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RECOVERY OF FERMENTATION PRODUCTS FROM DILUTE AQUEOUS SOLUTION

T.K. Murphy*, H.W. Blanch, and C.R. Wilke
(*Ph.D. Thesis)

April 1984

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*Ph.D. Thesis

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April 1984

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Recovery of Fermentation Products from Dilute Aqueous Solution

Thomas Kevin Murphy

ABSTRACT

The recovery of fermentation products from dilute aqueous solution is an important part of the field of biochemical engineering. After a brief survey of the techniques employed for product recovery, this thesis concentrates on ethanol recovery by liquid-liquid extraction as a model system. The potential benefits of this recovery method relative to distillation, the standard means of recovering ethanol produced by fermentation, are shown to be the reduction in the energy requirement of the recovery and the economic advantages which could be realized in an extractive fermentation.

The selection of a solvent is the key to the development of a process using liquid-liquid extraction. Several criteria for the selection are established for the analysis of solvent properties, the most important being the ethanol distribution coefficient (a measure of the capacity of the solvent) and the separation factor (a measure of the selectivity of the solvent for ethanol over water). Experimental data for a number of solvents are presented and discussed. Distribution coefficients for ethanol are generally low (none greater than 1.3) and separation factors are low for those solvents having the highest distribution coefficients. Alcohols and secondary amines (particularly saturated heterocyclicccompounds) are shown to have the most potential for use in an economical ethanol extraction process. In the case of the alcohols, the effects of branching of the carbon chain and of the position of the OH group are

interpreted in terms of their influence on the microstructure of the solutions. The results of experimental tests of the toxicity of various solvents to yeast indicate that nontoxic solvents are ones which have high molecular weights or an absence of polar groups, resulting in very low solubilities in water.

Modelling of liquid-liquid equilibria for systems of ethanol, water, and solvents is treated by both empirical and theoretical approaches. The effects of aqueous ethanol concentration and of temperature on the liquid-liquid equilibria can be represented accurately over the ranges of interest by simple empirical models. The theoretical approach has the potential advantage of allowing prediction of solvent properties in the absence of experimental data. The UNIFAC and UNIQUAC models are shown to give estimates of solvent properties which would be useful in a qualitative screening of solvents, even though they fail to make accurate predictions.

A review of previously proposed processes involving liquid-liquid extraction of ethanol reveals that the low selectivity of solvents with reasonable distribution coefficients limits the energy efficiency of the extraction process. This leads to the proposal of a new process involving the selective removal of water from the extract by contact with a suitable solid sorbent. The proposal includes regeneration of the sorbent by the hot solvent (after ethanol recovery).

Investigations of this process proposal through experiments and mathematical modelling are presented. The experimental results show that it is feasible to remove practically all of the water from a mixture of ethanol and water in a typical extraction solvent. Ion

exchange resins in metallic salt forms appear to have the desired properites of high water capacity and low ethanol uptake. Modelling of large scale column performance indicates that a sorption-regeneration cycle would be practical within the temperature limits of the sorbents and that such a cycle should be easily amenable to automatic process control.

Economic analysis of the proposed process relative to distillation indicates that it is competitive only under special conditions. While the cost of liquid-liquid contacting can be reduced by operating a process at lower recovery fractions (as would be the case in an extractive fermentation), the capital and energy requirements of the other parts of the process are equally significant. Extensive optimization could result in a more economical process, and specific areas recommended for further study include the use of other solvents, distillation optimization, and the use of inert gas stripping to regenerate the solvent and recover the product.

Dedication

This thesis is dedicated to my parents, Thomas V. and Carol E. Murphy, whose loving encouragement of my far-ranging curiosity started me on the path, and to my wife, Katherine, whose patient support and help were essential to its completion.

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1. FERMENTATION PRODUCT RECOVERY

A large part of the field of biochemical engineering involves the use of organisms or enzymes to carry out chemical reactions. In general, the study of such systems might be regarded as catalytic reaction engineering. However, there are many attributes of biochemical engineering systems which set them apart from conventional catalytic reaction engineering, attributes primarily related to the special nature of the catalysts involved. Whether these catalysts are microorganisms, enzymes, plant cells or animal cells, they have characteristics which are very different from those catalysts found in the typical petrochemical industry catalytic reactor. They are often very specific and selective in the conversions they perform. In the cases of the living organisms, they are capable of self-reproduction (a behavior opposite to the deactivation often encountered with inorganic catalysts), and of syntheses of large and complex products from relatively simple precursors, often involving many reaction steps.

These desirable aspects of using biochemical catalysts do not come without disadvantages, however. The biocatalysts have quite stringent environmental requirements which must be met if they are to function. Probably the most significant of these is the need for water. All living organisms and most enzymes can only remain catalytically active in the presence of at least some liquid water. As a consequence, the products of biochemically catalyzed reactions must be recovered from aqueous solutions which are most often quite dilute. In addition, other requirements of the catalysts generally include a variety of organic and inorganic compounds which serve as nutrients.

These compounds, together with unreacted substrate, the catalysts (organisms) themselves, and possibly byproducts make the typical crude bioreactor product stream a complex multicomponent mixture. The problem of recovering and purifying one or more compounds from such a mixture can be very different from separations problems encountered in the more traditional disciplines of chemical engineering. The challenges inherent in biochemical engineering separations provide ample opportunity for scientific research and invention, as the industry seeksto improve the efficiency of its existing separation techniques and to develop new ones for a growing and changing product spectrum. It is an objective of this thesis to contribute to the study of product recovery from dilute aqueous fermentation broths.

This chapter serves to review the role of product recovery in relation to the other operations of biochemical engineering. It describes the variety of recovery techniques available, focusing on one chosen for detailed study in this work, liquid-liquid extraction. Finally, the model product for this study, ethanol, is introduced, and the reasons for its choice discussed.

1.1 The Role of Product Recovery

The importance of product recovery to a biochemical engineering process varies considerably. The cost of recovery as a fraction of the total process cost may range from practically zero, for some fermented food products, to up to 60% for some organic and amino acids (Bailey and Ollis, 1977). A large number of biochemical products, especially health care products such as antibiotics, have a very high unit value when compared to even specialty products of the nonbiolo-

gical chemical industry. Others, including ethanol, organic acids, and other commodity-type chemicals, are characterized by the dominance of their cost of manufacture by the cost of the substrate used for their production. While the stoichiometric yields of product from substrate in the fermentation are much more important in the latter class of products, both classes have strong economic incentive to employ recovery processes that efficiently yield the maximum amount of product available.

There are cases of fermentation products which are not commercially successful primarily due to the lack of an efficient, economical recovery process. Butanediol is an example. In the continuing research efforts to develop methods of utilizing renewable biomass resources for the production of fuel and chemicals, the problem of effective use of the xylose, which makes up 10 to 25 percent of most kinds of plant biomass (Wilke et al, 1981), is the focus of much work (Rosenberg, 1980). It has long been known, however, that xylose can be efficiently fermented to produce a mixture of ethanol and butanediol (Ward et al, 1944). The difficulty of recovering the butanediol without excessive energy expenditure (Wheat et al, 1948) is a major reason that this product is not considered a viable one for a biomass utilization process, in which processing costs must be kept low.

The advent of genetic engineering, with its vast potential for new products for the biochemical engineering industries, is posing new recovery problems as well. Debate continues on the subject of whether it is better to develop an organism which secretes the product it makes (commonly a protein) and thereby avoid having to lyse or disrupt

the cell, or to have it retain the product in the cell. The advantage of the latter alternative is that it allows primary recovery, with a large reduction in the volume of the stream to be treated, by a relatively simple cell concentration technique such as ultrafiltration or centrifugation. The required purity of many of the products produced by gene-splicing techniques necessitates the development of new methods of purification, such as the use of monoclonal antibodies in affinity chromatography, and the development of procedures for the reliable scale-up of these methods.

There is a growing awareness of the importance of integrating the development of recovery processes for fermentation products with the optimization of the fermentation conditions and raw materials selection. Such integration is important in the efficient optimization of the overall production process. In many cases, there may be benefits to be realized from fully integrating the fermentation and recovery parts of the process. The simultaneous production and recovery of a product by removing it directly from a continuous fermentation can increase the yields and productivity of a fermentation by mitigating the effects of product inhibition and product degradation. Such beneficial effects have been reported in laboratory-scale work with lactic acid (Abbott and Gerhardt, 1970), ethanol (Cysewski and Wilke, 1977; Maiorella et al, 1979; Lee and Wang, 1982; Minier and Goma, 1982), and the antibiotic cycloheximide (Wang et al, 1981). While such schemes may place restrictions on the type and nature of the recovery method used, the potential economic benefits make their consideration worthwhile.

1.2 Survey of Recovery Techniques

There are a number of industrially important fermentation processes which require little in the way of product recovery. Notable among these are the production of fermented foods, such as yogurt, cheese, and other fermented dairy products, soy sauce, vinegar, beer, and wine. These need only filtration and pasteurization, in some cases, before being packaged for sale and consumption. Other products simply need to be concentrated to make their shipment more economical; an example being xanthan whole broth concentrates used for enhanced oil recovery. Still others, such as microbial biomass for food or feed, require a relatively simple recovery process including concentration by filtration or centrifugation followed, perhaps, by spray drying. Most chemical products of the fermentation industries, however, are required to be isolated from the medium in which they are produced and are often required to have a much greater degree of purity than can be achieved with such simple methods. There is a variety of more sophisticated separation techniques which are used in those cases.

It has been stated (King, 1980) that when considering separation process options, one of the first questions that should be asked is "Why not distillation?". Yet this operation is used for recovery of only a very small number of fermentation products. With the exceptions of ethanol, acetone, and some organic acids which have been purified by the distillation of their esters, fermentation products do not lend themselves easily to recovery by this workhorse of the petrochemical industry. It is true that the concentration of products by evaporation is quite common, but it is almost always followed by some

other operation (e.g. crystallization) to actually recover the product. The reasons for this are mainly related to the fact that fermentation is used mostly to manufacture more complex molecules than can be readily synthesized from petrochemicals. These materials tend to be high in molecular weight, with one or more polar functional groups. Consequently, they are nonvolatile, especially relative to water, and often sensitive to thermal degradation. So distillation is rarely applicable to their recovery. Instead, other operations are used which remove the products from the dilute solutions in which they are produced or from concentrated solutions made by evaporation or ultrafiltration of the dilute ones.

One such operation, mentioned above, is crystallization. It is most useful in cases where the product can be produced in rather high concentration in the fermentation. Commercially important examples include some of the amino acids. The mechanism used to induce crystallization at the desired point in the process varies. In the case of amino acids, it involves adjustment of the pH of the solution to the isoelectric point of the amino acid, at which it is least soluble in water. This may be accompanied, as in the case of glutamic acid production for monosodium glutamate, by cooling of the hot concentrate from a prior evaporation. In most cases, a crude crystallization serves as a primary recovery, concentrating and purifying the product somewhat. It is then followed by one or more additional purification steps, perhaps including impurity removal by carbon adsorption or ion exchange (after dissolution), recrystallization, and drying. Indeed, most chemical products must be crystallized and dried before they are sold, so this operation is a ubiquitous one; its

application as a primary recovery method is much less common.

A recovery operation similar to crystallization in some respects is precipitation. It differs from crystallization primarily in that it requires the addition of a mass separating agent which is added to the fermentation broth in amounts which are stoichiometrically related to the product or greater. A well-known example is the use of calcium hydroxide to precipitate citric acid as its calcium salt. Enzymes and other protein products are commonly recovered by ammonium sulfate precipitation. As in the case of crystallization, the crude precipitate must generally be further purified or treated. Citric acid, for example must be regenerated in an operation which consumes sulfuric acid and makes calcium sulfate. Proteins are purified by chromatographic techniques or special separation methods such as electrophoresis. The costs of the separating agent, and of the disposal or recycle of its residue in the spent broth, can be major contributors to the cost of manufacture in this type of recovery.

A more desirable approach, in general, to the problem of initial product recovery involves the selective removal of the product from the aqueous medium by its transfer to another phase which may be physically separated easily from the bulk of the broth. One such recovery method is the use of solid sorbents. Activated carbon, ion exchangers, and nonionic polymeric resins have all found applications in the recovery of fermentation products. Several kinds of antibiotics, amino acids, organic acids, and other compounds are recoverable by this method. It is being currently investigated as a recovery method for ethanol, as will be discussed in section 1.4. The use of solids, whether sorbents or ion exchangers, has some inherent

advantages over the use of liquids as separate phase extractants. These include the reduction or elimination of the problems of solvent recovery from the broth raffinate and an increased flexibility in the choice of regeneration methods (e.g. the use of solvents). They also are normally not toxic, making their use in extractive fermentation applications attractive. These properties all stem from the solid nature of the materials, which implies that, although they may swell in liquids, they will not dissolve. The fact that they are solids does, however, have disadvantages as well. Chief among these is the difficulty of handling solids in continuous processing (King, 1980), leading to the use of most solid sorbents or ion exchangers in fixed beds. There they may encounter problems with fouling of their surfaces, particularly with fermentation broths, which generally are high in particulates, polymeric substances, and surface active materials. Even without fouling, the mass transfer resistance of solids is normally much greater than that of liquids. This high resistance to mass transfer coupled with fixed bed operation means that large inventories of the solid sorbent or ion exchanger are generally required, and they are costly. Nevertheless, because of the advantages mentioned above, and the fact that they can provide superior selectivity for the product in some cases, recovery by the use of solids is the method of choice in some applications.

1.3 Liquid-Liquid Extraction of Fermentation Products

This recovery method, the one which is the subject of this thesis, has been used extensively for fermentation products. Probably the most economically important application is the use of solvent

extraction in the recovery of antibiotics. A good example is the extraction of penicillins from fermentation broths with butyl or amyl acetate (Queener and Swartz, 1979). Liquid-liquid extraction is also being used by one manufacturer to replace the costly calcium salt recovery process mentioned above for citric acid (Alter and Blumberg, 1981). It has been investigated for the recovery of other organic acids including acetic (King, 1981), lactic (Weiser and Geankopolis, 1955), and propionic and butyric (Playne, 1983). It has also received attention as a possible solution to the problem of efficient recovery of butanediol (Othmer et al, 1945). Previous work on its application to recovery of ethanol produced by fermentation will be discussed in chapter 5.

The same characteristics of fermentation broths which tend to foul solids can cause the formation of stable emulsions in liquid-liquid contacting. Removal of cell mass and other particulates is sometimes necessary, but the successful extraction of whole broths in a variety of types of contacting equipment has been reported (West and Patterson, 1981). The additional problems of solvent recovery and regenerability must be addressed in solvent extraction processes. If these can be solved, however, liquid extraction offers the advantages of the ease of handling fluids in a continuous process and the improved mass transfer characteristics relative to solids. The latter is due not only to intrinsically higher diffusion coefficients, but also to the continual renewal of the interface for mass transfer.

1.4 Ethanol Recovery - a Model System

In this thesis, the subject of fermentation product recovery has been investigated through the detailed examination of a model system, the recovery of ethanol produced by fermentation. The relative ease with which ethanol fermentations can be run, and the relative ease of analysis for this product when compared to others make it a good choice for a model. In addition, however, there is practical interest in developing recovery methods for ethanol which are more efficient, in terms of energy consumption as well as cost, than distillation, which is essentially the only method used today. Solvent extraction was chosen for study in this work after an examination of some other alternatives. Before proceeding with the discussion of solvent extraction, however, a brief review of some of the other alternatives to distillation is in order.

1.4.1 Supercritical Carbon Dioxide Extraction

This process is actually a special case of solvent extraction in which regeneration of the solvent is accomplished by a pressure swing. It has been claimed by its proponents to be a low-energy, economical process for ethanol recovery from dilute solutions including fermentation broths (De Filippi and Moses, 1982). However, independant analysis has revealed some important flaws in the process. The main one of these is that distribution coefficients for the system are in the neighborhood of 0.1, less than those obtainable with many ordinary liquid solvents (to be discussed in chapter 3). In addition, the high solubility of CO_2 (7 to 8 wt.%) at the pressures employed (>900 psi), means that significant solvent losses will be experienced. Proponents

of the process minimize this aspect, however, by pointing out that the fermentation produces plenty of makeup CO_2 as a byproduct. Although the selectivity of the supercritical CO_2 is relativly high, it is not high enough to produce ethanol concentrations greater than about 90 wt.% from feed concentrations which are reasonable for fermentation. Because the ethanol distribution coefficient is low, high selectivity would seem to be the only way to justify the high capital costs of the process and the safety problems associated with such high pressures.

1.4.2 Solid Ad/Absorption

There are a number of proposed processes which involve the use of a solid to adsorb or absorb ethanol from a dilute solution. Most do not seem to be viable alternatives to distillation, however. Research aimed at finding a polymer capable of selectively "imbibing" ethanol has produced none with distribution coefficients high enough for a practical process (Lawton and Moore, 1982). Other studies, involving the adsorption of ethanol on activated carbon, showed low selectivity, such that the concentration of desorbed product reported was less than that which could have been obtained by conventional stripping of the feed with lower energy input (Lee and Wang, 1982; Huibers et al, 1982). A recent patent on a method employing esterified silica (Kulprathipanja and Neuzil, 1982) amounts to a scaled-up liquid chromatography process and seems very unlikely to be practical for fermentation ethanol recovery. Work on the use of Silicalite, a hydrophobic molecular sieve, has shown distribution coefficients between 1 and 2 for dilute aqueous solutions of ethanol (Milestone and

Bibby, 1981; Abraham, 1982). Apparent selectivities are reported to be decreased by interstitial water when adsorption is from the liquid phase, so vapor phase sorption (with recycle of steam) was proposed. The use of vapor phase sorption would also avoid another problem; that is the fouling of a bed of solid sorbent by solids and surface active components in the fermentation broth. The most detailed proposal published to date, however, does not make the process look attractive relative to distillation (Pitt et al, 1983). In that work, which looked at commercially available styrene-divinylbenzene copolymers and a hydrophobic molcular sieve as sorbents, the reported concentrations of desorbed product obtained from stripping beds which had sorbed ethanol from 10 wt.% solutions were only 60 wt.%. Since simple stripping of the same solution would produce over 50 wt.% ethanol, it is difficult to see motivation to use the sorbents. Furthermore, the process analysis done in that study showed a savings of energy use compared to distillation, but over half of the energy used in the sorption process was electrical. Since electrical energy is four to five times as expensive as thermal energy in general, the sorption process would have to pay more for energy than a distillation. Capital costs were not estimated, but they would almost certainly make the economic analysis even worse for the sorption process.

1.4.3 Use of Permselective Membranes

Membranes have been found which will preferentially pass either water or ethanol (Southern Research Institute, 1982; Gregor and Jeffries, 1979). However, it has been pointed out (Eakin et al, 1981) that pressure limitations of conventional membranes limit concentration of dilute ethanol by the former type of membrane to

about 14 wt.% due to the high osmotic pressure gradients developed. The low fluxes and high membrane costs of both types make their application to ethanol recovery unattractive, especially considering the likelihood of fouling of the membrane surfaces by fermentation components.

1.4.4 Fractional Freezing

This method for removing water from an aqueous solution is also not suitable for ethanol concentration. The very low freezing point of ethanol and its resultant freezing point depression of aqueous solutions mean that fractional freezing could only be used practically to concentrate dilute ethanol to moderate concentrations, perhaps 10 wt.%. The energy savings compared to distillation are very small, however, and are not worth the investment in equipment that would be required to perform such an operation.

The following chapter discusses liquid-liquid extraction as an alternative to distillation for ethanol recovery. Previously proposed processes using liquid-liquid extraction are reviewed in chapter 5.

REFERENCES

1. Abbott, B.S., and Gerhardt, P. (1970), Biotech. Bioeng. **12**:577

2. Abraham, W. (1982) "Ethanol Purification by Adsorption", report presented at S.E.R.I. contractors meeting May, 1982 San Francisco, CA for Ames Laboratory, Ames, Iowa

3. Alter, J.E., and Blumberg, R. (1981) U.S. Pat. 4,251,671 (Chem. Abs., **95**:61507d)

4. Bailey, J.E., and Ollis, D.F. (1977), Biochemical Engineering Fundamentals, McGraw-Hill, New York

5. Cysewski, G.R., and Wilke, C.R. (1977), Biotech. Bioeng. **19**:1125

6. De Filippi, R.P., and Moses, J.M. (1982) Biotech. Bioeng. Symp. Ser., **12**:205

7. Eakin, D.E., Donovan, J.M., Cysewski, G.R., Petty, S.E., and Maxham, J.V. (1981) Preliminary Evaluation of Alternative Ethanol/Water Separation Processes, Battelle Pacific Northwest Laboratory, N.T.I.S. no. PNL-3825

8. Gregor, H.P., and Jeffries, T.W. (1979) Ann. New York Acad. Sci. **326**:273

9. Huibers, T.A., Jenq, C.Y., and Noack, C.M. (1982) "Energy Efficient Ethanol Separation by Two-Stage Adsorption - Project Summary" presented at S.E.R.I. contractors meeting May 1982, San Francisco, CA for Hydrocarbon Research, Inc. Lawrenceville, New Jersey

10. King, C.J. (1980) Separation Processes, 2nd ed., McGraw-Hill, New York

11. King, C.J. (1981) "Complexing Extractants for Recovery and Separation of Polar Organics", presented at the First Engineering Foundation Conference on Advances in Fermentation Recovery Process Technology, June 1981, Banff, Alberta

12. Kulprathipanja, S., and Neuzil, R.W. (1982) Use of Esterified Silica for Separation of Ethanol from Water, U.S. Pat. 4,343,623

13. Lawton, E.A., and Moore, G.W. (1982) "Removing Alcohol from Water by Selective Absorption", presented at S.E.R.I. contractors meeting May, 1982, San Francisco, CA for Shock Hydrodynamics Division of Whittaker Corp.

14. Lee, S.S., and Wang, H.Y. (1982) Biotech. Bioeng. Symp. Ser. **12**:221

15. Maiorella, B.L., Blanch, H.W., and Wilke, C.R. (1979), "Rapid Ethanol Production via Fermentation", Lawrence Berkeley Laboratory Report 10219, presented at A.I.Ch.E. meeting of November, 1979 San Francisco

16. Milestone, N.B., and Bibby, D.M. (1981) J. Chem. Tech. Biotechnol., **31**:732

17. Minier, M., and Goma, G. (1982) Biotech. Bioeng., **24**:1565

18. Othmer, D.F. et al (1945) Ind. Eng. Chem., **37**(9):890

19. Pitt, W.W., Haag, G.L., and Lee, D.D. (1983) Biotech. Bioeng. **25**(1):123

20. Playne, M.J. (1983) "Propionic and Butyric Acids" in Comprehensive Biotechnology, v.2 Pergamon Press (in press)

21. Queener, S., and Swartz, R. (1979) "Penicillins: Biosynthetic and Semisynthetic" in Economic Microbiology, v. 3, A.H. Rose, ed. Academic Press New York, N.Y.

22. Rosenberg, S.L. (1980), Enzyme Microb. Technol. **2**:185

23. Southern Research Institute (1982) "Summary of Progress on the Devolpment of Ethanol-Selective Membranes", presented at S.E.R.I. contractor's meeting May, 1982 San Francisco, CA

24. Wang, H.Y., Kominek, L.A., and Jost, J.L. (1981), "Proc. 6th Int. Ferment. Symp." London, Ont., July 1980 v. 1 p. 601, published by Advances in Biotechnology, M. Moo-Young and C.W. Robinson, eds.

25. Ward, G.E., Pettijohn, O.G., Lockwood, L.B., and Coghill, R.D. (1944), J. Am. Chem. Soc. **66**:541

26. Weiser, R.B., and Geankopolis, C.J. (1955) Ind. Eng. Chem., **47**(4):858

27. West, J.M., and Patterson, A. (1981) "Whole Broth Extraction", presented at the First Engineering Foundation Conference on Advances in Fermentation Recovery Process Technology Banff, Alberta, June, 1981

28. Wheat, J.A., Leslie, J.D., Tomkins, R.V., Mitton, H.E., Scott, D.S., and Ledingham, G.A. (1948), Can. J. Res. **26F**:469

29. Wilke, C.R., Yang, R.D., Sciamanna, A.F., and Freitas, R.P. (1981) Biotech. Bioeng. **23**(1):163

2. APPLICATION OF SOLVENT EXTRACTION TO ETHANOL RECOVERY

Liquid-liquid extraction represents one possible alternative to distillation as the conventional method for recovering ethanol from aqueous solutions. This chapter discusses the reasons for considering extraction and the situations in which it may be an attractive process. This will allow the establishment of some criteria to be applied in addressing the key issue in the design of a liquid-liquid extraction process, that is, the problem of solvent selection.

2.1 Conventional Ethanol Recovery by Distillation

Because distillation is so well established as the method of recovering ethanol from aqueous solution, it will be the standard against which any new process proposal will be judged. It is natural, then, to include here a brief review of this process.

The characteristics of the separation of ethanol from water by distillation are governed by the vapor-liquid equilibrium relations of the two compounds. The vapor-liquid equilibrium curve for the binary system at atmospheric pressure is shown in the x-y diagram of Figure 2-1. The relative volatility of ethanol is large at low ethanol concentrations, making the situation appear favorable for ethanol recovery. However, the relative volatility decreases as ethanol concentration increases until, at the azeotrope, it becomes less than one. Of course, this means that pure ethanol cannot be recovered from water at atmospheric pressure by means of ordinary distillation alone. Additional process steps, such as azeotropic distillation or selective

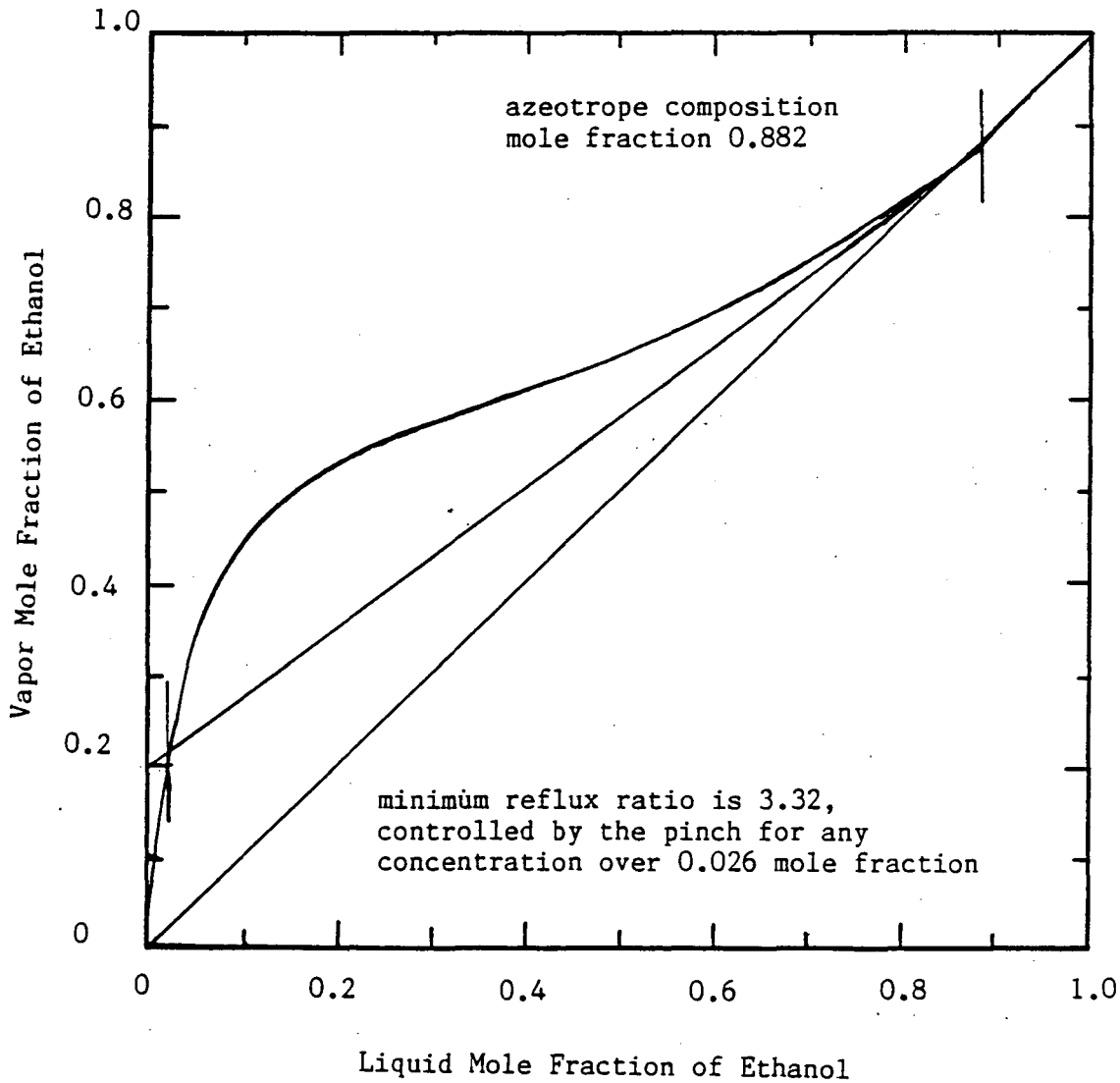
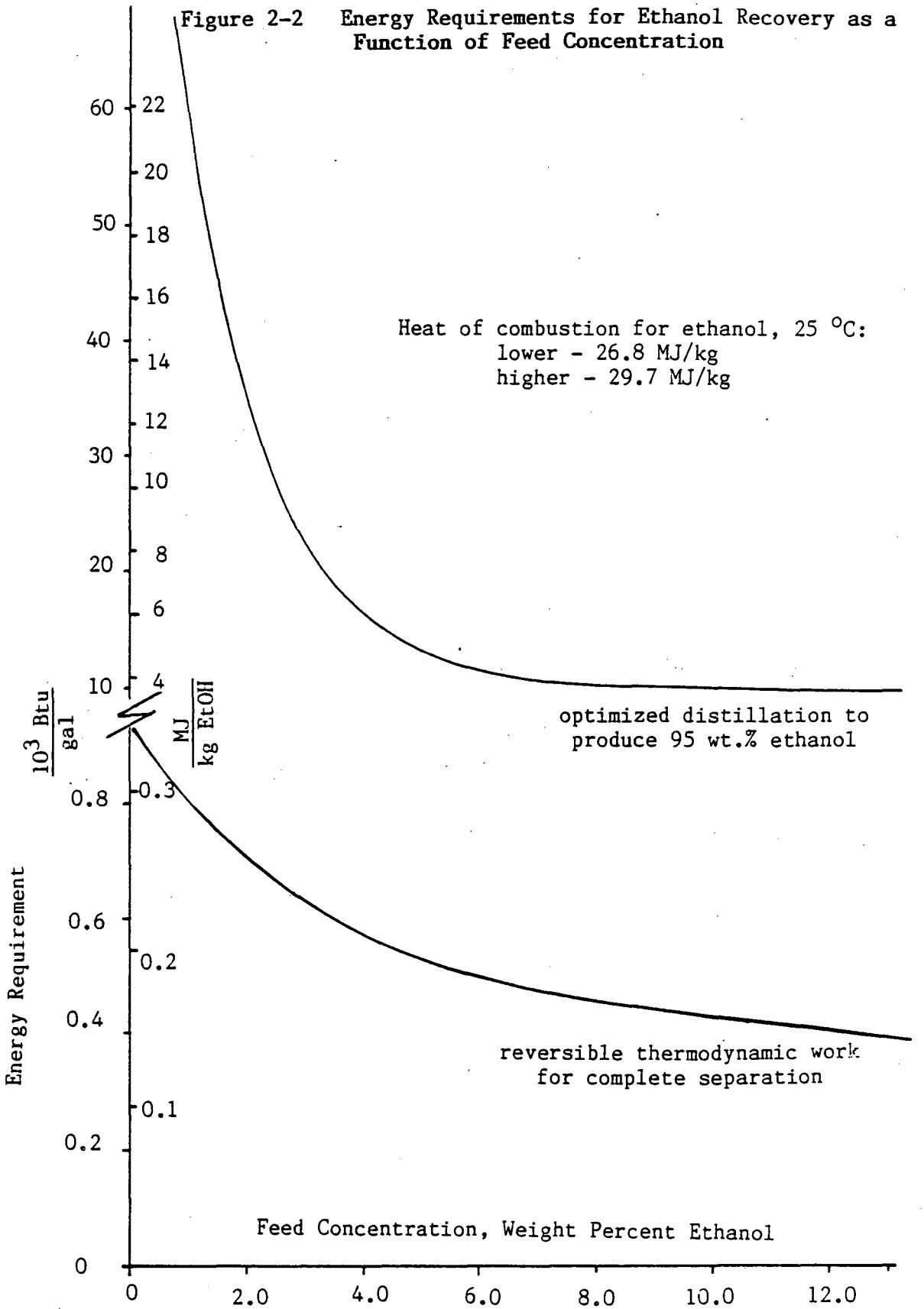


Figure 2-1 Vapor-Liquid Equilibrium Diagram for Ethanol and Water at Atmospheric Pressure

adsorption must be employed to produce anhydrous alcohol. Of even greater significance, however, is the large slope of the x-y curve in the vicinity of the azeotropic composition. This characteristic implies that a large reflux ratio must be used to obtain a distillate with a concentration near the azeotrope even if the feed is fairly concentrated. This pinch restriction on the operation of the distillation is the cause of the high energy consumption by the process. By operating at presures lower than atmospheric, however, it is possible to change the vapor-liquid equilibria of the system such that the azeotropic composition moves to a higher ethanol concentration and the slope of the x-y curve at that point decreases somewhat. An extensive study of the economic optimization of the distillation of ethanol water mixtures to produce 95 wt.% ethanol has been carried out by Maiorella (1983), in which the pressure, reflux ratio, and other operating parameters were optimized as a function of the ethanol concentration in the feed. The resulting optimum energy use as a function of feed ethanol concentration is presented in Figure 2-2. Of course, the optimum energy use is a function of the relative costs of equipment and utilities and the values shown are those for a base case. However, Maiorella's investigation of the sensitivity of his results to energy costs shows that the optimal energy consumption will not change dramatically as those costs change. Shown also in Figure 2-2 for comparison is the minimum work required to separate ethanol from water as a function of the ethanol concentration. The values on this curve were calculated from the thermodynamic expression for the Gibbs free energy change involved. The equation used for these calculations is that for an isothermal separation (King, 1980);

Figure 2-2 Energy Requirements for Ethanol Recovery as a Function of Feed Concentration



$$W_{min} = -RT\ (x_E \ln(x_E Y_E) + x_W \ln(x_W Y_W)),$$

in which W_{min} is the minimum work required for the separation to pure products, R is the universal gas constant, T is the temperature in ^{o}K, x_E and x_W are the feed mole fractions of ethanol and water respectively, and Y_E and Y_W are the activity coefficients of ethanol and water. The activity coefficients were taken from the work of Pemberton and Mash (1978). It is evident that the optimal energy consumption for the production of even 95 weight percent ethanol by distillation is approximately an order of magnitude greater than the thermodynamic requirement, regardless of the ethanol feed concentration. The energy consumed for the separation is a significant fraction of the energy available from combustion of the ethanol product (LHV is 76,240 BTU per gallon at 25 ^{o}C). Actual energy consumption of the distillation as practiced commercially is roughly twice as high as indicated in Figure 2-2 because vacuum distillation is not widely used, particularly by small producers who fear control problems (Nowlin, 1981). The other main point to be made about Figure 2-2 is that the distillation energy use curve has two distinct regions. Above a critical ethanol feed concentration, in the neighborhood of 5 to 6 weight percent, the energy use curve levels off at around 12,000 BTU per gallon. This is due to the pinch limitation discussed previously. Below this critical feed concentration, the energy use increases very rapidly as feed concentration decreases. This is due to the increasing amounts of water that must be vaporized with the ethanol when it is stripped from the dilute solution.

2.2 Potential Benefits of Ethanol Extraction

The preceeding discussion points to one of the potential benefits of using extraction for ethanol recovery, the possibility of reducing the energy requirements of the process. Because the cost of energy is the greatest contributor to the cost of distilling ethanol, there exists the hope that an extraction process, with a smaller energy requirement, could be economically competitive, especially as the cost of energy seems likely to continue to increase at a greater rate than the costs of labor and process equipment.

There are a number of ways in which a solvent extraction process could be operated to realize an energy use advantage over conventional distillation. An example is an idealized case in which a solvent that has a high boiling point and very high selectivity for ethanol is used to extract it from aqueous solution. The subsequent distillation to recover the ethanol could have an energy requirement only slightly greater than the latent heat of ethanol vaporization (2485 BTU per gallon of pure ethanol). Unfortunately, as the following chapter will show, no such solvent exists. Many other process alternatives are possible, however, and some of these will be presented in the review of work in this area which follows in chapter 5.

Because of the manner in which the energy requirement for the distillation increases as the ethanol feed concentration decreases, the advantage of using extraction might be expected to be greatest for dilute feeds. This is of interest because there are some sources of fermentable sugars which are quite dilute, such as cheese whey, some paper pulping wastes, and the products of some proposed schemes for hydrolysis of cellulosic materials. However, there is another

potentially important application of extraction which involves the opposite extreme, highly concentrated feeds. This is concept of extractive fermentation, in which ethanol is removed from the fermentation as it is produced. This removal can increase the productivity of the fermentation by alleviating the product inhibition encountered in conventional operation. In addition, Maiorella (1983) has shown that the reduction in the stillage handling and waste treatment costs provide considerable economic incentive for the use of processes utilizing selective ethanol removal. Other ways of accomplishing this have been proposed, including vacuum fermentation (Ramalingan and Finn, 1977; Cysewski and Wilke, 1977), flash fermentation (Maiorella et al, 1979), and the use of permselective membranes (Gregor 1979;Hahn-Hagerdal et al, 1981). Solvent extraction may compete with these, though its use in a fermentation places a toxicity restriction on the solvent selection.

2.3 Desirable Properties of an Ethanol Extraction Solvent

There are many desirable properties which can be identified as important for any liquid-liquid extraction process (Gerster, 1966; King, 1980). An obvious prerequisite is that the solvent have only limited miscibility with the stream to be extracted under the range of operating conditions employed. Apart from this, the most important general features desirable in a solvent are the following:

1. The solvent must have a high capacity for the compound being extracted. This is the same as requiring that the distribution coefficient for the compound, a ratio of the equilibrium concentration of the compound in the solvent phase to its equilibrium

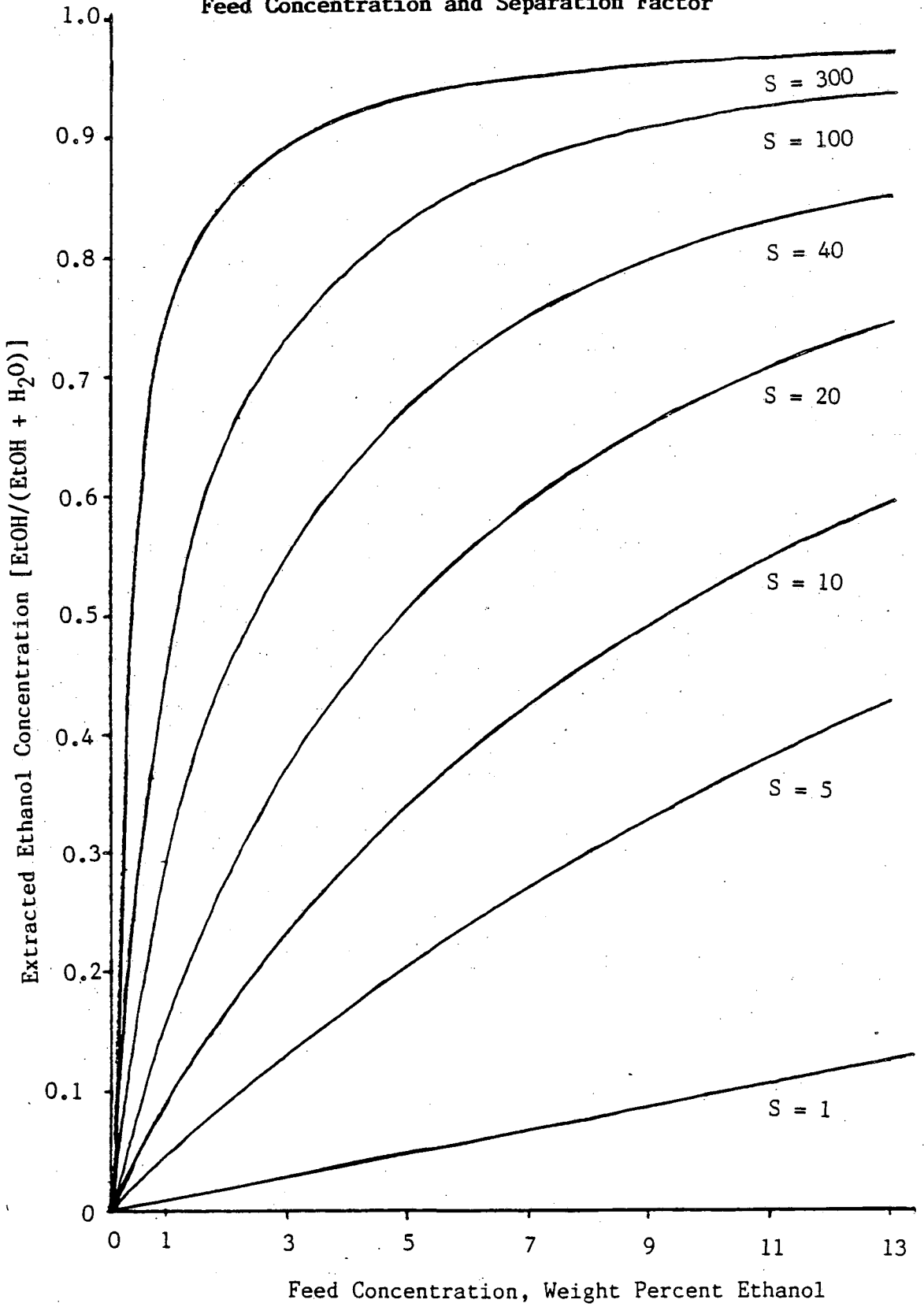
concentration in the feed mixture of interest, be large. In this thesis, the distribution coefficient for ethanol is represented by KE, defined as the weight fraction of ethanol in the solvent phase divided by the weight fraction of ethanol in the aqueous phase at equilibrium.

2. The solvent should be selective for the desired compound. This can be expressed as a requirement of a large separation factor, which is the ratio of the distribution coefficient for the desired compound to the distribution coefficient for the major component of the feed mixture. In this thesis, the separation factor is represented by S, defined as the ratio KE/KW, where KW is the distribution coefficient for water in terms of weight fractions, analagous to KE defined above. The significance of this parameter may be seen in Figure 2-3, which shows the effective concentration of ethanol (concentration on a solvent-free basis) that can be obtained by solvent extraction as a function ofthe aqueous feed concentration and the solvent separation factor.

Since both of these criteria concern the phase equilibrium properites of liquid mixtures, it is appropriate to consider them together in a search for potential solvents. It is generally true, as pointed out by King (1980), that in the absence of specific interactions, the goals of high capacity and high selectivity tend to be mutually exclusive. The best solvent choice for a given application will therefore represent a compromise, taking into account also the other important factors such as the following:

3. The density of the solvent should be as different as possible from the density of the solute-containing liquid, in this case water.

Figure 2-3 Extracted Ethanol Concentration as a Function of Feed Concentration and Separation Factor



This allows easier separation of the phases, resulting in lower equipment costs.

4. The viscosity of the solvent should be as low as possible to allow ease of handling (pumping) and, because diffusivities are generally inversely proportional to viscosities, to minimize mass transfer resistance.
5. The solvent should be nontoxic and noncorrosive. The toxicity of the solvent to the process operators is always of concern. Additionally, in those processes involving either direct extraction from the active fermentation or recycle of the raffinate to provide water for the process, the toxicity of the solvent to the fermentation organisms is a determining factor in its selection.
6. The solubility of the solvent in water should be as low as possible. Alternatively, the solvent should be easily recoverable from water in that its recovery should require little additional equipment or energy use. These considerations stem from the need to keep solvent losses low in order to avoid excessive costs for solvent replacement and to avoid environmental pollution or extra waste treatment costs. Some extraction process economics are dominated by the cost of solvent recovery (Lo, 1979). Of course, if the raffinate stream can be recycled in the process, solvent losses can be practically eliminated, but this places other restrictions on the solvent and on the process. The potential for water recycle in ethanol fermentation has been reviewed elsewhere (Murphy et al, 1982), and seems promising.
7. Related to the solvent recovery issue and to the ease of phase separation is the requirement that the solvent not form stable

emulsions with the process feed. In a general sense, this requirement is related to the interfacial tension of the solvent-feed interface. This tension must not be too low if emulsion formation is to be avoided. However, the rate of mass transfer between phases has been correlated with the reciprocal of the interfacial tension (Treybal, 1963), so there is a compromise to be made. The problem of emulsion formation is particularly severe and unpredictable in the case of fermentation broth extraction due to the ubiquitous presence of dissolved proteins, fatty acids, and other materials which are effective surfactants, and to the presence, depending on the process, of organisms themselves.

8. The cost of the solvent is important from the standpoint of the initial investment in the process and in connection with the issue of solvent recovery. If essentially quantitative recovery can be achieved without undue expense, then one can afford to consider the use of a more expensive solvent, particularly if significant advantages in capacity or selectivity are to be gained.
9. Finally, the solvent must be easily regenerable. This certainly means that the solvent must not react irreversibly with the product or with any other components of the feed. What it implies about other solvent properties depends very much on the details of the process configuration. For the case of ethanol recovery, most schemes involve the ultimate recovery of the ethanol by stripping or distilling it from the solvent. So ease of regenerability implies a boiling point significantly higher than that of ethanol, and the absence of azeotrope formation. Other possibilities will be discussed later in conjunction with specific processes.

REFERENCES

1. Cysewski, G.R., and Wilke, C.R. (1977) Biotech. Bioeng. **19**:1125

2. Gerster, J.A. (1966) Chem. Eng. Prog., **62**(9):62

3. Gregor, H. (1979) Proc. 3rd Ann. Biomass Energy System Conf. p. 39 D.O.E./S.E.R.I. Golden, Colorado (June 5, 1979)

4. Hahn-Hagerdal, B., Andersson, E., Lopez-Leiva, M., and Mattiasson, B. (1981) Biotech. Bioeng. Symp. Ser., **11**:651

5. King, C.J. (1980) Separation Processes, 2d ed., McGraw-Hill, New York

6. Lo, T.C. (1979) "Commercial Liquid-Liquid Extraction Equipment", section 1.10 of Handbook of Separation Processes for Chemical Engineers, P.A. Schweitzer, ed. McGraw-Hill, N.Y.

7. Maiorella, B.L. (1983) Ph.D.Thesis, Department of Chemical Engineering, University of California at Berkeley

8. Maiorella, B.L., Blanch, H.W., and Wilke, C.R. (1979) "Rapid Ethanol Production via Fermentation" Univ. of California, Lawrence Berkeley Laboratory Report 10219. Presented at A.I.Ch.E. meeting, November, 1979 San Francisco

9. Murphy, T.K., Blanch, H.W., and Wilke, C.R. (1982) Process Biochem., 17(6):6

10. Nowlin, R.L. (1981) personal communication (Nowlin is an owner of L. & A. Engineering, Turlock, CA, which builds and installs equipment for ethanol production)

11. Pemberton, R.C., and Mash, C.J. (1978) J. Chem. Thermodynamics **10**:867

12. Ramalingham, A., and Finn, R.K. (1977) Biotech. Bioeng. **19**:583

13. Treybal, R.E. (1963) Liquid Extraction, 2d ed. McGraw-Hill, New York

3. PROPERTIES OF POTENTIAL EXTRACTION SOLVENTS

The first step in designing a liquid-liquid extraction process of any kind is to select a suitable solvent. The feasibility of a proposed process can depend almost entirely on whether or not a solvent with desirable properties can be found. With this in mind, a primary purpose of this chapter is to examine the phase equilibrium data, obtained from published literature and from experiments in this work, for systems involving ethanol, water, and potential extraction solvents. These data will provide the basis for later evaluation of the feasibility of using a liquid-liquid extraction process for the recovery of ethanol from dilute aqueous solutions, including fermentation broths.

In addition to phase equilibrium data, other properties which will have a significant bearing on the configuration and feasibility of a process employing a given solvent are its boiling point, density, and solubility in water. These properties are available in the literature for many compounds of interest. One other property of interest, particularly if an extractive fermentation is considered, is the toxicity of the solvent. A limited amount of experimental work was performed to investigate the toxicity of some solvents with respect to ethanol fermentation since data on this subject are rare.

3.1 Physical Property Data and Analysis

A compilation of available data on liquid-liquid equilibria for systems involving ethanol, water, and partially miscible solvents is presented in Table 3-1. Only data for ethanol aqueous phase concentrations less than or equal to 15 weight percent are included in the table. The table is organized by solvent classes and contains information, when available, on the mutual solubilities of water with the solvents. Discussion of the data below follows the same solvent class groupings that appear in the table.

The experiments which provided the data referenced to this work were batch equilibrium studies. Weighed amounts of a solvent and a standard solution of ethanol in distilled water (normally about 2 milliliters of each) were added to a tared 5 dram screw cap vial. The sample was shaken periodically over a minimum 24 hour incubation period at the temperature of equilibration. Concentrations in both phases were analyzed by gas chromatography as detailed in Appendix A. To ensure that equilibrium had been reached, samples were reanalyzed after an additional 24 hours and the concentrations compared to the first set. No attempt was made to separate the phases for analysis. Instead, aliquots of the phases were carefully withdrawn using a syringe.

In Table 3.1, the densities given are those for the pure compounds at 25 ^{o}C. Densities of the water-saturated compounds will of course be different. Molecular weights and normal boiling points given are those cited in the C.R.C. Handbook of Chemistry and Physics (Weast, 1975). In many cases, a value is given for the distribution coefficient of water at zero ethanol concentration. This is a value

Table 3.1 - Properties of Pure Solvents for Ethanol Extraction

Abbreviations Used in the Table

MW - Molecular Weight
BP - Normal Boiling Point, °C
AS - Aqueous Solubility, wt.%
DEN - Density, g/cc
T - Temperature, °C
AEC - Aqueous Ethanol Concentration, wt.%
id - infinite dilution
KE - Ethanol Distribution Coefficient, aq.wt.%/org.wt.%
KW - Water Distribution Coefficient, aq.wt.%/org.wt.%
S - Separation Factor, KE/KW
Ref - Reference, see list at end of Table
nr - not reported

Solvent Name	MW	BP	AS,Ref	DEN	T	AEC	KE	KW	S	Ref
Aliphatic Hydrocarbons										
n-pentane	72.2	36	4.0e-3,SA	.630	25	0.0	-	1.1e-5		SA
					20	0-.9	.013	nr	-	KC
cyclohexane	84.2	81	5.6e-3,SA	.779	25	0.0	-	7.e-5		SA
					20	0-.9	.010	nr	-	KC
					20	0.5	.006	3.e-5	180	R1
					25	5.0	.008	3.e-5	310	R1
					40	0.5	.018	1.e-4	170	R1
n-hexane	86.2	69	1.3e-3,SA	.659	25	0.0	-	1.3e-4		SA
					20	0.5	.012	nr	-	KC
					25	0.5	.013	9.e-5	140	R2
					25	1.4	.013	1.e-4	130	R2
					25	4.7	.013	1.e-4	105	R2
					25	12.0	.013	2.e-4	70	R2
n-heptane	100.2	98	2.8e-4,SA	.684	25	0.0	-	1.3e-4		SA
					20	0-.9	.012	nr	-	KC
					25	0-20	.011			R2
n-octane	114.2	126	7.0e-5,SA	.703	25	0.0	-	1.3e-4		SA
					20	0-.9	.011	nr	-	KC
					25	0-20	.010			R2
2,2,4-trimethyl pentane	114.2	99	2.2e-4,SA	.692	25	0.0	-	1.3e-4		SA
					25	6.4	.008			TW
n-decane	142.3	174		.730	25	0.0	-	7.2e-5		SA
					20	0-.9	.011	nr	-	KC
					25	0-20	.008			R2

Table 3.1, continued

Solvent Name	MW	BP	AS,Ref	DEN	T	AEC	KE	KW	S	Ref
n-tetradecane	198.4	253		.765	40	0.0	-	1.1e-4		SA
					25	0-20	.007			R2
					23	9.0	.006	7.e-5	85	TW
					65	9.0	.028	4.7e-4	59	TW
					90	9.0	.054	.0011	49	TW
n-hexadecane	226.4	288		.774	25	0.0	-	7.5e-5		SA
					25	0-20	.007			R2
Aromatic Hydrocarbons										
benzene	78.1	80	0.17, SA	.879	25	0.0	-	6.9e-3	-	SA
					20	0-.9	.027	nr		KC
					23	5.0	.051	.0012	41	TW
					20	0.5	.044	5.2e-4	85	R1
					25	4.6	.052	4.9e-4	110	R1
					30	0.7	.058	5.0e-4	115	MK
					40	0.5	.071	8.4e-4	85	R1
toluene	92.1	111	0.054,SA	.867	25	0.0	-	5.4e-4		GS
					20	0-.9	.023	nr		KC
					20	0.5	.036	3.4e-4	110	R1
					40	0.5	.065	7.1e-4	92	R1
					25	4.6	.039	3.9e-4	100	R1
					30	0.7	.040	4.0e-4	100	MK
m-xylene	106.2	139	0.017,SA	.864	25	0.0	-	4.3e-4		SA
					20	0.5	.029	2.5e-4	110	R1
					25	4.6	.035	3.8e-4	91	R1
					40	0.5	.054	5.1e-4	110	R1
					20	0-.9	.008	nr		KC
ethylbenzene	106.2	136	0.017,SA	.867	25	0.0	-	4.3e-4		SA
					25	4.6	.033	3.5e-4	97	R1
					20	0-.9	.008	nr		KC
1,4-diethyl-benzene	134.2	184		.861	25	0.0	-	3.8e-4		EN
					20	0.5	.023	2.2e-4	110	R1
					25	4.6	.026	2.1e-4	120	R1
					40	0.5	.042	4.2e-4	100	R1
triethyl-benzene	162.3	216		.863	23	1-10	.025	.002	13	TW
					23	5.4	.026	.0016	16	TW
					60	1-10	.06	.002	30	TW
					90	1-5	.08	.003	27	TW

Table 3.1, continued

Solvent Name	MW	BP	AS,Ref	DEN	T	AEC	KE	KW	S	Ref
Alcohols										
1-pentanol	88.2	138	2.19, G1	.817	25	0.0	-	.10		SA
				.830	25	4.0	0.60	.11	5.5	01
				.835	25	11.6	0.86	.15	5.7	01
3-methyl-1-butanol	88.2	131	2.60, SA	.809	25	0.0	-	.15		SA
					25	0-15	1.2	.15	8	01
1-hexanol	102.2	158	.588, SA	.814	25	0.0	-	.068		SA
					25	0.7	1.0	.105	9.5	MK
					25	0.3	.63	nr		ZA
					30	0.7	1.2	.130	9.2	MK
					23	1.3	0.72	.09	8.0	TW
2-ethyl-butanol	102.2	146		.833	25	5.0	0.83	.028	30	R1
					30	0.7	0.97	.049	20	MK
					23	1.3	0.70	.059	12	TW
					23	4.0	0.64	.046	14	TW
2-methyl-1-pentanol	102.2	148	0.31, PR	.825	25	0.0	-	.054		PR
					23	1.4	0.68	.062	11	TW
3-methyl-3-pentanol	102.2	122	4.26, G2	.826	25	0.0	-	.108		G2
					30	0.7	1.3	.10	13	MK
4-methyl-2-pentanol	102.2	133	1.60, SA	.807	30	0.0	-	.054		SA
					30	0.7	1.1	.065	17	MK
					30	5.0	1.21	.060	20	DC
					30	9.0	1.20	.074	15	DC
					30	12.5	1.15	.093	12	DC
3,3-dimethyl-2-butanol	102.2	120	2.43, G2	.812	25	0.0	-	.075		G2
					23	1.5	.80	.092	8.7	TW
2-methyl-cyclo-hexanol	114.2	166		.93	30	0.7	0.93		15	MK
3-heptanol	116.2	159	0.6, OV	.822	25	0.0	-	.036		OV
					25	6.0	0.78	.040	20	OV
					25	11.0	0.85	.043	20	OV
2,4-dimethyl-3-pentanol	116.2	139	0.70, G3	.829	25	0.0	-	.033		G3
					25	4.6	0.71	.023	31	R1
3-ethyl-3-pentanol	116.2	143	1.68, G3	.841	25	0.0	-	.059		G3
					23	3.3	0.93	.081	11	TW
					66	3.0	1.13	.086	13	TW
					30	0.7	1.1	.061	18	MK
2,4-dimethyl-phenol	122.2	210		.965	23	2.0	1.3	.097	13	TW

Table 3.1, continued

Solvent Name	MW	BP	AS,Ref	DEN	T	AEC	KE	KW	S	Ref
1-octanol	130.2	194	0.051,SA	.827	23	0.0	-	.049		TW
					25	4.6	0.60	.052	12	R1
					20	4.1	0.58	nr		CO
					25	4.1	0.54	nr		ZA
					23	0.8	0.61	.049	12	TW
					23	4.0	0.60	.056	11	TW
					23	9.1	0.64	.068	9.4	TW
					60	0.7	0.96	.056	17	TW
					60	3.4	0.96	.064	15	TW
					60	8.1	0.92	.081	11	TW
					92	3.3	1.03	.069	15	TW
					30	0.7	0.64		11	MK
2-octanol	130.2	180	0.096,PR	.820	23	3.6	0.56	.043	13	TW
					64	3.1	0.83	.052	16	TW
					nr	5.0	0.7	.047	15	GT
					nr	10.0	0.75	.058	13	GT
2-ethyl-hexanol	130.2	185	0.07, PR	.833	25	0.0	-	.020		SA
					22	id	0.66	.033	20	ST
					35	id	0.64	.038	17	ST
					25	4.6	0.58	.021	23	R1
					30	0.7	0.66	.028	24	MK
					23	2.0	.49	.025	20	GT
					23	9.0	.57	.030	19	GT
					60	7.0	.81	.041	20	GT
					60	8.0	.88	.047	19	GT
					85	6.0	.85	.042	20	GT
					85	7.0	.99	.052	19	GT
2,2,4-trimethyl 1-pentanol	130.2	167		.823	23	0.0	-	.032		TW
					23	4.4	0.53	.033	16	TW
					67	3.8	0.76	.042	18	TW
2,3,4-trimethyl 3-pentanol	130.2				30	0.7	0.82		23	MK
3-phenyl-1-propanol	136.2	238		1.004	25	4.6	0.64	.022	29	R1
1-nonanol	144.3	213	0.013,SA	.827	25	0.0	-	.043		SA
					30	0.7	0.72	.055	13	MK
3-ethyl-3-heptanol	144.3	182		.838	25	4.6	0.44	.010	44	R1
2,4-dimethyl-3-heptanol	144.3			.835	25	4.6	0.38	.010	38	R1
2,6-dimethyl-4-heptanol	144.3	176	.06, PR	.809	25	0.	-	.010		PR
					30	0.7	0.53	.016	34	MK

Table 3.1, continued

Solvent Name	MW	BP	AS,Ref	DEN	T	AEC	KE	KW	S	Ref
1-decanol	158.3	229	.0037,SA	.830	25	0	-	.040		SA
					nr	5.0	0.52	.027	19	GT
					nr	10.0	0.55	.034	16	GT
					30	0.7	0.57	.044	13	MK
4-decanol	158.3	210		.826	25	4.6	0.32	.014	23	R1
2,2-dimethyl-3-octanol	158.3			.827	25	4.6	0.31	.009	34	R1
8-methyl-1-nonanol	158.3				35	i.d.	0.57	.06	9.5	ST
1-dodecanol	186.3	256	2.3e-3,SA	.831	25	0.	-	.029		TW
					23	7.4	0.35	.035	10	TW
					65	7.2	0.60	.041	15	TW
					90	4.4	0.64	.038	17	TW
					25	5.0	0.25	.012	21	R1
1-tridecanol	200.4			.822	20	0.5	0.22	.011	20	R1
1-heptadecanol	256.5	308		.841	25	0-20	0.29	.005	52	UV
Carboxylic Acids										
2-ethyl-butanoic acid	116.2	194		.923	23	4.0	1.03	.085	12	TW
n-hexanoic acid	116.2	205	1.06,SA	.927	30	0.0	-	.047		SA
					30	0.7	1.0	.067	15	MK
1-octanoic acid	144.2	239	0.068,PR	.909	23	0.0	-	.023		TW
					23	0.9	0.51	.031	16	TW
					23	4.7	0.54	.036	11	TW
					23	9.4	0.69	.081	8.5	TW
					60	0.0	-	.045		TW
					60	0.7	0.93	.059	16	TW
					60	4.0	0.84	.066	13	TW
					60	8.2	0.84	.083	10	TW
					30	0.7	0.60	.026	23	MK
2-ethyl hexanoic acid	144.2	230		.903	30	0.7	0.52	.012	44	MK
2-ethyl-4-methyl pentanoic acid	144				30	0.7	0.49	.0096	51	MK
7,7-dimethyl-octanoic acid	172.3				30	0.7	0.23	.0031	73	MK

Table 3.1, continued

Solvent Name	MW	BP	AS,Ref	DEN	T	AEC	KE	KW	S	Ref
Ketones and Aldehydes										
cyclohexanone	98.2	156	9.32,SA	.948	25	0.0	-	.065		SA
					23	2.3	0.57	.10	5.7	TW
2-ethyl-butyraldehyde	100.2			.810	23	4.7	0.36	.015	23	TW
4-methyl-2-pentanone	100.2	117	1.88,SA	.797	25	0.0	-	.020		SA
					22	id	0.52	.043	12	ST
					25	0.7	0.41	nr		ZA
					30	0.7	0.50	.033	15	MK
3-heptanone	114.2	147	0.41,SA	.818	25	0.0	-	.01		01
					25	2.1	0.59	.013	46	01
					25	8.6	0.46	.020	23	01
5-methyl-2-hexanone	114.2	144		.887	35	id	0.47	.045	11	ST
1-octanal	128.2	171	0.037,DV	.821	23	0.0	-	.009		TW
					23	0.6	0.69	.009	80	TW
					23	3.2	0.59	.012	49	TW
					23	4.2	0.63	.011	55	TW
					23	5.8	0.64	.016	40	TW
					60	3.3	0.42	.013	32	TW
					90	3.1	0.25	.015	17	TW
2-octanone	128.2	173		.820	23	4.1	0.20	.011	18	TW
					67	3.4	0.50	.021	24	TW
2,6-dimethyl-4-heptanone	142.2	168	0.17, SA	.805	24	0.0	-	.0043		SA
					25	4.6	0.11	.0058	19	R1
					24	5.0	0.18	nr		TW
					35	id	0.43	.036	12	ST
					30	0.7	0.19	.0054	35	MK
					25	11.0	0.21	.0081	26	GT
					70	6.0	0.46	.011	42	GT
					70	10.0	0.79	.03	26	GT
					80	1.0	1.3	.036	36	GT
					80	10.0	1.6	.042	38	GT
3,5,5-trimethyl 2-cyclohexen-1-one	138.2	214		.922	30	0.7	0.79	.053	15	MK
decanal	156.3	208		.829	23	4.0	0.48	.008	63	TW
					23	4.7	0.48	.006	81	TW
					72	4.2	0.41	.009	48	TW
2-methyl-4-dodecanone	198.3				30	0.7	0.13	.0031	42	MK

Table 3.1, continued

Solvent Name	MW	BP	AS,Ref	DEN	T	AEC	KE	KW	S	Ref
Esters										
ethyl acetate	88.1	77	7.36,SA	.900	25	0.0	-	.034		SA
					25	.69	0.54	nr		ZA
					20	.05	0.13	nr		KC
n-butyl acetate	116.2	126	0.64,SA	.882	25	0.0	-	.017		SA
					20	.05	0.10	nr		KC
					25	5.0	0.34	.025	14	R1
isobutyl acetate	116.2	112	0.85,SA	.870	25	0.0	-	.0134		SA
					25	4.6	0.21	.011	19	R1
t-butyl acetate	116.2	97		.866	25	4.6	0.24	.012	20	R1
amyl acetate	130.2	149		.875	22	id	0.5	.027	18	ST
isoamyl acetate	130.2	142	0.16, 01	.866	24	0.0	-	.028		01
					35	id	0.47	.043	11	ST
ethyl iso-valerate	130.2	135	0.17, SD	.865	20	0.0	-	.0046		SD
					25	5.9	0.39	.007	54	CM
ethyl hexanoate	144.2	168		.871	23	4.0	0.13	.0049	27	TW
dimethyl phthalate	194.2	284		1.190	23	5.6	0.16	-	-	TW
dibutyl phthalate	222.2	298		1.117	23	6.3	0.12	-	-	TW
					35	id	0.17	.005	33	ST
tri-n-butyl-phosphate	266.3	289		.972	20	0.05	0.44	nr		KC
					25	4.6	0.54	.065	8.3	R1
					25	4.5	0.47	nr		ZA
					35	id	0.79	.091	8.7	ST
					30	0.7	0.79	.066	12	MK
					23	.5-6	0.46	.063	7.3	TW
					60	.5-5	0.79	.070	11	TW
					90	.5-3	0.80	.07	11	TW
tri-isobutyl-phosphate	266.3	264		.968	25	4.6	0.65	.063	10	R1
diethyl carbonate	118.1	126		.974	35	id	0.43	.043	10	ST

Table 3.1, continued

Solvent Name	MW	BP	AS,Ref	DEN	T	AEC	KE	KW	S	Ref
Ethers										
di-isopropyl-ether	102.2	68	1.12, SA	.723	25	0.0	-	.0093		SA
					25	.88	0.22	nr		ZA
di-n-butyl-ether	130.2	142	0.185,01	.766	25	0.0	-	.0010		01
					25	2.1	0.15	.0016	93	01
					25	5.23	0.12	.0019	62	01
di-n-hexyl-ether	186.3	222		.790	25	5.0	0.04	.0007	50	R1
Nitrogen-Containing Compounds										
triethyl amine	101.2	89	7.29,SA	.727	25	0.0	-	.049		SA
					25	0.5	0.93	nr		ZA
quinoline	129.2	238		1.092	21	4.5	1.00	.17	5.8	FJ
					60	4.5	1.12	.15	7.5	FJ
					85	4.5	1.20	.14	8.8	FJ
					100	4.5	1.22	.13	9.4	FJ
5,6,7,8-tetra-hydroquinoline	133.2	251		1.030	21	4.5	1.05	.20	5.3	FJ
					85	4.5	1.30	.072	18	FJ
					100	4.5	1.32	.056	24	FJ
3,4-diethyl-pyridine	135.2				23	3.6	1.07	.167	6.4	TW
decahydro-quinoline	139.2	210		.95	21	4.5	0.94	.047	20	FJ
					60	4.5	1.04	.025	42	FJ
					85	4.5	0.92	.017	54	FJ
2-benzyl-pyridine	169.2	280		1.065	23	4.4	0.47	.061	7.7	TW
2,6-diisobutyl pyridine	191.2				23	5.6	0.015	8.e-4	19	TW
Adogen 364 (tertiary)					25	4.6	0.017	.0012	14	R1
Adogen 368 (tertiary)					30	0.7	0.040	.0089	4.5	MK
Adogen 464 (quaternary)					25	4.6	0.48	.21	2.3	R1
Amberlite XLA3					25	4.6	0.004	.029	.15	R1

Table 3.1, continued

Solvent Name	MW	BP	AS,Ref	DEN	T	AEC	KE	KW	S	Ref
Halogenated Hydrocarbons										
methylene chloride	84.9	40	1.94,SA	1.424	25	0.0	-	.0017		SA
					30	0.7	0.10	.0014	70	MK
					25	6.0	0.145	nr		TW
chloroform	119.4	62	0.78,SA	1.483	25	0.0	-	9.e-4		SA
					23	5.3	0.10	.0017	59	TW
					20	0-.9	0.095	nr		KC
					20	0.5	0.081	7.e-4	170	R1
carbon tetrachloride	153.8	77	.078,SA	1.594	25	0.0	-	9.5e-5		SA
					25	6.6	0.056	nr		TW
					30	0.7	0.021	1.5e-4	140	MK
					20	0.05	0.025	nr		KC
1,2-dichloro-ethane	99.0	83	.868,SA	1.234	25	0.0	-	.0014		SA
					20	0.05	0.025	nr		KC
					30	0.7	0.074	.0015	49	MK
1,2,3-trichlor-opropane	147.4	157		1.388	23	5.0	0.054	.0016	34	TW
1,1,2,2-tetra-chloroethane	167.9	146	.294,SA	1.595	25	0.0	-	.0011		SA
					23	5.1	0.12	.002	54	T2
					25	3.7	0.26	.0076	34	T4
					60	5.6	0.41	.010	41	T4
					30	0.7	0.12	.0008	150	MK
1,1,2-trichloro-trifluoroethane	187.4	48		1.564	20	0.5	0.0094	nr		R1
pentachloro-ethane	202.3	162	.047,SA	1.502	25	0.0	-	3.5e-4		SA
					23	5.0	0.033	4e-4	92	TW
chlorobenzene	112.6	132	.039,SA	1.105	25	0.0	-	3.9e-4		SA
					20	0-.9	0.018	nr		KC
o-dichloro-benzene	147.0	181		1.304	25	0.0	-	2.4e-4		SA
					20	0-.9	0.009	nr		KC
					23	5.5	0.02	7.e-4	25	TW

References for Table 3.1

CM - Chang and Moulton, 1953

CO - Collander, 1951

DC - Dakshinamurty et al, 1972

DV - Davis, 1968

EN - Englin et al, 1965

FJ - Feldman, 1982

G1 - Ginnings and Baum, 1937

G2 - Ginnings and Webb, 1938

G3 - Ginnings and Hauser, 1938

GS - Glasoe and Schultz, 1972

GT - Tedder, 1982

KC - Korenman and Chernorukova, 1974

MK - Munson and King, 1984

O1 - Othmer, White, and Trueger, 1941

OV - Oualline and Van Winkle, 1952

P - Perry and Chilton (eds.), 1973

PR - Peters, 1978

R1 - Roddy, 1981

R2 - Roddy and Coleman, 1981

SA - Sorensen and Arlt, 1979

SD - Seidell, 1941

ST - Soussi and Thyrion, 1981

TW - This Work

UV - Upchurch and Van Winkle, 1952

ZA - Zacchi et al, 1983

calculated from the cited mutual solubility data. It is presented as a distribution coefficient in order to be directly comparable to the other distribution coefficients reported for water.

3.1.1 Hydrocarbons

It is clear from the data in Table 3-1 that the hydrocarbons have distribution coefficients for ethanol at low concentrations which are very small. All aliphatic hydrocarbons have distribution coefficients near room temperature which are in the range of 0.006 to 0.013. Their separation factors, while large at low ethanol concentration, decrease rapidly as ethanol concentration increases. The solubility of water in the series of pure straight-chain hydrocarbons decreases slightly as the size of the chain increases, but the ethanol distribution coefficient also decreases, so the separation factor shows little variation among members of the class with different molecular weights. It is worth pointing out that the separation factor of 310 for cyclohexane is very likely an artifact or an error in Roddy's data. The water distribution coefficient measured in that case, despite the presence of a significant ethanol concentration which would tend to increase it, is less than half that reported by others for the pure solvent.

A number of researchers have examined, both theoretically and experimentally, the nature of alcohol/hydrocarbon solutions. An interesting example is a study of the solubility of water in ethanol-hydrocarbon blends (Kretschmer and Wiebe, 1945). The study determined the concentration of water necessary to cause phase separation in mixtures of ethanol and hydrocarbons to which it was added. The

conclusions were that water "tolerance" (solubility) increases with the volatility of the hydrocarbon. That is, higher molecular weight hydrocarbons containing ethanol will dissolve less water than lower molecular weight. In addition, the presence of any unsaturated bonds in the molecule increases the water solubility.

Solutions of alcohols in hydrocarbons have been studied by those interested in solution structure because they are classic examples of associated solutions. The alcohol forms complexes in solution which can be detected by vapor pressure effects, infrared or other spectroscopic measurements, or measurements of gross solution properties such as dielectric constant. Theoretical treatments of this behavior often involve the assumption of an equilibrium constant for the formation of the polymeric association complexes. Two well-known models of this type are the Mecke-Kempter model (Mecke and Kempter, 1939) and the Kretschmer-Wiebe model (Kretschmer and Wiebe, 1954). They differ only in their assumptions about the form of the equilibrium constant for consecutive addition of monomeric alcohols to a complex. However, a more recent study, involving measurements of the vapor pressure of ethanol over hexadecane solutions (Tucker and Christian, 1977), concluded that continuous association models, like the two mentioned, were inadequate to explain the results obtained. The least complex model that explained their observations involved one equilibrium constant for trimer formation and another for the sequential addition of further monomers to a complex. Practically no dimer is present in ethanol-hexadecane solutions greater than about 0.03 M (0.18 wt. %), according to their analysis. Of course, in equilibrium with dilute aqueous ethanol, the ethanol concentration would be 1/10 that or less.

The effect of the presence of water on the solution structure for alcohol-hydrocarbon mixtures has also been studied (Huyskens et al, 1980). While this study did not include ethanol, the behavior of water was examined in solutions of a series of alcohols from propanols to hexanol in cyclohexane, benzene, and carbon tetrachloride. The results show that the increased solubility of water in the nonpolar solvents with increased alcohol concentration was independant of the degree of self-association of the alcohol. In fact, for dilute alcohol solutions, less than approximately 1 M, the molar ratio of water to alcohol was found to be the same for all alcohols studied; very nearly 1 mole of water per 10 moles of alcohol for cyclohexane and carbon tetrachloride, and 1 mole of water per 5 moles of alcohol for benzene.

The most thorough study of ethanol-water-hydrocarbon systems published to date has been that of Roddy and Coleman (Roddy and Coleman, 1981). Much of the data for n-alkanes in Table 3.1 is from their reported results. It is noteworthy that these researchers found the same kind of linear relationship between water solubility and ethanol concentration that Huyskens et al (1980) reported. Even the ratio of moles of water per mole of ethanol (when considered as net water or total water minus the water that dissolves in pure hydrocarbon) is the same as reported in the previous study, 1:10. Roddy and Coleman used the model proposed by Tucker and Christian (1977) to correlate their data and obtained evidence from infrared studies of the solutions which they claim supports the physical interpretation suggested by those authors.

The effect of ethanol concentration in the aqueous phase on the distribution coefficient for ethanol is practically negligible over a large range of concentration in the dilute region. Above about 25 wt. pct. ethanol, however, the distribution coefficients increase rapidly with increasing ethanol concentration. This behavior is important to some process proposals (to be discussed later) which involve using a hydrocarbon extraction of a concentrated ethanol feed to break the ethanol-water azeotrope.

