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P.D. Mackenzie* and C.J. King
(*Ph.D. Thesis)

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(*Ph.D. Thesis)

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Simultaneous Stripping and Solvent Extraction for the Recovery of Ammonia and Acid Gases from Wastewaters

Patricia D. Mackenzie

Abstract

A processing approach is proposed which has the potential for reducing energy requirements for the recovery of ammonia and acid gases (e.g. CO_2 and H_2S) from wastewaters. Two separation processes, solvent extraction and steam stripping, are carried out simultaneously. One process preferentially removes the acid gases, the other the basic gas (NH_3). The key to the process is the identification of a suitable solvent for one of the components.

No common solvents were found to be effective for extraction of either CO_2 or H_2S at the usual pH of such wastewaters. Only liquid cation exchangers were found to be suitable extractants for ammonia. These compounds form ion pairs in the organic phase with the ammonium cation, the most prevalent form of ammonia at the pH of the wastewaters. They are commonly used in diluted form.

Values of the equilibrium distribution coefficient (K_c, organic-phase concentration/aqueous-phase concentration) for carboxylic-acid extractants are too low to be useful. Solvent mixtures containing dinonylnaphthalene sulfonic acid as extractant were not readily regenerable. Solvents containing an acid of intermediate strength, di-

2-ethylhexyl phosphoric acid (D2EHPA) have more favorable properties.

Diluent choice affected the properties of D2EHPA-containing solvents. The addition of alcohols and related compounds to the diluent increased K_c, improved aqueous/organic phase-separation properties, lowered D2EHPA aqueous solubility losses, but retarded solvent regenerability. These effects indicate that the alcohols solvate the ammonium/D2EHPA complex in the organic phase.

The addition of Lewis bases, such as amines and phosphine oxides, to the diluent decreased K_c, lowered D2EHPA aqueous solubility losses at a given pH and improved solvent regenerability. These effects indicate that the Lewis bases interact with free D2EHPA in the organic phase.

Batch experiments comparing solvent extraction/stripping with stripping alone confirmed that the former resulted in increased CO_2 volatility and served to isolate NH_3 from CO_2.

Analysis of the overall economics of the process indicates that costs for replenishment of D2EHPA due to aqueous solubility losses and for the energy to regenerate the solvent are dominant. An improved extractant is needed if this approach is to offer economical advantages over other established approaches for recovering and isolating ammonia from such water streams.

DEDICATION

To my sister and friend, Carol

"Home is just another word for you."

B. Joel

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I am fortunate to have had this opportunity to work with Professor C. Judson King. I have learned much from him, both academically and professionally. Throughout this work he has always managed to provide the balance between freedom and guidance that I needed. He has helped me to establish a solid foundation for my career, for which I am grateful.

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TABLE OF CONTENTS

TABLE OF CONTENTS, continued

TABLE OF CONTENTS, continued

TABLE OF CONTENTS, continued

TABLE OF CONTENTS, continued

TABLE OF CONTENTS, continued

TABLE OF CONTENTS, continued

LIST OF FIGURES

PAGE

CHAPTER 1

FIGURE

CHAPTER 2

FIGURE

CHAPTER 3

FIGURE

LIST OF FIGURES, continued

CHAPTER 4

FIGURE

CHAPTER 5

FIGURE

LIST OF FIGURES, continued

PAGE

CHAPTER 6

FIGURE

LIST OF FIGURES, continued

LIST OF TABLES

PAGE

CHAPTER 1

TABLE

CHAPTER 2

CHAPTER 3

TABLE

CHAPTER 4

TABLE

LIST OF TABLES, continued

CHAPTER 5

TABLE

CHAPTER 6

TABLE

LIST OF TABLES, continued

LIST OF TABLES, continued

PAGE

LIST OF TABLES, continued

CHAPTER 7

TABLE

LIST OF TABLES, continued

LIST OF TABLES, continued

APPENDIX I

TABLE

APPENDIX II

TABLE

LIST OF TABLES, continued

APPENDIX III

APPENDIX IV

CHAPTER 1

INTRODUCTION

Wastewaters containing volatile weak acids and volatile weak bases are generated in many energy-producing processes, specifically, solid fuel-conversion processes and petroleum refinery operations. The most common acid gases are H_2S and CO_2. The volatile weak base is usually ammonia. The energy requirements for removing and isolating these gases from wastewaters can be very high. This work proposes a new process for isolating NH_3 from the acid gases and presents some of the data required to evaluate the feasibility of this process.

