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Molecular Thermodynamics of Liquid-Liquid Equilibria of Electrolyte Solutions for Extractive Crystallization Processes

Interim Progress Report

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Abstract

In extractive crystallization, salts are precipitated from a saturated aqueous solution by extracting some of the water into a second liquid phase. Current electrolyte-thermodynamic models do not easily describe an equilibrium system with water, a partially miscible organic solvent and salt concentrations to saturation. We present a model based on Liu's local-composition/local-charge version of extended Debye-Hückel theory. The model has been extended to cover multisolvent systems and put into a framework for calculation of liquid-liquid phase equilibria. Results are presented for a system with application in extractive crystallization.

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1. Introduction

Within the last few years, there has been increasing interest in aqueous systems containing electrolytes and nonelectrolyte solvents. For systems where either the electrolyte or the nonelectrolyte is dilute in water, salting-out (Setschenow) coefficients (based on Henry's Law) can describe the effect of the salt on the solubility of the nonelectrolyte solvent. Recently the Gibbs-Duhem relation has been used in connection with Setschenow coefficients to show the effect of sparingly soluble, high-pressure gases on the solubility of a sparingly soluble salt (Corti *et al.*, 1989). For systems where neither the salt nor the nonelectrolyte can be considered dilute, other steps have to be taken.

Toward that end, two projects have been pursued in the Chemical Engineering Department at Berkeley. One project developed an equation of state valid for electrolyte-water-gas systems at elevated pressures where Henry's Law is insufficient as gas solubility becomes appreciable (Harvey and Prausnitz, 1988). Another project considers phase equilibria between two water-rich phases formed by mixtures of mutually-insoluble water-soluble polymers with salts and proteins (Haynes *et al.*, 1988). In both cases the activity of the nonelectrolyte components cannot be modeled by Henry's Law, nor can the interactions with the salt be described by simple salting-out coefficients.

In the previously discussed cases, the liquid phase(s) are mostly water. There remains a need for a thermodynamic description of electrolyte systems where the aqueous electrolyte is in equilibrium with a second liquid phase that is not mostly water. If the second liquid solvent is virtually immiscible with water, phase equilibrium can be described with a model based on Henry's Law; at present, however, no method exists for modeling phase equilibria for liquid-liquid systems where appreciable amounts of all three components (water, solvent, salt) can be found in both phases. Such systems are found, for example, in proposed extractive crystallization processes for energy-efficient recovery of salts from brines.

Extractive Crystallization for Recovery of Salts from Solution

At some stage in the recovery of many salts of industrial importance, the solid salt is recovered by crystallization from aqueous solution. In some cases, the salts are recovered from natural brines. In other cases, solid underground salt deposits are "solution-mined" by injecting water underground and recovering salt from the resulting brine. Even with conventionally-mined solid salts, coarse debris is removed by dissolving the salt and filtering the debris, and pure product is prepared by crystallization. For some salts, solubility varies appreciably with temperature such that salt can be precipitated by

heating or cooling a saturated solution. However, for many salts (*e.g.* NaCl and $NaHCO_3$), solubility does not vary appreciably with temperature, and the water must be removed by evaporation. For these salts, the energy required to evaporate the water is a significant factor in the overall process economics. (Industrial salts are typically low-cost, high-volume products.) The operating cost is reduced by using multi-effect evaporation, but this raises the capital cost of the plant. A more economic process would remove the water by extraction, without having to supply water's high heat of vaporization (Lynn and Hanson, 1984).

Recently, Weingaertner (1988) proposed precipitating salt by extracting some of the water from a saturated aqueous electrolyte solution into a second liquid phase. The second liquid phase must dissolve water (and relatively little salt), yet not be miscible with the aqueous salt solution. Ideally, little solvent should dissolve in the saturated brine. It must also be possible to regenerate the solvent without having to evaporate either water or the solvent; therefore, the solubility of water in the solvent should vary appreciably with temperature. It might be expected that a moderately polar organic solvent would fit the requirements; Weingaertner found promising results with small alcohols (propanol, butanol) and amines (di-isopropyl amine) for recovery of sodium bicarbonate and sodium chloride from water. Figures 1-1 and 1-2 show phase diagrams typical of those obtained by Weingaertner.

To design efficient separation processes, it is necessary to calculate liquid-liquid equilibria for a range of compositions and temperatures. There is at present no model capable of simultaneously describing an aqueous phase containing water, salt to saturation (perhaps 30 wt%) and 5-10 wt% organic solvent, as well as an organic phase containing solvent, about 30 wt% water and about 1 wt% salt. Because solvent regeneration occurs at temperatures significantly different from that for extraction, it is necessary that the model predict (or correlate) the effects of temperature on the coexistence curve. To illustrate, consider a model system for which there is a reasonable amount of data. Weingaertner reported data for the system water, Na_2CO_3, and n-butanol along the saturated coexistence curve from ambient temperature to the consolute temperature (about 125°C), and there are copious data for the water-salt and water-alcohol binaries. Unfortunately, because of the low solubility of salt in the organic phase, there are essentially no useful phase equilibrium data for the salt-solvent binary.

This report is concerned with development of a molecular-thermodynamic framework for describing liquid-liquid equilibria in a ternary system containing water, salt, and an organic solvent.

2. Thermodynamics of Liquid-liquid Equilibria (LLE) for Aqueous/Organic Systems with Electrolyte

To calculate compositions of coexisting phases for the extractive-crystallization process, we need to establish a basic thermodynamic framework. Most electrolyte activity-coefficient models are not directly concerned with phase equilibrium; they are generally concerned with calculating the activity of a single component. For some purposes, the desired quantity is the activity of the solvent (expressed by vapor pressure reduction or osmotic pressure), while for other purposes the desired quantity is the activity of the ions (*i.e.*, for electrochemical applications). In recent years, a few models have attempted to address vapor-liquid equilibrium (VLE); these are in general limited to systems where one of the nonelectrolytes is much more volatile than the other (*i.e.*, they are essentially used for calculating only the activity coefficient of the more volatile component) and none of the currently available models consider presence of the salt in the second fluid phase (Chen et al., 1979; Sander et al., 1986). For LLE, we must consider the presence of all components in both phases.

When we calculate phase equilibria, we equate, for each species, the chemical potential in the two phases. For electrolytes, we have a choice: either we treat each of the ions as a separate component, or we treat the neutral salt as a component. We can treat the salt as a single component because for practical purposes, the amounts of cation and anion in a phase are not independent. If one phase were appreciably enriched in, say, cations beyond what is required to balance the anions, a significant electrical potential difference between the phases would develop. The energy penalty for putting more cations into an already positively-charged phase is so high that at equilibrium, systems cannot have macroscopic charge imbalances. The requirement that the cations and anions in a given phase form an electrically neutral combination is called the assumption of electroneutrality. It does not mean that there cannot be microscopic charge separations or potential differences between phases, but it does mean that the overall composition of a phase cannot differ appreciably from neutral. For simplicity, we choose to treat the salt as a single component for calculating liquid-liquid equilibria; we calculate properties of the neutral salt by an appropriate combination of the properties of the individual ions.

Because we treat salt as a single component, we have three components (water, salt, solvent) and two phases. For a two-phase, three-component system, the phase rule gives us 3 degrees of freedom. If we fix temperature and pressure, we are left with one degree of freedom to define the system. That can be the overall composition, or the composition of one phase. Having fixed T and P, we have six composition unknowns:

mole fractions x_1, x_2, and x_3 in the two phases. We equate the chemical potentials of the three components (three equations), constrain the mole fractions to sum to unity (two equations) and fix the overall composition to define the problem.

Rather than calculating chemical potentials directly, it is convenient to refer the chemical potential μ_i of species i to a defined standard state and to express the difference from that standard state in terms of activity a_i:

$$\mu_i - \mu_i^o = RT \ln a_i \tag{2-1}$$

If we use the same standard state for i (the same μ_i^o, where superscript "o" refers to the standard state) in both phases, we can equate activities rather than chemical potentials. We can go on to relate activities to composition through the activity coefficient γ_i:

$$a_i = x_i \gamma_i \tag{2-2}$$

The equations of equilibrium are of the form:

$$(x_i \gamma_i)' = (x_i \gamma_i)'' \tag{2-3}$$

where ' and " refer to the two phases in equilibrium.

We calculate activity coefficients from an excess Gibbs energy model:

$$G^E = G - G^I = \sum_i n_i \bar{g}_i^E \tag{2-4}$$

Where superscript I refers to the ideal solution and E to the excess. Here n_i is the number of moles of component i. From the excess Gibbs energy we calculate activity coefficients:

$$RT \ln \gamma_i = \bar{g}_i^E = \left(\frac{\partial n_T g^E}{\partial n_i} \right)_{T,P,n_{j \neq i}} \tag{2-5}$$

Where g^E is the molar excess Gibbs energy and n_T the total number of moles. To calculate all the activity coefficients we need a model for G^E (or for G and G^I). The ideal Gibbs energy G^I is given by:

$$G^I = \sum_i n_i \mu_i^0 + \sum_i n_i RT \ln (x_i) \tag{2-6}$$

To calculate G^I, we need to establish standard states. When component i is in its standard state, $\gamma_i = 1$.