The effect of temperature on the distribution of ethanol and water between aqueous and hydrocarbon phases has received some attention. In this work, it was found that the ethanol distribution coefficient increased several-fold on increasing the temperature of equilibration from 23 ^{o}C to 65 ^{o}C and 90 ^{o}C. However, the separation factor was observed to decrease. A study of cyclohexane (Roddy, 1981) found that the separation factor decreased only slightly while the distribution coefficient tripled in going from 20 ^{o}C to 40 ^{o}C. Studies of a mixture of high molecular weight alkanes called Isopar L (Tedder, 1982) at high ethanol concentrations show similar increases in ethanol distribution coefficients with moderate temperature increases. The effective enthalpy of ethanol extraction can be estimated from the temperature dependance of the distribution coefficient, as will be discussed in the following chapter. Applying this idea to the data for tetradecane at dilute ethanol concentrations, a value of 7.1 kcal/gmol is obtained. This seems reasonable since it should be expected that, on average, at least one hydrogen bond, broken in the aqueous phase when ethanol leaves it, will not be reformed in the organic phase under dilute concentration conditions.

3.1.2 Aromatic Hydrocarbons

There are some discrepancies in the data presented for extraction properties of derivatives of benzene . While there is relatively good agreement among the various sources of data regarding ethanol distribution coefficients, the water distribution coefficients and resulting separation factors are problematic. The water distribution coefficients reported by Roddy (Roddy, 1981), and confirmed by Munson (Munson and King, 1984) in the cases of benzene and toluene, are significantly lower than the water distribution coefficients for the pure hydrocarbons. Results obtained in this work (for benzene only) show a water distribution coefficient about twice that reported by the others. One possible source of the discrepancies in the case of Roddy's work is an isotope effect not mentioned in his paper. Roddy used tritiated water in his work and there is evidence that a solubility difference of as much as 20 percent may exist between tritiated and normal water. That is the difference reported (Glasoe and Schultz, 1972) between the solubilities of D_2O (which has the same molecular weight as TOH) and H_2O in toluene. In Munson's work, the phases were separated and centrifuged before analysis; there may have been opportunity for evaporative loss of some water in this process. It should be recalled that the initial activities of water and ethanol in the organic phase after equilibration are equal to their aqueous phase activities, so the water (with an initial activity near 1.0) would be lost more quickly than the ethanol if evaporation occured.

In general, however, it can be noted that the distribution coefficients for ethanol into aromatic solvents, although they are roughly five times greater than those for aliphatic hydrocarbons, are

still quite small. The effect of adding substituents to the benzene ring is to decrease the ethanol distribution coefficient somewhat without a large effect on the separation factor. Substituents do markedly decrease the solubility of the compounds in water, however.

The temperature effects for these solvents are similar to those for the aliphatic hydrocarbons. The distribution coefficient for ethanol increases with increasing temperature while the separation factor is little changed.

3.1.3 Alcohols

This class of potential extraction solvents has received more attention than any other, as can be seen from the number of entries in this category in Table 3.1. One reason for this is the relatively high ethanol distribution coefficients which many investigators have found. There is considerable variation in the data for the distribution coefficients and separation factors presented in Table 3.1. Some of this is due to the different conditions of ethanol concentration and temperature employed by different investigators. Some may also be due to the presence of impurities or errors in identification of the solvent. For example, one reference (Roddy, 1981) lists 2-ethyl-heptanol in a table of data, but does not include it in a list of the sources of the solvents used. 2-ethyl-hexanol is included in the latter list, however, and it was assumed in this review that the data given for 2-ethyl-heptanol actually apply to 2-ethyl-hexanol. All the alcohol solvents for which experimental data were obtained in this work were checked to make sure that their

boiling points did not differ by more than 1 ^{o}C from values given in in the CRC Handbook of Chemistry and Physics (Weast, 1975).

The effect of temperature on the extraction properties can be deduced from the data obtained in this work for n-octanol and dodecanol. The ethanol distribution coefficients increase with increased temperature, practically doubling over a moderate temperature range in the case of the higher molecular weight alcohol. However, the separation factors remain the same or increase only slightly. These results indicate that the net enthalpy change for the transfer of ethanol into the alcohol solvent is positive. The extraction thus is apparently entropy-driven, so large distribution coefficients are not to be expected.

The differences among members of the alcohol class in distribution coefficients and separation factors have led to some interesting observations. As would be expected, the distribution coefficients for ethanol and for water decrease with the concentration of the polar OH group in the solvent. This is shown graphically in Figure 3-1. The water solubility in dodecanol measured in this work is felt supported in preference to that reported by Zhuraleva (Zhureleva et al, 1976) because of its consistency with the trend of the other alcohols. The data shown for heptadecanol are highly suspect because this alcohol is a solid below 54 ^{o}C, but the workers who gave the data for 30 ^{o}C mention no difficulties with keeping it liquified (Upchurch and Van Winkle, 1952).

As others have pointed out (Roddy, 1981; Munson and King, 1984) the effect of branching of the hydrocarbon chain is beneficial in that it gives increased ethanol distribution coefficients and separation

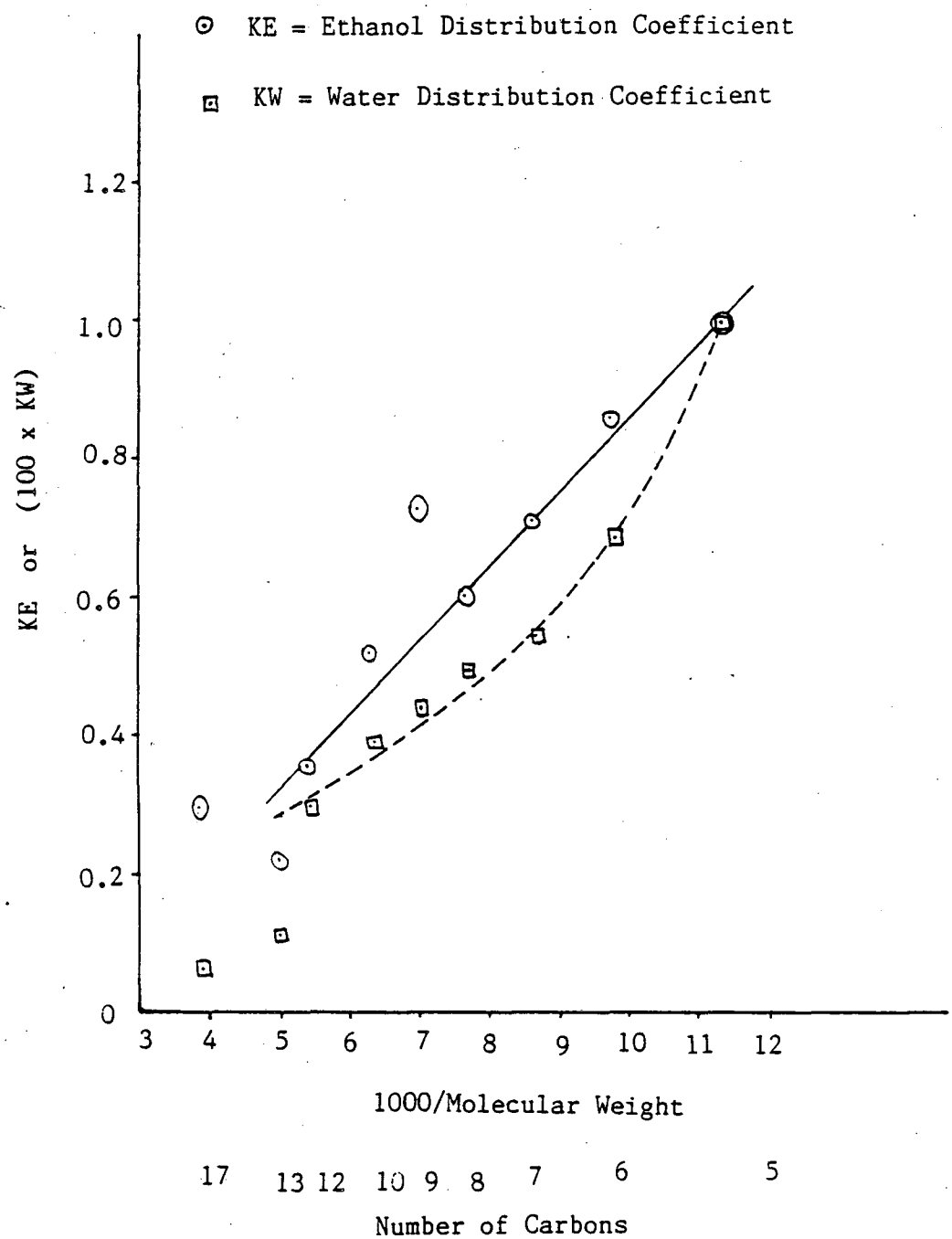


Figure 3-1 Ethanol and Water Distribution Coefficients for n-Alkanols as a Function of Molecular Weight

factors relative to the straight-chain alochol. The reasons for this are not intuitively obvious. Munson (Munson and King, 1984) has shown that a correlation exists between the separation factor and a parameter called the steric cone angle, calculated from the Van der Waals radii of the substituents of the hydroxyl carbon and meant to characterize the steric hindrance of the accessibility of the OH oxygen for hydrogen bonding. The increase in separation factor with the decrease in accessibility of the OH oxygen atom is said to result from the fact that ethanol is a stronger Lewis base than water and forms stronger hydrogen bonds with the OH hydrogen than does water.

There are problems with this interpretation, however. Although the data from Roddy's work (Roddy, 1981) for 3-heptanols and 3-octanols show very high separation factors for alcohols in general, the data for 3-pentanols, which have similar steric cone angles, show average or below average separation factors. In addition, the assertion that ethanol is a stronger Lewis base than water must be considered to be dependant upon the environment of the molecules. It has been pointed out (Huyskens et al, 1980) that the basicity of methanol, as measured by proton affinity, is greater than that of water in the vapor phase, but much less than water's basicity when each is dissolved in t-butanol. This is due to the fact that the water molecule can be stabilized by four hydrogen bonds while the methanol molecule can form only three. The formation of a hydrogen bond polarizes the OH group, making the formation of additional hydrogen bonds more favorable. Thus, in a solvent which can act as a donor or a receptor of hydrogen bond formation, such as an alcohol, water will be a stronger base (and a stronger acid) relative to

ethanol because of the extra synergism which takes place in its case. A final difficulty with Munson's model is that there really should be no more hindrance of hydrogen bond formation to the oxygen electron pairs than to the hydrogen of the solvent OH group. The oxygen is in an sp^3 hybrid state with the two lone pair orbitals, the bond to hydrogen and the bond to carbon arranged in an approximately tetrahedral geometry. The oxygen atom of an OH group approaching to form a hydrogen bond must reach the same distance from the oxygen of the solvent OH group whether it acts as a donor or as an acceptor. In other words, there doesn't seem to be any steric reason for preferential participation of the solvent OH as a donor or acceptor. If any steric effects would be predicted, they would favor the hydrogen bonds formed with water because of the interference of the ethyl group on ethanol with the solvent chain. Despite these shortcomings of the interpretation, Munson's correlation does point out an interesting trend which merits analysis. It seems that an explanation for the behavior may lie in the microstructure of the solutions.

The behavior of water in solutions of alcohols has been a subject of intense study, especially by Alessandro D'Aprano and coworkers at the Istituto di Chimica Fisica in Palermo, Italy. In studies of water in n-alkanols, these researchers have shown that the excess volume of mixing water into dry alkanols is negative (D'Aprano et al, 1978), that the dielectric constant of n-alkanols greater than four carbons long decreases with water addition (D'Aprano, Donato, and Caponetti, 1979), and that the viscosity of n-alkanols greater than C4 decreases with water addition (D'Aprano et al, 1979). All of these phenomena are interpreted by a model which proposes the formation of clusters,

most probably tetrahedral, of solvent alcohol around central water molecules. Of course, the addition of water into the linear or cylic chains of solvent alcohol is recognized, but the observations strongly suggest that a structure of reduced net volume and dipole moment is formed. The tetrahedral complex proposed seems likely in light of the synergistic effects of hydrogen bonding mentioned previously.

The most interesting study of this type, however, involves a comparison of the solution properties of six isomeric pentanols with varying amounts of added water (D'Aprano, Donato, and Agrigento, 1982). In this study, 3 primary pentanols, 2 secondary pentanols, and 1 tertiary pentanol were the subjects of viscosity and dielectric constant measurements at a number of water concentrations up to near saturation. The results are summarized in Figure 3-2. The primary and secondary alcohols all show significant decreases in dielectric constant and viscosity with water addition. In the case of dielectric constant, there is a minimum observed for these alcohols at a water mole fraction of 0.2 (when the molar ratio of solvent to water is 4:1). The tertiary alcohol, however, shows behavior opposite to the rest, its dielectric constant and viscosity increasing monotonically with water addition. The authors point out that the branching and position of the OH on the chain have marked effects on the water-solvent interactions, but stop short of drawing general conclusions.

It seems, however, that general conclusions can be drawn concerning the effects of steric hindrance of the OH group on alcohol-water solutions. The amount of steric hindrance determines what the structure of the alcohol-water solution will be. For primary and secondary alcohols water can either insert into the association chains

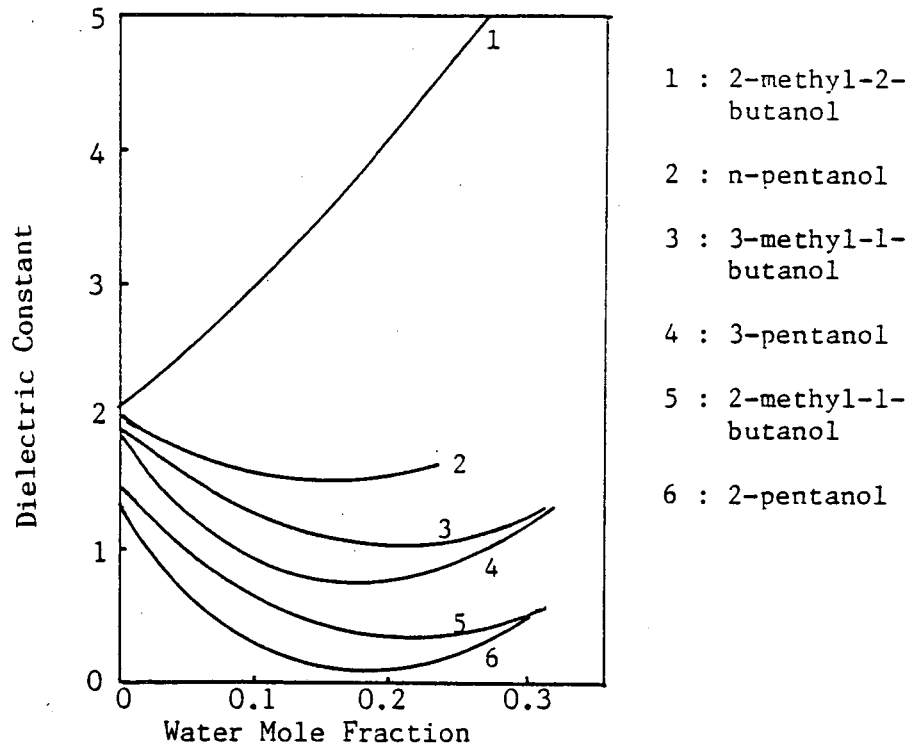


Figure 3-2(a) - Dependence of the Dielectric Constant for Pentanol Solutions on Water Mole Fraction

data from D'Aprano et al (1981)

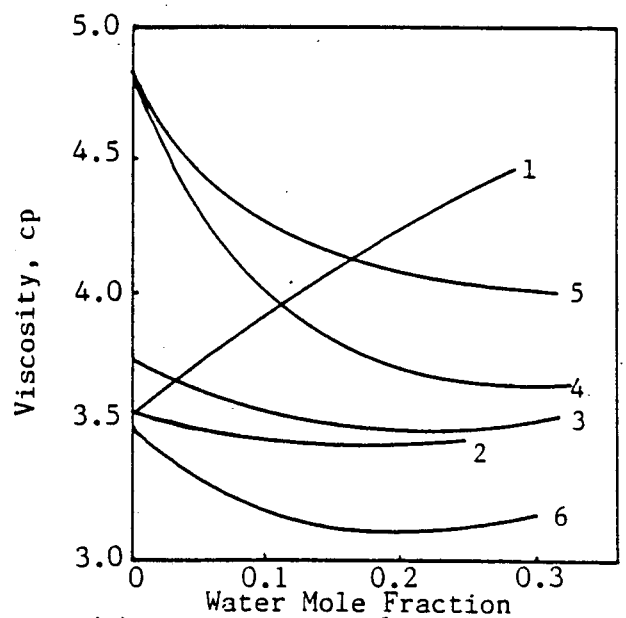


Figure 3-2(b) - Dependence of Viscosity of Pentanol Solutions on Water Mole Fractions

data from D'Aprano et al (1981) .

present in the alcohol or form nuclei for the tetrahedral complexes of solvent molecules. As the degree of steric hindrance increases, the tetrahedral complex is favored. As one goes from the straight chain primary to branched primary to end-locus secondary to middle-locus secondary, the tendency to form the tetrahedral complex increases. However, the tertiary alcohol is apparently too sterically hindered to allow the tetrahedral complex formation, so it remains unassociated and water hydrogen bonds to its OH groups randomly. Further evidence for this model comes from the saturation solubilities of water in alcohol isomers reported by Ginnings and coworkers. In measurements of mutual solubilities for water and the isomers of pentanol (Ginnings and Baum, 1937), the lowest solubility of water is found in 3-pentanol (except for the value reported for n-pentanol, which is lower than that reported by other workers). The greatest water solubility, nearly twice that of the next greatest, was found for the tertiary isomer, 2-methyl-2-butanol. In a study of some isomeric hexanols (Ginnings and Webb, 1938) the lowest water solubilities were found in a branched chain primary, 2,2-dimethyl butanol, followed by a middle-locus secondary, 3-hexanol, while the highest solubilities, nearly equal in all cases, were found for three tertiary isomers. In a study of heptanol isomers, seven tertiary isomers all had water saturation levels between 27 and 31 mole percent while two secondary alcohols had levels of 17 and 18 percent (Ginnings and Hauser, 1938).

Applying this model to an ethanol extraction situation, it can be postulated that ethanol is capable of replacing a solvent alcohol molecule in the formation of tetrahedral clusters. In fact, some alcohols which are too sterically hindered to form clusters themselves

may be able to do so when only three solvent molecules and one ethanol are involved. The formation of the clusters is desirable as this gives rise to the highest separation factors obtainable since the ratio of water to solvent is kept to a minimum. So there is an optimum amount of steric hindrance of the OH group in an alcohol which is to be used to extract ethanol. Too little or too much favors the formation of the linear or cyclic chains into which water can insert readily, lowering the separation factor. This thesis is borne out by the data in Table 3.1, with the single exception of the data reported by Roddy for 3-ethyl-3-heptanol. Discounting that data, the best separation factors for ethanol extraction are those of middle-locus secondary alcohols.

3.1.4 Carboxylic Acids

The limited amount of data on carboxylic acids does not allow one to draw too many general conclusions about their usefulness as extractants. It may be noted that their ethanol distribution coefficients and their solubilities in water are about the same as those of alcohols with similar size and stucture. However, the separation factors of n-octanoic acid, which are higher than those of the corresponding alcohol at low ethanol concentration, fall off much more dramatically as ethanol concentration increases. This may be rationalized by postulating that the n-alkanoic acid does not form the water-centered complex described above for the alcohols. In that case, an ethanol molecule which becomes hydrogen bonded to an acid group increases the net number of sites for potential hydrogen bonding by one, making the organic phase environment more attractive to water.

It should be pointed out that the boiling points of carboxylic acids are much higher than those of the corresponding alcohols. In addition, there is the possibility, if a carboxylic acid is used to recover ethanol, of forming the ethyl ester of the acid. Although tests with pure solvents (Munson, 1983) indicate that the rate of ester formation would be extremely slow, the effect of trace components in a fermentation broth on the rate is unknown. There should be little problem with esters forming as long as water is present, but its presence during the solvent regeneration depends upon the details of the regeneration process.

3.1.5 Ketones and Aldehydes

Ketones have been used as extraction solvents in a number of industrial applications. With respect to ethanol, however, the data in Table 3.1 show that the ketones do not have distribution coefficients as high as some of the alcohols. The separation factors show the same type of ethanol concentration dependance as seen with the carboxylic acids, probably for the same reason.

The aldehydes are a special case of ethanol extraction solvents. The data for octanal and decanal in Table 3.1 shows that these solvents have ethanol distribution coefficients as high as those of the corresponding alcohols at room temperature, and separation factors which are as much as four times greater. The temperature dependance of these properties, however, is exactly the opposite of that for the alcohols and most other solvents. While most solvents show increases of distribution coefficient with temperature, the aldehydes show significant decreases. The most likely explanation for this behavior

is that the ethanol and aldehyde react in the organic phase to form an acetal. Acetal formation is reported to be quite exothermic (Streitweiser and Heathcock, 1981), which can explain the temperature effect on the distribution coefficient. The reaction is reversible, however, so that quantitative recovery of ethanol would be possible. Unfortunately, the high reactivity of the aldehydes responsible for their good ethanol extraction properties probably also preclude their use in a practical industrial process. The oxidation of aldehydes occurs readily in air (Sherman, 1978), but need not be a serious problem since the oxygen level in the anaerobic ethanol fermentation broth is extremely low and there is no reason to expose the solvent to air in a continuous process. The real problem is with the aldol condensation reaction. This reaction, catalyzed by acid or base, can result in polymeric materials, and has produced tar in distillation of aldehyde-containing mixtures (Morrell et al, 1952). The usual method of inhibiting the reaction for the purposes of organic syntheses is to form acetals (Sherman, 1978), but this would, of course, destroy the desirable ethanol extraction properties of the aldehyde. So, the aldehydes, though they have some interesting chemistry with regard to ethanol, are unlikely solvents for an extraction process.

3.1.6 Esters

The use of esters as extraction solvents is well known in the pharmaceutical industry where they are used, for example, to recover penicillin from fermentation broth (Queener and Swartz, 1979). Inspection of the data for this class of solvents in Table 3.1, however, reveals that their distribution coefficients for ethanol are

relatively low and (with the exception of ethyl isovalerate) separation factors are small. The organic phosphates, esters of a special type which are used in extraction processes in the metals recovery industries, have higher ethanol distribution coefficients than the other esters, but even lower separation factors. Diethyl carbonate is very similar to the phosphates in its properties.

The extraction equilibria for esters show no advantages over those for alcohols. In addition, just as carboxylic acids are susceptible to ester formation, the esters are susceptible to hydrolysis, forming the constituent acids and alcohols. The moderately acidic conditions of a typical ethanol fermentation would tend to promote the latter reaction.

3.1.7 Ethers

The small amount of data in Table 3.1 on the ethanol extraction properties of ethers is enough to suggest why this class of compounds has received relatively little attention with regard to ethanol extraction. Although water is not very soluble in ethers, resulting in high separation factors, the ethanol distribution coefficients are quite low, making them unsuitable for consideration in a recovery process.

3.1.8 Nitrogen-Containing Compounds

Data in Table 3.1 on the ethanol extraction properties of nitrogen compounds can be categorized according to the degree of substitution of the nitrogen atom. The primary amine, Amberlite XLA3, shows a very low ethanol distribution coeffient and a separation

factor that is less than one, clearly an undesirable solvent for ethanol recovery.

The data on tertiary amines is intriguing. Triethyl amine has a relatively high reported ethanol distribution coefficient. Its separation factor, inferred from the water miscibility data, would be expected to be 19 or less. It is typical of the amines in showing a decrease in water miscibility with increasing temperature. In fact, it is completely miscible with water below about 19 ^{o}C. Higher molecular weight tertiary amines, the two Adogen products, show much lower ethanol distribution coefficients. This decrease compared to the triethyl amine is far more than can be explained by the decrease in the organic phase concentration of the polar nitrogen atom. The fact that the high distribution coefficients are reported to be recovered in the pyridine derivatives suggests that steric hindrance plays a role in producing the low coefficients of the long chain alkyl-substituted tertiary amines. The high distribution coefficients reported for the quinoline derivatives by Feldman in his patent disclosure (Feldman, 1982) are supported by the data of this work for 3,4-diethyl pyridine. Again, the importance of steric hindrance is brought out by the differences between 3,4-diethyl and 2,6-diisobutyl pyridines. The aromatic nature of the pyridine or quinoline rings are responsible for the low separation factors observed. The improvement seen when this feature is removed makes decahydroquinoline a very interesting solvent for ethanol extraction. Its cost and toxicity are not known, however. Decahydroquinoline is actually a secondary amine, the only one for which ethanol extraction data have been reported.

The one quaternary amine for which data appear in the table shows a reasonable ethanol distribution coefficient, but a very low separation factor. This is not surprising in view of the ionic nature of the compound. More discussion of this type of solvent is given in section 3.3.2.

3.1.9 Halogenated Hydrocarbons

From the data in Table 3.1, it can be seen that halogenated hydrocarbons as a group have relatively large separation factors, but small ethanol distribution coefficients. Only those which have at least one hydrogen atom have distribution coefficients which are high enough to be considered for use in ethanol recovery. This points to the need for a hydrogen bonding site in the solvent. Of the three chlorinated ethanes for which data are presented, the one with the best distribution coefficient is the tetrachloroethane. It has enough electron withdrawing chlorine substitution to make the hydrogen atoms polar, and has twice the number of bonding sites as the pentachloroethane. Increase of the equilibration temperature causes an increase in the distribution coefficient, but a decrease in the separation factor. The relatively high separation factors observed for those halocarbons containing hydrogen supports the contention that ethanol is a better Lewis base than water. It should be mentioned again, however, that this is true only in a nonpolar environment or an environment containing only hydrogen bond donors. The hydrogen containing halocarbons are solvents of the latter type. It would be interesting to test this idea further by examining the ethanol extraction properties of partially fluorinated hydrocarbons to obtain donor-only

solvents of stronger Lewis acidity. Unfortunately, such materials are not commercially available.

In summary, the collected data for pure solvents indicates that the most likely candidates for a successful extraction process for ethanol recovery, based on phase equilibrium considerations, are branched chain alcohols or the secondary amines, particularly decahydroquinoline.

3.2 Solvent Mixtures

There are a number of reasons for considering the use of a solvent mixture for an extraction process. One of these is that it allows the use of components which otherwise could not be used because their viscosities are too high or they are solids at the extraction temperature. Two examples of the latter type of situation have been investigated in this work. One is the use of organic salts to modify extractant properties, a topic to be discussed in section 3.3.2. The other is the use of substituted phosphine oxides as extractants in various diluents.

Table 3.2 contains a summary of data obtained for the ethanol extraction properties of trioctyl phosphine oxide (TOPO) and several other phosphine oxides. The first entry in the table is an estimate of the distribution coefficient of solid TOPO which was obtained by measuring the change in aqueous phase ethanol concentration of a solution equilibrated over a period of several weeks with a finely

divided sample of the waxy solid. The result is probably only accurate to within 20%. Of course, the water distribution coefficient could not be measured. The next entries show the the effect on the ethanol distribution coefficient of adding TOPO to 4-methyl-2-pentanone (methyl isobutyl ketone). There is an increase, relative to the solvent with no additive, which is greatest at the lowest ethanol concentration and falls off as ethanol concentration increases. If the ketone is assumed to extract the same amount of ethanol with or without the TOPO present, then the "extra" amount of ethanol extracted by the TOPO can be calculated by difference. When this is done, it is found that the ratios of the "extra" moles of ethanol extracted to the moles of TOPO present are 0.2, 0.57, and 0.68 for the aqueous ethanol concentrations of 1.8, 7.0, and 15.0 wt.%, respectively. Although the ratio does increase with ethanol concentration, it would appear that a saturation is being approached at less than one mole of ethanol per mole of TOPO. This is reasonable, considering that TOPO can probably form hydrogen bonds with only two H-donors and water is a stronger Lewis acid than ethanol. Support for this view is provided by a study (Roddy and Coleman, 1983) of ethanol extraction by solutions of tributyl phosphate in n-octane. In that study, also, ethanol distribution coefficients were found to decrease as aqueous ethanol concentration was increased, although they increased again at higher concentrations (>15 wt.%). The water distribution coefficient increased 1.5 times as much as the ethanol distribution coefficient as the concentration of TBP in the octane was increased. Separation factors were unfortunately not measured in the ketone studies. However, the data for TOPO in hexadecane show that the separation factor is relatively

Table 3.2 - Ethanol Extraction with Solutions of Phosphine Oxides

KE = Ethanol Distribution Coefficient, org.wt.fr./aq.wt.fr.

S = Separation Factor, ethanol dist. coeff./water dist. coeff.

Phosphine Oxide	Diluent	Phosphine Ox. Wt.%	Aqueous EtOH Wt.%	KE	S
trioctyl	none	100.0	6.2	0.4	-
none	MIBK[1]	-	2.2-15.0	0.18	-
trioctyl	MIBK	25.0	1.9	0.48	-
trioctyl	MIBK	25.0	7.0	0.38	-
trioctyl	MIBK	25.0	15.0	0.27	-
trioctyl	tetradecane	10.9	3.7	0.10	35
trioctyl	hexadecane	17.0	5.1	0.15	23
trioctyl	octanal	38.1	3.3	1.06	36
trioctyl	tetrachloroethane	30.2	3.5	0.28	23
dioctyl	octanal	28.1	3.6	0.78	37
dioctyl	tetrachloroethane	14.6[2]	4.6	0.19	33
tributyl	hexadecane	8.2	5.1	0.02	18
triphenyl	triethylbenzene	3.5	5.6	0.04	22

1) MIBK = methyl isobutyl ketone

2) two organic liquid phases present before and after aqueous ethanol addition

low. It is similar for the other cases of phosphine oxides in nonpolar diluents. The solubilities of the other phosphine oxides in nonpolar diluents is quite low. Dioctyl phosphine oxide has so little solubility in hexadecane that the saturated solution had extraction properties indistinguishable from hexadecane itself. In the polar diluents, however, it is soluble and has effects similar to those of TOPO, increasing the ethanol distribution coefficient and decreasing the separation factor relative to the pure diluent. The octanal diluent cases are notable in that the ethanol distribution coefficients obtained are greater than those of either pure component (even allowing for 20% error in the estimate of the pure TOPO coefficient).

The hope of finding that kind of synergistic effect is another motivation for considering the use of solvent mixtures. Such effects have been reported in a few other cases. Researchers at Texas Technical University (Clements, 1982) reported enhancement of ethanol distribution coefficients of up to 80% relative to the pure components for mixtures of ketones and alcohols. Details of the work are not known, however. Munson found that some mixtures of carboxylic acids and ketones show synergistic effects with regard to their ethanol distribution coefficients (Munson and King, 1984). The most notable example is the system of 2-ethylhexanoic acid and methyl isobutyl ketone in which a 56% increase of the ethanol distribution coefficient over those for the pure compounds (both have KE of about 0.5) is observed for a mixture which is 63 wt.% (54 mole%) acid. No enhancement of separation factor is observed however. A possible explanation for this behavior can be offered, recognizing that carboxylic acids are known to form doubly hydrogen bonded dimers in

the liquid phase. The ketone, by providing alternate hydrogen bonding sites for the acid hydrogen, could break up the dimers. A ketone-acid dimer has the same number (4) of free hydrogen bond acceptor sites as an acid-acid dimer, but the sites could be much less sterically hindered in the former. In accord with this picture, the greatest enhancement of distribution coefficient is greatest when the ketone substituents are least bulky, and the separation factor does not improve because water is a stronger Lewis acid than ethanol, better able to act as a hydrogen bond donor. In fact, for neodecanoic acid in isobutyl hexyl ketone, the separation factor of an equal weights mixture is less than a linear combination of the pure compound factors, probably because the water is less affected by steric hindrance of the large ketone chains.

Far more common than the occurance of synergism is a simple mixing of the properties of pure solvents when they are combined. This is especially true when one of the solvents is a nonpolar diluent. A typical example is illustrated in Figure 3-3, which shows the dependence of ethanol distribution coefficients and separation factors on solvent composition for the system of dodecanol in tetradecane. It can be seen that the ethanol distribution coefficients are very nearly linear combinations of those of the pure components while the water distribution coefficient increases almost exponentially with increasing dodecanol concentration. There is a nearly linear relationship, however, between the ethanol concentration in the organic phase on a solvent-free basis and the solvent composition. In a similar study of mixtures of tridecanol and Norpar-12 (a mixture of high molecular weight alkanes), the same linear relationship between

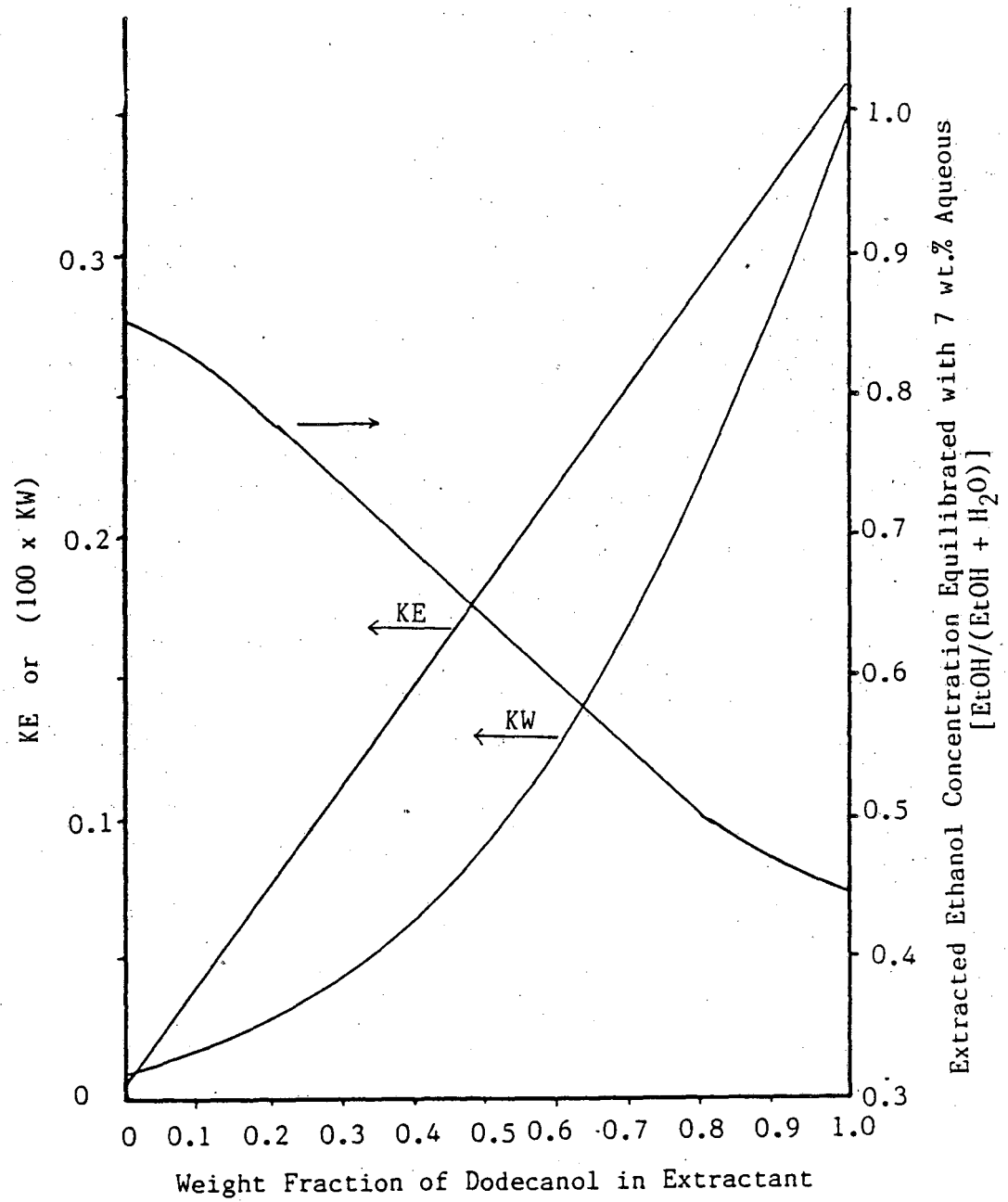


Figure 3-3 Ethanol and Water Extraction by Mixtures of Dodecanol and Tetradecane

ethanol distribution coefficient and mixture composition was observed for extraction from 10 wt.% aqueous ethanol (Tedder, 1982). The water distribution coefficient, however, increased more rapidly with increasing alcohol in the solvent, resulting in the separation factor reaching practically the same value at 50 wt.% tridecanol as at 100 wt.%. In studies of carboxylic acids in toluene, both ethanol distribution coefficients and separation factors were found to vary linearly with weight fraction of the acid in the solvent when the extraction was from aqueous ethanol of less than 1 wt.% (Munson and King, 1984). The aqueous concentration of ethanol has a large effect on separation factors, a fact pointed out by the authors of the tributyl phosphate mixtures study previously mentioned (Roddy and Coleman, 1983). That study, too, found a linear dependance of ethanol distribution on the concentration of the polar extractant. The exact behavior of the water distribution coefficient in mixtures of polar and nonpolar solvents must be regarded as difficult to predict. However, it is obviously possible, using solvent mixtures, to produce an extractant which has properties that can be varied along a continuum, increasing ethanol distribution coefficient at the cost of decreasing separation factor or vice-versa.

3.3 Salt Effects

Because the ethanol distribution coefficients, even for those solvents which have the highest ones, are low by the standards of conventional liquid-liquid extraction process technology, it is natural to search for methods of increasing them. The ability of salts to modify phase equilibria is well known. Thus, the possibility

of applying salt effects in the recovery of ethanol by extraction was investigated.

3.3.1 Aqueous Phase Effects

The phenomenon of "salting out" is one that has been known and studied for nearly a century (Furter, 1977; Furter and Cook, 1967). Most inorganic salts, when added to an aqueous solution of a nonelectrolyte, reduce the activity of the water and increase that of the nonelectrolyte as the water molecules become engaged in the strong hydration interaction with the salt ions. The degree of these effects is dependant on the nature of the salt and of the nonelectrolyte. It is often characterized by the use of a parameter called the Setchenow constant, defined for liquid-liquid equilibrium by the expression;

$$\ln S = k\ c$$

in which S is the separation factor previously defined, c is a measure of the aqueous salt concentration, often mole fraction, and k is the Setchenow constant.

The problem with using salt as a separating agent lies in the fact that high concentrations are needed to realize significant improvements in the separation. Due to the cost of the salt and to environmental considerations, the large amounts of salt used must be recycled in any practical process. So the process that uses salting out must either add a salt recovery operation to separate the salt from the water, or recyle the water and salt together. The former alternative has been used in ethanol recovery on an industrial scale, but only to break the ethanol-water azeotrope. The Hiag distillation uses acetate salts to accomplish this in a process that reuses the

heat required to evaporate the water from the salt mixture (Gorhan, 1933). The application of the idea to direct recovery from a dilute ethanol stream, however, is totally uneconomical. The cost of energy alone to evaporate the amounts of water that must be evaporated from the salt make such a process more expensive than distillation for any feed ethanol concentration which could be produced by fementation.

The other possibility, that of recycling the water and salt in the overall process, is feasible only if the salt does not have deleterious effects on the rest of the process. This is of concern in the case of ethanol production by fermentation because the microorganisms used to carry out the fermentation are easily affected by changes in the conditions of their environment. A study of this idea was carried out and published (Murphy et al, 1982). It shows that, for a common ethanol producing organism, Saccharomyces cerevisae, ethanol yield is too adversely affected by even moderate salt concentrations to allow the realistic proposal of such a process. It leaves open the question, however, of whether any other organisms could be found to operate a salting-out fermentation successfully. Salt-tolerant yeast able to ferment sugars in solutions of sodium and potassium chlorides up to 4 M have been reported, but no details of product yields were given (Yamagata and Fujita, 1974).

3.3.2 Organic Salts as Solvent Modifiers

In the course of an investigation of the literature on salt effects for ethanol and water systems, it was noticed that there are some salts which have effects opposite to the normal salting out observed with most inorganic salts. These are salts of organic mole-

cules, especially quaternary ammonium derivatives, which decrease the relative volatility of ethanol to water when dissolved in aqueous ethanol solutions (Burns and Furter, 1976). Most tetraalkyl ammonium salts are more soluble in ethanol than in water, in keeping with the tendency for salt effects to follow relative solubility. In addition, a study of the hydration of a wide variety of ions in nonaqueous media showed that the hydration of tetrabutyl (and other tetraalkyl) ammonium cations is practically negligible in solutions of salts of these ions in nitrobenzene and o-dichlorbenzene (Arnett, 1977). The same study found only one anion which showed negligible hydration, the tetraphenyl boron anion. These facts led to a hypothesis that organic salts might be effective extractant modifiers for ethanol extraction. Accordingly, a series of experiments was carried out to test this idea.

The tetramethyl, tetraethyl, tetrabutyl, and dodecyl trimethyl ammonium salts of tetraphenyl boron were prepared by mixing aqueous solutions of sodium tetraphenyl boron (from Aldrich Chemicals) and the tetraalkyl ammonium bromides (from Eastman Chemicals). The organic salts precipitated out and were collected by filtering. After drying, the salts were redissolved in hot ethanol and crystallized by cooling and the addition of water. Solutions of the salts in o-dichlorobenzene, Isopar L (a mixture of high molecular weight alkanes), tetrachloroethane, n-octanol, and octanal were equilibrated with aqueous ethanol solutions and analyzed by the methods of Appendix A. In no case, however, was there found any significant change in the ethanol distribution coefficient or separation factor relative to those of the pure solvents. The solubilities of the salts in the solvents were

uniformly very low, in the range 0.1 wt.% (or less) to 1.5 wt.%. This is probably the major reason for their ineffectiveness. If an anion could be found that was smaller than tetraphenyl boron, yet still nonhydrating, it could allow much greater organic salt solubilities in solvents and thus make better ethanol extractants. The other tetraalkyl boron salts are not as stable, however. Attempts to prepare tetraalkyl ammonium salts from lithium tetraethyl boron and sodium tetrabutyl boron (both from Aldrich) were hampered by the fact that these salts are pyrophoric. Crude precipitates of their tetraalkyl ammonium salts were, however, tested for ethanol extraction solvent modifying ability. They decreased separation factors without changing the ethanol distribution coefficients relative to the pure solvents. It is not known whether these results are due to hydration of the tetraalkyl boron anions or to the presence of other species, such as partial hydrolysis products formed during the precipitations.

3.4 Toxicity of Some Solvents to Yeast

The toxicity of potential extraction solvents to the microorganisms of the fermentation is of interest because of the possibilities of recovering ethanol directly from the fermentation as it is produced or of recycling the raffinate stream from an extraction process. Little work has been reported, however, on the effects of potential solvents on yeast, the organisms most commonly used to produce ethanol. One useful study determined the effects of compounds from four homologous series on three species of yeast (Gill and Ratledge, 1972). Although the results varied somewhat from species to

species, generally no inhibition of respiration or growth was found for alkanes of 10 or more carbon atoms, alkenes of 12 or more carbons, alkyl-1-bromides of 11 or more carbons, and 1-alkanols of 14 or more carbons. Of the three species tested, the best ethanol producer (Saccharomyces carlsbergensis) was the least resistant to toxic effects of the solvents. A recent study of extractive fermentation for ethanol production (Minier and Goma, 1982) tested the effects of the n-alkanols on Saccharomyces cerevisae strain UG5. All the n-alcohols between 4 and 11 carbons were found to completely inhibit growth and ethanol production. Dodecanol, tridecanol, tetradecanol, and commercial mixtures of these were found to have practically negligible effects. Another study found several normal and branched chain alcohols of 6 to 8 carbons to be completely toxic to an unidentified yeast, but found that growth and ethanol production continued in the presence of a high molecular weight polypropylene glycol (Pye and Humphrey, 1979).

In this work, the toxicities of a number of solvents were checked in screening experiments. The experimental procedure has been described elsewhere (Murphy et al, 1982). The results of these experiments are summarized in Table 3-3. They show that the hydrocarbons tested, dibutyl phthalate, and trioctyl phosphine oxide are not toxic at all (cell concentration data weren't obtained in the case of dibutyl phthalate due to the formation of a stable emulsion). It is interesting to note that these results parallel those of Playne and Smith (1983), who studied the toxicities of a variety of compounds on a mixture of facultatively anaerobic bacteria. The other solvents tested in this work show varying degrees of toxicity, including

Table 3-3 - Toxicities of Solvents to *S. cerevisae*

solvent concentration	saturation						1/10 saturation			
	f.a.s.c[1]			cell conc.[2]			f.a.s.c		cell conc.	
time (hr.)	22	42	96	22	42	96	22	44	22	44
solvent										
cyclohexane	.95	1.0		.97	.97		.95	1.0	.96	.97
tetradecane	1.0	1.0		1.0	1.0		1.0	1.0	1.0	1.0
tetralin	.10	.10		.05	.05		.82	.98	.79	.87
triethyl benzene	.26	.98		.47	.77		.85	.98	.80	.83
benzoic acid	.04	.04		.10	.11		.74	.91	.33	.37
triethyl citrate	.01	.05		.09	.11		.55	.98	.70	.83
dibutyl phthalate	.97	.99		-	-		1.0	1.0	1.0	1.0
tributyl phosphate	.58	.65		.67	.68		.62	.62	.62	.62
trioctyl phosphine oxide	.99	-	1.0	.95	.96	1.0	-	-	-	-
pentachloro-ethane	.01	-		0.0	-		.90	-	.84	-
dodecanol	.01	-	.99	0.4	.99	1.0	.99	-	.97	-
224tmp/hxn[3]	0.0	-	.81	.02	.80	.46				
dal/hxn[4]	0.0	-	.98	.01	.21	.64				

(1) fraction of available sugar consumed, relative to control

(2) cell concentration by optical density, relative to control

(3) 5 vol.% 2,2,4 trimethylpentanol in hexadecane

(4) 5 vol.% decanal in hexadecane

dodecanol. The difference between the result for dodecanol shown here and that obtained by Minier and Goma may be the result of using a different strain of the organism or the result of adaptation in the latter case. In the study by Gill and Ratledge (1972), dodecanol was found to be completely toxic to Candida 107 and to Saccharomyces carlsbergensis, but not at all toxic to C. tropicalis. Dodecanol, like several of the other solvents, apparently induces an extended lag phase on the yeast when contact is made. This effect has been noted also in a study of the toxicities of extraction solvents on algae and bacteria (Dave et al, 1979). The observed effects of tributyl phosphate are unusual in that growth and sugar utilization apparently stopped before completion after a significant period of activity. Evaporation of some of the solvents over the several-day experiment may be partially responsible for the increased growth seen late in some of the runs, particularly the mixed solvents for which data are given at the bottom of Table 3-3. Alternatively, this growth may be an effect of the reduced activity of the toxic solvent in the aqueous phase due to the presence of the inert cosolvent. Such effects were clearly demonstrated in a number of cases by Gill and Ratledge (1972). They suggest a method for using a toxic solvent in an extractive fermentation or an extraction with water recycle. That is, treatment of the raffinate from the toxic solvent extraction with an inert solvent could be used to remove enough of the toxic compound from the stream to allow recycle without toxic effects. The use of such a dual solvent extraction process has been proposed previously for the recovery of effective solvents having significant solubilities in water (Earhart et al, 1977).

REFERENCES

1. Arnett, E.M., Chawla, B., and Hornung, N.J. (1977) J. Soln. Chem., **6**(12):781

2. Burns, J.A., and Furter, W.F. (1976) Adv. Chem. Ser. **155**:99

3. Chang, Y., and Moulton, R.W. (1953) Ind. Eng. Chem., **45**(10):2350

4. Clements, L.D. (1982) "Executive Summary of Research Presented at SERI Alcohol Fuels Contractor's Meeting, May 1982", Center for Energy Research, Texas Tech University

5. Collander, R. (1951) Acta Chim. Scand., **5**:774

6. Dakshinamurty, P., Chiranjivi, C., Rao, P.V., and Subrahmanyam, V. (1972) J. Chem. Eng. Data, **17**(3):379

7. D'Aprano, A., Donato, D.I., and Agrigento, V. (1982) J. Soln. Chem., **11**(4):259

8. D'Aprano, A., Donato, D.I., and Caponetti, E. (1979) ibid., **8**(2):135

9. D'Aprano, A., Donato, D.I., Caponetti, E., and Agrigento, V. (1978) Gazzetta Chimica Italiana, **108**:601

10. D'Aprano, A., Donato, D.I., Caponetti, E., and Agrigento, V. (1979) J. Soln. Chem., **8**(11):793

11. Dave, G., Blanck, H., and Gustafsson, K. (1979) J. Chem. Tech. Biotech., **29**:249

12. Davis, P.L. (1968) J. Gas Chrom., **6**:518

13. Earhart, J.P., Won, K.W., Wong, H.Y., Prausnitz, J.M., and King, C.J. (1977) Chem. Eng. Prog., **73**(5):67

14. Englin, B.A., et al (1965) Khim. Tekhnol. Topl. Masel, **9**:42

15. Feldman, J. (1982) Process for Recovering Ethanol from Dilute Aqueous Solutions Employing Liquid Extraction Media U.S. Patent number 4,346,241

16. Furter, W.F. (1977) Can. J. Chem. Eng., **55**:229

17. Furter, W.F., and Cook, R.A. (1967) Int. J. Heat Mass Transfer, **10**:23

18. Gill, C.O., and Ratledge, C. (1972) J. Gen. Microbiol., **72**:165

19. Ginnings, P.M., and Baum, R. (1937) J. Am. Chem. Soc., **59**:1111

20. Ginnings, P.M., and Hauser, M. (1938) ibid., **60**:2581

21. Ginnings, P.M., and Webb, R. (1938) ibid., **60**:1388

22. Glasoe, P.K., and Schultz, S.D. (1972) J. Chem. Eng. Data, **17**:66

23. Gorhan, A. (1933) Int. Sug. J., **35**:266

24. Huyskens, P.L., Haulait-Pirson, M., Hanssens, I., and Mullens, J. (1980) J. Phys. Chem., **84**(1):28

25. Korenman, I.M., and Chernorukova, Z.G. (1974) J. Appl. Chem. U.S.S.R., **47**(11, pt.2):2595

26. Kretschmer, C.B., and Wiebe, R. (1945) Ind. Eng. Chem., **37**(11):1130

27. Kretschmer, C.B., and Wiebe, R. (1954) J. Chem. Phys., **22**:425

28. Mecke, A., and Kempter, H. (1939) Naturwissenschaften, **28**:583

29. Minier, M., and Goma, G. (1982) Biotech. Bioeng., **24**:1565

30. Morrell, C.E., Carkson, C.S., McAteer, J.H., Robey, R.F., and Smith, P.V.,Jr. (1952) Ind. Eng. Chem., **44**:2839

31. Munson, C.L. (1983) personal communication of unpublished data

32. Munson, C.L., and King, C.J. (1984) Ind. Eng. Chem. Process Des. Dev., **23**(1):109

33. Murphy,T.K., Blanch, H.W., and Wilke, C.R. (1982) Process Biochem., **17**(6):6

34. Othmer,D.F., White,R.E.,and Trueger, E. (1941) Ind. Eng. Chem. **33**(10):1240

35. Oualline, C.M., and Van Winkle, M. (1952) Ind. Eng. Chem., **44**(7):1668

36. Perry, R.H., and Chilton, C.H., eds. (1973) Chemical Engineer's Handbook, 5th Edition, McGraw-Hill, New York

37. Peters, R.A. (1978) "Alcohols, Higher Aliphatic" in Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed, v. 1, p. 716 John Wiley & Sons, Inc., New York

38. Playne, M.J., and Smith, B.R. (1983) Biotech. Bioeng., **25**:1251

39. Pryde, E.H. (1978) "Carboxylic Acids" in ibid., v. 4, p. 814 John Wiley & Sons, Inc., New York

40. Pye, E.K., and Humphrey, A.E. (1979), "The Biological Production of Liquid Fuels from Biomass", report for D.O.E. contractors meeting Sept. 1979, University of Pennsylvania

41. Queener, S., and Swartz, R. (1979) "Penicillins: Biosynthetic and Semisynthetic" in Economic Microbiology, v.3, A.H. Rose, ed. Academic Press, New York

42. Roddy, J.W. (1981) Ind. Eng. Chem. Process Des. Dev. **20**(1):104

43. Roddy, J.W., and Coleman, C.F. (1981) Ind. Eng. Chem. Fundam. **20**(3):250

44. Roddy, J.W., and Coleman, C.F. (1983) Ind. Eng. Chem. Fundam. **22**(1):51

45. Seidell, A. (1941) Solubilities of Organic Compounds, Van Nostrand Co., New York

46. Sherman, P.D. (1978) "Aldehydes" in Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., John Wiley & Sons, New York

47. Sorensen, J.M., and Arlt, W. (1979) Liquid-Liquid Equilibrium Data Collection, Binary Systems Chemistry Data Series, vol. 5, part 1 DECHEMA, Frankfurt

48. Soussi, A., and Thyrion, F.C. (1981) Proc. World Congress Chem. Eng. **4**:443

49. Streitwieser, A,Jr., and Heathcock, C.H. (1981) Introduction to Organic Chemistry, MacMillan, New York

50. Tedder, D.W. (1982) "Fuel-Grade Ethanol Recovery by Solvent Extraction - Technical Progress Report" Solar Energy Research Institute contract number XK-0-9082-1

51. Tucker, E.E., and Christian, S.D. (1977) J. Phys. Chem., **81**(13):1295

52. Upchurch, J.C., and Van Winkle, M. (1952) Ind. Eng. Chem., **44**(3):618

53. Weast, R.C., ed. (1975) CRC Handbook of Chemistry and Physics, 56th ed., CRC Press, Cleveland

54. Yamagata, K., and Fujita, T. (1974) J. Ferm. Technol., **52**(4):217

55. Zacchi, G., Aly, G., and Wennersten, R. (1983) "Investigation of Ethanol Extraction from Fermentation Liquors" presented at A.I.Ch.E. International Solvent ExtractionConference, Denver, Colorado Paper no. 366

56. Zhuraleva, I.K., Zhuralev, E.F., and Salamatin, L.N. (1976) Zh. Obshch. Khim., **46**:121

4. MODELLING OF LIQUID-LIQUID EQUILIBRIA

There are several reasons for developing models for liquid-liquid equilibrium behavior. The most obvious is the need to interpolate and extrapolate experimental data for systems of interest. That need arises in the design of processes involving liquid-liquid contacting, especially solvent extraction processes. It will be shown in this chapter that relatively simple models can be used to correlate equilibrium data for the systems of interest in the extraction of ethanol from dilute aqueous solution.

Nevertheless, there are reasons to consider the use of more complex models of liquid-liquid equilibria, particularly those with a theoretical foundation in the statistical thermodynamics of liquid mixtures. It is useful, of course, to have a theoretical format for the interpolation and extrapolation of experimental data. Beyond this, however, the methods considered have some ability to predict experimental results even in the absence of any data for the system of interest. This ability is worth critical evaluation because it could be used to reduce the number of systems for which one would need to gather experimental data, and allow prediction of phase equilibrium properties for solvent systems which could be synthesized. If methods such as these could be perfected, it would be possible to use calculational procedures to select extraction solvents and perhaps even to design new, efficient extraction solvents from a molecular approach. This chapter, therefore, includes analysis of a theoretical approach as well as empirical methods useful in modelling the equilibrium behavior of ethanol, water, and extraction solvents.

4.1 Empirical Correlations of Ethanol and Water Extraction Data

There are two variables which can have effects of practical importance on the phase equilibrium behavior of systems containing one solvent in equilibrium with dilute aqueous ethanol. These are the temperature of the system and the ethanol concentration. While the pressure of the system can theoretically affect liquid-liquid equilibria, for pressures below 100 atmospheres these effects are not significant. One consequence of this is that there can be no thermodynamic consistency test for liquid-liquid equilibria as there is for vapor-liquid equilibria (Sorensen and Arlt, 1979). In addition, the pressure independance of liquid-liquid equilibria decreases the amount of information required to specify a system. According to Gibb's Phase Rule (Prausnitz, 1969), there are three degrees of freedom in a system with three components and two phases. If the temperature and pressure of the system are fixed, then specification of the mole fraction of a single component in either phase serves to completely fix the remaining variables of the system. Because pressure has so little effect on the equilibrium behavior, it can be considered constant even if it actually changes with system composition. The phase rule does not necessarily imply that any of the component mole fractions is sufficient, however; only that one of them must be. For systems in which the three components form two miscible pairs and one partially miscible pair (often referred to as Type 1 systems), it seems logical that the component which forms two miscible pairs should allow specification of the system. Thus, for the ternary systems of interest in this study, the temperature and the ethanol concentration should suffice to determine the other concentrations. Empirical

correlations have been developed for describing the effects of these variables on the equilibrium behavior. For systems in which the solvent is a mixture of two or more components, the solvent composition is obviously a third important variable. This subject was discussed in the previous chapter (section 3.2), however, and will not be treated here.

4.1.1 Effects of Ethanol Concentration

The ethanol distribution coefficients for pure solvents change very little over the aqueous ethanol concentration range of interest, 0 - 15 wt.%. For nonpolar solvents, the distribution coefficient is quite constant. Since the activity coefficient of ethanol in the aqueous phase decreases with increasing ethanol concentration (see Figure 4-4), there must be a concomitant decrease in the ethanol activity coefficients in the nonpolar solvent. This is probably due to the formation of complexes, as discussed in section 3.1.1. Since ethanol has a higher concentration of polar groups per unit volume than even the polar solvents, increasing its concentration in a solvent tends to increase its distribution coefficient by increasing the effective concentration of polar groups (see Figure 3-1).

While this holds the ethanol distribution coefficient constant or to moderate increases with increasing ethanol concentration, it has a more dramatic effect, in general, on the water distribution coefficient. Thus, despite the fact that the water activity in the aqueous phase decreases as ethanol concentration increases, the water distribution coefficient increases enough to make separation factors a decreasing function of ethanol concentration.

The behavior of distribution coefficients as a function of ethanol concentration has been characterized by the use of an empirical equation of the form (Tedder, 1982);

$$\ln KE \text{ (or } \ln KW) = a + b\, X_e \quad , \qquad (4\text{-}1)$$

where **KE** is the ethanol distribution coefficient, **KW** the water distribution coefficient, X_e the equilibrium aqueous ethanol weight fraction, and **a** and **b** are empirical constants for a given solvent at a given temperature. An example is shown in Figure 4-1 which shows data for 2-octanol. The empirical equations fit by Tedder and coworkers are also shown on the plot. It can be seen that the ethanol distribution coefficient increases very little over the dilute concentration range, but the water coefficient increases significantly. The result is typical for polar solvents. The constant **b** in the ethanol distribution coefficient correlation is less than 2.0 for most solvents that have been characterized, indicating that the distribution coefficient increases by a maximum of 35% as ethanol concentration increases from 0 to 15 wt.%. On the other hand, the constant **b** for water is generally in the range of 5 to 9, and for a value of 7 the water distribution coefficient almost triples in the same range of aqueous ethanol concentration.

An alternative correlation method can be derived from the hypothesis that, in the dilute concentration range, there is a proportionality between the number of moles of ethanol in the organic phase and the number of moles of water "extracted" into the phase. That is, the amount of water in the solvent above the amount dissolved in the absence of ethanol is taken to be a constant factor times the ethanol concentration. This idea leads to the following equation for the

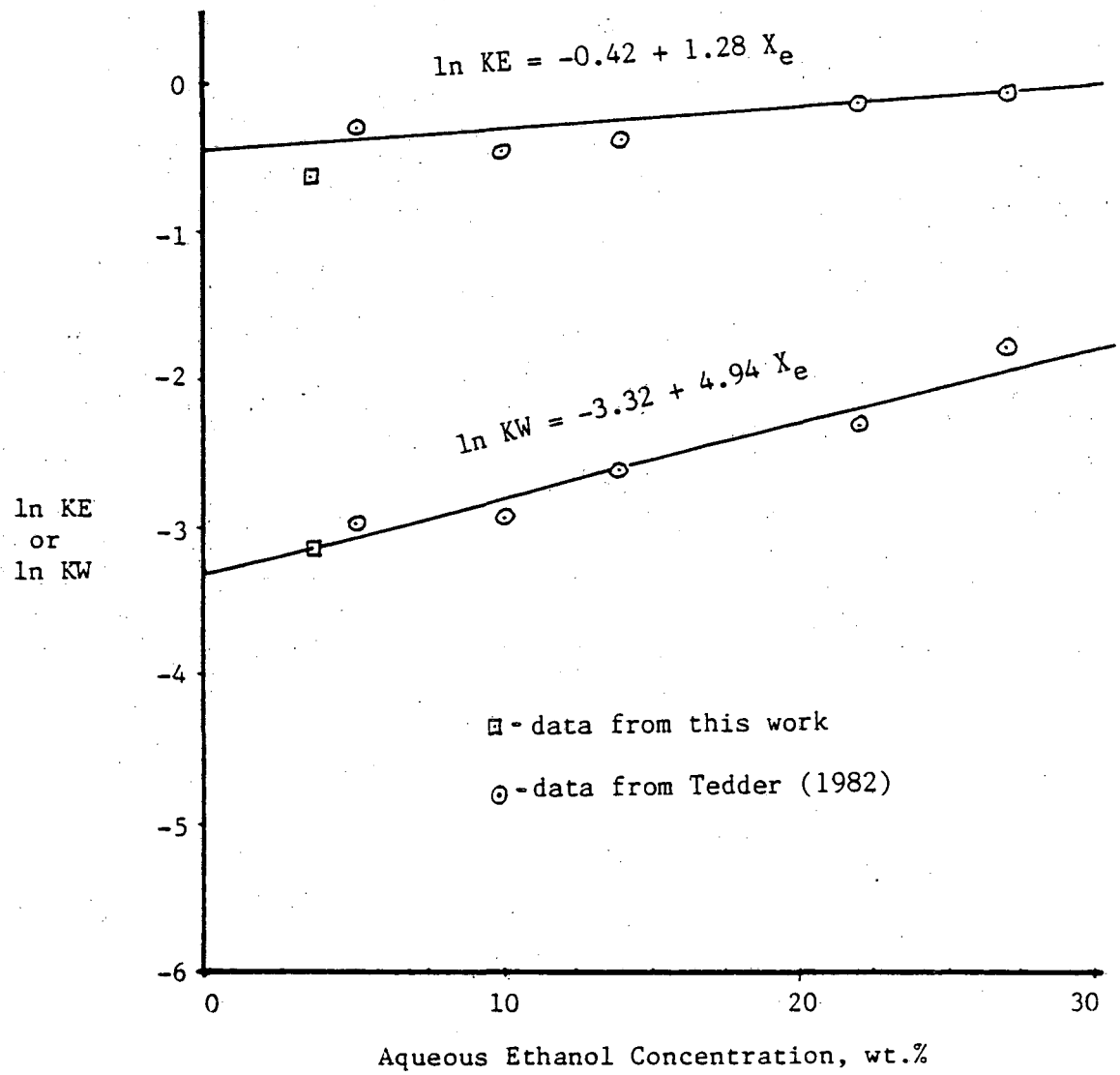


Figure 4-1 - Effect of Aqueous Ethanol Concentration on Distribution Coefficients for 2-Octanol

water distribution coefficient;

$$KW = \frac{KW(0) + r\ X_e}{1 - X_e} \tag{4-2}$$

in which **KW(0)** is the water solubility in the solvent with no ethanol present, **r** is the weight ratio of extra water to ethanol in the solvent phase, and the other terms are the same as those defined above. The solubility of the solvent in the aqueous phase has been neglected as it is generally small enough to ignore. Using this expression in the definition of the separation factor, and taking the ethanol distribution coefficient to be constant for simplicity, the following relation can be derived for the ratio of the separation factor at a dilute ethanol concentration to its value at infinite dilution;

$$\frac{S}{S(0)} = \frac{1 - Xe}{1 + S(0)\ r\ X_e} \tag{4-3}$$

in which **S(0)** is the separation factor at infinite dilution and the other terms are as previously defined. The behavior of this model is shown in Figure 4-2. Two cases are presented. The higher curves of organic ethanol concentration are those for a solvent with an infinite dilution separation factor of 100 and **r** values of 0 and .039. The latter corresponds to a ratio of one extra mole of water extracted for each ten moles of ethanol in the organic phase. This is the ratio, and a typical separation factor, that have been observed for nonpolar solvents, including aliphatic and aromatic hydrocarbons, that have been discussed in chapter 3. The second case in Figure 4-2 is for a solvent with an infinite dilution separation factor of 20 and **r** of 0.195 (0.5 mole of extra water per mole of ethanol). The behavior is characteristic of some polar solvents such as alcohols and ketones. In both cases, the curve for **r**=0 is shown for comparison. Also

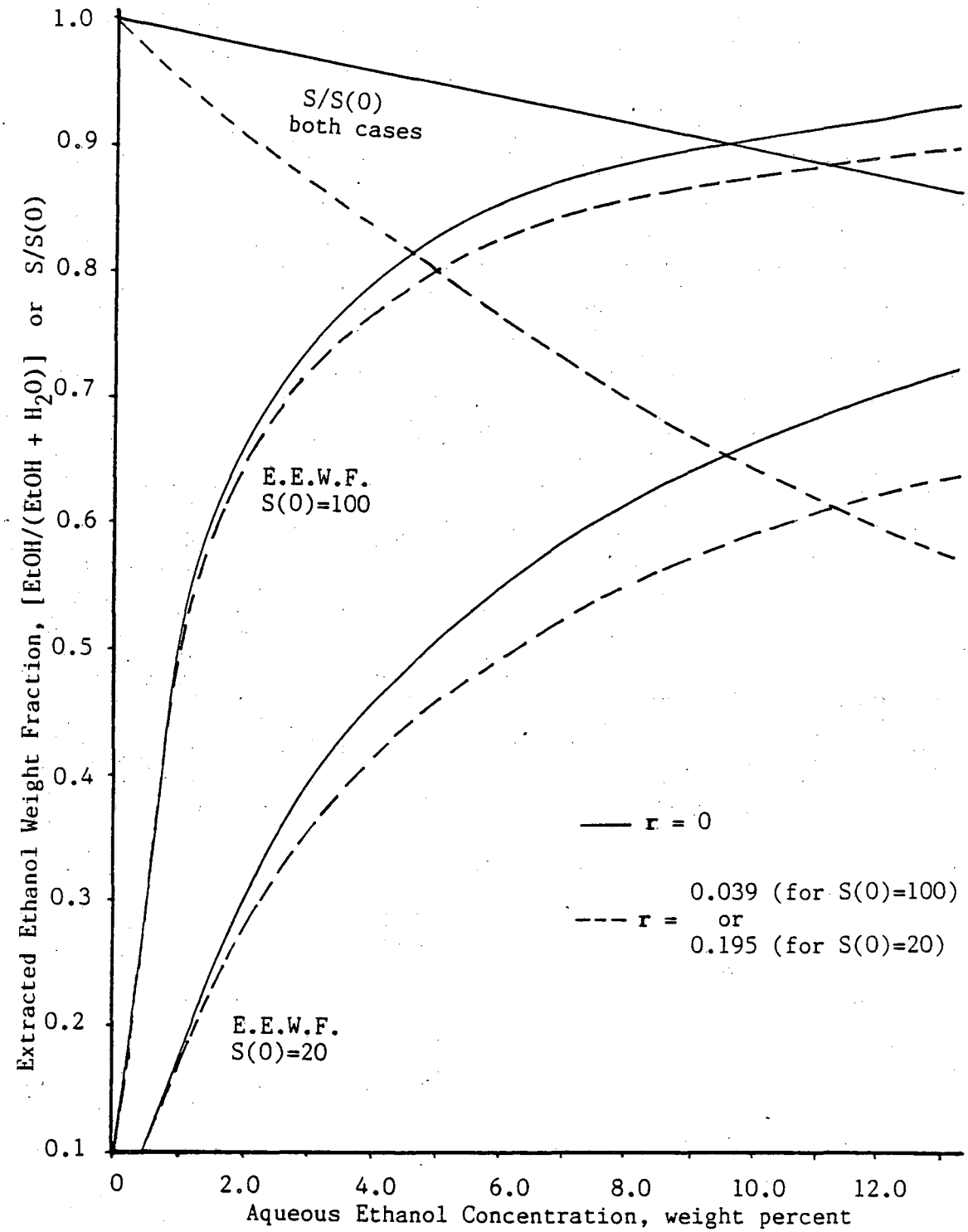


Figure 4-2 Effect of Aqueous Ethanol Concentrations on Separation Factors and Extracted Ethanol Concentrations Predicted by a Constant Molar Ratio Model

plotted in the figure are the ratios of the separation factors to the infinite dilution values. In both cases, when r=0 the separation factor ratio is a linearly decreasing function of X_e. In addition, because of the parameters used, the ratios for the two cases with finite **r** values are also the same. They show the dramatic lowering of separation factor caused by the coextraction of water. Figure 4-3 shows water distribution coefficient data for two octanols and the curves calculated using this method. The **r** values for the two cases correspond to molar ratios of extra water to ethanol of .35 and .44 for the n-octanol and 2-octanol respectively. Other solvents show different ratios, but **r** values for polar solvents seem to lie in the range of 0.1 to 0.3. The correlation does not work well at higher concentrations, however. Parameters obtained from data at dilute concentrations will always underestimate the water distribution coefficient at higher concentrations. For aqueous concentrations greater that 15 wt.%, Tedder's exponential form gives better results.

4.1.2 Temperature Effects

The data reviewed in the previous chapter show that the temperature of equilibration has large effects on the phase equilibrium behavior. Except for the aldehydes, which were discussed in section 3.1.5, most solvents show increases in the ethanol distribution coefficient with increased temperature. While the water distribution coefficient also increases with temperature for most solvents (except for many of the amines), the separation factor changes little, tending to decrease slightly in the cases of nonpolar solvents and to increase slightly in the cases of polar solvents.

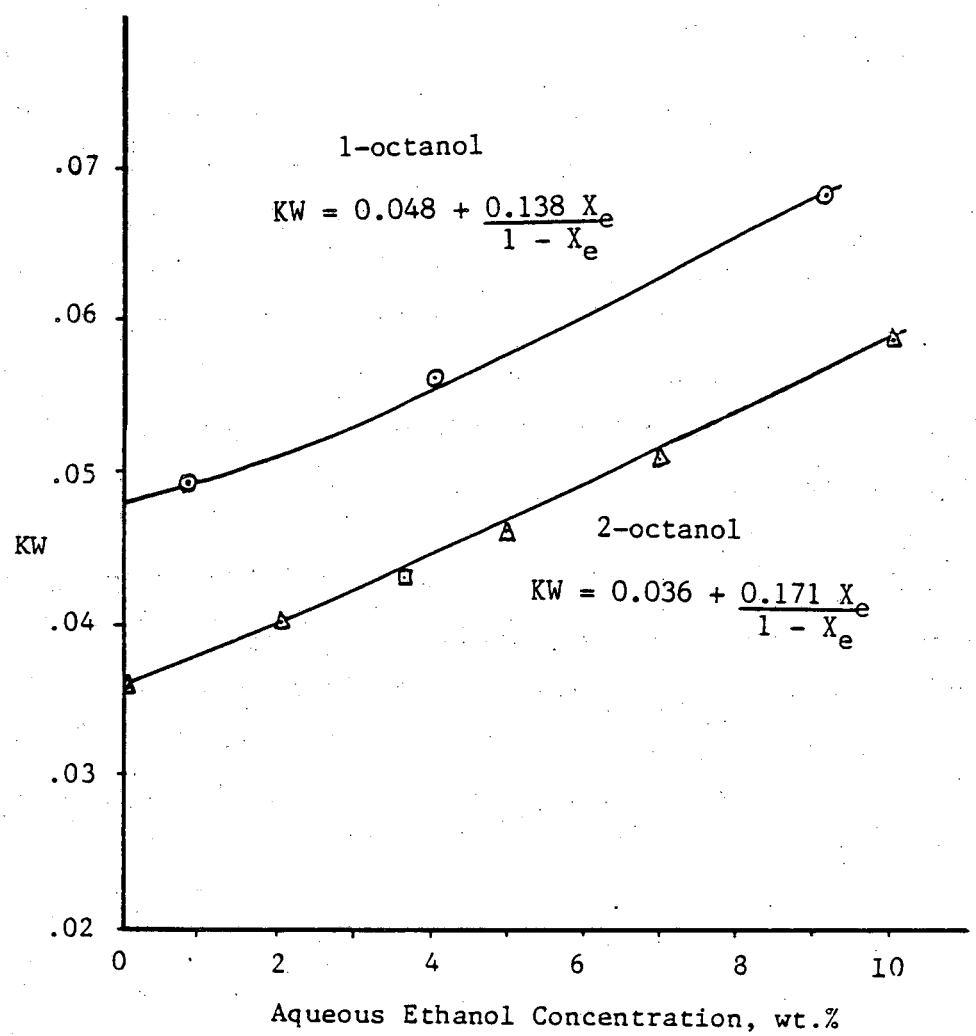


Figure 4-3 - Effect of Aqueous Ethanol Concentration on Water Distribution Coeffecient for Two Octanols

Because the increases in distribution coefficients are seen over a wide variety of solvent types, it is logical to examine the aqueous phase in seeking an explanation for the behavior. Recalling that the distribution coefficient for a component is determined by the ratio of the activity coefficients in the two phases, it is of interest to note the effect of temperature on the activity coefficients of ethanol and water in binary aqueous solutions. Figure 4-4 shows these parameters at two temperatures, 30 ^{o}C and 90 ^{o}C, as calculated from vapor pressure data (Pemberton and Mash, 1978). As shown in the figure, the activity coefficient of ethanol at low concentrations does increase with temperature, but by a maximum of 50%. This may provide a partial explanation for the increases in ethanol distribution coefficients observed. It is a somewhat unusual situation, because it is more common for solutions to behave more ideally as the temperature increases, with activity coefficients tending to approach unity. This must be case in the organic phase to explain the temperature dependance of the distribution coefficients. The activity coefficient for water in the organic phase is of course very large, as it must be to maintain partial miscibility, and decreases with increasing temperature for most solvents as reflected in increasing water solubility with temperature (except for many amines, again, which show the opposite behavior). The activity coefficient for ethanol in the solvent phase will probably be close to what it would be in a binary system. The infinite dilution activity coefficients of ethanol have been measured by differential ebulliometry (Thomas et al, 1982) in a number of solvents. Without exception, the ethanol activity coefficients at infinite dilution decreased with increases in temperature

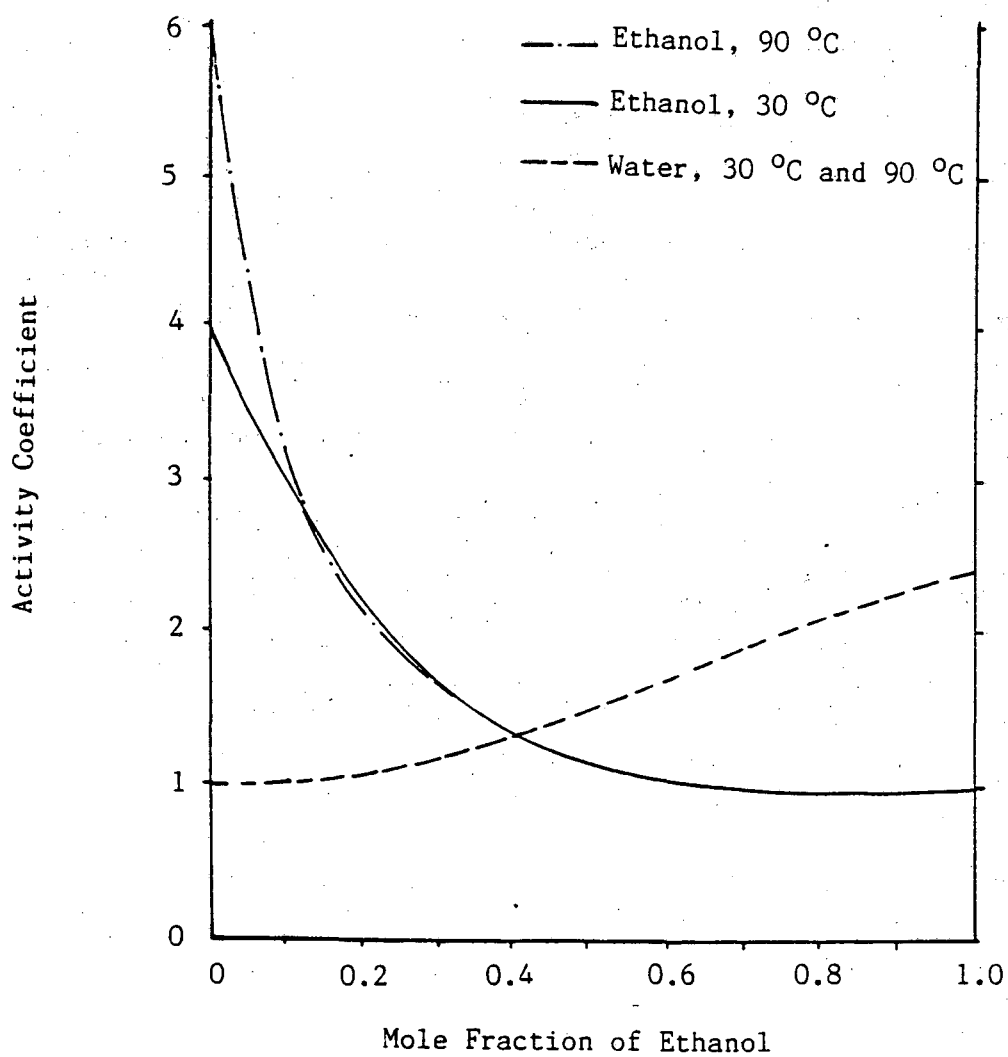


Figure 4–4 Activities of Ethanol and Water in Binary Mixtures

for the systems measured. The effect is most dramatic for the most nonpolar solvents. Thus, the infinite dilution activity coefficient of ethanol in hexane was found to decrease from 38 at 32 ^{o}C to 23 at 50 ^{o}C. In a polar solvent the effect is less dramatic, as in the case of 2-butanone the coefficient decreases from 2.26 at 42 ^{o}C to 1.74 at 75 ^{o}C. For an alcohol, n-decanol, vapor-liquid equilibria measurements (Singh and Benson, 1968) have shown that the ethanol activity coefficient of ethanol at a concentration of 3 wt.% decreases from 1.3 at 20 ^{o}C to 1.25 at 50°C. Thus, the increases in distribution coefficients observed with increases in temperature may be due to decreases in the solvent phase activity coefficients while the aqueous phase coefficients remain constant or, in the case of ethanol when it is quite dilute, actually increase.