In this chapter some background information is given on conventional methods for treating these wastewaters and the concepts behind the proposed process are developed.

A. WASTEWATERS FROM SOLID-FUEL CONVERSIONS

Coal-gasification, coal-liquefaction and oil-shale retorting processes can produce gaseous and liquid fuels from solid feedstocks. Interest in such processes fluctuates with the price structure of world energy supplies, as well as both the world and national political environments. In any event, it is important to have good engineering designs of these processes for when they are needed. An important part of these designs is processing of the water streams which they generate.

In the Lurgi high-BTU coal-gasification process coal, steam and oxygen react to produce CH_4, H_2, CO, CO_2, H_2O, and various other byproducts. The reactor effluent is first quenched with cooling water, and then a portion of the excess CO in the gas is converted to CO_2 through the water-gas shift reaction. Again the gas is cooled, CO_2 is removed by scrubbing, and then the CO and H_2 are reacted to produce CH_4 and water. The principal sources of water streams are the process condensates from the two gas-cooling steps.

The process condensates have been in direct contact with organic materials at high temperatures and are contaminated with organic species. For low-temperature gasification processes, such as the Lurgi process, the Chemical Oxygen Demand (COD), a measure of the level of dissolved organic species, ranges from 5,000 to 90,000 ppm (King et. al., 1981). This COD is composed mostly of phenols and related compounds. The actual organic composition of the wastewater depends on the process, the operating conditions and the coal used, among other things. High-temperature gasification processes (e.g. the Texaco entrained-bed gasifier) produce waters that are much less contaminated. Much attention has been focused on accurately characterizing the organic contaminants of the wastewaters (Mohr and King, 1983).

In addition to organic contaminants, these wastewaters contain significant amounts of dissolved gases. Ammonia is universally present, being produced from the nitrogen-containing groups in the fuel. Ammonia is very soluble in water and absorbs into the condensate waters in the cooling step. Since ammonia is a weak base its presence in the wastewater enhances the solubilities of acid gases, such as CO_2 and H_2S. In gasification plants, CO_2 is the predominant gas, but H_2S will also be present if the sulfur content of the fuel is high. In liquefaction plants, H_2S is predominant.

Ranges of typical concentrations for NH_3, CO_2, and H_2S in these wastewaters are presented in Table 1.1 (King et. al., 1981).

Non-volatile salts can also be present in the wastewaters. Among the non-volatile ionic species oil-shale retorting waters contain sodium cations, while coal-conversion wastewaters may contain chloride anions (King et. al., 1981). The non-volatile cation-to-anion balance is important as it affects the ease of removal of the dissolved gases. The effect of these salts on the treatment of the wastewaters is discussed later.

The volume of water to be managed can be very large. Estimated process condensate flows from a 250 MM SCFD (standard cubic feet per day) plant range from 160 gpm for the SRC liquefaction process to 2600 gpm for the Lurgi gasification process (King et. al., 1980).

The usual proposal for treating these waters includes solvent extraction for bulk removal of organics and stripping to remove the dissolved gases. These are followed by biotreatment for degradation of residual organics and carbon adsorption as a finishing step (King et. al., 1981).

1. TREATMENT GOALS FOR WASTEWATERS FROM SOLID-FUEL PROCESSES

The concern of the present work is the removal of the dissolved gases from recycle or effluent water streams. Hence the rest of this discussion will focus on that problem.

The concentration levels to which each of these gases must be lowered depend on the end use of the treated water. The two main end-use possibilities are release of the water to the environment and recycle of the water back to the process. If the water is to be

TABLE 1.1

CONCENTRATIONS OF DISSOLVED GASES (ppm)

		EFFLUENT LIMITS	
SPECIES	FEED	RELEASE	RECYCLE TO COOLING TOWER
AMMONIA	1000-30,000	1-15	5-100
SULFIDE	20-30,000	0.1-10	1-5
CARBONATE (as $CaCO_3$)	1500-25,000	-	10-350
pH	7.5-9.5	6-8.5	7-8.5

Source: King et. al., 1981.

released to the environment, the levels of NH_3 and H_2S must be very low.

