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EXTRACTION OF PHENOLS FROM WATER WITH TRI-OCTYL PHOSPHINE OXIDE

John Douglas MacGlashan
(M.S. thesis)

March 1982

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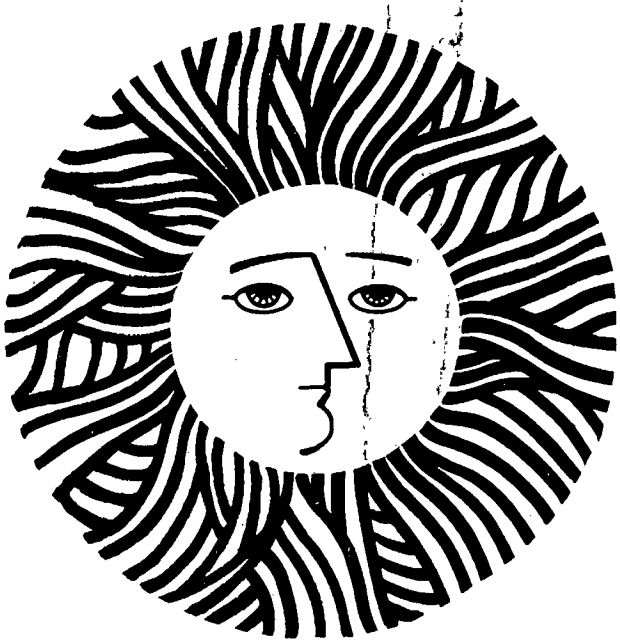

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Berkeley, CA 94720

This work was supported by the Assistant Secretary for Environmental Protection, Safety and Emergency Preparedness, Office of Environmental Progress, Environmental Technology Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

John Douglas MacGlashan

Extraction of Phenols from Water with Tri-octyl Phosphine Oxide

Abstract

Tri-octyl phosphine oxide (TOPO) was examined as an extractant for removing phenol; the dihydric phenols catechol, resorcinol, and hydroquinone; and the trihydric phenols pyrogallol, phloroglucinol, and 1,2,4-benzenetriol from water. Distribution coefficients were measured and results modelled for extractions with different diluents, solvent compositions, temperatures, and extractant-to-solute stoichiometric ratios.

The distribution coefficients (K_D) for all the solutes into TOPO are quite large. They range from 24.3 for the extraction of a 5000 ppm solution of 1,2,4-benzenetriol into 25 weight percent TOPO with di-isobutyl ketone (DIBK) as a diluent, at a water-to-solvent volume phase ratio of 5.23 to 1, to 813 for the extraction of a 5000 ppm phenol solution into 25 weight percent TOPO/DIBK at a water-to-solvent phase ratio of one to one. The K_D values are typically one to two orders of magnitude larger than values obtained with conventional solvents, indicating that strong complexes are formed between TOPO and the solutes, and that TOPO is a promising extractant for removing these compounds from wastewater streams.

Modelling of the results indicates that the extraction mechanism is complicated, with the diluent probably playing an important role. The most effective diluents are those that have some electron-donating ability and are thus able to solvate the solute-TOPO complex, without competing with the solute for the phosphoryl oxygen on TOPO.

The distribution coefficients decrease with increasing temperature, and show a linear dependence when plotted as $\ln(K_D)$ vs. $1/T$.

To my mother and father,

for their unswerving love and support

Acknowledgements

I would first like to thank my research director, C. Judson King. I have thoroughly enjoyed working with Dr. King the past two years, and have profited from it in both a personal and professional sense.

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-Gloria Pelatowski, for accurate and speedy drawing of the figures and graphs;

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Chapter I: Introduction

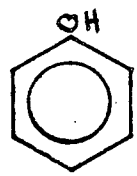
A. Uses and Production of Phenols

Phenol and some of the di- and trihydric phenols are commonly-used industrial chemicals, as well as water-pollution hazards. Phenol is used primarily as an intermediate in the manufacture of phenolic resins, as well as a disinfectant and a raw material for making pharmaceuticals. The di- and trihydrics are used as antioxidants, and in photography, printing, and the making of dyes. Table 1 gives the structures, common names, and IUPAC names for the non-alkylated mono-, di-, and trihydric phenols, while Table 2 lists typical uses for each of these compounds.

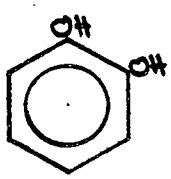
The production of synthetic phenol in 1975 was about 1.75×10^9 lbs., ranking it 38th among chemicals produced in the United States.[44] Sales volume was about $\$123 \times 10^6$, ranking it 15th among organic chemicals.[44] 1980 production was 2.46×10^9 lbs., making it the 37th highest of top U.S. produced chemicals.[7] Production data for the di- and trihydric phenols are much scarcer. For example, in U.S. Government statistics the production figures for hydroquinone are usually combined with those of other photographic chemicals, making hydroquinone production virtually impossible to determine. In the past, the U.S. Tariff Commission has kept production data for catechol confidential,

Table 1

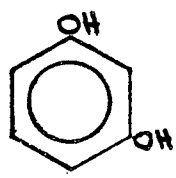
Chemical Structures of Phenols



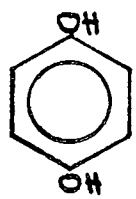
Phenol(Hydroxybenzene)



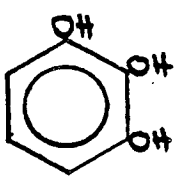
Catechol(1,2-dihydroxy-benzene)



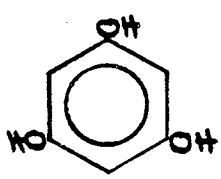
Resorcinol(1,3-dihydroxy-benzene)



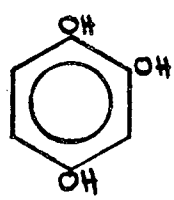
Hydroquinone (1,4-dihydroxy-benzene)



Pyrogallol (1,2,3-tri-hydroxy-benzene)



Phloroglucinol (1,3,5-tri-hydroxybenzene)



1,2,4-Benzene-triol(1,2,4-trihydroxy-benzene)

Table 2

Industrial Uses of Phenols

PHENOL

Phenolic Resins
Petroleum Refining
Disinfectants
Insecticides
Pharmaceuticals

CATECHOL

Antioxidant
Photographic Developer

RESORCINOL

Dyes
Pharmaceuticals
Resins
Rubber

HYDROQUINONE

Antioxidant
Photographic Developer

PYROGALLOL

Photography
Pharmaceuticals
Dyes

PHLOROGLUCINOL

Printing
Dyes

1,2,4-BENZENETRIOL

None Reported

since at times only one company has reported production figures. However, some older production figures are available. In 1951 4.5 million lbs. of resorcinol and 35,000 lbs. of pyrogallol were produced. In comparison, production of phenol in that year was about 500 million lbs.[25]

B. Hazardous Properties of Phenols

Phenol is a highly toxic chemical. Death has resulted from absorption of solutions of phenol through a skin area as small as 64 square inches. Absorption is extremely rapid, with death occurring in 30 minutes to several hours.[34] Long-term exposure to low concentrations of the vapor or mist can result in death due to extensive damage to the kidneys, liver, or spleen. In wastewaters, phenol is toxic to fish at concentrations as low as 5 ppm,[33a] and causes an objectional taste in drinking water at concentrations of 2 ppm.[46] Phenol can also react with chlorine, which is used as a disinfectant in drinking water, to form chlorophenols, which impart a medicinal taste to the water at ppb levels.[19] In toxicity, the di- and trihydric phenols range from phloroglucinol, which is moderately toxic and primarily a skin irritant, to catechol, which is highly toxic and has an LD_{50} of 0.05 g/kg of body weight when orally administered to dogs.[25] Table 3 lists the toxic properties of each of these compounds.

In addition to being highly toxic, phenol is a widespread industrial pollutant. An Environmental Protection Agency

Table 3

Toxic Properties of Phenols

PHENOL: HIGHLY TOXIC: "MAY CAUSE DEATH OR PERMANENT INJURY AFTER VERY SHORT EXPOSURE TO SMALL AMOUNT"
TLV: 5 PPM/AIR (19 MG/M^3)
READILY ABSORBED THROUGH SKIN

CATECHOL: HIGHLY TOXIC
LD_{50}(ORAL,DOGS): 0.05 G/KG BODY WEIGHT

RESORCINOL: MODERATELY TOXIC: "MAY INVOLVE BOTH IRREVERSIBLE AND REVERSIBLE CHANGES, NOT SEVERE ENOUGH TO CAUSE DEATH OR PERMANENT INJURY"
PRIMARILY A SKIN IRRITANT

HYDROQUINONE: SLIGHTLY-MODERATELY TOXIC
LETHAL DOSE: 60-100 MG/KG BODY WEIGHT

PYROGALLOL: HIGHLY TOXIC
READILY ABSORBED THROUGH SKIN

PHLOROGLUCINOL: MODERATELY TOXIC
SKIN IRRITANT

1,2,4-BENZENETRIOL: MODERATELY TOXIC
SKIN IRRITANT

Source: Sax[34]

(EPA) study[17] found phenol in 25 out of 32 industrial categories and in 26% of all samples analyzed. Because phenol is both toxic and widespread, it has been classified as a Priority Pollutant by the EPA.

Phenol and the di- and trihydric phenols appear in significant quantities in both coke oven effluent waters and in coal conversion process waters. Table 4 lists the phenols content of several of these process waters. The phenol concentration of a typical coke plant effluent water is a few thousand parts per million.[12] Two points are worthy of note from Table 4--first, that these compounds can appear at high concentrations; and second, that the concentration can vary a great deal from sample to sample.

Removal of these compounds is critical for the success of coal conversion processes, since they use large quantities of water and will probably be located in arid areas. A typical coal liquefaction plant (solvent refined process at 10,000 tons/day) produces about 700 gallons of wastewater per minute,[43] while a coal gasification plant (Lurgi process at 250 x 10^6 SCFD of SNG) produces about 2700 gallons per minute.[5]

C. Current Treatment Practices

Various methods are currently in use or have been proposed to treat phenol. Since the di- and trihydrics appear less frequently in wastewaters and are difficult or impossible to analyze by standard gas-chromatographic methods,

Table 4

Occurrence of Phenols in Synthetic Fuels
Process-Condensate Water

I. Synthane Gasification Process[43]

	Illinois No. 6 Coal	Wyoming Sub-Bituminous Coal
Phenol	3400 ppm	4050 ppm
Dihydric Phenols	250 ppm	530 ppm

II. Solvent Refined Coal Process[43]

Phenols (as phenol): 5000 ppm

III. Exxon Doner-Solvent Liquefaction Condensate Water[10]

Phenol	2130 ppm
Resorcinol	3830 ppm

IV. SRC Condensate Water[14]

Phenol	6700 ppm
Resorcinol	2360 ppm
Phloroglucinol	610 ppm

V. GFETC Slagging Fixed-Bed Gasifier Condensate Water[29]
(Stored for 6 Weeks at pH=8.5)

Phenol	7415 ppm
Catechol	903 ppm
Resorcinol	28 ppm
Hydroquinone	25 ppm

not as much attention has been paid to them. With the development of synthetic fuels, however, effective methods must be found to deal with these compounds.

Biological oxidation of phenol is a common treatment method. It is usually used as a final treatment step to reduce phenol to very low levels. This method does have some drawbacks. Unless phenol-acclimatized bacteria are used, the tolerance level of the bacteria is about 50 ppm.[23,27] The bacteria are also sensitive to the presence of ammonia, cyanides, thiocyanates, and tars, all of which appear in significant amounts in coal processing waters. Various compounds, including chlorophenol and the trihydric phenols, are resistant to biological oxidation. Since biotreatment systems are especially sensitive to inlet phenol concentration, a sudden surge of phenol ("shockload" conditions) can cause the system to fail. Finally, biotreatment is a degradation process, and thus the economic value of the unrecovered phenol is lost.

Carbon adsorption is a second method that is useful for taking a pretreated water and further reducing the phenol content to acceptably low levels. If the adsorption process is reversible, the phenol can be recovered for sale or reuse. Energy costs are high, however, if thermal regeneration is used. Carbon losses of 5 to 15 percent per cycle are not unusual.[15] If pH-change regeneration is used, large quantities of phenolates are generated, which are themselves

a disposal problem. It is for this reason that back-extraction into caustic, once a common practice, is no longer popular.

Adsorption onto polymeric resins is similar in principle to carbon adsorption. Since resins have very durable matrices, they are not subject to the physical breakdown problems which affect carbon adsorbents. Also, whereas in carbon adsorption the regeneration procedure is limited, several solvents are available for efficient resin regeneration. Acetone is commonly used to remove phenol.[13] Again, resin adsorption would be useful for polishing a pretreated wastewater stream.

Steam stripping of phenol is limited in utility because phenol forms an azeotrope with water at 9.2 weight percent phenol. Air stripping is precluded because the vapor pressures of phenol and the di- and trihydric phenols are low and their water solubilities relatively high. Other, less common methods, such as liquid ion-exchange amines [32] and reverse osmosis[11] have also been suggested for phenol separation. Neither of these methods are currently viable on an industrial scale, however.

Liquid-liquid extraction is a well extablished method for removal of phenols at higher concentrations. A preliminary study by the Department of Energy[20] which compared different methods for purifying wastewater streams from synthetic fuels processes concluded that solvent extraction had

several attractive aspects, in particular its lack of sensitivity to variations in feed concentrations and its ability to remove a wide variety of compounds with the proper solvent selection.

At least two solvent extraction processes are presently in use on a very large scale to remove phenol from coke-oven waters. The Phenosolvan process, developed by Lurgi and first commercialized in about 1940,[5] uses di-isopropyl ether (DIPE) as a solvent. Figure 1 is a process diagram of the Phenosolvan process. The wastewater is first treated with lime to free ammonia for subsequent stripping, is filtered to remove tars, and then is extracted with DIPE. The solvent in the extract is recovered using distillation, while residual DIPE in the raffinate is removed by nitrogen stripping.

A second process, licensed by the Chem-Pro Equipment Corporation, uses a proprietary solvent which is thought to be methyl iso-butyl ketone (MIBK).[35] This process has claimed 99.7 to 99.9 percent phenol removal using very small solvent-to-feed ratios.[30] As in the Phenosolvan process, the solvent is regenerated by distillation. Residual solvent is removed from the raffinate by using steam stripping. The capital costs for this process are appreciably lower than for the Phenosolvan process, while the operating costs are slightly higher.[6] Burns et al[6] have suggested an improvement in the Chem-Pro process by which vacuum steam stripping signifi-

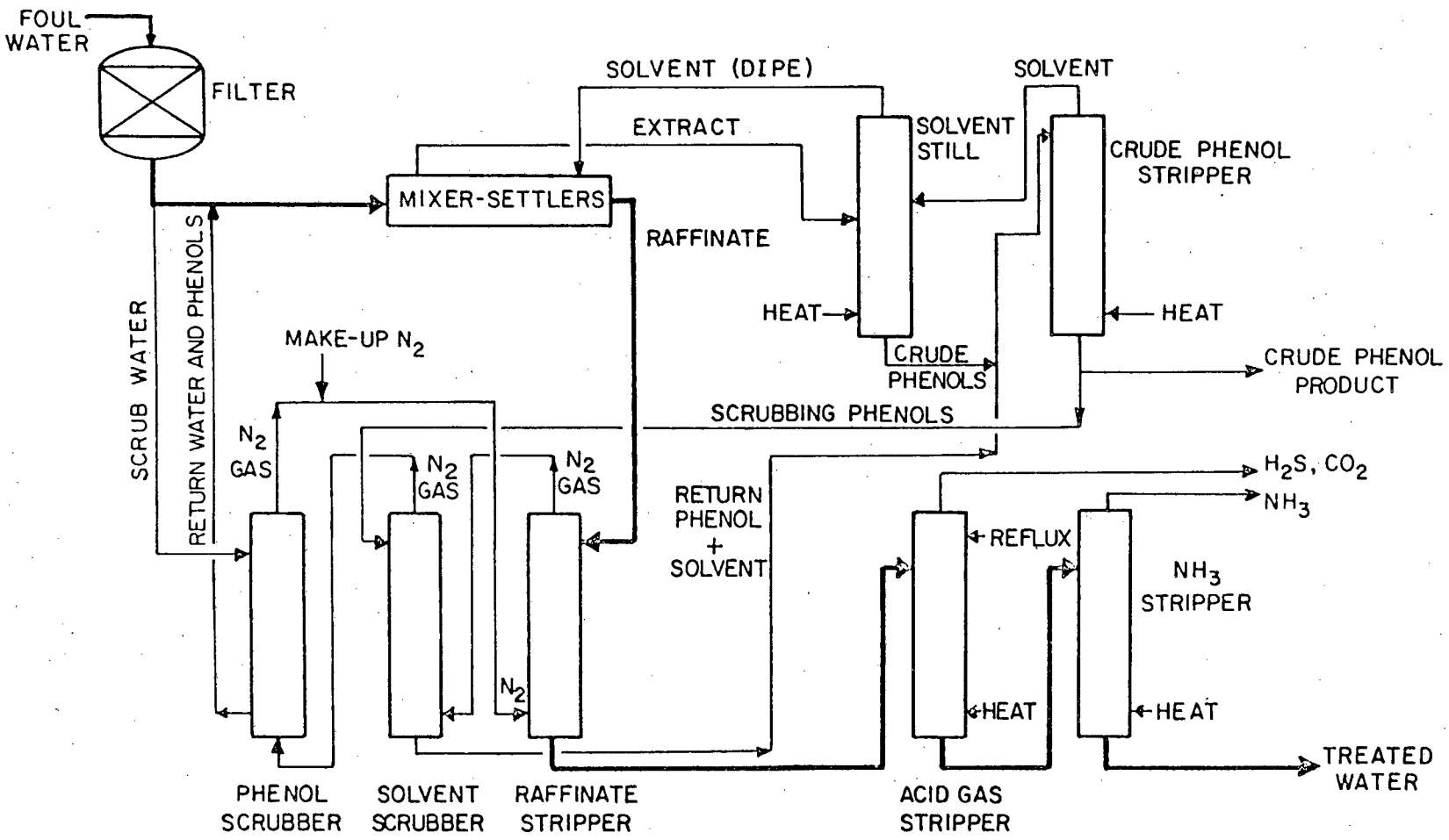


Figure 1: Phenosolvan Process Flow Diagram[5,48]

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cantly reduces energy requirements and thus operating costs.