Standard States and Reference States

A reference state is a precisely specified physical state of matter (or a well-defined limiting condition, such as the limit of infinite dilution) in which we can measure some properties of interest. A thermodynamic standard state is the state from which we measure or calculate changes in state properties such as chemical potential. A standard state need not be physically realizable, but must be well-defined. The distinction between a standard state and a reference state becomes important for our system because we cannot use the same reference or standard state for all our species. For water, we use pure liquid water at system temperature and pressure as our reference state, but we cannot do so for salt, which does not exist as a pure liquid at system temperature. For our salt, the physical state to which we refer is the limit of infinite dilution in water -- in this limit the ratio of activity to concentration (in our case, mole fraction) approaches a physical limit, the infinite dilution activity coefficient γ_i^∞. This physical state is not appropriate for a thermodynamic standard state, however, since in the limit of infinite dilution, the chemical potential of the solute approaches $-\infty$. We therefore choose a hypothetical standard state, the "ideal dilute solution of unit concentration." This is a hypothetical standard state with a concentration of 1 (mole fraction in our case, though molality is commonly also used for salts) and an activity coefficient equal to the infinite-dilution limit. Figure 2-1 illustrates this choice with a plot of activity as a function of concentration for a typical electrolyte. As electrolyte concentration goes to zero, the ratio of activity to concentration approaches a finite limit (γ_i^∞). The dashed line is tangent to the experimental curve of activity as a function of concentration at zero concentration. Point A is the thermodynamic standard state. It is hypothetical because the experimental (or extrapolated) curve of activity *vs.* concentration does not necessarily pass through A, even if it were possible to make a solution with unit concentration. At point B the activity coefficient happens to be 1, but B is of no special significance. In sparingly soluble electrolytes, the solubility limit is reached before the curve crosses the dashed line.

For water, the thermodynamic standard state is pure liquid water at system temperature and pressure. We use the "ideal dilute solution of unit concentration" as the reference state for both salt and for organic solvent; the physical reference state for both is infinite dilution in water. This framework considers the organic solvent as a second solute, parallel to the salt, rather than to the water. By assigning solute status to the nonaqueous solvent, we avoid the complications that arise from trying to combine infinite-dilution

reference states for a solute in multiple solvents discussed by Van Ness and Abbott (1979). In our framework, we need not directly refer to the state where salt is infinitely dilute in the organic solvent. When calculating liquid-liquid equilibria, we use the same reference state (pure water for water and ideal dilute solution for salt and organic solvent) to calculate activities in both the aqueous and the nonaqueous phase. This allows us to use Equation 2-3 as our equilibrium condition.

Electrolyte Compositions and Activity Coefficients

Although we calculate phase equilibria with the neutral salt as a component, we need to refer to the individual ions when we calculate Gibbs energies from a molecular-thermodynamic model. We need to consider how to calculate mole fractions for both salts and ions, as well as how to combine ionic activity coefficients to obtain overall salt coefficients.

A strong electrolyte MX dissociates in solution to form ν_+ cations and ν_- anions:

$$MX \Rightarrow \nu_+ M^+ + \nu_- X^- \tag{2-7}$$

Because the solid salt is electrically neutral, the charges sum to zero:

$$\nu_+ z_+ + \nu_- z_- = 0 \tag{2-8}$$

where z_i is the algebraic charge on ion i. The chemical potential of the salt is related to those of the ions:

$$\mu_{MX} = \nu_+ \mu_+ + \nu_- \mu_- \tag{2-9}$$

Introducing activity coefficients:

$$\mu_{MX} = \nu_+ (\mu_+^0 + RT \ln (x_+ \gamma_+)) + \nu_- (\mu_-^0 + RT \ln (x_- \gamma_-)) \tag{2-10}$$

Rearranging, we obtain:

$$\mu_{MX} = (\nu_+ \mu_+^0 + \nu_- \mu_-^0) + RT \ln [(x_+ \gamma_+)^{\nu_+} (x_- \gamma_-)^{\nu_-}] \tag{2-11}$$

Collecting terms corresponding to standard states, composition, and activity coefficients:

$$\mu_{MX} = \mu_{MX}^0 + RT \ln [(x_+^{\nu_+} x_-^{\nu_-})(\gamma_+^{\nu_+} \gamma_-^{\nu_-})] \tag{2-12}$$

The standard-state chemical potential of the salt, μ_{MX}^{o} is that defined for the ideal dilute solution (in water) at unit mole fraction; when we calculate phase equilibria we use the same standard state for both phases. Often we are only interested in $\gamma_{\pm}$, the mean activity coefficient of the neutral salt, defined by:

$$\gamma_{\pm}^{\nu} = (\gamma_{+}^{\nu_{+}} \gamma_{-}^{\nu_{-}}) \tag{2-13}$$

where $\nu = \nu_{+} + \nu_{-}$.

When a strong electrolyte is dissolved in a mixed solvent, it is easy to define the mole fractions of the ions and the solvents; for each species:

$$x_i = n_i / (n_{+} + n_{-} + n_w + n_s) \tag{2-14}$$

There are two conventions for defining the mole fraction of the salt, x_{MX}. For aqueous solutions, Robinson and Stokes (1965) write:

$$x_{MX} = \frac{\nu n_{MX}}{\nu n_{MX} + n_w}$$

or

$$x_{MX} = \frac{n_{MX}}{\nu n_{MX} + n_w} \tag{2-15}$$

Robinson and Stokes prefer the second definition (Eq. 2-15), so that the mole fraction of salt is related to the mole fractions of the ions by:

$$\nu x_{MX} = \nu_{+} x_{+} + \nu_{-} x_{-} \tag{2-16}$$

We follow this choice. The salt mole fraction defined by Equation 2-15 cannot equal unity; for pure salt it becomes $1/\nu$. This means our thermodynamic standard state for salt (ideal dilute solution at unit mole fraction) must always be hypothetical. If there is also an organic solvent, we extend Eq. 2-15:

$$x_{MX} = \frac{n_{MX}}{\nu n_{MX} + n_w + n_s} \tag{2-17}$$

From equation 2-17 it follows that:

$$x_w + x_s + \nu\, x_{MX} = 1 \qquad (2\text{-}18)$$

rather than $$x_w + x_s + x_{MX} = 1$$

where x_w and x_s are the mole fractions of water and the organic solvent. Keeping in mind that x_{MX} is defined by Eq. 2-15, we can now write $x_+ = \nu_+ x_{MX}$ and $x_- = \nu_- x_{MX}$; substituted into equation 2-12 that gives:

$$\mu_{MX} - \mu^0_{MX} = RT \ln [(\nu_+^{\nu_+} x_{MX}^{\nu_+})(\nu_-^{\nu_-} x_{MX}^{\nu_-})\gamma_\pm^{\nu}] \qquad (2\text{-}19)$$

which we can rearrange to give:

$$\mu_{MX} - \mu^0_{MX} = \nu RT \ln [x_{MX}\, \gamma_\pm] + RT(\nu_+ \ln \nu_+ + \nu_- \ln \nu_-) \qquad (2\text{-}20)$$

In Eq. 2-20, the last term in parentheses is zero for 1-1 electrolytes. For electrolytes with higher charges, the term is non-zero, but when we equate the salt chemical potential in one phase to that in the other, it will cancel.

We use Eq. 2-20 to define chemical potential of the salt. Given that we use the same standard state for salt in two liquid phases ' and ", the equations of equilibrium are:

$$(x_{MX}\, \gamma_\pm)' = (x_{MX}\, \gamma_\pm)'' \qquad (2\text{-}21)$$

for the salt, where x_{MX} is defined as in Eq. 2-15. For the water:

$$(x_w\, \gamma_w)' = (x_w\, \gamma_w)'' \qquad (2\text{-}22)$$

and for the solvent:

$$(x_s\, \gamma_s)' = (x_s\, \gamma_s)'' \qquad (2\text{-}23).$$

3. Excess Gibbs Energy Model

We calculate the Gibbs energy of the system by summing the contributions of each species in solution. Although each molecule or ion in solution can interact with every other, intermolecular forces (other than electrostatic) are short range giving rise to local contributions to the Gibbs energy. We calculate the Gibbs energy of each particle by constructing an arbitrary division between the volume immediately surrounding a particle (in which both short and long range forces act) and the range outside that volume (in which only long range electrostatic forces act). Figure 3-1 gives a schematic picture showing the domain of short-range interactions.

We express the excess Gibbs energy of the system as the sum of local and electrostatic terms:

$$G^E = G^{lc} + G^{el}$$

The volume of a local cell (*i.e.*, a region in space containing a species plus its first coordination shell) is defined by a cutoff radius r*, somewhat larger than that of the central species. The value of r* only affects the calculation of the electrostatic contribution to the excess Gibbs energy. The significance of the cutoff radius is indicated by Equation 3.2-8.

Our model is similar to that of Liu, (1988). The average composition within the local cell is the "local composition" around a given species. Each species has a "coordination number," the number of particles within the first coordination shell. Each species can have a different coordination number, and the sizes of the species can be taken into account by using volume fraction for the local composition. Although this flexibility is built into the model, we fix the coordination number for all species at 6 and use simple mole fractions rather than volume fractions for these first calculations.