Unionized ammonia is acutely and chronically toxic to many freshwater and marine aquatic organisms, and it is readily oxidized to nitrite which is also toxic to fish. However, unionized ammonia is not carcinogenic, teratogenic nor mutagenic in man or in other animals, although it is capable of causing death or permanent injury due to exposures of normal use (Federal Register, 1980; Sax, 1979).

Unionized ammonia is approximately 50 times more toxic than ionized ammonia. The ratio of NH_3 to NH_4^+ ions in an aquatic environment depends on the prevailing pH, temperature, and ionic strength. The U.S. Environmental Protection Agency (EPA) criterion for the concentration of unionized NH_3 in water is 20 ppm. Total ammonia concentrations in surface waters are between 180 and 500 ppm. Because the level of unionized ammonia in surface waters is dependent on environmental conditions which cannot be easily controlled, the EPA has proposed listing ammonia as a toxic pollutant (Federal Register, 1980). As a toxic pollutant under the Clean Water Act, ammonia would not be eligible for waivers from effluent standards based on Best Available Technology Economically Achievable and it may be subject to very stringent effluent standards.

H_2S is an irritant and an asphyxiant. Prolonged exposure results in pulmonary edema. At very high concentrations, it paralyzes the respiratory center. An exposure to 800 to 1000 ppm for 30 minutes can be fatal. At even higher concentrations, death can be instant (Sax, 1979).

Rather than being directly released to the environment, it is more likely that these waters would be recycled back to the process. This is particularly desirable in arid lands of the western United States because it reduces water consumption and decreases the amount of water released to low-volume waterways. Water may be recycled as boiler-feed water, as cooling-tower make-up water, as steam to the gasifier, and as quench water for the reactor effluent. The latter choice requires very little processing of the water. The most likely scheme is to use the purge from the quench water recycle as cooling-tower make-up. If the water is recycled the treatment goals can be less stringent (Goldstein et. al., 1981).

Since NH_3 normally would not concentrate in the cooling tower, its effluent concentration from a treatment process is probably determined by odor limits in the cooling tower drift. The threshold odor limit for ammonia in air is about 20 ppm (Arthur D. Little, Inc., 1968).

For H_2S the limit for recycle to the cooling tower is influenced by odor limitations in the drift, corrosion effects and possible degradation of chromate corrosion inhibitors in the tower.

For CO_2, prevention of carbonate precipitation determines its concentration limit in the cooling-tower make-up water.

A general consensus of treatment goals for these wastewaters is presented in Table 1.1. Estimated limits for release to the environment and for recycle to the cooling tower are given (King et. al., 1981).

The dissolved gases will normally be removed in some combination of steam strippers. The effluent requirements from the stripper may be dictated by downstream biotreatment. Ammonia may be required as a nutrient to the biotreatment plant but certainly at a level well below that in the untreated water, so some NH_3 stripping will be necessary. On the other hand H_2S will probably be toxic to the microorganisms in the biotreatment plant and so must be nearly completely removed in the stripper.

A further motivation for removal of ammonia and H_2S from these wastewaters is recovery of the NH_3 and H_2S in usable or salable form. This requires isolation of ammonia from the H_2S. In addition to eliminating the loss of valuable NH_3 by burning in a Claus sulfur-recovery unit, this isolation lessens the burden on the Claus plant by reducing air, cooling and tail-gas clean up requirements. Further, if NH_3 and H_2S are not present together at the top of the stripper, plugging of the overhead system with ammonium sulfide salts is not a problem, and the temperature of the gas leaving the stripper may therefore be lower. This reduces the amount of water vapor in the gas feed to the Claus plant, which improves the operation of that plant (Cahn et. al., 1978).

One final incentive for removing the dissolved gases is to eliminate their buffering effect. The presence of significant amounts of CO_2, H_2S, and NH_3 in the wastewater produces a solution buffered in the pH range of 7.5 to 9.5. Adjusting the pH for some downstream process would require an economically prohibitive chemical consumption. Carrying out the same pH change in a treated water may be more tractable.