The capabilities of the Chem-Pro or Phenosolvan processes for treating coal conversion wastewaters are matters of some debate. Beychok[5] has claimed that the Phenosolvan process is capable of removing 70 percent of the catechol and 99.9 percent of the phenol from a wastewater stream. Beychok assumed nine equilibrium stages in the extractor, a solvent-to-feed ratio (mass/mass) of 1:10, and distribution coefficients (K_D) of 20 and 7.0 for phenol and catechol, respectively.

Greminger and King,[14] however, pointed out that phenols are weak acids which ionize at high pH, and that it is the unionized species that is extractable. The K_D values drop sharply at a pH close to or above the pK_a of the solute. Beychok's choice of K_D for phenol reflects this decrease and corresponds to a pH of 9.8, which is a reasonable pH for a coal process wastewater. The K_D postulated by Beychok for catechol is much too high, however. A more realistic value is about 1.6[14]. The removal of catechol with this K_D and the same conditions as above is only about 16 percent. The removals of the other di- and trihydric phenols would be even lower, since their distribution coefficients are smaller.

With MIBK the recovery of catechol would be greater because of the higher K_D, which at pH 9.8 is 6.05 versus 1.6 for DIPE. With the same conditions as above, catechol recovery is about 60 percent. Again, recovery would be lower

for the remaining di- and trihydric phenols. Thus, the development of a solvent giving higher K_D values for these compounds would be highly desirable.

D. Previous Measurements of Equilibrium Distribution Coefficients for Phenols

Since phenol is a commonly-encountered chemical and is often removed from water by solvent extraction, equilibrium and liquid-liquid extraction data for it are widespread. Wisniak and Tamir,[45] for example, list published equilibrium data for over 300 systems in which phenol is a component. Data for the di- and trihydric phenols are much scarcer. According to the same source, equilibrium data for only nine systems involving pyrogallol appear in the literature.

Kiezyk and Mackay[18] have also reviewed the literature for phenol liquid-liquid extraction data, while Korenman[21] has reported distribution coefficients for all the dihydric phenols into several esters, alcohols, and DIPE. Luecke[24] has measured K_D values for the dihydrics and pyrogallol into 3-heptanone, 2-octanone, 1-octanol, DIPE, and n-butyl acetate. Won and Prausnitz[47] determined distribution coefficients for resorcinol and catechol into MIBK and n-butyl acetate.

As previously mentioned, Greminger and King[14] measured distribution coefficients for phenol and the di- and trihydric phenols into both MIBK and DIPE. They also studied the effect of pH on the extraction equilibria of phenol, re-

sorcinol, and hydroquinone into DIPE and of hydroquinone into MIBK. They showed that the distribution coefficient dropped sharply at a pH approximately equal to the pK_a of the solute, and found that the following equation modelled the data well:

$$(1) \qquad K_{D\ apparent} = \frac{K_{D\ low\ pH}}{\frac{K_a}{(H^+)} + 1}$$

where:

$K_{D\ low\ pH}$ = distribution coefficient at pH much less than pK_a
$K_{D\ apparent}$ = distribution coefficient at a given pH
K_a = dissociation constant of the solute
(H^+) = hydrogen ion concentration (moles/L)

Burns et al[6] measured distribution coefficients for the phenol-water-MIBK system at 30, 50, and 70 °C. They also investigated possible energy savings by coupling MIBK extraction with the use of vacuum steam stripping to recover residual dissolved solvent from water. Pittman[31] made preliminary investigations of less conventional, chemically-complexing solvents, and in particular high-molecular weight primary, secondary, and tertiary amines, for extracting phenol from dilute aqueous solutions. Bell[4] measured distribution coefficients for resorcinol into tertiary amines with various diluents; for phenol, resorcinol, and pyrogallol into diluted and undiluted tri-cresyl phosphate (TCP); and for

pyrogallol into tri-octyl phosphine oxide (TOPO) dissolved in di-isobutyl ketone (DIBK). For extraction with the amines, she found values of K_D that were not much higher than occurred with the diluents alone. There was also strong evidence of an irreversible degradation reaction. For these reasons, extraction of polyhydric phenols with amines was not considered to be promising. In the case of extraction with TOPO/DIBK, very high values of K_D (about 110) were obtained for removal of pyrogallol. That extraction also proved to be reversible, with no apparent degradation. The purity of the TOPO used was questionable, however. The pH of the aqueous phase dropped from 6 to 3.3 during the course of the extraction, indicating that an acidic impurity was possibly present.

Tables 5 and 6 list K_D values for phenol and the di- and trihydric phenols which are of particular interest in this work.

E. Previous Work Involving Phenol and Phosphorus Compounds

Several workers have investigated various phosphorus compounds for their ability to form complexes with phenol. Aksnes[1] determined that it is the phosphoryl group which participates in hydrogen bonding with phenol. He measured association constants for the phenol-triethylphosphate-carbon tetrachloride system and the phenol-N diethylacetamide-carbon tetrachloride system by measuring the free phenol concentration with IR spectroscopy. The large association

Table 5

Distribution Coefficients for Phenol into Various Organic Solvents

Solvent	K_D	Source
n-Butyl Acetate	65	47
	55	21
	62	28
	56	32
Kerosene	0.20	28
2-Ethyl Hexanol	28.5	4
Amberlite XLA-3*	58	32
TCP	72	4
MIBK	110	47
DIPE	33	47

*A primary aliphatic liquid amine produced by Rohm and Haas

Table 6

Distribution Coefficients for the Di- and Trihydric Phenols into MIBK and DIPE

Solute	K_D MIBK	K_D DIPE
Catechol	18.7	4.86
Resorcinol	17.9	2.06
Hydroquinone	9.92	1.03
Pyrogallol	3.58	---
Phloroglucinol	3.92	---
1,2,4-Benzenetriol	5.01	0.181

All values at a pH much less than the pK_a of the solute

Source: Greminger and King[14]

constants and wavelength shifts in the phenol hydroxyl band indicated that strong complexes are formed. Aksnes and Gramstad[3] came to similar conclusions in measuring the association constants involving phenol and 18 organophosphorus compounds. They also interpreted the relative magnitude of the association constants in terms of the nature of the substituents surrounding the phosphoryl group.

Shvets et al[37] studied the shifts in the hydroxyl absorption of phenol in the formation of complexes with triaryl phosphine oxides. They found that triaryl phosphine oxides form extremely strong hydrogen bonds with phenol, surpassing such organic bases as ether, tetrahydrofuran, and dimethyl sulfoxide, and of the same order as pyridine 1-oxide and pyridine. They explained the high strength of these bonds on the basis of the steric accessibility of the phosphoryl oxygen.

Matysik and Soczewinski[26] looked at the extraction of various phenolic acids from water by liquid-liquid partition chromatography with tributyl phosphate in various diluents. They noted the effects of chemically interacting diluents on results. Soczewinski and Matysik[39] modelled results for systems where more than one solute-solvent complex is formed.

Stuurman et al[41] extracted phenol and other hydrophilic organic acids from water using TOPO in n-decane coated on a liquid chromatography column. They modelled results and determined the number of moles of TOPO complexing a mole of solute for each of the compounds.

F. Objectives

This work was primarily concerned with examining the use of tri-octyl phosphine oxide as a chemically complexing extractant for removal of phenol and the di- and trihydric phenols from water. The K_D value of 110 measured by Bell[4] for extraction of pyrogallol into a 25 weight percent solution of TOPO in DIBK, mentioned above, indicated that TOPO is a promising extractant. In comparison, K_D values for pyrogallol into TCP and MIBK are 1.6 and 3.6, respectively. A solvent giving a high K_D is desirable, since it can allow use of a lower solvent-to-water flow ratio. This factor is particularly pertinent for coal-conversion processes because of the large volumes of water involved. Smaller solvent flow rates result in reduced solvent inventory and equipment size.

TOPO is a solid at room temperature (MP=56 °C, BP=460 °C), which means that it must be dissolved in a liquid diluent. The choice of diluent is influenced by several factors. The diluent-TOPO mixture should give high values of K_D for the reasons mentioned above. The diluent should have a low solubility in water to minimize diluent loss. TOPO itself has a very low solubility in water[16], but it is important to select a diluent which minimizes solvent losses through emulsification or entrainment. This is crucial, since TOPO is relatively expensive (1981 price= $7.40/lb., American Cyanamid Company). The diluent should be relatively inexpensive and readily available. The diluent-TOPO mixture

should also have a sufficiently low viscosity to prevent contacting problems. The density difference between it and water should be great enough to avoid settling problems.

An important factor in diluent choice is the solvent regeneration method chosen. If distillation is used, a diluent with a higher boiling point than the solute would be desirable. Less energy would be required, since only the solutes are taken overhead in that case. If a lower-boiling diluent is used, more energy will be needed to take it overhead, and a second separation will be required, since the diluent and TOPO would appear in separate products. A low-boiling solvent is sometimes used to avoid build-up of heavy impurities in the recycle solvent. However, TOPO as an extractant is inherently high-boiling, and any problem of build-up of heavy impurities will have to be solved through a purge, with possible further processing and recycle of the TOPO in the purge stream.

Finding a diluent with a higher boiling point than phenol (182 °C) would not pose too serious a problem. Resorcinol, however, boils at 281 °C. It is doubtful a convenient and effective diluent exists with a higher boiling point than that of this compound. One possible solution is to separate the di- and trihydric phenols from the TOPO/diluent mixture by using back-extraction into an aqueous NaOH solution, or possibly a back-extraction into water at a much higher temp-

erature, if the K_D values for these compounds decrease sharply with increasing temperature. In the case of back-extraction into NaOH, loss of the solutes due to conversion into phenolates would probably not be a serious problem, since the di- and trihydric phenols have much less market value than phenol. However, disposal of the resulting phenolates could be a problem.

With the above factors in mind, DIBK was chosen as the diluent for most of the extractions in this work. Ricker et al[33] found that TOPO/ketone mixtures give higher K_D values for acetic acid than either TOPO/Chevron 25 (a mixture of alkylated aromatics) or TOPO/2-ethyl hexanol mixtures, and that DIBK is an effective diluent for either TOPO or tertiary amines as extractants for acetic acid. DIBK also has a relatively small solubility in water (about 300 ppm at 30 °C)[36] and is inexpensive ($0.52/lb. in large quantities)[9] and readily available. DIBK does have a lower boiling point than phenol (168 °C); thus in an actual extraction process it would come out as a separate, light product. In order to keep the diluent in the same product stream as the TOPO extractant, a higher-molecular weight ketone with a higher boiling point might be used instead as a diluent. Acetophenone, for example, boils at 202 °C and costs a reasonable $0.74/lb.[9] This study was concerned primarily with the chemical nature of the diluent and its effect on distribution coefficients. Thus, any shortcomings associated with the

boiling point of DIBK were overlooked.

In light of this discussion, the specific objectives of this work were as follows: (1) to examine the feasibility of TOPO as an extractant for removing phenol and the di- and trihydric phenols from water, using fresh, uncontaminated TOPO; (2) to vary TOPO/DIBK ratios in a mixed solvent and initial TOPO-to-phenol molar ratios, in order to gain insight into the extraction mechanism; (3) to vary the nature of the diluent and to note and interpret the effect of the diluent on K_D; (4) to examine the relationship between temperature and K_D for phenol and other solutes; and (5) to investigate the relative proportions of uncomplexed and complexed phenol in the solvent phase, using IR spectroscopy.

Chapter II

Experimental Procedure and Analytical Methods

A. Introduction

The focus of this work was on measuring equilibrium distribution coefficients, by first contacting the organic and aqueous phases using batch extraction, and then measuring the concentration of the solute in the final aqueous phase (raffinate) using liquid-liquid chromatography. In addition, some IR measurements were taken to determine the concentration of uncomplexed phenol in the organic phase.

Although distribution coefficients can be defined in several ways, two are of particular interest here: (1) K_D, a weight fraction distribution coefficient, defined as the weight fraction of the solute in the organic phase divided by the weight fraction solute in the aqueous phase, at equilibrium and at high dilution. Typical weight fraction units are parts per million (ppm); (2) K_M, a molar distribution coefficient, defined as the concentration (in moles per liter) of the solute in the organic phase divided by the concentration of solute in the aqueous phase, again at equilibrium and at high dilution. Weight fraction distribution coefficients are useful for predicting solute removal from an aqueous stream for a given extractor, or for designing an extractor for a given solute removal, with streams in mass flow rates; molar distribution coefficients

are useful for modelling data and explaining mechanisms.

There are several available methods for experimentally measuring distribution coefficients. One involves adding the solute initially to the water phase, contacting this phase with a solvent, and measuring the solute concentrations in both the feed and raffinate. A second method consists of placing the solute in the solvent phase, contacting it with solute-free water, and calculating K_D or K_M from the initial and final solvent phase concentrations. In either method, a concentration measurement for the other product phase, as well, allows a mass balance. Other methods involve placing the solute initially in the solvent or aqueous phase, contacting this phase with a sufficiently small amount of water or solvent to cause relatively little depletion of the solute, and calculating K_D from its definition ($=C_s/C_w$) and measured solute concentrations in the two phases.

The first method, which was used in this study, has several advantages: (1) previous work[14] suggested that it was easier to measure aqueous phase concentrations rather than solvent phase concentrations; (2) the first method directly simulates an actual extraction process, since the solute would initially be in the aqueous phase; and (3) for high distribution coefficients, the second method results in only a small percentage removal of solute from the solvent phase, which leads to an imprecise calculation of K_D.

A mass balance on the solute yields the following equation:

$$(1) \qquad W(C_{wo} - C_w) = S \cdot C_s$$

where C_s, C_w, and C_{wo} are the concentrations in ppm (w/w) of solute in the final solvent (extract), raffinate, and initial aqueous (feed) phases, respectively, and W and S are the aqueous and solvent phase weight or mass. The simplest use of this equation assumes no solubility of water in the solvent phase or of solvent in the aqueous phase, i.e., S and W equal to the amounts fed initially. Also, it is assumed in Equation 1 that C_{so}, the concentration of solute initially in the solvent, is zero. Since K_D is defined as $K_D = C_s/C_w$, substituting for C_s in Equation 1 and rearranging yields:

$$(2) \qquad K_D = \frac{W(C_{wo} - C_w)}{S \quad C_w}$$

A similar equation can be written for K_M if the concentrations are in moles or mass per liter and W and S are the aqueous and solvent phase volumes, in liters.

For a given C_{wo}, the range of W/S which yields acceptable results is limited by a number of factors. An upper limit on W/S is dictated by solvent loading, i.e., the amount of solute extracted into the organic phase. If W/S

is too high, the concentration of solute in the solvent can be large enough for the activity coefficient of the solute to be a function of concentration. On the basis of past experience, an acceptable limit on solvent loading is typically about 1 to 2 weight percent (10,000 to 20,000 ppm).

A lower limit on W/S is determined by the lower limit of detectability of the solute in the aqueous phase. Smaller values of W/S can deplete the aqueous phase of solute to an extent that it can no longer be reliably detected. The lower limit of solute detectability, which was taken to be the smallest concentration of solute which could be distinguished from detector noise, was about 10 ppm in the present work.

In some cases the constraints imposed by these limits are very narrow or actually cross. This is especially true when distribution coefficients are large. For example, when investigating the effect of stoichiometric ratio on K_D for phenol in the present work, it was necessary to go to as high a solvent loading as 9 percent. In all other cases, however, solvent loading was typically less than 3 percent.

B. Batch Extractions

Extractions were performed in a variety of ways, depending largely upon the equipment available. In initial phases of the work, the aqueous and organic phases were mixed in 125 mL separatory funnels at ambient temperature, on a

Lab Line Junior Orbit shaker set at 300 rpm. After 30 minutes of agitation, the phases were allowed to settle under the impetus of gravity for about 1 hour. The raffinate phase was withdrawn with a 5 mL syringe and transferred to a 10 mL centrifuge tube. The raffinate was then centrifuged for about 30 minutes to separate any entrained solvent, using an International Clinical centrifuge (Model X-4543). All of the initial extractions involving phenol, with the exception of those performed at temperatures other than ambient, were carried out in the above manner.

It was noted that during these extractions ambient temperature ranged from 20 to 25 °C. The temperature dependence of K_D for phenol can be significant. For example, Burns et al[6] found that K_D for the phenol-water-methyl isobutyl ketone system dropped from 129 to 73 at about 5 weight percent solvent loading as T rose from 30 to 50 °C. It was thus decided to keep the temperature constant for subsequent extractions.

Extractions involving the di- and trihydric phenols were carried out in 125 mL Erlenmeyer flasks at ambient temperature on the Lab Line Junior Orbit shaker for 30 minutes. The flasks were then held in a thermostatted temperature bath at 30 °C for 1 hour. About half way through this settling period the flasks were removed, shaken vigorously by hand for about five minutes, and then returned to the bath. After settling, the raffinate was withdrawn with a 5 mL

syringe and centrifuged for 30 minutes. After centrifuging, the tubes were placed in the temperature bath for about 20 minutes prior to analysis.

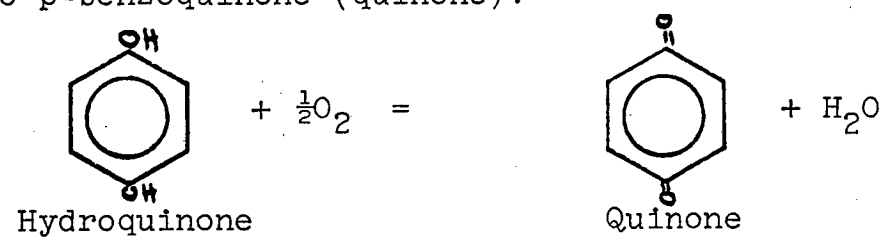
A final set of extractions was performed using a Precision Scientific Model 50 temperature-controlled shaker bath. The phases were mixed in 125 mL Erlenmeyer flasks for 30 minutes at a shaker speed of about 180 oscillations per minute. After a 30 minute settling time, the raffinate was withdrawn with a syringe and centrifuged as above. Extractions for all the conditions involving phenol, as well as the temperature-dependence extractions for catechol, were performed in this manner. Some discrepancies were noted between K_D values measured for phenol using this method and those measured using the first method mentioned. These are discussed at length later in this report.

