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J.L. Bixby* and C.J. King
(*M.S. Thesis)

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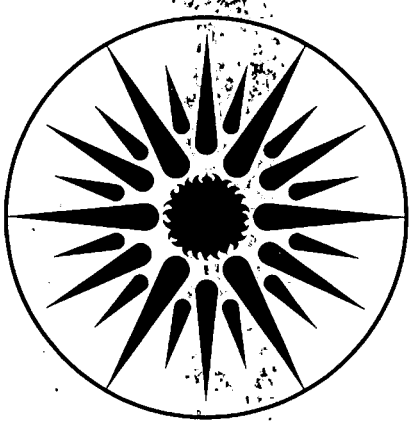

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James Lawrence Bixby

"The Regeneration of Tri-octyl Phosphine Oxide Solutions Used to Extract Phenol from Water"

ABSTRACT

Several potential extractant diluents were examined in terms of physical properties relevant to both extraction of the solute from water and subsequent solvent regeneration. Distillation was investigated as a unit operation to regenerate tri-octylphosphine oxide solutions loaded with phenol. Relative volatilities of phenol to the diluent were measured for the diluents isobutyl-heptyl ketone and dimethylnaphthalene, at both varying solute-to-extractant mole ratios and extractant concentrations in the solvent. A simple model based on the chemical complexation between the solute and extractant is proposed to explain the observed trends in the data, and the equilibruim constant for this reaction was determined to be roughly 5 L/gmole.

Equilibrium distribution coefficients were also measured for the extraction of phenol from both pure water and coal-gasification condensate water, by a mixed TOPO solvent having acceptable regeneration capabilities. These data are consistent with the extraction mechanism model previously proposed by MacGlashan (1982). Losses of the extractant into the aqueous raffinates are also reported.

Both the observed high distribution coefficients at low solute-to-extractant mole ratios, and the low relative volatilities indicate that the association between phenol and TOPO is strong.

Hence, a high boiling diluent is needed for favorable regeneration via distillation. TOPO-based solvent extraction appears to be best suited for treatment of aqueous solutions having phenol concentrations on the order of 100 parts per million.

To my parents and family - For helping me get this far ahead in life.

To Jack, Jim, Phil, Kristi, and Sue - When you look up "friends" in my dictionary, you will find a picture of them.

"There is no manufacturing a strong will."

- R.W. Emerson, "Fate", 1860.

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INTRODUCTION

A.) Sources and Extent of Phenol in Water

Phenol, otherwise known as monohydroxybenzene, is a common constituent of waste streams produced from a variety of industrial processes. In fact, its presence in waste effluents, at concentrations typically ranging from several parts per million (PPM) to several percent is so widespread that phenol has been classified by the Environmental Protection Agency (EPA) as an organic priority pollutant. In the process of establishing limitation guidelines for the 129 priority pollutants, EPA conducted a comprehensive program of screening waste effluents from 21 industries. Through October 1979, at which point over 3100 individual samples from 35 industrial categories and subcategories had been analyzed, phenol had been identified in 24% of these samples, spanning over two dozen categories, and consequently was ranked as the sixth most prevalent organic pollutant.[56] Most commonly, phenol, as well as other compounds of its class (which contain one or more hydroxyl groups attached to an aromatic ring), are present in waste liquors from industrial operations such as petroleum refining, processing and manufacture of phenol, production of phenolic resins, creosoting, coal processing, and coking, employed in the production of iron and steel.

B.) Justification for Recovery

One reason why the prevalence of phenol as a pollutant poses a significant problem is the harmful effects possessed by aqueous

solutions of phenols. The odor and taste concentration thresholds of phenols in water are quite low, ranging from 10 to 1,000+ parts per billion (PPB) and 0.04 to 200 PPB, respectively.[16] Because the common treatment practice of chlorinating wastewaters often produces chlorophenols, which impart a distinctive medicinal taste to drinking water, it is also noteworthy that these compounds have the lowest odor and taste threshold concentrations of the phenols. Baker (7) has documented the effects of phenol poisoning due to the consumption of contaminated drinking water by humans. Phenols are also toxic to a variety of aquatic biota. Most significantly, the toxicty threshold concentrations of phenols to fish are generally 10 to 100 times the odor threshold concentrations listed above.[16] Degraeve (15) and Parkhurst (55) have investigated the toxicity of phenolic compounds to rainbow trout and flathead minnows, and Daphnia magna (water fleas), respectively. For the aforementioned reasons, the specifications for phenol in effluents are quite low, generally a few PPB.

The predominance of phenol in industrial wastes can also represent the loss of a valuable resource. Phenol, which has a current market price of $0.325/lb[12], ranked as the 35th largest volume chemical in the U.S. as of 1981, with a sales volume of 2.55 billion lb/yr. The projected demand by 1984, which hinges to a large extent on the recovery of the housing and automotive industries from the recent recession, is 3.27 billion lb/yr.[39] Although a specific dollar amount is difficult to estimate accurately because of uncertainties in the volume of phenolic wastes produced annually in the United States, the economic incentive for recovery is significant. For comparison, in

1966, coke-oven plants is Germany alone produced at least 65 million cubic meters of phenolic wastes at a concentration level of about 400 mg/l (i.e. 400 PPM).[76] Roughly 8,000 tons of phenols were recovered annually from these wastes at that time, which at today's market price translates into 5 million dollars. This represents only a small fraction of what could be presently recovered in the U.S. each year. Thus if one also considers the cost associated with the destructive treatment methods commonly used for phenols, a process to recover phenol from dilute aqueous solutions could certainly be more cost effective. Hence, in conclusion, both environmental considerations and economic advantages make the recovery of phenol desirable.

C.) Present Treatment Techniques

1.) Biochemical Oxidation

A variety of treatment methods can be used to treat aqueous solutions of phenols. For example, biochemical oxidation is one relatively simple and inexpensive method which can be successful in treating phenolic wastes up to 2,000 to 3,000 mg/l, under the proper conditions.[48] In the past, this technique has been used reliably to treat coking process effluents as well as industrial and municipal wastewaters. More generally, biochemical oxidation has been employed as a terminal method for treating solutions containing hundreds of mg/l of phenol.[17] The cost of treatment is reduced as the input pollutant level decreases, since the treatment residence time required also declines accordingly. The extent of biodegradation is strongly influenced by both the treatment temperature and the opportunity for acclimation of the bacteria.[56] Although considerable quantities of other toxic organics can be tolerated if acclimation can occur,

concentrations down to only 50 mg/l of phenolics alone can be toxic to the microorganisms unless special precautions are taken.[48] Efficient operation of the bioreactor hinges on a continuous effluent source consistent in concentration. This destructive method is also useful in treating many other organics in water, and is best applied to polishing large volumes of dilute wastes.

2.) Chemical Oxidation

Chemical oxidation is a second technique commonly used to remove phenol from wastewaters. Chlorine, ozone, and hydrogen peroxide are all oxidants widely used today, although other agents, such as air, potassium permanganate, and chlorine dioxide can be employed. Oxidation of phenols in wastewaters via chlorination has been practiced for some time. Phenol can be completely decomposed by chlorine to tasteless oxidation products at a pH above 7.7 if the reaction time is long enough and at least a stoichiometric amount of chlorine is used.[17] Chlorine is presently the cheapest practical oxidant in use, but because of uncertainties in knowledge of chlorination products and their relative toxicity, the true value of this agent is debatable. Ozone has also proved effective in the oxidation of phenols; in fact, it is useful in removing chlorinated phenols from drinking water.[17] Presently, however, it is not cost effective relative to chlorine per unit of available active oxygen produced. Hydrogen peroxide is yet a more expensive oxidizing agent, and will oxidize phenol in the presence of certain transition metal salt catalysts. Air is potentially the most desirable oxidant since it is the least expensive, but its relatively low efficiency and slow speed of reaction generally make it impractical.[17] It should be noted that the chemical oxidation of

phenols produces intermediates such as catechols, hydroquinones, and quinones, which are more biologically refractive than the initial phenols.[40] However, the main shortcoming of chemical oxidants is the high cost of their oxidizing power, and thus effluent polishing is regarded as their niche.[22]

3.) Wet Air Oxidation and Incineration

Wet air oxidation and incineration are ultimate destructive methods for removing phenol from aqueous solutions. Both are best applied to detoxification of waste waters containing a wide variety of hazardous organics. For example, Eisenhauer notes that a coke effluent containing 5,000 mg/l phenol was rendered harmless by incineration at 900°C and 45 psig.[17] Wet air oxidation is a more versatile technique wherein conditions can be altered to achieve the degree of oxidation sought. (The high solubility of oxygen in aqueous solutions at elevated temperatures provides a strong driving force for oxidation.) At 275°C, over 99.7% of phenol in aqueous solutions having g/l range concentrations is oxidized by this treatment.[72] However, as with all destructive methods, any possible by-product credit from the sale of recovered phenol is foregone when wastes are incinerated or oxidized.

4.) Steam Stripping

Dephenolization of waste waters by steam stripping is one mode which can recover phenol for subsequent sale. In fact, a process for this purpose was developed around 1925 in which phenols were steam-stripped from high-temperature carbonization ammoniacal liquors and were subsequently recovered in hot caustic solution.[60] The phenolates were converted back to phenols by sparging carbon dioxide through

solution. This process was not effective for low temperature carbonization waters because the higher boiling phenols were not stripped from solution. It is noteworthy that the overhead product from a column designed to strip phenol from dilute aqueous streams is limited, for operating pressures of 1 atm and below, to less than 10% phenol by weight due to the formation of a binary azeotrope.[28] Since recovery of the solute in its most concentrated form is desirable, further purification steps are necessary when stripping is used. In addition, relative to other techniques, steam stripping is not an efficient way to remove phenolic compounds from water.

5.) Adsorption

A second non-destructive phenol removal technique is adsorption. Activated carbon has been shown to be quite efficient for this purpose, commonly producing an effluent of only 1 PPM phenol.[22] However, in practice, regeneration procedures for the recovery of adsorbed chemicals have been problematic. In the past, the spent carbon was either discarded or regenerated by burning off adsorbed species, which caused carbon losses of up to 10% per cycle.[22] More recently, a solvent wash or change in pH has been used to desorb organics. In 1930, Lurgi developed a process to purify high temperature carbonization waste waters down to 50 mg/l by passing them through coke and activated carbon; the loaded adsorbent was regenerated by washing with benzene. However, this process was not competitive with others, due in part to fouling of the carbon.[60] The presence of other organics in the effluent can seriously affect the phenol removal efficiency due to competition between species for active sites. However, activated carbon does remove a wider variety of chemicals

from water than does biochemical oxidation. The use of this adsorbent is still generally regarded as a final polishing step, economical for removing very low concentrations of phenol from water.

Polymer resin adsorbents have become increasingly popular in the clarification of water to meet stringent new standards. These resins are physically much more durable than activated carbon and are also easier to regenerate since they bind organic molecules less strongly in many cases. Regeneration is typically accomplished by washing the adsorbed species from the polymer surface with an organic solvent, an aqueous acid or base, or steam. Fox (19, 20, 21) has documented the use of polymer adsorbents to recover phenol from aqueous wastes at concentrations ranging from 0.75% to 2%. The phenol effluent concentration typically is on the order of 1 PPM, and the estimated resin life is high, about 5 years. In fact, after 3 years and over 1800 cycles of commercial use, the original resin charge in one process showed no decrease in performance.[19] The practical use of polymer resins to recover phenol from wastes hinges mainly on favorable economics of solvent or chemical regeneration.

6.) Liquid-Liquid Extraction

Liquid-liquid extraction has enjoyed a long history of success in recovering phenol from process waste streams. One of the first processes, developed over 55 years ago for treatment of phenolic ammonia liquors from coke-oven plants, used benzene as the extraction solvent. The loaded benzene was regenerated by washing it with aqueous sodium hydroxide, producing sodium phenolate, which was subsequently converted back to phenol by bubbling carbon dioxide through solution. The process generally became obsolete because

large volumes of benzene were required for substantial phenol removal, and the steam stripping costs for recovery of dissolved benzene from wastewaters were high. Because of its lower water solubility, middle oil from low-temperature carbonization plants was sometimes used instead, but emulsions became a stubborn problem in this case.[60]

A second process was subsequently developed based on tri-cresyl phosphate, because its higher distribution coefficients for phenols reduced the solvent requirement for extraction by a factor of over 10.[5] Vacuum distillation recovered the phenols in the distillate and produced the high boiling solvent as the bottoms product. Although several plants were constructed, this process never became widely used because high boiling residues accumulated in the tri-cresyl phosphate, particularly in the treatment of low-temperature carbonization waste waters. This eventually decreased the extraction efficiency of the solvent, increased its viscosity, and caused emulsification problems. Frequent purification of the solvent with sulfuric acid was costly.[60]

Around 1940, as low-temperature coal carbonization plants began to grow in both size and number, the Phenosolvan process was developed to treat the resulting waste waters produced. Soon thereafter, this process was applied to phenolic resin effluents of the chemical industry; and, as of about 1958, it was first used on coke-oven plant effluents. The first solvent used in this process was butyl acetate. However, its relative ease of saponification, e.g. by ammonia at concentrations above 3,000 mg/l,[42] along with comparatively higher costs for solvent regeneration and solvent recovery from water, subsequently made di-isopropyl ether a better solvent choice. In

this process, regenerated solvent is recovered overhead by distillation, and the 0.8% residual solvent in the aqueous phase is recovered by stripping with steam or an inert gas. The Phenosolvan process typically removes 99% of phenol from solution and reduces the effluent concentration to below 10 mg/l.[76] This process is still used today in more than 30 plants worldwide.

The most recent process developed for the extraction of phenol from water is the Chem-Pro Equipment Corporation process, wherein the solvent is believed to be methyl-isobutyl ketone.[71] As in the Phenosolvan process, the solvent is regenerated via distillation, but in the Chem-Pro process, recovery of solvent dissolved in the raffinate is much simpler, and so results in lower capital costs. Extraction efficiences of nearly 100% have been achieved by reducing the phenol content of a 1500 PPM feed to less than 4 PPM at a solvent to water ratio of only 1:18.[53] Accordingly, the Chem-Pro process is probably the most efficient solvent extraction process for phenol recovery in wide use today.

Burns and Lynn, et. al., (25) studied the recovery of residual solvent from the aqueous raffinate in both the Phenosolvan and Chem-Pro processes. They conceived a process to extract phenol from water which retained the simple solvent recovery scheme of the Chem-Pro process while reducing its relatively high operating costs. Significant savings were demonstrated by utilizing waste heat from the warm, foul water extractor feed to strip residual solvent from the dephenolized raffinate under vacuum. Because its physical properties satisfied solvent selection criteria necessary to realize these benefits, methyl-isobutyl ketone (MIBK) was nearly ideal for this

process, while di-isoprpyl ether (DIPE) was unsatisfactory. Operating costs for this process using MIBK as the solvent were lower than for either commercial process.