A qualitative explanation of the behavior can be proposed, based on a consideration of the intermolecular forces involved. The strength of dipole-dipole interactions, including hydrogen bonding, is inversely dependant on temperature because it depends upon favorable orientations between molecules (Prausnitz, 1969). Higher temperatures randomize the intermolecular orientations by increasing the rotational energy of the molecules. For a given rotational energy, however, the rotational velocity of a molecule is inversely proportional to the square root of its moment of inertia. Since the molecules of solvents considered for use in ethanol extraction are all larger than ethanol (and water), they will have larger moments of inertia and their rotational velocities at a given temperature will be less. Hence, the disruption of dipolar interactions in the solvent phase might be expected to be less than in the aqueous phase. There is no direct

effect of temperature on the induced dipole and dispersion forces between molecules, so the forces acting on ethanol and water in a nonpolar solvent, while much weaker than those in a polar one, are not decreased by increasing temperature.

Empirical correlation of temperature effects on distribution coefficients has been obtained with the use of equations of the following form (Tedder, 1982);

$$\ln KE \text{ (or } KW) = a + bX_e + c/T \qquad (4\text{-}4)$$

in which the empirical constants **a** and **b** are different from the ones used in equation (4-1) and the temperature T is in ^{o}K. The use of the equation is based on the observation that a plot of the logarithm of the distribution coefficients versus the reciprocal of absolute temperature yields a straight line in most cases. However, only a relatively small range of temperature, 20-90 ^{o}C, has been investigated. The constant **c** typically is in the range of -1000 to -3000 ^{o}K, with the values for water and ethanol being close for a given solvent. "Apparent" thermodynamic properties have been calculated from these values. These calculations should be based on distribution coefficients which are in terms of mole fractions because they are based on the temperature dependance of activity coefficients. For any component i, the activity coefficient, Y_i is related to the excess partial molar excess Gibb's free energy, g^E_i, by the equation;

$$g^E_i = RT \ln Y_i \qquad (4\text{-}5)$$

The partial molar excess enthalpy of the component, h^E_i, can be found from the temperature derivative;

$$\frac{\partial g^E i/RT}{\partial 1/T} = \frac{\partial \ln(Yi)}{\partial 1/T} = \frac{h^E_i}{R} \qquad (4\text{-}6)$$

Since the mole fraction distribution coefficient is the ratio of the activity coefficient in the aqueous phase to that in the organic phase, the derivative of its logarithm with respect to reciprocal absolute temperature gives the difference between the partial molar excess enthalpies of the component in the two phases;

$$\frac{\partial \ln Ki(mol)}{\partial 1/T} = \frac{h^E i(aqueous) - h^E i(solvent)}{R} \qquad (4\text{-}7)$$

The distribution coefficient on a weight fraction basis can be expressed as a factor, which depends on concentration, times the mole fraction distribution distribution coefficient. The conversion factor drops out when the temperature derivative is taken. Thus, apparent enthalpies for the transfer of ethanol and water from the aqueous phase to the solvent can found from the values of **-c** used in equation (4-4). These values are positive, ranging from 2 to 7 kcal per mole of ethanol or water. Negative values reported by Tedder (1982) were the result of treating the extraction as a reaction and setting the derivative of the log of **KE** equal to an apparent enthalpy change for the process, an obviously erroneous approach. In the same work, apparent values of Gibb's energy change for the extraction were calculated using a similar approach. In this case, however, the factor which converts from weight fraction to mole fraction basis does not drop out because the relevant relation is;

$$\mathbf{RT \ln K_i(mol) = g^E{}_i(aqueous) - g^E{}_i(solvent)} \qquad (4\text{-}8)$$

When the ethanol concentration and mutual solubilities of water and the solvent are low, the mole fraction distribution coefficient will be approximately the weight fraction distribution coefficient times the ratio of molecular weights of solvent to water. Using this fact allows calculation of apparent Gibb's energies of transfer of ethanol

and water from the aqueous to the solvent phase for a case of infinite ethanol dilution from the values of **a** and **c** of equation (4-4). For example, for 2-ethyl-hexanol, Tedder (1982) gives values for **a** and **c** for ethanol as 2.8 and -1063, and for water as -.76 and -973. These values lead to estimates of the excess Gibb's energy of transfer from the aqueous to the organic phase at 25 ^{o}C of -716 cal/gmol for ethanol and 1.2 kcal/mole for water. The estimated enthalpy changes for the transfer are 2.1 kcal/mole for ethanol and 1.9 kcal/mole for water. This leads to apparent excess entropy changes of 9.4 cal/gmol-^{o}K for ethanol and 2.3 cal/gmol-^{o}K for water. The other calculation method (by analogy to reaction) leads to negative entropy changes for the extraction of ethanol (Tedder, 1982), which cannot be correct since the extraction does occur spontaneously. In fact, since the enthalpy changes for extraction are positive, it is the entropy increase which actually provides the driving force for the extraction, even in those cases for which the ethanol distribution coefficients are highest.

4.2 Prediction of Liquid-Liquid Equilibria with UNIQUAC and UNIFAC

As discussed at the beginning of this chapter, a theoretical model of liquid-liquid equilibria is desirable for several reasons. In the case of modelling the equilibria involved in the extraction of ethanol from dilute aqueous solutions, there is little need to adopt a complicated model for the purpose of correlating experimental data. As shown in the previous section, simple empirical expressions do an adequate job over the concentration range of interest. Instead, the main impetus for a theoretical approach in the situation at hand is

the desire to be able to predict liquid-liquid equilibria from available data for the binary pairs of the system, or ideally from the molecular properties of the components.

A theoretical model for liquid-liquid equilibria must involve a method for calculating activity coefficients for the components of a liquid mixture as a function of the composition. This allows solution of the governing equations for liquid-liquid equilibria (Prausnitz, 1969), which are, for each component i;

$$x_i \, Y_i^{\,1} = x_i \, Y_i^{\,2} \qquad (4\text{-}8)$$

in which x_i is the mole fraction and Y_i is the activity coefficient of component i and the superscript numbers refer to the two phases. For the purposes of predicting ternary equilibria , the model used should involve only the use of pure component parameters and parameters which can be determined from binary data.

A number of models which meet these criteria are available. In this work, however, there are a number of reasons to favor one of these, the UNIQUAC equation (Abrams and Prausnitz, 1975). UNIQUAC is an acronym for Universal Quasi-Chemical and the equation was derived from a lattice theory of liquid mixtures. It has been shown to be capable of excellent correlation of liquid-liquid equilibrium data for a wide variety of systems, including ones involving water and ethanol (Anderson and Prausnitz, 1978). While predictions from binary vapor-liquid equilibrium data alone are not always good, Anderson and Prausnitz (1978) have described a method for including ternary liquid-liquid equilibrium data, which may be as little as one tie line, to obtain fairly accurate predictions of liquid-liquid equilibria over the whole range of concentrations. The fact that temperature-dependant

UNIQUAC parameters for the ethanol-water binary system have been determined for the temperature range of interest (Maiorella et al, 1982) makes the use of UNIQUAC attractive. Also relevant to the present intended purpose of the model is a recent study of the use of UNIQUAC to predict distribution coefficients from binary data only (Simonetty et al, 1982). In comparing UNIQUAC for this purpose with two other well-known models (NRTL and LEMF), the authors used a set of ten ternary systems. Although the average error in the prediction of distribution coefficients for the ten-system set was found to be less with the other models, for the two systems containing ethanol and water (benzene and ethyl acetate were the two solvents) the UNIQUAC equation was found to be best, with average percentage errors in predicted distribution coefficients of 14% for ethyl acetate and 21% for benzene. Perhaps the greatest incentive for choosing the UNIQUAC model, however, is that it has been extended to a group contribution method called UNIFAC, for Universal (quasichemical) Functional group Activity Coefficients (Fredenslund et al, 1975). This development has made it possible to predict phase equilibria even in the absence of experimental data, provided the components contain only combinations of the groups for which UNIFAC parameters have been determined.

The details of the UNIQUAC and UNIFAC models are given in the references cited above. In addition, a succinct statement of the equations involved is available (Fredenslund et al, 1977a). In both UNIQUAC and UNIFAC, the excess Gibbs free energy of a mixture, and hence the activity coefficient of any of its components, is modelled as the sum of two contributions. The first, called the combinatorial part, is due only to differences in the sizes and shapes of the

molecules and is calculated from pure component parameters only. Those parameters represent the volume and surface area of a molecule and are found as the sum of standard values for the groups in the molecule. The combinatorial contribution is thus exactly the same in the UNIFAC and UNIQUAC equations. The other contribution to the activity coefficients is the residual contribution, which accounts for the role of molecular forces. It depends on the energies of interaction among the components as well as the surface areas. It is the energies of interaction which are characterized by empirical parameters. In the UNIQUAC equation, there are two empirical parameters for each binary pair of molecular species. In the UNIFAC treatment, the interaction energy for a molecule in a mixture is taken to be the sum of contributions of its groups interacting with all other groups in the mixture, so two binary interaction parameters for all possible pairs of groups in the mixture are required. Fortunately, the developers of the UNIFAC method have prepared and published values of the parameters for a large number of groups of common interest. Initially, the parameters were based mainly on vapor-liquid equilibrium data. While these should theoretically have been able to predict liquid-liquid equilibria, the results of such predictions were often unreliable. This is because the parameters derived depend strongly on the data used, due to the fact that UNIFAC is not a perfect model of the real situation. Recently, however, a set of parameters based on liquid-liquid equilibrium data was made available (Magnussen et al, 1981). The authors showed that with the new parameters, UNIFAC was able to predict liquid-liquid equilibria for many systems of interest with considerable accuracy.

The ability of the UNIQUAC/UNIFAC system to predict distribution coefficients and separation factors of ethanol extraction solvents was tested in two ways. First, the predictions of UNIFAC alone were calculated using the binary interaction parameters for liquid-liquid equilibria given by Magnussen et al (1981). In the second method, UNIFAC was used to generate UNIQUAC parameters for the ethanol-solvent binary interaction only. This was done by using UNIFAC to generate infinite dilution activity coefficients for each component in the other, then solving the UNIQUAC equations for the binary parameters which yield the same coefficients. The UNIQUAC binary interaction parameters for the ethanol-water pair were those derived from vapor-liquid equilibrium data by Maiorella et al (1982), while those for the solvent-water pair were calculated from data on the mutual solubilities (knowing all four composition variables allows the two activity coefficient ratio equations for such a sytem to be solved simultaneously, yielding the two parameters). The calculations for all of these steps were facilitated by the use of computer programs listed and discussed in Appendix B. The results of the predictions are compared to experimental results in Table 4.1. In that table and in the figures to follow, UNIFAC refers to the first method just described while UNIQUAC refers to the second.

There are several points to be made about these results. First, though the quantitave predictions are not very good, the relative merits of the solvents as extractants for ethanol are predicted rather well. This suggests that, although the techniques in their present form are not accurate enough to be useful for design purposes in the absence of experimental data, they are of potential benefit in

Table 4.1

Comparison of Predicted and Experimental Distribution Coefficients and Separation Factors for Ethanol Extraction by Several Solvents

Temperature 25 °C Aqueous Ethanol Concentration 5 wt.%

Solvent	Experiment KE	Experiment S	UNIFAC KE	UNIFAC S	UNIQUAC KE	UNIQUAC S
n-hexanol	.85[a]	9	1.58[b]	17	1.12	14
n-octanol	.60	12	1.10	17	.87	16
n-decanol	.52	16	.81	21	.68	24
n-dodecanol	.35	12	.63	24	.59	17
octyl aldehyde	.63	50	1.33	160	1.41	94
octanoic acid	.55	11	.75	28	.56	21
butyl acetate	.34	14	.70	32	.56	30
3-heptanone	.53	32	.46	55	.44	34
di-n-butyl ether	.12	62	.29	45	.32	118
1,1,2,2-tetra-chloroethane	.12	54	.50	211	.50	172
benzene	.05	60	.05	65	.05	68
dibutyl pyridine	(1.0	8)[c]	1.05	25	-	-

a) data averaged or interpolated

b) extrapolated; UNIFAC unable to predict a phase split at 5%

c) extrapolated from results for diethyl as the results for 1,6-diisobutyl (Table 3.1) are unusual due to steric effects

conducting a screening process that would limit the amount of experimental work required. The distribution coefficients predicted by the UNIQUAC method are generally lower than those predicted by UNIFAC alone, probably because the aqueous phase ethanol-water interaction is modelled better by the former. As shown in Figure 4-5, both methods predict almost constant distribution coefficients for most solvents over the range of dilute ethanol concentration. With the exception of octanoic acid, the UNIFAC predictions of distribution tend to decrease slightly with increase in aqueous phase ethanol concentration, while the UNIQUAC predictions tend to increase slightly. Experimental results most often show significant increases. The behavior of the predicted separation factors as a function of aqueous ethanol concentration is shown in Figure 4-6. In agreement with experiment, the solvents with low separation factors at low ethanol concentration show a much smaller fractional decrease of separation factor with increasing ethanol concentration than do solvents with high initial separation factors. The fact that the UNIQUAC method gives only a modest improvement over the use of UNIFAC alone suggests that accurate modelling of the aqueous phase is not as important to accurate prediction as the characterization of the ethanol-solvent interaction. This could be done by using vapor-liquid equilibrium data or infinite dilution activity coefficient data, but it would defeat the purpose of the prediction since liquid-liquid equilibrium data are generally easier to obtain than either of the other types.

Two shortcomings of these models, in addition to the failure to accurately predict the distribution coefficients and separation factors, are their predictions of the effects of branching in the

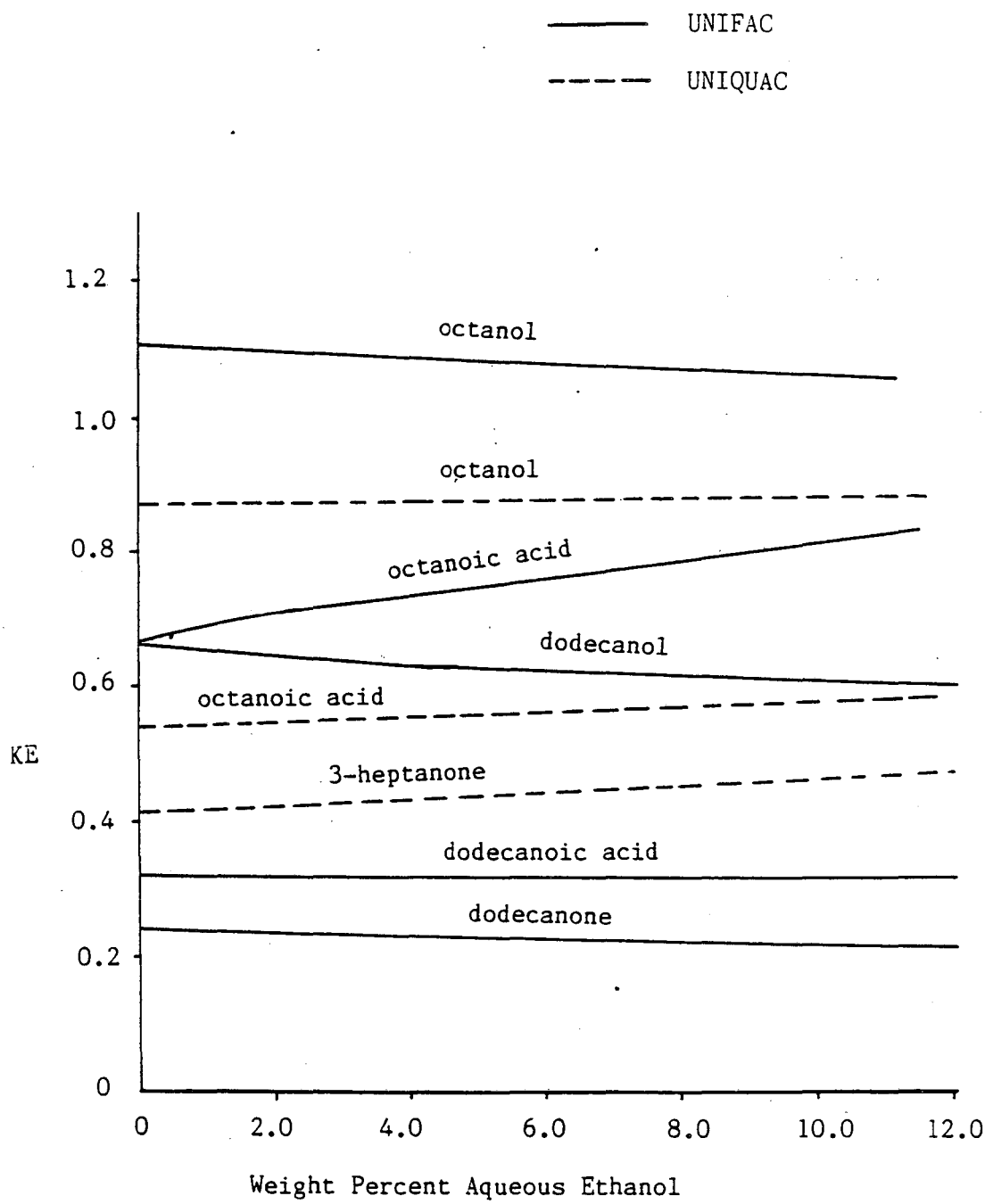


Figure 4-5 Effects of Aqueous Ethanol Concentration on Distribution Coefficients at 25 °C Predicted by UNIFAC and UNIQUAC

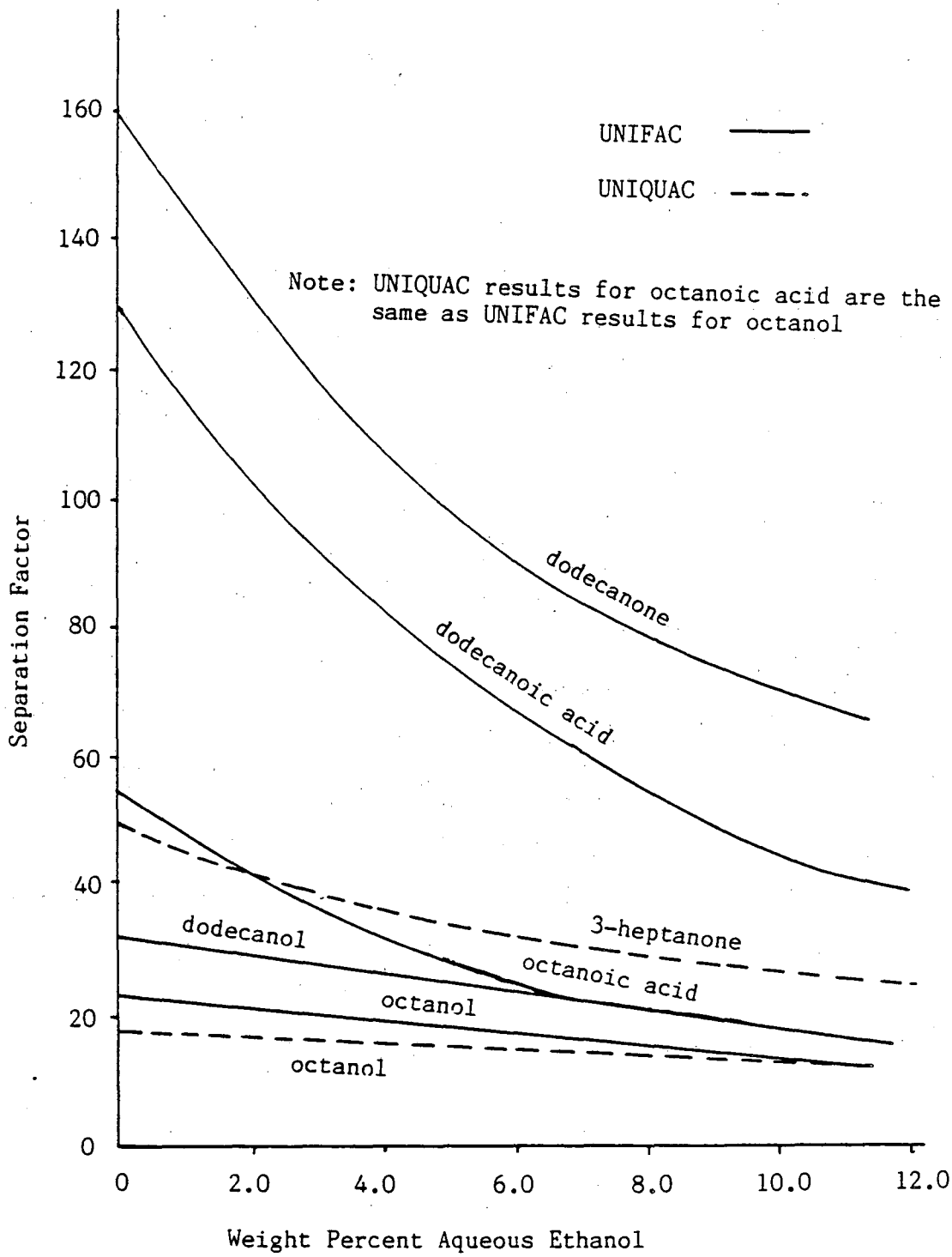


Figure 4-6 Effects of Aqueous Ethanol Concentration on Separation Factors Predicted by UNIFAC and UNIQUAC

hydrocarbon chain of a given solvent and of the effects of temperature. Many isomers of a given carbon number alcohol, for example, are described by the same redundant set of UNIFAC groups. Even in those cases where the structural group parameters differ, the interaction parameters are the same, leading the model to predict very little difference between the extraction behavior. In tests with the acid, alcohol, and ketone groups, the predicted extraction properties showed negligible changes when the numbers of CH_3, CH_2, and CH groups were varied, as long as the total number of carbons was kept the same. Similarly, the predicted effects of temperature are much smaller then those seen in experimental results. For the UNIFAC-only method, the ethanol distribution coefficients show a slight tendency to decrease as the temperature is increased, a trend opposite to experimental results. This limitation is recognized by Magnussen et al (1981), who recommend use of the UNIFAC liquid-liquid equilibrium parameters only in the range of 10-40 ^{o}C. Even when the UNIQUAC method is used with the temperature-dependant interaction parameters for the ethanol-water pair, the predicted effects of temperature on ethanol extraction are too small. The temperature dependance of the ethanol-organic solvent interaction must apparently be modelled with temperature-dependant parameters if the predictions are to correspond with experiments.

REFERENCES

1. Abrams, D.S., and Prausnitz, J.M. (1975) AIChE J., **21**(1):116

2. Anderson, T.F., and Prausnitz, J.M. (1978) Ind. Eng. Chem. Process Des. Dev., **17**(4):561

3. Fredenslund, A., Gmehling, J., Michelsen, M.L., Rasmussen, P., and Prausnitz, J.M. (1977a) Ind. Eng. Chem. Process Des. Dev., **16**(4):450

4. Fredenslund, A., Gmehling, J., and Rasmussen, P. (1977b) Vapor-Liquid Equilibria Using UNIFAC Elsevier, New York

5. Fredenslund, A., Jones, R.L., and Prausnitz, J.M. (1975) AIChE J., **21**:1086

6. Magnussen, T., Rasmussen, P., and Fredenslund, A. (1981) Ind. Eng. Chem. Process Des. Dev., **20**(2):331

7. Maiorella, B., Blanch, H., and Wilke, C. (1982) "Ethanol/Water Physical and Chemical Properties for Separation Process Design" Lawrence Berkeley Laboratory Report LBL-14220

8. Pemberton, R.C., and Mash, C.J. (1978) J. Chem. Thermodynamics, **10**:867

9. Prausnitz, J.M. (1969) Molecular Thermodynamics of Fluid Phase Equilibria Prentice-Hall, Englewood Cliffs, New Jersey

10. Prausnitz, J.M., Anderson, T.F., Grens, E.A., Eckert, C.A., Hsieh, R., and O'Connell, J.P. (1980) Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria Prentice-Hall, Englewood Cliffs, New Jersey

11. Simonetty, J., Yee, D., and Tassios, D. (1982) Ind. Eng. Chem. Process Des. Dev., **21**(1):174

12. Singh, J., and Benson, G.C. (1968) Can. J. Chem., **46**:1249

13. Sorensen, J.M., and Arlt, W. (1979) "Liquid-Liquid Equilibrium Data Collection - Binary Systems", Chemistry Data Series, vol. 5, part 1 DECHEMA, Frankfurt, F.R. Germany

14. Thomas, E.R., Newman, B.A., Nicolaides, G.L., and Eckert, C.A. (1982) J. Chem. Eng. Data, **27**:233

15. Tedder, D.W. (1982) "Fuel-Grade Ethanol Recovery by Solvent Extraction" Technical Progress Report under S.E.R.I contract XK-0-9082-1, Georgia Institute of Technology, September 1982

5. REVIEW OF PREVIOUSLY PROPOSED EXTRACTION PROCESS ALTERNATIVES

In this chapter, the proposals of others who have worked or are working on the development of an extraction process for ethanol recovery are critically reviewed. Before proceeding specific process proposals, however, a recent study of the feasibility of applying liquid-liquid extraction to this separation should be mentioned. This study concluded that there is no energy-saving incentive to use extraction for ethanol recovery at any practical ethanol feed concentration (Zacchi et al, 1983). Since this conclusion, if correct, would eliminate one of the potential advantages that an extraction process might have over conventional distillation of the aqueous ethanol, it bears closer scrutiny.

The authors considered two types of process for the recovery of ethanol using liquid-liquid extraction. These were a low-boiling solvent process, in which the solvent is distilled overhead after it extracts the ethanol, and a high-boiling solvent process, in which the ethanol is distilled from the solvent. In the former process, the minimum energy requirement was estimated by calculating the amount of energy required to simply evaporate the solvent, with no allowance for reflux. The results showed that, in order to have this minimum energy requirement equal to the actual energy requirement of a conventional distillation, distribution coefficients approximately 6 to 8 times larger than any obtainable with known low-boiling solvents would be required. The conclusion drawn, that a low-boiling solvent process is not practical for ethanol recovery from dilute solutions, is undoubtedly a valid one.

In the investigation of the high-boiling solvents process, however, the results obtained by Zacchi and coworkers are questionable. The process considered was essentially the same as that shown in Figure 5-1. The solvents considered included hexanol, octanol, and 4-methyl-2-pentanone (methyl isobutyl ketone). However, the energy requirements were apparently calculated in a peculiar way. Instead of calculating the energy required to directly distill the product (93.5 wt.% ethanol) from the extract stream, that distillation was 'modelled' as two separate distillations; one to separate the extracted ethanol and water from the solvent which was approximated as a water-solvent binary distillation, and another to produce the concentrated ethanol product from the water-ethanol-solvent mixture. Thus the ethanol was required to be vaporized twice, and the energy requirements found by this method were naturally much higher than those for a conventional ethanol-water distillation, regardless of the feed concentration. In a check on the method, a more sophisticated distillation program was used by the same authors to model the ternary system and the production of concentrated ethanol directly from the extract. The results gave an even higher energy requirement than the simple approach, but this is almost certainly due to the fact that the number of theoretical stages was not allowed to vary in the ternary system calculations. Instead, the location of the feed plate and the reflux ratio were varied until the product concentrations met specifications. This resulted in very large reflux ratios and correspondingly large energy requirements. The conclusion drawn was that high-boiling solvents also would be unfeasible for use as extractants to recover ethanol.

5.1 The Othmer Process

One of the most detailed studies to date of the application of solvent extraction to the problem of ethanol recovery was made during the mid- 1940's. Donald Othmer and coworkers (Othmer and Ratcliffe, 1943; Othmer and Truegar, 1941; Othmer et al, 1941) investigated the use of solvent extraction to recover acetone as well as ethanol from dilute aqueous solutions. In the case of ethanol, the process of choice was that shown schematically in Figure 5-1. A partially miscible solvent recovers ethanol from the aqueous feed in a counter-current extraction. The extract goes to a distillation in which the extracted ethanol is recovered as the top product at a 95 wt.% concentration while the solvent and remaining extracted water form the bottom product, sent to a decanter. The raffinate and the aqueous layer from the decanter go to a stripping column in which the solvent is stripped from the water as an azeotrope. The heat required to do this is recovered for use in the main distillation by the simple expedient of recycling the stripper vapors to the bottom of that distillation. It is apparent that the idea behind this scheme is to replace one costly distillation, of ethanol from a dilute aqueous feed, with two less costly ones, ethanol from the solvent and the solvent from water. The success of the idea depends on identifying a solvent which has two characteristics: (1) a high enough separation factor to give an effective ethanol concentration in the extract (ethanol-water binary basis) which is to be at or above the pinch-limited concentration for the ethanol-water distillation, and (2) low enough aqueous solubility and high enough concentration in the azeotrope to make the energy requirement for the solvent stripping

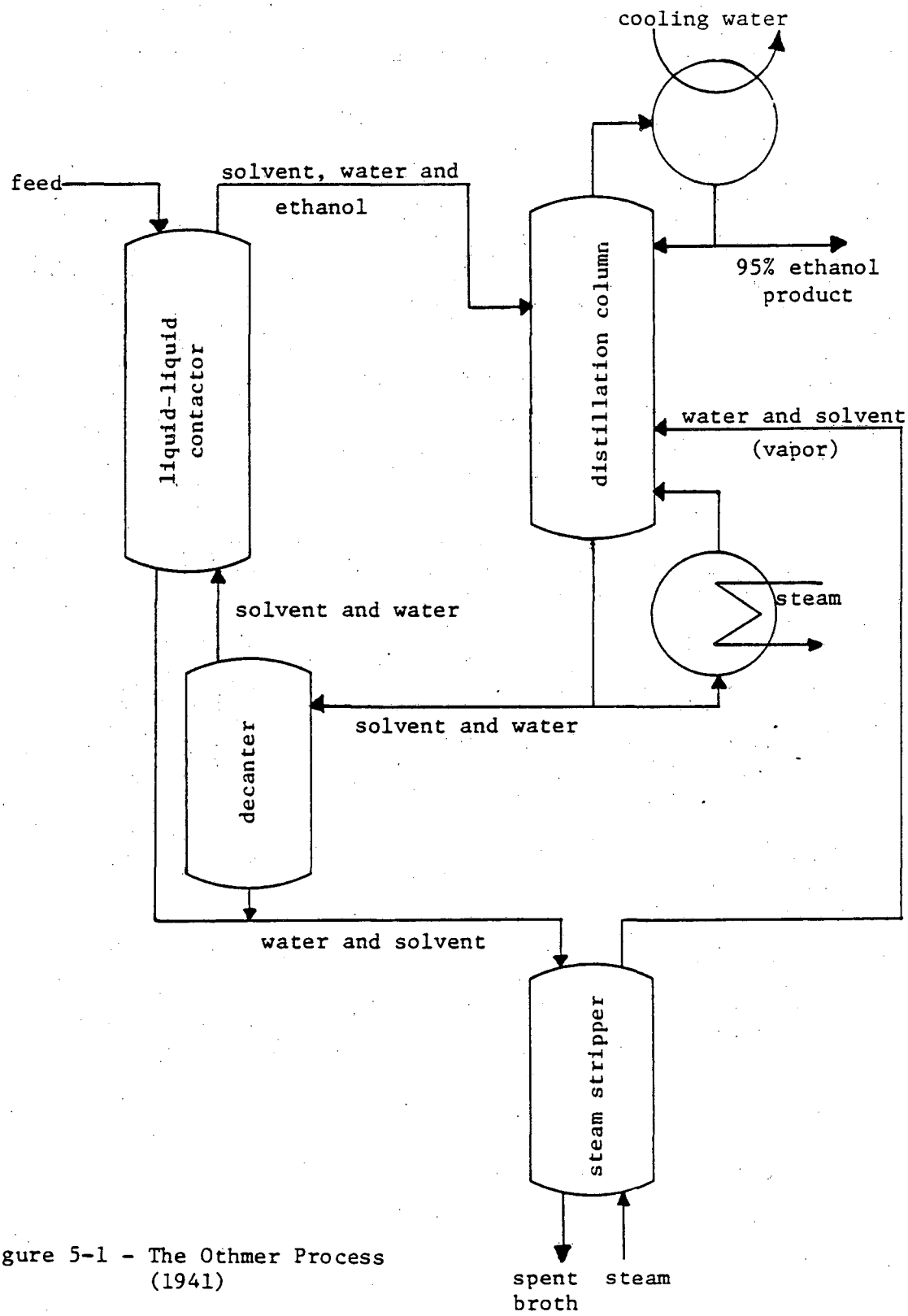


Figure 5-1 - The Othmer Process
(1941)

less than or equal to that for the main distillation. Of course, the solvent should also have a high distribution coefficient for ethanol to ensure that the solvent flow rates are practical. Based on these criteria, Othmer and his coworkers identified isoamyl alcohol as a solvent with the potential to reduce the cost of ethanol recovery compared to ordinary distillation. They showed, by calculation and experiment, that significant energy savings would be realized by using the process for aqueous ethanol feeds more dilute than the pinch-limiting concentration. In their work, using atmospheric pressure distillation and a reflux ratio of 1.5 times the minimum, the pinch limiting concentration was 5 wt.%. For a 2 wt.% feed, the savings in energy by using an isoamyl alcohol extraction process versus straight distillation were over 56%. Capital costs for the extraction process would necessarily be much larger, however, and an overall economic analysis was not performed.

It is apparent that these results contradict the computer simulations of Zacchi et al (1981). In the latter work, the energy requirement found for the use of octanol as a solvent was about twice the requirement of a conventional distillation (for a range of feed concentrations from 3 to 10 wt.%) while that for hexanol was about three times. By extrapolation, their method would probably yield even greater energy requirements for the use of isoamyl alcohol. Yet the experimental results show that significant energy savings would be possible, depending on the feed concentration. Some of the possible problems with the study by Zacchi and coworkers have been mentioned above. Another may be that the effect of a side stream withdrawal on the distillation energy requirements was not apparently considered in

that work, while it was used by Othmer and coworkers in their isoamyl alcohol process. In addition, the methods used by the Swedish researchers to model the complex vapor-liquid equilibria of the ternary systems may not have been adequate to accurately represent them. The problems encountered in modelling such systems have led others to the conclusion that ternary data are required to achieve accuracy.

5.2 The G.I.T. Process

The properties of solvents for ethanol extraction, reviewed in chapter 3, are such that there is no solvent which has both a high distribution coefficient and a high separation factor when in contact with an aqueous ethanol solution as dilute as those normally produced by fermentation. As a consequence of this, the energy requirements to produce concentrated ethanol (95 wt.% or greater) from a dilute stream using a solvent extraction process may be greater than that for distillation of the same solution, depending on its concentration. If a low separation factor solvent is used, and the product from a simple distillation to regenerate the solvent is 95 wt.% ethanol, then there will be no energy savings unless the feed stream is very dilute. This is the situation for the Othmer process. The reason for this, of course, is that the recovery distillation cannot be more efficient than a conventional distillation without the use of extraction since, when both are used to produce the same product concentration, both are subject to the same pinch limitation for ethanol concentrations (on a solvent-free basis) greater than the critical concentration, as discussed in chapter 2. If a very high separation factor solvent could be used, such that the ethanol concentration on a solvent free

basis could exceed 95 wt.% in the extract stream, then a lower reflux ratio with concommitant energy savings might be possible in the recovery distillation, provided the solvent had a high boiling point and no azeotrope-forming tendency. However, there are other factors which militate against the use of high separation factor solvents. These include the size and cost of equipment required and the sensible heat requirements of the solvent cycle, both consequences of the low distribution coefficients that must be accepted if a high separation factor is required.

One way around this dilemma is to produce an intermediate product which is less than 95 wt.%, then subject it to further treatment. If the energy required to vaporize the ethanol and water in an extract stream is taken as a minimum, it can be easily shown that the extract stream ethanol concentration need only be greater than 41 wt.% on a solvent free basis for this minimum stripping energy to be less than the minimum energy required by optimized vacuum distillation. Such an extract concentration requires only moderate separation factors, ranging from 35 for a 2 wt.% aqueous ethanol feed to 5 for a 12 wt.% feed. Many of the solvents in Table 3.1 have separation factors greater than these values.

This concept is behind a process proposal being currently being developed at the Georgia Institute of Technology (Tedder, 1982). It has been called the two-cycle process, and is shown schematically in Figure 5-2. The first cycle, called the recovery cycle, involves conventional solvent extraction of the fermentation broth in a liquid-liquid contactor, followed by distillation to regenerate the solvent and produce an intermediate ethanol-water product mixture. The

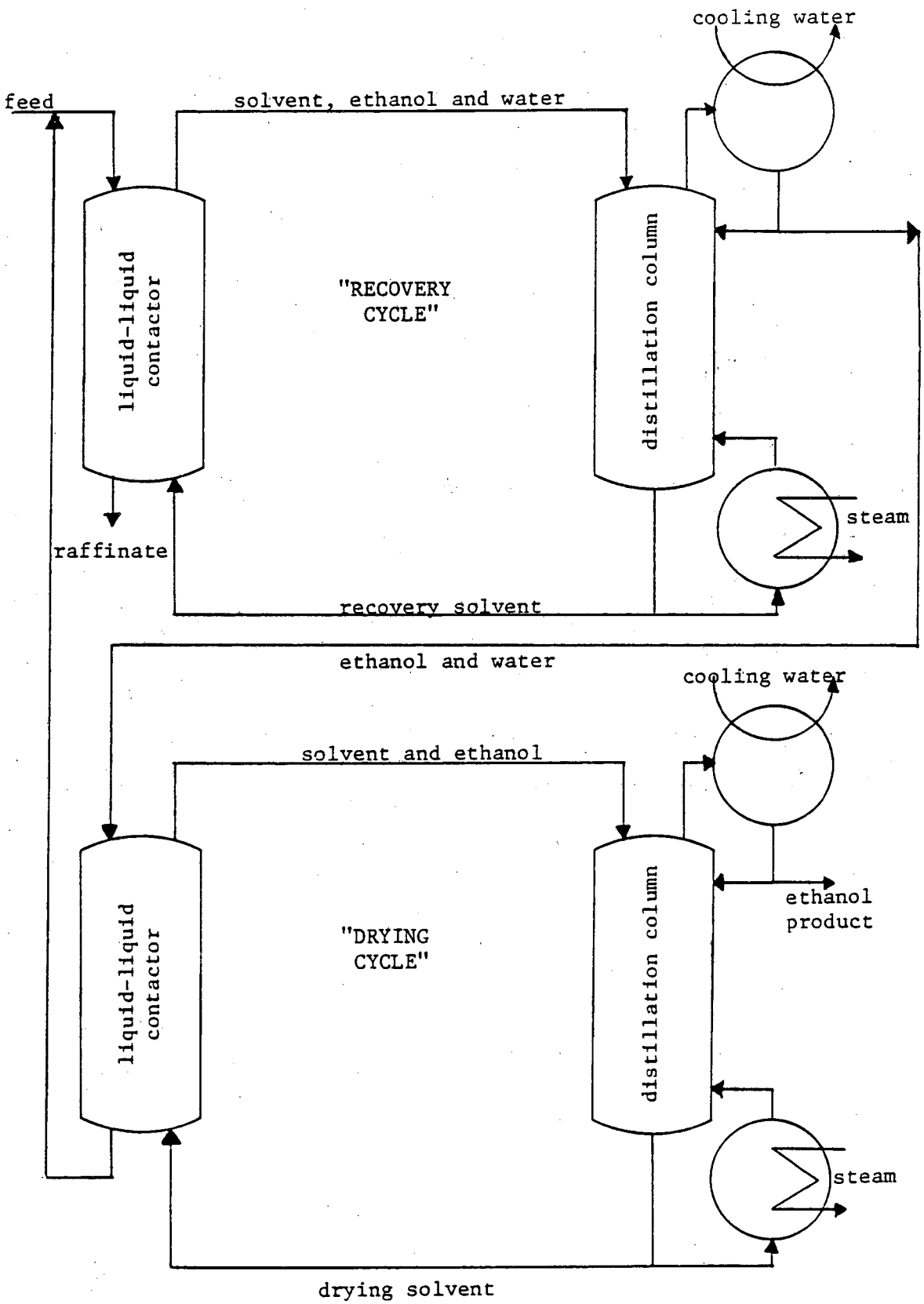


Figure 5-2 - The G.I.T. Two-Cycle Process (Tedder, 1982)

solvent used in this cycle would be chosen to obtain a high distribution coefficient at the expense of a moderate separation factor. Examples include 2-ethylhexanol and mixtures of tridecanol in alkanes. The intermediate product composition would depend on the solvent and the feed composition, but would be in the range of 30-70 wt.% ethanol. The second cycle, called the drying cycle, involves a second liquid-liquid extraction, this time of the intermediate product, using a different solvent. The drying solvent, as it is called, is a mixture of alkanes having a low distribution coefficient for ethanol, but a high selectivity. The extract stream contains ethanol in high enough proportion relative to water that its subsequent distillation produces 98 wt.% ethanol or greater, thus avoiding the azeotropic distillation step normally required to produce ethanol concentrated enough to be used directly as a fuel additive to gasoline. Parts of the process have been tested on a laboatory scale with successful results. There were reports of interest in developing the technology for commercial application (Anonymous, 1983). A better assessment of the merits of the process should be possible if that occurs.

5.3 Extractive Fermentation

The beneficial effects of recovering ethanol directly from an active fermentation as it is produced have been discussed previously. Several approaches to this concept have been and are being explored.

Work at the University of Pennsylvania examined extractive fermentation for ethanol production (Pye and Humphrey, 1979). The process proposed involved the use of a "diffusion cell" in which a membrane would separate the extractant from the fermentation broth, presumably to avoid problems with emulsion formation. Results of

solvent screening tests led to identification of a high molecular weight polypropylene glycol as the only solvent with a reasonable distribution coefficient and acceptable toxicity to the yeast used in fermentation. No separation factor was given for this solvent, but it is certainly quite low.

The result of using a low selectivity solvent would give a process similar to the proposed use of a two-phase aqueous system (Kuhn, 1980; Hahn-Hagerdal et al, 1981). In the two-phase aqueous work, dextran and polyethylene glycol were added to a fermentation, causing the formation of two aqueous phases. The yeast cells remain in the dextran-rich phase while ethanol distributes to approximately equal compositions in both phases. Such a system has shown improved yields over a normal one-phase solution in simultaneous saccharification and fermentation experiments (Hahn-Hagerdal et al, 1981). It was shown by Inger (1980) that the polyethylene glycol (PEG)-rich phase could be removed, stripped of ethanol by distillation, and returned to the fermentation, allowing a continuous extractive fermentation to be run. It was found that nonvolatile components, including glycerol, accumulated in this operation to the point that they caused significant inhibition of growth and ethanol production after about 10 cycles of glucose addition, fermentation, and PEG regeneration. Neither dialysis of the PEG phase nor addition of fresh viable yeast alone could overcome this inhibition, but both treatments together resulted in restoration of the original productivity. This illustrates the importance of removing the byproducts of fermentation in an extractive fermentation scheme. The use of the two-phase aqueous fermentation process, however, would seem to be a

rather complex way to achieve cell recycle in an ethanol fermentation. Little or no separation of ethanol from water is obtained by the extraction of ethanol in an aqueous polymer solution. The use of the two-phase system serves only to retain the cells in the fermentor, a function probably performed just as well by more conventional means, such as centrifugation, ultrafiltration, or some type of facilitated cell settling. Fermentor productivities in the experimental studies cited were quite low, but this is due to their use of large volumes of the inert PEG phase, which presumably could be reduced by as much as an order of magnitude if the two-phase extraction were run in a continuous fashion.

The use of high molecular weight alcohol as a solvent for ethanol extractive fermentation has also been recently reported (Minier and Goma, 1982). In that work, dodecanol was used to continuously extract ethanol from a pulsed column fermentor in which yeast cells were immobilized by adsorption on crushed brick. An increase in ethanol yield was reported for the extractive fermentation relative to controls. In fact, the ethanol yield for the extractive runs was nearly equal to the theoretical yield. This implies a reduction in cell mass production, since other carbon sources in the medium used were practically negligible compared to glucose. However, increases in cell yield were also reported, and the authors were unable to offer any explanation of their observations. In the extractive fermentation, the dodecanol extractant was regenerated by back extraction with water, obviously not a practical recovery technique. Recognizing the need for ethanol recovery, however, the authors propose the development of a permselective membrane process. Unfor-

tunately, the chemical similarity between ethanol and dodecanol and relatively small difference between their molecular weights make such a development seem unlikely.

Other examples of extractive fermentation applied to ethanol recovery have been investigated by Wang and coworkers at the University of Michigan (Wang et al, 1981; Lee and Wang, 1982). In the first of these investigations, the use of n-decanol as an extractive fermentation solvent was examined. While the authors stated that dissolved decanol had little adverse effects on the yeast in the fermentation, the very limited data reported for experiments on the subject do not support that claim. Data were obtained from an experiment which involved batch growth of the yeast on a sugar-rich medium, followed by centrifugation of the yeast, extraction of the broth with decanol, and the addition of more sugar along with the yeast to restart the fermentation. The fermentation did start, but came to practically a complete halt after only partial utilization ofthe added sugar. In light of the toxicity results obtained by Minier and Goma (1982) for decanol on the same yeast species, it seems likely that the fermentation activity observed after saturation of the medium with decanol was due to enzymes released into the medium, rather than to viable cells. In other work, however, viability of yeast cells was maintained in a similar fed-batch extractive fermentation with the use of activated carbon as the extractive agent (Lee an Wang, 1982). While not a liquid-liquid extraction, the principle of extractive fermentation was the same. Unfortunately, in addition to being subject to the solids handling problems mentioned in chapter 1, the activated carbon has a low selectivity for ethanol (separation factor

of approximately 2.7) and a relatively low capacity (distribution coefficient of 0.1 to 0.2). Thus, not only would large amounts of it need to be cycled to extract ethanol, but the energy requirements for its regeneration would exceed those of a conventional distillation to concentrate the ethanol directly from the fermentation. Furthermore, as the Lee and Wang study showed, fouling or some other capacity loss mechanism was very significant when actual fermentation broths were used in adsorption capacity studies. This is a general problem to be expected with the use of solid extractive agents in fermentation.

5.4 Azeotrope-Breaking Processes

Because of the shape of the ethanol-water vapor-liquid equilibrium curve, as discussed in chapter 2, a distillation of a feed containing a reasonably high ethanol concentration, greater than about 5 wt.%, to produce a concentrated ethanol product that is less than the azeotrope concentration does not need to consume very much energy. To further purify the ethanol with conventional technology, however, requires additional energy input and equipment. To reduce the cost of the azeotrope-breaking step, some researchers have suggested the use of liquid-liquid extraction.

One such proposal involved the use of fractional liquid extraction (Scheibel, 1950). In this scheme, ethanol from a dilute feed is concentrated in a conventional distillation to 90 wt.% or more, then fed to the middle of a fractional liquid-liquid extraction column. In the column, a highly polar solvent (ethylene glycol) and a relatively nonpolar solvent (methyl amyl ketone and o-xylene were investigated) flow countercurrently. The water is selectively

extracted by the polar solvent while the ethanol dissolves preferentially in the nonpolar. Both solvents are regenerated by distillation, producing pure ethanol and water product streams. In a careful analysis of the proposed process, Scheibel found that the ketone would be the preferred nonpolar solvent because of a pinch limitation on the purity of the ethanol produced using xylene. The energy requirements were calculated to be 3.5 MJ/kg ethanol produced, about the same those for conventional azeotropic distillation with benzene. No estimate of the capital cost of the process was made, but one would probably show the fractional extraction process to be more expensive, since it uses the same number of columns as the benzene distillation, three, and one of these is the liquid-liquid extraction column, which would be very large. So, while it remains an interesting example of the application of fractional liquid-liquid extraction, there would seem to be little incentive to consider the use of Scheibel's process for practical applications.

A process with more potential for application, albeit in a special situation, is the proposed extraction of concentrated ethanol directly into gasoline to produce gasohol (Leeper and Wankat, 1982). This proposed process was demonstrated in experiments with pure hydrocarbon components of gasolines and with actual gasolines in commercial use. It is necessary to use a feed concentration of 90 wt.% ethanol or greater to obtain distribution coefficients high enough to produce the nominal 10 wt.% gasohol mixture. Dilute ethanol feeds cannot be directly extracted, as is obvious from the low distribution coefficients of hydrocarbons for ethanol discussed in chapter 3. Leeper and Wankat showed that considerable energy savings

should be possible if gasoline extraction is used to replace a conventional azeotropic distillation to produce anhydrous alcohol for fuel blending use. These results considered the need to recover gasoline components from the ethanol-water raffinate and the recycle of that raffinate back to the concentrating distillation. The concept would seem to be a promising one for the production of fuels with ethanol added.

5.5 Other Processes

The extraction of ethanol with supercritical CO_2 has been discussed in chapter 1. Although pilot plant tests have shown that process to be capable of producing concentrated ethanol from dilute aqueous feeds including fermentation broths, capital costs for the process are likely to be high due to the extremely high pressures involved and to the low distribution coefficients obtained.

One other process proposal which should perhaps be mentioned is one which appeared as a letter to the editor of Chemical and Engineering News (Myers, 1980). Diethyl ether, methyl chloride, and other low-boiling solvents were suggested for ethanol recovery by solvent extraction. However, the distribution coefficients of the compounds, some of which are given in Table 3.1, are uniformly low. In addition, the assertion by Myers that distillation of the solvents would "require virtually no energy" is clearly incorrect. As the analysis of Zacchi et al (1983) has shown, no low-boiling solvent suitable for application to the problem of ethanol recovery from dilute solutions has been found.

REFERENCES

1. Anonymous (1983) Chem. Eng., **90**(11):18 (May 30, 1983)

2. Hahn-Hagerdal, B., Andersson, E., Lopez-Leiva, M., and Mattiasson, B. (1981) Biotech. Bioeng. Symp. Ser., **11**:651

3. Kuhn, I. (1980) Biotech. Bioeng., 22:2393

4. Lee, S.S., and Wang, H.Y. (1982) Biotech. Bioeng. Symp. Ser., 12:221

5. Leeper, S.S., and Wankat, P.C. (1982) Ind. Eng. Chem. Process Des. Dev., **21**(2):331

6. Minier, M., and Goma, G. (1982) Biotech. Bioeng., 24:1565

7. Myers, R.T. (1980) Chem. Eng. News, **58**(17):4

8. Othmer, D.F., and Ratcliffe, R.L. (1943) Ind. Eng. Chem., 35(7):798

9. Othmer, D.F., and Trueger, E. (1941) Trans. A.I.Ch.E., **37**:597

10. Othmer, D.F., White, R.E., and Trueger, E. (1941) Ind. Eng. Chem. **33**(10):1240

11. Pye, E.K., and Humphrey, A.E. (1979) "The Biological Production of Liquid Fuels from Biomass", University of Pennsylvania Interim Report for D.O.E. contractors meeting September, 1979, University of Connecticut, Storrs

12. Scheibel, E.G. (1950) Ind. Eng. Chem., 42(8):1497

13. Tedder, D.W. (1982) "Fuel-Grade Ethanol Recovery by Solvent Extraction - Technical Progress Report" Solar Energy Research Institute contract number XK-0-9082-1, Georgia Institute of Technology contract numbers E-19-621/G-33-609

14. Wang, H.Y., Robinson, F.M., and Lee, S.S. (1981) Biotech. Bioeng. Symp. Ser., **11**:555

15. Zacchi, G., Aly, G., and Wennersten, R. (1983) "Investigation of Ethanol Extraction from Fermentation Liquors", presented at A.I.Ch.E. International Conference on Solvent Extraction, Denver (August 1983) paper # 366

6. INVESTIGATIONS OF A NEW PROCESS PROPOSAL

In the previous chapter, the problem of achieving an energy efficient extraction process with low separation factor solvents was discussed. The scheme proposed by Tedder of G.I.T. process was seen to be an attempt to overcome this limitation. Another approach involves selectively removing the water from the extract stream before the ethanol recovery distillation. This would remove the ethanol-water pinch limitation, allowing concentrated ethanol to be recovered directly from the solvent regeneration distillation. If a method of accomplishing the selective water removal could be found that did not involve evaporating the water, the energy requirements for this process could be less than those of an intermediate product recovery process, such as the G.I.T. proposal.

6.1 Description of the Proposed Process

To selectively remove water from an extract stream containing ethanol and water in an organic liquid requires that the water be transferred to another phase. To minimize energy requirements, the phase should not be vapor. If a liquid were used to extract the water from the mixture, complications could arise due to amounts, however small, of mutual solubilities of the extraction solvent and the water removal solvent. So, to keep the process as simple as possible, the use of a solid which is completely insoluble in the extraction solvent is preferred to remove the water from theextract stream.

A schematic flow diagram for the proposed process is shown in Figure 6-1. The process would involve extraction of the dilute

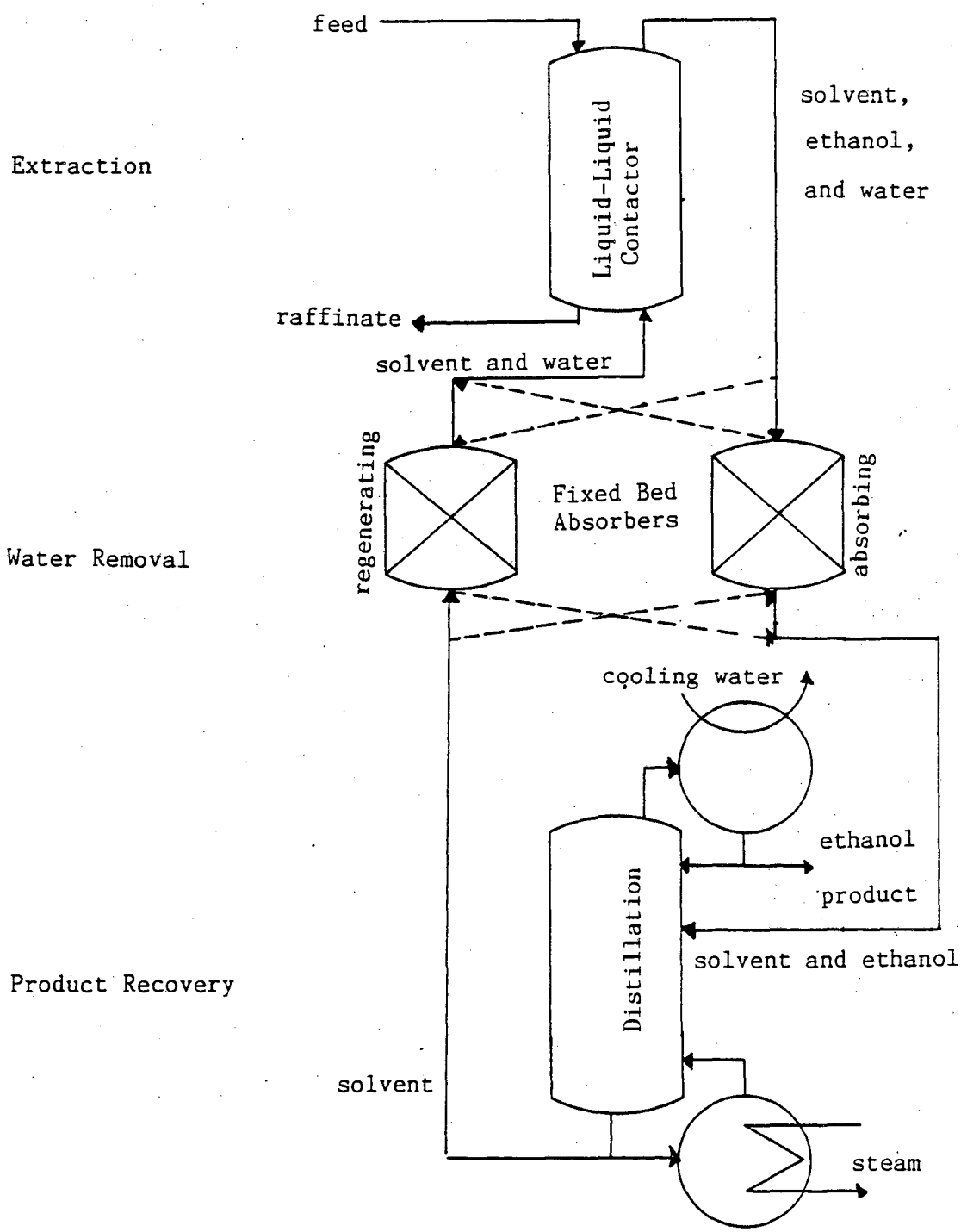


Figure 6-1 Proposed Process for Ethanol Recovery Using Liquid-Liquid Extraction and Selective Water Removal

fermentation broth, followed by selective water removal in a fixed bed of solid sorbent, and a distillation to recover ethanol and regenerate the solvent. The solvent from the bottom of the distillation column, at a higher temperature than the extraction temperature, would be passed through a water-saturated bed to regenerate it. The solvent from the bed being regenerated would be cycled back to the fermentation broth extraction, presaturated with water. Not shown in the figure are heat exchangers and an operation to recover solvent from the raffinate, which may be needed, depending on the details of the solvent and sorbent characteristics. The fact that the solvent would be saturated with water before contacting the fermentation broth should have no adverse effects on the extraction.

The solvent must be at a higher temperature to regenerate the bed of sorbent than when it is contacted with the sorbent for water removal for two reasons. The first is that the desorption will be an endothermic process and the energy to perform it must come from the sensible heat of the solvent. The second reason is that the fugacity of water in the solvent will be higher in the absence of ethanol than when the ethanol is present, so the solubility of water in the pure solvent at the same temperature would be lower. In most solvents, the solubility of water increases with increasing temperature (some nitrogen-containing compounds are notable exceptions, however). Hence, to maintain a steady state mass balance, the solvent must either leave the regeneration bed supersaturated with water at the extraction temperature or leave at a higher temperature with the same amount of water, but at or less than the saturation concentration.

It should be mentioned that this process resembles in some respects a recently proposed process for dehydration of the ethanol azeotrope (Garg and Ausikaitis, 1983). In that process, molecular sieves are used to adsorb water from a vapor containing up to 20 wt.% water. The heat of adsorption, which can be up to 1000 cal/gram of water, causes a large temperature rise in the bed. The key to the process is the storage of this significant amount of heat in the solid bed. The regeneration, with a hot purge gas, is done countercurrent to the adsorption, so that the heat stored in the bed can be used to help provide the required energy for desorption of the water. The authors of this proposal claim that it can be used to produce anhydrous ethanol with only a fraction of the energy input of the conventional processes.

A qualitative comparison of the two process proposals can be made. The azeotrope dehydration process necessarily involves distillation of dilute ethanol to produce a concentrated vapor, so the energy requirements of that overall process appear to be intrinsically higher. In addition, the high temperatures involved in the vapor phase water removal require the use of inorganic sorbents, such as the mole sieves proposed. As will be shown in the next section, however, the water capacity of these materials is low compared to that of other materials suitable for use in the liquid phase dehydration. This means that, based on equilibrium considerations, greater quantities of the sorbent would be required for the same water removal using the vapor phase process. Balancing that aspect are the higher rates of mass transfer in the vapor at high temperature, and the potential for higher product recoveries due to lower holdup in the vapor process.

6.2 Experimental Investigations

A number of experimental studies were carried out to test the feasibility of the above proposal. These included screening tests to identify a solid sorbent with high selectivity and water capacity, the determination of sorbent characteristics as functions of concentrations and temperature, some column breakthrough studies, and measurement of the heat of water sorption for a typical sorbent. The experimental determination of ethanol and water concentrations in these studies were made using the methods detailed in Appendix A. The ion exchange resins used in these studies were converted to the desired ionic forms by following manufacturer's recommended procedures. These included initial conversion to the protonated form (for cation exchangers) by washing in a column with a ten-fold excess of 1 M hydrochloric acid, followed by conversion to the desired cation by washing with a three-fold excess of the appropriate hydroxide salt. In the cases of divalent and trivalent cations, for which hydroxide salts were unsuitable for use, the resin was first converted to the sodium form by using sodium hydroxide, then converted to the multivalent ion form by using a ten-fold excess of a soluble salt of the multivalent cation. Anion exchangers were treated in analogous fashion, with the initial conversion being to the hydroxide form, using 1 M sodium hydroxide, and subsequent conversion with the corresponding acid where possible. All conversions were followed by a minimum twenty volume wash with distilled water to remove free electrolytes.

6.2.1 Preliminary Sorbent Screening

An initial screening of likely solid sorbents was conducted by testing the ability of several materials to remove water from a solution of 95.1 wt.% ethanol. Small amounts of the solids were placed in one dram vials and kept in a 70 ^{o}C oven over a period of several days, till they reached a constant weight. A weighed amount of the ethanol-water solution was then added to each vial. The water concentration in the liquid was measured and, after equilibrium had been reached, the amount of water taken up by the solid was estimated, assuming that the amount of ethanol taken up was small enough to have a negligible effect on the liquid concentrations. The results are shown in Table 6.1. It is clear that dehydration of the liquid phase occurred to some extent with all of the materials. It should be pointed out that the drying of the solids before the test was not rigorous, and different results might have been obtained if different drying conditions had been used. In particular, the result for the 3A molecular seive may have been at least partially due to the fact that it takes much higher temperatures to dry that material (Lee, 1979). Under the conditions that were used, however, the ion exchange resins gave the best results. The simple salt, potassium fluoride, was an effective dehydrating agent, but its use in the process would probably not be feasible since it would liquefy as it equilibrated with a water saturated organic phase. The results for the ion exchange resins show a strong dependance on the ionic form of the exchanger. This result is different from the results of a study of the drying of dioxane, toluene, and dichloromethane by cation exchangers (Burfield and Smithers, 1980), in which little dependance on ionic form was found.

Table 6.1 - Results of Sorbent Screening

Sorbent and source	final wt.% water in ethanol[1]	pseudo-distribution coefficient[2]
3A molecular seive, pellet form, Union Carbon (Linde)	4.36	0.08
potassium fluoride crystals, Baker analytical reagent	3.69	0.69
potassium carbonate crystals, Baker analytical reagent	4.14	0.18
potassium polyvinysulfate, Sigma Chemical (98%)	3.77	0.39
Dowex-50[3], lithium form (Dow Chemical)	4.16	0.41
Dowex-50, magnesium form	2.48	1.34
Dowex-50, aluminum form	1.70	2.53
Amberlite IRC-50[4], lithium form (Rohm and Haas)	3.80	1.36
Amberlite IRC-50, magnesium form	3.49	0.82

1) initial water concentration of liquid was 4.88 wt.%

2) defined as the ratio of the loading of the solid, grams of water per gram of dry solid, to the weight fraction of water in the liquid

3) Dowex-50 is a strong acid cation exchange resin which is a sulfonated copolymer of styrene and divinylbenzene

4) Amberlite IRC-50 is a weak acid cation exchange resin which is a copolymer of acrylic acid and divinylbenzene

The ethanol and water sorption properties of ion exchangers were further investigated by measuring the maximum loadings of each compound in a series of exchangers of various ionic forms. An isopiestic technique was used. Small samples of the exchange resins, 0.5 to 1.5 grams, were placed in vials and dried to constant weight by incubation under reduced pressure in a dessicator with phosphorous pentoxide. The samples were then placed in a dessicator with either water or pure ethanol present as a liquid in the bottom. The gain in weight of the samples with time was measured and assumed to be due only to sorption of the water or ethanol. The results of the measurements are shown in Table 6.2. The samples took a long time to equilibrate as there was no stirring of the vapor in the dessicator. The results are shown for a four day incubation period and in some cases for the constant weight reached after a period of several weeks. The anion exchangers gave off a distinct ammonia odor during the tests. Use of these resins in a dehydrating process was deemed impractical because of their apparent instability, as well as their significant ethanol uptake. Among the cation exchangers, good selectivity for water was observed for both kinds of resin in any ionic form other than hydrogen. There was relatively little variation among the water capacities in the polstyrene sulfonate samples, but ethanol capacity did decrease as ionic valence increased. Thus, a competition from ethanol for ionic sites is probably why the differences in ethanol dehydrating ability for this resin observed in this work were not seen in the study of dehydration of other solvents. The water capacity of the polyacrylate resin, which has a higher charge density than the polystyrene sulfonate resin, was considerably higher than the water

Table 6.2 - Sorption of Pure Water and Ethanol by Ion Exchangers

Resin, ionic form	Sorption in 4 days grams/gram dry resin		Sorption to constant weight grams/dry gram
	ethanol	water	water only
IRA-401S[1], chloride	.77	.60	-
, iodide	.22	.88	-
, sulfate	.60	.64	-
, benzoate	.87	.55	-
IRC-50[2], hydrogen	.71	.31	-
, lithium	-	1.13	1.65
, potassium	.05	1.11	1.56
, magnesium	-	.41	.62
, calcium	.03	.59	1.04
, tetrapropylammonium	.37	.28	-
Dowex 50[3], hydrogen	.97	.73	-
, lithium	-	.69	.91
, sodium	.07	.66	1.21
, potassium	.06	.58	.96
, magnesium	-	.70	.87
, calcium	.04	.53	.97
, aluminum	.03	.62	1.02
, tetrapropylammonium	.48	.42	-

1) Amberlite polystyrene quaternary ammonium anion exchanger

2) Amberlite polymethacrylate cation exchanger

3) Dow Chemical polystyrene sulfonate cation exchanger

capacity of the polystyrene sulfonate in monovalent ionic forms, but much lower in multivalent forms. The cation exchange resins were also tested for water absorption at a higher temperature, 72 ^{o}C, using the same method. While there was more uncertainty in the results, due to condensation of liquid water on the vials of some of the samples, there were no significant differences between the amounts of water absorbed at 72 ^{o}C and the amounts absorbed at 23 ^{o}C.

The polacrylic acid resin in the hydrogen form was actually selective for ethanol, in agreement with observations of other researchers (Hellferich, 1962). In a separate experiment, this material was shown to be able to concentrate ethanol from dilute aqueous solutions. The distribution coefficient, about 0.02, was too low to be of practical interest, however.

6.2.2 Equilibrium Isotherms for Selected Sorbents

While the screening tests were useful for identifying some sorbents for potential application, they do not establish whether or not a sorbent can selectively remove water from an organic phase containing both ethanol and water. To resolve this, equilibrium isotherms for several of the sorbents were determined.

In the first set of experiments, a number of different sorbents were used. These included 3A molecular sieves (Linde), silica gel (Fisher), the ion exchange resin Dowex-50 in the aluminum form, and two water absorbent polymers, SGP 502S (a trademark of Henkel Corporation for a starch modified with polyacrylonitrile, also known as HSPAN or "super slurper"), and Stasorb 372 (a trademark of Staley Corporation for a starch modified with potassium polyacrylate). The SGP 502S was shown recently to be able to dehydrate ethanol containing

up to 20 wt.% water when the mixture was in contact with gasoline (Fanta et al, 1980). To dry the sorbents, the mole sieve and the silica gel were kept in a 300 ^{o}C oven for 48 hours and the others were stored in a dessicator under vacuum in the presence of P_2O_5 for over a week. The solvent used in the tests was 2,2,4-trimethylpentanol (Eastman). It was distilled before use and dried by storage over 4A molecular sieves. Two sets of samples were prepared; one set containing 4 wt.% ethanol in the dry solvent before sorbent addition and another set with no ethanol added. In a series of additions, water was added to the samples with accurate weighings before and after to measure the amounts. The liquid phase concentrations were monitored using gas chromatography according to the method given in Appendix A.

Results for low water concentrations are shown in Figure 6-2 for the samples without added ethanol. The slope of the curves indicates the affinity of the sorbent for water. The water saturation concentration in the solvent at 23 ^{o}C is 3.2 wt.%. The most effective sorbent in the low concentration range is clearly the 3A mole sieve. However, it reaches a maximum capacity at about 0.2 grams of water per gram of dry sorbent. The silica gel has a low capacity over the whole range. The water-absorbent polymers are nearly as good as the ion exchangers for water absorption at low concentrations. However, as the saturation concentration is approached, these materials swell to become viscous gels. Their application in a fixed bed process would be difficult in that condition.

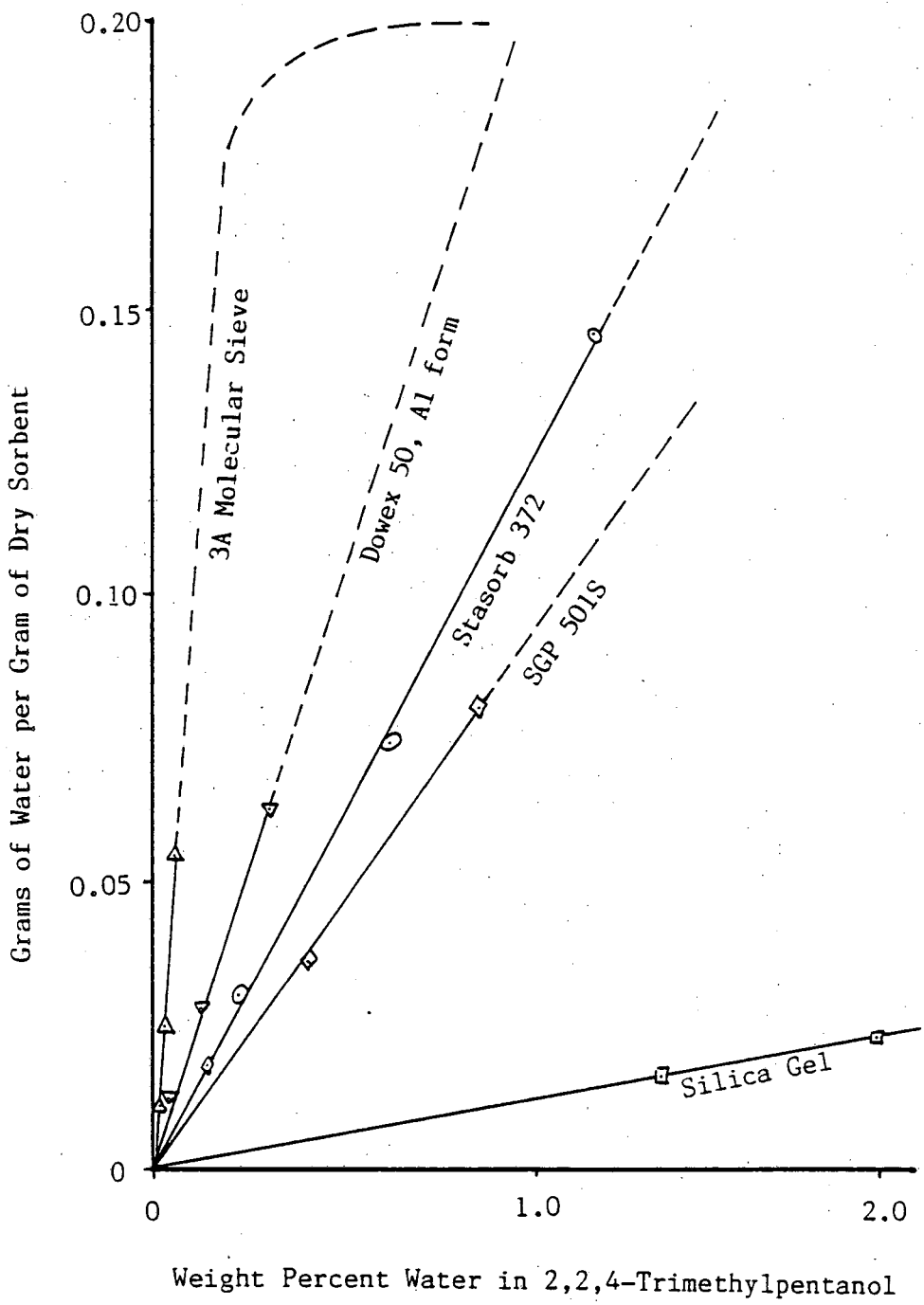


Figure 6-2 Water Sorption Isotherms for Several Sorbents in a Moderately Polar Solvent

The samples containing ethanol provided more reasons to favor the ion exchangers as sorbents. The curves for water uptake followed the same trends as seen in Figure 6-2 for the samples without water. However, the water sorption for a given liquid concentration of water were about 10% lower in all cases except the molecular sieve. This was expected because the activity of water at a given concentration is decreased by the presence of the ethanol. The reason for the different behavior of the molecular sieve is that the ethanol was practically all adsorbed from the solution by that material. Table 6.3 shows the amount of ethanol sorption observed for all the samples. The molecular sieve adsorbed most of the ethanol from the solvent even before any water was added. The silica gel also showed a significant amount of sorption when dry. The other samples showed very little ethanol sorption in the dry condition, but increasing amounts as the water level increased. The ratios of increase in ethanol sorption to water sorption shown in the table apply only to the dilute region. For most of the materials, the ratios change little up to saturation. However, for the water-absorbent polymers, the ratios increase as they swell to the gel state mentioned previously. Shown also in the table are the results for a polymethacrylate resin, IRC-50 in the potassium form. It is apparent that this material is superior in selectivity to the other ion exchange resin. Again, this is probably due to the higher charge density inherent in the polymethacrylate structure relative to the sulfonated polystyrene structure.