B. WASTEWATERS FROM REFINERY OPERATIONS

The wastewaters of interest from these operations are sour waters, which contain NH_3 and H_2S. They result from scrubbing a number of refinery gas streams to remove NH_3 from the feeds to gas-cleaning units that do not tolerate ammonia. NH_3 is very soluble in the water scrub and, as with the coal-conversion wastewaters, enhances the solubility of acid gases, mainly H_2S. In addition to significant quantities of NH_3 and H_2S, sour waters may contain organic acids, mercaptans, disulfides, phenols, oils, metal ions and non-volatile anions, such as chloride anions (Darton et. al., 1978).

After treatment, the water is recycled as desalter water, process wash water, cooling-tower make-up water and boiler feed water. Treatment goals for these wastewaters are similar to those for the solid-fuel-conversion wastewaters. The economic incentive to recover NH_3 and H_2S is also present, especially in view of the high likelihood of an on-site sulfur recovery plant (Verhoff and Choi, 1979).

C. DESIGN OF WASTEWATER STRIPPERS

NH_3, CO_2, and H_2S are usually removed from water streams by steam stripping. Figure 1.1 shows a typical steam stripper. The water enters the column and is contacted countercurrently with steam, either live or from a reboiler. Clean water exits the tower bottom and is used to preheat the feed. The gas leaving the top of the stripper contains water, NH_3 and the acid gases. The exit gases may be incinerated directly, but more commonly they are partially condensed, and the reflux is returned to the column. Refluxing to a short rectifying section offers the advantage of enriching the off-gas in the more volatile components and so decreasing the amount of water lost overhead. The disadvantages of refluxing are an increase in steam consumption for a given column and degree of contaminant removal and the need to provide cooling water and a condenser. When reflux is used, it is beneficial to provide a rectifying section above the feed tray. This becomes less

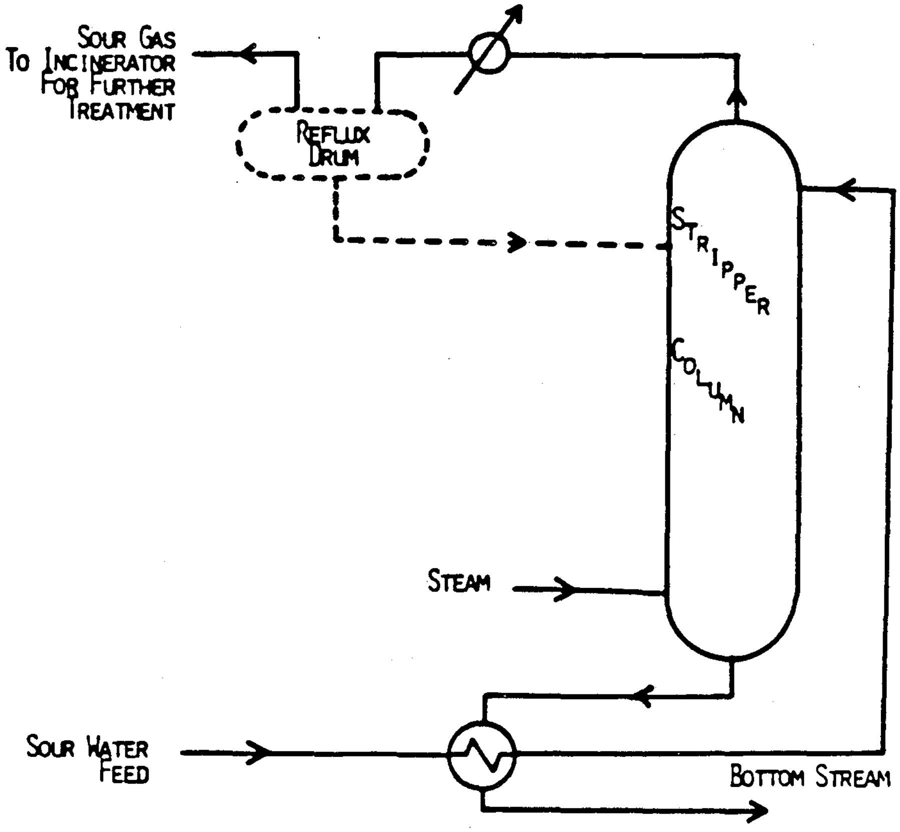

FIGURE 1.1: SOUR WATER STRIPPER.