At the present time, solvent extraction is generally a primary treatment method capable of recovering high percentages of phenol from waste waters. A subsequent polishing step is required because processes using conventional solvents are unable to reduce the raffinate concentration below the strict pollutant discharge levels. Another drawback is that stripping of residual solvent from the raffinate often becomes costly for large volumes of waste water. Extraction is best suited as a complementary treatment step for selected, concentrated feeds prior to combination of dilute wastes for biological oxidation or adsorption; extraction cannot compete with either of these two techniques in treating large amounts of very dilute wastes.

Other methods, including foam fractionation, reverse osmosis, chemical precipitation, and most notably, liquid ion-exchange, have also been used to treat phenolic wastes in certain instances.[17]

D.) TOPO Based Solvent Extraction

Within the past nine years, tri-alkyl phosphine oxides, most notably tri-octyl phosphine oxide (TOPO), have been used, at least on a developmental scale, to extract acetic acid from dilute aqueous solutions, typically below 5% by weight.[23,26,68] (See Appendices A and B for information on TOPO.) Common organic extractants used for recovery of acetic acid are not economical for processing dilute aqueous solutions because their water solubilities are relatively high, due to their polar nature, which is required for favorable

extraction of this polar acidic solute, and because their extraction capacities are not great enough. TOPO presents a unique solution to this problem because although it is polar, due to the phosphoryl group, its solubility in water is extremely low (below 4 PPM).[4,26] The phosphoryl oxygen of TOPO has a strong affinity for acidic hydrogen atoms of solute molecules, and the resulting hydrogen bonds can effectively concentrate a hydrophilic solute into a less polar organic phase. In general, this hydrogen bonding ability depends on both the electron donor properties of the extractant and steric effects.[47] Since TOPO is a strong Lewis base, even stronger than corresponding alkyl phosphates and sulfoxides, it is very effective in extracting lower carboxylic acids from dilute water solutions. However, the long alkyl groups of TOPO, which are responsible for its hydrophobic nature, may hinder its extraction capabilities for larger, more complex solute molecules.

Aksnes (1,2,3) has investigated the association of phenol with organic phosphoryl compounds, and has measured the equilibrium constants of the dimeric hydrogen bond complexes which are formed. For open chain phosphine oxides, the equilibrium constants range from a high of 1000 at 25°C to a low of 200 at 50°C, while the ΔH for the complexation reaction is about -9.5 kcal/gmole. Extrapolation of Aksnes' Arrhenius plot for tri-butyl phosphine oxide predicts that the equilibrium constant will drop sharply with increasing temperature, down to 38 at 100°C and to 2.5 at 200°C. These findings suggest, at least in theory, that the association of phenol with phosphine oxides, e.g. TOPO, is a thermally reversible chemical complexation[36] which could be used to extract phenol from water in

a process similar to that for acetic acid.

E.) Previous Work Involving the Extraction of Phenols

Greminger, et. al., (25) investigated the extraction of phenols from coal conversion process condensate waters using di-isopropyl ether (DIPE) and methyl-isobutyl ketone (MIBK), both solvents which are used in commercial processes. He found that the distribution coefficients for poly-hydroxybenzenes were about an order of magnitude higher for MIBK than for DIPE. He concluded that MIBK was the best physical solvent for the extraction of phenols from coal conversion condensate waters, based on its performance, cost, energy efficiency, and lack of reactivity. Greminger also noted that the pH of the aqueous phase had a dramatic effect on the extractability of the weakly acidic phenols. A simple model combined the aqueous acid ionization equilibrium with the phase distribution equilibrium between organic and non-ionized aqueous phase phenol, and allowed for the sharp drop in the observed distribution coefficient at a pH above the pK_a of the phenol, as shown in equation 1-1,

$$K_{D,apparent} = \frac{K_{D,true}}{(K_a/[H^+]) + 1} \qquad (1\text{-}1)$$

where K_a is the dissociation constant for the weak acid ionization. Because only their un-ionized forms are extracted, the removal of phenols from high pH coal conversion condensate waters will be much less than would be predicted using K_D's measured at low pH. Thus, the pH of such waters should be reduced accordingly, e.g. by removal of ammonia prior to the extraction of phenols, in a comprehensive

water treatment process in order to obtain the most benefit from the extraction and any subsequent steps.

Because the K_D's for methyl-isobutyl ketone are more favorable than those for di-isopropyl ether, a somewhat weaker Lewis base, one might reason that successively stronger Lewis bases (e.g. $(RO)_3PO$, R_3PO, and R_3N) should give progressively higher K_D's, since phenols are weakly acidic. Accordingly, Bell (8) tested three Lewis bases, one from each group listed above, as extraction solvents for phenolic compounds commonly found in coal conversion process condensate waters. Mixed solvents of Alamine 336 (a viscous, C_8- C_{10} tertiary amine marketed by Henkel Corp.) in a variety of diluents (2-ethyl-1-hexanol, Chevron 25, di-isobutyl ketone, and kerosene) gave K_D's of at most 6 for resourcinol and 1 for pyrogallol. The corresponding distribution coefficients for tri-cresyl phosphate were roughly twice as high, but were still significantly lower than those for MIBK, which are 18 and 3.6, respectively. However, the distribution coefficient for pyrogallol into a mixed solvent of 25% by weight tri-octyl phosphine oxide (TOPO) in di-isobutyl ketone (DIBK) was 110, roughly two orders of magnitude above that for MIBK.

MacGlashan (43) studied the extraction of phenols from water with mixed solvents containing TOPO in more depth. His results clearly showed that the distribution coefficients for phenol, and more importantly the di- and tri-hydric phenols, between water and TOPO in DIBK were significantly higher than those for both DIPE and MIBK. (The extractability of the phenols from water decreases with the number of hydroxyl groups present.) Furthermore, as long as TOPO has a high enough solubility in the diluent, and its basic (i.e.,

electron donating) character is not reduced, the diluent used has only a minor effect on these distribution coefficients. Referring to Table 1-1 for example, one can see that for the conditions listed, the K_D's for TOPO in the diluents n-butyl acetate, DIBK, and Chevron 25 (a mixture of short chain alkyl-benzenes) are roughly 400. However, the K_D's for TOPO in both 2-ethyl hexanol and kerosene are significantly lower. This is explained, in the former case, by the -OH group of the alcohol diluent, which probably preferentially complexes with the phosphoryl oxygen of TOPO and hence competes with phenol for these active sites. In the latter instance, the aliphatic, highly non-polar nature of kerosene leads to low solubility of TOPO, which in turn gives a low K_D and thus limits the usefulness of such a diluent. These results are significant since they indicate that a mixed solvent of TOPO in the proper diluent could be used to extract phenols from wastewaters at lower solvent-to-water ratios than solvents presently used in commercial processes for this purpose.

F.) Objectives of This Work

The high distribution coefficients observed for phenol between TOPO-containing solvents and water confirm tnat the complexation of phenol with TOPO is relatively strong. This, in turn, implies that regeneration of the loaded solvent after extraction might be the critical factor governing the feasibility of any TOPO-based solvent. In addition, solvent losses will be vital to the process economics due to the high cost of TOPO (about $8/lb).

Accordingly, the principal objective of this work was to investigate the regeneration of TOPO-based solvents. The approach taken was first to study TOPO/diluent mixtures for which previous

Table 1-1

Previous Data for the Extraction of Phenols from Water (43)

Distribution Ratios for Extraction of Phenol with Various Solvents

Pure Diluent		With TOPO	
Solvent	K_D	% TOPO in Mixed Solvent	K_D
n-Butyl Acetate	58	25	390
2-Ethyl Hexanol	28	25	56
Chevron 25	1.8	25	340
Kerosene	0.15	5	90
n-Butyl Ether	14	15	320
Di-isobutyl Ketone (DIBK)	46	5	160
		15	330
		25	460
Methyl-isobutyl Ketone (MIBK)	110	--	
Di-isopropyl Ether (DIPE)	33	--	

Distribution Ratios for Di- and Tri-hydric Phenols

Pure Diluent		With TOPO	
Solvent	K_D Range	% TOPO in Mixed Solvent	K_D Range
DIBK	7.0 - 0.12	25	204 - 20.8
DIPE	4.9 - 0.18	-	
MIBK	18.7 - 3.6	-	

Initial Aqueous Solute Concentration = 5000 PPM T = 22.5 °C

Solute/TOPO Mole Ratio 1:2.5 K_D's Based on Weight Fractions

measurements of distribution coefficients had been made. The next step was to identify specific new diluents which might be more favorable in terms of regeneration, and in retrospect, to show that these TOPO/diluent combinations were still promising for extraction. Finally, the magnitude of TOPO losses into the aqueous phase was studied to determine the significance of any solvent losses.

Chapter II

EXPERIMENTAL PROCEDURE AND ANALYTICAL TECHNIQUE

A.) Solvent Regeneration

1.) Separation Factors

The separation factor, $\alpha_{i,j}$, between any two components of a mixture involved in a separation process is defined as the ratio of component i to component j in phase 1, divided by that for phase 2, as shown in equation 2-1,

$$\alpha_{i,j} = \frac{x_{i,1}}{x_{j,1}} \Bigg| \frac{x_{i,2}}{x_{j,2}} \qquad (2\text{-}1)$$

where the x's are all either mole or weight fractions, or molar or mass flow rates. For the specific case of distillation, the separation factor is commonly referred to as the relative volatility, and phases 1 and 2 are the distillate and bottoms products, respectively, obtained from one ideal, equilibrium stage. One can calculate the relative volatility by directly measuring the equilibrium concentrations of the components of interest in both product phases. In addition, for a simple distillation in which the feed is separated into two product phases, the relative volatility can be determined from knowledge of one product phase composition and the feed composition.

Specifically, a material balance for any component in such a system gives equation 2-2,

$$Fx_{F,i} = Dx_{D,i} + Bx_{B,I} \qquad (2\text{-}2)$$

where F, D, and B are the respective amounts of the feed, the distil-

late, and the bottoms, and the x's are the corresponding weight or mole fraction compositions. This expression can be rearranged, for example, to express the bottoms compostion in terms of the distillate and feed compositions (see equation 2-3).

$$x_{B,i} = (Fx_{F,i} - Dx_{D,i})/B \qquad (2\text{-}3)$$

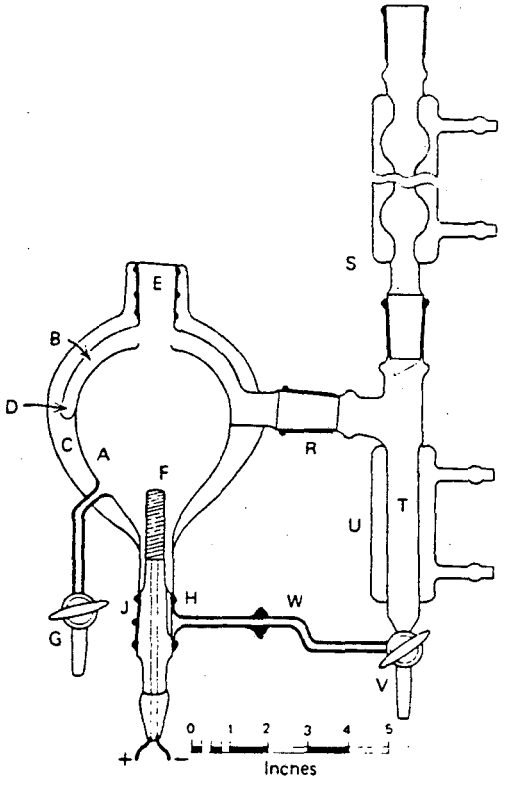
Consequently, the relative volatility can be calculated indirectly, without directly measuring the composition of the bottoms.

2.) Theory of Equilibrium Stills

A vapor-recirculating equilibrium still, model CG MES-100 by Cal Glass, was used to study the vapor-liquid equilibrium between phenol and the TOPO diluents in loaded solvent mixtures. This still is a modification of the design described by Hipkin and Meyers (27) who sought to eliminate the operating difficulties associated with previous still designs. In a liquid-recirculating still, of which the well-known Othmer design (1928) is an example, the liquid is boiled, condensed, and then recycled directly to the reboiler (see figure 2-1). The most noteworthy point of the Othmer still is the nearly perfect adiabatic jacketing of its boiling pot, which eliminates the possibility of condensation and rectification of vapors upon contact with the walls. Because of this, active boiling is possible with a minimum heat input, well below the point of significant superheating or entrainment.[46] However, considerable debate over the years has been focused upon whether or not the boiling action of the liquid in the pot is sufficient to mix the returning condensate well enough to obtain a homogeneous liquid composition. This can be a problem because if any portion of the low-boiling recycled condensate vapor-

Figure 2-1

Othmer Still[46]



The Othmer still with an integral jacketing arrangement to minimize heat losses from the pot: A, still body; B, vapor jacket; C, vacuum jacket; D, drain trough; E, thermometer part; F, glass immersion heater; G, liquid sample stopcock; H, groove in heater joint; J, heater joint; R, vapor line joint; S, condenser; T, condensate receiver; U, condensate cooler; V, condensate sample stopcock; W, capillary return line

izes before it mixes intimately with the liquid in the still, true equilibrium will not be reached.[27]