Table 6-3 - Uptake of Ethanol from Solvent by Water Sorbents

Initial ethanol concentration was 4.0 wt.% in the solvent, 2,2,4-trimethylpentanol

Sorbent	before water addition EtOH wt.%	gm EtOH/gm sorbent	increase with water gm EtOH/gm H_2O sorbed
3A mol. sieve	0.33	.041	.067
silica gel	3.11	.022	.067
SGP 502S	3.99	.0001	.052
Stasorb 372	3.99	.0001	.014
Dowex-50 (Al)	3.99	.0001	.193
IRC-50 (K)	3.99	.0001	.042

Because the polymethacrylate ion exchange resin seemed to have a desirable combination of properties for selective water sorption, a set of experiments was carried out to determine the effects of ionic form on these properites for that resin. Isotherms for water and ethanol sorption from 2,2,4-trimethylpentanol were determined at 23 ^{o}C for the IRC-50 resin in the lithium, potassium, magnesium, and aluminum forms. The results are shown in Figure 6-3. As observed in the initial screening experiments, the capacity for water sorption decreases as the ionic valence increases. The lithium form had the highest capacity; whereas the isotherms for the other forms are nearly linear, the curve for lithium bends upward at higher water concentrations. The ethanol sorption of the resins is practically negligible when they are dry. As water is added, the ethanol sorption increases, but it reaches an asymptotic value for each resin at a water sorption of about 0.2 grams/gram of sorbent. The values reached are 0.011, 0.008, 0.007, and 0.017 grams of ethanol per gram of sorbent for the lithium, potassium, magnesium, and aluminum forms, respectively. When these figures are divided by the respective water capacities of the resins at saturation, the selectivities are found to be about the same for the lithium, potassium, and magnesium forms; approximately 0.006 grams of ethanol per gram of water sorbed. The selectively for the aluminum form is not as good; 0.023 grams of ethanol per gram of water. While the lithium form of this resin would seem to have the best properties for selective water removal in a process of the type being considered, salts of lithium are relatively expensive, and the potassium or sodium forms may be the best from an economic standpoint.

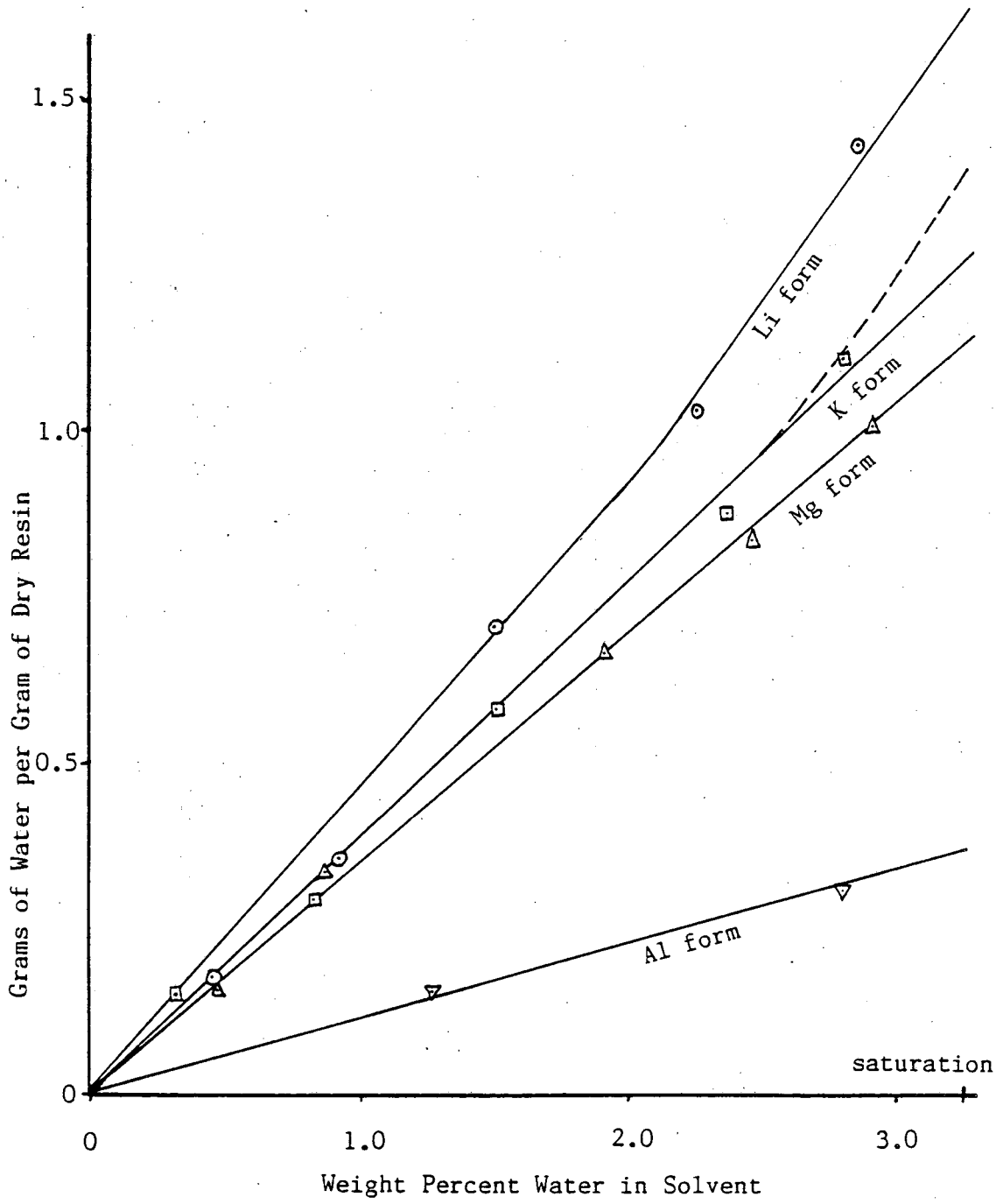


Figure 6-3 Water Sorption Isotherms for a Polymethacrylate Resin in Various Ionic Forms

The effect of temperature on the sorption of water was investigated briefly. During the isotherm determinations just described, samples were placed in an incubator at 63 ^{o}C to equilibrate. At that temperature, the solubility of water in pure 2,2,4-trimethylpentane increased about 30% relative to room temperature, 23 ^{o}C (from 3.2 to 4.1 weight percent water). The effect on the sorption of water by the samples tested was to shift the curves over by a corresponding amount. The concentration of water in equilibrium with a given sorbent loading was roughly 30% greater at 63 ^{o}C than at 23 ^{o}C. This is in keeping with the observation that the amount of water uptake by the sorbents at saturation changes little with moderate temperature increases. The upper limit of operating temperature recommended by the manufacturers for the ion exchange resins is 100 ^{o}C (Dow, Amberlite).

The effect of the solvent on water sorption was not examined in depth. It would be expected, however, that sorption curves would be the same for all solvents when the water concentration is expressed as a fraction of the saturation concentration. This assumes that the solvent is large enough or nonpolar enough that it is not sorbed by the solid itself, a good assumption for any solvent which is required to be only partially miscible with water. Results for the sorption of water by ion exchange resins from n-octanol and from the aldehyde, decanal, supported this expectation. In the latter case, the low water solubility in the solvent made the dehydration of ethanol extracts easy to accomplish. However, the ion exchange resin (particularly Dowex-50) in the aluminum form, apparently catalyzed a reaction of the decanal as viscous, miscible products were observed in samples stored at room temperature for several weeks.

6.2.3 Column Breakthrough Studies

The equilibrium properties of cation exchange resins showed these materials to be potentially useful materials for selective removal of water from ethanol extraction streams. The next logical step was to demonstrate such a water removal process on a laboratory scale. This was done initially with the Dowex-50 resin in the aluminum form and n-octanol as the solvent. A small sample of resin was dried at 70 ^{o}C and for four days in a dessicator with P_2O_5. A 1.58 gram sample of this was placed in a glass column with 1.02 grams of n-octanol dried to a water content of 0.17 wt.%. The column was then fed a solution of octanol with 4.63 wt.% water and 2.15 wt.% ethanol (from a batch extraction of a dilute aqueous ethanol solution). A flow rate of about 5 grams per hour was used. The first void volume of effluent contained 0.2 wt.% water, more than the partially dried octanol put into the bed initially. This showed that the resin had not been dried sufficiently. After two void volumes of feed, the effluent contained close to the feed concentration of ethanol and nearly 10% of the feed concentration of water. These levels remained unchanged until the run was stopped after about seven void volumes. Water breakthrough was not seen. Rather, the incomplete drying of the resin before the experiment resulted in only partial water removal. One reason the run was stopped after a short period was that the flow rate from a constant head source was practically stopped due to increased flow resistance in the column. Closer inspection revealed that swelling of the resin beads had compacted the resin in the top of the column into a solid mass which could not be dislodged with a glass rod. Forcing dry octanol through it caused it to loosen again, but the behavior was

unusual in that there was room in the column for the resin to swell in the axial direction. In subsequent tests with the polymethacrylate ion exchange resin, instead of the polystyrene sulfonate, no such behavior was observed for resin beads of about the same particle size. It was seen, though, in an attempted run with a very small particle size (400 mesh) of the polymethacrylate resin. That run had to be abandoned when the flow of liquid through the column was completely halted by the effect.

The polymethacrylate resin in the potassium form was used in another column experiment to obtain a water breakthrough curve. The column used was fitted with two thermocouples to detect possible temperature rise due to the exothermic water sorption. The setup is sketched in Figure 6-4. The IRC-50 resin in the potassium form was dried extensively over P_2O_5 and 10.02 grams was placed in the column. The feed to the column was 2,2,4-trimethylpentanol containing 3.95 wt.% water and 3.35 wt.% ethanol. The column was first filled with dry solvent. Then the feed was started and the effluent was collected in fractions that were weighed. The average flow rate was 0.4 grams per minute. The breakthrough curves are shown in Figure 6-5 along with the calculated equilibrium capacity of the column. For most of the run, the water removal was greater than 95%, resulting in a stream containing over 95 wt.% ethanol on a solvent free basis. More than 70% of the equilibrium capacity before the water concentration began to rise above this level. The breakthrough was quite gradual, especially considering the low flow rate, suggesting significant mass transfer resistance in the column. Though both of the thermocouples were monitored continuously through the run, the maximum temperature

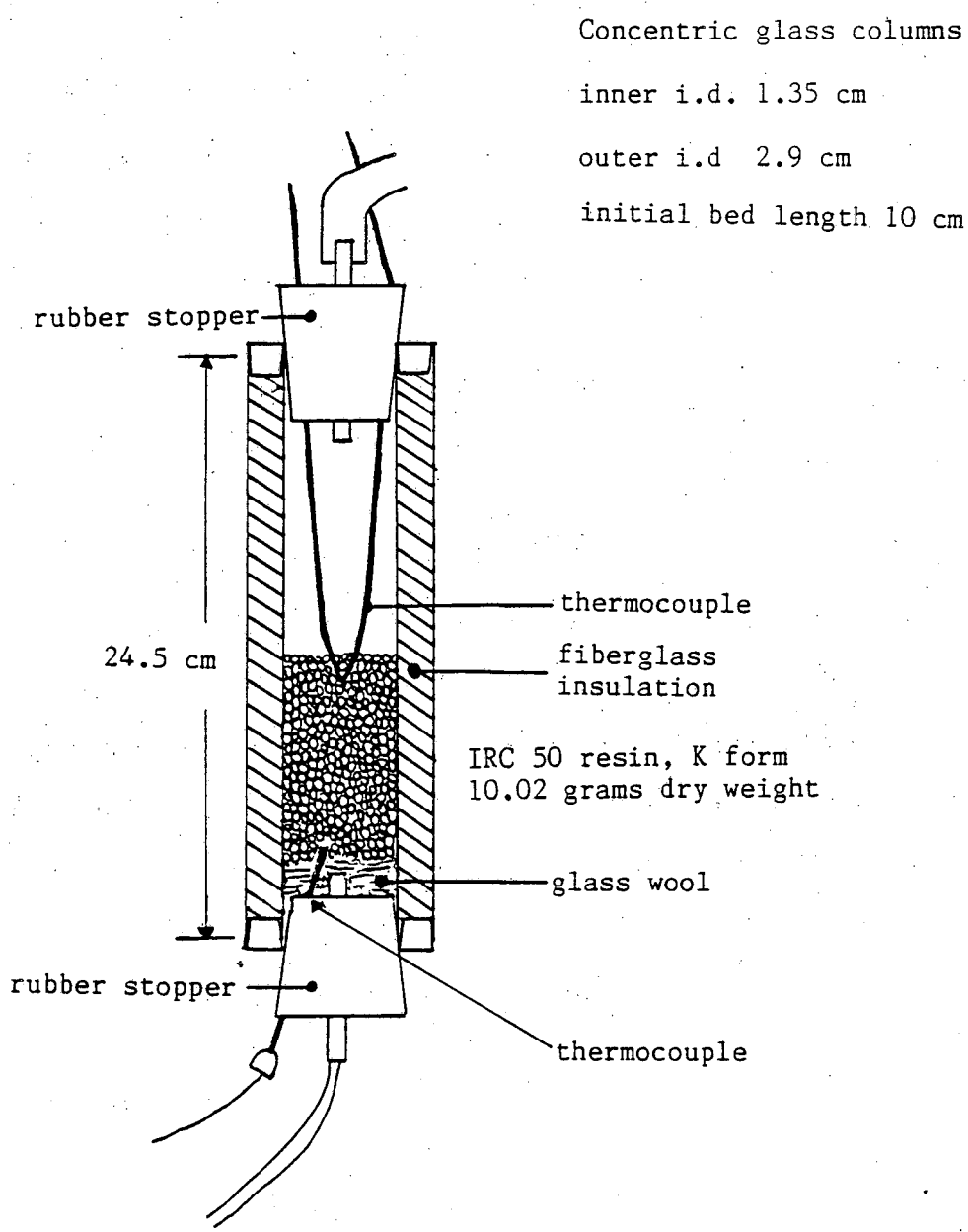


Figure 6–4 Experimental Apparatus for Fixed Bed Water Removal Study

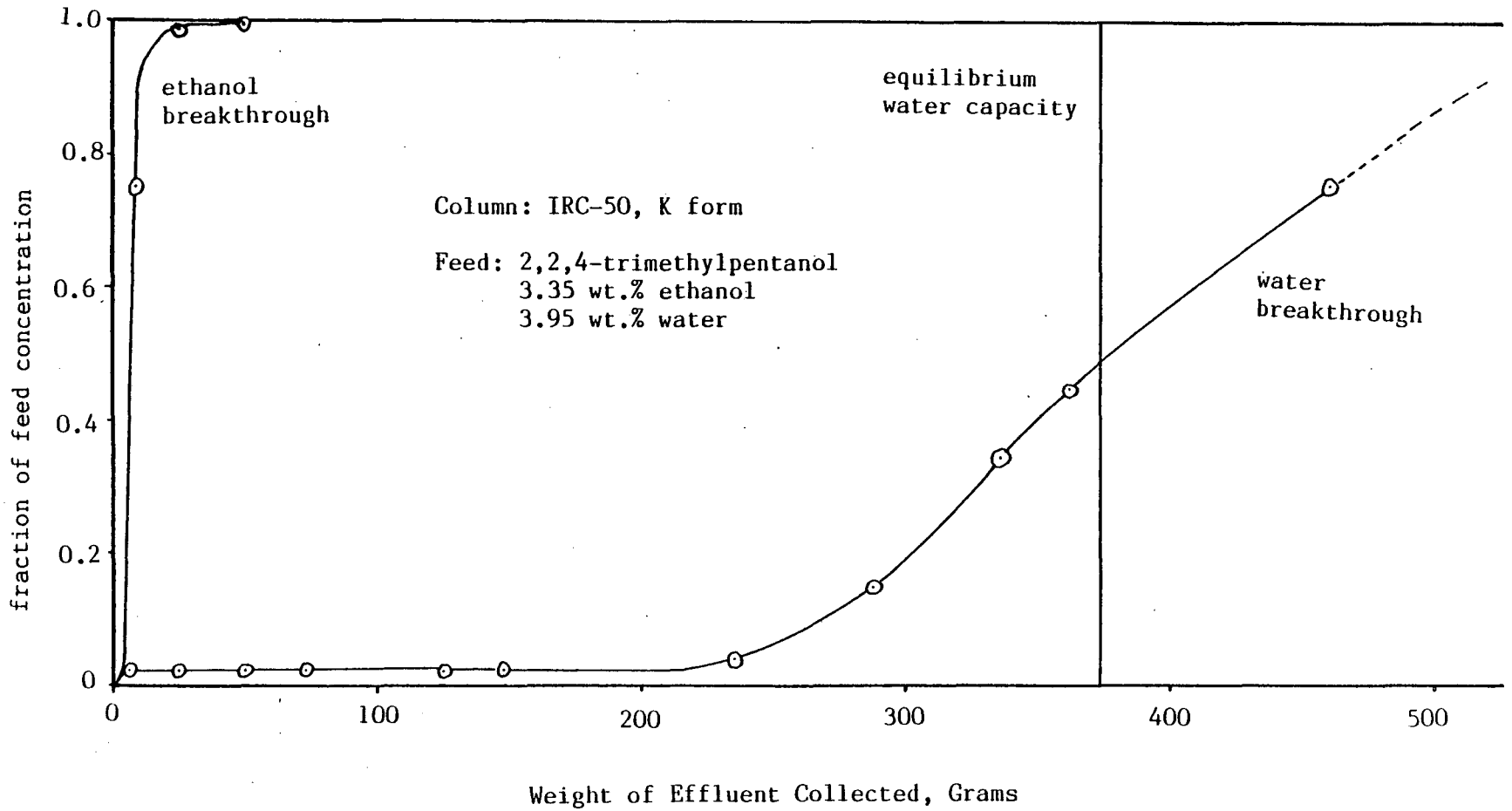


Figure 6-5 Effluent Concentration Profiles from Column Breakthrough Experiment

increase observed was only 2 ^{o}C. Despite the precautions taken to avoid heat losses, they still dissipated the heat of absorption too rapidly for any significant temperature rise to occur.

6.2.4 Batchwise Adiabatic Sorption

While the heat of water sorption had no effect on the small laboratory scale columns used in this work, its effects would be significant in the large columns that would be needed if this process were used on an industrial scale. Because the amount of heat released is important to the design of the system and the modelling which was done, it was necessary to estimate this quantity. A crude but effective calorimetric technique was used to do this.

A 10 gram sample of the IRC-50 resin in the potassium form, dried thoroughly over P_2O_5, was used in the experiment. Twenty grams of an aqueous ethanol solution saturated with 2,2,4-trimethylpentanol and 3 grams of the organic phase in equilibrium with it were placed in a 50 ml roundbottom flask. The flask was wrapped with roughly 5 cm of fiberglass insulation and the temperature of the liquid inside was measured with a thermocouple. Then the resin was added and a rubber stopper, fitted with the thermocouple, was used to seal the flask. The temperature rose to a maximum of 48 ^{o}C from its initial value of 20.5 ^{o}C. Using the known heat capacities of the pure liquids and estimating the contribution of the dry resin to be .75 cal/gm-^{o}C, the total heat capacity of the contents of the flask was about 30 cal/^{o}C. Thus, a minimum of 825 calories were released. Assuming that this was due to the sorption (in the first minute) of 1 gram of water per gram of dry sorbent, a minimum value of 83 calories per gram of waterwas estimated for the heat of sorption. Allowing for wall effects and

losses, the average heat released on absorption of water by this resin is probably close to 100 calories per gram of water.

No prior measurements of the heat of swelling for this resin were found, but several researchers have measured the heat of water swelling of the polystyrene sulfonate resins. In studies that calculated the heat of swelling from the temperature dependance of a water sorption isotherm, average heats of swelling were found to be as high as 220 cal/gm of water for the hydrogen form of the resin (Sundheim et al, 1959). However, that method cannot be expected to be very accurate since the changes in water sorption with temperature are very small. Other investigators, using a direct calorimetric technique, found average heats of water sorption to be 50 to 55 cal/gram of water for hydrogen and sodium forms of the same type of resin (Lapanje and Dolar, 1959). The polymethacrylate resin might be expected to have a higher average heat of water sorption, by the analogy to heats of dilution, because its charge density is nearly twice as high as that of the polystyrene sulfonate resins.

It should be pointed out that this heat must be supplied to desorb the water from the resin. However, it is less than 1/5 of the heat of vaporization of water. In addition, if there is a concentration driving force, it is possible to supply this heat of desorption from the relatively low grade heat present as sensible heat of the solvent.

6.4 Modelling Large Scale Column Behavior

In order to better understand the operation of the fixed bed water removal process and to provide a basis for the design of large scale systems, some mathematical models of the process were investigated. This section discusses the reasons for seeking a model, the activities of others who have modelled similar systems, and the approach and results of the present work.

6.4.1 The Need for Modelling

The laboratory scale experiments with fixed bed water removal described in the previous section demonstrated that, despite the exothermic nature of the water sorption, the operation of the column remained practically isothermal. Thus, thermal effects were practically negligible in such a small system. In a large diameter column, such as those which would be required for an industrial scale application, the operation would become practically adiabatic for most of the column, so thermal effects would be significant. The laboratory experiments have shown, though, that there are sorbents which will selectively remove water, in batch or fixed bed systems, from moderately polar solvents containing water and ethanol. Thus, the key questions that remain are primarily concerned with the process dynamics. For example, the temperature of the solvent entering the regeneration phase of operation is an important parameter to be determined. In addition, the size of the beds is important, because their capital cost may be very significant.

The bed size is often set by choosing a cycle time long enough to fit conveniently into operating labor shift cycles. The optimum bed size would, however, be driven by capital cost and pressure drop

considerations to a minimum. To operate a small bed with a short cycle time would require good process control. Fortunately, though, the properties of the system suggest the possibility of implementing a process control scheme based on temperature measurement rather than direct measurement of water concentration breakthrough. A good model of the process would be required to do this.

6.4.2 Previous Work

Most of the literature on absorption and adsorption that involves modelling deals with the isothermal subset of the problem. It is relatively easy to deal with compared to a full treatment because the inclusion of thermal effects is complicated by the fact that the phase equilibrium is a strong function of temperature. Because the problem at hand involves fairly high concentrations of absorbing species and the expected temperature changes are of interest, a nonisothermal model is required. The logical starting point is the opposite extreme from the isothermal approach; an adiabatic model.

The basic equations describing the one-dimensional absorption problem have been developed by many (Acrivos, 1956; Meyer and Weber, 1967; Vermeulen et al, 1973, others). The assumptions used to obtain a tractable model include the following:

1. Only one component changes phase.
2. Radial gradients can be neglected (one-dimensional problem).
3. Axial diffusion and conduction are negligible compared to convection.

Furthermore, in the case of interest, the density of the fluid varies with the concentration of the absorbing species. The mass of solvent per unit volume and the superficial velocity remain approximately

constant, however. It is thus convenient to use mass ratio concentration variables. Assuming constancy of solvent density and superficial velocity, a material balance on the absorbing species gives equation (6-1);

$$v \rho_f \frac{\partial X}{\partial s} + \varepsilon \rho_f \frac{\partial X}{\partial t} = -\rho_b \frac{\partial Y}{\partial t} \tag{6-1}$$

A balance on enthalpy leads to equation (6-2);

$$v C_f \rho_f \frac{\partial T_f}{\partial s} + \varepsilon C_f \rho_f \frac{\partial T_f}{\partial t} = -C_s \rho_b \frac{\partial T_p}{\partial t} + \rho_b \frac{\partial H}{\partial Y} \frac{\partial Y}{\partial t} \tag{6-2}$$

The meanings of the symbols in these equations are given in Table C.1 in Appendix C. Solution of these equations necessarily involves assumptions about the rates of mass and heat transfer between the fluid and solid phases. It is interesting to briefly review some of the approaches taken by others before going on to the present work.

One simple approach is to ignore the thermal effects on the equilibrium. Concentration profiles can then be calculated using an isothermal treatment and it may be possible (depending on the complexity of the models for mass transfer) to obtain an analytical solution (Vermuelen et al, 1973). In some cases, including the absorption step of the system of interest here, this may be a reasonably accurate approach because the thermal wave travels through the bed faster than the concentration wave, effectively uncoupling the two variables for most of the absorption region. In the general case, though, an isothermal treatment will produce serious errors (Lee and Weber, 1969).

If a nonisothermal treatment is to be employed, the simplest approach is to assume that the two phases are in equilibrium at every point and time in the process. This route has been studied extensively by Rhee and Amundsen (1970), and by Rhee et al (1970), among others. While it is very useful for characterizing the behavior of systems, such as the occurence of sharp or broad fronts and plateau regions, it naturally will not reflect accurately the behavior of real systems with finite rates of heat and mass transfer (Cooney, 1974). The departure from equilibrium will be especially great in the system under consideration here because it is a liquid system and involves absorption into solid particles rather than adsorption from a gas.

There are not very many investigations of the nonisothermal case with finite rates of heat and mass transfer. Among these, the work of Meyer and Weber must be considered a landmark (Meyer and Weber, 1967). This work involved using a detailed model for intraparticle mass transfer, a variable gas flow rate, and included heat transfer to the walls of the bed. A set of six partial differential equations describing the system was solved using implicit numerical integration along characteristic paths. At the time, however, the utility of the model was severely restricted by its computer time requirements. While that limitation has probably been mitigated in the interim, another objection to the model, that it contained too many unknown (therefore adjustable) parameters, would seem to remain valid.

A somewhat simpler approach was taken by Chi and Wasan (1970). In their model, linear driving force approximations with constant coefficients for heat and mass transfer were assumed. They also used the method of characteristics to solve the equations numerically.

Their results showed good agreement with experimental data when limited data was used to establish the coefficients needed to simulate an entire run.

More recently, the same kind of model was investigated using a straightforward finite differences technique for the numerical solution (Cooney, 1974). Interestingly, the application of the technique was limited to high gas pressures (500 psig) because numerical instabilities were encountered in the equation involving heat generation by adsorption at lower pressures.

It is to be noted that all these previous studies of real systems involved gas-solid systems. While the principles to be applied to a liquid-solid system are no different from those developed for gas-solid,very different resultscan be obtained, as noted above.

6.4.3 Local Equilibrium Approximation

As a first step in seeking information about the system, the local equilibrium approximation was investigated. A finite differences technique was used to solve equations equations (6-1) and (6-2) with the asumptions of local equilibrium for tempearture and concentrations. Those assumptions are that, at any point in the bed at any time, the temperatures of the fluid and the particles are the same and the concentrations in the two phases are simply related by the equilibrium at that temperature. The details of the model used to describe the temperature-dependant equilibrium are given in Appendix C. An interval halving scheme was used to determine concentrations and temperatures at each grid point. This simple method gave quick convergence for the system of interest. The computer program used to perform the calculations is listed and explained in Appendix C.

A typical result from the local equilibrium approximation model is shown in Figure 6-6. The case shown is for a linear isotherm, so the fact that the concentration variables are not equal in the fluid and solid phases is due only to the effect of temperature on the equilibrium. There is a separation of the thermal wave from the concentration wave apparent in the model prediction even after a relatively short time. This occurs because the ratio of the water capacity of the solid sorbent to that of the fluid is much larger than the ratio of the heat capacities of the two phases. Thus, the heat generated by the sorption is carried forward in the bed by the fluid, keeping most of the mass transfer zone close to the inlet temperature of the fluid. This is a fortunate result from the process design aspect because a higher temperature in that zone would spread the front and decrease the capacity of the sorbent. Comparison with a run in which the same parameters were used, but the heat of absorption was set equal to zero, shows that the length of the mass transfer zone in the adiabatic case is about three times as long as in the isothermal case, due to the spreading effect of temperature. The equilibrium is represented by a contant separation factor **R**, described in Appendix C. When an R value of 0.6 is used to represent a slightly favorable equilibrium instead of the linear one, the mass transfer zone for the absorption shrinks, as would be expected. In addition, the length of the zone remains constant as it moves down the bed in the case of a favorable isotherm, but the length increases with distance in the bed for the linear case. Desorption, however, is more difficult if an isotherm favorable for absorption is used.

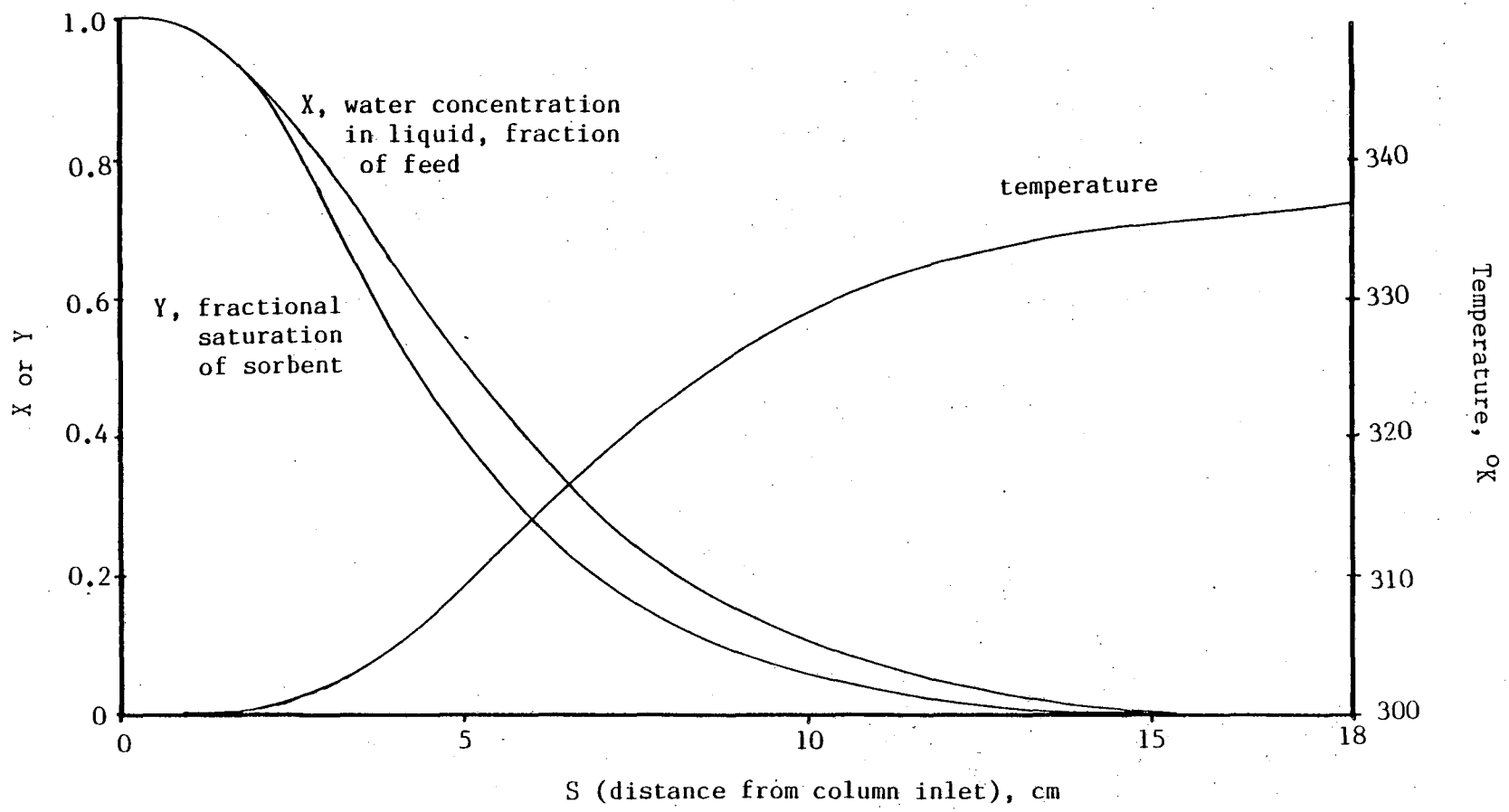


Figure 6-6 Adiabatic Water Sorption Modelled by Local Equilibrium Approximation

The results of modelling a desorption with the local equilibrium approximation are shown in Figure 6-7. The system is the same as that of Figure 6-6, with the initial conditions and feed temperature changed. While the peak in the fluid concentration is unrealistically high (implying a doubling in solubility with a 30 ^{o}C temperature increase), this is due to the nature of the equilibrium model used. The qualitative behavior of the concentration profiles should be accurate. It can be noted that the drop from the inlet temperature to the middle temperature plateau is the same as the temperature rise seen in the absorption model. This temperature plateau moves ahead through the bed with time in a behavior similar to the separation of the temperature and concentration waves seen previously. The slight rise in temperature toward the end of the plateau region is an artifact of the model, due to the form of the enthalpy function and the fact that resorption of the water desorbed upstream in the bed is taking place in that region.

The local equilibrium approximation should be a good one if very small particles and very low liquid flow rates could be used in the process. For such a case, the model shows that the fixed bed water removal process should work quite well when the minimum temperature of the regenerating stream is the temperature reached at the bed outlet during the sorption step. In addition, the predicted temperature and concentration profiles are simple enough to offer good potential for automatic process control by using temperature measurements. However, a more stringent test of the process concept must account for finite rates of heat and mass transfer, because the conditions of local equilibrium are not likely to be met by an economical process.

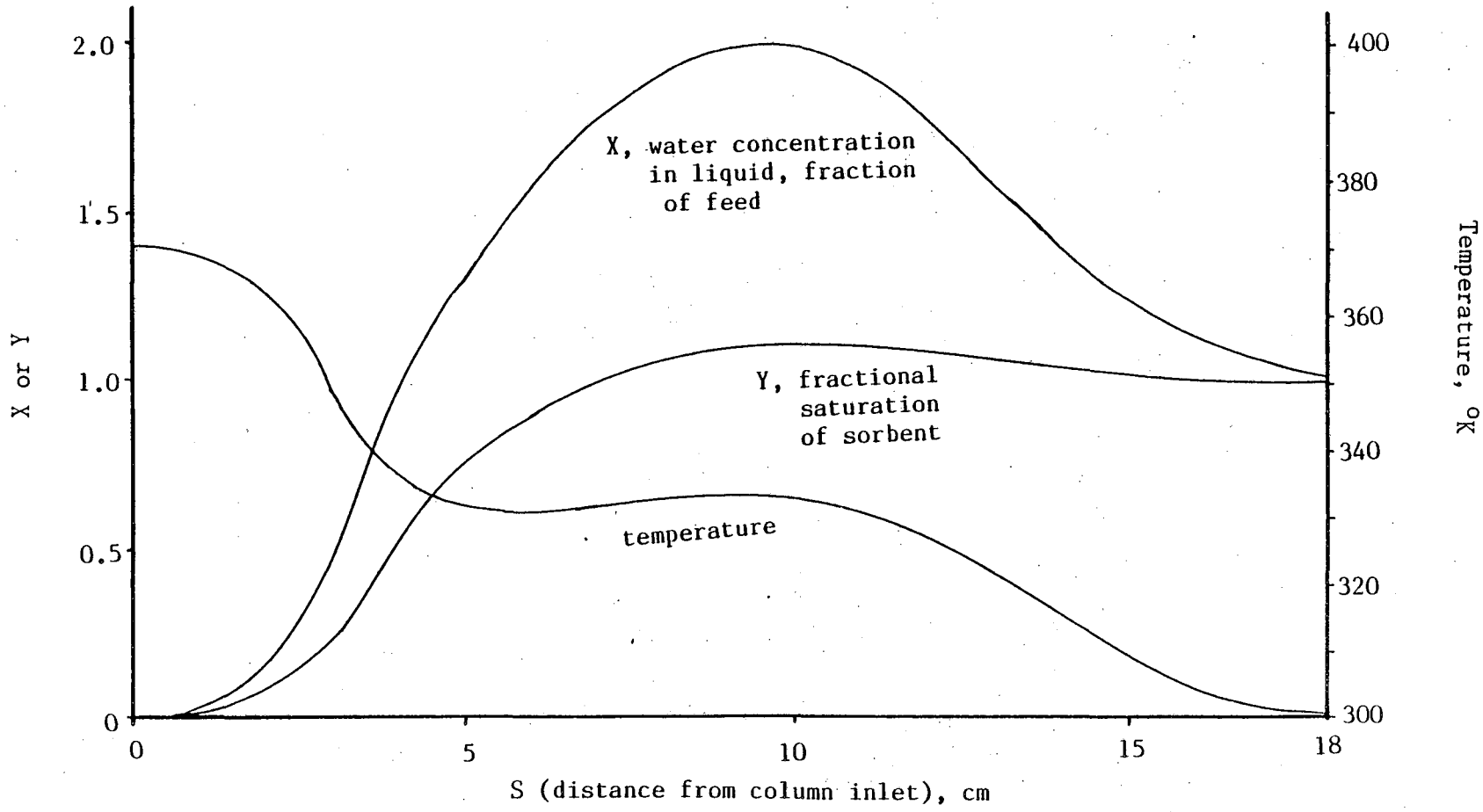


Figure 6-7 Adiabatic Desorption of Water Modelled by Local Equilibrium Approximation

6.4.4 Dynamic Modelling by the Method of Characteristics

The solution to the problem with finite rates of heat and mass transfer is accomplished using a model based on the assumptions discussed above. It was decided to adopt a solution technique similar to that of Chi and Wasan (1970), using the method of characteristics to solve equations for a constant coeficient linear driving forces model. A further simplification is the neglect of swelling of the solid phase, which is in fact significant for the systems of interest. Swelling mainly affects the region of the bed which has reached equilibrium with the feed, however, and not the region of interest which is the zone of active mass transfer.

The method developed here follows very closely that proposed by Acrivos (1956). Once again, the symbols used in the equations are defined in Appendix C, Table C.1. The first steps involve a few simple variable transformations. The concentrations are nondimensionalized by defining;

$$x = X/X_s \quad \text{and} \quad y = Y/Y_s \tag{6-3}$$

It is also useful to change the independant variables by defining;

$$z = s/v \quad \text{and} \quad n = t - \varepsilon\, s/v \tag{6-4}$$

so that **z** measures position in the bed by the time required to reach it from the bed inlet travelling at the superficial velocity of the fluid, and **n** is the time corrected for filling time or measured from when the first element of fluid to enter the bed reaches the specified bed position. With these definitions, the partial derivatives in equation (6-1) are transformed as follows;

$$\frac{\partial X}{\partial s} \rightarrow X_s \left[\frac{\partial x}{\partial n}\frac{\partial n}{\partial s} + \frac{\partial x}{\partial z}\frac{\partial z}{\partial s}\right] = X_s \left[\frac{\partial x}{\partial z} - \frac{\partial x}{\partial n}\right] \tag{6-5}$$

$$\frac{\partial X}{\partial t} \rightarrow X_s \left[\frac{\partial x}{\partial n}\frac{\partial n}{\partial t} + \frac{\partial x}{\partial z}\frac{\partial z}{\partial t}\right] = X_s \frac{\partial x}{\partial n} \tag{6-6}$$

and equation (6-1) can be expressed as the two equations;

$$\frac{\partial x}{\partial z} = \frac{-\rho b\ Y_s}{\rho f\ X_s} Rm \tag{6-7}$$

$$\frac{\partial y}{\partial n} = R_m \tag{6-8}$$

where R_m is a known function of the temperatures and concentrations. In a completely analagous fashion, equation (6-2) is transformed into;

$$\frac{\partial T_f}{\partial n} = \frac{-Rh}{C_f\ \rho_f} \tag{6-9}$$

$$\frac{\partial T_p}{\partial n} = \frac{Rh + Rg}{C_s\ \rho_b} \tag{6-10}$$

where R_h is the rate of heat transfer from fluid to solid phase and R_g is the rate of heat generation due to absorption, both known functions of the temperatures and concentrations (and the rate of mass transfer in the case of R_g). The reason for the variable changes is now apparent. Along the characteristics,

$$n = \text{constant} \tag{6-11}$$

the partials of equations (6-7) and (6-9) may be treated as ordinary differentials. Similarly, along the characteristics,

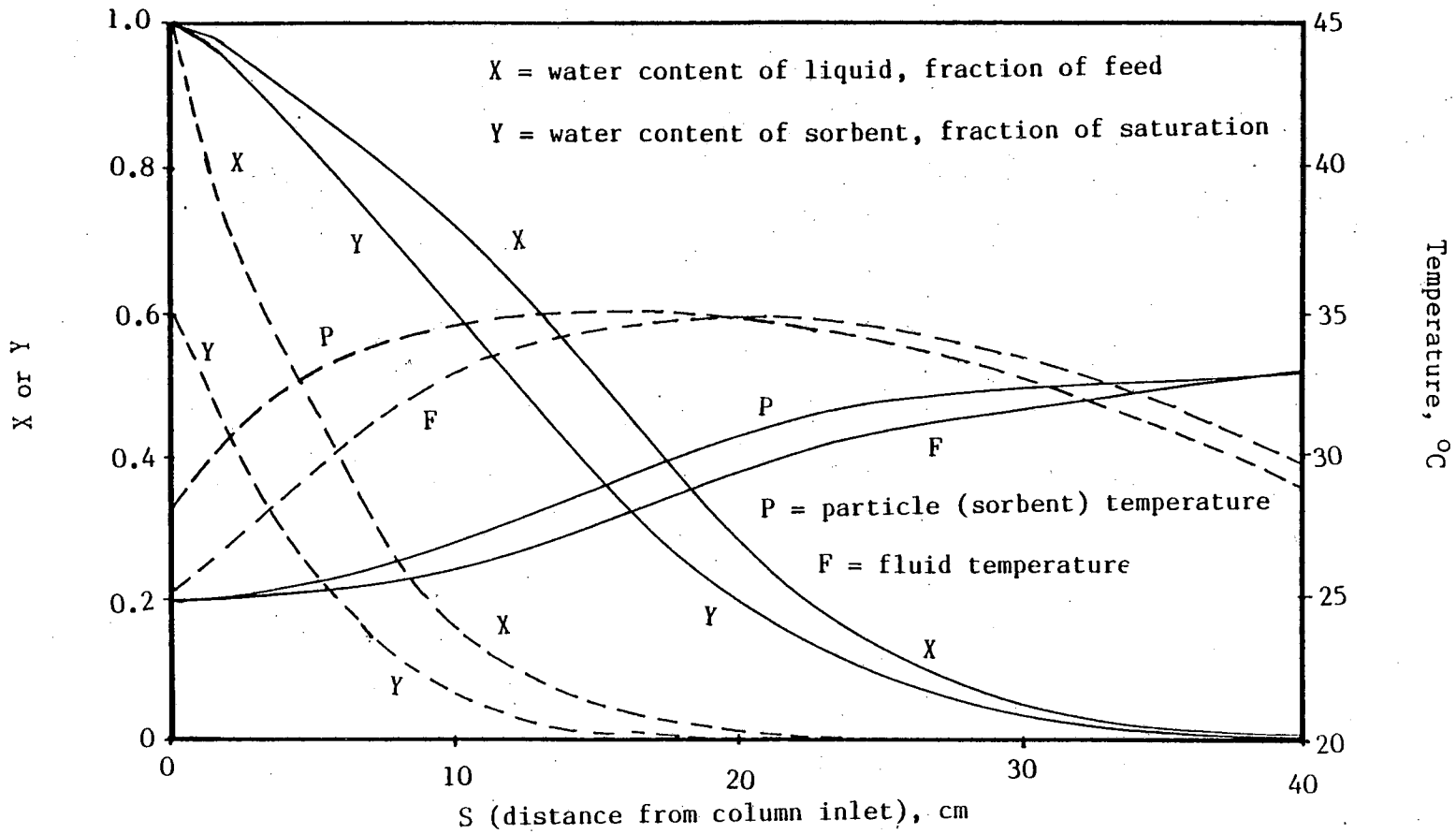
$$z = \text{constant} \tag{6-12}$$

equations (6-8) and (6-10) may be treated as ordinary differential equations. Thus, numerical integration of the set can be accomplished by stepping through a grid in **n** and **z**, calculating unknown values of the dependant variables, **x**, **y**, T_f, and T_p, from a knowledge of their derivatives, R_h and R_m (R_g being a function of **Rm**), at previously determined grid points. The detailed models and numerical methods used to carry out these integrations are given in Appendix C, along

with a listing and explanation of the computer program used for the calculations.

The results of some calculations for water sorption from an organic solvent by an ion exchange resin are shown in Figure 6-8. Comparing these with the local equilibrium results, one sees that the mass transfer zone is much longer when finite rates of transfer are used. The length of the mass transfer zone in cm for the linear equilibrium isotherm case is about 40 times the superficial velocity in cm/s. This is for a particle diameter of .03 cm and a soild phase diffusivity of 10^{-6} cm^2/s. The case shown included only particle side mass transfer resistance, but the results would be the same if the resistance had been divided between fluid and particle phases because of the linear isotherm used. The temperature rise is much smaller than that observed in the local equilibrium model result even though the system properties are practically the same. This is due to the fact that the heat release takes place over a longer time and a longer length of bed when the effect of a finite rate of mass transfer is included in the analysis. There is still a separation of the thermal wave from the concentration wave in the bed, however, with a maximum temperature rise of about 10 ^{o}C for the case shown.

Problems with the stability of the solution were encountered with the modified Euler method used in the calculations. For a time increment of 1 second, the heat transfer coefficients calculated by the method given in Appendix C led to unstable, physically unrealistic behavior. It was necessary to reduce the heat transfer coefficient by a factor of 5 or more to obtain stable solutions. As the results show, however, the fluid and particle temperatures never differ by



— — — t = 40 sec ——— t = 200 sec

Figure 6-8 Adiabatic Water Sorption Modelled by the Method of Characteristics

more than 5 ^{o}C with the reduced heat transfer coefficient, so increasing it would not change the results very much. It would be possible to use a higher heat transfer coefficient if the time step size were reduced (Meyer and Weber, 1967; Chi and Wasan, 1970), but this would of course require more calculation for a given solution. Improvement of the stability of the method might be realized by going to an implicit integration technique. A simpler alternative, however, would be to use the local equilibrium approximation for the temperature and the method of characteristics only for the concentrations. In this work, though, the desired information could be obtained with the slight modification of the heat transfer coefficients, so other approaches were not pursued.

The numerical solution of the desorption step for the system of Figure 6-8 is shown in Figure 6-9. The similarity of the curves for the short time shown to the local equilibrium curve of Figure 6-7 is apparent. At the longer time, the drop to a temperature plateau is by the same amount, roughly 9 ^{o}C, as the temperature rise seen in the sorption step. As in the local equilibrium case, the fluid phase concentration during the desorption reaches values which may be unrealistically high, due to the nature of the model used for the temperature dependance of equilibrium. However, reducing the solubility at higher temperature simply shifts the concentration profiles to lower values. It may be noted that the length of the mass transfer zone is shorter in this case than in the case of the corresponding absorption, so reducing the high temperature solubility somewhat would still result in regeneration times which are roughly equal to the loading time.

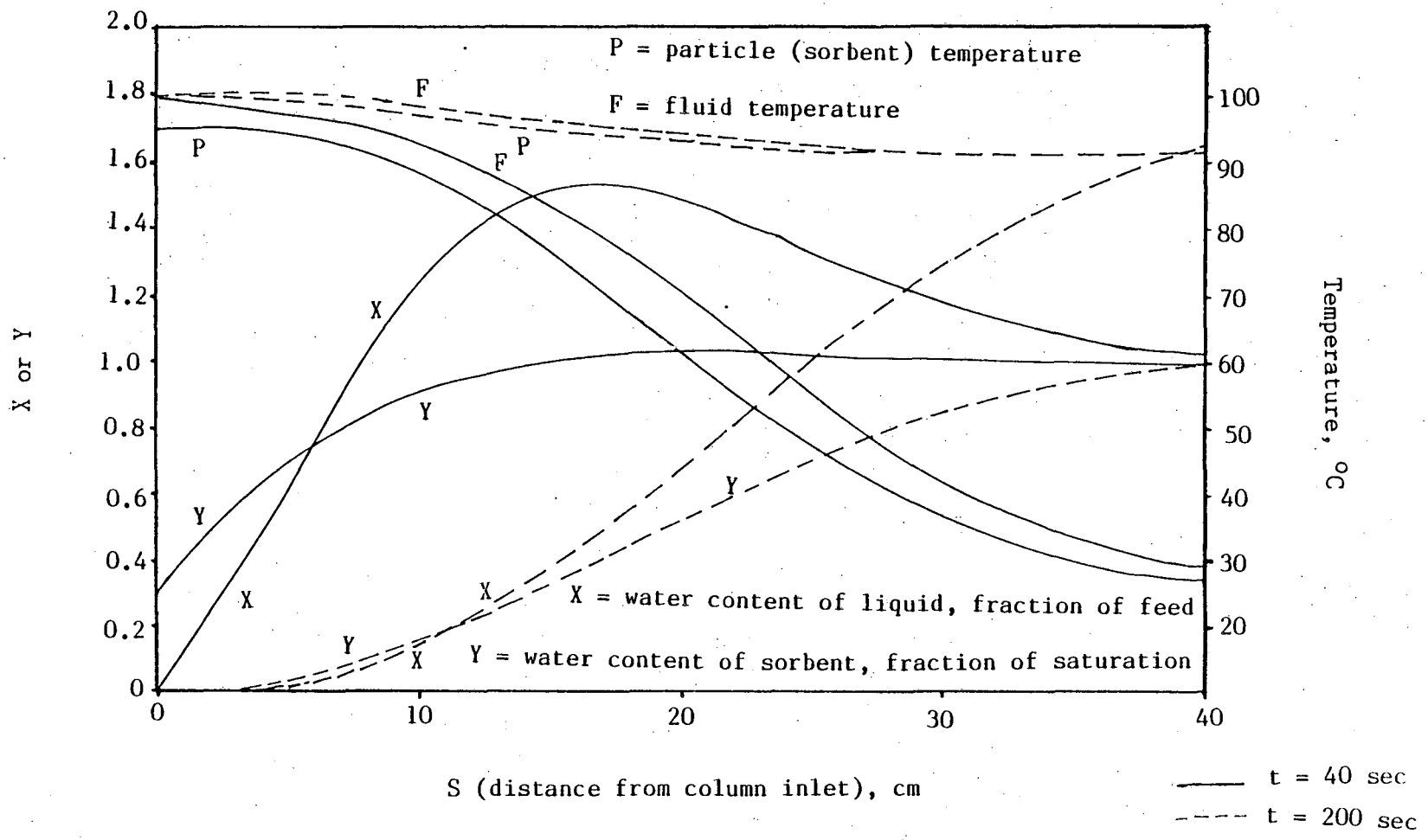


Figure 6-9 Adiabatic Water Desorption Modelled by the Method of Characteristics

A possible problem exists, however, with the assumption of constant diffusivity of the water in the sorbent. Diffusion through the water-swollen ion exchanger is rapid, so the absorption step can be expected to be modelled well by a constant coefficient. During desorption, however, the outside of a resin particle dries first, forming a layer of dry polymer which may offer significantly more resistance to water diffusion than the water-swollen form. Counteracting this, though, is the fact that the diffusivity should increase rapidly with temperature, so the high temperature of the desorption may overcome the drying effect. In the absence of experimental information, the effects have been assumed, in this work, to cancel each other.

Conclusions from this work are that it appears technically feasible to operate a water removal process of the kind depicted in Figure 6-1 and that its thermal characteristics should allow the use of automatic control of the process based on temperature measurements. For design purposes, the length of the mass transfer zone for both sorption and desorption will be approximately forty times the superficial velocity (measured with seconds as the time unit). The temperatures required for desorption are within the operating limits of the polymethacrylate ion exchange resins found to be the best candidates for sorbents for the process.

REFERENCES

1. Acrivos, A. (1956) Ind. Eng. Chem., **48**:703

2. Burfield, D.R., and Smithers, R.H. (1980) J. Chem. Tech. Biotechnol., **30**:491

3. Chi, C.W. and Wasan, D.T. (1970) AIChE Journal, **16**(1):23

4. Cooney, D.O. (1974) Ind. Eng. Chem. Proc. Des. Dev., **13**(4):368

5. Fanta, G.F., Burr, R.C., Orton, W.L., and Doane, W.M. (1980) Science, **210**(7):646

6 Garg, D.R., and Ausikaitis, J.P. (1983) Chem. Eng. Prog., **nn**:60

7. Helfferich, F. (1962) Ion Exchange, McGraw-Hill New York

8. Lapanje, S., and Dolar, D. (1959) Z. Phys. Chem. (Frankfurt), **21**:376

9. Lee, M.N.Y. (1979) "Novel Separations with Molecular Sieves Adsorption" in Recent Developments in Separation Science, vol. 1, N.N. Li, ed. CRC Press, Cleveland, Ohio

10. Lee, R.G. and Weber, T.W. (1969) Can. J. Chem. Eng., **47**(2):60

11. Meyer, O.A. and Weber, T.W. (1967) AIChE Journal, 13(3):457

12. Rhee, H.K. and Amundsen, N.R. (1970) Chem. Eng. J., **1**:241

13. Rhee, H.K., Heerdt, E.D., and Amundsen, N.R. (1970) Chem. Eng. J., **1**:279

14. Sundheim, B.R.,Waxman, M.H., and Gregor, H.P.(1953) J. Phys. Chem., **57**:974

15. Vermuelen, T., Klèin, G., and Hiester, N.K. (1973) "Adsorption and Ion Exchange" in Chemical Engineer's Handbook, 5th Edition, Perry, R.H. and Chilton, C.H. eds., 16-18 ff. McGraw-Hill

7. Economic Analyses

The ultimate value of any proposed process for recovery of ethanol or any other fermentation product is measured in terms of its economic impact. The purpose of this chapter is to report estimates of the economic worth of the new proposed process, comparing it to distillation and to other processes for ethanol recovery.

7.1 Methods and Base Case Assumptions

The economic analyses in this work involve a number of different process configurations. Because it is desirable to compare them on as equal a basis as possible, standard methods of designing equipment and estimating its costs should be adopted. This fact, coupled with the desire to examine the effects of varying a rather large number of the process parameters for some processes, led to the development of a flexible system of computer programs to facilitate the calculations. The details of the programs used, including listings, input data format, and samples of output, are given in Appendix D. In summary, they consist of an executive main program which handles data input, keeps track of process streams, and calls subroutines which correspond to the various unit operations used in a given process. A special subroutine for economic analysis collects information generated by the unit operations modules and calculates total costs for running the process. This economic analysis subroutine (**econom**) naturally uses a number of costs and estimating factors which must be supplied as input variables. Since the values of these variables directly determine the calculated process costs, it is important to establish a set for use

as a base case in comparing costs of different processes. A list of the set of economic variables used as a base case in this work is given in Table 7.1. While most of the items in the table are self-explanatory, those pertaining to the capital cost estimating and accounting are worth clarifying. The procedure used here is quite similar to that used by Maiorella et al (1983) in estimation of ethanol distillation costs. The cost estimates for main items of purchased equipment are adjusted for inflation by applying the appropriate ratio of the Marshall-Swift equipment cost index as reported in the publication Chemical Engineering (McGraw-Hill, New York). The base for this work is the first quarter of 1983, for which the M-S index is 751. The total fixed capital cost of a process is estimated by the "Lang factor" method; as the product of a fixed multiplier (the Lang factor) and the sum of purchased equipment costs. The contribution of capital cost to product cost is then estimated as the sum of two contributions. The first is the capital-related cost of manufacture, including depreciation, maintenance, insurance, and local taxes. It is estimated as the product of a "capital factor" and the total fixed capital estimate. The 0.156 value of the capital factor, for example, was the result of assuming 18 year, straight-line depreciation, 6% annual maintenance cost, 1% annual insurance premium, and 3% annual local tax. The second contribution of capital to product cost is a profit factor and is equal to the desired simple rate of return on investment before tax. Working capital requirements have been omitted in these analyses, so the rate of return on the total investment would be slightly lower than the input factor.

Table 7.1 - Base Case Economic Variables

Variable	Value
Marshall-Swift index, inflation adjuster for equipment cost (base period: first quarter 1983)	751
Lang factor, multiplies total purchased equipment cost to give total fixed capital cost	4.90
Capital factor, multiplies total fixed cost to give annual capital-related cost of manufacture	0.156
Profit factor, multiplies total fixed cost to give profit before tax	0.30
Labor cost (operating), $ per man-year	30,000
Labor factor, multiplies base labor cost to give total labor cost (including supervision)	1.65
Hours of operation per year	8000
Temperature of low pressure steam (saturated), ^{o}C	180 (150 psi)
Cost of low pressure steam, $ per 1000 lb.	5.00
Temperature of high pressure steam (saturated), ^{o}C	300 (1250 psi)
Cost of high pressure steam, $ per 1000 lb.	7.50
Cooling water temperature, ^{o}C	25
Maximum cooling water return temperature, ^{o}C	40
Cooling water cost, cents per 1000 gallons	25.0
Electricity cost, cents per kilowatt-hour	5.0

7.2 The Cost of Distillation for Ethanol Recovery

As stated in previous chapters, distillation is the standard process for ethanol recovery. The economics of ethanol distillation are thus a logical place to begin a discussion of ethanol recovery process analyses.

The cost of a process to recover ethanol by distillation is a function of a number of variables. The most important of these are the feed concentration and the desired product concentration, which interact through the pinch limitation discussed in chapter 2. Also important in determining the cost, however, are the scale of the process, the detailed configuration (the number of columns and the use of heat recovery, as examples), the pressure of the distillation, and the reflux ratio. The economic optimization of the recovery of ethanol by distillation is a complex problem. Fixing the product concentration simplifies the problem somewhat. This approach was used in a recent study (Maiorella et al, 1983) which involved a detailed optimization of the distillation to produce 95 wt.% ethanol over a range of feed concentration. This approach is a practical one, since 95 wt.% ethanol is a commercial product. Furthermore, while it is not necessarily the optimum intermediate concentration for the production of anhydrous ethanol (by azeotropic distillation, selective sorption, or other method), it is probably close to the optimum.

The cost of optimized distillation to produce 95 wt.% ethanol is shown as a function of feed concentration in Figure 7-1. The scale is 25 million gallons per year. Two curves are shown in the figure. The lower was generated by adjusting the costs calculated in the above-mentioned study (Maiorella et al, 1983) to reflect the different base

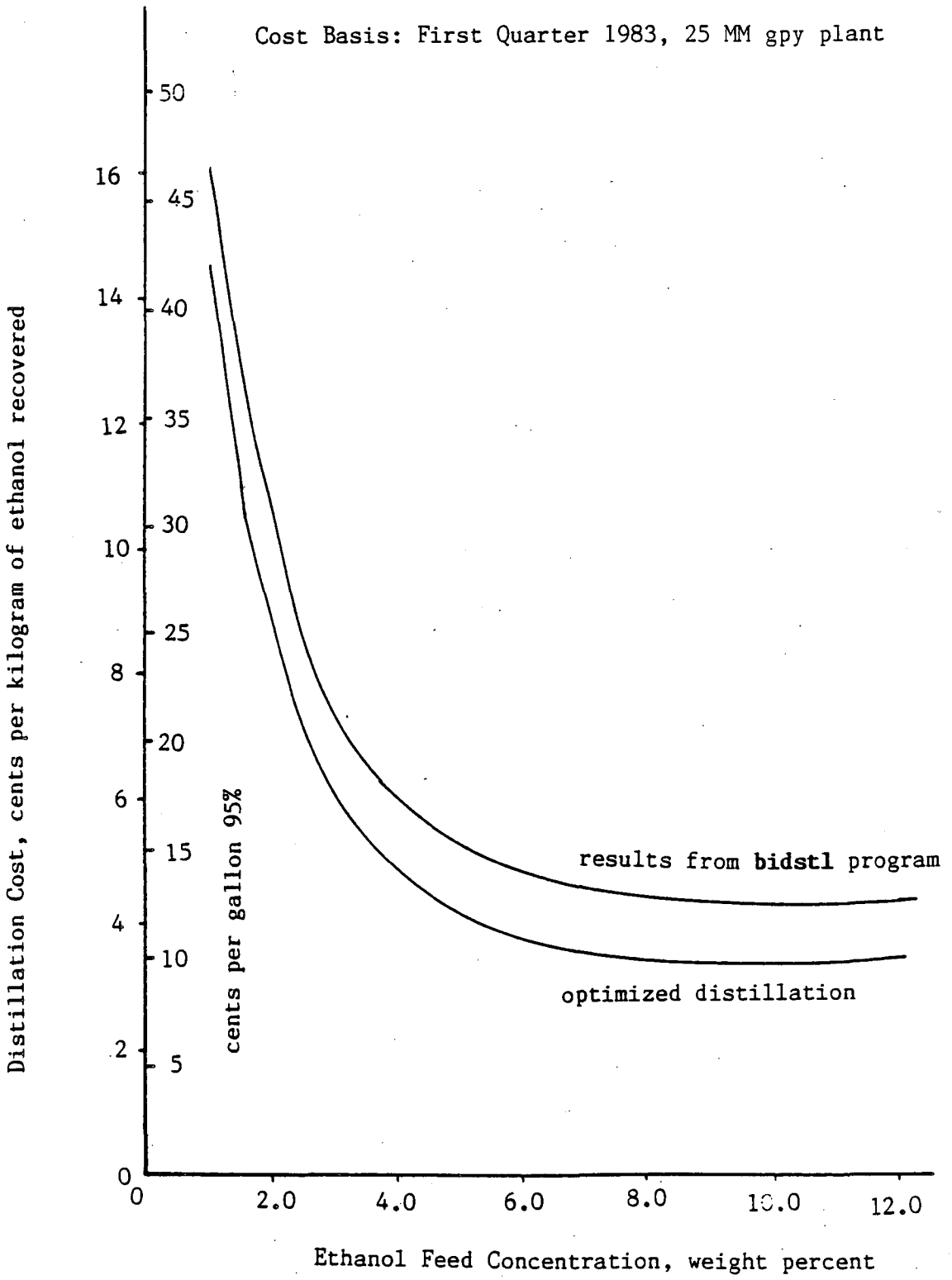


Figure 7-1 Estimated Costs of Distillation to Produce 95 Weight Percent Ethanol as a Function of Feed Concentration

case assumptions used in this thesis. This involved increasing the steam cost by a much larger factor than the capital cost; steam cost was raised from $3.15 to $5.00 per 1000 lb. while the capital costs were adjusted by the Marshall-Swift ratio 751/717. However, Maiorella et al (1983) have shown that the optimum steam consumption is not affected very much by the cost of steam, so the adjusted costs shown in Figure 7-1 are likely to be near the optimal values. The higher curve shown in Figure 7-1 shows the results obtained by using the **bidstl** program (given in Appendix D) to calculate the distillation costs, optimizing only the reflux ratio. The costs are shown in cents per kilogram of ethanol recovered to facilitate comparison with results for other processes which do not necessarily produce 95 wt.% product. The distillation cost per kilogram of 95% ethanol is 95% of the cost on the left axis of Figure 7-1. On the right axis, the cost is shown in cents per gallon of the 95% ethanol.

The costs produced by the **bidstl** calculations are 15 to 27% greater than the optimal cost estimates. This is primarily due to the fact that a suboptimal process configuration is used in the case of the **bidstl** calculations. The optimal process configuration involves the use of an atmospheric pressure stripper and a separate vacuum distillation column with a heat exchanger to transfer the latent heat of the stripper vapors to the vacuum column (a combined condenser and reboiler). The pressure of the vacuum column is one of the variables optimized in the more thorough treatment. In contrast, the **bidstl** program assumes a conventional single fractionating column operation and the pressure in the column is set by fixing the temperature at the condenser (45 ^{o}C in this case).

Despite its relative simplicity, however, the **bidstl** program gives results for the ethanol distillation cost which show the same trends as those seen in the more detailed optimization. A breakdown of the components of some of the costs plotted in Figure 7-1 is given in Table 7.2. It is clear that the cost of energy (as steam) is the

Table 7.2 - Costs of Ethanol Distillation Estimated Using BIDSTL

	Ethanol Feed Concentration, Wt.%		
	2.0	6.0	10.0
Steam cost, cents/kg EtOH	7.05	2.68	2.36
Capital-related cost, cents/kg EtOH	2.52	1.55	1.46
Cooling water cost, cents/kg EtOH	0.43	0.31	0.25
Labor cost, cents/kg EtOH	0.36	0.36	0.36
Total, cents/kg EtOH	10.36	4.90	4.43

greatest part of the process cost. Hence the cost curves have shapes similar to that of the plot of optimum energy consumption versus feed concentration given in Figure 2-2. The same kind of transition is seen at a feed concentration between 5 and 6 weight percent. Above this concentration, the distillation is governed by the pinch at the high ethanol concentration (top of the column) and the energy consumption and process cost level out. Below the transition, the distillation is governed by the amount of water which is vaporized with the ethanol in the feed as it is stripped. So the energy consumption and process cost rise rapidly as the feed concentration becomes more dilute.

7.3 Costs of Liquid-Liquid Contacting

Probably more kinds of equipment have been developed for liquid-liquid extraction than for any other chemical engineering unit operation. The profusion of available contactor designs has been surveyed and classified in recent reviews (Bailes et al, 1976; Lo, 1979). Five major categories can be identified, as follows:

1. Mixer-settlers - characterized by a high degree of flexibility with regard to processing parameters and ease of scale-up, but generally limited to applications requiring few theoretical stages for mass transfer.
2. Unagitated columns - includes spray columns, packed columns, and perforated plate columns, characterized by simplicity and low cost, but also low efficiency.
3. Pulsed columns - pulsation of the liquid in packed or perforated plate columns increases contacting efficiency at the expense of a significant energy input.
4. Agitated columns - includes rotary agitated columns such as Scheibel columns and rotating disk contactors as well as reciprocating plate or Karr columns; characterized by high efficiency and capacity, but difficult to design and scale up.
5. Centrifugal contactors - more costly than other types, but used in special applications in which short residence times are required or phase separation difficulties are encountered.

Selection of the most economical contactor for application to the recovery of ethanol by liquid-liquid extraction is a complex problem. Some guidelines for preliminary selection of liquid-liquid contactors have been proposed (Hanson, 1968; Reissinger and Schroter, 1978;

Robbins, 1979). These, however, reflect the observation that "it is impossible to give anything but the most general guide to contactor selection..,"(Bailes et al, 1976). Because the performance of the various types of extractors is affected differently by the properties of the liquids involved and because these properties can be altered dramatically by the presence of even trace impurities, final selection and design of a contactor can be based only on experiments (Reissinger and Schroter, 1978). The feasibility of the extraction process concept can be investigated without such experiments, however, by assuming the applicability of a contactor and developing a preliminary economic assessment on that basis. That is the approach taken in this thesis.

From the data presented in chapter 3, it is apparent that a relatively low distribution coefficient is unavoidable in a liquid-liquid extraction process for ethanol recovery. For this reason, a moderate to large number of theoretical stages of contacting will be required. In such a situation, some type of column contactor is generally more economical than either a mixer-settler or centrifugal contactor (Bailes et al, 1976; Reissinger and Schroter, 1978; Lo, 1979). As a basis for economic estimates in this work, the unagitated perforated plate column extractor was chosen. This choice is in keeping with the attitude expressed by Robbins (1979) that, "the least complicated contactor which will perform the extraction with low maintenance is preferred for an industrial process". In addition, a detailed design procedure has been published for the perforated plate extractor (Treybal, 1980). That procedure, with certain simplifying assumptions, described in Appendix D, was used in this work.

A typical result for the estimated cost of liquid-liquid contacting calculated using the perforated plate extractor model is illustrated in Figure 7-2. Shown are cost estimates, per kilogram of ethanol extracted, for only the liquid-liquid extraction step of the process. The solvent in this example is n-octanol, which has a distribution coefficient for ethanol of 0.6 and a solubility in water of 0.05 weight percent. The extraction costs are plotted as a function of the fraction of ethanol recovered in the extract. The amount of ethanol in the extract is the same in all cases, 9311 kg/hr corresponding to 25 million gallons per year. The size of the feed stream to the extractor increases with decreasing recovery fraction, since the ethanol concentration in the feed is fixed at five weight percent. The weight ratio of solvent to feed is also fixed in the example at 2.08, which corresponds to an extraction ratio (solvent/feed ratio times distribution coefficient) of 1.25. Two curves are shown in the figure. One is the total cost for the extraction step, while the other shows the contribution of the capital cost alone. The difference between them is primarily due to the value of solvent which is removed from the process by being dissolved in the raffinate (labor cost, with the assumptions used, amounts to only a constant 0.06 cents per kilogram). The unit cost of the solvent is an assumed $1.00 per kilogram.

Figure 7-2 illustrates some points to be made about the cost of liquid-liquid contacting. The cost curves rise very steeply as the recovery fraction approaches 1.0; the end points of the curves are actually at a recovery fraction of 0.998, a recovery fraction acheived routinely in ordinary distillation of ethanol. At this recovery

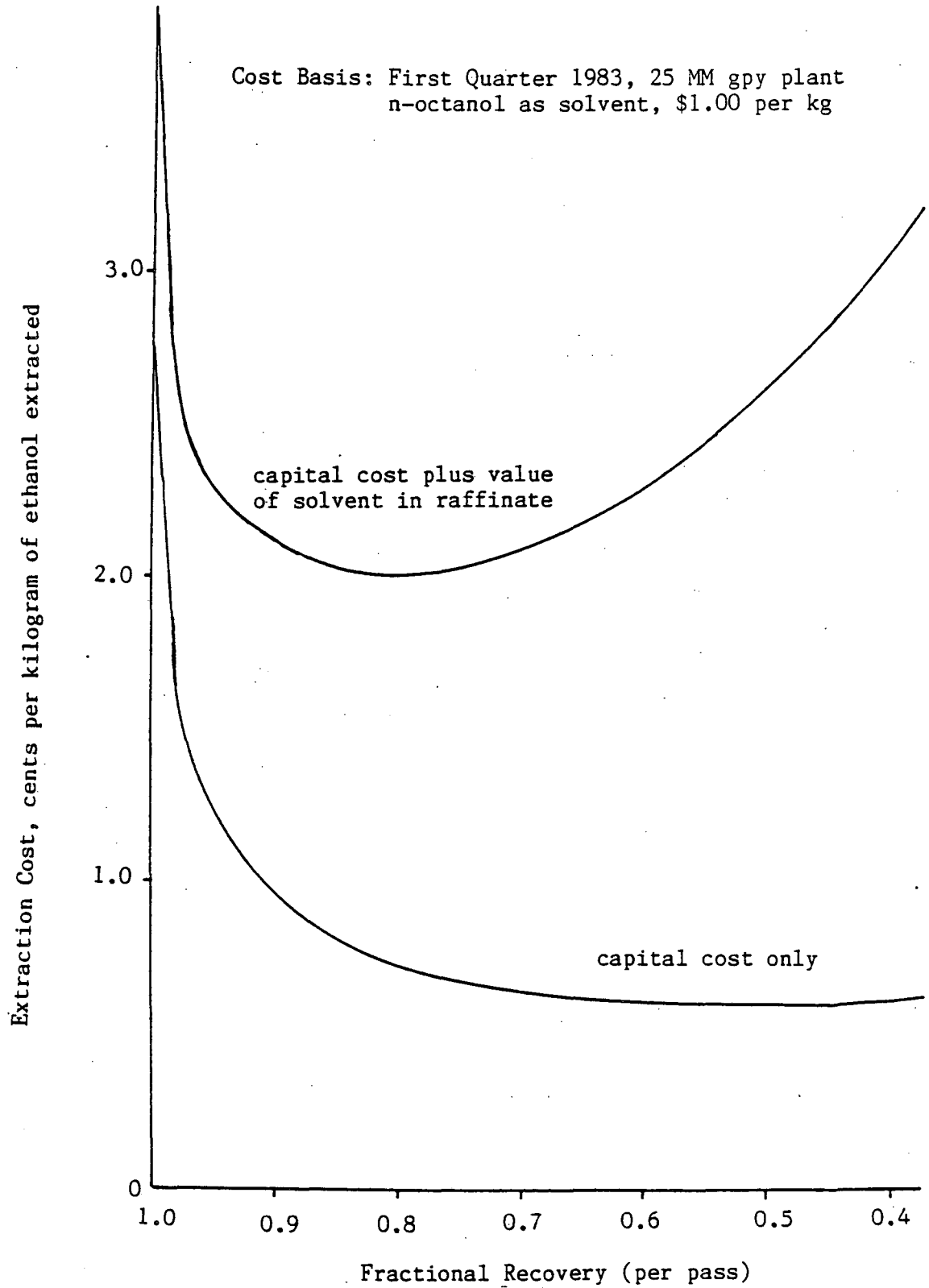


Figure 7-2 Cost of Liquid-Liquid Contacting as a Function of Fractional Recovery

fraction, the capital cost alone for the extraction process is over half the total cost of the optimized distillation at the same feed concentration (Figure 7-1). Comparing this case to that involving a recovery fraction of 0.9, the required throughput increases roughly 10%, but the theoretical stage requirement decreases from over 20 to 4.3. The resulting decrease in the size of the columns required is evident in the capital cost difference. The capital cost contribution continues to decrease with decreasing recovery fraction until the minumum column height (corresponding to less than one theoretical stage) is reached at a recovery fraction of about 0.5. Offsetting this trend, however, is the cost of solvent lost to the raffinate. This cost rises in proportion to the volume of liquid feed to the extractor and thus dominates the total cost as the recovery fraction decreases.

It must be emphasized, however, that the above results apply only in a situation where recycle of the unrecovered ethanol to the upstream process can be employed. Otherwise, the cost of wasted ethanol would dominate the economics at all but the highest recovery fractions. In this situation, of course, the solvent is not necessarily wasted. If the solvent does not adversely affect the upstream process (particularly if it is nontoxic to the fermentation) it may be recycled with the unrecovered ethanol. In other cases it may be recovered in a separate operation. Though it would appear that a very low recovery fraction would be favored in such cases, the costs of solvent recovery in the latter case will be proportional to the size of the raffinate stream and will increase with decreasing recovery fraction in the same way that the value of the solvent in the raffi-

nate is shown to increase in Figure 7-2. In addition, it must be recalled that ethanol itself has an inhibitory effect on the fermentation. So overall process optimization would tend to favor the higher recovery fractions than those appearing most economical from the standpoint of liquid-liquid contacting alone. By using a reduced extraction ratio (lower solvent to feed ratio) with the lower recovery fraction, the size and cost of the liquid-liquid contacting equipment can be kept to a minimum while still obtaining reasonably high ethanol concentration in the extract.