The initial aqueous phase for each extraction was prepared by dissolving an appropriate amount of solute in water to make a 5000 ppm (by weight) solution. Distilled water was filtered through a Milli-Q Water Purification System (Millipore Corp.) prior to use, to remove organics, inorganics, and particulates. A few drops of KH_2PO_4-H_3PO_4 buffer were added to keep the pH sufficiently low to prevent ionization, and thus oxidation, of the solute.

For the di- and trihydric phenols, the water was also sparged with nitrogen for about 30 minutes to remove dissolved oxygen and thus further discourage oxidation. All solutions were filtered using Millipore cellulose acetate

(0.45 μm pore diameter) filters to remove particulates. Removal of particulates was particularly important to avoid plugging the liquid chromatography column used in analysis. The solvents were prepared by dissolving the appropriate amount of TOPO in diluent and then filtering these solutions using Millipore fluorocarbon (0.5 μm pore diameter) filters. Table 1 lists the sources of chemicals used in this work.

The above method of feed phase preparation was successful for all the compounds except hydroquinone and 1,2,4-benzenetriol. These compounds discolored almost immediately upon mixing with water, even when the mixing was done in a darkened flask with water that had been sparged with nitrogen for two hours or more. Hydroquinone oxidizes readily to p-benzoquinone (quinone):



A similar reaction is undergone by 1,2,4-benzenetriol. Apparently the discoloration was associated with the formation of these oxidation products, or polymers of these substances, all of which are highly conjugated.

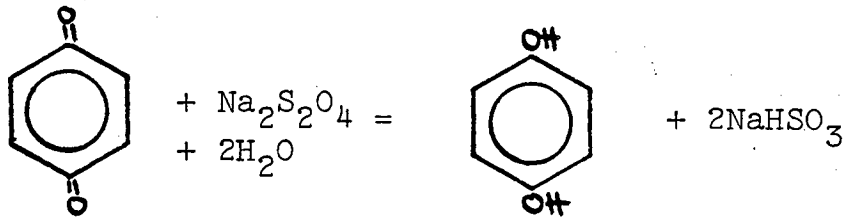
Fortunately, these reactions are reversible, and quinone is nearly quantitatively reduced to hydroquinone by a variety of reducing agents.[8] A few drops of a 1 molar solution of $Na_2S_2O_4$ (sodium hydrosulfite) in water was found

Table 1

Sources of Chemicals Used in Experiments

Chemical	Source
Phenol	Mallinckrodt, Inc.
Catechol	Aldrich Chemical Co.
Resorcinol	Aldrich Chemical Co.
Hydroquinone	Matheson, Coleman and Bell
Pyrogallol	Aldrich Chemical Co.
Phloroglucinol (dihydrate)	Aldrich Chemical Co.
1,2,4-Benzenetriol	Aldrich Chemical Co.
TOPO	Eastman Kodak Co.
DIBK	Eastman Kodak Co.
Kerosene	Giauque Low Temperature Laboratory
Chevron 25	Chevron Chemical Company
n-Butyl Ether	Matheson, Coleman and Bell
2-Ethyl Hexanol	Matheson, Coleman and Bell
n-Butyl Acetate	Matheson, Coleman and Bell
Methanol	Mallinckrodt, Inc.
Dichloromethane	Mallinckrodt, Inc.
n-Heptane	Mallinckrodt, Inc.
MIBK	Matheson, Coleman and Bell
2-Heptanone	Aldrich Chemical Co.
4-Heptanone	Aldrich Chemical Co.
1-Heptanol	Matheson, Coleman and Bell

to be successful in this case, with reduction occurring by the following reaction:



Upon addition of the $Na_2S_2O_4$ the solution turned from a bright yellow, which is characteristic of quinone, to colorless.

C. Liquid Chromatography

The concentrations of solute in the raffinate and feed were measured using high-pressure reverse-phase liquid chromatography, which is defined as high-pressure liquid chromatography using a nonpolar stationary phase and a polar mobile phase. The more nonpolar a compound, the less strongly it associates with the mobile phase, and the more slowly it elutes from the chromatography column. Thus, compounds can be separated and analyzed on the basis of their polarity. Greminger and King[14] found that phenol and the di- and trihydric phenols can be successfully analyzed in this manner. They also found that the di- and trihydric phenols are too polar to elute from common gas chromatography columns; thus gas chromatography is precluded for measuring concentrations of these compounds. Phenol, however, can be analyzed using gas chromatography. To be consistent, liquid chromatography was used in all cases in the present

work.

The liquid chromatography system consisted of a Spectra-Physics Model 740 high-pressure liquid chromatography pump, a Spectra-Physics 10-μL sample-injection valve, a Waters Associates μBondapak C_{18} column, and a Waters Associates Model 440 ultraviolet absorbance detector, set at 254 nm. The column was 3.9 mm in diameter and 30 cm long. It was filled with 10-μm silica particles onto which $C_{18}H_{37}$ was bonded. In addition, a Perkin-Elmer M-2 digital integrator and a Sargent-Welch Model XKR chart recorder were used to measure peak areas. The peak width at half height on the integrator was set at 10 seconds.

Forty volume percent methanol in water was chosen as the mobile phase for all compounds, with the exception of hydroquinone and 1,2,4-benzenetriol. Twenty volume percent methanol in water was chosen for these compounds, to give better peak resolution between the compound and an oxidation product which was present. These mobile phases seemed to give reasonable elution times, which are usually taken to be approximately 2.5 to 7 times the column void volume.[38] Since the column void volume was about 1.5 mL and a mobile phase pumping rate of 2.0 mL/min. was used, a reasonable elution time would be from 112 to 315 seconds. In the present work, retention times ranged from 115 seconds (pyrogallol) to 210 seconds (phenol). The mobile phases were prepared by mixing the appropriate amounts of methanol and

water, and filtering the resulting solution through a Millipore fluorocarbon (0.5 μm pore diameter) filter.

A number of solvents were used to clean the column at periodic intervals. The following elutropic series was found to remove most column contaminants: water, methanol, dichloromethane, n-heptane, and then back to water in the reverse order. A fifty volume percent mixture of the adjacent solvents in the above series was used in between the pure solvents to minimize heat of mixing effects, which can cause channeling due to shifts in the column packing.

In all cases the raffinate was analyzed, rather than the extract. Since the extract was not soluble in the mobile phase, two-phase flow in the column would have resulted. Also, TOPO is such a large molecule that it might have problems eluting from the column even if a mobile phase were used in which it was soluble. The concentration of solute in the extract was calculated from the difference between the feed and raffinate concentrations. Complete mass balance closure was assumed, but could not be checked.

A calibration curve was constructed for each solute to insure that the concentration-peak area relationship was linear in the concentration ranges used. In all cases it was found that the relationship was indeed linear. For each extraction a sample of the feed was injected as a check on the concentration as calculated from the known weight of solute and volume of water. This figure differed from that

given by the integrator by up to ± five percent. The differences were presumably due to variations in the pump flow rate. The feed and raffinate were each injected from three to five times, and the mean was used in further calculations. Good reproducibility was observed in all cases. The standard deviation was typically less than two percent.

D. IR Spectroscopy

A number of IR measurements were performed to determine the concentrations of free and complexed phenol in the organic phase. Solutions containing phenol in carbon tetrachloride, DIBK, and 25 weight percent TOPO in DIBK were prepared, and the free phenol concentration was measured using a Cary 14 spectrophotometer. Cylindrical quartz absorption cells were used, with a path length of 10 mm. The reference cell contained the phenol-free solvent. The first overtone band of the hydroxyl group of phenol was employed, at 7052 cm^{-1}, as recommended by Aksnes and Gramstad.[3]

Chapter III: Results and Discussion

A. Spectroscopy Measurements

The results of spectroscopy measurements are shown in Figure 1. The peak height of free phenol in carbon tetrachloride, measured at 7052 cm^{-1}, is presented as a function of the concentration of phenol dissolved in the solvent. The curvature is probably due to dimerization of the phenol at higher concentrations. No free phenol could be detected in any of the solutions of phenol in DIBK or in TOPO/DIBK.

B. Extraction of Phenol with TOPO/DIBK

As previously mentioned, extractions of phenol into TOPO with DIBK as a diluent were performed in two manners. Initially, the extractions were carried out with the Orbit shaker at ambient temperature in separatory funnels, while later extractions were carried out with the shaker bath in Erlenmeyer flasks at 22.5 °C. In all cases the distribution coefficients were larger for the latter method, with the difference becoming smaller at larger water-to-solvent phase ratios. In order to resolve these anomalies, a number of experiments were performed, the results of which are shown in Table 1.

The effect of shaking time on distribution coefficient was first examined, to see whether the differences were due to a slow chemical reaction or some other rate-limit-

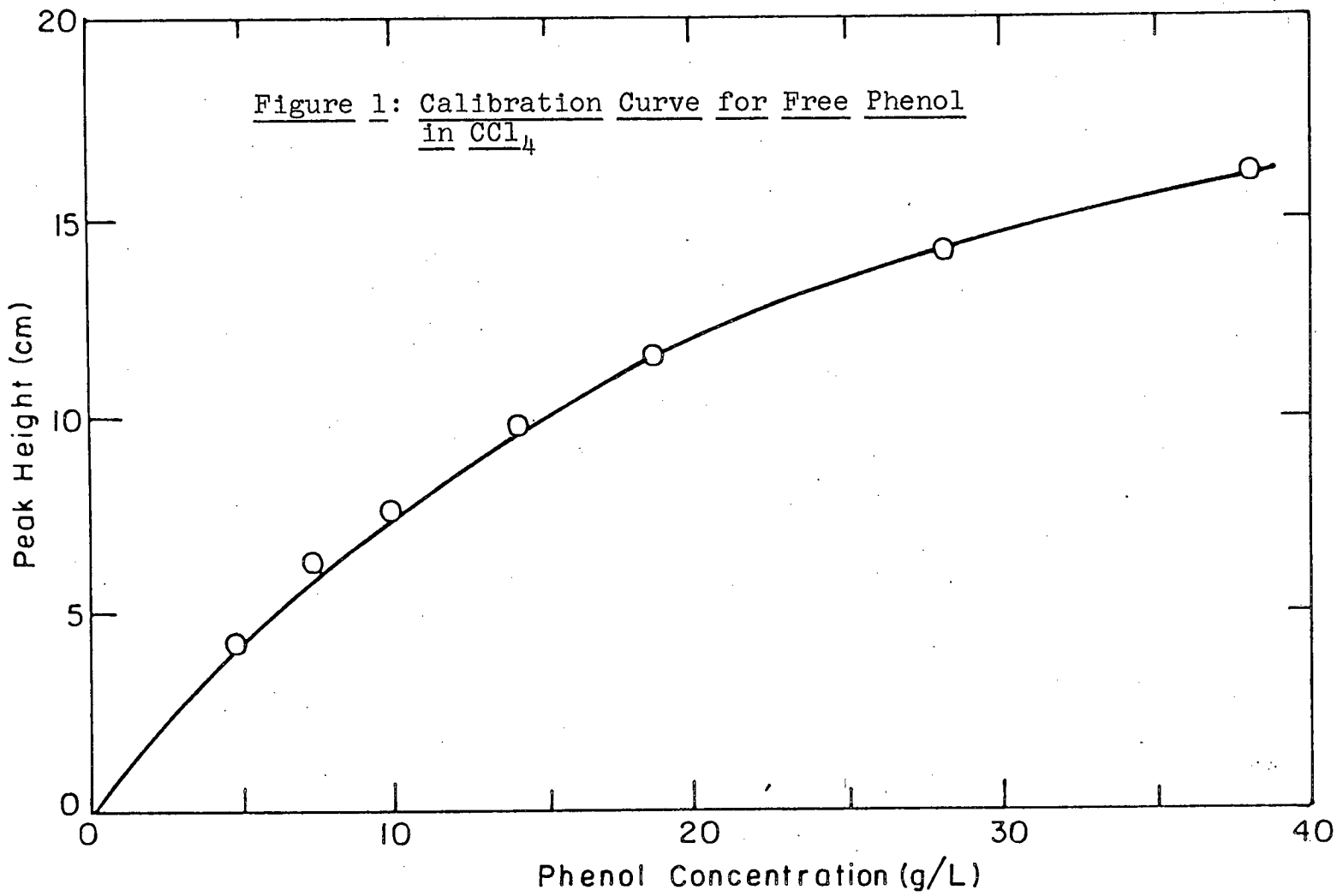


Figure 1: Calibration Curve for Free Phenol in CCl_4

XBL 822-5196

Table 1: Effect of Shaking and Phase Separation Methods on K_D

Inlet Phenol Concentration = 5000 ppm
Moles TOPO/Mole Phenol = 2.5:1 (except where noted)
Solvent = 25 weight percent TOPO/DIBK
T = 22.5 °C (except where noted)
Water-to-Solvent Volume Ratio = 4:1 (except where noted)

I. Effect of Shaking Time on K_D

Extractions Performed with Precision Scientific Shaker Bath and Erlenmeyer Flasks
Settling Time = 20 Minutes
Centrifuge Time = 30 Minutes

Shaking Time (Minutes)	K_D	K_M
10	430	361
10	443	371
20	442	371
20	433	363
40	434	364
40	435	365

II. Effects of New TOPO on K_D

Extractions Performed with Shaker Bath and Erlenmeyer Flasks
Shaking Time = 20 Minutes
Settling Time = 20 Minutes
Centrifuge Time = 30 Minutes

K_D	K_M
448	376
444	373

III. Effect of Ultracentrifuging the Raffinate on K_D

Extractions Performed with Shaker Bath and Erlenmeyer Flasks
Shaking Time = 40 Minutes
Settling Time = 20 Minutes
Centrifuge Time = 1 Hour

K_D	K_M
438	367
454	381

Table 1 (cont.)

IV. Comparison of Orbit Shaker and Shaker Bath

T = 20.1 °C
Shaking Time = 20 Min.
Settling Time = 20 Minutes
Centrifuge Time = 20 Minutes
Extractions Performed in Erlenmeyer Flasks

Shaker Type	K_D	K_M
Orbit	452	379
Precision Scientific	455	379
Precision Scientific	469	393

V. Extractions in Separatory Funnels Followed by Ultra-Centrifuging Raffinate

Shaking Time = 20 Minutes
Settling Time = 20 Minutes
Centrifuge Time = 1 Hour
T = 19.7 °C
Extractions Performed with Orbit Shaker

K_D	K_M
433	363
455	381

VI. Back Extraction Results

Extractions Performed with Shaker Bath and Erlenmeyer Flasks
Shaking Time = 20 Minutes
Settling Time = 20 Minutes
Centrifuge Time = 30 Minutes

	K_D	K_M
Forward Extraction	433	363
Back Extraction	443	371

Table 1 (cont.)

VII. Non-Equilibrium Results for Extraction of Phenol into TOPO/DIBK

Water-Solvent Volume Ratio	Stoichiometric Ratio (Moles TOPO/ Mole Phenol)	K_D	T(°C)
1:1	9.84:1	520	20.4
1:1	9.84:1	515	20.8
2:1	4.91:1	431	22.5
2:1	4.91:1	435	22.5
4:1	2.46:1	345	21.1
4:1	2.46:1	286	22.8
4:1	2.46:1	374	22.9
8:1	1.24:1	240	21.7
8:1	1.24:1	224	22.7
8:1	1.24:1	244	22.0
16:1	0.617:1	103	24.2
16:1	0.617:1	107	23.3
25:1	0.395:1	72.4	23.3
25:1	0.395:1	71.5	24.5

VIII. Non-Equilibrium Results for the Extraction of Phenol into Various Weight Percent TOPO/DIBK Mixtures

Wt. % TOPO/ DIBK	Water-Solvent Volume Ratio	K_D	T(°C)
15	2.33:1	284	24.5
15	2.33:1	288	24.5
5	0.775:1	132	22.0
5	0.775:1	131	22.0
0	1:1	43.7	22.2
0	1:1	44.0	22.0

ing phenomenon. No effect was observed (Table 1, Part I). In addition, a back extraction into Milli-Q water gave a distribution coefficient equal to that of the forward extraction (Table 1, Part VI), which further rules out this explanation. An extraction was also performed using a fresh, unopened bottle of TOPO (Table 1, Part II), to check whether the differences were due to some impurity in the TOPO. This too gave unchanged distribution coefficients.

It was therefore postulated that the differences in K_D values were due to incomplete phase separation in the Orbit shaker runs. Extractions were carried out on the Precision Scientific shaker bath in Erlenmeyer flasks followed by centrifuging the raffinate in a Sorvall Model No. RC-2 ultracentrifuge at 20,000 RPM (Table 1, Part III); on the Orbit shaker in Erlenmeyer flasks followed by normal centrifuging (Table 1, Part IV); and on the Orbit shaker in separatory funnels followed by ultracentrifuging (Table 1, Part V). In all cases the distribution coefficients showed little or no variation. It was thus concluded that the lower K_D values obtained originially with the Orbit shaker were due to incomplete phase separation, which in turn was due to using separatory funnels and centrifuging for an insufficient amount of time. The differences in K_D values are larger at higher solvent-to-water phase ratios because at these conditions the concentration of solute in the raffinate is extremely small. Only a small amount of entrained

extract is necessary to cause a large relative change in this concentration, and thus a large change in the apparent distribution coefficient. The only objection to this explanation is that good consistency was obtained for the extractions on the Orbit shaker, which means that the same degree of entrainment was present in all cases.