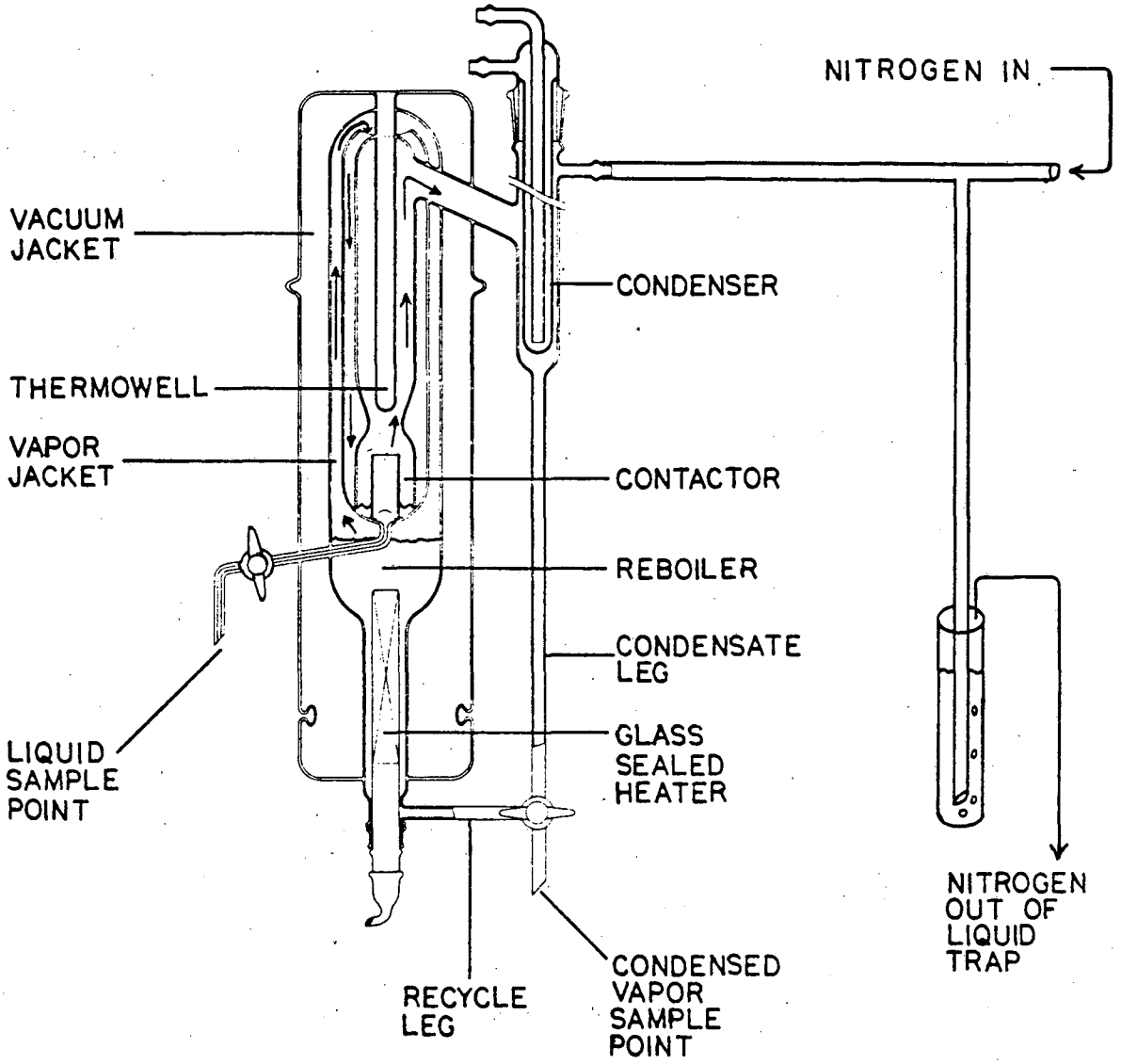
In theory, a vapor-recirculating still is a better design since it circumvents this problem. The idea in such a design is to vaporize the returning condensate so that it in effect has the equilibrium phase conditions as it enters the contactor[27] (see figure 2-2). The equilibrium vapor merely bubbles through the liquid here on its way to the condenser and is then recycled. However, the contactor section must be kept adiabatic to maintain steady state operation, which generally makes vapor-recirculating stills difficult to control.[27] The particular design shown avoids this control problem by completely insulating the contactor with its own vapor, by forcing the vapor to flow as diagrammed, as opposed to using an external winding to heat this area when necessary. In addition, the entire still is enclosed in a vacuum jacket by means of silvered glass walls which reduce radiation losses (as in a common Dewar flask.) A one-half inch wide, unsilvered strip on one side of the still serves as a window which permits observation of the boiling occuring inside.

3.) Procedure

The general procedure used was to charge the still with a known amount of loaded solvent, which was prepared synthetically by adding phenol to the mixed (TOPO/diluent) solvent of interest, and then turn on both the cooling water supply to the condenser and the power to the electrical heater. The temperature within the still was monitored by means of an Omega model 412-AJF digital temperature indicator equipped with an iron-constantan thermocouple, which was checked for accuracy to within less than one degree Fahrenheit at the freezing point of

Figure 2-2

Vapor-Recirculating Equilibrium Still[11]



water (32° F), and the boiling point of acetone (134° F). Once steady state was attained and held for at least 45 minutes, as evidenced by nearly constant temperature readings and a steady condensation rate, equilibrium was assumed to exist in the contacting section of the still, since the boiling action caused vigorous mixing here. At this point, the power to the heater was discontinued and the subcooled distillate was drained from the condensate leg of the column. The remaining liquid samples, in both the contactor and reboiler, stopped boiling as soon as the heat was cut off, and were drained off only after cooling to room temperature, so as to avoid changes in composition due to loss of hot vapor at the sampling points. A representative sample drop of the condensate, for subsequent analysis, was always obtained after first drawing off about half of it, in order to allow the Teflon valve and the glass tubing to be flushed out. It was not necessary to follow this procedure for the contactor and reboiler liquid samples because of their relatively large volumes and since the valve and tubing at the contactor liquid sample point were clean. (Samples were taken from the entire recovered volumes of these liquids.) Liquid samples which were not analyzed within a few hours after removal from the still were stored at 1 °C in one-dram, tight-seal sample vials covered with parafilm, until analysis for phenol and TOPO diluents was carried out. In addition, liquid samples from all three regions of the still were analyzed for TOPO, generally within a week.

It should be noted that some problems were encountered during operation of the still, and led to a few modifications. First, the synthetic loaded solvent solutions became successively darker in color

upon repeated distillation. This may have been due to the presence of phenol in solution, an effect of heat on the diluent itself, or a combination of both. (The presence of 25% TOPO (w/w) in dimethylnaphthalene (DMN) prevented its discoloration at room temperature for six months; however, solutions of this solvent containing over 6% phenol (w/w) and phenol-free solutions of DMN containing less than 5% TOPO both darkened with time.) In response to this phenomenon, the still was blanketed with nitrogen, to reduce the degree of discoloration (i.e. oxidation), as shown in figure 2-2. In addition, loaded solvent solutions were distilled only once to obtain relative volatilities. These measures lessened this effect enough so that the problem was consciously ignored thereafter.

Secondly, for high boiling mixed solvents (i.e. mixtures containing dimethylnaphthalene and TOPO), the rate of heat loss from the still was much greater than the heating rate required to boil the liquid samples within. In fact, the line between inadequate boiling and running the contactor dry, as determined by the hand-dialed heat rate setting on the variac, was so fine that several runs had to be terminated before steady state was reached, because the liquid in the contacting pool dropped to a level too low to assure that the rising vapor from below would bubble through it. This predicament was alleviated by attaching a one-inch layer of Owens-Corning fiberglass insulation to the outside of the still. However, although this significantly reduced heat losses, some heat loss from the still window near the reboiler remained noticeable.

Finally, despite these precautions, the distillation of high boiling, mixed solvent solutions loaded with relatively high amounts

of phenol (above 5.7% w/w) could not be carried out satisfactorily, because the majority of liquid in the contacting pool would inevitably bump over into the condensate leg, negating any degree of separation achieved up to that point. Because the boiling temperature of the reboiler liquid was significantly higher than that of the phenol-enriched, TOPO-free distillate, the condensate would begin boiling in the return leg of the still. Hence, this vapor became superheated as it moved closer to the heater and so expanded rapidly, which in turn caused the pressure in the lower region of the still to increase quickly. This sudden change in pressure between the two main sections of the still could not be maintained by the weight of the contacting liquid, and so it was violently forced over into the condensate leg. This behavior of the system effectively set an upper limit of 1.0 on the phenol/TOPO mole ratio in the loaded solvent feed.

It should be noted that Joshi (32) measured the relative volatility of heptane to toluene at 1 atmosphere using this particular equilibrium still. At a temperature of 102 °C, he found liquid and vapor samples in equilibrium contained 42.7 and 51.8 mole percent heptane, respectively. This corresponds to a relative volatility of 1.43, compared to a value of 1.45 published in the literature.[27] Hence, this vapor-recirculating still reproduced the previous equilibrium measurement for this binary system reasonably well.

B.) Liquid-Liquid Extraction

1.) Distribution Coefficients

For separation processes involving the equilibration of immiscible phases, the equilibrium distribution ratio is defined as the ratio of component i in phase 1 to that in phase 2. In the case of liquid-

liquid extraction, two different equilibrium distribution coefficients are commonly used. The molar distribution coefficient, K_M, is defined in terms of mole fractions and is useful in explaining solute-solvent interactions. In contrast, a distribution coefficient based on weight fraction compositions, K_D, is generally preferable for design calculations. (The two are directly related by a ratio of molecular weights.) The distrbution coefficient can be expressed in terms of activity coefficients of the solute in each liquid phase, as in equation 2-4,

$$K_M = x_{i,1}/x_{i,2} = \gamma_{i,2}/\gamma_{i,1} \qquad (2\text{-}4)$$

In general, the distribution coefficient is dependent upon concentration because these activity coefficients are functions of the solute concentration in the respective phases. However, the activity coefficients are constant for dilute solutions of the solute, typically below 1 or 2% by weight, and so the distribution ratio is also constant in this case.

Several experimental methods can be used to determine distribution coefficients. In this work, the solute of interest, phenol, was initially added to a water phase which was then contacted with solute-free solvent. The material balance for the solute before and after equilibration is given by equation 2-5,

$$Fw_F = Rw_R + Ew_E \qquad (2\text{-}5)$$

in which F, R, and E denote the weights of the aqueous feed, the raffinate, and the extract phases, respectively, and w_F, w_R, and w_E stand for the weight fraction of solute in the corresponding phases. This equation can be rearranged to express w_E in terms of the other

variables, as shown in equation 2-6.

$$w_E = (Fw_F - Rw_R)/E \tag{2-6}$$

If the aqueous and solvent phases have low mutual solubilities and are dilute in the solute, the amounts of these phases remain essentially constant during extraction, and equation 2-6 can be simplified to equation 2-7,

$$w_E = \frac{W}{S}(w_F - w_R) \tag{2-7}$$

where W and S denote the constant weights of the water and solvent phases. Substitution of this expression for w_E into the defining relation for K_D, equation 2-8,

$$K_D = w_E/w_R \tag{2-8}$$

gives an expression for K_D involving only aqueous phase compositions, equation 2-9.

$$K_D = \frac{W}{S}(w_F - w_R)/w_R \tag{2-9}$$

Thus, K_D can be calculated from the feed and raffinate solute weight fractions and the weights of both phases. In addition, analysis of the solute content of the extract phase permits the material balance to be checked, e.g. via equation 2-7.

Back extraction of a solute from solution in a solvent phase into a solute-free water phase can be used to check for possible mass transfer limitations or irreversible chemical reactions. In the absence of such effects, and K_D is independent of concentration, the extraction will be reversible; the K_D's measured for extraction in

for both directions will match to within experimental error. A derivation analogous to that for extraction in the forward direction yields the following expression for K_D, equation 2-10,

$$K_D = (Sw_F - Ww_R)/Sw_R \qquad (2\text{-}10)$$

where w_F now refers to the solute concentration in the solvent feed.

Several points should be considered in carrying out the experimental precedure used to determine K_D's. The liquid samples analyzed must be representative of the equilibrium distribution of the solute between the liquid phases. Vigorous contact between the solvent and water phases will permit chemical and thermal equilibrium to be reached in a reasonable length of time. Next, the phases must be completely separated to avoid analysis errors caused by entrained liquid of the complimentary phase. Also, any loss of material from the system can adversely affect the results when a material balance is assumed in calculating K_D's. In addition, all extractions should be carried out at the same temperature to permit direct comparison of the results, because K_D's vary sharply with this variable.

Other constraints can affect the experimental results, even if proper precautions are heeded to obtain samples for analysis. For a given feed concentration, either or both of two opposing effects can be encountered depending on the solvent to water ratio used. If S/W is too low, the solvent phase will become concentrated enough in the solute so that K_D is no longer equal to the infinite-dilution value, due to previously discussed reasons. If S/W is too high, the raffinate phase will become depleted in the solute below the limit of accurate, quantitative detection. This level was on the order of 5 PPM in this

work. Increasing the solute feed concentration can help overcome the latter problem, up to the point where the solubility limit of the solute is reached. In addition, water-soluble solvent impurities can interfere with trace solute analysis of the raffinate. Finally, a sufficiently high value for ($w_F - w_R$) is desirable for precise results.

2.) Procedure

The distribution coefficients were determined using the following precedure. For forward extractions, phenol was added to water purified by a Milli-Q™ filtration system to yield an aqueous feed solution containing 5,000 PPM phenol. For back extractions, the same weight of phenol was added to the solvent phase instead. The aqueous and organic phases were added to either a screw-top flask or a jar, which was then secured to a Lab Line Junior Orbit shaker set at 270 r.p.m. for 10-30 minutes, which caused intense phase contact. The closed container was then placed in a Precision Scientific model 50 temperature controlled shaker bath, set at 30 °C and about 120 oscillations/min., for 30 minutes. After allowing the phases to settle at this temperature for at least another hour, aqueous (and on occasion, organic) samples were removed with a pipette for analysis. These samples were then centrifuged in an International Clinical centrifuge, model X-4543, at 3300 r.p.m. for 30 minutes in order to ensure complete phase separation. Finally, 2 ml of liquid was withdrawn from the centrifuge tube and analyzed for phenol within a day via gas chromatography.

C.) Analytical Methods

1.) Organic Solutions

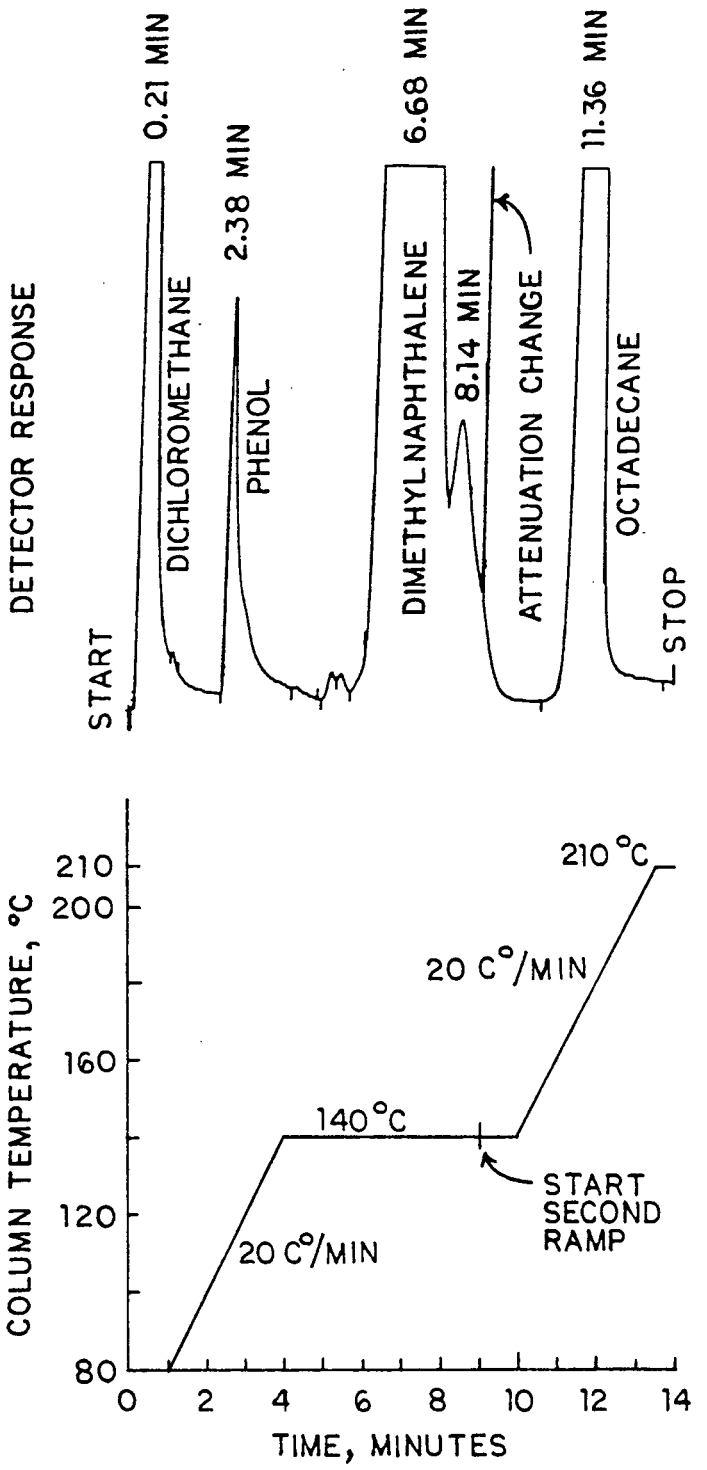
Analytical measurements for phenol and organic diluents were carried out using a Varian model 3700 gas chromatograph equipped

with a flame ionization detector (FID), a Gould model 110 chart recorder, and a Hewlett Packard model 3390A integrator. The flow rates for the nitrgen carrier gas, hydrogen, and air were 30, 30, and 300 cm^3/min, respectively. For nearly all of this work, a 54-inch long, one-eighth-inch O.D. stainless steel column packed with 5% OV-17 on an acid-washed, DMCS-treated 80-100 mesh Chromosorb® W support was used to analyze organic solvent solutions. In order to analyze solvent solutions containing TOPO without permanently contaminating the column, a sacrificial precolumn, containing 3 inches of this same packing, was connected to the front end of the main column via a Swagelock tubing union. This sacrificial precolumn was replaced as necessary when buildup of TOPO increased the normal retention times of the compounds of interest. In addition, the presence of TOPO in analyzed solutions also called for periodic cleaning of the injector port with acetone and replacement of the injector septum.