While it is true that the cost of the optimized distillation would also be reduced by operating at a lower recovery fraction, the effects in that case are not as pronounced. The energy consumption of the distillation is not reduced by such a change, so the effect is only to reduce the capital cost by decreasing the size of the stripping column. Since this column typically accounts for 30% or less of the purchased equipment cost and the total capital cost contribution is less than 30% of the distillation cost, it is apparent that the curves of Figure 7-1 would be shifted only slightly by reducing the recovery fraction for the distillation.

7.4 Costs of the Process Proposed for Ethanol Recovery

The overall process proposed in this thesis as an alternative to distillation for ethanol recovery is depicted schematically in Figure 7-3. It involves liquid-liquid extraction of the ethanol, selective water removal by fixed bed absorption, and distillation to produce the ethanol product and regenerate the solvent. It allows for the recovery of solvent from the raffinate stream by vacuum steam

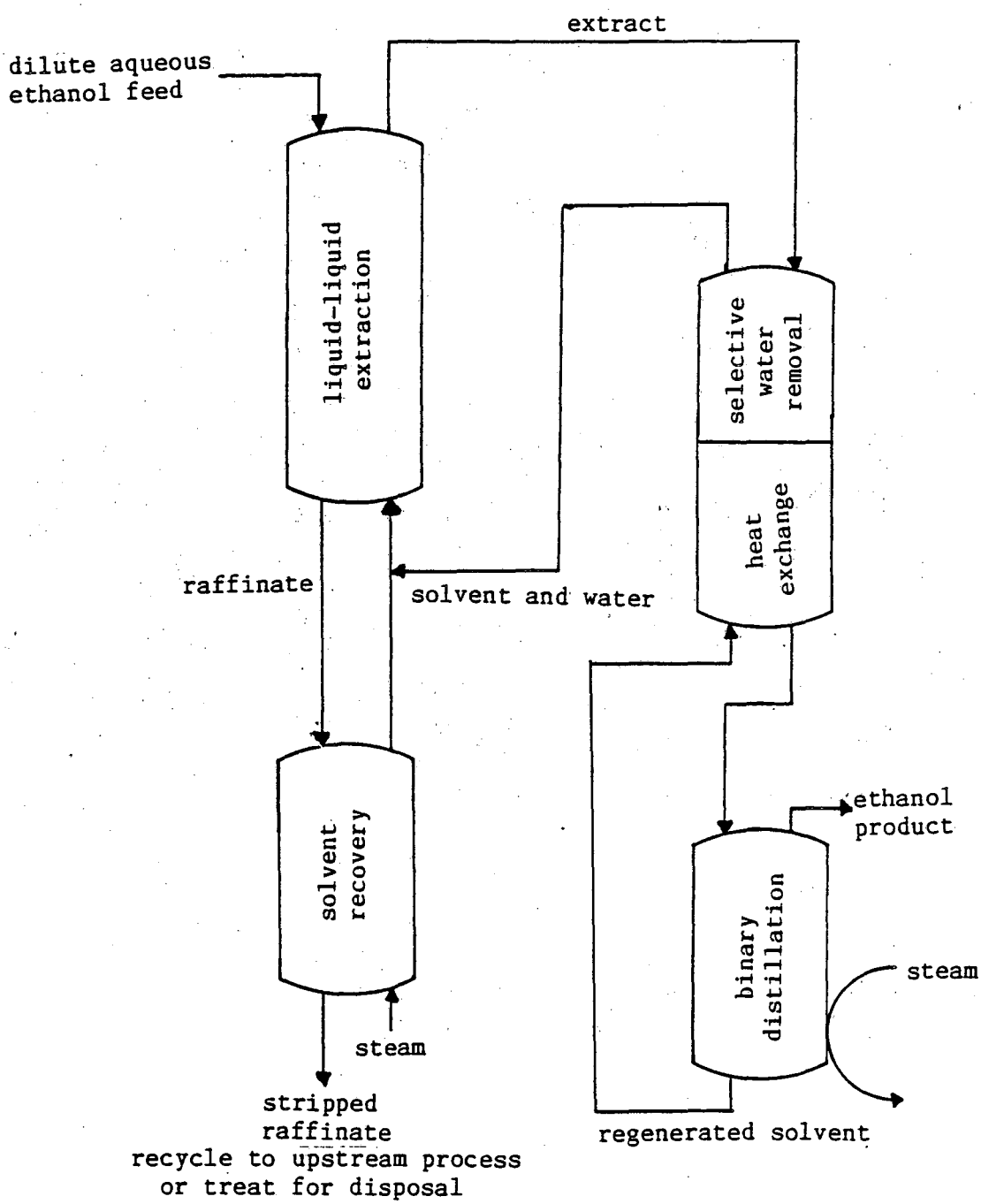


Figure 7-3 Schematic Flow Diagram for the Proposed Ethanol Recovery Process Using Liquid-Liquid Extraction

stripping (since this will be necessary in most cases), and incorporates heat exchange as required to minimize the use of energy and cooling capacity caused by cycling the solvent between different temperatures. The heat exchange and water removal operations are shown together because they are interdependant and the exact process configuration for them will depend on the solvent used and temperatures of the streams involved. The regenerated solvent leaving the bottom of the distillation column at elevated temperature can either be used directly for regeneration (drying) of the water removal beds, or be used first to preheat the distillation column feed.

The number of variables in the process is quite large. The most important of these, of course, is the identity of the solvent used. Even for one solvent, however, the problem of optimizing the total process is a complex one. To simplify matters somewhat, a number of decisions were made to fix certain variables in the process. Those regarding liquid-liquid contacting have been addressed above, but some assumptions were required in the other parts of the process as well. The details of these are contained in Appendix D, but some of the major points will be mentioned here, grouped according to the unit operation involved;

1. Distillation - the following parameters were fixed;
    a. The reflux ratio (ratio of condensate returned to the column to product taken) was fixed at 10% greater than the minimum determined by the vapor-liquid equilibrium.
    b. The product specification was set at 99.99 wt.% ethanol.
    c. The bottom product specification (the degree of regeneration of the solvent) was set at 99.9 wt.%.

d. The pressure of the column was set by fixing 45 ^{o}C as the temperature at the top of the column.

e. The tray efficiency was fixed at 70% for most runs, though efficiencies estimated by the O'Connell method were lower.

f. The heat transfer coefficients of the condenser and reboiler were assumed to be 300 Btu/hr-sq.ft.-^{o}F in all cases.

2. Water removal - the design of the fixed beds included the following assumptions;

a. Three beds were assumed required to allow for inefficiencies in regeneration.

b. Utilization of a bed's capacity before water breakthrough was taken to be 50%.

c. Time on-stream for a bed was fixed at 1/2 hour per cycle.

d. The cost of the sorbent (assumed to be an ion exchange resin) was assumed to be $3.00 per pound, on a dry basis.

3. Solvent recovery - vacuum steam stripping with the following set;

a. Recovery of solvent fixed at 99.0%.

b. The pressure of the stripper fixed by the temperature of the extractor raffinate fed to it.

c. The approach to equilibrium at the top of the stripper was set to 90.0%.

d. A constant tray efficiency of 60% was assumed.

4. Heat exchange - optimized by the program **hxcng**, with the following assumed overall heat transfer coefficients;

a. Exchanger between process streams - 250 Btu/hr-sq.ft.-^{o}F

b. Cooler (water and a process stream) - 250 Btu/hr-sq.ft.-^{o}F

c. Heater (steam and a process stream) - 350 Btu/hr-sq.ft.-^{o}F

Two other assumptions were made which affected most of the units in the process. The first of these was that ordinary carbon steel would have adequate corrosion resistance to be used for process equipment. Typical ethanol fermentation broths are slightly acidic, but the parts of the process which involve contact with a broth are at low to moderate temperature. The second assumption was the cost of the solvent. It was fixed at $1.10 per kilogram, which is a typical figure for the higher molecular weight alcohols which were the solvents of principle interest.

With these assumptions, it was possible to evaluate the relative importance of the various solvent properties in the overall process economics. Of course, the effect of the solvent's ethanol distribution coefficient was found to be dramatic. This is because the distribution coefficient is the primary determinant of the size of the organic solvent streams in the process and most of the process expenses are proportional to the size of those streams. An example of this effect is shown in Figure 7-4. The figure shows the costs calculated for recovering ethanol from a 5 wt.% feed using the proposed process. The properties of the solvent are those of 1-octanol except that the ethanol distribution coefficient was varied as shown and the ethanol-water separation factor was set equal to 25. A constant extraction ratio (the ratio of solvent to feed times the distribution coefficient) of 1.25 was used. That fact is responsible for the increases in product cost seen as the recovery fraction is decreased to below 0.85. If the extraction ratio is decreased along with the recovery fraction, the cost curves level out instead of rising on the right side of the figure. Nevertheless, the figure demonstrates the

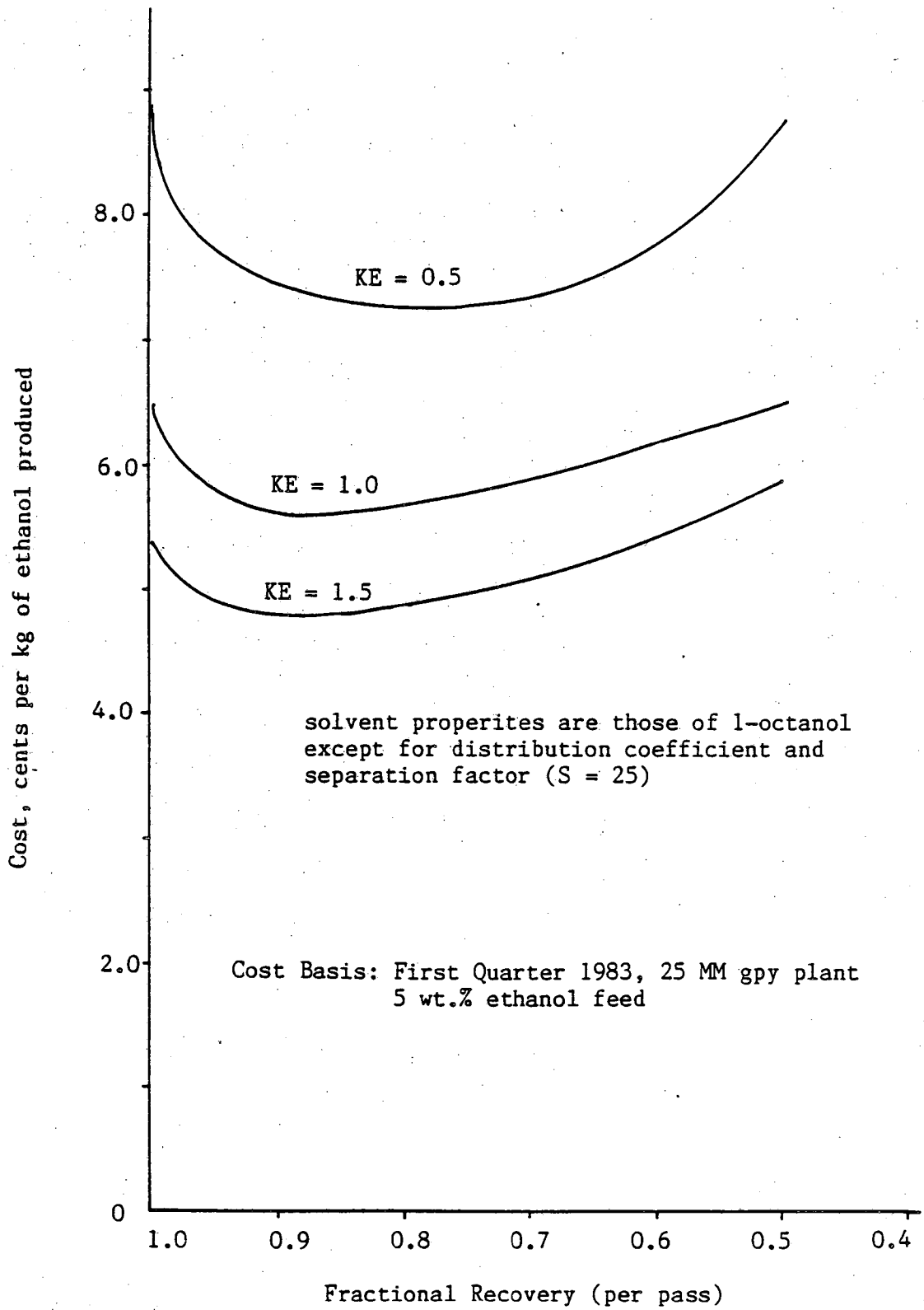


Figure 7-4 Estimated Costs of Proposed Ethanol Recovery Process as a Function of Distribution Coefficient and Recovery Fraction

decreases in process cost associated with increases in the ethanol distribution coefficient of the solvent. It also shows that the relative benefits of operating at a reduced recovery fraction are greater for a lower distribution coefficient solvent than for a higher. The actual distribution coefficient of 1-octanol at ambient temperature is about 0.6, but its separation factor is only about 12. Thus, its process costs are roughly the same as those shown in Figure 7-4 for the case of a 0.5 distribution coefficient.

While the ethanol distribution coefficient does have a major effect on the overall process economics, other solvent properties can be at least as important. This was found in calculations of the process economics for a variety of actual solvents. Due to the limited availability of data on the required physical properties of some solvents, this work was restricted to the study of various alcohols as solvents. The values of the key properties for five of these are listed in Table 7.3. These properties were used to calculate process costs for each of the solvents as a function of the concentration of the ethanol feed, the extraction ratio, and the recovery fraction. Results are shown in Figure 7-5. The best combination of extraction ratio and recovery factor varied among the solvents and with feed concentration for a given solvent. However, it was generally found that a recovery factor in the vicinity of 0.9 and extraction ratio in the range of 1.00 to 1.15 were optimal. Shown in the figure for comparison purposes are two curves for the cost of distillation. One is the optimal distillation cost for the production of 95 wt.% ethanol (from Figure 7-1). The proposed process using extraction with water removal produces anhydrous ethanol as the

Table 7.3 - Key Extraction Solvent Properties for Five Alcohols

solvent	KE[1]	S[2]	BP[3]	SW[4]	AZ[5]
4-methyl-2-pentanol	1.2	10	133	1.60	57
2-methyl-1-pentanol	1.0	20	147	0.31	42
1-hexanol	1.0	10	158	0.59	40
2-ethyl-1-hexanol	0.75	25	185	0.07	20
1-dodecanol	0.35	20	256	0.0023	-

1) KE = ethanol distribution coefficient, weight fractions

2) S = separation factor (KE/KW)

3) BP = boiling point, ^{o}C

4) SW = solubility in water, weight percent

5) AZ = solvent content in the solvent-water azeotrope, wt.%

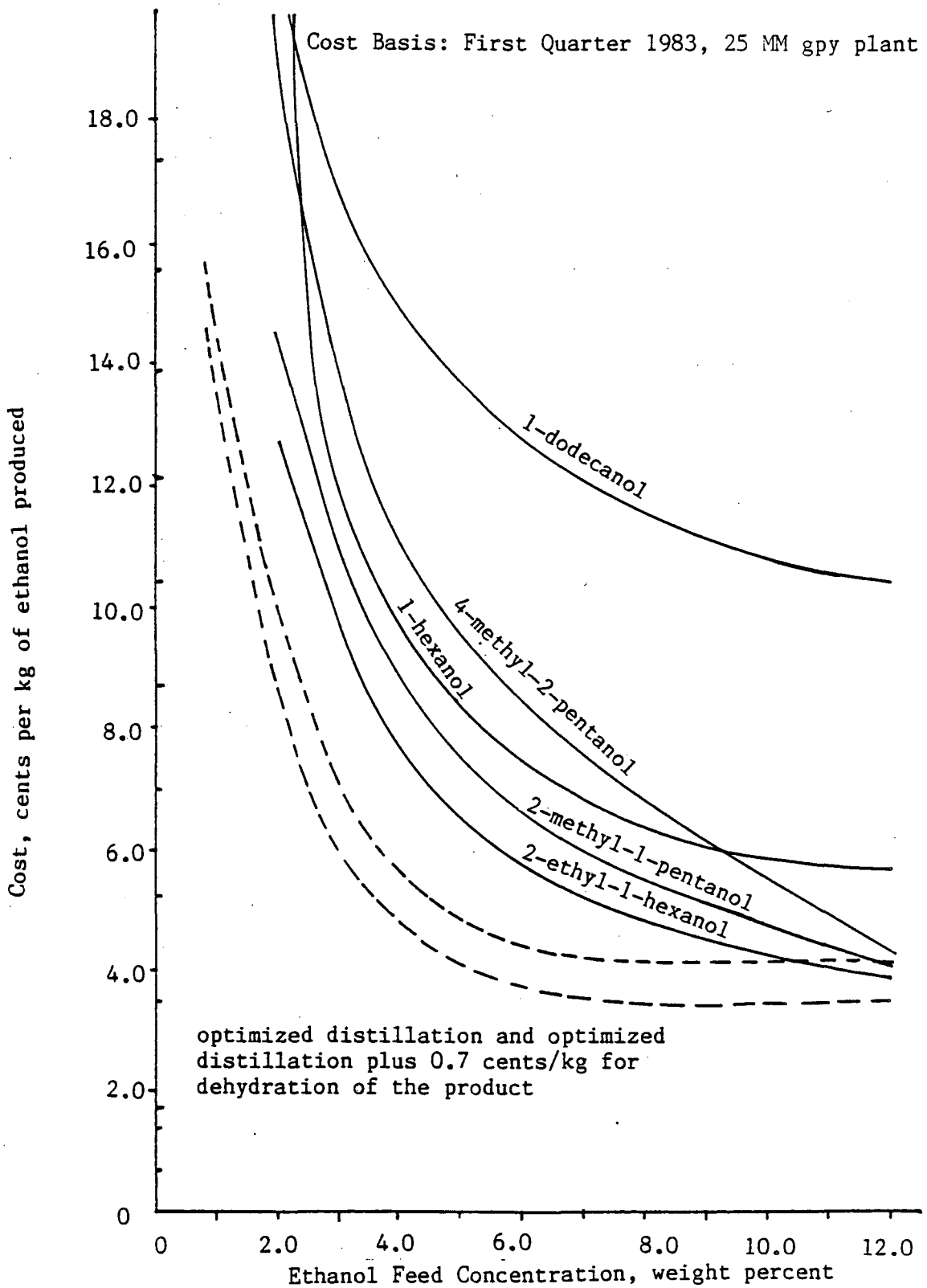


Figure 7-5 Cost Estimates for the Proposed Ethanol Recovery Process as a Function of Feed Concentration for Several Alcohol Solvents

product, however. So the second curve shows an increase in the distillation cost to break the azeotrope and produce anhydrous ethanol from a 95 wt.% intermediate. The increase, a constant 0.7 cents per kilogram of ethanol, is an estimate of the cost, using either azeotropic distillation (benzene, pentane, or diethyl ether as entrainer) or molecular sieve adsorption. While it is beyond the scope of this work to optimize the production of anhydrous ethanol by distillation, it is felt that this cost estimate is fair and useful for the present purpose.

The results shown in Figure 7-5 appear to indicate that the extraction process, as proposed, is not competitive with distillation for the production of anhydrous ethanol except at the highest feed concentrations studied. However, it must be remembered that the process has not been fully optimized with respect to the solvent used and the parameters of operation. The results for 2-ethyl-1-hexanol are the best of all solvents tested, but a number of promising alternatives were not evaluated because some required data were not available. To determine what the properties would be required of a solvent to make the process more economical, it is worth examining the results of Figure 7-5 in more detail.

Some details of the process costs for the case of a 5 wt.% ethanol feed are presented in Table 7.4. The costs are broken down in two ways; one showing the costs grouped according to the kind of expense and the other showing the costs attributable to each of the five major parts of the process. A breakdown of the optimized distillation cost (for production of 95 wt.% ethanol only) is also provided for comparison. It is clear from the expense category

Table 7.4 - Breakdown of Costs for Recovery of Ethanol from 5 wt.% Feed by the Proposed Process

All costs are expressed in cents per kilogram of ethanol produced.

	Expense Category					
Solvent	capital	steam	cooling water	labor	solvent losses	total
4-methyl-2-pentanol	4.62	2.86	0.43	0.39	0.35	8.68
2-methyl-1-pentanol	4.27	2.37	0.22	0.41	0.08	7.34
1-hexanol	5.34	2.24	0.20	0.40	0.14	8.32
2-ethyl-1-hexanol	3.79	1.92	0.17	0.40	0.02	6.30
1-dodecanol	2.72	9.50	0.88	0.39	0.14	13.65
optimized distillation (95 wt.% product)	1.17	2.35	0.30	0.36	-	4.19

	Unit Operation					
Solvent	extr'n.	water remvl.	distln.	heat exch.	solv. rec'y.	total
4-methyl-2-pentanol	0.99	2.28	3.29	0.62	1.51	8.68
2-methyl-1-pentanol	1.52	1.07	2.56	0.71	1.29	7.34
1-hexanol	1.09	2.26	2.83	0.98	1.16	8.32
2-ethyl-1-hexanol	1.26	0.69	2.24	1.07	1.04	6.30
1-dodecanol	1.55	0.74	10.20	1.06	-	13.65

breakdown that the extraction process is plagued high capital cost relative to distillation. In addition, the process does not use significantly less energy than the optimized distillation, even in the best case (2-ethyl-hexanol as solvent). Unless an energy savings relative to distillation can be realized by an extraction process, there will be no way to offset the higher capital cost. Examining the cost breakdown by unit operations, it may be noted that a significant portion of the capital cost is due to the water removal system. It is this fact which gives the solvents with higher separation factors advantages over those with lower separation factors, even though the latter have higher ethanol distribution coefficients. The result for dodecanol is instructive because it shows the problem with solvents of very high molecular weight. Dodecanol has a very low water solubility and is nontoxic to some ethanol-producing microorganisms, so solvent recovery is not needed. However, its boiling point is so high that high pressure steam (with its significantly greater cost) is required for the distillation. The steam requirement is large due to the amount of sensible heat that must be added to the solvent in the distillation column; the temperature gradient in that column is extreme despite operation under vacuum. In contrast, the boiling point of 2-ethyl-hexanol is high enough to allow an efficient separation from ethanol, but not so high that temperatures requiring the use of high pressure steam are involved. While its water azeotrope is less concnetrated in solvent than those of the hexanols, its much lower solubility in water acts to keep the cost of solvent recovery down. The desirability of 2-ethyl-hexanol as a solvent is due to the interplay of all these factors rather than any one alone.

7.5 Conclusions and Recommendations

The results of the preceding section lead to the conclusion that liquid-liquid extraction does not appear to be competitive with distillation for the recovery of ethanol from dilute aqueous solutions, at least in the form of the process developed in this thesis. There are some things which have the potential to change that conclusion, however. The following topics were beyond the scope of this work, but would seem to be worthy of future investigation:

1. The use of a better solvent than 2-ethyl-hexanol could, of course, improve the process economics. Especially recommended for further study are decahydroquinoline and similar compounds. More data on their physical properties, especially vapor-liquid equilibrium with ethanol, are required for their evaluation.
2. Experimental evaluation of the liquid-liquid contacting options available could show that a significant decrease in that part of the process is possible. While the results of such a study would probably be of limited application, due to the variability of the important properties of the liquids in fermentation broths, it would provide a basis for more realistic assessment of the likely cost of this key operation.
3. More extensive optimization of the process, especially of the distillation, could also result in significant improvements. For example, decreasing the fractional regeneration of the solvent could significantly decrease both capital and energy requirements of the distillation, but would have to be balanced against an increased throughput and reduced liquid-liquid contacting driving force. The latter involves interaction with the liquid-

liquid extraction recovery fraction, leading to a more complicated optimization problem.

4. The use of inert gas stripping of the dewatered extract should be considered instead of a distillation as proposed. This would avoid the large temperature gradients of the distillation and could result in considerable reduction of the energy requirement. It would also require the use of refrigeration to condense the product, however, so its cost-effectiveness would need to be carefully evaluated. It would allow the use of the high molecular weight solvents, such as dodecanol, with the associated lack of toxicity. That, in turn, makes an extractive fermentation, with the benefits of increased productivity and reduced waste treatment costs, an attractive possibility.

So there are a number of avenues which could be explored to attempt to make liquid-liquid extraction a competitive alternative to distillation for ethanol recovery. It is hoped that the work of this thesis will be of use to others continuing to investigate this area. In addition, the models and process principles developed herein will hopefully be applied to the solution of other problems in the recovery of fermentation products.

REFERENCES

1. Bailes, P.J., Hanson, C., and Hughes, M.A. (1976) Chem. Eng. **83**:2 p. 86

2. Lo, T.C. (1979) "Commercial Liquid-Liquid Extraction Equipment", section 1.10 of Handbook of Separation Techniques for Chemical Engineers, P.A. Schweitzer, ed. McGraw-Hill, New York

3. Maiorella, B.L., Blanch, H.W., and Wilke, C.R. (1983) "Vacuum Ethanol Distillation Technology" Lawrence Berkeley Laboratory report 15752, University of California, Berkeley

4. Reissinger, K.-H., and Schroter, J. (1978) Chem. Eng. **85**:25, 109

5. Robbins, L.A. (1979) "Liquid-Liquid Extraction", section 1.9 of Handbook of Separation Techniques for Chemical Engineers, P.A. Schweitzer, ed. McGraw-Hill, New York

6. Treybal, R.E. (1980) Mass Transfer Operations McGraw-Hill, New York

Appendix A

Determination of Concentrations in Liquid Mixtures

Much of the experimental work done in the course of this thesis research involved determining the concentrations of ethanol and water in liquid mixtures. This was necessary in the measurement of liquid-liquid equilibria, in the analysis of fermentation yields, and in investigations of water removal from ethanol extracts by solid sorbents. This appendix gives the details of the methods used in these determinations.

All measurements were made using gas chromatography. The instrument used in this work was a Carle Instruments Model 311 gas chromatograph. This instrument had 1/8 inch diameter columns 6 feet in length. It was equipped with both flame ionization detection and thermal conductivity detection. Only the latter was used in this work, however, because it was desirable to measure the water concentration in all cases. Most of the analyses were done using a column of Porapak P (Waters) at a column temperature of 105 ^{o}C. Some early work was also done using a Porapak Q column at 160 ^{o}C. The gas chromatograph was equipped with an auxiliary heater for the injectors and this was used since all samples were injected as liquids. The temperature of the injectors was a function of the column temperature and was approximately 145 ^{o}C when the column temperature was 105 ^{o}C and 230 ^{o}C when the column was 160 ^{o}C. The injection ports of the instrument were modified by drilling them to a larger diameter. This was done to allow them to accomodate prefilters made of thin-walled glass tubing, approximately 5 cm long, in which glass wool was placed.

This was done to collect salts, yeast cell residues, and other nonvolatile materials which were injected with some liquid samples. The prefilters were held in place by tension between the spring-loaded septum of the injector and a Viton O-ring which formed a seal between the glass prefilter and the end of the metal column. Periodic cleaning of the filter and replacement of the glass wool kept the accumulation of solids to a minimum.

Analyses of the output of the gas chromatograph were facilitated by connecting that instrument directly to a Hewlett-Packard Model 3390-A digital integrator. The integrator was used with all of the default options of the standard software supplied by the manufacturer. An attenuation setting of 2 gave a relatively smooth baseline. The minimum area for peak recognition was set at 2500.

When analyses of aqueous phases were done, the concentrations of ethanol were correlated with the ratio of the areas of the ethanol and water peaks. This method was found to give better reproducibility since it was independant of the exact size of the sample injected. There was some variation in the ratios measured for a given concentration if samples of greatly different size were injected, however, so a standard injection size of 1/2 microliter was adopted. A Hamilton Gas-Tite 2 microliter syringe was used for injections. The same method, using peak ratios, was applied to the analysis of water content in very concentrated ethanol streams. In all cases, standard solutions were made by mixing carefully weighed amounts of distilled water and anhydrous (>99.8 wt.%) ethanol. The accuracy of the peak ratio method was estimated to be $\pm$ 0.05 weight percent of the dilute component.

The analyses of ethanol and water concentrations in an organic solvent were also done by direct injection of liquid samples. The solvents used had very long retention times under the column conditions used, so it was generally possible to perform a number of injections before the first solvent would break through to the detector. The ethanol and water peaks were not noticably affected by the presence of small amounts of solvent in the column, as evidenced by good reproducibility of results for the same sample injected at the beginning of a series and at the end. For these organic phase analyses, the absolute areas calculated by the integrator were correlated with ethanol and water concentrations in the solvent. The results were thus dependant on obtaining reproducible injection sizes. A standard size of 1.0 microliter was used, measured with a Hamilton 2 microliter syringe. At least two injections for each sample were made to insure reproducibility. The accuracy depended on the detector filament temperature used, but was estimated to be $\pm$ 0.2 wt.% for both ethanol and water for the temperature used in most of the work. The concentrations were correlated with peak areas by preparing standards. The standards were made by weighing amounts of water and anhydrous ethanol (or an aqueous ethanol solution of known concentration) when adding them to a weighed amount of solvent. Saturation concentrations of water in the solvents were found by linear extrapolation of results for concentrations close to to saturation. The presence of ethanol or water in a solvent did not affect the response of the analysis to the other component. Thus, calibration curves prepared for the pure components in a solvent were found to be valid when both were present.

Appendix B

Computer Programs Used in Modelling Liquid-Liquid Equilibria

The programs used to perform the calculations necessary for using UNIQUAC and UNIFAC are listed in this Appendix. For the most part, they are simply modified versions of Fortran programs published in the open literature. Details of their operations, including discussions of the equations and mathematical techniques used to solve them, are available in the original references. The purpose of providing the listings here is to show where modifications were made.

The first set of programs is for the prediction of liquid-liquid equilibria using UNIFAC. The main program and most of the subprograms are taken from the book "Vapor-Liquid Equilibria Using UNIFAC" by Fredenslund and Gmehling (1977). The **systm** subroutine was modified, however, to change the way parameter data are input. Other modifications are to allow the program to be run on the UNIX operating system at the University of California at Berkeley, using the F77 compiler/loader. Listings of the programs, with examples of input data and output are reproduced on the following pages.

```
c
c  The following three lines are a set of definitions which
c  are needed by most of the UNIFAC programs.  They reside in a
c  file called 'facdefs' and are put into the programs with the
c  us of the INCLUDE command in Fortran 77.
c
      dimension para(8,8),parb(8,8),henry(5,5)
      dimension itab(5,20),cc(5,5),dd(5,5),gamc(5,5)
      common/grpprm/ny(5,8),r(8),q(8),rs(5),qs(5),xl(5),nr
```

```
c
c   The following program, called llefac, uses UNIFAC
c   for predicting liquid-liquid equilibrium compositions. It
c   is a modified version of a program
c   taken from 'V.L.E. Using UNIFAC', Fredenslund et al (1977)
c
c   reads from file 'fledata',unit 5
c   writes to file 'lefout', unit 7
c   must be loaded with subroutines unifa, systm,
c        gres, gcomb, and gref
c
c   input data
c
c   text - up to 80 characters
c   nk,ng - number of components and groups, respectively
c   itab(i,20) - 20 integers specifying the number of groups
c           of each type in component i, one line for each
c           component
c   t,(z(i),i=1,nk) - temperature (K) and total moles of each
c           component
c      the last line may be repeated any number of times
c      input ends with 3 blank lines
c
      implicit double precision (a-h,o-z)
      dimension z(5),fd(5),fdd(5),xd(5),xdd(5),gamd(5),gamdd(5),
     1   xdn(5),xddn(5)
      dimension itab(5,20)
      character text*80
      common/grpprm/ ny(5,8),r(8),q(8),rs(5),qs(5),xl(5),nr
  100 format(40i2)
  101 format(6f10.4)
  102 format(//,a80,/,4x,'mole fractions',26x,'activity coefficients',
     1 /)
  103 format(f10.4,4x,f10.4,6x,f10.2,4x,f10.2)
  104 format('unifac is unable to predict the phase split ',/
     1 '  the composition is ',/,5f10.4)
  105 format(a80)
  106 format(1h0,/,' the total composition of the system is',/,5f10.4)
  107 format(1h0,/,' the amount of phase 1 is ',2x,f10.4,/,' the amount
     1 of phase 2 is ',2x,f10.4,//)
      nt=20
  199 open(unit=5,file='fledata')
      rewind 5
      read(5,105) text
      read(5,100) nk,ng
```

```
      if (nk.eq.0) go to 99
      nk1=nk+1
      nr=0
      delta1=0.001
      delta2=0.0001
      do 1 i=1,nk
    1 read(5,100) (itab(i,j),j=1,nt)
   98 read(5,101) t,(z(i),i=1,nk)
      if (t.eq.0.) go to 99
      s=0.
      do 2 i=1,nk
    2 s=s+z(i)
      do 3 i=1,nk
    3 fd(i)=.5*z(i)
      fd(1)=.9*z(1)
      fd(nk)=.1*z(nk)
      sfd=0.
      sfdd=0.
      do 4 i=1,nk
      fdd(i)=z(i)-fd(i)
      sfd=sfd+fd(i)
    4 sfdd=sfdd+fdd(i)
      do 5 i=1,nk
      xd(i)=fd(i)/sfd
    5 xdd(i)=fdd(i)/sfdd
    6 continue
      call unifa(nk,ng,itab,t,xd,gamd)
      nr=nr+1
      call unifa(nk,ng,itab,t,xdd,gamdd)
      tsfd=0.
      tsfdd=0.
      do 7 i=1,nk
      fd(i)=z(i)/(1.+sfdd*gamd(i)/sfd/gamdd(i))
      fdd(i)=z(i)-fd(i)
      tsfd=tsfd+fd(i)
      tsfdd=tsfdd+fdd(i)
    7 continue
      do 8 i=1,nk
      xdn(i)=fd(i)/tsfd
    8 xddn(i)=fdd(i)/tsfdd
      do 9 i=i,nk
      if(dabs(xd(i)-xdn(i)).gt.delta1) go to 10
    9 continue
      if(dabs(tsfd-sfd).gt.delta2) go to 10
      go to 12
```

```
   10 do 11 i=1,nk
      xd(i)=xdn(i)
   11 xdd(i)=xddn(i)
      sfd=tsfd
      sfdd=tsfdd
      go to 6
   12 open(unit=7,file='lefout')
      write(7,102) text
      if(dabs(xd(1)-xdd(1)).le..01) write(7,104)(xd(i),i=1,nk)
      do 13 i=1,nk
      fd(i)=xd(i)*gamd(i)-xdd(i)*gamdd(i)
   13 write(7,103) xd(i),xdd(i),gamd(i),gamdd(i),fd(i)
      write(7,106) (z(i),i=1,nk)
      write(7,107) tsfd,tsfdd
      close(unit=7)
      go to 98
   99 close(unit=5)
      stop
      end
```

```
      subroutine unifa(nk,ng,itab,t,x,xa)
c
c  This subroutine calculates the activity coefficients, xa,
c   for a given temperature, t (K), and composition, x.  It
c   uses the subroutines systm, gref, gres, and gcomb.
c
      implicit double precision(a-h,o-z)
      dimension para(8,8),parb(8,8),gamc(5),gamrf(5),gamr(8),x(5),
     1 xa(5),itab(5,20)
      common/grpprm/ny(5,8),r(8),q(8),rs(5),qs(5),xl(5),nr
      if(nr.ne.0) go to 10
      call systm(para,nk,ng,itab)
   10 continue
      call gref(gamrf,para,parb,t,nk,ng)
      call gres(parb,x,gamr,nk,ng)
      call gcomb(x,gamc,nk,ng)
      do 20 j=1,nk
   20 xa(j)=gamc(j)*gamr(j)/gamrf(j)
      return
      end
```

```
      subroutine systm(para,nk,ng,itab)
c
c  This subroutine reads the data for group size and
c   interaction parameters and stores the required
c   values in the common block 'grpprm' and the matrix
c     para
c
c   reads from 'grpsizes' and 'grpntpms'  both unit 4
c   writes to 'sysout' unit 6
c
      implicit double precision (a-h,o-z)
      dimension arr(20,20),rr(20),qq(20),ktab(8)
      include 'facdefs'
      nt=20
      open (unit=4,file='grpsizes')
      rewind 4
      do 11 i=1,nt
      read(4,51) rr(i),qq(i)
   51 format(10x,2f15.5)
   11 continue
      close(unit=4)
      open (unit=4,file='grpntpms')
      rewind 4
      do 12 i=1,nt
      read(4,52)(arr(i,j),j=1,nt)
   52 format(10x,5f12.4)
   12 continue
      close(unit=4)
      open(unit=6,file='sysout')
      rewind 6
      m=0
      do 15 j=1,nt
      jj=0
      do 16 i=1,nk
   16 jj=jj+itab(i,j)
      if (jj) 15,15,17
   17 m=m+1
      ktab(m)=j
   15 continue
      ng=m
```

```
      do 20 j=1,ng
      jj=ktab(j)
      r(j)=rr(jj)
      q(j)=qq(jj)
      do 20 i=1,nk
   20 ny(i,j)=itab(i,jj)
      do 30 i=1,nt
      do 35 j=1,ng
      j1=ktab(j)
      if (j1-i) 35,36,35
   36 do 37 l=1,ng
      l1=ktab(l)
   37 para(j,l)=arr(i,l1)
   35 continue
   30 continue
      do 40 i=1,nk
      rs(i)=0
      qs(i)=0
      do 41 j=1,ng
      rs(i)=rs(i)+ny(i,j)*r(j)
   41 qs(i)=qs(i)+q(j)*ny(i,j)
   40 xl(i)=5.*(rs(i)-qs(i))-rs(i)+1.
      if (nr) 34,34,39
   34 write (6,80)
   80 format (//,' group constants and interaction parameters (r,q,and
     1 a(i,j)) ',/)
      do 81 i=1,ng
   81 write (6,82) r(i),q(i),(para(i,j),j=1,ng)
   82 format (2f10.4,8f10.2)
      write (6,83)
   83 format (//,3x,' molecular functional groups'/)
      do 84 i=1,nk
   84 write (6,85) i,(ny(i,j),j=1,ng)
   85 format (2i5,10i3)
   39 continue
      close(6)
      return
      end
```

```
c
c 'facsubs.f' contains subroutines gres, gref, gcomb, and hcon
c
      subroutine gres (p,x,gam,nk,ng)
c
c  This subroutine calculates the residual astivity
c  coefficients less the reference part (done by gref)
c
      dimension p(8,8),gam(5),s1(8),xg(8),s4(8),th(8),gaml(8),x(5)
      include 'facdefs'
      s3=0.
      s2=0.
      do 10 k=1,ng
      s1(k)=0.
      do 11 i=1,nk
   11 s1(k)=s1(k)+ny(i,k)*x(i)
   10 s2=s2+s1(k)
      do 13 k=1,ng
      xg(k)=s1(k)/s2
   13 s3=s3+q(k)*xg(k)
      do 15 k=1,ng
      s4(k)=0.
   15 th(k)=q(k)*xg(k)/s3
      do 16 k=1,ng
      do 16 i=1,ng
   16 s4(k)=th(i)*p(i,k)+s4(k)
      do 20 k=1,ng
      g=1.-dlog(s4(k))
      do 21 i=1,ng
   21 g=g-th(i)*p(k,i)/s4(i)
   20 gaml(k)=q(k)*g
      do 30 i=1,nk
      g=0.
      do 31 j=1,ng
   31 g=ny(i,j)*gaml(j)+g
   30 gam(i)=dexp(g)
      return
      end
```

```
      subroutine gref(gam,para,parb,t,nk,ng)
c
c  This subroutine calculates the residual reference
c  activity coefficients
c
      implicit double precision (a-h,o-z)
      dimension para(8,8),parb(8,8),x(5),gamx(5),gam(5)
      do 10 i=1,ng
      do 10 j=1,ng
   10 parb(i,j)=dexp(-para(i,j)/t)
      do 20 i=1,nk
      do 21 j=1,nk
   21 x(j)=0.
      x(i)=1.
      call gres(parb,x,gamx,nk,ng)
   20 gam(i)=gamx(i)
      return
      end
```

```
      subroutine gcomb(x,gamma,nk,ng)
c
c  This subroutine calculates the combinatorial part of the
c  activity coeffficients
c
      implicit double precision (a-h,o-z)
      dimension x(5),gamma(5)
      include 'facdefs'
      qss=0.
      rss=0.
      xls=0.
      do 10 i=1,nk
      qss=qss+qs(i)*x(i)
      rss=rss+rs(i)*x(i)
   10 xls=xls+xl(i)*x(i)
      do 20 i=1,nk
      a=5.*qs(i)*dlog(qs(i)/qss*rss/rs(i))+xl(i)-rs(i)/rss*xls
   20 gamma(i)=rs(i)/rss*dexp(a)
      return
      end
```

The following is a sample input file, 'fledata', for the UNIFAC liqui-liquid equilibrium program, llefac.

```
 l.l.e. for water, ethanol, 2-octanol
 3 6
 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
 1 1 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
 2 5 1 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
 298.0     50.0      0.0      50.0
 298.0     50.0      0.5      49.5
 298.0     49.0      2.0      49.0
 298.0     47.5      5.0      47.5
 298.0     45.0      10.0     45.0
0.
```

The following is a sample output file, 'lefout', from the UNIFAC liquid-liquid equilibrium program, llefac.

```
 l.l.e. for water, ethanol, 2-octanol
    mole fractions                                activity coefficients

    0.9998        0.2642            1.00            3.78
    0.0000
    0.            0.                6.09            0.98
    0.
    0.0002        0.7358         4522.39            1.04
    0.0000
0
 the total composition of the system is
   50.0000    0.        50.0000
0
 the amount of phase 1 is       32.0561
 the amount  of phase 2 is       67.9439
```

```
 l.l.e. for water, ethanol, octanol
    mole fractions                                activity coefficients

    0.9987        0.2656            1.00            3.76
    0.0000
    0.0011        0.0068            6.02            0.98
    0.0000
    0.0002        0.7276         4355.59            1.04
    0.0000
0
 the total composition of the system is
   50.0000    0.5000    49.5000
0
 the amount of phase 1 is       31.9736
 the amount  of phase 2 is       68.0264
```

```
 l.l.e. for water, ethanol, octanol
    mole fractions                                activity coefficients

    0.9953        0.2699            1.00            3.69
    0.0000
    0.0045        0.0268            5.82            0.98
    0.0000
    0.0002        0.7034         3891.02            1.05
    0.0000
0
 the total composition of the system is
   49.0000    2.0000   49.0000
0
 the amount of phase 1 is       30.3444
 the amount  of phase 2 is       69.6556
```

```
 l.l.e. for water, ethanol, octanol
    mole fractions                                activity coefficients

    0.9882        0.2786            1.00            3.55
    0.0000
    0.0116        0.0647            5.43            0.97
    0.0000
    0.0002        0.6567         3094.91            1.07
    0.0000
0
 the total composition of the system is
   47.5000    5.0000   47.5000
0
 the amount of phase 1 is       27.6762
 the amount  of phase 2 is       72.3238
```

The following is the output of the program mlwt which converts the above results from llefac, which are in mole fractions, to the corresponding weight fractions.

compound	a wt. fr.	b wt. fr.	k weight
water	0.99855642	0.04733274	0.04740117
ethanol	0.	0.	-1.00000000
octanol	0.00144358	0.95266726	659.93195607
Separation Factor:	-21.096526142983		
water	0.99575429	0.04793109	0.04813546
ethanol	0.00280459	0.00313804	1.11889250
octanol	0.00144112	0.94893087	658.46823907
Separation Factor:	23.244660460022		
water	0.98715337	0.04978015	0.05042798
ethanol	0.01141308	0.01264002	1.10750306
octanol	0.00143355	0.93757983	654.02601354
Separation Factor:	21.962076489235		
water	0.96948071	0.05368056	0.05537043
ethanol	0.02910128	0.03187866	1.09543830
octanol	0.00141800	0.91444077	644.87961968
Separation Factor:	19.783814392158		
water	0.93814862	0.06088614	0.06490031
ethanol	0.05976611	0.06491762	1.08619439
octanol	0.00208527	0.87419625	419.22404189
Separation Factor:	16.736350979222		

It should be mentioned that there is some confusion about the binary interaction parameters for the CH_2-OH pair in the paper by Magnussen et al (1981). The main table listing the parameters gives the ones shown on the previous pages. However, a table later in the paper (Table IV), given in discussion of the determination of parameters, lists the CH_2-OH pair as just the opposite as given in the main table. In other words, the CH_2-OH and OH-CH_2 parameters are switched. When the latter combination was tried in the liquid-liquid equilibrium prediction, however, the ethanol distribution coefficients were generally wrong by a about factor of 4 instead of by the factor of two seen in Table 4.1 of this work. Therefore, the parameters given in the main table by Magnussen et al (1981) were assumed correct and used throughout this work.

The programs listed on the following pages are for the estimation of UNIQUAC binary interaction parameters using UNIFAC. The source of the programs is again the book, "Vapor-Liquid Equilibria Using UNIFAC" (Fredenslund and Gmehling, 1977). Since the modified UNIQUAC equation was used (because of the availability of temperature-dependant parameters for ethanol-water with this equation), it was necessary to modify the following program to allow the specification of the modified surface area parameter, Q'. As given by Prausnitz et al (1981), Q' is 1.0 for water and .92 for ethanol.

```
c
c program nucfac - calculates uniquac parameters from
c  UNIFAC estimates of infinite dilution activity coefficients
c
c based on the program published by Fredenslund et al, "Vapor-
c   Liquid Equilibria Using UNIFAC", 1977
c modified to allow use of qp, the second area parameter used
c   in the modified UNIQUAC equation
c
c   input file-'qcfccs' unit 7
c   output file-'qcfcrt' unit 6
c
c   must be used with systm and facsubs subroutines,
c          the definitions file 'facdefs'
c          and the parameter files, 'grpntpms' and 'grpsizes'
c
c   input data file must contain;
c
c   text, 1 record up to 80 characters
c   temp, the temperature in degrees K
c   nk,ng - numbers of components and total groups, respectively
c          (no more than 5 components)
c   qp(i) - qp value for each component; if 0 is input, qp will
c          be set equal to qs, the regular UNIQUAC area param.
c   itab(i,j) - nk rows of nt integers, giving the number of
c          groups of type j in component i
c
c
      implicit double precision (a-h,o-z)
      character ntext*80
      include 'facdefs'
      dimension qp(5)
   86 format (40i2)
   87 format (//)
   88 format (40a2)
   89 format (3f10.2)
   98 format (a80)
      nr=0
      nt=10
      open(unit=7,file='qcfccs')
      rewind 7
      read(7,98) ntext
      read(7,89) temp
      read(7,86) nk,ng
      read(7,*) (qp(i),i=1,nk)
      do 22 i=1,nk
   22 read (7,86) (itab(i,j),j=1,nt)
      close(unit=7)
```

```
      call systm(para,nk,ng,itab)
      t=temp
      call hcon(para,parb,t,henry,gamc,nk,ng)
      open(unit=6,file='qcfcrt')
      rewind 6
      write(6,87)
      write(6,98) ntext
      write(6,12) temp
   12 format (/,'    *****  t = ',f10.2,' k',/)
      write(6,13)
   13 format (' infinite dilution activity coefficients '/)
      do 1 i=1,nk
      do 1 j=1,nk
    1 henry(i,j)=henry(i,j)*gamc(i,j)
      do 10 i=1,nk
   10 write (6,3) i,(henry(i,j),j=1,nk)
    3 format (' component ',i2,' is solvent ',5e12.4)
      write(6,15)
   15 format (/,'    tau(j,i)=exp(-delta(u)/rt)   ',/)
      write(6,*) 'gamc(1,1)=',gamc(1,1)
      do 5 i=1,nk
      do 5 j=1,nk
      write(6,*) 'gamc(',i,j,')=',gamc(i,j)
    5 henry(i,j)=henry(i,j)/gamc(i,j)
   21 nk1=nk-1
      do 30 i=1,nk1
      i1=i+1
      do 30 j=i1,nk
      write(6,*) 'henry(i,j)=',henry(i,j),' qs(j)=',qs(j),
     1 ' qp(j)=',qp(j)
      if(qp(j).eq.0.) qp(j)=qs(j)
      if(qp(i).eq.0.) qp(i)=qs(i)
      b1=1.-dlog(henry(i,j))/qp(j)
      b2=1.-dlog(henry(j,i))/qp(i)
      write(6,*) 'i=',i,' j=',j,' b1=',b1,' b2=',b2
      a=.001
      if(dabs(b1+b2-2.)-1.d-5)201,202,202
  201 a=1
      go to 36
  202 if(b1-1.)35,35,203
  203 if(b2-1.)35,35,204
  204 if(dexp(b2-1.).lt.b1) a=dexp(b1)
   35 s=dexp(b2-a)
      f=dlog(a)+s-b1
      df=s-1./a
      da=f/df
      a=a+da
```

```
      if (dabs(da)-1.d-4) 36,36,35
   36 cc(i,j)=a
   30 cc(j,i)=b1-dlog(a)
      do 60 i=1,nk
      cc(i,i)=1.
   60 write(6,85) (cc(i,j),j=1,nk)
   85 format(5e15.7)
      write(6,16)
   16 format(/,' delta(u)/r ',/)
      do 70 i=1,nk
      do 70 j=1,nk
   70 dd(i,j)=temp*(-dlog(cc(i,j)))
      do 71 i=1,nk
   71 write (6,84)(dd(i,j),j=1,nk)
   84 format(5e15.5)
      close (unit=6)
      stop
      end
```

```
      subroutine hcon(para,parb,t,henry,gamc,nk,ng)
c
c  This subroutine calculates infinite dilution activity
c  coefficients (Henry's constants)
c
      implicit double precision (a-h,o-z)
      dimension para(8,8),parb(8,8),henry(5,5),x(5),gam(5),gamx(5)
      dimension gamc(5,5),cgam(5)
      do 10 i=1,ng
      do 10 j=1,ng
   10 parb(i,j)=exp(-para(i,j)/t)
      do 20 i=1,nk
      do 21 j=1,nk
   21 x(j)=0.
      x(i)=1.
      call gcomb(x,cgam,nk,ng)
      call gres(parb,x,gamx,nk,ng)
      gam(i)=gamx(i)
      do 20 j=1,nk
      gamc(i,j)=cgam(j)
   20 henry(i,j)=gamx(j)
      do 25 i=1,nk
      do 25 j=1,nk
   25 henry(i,j)=henry(i,j)/gam(j)
      return
      end
```

Sample input data for program nucfac

```
uniquac parameters for etoh,octanol
 298.0
 2 3
 .92, 0.
 1 1 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
 1 7 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
```

Sample output from program nucfac

```
uniquac parameters for etoh,octanol

   *****  t =     298.00 k

 infinite dilution activity coefficients

 component  1 is solvent   0.1000d+01  0.1465d+01
 component  2 is solvent   0.1163d+01  0.1000d+01

   tau(j,i)=exp(-delta(u)/rt)

  gamc(1,1)=   1.0000000000000
  gamc(  1  1  )=   1.0000000000000
  gamc(  1  2  )=  0.69831136179356
  gamc(  2  1  )=  0.79894684138636
  gamc(  2  2  )=   1.0000000000000
  henry(i,j)=   2.0976438757120   qs(j)=   5.8280000000000   qp(j)=  0.
  i=  1   j=  2   b1=  0.87288696792896   b2=  0.59167364420415
  0.1000000d+01  0.1747125d+01
  0.3149153d+00  0.1000000d+01

 delta(u)/r

    0.      d+00   -0.16628d+03
    0.34432d+03    0.      d+00
```

The following is a sample of the parameter data file 'grpsizes', which contains the R and Q values the groups. Parameters shown are taken from the set given by Magnussen et al (1980).

1	ch3	0.9011	0.848
2	ch2	0.6744	0.540
3	ch	0.4496	0.228
4	oh	1.0	1.2
5	h2o	0.92	1.4
6	cooh	1.3013	1.224
7	ch3coo	1.9031	1.728
8	cho	0.998	0.948
9	ch2co	1.4457	1.18
10	ch2o	0.9183	0.780
11	ch2cl	1.4654	1.264
12	chcl	1.238	0.952
13	chcl2	2.0606	1.684
14	ccl2	1.8016	1.448
15	ccl3	2.6401	2.184
16	ach	0.5313	0.40
17	acch2	1.3096	0.660
18	acoh	0.8952	0.680
19	accl	1.1562	0.844
20	c5h3n	2.667	1.553

The following is a sample of the parameter data file 'grpntpms', which contains the group interactions parameters. Parameter values shown are those given foe L.L.E. by Magnussen et al (1980).

1	ch3	0.0	0.0	0.0	644.6	1300.0
		139.4	972.4	158.1	472.6	662.1
		42.14	42.14	-243.9	-243.9	7.5
		156.5	-115.7	2255.0	924.8	-300.0
2	ch2	0.0	0.0	0.0	644.6	1300.0
		139.4	972.4	158.1	472.6	662.1
		42.14	42.14	-243.9	-243.9	7.5
		156.5	-115.7	2255.0	924.8	-300.0
3	ch	0.0	0.0	0.0	644.6	1300.0
		139.4	972.1	158.1	472.6	662.1
		42.14	42.14	-243.9	-243.9	7.5
		156.5	-115.7	2255.0	924.8	-300.0
4	oh	328.2	328.2	328.2	0.0	28.73
		-104.0	195.6	1409.0	67.07	262.5
		62.05	62.05	272.2	272.2	-61.57
		-9.21	1.27	-195.5	-597.1	183.3
5	h2o	342.4	342.4	342.4	-122.4	0.0
		-465.7	-6.32	-349.9	-171.8	64.42
		315.9	315.9	370.7	370.7	356.8
		372.8	203.7	344.5	-97.27	-873.6
6	cooh	1744.0	1744.0	1744.0	118.4	652.3
		0.0	-117.6	1051.0	-101.3	-96.62
		19.77	19.77	1670.0	1670.0	48.15
		75.49	147.3	-	874.3	-
7	ch3coo	-320.1	-320.1	-320.1	180.6	385.9
		1417.0	0.0	1090.0	58.84	-235.7
		-	-	108.9	108.9	-209.7
		114.8	-170.2	-337.3	629.0	-
8	cho	146.1	146.1	146.1	-431.3	623.7
		0.75	-245.8	0.0	128.0	-
		751.8	751.8	-	-	-
		-75.3	223.2	-	-	-
9	ch2co	66.56	66.56	66.56	216.0	634.8
		1247.0	258.7	-37.36	0.0	5.202
		1000.0	1000.0	-301.0	-301.0	12.01
		-78.31	-73.87	-568.0	902.6	-

10 ch2o	1571.0	1571.0	1571.0	137.1	212.8
	1402.0	461.3	-	52.38	0.0
	301.1	301.1	137.8	137.8	-154.3
	52.13	65.69	-	-	-
11 CCl	73.8	73.8	73.8	455.1	770.0
	337.1	-	-47.51	483.9	225.4
	0.0	0.0	110.5	110.5	249.2
	4.68	122.9	-	-	-
12 CCl	73.8	73.8	73.8	455.1	770.0
	337.1	-	-47.51	483.9	225.4
	0.0	0.0	110.5	110.5	249.2
	4.68	122.9	-	-	-
13 CCl2	27.9	27.9	27.9	669.2	740.4
	437.7	-132.9	-	550.6	-197.7
	-157.1	-157.1	0.0	0.0	-
	-	-	-	-	-
14 CCl2	27.9	27.9	27.9	669.2	740.4
	437.7	-132.9	-	550.6	-197.7
	-157.1	-157.1	0.0	0.0	-
	-	-	-	-	-
15 CCl3	21.23	21.23	21.23	418.4	793.2
	370.4	176.5	-	342.2	-20.93
	11.8	11.8	-	-	0.0
	288.5	33.61	-	-	18.98
16 ACH	156.5	156.5	156.5	703.9	859.4
	461.8	6.0	362.3	593.7	32.14
	-18.81	-18.81	-	-	-231.9
	0.0	167.0	1649.0	-878.1	-578.2
17 ACCH2	104.4	104.4	104.4	4000.0	5695.0
	339.1	5688.0	1218.0	916.7	213.1
	-114.1	-114.1	-	-	-12.14
	-146.8	0.0	292.6	-107.3	-390.7
18 ACOH	-159.8	-159.8	-159.8	-63.15	-595.9
	-	-898.3	-	-825.7	-
	-	-	-	-	-
	-473.2	-470.4	0.0	-	-637.3
19 ACCl	-59.06	-59.06	-59.06	1989.0	390.7
	1349.0	-246.3	-	190.5	-
	-	-	-	-	-
	777.8	-47.13	-	0.0	-387.7
20 C5H3N	-128.8	-128.8	-128.8	-319.2	203.0
	-	-	-	-	-
	-	-	-	-	-14.7
	-225.3	-124.6	-222.7	-906.5	0.0

The following programs are for the prediction of liquid-liquid equilibria using UNIQUAC. The heart of the set is the subroutine **elips**, which calculates the equilibrium phase compositions. That routine and the four other subroutines used were taken from the book, "Computer Calculations of Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria" by Prausnitz et al (1981). The modifications to the program are primarily to allow it to be run on VAX 780 rather than the CDC 6400 for which it was originally written. In addition, the data input subroutine, originally **parin** was changed to reduce the library size and the number of parameters read, since only a few of these are needed.

```
c
c  This program, called strtr, is a driver program for the UNIQUAC
c  liquid-liquid equilibrium calculation routine, ELIPS.  The latter
c  is from the book, "Computer Calculations for Multicomponent
c  Vapor-Liquid and Liquid-Liquid Equilibria" by Prausnitz et al
c  (1980).
c
c  The input data file for the program is called 'casefile' and
c   contains the following;
c
c  m - the number of components in the library 'pureprm'
c  iewopt - a special flag for the ethanol-water binary
c           if set to 1 the temperature-dependant parameters
c           found by Maiorella (1983) using VPLQFT on vapor-
c           liquid equilibria are used,  otherwise the parameters
c           for the pair in the 'binprm' file are used
c  n,t,(id(i),i=1,n) - the number of components, the temperature
c           in degrees K, and the i.d. number for each component
c  ncase - the number of cases to be run
c  ir,ie,(zt(kk,i),i=1,n) - the i.d. of the raffinate phase major
c           component, the i.d. of the extract phase major component
c           and the initial (i.e. total) mole fractons of al the
c           components
c     There should be as many records like the last one as there
c     are cases to be run (kk=1,ncase).
c
c
      dimension z(10),x(10),y(10),k(10),we(10),wr(10),wz(10),kw(10)
      dimension zt(10,10)
      integer id(10),er
      implicit double precision(a-d,f-h,k,o-z)
      integer key
      character nm1(100)*10,nm2(100)*10
      common/pure/nm1(100),nm2(100),wm(100),ru(100),qu(100),qp(100)
      common/binary/u(100,100)
      open(unit=7,file='casefile')
      rewind 7
      read(7,99) m
      read(7,99) iewopt
   99 format(i2,10x)
  200 read(7,02) n,t,(id(i),i=1,n)
   02 format(i2,8x,f10.2,10i5)
      if(n.eq.0) stop
      key=1
      read(7,99) ncase
      do 210 kk=1,ncase
  210 read(7,04) ir,ie,(zt(kk,i),i=1,n)
   04 format(2i5,(7f10.4))
      close(unit=7)
```

```
100 call newpin(m,t,er,iewopt)
    if(er.gt.0) stop
    do 918 ik=1,ncase
    do 122 i=1,n
122 z(i)=zt(ik,i)
    sz=0.
    do 212 i=1,n
212 sz=sz+z(i)
    if(sz.lt.0.999) go to 200
    open(unit=4,file='outquac')
    write(4,11) n,t
 11 format(///30h liquid/liquid equilibrium for,i3,23h component syste
   1m at t=,f4.0)
    write(4,12)
 12 format(/1x,'index',5x,'component',15x,'feed',6x,'r phase',5x,
   1  'e phase',8x,'k'/)
    call elips(n,id,key,ir,ie,z,t,v,x,y,k,ier)
    if(ier.gt.0) write(4,13) ier
 13 format(/9h ***error,i2,3h***/)
220 do 229 i=1,n
    ii=id(i)
    write(4,14) ii,nm1(ii),nm2(ii),z(i),x(i),y(i),k(i)
 14 format(2x,i3,2x,2a10,3f12.4,1pe14.2)
229 continue
    write(4,15) v
 15 format(/3x,'e/r = ',1pe9.2//)
    write(4,14)
    write(4,*) ' above values in mole fractions, those below in
   1 weight fractions'
    swr=0.0
    swe=0.0
    swz=0.
    do 300 i=1,n
    ii=id(i)
    wz(i)=z(i)*wm(ii)
    wr(i)=x(i)*wm(ii)
    we(i)=y(i)*wm(ii)
    swz=swz+wz(i)
    swr=swr+wr(i)
    swe=swe+we(i)
300 continue
```

```
      do 301 i=1,n
      ii=id(i)
      wz(i)=wz(i)/swz
      we(i)=we(i)/swe
      wr(i)=wr(i)/swr
      if(wr(i).eq.0.) wr(i)= -1.
      kw(i)=we(i)/wr(i)
      write(4,14) ii,nm1(ii),nm2(ii),wz(i),wr(i),we(i),kw(i)
  301 continue
      ww=v*swe/swr
      write(4,15) ww
  918 continue
      close(unit=4)
      stop
  900 write(4,19)
   19 format(/' error in parameter input deck'/)
      close(unit=4)
      stop
      end



      subroutine newpin(m,t,erin,iewopt)
*
* newpin reads pure component and uniquac binary parameters into
* common storage blocks /pure/ and /binary/ for a library of
* m components
*   see subroutine parin (Prausnitz et al, 1980) for formats
*
* if iewopt is equal to 1, the equations for ethanol-water
* binary interaction parameters as a funtion of temperature
* are used, otherwise the parameters in the 'binprm' file
* are used
*
      integer erin
      implicit double precision(a-d,f-h,k,o-z)
      character nm1(100)*10,nm2(100)*10
      common/pure/nm1(100),nm2(100),wm(100),ru(100),qu(100),qp(100)
      common/binary/u(100,100)
  100 erin=0
      if(m.gt.100) go to 900
* read in pure component parameters
      open(unit=7,file='pureprm')
      rewind 7
      do 109 i=1,m
* first card for pure component
      read(7,01) j,nm1(j),nm2(j),wm(j),ru(j),qu(j),qp(j)
   01 format(i3,2a10,4f6.3)
  109 continue
      close(unit=7)
      open(unit=7,file='binprm')
      rewind 7
```

```
*initially zero uniquac binary interaction parameters
  120 do 121 i=1,m
      do 121 j=i,m
  121 u(i,j)=0.
*read in u.b.p.s
  125 read(7,05) i,j,uij,uji
   05 format(2i5,2f10.2)
* terminate read on blank final card
      if(i.eq.0) go to 130
      u(i,j)=uij
      u(j,i)=uji
      go to 125
  130 continue
      if(iewopt.eq.0) go to 140
      u(1,2)=(-10845.01085+144.45463836*t-.69258891047*t**2+
     1 .00143459625*t**3-1.096233611d-06*t**4)
      u(2,1)=(38765.54177-475.05211071*t+2.141085409*t**2-
     1 .0042031659367*t**3+3.054583612d-06*t**4)
  140 close(unit=7)
      return
  900 erin=5
      return
      end
```

```
      subroutine elips(n,id,key,ir,ie,z,t,a,xr,xe,k,err)
*
* ELIPS calculates conjugate phase compositions xr and xe for
* partially miscible n component liquid systems (n.le.20) of overall
* composition z at given temperature t (K).
*       Indices of the components involved should
* be in the vector id.  ir and ie are the component nrs of the
* r and e phase solvents (should be set to 0 if no such solvents
* designated).  The fraction of the system going into the e phase is
* returned in a, with a being 0 or 1 (and xe=xr) if z is in a single
* phase region.  elips normally returns err=0, but if component
* combinations lacking data are involved it returns err=1, if
* convergence is not achieved err=2, and if z is too near the plait
* point for resolution err=7.  key should be 1 (or 9) for the first
* call with new systems, otherwise 2 (or 3-8,10).
*
      dimension z(n),xr(n),xe(n),k(n),gar(20),gae(20),k1(20),ks,kp,
     1  k2,rx(20),ex(20)
      implicit double precision(a-h,k,o-z)
      integer key,kee,kac,id(n),err,erl
  100 err=0
      kee=key
      if(ir.eq.0.or.ie.eq.0) go to 101
      go to(101,130,130,130,130,130,130,130,101,130),key
* for new systems without ir, ie specified, find ir, ie as least
*  soluble pair
  101 ks=1.
      kp=1.
  110 do 115 i=1,n
      xr(i)=0.
  115 xe(i)=0.
      j1=1
      if(ir.ne.0) go to 120
      if(ie.ne.0) go to 121
  116 do 119 j=2,n
      xr(j1)=0.
      xe(j1)=0.
      j1=j-1
      xr(j)=0.98
      xe(j)=0.02
      xr(j-1)=0.
      xe(j-1)=0.
      if(z(j).lt.0.10) go to 119
```

```
      do 118 i=1,j1
      xe(i)=0.98
      xr(i)=0.02
      if(i.gt.1) xe(i-1)=0.
      if(i.gt.1) xr(i-1)=0.
      if(z(i).lt.0.10) go to 118
      call lilik(n,id,kee,xr,xe,t,k,gar,gae,erl)
      if(erl.gt.1) go to 900
      kee=3
      if(k(i).le.ks) go to 117
      ks=k(i)
      is=i
  117 if(1./k(j).le.ks) go to 118
      ks=1./k(j)
      is=j
  118 continue
  119 continue
      xr(n)=0.
      xe(n)=0.
      xr(j1)=0.
      xe(j1)=0.
      go to 125
  120 if(ie.ne.0) go to 130
      is=ir
      go to 125
  121 is=ie
  125 xe(is)=0.98
      xr(is)=0.02
  126 do 129 j=1,n
      if(j.eq.is) go to 129
      xr(j)=0.98
      xe(j)=0.02
      if(j.eq.(is+1)) go to 128
      if(j.gt.1) xr(j-1)=0.
      if(j.gt.1) xe(j-1)=0.
  127 if(z(j).lt.0.10) go to 129
      call lilik(n,id,kee,xr,xe,t,k,gar,gae,erl)
      if(erl.gt.1) go to 900
      kee=3
      if(k(j).ge.kp) go to 129
      kp=k(j)
      ip=j
      go to 129
  128 if(j.gt.2) xr(j-2)=0.
      if(j.gt.2) xe(j-2)=0.
      go to 127
  129 continue
```

```
      ie=ip
      if(ir.ne.is) ie=is
      if(ir.ne.is) ir=ip
* initialize r and e phase compositions
  130 do 131 i=1,n
      xr(i)=0.
  131 xe(i)=0.
      xr(ir)=0.98
      xe(ir)=0.02
      xr(ie)=0.02
      xe(ie)=0.98
* get initial estimates for k values
  135 call lilik(n,id,kee,xr,xe,t,k,gar,gae,erl)
      if(erl.gt.1) go to 900
      sz=0.
  136 do 137 i=1,n
      sz=sz+z(i)
  137 k1(i)=k(i)-1.
      if(abs(sz-1.).gt.0.01) go to 903
* get initial estimate for a
      a=z(ie)/(z(ie)+z(ir))
      a=-a/k1(ir)+(a-1.)/k1(ie)
      if(a.lt.0.) a=0.
      if(a.gt.1.) a=1.
      ao=a
      it=0
      kac=0
* conduct iteration over phase composition (outer loop)
  200 it=it+1
      if(it.gt.50) go to 900
      aa=ao
      ao=a
      an=a
* conduct newton-raphson iteration for a at fixed k values
  300 do 319 m=1,10
      f=0.
      df=0.
  301 do 309 i=1,n
      k2=a*k1(i)+1.
      f=f+z(i)*k1(i)/k2
  309 df=df-z(i)*(k1(i)/k2)**2
      if(abs(f).lt.1.e-05) go to 210
      da=f/df
  310 an=a-da
* limit a to range 0 - 1 if it falls outside poles of f.
      if(an.lt.-1./k1(ir)) go to 312
      an=a+(1./k1(ir)+a)/2.
      go to 319
  312 if(an.gt.-1./k1(ie)) go to 319
      an=a+(1./k1(ie)+a)/2.
  319 a=an
```

```
      go to 900
  210 a=an
      sr=0.
      se=0.
* find new r and e phase compositions
  211 do 215 i=1,n
      xr(i)=z(i)/(a*k1(i)+1.)
      xe(i)=k(i)*xr(i)
      sr=sr+xr(i)
  215 se=se+xe(i)
  220 do 225 i=1,n
      xr(i)=xr(i)/sr
  225 xe(i)=xe(i)/se
* at alternate iterations after 3 accelerate phase compositions
* by wegstein method based on sum of deviations of component
* fugacities
  230 if(it.lt.3) go to 250
      if(it.le.5.and.(a.lt.0..or.a.gt.1.)) go to 250
      if(kac.ge.1) go to 239
      if(ss.gt.sl) go to 250
      if(ss.gt.0.2) go to 250
      kac=1
      wg=ss/(sl-ss)
      wk=1.+wg
      sr=0.
      se=0.
      do 235 i=1,n
      xr(i)=wk*xr(i)-wg*rx(i)
* allow no negative mol fractions
      if(xr(i).lt.0.) xr(i)=0.
      xe(i)=wk*xe(i)-wg*ex(i)
      if(xe(i).lt.0.) xe(i)=0.
      sr=sr+xr(i)
  235 se=se+xe(i)
* normalize accelerated compositions (to allow for xr(i)
* or xe(i) set to 0)
  236 do 237 i=1,n
      xr(i)=xr(i)/sr
  237 xe(i)=xe(i)/se
      go to 250
  239 kac=0
* get new k and gamma values
  250 call lilik(n,id,3,xr,xe,t,k,gar,gae,erl)
      if(erl.gt.1) go to 900
      ess=1.e-03
      if(it.le.5) go to 252
* check for vicinity of a plait point
      ppi=k(ir)/k(ie)+k(ie)/k(ir)
      if(ppi.gt.10..or.ss.gt.0.05) go to 251
```

```
* exit if too near plait point
      if(it.ge.20) go to 290
      if(ppi.gt.7.) go to 251
* check if calculation near plait point is probably in single
* phase region--if so continue
      de=ao
      if(de.gt.0.5) de=ao-1
      di=(aa-a)/de
      if(di.lt.0.1) go to 290
  251 if(ppi.lt.20) ess=2.e-04
  252 sl=ss
      ss=0
  253 do 255 i=1,n
      k1(i)=k(i)-1.
* calculate objective function
  255 ss=ss+abs(gae(i)*xe(i)-gar(i)*xr(i))
* check convergence
      if(ss.le.ess) go to 190
      if(a.ge.0..and.a.le.1.) go to 260
      if(it.lt.3.or.ss.gt.0.20) go to 260
      if(it.lt.5.and.ss.gt.0.05) go to 260
* check if a moving away from 0 - 1 region
      if((abs(a)-abs(ao)).gt.0.) go to 195
* save last phase compositions for use in acceleration
  260 do 265 i=1,n
      rx(i)=xr(i)
  265 ex(i)=xe(i)
      go to 200
* feed in vicinity of plait point--check if in two phase region
  290 if(a.ge.0..and.a.le.1.) go to 905
      go to 195
* do not allow convergence on accelerated iteration
  190 if (kac.eq.1) go to 260
* converged solution--check if in two phase region
  191 if(a.lt.0..or.a.gt.1.) go to 195
      err=erl
      write(4,*) ' activity coeficients '
      do 555 i=1,n
      write(4,*) gar(i),gae(i)
  555 continue
      return
* feed outside two phase region
  195 do 196 i=1,n
      xr(i)=z(i)
  196 xe(i)=z(i)
      if(a.lt.0.) a=0.
      if(a.gt.1.) a=1.
      err=erl
      return
```

```
* on failure to converge set a to -1 and err to 2
  900 err=2
      go to 910
* for bad data input set a to -1 and err to 5
  903 err=5
      go to 910
* for feed too near plait point set a to -1 and err to 7
  905 err=7
  910 do 911 i=1,n
      xr(i)=-xr(i)
  911 xe(i)=-xe(i)
      a=-1.
      return
      end
```

```
      subroutine lilik(n,id,key,xr,xe,t,k,gar,gae,err)
*
* lilik calculates two phase effective liquid equilibrium ratios k
* for all n components (n.le.20) whose indices appear in vector id,
* given temperature t(k) and estimates of phase compositions xr, xe
* (used without correction to evaluate activity coefficients gar and
* gae). lilik normally returns err=0, but if component combinations
* lacking data are involved it returns err=1; if a k is out of range
* then err=2.  key should be 1 on initial call for a system, 2 (or 6)
* on subsequent calls when all variables are changed, 3 if only
* compositions are changed, and 4 (or 7) if only t is changed.
*
      dimension xr(n),xe(n),k(n),gar(n),gae(n),x(20),y(20),
     1  gx(20),gy(20)
      integer id(n),idf(20),err,erg
      implicit double precision(a-d,f-h,k,o-z)
      integer key
  100 err=0
* convert composition vectors to dimension 20 to match lower level
* subroutines
  101 do 102 i=1,n
      x(i)=xr(i)
      y(i)=xe(i)
  102 idf(i)=id(i)
* get r and e phase activity coefficients
      call gamma(n,idf,key,x,t,gx,erg)
      call gamma(n,idf,3,y,t,gy,erg)
* convert activity coefficient vectors to dimension n
  110 do 119 i=1,n
      gar(i)=gx(i)
      gae(i)=gy(i)
      k(i)=gar(i)/gae(i)
      if(k(i).le.0..or.k(i).gt.1.e+19) go to 900
  119 continue
      err=erg
      return
* for a k value out of range set err to 2
  900 err=2
      do 905 i=1,n
  905 k(i)=0.
      return
      end
```

```
      subroutine gamma(n,id,key,x,t,gam,erg)
*
* gamma calculates liquid phase activity coefficients, gam, for all
* n components(n.le.20) whose  indices appear in vector id, given
* temperature t(k) and liquid composition x, using the uniquac model.
* for noncondensable components (u(i,i) set to 1.e+20) an unsymmetric
* convention is used to derive effective activity coefficients. gamma
* returns erg=0 unless binary data are missing for system, in which
* case it returns erg=1. key should be 1 for a new system, 3 for t
* unchanged, and 4 or 5 for x unchanged.
      dimension x(20),gam(20),pt(20),pts(20)
      integer id(20),erg
      implicit double precision(a-d,f-h,k,o-z)
      character nm1(100)*10,nm2(100)*10
      integer key
      common/pure/nm1(100),nm2(100),wm(100),ru(100),qu(100),qp(100)
      common/binary/u(100,100)
      common/gs/ier,rl(20),th(20),tp(20),gcl(20),tau(20,20)
      data z/10./
* skip system initialization on subsequent calculations
  100 go to(110,120,120,130,130,120,130,120,110,120),key
  110 erg=0
* calculate composition independent terms
  111 do 119 i=1,n
      ii=id(i)
  119 rl(i)=z*(ru(ii)-qu(ii))/2.-ru(ii)+1.
* calculate segment and area fractions for components in mixture
  120 sp=1.e-30
      st=1.e-30
      stp=1.e-30
      ss=0.
      sl=0.
  121 do 125 i=1,n
      ii=id(i)
      th(i)=x(i)*qu(ii)
      tp(i)=x(i)*qp(ii)
      sp=sp+x(i)*ru(ii)
      st=st+th(i)
      stp=stp+tp(i)
* skip for noncondensable components
      if(u(ii,ii).gt.1.e+19) go to 125
      ss=ss+x(i)
      sl=sl+x(i)*rl(i)
  125 continue
  126 do 129 i=1,n
      ii=id(i)
      th(i)=th(i)/st
      tp(i)=tp(i)/stp
      if(u(ii,ii).gt.1.e+19) go to 128
```

```
* calculate combinatorial comtribution to excess free energy
  127 gcl(i)=rl(i)-ru(ii)*sl/sp+dlog(ru(ii)*ss/sp)+z*qu(ii)
     1  *dlog(qu(ii))*sp/(ru(ii)*st))/2.
      go to 129
  128 gcl(i)=0.
  129 continue
      if(key.eq.3) go to 140
* get uniquac binary interaction parameter terms
  130 call taus(n,id,t,tau,ier)
* calculate residual contribution to excess free energy
  140 do 141 i=1,n
  141 pts(i)=0.
  142 do 149 i=1,n
      pt(i)=1.e-30
      do 143 j=1,n
  143 pt(i)=pt(i)+tp(j)*tau(j,i)
      do 145 j=1,n
  145 pts(j)=pts(j)+tp(i)*tau(j,i)/pt(i)
  149 continue
  150 do 159 i=1,n
      ii=id(i)
      if(u(ii,ii).gt.1.e+19) go to 155
* residual free energy for condensable components
      grl=qp(ii)*(1.-dlog(pt(i))-pts(i))
      go to 158
  155 grl=0.
      do 156 j=1,n
      jj=id(j)
* residual free energy for noncondensable components
  156 grl=grl+th(j)*(u(ii,jj)+u(jj,ii)/t)
* calculate activity coefficient
  158 gam(i)=dexp(gcl(i)+grl)
  159 continue
      if(iabs(ier).eq.1) erg=1
      return
      end
```

```
      subroutine taus(n,id,t,tau,ier)
*
* taus calculates temperature dependent interaction coefficients
* tau, for use in subroutine gamma.  if system data are missing
* (some required entry in matrix u in common/binary is zero)
* the corresponding tau is set to 1
* and ier is returned as +/- 1.  for noncondensables present
* ier is -2 or -1 (otherwise 0).
*
      dimension tau(20,20)
      integer id(20)
      implicit double precision(a-d,f-h,k,o-z)
      common/binary/u(100,100)
  100 ier=0
  110 do 119 i=1,n
      ii=id(i)
* check if any component is a noncondensable and flag ier
      if(u(ii,ii).gt.1.e+19) ier=isign(ier**2-2,-1)
      do 119 j=1,n
      if(j.eq.i) go to 115
      jj=id(j)
      write(4,*) 'u',ii,jj,'=',u(ii,jj)
* check if binary pair are both noncondensables.
      if(u(ii,ii).gt.1.e+19.and.u(jj,jj).gt.1.e+19) go to 115
* check if binary data are missing
      if(abs(u(ii,jj)).lt.1.e-19) go to 112
* check if either component in binary pair is a noncondensable
      if((u(ii,ii)+u(jj,jj)).gt.1.e+19) go to 115
* calculate interaction term
      tau(i,j)=dexp(-u(ii,jj)/t)
      go to 119
  112 ier=isign(1,ier)
* set interaction term equal to unity for pair with missing data
  115 tau(i,j)=1.
  119 continue
      return
      end
```

The following is a sample data file, 'casefile' for the UNIQUAC liquid-liquid equilibrium programs (strtr, elips).

```
17  libsize
 1  (iewopt, =0 for pars in binprm, 1 for b.m. curves)
03        298.0          1    2    9
 6  ncase
    2    3   0.0        0.50       0.50
    2    3   0.01       0.50       0.49
    2    3   0.05       0.50       0.45
    2    3   0.10       0.50       0.40
    2    3   0.15       0.45       0.40
    2    3   0.20       0.40       0.40
```

The following is a sample output file, 'outquac', produced by the UNIQUAC liquid-liquid equilibrium programs.

```
 liquid/liquid equilibrium for  3 component system at t=298.

 index      component       feed       r phase      e phase        k

  u  1  2  =   17.310585578135
  u  1  9  =  -159.96000000000
  u  2  1  =   194.99548313256
  u  2  9  =   191.17000000000
  u  9  1  =   288.27000000000
  u  9  2  =   269.11000000000
   activity coeficients
   4.7775784239316  0.98873512685393
   1.0000339992784   3.4467155760797
   714.76063684331   1.0489357142181
    1  ethanol          0.          0.          0.          4.83d+00
    2  water            0.5000      0.9990      0.2898      2.90d-01
    9   hexanol         0.5000      0.0010      0.7102      6.81d+02

   e/r =  7.04d-01


   above values in mole fractions, those below in weight fractions
    1  ethanol          0.         -1.0000      0.          0.  d+00
    2  water            0.1499      0.9941      0.0671      6.75d-02
    9   hexanol         0.8501      0.0059      0.9329      1.59d+02

   e/r =  3.02d+00
```

liquid/liquid equilibrium for 3 component system at t=298.

index	component	feed	r phase	e phase	k

u 1 2 = 17.310585578135
u 1 9 = -159.96000000000
u 2 1 = 194.99548313256
u 2 9 = 191.17000000000
u 9 1 = 288.27000000000
u 9 2 = 269.11000000000

activity coeficients

3.4626379048584 0.97666701241311
1.0120861259295 3.0290803135482
237.79682031846 1.1264038018392

1	ethanol	0.2000	0.0627	0.2224	3.55d+00
2	water	0.4000	0.9351	0.3125	3.34d-01
9	hexanol	0.4000	0.0022	0.4651	2.11d+02

e/r = 8.59d-01

above values in mole fractions, those below in weight fractions

1	ethanol	0.1608	0.1448	0.1616	1.12d+00
2	water	0.1258	0.8439	0.0888	1.05d-01
9	hexanol	0.7134	0.0113	0.7496	6.65d+01

e/r = 2.73d+00

The following is a sample of a library of pure component parameters used by the UNIQUAC liquid-liquid equilibrium programs. It is stored in the file 'pureprm'.
The parameters are molecular weight, R value, Q value, and Q prime value for each component.