Within the cutoff radius, we make no attempt to calculate the energies between species from first principles; we follow the tradition of local-composition models (*e.g.* NRTL, Wilson, and UNIQUAC) by using Boltzmann factors in conjunction with exchange energies (when one particle is exchanged for another within the first coordination shell) as adjustable parameters.

Molecular species are assumed to interact only with immediate neighbors. Because electrostatic potentials between ions decline as $1/r$ (rather than as $1/r^6$ for neutral species), ions interact not only with neighbors in the first coordination shell (FCS) but with a large sea of charged species around them. We calculate the electrostatic interaction energies by solving the Poisson-Boltzmann Equation for the distribution of the charged species with an approximation similar to that of Debye and Hückel. The key difference is in the boundary

conditions: we apply the Poisson-Boltzmann equation only outside the cutoff radius and require the integrated charge density to balance the *net local* charge (within the short-range volume) rather than the charge of the central ion. For ions within the FCS, both electrostatic and nonelectrostatic energies are included in the local-composition energy term. Our model differs from earlier models (Chen *et al.*, 1979, Haghtalab and Vera, 1988, Sander *et al.*, 1986) that mix electrostatic with nonelectrostatic energy in two ways: (1) the earlier models constrain local compositions to be electrically neutral, and (2) they calculate electrostatic interactions between all ions in the system *including* nearest neighbors.

An important advantage of our model is that by separating Gibbs energy calculations as indicated above, we extend the valid concentration range for the approximation of Debye and Hückel by reducing the apparent charge density. The amount by which charge density is reduced depends on both the system and the concentration. At low salt concentration, almost all ions are surrounded by water; the electrostatic contribution then collapses to the Debye-Hückel limiting law. At higher salt concentrations, the number of counterions near each ion rises, reducing or even eliminating the electrostatic contribution as the cells become neutral. For some salts at higher concentrations, the number of counterions in the FCS can more than cancel the charge of a central ion.

Our method of dividing the energy contributions was first suggested by Liu *et al.* , (1988). It gives significantly improved results compared with those of other methods for combining electrostatic and local-composition models (Liu *et al.*, 1989). The model of Liu *et al.* was developed for single salts in water; they only report an explicit expression for the mean ionic activity coefficient. We have extended that work to ternary (water/salt/solvent) systems; we derive explicit expressions for the activity coefficients of all species present. The short-range local-composition model is described in Section 3.1; electrostatic contributions are described in Section 3.2.

Our model does not address the issue of how to combine consistently an electrostatic contribution to free energy derived in the statistical-mechanical framework of MacMillan and Mayer with a contribution due to short range forces calculated in the usual framework of Lewis and Randall. Although questions about the proper way to combine such terms have been raised by Cardoso and O'Connell (1987), the electrostatic contributions in our case are not rigorously derived in the framework of MacMillan and Mayer. Our model is not rigorous in a statistical-mechanical sense; it must be considered as a phenomenological model based on insight from molecular physics.

3.1 Local-Composition Model

We calculate the total potential energy U due to forces between nearest neighbors by summing the contributions of each component in the system:

$$U = \sum_i n_i \langle u \rangle_i \tag{3.1-1}$$

where n_i is the number of moles of species i, and $\langle u \rangle_i$ the average energy of a mole of i. The average energy of a particle i depends on the values of the interaction energies and on the average composition of the FCS. We express the composition of the FCS in terms of the local mole fraction of species j around central species i, x_{ji}. The average energy of a mole of i can then be expressed in terms of the sums of the microscopic energy terms:

$$\langle u \rangle_i = N_A \frac{Z_i}{2} (x_{wi}\varepsilon_{wi} + x_{si}\varepsilon_{si} + x_{ci}\varepsilon_{ci} + x_{ai}\varepsilon_{ai}) \tag{3.1-2}$$

where ε_{ji} is the pair interaction energy of a molecule (or ion) of j near molecule (or ion) i and subscripts w, s, c, and a refer to water, solvent, cation, and anion respectively. N_A is Avogadro's Number. The coordination number Z_i is the number of nearest neighbors of i; the factor of 2 is necessary because only half of the energy of a pair interaction can be associated with each member of the pair. Following Wilson (1964), we relate the local compositions x_{ji} to overall composition through Boltzmann factors:

$$\frac{x_{ji}}{x_{ki}} = \frac{x_j}{x_k} \exp\left[\frac{-(\varepsilon_{ji} - \varepsilon_{ki})}{c\,RT}\right] \equiv \frac{x_j}{x_k} \Lambda_{jki} \tag{3.1-3}$$

For consistency with Wilson's three parameter equation, we have incorporated a proportionality factor c (Renon and Prausnitz, 1969). Equation 3.1-3 gives only ratios of local mole fractions; to calculate individual local mole fractions we must normalize. For example, to calculate the local mole fraction of a species i about a water molecule, we use Equation 3.1-3 to give the ratio of the local mole fraction of *each* species near water to the local mole fraction of water about water (x_{iw}/x_{ww}):

$$\frac{x_{jw}}{x_{ww}} = \frac{x_j}{x_w} \exp\left[\frac{-(\varepsilon_{jw} - \varepsilon_{ww})}{c\,RT}\right] \equiv \frac{x_j}{x_w} \Lambda_{jww} \tag{3.1-3a}$$

We require that the sum of all the local mole fractions about water be unity ($x_{ww} + x_{sw} + x_{aw} + x_{cw} = 1$). Dividing by the sum of the four local mole fractions about water gives the following:

$$x_{iw} = \frac{x_i \Lambda_{iww}}{x_w + x_s \Lambda_{sww} + x_c \Lambda_{cww} + x_a \Lambda_{aww}} \qquad (3.1\text{-}4)$$

Here we have arbitrarily used water as the reference species, *i.e.* we have used the difference between ε_{iw} and ε_{ww} to determine the ratio of the local mole fraction of each species to the local mole fraction of water. Since we normalize, we could have used *any* species as the basis for our ratios. Using water is merely a notational convenience; it is unrelated to the choice of thermodynamic reference state.

Note that we do not make the assumption of local electroneutrality used in many electrolyte activity coefficient models (Chen *et al.*, 1979; Haghtalab and Vera, 1989); the net local charge is a parameter we use in our model of electrostatic interactions. We can go on to calculate local energies:

$$\langle u \rangle_w = \left(\frac{N_A Z_w}{2} \right) \frac{x_w \varepsilon_{ww} + x_s \varepsilon_{sw} \Lambda_{sww} + x_c \varepsilon_{cw} \Lambda_{cww} + x_a \varepsilon_{aw} \Lambda_{aww}}{x_w + x_s \Lambda_{sww} + x_c \Lambda_{cww} + x_a \Lambda_{aww}} \qquad (3.1\text{-}5)$$

This equation gives us species energies as a function of T and overall composition. To calculate Helmholtz energy, we use the Gibbs-Helmholtz relation:

$$\frac{\partial(A/T)}{\partial(1/T)} = U \quad \text{or} \quad \frac{\partial(A^E/T)}{\partial(1/T)} = U^E \qquad (3.1\text{-}6)$$

To find A^E we need a relationship for U^E; but U^E is $U - U^o$. Since the standard state for water is pure water and the standard state of the ions and the alcohol is infinite dilution at unit concentration, the excess energy for any molecule or ion is its energy in the real system less that when surrounded by water.

$$U^E = U - U^o = U - N \sum_i \frac{x_i Z_i}{2} \varepsilon_{wi} \qquad (3.1\text{-}7)$$

Assuming that the energy parameters ε_{ij} do not depend on temperature, we can integrate equation (3.1-6):

$$\frac{A^E}{T} - \frac{A^E}{T^*} = \int_{1/T^*}^{1/T} U^E \, d(1/T) \qquad (3.1\text{-}8)$$

Where T* is an arbitrary reference temperature; we let $1/T^* = 0$. At the lower limit of integration, all Λ go to unity and local composition is the same as global composition. Since A^E is finite at T*, A^E/T^* is zero. For a liquid system at near-atmospheric pressure, the PV product is small relative to interaction energies and the Helmholtz energy of mixing at constant volume is approximately equal to the Gibbs energy of mixing at constant pressure (Hildebrand and Scott, 1950).

For the four-component (water, solvent, cation, anion) system, the contribution of short-range forces to the molar excess Gibbs energy g^E is given by:

$$\frac{g^E}{RT} = \frac{-c}{2}\left[\begin{array}{l} Z_w x_w \ln(x_w + x_s\Lambda_{sww} + x_c\Lambda_{cww} + x_a\Lambda_{aww}) \\ + Z_s x_s \ln(x_w + x_s\Lambda_{sws} + x_c\Lambda_{cws} + x_a\Lambda_{aws}) \\ + Z_c x_c \ln(x_w + x_s\Lambda_{swc} + x_c\Lambda_{cwc} + x_a\Lambda_{awc}) \\ + Z_a x_a \ln(x_w + x_s\Lambda_{swa} + x_c\Lambda_{cwa} + x_a\Lambda_{awa}) \end{array}\right] \quad (3.1\text{-}9)$$

Before we differentiate this expression to obtain activity coefficients, let us pause to consider the number of adjustable parameters we have introduced.