In order to reduce the required analysis time, linear temperature programming was usually employed for solvent phase analysis. However, for solutions containing phenol, dimethylnaphthalene, and octadecane, whose boiling points span a temperature range of 136 C°, two temperature ramps were executed during the course of analysis, in order to obtain complete peak resolution and the best peak shapes. Since this is not a normal operating procedure for this gas chromatograph, a change in attenuation was programmed into the timed events table of the integrator to signal when the second temperature program should start, and thus ensure a reproducible column temperature history (see figure 2-3). Also, for peaks which were not consistently interpreted correctly by the integrator using default construction, chromatogram

Figure 2-3

Matrix Temperature Program and Corresponding Chromatogram for Loaded Mixed Solvent



baseline construction was controlled by programmed integrator events. For example, it was appropriate to program the integrator to interpret the phenol peak always as a solvent peak, since it would otherwise be interpreted as a tangent-skimmed peak below a certain concentration range by default, but as a solvent peak at higher concentrations.

The composition of organic liquid samples was determined using the following procedure. First, a known weight of the sample was diluted with a known weight of solvent (methanol, acetone, or dichloromethane) to a concentration level low enough for accurate detection by FID, typically below 2% by weight. A one microliter Hamilton syringe, equipped with a Chaney adapter to guarantee a reproducible sample size, was rinsed with this solution several times, after any air bubbles adhering to the needle were knocked loose. Then the sample volume to be injected was drawn up into the syringe, and the needle was wiped clean. Within a timed 6-second interval, the needle was inserted as far as possible into the injector port, the integrator was started, the sample was injected, the temperature program was initiated, and the needle was removed, in that sequence. The average peak area for each component of interest, obtained from integrator outputs for 3 or more injections, was entered into an HP-41 CV programmable calculator which then calculated the concentration in the diluted sample. (The analytical expression relating peak area to concentration was obtained from a polynomial regression fit of the logarithms of peak areas and concentrations for TOPO-free calibration solutions, which covered at least an order of magnitude of concentration for each component. The standard deviation of this curve fit was always less than 2%.) The weight fraction of each component in the original liquid sample was

subsequently calculated from the known dilution ratio.

In the initial phases of this work, organic liquid samples were diluted with an unknown weight of solvent and analyzed only for phenol-diluent ratios, which were adequate for calculation of relative volatilities. However, once it became desirable to determine weight fractions of the components in solution in order to check various material balances, the amount of solvent used was measured. It should also be noted that although GC analysis of known solutions generally gave results accurate to within at least 6% of the true value, the measured concentration of phenol checked in known solutions containing 25% (w/w) or more TOPO was always low, generally by 5% to 15%. This point will be discussed further later in this report.

2.) Aqueous Solutions

A 16-inch long, one-eighth inch O.D. column packed with 100-120 mesh Poropak® Q was used to analyze aqueous solutions for phenol. Isothermal operation at 210 °C resulted in a linear calibration from 9 to 5200 PPM phenol. Because the phenol content of the aqueous extraction raffinates was already within this range, dilution was unnecessary for any of these samples. In addition, contamination of this column with TOPO was not a problem due to this compound's low water solubility. Otherwise, the procedure used for aqueous phase analysis was the same as that for organic samples.

3.) Analysis for TOPO

Initially, the weight fraction of TOPO in organic solutions was indirectly determined from the phosphorus content. The method of analysis used for phosphorus is based upon the weight of the ammonium phosphomolybdate precipitate obtained.[24] Since this compound has a

molecular weight is which is 63 times the atomic weight of the phosphorus which it contains, the method is typically highly accurate, to within ± 0.1%. From the determined weight percent phosphorus in solution, the weight fraction of TOPO was calculated with the assumption that all phosphorus detected was due only to this compound. Analyses of known organic solutions containing up to 25% TOPO gave results which were accurate to within +0.5%.

Determination of the trace TOPO content of aqueous solutions in this way gave values higher than the known solubility of TOPO in water.[4,26] The 3% impurity in the technical grade TOPO used in these experiments may account for this inconsistency, which could be caused by water-soluble TOPO contaminants. Hence, the utility of gas chromatography as an analytical technique was subsequently investigated. Although its full benefits have not been realized due to time constraints, gas chromatography produced valuable information about the TOPO content of raffinates; the OV-17 column previously mentioned was used isothermally at 280 °C for this analysis.

Chapter III

RESULTS AND DISCUSSION

A.) Considerations for Use of TOPO as an Extractant

In order to extract phenol from dilute aqueous solutions with a minimum of solvent, a high distribution coefficient is necessary. Because the activity coefficient of phenol in water at infinite dilution is independent of the solvent, the distribution ratio for phenol depends only on the activity coefficient of phenol in the solvent (refer back to equation 2-4). A low value of this activity coefficient is usually due to association between phenol and the solvent and results in a high distribution coefficient. Unfortunately, however, the factors which promote a high value of K_M also generally cause the solvent to be more soluble in water. Yet, as in the case for acetic acid, TOPO potentially avoids this shortcoming of conventional phenol solvents, although it is a solid at ambient conditions.

Ideally, one would like to use an extractant in its most concentrated form for removal of a solute from a liquid phase. However, the use of pure solid or viscous liquid extractants is impractical due to both mass transfer limitations and general handling problems. Consequently, in these cases, a liquid diluent is added to the extractant to yield a homogeneous, non-viscous mixed extraction solvent. While such solvents are necessarily subject to all the criteria for an acceptable pure liquid solvent, as listed in Table 3-1, additional factors become involved in the selection of a suitable diluent. For example, the diluent must be able to dissolve and retain in solution both the uncomplexed and complexed extractant.[6]

Table 3-1

Extraction Solvent Selection Criteria[36,57,65]

1.) High Solute Capacity

2.) High Distribution Coefficient

3.) Available at Low Cost

4.) Low Solubility in Raffinate Phase

5.) Density Difference from Complementary Phase

6.) High Interfacial Tension (Low Emulsion Tendencies)

7.) Easily Regenerated

8.) High Selectivity

9.) Nontoxic

10.) Thermally and Chemically Inert

11.) Low Viscosity, Vapor Pressure, and Freezing Point

Although the diluent is often considered to be an inert medium for the extractant, this may not be the case. So, the diluent chosen should not significantly detract from the extractant's capabilities; in some cases it can enhance these. The diluent should also have a low enough volatility so that the mixed solvent does not become progressively concentrated in the extractant. All these factors can often incite consideration of obscure or tailor-made diluents, but price and availability constraints must be considered as overriding factors for the use of more common diluents. (Experimental data for extractions are summarized in Appendix D.)

The regeneration of mixed solvents loaded with extracted solutes is also somewhat more involved than for common solvents. Distillation, generally the most common regeneration method employed, can be affected by TOPO, which is essentially nonvolatile. For the case of solvents with diluents having higher boiling points than phenol, a distillation column could effectively strip phenol from the mixed solvent to yield the former as a nearly pure overhead product and the latter as a bottoms product. (This is the same as for the case of a high boiling conventional solvent.) The possible buildup of coextracted heavy organics would necessitate a periodic purge of the mixed solvent which would increase solvent costs somewhat. In addition, any reduction in the volatility of the solute caused by the extractant must be taken into account.

For mixed solvents with TOPO diluents having lower boiling points than the extracted solute, a single distillation column could at best produce a nearly pure distillate of the diluent, and a mixed phenol-TOPO bottoms product, thereupon separating the components of

the mixed solvent. One possible disadvantage here is that the utility requirements to vaporize and condense the diluent can be high, depending on the required solvent flow. A stronger objection is that another step, which cannot be a common distillation, will be required to separate the phenol and TOPO, for reuse of the latter (by redissolving in the recovered diluent) and possible sale of the former. In this instance, stripping of the loaded extractant solution with water or an aqueous base would probably be preferable to distillation for regeneration. However, stripping with water essentially reverses the extraction and may not be at all advantageous, especially if coextracted organics also co-strip. Stripping with aqueous base is much more water efficient, but may not be amenable to ultimate solute recovery for sale and also incurs expenses for consumed chemicals. Also, TOPO forms stable emulsions upon contact with aqueous solutions of many common bases, such as NaOH and KOH. (Experimental data for solvent regeneration are summarized in Appendix C.)

B.) 25% TOPO in Di-isobutyl Ketone (DIBK)

Because of its demonstrated ability to extract phenols, the regenerability of this mixed solvent was studied first. Regeneration by back extraction into water is not attractive because the distribution coefficient for phenol is still high at increased temperatures (e.g. the distribution coefficient is about 150 at 60°C[43]). Thus, distillation was chosen as the regeneration method to investigate, even though the normal boiling point of DIBK (167 °C) is below that of phenol (182 °C).

For a feed solution of 25% TOPO in DIBK having a phenol-to-TOPO mole ratio of 0.5, the phenol-DIBK relative volatility was

determined, by the material balance method, to be greater than the ideal-solution value of 0.67 at the regeneration temperature of 170 °C. However, the presence of TOPO in solution would be expected to cause negative deviations from ideality and so reduce the relative volatility. Upon further investigation, an impurity of roughly 3% in the DIBK used was found to have the same residence time as phenol on the Poropak® Q column used for analysis. This impurity was not discovered earlier because the calibration solutions contained, by choice, both phenol and DIBK, in a 1:1 ratio; this masked the contaminant. The detected phenol content of the distillate was typically 3% by weight, and since the peak height at the phenol retention time varied with both phenol and DIBK concentrations (because the impurity level varied with DIBK concentration), the quantitative detection of phenol was faulty and could not be properly corrected for. Different columns were tested, in vain, for adequate resolution of the phenol and impurity peaks. Since no purer source of DIBK could be purchased, purification of the practical grade on hand was attempted by washing it first with 0.1 N NaOH, then 0.1 N HCl and finally, contacting it with silica gel adsorbent. This also had no effect, and at this point other high-boiling diluents were explored.

C.) 25% TOPO in Isobutyl-heptyl Ketone (IBHK)

Isobutyl-heptyl ketone (IBHK) was selected as an alternative TOPO diluent because of its similar chemical nature, commercial availability and higher boiling point, 218°C. At this temperature, the ideal-solution phenol-IBHK relative volatility (i.e. the ratio of vapor pressures) is 2.5. Based on the material balance method, relative volatilies of phenol to IBHK in synthetic loaded solvent mixtures

were determined to be 0.87 and 1.11, respectively, for phenol-TOPO mole ratios of 1.0 and 2.0 in the feed. These values are too low for economical regeneration of the loaded solvent produced by extraction of phenol from dilute aqueous solutions, and indicate that the complexation of phenol with TOPO at the measured distillation temperature of 218 °C is still quite strong. Thus, an even higher boiling diluent is required to obtain high enough separation factors at the phenol-TOPO mole ratios typical for a loaded solvent, i.e. less than 1.0.

It should be noted that the material balance method used to calculate these relative volatilities is based on the formation of two products, the distillate and bottoms, at equilibrium during distillation. However, in the vapor recirculating still used to obtain vapor-liquid equilibrium data, the feed is allocated to three separate regions. The theory behind this still implies that if the liquids in the condensate leg, the reboiler, and the contactor all have the same initial composition, then the liquids in the contactor and the reboiler should have very nearly the same composition at all times. Yet this was subsequently found not to be the case; liquid samples from these two regions of the still varied significantly in composition for distillation of loaded solvent mixtures containing phenol, TOPO, and dimethylnaphthalene (DMN). This is important because knowledge of the feed and distillate compositions no longer gives the composition of the equilibrium liquid by material balance under these conditions. Thus, the accuracy of the phenol-IBHK relative volatilities is limited because of this. (The degree of error this introduces is covered for the case of DMN in Appendix C.)

D.) 25% TOPO in Dimethylnaphthalene (DMN)

A mixture of dimethyl-naphthalene (DMN) isomers, having a boiling range of 262-269 °C, was selected for study as an even higher boiling TOPO diluent. DMN, a non-viscous liquid of low water solubility at ambient conditions, represents a practical limit for a high boiling diluent in terms of its physical properties. Compounds having higher boiling points are invariably solids or very viscous liquids at room temperature. Tables A-4a and b list some physical properties of TOPO diluents that were seriously considered. Since no single candidate is ideal in all aspects, a second component could be used to improve the physical properties of the diluent. In fact, octadecane, a high boiling alkane, was used as a co-diluent with DMN in this work to reduce the specific gravity of the mixed solvent. In like manner, one might choose to alter the diluent viscosity, water solubility, or melting point, while heeding economic and availability constraints.

DMN comprises approximately 10% by weight of Hi-Sol 4-2, a hydrocarbon solvent mixture manufactured by Ashland Chemical Company.[61] Accordingly, hydrocarbon solvents rich in DMN are probably commercially available at an inexpensive price. Thus, DMN was chosen as a representative substance to demonstrate the efficacy of a high boiling diluent. Preliminary regeneration studies with HiSol 4-2, which has a boiling point range of 78 C°, showed that its most volatile components became concentrated in the distillate and interferred with the gas-chromatographic analysis for phenol, making this diluent unsuitable for experimental purposes. In practice, it may be most prudent to use a narrow boiling range cut of such a solvent mixture.