Source: Verhoff and Choi, 1979

important as the feed composition approaches the reflux composition (Melin et. al., 1975).

A water wash may be added to the top of the column to suppress the stripping of less volatile components such as organics and NH_3.

Many procedures are available in the literature for the design of strippers for the treatment of wastewaters containing NH_3, CO_2, and H_2S. Beychok (1967) provides a quick and simple procedure, while Verhoff and Choi (1979) have developed a computer-aided design program which still ignores energy-balance considerations. More rigorous design procedures have been developed by Seufert et. al. (1979) Melin et. al. (1975) and Pawlikowski (1981).

These design procedures are generally stage-to-stage calculations combining material and energy balances with vapor-liquid equilibrium models for the system. The intricacies of the vapor-liquid equilibrium models are complicating factors in the design of strippers for these wastewaters.

D. VLE MODELS FOR NH_3-CO_2-H_2S-H_2O-SYSTEM

CO_2 and H_2S are weak acids and NH_3 is a weak base. In an aqueous solution these electrolytes can react to form several ionic species: HCO_3^-, CO_3^{2-}, HS^-, $S^{\ -}$, NH_4^+, NH_2COO^-, H^+, and OH^-. The exact distribution of ionic and molecular, or unionized, species depends on the total amount of CO_2, H_2S, and NH_3 present and also on the concentration of any other acidic or basic components, the temperature and the ionic strength of the solution.

These species dissociate according to the following equilibria:

$$\frac{(NH_4^+)\ (OH^-)}{(NH_3)} = K_b \qquad (1.1)$$

$$\frac{(HCO_3^-)\ (H^+)}{(CO_2)} = K_{1c} \qquad (1.2)$$

$$\frac{(CO_3^{2-})\ (H^+)}{(HCO_3^-)} = K_{2c} \qquad (1.3)$$

$$\frac{(NH_2COO^-)}{(NH_3)\ (HCO_3^-)} = K_{3c} \qquad (1.4)$$

$$\frac{(HS^-)\ (H^+)}{(H_2S)} = K_{1s} \qquad (1.5)$$

$$\frac{(S^{2-})\ (H^+)}{(HS^-)} = K_{2s} \qquad (1.6)$$

$$(H^+)\ (OH^-) = K_w \qquad (1.7)$$

Properly, these equations should be written in terms of activities. Activity is the product of concentration and an activity coefficient (γ). The activity coefficients may be grouped into the equilibrium constants and these new "constants" will then be functions of solution ionic strength and species concentrations as well as temperature. Values of equilibrium constants for dilute solutions are given in Table 1.2 (Edwards et. al., 1978).

For a given concentration of total NH_3, CO_2, and H_2S, the concentrations of the various ions in solution and the solution pH may be calculated. This is done by combining the above chemical equilibria with a mass balance for each species and an equation representing electroneutrality in the system. For instance, for CO_2 the species mass

TABLE 1.2

DILUTE SOLUTION EQUILIBRIUM CONSTANTS

$pK^{(a)}$	TEMPERATURE 298K	TEMPERATURE 373K
pK_b	4.75	4.84
pK_{1c}	6.36	6.64
pK_{2c}	10.33	10.15
pK_{3c}	-0.32	-0.11
pK_{1s}	7.00	6.47
pK_{2s}	15.74	14.00
pK_w	14.0	12.3

(a): pK ≡ (-log K); see text for definition of subscripts

Source: Edwards et. al., 1978

balance is:

$$\text{Total } CO_2 = (CO_2) + (HCO_3^-) + (CO_3^{2-}) + (NH_2COO^-) \quad (1.8)$$

The electroneutrality equation is:

$$\sum z_+ m_+ = \sum z_- m_- \quad (1.9)$$

where z represents the charge on a species and m represents its concentration.

The distribution of a species between a vapor phase and a liquid phase is determined by its Henry's Law constant. At equilibrium, the fugacity of a given species is equal in both phases. Thus:

$$f_i^v = f_i^l \quad (1.10)$$

or:

$$y_i \phi_i P = m_i \gamma_i H_i \quad (1.11)$$

where f represents fugacity, y vapor phase mole fraction, ϕ vapor phase fugacity coefficient and H the Henry's Law constant. At the temperatures of interest, ionic species are not volatile, so Equation 1.11 applies only to molecular CO_2, molecular NH_3 and molecular H_2S.