Our ternary (water/salt/solvent) system has four species in the Gibbs energy model. That gives 16 possible energy parameters ε_{ij}. We can reduce this considerably. First, we use Brønsted's rule to set x_{cc} and x_{aa} to zero (or equivalently, set ε_{cc} and ε_{aa} arbitrarily high). For each binary, we can also set $\varepsilon_{ij} = \varepsilon_{ji}$. That leaves 8 parameters, but not all of them are independent. Because only differences in ε_{ij} show up, we are free to set one of the 8 ε_{ij} arbitrarily; alternatively we can set ε_{ww} for water and and ε_{ss} for the solvent to give the correct energies of vaporization (see Appendix II). If we do that, we are left with only 6 adjustable parameters for the ternary system, and all but ε_{as} and ε_{cs} can be fit to readily available binary data. (For many systems there are little or no useful data for the salt/solvent binary).

We also have to fix the 4 coordination numbers Z_i. Liu *et al.* (1988), showed that within a reasonable range of values, adjusting the coordination number had little effect on the ability of the model to fit activity coefficient data. We fix Z_i at 6 for all components. The coordination numbers Z_i play a role equivalent to the c parameter in the three-parameter Wilson equation (Renon and Prausnitz, 1968). With the coordination numbers set to 6, it is not necessary to also adjust the parameter c to allow calculation of liquid-liquid phase splitting. We set the value of c to unity.

We can now proceed to calculate activity coefficients by differentiation of our excess Gibbs energy expression.

$$\ln \gamma_i^{lc} = \frac{1}{RT}\left(\frac{\partial n_T g^E}{\partial n_i}\right)_{T,P,n_{j\neq i}} \tag{3.1-10}$$

Applying Equation 3.1-10 to Equation 3.1-9, we obtain for the cation:

$$\ln \gamma_c^{lc} = \frac{-1}{2}\left[\begin{array}{c} \dfrac{Z_w x_w \Lambda_{cww}}{x_w + x_s \Lambda_{sww} + x_c \Lambda_{cww} + x_a \Lambda_{aww}} \\ + \dfrac{Z_s x_s \Lambda_{cws}}{x_w + x_s \Lambda_{sws} + x_c \Lambda_{cws} + x_a \Lambda_{aws}} \\ + \dfrac{Z_a x_a \Lambda_{cwa}}{x_w + x_s \Lambda_{swa} + x_c \Lambda_{cwa}} \\ + Z_c \ln (x_w + x_s \Lambda_{swc} + x_a \Lambda_{awc}) \\ - (Z_w x_w + Z_s x_s + Z_c x_c + Z_a x_a) \end{array}\right] \tag{3.1-11}$$

Similarly, for the anion:

$$\ln \gamma_a^{lc} = \frac{-1}{2}\left[\begin{array}{c} \dfrac{Z_w x_w \Lambda_{aww}}{x_w + x_s \Lambda_{sww} + x_c \Lambda_{cww} + x_a \Lambda_{aww}} \\ + \dfrac{Z_s x_s \Lambda_{aws}}{x_w + x_s \Lambda_{sws} + x_c \Lambda_{cws} + x_a \Lambda_{aws}} \\ + \dfrac{Z_c x_c \Lambda_{awc}}{x_w + x_s \Lambda_{swc} + x_a \Lambda_{awc}} \\ + Z_a \ln (x_w + x_s \Lambda_{swa} + x_c \Lambda_{cwa}) \\ - (Z_w x_w + Z_s x_s + Z_c x_c + Z_a x_a) \end{array}\right] \tag{3.1-12}$$

The local-composition contribution to the mean ionic activity coefficient for a 1:1 electrolyte is therefore:

$$\ln \gamma_{\pm}^{lc} = \frac{-1}{4} \left[\begin{array}{c} \dfrac{Z_w x_w (\Lambda_{aww} + \Lambda_{cww})}{x_w + x_s \Lambda_{sww} + x_c \Lambda_{cww} + x_a \Lambda_{aww}} \\[2ex] + \dfrac{Z_s x_s (\Lambda_{cws} + \Lambda_{aws})}{x_w + x_s \Lambda_{sws} + x_c \Lambda_{cws} + x_a \Lambda_{aws}} \\[2ex] + \dfrac{Z_c x_c \Lambda_{awc}}{x_w + x_s \Lambda_{swc} + x_a \Lambda_{awc}} + \dfrac{Z_a x_a \Lambda_{cwa}}{x_w + x_s \Lambda_{swc} + x_c \Lambda_{cwa}} \\[2ex] + Z_c \ln (x_w + x_s \Lambda_{swc} + x_a \Lambda_{awc}) \\ + Z_a \ln (x_w + x_s \Lambda_{swa} + x_c \Lambda_{cwa}) \\[2ex] -2 (Z_w x_w + Z_s x_s + Z_c x_c + Z_a x_a) \end{array} \right] \qquad (3.1\text{-}13)$$

Expressions for the contribution of short-range forces to the activity coefficients for water and solvent are similar to those for the anion and cation; they are given in Appendix I.

3.2 Electrostatic Interactions

There are two contributions to the electrostatic energy of an ion. The first is the "Born" energy, which arises when an ion is in a medium with a dielectric constant different from that of water (the standard state). This energy can often be neglected since it is usually much smaller than energies due to ion solvation (Harvey, 1989). The second contribution is due to ion-ion interactions. The electrostatic interaction-energy model we use is similar in form to the extended Debye-Hückel model. However, when calculating the energetic contributions to the Helmholtz energy of an ion, we do not include the contributions from ions that are in the first coordination shell. Those energies are included in the local-composition term. (They do not show up explicitly, since we do not calculate exchange energies from first principles; but since we exclude them here, they are automatically included when the ion-ion nearest-neighbor energy parameters ε_{ca} and ε_{ac} are regressed.) We start by applying the Poisson-Boltzmann equation to our system.

Poisson's equation (given here in radial coordinates) relates the divergence of the electric field $\nabla^2\psi$ to the local charge density ρ and the dielectric constant D:

$$\nabla^2\psi = \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{\partial\psi}{\partial r}\right) = \frac{-4\pi\rho}{D} \qquad (3.2\text{-}1)$$

We assume that ions arrange themselves in the field in a Boltzmann distribution:

$$\rho = \frac{1}{V}\sum_i n_i z_i e \exp\left(\frac{-z_i e \psi}{kT}\right) \qquad (3.2\text{-}2)$$

where n_i is the number of ions of charged species i and V is the total volume. Combining 3.2-1 and 3.2-2 gives the Poisson-Boltzmann equation:

$$\nabla^2\psi = \frac{-4\pi}{DV}\sum_i n_i z_i e \exp\left(\frac{-z_i e \psi}{kT}\right) \qquad (3.2\text{-}3)$$

We expand the exponential:

$$\sum_i n_i z_i e \exp\left(\frac{-z_i e \psi}{kT}\right) = \sum_i n_i z_i e - \sum_i n_i z_i e\left(\frac{-z_i e \psi}{kT}\right) + \sum_i \frac{n_i z_i e}{2!}\left(\frac{-z_i e \psi}{kT}\right)^2 + \ldots$$

...(3.2-4)

The first term in the series is zero because the solution as a whole is electrically neutral.; we keep the second and neglect the third (which is also zero for symmetrical electrolytes):

$$\nabla^2 \psi = \frac{4\pi e^2}{DVkT} \sum_i n_i z_i^2 \psi \equiv \kappa^2 \psi \qquad (3.2\text{-}5)$$

Equation 3.2-5 defines κ, the inverse Debye length. This differential equation has the solution:

$$\psi = \frac{A \exp(-\kappa r)}{r} + \frac{B \exp(+\kappa r)}{r} \qquad (3.2\text{-}6)$$

where A and B are constants to be determined by the boundary conditions. To keep ψ finite as $r \rightarrow \infty$, we set $B = 0$. Constant A is found by requiring that the charge outside r* (the radius of a local cell) balance the *net charge of the cell* (which we calculate from our local composition expression). By contrast, in the classical Debye-Hückel derivation, the charge outside the ion is required to balance the *charge of the ion.* For the charge distribution around a cation we have:

$$\rho_c = \frac{-D}{4\pi r^2} \frac{d}{dr}\left(r^2 \frac{d\psi}{dr}\right) = -\frac{AD\kappa^2}{4\pi r} \exp(-\kappa r) \qquad (3.2\text{-}7)$$

To balance charge we require:

$$\int_{r_c^*}^{\infty} 4\pi r^2 \rho_c \, dr = -e\,(z_c + Z_c x_{ac} z_a) \qquad (3.2\text{-}8)$$

where r* is the radius of the first coordination shell. Following Liu, we use $r_c^* = (r_c + 1.5r_a)$ and $r_a^* = (r_a + 1.5r_c)$. Substituting the equation 3.2-7 for ρ, we can solve for the constant A:

$$A = -\frac{e\,(z_c + Z_c x_{ac} z_a)}{D\,(1 + \kappa r^*)} \exp(\kappa r^*) \qquad (3.2\text{-}9)$$

and the electric field ψ_c about a cation is:

$$\psi_c = -\frac{e}{D}\left(z_c + \frac{Z_c z_a x_a \Lambda_{awc}}{x_w + x_s \Lambda_{swc} + x_a \Lambda_{awc}}\right) \frac{\exp[\kappa(r_c^* - r_c)]}{(1+\kappa r_c^*) r_c} \qquad (3.2\text{-}10)$$