Table 1 also presents the non-equilibrium results, performed on the Orbit shaker, for extractions at 25 weight percent TOPO/DIBK and 5000 ppm inlet phenol concentration, with varying water-to-solvent phase ratio, and thus TOPO-to-phenol stoichiometric ratio; and at constant stoichiometric ratio (= 2.5) and inlet phenol concentration (= 5000 ppm), but varying solvent composition. Tables 2 and 3 present similar results for the true (i.e., equilibrium) distribution coefficients, performed with the shaker bath.

C. Models of the Extraction Mechanism

Several different approaches were used to model the extraction mechanism. The simplest model assumes no interaction of the phenol and diluent, no variation in phenol activity coefficient with concentration (i.e., the system is dilute), no extraction of water into the organic phase, and only a single TOPO-phenol complex being formed. The phenol is first assumed to transfer from the aqueous phase to the organic phase:

$$Ph_{aq} \rightleftarrows Ph_{org}$$

Table 2: True Distribution Coefficients for the Extraction of Phenol into 25 Wt. % TOPO/DIBK

Inlet Phenol Concentration = 5000 ppm
Extractions Performed with Precision Scientific Shaker Bath
T = 22.5 °C

Water-Solvent Volume Ratio	Moles TOPO/ Mole Phenol	K_D	K_M
1:1	9.96:1	791	652
1:1	9.96:1	834	687
2:1	4.98:1	628	521
2:1	4.98:1	674	559
3.9:1	2.52:1	468	392
3.9:1	2.52:1	456	382
8:1	1.24:1	252	216
8:1	1.24:1	257	220
16:1	0.615:1	109	96.7
16:1	0.615:1	110	97.5
25:1	0.398:1	75.5	68.6
25:1	0.398:1	76.8	69.9

Table 3

True Distribution Coefficients for the Extraction of Phenol into Various Weight % TOPO/DIBK Mixtures

Wt. % TOPO/ DIBK	Water-Solvent Volume Ratio	K_D	K_M
15	2.37:1	313	259
15	2.37:1	327	270
5	0.789:1	162	133
5	0.789:1	156	127
0	1:1	45.3	36.7
0	1:1	47.2	38.2

Inlet Phenol Concentration = 5000 ppm
Extractions Performed with Precision Scientific Shaker Bath
Moles TOPO/Mole Phenol = 2.50:1
T = 22.5 °C

with

$$(1) \qquad K_P = (Ph)_{org}/(Ph)_{aq}$$

where K_P is a physical distribution coefficient which is assumed to be a function of temperature only, and the quantities in parentheses are phenol concentrations in moles/liter in the organic and aqueous phases.

The phenol then complexes with an unknown number n of TOPO molecules:

$$Ph_{org} + n\ TOPO = complex$$

with

$$(2) \qquad K_R = \frac{(complex)}{(Ph)_{org}(TOPO)^n}$$

where:

K_R = reaction equilibrium constant = K(T) only
(complex) = phenol-TOPO complex concentration, mol/l
$(Ph)_{org}$ = free phenol concentration in the organic phase, mol/l
(TOPO) = uncomplexed TOPO concentration in the organic phase, mol/l

By definition, the distribution coefficient is:

$$(3) \qquad K_M = \frac{(complex) + (Ph)_{org}}{(Ph)_{aq}}$$

In the present case it is assumed that (complex) is much larger than $(Ph)_{org}$. Thus:

$$(4) \qquad K_M = (complex)/(Ph)_{aq}$$

When these equations are combined, one arrives at the following result:

$$(5) \quad K_M = K_R \, K_P \, (TOPO)^n$$

Taking the natural logarithm of both sides of the above equation yields:

$$(6) \quad \ln(K_M) = n \ln(TOPO) + \ln(K_P \, K_R)$$
$$= n \ln(TOPO) + \text{constant}$$

Thus, graphing $\ln(K_M)$ vs. $\ln(TOPO)$ should yield a straight line with a slope equal to n. It is necessary to assume a value for n and calculate the concentration of uncomplexed TOPO from a mass balance: uncomplexed TOPO = original TOPO - n(phenol in extract). This mass balance again neglects physically dissolved phenol in the extract. The amount of phenol in the extract for use in this equation is calculated from a mass balance and the known values of phenol in the feed and raffinate. The guessed value of n can then be checked from the slope of the resultant line.

Figure 2 shows results for assumed values of n equal to 1, 1.5, and 2. A curve results for n equal to 1. Both n equal to 1.5 and 2 yield straight lines, but with slopes equal to 0.68 and 0.51, respectively. The curvature is even more pronounced for values of n less than 1. The aforementioned model is thus not valid. This is probably

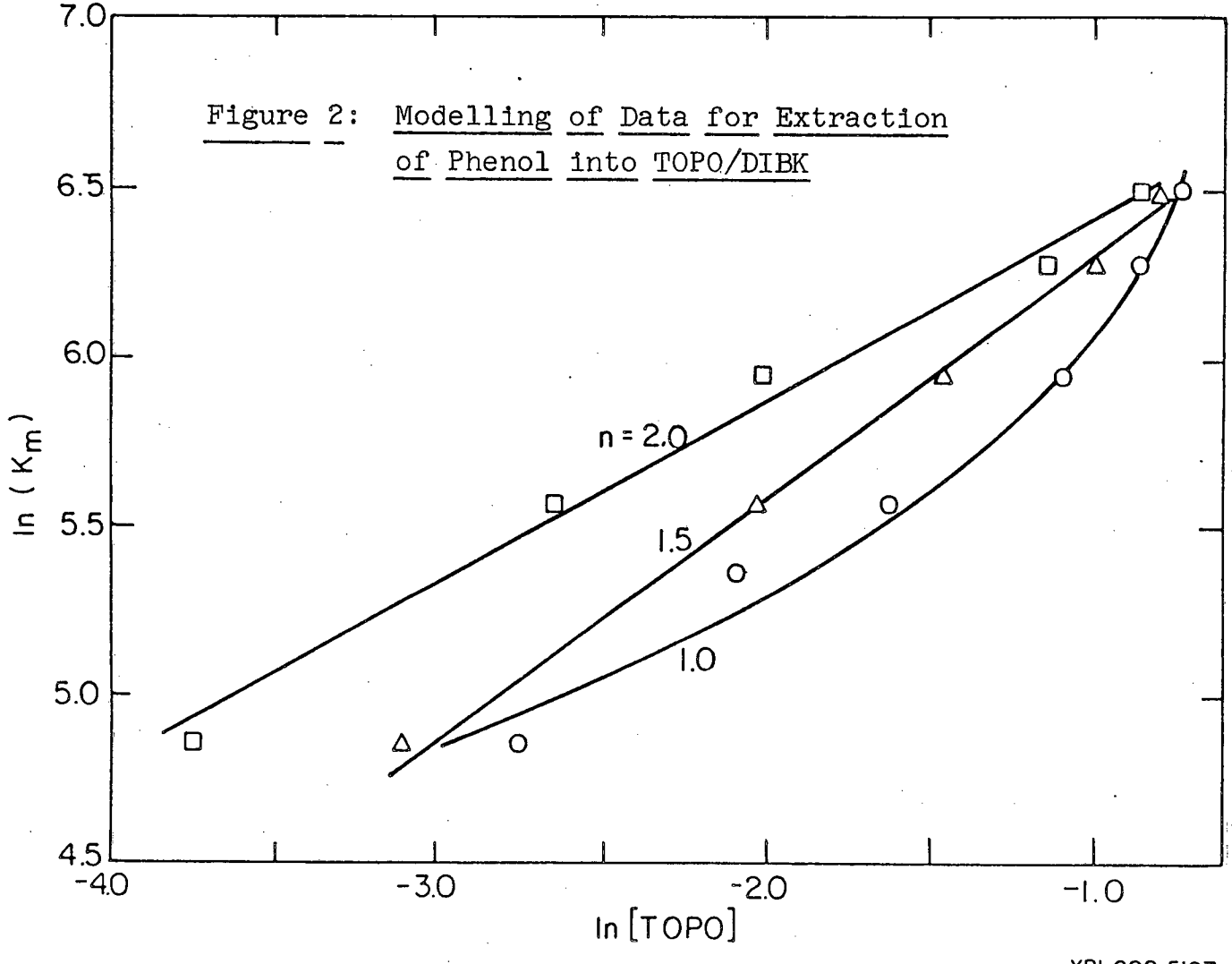


Figure 2: Modelling of Data for Extraction of Phenol into TOPO/DIBK

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due to several factors. The assumption that DIBK is a non-interacting diluent is not a good one, as evidenced by the high distribution coefficient of phenol into it. The curve for n equal to one is typical of systems where the diluent plays a complexing role along with the extractant.[26,40] The spectroscopy results also indicate that DIBK can effectively complex phenol.

A second factor could be that several complexes are present in the organic phase, rather than just a single one. Although a value of n equal to one is a reasonable estimate, and is reported by Stuurman et al[41] for the phenol-TOPO-n-hexane system, it is not unlikely that several complexes exist in the organic phase, with the dominant species changing with solvent composition or water-to-solvent phase ratio. Curves of this type have been derived on a theoretical basis by Soczewinski and Matysik.[39]

A second, more complicated model, which does not neglect the solubility of the phenol in the diluent, can also be derived. With the assumption of a complexation number, n, equal to one, from the definition of the complexation, physical distribution, and equilibrium distribution coefficients, and writing a mass balance on the solute, the following equation (see Appendix A) results:

$$R = \frac{T_{io}}{P_{iw} K_M} \left[\frac{(K_M - K_P)(K_P K_R P_{iw})}{K_P K_R T_{io} - (K_M - K_P)} - 1 \right] \tag{7}$$

where:

K_M = molar distribution coefficient = $\frac{(P\ T)_o + P}{P_w}$

K_P = physical distribution coefficient = P_o/P_w

K_R = complexation constant = $(P\ T)_o/(P_o)(T_o)$

T_{io} = concentration of TOPO initially in the organic phase, mol/l

P_{iw} = concentration of phenol initially in the aqueous phase, mol/l

R = stoichiometric ratio of TOPO to phenol = $\frac{T_{io}\ S}{P_{iw}\ W}$

P_o = concentration of phenol in the organic phase, mol/l

P_w = concentration of phenol in the aqueous phase, mol/l

$(P\ T)_o$ = concentration of phenol-TOPO complex in the organic phase, mol/l

S = volume of the initial organic phase, assumed = final volume

W = volume of the initial aqueous phase, assumed = final volume

Equation 7 can be used to extract useful information about K_P and especially K_R. From Equation 7, one can calculate R vs. the experimentally obtained values of K_M for various assumed values of K_P. Figure 3 shows results for K_P equal to 25, 35, and 45. Only the experimental results for constant solvent composition (Table 2) were used, because in this set of data the variation of the activity coefficient of phenol is probably less than in the data at changing solvent composition (Table 3).

Figure 3 shows that the graph consists of two asymptotic regions and a transition zone between these two regions. For small R, the value of K_M approaches K_P. For

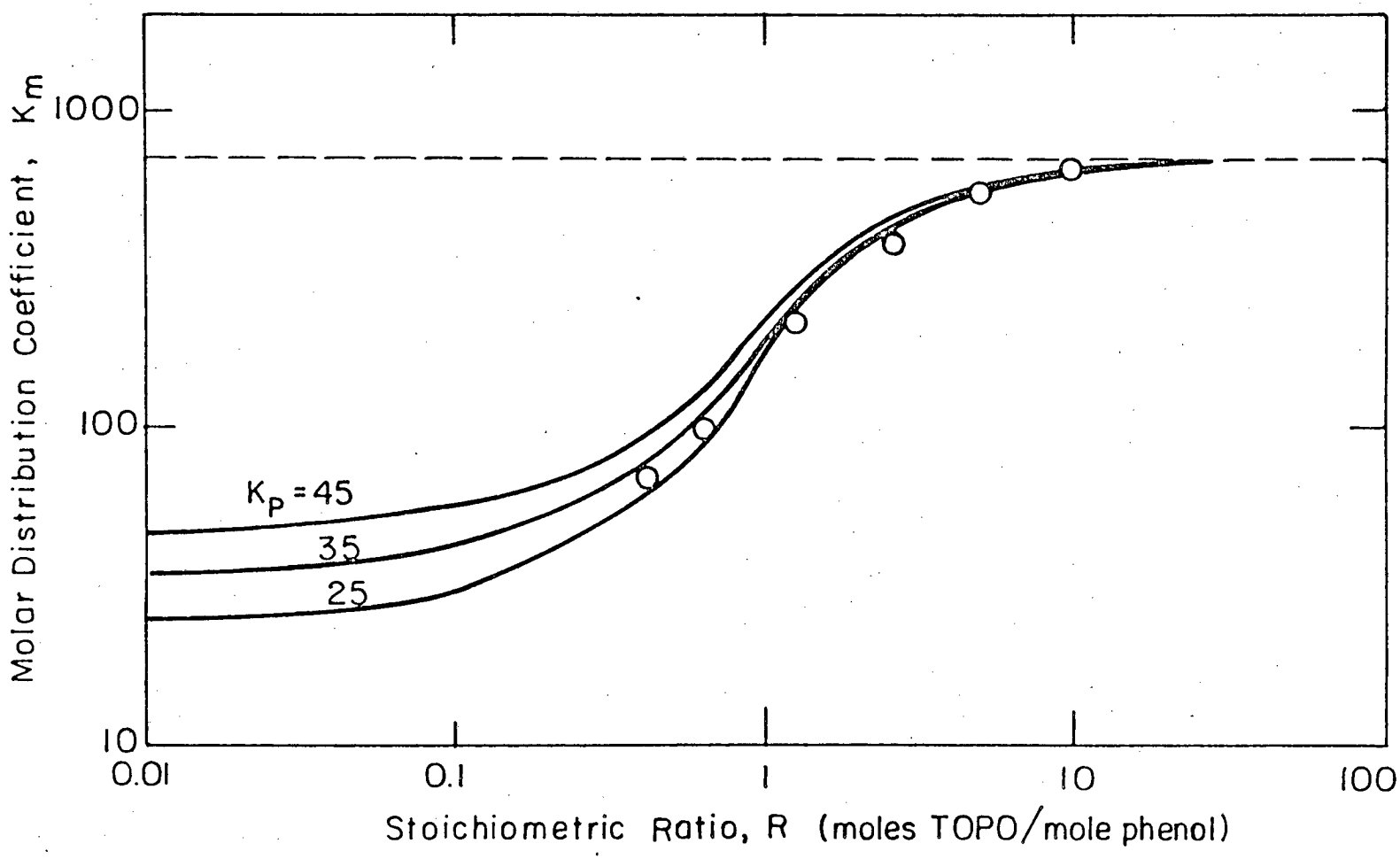

Figure 3: Modelling of Phenol Data with More Complicated Model

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large R, the value of $K_P + K_P K_R T_{io}$ approaches a constant value of about 700. The complexation constant thus appears to be in the range of 27 to 51. These values are much smaller than the values of K_R for complex formation involving phenol and phosphoryl compounds which are reported by Aksnes and Albriktsen.[2] These workers report a value of 1000 for phenol and tri-butyl phosphine oxide in carbon tetrachloride at 25 °C. The values of K_R in the present work could be low because the ratio of activity coefficients of phenol to extractant-phenol complex might be less in DIBK than in a system with a non-interacting diluent (e.g., CCl_4).

Appendix A discusses the development and use of Equation 7 in more detail.

D. Extraction of Phenol into TOPO with Other Diluents

Tables 4 and 5 list distribution coefficients for phenol into solvents composed of TOPO dissolved in various diluents and into the pure diluents, measured using the shaker bath. Results for the Orbit shaker are shown in Table 6. The results with the Orbit shaker again represent non-equilibrium conditions, since in all cases the distribution coefficients are lower than the values obtained with the shaker bath. The concentration of TOPO is 25 weight percent except for the cases of n-butyl ether and kerosene as diluents, for which it is 15 and 5 weight percent, respectively. This is due to solubility limitations of TOPO in these liquids.