001ethanol	46.07	2.11	1.97	0.92
002water	18.016	0.92	1.40	1.00
0031-dodecanol	186.33	8.85	7.372	7.372
004tetradecane	198.38	9.895	8.176	8.176
5224-trimethylpentane	114.0	5.85	4.94	4.94
6furfural	96.08	3.17	2.48	2.48
7cyclohexane	84.16	3.97	3.01	3.01
8benzene	78.11	3.19	2.40	2.40
9 hexanol	102.2	4.80	4.13	4.13
10 octanol	130.2	6.15	5.21	5.21
11 decanol	158.3	7.50	6.01	6.01
12 octanoic acid	144.2	6.25	5.33	5.33
13 octanal	128.2	5.95	5.04	5.04
14 dibutyl ether	130.2	6.09	5.18	5.18
15 3-heptanone	114.2	5.27	4.50	4.50
16 butyl acetate	116.2	4.83	4.20	4.20
17 tetrachloroethane	167.9	4.12	3.37	3.37

The following is a sample of a library of binary interaction parameters used by the UNIQUAC liquid-liquid equilibrium programs. It is stored in the file 'binprm'.
The numbers in the first two groups are the component i.d. numbers and correspond to the numbering in 'pureprm'. The parameters are Aij and Aji, respectively, where i is the first i.d. number and j the second.

1	2	-90.19	254.55
2	3	326.3	347.30
1	3	-168.09	423.46
1	4	-34.876	279.98
2	4	342.40	1300.0
3	4	-63.71	108.55
5	6	410.08	-4.98
5	7	141.01	-112.66
6	7	41.17	354.83
1	8	115.13	500.0
2	8	369.01	860.81
1	9	-159.96	288.27
2	9	191.17	269.11
1	10	-166.28	344.32
2	10	253.63	276.16
1	11	-168.07	387.86
2	11	301.5	238.6
1	12	-183.19	493.7
2	12	183.48	508.96
1	13	-341.51	600.17
2	13	203.9	774.78
1	14	-161.44	640.22
2	14	85.287	1505.1
1	15	-174.07	596.11
2	15	93.586	856.72
1	16	-216.41	557.72
2	16	120.99	677.09
1	17	-312.0	712.38
2	17	239.08	1165.4

The final set of programs used in the modelling of liquid-liquid equilibria is for the estimation of UNIQUAC binary interaction parameters from mutual solubility data. The program used is based extensively on the **solpa** program written by T.F. Anderson in the course of his Ph.D. thesis in the Department of Chemical Engineering at the University of California at Berkeley. Again, modifications were necessary to allow the program to be run on the VAX 780. In addition, the data input was changed somewhat to take advantage of the interactive nature of the UNIX system.

```
c
c program solpa
c
c  This program uses mutual solubility data to determine binary
c  parameters for the modified UNIQUAC equation.  It is a
c  modified version of a program from the Ph.D. thesis of
c  T.F. Anderson, Dept. of Chem. Eng., University of California
c  at Berkeley.
c
c  The subroutines DRVT, ACTIV, and PAREST must be loaded with this
c  program.  It reads from an input file called 'solpadata' and writes
c  output to a file called 'solpaout'.
c
      implicit double precision (a-h,o-z)
      real mw
      dimension a(2,2),std(2),cov(2,2),p(5),mw(2)
      character rf1*60,rf2*60,nm1(2)*10,nm2(2)*10
      common/size/r(2),q(2),qp(2),el(2)
      common/diff/dp(5),dx
      common/data/temp,x1b,x2b,x1a,x2a
      common/cntrl/itmax,ll,iprt,sf,tol
c replacing first read with data
      data tol,sf,dp(1),dp(2),dx,itmax,iprt,ll/1.e-6,1.0,0.1,0.1,.00001,
     1   15,3,2/
c read data for first system
      open(unit=5,file='solpadata')
      rewind 5
   10 read(5,1001) num,iref,icmp
 1001 format(3i2)
      if(num.eq.0) go to 60
      read(5,1002) rf1
 1002 format(a60)
      if(iref.gt.0) read(5,1002) rf2
      do 12 i=1,2
      read(5,1003) nm1(i),nm2(i),r(i),q(i),qp(i),mw(i),std(i)
 1003 format(2a10,6f10.2)
      if (qp(i).lt.1.e-6) qp(i)=q(i)
   12 continue
      read(5,1004) (p(i),i=1,ll)
 1004 format(8f10.2)
```

```
      open(unit=4,file='solpaout')
      write(4,2001)
 2001 format(10x,'uniquac parameters fit to mutual solubility data',//)
      write(4,2002) rf1
 2002 format(1x,'ref - ',a60)
      if(iref.gt.0) write(4,2015) rf2
 2015 format(7x,a60)
      write(4,2003)
 2003 format(//1x,'no',6x,'name',15x,'l',6x,'r',6x,'q',5x,'qp',2x,
     1 'mol wt'/)
      z=10.0
      do 15 i=1,2
      el(i)=(z/2.)*(r(i)-q(i))-(r(i)-1.)
   15 write(4,2004) i,nm1(i),nm2(i),el(i),r(i),q(i),qp(i),mw(i)
 2004 format(1x,i2,1x,2a10,2x,f5.2,2x,f5.2,2x,f5.2,2x,f5.2,2x,f6.2/)
      write(4,2005)(p(i),i=1,11)
 2005 format(1x,'initial estimates of parameters'//5x,'a12 =',f10.2/
     1 5x,'a21 =',f10.2)
c
c
      do 50 ii=1,num
      read(5,*) temp,x1b,x2a
      if(icmp.eq.0) go to 20
      const=(1.-x1b)*mw(1)/(x1b*mw(2))
      x1b=1./(1.+const)
      const=(1.-x2a)*mw(2)/(x2a*mw(1))
      x2a=1./(1.+const)
   20 continue
      write(4,2006) temp
 2006 format(1x,'measured solubilities and estimated standard deviations
     1 at ',f6.2,' degrees c'/)
      write(4,2007) nm1(1),nm2(1),nm1(2),nm2(2),x1b,std(1)
      write(4,2007) nm1(2),nm2(2),nm1(1),nm2(1),x2a,std(2)
 2007 format(1x,'mole fraction of ',2a10,' in ',2a10,' rich phase is ',
     1 g15.5,'(+/-',g10.3,')'/)
      temp=temp+273.16
      x2b=1.-x1b
      x1a=1.-x2a
c
c
      call parest(p,it)
c
```

```
      call drvt(1,p,f,g,f1,f2,f3,f4,g1,g2,g3,g4)
      del=f3*g4-f4*g3
      a(1,1)=-(f1*g4-f4*g1)/del
      a(1,2)=-(f2*g4-f4*g2)/del
      a(2,1)=-(f3*g1-f1*g3)/del
      a(2,2)=-(f3*g2-f2*g3)/del
      do 40 i=1,2
      do 40 j=1,i
      cov(i,j)=0.0
      do 35 k=1,2
   35 cov(i,j)=cov(i,j)+a(i,k)*a(j,k)*std(k)**2
      cov(j,i)=cov(i,j)
   40 continue
      stdp1=dsqrt(cov(1,1))
      stdp2=dsqrt(cov(2,2))
      write(4,2008) it
 2008 format(/1x,'converged successfully requiring ',i3,' iterations'/)
      write(4,2009)
 2009 format(//1x,'final parameters and estimates of their std dev'/
     1 1x,'no',10x,'parameter',10x,'std dev'/)
      write(4,2010) p(1),stdp1,p(2),stdp2
 2010 format(1x,'a12 =',g15.5,2x,'(+/-',g10.3,')'/1x,'a21 =',g15.5,2x,
     1 '(+/-',g10.3,')'/)
      write(4,2011)
 2011 format(//1x,'covariance matrix'/)
      do 45 i=1,2
   45 write(4,2012) (cov(i,j),j=1,2)
 2012 format(1x,5g15.5/)
      a(1,1)=1.0
      a(2,2)=1.0
      a(1,2)=cov(1,2)/stdp1/stdp2
      a(2,1)=a(1,2)
      write(4,2013)
 2013 format(//1x,'corelation matrix'/)
      do 47 i=1,2
   47 write(4,2012) (a(i,j),j=1,2)
      con1=(cov(1,1)+cov(2,2))/2.
      con2=cov(1,2)**2-cov(1,1)*cov(2,2)
      e1=con1+dsqrt(con2+con1**2)
      e2=con1-dsqrt(con2+con1**2)
      write(4,2014) e1,e2
 2014 format(//1x,'eigenvalues'/1x,'e1 is',g15.5,5x,'e2 is',g15.5)
   50 continue
      go to 10
   60 stop
      end
```

```
      subroutine parest (p,it)
      implicit double precision (a-h,o-z)
      dimension p(5)
      common/cntrl/itmax,ll,iprt,sf,tol
      it=0
   15 it=it+1
      sfp=sf
      if (it.gt.itmax) go to 30
      call drvt(0,p,f,g,f1,f2,f3,f4,g1,g2,g3,g4)
      del=f3*g4-f4*g3
      delp1=-(f*g4-f4*g)/del
      delp2=-(f3*g-f*g3)/del
   17 continue
      if (sfp.lt.1.e-4) go to 30
      if ((abs(delp1*sfp).lt.500.0).and.(abs(delp2*sfp).lt.500.0))
     1     go to 18
      sfp=sfp/5.0
      go to 17
   18 continue
      p(1)=p(1)+delp1*sfp
      p(2)=p(2)+delp2*sfp
      if (iprt.lt.1) go to 20
      write (4,2001) it,p(1),p(2),delp1,delp2,f,g
 2001 format (1x,i2,6g15.4)
   20 continue
      if (abs(delp1/p(1)).gt.tol.or.abs(delp2/p(2)).gt.tol) go to 15
      if (abs(f).gt.tol.or.abs(g).gt.tol) go to 15
      return
   30 write (4,2002) it
 2002 format (1x,'did not converge, it= ',i2)
      return
      end
```

```
      subroutine drvt (ict,p,f,g,f1,f2,f3,f4,g1,g2,g3,g4)
c
c  This subroutine evaluates the objective function and calculates
c  the derivatives with respect to the parameters numerically,
c  using central differences.
c
      implicit double precision (a-h,o-z)
      common/data/temp,x1b,x2b,x1a,x2a
      common/cntrl/itmax,ll,iprt,sf,tol
      common/diff/dp(5),dx
      dimension p(5),pr(5),gam(2)
      fnc1(xa,xb,aca,acb)=dlog(xa*aca)-dlog(xb*acb)
      do 10 i=1,ll
   10 pr(i)=p(i)
c     evaluate error functions f & g
      call activ(x1a,x2a,pr,temp,gam)
      g1a=gam(1)
      g2a=gam(2)
      call activ(x1b,x2b,pr,temp,gam)
      g1b=gam(1)
      g2b=gam(2)
      f=fnc1(x1a,x1b,g1a,g1b)
      g=fnc1(x2a,x2b,g2a,g2b)
c     calculate partial derivatives wrt p(1) using central diff
      pr(1)=p(1)+dp(1)
      call activ(x1a,x2a,pr,temp,gam)
      g1a=gam(1)
      g2a=gam(2)
      call activ(x1b,x2b,pr,temp,gam)
      g1b=gam(1)
      g2b=gam(2)
      fp=fnc1(x1a,x1b,g1a,g1b)
      gp=fnc1(x2a,x2b,g2a,g2b)
      pr(1)=p(1)-dp(1)
      call activ(x1a,x2a,pr,temp,gam)
      g1a=gam(1)
      g2a=gam(2)
      call activ(x1b,x2b,pr,temp,gam)
      g1b=gam(1)
      g2b=gam(2)
      fm=fnc1(x1a,x1b,g1a,g1b)
      gm=fnc1(x2a,x2b,g2a,g2b)
      pr(1)=p(1)
      f3=(fp-fm)/(2.*dp(1))
      g3=(gp-gm)/(2.*dp(1))
```

```
c     calculate partial derivatives wrt p(2) using central diff
      pr(2)=p(2)+dp(2)
      call activ(x1a,x2a,pr,temp,gam)
      g1a=gam(1)
      g2a=gam(2)
      call activ(x1b,x2b,pr,temp,gam)
      g1b=gam(1)
      g2b=gam(2)
      fp=fnc1(x1a,x1b,g1a,g1b)
      gp=fnc1(x2a,x2b,g2a,g2b)
      pr(2)=p(2)-dp(2)
      call activ(x1a,x2a,pr,temp,gam)
      g1a=gam(1)
      g2a=gam(2)
      call activ(x1b,x2b,pr,temp,gam)
      g1b=gam(1)
      g2b=gam(2)
      fm=fnc1(x1a,x1b,g1a,g1b)
      gm=fnc1(x2a,x2b,g2a,g2b)
      pr(2)=p(2)
      f4=(fp-fm)/(2.*dp(2))
      g4=(gp-gm)/(2.*dp(2))
      if (ict.lt.1) return
c     calculate partial derivatives wrt x1b using central diff
      x1=x1b+dx
      x2=1.-x1
      call activ(x1a,x2a,pr,temp,gam)
      g1a=gam(1)
      g2a=gam(2)
      call activ(x1,x2,pr,temp,gam)
      g1b=gam(1)
      g2b=gam(2)
      fp=fnc1(x1a,x1,g1a,g1b)
      gp=fnc1(x2a,x2,g2a,g2b)
      x1=x1b-dx
      x2=1.-x1
      call activ(x1a,x2a,pr,temp,gam)
      g1a=gam(1)
      g2a=gam(2)
      call activ(x1,x2,pr,temp,gam)
      g1b=gam(1)
      g2b=gam(2)
      fm=fnc1(x1a,x1,g1a,g1b)
      gm=fnc1(x2a,x2,g2a,g2b)
      f1=(fp-fm)/(2.*dx)
      g1=(gp-gm)/(2.*dx)
```

```
c     calculate partial derivatives wrt x2a using central diff
      x2=x2a+dx
      x1=1.-x2
      call activ(x1,x2,pr,temp,gam)
      g1a=gam(1)
      g2a=gam(2)
      call activ(x1b,x2b,pr,temp,gam)
      g1b=gam(1)
      g2b=gam(2)
      fp=fnc1(x1,x1b,g1a,g1b)
      gp=fnc1(x2,x2b,g2a,g2b)
      x2=x2a-dx
      x1=1.-x2
      call activ(x1,x2,pr,temp,gam)
      g1a=gam(1)
      g2a=gam(2)
      call activ(x1b,x2b,pr,temp,gam)
      g1b=gam(1)
      g2b=gam(2)
      fm=fnc1(x1,x1b,g1a,g1b)
      gm=fnc1(x2,x2b,g2a,g2b)
      f2=(fp-fm)/(2.*dx)
      g2=(gp-gm)/(2.*dx)
      return
      end
```

```
      subroutine activ (x1,x2,pr,temp,gam)
c
c  This subroutine calculates activity coefficients at the
c  specified temperature and composition, using the current
c  best estimates of the interaction parameters.
c
      implicit double precision (a-h,o-z)
      double precision lgc,lgr
      dimension pr(5),gam(2),x(2),t(2,2),th(2),thts(2)
      common/size/r(2),q(2),qp(2),el(2)
      ncmp=2
      z=10.
      zot=z/2.
      t(1,2)=dexp(-pr(1)/temp)
      t(2,1)=dexp(-pr(2)/temp)
      t(1,1)=1.0
      t(2,2)=1.0
      x(1)=x1
      x(2)=x2
      elsum=0.0
      rsum=0.0
      qsum=0.0
      qsump=0.0
      do 30 i=1,ncmp
      qsum=qsum+q(i)*x(i)
      qsump=qsump+qp(i)*x(i)
      rsum=rsum+r(i)*x(i)
      elsum=elsum+x(i)*el(i)
   30 continue
      do 40 i=1,ncmp
      th(i)=qp(i)*x(i)/qsump
   40 continue
      do 50 i=1,ncmp
      thts(i)=0.0
      do 50 j=1,ncmp
      thts(i)=thts(i)+th(j)*t(j,i)
   50 continue
      do 70 i=1,ncmp
      sum=0.0
      do 60 j=1,ncmp
      sum=sum+th(j)*t(i,j)/thts(j)
   60 continue
      lgc=dlog(r(i)/rsum)+zot*q(i)*dlog(q(i)*rsum/(r(i)*qsum))
     1     +el(i)-r(i)*elsum/rsum
      lgr=qp(i)*(1.0-dlog(thts(i))-sum)
      gam(i)=dexp(lgc+lgr)
   70 continue
      return
      end
```

The following is a sample input data file, 'solpadata', for the program solpa, used for calculating UNIQUAC binary interaction parameters from mutual solubility data.

```
1
title
water                   0.92      1.4       1.0       18.016    0.005
1-octanol               6.152     5.212     5.212     130.2     1.d-6
302.      239.
25.0      .272          7.03d-5
```

The following is a sample output data file, 'solpaout' created by the program solpa.

```
          uniquac parameters fit to mutual solubility data

 ref - title

            me                 l       r       q      qp  mol wt

  1 water                    -2.32   0.92    1.40    1.00   18.02

  2 1-octanol                -0.45   6.15    5.21    5.21  130.20

 initial estimates of parameters

     a12 =     302.00
     a21 =     239.00
solubilities and estimated standard deviations at  25.00 degrees c

 mole fraction of water          in 1-octanol        rich phase is
    0.27200    (+/- 0.500d-02)

 mole fraction of 1-octanol      in water            rich phase is
    0.70300d-04(+/- 0.100d-05)

  1      253.7          273.6          -48.27          34.65
       0.3054d-01     0.5752
  2      253.6          276.2        -0.9589d-01       2.510
       0.5921d-02    -0.1544d-01
  3      253.6          276.2         0.3871d-02     0.1065d-02
       0.7782d-05    -0.7469d-04
  4      253.6          276.2        -0.5880d-08     0.1717d-07
       0.3335d-10    -0.1350d-10

 converged successfully requiring   4 iterations
```

final parameters and estimates of their std dev

no	parameter	std dev
a12 =	253.63	(+/- 2.85)
a21 =	276.16	(+/- 7.69)

covariance matrix

8.1171	-20.932
-20.932	59.065

corelation matrix

1.0000	-0.95597
-0.95597	1.0000

eigenvalues

e1 is 66.562 e2 is 0.62029

References for Appendix B

1. Fredenslund, A., Gmehling, J., and Rasmussen, P. (1977) Vapor-Liquid Equilibria Using UNIFAC Elsevier, New York

2. Magnussen, T., Rasmussen, P., and Fredenslund, A. (1981) Ind. Eng. Chem. Process Des. Dev., **20**(2):331

3. Prausnitz, J.M., Anderson, T.F., Grens, E.A., Eckert, C.A., Hsieh, R., and O'Connell, J.P. (1980) Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria Prentice-Hall, Englewood Cliffs, New Jersey

Appendix C

Details of Calculations for Adiabatic Sorption Models

This appendix gives the details of the calculations used to model water removal by solid sorbent in an adiabatic fixed bed process. The first section describes the local equilibrium approximation method and the second describes the method of characteristics. A list of the symbols used in all equations and an explanation of their meanings is provided in Table C.1.

C.1 Local Equilibrium Approximation

In order to integrate equations (6-1) and (6-2) numerically, the local equilibrium approximation was used to reduce the number of dependant variables. Equilibrium between the water concentrations was assumed to be described by the equation;

$$x = \frac{Ry}{f\ (1+Ry-y)} \qquad y = \frac{x}{R/f + x - Rx} \tag{C-1}$$

in which **R** is a constant which characterizes the sorption. **R** less than 1.0 signifies a favorable isotherm, meaning high affinity of the sorbent for the sorbate. **R** greater than 1.0 represents an unfavorable sorption, and **R** equal to 1.0 is a linear isotherm. The above expressions are a modified form of the constant separation factor relation, equivalent to the Langmuir relation (Vermuelen et al, 1973). It is modified by the inclusion of temperature dependance through the factor **f**, defined by;

$$f = \exp\ \frac{\Delta H}{GC}\left[\frac{1}{T_r} - \frac{1}{T_p}\right] \tag{C-2}$$

in which **H** is on a molar basis, **GC** is the universal gas constant, and the temperatures are converted to absolute (^{o}K). The behavior of the

Table C.1

List of Symbols Used and Their Meanings in Chapter 6 and Appendix C

a = interfacial area per unit bed volume, cm^2/cm^3
C_f = fluid heat capacity, cal/g-^oC
C_p = heat capacity of dry absorbent, cal/g-^oC
C_s = heat capacity of absorbent plus absorbed species, cal/g-^oC ($C_s = C_p + y\ C_w$)
d = particle diameter, cm
D_f = fluid phase diffusivity, cm^2/s
D_p = solid phase diffusivity. cm^2/s
C_w = heat capacity of absorbed species, cal/g-^oC
h = overall heat transfer coefficient, cal/cm^2-s-^oC
ΔH = enthalpy of absorption, cal/g absorbent (from dry to saturated)
k_f = fluid side mass transfer coefficient, cm/sec
k_p = particle side mass transfer coefficient, cm/sec
K = fluid phase thermal conductivity, cal/sec-cm-^oC
n = position dependant time variable, sec ($n = t - \varepsilon s/v$)
R = equilibrium constant defined in equation (C-1)
R_h = rate of heat transfer between phases, cal/sec-cm^3 (of bed)
R_m = rate of mass transfer between phases, dy/dt, sec^{-1}
s = distance along absorbent bed, cm (inlet is s=0)
t = time, sec
T_f = fluid temperature (average bulk), ^oC
T_p = absorbent temperature (average particle), ^oC
T_r = reference temperature for equilibrium, ^oC
v = superficial velocity of fluid, cm/sec
X = mass ratio of absorbate to dry carrier (fluid), g/g
X_s = saturation X at the reference temperature
x = fractional saturation of carrier (fluid), X/X_s
Y = mass ratio of absorbate to dry absorbent, g/g
Y_s = saturation Y at reference temperature
y = fractional saturation of absorbent, Y/Y_s
z = bed position variable, sec ($z = s/v$)

ε = void fraction in absorbent bed
μ = fluid viscosity, g/cm-s
ρ_b = density of dry empty bed, g/cm^3
ρ_f = grams of carrier (solvent fluid) per cm^3 of fluid
ρ_s = density of dry absorbent, g/cm^3
ψ_p = particle side mass transfer coefficient correction factor

function is sketched in Figure C-1 where it may be seen that the fluid phase concentration variable may exceed 1.0 as the temperature is increased. This corresponds, in the case of water sorption from an extraction solvent, to increased water solubility in the solvent with increasing temperature.

The functional form used for the release of heat during water absorption was the following;

$$H(y) = 2\ \Delta H\ (y - y^2/2) \qquad \text{(C-3)}$$

This form was chosen empirically because its shape, sketched in Figure C-2, resembles the shape of experimental curves reported by several researchers for water sorption by ion exchangers. Specifically, most of the heat release occurs in the first part of the sorption and the derivative of heat release with respect to fractional saturation of the sorbent goes to zero as the latter variable approaches one.

The calculation method used in the local equilibrium model was a backward finite differnces method. A flow diagram for the calculations is given in Figure C-3. Briefly, the calculation starts at each point in time and bed distance with a calculation ofthe convective terms. Then, two convergence loops are used to establish the local equilibrium condition. The inner loop uses a Newton-Raphson method to solve for the **x** and **y** which satisfy the material balance and equilibrium constraints. The outer loop calculates the heat released and solves for the equilibrium temperature using interval halving. Unnecessary computation is avoided by preliminary checks on the derivatives of the convection terms. Storage requirements are kept to a minimum by keeping only the currently calculated and immediately previous values of **x**, **y**, and **T** at all points **s**.

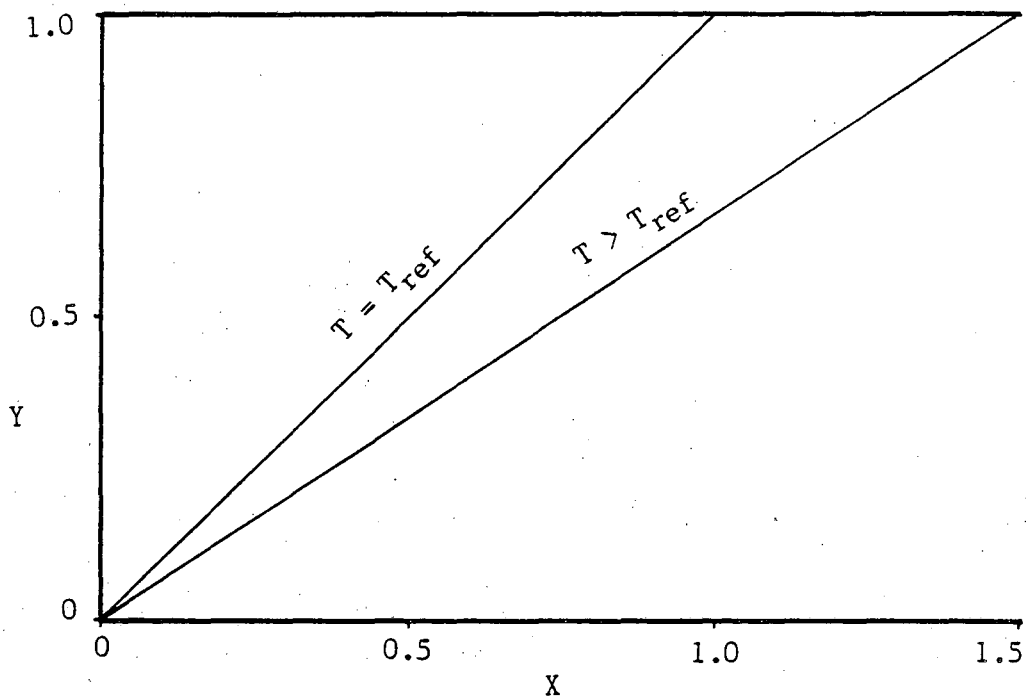


Figure C-1 Temperature Dependant Sorption Equilibrium

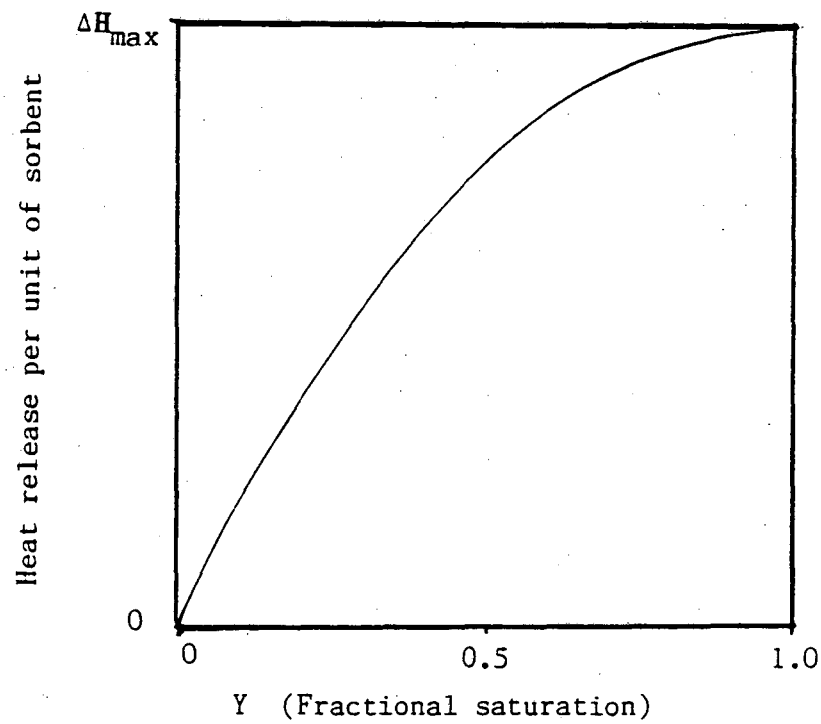


Figure C-2 Heat of Water Sorption as a Function of Fractional Saturation

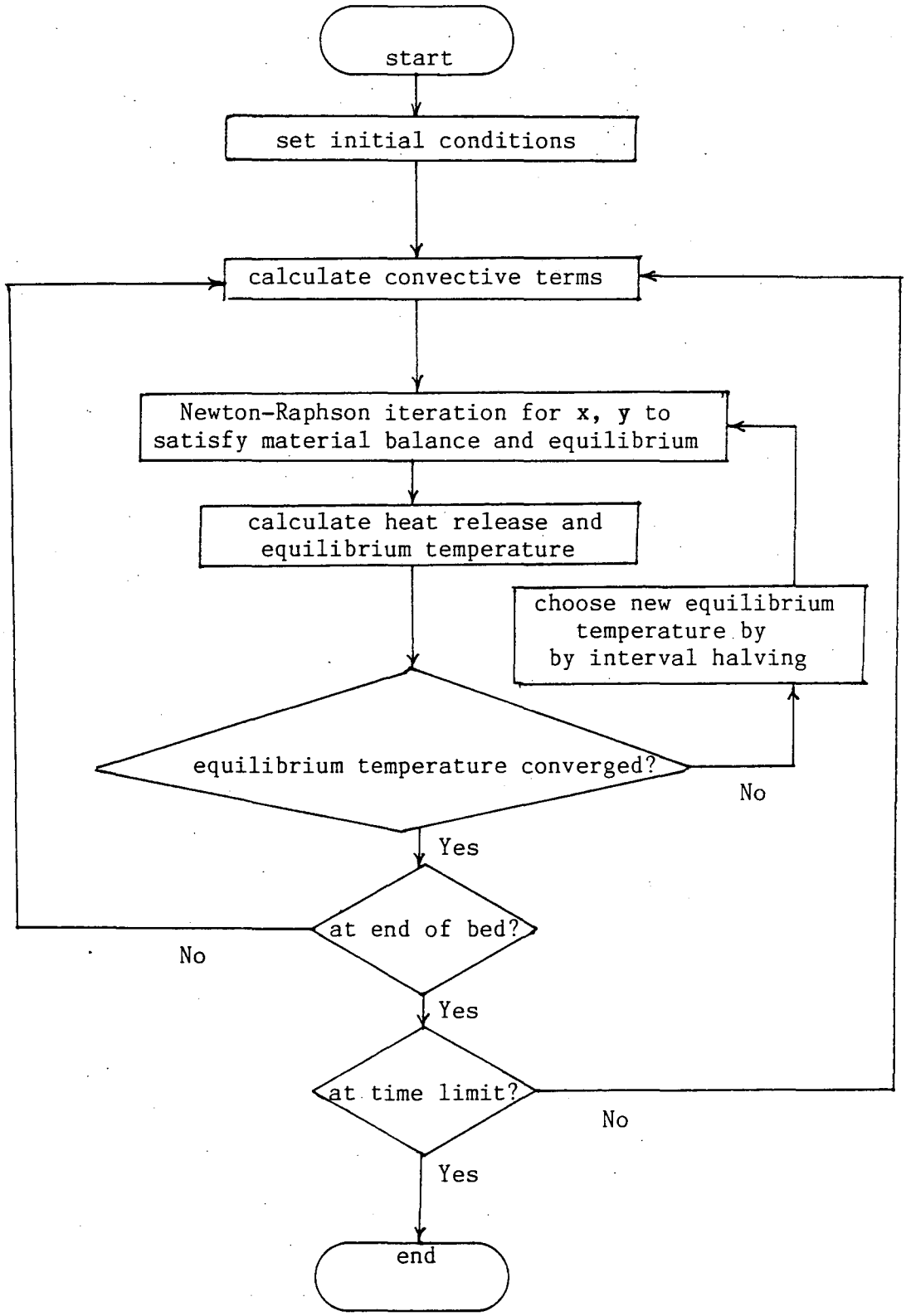


Figure C-3 - Flow Diagram for Calculation of Adiabatic Sorption by Local Equilibrium Approximation

The calculations were carried out on a VAX 780 computer using Fortran programs. Listings are given on the following pages of the main program, **drvsb**, and the subroutine, **thrmsb**, which actually does the calculations and prints the results. The main program simply reads data and calls **thrmsb**. Samples of input data and output from the programs are also listed.

```
c
c The following programs are for the modelling of adiabatic
c   fixed bed absorption ny the local equilibrium approximation.
c   They were written by T.K. Murphy, December 1982.
c
c This is the driver program for thrmsb. It reads data and calls the
c   subroutine 'thrmsb' to do the actual calculations.
c
c As given, it includes file definitions to allow it to be run as an
c   f77 Fortran program on a VAX 780 with UNIX operating system.
c
c   The output file is called 'sbout'.
c
c   The input file is called sbdata and must contain the following,
c     all in a format(20x, f10.5);
c
c   xfd, feed concentration of fluid, fraction of saturation
c   ybd, fractional saturation of bed initially, assumed uniform
c   tfd, feed temperature, degrees K
c   tbd, bed temperature, degrees K
c   r, equilibrium isotherm parameter, < 1 favorable, > 1 unfavorable
c   tref, reference temperature for equilibrium, deg. K
c   dhmx, heat release in calories for saturation of 1 cc of dry bed
c   cpf, heat capacity of fluid, cal/g-deg.C
c   cps, heat capacity of solid, cal/g dry solid-deg.C
c   fcap, fluid capacity, grams of sorbate per gram of pure solvent
c   scap, sorbent capacity, grams of sorbate per gram of dry sorbent
c   u, velocity of fluid in bed, distance increments/time increment
c   imax, maximum number of time increments
c   jmax, maximum number of distance increments
c   itell, print control, 0 to minimize reporting
c
```

```
c
      implicit double precision (a-h,o-z)
      common/param/xfd,ybd,tfd,tbd,r,tref,dhmx,cpf,cps,fcap,scap,u
      open(unit=5,file='sbdata')
      rewind 5
      read(5,99) xfd
   99 format(20x,f10.5)
      read(5,99) ybd
      read(5,99) tfd
      read(5,99) tbd
      read(5,99) r
      read(5,99) tref
      read(5,99) dhmx
      read(5,99) cpf
      read(5,99) cps
      read(5,99) fcap
      read(5,99) scap
      read(5,99) u
      read(5,98) imax
   98 format(20x,i3)
      read(5,98) jmax
      read(5,98) itell
      close(unit=5)
      open(unit=6,file='sbout')
      write(6,*) 'finite differences calc. of nonisothermal
     1 absorption'
      call thrmsb(imax,jmax,itell)
      close(unit=6)
      end
```

```
      subroutine thrmsb(imax,jmax,itell)
c This routine uses finite differences to calculate unsteady state
c profiles of fluid and solid concentrations and temperature in an
c adiabatic fixed bed absorption.
c
      implicit double precision (a-h,o-z)
      dimension x(2,200),y(2,200),t(2,200)
      common/param/xfd,ybd,tfd,tbd,r,tref,dhmx,cpf,cps,fcap,scap,u
      cmw=18.
      hmr=cmw*dhmx/(1.986*scap)
      hcpr=cps/cpf
      capr=fcap/scap
      xbd=ybd*r/(1.+(r-1.)*ybd)
c initialize x,y,and t
      jmx2=jmax+2
      do 10 j=2,jmx2
      y(1,j)=ybd
      t(1,j)=tbd
      x(1,j)=xbd
   10 continue
      x(1,1)=xfd
      x(2,1)=x(1,1)
      y(1,1)=dexp(hmr*(1./tref-1./tfd))*xfd/(r+xfd-r*xfd)
      y(2,1)=y(1,1)
      t(1,1)=tfd
      t(2,1)=t(1,1)
      write(6,*) "time=0"
      write(6,*) "x(0,j): ",(x(1,j),j=1,jmax)
      write(6,*) "y(0,j): ",(y(1,j),j=1,jmax)
      write(6,*) "t(0,j): ",(t(1,j),j=1,jmax)
      do 500 i=1,imax
      do 400 j=2,jmax
      m=j-1
      n=j+1
      dxdz=(x(1,j)-x(1,m))
      dtdz=(t(1,j)-t(1,m))
      if ((dabs(dxdz)).ge.0.001) goto 100
      if ((dabs(dtdz)).ge.0.001) goto 100
      x(2,j)=x(1,j)
      y(2,j)=y(1,j)
      t(2,j)=t(1,j)
      goto 400
  100 continue
```

```
  110 if(x(1,j).ge.0.) goto 120
      x(2,j)=0.
      y(2,j)=0.
      t(2,j)=t(1,j)-u*dtdz/(1.+hcpr)
      goto 400
  120 xinit=x(1,j)-u*dxdz
      tinit=t(1,j)-u*dtdz/(1.+hcpr)
      tc=tinit
c initialize convergence with r=1 case
      yc=(y(1,j)+capr*xinit)/(1.+capr)
      do 300 l=1,20
      f=dexp(hmr*(1./tref-1./tc))
      a=f*(xinit+y(1,j)/capr)
      b=f/capr
      c=r+(1.-r)*(xinit+y(1,j)/capr)
      d=(1.-r)/capr
c converge on y to satisfy mtl. balance and equilibrium
      do 200 k=1,20
      xc=xinit+(y(1,j)-yc)/capr
      ck=yc-f*xc/(r+xc-xc*r)
      if(dabs(ck).gt.0.001) goto 190
      if(icon.eq.1) goto 210
      icon=1
      goto 200
  190 dckdy=1.-(a*d-b*c)/(c-d*yc)**2
      yc=yc-ck/dckdy
  200 continue
      write(6,*) "inner loop y doesn't converge"
  210 if(itell.eq.0) goto 220
      write(6,*) "inner loop y converges, y=",yc," k=",k
  220 delh=2.*dhmx*(y(1,j)-yc-(y(1,j)**2-yc**2)/2.)
      tn=tinit+delh/(cps+cpf)
      delt=tn-tc
      if((dabs(delt)).ge.0.1) goto 290
      if(jcon.eq.1) goto 310
      jcon=1
      goto 300
  290 tc=(tn+tc)/2.
  300 continue
      write(6,*) "outer loop t doesn't converge"
  310 if(itell.eq.0) goto 320
      write(6,*) 'outer loop t converges, t=',tc,' l=',l
  320 t(2,j)=tc
      x(2,j)=xc
      y(2,j)=yc
  400 continue
```

```
      write(6,*) "time=",i
      write(6,*) "x(i,j): "
      write(6,99) (x(2,j),j=1,jmax)
      write(6,*) "y(i,j): "
      write(6,99) (y(2,j),j=1,jmax)
      write(6,*) "t(i,j): "
      write(6,99) (t(2,j),j=1,jmax)
 99   format(5x,f10.5,4x,f10.5,4x,f10.5,4x,f10.5,4x,f10.5)
      do 450 ij=1,jmax
      x(1,ij)=x(2,ij)
      y(1,ij)=y(2,ij)
      t(1,ij)=t(2,ij)
450   continue
500   continue
      return
      end
```

The following is a sample input data file, 'sbdata', for the local equilibrium approximation model of adiabatic sorption in a fixed bed. See the program comments for definitions of the variables and units used.

```
x of feed fluid      1.0
y of bed (initial)   0.0
feed temp. (deg.K)   300.0
initial bed temp.    300.0
constant R value     1.0
ref. temp. for R     300.0
max. delta H (vol)   0.0
fluid heat cap (bd)  0.4
solid heat cap (bd)  0.4
fluid sat. (vol)     0.05
solid sat. (bd.vol)  0.5
velocity             1.0
max. time incr.       50
max. distance incr.   20
itell                  0
```

The following is a sample of output data from the program, 'thrmsb', for the calculation of adiabatic fixed bed sorption using the local equilibrium approximation.

```
finite differences calc. of nonisothermal absorption
time=0
x(0,j):     1.0000000000000  0.  0.  0.  0.  0.  0.  0.  0.
   0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.
y(0,j):     1.0000000000000  0.  0.  0.  0.  0.  0.  0.  0.
   0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.
t(0,j):     300.00000000000   300.00000000000   300.00000000000
 300.00000000000   300.00000000000   300.00000000000   300.0000
 300.00000000000   300.00000000000   300.00000000000   300.0000
 300.00000000000   300.00000000000   300.00000000000   300.0000
 300.00000000000   300.00000000000   300.00000000000   300.0000
 300.00000000000
time=  1
x(i,j):
   1.00000       0.09091       0.            0.            0.
   0.            0.            0.            0.            0.
   0.            0.            0.            0.            0.
   0.            0.            0.            0.            0.
y(i,j):
   1.00000       0.09091       0.            0.            0.
   0.            0.            0.            0.            0.
   0.            0.            0.            0.            0.
   0.            0.            0.            0.            0.
t(i,j):
 300.00000     300.00000     300.00000     300.00000     300.00000
 300.00000     300.00000     300.00000     300.00000     300.00000
 300.00000     300.00000     300.00000     300.00000     300.00000
 300.00000     300.00000     300.00000     300.00000     300.00000
```

```
time=  2
x(i,j):
   1.00000        0.17355        0.00826        0.             0.
   0.             0.             0.             0.             0.
   0.             0.             0.             0.             0.
   0.             0.             0.             0.             0.
y(i,j):
   1.00000        0.17355        0.00826        0.             0.
   0.             0.             0.             0.             0.
   0.             0.             0.             0.             0.
   0.             0.             0.             0.             0.
t(i,j):
 300.00000      300.00000      300.00000      300.00000      300.00000
 300.00000      300.00000      300.00000      300.00000      300.00000
 300.00000      300.00000      300.00000      300.00000      300.00000
 300.00000      300.00000      300.00000      300.00000      300.00000
```

```
time=  50
x(i,j):
   1.00000        0.99148        0.94889        0.84454        0.67757
   0.48139        0.30088        0.16549        0.08037        0.03459
   0.01320        0.00439        0.00114        0.             0.
   0.             0.             0.             0.             0.
y(i,j):
   1.00000        0.99148        0.94889        0.84454        0.67757
   0.48139        0.30088        0.16549        0.08037        0.03459
   0.01320        0.00439        0.00114        0.             0.
   0.             0.             0.             0.             0.
t(i,j):
 300.00000      300.00000      300.00000      300.00000      300.00000
 300.00000      300.00000      300.00000      300.00000      300.00000
 300.00000      300.00000      300.00000      300.00000      300.00000
 300.00000      300.00000      300.00000      300.00000      300.00000
```

C.2 Method of Characteristics

The model used for the calculation of adiabatic absorption by the method of characteristics assumes linear driving forces for mass and heat transfer with constant coefficients. For mass transfer, the rate of increase of dimensionless solid phase concentration, R_m, can be modelled solid phase resistance, fluid phase resistance, or both. The expression for the solid phase is;

$$R_m = \Psi_p \, k_p \, a \, (y^* - y) \qquad \text{(C-4)}$$

and for the fluid phase;

$$R_m = k_f \, a \, (x - x^*) \qquad \text{(C-5)}$$

where the quanitities marked with * are interfacial and assumed to be in equilibrium with each other if both resistances are used, or with the opposing phase bulk (average) concentration if one resistance is neglected. Mass transfer coefficients are estimated using methods given by Vermuelen et al (1973). For particle side mass transfer;

$$k_p \, a = 60 \, D_p/d^2 \qquad \text{(C-6)}$$

and Ψ_p, a correction factor for the linear driving force approximation, is given (for $R \leq 1.0$) by;

$$\Psi_p = 0.894/(1 - .106 \, R^{.25}) \qquad \text{(C-7)}$$

For the fluid phase;

$$k_f \, a = \frac{10.9 \, v \, (1-\varepsilon)}{d} \left(\frac{D_f}{d \, v}\right)^{.51} \left(\frac{D_f \rho_f}{\mu}\right)^{.16} \qquad \text{(C-8)}$$

The subroutine **rmas**, listed at the end of this appendix, calculates the rate, performing an iterative determination of the interfacial concentrations if necessary.

The heat transfer rate between phases, R_h, is given by;

$$R_h = h\ a\ (T_f - T_p) \tag{C-9}$$

The heat transfer coefficient is also estimated using equation (C-8) by replacing D_f with α , the thermal diffusivity given by;

$$\alpha = K/(\ _f\ C_f) \tag{C-11}$$

The heat generation rate is found from the mass transfer rate and the derivative of the heat release function of equation (C-3). The equation expressing this relationship is;

$$R_g = \rho_b\ R_m\ 2\Delta H\ (1-y) \tag{C-10}$$

The equilibrium relation is given again by equations (C-1) and (C-2). In this case, equilibrium relations are calculated by a subroutine, **eqlb**, which can calculate either **x** or **y** from the other and the temperature. A listing of the routine is included in the following pages.

Figure C-4 gives a flow diagram for the calculation using the method of characteristics. Listings of the main program, subroutines, and samples of input data and output follow.

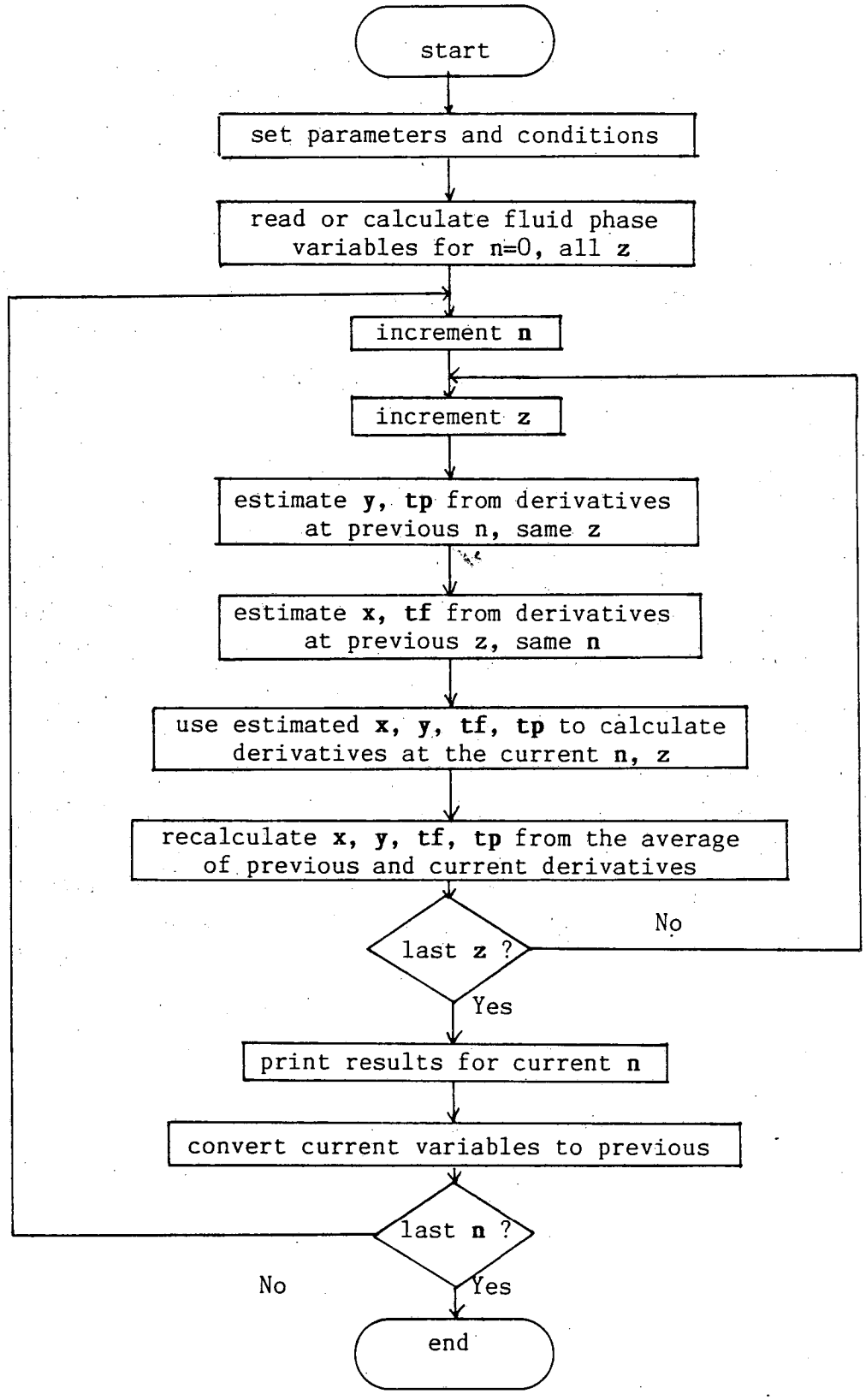


Figure C-4 - Flow Diagram for Calculation of Adiabatic Sorption by the Method of Characteristics

```
c  This program uses the method of characteristics to calculate the
c  temperature and concentration profiles in a fixed bed during
c  adiabatic absorption or desorption.   The method used is similar
c  to that given by Acrivos (Ind. Eng. Chem., April 1956).  The
c  program was written by T.K. Murphy, March, 1983.
c
c  The model assumptions limit its application to dilute solutions of
c  one absorbing component.
c
c  The output file is called 'moc'.
c
c  The input data file, called 'adata', contains the following;
c
c  ys,rob,xs,rof - format(30x,4f10.5)
c     ys is sorbent saturation content, g sorbate/g dry sorbent
c     rob is the density of the dry sorbent (no fluid present), g/cc
c     xs is solvent (fluid) saturation, g sorbate/g pure solvent
c     rof is dry solvent density, g/cc (the fluid density is assumed
c           to increase linearly with sorbate concentration)
c  r,deltah,tref,wm - format(30x,4f10.5)
c     r is equilibrium parameter, <1 for favorable isotherm
c     deltah is heat released, cal, on sat. of 1 gram of dry sorbent
c     tref is reference temperature for equilibrium, deg. C
c     wm is molecular weight of sorbate (i.e. 18 for water)
c  cf,cp,cw - format(30x,3f10.5)
c     cf is heat capacity of pure solvent, cal/g-deg.C
c     cp is heat capacity of dry sorbent, cal/g-deg.C
c     cw is heat capacity of sorbate, cal/g-deg.C
c  xfac,yfac,tfac - format(30x,3f10.5)
c     xfac is fluid side mass transfer coefficient, 1/sec
c       (xfac = kf*a*Xs*rof/(Ys*rob))
c     yfac is particle side mass transfer coefficient, 1/sec
c       (yfac = kp*a)
c     tfac is heat transfer coefficient, assumed fluid side
c        dominated, cal/cc-s (tfac = h*a)
c  xfd,tfd,nz,nn,krd - format(30x,2f10.5,3i5)
c     xfd is fractional saturation of feed fluid, 0-1
c     tfd is feed temperature, degrees C
c     nz is number of z increments to run, z is bed distance param.
c     nn is number of n increments to run, n is time measure
c     krd is read control, if krd is 0, read only one set of
c         variables and use them for the whole bed,
c         if krd other than 0, read a set of variables for every z
```

```
c  x(1,j),tf(1,j),y(1,j),tp(1,j) - format(30x,4f10.5)
c     x(1,j) is the fractional fluid saturation at z=j
c     tf(1,j) is the fluid temperature at z=j
c     y(1,j) is the fractional sorbent saturation at z=j
c     tp(1,j) is the particle temperature at z=j
c   The first subscript in the above variables refers to the n
c     value; 1 is the previous value and 2 is the next
c
c  If krd=0, no more data is required.  If krd is not 0, (z-1) more
c     records like the last one above must be available.
c
c
      common/an1/ x(2,100),y(2,100),tf(2,100),tp(2,100)
      common/an2/ rm(2,100),rh(2,100)
      common/mt/ xfac,yfac
      common/eq/ delhr,tref,r
      open(unit=5,file='adata')
      rewind 5
c
c      read system properties
c
      read(5,71) ys,rob,xs,rof
   71 format(30x,4f10.5)
      crm=-ys*rob/(xs*rof)
      read(5,71) r,deltah,tref,wm
      delh=deltah*rob
      delhr=deltah*wm/(ys*1.986)
      read(5,72) cf,cp,cw
   72 format(30x,3f10.5)
      read(5,72) xfac,yfac,tfac
c
c      read feed and bed conditions and array sizes
c
      read(5,73) xfd,tfd,nz,nn,krd
   73 format(30x,2f10.5,3i5)
      read(5,71) x(1,1),tf(1,1),y(1,1),tp(1,1)
      do 20 j=2,nz
      if(krd.gt.0) goto 10
      y(1,j)=y(1,1)
      tp(1,j)=tp(1,1)
      rm(1,j)=0.
      rh(1,j)=0.
      goto 20
   10 read(5,71) x(1,j),y(1,j),tf(1,j),tp(1,j),rm(1,j),rh(1,j)
   20 continue
```

```
      do 30 i=1,2
      x(i,1)=xfd
      tf(i,1)=tfd
   30 continue
      close(unit=5)
      open(unit=6,file='moc')
c
      if(krd.gt.0) goto 60
c
c     if starting from an empty bed,
c      calculate x and tf values for n=0 at z=2,nz
c
      call rmas(x(1,1),y(1,1),tf(1,1),tp(1,1),rm(1,1))
      rh(1,1)=tfac*(tf(1,1)-tp(1,1))
      do 40 i=2,nz
      j=i-1
      x(1,i)=x(1,j)+crm*(rm(1,j))
      tf(1,i)=tf(1,j)-rh(1,j)/(rof*cf)
      if(x(1,i).lt.0.) x(1,i)=0.
      if(tf(1,i).lt.0.) tf(1,i)=0.
      call rmas(x(1,i),y(1,i),tf(1,i),tp(1,i),rm(1,i))
      rh(1,i)=tfac*(tf(1,i)-tp(1,i))
      x(1,i)=x(1,j)+crm*(rm(1,j)+rm(1,i))/2.
      tf(1,i)=tf(1,j)-(rh(1,j)+rh(1,i))/(rof*cf*2.)
   40 continue
   60 continue
c
c      print results as calculations proceed
c
      write(6,*)' Adiabatic Absorption Results'
      write(6,*) ''
      call prnt(0,nz,1)
c
```

```
c       begin numerical integration along characteristics
c       inner loop steps in bed position,
c       outer loop steps in time
c
      do 200 i=1,nn
      do 180 j=1,nz
c
      k=j-1
      y(2,j)=y(1,j)+rm(1,j)
      if(y(2,j).lt.0.) y(2,j)=0.
      ya=y(2,j)
      dhdy=2.*delh*(1.-ya)
      tp(2,j)=tp(1,j)+(rh(1,j)+dhdy*rm(1,j))/(rob*(cp+ya*cw))
      if(tp(2,j).lt.0.) tp(2,j)=0.
      if(j.eq.1) goto 110
      x(2,j)=x(2,k)+crm*rm(2,k)
      if(x(2,j).lt.0.) x(2,j)=0.
      tf(2,j)=tf(2,k)-rh(2,k)/(rof*cf)
      if(tf(2,j).lt.0.) tf(2,j)=0.
  110 call rmas(x(2,j),y(2,j),tf(2,j),tp(2,j),rm(2,j))
      rh(2,j)=tfac*(tf(2,j)-tp(2,j))
      y(2,j)=y(1,j)+0.5*(rm(2,j)+rm(1,j))
      if(y(2,j).lt.0.) y(2,j)=0.
      ya=y(2,j)
      dhdy=2.*delh*(1.-ya)
      tp(2,j)=tp(1,j)+0.5*(rh(1,j)+rh(2,j)+dhdy*(rm(1,j)+rm(2,j)))/
     1   (rob*(cp+ya*cw))
      if(tp(2,j).lt.0.) tp(2,j)=0.
      if(j.eq.1) goto 180
      x(2,j)=x(2,k)+crm*(rm(2,j)+rm(2,k))/2.
      tf(2,j)=tf(2,k)-(rh(2,j)+rh(2,k))/(rof*cf*2.)
      if(x(2,j).lt.0.) x(2,j)=0.
      if(tf(2,j).lt.0.) tf(2,j)=0.
  180 continue
      call prnt(i,nz,2)
      do 190 m=1,nz
      x(1,m)=x(2,m)
      y(1,m)=y(2,m)
      tf(1,m)=tf(2,m)
      tp(1,m)=tp(2,m)
      rm(1,m)=rm(2,m)
      rh(1,m)=rh(2,m)
  190 continue
  200 continue
      close(unit=6)
      end
```

```
      subroutine rmas(x,y,tf,tp,dydt)
c  This subroutine calculates the rate of concentration increase,
c  dy/dt, for the particle phase in fixed bed absorption given the
c  local bulk fluid phase concentration, x, and particle phase
c  concentration, y, local fluid and particle temperatures (C),
c  tf and tp.  The coefficients for the linear driving force models
c  for the fluid and solid phases are stored in common/mt/ as xfac
c  and yfac respectively.  If either one is set equal to zero, the
c  mass transfer resistance in that phase is assumed negligible.
c  The interfacial concentrations is taken to be in equilibrium
c  in all cases.  The equilibrium relations are found by calling
c  subroutine eqlb(flag,x,y,tp).
c
      common/mt/ xfac,yfac
      if(xfac.gt.0.) goto 30
      call eqlb(1.,x,yi,tp)
      dydt=yfac*(yi-y)
      return
   30 if(yfac.gt.0) goto 40
      call eqlb(-1.,xi,y,tp)
      dydt=xfac*(x-xi)
      return
c
   40 call eqlb(-1.,xeq,y,tp)
      xi=(xfac*x+yfac*xeq)/(xfac+yfac)
      xmx=x
      xmn=xeq
      n=1
   50 if(n.eq.20) goto 100
      n=n+1
      call eqlb(1.,xi,yi,tp)
      cx=xfac*(x-xi)
      cy=yfac*(yi-y)
      if(abs(cx/cy-1.).le.0.01) goto 80
      if(cx/cy.gt.1.) goto 60
      xmn=xi
      xi=(xmx+xi)/2.
      goto 50
c
   60 xmx=xi
      xi=(xmn+xi)/2.
      goto 50
c
   80 dydt=(cx+cy)/2.
      return
c
  100 write(6,*) 'rmas: iterative search for xi fails to converge'
      return
      end
```

```
      subroutine eqlb(f,x,y,t)
c
c  This subroutine calculates temperature-dependant equilibrium
c  relations for a fluid-solid system.  If the flag, f, is zero or
c  negative, then x, the fluid concentration, is calculated from
c  y, the solid concentration, and the temperature t (C).  If f is
c  positive, y is calculated from x.  The routine must have the
c  variables delhr (delta H over R), tref (reference temperature, C)
c  and r (constant separation factor) stored in common/eq/.
c
      common/eq/delhr,tref,r
      tdp=exp(delhr*(1./(t+273.16)-1./(tref+273.16)))
      if (f.gt.0.) goto 20
      x=r*y/(tdep*(1.+r*y-y))
      return
   20 y=x/(r/tdp+x-r*x)
      return
      end
```

```
      subroutine prnt(nt,nz,i)
      common/an1/ x(2,100),y(2,100),tf(2,100),tp(2,100)
      common/an2/ rm(2,100),rh(2,100)
      write(6,91) nt
   91 format(/ ' Time step: ',i5/)
      write(6,92)
   92 format('  z',9x,'x',9x,'y',9x,'tf',8x,'tp',8x,'rm',8x,'rh'//)
      do 99 j=1,nz
      write(6,93) j,x(i,j),y(i,j),tf(i,j),tp(i,j),rm(i,j),rh(i,j)
   93 format(i4,6f10.4)
      m=j-1
      k=j-2
      if(k.le.0) goto 99
      if((x(i,k).ne.x(i,j)).or.(x(i,m).ne.x(i,j))) goto 99
      if((tf(i,k).ne.tf(i,j)).or.(tf(i,m).ne.tf(i,j))) goto 99
      j=nz
   99 continue
      return
      end
```

The following is a sample input data file, 'adata', for the method of characteristics modelling program, nmc.

ysat,rhobed,xsat,rhofluid	1.0	0.5	0.04		0.80
R(eq.),deltaH,tref(C),m.w.	1.0	100.0	25.0		18.0
heat caps.;fluid,solid,abs.	0.7	0.75	1.0		
xfac,yfac,tfac (Vo/htu)	0.0	0.03	0.15		
xfeed,tfd,nz,nn,krd	0.0	100.0	50	300	0
initial x,tf,y,tp	1.0	25.0	1.0		25.0

The following is a sample output data file, 'moc', from the method of characteristics modelling program. Only the first and last portions of the file are reproduced here.

Adiabatic Absorption Results

Time step: 0

z	x	y	tf	tp	rm	rh
1	0.	1.0000	100.0000	25.0000	-0.0300	11.2500
2	0.3589	1.0000	82.6012	25.0000	-0.0159	8.2366
3	0.5753	1.0000	69.5025	25.0000	-0.0118	6.4340
4	0.7237	1.0000	59.3365	25.0000	-0.0072	4.9520
5	0.8184	1.0000	51.5007	25.0000	-0.0049	3.8240
6	0.8813	1.0000	45.4518	25.0000	-0.0031	2.9508
7	0.9222	1.0000	40.7837	25.0000	-0.0021	2.2774
8	0.9491	1.0000	37.1811	25.0000	-0.0014	1.7576
9	0.9667	1.0000	34.4008	25.0000	-0.0009	1.3564
10	0.9782	1.0000	32.2551	25.0000	-0.0006	1.0468
11	0.9857	1.0000	30.5992	25.0000	-0.0004	0.8079
12	0.9906	1.0000	29.3212	25.0000	-0.0002	0.6235
13	0.9939	1.0000	28.3349	25.0000	-0.0002	0.4812
14	0.9960	1.0000	27.5737	25.0000	-0.0001	0.3713
15	0.9974	1.0000	26.9863	25.0000	-0.0001	0.2866
16	0.9983	1.0000	26.5329	25.0000	-0.0000	0.2212
17	0.9989	1.0000	26.1830	25.0000	-0.0000	0.1707
18	0.9993	1.0000	25.9130	25.0000	-0.0000	0.1317
19	0.9995	1.0000	25.7046	25.0000	-0.0000	0.1017
20	0.9997	1.0000	25.5438	25.0000	-0.0000	0.0785
21	0.9998	1.0000	25.4197	25.0000	-0.0000	0.0606
22	0.9999	1.0000	25.3239	25.0000	-0.0000	0.0467
23	0.9999	1.0000	25.2500	25.0000	-0.0000	0.0361
24	0.9999	1.0000	25.1929	25.0000	-0.0000	0.0278
25	1.0000	1.0000	25.1489	25.0000	-0.0000	0.0215
26	1.0000	1.0000	25.1149	25.0000	-0.0000	0.0166
27	1.0000	1.0000	25.0887	25.0000	-0.0000	0.0128
28	1.0000	1.0000	25.0684	25.0000	-0.0000	0.0099
29	1.0000	1.0000	25.0528	25.0000	-0.0000	0.0076
30	1.0000	1.0000	25.0408	25.0000	-0.0000	0.0059

45	1.0000	1.0000	25.0008	25.0000	0.	0.0001
46	1.0000	1.0000	25.0006	25.0000	0.	0.0001
47	1.0000	1.0000	25.0005	25.0000	0.	0.0001
48	1.0000	1.0000	25.0004	25.0000	0.	0.0001
49	1.0000	1.0000	25.0003	25.0000	0.	0.0000
50	1.0000	1.0000	25.0002	25.0000	0.	0.0000

Time step: 1

z	x	y	tf	tp	rm	rh
1	0.	0.9704	100.0000	36.8451	-0.0291	9.3035
2	0.3609	0.9835	85.1420	33.9528	-0.0171	7.3374
3	0.5894	0.9880	73.2802	32.1076	-0.0121	5.9479
4	0.7444	0.9925	63.6862	30.5885	-0.0077	4.7973
5	0.8438	0.9950	55.9556	29.4011	-0.0050	3.8610
6	0.9078	0.9968	49.7382	28.4642	-0.0032	3.1026
7	0.9479	0.9980	44.7458	27.7263	-0.0020	2.4889
8	0.9726	0.9987	40.7435	27.1450	-0.0012	1.9937
9	0.9874	0.9992	37.5394	26.6871	-0.0007	1.5949
10	0.9959	0.9995	34.9777	26.3266	-0.0004	1.2742
11	1.0006	0.9997	32.9322	26.0429	-0.0002	1.0168
12	1.0030	0.9998	31.3006	25.8195	-0.0001	0.8106
13	1.0039	0.9999	30.0005	25.6438	-0.0000	0.6455
14	1.0041	0.9999	28.9657	25.5057	0.0000	0.5135
15	1.0039	1.0000	28.1428	25.3970	0.0000	0.4082
16	1.0035	1.0000	27.4889	25.3116	0.0000	0.3242
17	1.0030	1.0000	26.9698	25.2445	0.0000	0.2572
18	1.0025	1.0000	26.5580	25.1918	0.0000	0.2040
19	1.0021	1.0000	26.2315	25.1505	0.0000	0.1616
20	1.0017	1.0000	25.9729	25.1180	0.0000	0.1280
21	1.0014	1.0000	25.7682	25.0925	0.0000	0.1013
22	1.0011	1.0000	25.6063	25.0725	0.0000	0.0801
23	1.0009	1.0000	25.4783	25.0568	0.0000	0.0633
24	1.0007	1.0000	25.3771	25.0445	0.0000	0.0500
25	1.0005	1.0000	25.2972	25.0348	0.0000	0.0395
26	1.0004	1.0000	25.2341	25.0273	0.0000	0.0312
27	1.0003	1.0000	25.1843	25.0214	0.0000	0.0246
28	1.0003	1.0000	25.1451	25.0167	0.0000	0.0194
29	1.0002	1.0000	25.1142	25.0131	0.0000	0.0153
30	1.0002	1.0000	25.0898	25.0102	0.0000	0.0120
31	1.0001	1.0000	25.0706	25.0080	0.0000	0.0095
32	1.0001	1.0000	25.0555	25.0063	0.0000	0.0075
33	1.0001	1.0000	25.0436	25.0049	0.0000	0.0059
34	1.0001	1.0000	25.0342	25.0038	0.0000	0.0046
35	1.0000	1.0000	25.0269	25.0030	0.0000	0.0036

Time step: 300

z	x	y	tf	tp	rm	rh
1	0.	0.0001	100.0000	99.9973	-0.0000	0.0004
2	0.0001	0.0004	99.9985	99.9910	-0.0000	0.0012
3	0.0004	0.0011	99.9947	99.9760	-0.0000	0.0031
4	0.0011	0.0023	99.9867	99.9496	-0.0001	0.0060
5	0.0022	0.0042	99.9724	99.9089	-0.0001	0.0101
6	0.0041	0.0068	99.9495	99.8507	-0.0001	0.0155
7	0.0069	0.0104	99.9156	99.7721	-0.0002	0.0224
8	0.0108	0.0151	99.8680	99.6700	-0.0003	0.0308
9	0.0160	0.0211	99.8042	99.5420	-0.0004	0.0406
10	0.0228	0.0284	99.7217	99.3861	-0.0005	0.0518
11	0.0315	0.0371	99.6180	99.2009	-0.0006	0.0642
12	0.0421	0.0475	99.4914	98.9857	-0.0008	0.0776
13	0.0550	0.0594	99.3401	98.7406	-0.0009	0.0918
14	0.0703	0.0730	99.1630	98.4663	-0.0011	0.1065
15	0.0880	0.0883	98.9597	98.1647	-0.0012	0.1212
16	0.1084	0.1054	98.7302	97.8380	-0.0014	0.1358
17	0.1316	0.1241	98.4753	97.4894	-0.0016	0.1498
18	0.1574	0.1443	98.1962	97.1225	-0.0017	0.1628
19	0.1859	0.1662	97.8948	96.7413	-0.0019	0.1747
20	0.2172	0.1894	97.5737	96.3502	-0.0021	0.1850
21	0.2510	0.2140	97.2358	95.9538	-0.0022	0.1935
22	0.2872	0.2398	96.8843	95.5565	-0.0024	0.2001
23	0.3258	0.2666	96.5228	95.1626	-0.0025	0.2047
24	0.3665	0.2943	96.1550	94.7763	-0.0027	0.2072
25	0.4091	0.3227	95.7845	94.4011	-0.0028	0.2077
26	0.4534	0.3517	95.4151	94.0402	-0.0029	0.2061
27	0.4991	0.3811	95.0500	93.6964	-0.0030	0.2027
28	0.5461	0.4107	94.6926	93.3717	-0.0030	0.1976
29	0.5940	0.4404	94.3457	93.0677	-0.0031	0.1909
30	0.6426	0.4701	94.0119	92.7857	-0.0031	0.1830
31	0.6916	0.4995	93.6931	92.5260	-0.0032	0.1740
32	0.7409	0.5286	93.3912	92.2891	-0.0032	0.1641
33	0.7902	0.5573	93.1075	92.0746	-0.0032	0.1537
34	0.8394	0.5854	92.8428	91.8820	-0.0031	0.1428
35	0.8881	0.6129	92.5977	91.7106	-0.0031	0.1317
36	0.9362	0.6397	92.3725	91.5595	-0.0031	0.1206
37	0.9836	0.6657	92.1670	91.4274	-0.0030	0.1096
38	1.0301	0.6909	91.9809	91.3132	-0.0029	0.0988
39	1.0756	0.7153	91.8137	91.2155	-0.0029	0.0884
40	1.1199	0.7387	91.6647	91.1331	-0.0028	0.0785

References for Appendix C

1. Acrivos, A. (1956) Ind. Eng. Chem., **48**:703

2. Vermeulen, T., Klein, G., and Hiester, N.K. (1973) "Adsorption and Ion Exchange" in Chemical Engineer's Handbook, 5th Edition, Perry, R.H. and Chilton, C.H., eds. 16-18 ff. McGraw-Hill New York

Appendix D - Process Simulation/Economics Programs

The basis for the system of programs used for the economic analysis estimates made in this work is a modified version of a process simulation program developed by Professor Cameron Crowe and coworkers at McMaster University. The executive program, called GEMCS for General Engineering Management Computation System, handles data input and calls subroutines (referred to as modules) that correspond, in most cases, to unit operations in a process. GEMCS also keeps track of the streams in the process, which exist in the program as vectors containing temperature, pressure, and component flowrates, and supplies the modules with the needed input and output streams when they are called. The intent of GEMCS is to be used as a material and energy balance calculation tool and it is designed to cycle through a sequence of modules until the material and energy balances meet specified convergence criteria. However, in this work, the modules have been written in such a manner that they need to be called at most two times, so a simple, once-through calculation is used.