This expression for the electric field is valid outside the cell radius r*; it includes the effects of the central cell and the ions external to it. Because we want to calculate the contribution of each ion to the total energy, we need to calculate the electric field at the surface of the central ion due to all other ions. Since the field we have calculated is the total field due to all ions in the system, we must subtract the contribution of the central ion itself to the field. (The so-called self-energy due to the ion's "interaction" with its own electric field should not be counted here; it belongs in the standard state or in the Born term). The field around a point charge is:

$$\psi_{self} = \frac{z\,e}{Dr} \tag{3.2-11}$$

The energetic contribution per ion due to the arrangement of ions is given by the product of each ion's charge with the net external field at its radius. For a cation:

$$\varepsilon_c^{el} = \frac{z_c\,e\,(\psi_c - \psi_{self})}{2} \tag{3.2-12}$$

The factor of 1/2 is necessary to avoid double counting of ions -- once as a central ion and once as part of the field. Substituting 3.2-9 and 3.2-10 into the above expression yields:

$$\varepsilon_c^{el} = \frac{z_c\,e^2}{2Dr_c}\left[\left(z_c + \frac{Z_c z_a x_a \Lambda_{awc}}{x_w + x_s\Lambda_{swc} + x_a\Lambda_{awc}}\right)\frac{\exp\,[\kappa(r_c^* - r_c)]}{(1+\kappa r_c^*)} - z_c\right] \tag{3.2-13}$$

where r_c is the radius of the cation. We sum these contributions over all the charged species to get the electrostatic contribution to the Helmholtz energy of the system, and differentiate to get activity coefficients for all species. The electrostatic contribution to the Helmholtz energy is:

$$\frac{A^{el}}{N_A} = \frac{n_c z_c e^2}{2Dr_c}\left[\left(z_c + \frac{Z_c z_a x_a \Lambda_{awc}}{x_w + x_s\Lambda_{swc} + x_a\Lambda_{awc}}\right)\frac{\exp\,[\kappa(r_c^* - r_c)]}{(1+\kappa r_c^*)} - z_c\right]$$
$$+ \frac{n_a z_a e^2}{2Dr_a}\left[\left(z_a + \frac{Z_a z_c x_c \Lambda_{cwa}}{x_w + x_s\Lambda_{swa} + x_c\Lambda_{cwa}}\right)\frac{\exp\,[\kappa(r_a^* - r_a)]}{(1+\kappa r_a^*)} - z_a\right] \tag{3.2-14}$$

For the cation, the electrostatic contribution to the activity coefficient is given by:

$$\ln \gamma_c^{el} = \frac{z_c e^2}{2Dr_c kT}\left[\left(z_c + \frac{Z_c z_a x_a \Lambda_{awc}}{x_w + x_s\Lambda_{swc} + x_a\Lambda_{awc}}\right)\frac{\exp\left[\kappa(r_c^*-r_c)\right]}{(1+\kappa r_c^*)} - z_c\right] \quad (3.2\text{-}15)$$

Using similar arguments, the electrostatic contribution to the activity coefficient of the anion is:

$$\ln \gamma_a^{el} = \frac{z_a e^2}{2Dr_a kT}\left[\left(z_a + \frac{Z_a z_c x_c \Lambda_{cwa}}{x_w + x_s\Lambda_{swa} + x_c\Lambda_{cwa}}\right)\frac{\exp\left[\kappa(r_a^*-r_a)\right]}{(1+\kappa r_a^*)} - z_a\right] \quad (3.2\text{-}16)$$

There are two comments about the differentiation of G^E to give γ. Properly, the activity coefficient is given by:

$$\ln \gamma_i = \frac{1}{RT}\left(\frac{\partial n_T g^E}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \frac{1}{RT}\left(\frac{\partial n_T a^E}{\partial n_i}\right)_{T,V,n_{j\neq i}} \quad (3.2\text{-}17)$$

where the differentiation is with respect to n_i at constant $n_{j\neq i}$. This constraint presents a problem for electrolytes if individual ionic activity coefficients are calculated. If we were to compute the actual change in Gibbs energy needed to add cations at constant number of anions, we would have a huge contribution due to charging the solution as a whole; subsequent addition of the appropriate number of anions would cancel this contribution. The experiment implied by the differentiation in equation 3.2-26 is not physically achievable; we can only add or remove neutral combinations of ions to a phase. Since each phase is electrically neutral and we only use mean ionic activity coefficients for neutral combinations of charged species, there is no energy due to charging a phase; neglecting net charge gives the correct phase equilibria. We follow the normal procedure of ignoring the energy due to charge imbalance implied in the above equation.

Second, and possibly more serious, we follow Liu in that we do not carry the differentiation with respect to n_i into the local composition term. If we apply the chain rule for differentiation to equation 3.2-15, we realize that the charge of a local cell depends on overall composition; the local-cell charge should therefore be a function of n_i as well.

4. Results for Extractive Crystallization Systems

Weingaertner (1988) studied a number of alternatives for using extractive crystallization to produce industrial salts. To determine whether the preliminary version of the model is able to describe these systems, we attempted to fit phase equilibrium data for one of the systems he measured. The process Weingaertner developed to produce Na_2CO_3 uses normal butanol to extract water from a saturated Na_2CO_3 solution.

For the butanol/water/Na_2CO_3 system, we first fit the four parameters for the butanol-water binary. The butanol-butanol and water-water parameters were set to give the correct molar energy of vaporization at 25 °C as shown in Appendix II. Then the butanol-water and water-butanol parameters were adjusted to fit the salt-free liquid-liquid equilibrium curve. To reproduce the salt-free LLE data with sufficient accuracy, it was necessary to make the two cross-parameters temperature dependent. The parameters were fit to LLE data from 25 to 111 °C; the consolute point is at 125 °C. Results of the fit are shown in Figure 4-1.

There are six unknown energy parameters in the water-salt binary. To reduce the number of fitted parameters, we set $\varepsilon_{ij} = \varepsilon_{ji}$, reducing the number of parameters to three. There are also a number of physical parameters in the electrolyte model: the dielectric constant of water and the solution molar density, which go into the Debye-Hückel constant, and the radii of the two ionic species. The properties of water were set to their usual values at 25°C (Robinson and Stokes, 1965); ionic radii were arbitrarily fixed at 2 Å. The three energy parameters were then adjusted to fit mean ionic activity coefficient data (Robinson and Stokes, 1965) for the aqueous salt solution at 25 °C. The results of the fit are shown in figure 4-2. The fit is relatively poor, principally as a result of arbitrarily fixing the ionic radii at 2 Å, rather than using fitted radii. At the low salt concentration limit, some deviations may also be due to neglecting the combination of some of the carbonate ion with water to form bicarbonate and hydroxide. These parameters were not considered to depend on temperature.

With water-salt and water-alcohol parameters fit to the binary data, we then used the available ternary data to determine the salt-alcohol parameters. Two parameters, the butanol-cation and butanol-anion interaction energies, were fit to the available data. Values of all fitted parameters are given in Table 4-1. In the temperature range for which the butanol-water binary was adequately fit, Weingaertner measured seven ternary LLE points. Three points (at 50, 100, and 150 °C) were for the two-liquid system saturated with salt; four more (all at 100 °C) were for various degrees of subsaturation with respect to salt.

Results for all seven points are given in Table 4-2; the results for the salt-saturated points are shown in Figure 4-3.

The equations given in this report do not allow us to predict the solid salt-liquid equilibrium. When calculating our liquid-liquid equilibria we fix the *total* amount of salt in the liquid feed to our flash calculation at a value that will allow a match to the measured solubility. Salt is free to distribute between the liquid phases. Agreement with experiment is quite good, although the data show more salting out of the butanol from the aqueous phase than the model, especially at 150 °C. This upper temperature is beyond that at which the salt-free model is reliable, however; the consolute temperature for the salt-free binary is about 125 °C, and we only fit data to 111 °C. We cannot evaluate our ability to fit the salt content of the organic phase, since that was below the detection limit in all of Weingaertner's experimental points. We calculate values that are also below the detection limit. The model does a good job of predicting the water content of the organic phase.

5. Conclusions

The model of Liu *et al.* has been extended for use in liquid-liquid equilibrium calculations needed for extractive crystallization process design. To do this, the model was modified to include a second solvent and explicit expressions were derived for the activity coefficients of all components. Thermodynamic standard states were defined that allow us to perform phase equilibrium calculations using activity coefficients from a semi-empirical model for the excess Gibbs energy. Computer programs have been written that allow calculation of activity coefficients from composition given fixed energy parameters; this forms the basis for another program that calculates liquid-liquid equilibria. In addition, separate programs have been written to allow energy parameters to be fit to salt-free LLE data, to electrolyte activity-coefficient data, or to ternary salt/water/solvent LLE data.