Table 4

Distribution Coefficients for the Extraction of Phenol into TOPO Dissolved in Various Diluents

Diluent	Wt.% TOPO	Water-Solvent Volume Ratio	Moles TOPO/ Mole Phenol	K_D	K_M
n-Butyl Acetate	25	4.25:1	2.49:1	380	338
n-Butyl Acetate	25	4.25:1	2.49:1	395	352
2-Ethyl Hexanol	25	4.05:1	2.49:1	56.4	48.0
2-Ethyl Hexanol	25	4.05:1	2.49:1	56.2	47.8
Chevron 25	25	4.25:1	2.49:1	345	308
Chevron 25	25	4.25:1	2.49:1	339	302
Kerosene	5	0.75:1	2.52:1	88.9	69.6
Kerosene	5	0.75:1	2.52:1	95.4	74.7
n-Butyl Ether	15	2.27:1	2.49:1	322	253
n-Butyl Ether	15	2.27:1	2.49:1	313	247
DIBK	25	3.90:1	2.52:1	468	392
DIBK	25	3.90:1	2.52:1	456	382
DIBK	15	2.37:1	2.50:1	313	259
DIBK	15	2.37:1	2.50:1	327	270
DIBK	5	0.789 :1	2.50:1	162	133
DIBK	5	0.789 :1	2.50:1	156	127

Inlet Phenol Concentration for All Extractions = 5000 ppm
T = 22.5 °C
Extractions Performed with Shaker Bath and Erlenmeyer Flasks

Table 5

Distribution Coefficients for the

Extraction of Phenol into Various Diluents

Diluent	Water-Solvent Volume Ratio	K_D	K_M
n-Butyl Acetate	1.33:1	57.8	51.4
n-Butyl Acetate	1.33:1	59.3	52.7
2-Ethyl Hexanol	1:1	28.2	23.7
2-Ethyl Hexanol	1:1	28.5	23.9
Chevron 25	1:1	1.81	1.58
Chevron 25	1:1	1.87	1.63
Kerosene	1:1	0.15	0.12
Kerosene	1:1	0.15	0.12
n-Butyl Ether	1:1	14.0	11.1
n-Butyl Ether	1:1	14.2	11.3
DIBK	1:1	45.3	36.7
DIBK	1:1	47.2	38.2

Inlet Phenol Concentration for all Extractions = 5000 ppm
T = 22.5 °C
Extractions Performed on Shaker Bath with Erlenmeyer Flasks

Table 6

Non-Equilibrium Results for the Extraction of Phenol into TOPO Dissolved in Various Diluents

Diluent	Wt. % TOPO	Water-Solvent Volume Ratio	Moles TOPO/ Mole Phenol	K_D	K_M	T(°C)
n-Butyl Acetate	25	4.15:1	2.55:1	331	295	22.0
n-Butyl Acetate	25	4.15:1	2.55:1	316	282	22.0
2-Ethyl Hexanol	25	4.00:1	2.52:1	57.5	48.9	22.0
2-Ethyl Hexanol	25	4.00:1	2.52:1	57.8	49.2	22.0
Chevron 25	25	4.17:1	2.54:1	287	256	20.0
Chevron 25	25	4.17:1	2.54:1	293	261	20.0
Kerosene	5	0.75:1	2.56:1	80.4	63.0	20.0
Kerosene	5	0.75:1	2.56:1	79.2	62.1	20.0
n-Butyl Ether	15	2.22:1	2.58:1	221	174	20.0
DIBK	25	4.00:1	2.46:1	345	289	21.1
DIBK	25	4.00:1	2.46:1	286	240	22.8
DIBK	25	4.00:1	2.46:1	374	314	22.9
DIBK	15	2.33:1	2.50:1	284	234	24.5
DIBK	15	2.33:1	2.50:1	288	237	24.5
DIBK	5	0.775:1	2.50:1	132	108	22.0
DIBK	5	0.775:1	2.50:1	131	107	22.0

Inlet Phenol Concentration for all Extractions = 5000 ppm
Extractions Performed with Orbit Shaker and Separatory Funnels

The inlet phenol concentration is 5000 ppm, while the stoichiometric ratio of TOPO to phenol is held at about 2.5:1. With the exception of 2-ethyl hexanol, the distribution coefficients into the TOPO/diluent mixture are at least an order of magnitude larger than into the pure diluent, which indicates that TOPO forms strong hydrogen bonds with phenol.

Chevron 25, n-butyl acetate, n-butyl ether, and DIBK all appear to be good diluents for TOPO, which means they all effectively solvate the TOPO-phenol complex. The latter three diluents evidently are effective because of the ready availability of the unshared electrons on the oxygen atom, while in Chevron 25 the pi electrons are available for bonding. Kerosene is not as effective a diluent because it lacks free electrons for solvating the complex. 2-ethyl hexanol, which gives distribution coefficients nearly a factor of 10 lower than DIBK, probably competes with phenol for the phosphoryl group in TOPO, with complexation occurring between the phosphoryl oxygen and the hydroxyl group hydrogen atom. Ricker et al[33] observed the same phenomenon for extraction of acetic acid from water; TOPO/2-ethyl hexanol gave lower distribution coefficients than either TOPO/2-heptanone or TOPO/Chevron 25.

It is of some interest that the value of K_D for phenol into n-butyl ether is much lower than into DIBK (14.1 vs. 46.2), while the distribution coefficients into the TOPO/diluent mixtures are nearly equal (318 for TOPO/n-butyl ether

vs. 320 for TOPO/DIBK, both for 15 weight percent solvent mixtures). In the case of the pure diluent, the ether is a poorer solvent because its oxygen is less of an electron donor than the carbonyl oxygen on the ketone. Also, bonding is less sterically hindered for the ketone than for the ether.

Aksnes[1] has shown that the phosphoryl group participates in hydrogen bonding when triethyl phosphate complexes phenol. In all likelihood a similar situation exists between TOPO and phenol. One would think that this complex would be more effectively solvated by DIBK than by n-butyl ether, since DIBK is both more polar and a better electron donor. This is not the case, however. Apparently it makes little difference to the complex what diluent is present as long as it has some basic (electron-donating) character and does not preferentially associate with the phosphoryl group.

Values of the reaction constant, K_R, can be calculated for the various TOPO/diluent systems by using an analysis similar to that of the previous section (see Appendix A). Since the extractions were performed at a stoichiometric ratio of about 2.5 moles of TOPO per mole of phenol, which corresponds to a value of R not quite in the upper asymptotic region, the values of K_R are only rough estimates.

These values are presented in Table 7. They range from roughly 2 (2-ethyl hexanol) to over 9000 (kerosene). The large value obtained for kerosene, which is a non-interacting diluent, is a good indication of the very strong

Table 7

Calculated Equilibrium Constants for the Association Reaction Between Phenol and TOPO Dissolved in Various Diluents

Solvent	K_R	$K_P K_R T_{io}$	K_P
25 Wt. % TOPO/DIBK	27.3	543	37.5
15 Wt. % TOPO/DIBK	28.8	343	37.5
5 Wt. % TOPO/DIBK	32.9	129	37.5
25 Wt. % TOPO/n-Butyl Acetate	15.1	442	52.0
25 Wt. % TOPO/2-Ethyl Hexanol	2.31	29.6	23.8
25 Wt. % TOPO/Chevron 25	555	501	1.60
15 Wt. % TOPO/n-Butyl Ether	114	385	11.2
5 Wt. % TOPO/Kerosene	9781	119	0.12

Inlet Phenol Concentration for All Extractions = 5000 ppm
T = 22.5 °C
Extractions Performed with Shaker Bath and Erlenmeyer Flasks

hydrogen bonds formed between phenol and TOPO.

The distribution coefficients measured for phenol into several of the pure diluents (Table 5) agree well with those found by other workers. The value for K_D into kerosene (0.15) is close to that measured by Medir and Mackay[28] (0.20). The K_D values for phenol into n-butyl acetate range from 55 to 65 (see Table 5, Introduction), and compare favorably with the value of 58.6 determined in this work. The value of K_D equal to 28.4 for 2-ethyl hexanol closely matches the value (28.1) reported by Bell[4], who calculated it from the data of Pittman[31] at high pH, using Greminger and King's[14] model for the change in K_D for an ionizing solute with changing pH.

E. Extraction of the Dihydric Phenols into TOPO/DIBK

The results of extracting the dihydric phenols into 25 weight percent TOPO/DIBK and into pure DIBK are shown in Tables 8 and 9. The extractions were performed with the Orbit shaker in Erlenmeyer flasks at ambient temperature, followed by holding the flasks in a temperature bath at 30 °C for ½ hour. This method of extraction gave K_D values close to those with the shaker bath for catechol (see Section G), which indicates that the K_D values are true equilibrium values.

The effect of stoichiometric ratio on K_M was investigated for catechol. Using the same model and assumptions as for phenol, one arrives at a similar equation:

Table 8

Extraction of Catechol into 25 Wt. % TOPO/DIBK

Water-Solvent Volume Ratio	Moles TOPO/ Mole Catechol	K_D	K_M	T(°C)
9.17:1	1.27:1	92.1	80.3	30
9.17:1	1.27:1	91.2	79.4	30
4.58:1	2.57:1	202	170	30
4.58:1	2.57:1	204	172	30
2.29:1	5.04:1	267	223	30
2.29:1	5.04:1	277	231	30

Inlet Catechol Concentration = 5000 ppm
Extractions Performed on Orbit Shaker in Erlenmeyer Flasks
Followed by Thermostatting at 30 °C

Table 9

Extraction of the Dihydric Phenols
into 25 Wt. % TOPO/DIBK and into DIBK

Isomer	Wt. % TOPO/ DIBK	Water-Solvent Volume Ratio	Moles TOPO/ Mole Solute	K_D	K_M
Catechol	25	4.58:1	2.57:1	202	170
Catechol	25	4.58:1	2.57:1	204	172
Resorcinol	25	4.58:1	2.54:1	99.5	83.6
Resorcinol	25	4.58:1	2.54:1	97.1	81.6
Hydroquinone	25	4.58:1	2.54:1	37.1	31.1
Hydroquinone	25	4.58:1	2.54:1	32.7	27.5
Catechol	0	1:1	--	6.97	5.64
Catechol	0	1:1	--	6.91	5.59
Resorcinol	0	1:1	--	4.33	3.50
Resorcinol	0	1:1	--	4.17	3.37
Hydroquinone	0	1:1	--	2.06	1.67
Hydroquinone	0	1:1	--	2.04	1.65

Inlet Solute Concentration = 5000 ppm
T = 30 °C
Extractions Performed with Orbit Shaker in Erlenmeyer Flasks Followed by Thermostatting at 30 °C

$$(8) \quad \log(K_M) = n \log(TOPO) + constant$$

A logical choice for n is 1. Sodewinski and Matysik[39] found this to be so for extractions of catechol into tributyl phosphate/n-hexane and into tributylamine/n-hexane. Apparently the formation of (catechol)$(TOPO)_2$ complexes is hindered by the close proximity of the adjacent OH groups. The graph for n equal to 1 is shown in Figure 4. Again a curve rather than a straight line results. The model probably breaks down for the same reason as for phenol, i.e., DIBK is itself interacting with the catechol.

The more complicated model used for phenol can also be applied to the catechol data. Figure 5 shows the results of using Equation 7 to model the data for values of K_P equal to 4.5, 5.5, and 6.5. The reaction constants, K_R, range from 71.9 to 106.

The distribution coefficients for all the isomers into TOPO/DIBK are an order-of-magnitude larger than those into the pure diluent. Again, this is a good indication that the hydrogen bonds formed between the solutes and TOPO are quite strong. The large K_D values also indicate that TOPO is a promising solvent for the removal of phenols from coal conversion wastewaters. A calculation with conditions similar to those of Beychok[5] (see Appendix A) results in 99 percent catechol removal for a nine (ideal) stage extractor at a solvent-to-water ratio of about 1 to 10 on a mass basis. This compares favorably with both DIPE (15 percent removal)

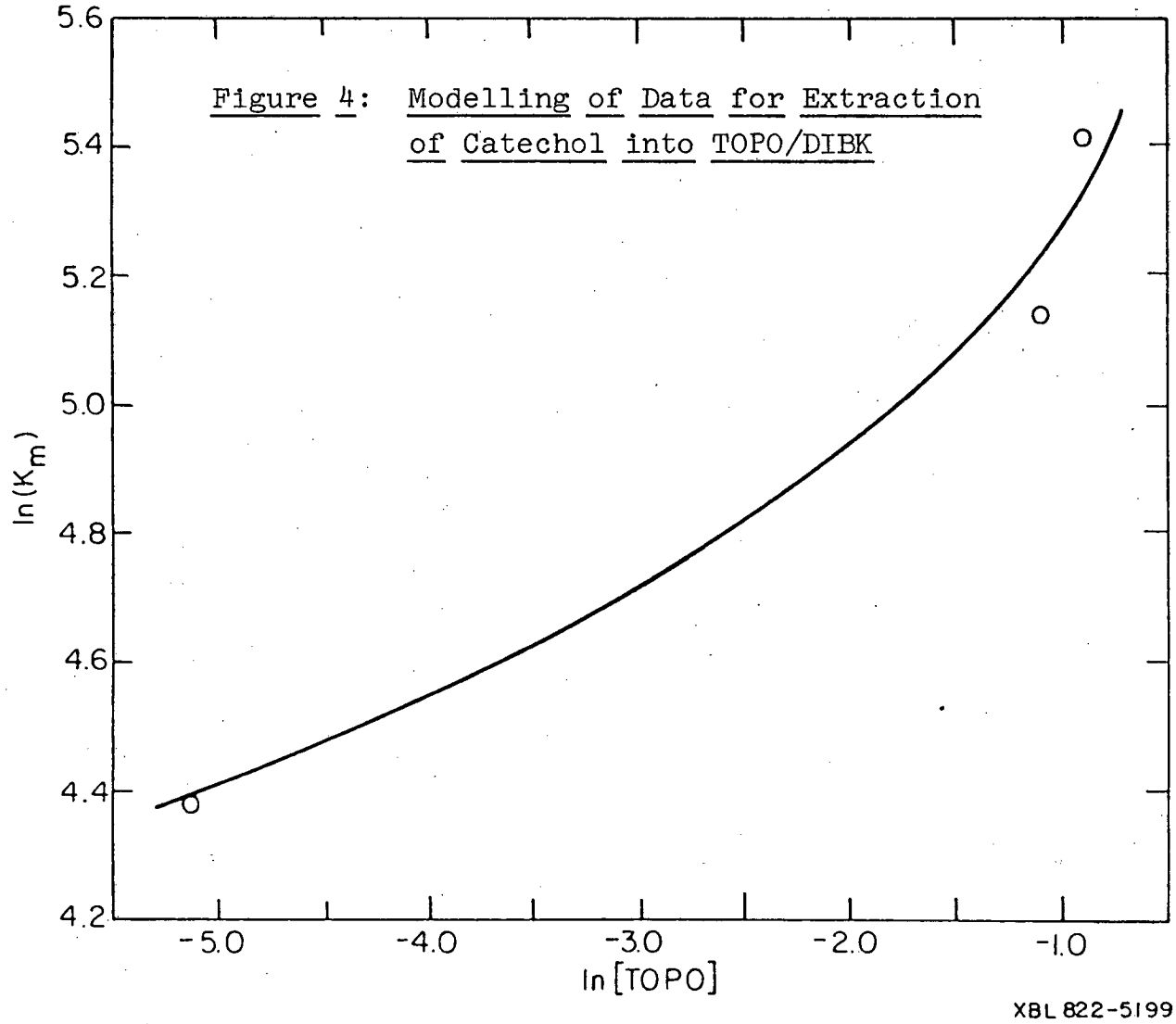

Figure 4: Modelling of Data for Extraction of Catechol into TOPO/DIBK

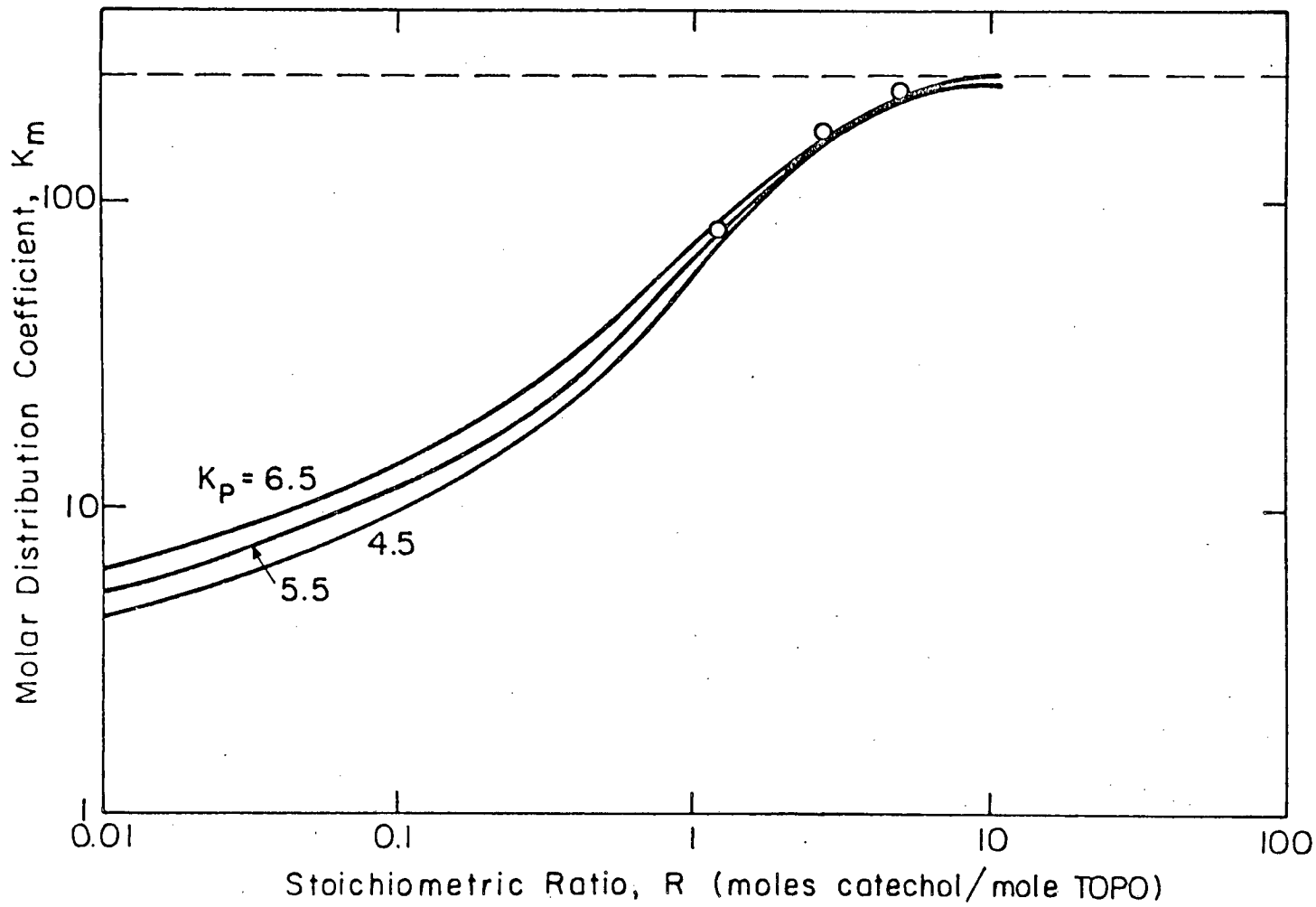

Figure 5: Modelling of Catechol Data with More Complicated Model

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and MIBK (70 percent removal). The removal would be lower for resorcinol and hydroquinone, since they have lower distribution coefficients, but still substantially higher than for conventional solvents.