D.1 GEMCS Executive, GEMCS Subroutines, and General Input Format

The procedure for using GEMCS begins with the establishment of a process flow diagram. Each unit operation on the diagram should have a corresponding module (subroutine) available to be called by GEMCS. Streams in the flow diagram are numbered and these numbers are used to identify the connections between process modules as they will be inputs to one and outputs from another. A feed stream generally must be specified and other streams may be specified as well. The jobs of

reading all of the input information and of keeping track of the process stream information and supplying it to the modules when they are called are handled by the GEMCS main program and a set of five subroutines.

Shown in Figure D-1 is a schematic flow diagram illustrating the functions of the GEMCS main program and its subroutines. A list of the principal variables used and a program listing follow. In the listing, the statements in all capital letters are those from the original program as developed by Crowe and coworkers. Those in small letters represent modifications made in this work. Some modifications allowed it to be run on the Berkeley UNIX system (on a DEC VAX 750 or 780). Other modifications were to incorporate a physical properties array and the capability for economic evaluation by a special module. Following the program listing is a list of the input data format for a generalized case.

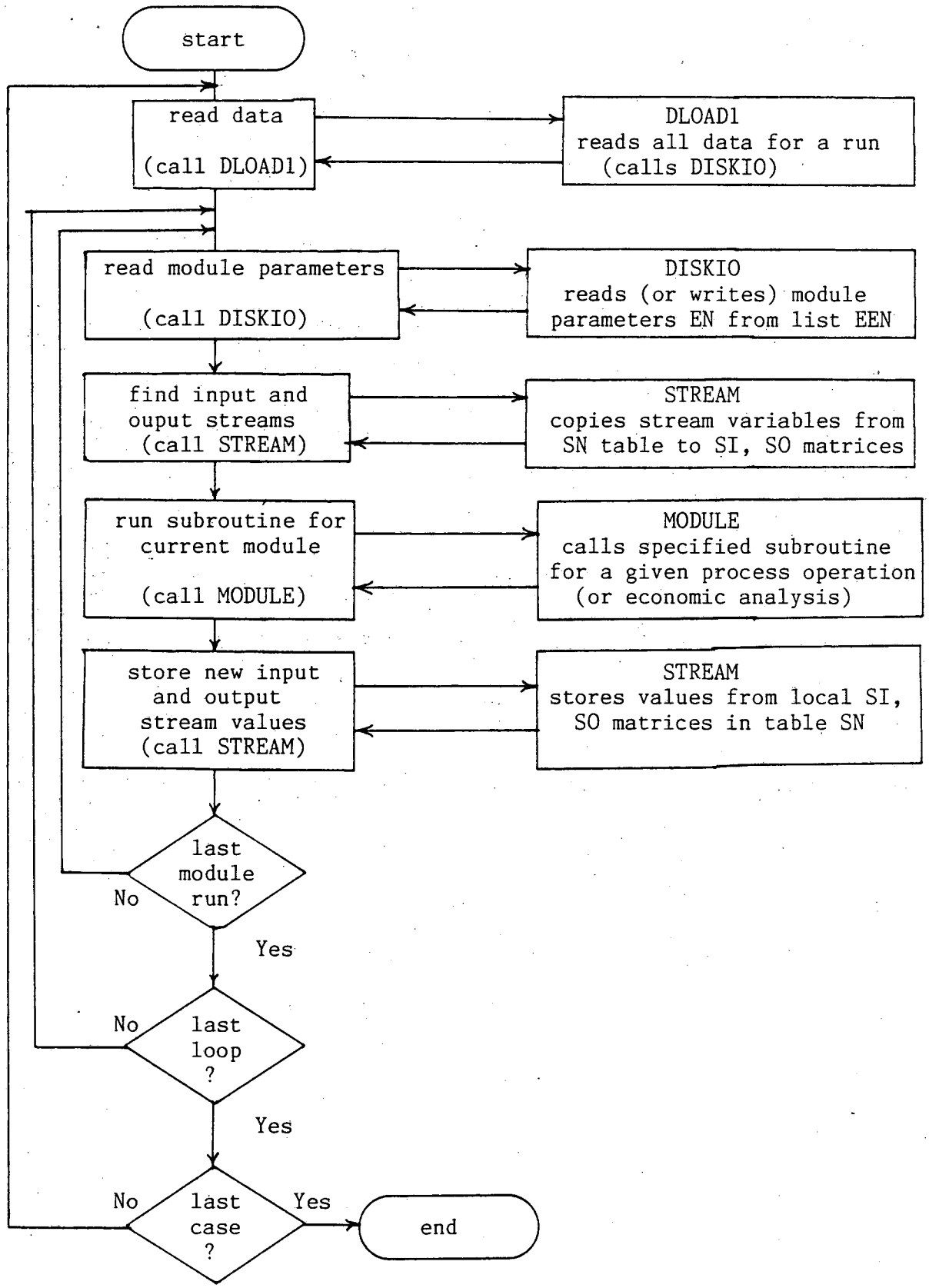


Figure D-1 Flow Diagram for GEMCS and Subroutines

Principal Variables
GEMCS and GEMCS Subroutines

EEN - master list (vector) of individual equipment list vectors (EN)

EN - equipment list, parameters for current module

III - number of stream lists for the total process

JJ - length of stream lists, equal to (NOCOMP + 5) or 9, whichever is greater

KPRNT- vector of print controls

LLST - calculation sequence, vector of unit numbers

LOOP - current iteration number (set to 999 for last iteration)

NC - current position in calculation sequence

NCALC - length of calculation sequence

NE - current equipment unit number

NIN - number of input streams for the current unit

NOCOMP - number of components

NOPROPS - number of physical properties used (read)

NOUT - number of output streams for the current unit

NS - vector of stream codes which govern storage of stream information

PROPS - matrix of physical properties (NOCOMP x NOPROPS)

SI - matrix of input stream lists for current unit (NIN x JJ)

SO - matrix of output stream lists for current unit (NOUT x JJ)

SN - master matrix of stream lists (III x JJ)

```
c  The following are common statements needed by GEMCS and
c    many of the subroutines used with it. It is put into
c    the programs where it is needed by the INCLUDE statement
c    of F77.  Its file name is 'cmns'.
C
      COMMON/gmc1/ LLST(40),NS(40),EN(60),SI(5,15),SO(5,15)
      common/gmc2/sN(20,15),EEN(500)
      common/gmc3/is,ne,jj,LOOP,NIN,NOUT,MSN,MODE,NPLNT,ISP,NC,III
      COMMON/gmc4/ KPRNT(10),NCALC,NOCOMP,NSR,npoint(40,2),ncount
C
      common/pps/props(10,25)
      common/econ/hpy,cftr,cmsi,sp1,sp2,ep,cwp,plab,st1,st2,tcw,twmx
c
C       ***NOTE*** ACHANGE IN THE SN SIZE REQUIRES A CHANGE IN III TO
C       MATCH THIS CHANGED SIZE
C        *** NOTE*** THE SIZE OF THE SN TABLE MUST BE THE NUMBER OF
C      STREAMS WHICH HAVE A 1,2,OR3 STREAM TYPE LABEL PLUS THE MAXIMUM
C      NUMBER OF OUTPUT STREAMS FROM AN EQUIPMENT MODULE WHICH HAVE A
C      7 LABEL
c
```

```
c      GEMCS - modified by T.K. Murphy
C
      include 'cmns'
c
C
c      The following are file definitions which allow the program to
c       be run with the f77 compiler on UNIX.
      open(unit=5,file='gdata')
      rewind 5
      open(unit=6,file='out')
      READ (5,100) NCASE,iii
      write(6,*) 'No. of cases: ',ncase,' No. of process streams',iii
C     NCASE=NUMBER OF CASES TO BE RUN.
c     NOTE THIS IS FIRST CARD IN DATASET.
c     iii=number of streams in  flow diagram, .le. 1st dim. in sn
C     FORMAT IS 2I5
      ISP=0
       IQE=1
  755  WRITE (6,101)  IQE
      NCOUNT=0
      CALL  DLOAD1
C
C     CALCULATING EQUIPMENT IN CALCULATION ORDER LIST
C
      NC=1
      NCLAST = 0
      KTEST =0
C
C     PRINT SN TABLE
C
```

```
  707 IF(LOOP.EQ.999) KTEST=1
      IF(KPRNT(4).NE.1.OR.NCLAST.LT.NC) GO TO 710
      WRITE(6,112) LOOP
  112 FORMAT(1H0,25HSN TABLE ON ENTERING LOOP,I5)
      DO 111 IKE=1,III
      IF(SN(IKE,1).LE.0.) GO TO 111
      WRITE(6,103) (SN(IKE,J),J=1,JJ)
      WRITE (6,115)
  111 CONTINUE
      CALL STREAM(-S)
      IF(IS.LE.III)  GO TO 43
      SI(I,1)=S
C        IF NO STREAM AVAILABLESET SI(1,-) =0.
      DO 45 J=2,JJ
   45 SI(I,J)=0.
      GO TO 41
   43 DO 44 J=1,JJ
   44 SI(I,J)=SN(IS,J)
      IF (NS(M).LT.6)  GO TO 41
      SN(IS,1)=0.
   41 CONTINUE
      IF (KPRNT(4).NE.1) GO TO 714
      WRITE(6,107) NE
  107 FORMAT(1H0,24HINPUT STREAMS FOR MODULE,I5)
      DO 108 IKE=1,NIN
      WRITE(6,103)(SI(IKE,J),J=1,JJ)
  108 WRITE(6,115)
  714 CONTINUE
C
C      READ EN VECTOR
C
  710 NE=LLST(NC)
      MM=NE
      CALL DISKIO(1,MM)
      NN=EN(3)+.001
      NIN=EN(6)+.001
      NOUT=EN(11)+.001
      NTYPE = ABS(EN(2)) + .001
      KSW=0
      IF (EN(2).LE.0.) KSW=1
      IF (KPRNT(4).NE.1) GO TO 40
      WRITE(6,106) NE
  106 FORMAT(1H0,19HMODULE SET FOR UNIT,I5)
      WRITE(6,103)(EN(I),I=1,NN)
C
C      FINDING INPUT STREAMS
C
   40 IF (NIN.LE.0) GO TO 714
      DO 41 I=1,NIN
      S=EN(I+6)
      M = INT(ABS(S)+0.001)
      IF (M.EQ.0) GO TO 41
C
C     FINDING OUTPUT STREAMS
C
      IF (NOUT.LE.0) GO TO 465
      DO 46 I=1,NOUT
      S=EN(I+11)
      IF (INT(ABS(S)+0.001).EQ.0)  GO TO 46
      CALL STREAM(-S)
      IF (IS.GT.III) GO TO 46
```

```
      DO 49 J=2,JJ
   49 SO(I,J)=SN(IS,J)
   46 SO(I,1)=S
  465 CONTINUE
      NCLAST = NC
C
C
C     CALLING MODULES
C
      CALL MODULE(NTYPE)
C
C
C
C     STORING OUTPUT STREAMS AND PRINTING
C
      IF (NOUT.LE.0) GO TO 68
      DO 60 I=1,NOUT
      S=EN(I+11)
      M=S+.001
      IF(NS(M).NE.3) GO TO 64
      IF(ISP.EQ.0) GO TO 64
      WRITE(6,120)M
  120 FORMAT(1H0,26H OUTPUT FOR PRODUCT STREAM,I5)
      WRITE(6,103) (SO(I,J),J=1,JJ)
   64 IF (NS(M).EQ.6) GO TO 60
      CALL STREAM(-S)
      IF(IS.LE.III) GO TO 62
C       STORES IN NEXT LOCATION AVAILABLE IN SN
      CALL STREAM(0.)
      IF (IS.LE.III) GO TO 62
C      IF NO SPACE AVAILABLE IN SN WRITE (6,102)
      WRITE(6,102)
      GO TO 60
C      IF NS(M) =7,SO"S STORED IN SN TABLE TEMPORARILY FOR
C      USE IN NEXT CALCULATION
C      IF NS(M) =1,2,OR 3 THEN STORED PERMANENTLY
   62 DO 63 J=1,JJ
   63 SN(IS,J)=SO(I,J)
   60 CONTINUE
      IF (ISP.LE.0)GO TO 68
      IF (LOOP.GE.999) GO TO 68
      WRITE (6,109) NE
  109 FORMAT(1H0,25HOUTPUT STREAMS FOR MODULE,I5)
      DO 110 IKE=1,NOUT
      WRITE(6,103)(SO(IKE,J),J=1,JJ)
  110 WRITE (6,115)
C      STORE INPUT STREAMS IF DESIRED
   68 CONTINUE
      IF(NIN.LE.0) GO TO 6899
      DO 699 I=1,NIN
      S=EN(I+6)
      M=S+0.001
      IF(NS(M).GE.6) GO TO 699
      CALL STREAM(-S)
      IF(IS.LE.III) GO TO 6299
      CALL STREAM (0.)
      IF(IS.LE.III) GO TO 6299
      WRITE(6,102)
      GO TO 699
 6299 DO 6399 J=1,JJ
 6399 SN(IS,J)=SI(I,J)
  699 CONTINUE
 6899 CONTINUE
```

```
      IF(LOOP.LT.999) GO TO 99
       IF (KSW.NE.0) GO TO 99
      WRITE(6,114) NE
  114 FORMAT(1H0,31HFINAL OUTPUT STREAMS FOR MODULE,I5)
      IF (NOUT.LE.0) GO TO 99
      DO 116 IKE=1,NOUT
      WRITE(6,103)(SO(IKE,J),J=1,JJ)
  116 WRITE (6,115)
   99 NC=NC+1
      IF(NC.LE.NCALC) GO TO 707
C
      IF (LOOP.LT.999) GO TO 70
      IF(KTEST.GT.0) GO TO 728
      DO 729 IG=1,5
  729 KPRNT(IG)=0
      KTEST=1
   70 NC=1
      GO TO 707
  728 WRITE(6,104)
       IQE=IQE+1
      IF(IQE.GT.NCASE) goto 777
      GO TO 755
  777 close(unit=5)
      close(unit=6)
  100 FORMAT(2I5)
  101  FORMAT(1H1,10X,4HCASE,1X,I5//)
  102 FORMAT(1H ,11HERROR IN SN)
  103 FORMAT(1H ,5F15.5)
  104 FORMAT(1H0,16HEND OF EXECUTION)
  115 FORMAT(/,1H ,'----')
      END

      SUBROUTINE STREAM(S)
c
      include 'cmns'
c
      K1 = INT(ABS(S) + 0.001)
      DO 11 IS1=1,III
      IS=IS1
      IF (INT(SN(IS1,1)+0.001).EQ.K1) GO TO 2
   11 CONTINUE
      IS=IS+1
      IF (S.LE.0.) GO TO 2
      WRITE(6,400)S
  400 FORMAT(1H0,14HERROR...STREAM,F3.0,16HNOT IN SN MATRIX)
    2 IF(KPRNT(5).GT.0) WRITE (6,401) IS
  401 FORMAT(1H0,3HIS= ,I3)
      RETURN
      END
```

```
      SUBROUTINE DISKIO(IPNT,MM )
C
C     THIS SUBROUTINE SIMULATES DISKIO ON360/30
C     IF IPNT=1.  READS FROM MODULE SETS TABLE
C     IF IPN=2. WRITES ONTO MODULE SETS TABLE
C
      include 'cmns'
c
      MQ=NPOINT(MM,1)
      ML=NPOINT(MM,2)
      IF(IPNT.NE.1) GO TO 2
      DO 11 I=1,ML
   11 EN(I)=EEN(MQ+I)
      GO TO 70
    2 IF(IPNT.NE.2) GO TO 4
      DO 33 I=1,ML
   33 EEN(MQ+I)=EN(I)
      GO TO 70
    4 WRITE(6,100)IPNT,MM
  100 FORMAT(1H0,22H DISKIO ERROR-IPNT,MM=,I5,1X,I5)
   70 RETURN
      END
```

```
      SUBROUTINE DLOAD1
C
C
      include 'cmns'
      COMMON/CC/ KRUN
      Character cname(10)*20,mdlbl1(10)*20,mdlbl2(10)*20
C
C
C     ***** PRINTING CONTROL CHARACTERS *****
C
C     KPRNT(1)=1  CAUSES PRINTING OF NCONT,LLST,NS
C     KPRNT(1)=0  SUPPRESSES ABOVE PRINTING
C     KPRNT(2)=1  CAUSES PRINTING OF INITIAL STREAMS
C     KPRNT(2)=0  SUPPRESSES ABOVE PRINTING
C     KPRNT(3)=1  CAUSES PRINTING OF MODULES SETS and comp. props.
C     KPRNT(3)=0  SUPPRESSES ABOVE PRINTING
C     KPRNT(4)=1  CAUSES PRINTING OF SN TABLE ON ENTERING LOOP
C     KPRNT(4)=1  CAUSES PRINTING OF EN VECTOR FOR SPECIFIED MODULE
C     KPRNT(4)=1  CAUSES PRINTING OF SI MATRIX FOR SPECIFIED MODULE
C     KPRNT(4)=1  CAUSES PRINTING OF STREAM NUMBERS ENTERING AND
C        LEAVING SPECIFIED MODULES(RE- PIECE OF EQUIPMENT)
C     KPRNT(4)=0  SUPPRESSES ABOVE PRINTING
C
      DIMENSION TITLE(18)
C
C
      DIMENSION DUMMY(1)
      EQUIVALENCE (EN(1),DUMMY(1))
      DO 7070 I=1,860
C      ***NOTE*** THE LIMIT ON THIS DO STATEMENT MUST CORRESPOND TO
C       TOTAL LENGTH OF EN,SI,SO,SN AND EEN VECTORS
```

```
7070  DUMMY(I) = 0.
      READ(5,*) KRUN
  116 FORMAT(/,1H ,'RUN NUMBER',I5,/)
      WRITE(6,116) KRUN
      READ(5,100) TITLE
      WRITE(6,101) TITLE
      READ(5,100) TITLE
      WRITE(6,101) TITLE
      READ (5,*) (KPRNT(i),i=1,10)
C
C     REPORT ON PRINTING EXPECTED
C
      IF (KPRNT(1).EQ.1) WRITE (6,103)
      IF (KPRNT(2).EQ.1) WRITE (6,104)
      IF (KPRNT(3).EQ.1) WRITE (6,105)
C
C     READ NO. OF MODULES IN CALCULATION ORDER, AND NO. OF CONPOMENTS
c      and number of components to be read
      READ (5,*) NCALC,NOCOMP,nprops
      do 200 i=1,nocomp
      read (5,102) cname(i)
      read (5,*) (props(i,j),j=1,nprops)
  200 continue
      IF(KPRNT(1).EQ.1) WRITE (6,107) NCALC,NOCOMP,nprops
      if(kprnt(3).ne.1) goto 500
      do 210 i=1,nocomp
      write(6,102) cname(i)
      write(6,113) (props(i,j),j=1,nprops)
  210 continue
  500 IF(NCALC.GT.0) GO TO 510
      NCALC=-NCALC
      LOOP=999
      GO TO 511
  510 LOOP=1

C
C     READ CALCULATION ORDER
C
511    READ (5,*) (LLST(I),I=1,NCALC)
      WRITE(6,118)
      IF (KPRNT(1).EQ.1) WRITE (6,109) (LLST(I),I=1,NCALC)
C
C     READ STREAM CODES,MSN IS THE MAXIMUM STREAM NUMBER, IF NEGATIVE
C     OUTPUT STREAMS WILL BE PRINTED DURING EXECUTION
C
      READ(5,*) MSN
      IF (MSN.GT.0) GO TO 520
      MSN=-MSN
      ISP=1
  520 READ(5,*) (NS(I),I=1,MSN)
      IF (KPRNT(1).NE.1) GO TO 18
      WRITE (6,110) MSN
      WRITE (6,109) (NS(I),I=1,MSN)
   18 JJ=NOCOMP+5
      if(jj.lt.9) jj=9
      READ(5,*) NSR
      IF (KPRNT(2).EQ.1) WRITE (6,111) NSR
      DO 530 I=1,NSR
      READ(5,*)(SN(I,J),J=1,JJ)
      IF(KPRNT(2).NE.1) GO TO 530
      WRITE(6,113)(SN(I,J),J=1,JJ)
      WRITE (6,115)
  530 CONTINUE
```

```
C
C     READING MODULE SETS,NOE IN NUMBER
C
      READ(5,*) NOE
      IF (KPRNT(3).EQ.1) WRITE (6,114) NOE
      DO 540 I=1,NOE
      read (5,102) mdlbl1(i)
      read (5,102) mdlbl2(i)
      READ(5,*)(EN(N),N=1,5)
      NN=EN(3)
      NCOUNT=NCOUNT+NN
      READ(5,*)(EN(N),N=6,NN)
      IF(KPRNT(3).NE.1) GO TO 26
      write(6,102) mdlbl1(i)
      write (6,102) mdlbl2(i)
      WRITE(6,113)(EN(N),N=1,NN)
      WRITE (6,115)
   26 MM=EN(1)+.001
      NPOINT(MM,1)=NCOUNT-NN
      NPOINT(MM,2)=NN
  540 CALL DISKIO(2,MM )
      IF(KPRNT(5).NE.1) GO TO 768
       DO 767 I=1,NOE
767    WRITE(6,106) (NPOINT(I,J),J=1,2)
768    CONTINUE


C     FORMAT STATEMENTS FOR DLOAD
C
  100 FORMAT (18A4)
  101 FORMAT(1H ,18A4)
  102 format(a20)
  103 FORMAT (1H0,22HPRINTING NCONT,LLST,NS)
  104 FORMAT (1H0,24HPRINTING INITIAL STREAMS)
  105 FORMAT (1H0,20HPRINTING MODULE SETS)
  106 FORMAT (2I5)
  107 FORMAT(1H0,I5,12H MODULE SETS,I5,11H COMPONENTS,I5,7H PROP'S//)
  118 FORMAT(24H CALCULATION ORDER LIST-)
  108 FORMAT (10I5)
  109 FORMAT (1X,10I5)
  110 FORMAT (1H0,I5,22HSTREAM CODES ARE READ-)
  111 FORMAT (1H0,I5,25HINITIAL STREAMS ARE READ-)
  113 FORMAT (1X,5F15.5)
  114 FORMAT (1H0,I5,21HMODULE SETS ARE READ-)
  115 FORMAT(/,1H ,'----')
      IF (KPRNT(6).EQ.1) CALL SLIST
      RETURN
      END
```

```
      SUBROUTINE MODULE(NT)

      GO TO (1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22
     123,24,25,26,27,28,29,30,31,32,33),NT
    1 CONTINUE
      CALL econom
      RETURN
    2 CONTINUE
      CALL hxcng
      RETURN
    3 CONTINUE
      CALL extrtr
      RETURN
    4 CONTINUE
      CALL bidstl
      RETURN
    5 CONTINUE
      CALL fbdabs
      RETURN
    6 CONTINUE
      CALL strip
      RETURN
    7 CONTINUE
      RETURN
    8 CONTINUE

        .
        .
        .
        .

   31 CONTINUE
      RETURN
   32 CONTINUE
      RETURN
   33 CONTINUE
      RETURN
      END
```

General Input Data Format for GEMCS

Data		Format
Number of cases(IQE), number of streams(III)		2I5
Run number		free
Title (line 1)		18A4
Title (line 2)		18A4
Print controls (KPRNT(i), i=1,10)		free
NCALC, NOCOMP, NOPROPS		free
For each component	Component name	A20
	PROPS(i,j), j=1,NPROPS	free
Calculation order list, LLST(i), i=1,NCALC		free
Maximum stream number, MSN		free
Stream type codes, NS(i), i=1,MSN		free
Number of streams to be read as input, NSR		free
For each input stream	SN(i,j), j=1,JJ i=1,NSR	free
Number of module sets to be read, NOE		free
For each module set	Module label line 1	A20
	Module label line 2	A20
	EN(i), i=1,NN (NN=EN(3))	free

Positions of Physical Properties in Matrix PROPS as Used in This Work

Most property values used in this work were taken from the reference work, The Properties of Gases and Liquids, 3rd Edition by R.C. Reid, J.M. Prausnitz, and T.K. Sherwood (1977) McGraw-Hill, New York.

Numbers are j values in the matrix PROPS(i,j). "i" is component index.

1. Molecular weight
2. Critical temperature, degrees C.
3. Critical pressure, atmospheres
4. Critical volume, $cm^3/gmol$
5. Pure liquid density at 20 ^oC, g/cm^3
6. Liquid density temperature coefficient, g/cm^3-^oC
7. Liquid heat capacity (average of T range of interest), cal/g-^oC
8. Liquid thermal conductivity (not used in this work)
9. VISB log(viscosity, cp) = VISB*(1/T(^oK)-1/VISTO)
10. VISTO
11. Normal boiling point, ^oC
12. Latent heat of vaporization, cal/gmol
13. ANTA ln(vapor pressure, mm Hg) = ANTA-ANTB/(T^oK)+ANTC)
14. ANTB
15. ANTC

D.2 Modular Subprograms for Process Unit Operations

The following pages contain listings of the subprograms used for calculations of the material and energy balances and cost estimates of the various unit operations use din the processes analyzed. Six module routines (called by the GEMCS MODULE subroutine) are included;

1. **econom** - economic analysis of overall process
2. **extrtr** - design of liquid-liquid extraction operation
3. **bidstl** - design of binary distillation equipment
4. **strip** - design of solvent recovery by steam stripping
5. **fbdabs** - design of fixed bed water sorption units
6. **hxcng** - optimization of heat exchange between two streams

In the case of each of these modules, the EN list is documented in the beginning of the program listing and serves to identify the principle variables used and their meanings. In the same way, the other subroutines, called by those listed above, contain statements of documentation to clarify their purposes and the meanings of the variables used in each. A sample of input data and resulting output follows the program listings. In addition, an index of the program and subprogram names in this appendix is provided on page 333 to assist in cross-referencing, since many subroutines are called by more than one program.

```
      subroutine econom
c
c  EN list
c  1. unit number (first and last)
c  2. unit type=1
c  3. number of elements=32
c  4. number of elements in c.o.m. 'stream lists' (9)
c  5. product component number (1-nocomp)
c  6. number of input streams (1-4) including product stream
c  7. number of product stream
c  8.-10. stream numbers of input streams
c  11. number of other input streams (0-4), no outputs
c  12.-15. stream numbers of extra input streams
c  16. Lang factor, multiplies p.e.c to give t.f.c. (4.9)
c  17. capital-related c.o.m. (multiplies tfc to give annual cost)
c       - accounts for depreciation, maintenance, insurance, and
c                      local tax
c  18. profit factor (also multiplies total fixed capital)
c       - required ROI divided by income tax rate (e.g. .15/.5=.3)
c  19. cost of labor, $/man-year
c  20. labor factor, multiplies op. labor to give total labor
c  21. hours of operation per year
c  22. current Marshall-Swift index
c  23. temperature of low pressure steam (C)
c  24. cost of low pressure steam, $/1000#
c  25. temperature of high pressure steam (C)
c  26. cost of high pressure steam, $/1000#
c  27. temperature of cooling water (C)
c  28. maximum temperature of cooling water returned (C)
c  29. cost of cooling water, cents/1000 gal
c  30. cost of electricity, cents/kwh
c  31. conversion factor for product from kg to desired units
c  32. loop flag; 0. leaves LOOP unchanged, 1. sets LOOP=999
      include 'cmns'
      dimension cm(10,10),com(10,2)
      if(loop.eq.999) goto 100
      cftr=en(16)*(en(17)+en(18))
      plab=en(19)
      flb=en(20)
      hpy=en(21)
      cmsi=en(22)
      st1=en(23)
      sp1=en(24)
      st2=en(25)
      sp2=en(26)
      tcw=en(27)
      twmx=en(28)
      cwp=en(29)
      ep=en(30)
      if(en(32).eq.0.) goto 90
      loop=999
   90 return
  100 np=int(en(5))+5
      yp=si(1,np)*hpy*en(31)
      ni=int(en(4))
      lim=int(en(6))-1
      if(yp.eq.0.) yp=1.
      do 110 i=1,lim
      n=i+1
      do 110 j=1,ni
      k=j+2
  110 cm(i,j)=si(n,k)
      if(en(11).eq.0.) goto 130
      n=int(en(11))
      lmt=lim+n
```

```
      do 120 i=1,n
      ik=i+lim
      do 120 j=1,ni
      k=j+2
  120 cm(ik,j)=so(i,k)
      goto 140
  130 lmt=lim
c
c
  140 write(6,*) 'economics summary'
      do 300 i=1,lmt
      if(kprnt(1).eq.0) goto 200
      write(6,*) ''
      write(6,*) 'unit number: ',i
      write(6,*) 'purchased equipment cost:        ',cm(i,1)
      write(6,*) 'low pressure steam, lb/hr:       ',cm(i,2)
      write(6,*) 'high pressure steam, lb/hr:      ',cm(i,3)
      write(6,*) 'electricity, kw:                 ', cm(i,4)
      write(6,*) 'cooling water, gpm:              ',cm(i,5)
      write(6,*) 'other operating expenses, $/yr: ',cm(i,6)
      write(6,*) 'labor requirement, men/shift:    ',cm(i,7)
c
  200 ecs=ecs+cm(i,1)
      s1s=s1s+cm(i,2)
      s2s=s2s+cm(i,3)
      els=els+cm(i,4)
      cws=cws+cm(i,5)
      ots=ots+cm(i,6)
      slb=slb+cm(i,7)
  300 continue
      write(6,*) ''
      write(6,*) 'Total costs by category'
      tfc=en(16)*ecs
      write(6,*) '     (total fixed capital: ',tfc,')'
      write(6,*) ' category, annual cost ($/yr), cost per unit product'
      write(6,*) ''
      crt=ecs*cftr
      crtu=crt/yp
      write(6,*) ' capital related:     ',crt,crtu
      s1t=s1s*hpy*sp1/1000.
      s1tu=s1t/yp
      s2t=s2s*hpy*sp2/1000.
      s2tu=s2t/yp
      elt=els*hpy*ep/100.
      eltu=elt/yp
      cwt=cws*hpy*cwp*0.0006
      cwtu=cwt/yp
      otu=ots/yp
      tlb=slb*plab*flb
      tlbu=tlb/yp

      write(6,*) ' low pressure steam : ',s1t,s1tu
      write(6,*) ' high pressure steam: ',s2t,s2tu
      write(6,*) ' electricity:         ',elt,eltu
      write(6,*) ' cooling water:       ',cwt,cwtu
      write(6,*) ' other costs:         ',ots,otu
      write(6,*) ' labor costs:         ',tlb,tlbu
      tt=crt+s1t+s2t+elt+cwt+ots+tlb
      ttu=tt/yp
      write(6,*) '-------------------------------------------------'
      write(6,*) ' TOTAL:               ',tt,ttu
      write(6,*) ''
      write(6,*) 'Total costs by process unit'
      write(6,*) '  process unit, annual cost, cost per unit product'
      write(6,*) ''
```

```
      do 350 i=1,lmt
      j=i+1
      com(i,1)=cm(i,1)*cftr+hpy*(cm(i,2)*sp1+cm(i,3)*sp2)/1000.
      com(i,1)=com(i,1)+hpy*(cm(i,4)*ep/100.+cm(i,5)*cwp*0.0006)
      com(i,1)=com(i,1)+cm(i,6)+cm(i,7)*plab*flb
      com(i,2)=com(i,1)/yp
      comt=comt+com(i,1)
      comtu=comtu+com(i,2)
      write(6,*) 'unit # ',i,com(i,1),com(i,2)
  350 continue
      write(6,*) '-----------------------------------------------'
      write(6,*) 'TOTAL:                ',comt,comtu
c
c
      return
      end
```

```
      subroutine traycs(att,tn,tmtl,trcst,tar)
c  This subroutine calculates the Jan. 1981 estimates of sieve tray
c  costs using the correlation of Maiorella. ATT is tray area (sq.ft.)
c  TN is number of trays, TMTL is material of construction flag, 0 for
c  c.s. or 1 for s.s.  TRCST is a vector with the following elements:
c       1. number of maximum size tray columns
c       2. cost of the maximum size tray
c       3. cost of any sub-maximum size tray for a sub-max diam. column
c       4. total cost of all trays,  TN*(1.*2. + 3.)
c  TAR contains the areas (sq.ft.) of the max tray size, TAR(1), and
c  the other required tray size, TAR(2).
c
      dimension trcst(4),tar(4)
      data pre,exp,amin,amax,ssf/10.258,.8685,3.,201.,4./
      do 5 i=1,4
      trcst(i)=0.
    5 tar(i)=0.
      ar=att
   10 if(ar.gt.amin) goto 20
      ar=amin
      goto 40
   20 if(ar.le.amax) goto 40
      trcst(1)=trcst(1)+1.
      tar(1)=amax
      trcst(2)=(1.+tmtl*ssf)*pre*amax**exp
      ar=ar-amax
      goto 10
   40 trcst(3)=(1.+tmtl*ssf)*pre*ar**exp
      tar(2)=ar
      trcst(4)=tn*(trcst(1)*trcst(2)+trcst(3))
      return
      end
```

```
      subroutine colcs(tn,ar,tmtl,shcst)
c  This routine is given TN, the number of trays in a sieve column,
c  AR, the area of the trays, TMTL, a material flag (0 for c.s. or 1
c  for s.s) and calculates the vector shcst with the elements:
c     1. diameter of column, ft.
c     2. height of column, ft.
c     3. weight of column shell, lb. (costing basis)
c *   4. shell cost
c     5. fittings cost
c     6. total cost exclusive of trays, Jan. 1981 basis
c
c
      dimension shcst(6)
      data pre,exp,ssf/109.83,0.6126,1.0/
c
c  determine diameter in feet
c
      di=sqrt(1.27324*ar)
      shcst(1)=di
c
c  calculate tray spacing (rec. of Treybal, 1981) and total height
c
      tsp=3.
      if(di.lt.12.) tsp=2.5
      if(di.lt.10.) tsp=2.
      if(di.lt.4.) tsp=1.667
      ht=tsp*(tn+3.)
      shcst(2)=ht
c
c  calculate thickness based on 50 psi stress (inches)
c   round to nearest 1/8 in. and allow 1/4 in. corrosion allowance
c
      th=0.0625*di+0.25
      th=float(int((th+.0625)/.125))*.125
c
c  calculate shell weight, allow extra 12% for heads and skirt
c
      ws=131.2*di*ht*th
      wt=ws*1.12
      shcst(3)=wt
      shcst(4)=(1.+tmtl*ssf)*pre*wt**exp
c
c  calculate cost for 18 in. flanged manholes
c   NOTE; equation should have a factor of 18 in it following P&T
c         this is left out below to correspond to B.M.'s work
c
c  number of manholes is an arbitrary decreasing function of
c    tray number
c
      tnm=3.*sqrt(tn)
      cp=(76+50*th)*1.
      shcst(5)=tnm*cp
      shcst(6)=shcst(4)+shcst(5)
      return
      end
```

```
      subroutine hxcst(a,tmtl,numx,xare,xcst)
c     Given area and mtl. of construction (tmtl=1 for stainless, 0 for
c     carbon) hxcst calculates the number, size(s), and area(s) of
c     required exchangers.  As given, it uses cost correlations
c     established by Maiorella (Perez) for Jan. 1981 costs (MSI=717).
c
      dimension xare(3),xcst(3)
      data pre,exp,amin,amax,ssf/416.7,.5528,100.,7000.,0.6/
      if (a.ge.amin) goto 10
      write(6,*) 'hxcst: a.lt.amin, a=',a,' amin=',amin
      a=amin
   10 nm1=int(a/amax)
      xn=float(nm1)
      numx=nm1+1
      xare(1)=amax
      xare(2)=a-xn*amax
      xare(3)=a
      xcst(1)=pre*amax**exp
      xcst(2)=pre*xare(2)**exp
      xcst(3)=xn*xcst(1)+xcst(2)
      do 5 i=1,3
      xcst(i)=xcst(i)*(1.+tmtl*ssf)
    5 continue
      return
      end
```

```
      subroutine extrtr
c
c  Given a specified feed stream, a solvent-to-feed ratio, and desired
c  fractional recovery of the extracted component (component 2), this
c  routine calculates the solvent flows and the theoretical stage
c  requirement for a liquid-liquid contactor.  It calls the subroutine
c  "exdsn" to design and estimate the cost of the equipment.
c
c  Note: component 1 is water (or main feed component)
c        component 2 is extracted component
c        Kd and S are weight fraction based
c
c  An input stream, the fresh solvent feed, must have the relative
c  concentrations of all components specified by the stream
c  initializing procedure.  Only the relative concentrations matter,
c  the actual flows are determined in this routine.
c
c  EN LIST
c 1. unit number on process flow sheet
c 2. unit type=3
c 3. number of elements=26
c 4. temperature of extraction (same as all inlet and outlet streams)
c 5. tmtl for extractor, 0 for c.s., 1 for s.s
c 6. number of input streams=2
c 7. feed stream containing material to be extracted
c 8. solvent stream (relative amounts of all components must be set)
c 9.-10. not used
c 11. number of output streams=3
c 12. raffinate stream
c 13. extract stream (solvent plus extracted material)
c 14. output stream (information) to econ subroutine
c 15. solvent cost, $/kg (average if multicomponent)
c 16. distribution coefficient A , Kd= A + B ln (wt. fr. product)
c 17. distribution coefficient B
c 18. separation factor A , S = A + B ln (wt.fr. product)
c 19. separation factor B
c 20. solubility of solvent in water at extraction temperature, wt.fr.
c 21. extraction ratio = Kd(feed)*solvent flow/total feed flow
c 22. recovery factor = wt. fraction of product recovered from feed
c 23.-25. parameters used by "exdsn", see exdsn listing for meanings
c
      include 'cmns'
      dimension sum(2)
      dcf(w)=en(16)+en(17)*alog(w)
      sfr(w)=en(18)+en(19)*alog(w)
c
c  check input streams for material balance
c
      do 7 i=1,2
      sum(i)=0.
      do 5 j=6,jj
    5 sum(i)=sum(i)+si(i,j)
      if(abs(sum(i)-si(i,3)).le.sum(i)*.001) goto 7
      write(6,*) 'extrtr: error in mat. bal. for input ',i
      si(i,3)=sum(i)
    7 continue
c
c  set all temperatures to extraction temperature,
c      pressures to input press.
c
```

```
      do 8 i=1,2
      si(i,4)=en(4)
      si(i,5)=si(1,5)
      so(i,4)=en(4)
    8 so(i,5)=si(1,5)
c
c  calculate input solvent flow rates
c
      fw=si(1,7)/si(1,3)
      fdcf=dcf(fw)
      tsf=en(21)*si(1,3)/fdcf
      if(kprnt(4).eq.0) goto 9
      write(6,*) 'extrtr; input solvent component flows'
    9 do 10 j=6,jj
      si(2,j)=si(2,j)*tsf/si(2,3)
      if(kprnt(4).eq.0) goto 10
      write(6,*) 'si(2,',j,')= ',si(2,j)
   10 continue
      si(2,3)=tsf
c
c  calculate output streams
c
      ext=en(22)*si(1,7)
      so(2,7)=si(2,7)+ext
      so(1,7)=si(1,7)-ext
c
c  water and solvent balance (approximate)
c
      wrf=si(1,6)
      srf=en(20)*(wrf+so(1,7))/(1.-en(20))
      sex=0.
      do 20 i=8,jj
   20 sex=sex+si(1,i)+si(2,i)
      sex=sex-srf
      wfwo=fdcf*si(1,6)/(sfr(fw)*si(1,3))
c  wfwo is weight fraction of water in the extract output
      so(2,6)=wfwo*(sex+so(2,7))/(1.-wfwo)
      so(1,6)=si(1,6)+si(2,6)-so(2,6)
      srf=en(20)*(so(1,6)+so(1,7))/(1.-en(20))
c  srf is total solvent dissolved in the raffinate
c   (all components assumed equally soluble in this treatment)
      sum1=0.
      sum2=0.
      do 30 j=8,jj
      so(1,j)=srf*si(2,j)/(si(2,3)-si(2,6)-si(2,7))
      so(2,j)=si(1,j)+si(2,j)-so(1,j)
      sum1=sum1+so(1,j)
   30 sum2=sum2+so(2,j)
      so(1,3)=so(1,6)+so(1,7)+sum1
      so(2,3)=so(2,6)+so(2,7)+sum2
c
c  calculate theoretical stage requirements by KSB method
c
c   Note: assuming dilute concentrations of extractable and fairly
c         constant distribution coefficient.  Calculation could be
c         subdivided to use the same method over smaller concentration
c         changes, for which the assumptions would be okay.
c
      rf=so(1,7)/so(1,3)
      sf=si(2,7)/si(2,3)
      ex=so(2,7)/so(2,3)
      sfp=sf/dcf(sf)
      do 40 i=1,10
      if(sfp.eq.0.) goto 50
      fn=dcf(sfp)-sf/sfp
      if(fn.le.(.01*sf/sfp)) goto 50
      drv=(en(17)+sf/sfp)/sfp
```

```
   40 sfp=sfp-fn/drv
      write(6,*) 'extrtr: NR search for sfp fails; sf,sfp',sf,sfp
   50 if(sf.lt.(dcf(rf)*rf)) goto 70
      write(6,*) 'extrtr:  insuff. regen. for rec.frac.',en(22)
      return
   70 continue
c
c  material balance complete - exit unless in final loop
c
      if(loop.lt.990) goto 100
      z=(fw-rf)/(fw-sfp)
      u=en(21)
      xn=(alog((u-z)/(u-z*u)))/alog(u)
c
c  xn is the number of theoretical stages required
c
      write(6,*) 'calling exdsn, xn = ',xn
      call exdsn(xn)
      so(3,8)=srf*hpy*en(15)
      if(kprnt(4).eq.0) goto 100
      write(6,*) '      solvent loss cost, $/yr: ',so(3,8)
  100 return
      end
```

```
      subroutine exdsn(xn)
c  This routine, called by EXTRTR, calculates the size and cost of a
c   seive tray extraction column to provide the necessary stage
c   requirements estimated by EXTRTR.  XN is the theoretical stage
c   requirement.
c
c   There are three parameters which must be included in the EN list
c    of EXTRTR for use by this routine;
c         en(23): cf, factor which multiplies density differences to
c                     give terminal velocity for a .5mm drop
c         en(24): hole velocity for trays, cm/s
c         en(25): overall efficiency for the column
c
c   Input stream 1 is assumed to be the continuous phase, 2 the
c    dispersed.
c
c   Calls costing subroutines TRAYCS and COLCS.  Writes the output
c    stream for the ECONOM subroutine in SO(3,j).
c
      include 'cmns'
      dimension v(2),ro(2),dn(10),trcst(4),tar(4),shcst(6)
c
c  find average densities of both phases assuming Amagat's Law holds
c
      do 15 i=1,2
      v(i)=0.
      do 10 k=1,nocomp
      j=k+5
      dn(k)=props(k,5)+props(k,6)*(en(4)-20.)
      v(i)=v(i)+(si(i,j)+so(i,j))/dn(k)
   10 continue
      ro(i)=(si(i,3)+so(i,3))/v(i)
      v(i)=v(i)/2.
   15 continue
c
c  downcomer area sized by setting continuous phase velocity, UCON, to
c   90% of the terminal velocity of a 0.5mm drop (treated as solid)
c   DNAR is downcomer area in sq.meters
c
      cf=en(23)
      ucon=abs(ro(2)-ro(1))*cf
      dnar=v(1)/(36000.*ucon)
c
c  hole velocity set by following procedure of Treybal (1980)
c   active area = 10 times hole area (triangular pitch, 3 diam. spacing)
c
      uhol=en(24)
      acar=v(2)/(3600.*uhol)
c
c  total tray = 2 times downcomer area plus active area plus 5%
c   ATT is total area in sq. ft.
c
      att=(2*dnar+acar)*1.05*10.765
```

```
c
c  overall efficiency is EFF,  trays are assumed to be stainless steel
c
      eff=en(25)
      tn=xn/eff
      tmtl=1.
      if(kprnt(4).eq.0) goto 20
      write(6,*) ''
      write(6,*) 'exdsn: Costs of sieve tray liquid extractor'
      write(6,*) '        ',xn,' th. stages, ',tn,' actual trays'
      write(6,*) ''
   20 call trayes(att,tn,tmtl,trcst,tar)
      do 30 i=2,4
   30 trcst(i)=trcst(i)*cmsi/717.
      btc=tn*trcst(2)
      stc=tn*trcst(3)
      tmtl=en(5)
      if(trcst(1).eq.0.) goto 50
      ar=tar(1)
      call colcs(tn,ar,tmtl,shcst)
      do 40 i=4,6
   40 shcst(i)=shcst(i)*cmsi/717.
      tc=shcst(6)*trcst(1)+trcst(4)-stc
      if(kprnt(4).eq.0) goto 50
      write(6,*) '        ',trcst(1),' column of diam: ',shcst(1),' ft'
      write(6,*) '         height: ',shcst(2),' ft '
      write(6,*) '         weight: ',shcst(3),' lb '
      write(6,*) '       costs, shell:',shcst(4),' fittings:',shcst(5)
      write(6,*) '              trays, each: ',trcst(2),' total: ',btc
      totl=shcst(6)+btc
      write(6,*) '       total: ',totl
   50 if(tar(2).gt.0.) goto 60
      if(tar(1).gt.0.) goto 85
      write(6,*) 'exdsn: error - no column area after TRAYCS, COLCS'
      return
   60 ar=tar(2)
      call colcs(tn,ar,tmtl,shcst)
      do 70 i=4,6
   70 shcst(i)=shcst(i)*cmsi/717.
      if(kprnt(4).eq.0) goto 80
      write(6,*) '         one column of diam: ',shcst(1),' ft'
      write(6,*) '         height: ',shcst(2),' ft '
      write(6,*) '         weight: ',shcst(3),' lb '
      write(6,*) '       costs, shell:',shcst(4),' fittings:',shcst(5)
      write(6,*) '              trays, each: ',trcst(3),' total: ',stc
      totl=shcst(6)+stc
      write(6,*) '       total: ',totl
   80 tc=tc+shcst(6)+stc
   85 write(6,*) 'exdsn: TOTAL PURCHASE COST: ',tc
      so(3,3)=tc
      do 90 i=4,8
   90 so(3,i)=0.
      so(3,9)=1.
      return
      end
```

```
      subroutine bidstl
c  This routine calculates the sizes and costs of the equipment and
c  utility streams necessary to carry out a specified binary
c    distillation.
c  While strictly applicable only to a binary feed mixture, it will
c   handle more
c  components if these can be treated as "light products", assumed
c  all recovered in the distillate, or "nonvolatiles", assumed all
c      recovered
c  in the bottoms.  Up to three of each type is allowed and all
c  components present must be identified as the light key, heavy key,
c  or one of the other two types.
c
c  EN list
c  1. unit number
c  2. unit type = 4.
c  3. number of elements = 34
c  4. light key component number, 1-nocomp
c  5. heavy key component number, 1-nocomp
c  6. number of input streams = 1
c  7. input stream number
c  8. light product component # (0 if none)
c  9. light product component # (0 if no more)
c 10.    "      "       "              "
c 11. number of output streams = 3
c 12. distillate stream #
c 13. bottoms stream #
c 14. economics information "stream" #
c 15. nonvolatile component # (0 if none)
c 16.    "          "            "
c 17.    "          "            "
c 18. mode- 1 for compositions specified or 0 for recoveries spec.
c 19. recovery of light key in distillate, wt.fr. (mode 0) OR
c       wt.fr. of light key in distillate, binary basis (mode 1)
c 20. recovery of heavy key in bottoms, wt.fr. (mode 0)  OR
c       wt.fr. of heavy key in bottoms, binary basis (mode 1)
c 21. actual reflux ratio (L/D) divided by minimum reflux ratio
c 22. solvent loss parameter, $/kg + (1000 if light key) or
c                 (2000 if heavy)
c 23. temperature at top of column, deg. C
c 24. temp. of refrigerant, if required
c 25. cost of refrigerant, if required ($/ton = $/280,000 BTU)
c 26. overall heat transfer coefficient in condenser, BTU/hr-sq.ft.-F
c 27. initial guess for saturation feed temperature, deg. C
c 28. initial guess for reboiler temperature, deg. C
c 29. overall heat transfer coefficient in reboiler, BTU/hr-sq.ft.-F
c 30. tmtl for column construction, 0. for c.s. or 1. for s.s
c 31. pinch tolerance; required mole fraction increase per
c                   theoretical stage
c 32. maximum iteration number on tray temperature finding loop
c 33. rectifying section efficiency (0. to use O'Connell correlation)
c 34. stripping section efficiency (0. to use O'Connell correlation)
c
      include 'cmns'
      dimension ilp(3),ihp(3),f(2,3),x(2,3),px(2,3)
      dimension rtcs(4),rtar(4),rshcs(6),stcs(4),star(4),sshcs(6)
      dimension cnar(3),cncs(3),rbar(3),rbcs(3)
      mlp=int(en(32))
```

```
c
c  initialize output streams
c
      do 30 i=1,2
      do 30 j=3,jj
   30 so(i,j)=0.
      kl=int(en(4))
      kh=int(en(5))
      nkl=kl+5
      nkh=kh+5
c
c  do material balance according to specified mode
c
      if(en(18).eq.1.) goto 50
      if(en(18).eq.0.) goto 40
      write(6,*) 'bidstl: error- EN(18) must be zero or one to
     1 set mode'
      return
   40 so(1,nkl)=en(19)*si(1,nkl)
      so(2,nkl)=si(1,nkl)-so(1,nkl)
      so(2,nkh)=en(20)*si(1,nkh)
      so(1,nkh)=si(1,nkh)-so(2,nkh)
      goto 60
   50 wtl=en(19)
      wth=1.-wtl
      wbh=en(20)
      wbl=1.-wbh
      t=(si(1,nkh)*wbl-si(1,nkl)*wbh)/(wth*wbl-wbh*wtl)
      b=(si(1,nkh)-wth*t)/wbh
      so(1,nkl)=wtl*t
      so(1,nkh)=wth*t
      so(2,nkl)=wbl*b
      so(2,nkh)=wbh*b
c
c  distribute non-key components according to specified types
c
   60 nlp=0
      nhp=0
      do 70 i=1,3
      j=i+7
      k=i+14
      if(en(j).le.0.) goto 65
      nlp=nlp+1
   65 ilp(i)=int(en(j))
      if(en(k).le.0.) goto 70
      nhp=nhp+1
   70 ihp(i)=int(en(k))
      if((nhp+nlp+2).eq.nocomp) goto 90
      write(6,*) 'bidstl: error- nhp+nlp must equal nocomp - 2'
      return
   90 if(nlp.eq.0) goto 100
      do 95 i=1,nlp
      k=ilp(i)+5
      so(1,k)=si(1,k)
   95 so(2,k)=0.
  100 if(nhp.eq.0) goto 110
      do 105 i=1,nhp
      k=ihp(i)+5
      so(2,k)=so(1,k)
  105 so(1,k)=0.
  110 do 115 i=1,2
      so(i,3)=0.
      do 115 j=6,jj
  115 so(i,3)=so(i,3)+so(i,j)
      so(1,4)=en(23)
```

```
c
c  end of material balances, proceed with size/cost work if
c       in last loop
c
      if(loop.eq.999) goto 120
      return
c
c  Calculate the distillation tray requirements and reflux ratio
c       using the
c   Modified Latent Heat of Vaporization Method (King, 1981) to
c   obtain straight operating lines.  Heavy component is assigned
c   the pseudo molecular weight.
c
  120 wml=props(kl,1)
      wmh=props(kh,1)
      hvl=props(kl,12)
      hvh=props(kh,12)
c
c  latent heats are in cal/gmol and assumed constant
c
      beta=hvh/hvl
c
c  i is component index, 1 = light, 2 = heavy
c  j is position index, 1 = feed, 2 = distillate, 3 = bottoms
c
c  f(i,j) are liquid molar flows in kgmoles/hr
c
      f(1,2)=so(1,nkl)/wml
      f(2,2)=so(1,nkh)/wmh
      f(1,3)=so(2,nkl)/wml
      f(2,3)=so(2,nkh)/wmh
      f(1,1)=si(1,nkl)/wml
      f(2,1)=si(1,nkh)/wmh
      if(kprnt(4).eq.0) goto 128
      write(6,*) 'Binary Distillation Calculations'
      write(6,*) '      binary mole frac. of feed, distillate, bottoms'
  128 do 130 j=1,3
      do 130 i=1,2
      k=abs(i-2)+1
      x(i,j)=f(i,j)/(f(i,j)+f(k,j))
  130 if(kprnt(4).ne.0) write(6,*) '      x(',i,j,') = ',x(i,j)
c
c  x(i,j) are actual mole fractions on a binary basis
c  px(i,j) are pseudo mole fractions on a binary basis
c
      if(kprnt(4).eq.0) goto 135
      write(6,*) '      pseudo mole frac. of feed,distillate,bottoms'
  135 do 140 j=1,3
      px(1,j)=x(1,j)/(x(1,j)+beta*x(2,j))
      px(2,j)=1.-px(1,j)
  140 if(kprnt(4).ne.0) write(6,*) '      j= ',j,'  x1, x2: ',px(1,j),
     1       px(2,j)
c
c  Start by assuming no pinch exists and that feed is close to
c           saturation
c
c  Set pseudo L/V by using the specified multiple of L/D (actual L/D
c    equals pseudo L/D since compositions of L and D are equal).
c
      t=en(27)
      call binvle(t,px(1,1),kl,kh,pypn,pfd)
      pxpn=px(1,1)
      ypn=beta*pypn/(pypn*beta+(1.-pypn))
```

```
c
c  estimate efficiency using O'Connell correlation
c
      alph=(ypn*x(2,1))/(x(1,1)*(1.-ypn))
      vis1=props(kl,9)*(1./(si(1,4)+273.16)-1./props(kl,10))
      vis1=10.**vis1
      vis2=props(kh,9)*(1./(si(1,4)+273.16)-1./props(kh,10))
      vis2=10.**vis2
      vav=x(1,1)*vis1+x(2,1)*vis2
      ebase=0.4677/(alph*vav)**.25
      if((alph*vav).gt.10.) ebase=.25
      write(6,*) '     estimating efficiency, alph,vav,ebase: ',alph,
     1    vav,ebase
c
c  find minimum reflux
c
  200 fvm=(px(1,2)-pypn)/(px(1,2)-pxpn)
      rrm=fvm/(1.-fvm)
c
c  set operating reflux ratio and constant pseudo L/V
c
      rr=en(21)*rrm
      fv=rr/(1.+rr)
      pyint=px(1,2)-fv*(px(1,2)-px(1,1))
c
c  Start by calculating top of column.  Initialize by using
c   (input) guessed temp. as feed tray temp.;
c   iterate until top temp. matches desired value.  Allow
c   pressure drop for each actual tray based on Peters & Timmerhaus
c   guidelines (empirical correlation below).  Take actual trays as
c   theoretical trays divided by efficiency.
c
      xinit=px(1,1)
      yfin=px(1,2)
      yp=pyint
      tinit=en(27)
      tfin=en(23)
      tmax=tinit
      tmin=en(23)
      ctmin=tmin
      eff=ebase*fv**0.3
      if(fv.lt.0.4) eff=ebase*.7
      if(en(33).gt.0.01) eff=en(33)
      rectn=0.
      dr=1.
      muflg=0
      mdflg=0
c
c  start of loop iterating to find tinit
c
      itlp=0
  250 call binvle(tinit,xinit,kl,kh,yy,pa)
      write(6,*) ''
      xx=xinit
      tt=tinit
      eqtrn=1.
      trn=1./eff
      if(rectn.gt.0.) pyrb=yy
      prb=pa
      if(rectn.le.0.) pfd=pa
c
c  start of tray-to-tray stepping loop
c
  260 if(kprnt(4).eq.0) goto 261
      write(6,*) '      tray number, eq.: ',eqtrn,' actual: ',trn
      write(6,*) '            xx,yp,yy,tt,pa: ',xx,yp,yy,tt,pa
```

```
  261 if(yy.ge.yfin) goto 340
      pdp=0.8*alog(pa)
      pa=pa-pdp/eff
      xx=xx+(yy-yp)/fv
      yp=yy
c
c  iterate to find temperature on current tray
c
      do 280 i=1,mlp
      call binvle(tt,xx,kl,kh,yy,pi)
      if(abs(pi-pa).le.1.) goto 290
      if(pi.lt.pa) goto 270
      tmax=tt
      if((tt-tmin).le.1.) tmin=tmin-5.
      tt=(tt+tmin)/2.
      goto 280
  270 tmin=tt
      tt=(tt+tmax)/2.
  280 continue
      write(6,*) 'bidstl: temp. on tray doesnt convg. in ',mlp,' it'
      write(6,*) 'tinit,ctmin,tt: ',tinit,ctmin,tt
      return
  290 tmin=ctmin
      if(yy.gt.(yp+en(31))) goto 300
      write(6,*) 'bidstl:pinch exists , increasing fv'
      if(rectn.eq.0.) goto 291
      write(6,*) ' pinch is in stripper section - cant cope'
      return
  291 pypn=yy
      pxpn=xx
      goto 200
c
  300 eqtrn=eqtrn+1.
      trn=trn+1./eff
      if(eqtrn.le.50.) goto 260
      write(6,*) 'bidstl: more than 50 equil. stages - I quit'
      return
c
c  end of tray-to tray stepping loop
c  check for temperature convergence
c
  340 if(itlp.le.20) goto 341
      write(6,*) 'bidstl: tinit loop doesnt cnvg. in 20;tinit:',tinit
      return
  341 itlp=itlp+1
      if(abs(tt-tfin).le.1.) goto 350
      yp=pyint
      if(rectn.ne.0.) yp=px(1,3)
      if(tt.lt.tfin) goto 345
      if(muflg.eq.1) dr=dr+1.
      tinit=tinit-5./dr
      mdflg=1
      goto 250
  345 if(mdflg.eq.1) dr=dr+1.
      tinit=tinit+5./dr
      muflg=1
      goto 250
c
c  temperatures converge, proceed with calculation of column diameter
c
  350 if(rectn.ne.0.) goto 500
      si(1,4)=tinit
      rectn=float(int(trn))
      reqtn=eqtrn
      reclv=fv
```

```
c
c  first calculate an area for the top of the rect. section
c
c  calculate actual and pseudo flows of binary vapor and liquid
c    all in kgmole/hr
c
      vod=rr+1.
      acbv=vod*so(1,nkl)/(wml*x(1,2))
      psbv=acbv*(x(1,2)+beta*x(2,2))
      acbl=reclv*acbv
      psbl=reclv*psbv
      vac=0.
      hcon=0.
      vlq=0.
      do 355 i=1,nocomp
      j=i+5
      vlq=vlq+rr*so(1,j)*9.81e-6/(props(i,5)+props(i,6)*(tfin-20.))
      vfm=vod*so(1,j)/props(i,1)
      vac=vac+vfm
  355 hcon=hcon+vfm*props(i,12)*3.97
c
c  hcon is condenser duty in BTU/hr
c
      call binvle(tfin,px(1,2),kl,kh,y,ptop)
      vvf=vac*.61183*(tfin+273.16)/ptop
      vmf=so(1,3)*vod*6.125e-4
      vden=vmf/vvf
      denl=rr*so(1,3)*6.125e-4/vlq
      write(6,*) 'vvf,vden,vlq,denl: ',vvf,vden,vlq,denl
      call colsiz(vvf,vden,vlq,denl,treca)
      write(6,*) 'treca: ',treca
c
c  check area required at bottom of rect. section
c
      y=beta*pyint/(beta*pyint+(1.-pyint))
      bbv=psbv/(y+beta*(1.-y))
      vac=vac-acbv+bbv
      write(6,*) 'pfd: ',pfd
      vvf=vac*.61183*(tinit+273.16)/pfd
      vmf=vmf+6.125e-4*(bbv*(y*wml+(1.-y)*wmh)-acbv*(x(1,2)*
     1      wml+x(2,2)*wmh))
      vden=vmf/vvf
      bbl=psbl/(x(1,1)+beta*x(2,1))
      wll=bbl*x(1,1)*wml*6.125e-4
      dll=(props(kl,5)+props(kl,6)*(tinit-20.))*62.43
      whl=bbl*x(2,1)*wmh*6.125e-4
      dhl=(props(kh,5)+props(kh,6)*(tinit-20.))*62.43
      vlq=wll/dll+whl/dhl
      write(6,*) 'vlq: ',vlq
      denl=(wll+whl)/vlq
      write(6,*) 'vvf,vden,vlq,denl: ',vvf,vden,vlq,denl
      call colsiz(vvf,vden,vlq,denl,breca)
      reca=breca
      if(treca.gt.breca) reca=treca
      if(kprnt(4).eq.0) goto 395
      write(6,*) ''
      write(6,*) ' areas calc. for rect. sec.; top,bot.; ',treca,breca
  395 if(abs(treca-breca).lt.(.4*reca)) goto 400
      write(6,*) ' rec. sec. areas very different top and bot.'
```

```
c
c  proceed with calculation of stripping section of column
c
c  set pseudo L/V ; note that heat requirements take light products
c   into account but equilibrium stage requirements and area
c    calculations for the stripping section don't account for increased
c    vapor flow necessary to carry extra heat up to rectifying section
c
  400 fv=(pyint-px(1,3))/(px(1,1)-px(1,3))
c
c  recalculate efficiency
c
      eff=ebase*fv**0.3
      if(fv.gt.8.) eff=ebase*1.86
      if(en(34).gt.0.01) eff=en(34)
      xinit=px(1,3)
      yfin=pyint
      yp=px(1,3)
      tinit=en(28)
      tfin=si(1,4)
      tmax=tinit
      tmin=tfin
      ctmin=tmin
      dr=1.
      muflg=0
      mdflg=0
      itlp=0
      goto 250
c
c  find area of stripping section by checking bottom first
c
  500 seqtn=eqtrn
      strtn=float(int(trn))
      so(2,4)=tinit
c
c  find actual and pseudo binary flows, kgmol/hr
c
      write(6,*) 'fv: ',fv
      acbl=so(2,nkl)/(wml*x(1,3))
      psbl=acbl*(x(1,3)+beta*x(2,3))
      psbv=psbl/fv
      yrb=beta*pyrb/(beta*pyrb+(1.-pyrb))
      acbv=psbv/(yrb+beta*(1.-yrb))
c
c  find total actual liquid and vapor flows and densiites
c
      tvl=0.
      do 510 i=1,nocomp
      j=i+5
  510 tvl=tvl+9.81e-6*so(2,j)/(props(i,5)+props(i,6)*(tinit-20.))
      denl=6.125e-4*so(2,3)/tvl
      vvf=acbv*.61183*(tinit+273.16)/prb
      vmf=6.125e-4*acbv*(yrb*wml+(1.-yrb)*wmh)
      vden=vmf/vvf
      write(6,*) 'vvf,vden,tvl,denl: ',vvf,vden,tvl,denl
      call colsiz(vvf,vden,tvl,denl,tstra)
```

```
c
c  check area required at top of stripping section
c
      tvl=0.
      twl=0.
      usbl=psbl/(x(1,1)+beta*x(2,1))
      wflk=6.125e-4*usbl*x(1,1)*wml
      vflk=wflk/(62.43*(props(kl,5)+props(kl,6)*(tfin+20.)))
      wfhk=6.125e-4*usbl*x(2,1)*wmh
      vfhk=wfhk/(62.43*(props(kh,5)+props(kh,6)*(tfin-20.)))
      if(nhp.eq.0) goto 550
      do 530 i=1,nhp
      j=ihp(i)
      k=j+5
      twl=twl+so(2,k)*6.125e-4
  530 tvl=tvl+so(2,k)*9.81e-6/(props(j,5)+props(j,6)*(tfin-20.))
  550 twl=twl+wflk+wfhk
      tvl=tvl+vflk+vfhk
      denl=twl/tvl
      acbv=usbl/fv
      vvf=acbv*.61183*(tfin+273.16)/pfd
      vmf=6.125e-4*acbv*(x(1,1)*wml+x(2,1)*wmh)
      vden=vmf/vvf
      write(6,*) 'vvf,vden,tvl,denl: ',vvf,vden,tvl,denl
      call colsiz(vvf,vden,tvl,denl,bstra)
      stra=tstra
      if(bstra.gt.tstra) stra=bstra
      if(abs(bstra-tstra).le.(.4*stra)) goto 560
      write(6,*) 'bidstl; stripper areas differ widely;b,t; ',bstra
     1           ,tstra
  560 if(kprnt(4).eq.0) goto 565
      write(6,*) 'bidstl: Costs of Distillation Equipment'
      write(6,*) '       Rectifying Column'
      write(6,*) '        ',reqtn,' theor., ',rectn,' actual trays'
  565 ttc=0.
      call trayes(reca,rectn,1.,rtcs,rtar)
      do 569 i=2,4
  569 rtcs(i)=rtcs(i)*cmsi/717.
      tmtl=en(30)
      if(rtar(1).eq.0.) goto 580
      call colcs(rectn,rtar(1),tmtl,rshcs)
      do 570 j=4,6
  570 rshcs(j)=rshcs(j)*cmsi/717.
      cn=rtcs(1)
      ttc=cn*(rshcs(6)+rectn*rtcs(2))
      if(kprnt(4).eq.0) goto 580
      call colprn(cn,rectn,rtcs(2),rshcs)
  580 if(rtar(2).ne.0) goto 585
      if(rtar(1).ne.0) goto 595
      write(6,*) 'bidstl: ERROR, zero area for rectifier'
      return
  585 call colcs(rectn,rtar(2),tmtl,rshcs)
      do 590 j=4,6
  590 rshcs(j)=rshcs(j)*cmsi/717.
      ttc=ttc+rectn*rtcs(3)+rshcs(6)
      if(kprnt(4).eq.0) goto 600
      call colprn(1.,rectn,rtcs(3),rshcs)
  595 if(kprnt(4).eq.0) goto 600
      write(6,*) ''
      write(6,*) '     Total rectifying col. purchase cost: ',ttc
      write(6,*) ''
      write(6,*) '     Stripping column'
      write(6,*) '     ',seqtn,' theor., ',strtn,' actual trays'
  600 btc=0.
      call trayes(stra,strtn,1.,stcs,star)
      do 605 i=2,4
  605 stcs(i)=stcs(i)*cmsi/717.
```

```
      if(star(1).eq.0) goto 620
      call colcs(strtn,star(1),tmtl,sshcs)
      do 610 j=4,6
  610 sshcs(j)=sshcs(j)*cmsi/717.
      cn=stcs(1)
      btc=cn*(sshcs(6)+strtn*stcs(2))
      if(kprnt(4).eq.0) goto 620
      call colprn(cn,strtn,stcs(2),sshcs)
  620 if(star(2).ne.0) goto 625
      if(star(1).ne.0) goto 640
      write(6,*) 'bidstl: ERROR, zero area for stripper'
      return
  625 call colcs(strtn,star(2),tmtl,sshcs)
      do 630 j=4,6
  630 sshcs(j)=sshcs(j)*cmsi/717.
      btc=btc+strtn*stcs(3)+sshcs(6)
      if(kprnt(4).eq.0) goto 640
      call colprn(1.,strtn,stcs(3),sshcs)
  640 tcc=ttc+btc
      if(kprnt(4).eq.0) goto 650
      write(6,*) '      Total stripping col. purch. cost: ',btc
      write(6,*) '      Total distillation column cost: ',tcc
      write(6,*) ''
      write(6,*) '   Condenser(s)'
  650 u=en(26)
      wuse=0.
      refcs=0.
      if(en(23).gt.(tcw+5.)) goto 720
      if((en(24).lt.(en(23)-5.)).and.(en(25).ne.0.)) goto 700
      write(6,*) 'bidstl: refrigeration needed for condenser, n.av.'
      return
c
c  design calls for refrigerated condenser, refrigerant provided
c
  700 delt=en(23)-en(24)
      ar=hcon/(u*delt*1.8)
      call hxcst(ar,tmtl,ncon,cnar,cncs)
      do 705 i=1,3
  705 cncs(i)=cncs(i)*cmsi/717.
      refcs=hcon*hpy*en(25)/2.8e5
      if(kprnt(4).eq.0) goto 750
      write(6,*) '      heat duty (BTU/hr): ',hcon
      if(ncon.eq.1) goto 710
      nb=ncom-1
      write(6,*) '      ',nb,' condenser of area (sq.ft.): ',cnar(1)
      write(6,*) '       purch. cost of each: ',cncs(1)
  710 write(6,*) '       one condenser of area (sq.ft.): ',cnar(2)
      write(6,*) '       purch. cost: ',cncs(2),'  TOTAL: ',cncs(3)
      write(6,*) '       cost of refrigeration ($/yr): ',refcs
      write(6,*) ''
      goto 750
c
c  cooling water can be used for condenser
c
  720 tin=en(23)
      call wtrclr(hcon,1,tin,tin,u,tmtl,tx,ncon,cnar,cncs,wuse,wc)
      if(kprnt(4).eq.0) goto 750
      write(6,*) '      heat duty (BTU/hr): ',hcon
      if(ncon.eq.1) goto 730
      nb=ncon-1
      write(6,*) '       ',nb,' condenser of area (sq.ft.): ',cnar(1)
      write(6,*) '       purch. cost of each: ',cncs(1)
  730 write(6,*) '       one condenser of area (sq.ft.): ',cnar(2)
```

```
      write(6,*) '       purch. cost: ',cncs(2),'  TOTAL: ',cncs(3)
      write(6,*) '       cooling water outlet T (C): ',tx
      write(6,*) '       cooling water use (gpm): ',wuse,' cost ($/yr)
     1: ',wc
      write(6,*) ''
c
c  calculate size and cost of reboiler
c
c   add sensible heat gain of bottom products to condenser duty to
c    estimate reboiler duty
c
  750 hsen=0.
      do 755 j=6,jj
      k=j-5
  755 hsen=hsen+so(2,j)*props(k,7)*(tinit-si(1,4))*3.97
      if(tinit.lt.(st2-5.)) goto 760
      write(6,*) 'bidstl: rb temp. too high for high p stm: ',tinit,
     1st2
      return
  760 tsm=st2
      if(tinit.lt.(st1-5.)) tsm=st1
      u=en(29)
      hrb=hcon+hsen
      call stmhtr(1,hrb,tinit,tinit,tsm,u,tmtl,nrb,rbar,rbcs,stus)
      do 765 i=1,3
  765 rbcs(i)=rbcs(i)*cmsi/717.
      if(kprnt(4).eq.0) goto 800
      write(6,*) '      Reboiler'
      write(6,*) '       heat duty(BTU/hr): ',hrb,' T (C): ',tinit
      if(nrb.eq.1) goto 770
      nb=nrb-1
      write(6,*) '       ',nb,' reboiler of area (sq.ft.): ',rbar(1)
      write(6,*) '       purch. cost: ',rbcs(1)
  770 write(6,*) '       one reboiler of area (sq.ft.): ',rbar(2)
      write(6,*) '       purch. cost: ',rbcs(2),' TOTAL: ',rbcs(3)
      write(6,*) ''
c
c  set output streams for econom routine
c
  800 so(3,3)=tcc+cncs(3)+rbcs(3)
      write(6,*) 'bidstl: total purch. eq. cost: ',so(3,3)
      so(3,4)=0.
      if(tsm.eq.st1) so(3,4)=stus
      so(3,5)=0.
      if(tsm.eq.st2) so(3,5)=stus
      so(3,6)=0.
      so(3,7)=wuse
      if((en(22)-1000.).ge.1000.) goto 810
      sls=so(2,nkl)*hpy*(en(22)-1000.)
      goto 825
  810 sls=so(1,nkh)*hpy*(en(22)-2000.)
  825 if(kprnt(4).eq.0) goto 830
      write(6,*) '      value of solvent lost ($/yr): ',sls
  830 so(3,8)=refcs+sls
      so(3,9)=1.
c
c  assigning one man per shift to run the distillation
c
      return
      end
```

```
      subroutine binvle(t,x,kl,kh,y,p)
c
c  Calculates y and p as a function of x and t for a binary mixture.
c  Assumes ideal gas behavior.  Calls 'binact' for activity coefficients.
c   x,y are pseudo mole fractions of light component
c
      include 'cmns'
      psl=props(kl,13)-props(kl,14)/(t+273.16+props(kl,15))
      psl=exp(psl)
      psh=props(kh,13)-props(kh,14)/(t+273.16+props(kh,15))
      psh=exp(psh)
c
c  convert from pseudo mole fraction to actual
c
      beta=props(kh,12)/props(kl,12)
      xl=beta*x/(beta*x+(1.-x))
      call binact(t,xl,acl,ach)
      xh=1.-xl
      ylp=psl*x*acl
      yhp=psh*xh*ach
      p=ylp+yhp
      yl=ylp/p
c
c  convert from actual mole fraction to pseudo
c
      y=yl/(yl+beta*(1.-yl))
      return
      end
c
```

```
c
c  Subroutine 'binact' calculates activity coefficients of both
c   components
c   in a binary mixture given the temperature (deg. C) and the mole
c   fraction of the light component, x.
c
c  The following routine is specifically for the ethanol-water binary.
c    It uses the UNIQUAC equation with the temperature dependant
c    binary parameters determined by Maiorella.
c
      subroutine binact(tc,xe,game,gamw)
      data z,z2,re,rw,qe,qw,qpe,qpw,rle,rlw/10.,5.,2.11,.92,1.97,1.4,
     1    .92,1.,-.41,-2.32/
      t=tc+273.15
      u12=-10845.0108+144.45463836*t-0.692588910446*t**2+
     1    0.00143459625212 *t**3-1.096233611d-6*t**4
      u21=38765.541772-475.05211078*t+2.141085409*t**2-
     1   0.00420316593674  *t**3+3.054583612d-6*t**4
      t12=exp(-u12/t)
      t21=exp(-u21/t)
      xw=1.-xe
      th1=xe*qe
      th2=xw*qw
      tp1=xe*qpe
      tp2=xw*qpw
      st=th1+th2
      the=th1/st
      thw=th2/st
      tpe=tp1/(tp1+tp2)
      tpw=tp2/(tp1+tp2)
      sp=re*xe+rw*xw
      sl=rle*xe+rlw*xw
      gcle=rle-re*sl/sp+alog(re/sp)+z2*qe*alog(qe*sp/(re*st))
      gclw=rlw-rw*sl/sp+alog(rw/sp)+z2*qw*alog(qw*sp/(rw*st))
      pte=tpe+tpw*t21
      ptw=tpw+tpe*t12
      ptse=tpe/pte+tpw*t12/ptw
      ptsw=tpw/ptw+tpe*t21/pte
      grle=qpe*(1.-alog(pte)-ptse)
      grlw=qpw*(1.-alog(ptw)-ptsw)
      game=exp(gcle+grle)
      gamw=exp(gclw+grlw)
c     open(unit=7,file='actcof')
c     write(7,*) 'temperature: ',tc,' uew:',u12,' uwe:',u21
c     write(7,*) 'mole fraction ethanol: ',xe
c     write(7,*) 'ethanol activity coefficient: ',game
c     write(7,*) 'water activity coefficient: ',gamw
c     write(7,*) ' '
c     close(unit=7)
      return
      end
```

```
c
c
c  Subroutine 'binact' calculates activity coefficients of both
c     components
c   in a binary mixture given the temperature (deg. C) and the mole
c   fraction of the light component, x.
c Ths version used for ideal mixtures, which is a good
c   approximation for ethanol in other alcohols.
c
      subroutine binact(t,x,acl,ach)
      acl=1.
      ach=1.
      return
      end
```

```
      subroutine colsiz(vvf,vden,vfl,denl,ar)
c
c  This subroutine estimates the required column area for a
c   distillation column given the volumetric flows of vapor, VVF, and
c   liquid, VFL, both in cu.ft./s and their densities in lb/cu.ft. The
c   area returned is the empty column cross sectional area in sq.ft.
c
      a=vvf/4.
      ic=0
   20 ic=ic+1
      tsp=1.5
      if(a.gt.12.57) tsp=2.
      if(a.gt.78.54) tsp=2.5
      if(a.gt.114.) tsp=3.
      fkv=.24+0.09333*(tsp-1.5)
      vmax=fkv*sqrt((denl-vden)/vden)
      v=.8*vmax
      ar=vvf/v
      if(abs(ar-a).le.0.5) goto 50
      if(ic.lt.11) goto 30
      write(6,*) 'colsiz: failure to converge on area : ',ar
      return
   30 if(ic.lt.5) goto 35
      a=(a+ar)/2.
      goto 20
   35 a=ar
      goto 20
c
c  check liquid flow
c
   50 diam=sqrt(1.273*ar)
      clf=vfl/diam
      if(clf.le..165) goto 70
      if(clf.le..35) goto 60
      write(6,*) 'colsiz: liq. loading on trays too high, clf: ',clf
      return
   60 write(6,*) 'colsiz: nonstandard trays reqd, clf: ',clf
      return
   70 continue
      return
      end
```

```
c
c  subroutine colprn is used to print size and cost information
c   about a column
c
      subroutine colprn(cn,tn,tc,shcst)
      dimension shcst(6)
      write(6,*) ''
      write(6,*) '     ',cn,' column of diam. : ',shcst(1),' ft.'
      write(6,*) '          height(ft.): ',shcst(2),' weight(lb):',
     1      shcst(3)
      write(6,*) '     Costs'
      write(6,*) '       shell: ',shcst(4),' fittings: ',shcst(5),
     1      ' sum: ',shcst(6)
      ttc=tn*tc
      write(6,*) '       trays, each: ',tc,'  total: ',ttc
      ttl=shcst(6)+ttc
      write(6,*) '      Total, per column: ',ttl
      write(6,*) ''
      return
      end
```

```
      subroutine strip
c  This routine estimates the size and cost of equipment and steam use
c   to recover an extracton solvent from an aqueous raffinate stream.
c   It applies only to solvents which form azeotropes with water.  The
c   azeotropic composition must be supplied as it is used to estimate
c   vapor-liquid equiliria.  The equilibrium is taken to be described
c   by a simple linear proportionality to weight fraction.  The weight
c   fraction of the raffinate feed is assumed to be the saturation
c   concentration.  If a second strippable component is present (i.e.
c   ethanol) it may be treated separately, the degree of removal
c     calculated
c   by a KSB procedure, using the same number of theoretical stages as
c   required by the specified solvent recovery.
c
c  EN list
c 1. unit number
c 2. unit type = 6
c 3. number of elements = 22
c 4. component number of solvent to be stripped (design basis)
c 5. second component to be stripped (zero if none)
c 6. number of input streams = 1
c 7. raffinate feed stream number
c 8. tmtl for column, 0. for c.s. or 1. for s.s.
c 9.
c 10.
c 11. number of outputs = 3
c 12. stripped raffinate stream number
c 13. stream number of recovered solvent (& steam), vapor
c 14. stream number of output to economics routine
c 15.
c 16. fractional recovery of solvent, 0.-1.
c 17. approach to equilibrium at top of stripper, 0.-1.
c 18. weight fraction of solvent in solvent-water azeotrope
c 19. equilibrium constant for second strippable component
c      (vapor wt.fr./liquid wt.fr.)
c 20. tray efficiency (assumed constant and the same for both
c            components)
c 21. cost of solvent, $/kg (match that in extrtr)
c 22. top temperature, deg. C;  set to -1 to default to feed temp.
c
c
      include 'cmns'
      dimension fm(10),fmf(10),shcs(6),tcst(4),tar(4)
c
c  check for input stream consistency
c
      ck=0.
      do 20 i=1,nocomp
      j=i+5
   20 ck=ck+si(1,j)
      if(abs(si(1,3)-ck).le.1.) goto 30
      write(6,*) 'strip: input flows inconsistent'
      return
c
c  material balance calculations
c     start by finding feed weight fractions
c
   30 nos=int(en(4))
      nas=nos+5
      ne=int(en(5))
      nae=ne+5
      wfs=si(1,nas)/si(1,3)
      wfe=si(1,nae)/si(1,3)
```

```
c
c  find column pressure at feed temperature
c
      tt=en(22)
      if(tt.lt.0.) tt=si(1,4)
c find mole fractions of all feed components
      sfm=0.
      do 50 i=1,nocomp
      j=i+5
      fm(i)=si(1,j)/props(i,1)
   50 sfm=sfm+fm(i)
      do 55 i=1,nocomp
   55 fmf(i)=fm(i)/sfm
      tk=tt+273.15
      pw=props(1,13)-props(1,14)/(tk+props(1,15))
      vms=en(18)*props(1,1)/(en(18)*(props(1,1)-props(nos,1))+
     1     props(nos,1))
      pt=fmf(1)*pw/(1-vms)
c
c  calculate L/V (rlv) and stripping ratio (sr)
c
      z=en(16)
      ae=en(17)
      rlv=ae*en(18)/(z*wfs)
      sr=z/ae
c
c  number of theoretical stages found by using KSB equation
c
      tsn=alog((sr-z)/(sr*(1.-z)))/alog(sr)
      tn=tsn/en(20)
      if(ne.eq.0) goto 100
c
c  find fractional removal of second component, if required
c
      sre=en(19)/rlv
      fre=(1.-sre)/(1.-sre**(tsn+1))
c
c  calculate output streams, latent heat requirement, heat capacity,
c       and volumetric flows
c
  100 so(1,3)=0.
      so(2,3)=0.
      hv=0.
      vl=0.
      vv=0.
      cp=0.
      do 120 i=1,nocomp
      j=i+5
      so(1,j)=si(1,j)
      if(i.eq.nos) so(1,j)=si(1,j)*(1.-z)
      if(i.eq.ne) so(1,j)=si(1,j)*(1.-fre)
      so(1,3)=so(1,3)+so(1,j)
      cp=cp+so(1,j)*props(i,7)
c vl is liquid volume in cu.ft./s
      vl=vl+si(1,j)*9.81e-6/(props(i,5)+props(i,6)*(tt-20.))
      so(2,j)=si(1,j)-so(1,j)
      if(i.eq.1) so(2,6)=si(1,nas)*z*(1./(en(18)*ae)-1.)
      so(2,3)=so(2,3)+so(2,j)
      hv=hv+so(2,j)*props(i,12)*3.97/props(i,1)
c vv is vapor volume in cu.ft./s
      vv=vv+so(2,j)*.61183*(tt+273.15)/(props(i,1)*pt)
  120 continue
      vden=so(2,3)*6.125e-4/vv
      denl=si(1,3)*6.125e-4/vl
```

```
c
c  find column area
c
      if(kprnt(4).eq.1) write(6,*) 'vv,vden,vl,denl: ',vv,vden,vl,denl
      call colsiz(vv,vden,vl,denl,ar)
      if(kprnt(4).eq.0) goto 565
      write(6,*) 'strip: Costs of Solvent Recovery Equipment'
      write(6,*) '       Stripping Column'
      write(6,*) '        ',tsn,' theor., ',tn,' actual trays'
  565 ttc=0.
      call traycs(ar,tn,1.,tcst,tar)
      do 569 i=2,4
  569 tcst(i)=tcst(i)*cmsi/717.
      tmtl=en(10)
      if(tar(1).eq.0.) goto 580
      call colcs(tn,tar(1),tmtl,shcs)
      do 570 j=4,6
  570 shcs(j)=shcs(j)*cmsi/717.
      cn=tcst(1)
      ttc=cn*(shcs(6)+tn*tcst(2))
      if(kprnt(4).eq.0) goto 580
      call colprn(cn,tn,tcst(2),shcs)
  580 if(tar(2).ne.0.) goto 585
      if(tar(1).ne.0.) goto 595
      write(6,*) 'strip: ERROR, zero area for stripper'
      return
  585 call colcs(tn,tar(2),tmtl,shcs)
      do 590 j=4,6
  590 shcs(j)=shcs(j)*cmsi/717.
      ttc=ttc+tn*tcst(3)+shcs(6)
      if(kprnt(4).eq.0) goto 600
      call colprn(1.,tn,tcst(3),shcs)
  595 if(kprnt(4).eq.0) goto 600
      write(6,*) ''
      write(6,*) '      Total stripping col. purchase cost: ',ttc
  600 write(6,*) ''
c
c  find pressure and temperature at bottom of column
c
      pdp=.8*alog(pt)
      pb=pt+tn*pdp
      tb=props(1,14)/(props(1,13)-alog(pb))-props(1,15)-273.15
c
c  estimate sensible heat requirement
c
      hs=cp*(tb-si(1,4))*3.97
c
c  find steam requirement, lb/hr
c
      tsm=st2
      if(tb.le.st1) tsm=st1
      ht=hv+hs
      slh=910.*((374.15-tsm)/225.26)**.3518
      stus=ht/slh
      aw=stus/2.205-so(2,6)
      so(1,6)=so(1,6)+aw
      so(1,3)=so(1,3)+aw
      if(kprnt(4).eq.0) goto 200
      write(6,*) '      Temperatures, top: ',tt,' bottom: ',tb
      write(6,*) '      heat requirements, latent: ',hv,' total: ',ht
      write(6,*) '      steam use (lb/hr): ',stus
  200 write(6,*) ''
      so(3,3)=ttc
      do 300 i=4,9
  300 so(3,i)=0.
      so(3,8)=-so(2,nas)*en(21)*hpy
      write(6,*) '      solvent recovery credit: ',so(3,8)
      write(6,*) ''
      if(tsm.eq.st1) so(3,4)=stus
      if(tsm.eq.st2) so(3,5)=stus
      return
      end
```

```
      subroutine fbdabs
c
c This routine calculates the size and costs of a fixed bed absorption
c  system for removal of one component from a given input stream.  If
c  desired, the regeneration of the bed can be calculated on the
c  first or on a subsequent call.
c  The regeneration stream must be given; the regeneration output is
c  calculated from material balance considerations only (no modelling).
c  The number of beds required (EN(26)) should reflect the difficulty
c  of regeneration, the need to fill an empty beds, etc..
c
c The routine assumes that, if there significant heat effects, the
c  properties of the system are such that there will be separation of
c  the thermal and concetration waves, which is a good assumption
c  for liquid streams and high bed capacities, but not for gases.
c
c EN list
c 1. unit number
c 2. unit type=5
c 3. number of variables in EN list = 29
c 4. mode flag; 0-stop after absorption calc's, 1-proceed to regen.
c 5. ad/absorbed component number, 1-nocomp
c 6. number of input streams, 2 or 3
c       three inputs may be used if it desired to transfer
c       information from one stream to another
c 7. stream number of absorbant feed stream
c 8. stream number of actual regeneration stream
c 9. stream number of upstream source of regen. stream, if needed
c 10. zero
c 11. number of output streams, either 3 or 4
c 12. regeneration effluent stream number
c 13. actual product stream number

c 14. downstream destination stream for product (if product info to
c         be transferred) or econom info stream
c 15. econom info stream or zero
c 16. ad/absorbent capacity, gm/gm 'dry' sorbent at feed conditions
c 17. density of 'dry' sorbent, lb/cu.ft
c 18. heat capacity of 'dry' sorbent, cal/g-C
c 19. swelling factor at saturation (vol. at sat./vol. 'dry')
c 20. void fraction of sorbent bed, assumed constant
c 21. average enthalpy of ad/absorption, cal/g ad/absorbate, positive
c         for exothermic sorption
c 22. fractional regeneration = fractional removal of sorbate (0.-1.)
c 23. cycle time, hours
c 24. efficiency of bed utilization (fraction of bed equilibrium cap.
c         used at breakthrough
c 25. temperature required of regeneration input stream (set negative
c         default to the input temperature of the regen. stream)
c 26. number of beds required (minimum of 2 for continuous operation)
c 27. height to diameter ratio of beds
c 28. material of bed shell and supports, 0. for c.s. or 1. for s.s.
c 29. cost of sorbent, current $/'dry' lb.
c
c
      include 'cmns'
      dimension shcst(6)
```

```
c
c  calculate product output
c
      na=int(en(5))
      nan=na+5
      tcp=0.
      vin=0.
      so(2,3)=0.
      do 50 i=1,nocomp
      j=i+5
      so(2,j)=si(1,j)
      vin=vin+si(1,j)*9.81e-6/(props(i,5)+props(i,6)*(si(1,4)-20.))
      if(i.eq.na) so(2,j)=si(1,j)*(1.-en(22))
      so(2,3)=so(2,3)+so(2,j)
   50 tcp=tcp+so(2,j)*props(i,7)
      aph=si(1,nan)*en(22)
      cp=tcp/so(2,3)
c
c  calculate product stream temperature
c    bhm is an estimate of the bed mass that must be heated
c    by the heat of sorption in addition to the fluid
c
      bhm=en(18)*en(23)*(816.3*vin*en(17)/en(20)-aph/en(16))
      trs=aph*en(21)/(tcp+bhm)
      so(2,4)=si(1,4)+trs
c
c  write product flows to downstream second stream if desired
c
      if(nout.lt.4) goto 100
      do 90 j=3,jj
   90 so(3,j)=so(2,j)

c
c  check mode; proceed to regeneration or not
c
  100 if(en(4).eq.1.) goto 150
      if(kprnt(4).eq.0) goto 300
      write(6,*) ''
      write(6,*) 'fbdabs: second output stream (product) flows'
      do 120 i=1,nocomp
      j=i+5
  120 write(6,*) '      component ',i,'  flow: ',so(2,j)
      write(6,*) ''
      return
c
c  calculate regeneration effluent stream
c
  150 if(nin.lt.3) goto 170
      do 160 j=3,jj
  160 si(2,j)=si(3,j)
  170 if(en(25).le.0) goto 175
      si(2,4)=en(25)
  175 tcp=0.
      so(1,3)=0.
      do 180 i=1,nocomp
      j=i+5
      so(1,j)=si(2,j)
      if(i.eq.na) so(i,j)=si(2,j)+aph
      tcp=tcp+so(i,j)*props(i,7)
  180 so(1,3)=so(1,3)+so(1,j)

c
c  calculate temperature drop neglecting bed heat effects
c
      tdp=aph*en(21)/(tcp+bhm)
      so(1,4)=si(2,4)-tdp
c
c  material, energy balance complete - proceed with cost calculations
c
  300 if(loop.eq.999) goto 305
      return
```

```
c
c  calculate bed size - bac is pounds of sorbent required per bed
c
  305 apb=aph*en(23)
      bmn=2.205*apb/en(16)
      bac=bmn/en(24)
c
c  sbcs is cost of sorbent per bed, vvs is vessel volume allowing for
c                                        swelling
c
      sbcs=bac*en(29)
      vbd=bac/en(17)
      vvs=vbd*en(19)
c
c  calculate bed dimensions, allow 2 extra feet of height for head space
c
      di=(vvs*1.27324/en(27))**(1./3.)
      ht=di*en(27)+2.
      ar=di**2./1.27324
      usf=vin/ar
      uac=usf/en(20)
      tsp=3.

      if(di.lt.12.) tsp=2.5
      if(di.lt.10.) tsp=2.
      if(di.lt.4.) tsp=1.667
      tn=ht/tsp-3.
      tmtl=en(28)
      call colcs(tn,ar,tmtl,shcst)
      do 320 i=4,6
  320 shcst(i)=shcst(i)*cmsi/717.
      cpb=sbcs+shcst(6)
      tcs=cpb*en(26)
      do 330 j=3,jj
  330 so(nout,j)=0.
      so(nout,3)=tcs
      if(kprnt(4).eq.0) goto 350
      write(6,*) ''
      write(6,*) 'Results of fixed bed sorption calcuations'
      write(6,*) '       ',en(26),' beds used'
      write(6,*) '       height (ft): ',ht,'  diam.(ft): ',di
      write(6,*) '       velocities of fluid, ft./s'
      write(6,*) '          superficial: ',usf,'  actual: ',uac
      write(6,*) '       temperatures, deg. C'
      write(6,*) '          input: ',si(1,4),'  product: ',so(2,4)
      write(6,*) '         regennt: ',si(2,4),' reg. eff.: ',so(1,4)
      write(6,*) '       Costs per bed'
      write(6,*) '          sorbent: ',sbcs,'  vessel: ',shcst(6)
      write(6,*) '       Total purchase cost of system: ',tcs
      write(6,*) ''
  350 continue
      return
      end
```

```
      subroutine hxcng
c
c  Given two specified process streams (in the SI matrix stored in a
c  common block by GEMCS), this routine finds the optimum combination
c  of heat exchange, heating, and cooling to achieve the required
c  temperature changes. It calls on the subroutines WTRCLR and STMHTR.
c
c  EN list
c  1. unit number on process flowsheet
c  2. unit type = 2
c  3. number of elements = 22
c  4. tmtl for exchanger, 0. for c.s., 1. for s.s.
c  5. phase change flag; 0 for none, 1 for one stream, -1 for both
c  6. number of input streams = 2
c  7. input stream to be cooled
c  8. input stream to be heated
c  9,10. -not used-
c  11. number of output streams = 3
c  12. output stream which was cooled
c  13. output stream which was heated
c  14. output stream to ECONOMICS subroutine
c  15. -not used-
c  16. overall heat transfer coefficient for exchanger (BTU/hr.sqft.F)
c  17. o.h.t.c. for heater (BTU/hr.sqft.dF)
c  18. tmtl for heater (as above)
c  19. o.h.t.c. for cooler (same units)
c  20. tmtl for cooler (as above)
c  21. limit on convergence loops
c  22. mode flag; 0. proceed with cost calc., 1 pass inputs to outputs
c        unchanged except for temperatures set to zero on outputs
c  23. check flag; 0 to check the material balance for inputs
c        equal outpus, 1 to use only input flows but input and
c        output temperatures


      include 'cmns'
      dimension c(3),cp(2),q(2),qmx(2),qo(3),t(2),exar(3),excst(3)
      dimension hare(3),hcst(3),clar(3),clcst(3)
      if(en(22).eq.0.) goto 10
      do 15 i=1,2
      so(i,3)=si(i,3)
      so(i,4)=0.
      do 15 j=5,jj
      so(i,j)=si(i,j)
   15 continue
      return
c
c  check material balance if desired
c
   10 if(en(23).gt.0) goto 30
      do 20 i=1,2
   20 if((abs(si(i,3)-so(i,3))).ge.1.) goto 25
      goto 30
   25 write(6,*) 'error in hxcng: input flow.ne.output flow'
c  calculate heat capacities and check stream flow sums
   30 do 35 i=1,2
      ck=0.
      cp(i)=0.
      do 40 j=6,jj
      k=j-5
      ck=ck+si(i,j)
   40 cp(i)=cp(i)+si(i,j)*props(k,7)/si(i,3)
      if(abs(ck-si(i,3)).le.1.) goto 35
      write(6,*) 'error in hxcng: sum of flows .ne. total, i=',i
   35 continue
```

```
c  calculate heat duties of each stream and find limiting heat duty
c  of the exchanger
      do 50 i=1,2
      j=1+iabs(i-2)
      q(i)=cp(i)*si(i,3)*(abs(si(i,4)-so(i,4)))*3.968
   50 qmx(i)=cp(i)*si(i,3)*(abs(si(i,4)-si(j,4))-1.)*3.968
      qlm=min(q(1),q(2),qmx(1),qmx(2))
c  start optimization at the constraint
      qo(3)=qlm
      qo(2)=.9*qlm
      qo(1)=.8*qlm
      count=0.
      qlo=0.
      qhi=qlm
      lim=int(en(21))
      i=1
      ilp=1
      ilc=0
      ihc=0
c  cost calculating subroutine follows
c
c  begin by setting temperatures
   90 do 100 j=1,2
  100 t(j)=si(j,4)+qo(i)*(so(j,4)-si(j,4))/q(j)
      dtc=t(1)-si(2,4)
      if(dtc.le.0.) goto 105
      dth=si(1,4)-t(2)
      if(dth) 105,105,110
  105 write(6,*) 'error in hxcng: temperature approach .le. zero '
      write(6,*) 'dtc: ',dtc,' dth: ',dth
      return

c  calculate exchanger size and cost
  110 dtlm=(dth-dtc)/alog(dth/dtc)
      a=qo(i)/(en(16)*dtlm*1.8)
      tmtl=en(4)
      call hxcst(a,tmtl,nhx,exar,excst)
      do 112 k=1,3
  112 excst(k)=excst(k)*cmsi/717.0
      c(i)=excst(3)*cftr
c  size and cost cooler, if needed
      qw=q(1)-qo(i)
      if(qw.ge.(.01*q(1))) goto 115
      ncl=0
      goto 120
  115 tin=t(1)
      tout=so(1,4)
      u=en(19)
      tmtl=en(20)
      call wtrclr(qw,0,tin,tout,u,tmtl,tx,ncl,clar,clcst,wuse,wc)
      do 117 k=1,3
  117 clcst(k)=clcst(k)*cmsi/717.
      c(i)=c(i)+clcst(3)*cftr+wc
c  size and cost heater, if needed
  120 qh=q(2)-qo(i)
      if(qh.ge.(.01*q(2))) goto 125
      nhtr=0
      goto 130
  125 tin=t(2)
      tout=so(2,4)
      u=en(17)
      tmtl=en(18)
      if(so(2,4).lt.st2) goto 126
      write(6,*) 'error in hxcng: desired T higher than steam T'
      return
```

```
  126 if(so(2,4).ge.st1) goto 127
      tstm=st1
      spc=sp1
      goto 129
  127 tstm=st2
      spc=sp2
  129 call stmhtr(0,qh,tin,tout,tstm,u,tmtl,nhtr,hare,hcst,stus)
      stc=stus*spc*hpy/1000.
      do 132 k=1,3
  132 hcst(k)=hcst(k)*cmsi/717.
      c(i)=c(i)+hcst(3)*cftr+stc
c
c  end of cost-calculating subroutine
c
  130 if(i.eq.3) ilp=0
      if(ilp.eq.0) goto 140
      i=1+i
      goto 90
  140 count=count+1.
      if(count.le.lim) goto 141
      write(6,*) 'hxcng: not converged in ',lim,' loops'
      return
  141 if(kprnt(4).eq.0) goto 142
      write(6,*) 'hxcng: loop number ',count
      write(6,*) 'qo(i): ',qo(1),qo(2),qo(3),' c(i): ',c(1),c(2),c(3)
  142 if(c(2).le.c(3)) goto 150
      if(c(1).lt.c(3)) goto 151
      if(qo(3).eq.qlm) goto 143
      qo(1)=qo(2)
      c(1)=c(2)
      qo(2)=qo(3)

      c(2)=c(3)
      qo(3)=(qo(2)+qhi)/2.
      i=3
      goto 90
  143 if((c(2)-c(3))/c(3).gt.0.01) goto 145
      if(ihc.eq.0) goto 144
      if(i.eq.3) goto 300
      i=3
      goto 90
  144 ihc=1
  145 qo(2)=(qo(2)+qo(3))/2.
      i=2
      ilp=1
      goto 90
c
  150 if(c(2).le.c(1)) goto 170
  151 if(qo(1).eq.0.) goto 155
      qo(3)=qo(2)
      c(3)=c(2)
      qo(2)=qo(1)
      c(2)=c(1)
      qo(1)=(qo(1)+qlo)/2.
      i=1
      goto 90
  155 if((c(2)-c(1))/c(1).gt.0.01) goto 165
      if(ilc.eq.0) goto 160
      if(i.eq.1) goto 300
      i=1
      goto 90
  160 ilc=1
  165 qo(2)=(qo(1)+qo(2))/2.
      i=2
      goto 90
```

```
c
c  middle point is lowest
c
  170 qlo=qo(1)
      qhi=qo(3)
      if(abs((2.*c(2)-c(1)-c(3))/c(2)).gt.0.01) goto 175
      if((i.eq.2).or.(c(3).eq.c(2))) goto 300
  175 continue
      if(c(3)-c(1)) 180,200,190
  180 qo(1)=qo(2)
      c(1)=c(2)
      goto 195
  190 qo(3)=qo(2)
      c(3)=c(2)
  195 qo(2)=(qo(3)+qo(1))/2.
      i=2
      ilp=0
      goto 90
  200 do 205 j=1,3
  205 qo(j)=(qo(j)+qo(2))/2.
      ilp=1
      i=1
      goto 90
c
c  end of optimization
c
  300 if(kprnt(3).eq.0) goto 350
      write(6,*) ''
      un=en(1)-1.
      write(6,*) 'hxcng results: unit number ',un
      write(6,*) 'input stream number ',en(7),' cooled'
      write(6,*) '  tin: ',si(1,4),' tout: ',so(1,4),' t1: ',t(1)
      write(6,*) 'input stream number ',en(8),' heated'
      write(6,*) '  tin: ',si(2,4),' tout: ',so(2,4),' t2: ',t(2)
      write(6,*) ''
      write(6,*) 'number of exchangers: ',nhx
      write(6,*) 'exchanger area: ',exar(3),'  cost: ',excst(3)
      write(6,*) 'number of coolers: ',ncl
      write(6,*) 'cooler area: ',clar(3),'  cost: ',clcst(3)
      write(6,*) ' cooling water use, gpm:',wuse,' cost, $/yr: ',wc
      write(6,*) 'number of heaters: ',nhtr
      write(6,*) 'heater area: ',hare(3),'  cost: ',hcst(3)
      write(6,*) ' steam temp. ',tstm,' use,lb/hr: ',stus,' cost: ',
     1 stc
c
c
  350 so(3,3)=excst(3)+clcst(3)+hcst(3)
      so(3,4)=0.
      so(3,5)=0.
      if(tstm.eq.st2) goto 360
      so(3,4)=stus
      goto 365
  360 so(3,5)=stus
  365 so(3,6)=0.
      so(3,7)=wuse
      so(3,8)=0.
      so(3,9)=0.
c
      return
c
      end
```

```
      subroutine wtrclr(q,iv,tin,tout,u,im,tx,ncl,clar,clcst,wuse,wc)
c     Given heat duty, q(btu/hr), and temperatures, wtrclr calculates
c     optimum cooler or condenser area and cooling water use (gpm).
c     Note: ivap must be 0 for cooling of a liquid, 1 for condensing.
c
c     Calls subroutine hxcst for heat exchanger costs.
c
c     Refers to common/econ for cooling water temp.(tcw), max. temp.
c     (twmx)(both deg. C), and price (cwp, cents/1000gal), and capital
c     factor (cftr), and current MSI (cmsi).
c
      dimension t(3),c(3),clar(3),clcst(3)
      common/econ/hpy,cftr,cmsi,sp1,sp2,ep,cwp,plab,st1,st2,tcw,twmx
      if(iv.eq.0) goto 20
      if(tin.eq.tout) goto 30
      write(6,*) 'wtrclr: ivap.ne.0, but tin.ne.tout'
      return
   20 if(tin.gt.tout) goto 30
      write(6,*) 'wtrclr: ivap=0, but tin.le.tout'
      return
   30 if(tout.gt.tcw) goto 40
      write(6,*) 'wtrclr: tout.le.tcw'
      return
   40 tmx=twmx
      if(tin.gt.tmx) goto 50
      tmx=tin-0.5
   50 dt2=tout-tcw

c
c   initialize optimization search; suspected optimum will be near tmx
c
      t(1)=(tcw+tmx)/2.
      t(3)=tmx
      t(2)=(t(1)+t(3))/2.
      tlo=tcw+1.
      thi=tmx
      j=0
      delt=2.
      count=1.
   45 ilp=1
      i=1
   55 if(j.gt.20) goto 100
c     write(6,*) 'i, t(i): ',i,t(i)
      dt1=tin-t(i)
      dtlm=(dt1-dt2)/alog(dt1/dt2)
c     write(6,*) 'dtlm: ',dtlm
      a=q/(u*dtlm*1.8)
c     write(6,*) 'a: ',a
      call hxcst(a,im,ncl,clar,clcst)
      ce=clcst(3)*cftr*cmsi/717.
      wuse=q/((t(i)-tcw)*899.75)
c     wuse is water use in gpm units
      wc=wuse*cwp*hpy*.0006
      c(i)=ce+wc
      if(i.eq.3) ilp=0
      if(ilp.eq.0) goto 60
      i=i+1
      goto 55
   60 j=j+1
c     write(6,*) 'c 1,2,3: ',c(1),c(2),c(3)
```

```
      if((c(2).lt.c(1)).and.(c(2).lt.c(3))) goto 85
      if(c(2).le.c(1)) goto 80
      if(c(2).le.c(3)) goto 70
      if(c(3).lt.c(1)) goto 80
   70 t(3)=t(2)
      t(2)=t(1)
      c(3)=c(2)
      c(2)=c(1)
      t(1)=(t(1)+tlo)/2.
      i=1
      ilp=0
      goto 55
   80 if(t(3).ne.tmx) goto 81
      if((j.gt.1).and.(i.eq.3)) goto 83
      t(1)=t(2)
      c(1)=c(2)
      t(2)=(t(1)+t(2))/2.
      i=2
      ilp=1
      goto 55
   83 tx=t(3)
      goto 115
   81 t(1)=t(2)
      t(2)=t(3)
      c(1)=c(2)
      c(2)=c(3)
      t(3)=(t(3)+thi)/2.
      i=3
      goto 55
   85 tlo=t(1)
      thi=t(3)
      delc=abs(c(1)+c(3)-2*c(2))/c(2)
      if(delc.le.0.01) goto 110
      if(c(3).le.c(1)) goto 90
      t(1)=(t(1)+t(2))/2.
      i=1
      ilp=0
      goto 55
   90 t(3)=(t(3)+t(2))/2.
      i=3
      goto 55
  100 continue
      write(6,*) 'wtrclr: optimization not converged, i=',i
  110 tx=t(2)
  115 wuse=q/((tx-tcw)*899.75)
      wc=wuse*cwp*hpy*.0006
      return
      end
```

```
      SUBROUTINE STMHTR(IVAP,Q,TIN,TOUT,TSTM,U,TMTL,NHTR,HARE,HCST,
     1 STUS)
c  Stmhtr is a subroutine for sizing and costing heaters or reboilers
c  using steam as the heat source. IVAP is a flag to signify
c   evaporation
c  (IVAP=1) or none (IVAP=0). Given heat duty, Q (BTU/hr), inlet and
c  outlet temperatures (note that these temperatures
c  must be equal if IVAP=1), steam temperature, (all temperatures in
c  degrees C), overall heat transfer coefficient (BTU/hr-sq.ft.-F) and
c  material of construction (TMTL=0. for carbon, 1. for stainless),
c  stmhtr calls hxcst to calculate the number, size(s), and
c  and cost(s) of exchangers required.
c
      DIMENSION HARE(3),HCST(3)
      data flim/15000./
c
c  flim is the limiting flux for a reboiler due to film boiling
c
      DO 5 I=1,3
      HARE(I)=0.
    5 HCST(I)=0.
      tsk=tstm+273.15
      STMLHT=910.*((647.3-tsk)/225.26)**0.3518
C
C STMLHT=LATENT HEAT OF STEAM AT TEMPERATURE TSTM
C


      STUS=Q/STMLHT
c stus=steam use, lb. per hour
      IF (IVAP) 10,10,20
   10 IF (TOUT.GT.TIN) GOTO 15
      WRITE(6,*) 'ERROR IN STMHTR, IVAP.LE.0 BUT TIN.GE.TOUT'
      GOTO 50
   15 DTLM=(TOUT-TIN)/ALOG((TSTM-TIN)/(TSTM-TOUT))
      GOTO 30
   20 IF(ABS(TOUT-TIN).LE.(0.1)) GOTO 25
      WRITE(6,*) 'ERROR IN STMHTR, IVAP.GT.0 BUT TIN.NE.TOUT'
      GOTO 50
   25 DTLM=TSTM-TOUT
C
   30 A=Q/(U*DTLM*1.8)
      if(ivap) 33,33,31
   31 flux=q/a
      if(flux.le.flim) goto 33
      a=q/flim
   33 CALL HXCST(A,TMTL,NHtr,HARE,HCST)
      IF (NHtr) 35,35,40
   35 WRITE(6,*) 'ERROR IN HXCST, Q=',Q,' A=',A
      GOTO 50
   40 continue
   50 RETURN
      END
```