Results to date are promising. Although the model is far from optimized, it is capable of describing the water-alcohol-salt system with a reasonable number of adjustable parameters. Further work will focus on tightening model assumptions (such as evaluating the quantitative contribution of the Born term), including better values for physical parameters (such as ion radii and mixture dielectric constants) and on using the model to describe other multisolvent electrolyte systems. Use of the model to calculate vapor-liquid equilibrium will also be explored. Ongoing experiments on other systems of interest for extractive crystallization will provide the more accurate data needed to test the model's ability to calculate the solubility of sparingly soluble salts in an organic phase.

6. Appendix I

The contribution of short-range forces to the activity coefficient of water and the solvent are given below:

$$\ln \gamma_s^{lc} = \frac{-1}{2} \left[\begin{array}{c} \dfrac{Z_w x_w \Lambda_{sww}}{x_w + x_s \Lambda_{sww} + x_c \Lambda_{cww} + x_a \Lambda_{aww}} \\ + \dfrac{Z_s x_s \Lambda_{sws}}{x_w + x_s \Lambda_{sws} + x_c \Lambda_{cws} + x_a \Lambda_{aws}} \\ + \dfrac{Z_c x_c \Lambda_{swc}}{x_w + x_s \Lambda_{swc} + x_a \Lambda_{awc}} \\ + Z_s \ln (x_w + x_s \Lambda_{sws} + x_a \Lambda_{aws} + x_c \Lambda_{cws}) \\ - (Z_w x_w + Z_s x_s + Z_c x_c + Z_a x_a) \end{array} \right] \qquad (I\text{-}1)$$

$$\ln \gamma_w^{lc} = \frac{-1}{2} \left[\begin{array}{c} \dfrac{Z_w x_w}{x_w + x_s \Lambda_{sww} + x_c \Lambda_{cww} + x_a \Lambda_{aww}} \\ + \dfrac{Z_s x_s}{x_w + x_s \Lambda_{sws} + x_c \Lambda_{cws} + x_a \Lambda_{aws}} \\ + \dfrac{Z_c x_c}{x_w + x_s \Lambda_{swc} + x_a \Lambda_{awc}} \\ + Z_w \ln (x_w + x_s \Lambda_{sww} + x_a \Lambda_{aww} + x_c \Lambda_{cww}) \\ - (Z_w x_w + Z_s x_s + Z_c x_c + Z_a x_a) \end{array} \right] \qquad (I\text{-}2)$$

Appendix II

We set the values of the interaction energy for water and solvent to match the known energy of vaporization:

$$\Delta U_i^{vap} = \frac{1}{2} N_A Z_i \varepsilon_{ii} \qquad \text{(II-1)}$$

The energy of vaporization is calculated from the readily available enthalpy of vaporization:

$$\Delta U_i^{vap} = \Delta H_i^{vap} - P\Delta V_i^{vap} \qquad \text{(II-2)}$$

The volume change of vaporization ΔV^{vap} is the molar volume of i in the vapor phase less the molar volume of i in the liquid phase. At temperatures remote from critical, the volume of the saturated liquid is negligible relative to that of the saturated vapor, so ΔV^{vap} is approximately equal to the vapor molar volume. Further, at the temperatures of interest, the saturated vapor is close enough to an ideal gas that we may substitute RT for PV^{vap}. This lets us write:

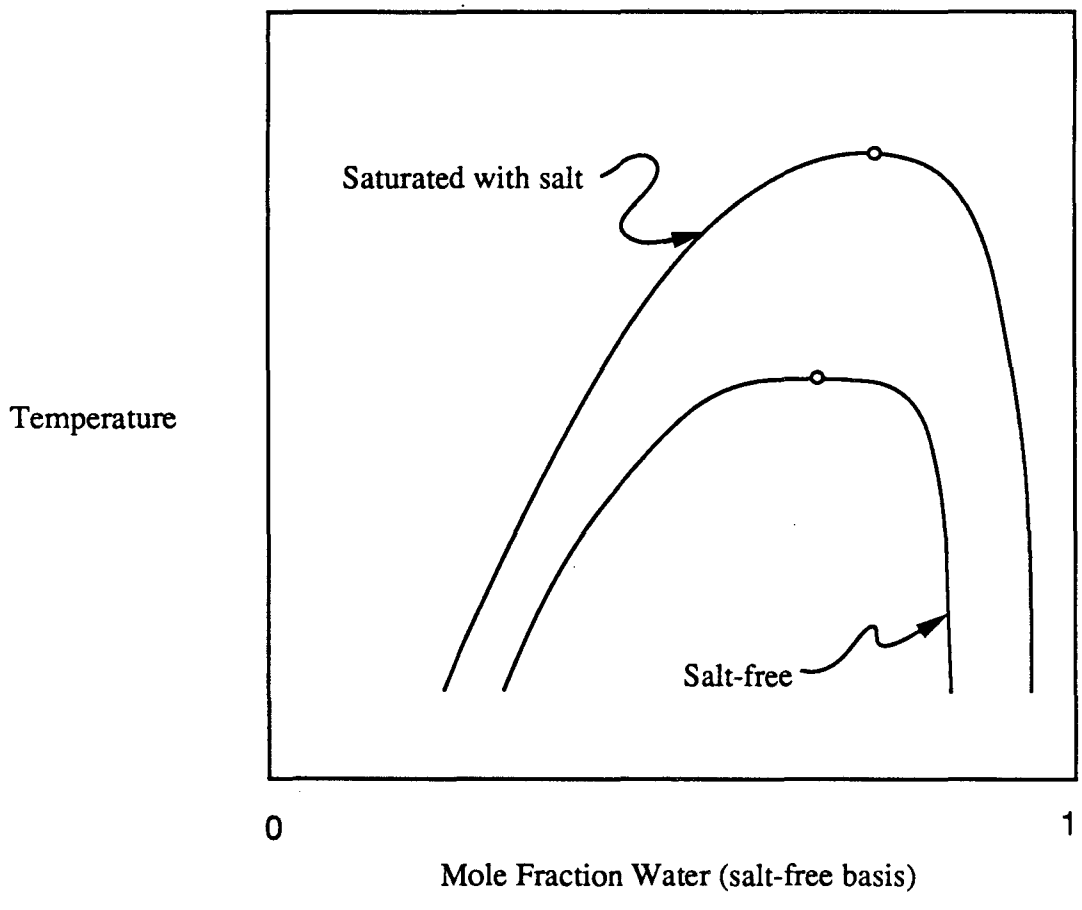
$$\Delta U_i^{vap} \approx \Delta H_i^{vap} - RT \qquad \text{(II-3)}$$

We substitute this value of the energy in Equation II-1 and solve:

$$N_A \varepsilon_{ii} = \frac{2(\Delta H_i^{vap} - RT)}{Z_i} \qquad \text{(II-4)}$$

Sample Calculation

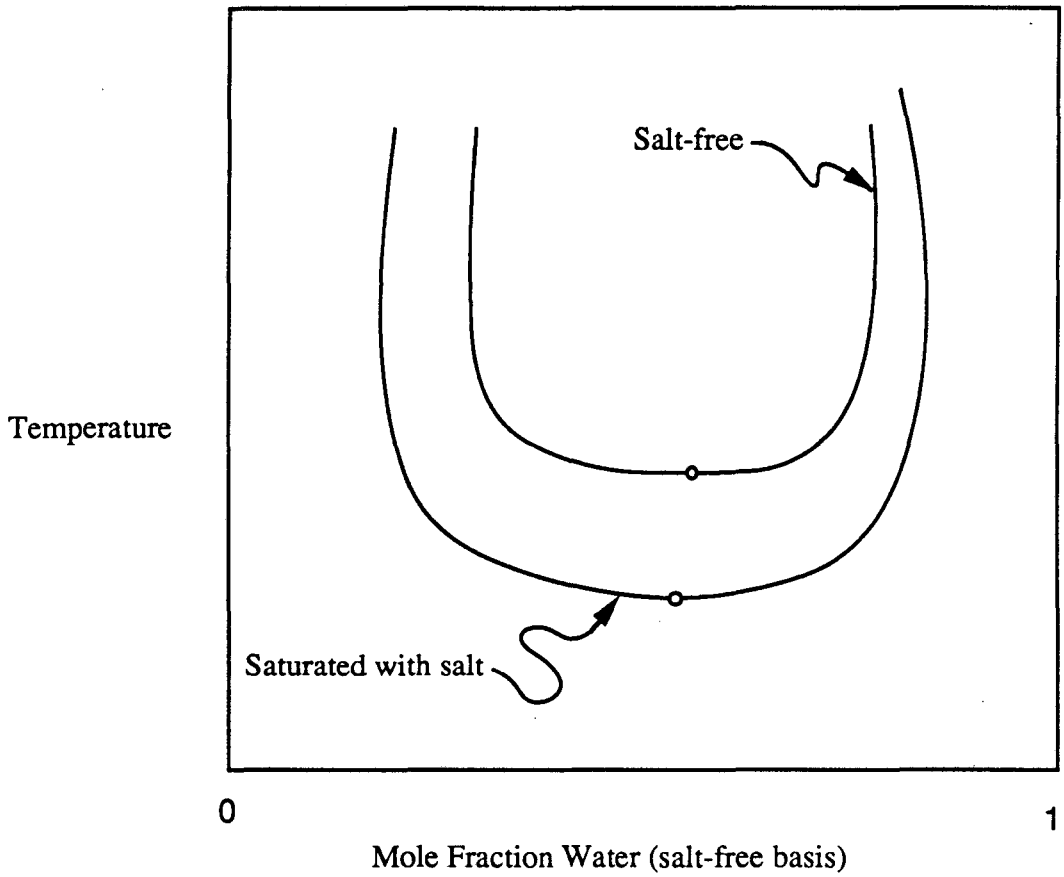
For normal butanol, the molar enthalpy of vaporization is 10300 cal/gmol at 391K (Reid, *et al.*, **Properties of Gases and Liquids**, 3rd Ed, 1977). The energy of vaporization is therefore 10300 - (1.987)(391) = 9523 cal/gmol. Divided by 6 (the coordination number), we obtain 1582 cal/gmol; twice this is the value we want: 3174 cal/gmol.