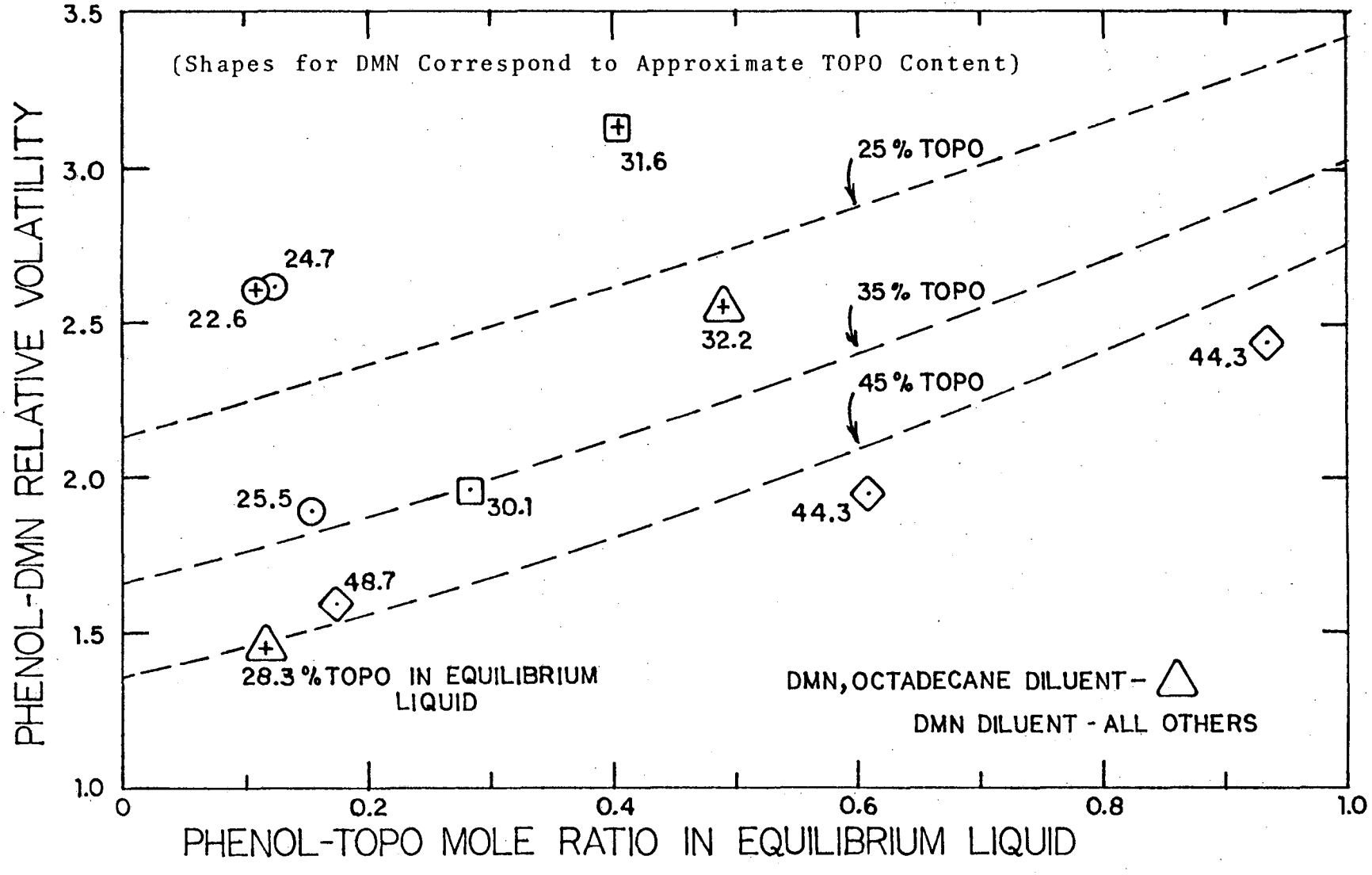
The relative volatility of an ideal phenol-DMN solution at

the measured regeneration temperature is 7.3. An attempt was made to measure the true separation factor for a TOPO-free solution of phenol and DMN for comparison, to determine the extent of non-ideality in the absence of TOPO, but the distillate became so enriched in phenol that it crystallized and clogged the condensate leg of the still at room temperature. However, at least qualitatively, this confirmed that the separation factor in the absence of TOPO is highly favorable, since one would expect phenol to have a relatively high solubility in DMN due to their similarities in chemical structure. Distillation of a phenol-free solution of 25% w/w TOPO in DMN showed that TOPO increases the boiling point of the solution by 46 °F above that for DMN alone. (If one assumes that the equilibrium liquid contained 25% TOPO, this corresponds to an activity coefficient of 0.68 for DMN in the presence of TOPO.) Due to phenol-TOPO complexation, the presence of TOPO would be expected to depress the volatility of phenol. Thus, the phenol-DMN relative volatility, for solutions containing all three compounds, will be determined by the relative strengths of two opposing effects - the vapor pressure difference between phenol and DMN on one hand, and the affinity of phenol for TOPO on the other.

Figure 3-1 shows the measured relative volatility of phenol to DMN, plotted as a function of the phenol-TOPO mole ratio in the equilibrium liquid. This ratio is a key variable because the dynamic hydrogen bonding which occurs between phenol and TOPO in solution on a molecular level implies, by Le Chatlier's principle, that the degree of phenol complexation should increase as the number of TOPO molecules available to associate with phenol increases. However, as is apparent

Figure 3-1

Phenol-DMN Relative Volatility as Function of Phenol-TOPO Mole Ratio



from the figure, this is not the only variable of significance. It was necessary, in order to interpret the data better, to introduce a second variable, the % TOPO in the equilibrium liquid, because the composition of this liquid was found to be substantially different from the 25% TOPO present initially in the loaded solvent feed. This change in liquid composition during distillation, due to both the apparatus used and the nature of the physical system studied, complicated the experimental design because the "independent" variables could be chosen only for the synthetic feed solution. In fact, distillation of identical feed solutions did not necessarily produce the same sample compositions at equilibrium.

The explanation for this behavior is tentative at best. Material balances for each component within each region of the still showed that: 1) In general, material accumulated in the reboiler at the expense of that in the contactor and condensate leg. 2) The absolute weight of TOPO present in the contactor remained unchanged during operation. 3) The distillate accumulated in the condensate leg was very nearly TOPO-free. (See Appendix C.) Apparently, during the transient attainment of steady-state operation, a heat transfer effect caused more liquid to boil off from the contactor than was replaced by the vapor condensing there from the reboiler. However, effects caused by boiling point elevation due to TOPO in solution or differences in latent heats of the contactor and reboiler liquids are implausible since the liquid within each region of the still had the identical composition at the onset. This net loss of material from the contactor caused the TOPO content of the liquid there to increase because TOPO is nonvolatile. Different steady state liquid

compositions might be produced from equivalent feed solutions if the time-heat input history during the start up period varied significantly between runs, which may have happened since the heating rate was not automatically controlled.

Although the data in Figure 3-1 show considerable scatter, some general trends can be explained by a simple model of the complexation between phenol and TOPO. Assuming an ideal vapor phase and neglecting liquid phase non-idealities for the diluent and for uncomplexed phenol, the partial pressure exerted by each component of interest in solution is given by Raoult's law, as shown in equations 3-1a and 3-1b,

$$p_1 = y_1 P_T = x_1^* P_1^\circ \qquad (3\text{-}1a)$$

$$p_2 = y_2 P_T = x_2 P_2^\circ \qquad (3\text{-}1b)$$

where the subscripts 1 and 2 denote phenol and the diluent (DMN), respectively, and x_1^* is the mole fraction of uncomplexed phenol in solution. By solving each of these equations for y and substituting the resulting expressions into the defining relation for the relative volatility, equation 2-1,

$$\alpha_{1,2} = (y_1/x_1)/(y_2/x_2) \qquad (2\text{-}1)$$

one obtains equation 3-2,

$$\alpha_{1,2} = (P_1^\circ/P_2^\circ)(x_1^*/x_1) \qquad (3\text{-}2)$$

in which the P°'s stand for the vapor pressures of the pure components. But since x_1^*/x is the fraction of free phenol in solution, f, and the ratio of vapor pressures is the ideal solution relative volatility,

equation 3-2 can be simplified further to yield equation 3-3.

$$\alpha_{1,2} = \alpha_{ideal}\, f \qquad (3\text{-}3)$$

This expression states that the measured relative volatility is directly proportional to the fraction of uncomplexed phenol in solution.

For a 1:1 stoichoimetry, the complexation of phenol at equilibrium is depicted by equation 3-4.

$$P + T \rightleftharpoons PT \qquad (3\text{-}4)$$

The equilibrium constant for this reaction is given by equation 3-5,

$$K_{eq} = \frac{[\,PT\,]}{[\,P\,]\,[\,T\,]} \qquad (3\text{-}5)$$

wherein [P], [T], and [PT] denote the respective molar concentrations of phenol, TOPO, and phenol-TOPO complex. If one lets P_o and T_o stand for the total concentrations of the solute and extractant in solution, the equilibrium constant can be expressed in terms of these variables and f, as shown in equation 3-6.

$$K_{eq} = \frac{1-f}{f[1-(1-f)P_o/T_o]T_o} \qquad (3\text{-}6)$$

Combination of equations 3-3 and 3-6 gives the equilibrium constant in terms of the relative volatility, the phenol/TOPO ratio, and the TOPO concentration, as shown in equation 3-7.

$$K_{eq} = \frac{[(\alpha_{ideal}/\alpha) - 1]}{\{1-[1-(\alpha/\alpha_{ideal})]P_o/T_o\}\,T_o} \qquad (3\text{-}7)$$

The equilibrium constant was estimated from the data for

the dimethylnaphthalene diluent (see Appendix C), using equation 3-7, and was found to be 5.1 L/gmole, with a standard deviation of 26%. (This value is an order of magnitude higher than that for tributyl phosphine oxide, as predicted by extrapolation of Asknes'[1] data to the measured regeneration temperatures.) Although K_{eq} would be expected to vary for different regeneration temperatures, the calculated K_{eq} values do not vary consistently with these measured temperatures (as predicted, for example, by an Arrhenius relation). Solution of equation 3-6 for f, and substitution of this expression into equation 3-3 allows one to predict the relative volatility from the phenol-TOPO mole ratio and the TOPO concentration, at a fixed temperature (i.e. a constant K_{eq}). The dashed curves shown in Figure 3-1 were calculated in this manner using the value of 5.1 for K_{eq}.

At constant temperature and TOPO concentration in the equilibrium liquid, the phenol-DMN relative volatility decreases with decreasing phenol-TOPO mole ratio. In the lower limit, as this ratio nears zero, the relative volatility also decreases to zero because essentially all the phenol is complexed. At the other extreme, as the phenol-TOPO ratio goes to infinity, the relative volatility will approach its binary value, since only an insignificant fraction of the phenol is complexed. In addition, for a given phenol-TOPO ratio, the separation factor will decrease with increasing TOPO content of the liquid.

Because the density of 25% TOPO in DMN (0.966 g/ml at 30 °C) is close to that water, octadecane was interchanged for 30% of the DMN to lower the density of the solvent to 0.914 g/ml at 30 °C. This substitution appears to reduce the phenol-DMN relative volatility

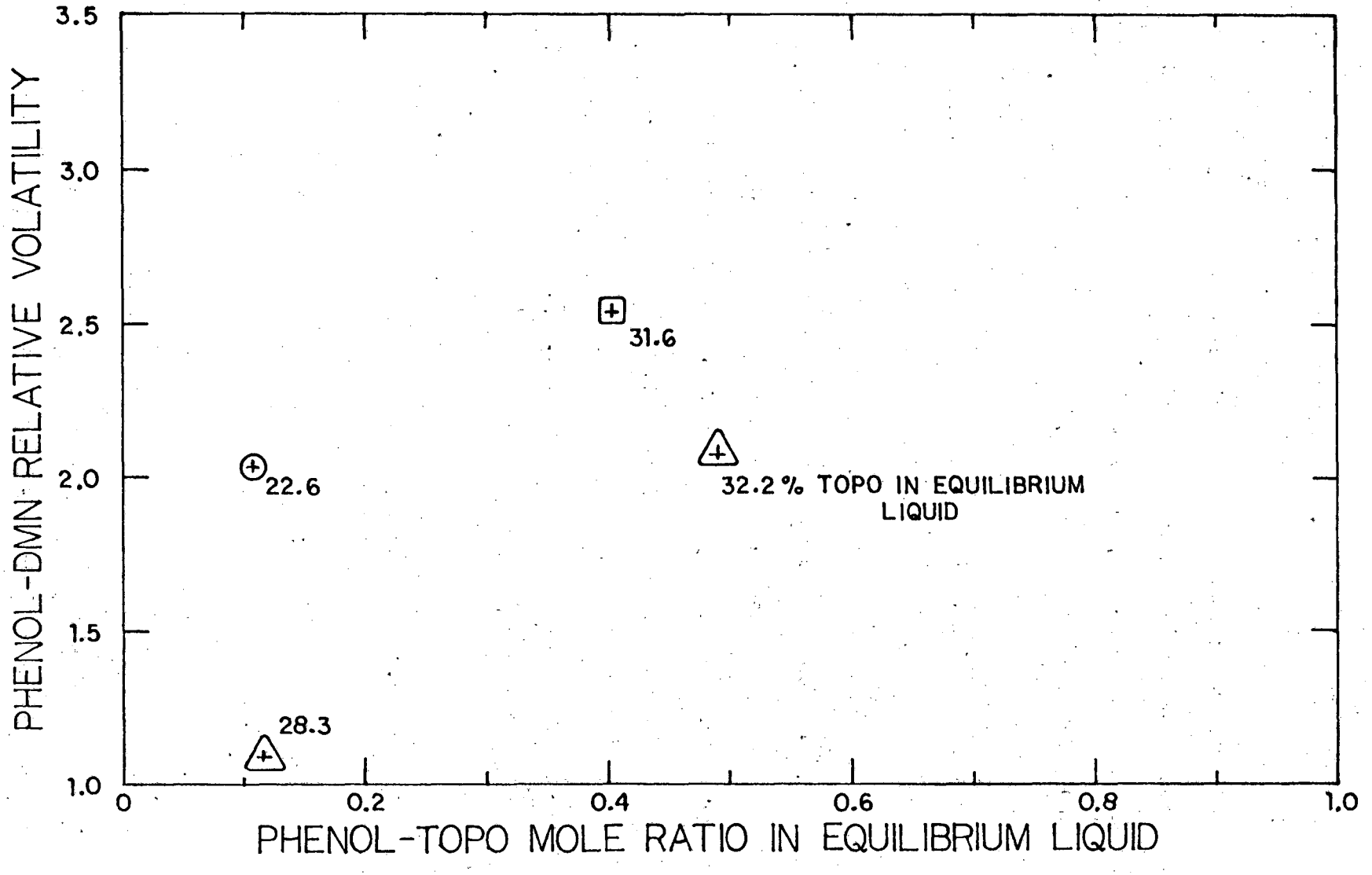
somewhat, as shown in figure 3-1.