The use of the preceding programs is illustrated by a example calculation reproduced in the following pages. The example is a calculation of the economics of the proposed ethanol recovery process using liquid-liquid extraction (n-octanol as the solvent) and selective water removal. The interconnections among the six modules used to model the process are shown in Figure D-2. The stream numbers are those used in the computer calculations and correspond to the following;

1. dilute aqueous ethanol feed
2. raffinate loaded with solvent
3. cooled water-loaded solvent recycled to extraction
4. extract (solvent containing ethanol and water)
5. extract after water removal by selective sorption
6. hot water-loaded solvent from bed regeneration
7. heated extract, water removed, for feed to distillation
8. hot regenerated solvent, distillation bottoms
9. ethanol product
10. information 'stream' from extraction for economic analysis
11. information 'stream' from water removal for economic analysis
12. information 'stream' from heat exchange for economic analysis
13. information 'stream' from distillation for economic analysis
14. information 'stream' from solvent recovery for econ. analysis
15. stripped raffinate (to recycle or waste treatment)
16. recovered solvent (plus water) recycled to extraction

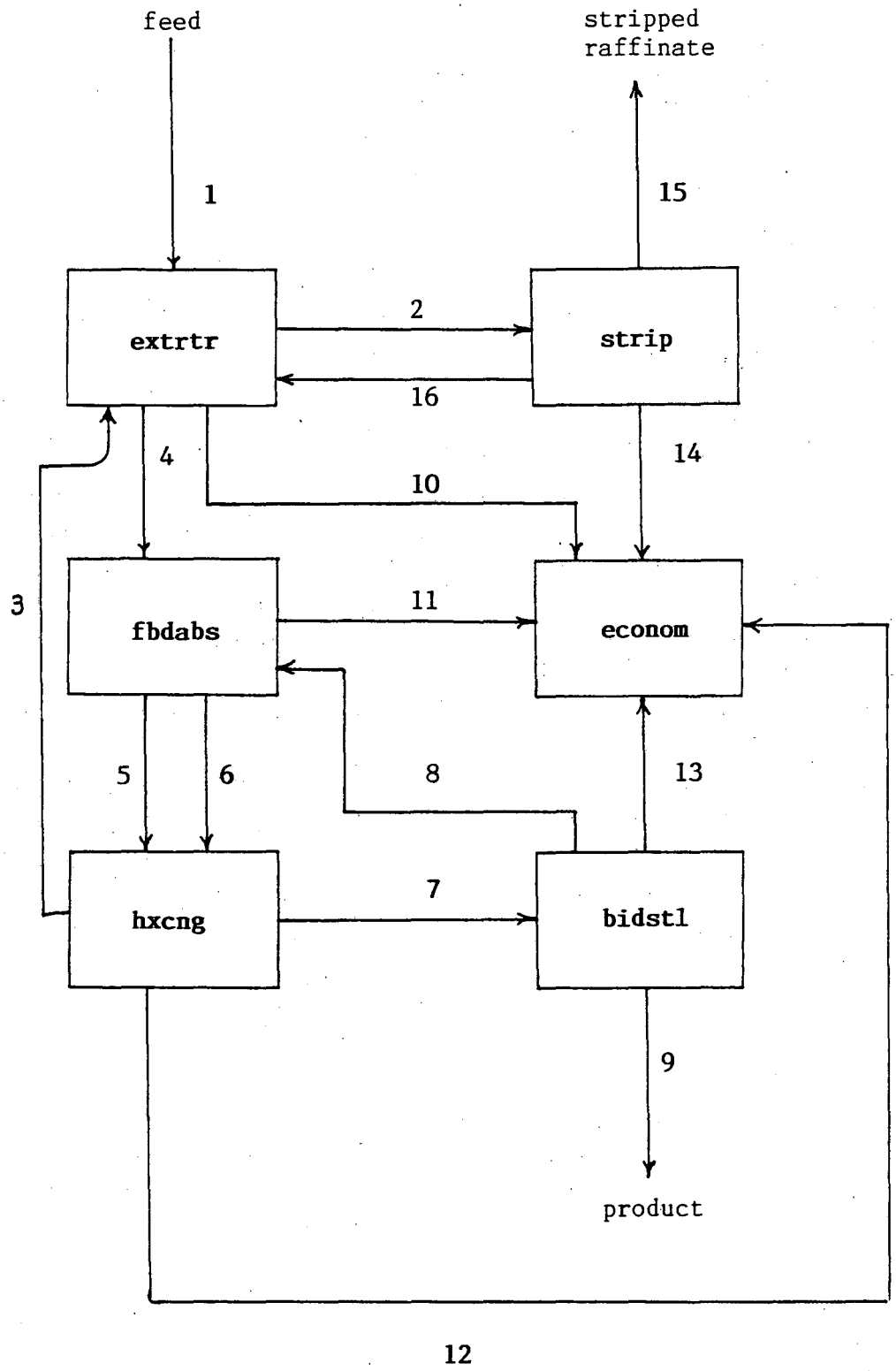


Figure D-2 Diagram of Stream Connections Among Process Modules in GEMCS Modelling of the Proposed Ethanol Recovery Process

```
    1    16      (ncase, iii=# of process streams in flow diagram)
    1
GEMCS calculation of ethanol recovery process economics
      Selective water removal process
1,1,1,1,0,0,0,0,0,0
8,3,20
 Water (H2O)
18.015, 374.1, 217.6, 56.0, .9982
4.98e-4, 1.0, 0.0, 658.25, 283.16
100.0, 9717., 18.3036, 3816.44, -46.13
7.701, 4.595e-4, 2.521e-6, -0.859e-9, 0.0
 Ethanol (C2H6O)
46.069, 243.0, 63.0, 167.0, .7893
8.5e-4, .586, 0.0, 686.64, 300.88,
78.4, 9260, 18.9119, 3803.98, -41.68
2.158, 5.113e-2, -2.004e-5, 0.328e-9, 0.0
2-methyl-1-pentanol (C6H14O)
102.18,610.,40.0,381.,.819
8.e-4,.5,0.,1179.4,354.94,
430.2,11600.,18.4337,4055.45,-76.49
0.,0.,0.,0.,0.
1,2,3,4,5,6,7,8
16
1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1
2
1,1,186232.0,35.,15.,176920.4,9311.6,0.,0.
3,1,100.,35.,15.,3.,0.,97.,0.
8

econom one
1,1,32,9,2
0,0,0,0,0
0,0,0,0,0
4.9,.156,.3,30000.,1.65
8000.,751.,180.,5.0,300.
7.5,25.,40.,25.,5.
1.0,1

extrtr
2,3,25,35.,0.
2,1,3,0,0,
3,2,4,10,1.10
1.00,0.,20.,0.,.0031
1.25,.900,50.,10.,.2

fbdabs
3,5,29,0,1
2,4,8,0,0
4,6,5,7,11
1.0,47.,0.8,2.,.4
100.,.99,.5,.50,-100.,
3.,1.,0.,3.

bidstl
4,4,34,2,3
1,7,1,0,0
3,9,8,13,0
0,0,1,.9999,.999
1.10,2001.1,45.,0.,0.,
300.,110.,130.,300.,0.
.00001,20.,.7,.7
```

```
fbdabs
5,5,29,1,1
2,4,8,0,0
3,6,5,11,0
1.0,47.,0.8,2.,.4
100.,.99,.5,.50,-100.,
3.,1.,0.,3.

hxcng
6,2,22,0,0
2,6,5,0,0
3,3,7,12,0
250.,350.,0,250.,0
10,0,1

strip
7,6,22,3,2
1,2,0,0,0
3,15,16,14,0
.99,.90,.42,4.,.6
1.10,-1

econom two
8,1,32,9,2
4,9,10,11,13
2,12,14,0,0
4.9,.156,.3,30000.,1.65
8000.,751.,180.,5.0,300.
7.5,25.,40.,25.,5.
1.0,1
```

```
  No. of cases:   1   No. of process streams  16
1          CASE     1


 RUN NUMBER    1

 GEMCS calculation of ethanol recovery process economics
       Selective water removal process
OPRINTING NCONT,LLST,NS
OPRINTING INITIAL STREAMS
OPRINTING MODULE SETS
0    8 MODULE SETS    3 COMPONENTS   20 PROP'S


 Water (H2O)
        18.01500      374.10001      217.60001       56.00000        0.99820
         0.00050        1.00000        0.           658.25000      283.16000
       100.00000     9717.00000       18.30360     3816.43994      -46.13000
         7.70100        0.00046       0.00000       -0.00000        0.
 Ethanol (C2H6O)
        46.06900      243.00000       63.00000      167.00000        0.78930
         0.00085        0.58600        0.           686.64001      300.88000
        78.40000     9260.00000       18.91190     3803.97998      -41.68000
         2.15800        0.05113       -0.00002        0.00000        0.
2-methyl-1-pentanol
       102.18000      610.00000       40.00000      381.00000        0.81900
         0.00080        0.50000        0.          1179.40002      354.94000
       430.20001    11600.00000       18.43370     4055.44995      -76.49000
         0.             0.             0.             0.             0.
```

```
 CALCULATION ORDER LIST-
     1    2    3    4    5    6    7    8
0   16STREAM CODES ARE READ-
     1    1    1    1    1    1    1    1    1    1
     1    1    1    1    1    1
0    2INITIAL STREAMS ARE READ-
         1.00000          1.00000    186232.00000        35.00000        15.000
    176920.40625       9311.59961        0.                0.

 ----
         3.00000          1.00000      100.00000         35.00000        15.000
         3.00000          0.            97.00000          0.

 ----
0    8MODULE SETS ARE READ-

econom one
         1.00000          1.00000       32.00000          9.00000         2.000
         0.               0.             0.               0.              0.
         0.               0.             0.               0.              0.
         4.90000          0.15600        0.30000      30000.00000         1.650
      8000.00000        751.00000      180.00000          5.00000       300.000
         7.50000         25.00000       40.00000         25.00000         5.000
         1.00000          1.00000

 ----

extrtr
         2.00000          3.00000       25.00000         35.00000         0.
         2.00000          1.00000        3.00000          0.              0.
         3.00000          2.00000        4.00000         10.00000         1.100
         1.00000          0.            20.00000          0.              0.003
         1.25000          0.90000       50.00000         10.00000         0.200


 ----

fbdabs
         3.00000          5.00000       29.00000          0.              1.0000
         2.00000          4.00000        8.00000          0.              0.
         4.00000          6.00000        5.00000          7.00000        11.0000
         1.00000         47.00000        0.80000          2.00000         0.4000
       100.00000          0.99000        0.50000          0.50000      -100.0000
         3.00000          1.00000        0.               3.00000

 ----

bidstl
         4.00000          4.00000       34.00000          2.00000         3.0000
         1.00000          7.00000        1.00000          0.              0.
         3.00000          9.00000        8.00000         13.00000         0.
         0.               0.             1.00000          0.99990         0.9990
         1.10000       2001.09998       45.00000          0.              0.
       300.00000        110.00000      130.00000        300.00000         0.
         0.00001         20.00000        0.70000          0.70000

 ----

fbdabs
         5.00000          5.00000       29.00000          1.00000         1.0000
         2.00000          4.00000        8.00000          0.              0.
         3.00000          6.00000        5.00000         11.00000         0.
         1.00000         47.00000        0.80000          2.00000         0.4000
       100.00000          0.99000        0.50000          0.50000      -100.0000
         3.00000          1.00000        0.               3.00000

 ----
```

```
hxcng
        6.00000        2.00000       22.00000        0.             0.
        2.00000        6.00000        5.00000        0.             0.
        3.00000        3.00000        7.00000       12.00000        0.
      250.00000      350.00000        0.           250.00000        0.
       10.00000        0.

 ----

strip
        7.00000        6.00000       22.00000        3.00000        2.00000
        1.00000        2.00000        0.             0.             0.
        3.00000       15.00000       16.00000       14.00000        0.
        0.99000        0.90000        0.42000        4.00000        0.60000
        1.10000       -1.00000

 ----

econom two
        8.00000        1.00000       32.00000        9.00000        2.00000
        4.00000        9.00000       10.00000       11.00000       13.00000
        2.00000       12.00000       14.00000        0.             0.
        4.90000        0.15600        0.30000    30000.00000        1.65000
     8000.00000      751.00000      180.00000        5.00000      300.00000
        7.50000       25.00000       40.00000       25.00000        5.00000
        1.00000        1.00000

 ----

OMODULE SET FOR UNIT     1
        1.00000        1.00000       32.00000        9.00000        2.00000
        0.             0.             0.             0.             0.
        0.             0.             0.             0.             0.
        4.90000        0.15600        0.30000    30000.00000        1.65000
     8000.00000      751.00000      180.00000        5.00000      300.00000
        7.50000       25.00000       40.00000       25.00000        5.00000
        1.00000        1.00000
OFINAL OUTPUT STREAMS FOR MODULE     1
OMODULE SET FOR UNIT     2
        2.00000        3.00000       25.00000       35.00000        0.
        2.00000        1.00000        3.00000        0.             0.
        3.00000        2.00000        4.00000       10.00000        1.10000
        1.00000        0.            20.00000        0.             0.00310
        1.25000        0.90000       50.00000       10.00000        0.20000
OINPUT STREAMS FOR MODULE     2
        1.00000        1.00000   186232.00000       35.00000       15.00000
   176920.40625     9311.59961        0.             0.

 ----
        3.00000        1.00000      100.00000       35.00000       15.00000
        3.00000        0.            97.00000        0.

 ----
  extrtr; input solvent component flows
  si(2,  6  )=    6983.70
  si(2,  7  )=   0.
  si(2,  8  )=    225806.
  si(2,  9  )=   0.
  calling exdsn, xn =     4.39381
```

```
exdsn: Costs of sieve tray liquid extractor
          4.39381   th. stages,    21.9691   actual trays

        one column of diam:    11.4930   ft
        height:    62.4227   ft
        weight:    105421.   lb
      costs, shell:   137368.   fittings:   1855.75
             trays, each:    3026.99   total:    66500.2
      total:    205724.
exdsn: TOTAL PURCHASE COST:    205724.
     solvent loss cost, $/yr:    4.73916e+06
OFINAL OUTPUT STREAMS FOR MODULE    2
        2.00000        0.        173722.78125       35.00000       15.0000
   172253.07813      931.16016      538.54059        0.

 ----
        4.00000        0.        245299.21875       35.00000       15.0000
    11651.02441     8380.43945   225267.75000        0.

 ----
       10.00000        0.        205724.39063        0.             0.
        0.             0.       4739157.00000        1.00000

 ----
OMODULE SET FOR UNIT    3
        3.00000        5.00000       29.00000        0.             1.0000
        2.00000        4.00000        8.00000        0.             0.
        4.00000        6.00000        5.00000        7.00000       11.0000
        1.00000       47.00000        0.80000        2.00000        0.4000
      100.00000        0.99000        0.50000        0.50000     -100.0000
        3.00000        1.00000        0.             3.00000

OINPUT STREAMS FOR MODULE    3
        4.00000        0.        245299.21875       35.00000       15.0000
    11651.02441     8380.43945   225267.75000        0.

 ----
        8.00000        0.             0.             0.             0.
        0.             0.             0.             0.

 ----

 fbdabs: second output stream (product) flows
      component   1    flow:    116.510
      component   2    flow:    8380.44
      component   3    flow:    225268.

OFINAL OUTPUT STREAMS FOR MODULE    3
        6.00000        0.        173722.78125       35.00000       15.00000
   172253.07813      931.16016      538.54059        0.

 ----
        5.00000        0.        233764.70313       40.16392       15.00000
      116.51013     8380.43945   225267.75000        0.

 ----
        7.00000        0.        233764.70313       40.16392       15.00000
      116.51013     8380.43945   225267.75000        0.

 ----
       11.00000        0.             0.             0.             0.
        0.             0.             0.             0.

 ----
```

```
OMODULE SET FOR UNIT     4
        4.00000        4.00000       34.00000        2.00000        3.00000
        1.00000        7.00000        1.00000        0.             0.
        3.00000        9.00000        8.00000       13.00000        0.
        0.             0.             1.00000        0.99990        0.99900
        1.10000     2001.09998       45.00000        0.             0.
      300.00000      110.00000      130.00000      300.00000        0.
        0.00001       20.00000        0.70000        0.70000
OINPUT STREAMS FOR MODULE     4
        7.00000        0.        233764.70313       40.16392       15.00000
      116.51013     8380.43945   225267.75000        0.

 ----
  Binary Distillation Calculations
       binary mole frac. of feed, distillate, bottoms
       x(  1  1  ) =    7.62240e-02
       x(  2  1  ) =   0.923776
       x(  1  2  ) =   0.999955
       x(  2  2  ) =    4.50961e-05
       x(  1  3  ) =    2.21525e-03
       x(  2  3  ) =   0.997785
        pseudo mole frac. of feed,distillate,bottoms
       j=   1    x1, x2:    6.17980e-02  0.938202
       j=   2    x1, x2:   0.999943   5.65052e-05
       j=   3    x1, x2:    1.76917e-03  0.998231
      estimating efficiency, alph,vav,ebase:    10.5156   2.61402  0.250000

       tray number, eq.:    1.00000   actual:    1.42857
            xx,yp,yy,tt,pa:    6.17980e-02  0.388629  0.409209   110.000
   315.753
       tray number, eq.:    2.00000   actual:    2.85714
            xx,yp,yy,tt,pa:    9.33807e-02  0.409209  0.537339   104.242
   309.176

       tray number, eq.:    3.00000   actual:    4.28571
            xx,yp,yy,tt,pa:   0.290014  0.537339  0.861465   83.4147   302.623
       tray number, eq.:    4.00000   actual:    5.71429
            xx,yp,yy,tt,pa:   0.787430  0.861465  0.988696   61.3407   296.095
       tray number, eq.:    5.00000   actual:    7.14286
            xx,yp,yy,tt,pa:   0.982682  0.988696  0.999345   56.1066   289.591
       tray number, eq.:    6.00000   actual:    8.57143
            xx,yp,yy,tt,pa:   0.999024  0.999345  0.999964   55.2345   283.113

       tray number, eq.:    1.00000   actual:    1.42857
            xx,yp,yy,tt,pa:    6.17980e-02  0.388629  0.422239   105.000
   260.099
       tray number, eq.:    2.00000   actual:    2.85714
            xx,yp,yy,tt,pa:   0.113378  0.422239  0.613725   96.1914   253.743
       tray number, eq.:    3.00000   actual:    4.28571
            xx,yp,yy,tt,pa:   0.407239  0.613725  0.927202   71.3956   247.416
       tray number, eq.:    4.00000   actual:    5.71429
            xx,yp,yy,tt,pa:   0.888312  0.927202  0.995399   54.3168   241.118
       tray number, eq.:    5.00000   actual:    7.14286
            xx,yp,yy,tt,pa:   0.992970  0.995399  0.999758   51.4053   234.849
       tray number, eq.:    6.00000   actual:    8.57143
            xx,yp,yy,tt,pa:   0.999659  0.999758  0.999989   50.6674   228.610

       tray number, eq.:    1.00000   actual:    1.42857
            xx,yp,yy,tt,pa:    6.17980e-02  0.388629  0.435968   100.000
   213.080
       tray number, eq.:    2.00000   actual:    2.85714
            xx,yp,yy,tt,pa:   0.134446  0.435968  0.680826   88.4619   206.953
       tray number, eq.:    3.00000   actual:    4.28571
            xx,yp,yy,tt,pa:   0.510215  0.680826  0.958305   61.7998   200.858
       tray number, eq.:    4.00000   actual:    5.71429
            xx,yp,yy,tt,pa:   0.936043  0.958305  0.997762   48.6750   194.798
```

```
    tray number, eq.:     5.00000   actual:     7.14286
         xx,yp,yy,tt,pa:   0.996596  0.997762  0.999893   46.8375   188.77
    tray number, eq.:     6.00000   actual:     8.57143
         xx,yp,yy,tt,pa:   0.999866  0.999893  0.999996   46.0369   182.78

    tray number, eq.:     1.00000   actual:     1.42857
         xx,yp,yy,tt,pa:    6.17980e-02  0.388629  0.450425   95.0000
173.570
    tray number, eq.:     2.00000   actual:     2.85714
         xx,yp,yy,tt,pa:   0.156633  0.450425  0.739526   80.7422   167.67
    tray number, eq.:     3.00000   actual:     4.28571
         xx,yp,yy,tt,pa:   0.600298  0.739526  0.974927   53.6563   161.82
    tray number, eq.:     4.00000   actual:     5.71429
         xx,yp,yy,tt,pa:   0.961552  0.974927  0.998814   43.8095   156.01
    tray number, eq.:     5.00000   actual:     7.14286
         xx,yp,yy,tt,pa:   0.998209  0.998814  0.999949   42.1130   150.23

    tray number, eq.:     1.00000   actual:     1.42857
         xx,yp,yy,tt,pa:    6.17980e-02  0.388629  0.443103   97.5000
192.453
    tray number, eq.:     2.00000   actual:     2.85714
         xx,yp,yy,tt,pa:   0.145396  0.443103  0.711574   84.4678   186.44
    tray number, eq.:     3.00000   actual:     4.28571
         xx,yp,yy,tt,pa:   0.557401  0.711574  0.967884   57.5993   180.46
    tray number, eq.:     4.00000   actual:     5.71429
         xx,yp,yy,tt,pa:   0.950744  0.967884  0.998387   46.1812   174.52
    tray number, eq.:     5.00000   actual:     7.14286
         xx,yp,yy,tt,pa:   0.997554  0.998387  0.999927   44.5356   168.62
    tray number, eq.:     6.00000   actual:     8.57143
         xx,yp,yy,tt,pa:   0.999918  0.999927  0.999998   43.7947   162.76

    tray number, eq.:     1.00000   actual:     1.42857
         xx,yp,yy,tt,pa:    6.17980e-02  0.388629  0.438326   99.1667
206.003
    tray number, eq.:     6.00000   actual:     8.57143
         xx,yp,yy,tt,pa:    1.88942e-02  0.112133  0.148822   123.736
383.813
    tray number, eq.:     7.00000   actual:     10.0000
         xx,yp,yy,tt,pa:    2.45874e-02  0.148822  0.188933   122.009
377.013
    tray number, eq.:     8.00000   actual:     11.4286
         xx,yp,yy,tt,pa:    3.08113e-02  0.188933  0.230359   120.224
370.233
    tray number, eq.:     9.00000   actual:     12.8571
         xx,yp,yy,tt,pa:    3.72393e-02  0.230359  0.270723   118.413
363.474
    tray number, eq.:     10.0000   actual:     14.2857
         xx,yp,yy,tt,pa:    4.35026e-02  0.270723  0.307969   116.608
356.736
    tray number, eq.:     11.0000   actual:     15.7143
         xx,yp,yy,tt,pa:    4.92820e-02  0.307969  0.340505   114.973
350.020
    tray number, eq.:     12.0000   actual:     17.1429
         xx,yp,yy,tt,pa:    5.43307e-02  0.340505  0.367457   113.611
343.325
    tray number, eq.:     13.0000   actual:     18.5714
         xx,yp,yy,tt,pa:    5.85127e-02  0.367457  0.389243   112.339
336.652

    tray number, eq.:     1.00000   actual:     1.42857
         xx,yp,yy,tt,pa:    1.76917e-03   1.76917e-03   1.55872e-02   125.000
345.033
    tray number, eq.:     2.00000   actual:     2.85714
         xx,yp,yy,tt,pa:    3.91332e-03   1.55872e-02   3.42297e-02   124.011
338.354
    tray number, eq.:     3.00000   actual:     4.28571
         xx,yp,yy,tt,pa:    6.80605e-03   3.42297e-02   5.89381e-02   122.706
```

```
     tray number, eq.:     2.00000    actual:     2.85714
          xx,yp,yy,tt,pa:    0.138065  0.438326  0.691376   87.1061    199.91
     tray number, eq.:     3.00000    actual:     4.28571
          xx,yp,yy,tt,pa:    0.526405  0.691376  0.961781   60.4608    193.85
     tray number, eq.:     4.00000    actual:     5.71429
          xx,yp,yy,tt,pa:    0.941379  0.961781  0.997992   47.8989    187.83
     tray number, eq.:     5.00000    actual:     7.14286
          xx,yp,yy,tt,pa:    0.996949  0.997992  0.999906   46.0871    181.85
     tray number, eq.:     6.00000    actual:     8.57143
          xx,yp,yy,tt,pa:    0.999885  0.999906  0.999997   45.3703    175.90
vvf,vden,vlq,denl:     592.676    2.45393e-02  0.186742   50.7494
treca:     56.8424
pfd:     206.003
vlq:    0.292554
vvf,vden,vlq,denl:     513.139    4.15052e-02  0.292554   55.0248

 areas calc. for rect. sec.; top,bot.;     56.8424    61.4762

     tray number, eq.:     1.00000    actual:     1.42857
          xx,yp,yy,tt,pa:     1.76917e-03    1.76917e-03    1.49062e-02    130.0C
 418.110
     tray number, eq.:     2.00000    actual:     2.85714
          xx,yp,yy,tt,pa:     3.80764e-03    1.49062e-02    3.18823e-02    129.03
 411.212
     tray number, eq.:     3.00000    actual:     4.28571
          xx,yp,yy,tt,pa:     6.44181e-03    3.18823e-02    5.34478e-02    127.91
 404.333
     tray number, eq.:     4.00000    actual:     5.71429
          xx,yp,yy,tt,pa:     9.78812e-03    5.34478e-02    8.01560e-02    126.67
 397.474
     tray number, eq.:     5.00000    actual:     7.14286
          xx,yp,yy,tt,pa:     1.39324e-02    8.01560e-02   0.112133    125.279
 390.634


 331.698
     tray number, eq.:     4.00000    actual:     5.71429
          xx,yp,yy,tt,pa:     1.06400e-02    5.89381e-02    9.07173e-02    121.235
 325.065
     tray number, eq.:     5.00000    actual:     7.14286
          xx,yp,yy,tt,pa:     1.55712e-02    9.07173e-02   0.129774    119.683
 318.454
     tray number, eq.:     6.00000    actual:     8.57143
          xx,yp,yy,tt,pa:     2.16317e-02   0.129774   0.175410    117.760
 311.868
     tray number, eq.:     7.00000    actual:     10.0000
          xx,yp,yy,tt,pa:     2.87129e-02   0.175410   0.225346    115.668
 305.305
     tray number, eq.:     8.00000    actual:     11.4286
          xx,yp,yy,tt,pa:     3.64614e-02   0.225346   0.276383    113.348
 298.766
     tray number, eq.:     9.00000    actual:     12.8571
          xx,yp,yy,tt,pa:     4.43808e-02   0.276383   0.324434    111.190
 292.252
     tray number, eq.:     10.0000    actual:     14.2857
          xx,yp,yy,tt,pa:     5.18369e-02   0.324434   0.366143    109.312
 285.763
     tray number, eq.:     11.0000    actual:     15.7143
          xx,yp,yy,tt,pa:     5.83089e-02   0.366143   0.400729    107.409
 279.300

     tray number, eq.:     1.00000    actual:     1.42857
          xx,yp,yy,tt,pa:     1.76917e-03    1.76917e-03    1.63293e-02    120.000
 283.020
     tray number, eq.:     2.00000    actual:     2.85714
          xx,yp,yy,tt,pa:     4.02847e-03    1.63293e-02    3.69244e-02    118.828
 276.567
```

```
    tray number, eq.:     3.00000    actual:     4.28571
         xx,yp,yy,tt,pa:    7.22420e-03   3.69244e-02   6.53974e-02   117.446
270.142
    tray number, eq.:     4.00000    actual:     5.71429
         xx,yp,yy,tt,pa:    1.16423e-02   6.53974e-02  0.103415   115.732
263.743
    tray number, eq.:     5.00000    actual:     7.14286
         xx,yp,yy,tt,pa:    1.75416e-02  0.103415  0.151445   113.834
257.372
    tray number, eq.:     6.00000    actual:     8.57143
         xx,yp,yy,tt,pa:    2.49943e-02  0.151445  0.208131   111.543
251.028
    tray number, eq.:     7.00000    actual:     10.0000
         xx,yp,yy,tt,pa:    3.37903e-02  0.208131  0.269861   108.861
244.713
    tray number, eq.:     8.00000    actual:     11.4286
         xx,yp,yy,tt,pa:    4.33688e-02  0.269861  0.330530   106.286
238.427
    tray number, eq.:     9.00000    actual:     12.8571
         xx,yp,yy,tt,pa:    5.27828e-02  0.330530  0.384858   103.721
232.171
    tray number, eq.:     10.0000    actual:     14.2857
         xx,yp,yy,tt,pa:    6.12128e-02  0.384858  0.428796   101.665
225.946

    tray number, eq.:     1.00000    actual:     1.42857
         xx,yp,yy,tt,pa:    1.76917e-03   1.76917e-03   1.71399e-02   115.0
230.694
    tray number, eq.:     2.00000    actual:     2.85714
         xx,yp,yy,tt,pa:    4.15424e-03   1.71399e-02   3.99773e-02   113.6
224.476
    tray number, eq.:     3.00000    actual:     4.28571
         xx,yp,yy,tt,pa:    7.69791e-03   3.99773e-02   7.29249e-02   112.1
218.289

    tray number, eq.:     4.00000    actual:     5.71429
         xx,yp,yy,tt,pa:    1.28104e-02   7.29249e-02  0.118607   110.159
212.134
    tray number, eq.:     5.00000    actual:     7.14286
         xx,yp,yy,tt,pa:    1.98989e-02  0.118607  0.177894   107.743
206.011
    tray number, eq.:     6.00000    actual:     8.57143
         xx,yp,yy,tt,pa:    2.90984e-02  0.177894  0.247891   105.063
199.922
    tray number, eq.:     7.00000    actual:     10.0000
         xx,yp,yy,tt,pa:    3.99597e-02  0.247891  0.322145   101.930
193.867
    tray number, eq.:     8.00000    actual:     11.4286
         xx,yp,yy,tt,pa:    5.14817e-02  0.322145  0.391802   98.7893
187.848
fv:    6.44456
vvf,vden,tvl,denl:    354.314   6.00812e-02   2.47167   55.8789
colsiz: nonstandard trays reqd, clf:   0.307698
vvf,vden,tvl,denl:    384.874   5.42275e-02   2.44097   55.1024
colsiz: nonstandard trays reqd, clf:   0.298093
bidstl: Costs of Distillation Equipment
      Rectifying Column
         6.00000   theor.,    8.00000   actual trays

        1.00000   column of diam. :    8.84725   ft.
         height(ft.):    22.0000   weight(lb):   21450.8
    Costs
      shell:    51794.6   fittings:    1008.75   sum:    52803.4
      trays, each:    1921.52    total:    15372.2
     Total, per column:    68175.5


    Total rectifying col. purchase cost:    68175.5
```

```
Stripping column
   8.00000   theor.,    11.0000   actual trays

   1.00000   column of diam. :    8.18939   ft.
     height(ft.):    28.0000   weight(lb):   25271.0
Costs
  shell:    57264.9   fittings:    1182.86   sum:    58447.8
  trays, each:    1680.18    total:    18482.0
 Total, per column:    76929.8

Total stripping col. purch. cost:    76929.8
Total distillation column cost:    145105.

Condenser(s)
  heat duty (BTU/hr):    1.93965e+07
   one condenser of area (sq.ft.):    3319.67
   purch. cost:    36837.0    TOTAL:    36837.0
   cooling water outlet T (C):    40.0000
   cooling water use (gpm):    1437.18   cost ($/yr):    172462.

   Reboiler
   heat duty(BTU/hr):    2.64848e+07   T (C):    115.000
   one reboiler of area (sq.ft.):    1765.65
   purch. cost:    27216.6   TOTAL:    27216.6

 bidstl: total purch. eq. cost:    209159.
      value of solvent lost ($/yr):    7178.11
OFINAL OUTPUT STREAMS FOR MODULE    4
      9.00000        0.          8272.27539       45.00000        0.
     116.51013     8154.95020       0.81571         0.

----
     13.00000        0.        209158.95313    30666.40039        0.
      0.          1437.17981     7178.10596       1.00000

----
OMODULE SET FOR UNIT    5
      5.00000        5.00000       29.00000        1.00000        1.00000
      2.00000        4.00000        8.00000        0.             0.
      3.00000        6.00000        5.00000       11.00000        0.
      1.00000       47.00000        0.80000        2.00000        0.40000
    100.00000        0.99000        0.50000        0.50000     -100.00000
      3.00000        1.00000        0.             3.00000
OINPUT STREAMS FOR MODULE    5
      4.00000        0.        245299.21875       35.00000       15.00000
  11651.02441     8380.43945   225267.75000        0.

----
      8.00000        0.        225492.42188      115.00000        0.
      0.           225.48952   225266.93750        0.

----

 Results of fixed bed sorption calcuations
      3.00000   beds used
    height (ft):    13.1280    diam.(ft):    11.1280
    velocities of fluid, ft./s
      superficial:    2.95653e-02    actual:    7.39133e-02
    temperatures, deg. C
      input:    35.0000    product:    40.1639
      regennt:    115.000   reg. eff.:    105.557
    Costs per bed
      sorbent:    76300.8    vessel:    52412.2
    Total purchase cost of system:    386139.
```

```
OFINAL OUTPUT STREAMS FOR MODULE     5
        6.00000          0.          237026.93750        105.55721        15.00000
     11534.51465       225.48952      225266.93750          0.

 ----
        5.00000          0.          233764.70313         40.16392        15.00000
      116.51013       8380.43945      225267.75000          0.

 ----
       11.00000          0.          386139.18750          0.                0.
        0.               0.               0.               0.

 ----
OMODULE SET FOR UNIT     6
        6.00000          2.00000        22.00000          0.                0.
        2.00000          6.00000         5.00000          0.                0.
        3.00000          3.00000         7.00000         12.00000           0.
      250.00000        350.00000         0.             250.00000           0.
       10.00000          0.
OINPUT STREAMS FOR MODULE     6
        6.00000          0.          237026.93750        105.55721        15.00000
     11534.51465       225.48952      225266.93750          0.

 ----
        5.00000          0.          233764.70313         40.16392        15.00000
      116.51013       8380.43945      225267.75000          0.

 ----
 hxcst: a.lt.amin, a=    52.2106    amin=    100.000
 hxcng: loop number     1.00000
 qo(i):     2.20378e+07    2.47925e+07    2.75472e+07    c(i):     518886.    386198.
  291920.
 hxcst: a.lt.amin, a=    26.5650    amin=    100.000
 hxcng: loop number     2.00000
 qo(i):     2.20378e+07    2.61698e+07    2.75472e+07    c(i):     518886.    325575.
  291920.
 hxcst: a.lt.amin, a=    13.4015    amin=    100.000
 hxcng: loop number     3.00000
 qo(i):     2.20378e+07    2.68585e+07    2.75472e+07    c(i):     518886.    297985.
  291920.
 hxcst: a.lt.amin, a=    6.73107    amin=    100.000
 hxcng: loop number     4.00000
 qo(i):     2.20378e+07    2.72029e+07    2.75472e+07    c(i):     518886.    292024.
  291920.
 hxcng: loop number     5.00000
 qo(i):     2.20378e+07    2.73750e+07    2.75472e+07    c(i):     518886.    281318.
  291920.
 hxcng: loop number     6.00000
 qo(i):     2.73750e+07    2.74611e+07    2.75472e+07    c(i):     281318.    286945.
  291920.
 hxcst: a.lt.amin, a=    53.7843    amin=    100.000
 hxcng: loop number     7.00000
 qo(i):     2.47064e+07    2.73750e+07    2.74611e+07    c(i):     390158.    281318.
  286945.
 hxcng: loop number     8.00000
 qo(i):     2.73750e+07    2.74181e+07    2.74611e+07    c(i):     281318.    284238.
  286945.
 hxcst: a.lt.amin, a=    29.0073    amin=    100.000
 hxcng: loop number     9.00000
 qo(i):     2.60407e+07    2.73750e+07    2.74181e+07    c(i):     330992.    281318.
  284238.
 hxcng: loop number     10.0000
 qo(i):     2.73750e+07    2.73966e+07    2.74181e+07    c(i):     281318.    282808.
  284238.
 hxcst: a.lt.amin, a=    16.3010    amin=    100.000
```

```
 hxcng: not converged in    10   loops
OFINAL OUTPUT STREAMS FOR MODULE     6
        3.00000          1.00000   232790.00000        35.00000        15.00000
     6983.70020          0.        225806.29688         0.

 ----
        7.00000          0.        233764.70313        99.16666        15.00000
      116.51013       8380.43945   225267.75000         0.

 ----
       12.00000          0.        386139.18750         0.              0.
        0.               0.             0.              0.

 ----
OMODULE SET FOR UNIT     7
        7.00000          6.00000       22.00000         3.00000         2.00000
        1.00000          2.00000        0.              0.              0.
        3.00000         15.00000       16.00000        14.00000         0.
        0.99000          0.90000        0.42000         4.00000         0.60000
        1.10000         -1.00000
OINPUT STREAMS FOR MODULE     7
        2.00000          0.        173722.78125        35.00000        15.00000
   172253.07813        931.16016      538.54059         0.

 ----
 vv,vden,vl,denl:     3294.84    4.29678e-04    1.69802    62.6642
 colsiz: nonstandard trays reqd, clf:    0.245365
 strip: Costs of Solvent Recovery Equipment
       Stripping Column
          24.1589   theor.,     40.2648   actual trays

         1.00000   column of diam. :     6.92105   ft.
           height(ft.):     86.5295   weight(lb):    55000.7

       Costs
         shell:     92212.9   fittings:     2138.46   sum:     94351.3
         trays, each:     1254.35    total:     50506.0
        Total, per column:     144857.


       Total stripping col. purchase cost:     144857.

       Temperatures, top:     35.0000   bottom:     38.3356
       heat requirements, latent:     2.83784e+06   total:     5.11915e+06
       steam use (lb/hr):     5927.40

       solvent recovery credit:    -4.69177e+06

OFINAL OUTPUT STREAMS FOR MODULE     2
       15.00000          1.00000   174099.56250        35.00000        15.00000
   174063.93750         30.24053        5.38540         0.

 ----
       16.00000          0.          2311.38330        99.16666        15.00000
 ----  877.30841       900.91962      533.15521         0.
       14.00000          0.        144857.29688      5927.39893         0.
        0.               0.      -4691766.00000         0.

 ----
OMODULE SET FOR UNIT     8
        8.00000          1.00000       32.00000         9.00000         2.00000
        4.00000          9.00000       10.00000        11.00000        13.00000
        2.00000         12.00000       14.00000         0.              0.
        4.90000          0.15600        0.30000     30000.00000         1.65000
     8000.00000        751.00000      180.00000         5.00000       300.00000
        7.50000         25.00000       40.00000        25.00000         5.00000
        1.00000          1.00000
```

```
0INPUT STREAMS FOR MODULE     8
        9.00000          0.          8272.27539        45.00000          0.
      116.51013       8154.95020        0.81571          0.

----
       10.00000          0.        205724.39063          0.               0.
        0.               0.       4739157.00000          1.00000

----
       11.00000          0.        386139.18750          0.               0.
        0.               0.             0.               0.

----
       13.00000          0.        209158.95313     30666.40039          0.
        0.            1437.17981     7178.10596          1.00000

----
 economics summary

 unit number:    1
 purchased equipment cost:          205724.
 low pressure steam, lb/hr:        0.
 high pressure steam, lb/hr:       0.
 electricity, kw:                  0.
 cooling water, gpm:               0.
 other operating expenses, $/yr:    4.73916e+06
 labor requirement, men/shift:      1.00000

 unit number:    2
 purchased equipment cost:          386139.
 low pressure steam, lb/hr:        0.
 high pressure steam, lb/hr:       0.

 electricity, kw:                  0.
 cooling water, gpm:               0.
 other operating expenses, $/yr:   0.
 labor requirement, men/shift:     0.

 unit number:    3
 purchased equipment cost:          209159.
 low pressure steam, lb/hr:         30666.4
 high pressure steam, lb/hr:       0.
 electricity, kw:                  0.
 cooling water, gpm:                1437.18
 other operating expenses, $/yr:    7178.11
 labor requirement, men/shift:      1.00000

 unit number:    4
 purchased equipment cost:          386139.
 low pressure steam, lb/hr:        0.
 high pressure steam, lb/hr:       0.
 electricity, kw:                  0.
 cooling water, gpm:               0.
 other operating expenses, $/yr:   0.
 labor requirement, men/shift:     0.

 unit number:    5
 purchased equipment cost:          144857.
 low pressure steam, lb/hr:         5927.40
 high pressure steam, lb/hr:       0.
 electricity, kw:                  0.
 cooling water, gpm:               0.
 other operating expenses, $/yr:   -4.69177e+06
 labor requirement, men/shift:     0.
```

```
Total costs by category
     (total fixed capital:    6.52689e+06  )
 category, annual cost ($/yr), cost per unit product

 capital related:        2.97626e+06   4.56205e-02
 low pressure steam :    1.46375e+06   2.24366e-02
 high pressure steam:   0.  0.
 electricity:           0.  0.
 cooling water:          172462.   2.64351e-03
 other costs:            54569.0   8.36440e-04
 labor costs:            99000.0   1.51748e-03
-----------------------------------------------------
 TOTAL:                  4.76605e+06   7.30545e-02

Total costs by process unit
  process unit, annual cost, cost per unit product

unit #   1   5.24833e+06   8.04470e-02
unit #   2   862790.    1.32249e-02
unit #   3   1.92314e+06   2.94781e-02
unit #   4   862790.    1.32249e-02
unit #   5  -4.13100e+06  -6.33205e-02
-----------------------------------------------
TOTAL:                  4.76605e+06   7.30545e-02
OFINAL OUTPUT STREAMS FOR MODULE    8
        12.00000        0.        386139.18750        0.              0.
         0.             0.             0.             0.


 ----
OEND OF EXECUTION
%
```

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