Liquid-liquid Coexistence
Curves with and without Salt

Curves are typical for systems such as butanol/water/sodium bicarbonate that exhibit upper critical solution temperatures. Circles indicate critical solution points.

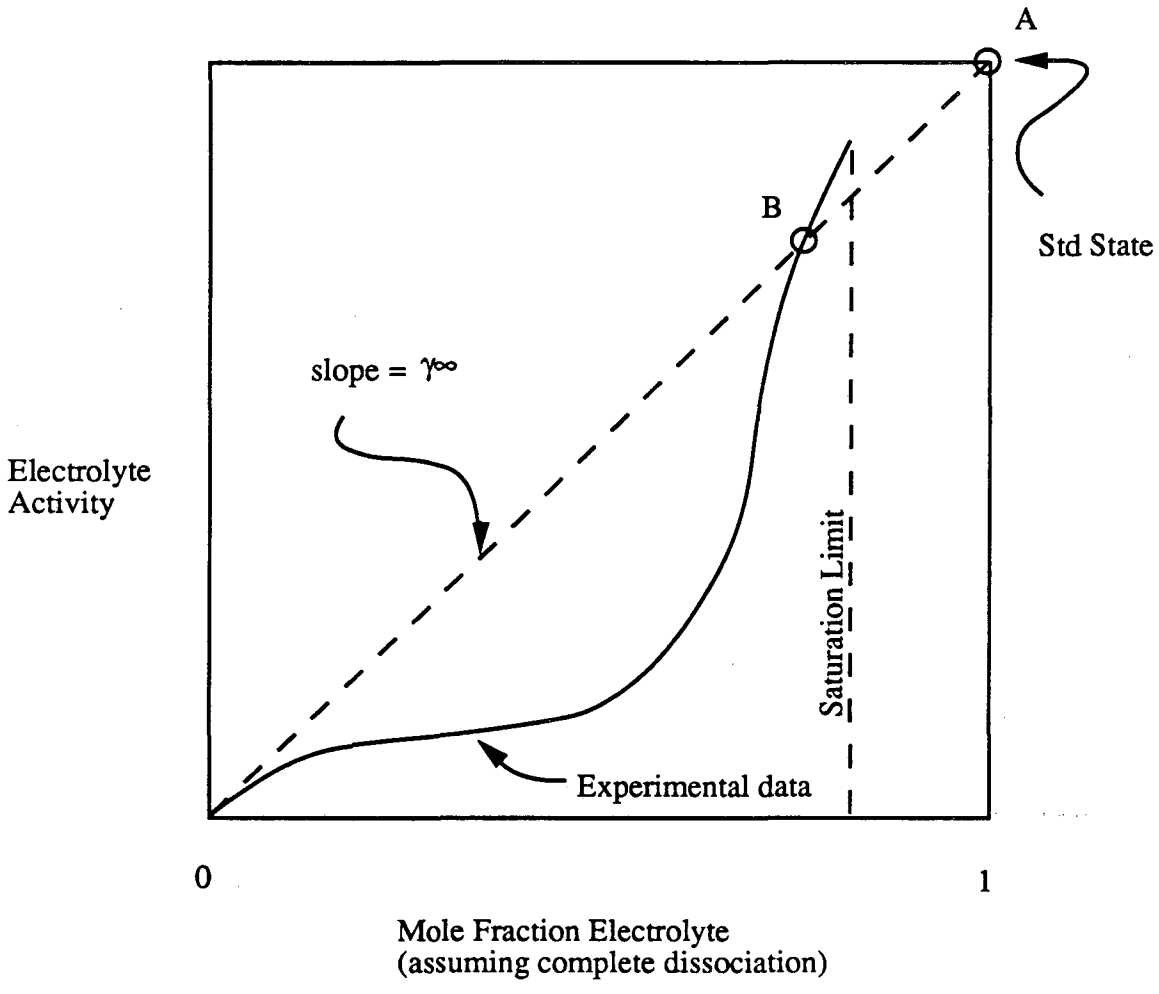
Figure 1-1



Liquid-liquid Coexistence
Curves with and without Salt

Curves are typical for systems such as diisopropyl amine/water/sodium chloride that exhibit lower critical solution temperatures. Circles indicate critical solution points.

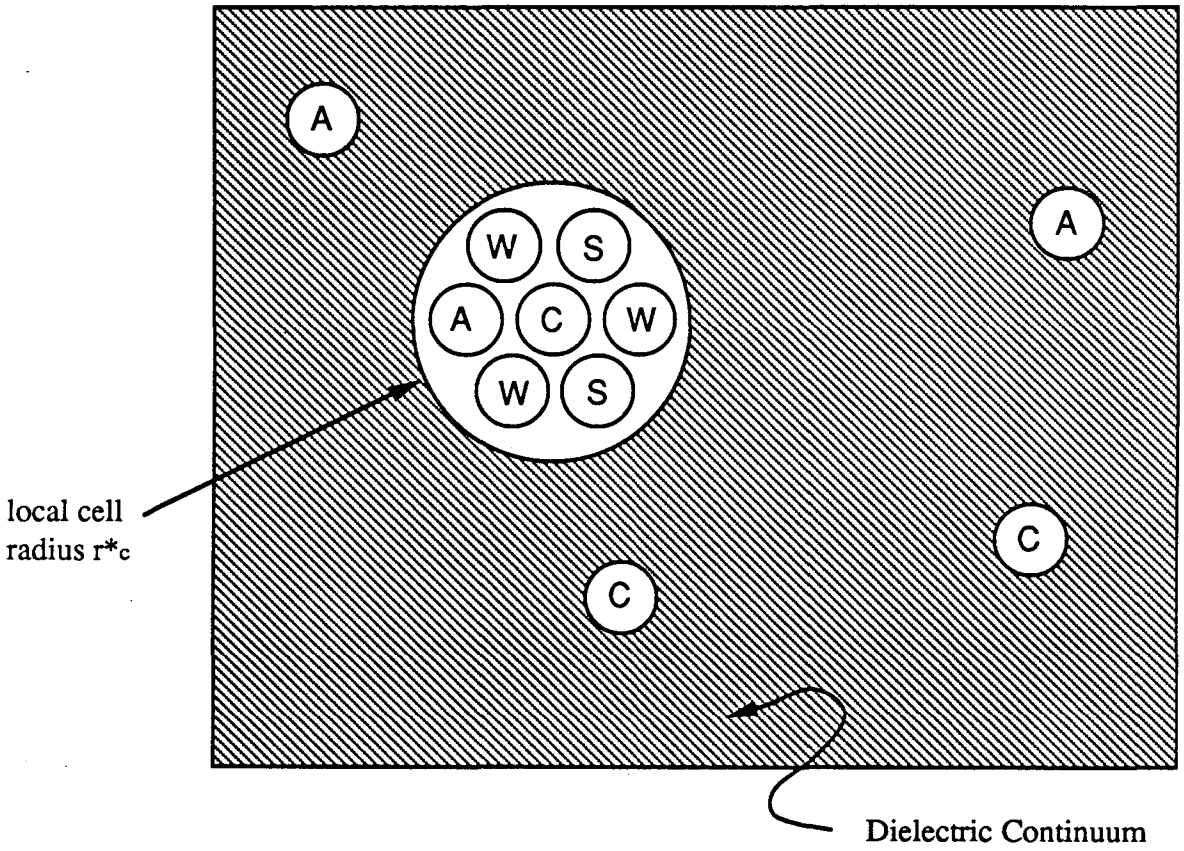
Figure 1-2



Activity as a Function of Concentration for a Typical Electrolyte in a Single-solvent System

The dashed line is tangent to the curve at salt mole fraction = 0 (the physical reference state). Point A is the thermodynamic standard state, found by extending the zero-concentration slope to a mole fraction of 1. B is a point where the experimental activity coefficient happens to be 1.

Figure 2-1



Schematic of a Local Cell and
Surrounding Dielectric Medium

Example of a cation-centered cell. Note that no other cations are in first coordination shell and that long-range forces act only between ions. S, W, C and A refer to solvent, water, cation and anion.