The distribution coefficients for the isomers into both pure DIBK and into TOPO/DIBK increase in the order hydroquinone< resorcinol < catechol. This same order was noted by Greminger and King[14] for extractions into both MIBK and DIPE. The magnitude of K_D is due to several factors, including the activity coefficients of the solutes in water, the complexing ability of the extractant, and the solvating ability of the solvent for complexed and uncomplexed solute. Activity coefficients for the solutes, at infinite dilution in water and at 25 °C, are as follows[42]: resorcinol, 0.61; catechol, 1.90; and hydroquinone, 4.3. On this basis alone one would expect the distribution coefficients to increase in the order resorcinol< catechol< hydroquinone. However, organic phase effects are important also. Catechol is the most polar of the dihydrics and would thus interact more strongly with DIBK or TOPO/DIBK than either resorcinol or hydroquinone. Hydroquinone, which has no net dipole moment, is the least polar and would interact the least strongly. Specific complexation effects are a factor also. The catechol-TOPO complex could be particularly strong, because two hydroxyl groups can interact with a molecule of TOPO, which might also happen to some lesser extent for

resorcinol. Hydroquinone, on the other hand, may self-associate into long chains and resist complexation.

F. Extraction of the Trihydric Phenols into TOPO/DIBK

Table 10 lists distribution coefficients for the trihydric phenols into 25 weight percent TOPO/DIBK and into pure DIBK. The extractions were performed at ambient temperature with the Orbit shaker in Erlenmeyer flasks followed by thermostatting in a temperature bath at 30 °C. The K_D values are about two orders of magnitude larger for TOPO/DIBK than for DIBK alone, which is again evidence of the very strong complexes formed with TOPO.

Pyrogallol has a higher K_D into DIBK than phloroglucinol even though its water solubility is much higher (62.5 g/100 g H_2O for pyrogallol vs. 1.13 g/100 g H_2O for phloroglucinol, both at 25 °C).[36] Water solubilities are a good inverse indication of activity coefficients in water, provided that the melting points and heats of fusion of the compounds in question are not too dissimilar. On this basis, then, phloroglucinol would be expected to have the higher K_D value. Organic phase effects must outweigh aqueous phase effects in this case, with the carbonyl oxygen on DIBK complexing the strongly polar pyrogallol molecule with its three adjacent OH groups more effectively than the less polar phloroglucinol.

For extractions into 25 weight percent TOPO/DIBK, the order is changed, to phloroglucinol < 1,2,4-benzenetriol <

Table 10

Extraction of the Trihydric Phenols into 25 Wt. % TOPO/DIBK and into DIBK

Isomer	Wt. % TOPO/ DIBK	Water-Solvent Volume Ratio	Moles TOPO/ Mole Solute	K_D	K_M
Phloroglucinol	25	5.23:1	2.55:1	21.0	17.5
Phloroglucinol	25	5.23:1	2.55:1	20.8	17.3
Pyrogallol	25	5.23:1	2.45:1	51.6	43.5
Pyrogallol	25	5.23:1	2.45:1	55.8	47.0
Pyrogallol*	25	2.00:1	11.4 :1	110	91.2
Pyrogallol*	25	2.00:1	11.4 :1	128	105
1,2,4-Benzenetriol	25	5.23:1	2.51:1	23.7	20.0
1,2,4-Benzenetriol	25	5.23:1	2.51:1	24.9	20.9
Phloroglucinol	0	1:1	--	0.370	0.298
Phloroglucinol	0	1:1	--	0.237	0.191
Pyrogallol	0	1:1	--	0.548	0.442
Pyrogallol	0	1:1	--	0.593	0.479
1,2,4-Benzenetriol	0	1:1	--	0.119	0.095
1,2,4-Benzenetriol	0	1:1	--	0.142	0.114

Inlet Solute Concentration = 5000 ppm
T = 30 °C
Extractions Performed with Orbit Shaker in Erlenmeyer Flasks Followed by Thermostatting at 30 °C

*Conditions Identical to those of Bell[4]

pyrogallol. The distribution coefficients for phloroglucinol and 1,2,4-benzenetriol are nearly equal. Presumably the order changes because DIBK solvates the TOPO-1,2,4-benzenetriol complex better than the TOPO-phloroglucinol complex, or because TOPO can interact more strongly with 1,2,4-benzenetriol, with its two adjacent OH groups, than it can with phloroglucinol, which has no adjacent OH groups.

Table 10 also lists the results for an extraction of 100 mL of a 3000 ppm pyrogallol solution into 50 mL of 25 weight percent TOPO/DIBK. These conditions are identical to those used by Bell[4] in earlier experiments. The measured distribution coefficient (K_D) of 119 agrees fairly well with Bell's value of 110.

G. Extraction of Phenol and Catechol at Various Temperatures

Tables 11 and 12 present distribution coefficients for phenol and catechol extracted from water into 25 weight percent TOPO/DIBK at temperatures ranging from 22.5 °C to 60 °C. The stoichiometric ratio and inlet solute concentration were kept constant at approximately 2.5 moles of TOPO per mole of solute and 5000 ppm, respectively. All extractions were performed with the Precision Scientific shaker bath.

The extraction of catechol at 30 °C yields a K_D of 194. This is slightly lower than the K_D of 203 obtained under the same conditions but with the Orbit shaker at room temperature and then holding the extraction flask in a thermo-

Table 11

Variation of K_D with Temperature for Phenol

T(°C)	K_D	K_M
22.5	468	392
22.5	456	382
30	352	295
30	347	291
40	262	220
40	258	216
50	198	166
50	189	159
60	148	124
60	148	124

Inlet Phenol Concentration = 5000 ppm
Solvent Composition = 25 Wt. % TOPO/DIBK
Moles TOPO/Mole Phenol = 2.5:1
Water-Solvent Volume Ratio = 3.9:1
Extractions Performed with Shaker Bath and Erlenmeyer Flasks

Table 12

Variation of K_D with Temperature for Catechol

T(°C)	K_D	K_M
22.5	248	209
22.5	253	213
30	195	164
30	192	162
40	147	124
40	147	124
40	148	125
40	153	128
50	101	85.4
50	99.0	83.4
50	102	85.9
50	103	86.8
55	89.7	75.5
55	86.4	72.7
55	84.4	71.0
55	84.6	71.2
60	69.8	58.9
60	69.6	58.6
60	68.9	57.9
60	69.4	58.4

Inlet Catechol Concentration = 5000 ppm
Solvent Composition = 25 Wt. % TOPO/DIBK
Moles TOPO/Mole Catechol = 2.5:1
Water-Solvent Volume Ratio = 4.58:1
Extractions Performed with Shaker Bath and Erlenmeyer Flasks

statted temperature bath at 30 °C. Thus, the latter method, which was used for all the di- and trihydric phenols, gives fairly accurate results.

The temperature dependence of K_D can be modelled in a straightforward manner. The activity coefficient of a component, γ_i, is defined as

$$(9) \qquad \ln(\gamma_i) = \bar{g}_i^E/RT$$

where $\bar{g}_i^E$ is the partial excess Gibb's energy of component i, R is the gas constant, and T is temperature. This expression can be differentiated with respect to T at constant pressure, P, and composition, x, to yield (see Appendix A):

$$(10) \qquad \left[\frac{\delta \ln(\gamma_i)}{\delta T}\right]_{P,x} = \frac{\bar{h}_i - h_{pure\ i}}{R\,T^2}$$

where $\bar{h}_i$ is the partial molar enthalpy of component i, and $h_{pure\ i}$ is the molar enthalpy of pure i. This expression can then be integrated and modified by using the thermodynamic criterion that $a_{ij} = a_{ik}$ at equilibrium, where a_{ij} is the activity of i in phase j and a_{ik} is the activity of i in phase k. The following equation results:

$$(11) \qquad \ln(x_{ik}/x_{ij}) = \frac{\bar{h}_{ij} - \bar{h}_{ik}}{RT} + \text{constant}$$

where x_{ik} and x_{ij} are the mole fractions of i in phase k and j, respectively, and $\bar{h}_{ij}$ and $\bar{h}_{ik}$ are the partial molar

enthalpies of i in phase j and k, respectively. At a constant inlet solute concentration, water-to-solvent ratio, and solvent composition, the following expression is valid:

$$(12) \qquad \ln(K_D) = \frac{\bar{h}_{ij} - \bar{h}_{ik}}{RT} + \text{constant}$$

Thus, a plot of $\ln(K_D)$ vs. 1/T should yield a straight line with slope equal to $\Delta\bar{h}/R$, where $\Delta\bar{h} = \bar{h}_{ij} - \bar{h}_{ik}$. Figure 6 is such a plot for both phenol and catechol. The graph for phenol is indeed a straight line, while that for catechol is composed of two straight lines, with a break occurring at about 44 °C. This break may be due to a change in complexation mechanism. Since the slope of the line is greater at higher temperature, $\Delta\bar{h}$ must be greater. This could be due to more moles of TOPO complexing with a mole of catechol; e.g., a change from n = 1 at lower temperatures to n = 2 at higher temperatures, or n = 2 becoming important along with n = 1.

By using a linear least squares regression technique, the slope using the phenol data yields a $\Delta\bar{h}$ of -5.91 kcal/mole. The value of the molar distribution coefficient at 22.5 °C (=387) can be used to obtain $\Delta\bar{g} = -RT\ln(K_M) = -3.49$ kcal/mole. $\Delta\bar{s}$, the change in partial molar entropy, can then be calculated from its definition ($= \frac{\Delta\bar{h} - \Delta\bar{g}}{T}$). Even though $\Delta\bar{h}$ and $\Delta\bar{g}$ reflect the overall extraction mechanism, $\Delta\bar{s}$, which is related to steric factors, is probably largely influenced by organic phase effects, and thus will be close

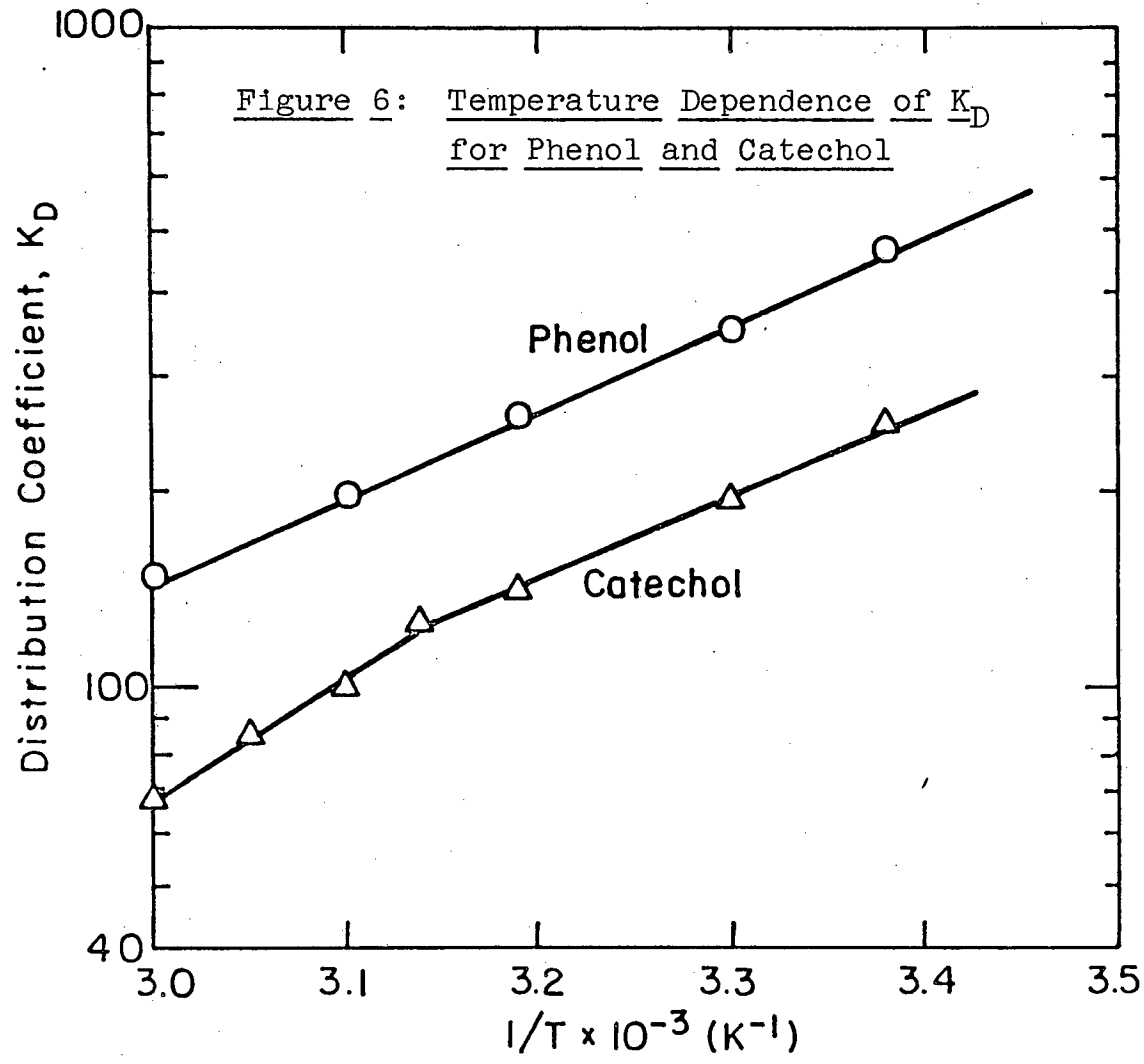

Figure 6: Temperature Dependence of K_D for Phenol and Catechol

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to the entropy change for the association reaction between phenol and TOPO or DIBK. From the above values of $\Delta\bar{h}$ and $\Delta\bar{g}$, a $\Delta\bar{s}$ value of -8.2 cal/mol °C results. This is significantly smaller than the Δs values reported by Aksnes and Albriktsen[2], which range from -14.2 to -27.7 cal/mol °C for the association reaction between phenol and various organic phosphoryl compounds in carbon tetrachloride.

The $\Delta\bar{s}$ value obtained in this study might be small for several reasons. Aksnes and Gramstad[3] interpret $\Delta\bar{s}$ to indicate the degree to which the solvent molecules order themselves around the complex. This degree of orientation in turn depends on the increase in polarity of the hydrogen bond complex as compared with the reactants. Since TOPO is a large molecule, it might have trouble ordering itself around the TOPO-phenol complex. The increase in polarity of the TOPO-phenol complex over that of the reactants might be small. Solvation of phenol by DIBK, as well as TOPO, could reduce ordering. Also, since the $\Delta\bar{g}$ and $\Delta\bar{h}$ values used to calculate $\Delta\bar{s}$ reflect the overall extraction process, $\Delta\bar{s}$ as calculated here might include aqueous phase effects.

The $\Delta\bar{h}$ value for the extraction of catechol with TOPO/DIBK in the temperature range from 22.5 °C to 45 °C is about -5.52 kcal/mole, while from 45 °C to 60 °C it is about -8.34 kcal/mole. At 22.5 °C, $\Delta\bar{g}$ (as calculated from the molar distribution coefficient) is -3.13 kcal/mole, while at

55 °C it is about -2.78 kcal/mole. The $\Delta\overline{s}$ values for the two temperature ranges are therefore about -7.74 cal/mol °C (22.5 - 45 °C) and -17 cal/mol °C (45 - 60 °C). The greater value at the higher temperatures may be due to the formation of $(TOPO)_2$(catechol) complexes, which results in a more ordered system and thus a greater negative entropy change.

H. Conclusions and Further Discussion

Tri-octyl phosphine oxide has been shown to be an effective solvent for extracting phenol and the di- and trihydric phenols from water. The choice of diluent is not crucial, as long as the diluent has some basic (electron-donating) character and does not associate preferentially with the phosphoryl group of TOPO.

The mechanism of extraction is complicated, with strong complexes being formed and with the diluent probably also playing an important role. An experimental method which could measure the concentration of solute-TOPO and solute-diluent complex(es) would be valuable for modelling data.

Whether TOPO can compete effectively with other, more conventional solvents for extraction of phenols depends upon the particular application and whether an effective solvent-regeneration method can be developed. The amount of co-extraction of water could also be an important factor. Residual solvent losses in the raffinate must also be kept to a minimum because of the relatively high cost of TOPO. The

solubility of TOPO in water is known to be very low[16], but entrainment and other losses must also be controlled.

Appendix A

Miscellaneous Calculations

I. Development and Use of Equation 7, Discussion

By definition,

(1) $$K_M = \frac{(P\ T)_o + P_o}{P_w}$$ (2) $$K_P = P_o/P_w$$

(3) $$K_R = (P\ T)_o/(P)_o(T)_o$$

A mass balance on phenol yields:

(4) $$W(P_{iw} - P_w) = S(\ (P\ T)_o + P_o)$$

while a mass balance on TOPO yields:

(5) $$(P\ T)_o + T_o = T_{io}$$

Combining Equations 2 and 3:

(6) $$(P\ T)_o = K_P\ K_R\ P_w\ T_o$$

Solving Equation 5 for T_o and substituting in Equation 6 yields:

(7) $$(P\ T)_o = K_P\ K_R\ P_w\ (T_{io} - (P\ T)_o)$$

This equation can then be solved for $(P\ T)_o$:

(8) $$(P\ T)_o = \frac{K_P\ K_R\ P_w\ T_{io}}{1 + K_P\ K_R\ P_w}$$

From Equation 1:

$$K_M = (P\ T)_o/P_w + P_o/P_w$$

or:

(9) $$K_M = (P\ T)_o/P_w + K_P$$

Substituting for $(P\ T)_o$ from Equation 8 yields:

$$(10) \qquad K_M = K_P + \frac{K_P \cdot K_R \cdot T_{io}}{1 + \dfrac{K_P \cdot K_R \cdot P_{iw}}{1 + K_M \cdot R \cdot \dfrac{P_{iw}}{T_{io}}}}$$

This equation can then be rearranged and solved for R to yield Equation 7 in the Discussion section:

$$(11) \qquad R = \frac{T_{io}}{P_{iw}\ K_M} \left[\frac{(K_M - K_P)(K_P\ K_R\ P_{iw})}{K_P K_R T_{io} - (K_M - K_P)} - 1 \right]$$

In order to use this equation, one must have values for $K_P K_R T_{io}$ and K_R for a given K_P. These can be obtained by combining the following two equations:

$$(9) \qquad K_M = (P\ T)_o / P_w + K_P$$

$$(12) \qquad (P\ T)_o / P_w = K_P \cdot K_R \cdot T_o$$

to yield:

$$(13) \qquad K_M = K_P \cdot K_R \cdot T_{io}\ (T_o / T_{io}) + K_P$$

Thus, a graph of K_M vs. T_o/T_{io} should yield a straight line with slope equal to $K_P K_R T_{io}$. For a given K_P and known T_{io}, K_R can also be calculated.