In summary, for an aqueous solution containing a known amount of total CO_2, H_2S, and NH_3, the equilibrium composition of the aqueous phase is determined by the relevant chemical equilibria, the species mass balances and the requirement of electroneutrality. The vapor phase equilibrium composition is determined by the Henry's Law constants and the concentration of unionized species.

Van Krevelen et. al. (1949) published a widely referenced work on the VLE of these systems. It is simple to use and gives satisfactory results for ammonia-rich solutions up to an ionic strength of 3 M.

More sophisticated and reliable VLE models for CO_2-H_2S-NH_3-H_2O systems have been developed recently (Pawlikowslki et. al., 1982a,b; Chen et. al., 1979; Edwards et. al., 1978; Beutier and Renon, 1978). In the present work a computer program, TIDES, developed by Pawlikowski, Newman, and Prausnitz (1982a,b) is used. The activity coefficient models used in TIDES are those developed by Edwards et. al. (1978). They are an extension of the Debye-Huckel theory and include three types of solute-solute interactions: molecule-molecule, molecule-ion, and ion-ion. The dependence of the Henry's Law constants on temperature is also taken from Edwards et. al. (1978). Vapor phase non-idealities are accounted for by vapor phase fugacity coefficients estimated by the method of Nakumara et. al. (1976). Direct substitution and a Newton-Raphson iteration are used to achieve convergence in TIDES. With TIDES, experimental results are predicted within 10% in the temperature range 0 to 170°C and the composition range from very dilute to 6 moles/kg. TIDES can also account for the presence of inert gas species and phenol.

For the current work, TIDES was modified to include the presence of excess anions and cations. To do this the equations for calculating ionic strength and total concentration of all solutes were corrected. Figures 1.2 and 1.3 show results of calculations using TIDES. Figure 1.2 shows the pH of an aqueous solution containing NH_3 and CO_2 as a