It should be noted that material balances, which were carried out for the last 5 regeneration runs, were consistently unable to account for roughly 20% of the phenol originally present in the feed. It was subsequently found that the presence of 25% TOPO in phenol-DMN solutions affected the peak area and retention time of phenol, but not those of DMN. The average integrated peak area for phenol in the presence of TOPO was 5% lower than that detected for a TOPO-free solution having the same concentration. In addition, the retention time for phenol was observed to increase by about 6 seconds for each of 4 successive injections of TOPO-containing samples. These results indicate the complexation of phenol with TOPO present on the sacrificial precolumn, and imply that the phenol concentration of TOPO-containing solutions were underestimated.

If one assumes that this discrepancy is due entirely to errors in analysis of TOPO-containing solutions, and allocates the unaccounted phenol in proportion to that detected in such solutions from the equilibrium still, corrected values of phenol-diluent relative volatilities can be calculated. These are shown in Figure 3-2. However, despite being the most pessimistic values one could calculate, they are still generally favorable enough to permit regeneration by distillation. In retrospect, if one accounts for all of the phenol in this manner, the weight fraction of phenol in solutions containing TOPO must have been from 22 to 40% higher than first estimated. This seems somewhat extreme, even with a buildup of TOPO on the precolumn, since it was replaced before any noticeable increases in the phenol peak width and retention time were observed. Analytical problems

Figure 3-2

Phenol-DMN Relative Volatility Corrected to Account for Phenol Mass Balance



certainly account for part of the phenol discrepancy, but one could also consider the possibility of phenol degradation at the high regeneration temperatures observed, between 497 to 567°F. However, because a more accurate analytical method is required before any final conclusions can be drawn, experiments relative to that possibility were not pursued further.

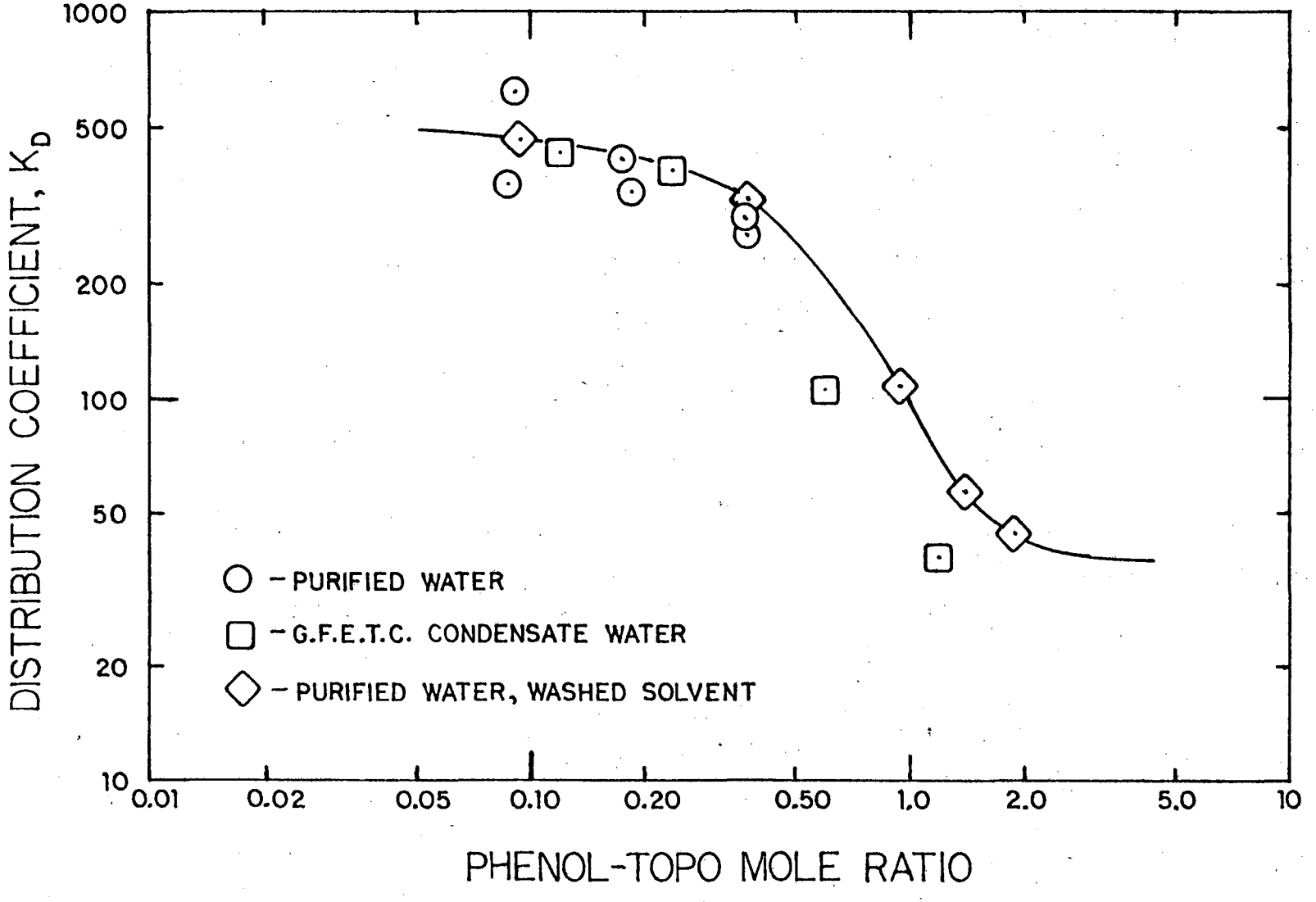
E.) Extraction of Phenol from Water with Mixed Solvent

At this point, since regeneration of the TOPO-DMN-Octadecane solvent combination was demonstrated to be feasible via distillation, the extraction capabilities of this solvent were investigated. The measured distribution coefficients for the extraction of phenol at 30 °C are plotted in Figure 3-3 as a function of the phenol to TOPO mole ratio in the system. The shape of the resulting curve is consistent with the formation of a dimeric phenol-TOPO complex, and can 43
be explained by the extraction mechanism model proposed by MacGlashan. For purified (Milli-Q™) water, the K_D's ranged from a high of 460 to a low of 44 at solvent to water ratios varying from 1.0 to 0.05, respectively. The disparity between K_D's for the forward and back extractions can be attributed, at least in part, to incomplete resolution of gas chromatogram peaks. Apparently, this was caused by a water-soluble impurity present in the solvent. Subsequent extractions carried out with solvent washed twice with water before use led to raffinate chromatograms without any extraneous peaks, and so these data are believed to be the most reliable.

To test the applicability of the solvent for treatment of an industrial effluent, distribution coefficients were also measured for the extraction of phenol from a condensate water sample from the

Figure 3-3

Extraction of Phenol from Water by Mixed TOPO Solvent at 30 °C



Grand Forks Energy Technology Center (GFETC) slagging fixed-bed coal gasifier. (The solvent was not washed in this case.) These K_D's compare reasonably well with the other data, and so are encouraging. However, the precision of the raffinate analysis decreased significantly with decreasing phenol concentration due to merged peaks caused by other components in this water sample. Thus, the uncertainty in these K_D's increases as the phenol-TOPO ratio decreases. In addition, it should be noted that emulsification occurred when the solvent was contacted with this water sample, whose pH was not altered from its value of 9 when received. Although centrifugation cleared the aqueous phase, the organic phase remained clouded with emulsified white particles less than 0.5 microns in diameter. Subsequent centrifugation of this phase at 10,000 r.p.m. for 40 minutes had no effect on the suspension.

For the extraction of phenol from purified water with unwashed solvent, the phosphorus content of the raffinate ranged from 31 to 90 PPM (w/w) at corresponding solvent to water ratios of 0.25 to 1.0. This corresponds to 400 to 1075 PPM TOPO if one assumes that all phosphorus detected is due to this compound. Since the true solubility of TOPO is no greater than 4 PPM, and the TOPO used was 97% pure, water-soluble phosphorus impurities originally present in TOPO were believed to account for the high phosphorus content of the raffinates. In addition, the phosphorus content of the coal condensate water raffinate was roughly four times higher than that for purified water at the same solvent to water ratio. Although the presence of other solutes in the aqueous phase may increase the solubility of phosphorus compounds, the fraction of this accounted for by TOPO is

unknown. Since the method used to produce the TOPO used in this work most likely yields acidic phosphorus side products, purification of the solvent by washing it with aqueous base was attempted with 0.1 N NaOH. However, emulsification of the solvent phase made it impractical for further experimental use.

Due to the aforementioned inconsistencies, gas chromatography was investigated as a means to analyze directly for trace amounts of TOPO. Reproducible chromatograms were obtained for dilute solutions of TOPO in acetone, below 1% by weight, using the same OV-17 column employed for analysis of organic solutions. Although the TOPO peak tailed badly, complete resolution was obtained at 280 °C. However, under the same conditions, the TOPO peak observed for aqueous raffinates was well merged with the preceeding peak. This was presumed to be due to traces of other high boiling organics, from the solvent, dissolved in the aqueous phase. However, the use of a low-boiling TOPO diluent, ethylbenzene, led to the same problem.

The general belief held for aqueous TOPO losses was that they were not much greater than the stated solubility of pure TOPO in water. Chromatograms of aqueous raffinates for extractions wherein the solvent was washed prior to use were nearly identical; i.e., the TOPO peak was the same shape and magnitude for both solvent to water ratios of 1.0 and 0.05. Thus, the aqueous phase became saturated to the same extent regardless of both the solvent-to-water ratio and the phenol-to-TOPO ratio. However, quantification of the merged TOPO peak was ambiguous. Since different chromatographic interpretations were equally plausible, the TOPO content of these raffinates could at best be demarcated to lie between 6 to 90 PPM. Nevertheless, even the

higher estimate is too low to account for the 15 PPM phosphorus in the in the raffinates, which corresponds to 190 PPM TOPO in the absence of other phosphorus-containing compounds. In addition, the phosphorus content of the fifth 50 ml water wash of 25 ml of mixed solvent was 11 PPM (or at most 137 PPM TOPO), as compared to 50 PPM (or at most 620 PPM TOPO) for the first water wash. This also supports the contention that water soluble TOPO impurities were present.

F.) Conclusions and Further Discussion

A vapor-recirculating still may not be the best design to use for determining VLE data for this particular system due to the change in TOPO content of liquid in the contactor. An Othmer still might be more appropriate for studying this system (or any other system containing a non-volatile component) because the experimental design would be simplified. In addition, if the phases attain equilibrium, relative volatilities could be obtained from knowledge of the feed composition and analysis of the TOPO-free distillate. However, the usefulness of the Othmer still would ultimately hinge upon how closely equilibrium is approximated.

An accurate means for analyzing for phenol in the presence of TOPO would be useful to check the material balance closure for phenol. This would permit investigation of possible phenol degradation during distillation at elevated temperatures. Also, a technique of analysis specific for TOPO would be valuable in interpreting the high phosphorus content of aqueous raffinates. Further use of gas chromatography for this purpose might define aqueous TOPO losses with greater accuracy than achieved here.

Regeneration of the loaded solvent by distillation at high temperatures appears to be feasible. Regeneration at decreased temperatures (and lower pressures) is probably not as favorable due to the corresponding increase in the equilibrium constant for TOPO-phenol complexation.

The distribution coefficients for the extraction of phenol from water are high for low phenol-TOPO mole ratios. Accordingly, the use of a TOPO based solvent would be best applied to dilute

aqueous feeds, having phenol concentrations on the order of hundreds of PPM.

APPENDIX A

SOURCES, GRADES, AND PHYSICAL PROPERTIES OF CHEMICALS USED

Table A-1

Sources and Grades of Chemicals Used

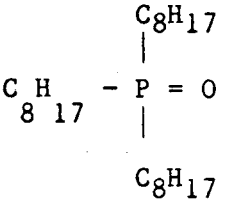
Chemical	Supplier	Grade
Tri n-Octylphosphine Oxide (TOPO)	American Cyanamid	Technical
Phenol	Mallinckrodt	Analytical
Di-isobutyl Ketone (2,6-dimethyl 4-heptanone)	Eastman Kodak	Practical
Isobutyl-heptyl Ketone (2-methyl 4-decanone)	Union Carbide	Technical
Dimethylnaphthalene (DMN)	Aldrich	Reagent
Octadecane	Aldrich	Reagent
Hi-Sol 4-2 (Commercial Hydrocarbon Mixture)	Ashland Chemical	Technical
Ethylbenzene	Matheson, Coleman, & Bell	Reagent

Table A-2

Physical and Toxological Properties of TOPO[4]

Formula: $C_{24}H_{51}PO$

Structure:



Purity of Grade Used:

93% n-isomer
4% other isomers
97% totyl octyl isomers

Molecular Weight: 386.65

Melting Point: 47 °C (56 °C [26])

Vapor Pressure: 0.1 mm at 200 °C
760 mm at 460 °C [26]

Water Solubility: < 4 PPM (1 PPM [26])

Specific Gravity: 0.88 at 25 °C
0.84 at 61 °C

LD_{50} (oral, rats): > 10 g/kg
(dermal, rabbits): 2.83 g/kg

Systemic toxic effects caused by skin absorption

Nonmutagenic

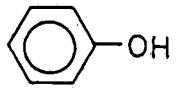
Appearance: Off-white waxy solid

TABLE A-3

Physical Properties of Phenol[46]

Formula: C_6H_6O

Structure:



Notes on Grade Used:

Water Content 0.125%

Preservative (H_3PO_2) 0.15%

Molecular Weight: 94.11

Melting Point: 41.0 °C

Vapor Pressure:

100 mm	at	121.4 °C	
200 mm	at	139.0 °C	
400 mm	at	160.0 °C	
760 mm	at	181.9 °C	
2 atm	at	208.0 °C	[57]
10 atm	at	283.8 °C	[57]

Water Solubility: 8.6% w/w at 25 °C

Specific Gravity:

1.132	at	25 °C
1.043	at	60 °C

Heat of Vaporization: 10.9 kcal/gmole at 182 °C

TABLE A-4a

Physical Properties of Diluents Used

Property	DIBK	IBHK	DMN	Octadecane
Formula	$C_9H_{18}O$	$C_{11}H_{22}O$	$C_{12}H_{12}$	$C_{18}H_{38}$
Molecular Weight	142.24	170.3	156.23	254.50
Melting Point	< 20 °C	< 20 °C	< 20 °C	29-30 °C
Vapor Pressure	100mm (104 °C)[63] 760mm (168 °C) 2692mm (225 °C) 6370mm (275 °C)	760mm (218 °C)	100mm (189 °C) 400mm (239 °C) 760mm (262-269 °C)	760mm (317 °C)
Water Solubility	0.06% w/w[51]	> 0.01% w/w (20 °C)	2.0-11.4 PPM[44] (25 °C)	2.1 PPB[64] (25 °C)
Solubility of Water in Solvent	-	0.2% w/w (20 °C)	-	-
Specific Gravity	0.9407 [5]1 (20/20)	0.818 (20/20)	1.010 (20/4)	0.777 (20/4)
Flash Point	140 °F[51]	-	101 °C (closed cup)	165 °C (closed cup)
Heat of Vaporization	9.54 kcal/gmole (168 °C)[63] 10.70 kcal/gmole (104 °C)			

TABLE A-4a (continued)

Physical Properties of Diluents Used

Property	Ethylbenzene
Formula	C_7H_{10}
Molecular Weight	106.17
Melting Point	-95 °C
Vapor Pressure	760mm (136°C)
Water Solubility	0.01% w/w (15 °C)
Solubility of Water in Solvent	-
Specific Gravity	0.867 (20/4)
Flash Point	22 °C

Reference for TABLES A-4a and b (except where otherwise noted):
Aldrich Catalog Handbook of Fine Chemicals, 1981-1982 ed., Aldrich Chemical Co., Inc Milwaukee (1980).