Figure 3-1

Coexistence Curve for the Butanol/Water System

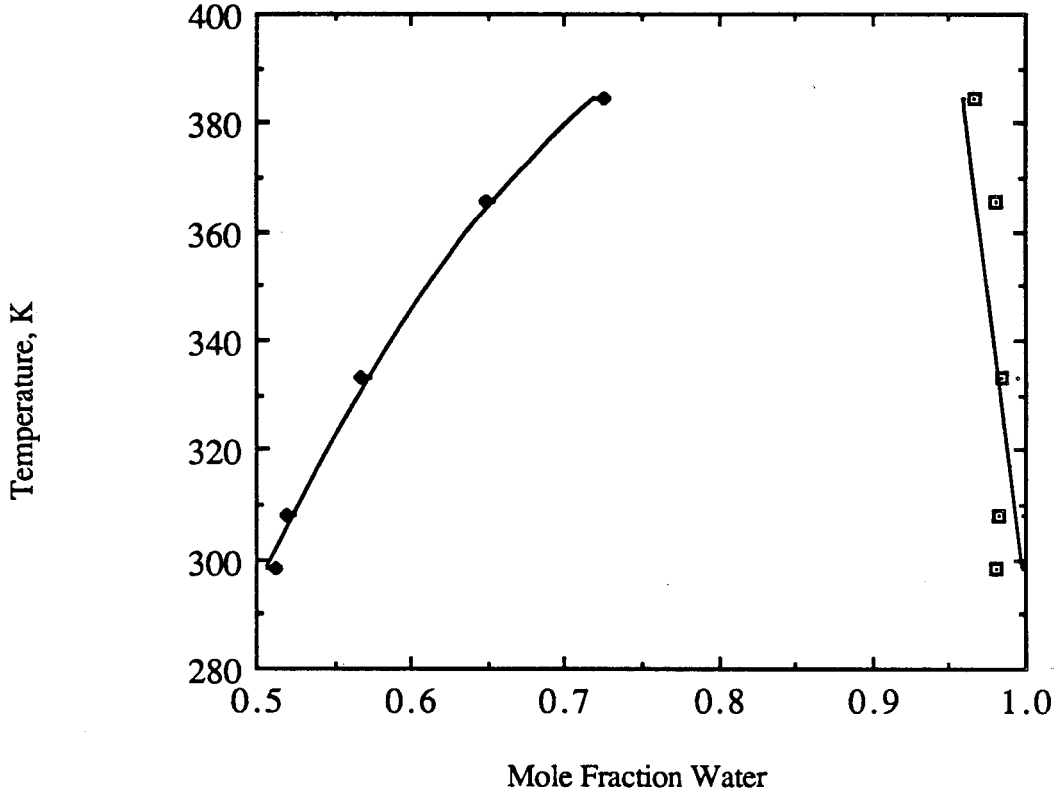


Figure 4-1

Fit of the Aqueous Na_2CO_3 Activity Coefficient

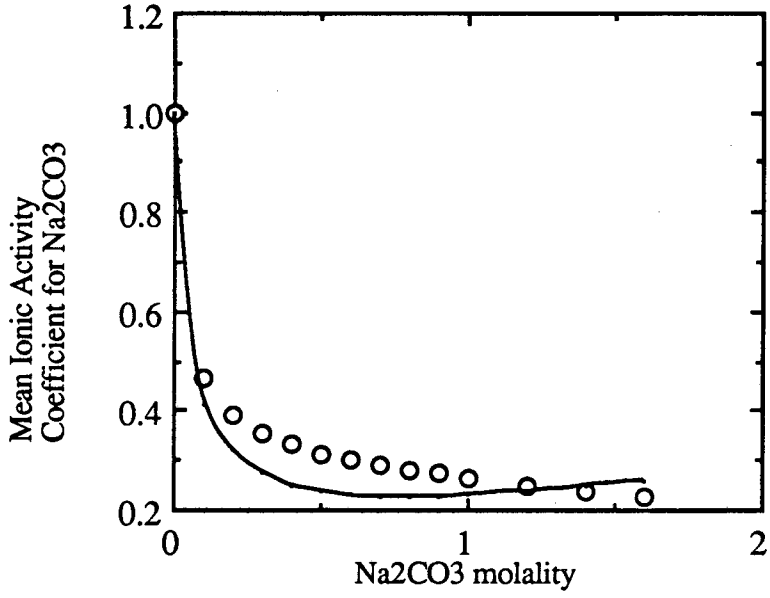


Figure 4-2

Coexistence Curve for the Butanol/Water/Na_2CO_3 System

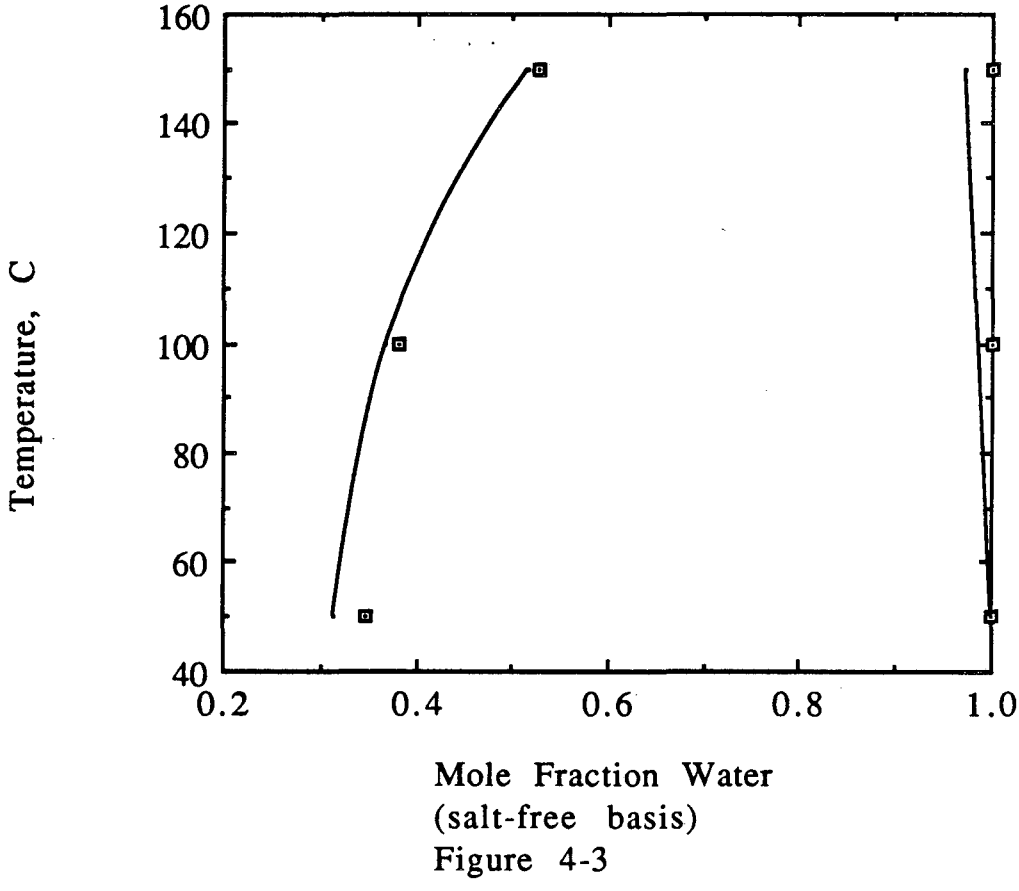


Figure 4-3

Table 4-1
Model Parameters

Water/Butanol/Sodium Carbonate system molar interaction parameters $N_A \varepsilon_{ij}$ at 25°C (energies in cal/gmol):

	Water	Butanol	Sodium	Carbonate
Water	-2997	-3392	-4276	443
Butanol	-1366	-3174	4935	-1526
Sodium	-4276	570	---	-1663
Carbonate	443	-1526	-1663	---

Values shown are for 25 °C; to better fit the alcohol-water system, temperature-dependent interaction parameters were needed:

$$\varepsilon_{wa} = -2624 + \frac{375{,}000}{T} \qquad \varepsilon_{aw} = -3770 + \frac{112{,}500}{T}$$

where T is in Kelvin. Ionic radii were fixed at 2Å.

Table 4-2
Fit to Ternary Data

Temp,°C	50	100	151	100	100	100	100
Measured Mole Fractions			(Weingaertner, 1988)				
x_w, aq	.866	.852	.889	.967	.948	.929	.902
x_s, aq	.00006	.0002	.0003	.008	.004	.002	.001
x_e, aq	.134	.147	.110	.025	.048	.069	.097
x_w, org	.348	.381	.527	.570	.524	.492	.453
x_s, org	.652	.619	.473	.430	.476	.507	.546
x_e, org	.0	.0	.0	.0	.0	.0	.0
Calculated Mole Fractions							
x_w, aq	.871	.853	.877	.968	.944	.921	.897
x_s, aq	.001	.004	.020	.011	.009	.008	.006
x_e, aq	.128	.143	.103	.021	.047	.070	.097
x_w, org	.315	.368	.516	.608	.554	.513	.459
x_s, org	.685	.632	.483	.386	.442	.486	.541
x_e, org	.00001	.00004	.001	.006	.004	.001	.00005

Here w, s, and e are water, solvent (butanol), and electrolyte (Na_2CO_3). The experimental values of x_e in the organic phase are less than about 0.1wt%.

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