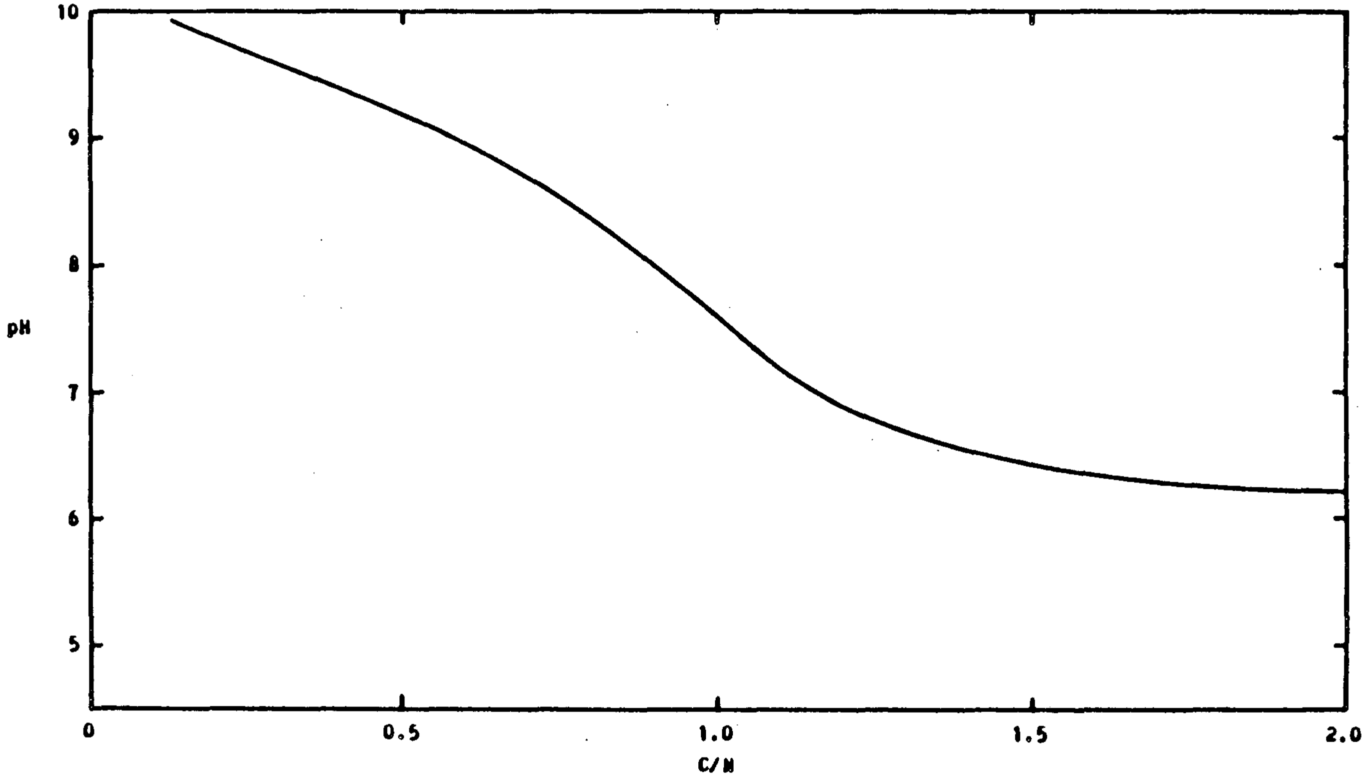

FIGURE 1.2: RESULTS OF TIDES: Prediction of pH as a function of total molar ratio of CO_2 to NH_3 (C/N).