TABLE A-4b

Physical Properties of Other Potential Diluents

Property	n-Hexyl Ether	Diethylene-glycol Dibutyl-ether	Dowtherm A	Tridecyl Alcohol
Formula	$C_{12}H_{26}O$	$C_{12}H_{26}O_3$	$C_{12}H_{10}O$ (73.5%) $C_{12}H_{10}$ (26.5%) w/w	$C_{13}H_{28}O$
Molecular Weight	186	218	-	200
Melting Point	-43 °C	-60 °C	12 °C	33 °C
Vapor Pressure	760mm (226 °C)	760mm (256 °C)	760mm (257 °C)	760 (252 °C-269 °C)
Water Solubility	0.01% w/w (20 °C)	0.3% w/w (20 °C)	"Insoluble"	-
Solubility of Water in Solvent	0.12% w/w (20 °C)	1.4% w/w (20 °C)	-	-
Specific Gravity	0.7942 (20/4)	0.8853 (20/4)	1.073 (20/20)	0.8454 (20/4)
Viscosity	1.7cp (20 °C) 1.0cp (50 °C)	-	5.0cp (50 °F) 2.9cp (100 °F)	382cp (15 °F) 47.5cp (68 °F) 2.6cp (210 °F)

TABLE A-5

Composition and Properties of Hi-Sol 4-2

Component	Weight %[61]
Alklybenxzenes	
C-7	0.3
C-8	0.7
C-9	2.1
C-10	17.2
C-11	11.5
C-12	3.4
C-13 to C-20	3.1
Tetralins	10.7
Dihydronaphthalenes	0.3
Naphthalene	7.5
Methylnaphthalenes	14.7
Dimethyl and Ethyl Naphthalenes	9.1
C-13 Alkyl Naphthalenes	4.0
C-14 Alkyl Naphthalenes	1.6
Biphenyls	6.1
Fluorenes	6.5
Phenanthrenes	2.1
Naphthenes	1.1

Normal Boiling Range: 395-535 °F[13]

Specific Gravity: 0.976[13] (60 °F)

Flash Point: 205 °C[13] (closed cup)

APPENDIX B

DESCRIPTION AND SOME APPLICATIONS OF TOPO AND RELATED COMPOUNDS

In general, tertiary phosphine oxides are prepared by oxidizing tertiary phosphines with agents such as hydrogen peroxide or nitric acid, as shown in equation B-1.[4]

$$(n\text{-}C_8H_{17})_3P \xrightarrow{H_2O_2} (n\text{-}C_8H_{17})_3PO \qquad \text{(B-1)}$$

Tri n-octylphosphine → Tri n-octylphosphine oxide

Tertiary phosphine oxides are odor-free solids characterized by their high thermal oxidative stability (due ultimately to their very strong phosphoryl bonds), weak basicity, and metal complexing ability. While the lower molecular weight homologs are hygroscopic and quite soluble in water, the higher phosphine oxides (C_8 and above) are insoluble in water and soluble in nonpolar solvents. Long chain unsymmetrical tertiary phosphine oxides are surface active agents.

Tertiary phosphine oxides are among the most stable organic compounds known; in fact, their decomposition temperatures are several hundred degrees higher than those of amine oxides.[4] Hence, many phosphine oxides make effective flame retardants, which can either be incorporated into the substrate as an additive, or even be added as part of a prepolymer, which can withstand the extreme conditions of polymer processing and ultimately become part of the polymer backbone. References 69 and 67 describe the use of certain phosphine oxides as flame retardants and UV stabilizers, respectively, for polyolefins.

Extraction of Uranium and Other Metals

Phosphine oxides generally form strong complexes with both the actinide (trans-uranic) and lanthanide (rare earth) elements. In addition, these phosphine compounds have greater hydrolytic stability and a lower water solubility than other metal extractants. TOPO, for example, is known to extract dozens of metals, e.g. Zn, Cu, Cr, and Fe, from sulphate, nitrate chloride and perchlorate solutions, by strong coordination with salts or organometallics. The solvent is usually regenerated by stripping with water or dilute aqueous acid, base, or salt solutions. The most well known use of TOPO in this regard is for uranium recovery from wet process phosphoric acid.[29,30] The solvent used is a synergistic extractant combination of di-2-ethyl-hexyl phosphoric acid (D2EHPA) and TOPO dissolved in kerosene, or sometimes another high boiling aliphatic diluent. In this particular case, the D2EHPA extracts the uranium, in its +6 valence state, primarily by cation exchange between the metal ion and acidic hydrogen atoms, to form a uranyl dialkyl phosphate complex. TOPO serves as a solvent modifier and enhances the extraction by combining with the D2EHPA-uranium complex. TOPO is the best neutral organophosphate for this purpose because, as a tertiary oxide, its phosphoryl oxygen has the greatest base strength.[10]

In the first cycle of the wet acid process, uranium is extracted from an aqueous oxidized solution of phosphoric acid by a mixed solvent of 0.5 M D2EHPA / 0.125 M TOPO in kerosene. This loaded solvent is stripped with a phosphoric acid solution containing ferrous (Fe^{+2}) iron which reduces the uranium to its less extractable U^{+4} state, which preferentially concentrates in the aqueous phase. After

reoxidation to its hexavalent state, the uranium in this aqueous solution is re-extracted, in the second cycle, with a 0.3 M D2EHPA / 0.075 M TOPO solution. This extract phase is subsequently stripped with an aqueous ammonium carbonate solution to precipate ammonium uranyl tricarbonate, which is then filtered and calcined to produce U_3O_8.[30]

APPENDIX C

EXPERIMENTAL DATA FOR SOLVENT REGENERATION

Calculation Procedures

1) TABLE C-1

% error for analyzed feed compositions

Example: solution F-10, w_{phenol}

$$\% \text{ error} = \frac{(0.0283 - 0.0295)}{0.0295} \times 100 = -4.4\%$$

2) TABLE C-2

Absolute weights from weight fractions

Example: solution M-10, grams DMN

From TABLE C-1, $w_{DMN} = 0.4096$

grams DMN = (34.82)(0.4096) = 14.263 g

3) TABLE C-4

Relative Volatility and Phenol-TOPO mole ratio

Example: Run #10

Using weight fractions from TABLE C-1,

$$\alpha = \frac{(0.1652/0.6853)}{(0.0385/0.4096)} = 2.565$$

Using absolute weights from TABLE C-2,

Phenol-TOPO mole ratio:

$$P_o/T_o = \frac{(1.340 \text{ g})}{(94.11 \text{ g/gmole})} \Big| \frac{(11.215 \text{ g})}{(386.65 \text{ g/gmole})} = 0.491$$

4) TABLE C-5

Corrected Relative Volatility

Example: Run #10

From TABLE C-2, 6.318 - 5.207 = 1.111 g phenol not accounted for. Assume measured phenol content of D-10 correct.

Calculation Procedures (continued)

(Very little TOPO in D-10.) Allocate phenol to M-10 and B-10.

Increment in g phenol for M-10 $= \frac{(1.340)}{(1.340 + 3.339)}(1.111) = 0.318$ g

Corrected g phenol = 0.318 + 1.340 = 1.658 g

Corrected final wt. components = 0.318 + 34.82 = 35.138 g

Corrected phenol wt. fraction = 1.658/35.138 = 0.0472

Corrected $\alpha = \frac{(0.1653/0.6854)}{(0.0472/0.4059)} = 2.075$

5) TABLE C-6

Equilibrium Constant and Fraction Free Phenol

Example: Run #8

Density of M-8 at regeneration temp. 545 °F?

Density of solvent at 30 °C = 0.914 g/ml

For Dowtherm A, $\frac{\rho\ (545\ °F)}{\rho\ (86\ °F)} = 0.788$

Estimated density of solvent at 545 °F

(0.914 g/ml)(0.788) = 0.761 g/ml

Using absolute weights from TABLE C-2,

$$T_o = \frac{(11.215\ g)/(386.65\ g/gmole)}{(34.82\ g)/(761\ g/L)} = 0.622\ gmole/L$$

Using data in TABLE C-3 and equation 3-7,

$$K_{eq} = \frac{(7.3/3.137 - 1)}{[1 - (1 - 3.137/7.3)(0.404)](0.622\ gmole/L)}$$

K_{eq} = 2.774 L/gmole

Using equation 3.3,

$f = \alpha / \alpha_{ideal}$

f = 3.137/7.3 = 0.430

Calculation Procedures (continued)

6) TABLE C-7

Predicted Relative Volatility

Example: 25% TOPO, $P_o/T_o = 0.50$

Solving Equation 3-6 for f,

$$f = \frac{-b + (b^2 - 4ac)^{1/2}}{2a}$$

where $a = K_{eq}T_o(P_o/T_o)$

$b = K_{eq}T_o(1 - P_o/T_o) + 1$

$c = -1$

Also, equation 3-3 is

$$\alpha = \alpha_{ideal} f \qquad (\alpha_{ideal} = 7.3)$$

Calculate T_o for 25% TOPO. From TABLE C-5, runs 7-10,

$$\frac{\%\ TOPO}{gmole/L} = 52.526 \pm 3.2\%$$

$$T_o = \frac{25\%}{(52.526\%\ /\ gmole/L)} = 0.476\ gmole/L$$

$K_{eq} = 5.061$ for all calculations.

7) Other Calculations

Relative volatility for DMN diluent using material balance to calculate equilibrium liquid composition from feed and distillate compositions

Example: Run 8

Using absolute weights form TABLE C-2, calculate weight fractions on a TOPO-free basis.

F-8: $w_{phenol} = \frac{6.562}{6.562 + 161.791} = 0.0390$

D-8: $w_{phenol} = \frac{0.434}{0.434 + 2.909} = 0.1298$

Calculation Procedures (continued)

Calculate phenol content in equilibrium liquid by equation 2-3.

$$w_{phenol} = \frac{(6.562 - 0.434)}{(6.562 + 161.791) - (0.434 + 2.909)}$$

$$w_{phenol} = 0.0371$$

$$\alpha = \frac{0.1298/(1 - 0.1298)}{0.0371/(1 - 0.0371)} = 3.87$$

Compare to $\alpha = 3.137$ using measured compositions in TABLE C-1.

Likewise, for run 7,

$$\alpha = \frac{0.0201/(1 - 0.0201)}{0.0078/(1 - 0.0078)} = 2.62$$

Compare to $\alpha = 2.615$ using measured compositions.

TABLE C-1

Measured Weight Fractions of Components in Solutions from Distillation of Loaded Solvents

Solution-Run #	w_{Phenol}	w_{DMN}	w_{OCT}	w_{TOPO}	Σw_i
F-10	$0.0283^{-4.4}$	$0.5099^{+0.1}$	$0.2184^{+0.1}$		
F-10*	0.0295	0.5095	0.2183	0.2430	1.0000
D-10	0.1652	0.6853	0.1246	0.0065	0.9816
M-10	0.0385	0.4096	0.2656	0.3221	1.0358
B-10	0.0192	0.5848	0.2330	0.2434	1.0805
F-9*	0.0061	0.5218	0.2236	0.2484	1.0000
D-9	0.0205	0.9164	0.1241	0.0069	1.0678
M-9	0.0078	0.5309	0.1818	0.2921	1.0126
B-9	0.0036	0.5239	0.2273	0.2497	1.0045
F-8	$0.0252^{-14.5}$	$0.7402^{+1.7}$			
F-8*	0.0295	0.7524		0.2426	1.0000
D-8	0.1219	0.8171		0.0045	0.9435
M-8	0.0304	0.6396		0.3158	0.9858
B-8	0.0214	0.7524		0.2468	1.0185
F-7	$0.0057^{-6.2}$	$0.7620^{+2.2}$			
F-7	$0.0058^{-3.9}$	$0.7015^{-5.9}$			
F-7	$0.0056^{-6.4}$	$0.7452^{0.0}$			
F-7*	0.0060	0.7455		0.2485	1.0000
D-7	0.0192	0.9399		0.0050	0.9641
M-7	0.0056	0.7101		0.2259	0.9416
B-7	0.0042	0.7488		0.2771	1.0302
F-X*	0.0294	0.7279		0.2428	1.0000
D-X	0.2759	0.8319		0.0057	1.1135
M-X	0.0404	0.8221		0.2958	1.1584
B-X	0.0219	0.9068		0.2921	1.2208

Key:

F = Feed D = Distillate M = Middle (contactor liquid)
B = Bottoms

* - known feed composition from weighed amounts of components

Superscripts denote % error of analyzed feed composition from true value.

Run X (not graphed) - 4th time solution was distilled

TABLE C-2

Calculated Absolute Weights of Components in Solutions from Distillation of Loaded Solvents

Solution-Run #	grams phenol	grams DMN	grams OCT	grams TOPO	Combined Weight of All Components: Final	Combined Weight of All Components: Initial
F-10	6.318	109.044	46.723	52.005	-	214.03
D-10	0.528	2.189	0.398	0.021	3.19	3.48
M-10	1.340	14.263	9.250	11.215	34.82	46.34
B-10	3.339	101.435	40.408	42.215	173.44	164.21
TOTAL	5.207	117.887	50.056	53.451	211.45	-
F-9	1.295	110.207	47.222	52.466	-	211.19
D-9	0.060	2.694	0.365	0.020	2.94	3.51
M-9	0.272	18.577	6.362	10.221	34.99	43.73
B-9	0.609	89.945	39.026	41.699	171.67	163.95
TOTAL	0.941	111.216	45.753	51.94	206.66	-
F-8	6.562	161.791		53.927	-	222.28
D-8	0.434	2.909		0.016	3.56	4.04
M-8	1.133	23.831		11.767	37.26	48.84
B-9	3.832	134.584		43.767	178.88	169.40
TOTAL	5.399	161.324		55.550	219.70	-
F-7	1.305	161.277		53.758	-	216.34
D-7	0.073	3.562		0.019	3.79	3.72
M-7	0.287	36.636		11.654	51.59	46.85
B-7	0.671	118.299		43.766	157.98	165.77
TOTAL	1.031	158.497		55.449	213.36	-
F-X	6.455	159.605		53.232	-	219.28
D-X	0.954	2.878		0.020	3.46	3.88
M-X	1.596	32.441		11.674	39.46	46.47
B-X	3.770	156.164		50.305	172.22	168.93
TOTAL	6.320	191.483		61.999	215.14	-

All weights for feed solutions (row 1) and combined weights of all components (columns 5 and 6) were measured directly.