To use Equation 13, it is also necessary to have values of T_o/T_{io}. These can be calculated from:

(14) $T_o/T_{io} = 1 - (\%\ \text{phenol complexed}/100R)$

The % phenol complexed for a given R (and thus K_M) can be estimated from:

(15) $$\%\ \text{phenol complexed} = \frac{(S/W)(K_M)}{(S/W)(K_M) + 1} \quad \frac{(K_M - K_P)}{K_M}$$

The results for phenol are presented below. A range of values is presented for both % phenol complexed and T_o/T_{io} for a corresponding range of K_P values from 25 to 45. K_P is probably close to the K_M value measured into pure DIBK (= about 37).

K_M	Water-Solvent Volume Ratio	% phenol complexed	R	T_o/T_{io}
670	1:1	95-97	9.96	0.903-0.905
540	2:1	93-96	4.98	0.807-0.813
387	3.9:1	90-94	2.52	0.627-0.643
218	8:1	81-88	1.24	0.290-0.347
97.1	16:1	55-68	0.615	0 - 0.106
69.2	25:1	36-52	0.398	0- 0.095

The range is closely bounded for large R. Similar results are presented below for catechol with the assumed K_P's ranging from 4.5 to 6.5

K_M	Water-Solvent Volume Ratio	% catechol complexed	R	T_o/T_{io}
79.8	9.17:1	83-84	1.27	0.339-0.346
171	4.58:1	94-95	2.57	0.630-0.634
227	2.29:1	96-97	5.04	0.808-0.810

$K_P K_R T_{io}$ can now be obtained from the slope of the graph of Equation 13. These graphs are shown in Figure A1 (phenol) and Figure A2 (catechol). They yield the following values:

	K_P	$K_P K_R T_{io}$	$K_R T_{io}$	K_R
phenol:	25	683	27.3	51.4
	35	658	18.8	35.4
	45	650	14.4	27.2
catechol:	4.5	252	56.0	106
	5.5	250	45.4	85.5
	6.5	248	38.2	71.9

Equation 11 for the various assumed values for K_P yields the following results:

(1) phenol:

K_M	$R_{experimental}$	R_{25}	R_{35}	R_{45}
670	9.96	17.29	27.10	24.24
540	4.98	3.86	4.00	3.83
387	2.52	1.96	1.93	1.84
218	1.24	1.19	1.12	1.04
97.1	0.615	0.727	0.603	0.480
69.2	0.398	0.538	0.377	0.219

(2) catechol:

K_M	$R_{experimental}$	$R_{4.5}$	$R_{5.5}$	$R_{6.5}$
227	5.04	8.33	8.52	8.72
171	2.57	2.81	2.80	2.80
79.8	1.27	1.22	1.20	1.18

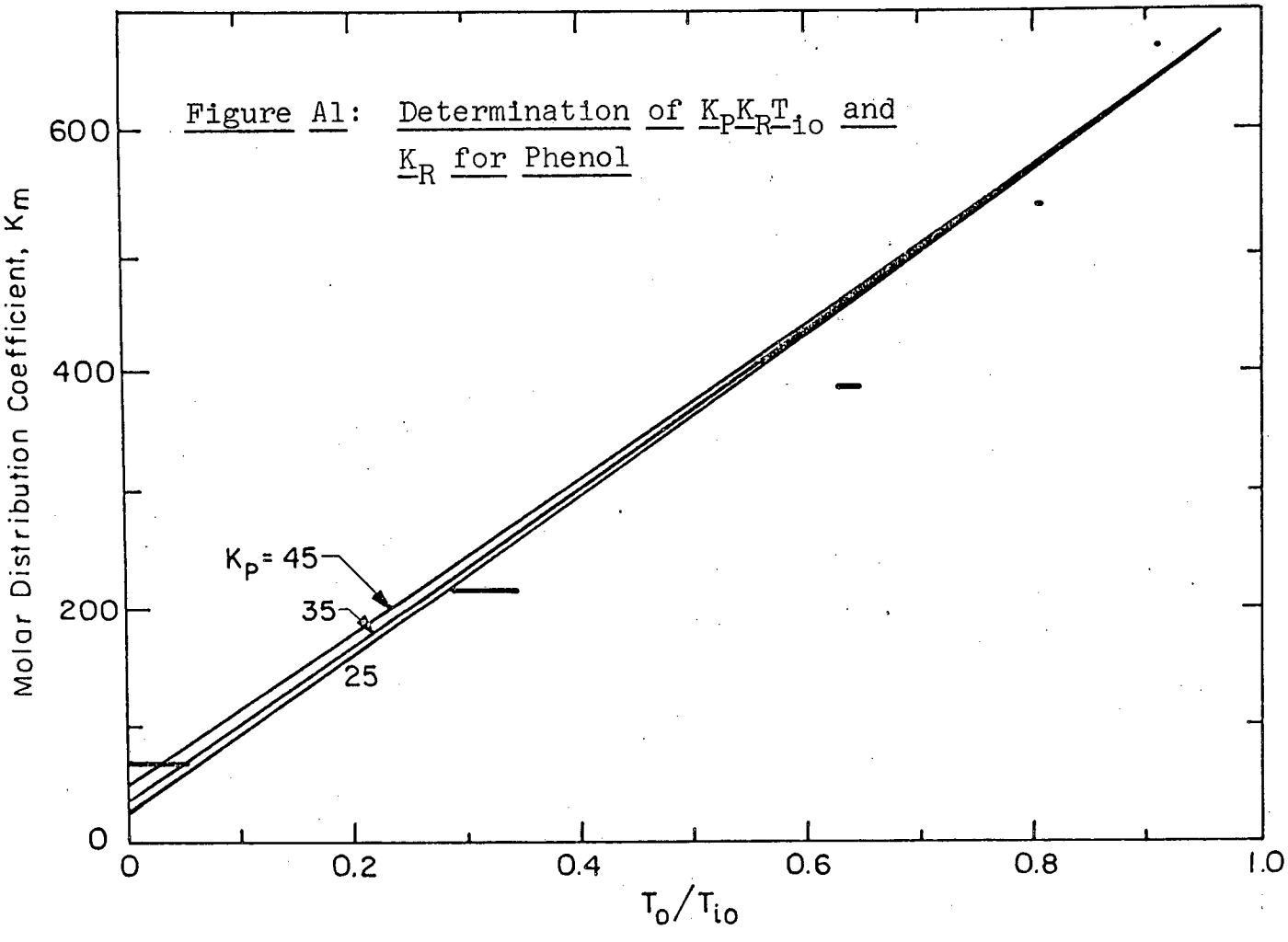

Figure A1: Determination of $K_P K_R T_{io}$ and K_R for Phenol

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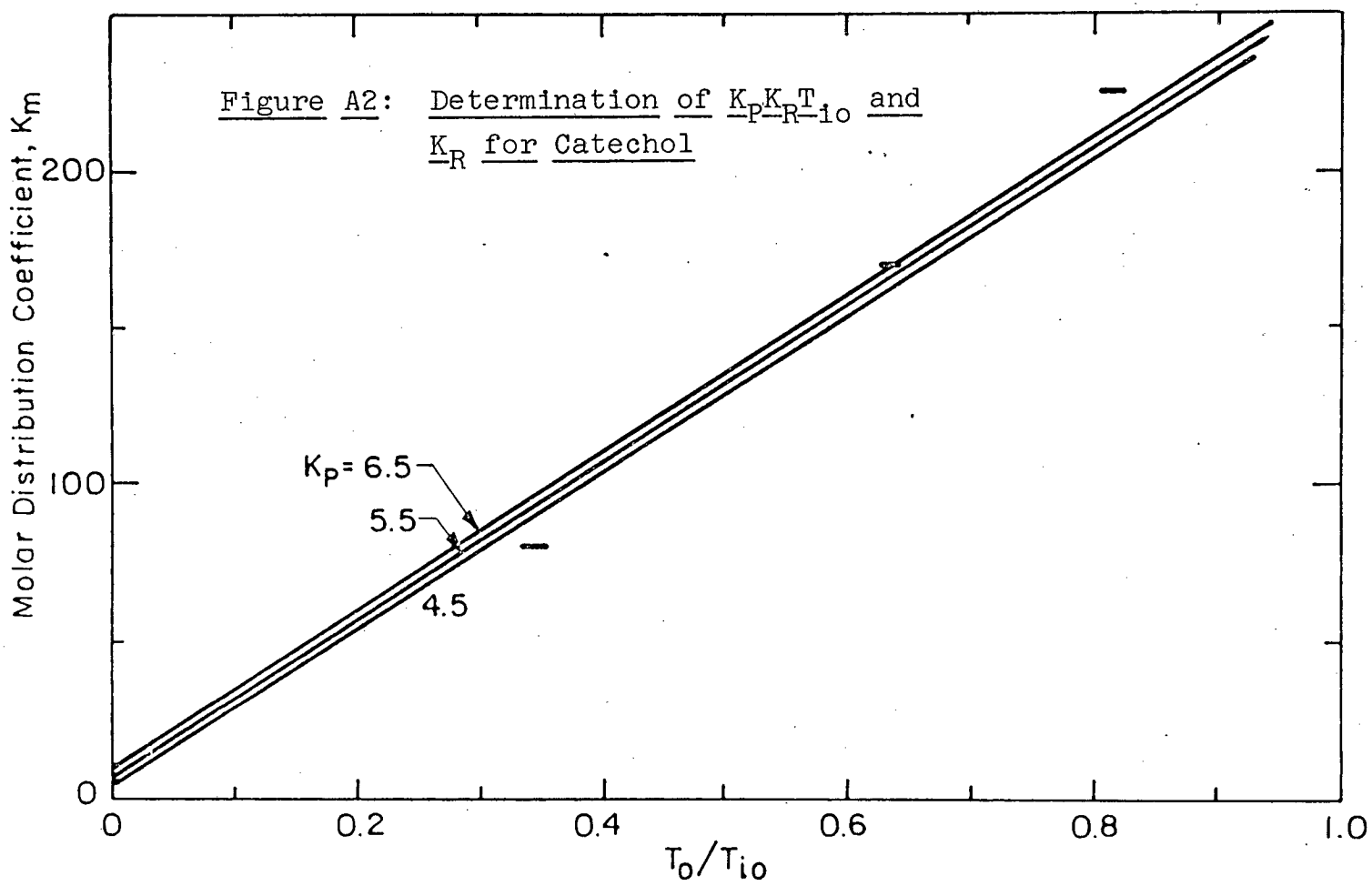

Figure A2: Determination of $K_P K_R T_{io}$ and K_R for Catechol

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These results are presented in Figure 3 and Figure 5 in the Discussion section. They indicate that regardless of the choice of K_P, the value of $K_P + K_P K_R T_{io}$ reaches an asymptotic value for large R. This value is about 700 for phenol and about 255 for catechol. From these values, a range of K_R values can be determined from an assumed range of K_P values. These values are presented below.

Phenol		Catechol	
K_P	K_R	K_P	K_R
25	51.4	4.5	106
35	35.4	5.5	86
45	27.2	6.5	71.9

Nomenclature

K_M = molar distribution coefficient = $\dfrac{(P\ T)_o + P_o}{P_w}$

K_P = physical distribution coefficient = P_o/P_w

K_R = complexation reaction constant = $(P\ T)_o/(P)_o(T)_o$

$(P\ T)_o$ = phenol-TOPO complex concentration in the organic phase, mol/liter

P_o = physically dissolved phenol concentration in the organic phase, mol/liter

P_w = phenol concentration in the aqueous phase, mol/liter

P_{iw} = initial phenol concentration in the aqueous phase, mol/liter

T_o = TOPO concentration in the organic phase, mol/liter

T_{io} = initial TOPO concentration in the organic phase, mol/liter

W = volume of aqueous phase, liters

Nomenclature (Cont.)

S = volume of organic phase, liters

R = stoichiometric ratio of TOPO to phenol = $\frac{T_{io}\ S}{P_{iw}\ W}$

II. Calculation of K_R for Various Diluents

The values for K_R were calculated from Equation 13 of the previous section, solved for K_R :

(1) $$K_R = \frac{K_M - K_P}{K_P} \quad (T_{io}/T_o)$$

K_P was assumed to equal K_M into the pure diluent. T_{io}/T_o was calculated from Equation 14 of the previous section:

(14) $$T_o/T_{io} = 1 - (\%\ \text{phenol complexed}/100R)$$

The % phenol complexed, in turn, was calculated from Equation 15:

(15) $$\%\ \text{phenol complexed} = \frac{(S/W)(K_M)}{(S/W)(K_M) + 1} \quad \frac{(K_M - K_P)}{K_M}$$

The results are shown below:

Solvent	% Phenol Complexed	T_o/T_{io}	$K_P K_R T_{io}$	K_R
25 Wt.% TOPO/DIBK	89.6	0.644	543	27.3
15 Wt.% TOPO/DIBK	85.1	0.660	343	28.8
5 Wt.%TOPO /DIBK	70.8	0.717	129.2	32.9
25 Wt.% TOPO/n-Butyl Acetate	83.9	0.663	442	15.1
25 Wt.% TOPO/2-Ethyl Hexanol	46.4	0.814	29.6	2.31
25 Wt.% TOPO/ Chevron 25	98.1	0.606	501	555

Solvent	% Phenol Complexed	T_o/T_{io}	$K_P K_R T_{io}$	K_R
15 Wt.% TOPO/ n-Butyl Ether	94.7	0.620	385	114
5 Wt.% TOPO/ Kerosene	98.8	0.608	119	9781

III. Calculation of Catechol Removal from a Wastewater Stream

The assumptions for this calculation were nine ideal stages in the extractor, an inlet water stream pH of 9.8, a solvent-to-water stream ratio of 1:11.4 (i.e., a TOPO-to-catechol stoichiometric ratio of 1.27:1), which corresponds to a K_D of 91.6, and a K_a for catechol[22] equal to $7.50\ 10^{-10}$. Catechol was assumed to exist either in its un-ionized or mono-ionized form. This is a safe assumption, since pK_{a2} for catechol equals 12.1.[22] These conditions are identical to those assumed by Beychok[5], with the exception of the solvent-to-water ratio, which in his case was 1:10. From Greminger and King's[14] model, K_D for catechol at a pH of 9.8 is:

$$(1) \qquad K_D = \frac{K_{D,\text{low pH}}}{\frac{K_a}{(H^+)} + 1}$$

$$= \frac{(91.6)}{\frac{7.50\ 10^{-10}}{10^{-9.8}} + 1}$$

$$= 16.0$$

The Kremser-Souders-Brown equation is:

$$(2) \qquad \frac{x_{in}}{x_{out}} = \frac{(K_D\ S/W)^{N+1} - 1}{(K_D\ S/W) - 1}$$

Substituting and solving yields:

$$\frac{x_{in}}{x_{out}} = \frac{(16.0/11.4)^{10} - 1}{(16.0/11.4) - 1}$$

$$= 80.3$$

The fraction removal of catechol is $\frac{x_{in} - x_{out}}{x_{in}}$ or :

$$1 - (1/80.3) = 0.9875$$

Thus, 98.75% of the catechol is removed.

Nomenclature

K_D = distribution coefficient
K_a = ionization constant of catechol
(H^+) = hydrogen ion concentration, mol/L
x_{in} = inlet catechol concentration to extractor
x_{out} = outlet catechol concentration from extractor
S = solvent flow rate, mass/time
W = water stream flow rate, mass/time
N = number of ideal stages in the extractor

IV. Derivation of K_D-Temperature Relation

From the definition of the activity coefficient:

(1) $$\ln(\gamma_i) = \bar{g}_i^E/RT$$

Differentiating with respect to T at constant P and x yields:

(2) $$\left[\frac{\delta \ln(\gamma_i)}{\delta T}\right]_{P,x} = \frac{(\delta \bar{g}_i^E/\delta T)_{P,x} RT - \bar{g}_i^E R}{R^2T^2}$$

$$= \frac{(\delta \bar{g}_i^E/\delta T)_{P,x} T - \bar{g}_i^E}{RT^2}$$

$$= \frac{-\bar{s}_i^E T - \bar{g}^E{}_i}{RT^2}$$

$$= \frac{-\bar{h}_i^E}{RT^2}$$

Integrating yields:

(3) $$\ln\left[\frac{\gamma_{ij}}{\gamma_{ik}}\right] = \frac{\bar{h}_{ij} - \bar{h}_{ik}}{RT} + \text{constant}$$

By definition, $\gamma_{ij} = a_{ij}/x_{ij}$ and $\gamma_{ik} = a_{ik}/x_{ik}$. At equilibrium, $a_{ij} = a_{ik}$. Thus, $\gamma_{ij}/\gamma_{ik} = x_{ik}/x_{ij}$, and

(4) $$\ln(x_{ik}/x_{ij}) = \frac{\bar{h}_{ij} - \bar{h}_{ik}}{RT} + \text{constant}$$

or $$\ln(K_M) = \frac{\bar{h}_{ij} - \bar{h}_{ik}}{RT} + \text{constant}$$

At a constant inlet phenol concentration, water/solvent ratio, and solvent composition, K_D and K_M are proportional. Therefore,

$$\ln(K_D) = \frac{\bar{h}_{ij} - \bar{h}_{ik}}{RT} + \text{constant}' \tag{5}$$

Nomenclature

γ_{ij} = activity coefficient of component i in phase j
γ_{ik} = activity coefficient of component i in phase k
$\bar{g}_i^E$ = excess partial molar Gibb's free energy
R = gas constant
T = temperature
P = pressure
x = composition
$\bar{s}_i^E$ = excess partial molar entropy
$\bar{h}_i^E$ = excess partial molar enthalpy
a_{ij} = activity of component i in phase j
a_{ik} = activity of component i in phase k
x_{ij} = mole fraction of component i in phase j
x_{ik} = mole fraction of component i in phase k

Appendix B: Experimental Data

Table B-1: Solvent Densities

Solvent	Density(g/mL)
25 Wt. % TOPO/DIBK	0.8194
15 Wt. % TOPO/DIBK	0.8134
5 Wt. % TOPO/DIBK	0.8129
25 Wt. % TOPO/n-Butyl Acetate	0.8715
25 Wt. % TOPO/2-Ethyl Hexanol	0.8325
25 Wt. % TOPO/Chevron 25	0.8716
5 Wt. % TOPO/Kerosene	0.7802
15 Wt. % TOPO/n-Butyl Ether	0.7774
DIBK	0.8052
n-Butyl Acetate	0.8825
2-Ethyl Hexanol	0.8328
Chevron 25	0.8692
n-Butyl Ether	0.7869
Kerosene	0.7797

Densities Measured by Weighing 25 mL of Solvent in a Tared Volumetric Flask

Table B-2: Extraction of Phenol into 25 Wt.% TOPO/DIBK

Water-Solvent Volume Ratio	Inlet Phenol Conc. (ppm)[1]	Inlet Phenol Conc. (ppm)[2]	Phenol Conc. in Raffinate (ppm)	K_D
1:1	5070	4985	11.6	520
1:1	5070	5192	12.2	515
2:1	5070	4946	27.5	431
2:1	5070	4954	27.3	435
4:1	5070	4999	68.2	345
4:1	5070	4883	80.1	286
4:1	5020	4776	60.1	374
8:1	5020	4778	179	240
8:1	5020	4899	196	224
8:1	5020	5004	184	244
16:1	5047	4939	736	103
16:1	5047	4707	682	107
25:1	5047	4933	1358	72.4
25:1	5047	4868	1355	71.5

ExtractionsPerformed on Orbit Shaker at Room Temperature.