TABLE C-3

Weight Fractions of Components for Distillations Prior to Complete Material Balance Checks

Solution-Run #	w_{phenol}	w_{DMN}	Deviation of GC Analysis (%)	w_{TOPO}
D-6	0.0547	0.9406	0.5	0.0048
M-6	0.0203	0.6848	0.3	0.3010
B-6	-	-	-	0.2549
D-5	0.0249	0.9685	1.3	0.0066
M-5	0.0073	0.7478	0.8	0.2467
B-5	-	-	-	0.2711
D-4	0.0599	0.9364	1.6	0.0037
M-4	0.0202	0.5029	1.1	0.4867
B-4	-	-	-	0.2372
D-3	0.0239	0.9761	-	<0.0012
M-3	0.0095	0.7383	-	0.2546
D-3	-	-	-	0.1073(?)
D-2	0.3059	0.6949	1.8	<0.0012
M-2	0.0915	0.5065	3.7	0.4425
B-2	-	-	-	0.2197
D-1	0.1871	0.8129	6.0	<0.0012
M-1	0.0617	0.5526	1.8	0.4430
B-1	-	-	-	0.2334

TOPO content of solutions measured directly.

Phenol and DMN weight fractions calculated from measured ratio and assumption that $\Sigma w_i = 1$.

TABLE C-4

Phenol-DMN Relative Volatilities at Measured Conditions

Run #		Phenol-TOPO Mole Ratio	% TOPO (w/w)	Boiling Range, °F	Duration at Temp (h:min)
1	1.951	0.610	44.30	497.3-508.7	1:01
2	2.439	0.935	44.25	513.9-533.5	1:05
3	1.897	0.155	25.46	557.3-559.2	0:51
4	1.598	0.174	48.67	550.4-552.6	1:47
5	2.629	0.123	24.67	557.1-558.5	1:25
6	1.966	0.283	30.10	511.9-512.6	2:22
7	2.615	0.109	22.59	556.6-558.5	1:03
8	3.137	0.404	31.58	540.3-548.9	0:58
9	1.458	0.117	28.25	563.5-567.4	1:17
10	2.565	0.491	32.21	557.8- ?	-
X	6.739(?)	0.459	29.59	543.8-547.7	1:32

Run X (not graphed) - 4th time solution was distilled

TABLE C-5

Relative Volatilities Corrected for Phenol Material Balance

Solution-Run #	Increment in Grams Phenol	Corrected Grams Phenol	Corrected Final Combined Weight of Components	Corrected Wt. Fractions		Corrected α	Uncorrected α
				Phenol	DMN		
D-10	+0	0.528	3.19	0.1653	0.6854	2.075	2.565
M-10	+0.318	1.658	35.138	0.0472	0.4059		
B-10	+0.793	4.132	174.233	0.0237	0.5822		
		6.318					
D-9	+0	0.060	2.94	0.0205	0.9164	1.089	1.458
M-9	+0.109	0.381	35.099	0.0109	0.5293		
B-9	+0.245	0.854	171.195	0.0050	0.5232		
		1.295					
D-8	+0	0.434	3.56	0.1219	0.8171	2.542	3.137
M-8	+0.265	1.398	37.525	0.0373	0.6351		
B-8	+0.898	4.730	179.778	0.0263	0.7486		
		6.562					
D-7	+0	0.073	3.79	0.0192	0.9399	2.033	2.615
M-7	+0.082	0.369	51.672	0.0071	0.7090		
B-7	+0.192	0.863	158.172	0.0055	0.7479		
		1.305					

TABLE C-6

Calculated Equilibrium Constants for Phenol-TOPO Complexation

Run #	α	% TOPO	ρ_3/ρ_{30}	ρ	T_o (gmole/L)	f	K_{eq}
1	1.951	44.30	-	-	0.8434[1]	0.267	5.878
2	2.439	44.25	-	-	0.8424[1]	0.334	6.269
3	1.897	25.46	-	-	0.4847[1]	0.260	6.639
4	1.598	48.67	-	-	0.9266[1]	0.219	4.457
5	2.629	24.67	-	-	0.4697[1]	0.360	4.106
6	1.966	30.10	-	-	0.5731[1]	0.269	5.968
7	2.615	22.59	0.776	0.750	0.4379	0.358	4.399
8	3.137	31.58	0.788	0.761	0.6217	0.430	2.774
9	"1.807"[2]	28.25	0.771	0.705	0.5323	0.248	6.265
10	"3.578"[2]	32.21	0.774	0.707	0.5894	0.490	2.354

Key: 1) TOPO concentration calculated from weight % TOPO.

2) Phenol-combined diluent relative volatility used in calculation.

3) Ratio of density at regeneration temp. to that at 30 °C for Dowtherm A. Used to estimate density of organic TOPO solvent at regeneration temperature.

For runs 1-8 (all DMN diluent), K_{eq} = 5.061 ± 26%

For runs 1-10, K_{eq} = 4.911 ± 31%

TABLE C-7

Relative Volatilities Predicted by Model

	25% TOPO (T_o = 0.476)		35% TOPO (T_o = 0.666)		45% TOPO (T_o = 0.857)	
P_o/T_o	f	α	f	α	f	α
0.01	0.2948	2.152	0.2301	1.680	0.1886	1.377
0.05	0.3008	2.196	0.2356	1.720	0.1938	1.414
0.10	0.3084	2.252	0.2429	1.773	0.2004	1.463
0.30	0.3410	2.489	0.2748	2.006	0.2307	1.684
0.50	0.3763	2.747	0.3114	2.273	0.2669	1.948
0.70	0.4133	3.017	0.3518	2.568	0.3088	2.254
0.90	0.4508	3.291	0.3945	2.880	0.3548	2.590
1.10	0.4876	3.559	0.4375	3.194	0.4023	2.937
1.50	0.5551	4.052	0.5176	3.778	0.4921	3.592
2.00	0.6247	4.560	0.5992	4.374	0.5826	4.253

All values calculated with K_{eq} = 5.061 and α_{ideal} = 7.3

APPENDIX D

EXPERIMENTAL DATA FOR EXTRACTIONS

Calculation Procedures

1) TABLE D-1

K_D from extraction data

Example: extraction 3-E

Using equation 2-9,

$$K_D = \frac{59.74 \text{ g water}}{2.70 \text{ g solvent}} \frac{(5{,}197 - 1{,}728)}{(1{,}728)} = 44.4$$

2) TABLE D-2

Maximum possible TOPO content of raffinate from phosphorus content

Example: fifth water wash of solvent

$$\text{Max} = (11 \text{ g P/ml}) \frac{(\text{gmole P})}{(30.974 \text{ g P})} \frac{(1 \text{ gmole TOPO})}{(\text{gmole P})} \frac{(386.65 \text{ g TOPO})}{(\text{gmole TOPO})}$$

Max = 137 g/ml TOPO i.e. 137 PPM TOPO

3) TABLE D-3

Weight and mole fractions of phenol in extracts and raffinates

Example: extraction 3-E

Absolute weight of solute transferred to solvent phase not negligible for such a low solvent-water ratio. (Magnitude of error from this assumption decreases as solvent-water ratio increases, i.e. this example shows worst case in this respect.)

i) Feed phase

From TABLE D-1,

g phenol = $(59.74 \text{ g})(5{,}197 \times 10^{-6})$ = 0.3105 g

g water = $(59.74 \text{ g})(1 - 5{,}197 \times 10^{-6})$ = 59.430 g

Total Feed = 59.74 g

Calculation Procedures (continued)

ii) Raffinate phase

Loss of phenol to solvent phase will also decrease weight of aqueous phase. This should be negligible, but take into account anyway.

By definition,

$$w_R = \frac{P}{P + W}$$

where w_R = phenol content of raffinate
P = g phenol
W = g water

Solve for P

$$P = W\,[w_R/(1 - w_R)]$$

Grams phenol left in raffinate

$$P = (59.430\text{ g})[1{,}728 \times 10^{-6}/(1 - 1{,}728 \times 10^{-6})$$

$$P = 0.1029\text{ g}$$

Total weight raffinate phase = 59.430 + 0.1029
= 59.53 g

Wt. fraction phenol in aqueous phase

$$w_R = \frac{0.1029}{59.53} = 0.001729$$

(Change in weight of aqueous phase was negligible.)

Mole fraction calculation similar to that for solvent phase, which follows.

iii) Solvent phase

g phenol transferred = 0.3105 - 0.1029 = 0.2076 g to solvent phase

2.70 g of solvent has composition

0.250	TOPO
0.525	DMN
0.225	Octad.
1.000	

$$\text{weight fraction phenol in solvent} = \frac{0.2076}{0.2076 + 2.70} = 0.07139$$

Calculation Procedures (continued)

Weight fraction of phenol

	grams	MW	moles
TOPO	2.70(0.250)	386.65	0.001746
DMN	2.70(0.525)	156.23	0.009072
Octad.	2.70(0.225)	254.50	0.002387
Phenol	0.2076	94.11	0.002206
			0.015411

$$x_{E,phenol} = \frac{0.002206}{0.015411} = 0.1431$$

Note: from weight fractions, $K_D = \frac{0.07139}{0.001728} = 41.3$

Compare to 44.4 assuming S constant.

4) Others

Minimum solvent Required for Extraction

The "pinch" condition occurs at the upper right portion of y-x diagram. Minimum solvent flow determined by slope of operating line at pinch condition.

Example: Assume i) 1728 PPM phenol in aqueous feed
ii) No phenol in entering solvent
iii) Exit raffinate concentration of 1 PPM

Using weight fractions from Table D-3,

$$\text{slope} = \Delta y / \Delta x = \frac{(0.07139 - 0)}{(0.001728 - 10^{-6})}$$

slope = 41.3 g water/g solvent

Minimum solvent to water ratio is about 1:40.

TABLE D-1

Summary of Extaction Data

Run #	Solvent-Water Phase Ratio (v/v)	Solvent-Water Phase Ratio (gram/gram)	Phenol-TOPO mole Ratio	PPM Phenol in Feed	PPM Phenol in Raff.	Stand. Dev. (%)	K_D	PPM Phosphorus in Raff.
1-A(f)	1:1	45.34/49.91	0.0858	4,743	32.2	0.8	161	-
1-A(b)	1:1	7.23/7.98	0.0945	- [1]	9.2	3.2	624	-
1-B(f)	1:2	29.88/65.70	0.1714	4,743	65.8	4.3	156	-
1-B(b)	1:2	7.29/15.99	0.1576	- [1]	22.7	3.5	420	-
1-C(f)	1:4	18.14/79.70	0.3424	4,743	87.3	6.0	234	-
1-C(b)	1:4	7.02/31.90	0.3703	- [1]	65.5	7.8	340	-
2-A(f)	1:1	67.84/74.84	0.0914	5,041	9.0	2.0	617	90
2-A(b)	1:1	68.18/74.71	0.0884	5,347 [2]	13.7	5.8	389	82
2-B(f)	1:2	45.66/99.76	0.1750	4,873	25.4	3.7	417	49
2-B(b)	1:2	45.95/99.57	0.1848	11,118 [2]	32.1	6.2	344	31
2-C(f)	1:4	26.95/119.68	0.3679	5,041	75.5	1.2	292	33
2-C(b)	1:4	27.55/119.65	0.3742	22,293 [2]	82.6	6.2	266	31

TABLE D-1 (continued)

Summary of Extaction Data

Run #	Solvent-Water Phase Ratio (v/v)	Solvent-Water Phase Ratio (gram/gram)	Phenol-TOPO mole Ratio	PPM Phenol in Feed	PPM Phenol in Raff.	Stand. Dev. (%)	K_D	PPM Phosphorus in Raff.
GFETC-A	1:2	18.10/40.78	0.1207	3,259[3]	17.0	34.6	430	217
GFETC-B	1:4	10.81/48.11	0.2384	"	37.0	7.0	388	118
GFETC-C	1:10	5.37/60.37	0.6021	"	317	8.0	104	53
GFETC-D	1:20	2.69/60.37	1.2020	3,259[3]	1201	1.5	38.5	32
3-A	1:1	27.15/29.87	0.0948	5,246	12.4	3.2	464	14
3-B	1:4	10.86/47.68	0.3784	5,246	68.9	3.6	330	-
3-C	1:10	5.39/59.70	0.9457	5,197	482	0.8	108	-
3-D	1:15	3.63/59.68	1.4038	5,197	1150	4.1	57.8	-
3-E	1:20	2.70/59.74	1.8892	5,197	1728	2.8	44.4	16

Key: f - forward extraction b - back extraction

1 - phenol concentration is that of extract produced from forward extraction
2 - same weight of phenol added to solvent feed phase as added to aqueous feed phase for forward extraction
3 - measured phenol content of GFETC condensate water

Solvent for extractions 3-A through 3-E washed twice with water before use.
None of data for run #1 plotted.
For all data - Solvent is 25% TOPO, 52.5% DMN, 22.5% Octadecane (wt. %'s) T = 30 °C

TABLE D-2

Additional Phosphorus Analyses

Sample	Detected PPM Phosphorus	Calculated Maximum PPM TOPO
Milli-Q™ water	< 1	< 13
Water saturated with solid TOPO	54.9	685
Water saturated with solvent (Water-solvent ratio = 5/3)	54	674
First water wash of solvent (W/S = 2)	49.5	618
Fifth water wash of solvent (W/S = 2 each time)	11.0	137

TABLE D-3

Phenol Weight and Mole Fractions in Raffinates and Extracts

Weight Fractions		Mole Fractions	
w_E	w_R	x_E	x_R
5.725×10^{-3}	1.24×10^{-5}	1.235×10^{-2}	2.374×10^{-6}
2.334×10^{-2}	6.89×10^{-5}	4.706×10^{-2}	1.319×10^{-5}
4.966×10^{-2}	4.817×10^{-4}	1.020×10^{-1}	9.227×10^{-5}
6.245×10^{-2}	1.150×10^{-3}	1.264×10^{-1}	2.205×10^{-4}
7.139×10^{-2}	1.728×10^{-3}	1.431×10^{-1}	3.314×10^{-4}

Values calculated from data for extractions 3-A through 3-E

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