1 Determined from Weighed Phenol and Known Volume of Water. Used to Determine Stoichiometric Ratios

2 From Digital Integrator. Used to Calculate K_D

Table B-3: Extraction of Phenol into 25 Wt. % TOPO/DIBK

Water-Solvent Volume Ratio	Inlet Phenol Conc. (ppm)[1]	Inlet Phenol Conc. (ppm)[2]	Phenol Conc. in Raffinate (ppm)	K_D
1:1	5001	4991	7.64	791
1:1	5001	4991	7.25	834
2:1	5001	4991	19.1	628
2:1	5001	4991	17.8	674
3.9:1	5064	4834	47.6	468
3.9:1	5061	4852	48.8	456
8:1	5001	4991	178	252
8:1	5001	4991	175	257
16:1	5067	4825	685	109
16:1	5067	4825	680	110
25:1	5011	4924	1315	75.5
25:1	5011	4924	1297	76.8

Extractions Performed on Precision Scientific Shaker Bath at T = 22.5 °C

1 Determined from Weighed Phenol and Known Volume of Water. Used to determine Stoichiometric Ratios.

2 From Digital Integrator. Used to Calculate K_D and K_M.

Table B-4: Extraction of Phenol into Various Wt. % TOPO/DIBK Mixtures

Wt. % TOPO/ DIBK	Water-Solvent Volume Ratio	Inlet Phenol Conc. (ppm)[1]	Inlet Phenol Conc. (ppm)[2]	Phenol Conc. in Raffinate (ppm)	K_D
15	2.33:1	5053	4826	47.6	284
15	2.33:1	5053	4826	47.0	288
5	0.775:1	5053	4805	34.2	132
5	0.775:1	5053	4805	34.6	131
0	1:1	5053	5018	138	43.7
0	1:1	5053	5018	137	44.0

Extractions Performed with Orbit Shaker at Room Temperature

1 Determined from Weight of Phenol and Known Volume of Water. Used to Determine Stoichiometric Ratios.

2 From Digital Integrator. Used to Calculate K_D and K_M.

Table B-5: Extraction of Phenol into Various Wt. % TOPO/DIBK Mixtures

Wt. % TOPO/ DIBK	Water-Solvent Volume Ratio	Inlet Phenol Conc. (ppm)[1]	Inlet Phenol Conc. (ppm)[2]	Phenol Conc. in Raffinate (ppm)	K_D
15	2.37:1	5011	4924	44.7	313
15	2.37:1	5011	4924	42.8	327
5	0.789:1	5011	4924	29.1	162
5	0.789:1	5011	4924	30.4	156
0	1:1	5067	4825	128	45.3
0	1:1	5067	4825	123	47.2

Extractions Performed on Precision Scientific Shaker Bath at T = 22.5 °C.

1 Determined from Weight of Phenol and Known Volume of Water. Used to Determine Stoichiometric Ratios.

2 From Digital Integrator. Used to Calculate K_D and K_M.

Table B-6: Effect of Shaking and Phase Separation Methods on K_D

I. Effect of Shaking Time (Performed with Shaker Bath at T = 22.5 °C)

Shaking Time (Minutes)	Water-Solvent Volume Ratio	Inlet Phenol Conc. (ppm)[1]	Inlet Phenol Conc. (ppm)[2]	Phenol in Raffinate (ppm)	K_D
10	4.00:1	4988	4796	52.6	430
10	4.00:1	4988	4796	51.1	443
20	4.00:1	4988	4796	51.2	442
20	4.00:1	4988	4796	52.3	433
40	4.00:1	4988	4796	52.1	434
40	4.00:1	4988	4796	52.0	435

II. Effect of New TOPO (Performed with Shaker Bath at T = 22.5 °C)

Water-Solvent Volume Ratio	Inlet Phenol Conc. (ppm)[1]	Inlet Phenol Conc. (ppm)[2]	Phenol in Raffinate (ppm)	K_D
4.00:1	4988	4996	53.0	444
4.00:1	4988	4996	52.6	448

III. Effect of Ultracentrifuging (Performed with Shaker Bath at T = 22.5 °C)

Water-Solvent Volume Ratio	Inlet Phenol Conc. (ppm)[1]	Inlet Phenol Conc. (ppm)[2]	Phenol in Raffinate (ppm)	K_D
4.00:1	4985	4967	53.5	438
4.00:1	4985	4967	51.6	454

Table B-6(Cont.)

IV. Comparison of Orbit Shaker and Shaker Bath

Shaker Type	Water-Solvent Volume Ratio	Inlet Phenol Conc. (ppm)[1]	Inlet Phenol Conc. (ppm)[2]	Phenol in Raffinate (ppm)	K_D
Orbit	4.00:1	4985	4756	49.7	452
Prec. Scientific	4.00:1	4985	4756	49.4	455
Prec. Scientific	4.00:1	4986	4756	47.9	469

V. Extractions in Separatory Funnels with Orbit Shaker Followed by Ultracentrifuging

Water-Solvent Volume Ratio	Inlet Phenol Conc. (ppm)[1]	Inlet Phenol Conc. (ppm)[2]	Phenol in Raffinate (ppm)	K_D
4.00:1	5011	4776	52.0	433
4.00:1	5011	4776	49.6	455

VI. Back-Extraction Data (Performed with Precision Scientific Shaker Bath at T = 22.5 °C)

Type	Water-Solvent Volume Ratio	Inlet Phenol Conc. (ppm)[1]	Inlet Phenol Conc. (ppm)[2]	Phenol in Raffinate (ppm)	K_D
forward	4.00:1	5025	4640	50.6	433
back*	4.00:1	----	----	48.9	443

*10 mL of extract from forward extraction contacted with 40 mL of Milli-Q Water

1 Determined from Weight of Phenol and Known Volume of Water. Used to Determine Stoichiometric Ratios.

2 From Digital Integrator. Used to Calculate K_D and K_M.

Table B-7: Extraction of Phenol into TOPO Dissolved in Various Diluents

Diluent	Wt. % TOPO	Water-Solvent Volume Ratio	Inlet Phenol Conc. (ppm)[1]	Inlet Phenol Conc. (ppm)[2]	Phenol in Raffinate (ppm)	K_D
n-Butyl Acetate	25	4.15:1	5017	4927	68.3	331
n-Butyl Acetate	25	4.15:1	5017	4927	71.4	316
2-Ethyl Hexanol	25	4.00:1	5017	4919	372	57.5
2-Ethyl Hexanol	25	4.00:1	5017	4919	370	57.8
Chevron 25	25	4.17:1	5017	4872	78.1	287
Chevron 25	25	4.17:1	5017	4872	76.6	293
Kerosene	5	0.75:1	4948	4868	57.3	80.4
Kerosene	5	0.75:1	4948	4868	58.1	79.2
n-Butyl Ether	15	2.22:1	4948	4856	61.3	221

Extraction Performed with Orbit Shaker at Room Temperature.

1 Determined from Weight of Phenol and Known Volume of Water. Used to Determine Stoichiometric Ratios.

2 From Digital Integrator. Used to Calculate K_D and K_M.

Table B-8: Extraction of Phenol into TOPO Dissolved in Various Diluents

Diluent	Wt. % TOPO	Water-Solvent Volume Ratio	Inlet Phenol Conc. (ppm)[1]	Inlet Phenol Conc. (ppm)[2]	Phenol in Raffinate (ppm)	K_D
n-Butyl Acetate	25	4.25:1	5016	4634	57.5	380
n-Butyl Acetate	25	4.25:1	5016	4634	55.3	395
2-Ethyl Hexanol	25	4.05:1	5016	4634	361	56.4
2-Ethyl Hexanol	25	4.05:1	5016	4634	362	56.2
Chevron 25	25	4.25:1	5016	4634	63.1	345
Chevron 25	25	4.25:1	5016	4634	64.3	339
Kerosene	5	0.75:1	5025	4721	50.3	88.9
Kerosene	5	0.75:1	5025	4721	46.9	95.4
n-Butyl Ether	15	2.27:1	5016	4760	42.2	322
n-Butyl Ether	15	2.27:1	5016	4760	43.3	313

Extractions Performed with Precision Scientific Shaker Bath at T = 22.5 °C

1 Determined from Weight of Phenol and Known Volume of Water. Used to Determine Stoichiometric Ratios.

2 From Digital Integrator. Used to Calculate K_D and K_M.

Table B-9: Extraction of Phenol into Pure Diluents

Diluent	Water-Solvent Volume Ratio	Inlet Phenol Conc. (ppm)[1]	Inlet Phenol Conc. (ppm)[2]	Phenol in Raffinate (ppm)	K_D
n-Butyl Acetate	1.33:1	4989	4944	125	57.8
n-Butyl Acetate	1.33:1	4989	4944	122	59.3
2-Ethyl Hexanol	1:1	5029	5029	204	28.2
2-Ethyl Hexanol	1:1	5029	5029	202	28.5
Chevron 25	1:1	5000	5000	1937	1.81
Chevron 25	1:1	5000	5000	1899	1.87
Kerosene	1:1	5029	5029	4505	0.15
Kerosene	1:1	5029	5029	4496	0.15
n-Butyl Ether	1:1	5000	5000	414	14.0
n-Butyl Ether	1:1	5000	5000	407	14.2

Extractions Performed on Precision Scientific Shaker Bath at T = 22.5 °C.

1 Determined from Weight of Phenol and Known Volume of Water. Used to Determine Stoichiometric Ratios.

2 From Digital Integrator. Used to Calculate K_D and K_M.

Table B-10: Extraction of Catechol into 25 Wt. % TOPO/DIBK

Water-Solvent Volume Ratio	Inlet Catechol Conc. (ppm)[1]	Inlet Catechol Conc. (ppm)[2]	Catechol Conc. in Raffinate (ppm)	K_D
9.17:1	5008	4916	510	92.1
9.17:1	5008	4916	515	91.2
4.58:1	4953	5034	132	202
4.58:1	4953	5034	131	204
2.29:1	5057	4957	50.6	267
2.29:1	5057	4957	48.8	277

Extractions Performed with Orbit Shaker at Room Temperature and Thermostatted in Temperature Bath at 30 °C.

1 Determined from Weight of Catechol and Known Volume of Water. Used to Determine Stoichiometric Ratio.

2 From Digital Integrator. Used to Calculate K_D and K_M.

Table B-11: Extraction of the Dihydric Phenols into 25 Wt.% TOPO/DIBK and into DIBK

Isomer	Wt. % TOPO DIBK	W/S (V/V)	Inlet Solute Conc. (ppm)[1]	Inlet Solute Conc. (ppm)[2]	Solute in Raffinate (ppm)	K_D
Catechol	25	4.58:1	4953	5034	132	202
Catechol	25	4.58:1	4953	5034	131	204
Resorcinol	25	4.58:1	5003	4927	256	99.5
Resorcinol	25	4.58:1	5003	4927	262	97.1
Hydroquinone	25	4.58:1	5001	5144	660	37.1
Hydroquinone	25	4.58:1	5001	5144	735	32.7
Catechol	0	1:1	5003	5189	781	6.97
Catechol	0	1:1	5003	5189	787	6.91
Resorcinol	0	1:1	4998	4734	1051	4.33
Resorcinol	0	1:1	4998	4734	1083	4.17
Hydroquinone	0	1:1	4979	4949	1854	2.06
Hydroquinone	0	1:1	4979	4949	1866	2.04

Extractions Performed on Orbit Shaker at Room Temperature Followed by Thermostatting in Temperature Bath at 30 °C

1 Determined from Weight of Solute and Known Volume of Water. Used to Determine Stoichiometric Ratio.

2 From Digital Integrator. Used to Calculate K_D and K_M.

Table B-12: Extraction of the Trihydric Phenols into 25 Wt.% TOPO/DIBK and into DIBK

Isomer	Wt. % TOPO/ DIBK	W/S (V/V)	Inlet Solute Conc. (ppm)[1]	Inlet Solute Conc. (ppm)[2]	Solute in Raffinate (ppm)	K_D
Phloroglucinol	25	5.23:1	5004	4960	1140	21.0
Phloroglucinol	25	5.23:1	5004	4960	1150	20.8
Pyrogallol	25	5.23:1	5219	5126	550	51.6
Pyrogallol	25	5.23:1	5219	5126	513	55.8
Pyrogallol	25	2.00:1	2925	2925	62.8	110
Pyrogallol	25	2.00:1	2925	2925	54.5	128
1,2,4-BT	25	5.23:1	5093	5036	1046	23.7
1,2,4-BT	25	5.23:1	5093	5036	1007	24.9
Phloroglucinol	0	1:1	4946	4950	3813	0.370
Phloroglucinol	0	1:1	4946	4950	4100	0.237
Pyrogallol	0	1:1	5126	5049	3502	0.548
Pyrogallol	0	1:1	5126	5049	3415	0.593
1,2,4-BT	0	1:1	5093	5036	4597	0.119
1,2,4-BT	0	1:1	5093	5036	4519	0.142

Extractions Performed with Orbit Shaker at Room Temperature Followed by Thermostatting in Temperature Bath at 30 °C

1 Determined from Weight of Solute and Known Volume of Water. Used to Determine Stoichiometric Ratio.
2 From Digital Integrator. Used to Calculate K_D and K_M.

Table B-13: Extraction of Phenol into 25 Wt. % TOPO/DIBK at Various Temperatures

T (°C)	Water-Solvent Volume Ratio	Inlet Phenol Conc. (ppm)[1]	Inlet Phenol Conc. (ppm)[2]	Phenol in Raffinate (ppm)	K_D
22.5	3.9:1	5064	4834	47.6	468
22.5	3.9:1	5064	4834	48.8	456
30	3.9:1	5061	4852	63.3	352
30	3.9:1	5061	4852	64.1	347
40	3.9:1	5061	4679	81.6	262
40	3.9:1	5061	4679	82.9	258
50	3.9:1	5061	5006	115	198
50	3.9:1	5061	5006	120	189
60	3.9:1	5061	5134	156	148
60	3.9:1	5061	5134	156	148

Extractions Performed with Precision Scientific Shaker Bath

1 Determined from Weight of Phenol and Known Volume of Water. Used to Determine Stoichiometric Ratios.

2 From Digital Integrator. Used to Calculate K_D and K_M.

Table B-14: Extraction of Catechol into 25 Wt.% TOPO/DIBK at Various Temperatures

T(°C)	Water-Solvent Volume Ratio	Inlet Catechol Conc. (ppm)[1]	Inlet Catechol Conc. (ppm)[2]	Catechol in Raffinate (ppm)	K_D
22.5	4.58:1	5009	5108	109.5	248
22.5	4.58:1	5009	5108	107.6	253
30	4.58:1	4999	5146	140	195
30	4.58:1	4999	5146	142	192
40	4.58:1	5002	5252	188	147
40	4.58:1	5002	5252	188	147
40	4.58:1	4999	5197	184	148
40	4.58:1	4999	5197	179	153
45	4.58:1	5002	5252	214.7	128
45	4.58:1	5002	5252	215.9	127
50	4.58:1	4988	5144	262	101
50	4.58:1	4988	5144	268	99.0
50	4.58:1	5010	5251	266	102
50	4.58:1	5010	5251	263.4	103
55	4.58:1	5010	5251	300.6	89.7
55	4.58:1	5010	5251	311.3	86.4
55	4.58:1	4988	5144	312	84.4
55	4.58:1	4988	5144	311	84.6

Table B-14(Cont.)

T(°C)	Water-Solvent Volume Ratio	Inlet Catechol Conc. (ppm)[1]	Inlet Catechol Conc. (ppm)[2]	Catechol in Raffinate (ppm)	K_D
60	4.58:1	5001	5597	404.4	69.8
60	4.58:1	5001	5597	405.7	69.6
60	4.58:1	4980	5169	379	68.9
60	4.58:1	4980	5169	376	69.4

Extractions Performed with Precision Scientific Shaker Bath

1 Determined from Weight of Catechol and Known Volume of Water. Used to Determine Stoichiometric Ratios.

2 From Digital Integrator. Used to Calculate K_D and K_M.

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