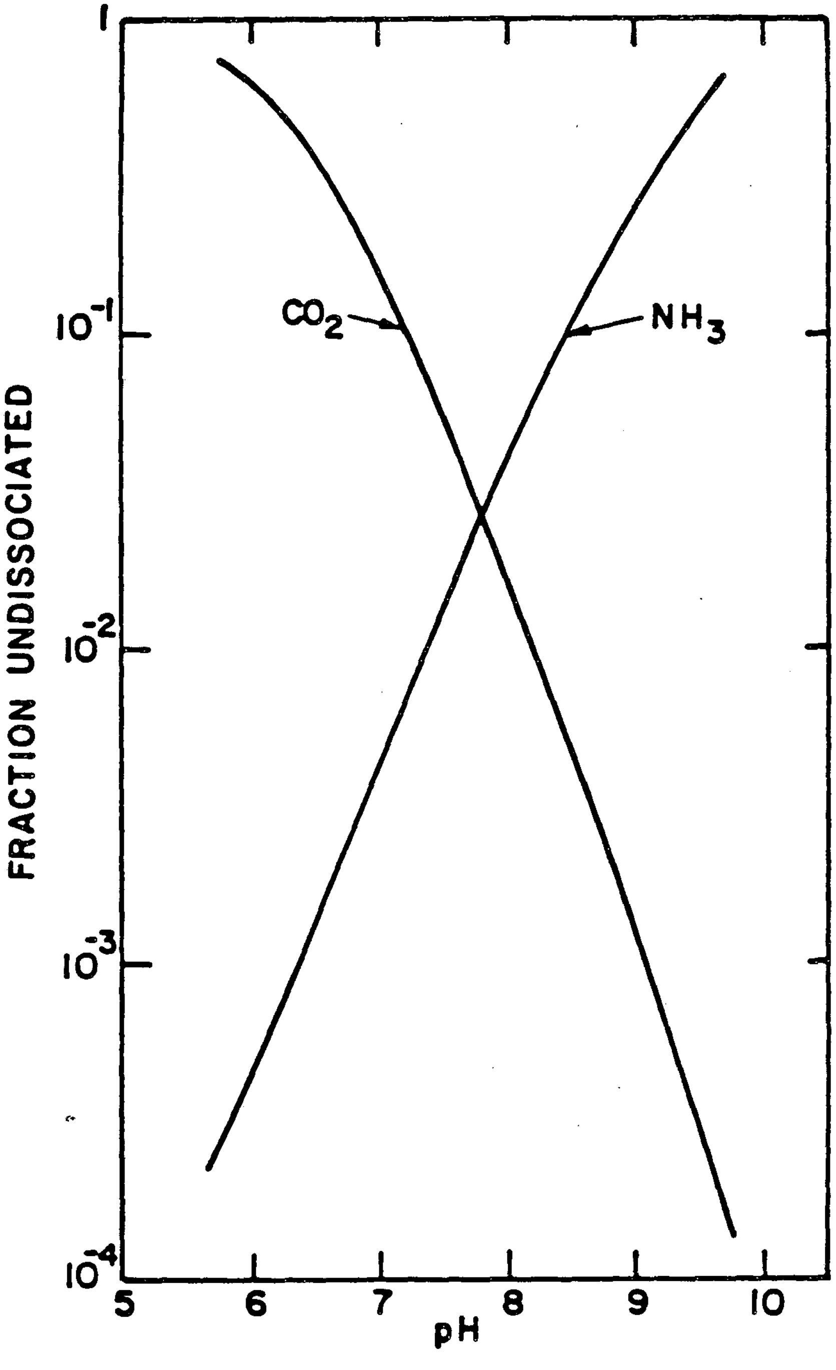

FIGURE 1.3: RESULTS OF TIDES: Prediction of Ratios of unionized species to total dissolved species.

function of the molar ratio of NH_3 to CO_2 at 298K. This is nearly independent of total concentration. Figure 1.3 shows the calculated ratios of molecular CO_2 to total CO_2 and molecular NH_3 to total NH_3 as a function of the aqueous phase pH at 298K.

E. STEAM STRIPPING OF NH_3-CO_2-H_2S WASTEWATERS

The steam requirements to remove a species from solution are directly related to the volatility of that species. For unionized NH_3, CO_2, and H_2S this is determined by the respective Henry's Law constants, values of which are given in Table 1.3 (Edwards et. al., 1978). Unionized CO_2 has the highest Henry's Law constant and unionized NH_3 has the lowest. Henry's Law constants increase with increasing temperature.

In the stripping process the concentrations of total CO_2, H_2S, and NH_3 are to be reduced. Since only the unionized portion is volatile, the ionization of a gas in an aqueous solution results in a reduction of its effective volatility. The greater the extent of ionization, the greater the decrease in volatility. This can be represented quantitatively by expressing the partial pressure of NH_3 as a function of the total concentration of ammonia in solution. Letting N equal the total ammonia concentration and ignoring the presence of the carbamate ion (NH_2COO^-), then:

$$N = (NH_3) + (NH_4^+) \tag{1.12}$$

from Equation 1.1 and 1.7:

$$(NH_4^+) = K_b \frac{(NH_3)}{(OH^-)} = \frac{K_b}{K_w} (NH_3)\ (H^+) \tag{1.13}$$

TABLE 1.3

DILUTE SOLUTION HENRY'S LAW CONSTANTS

(kg H_2O-atm/gmol)

SPECIES	TEMPERATURE 298K	 373K
NH_3	0.017	0.23
CO_2	28.4	94.5
H_2S	9.64	28.5

Source: Edwards et. al., 1978

Substituting into Equation 1.12 gives:

$$N = (NH_3)\left[1 + \frac{K_b}{K_w}(H^+)\right] \qquad (1.14)$$

This equation is the essence of Figure 1.3.

Using the Henry's Law relationship (Equation 1.11) and ignoring solution non-idealities:

$$P_{NH_3} = H_{NH_3}\,(NH_3) \qquad (1.15)$$

where P_{NH_3} is the equilibrium partial pressure of ammonia. Combining equations 1.14 and 1.15 yields:

$$P_{NH_3} = \frac{H_{NH_3}\,N}{\left[1 + \frac{K_b}{K_w}(H^+)\right]} \qquad (1.16)$$

For a given total ammonia concentration, at a high pH the concentration of NH_4^+ ions is low (Equation 1.13), nearly all of the ammonia exists in the molecular form and the partial pressure of ammonia is high (Equation 1.16). As the pH decreases, however, ammonia ionizes and the partial pressure of ammonia above the solution decreases according to Equation 1.16.

The opposite is true of the acid gases. For a given total concentration of CO_2, the partial pressure of CO_2 is highest at low pH and falls off at high pH. The same is true for H_2S.

In view of this, for a given total concentration of CO_2 or NH_3 the curves in Figure 1.3 are proportional to the partial pressure of the gas above an aqueous solution as a function of pH. The constants of proportionality are the Henry's Law constants.

Since the addition of CO_2 to a solution containing NH_3 lowers the pH and results in ionization of NH_3, the presence of CO_2 in solution decreases the volatility of NH_3 and consequently increases the steam requirements for stripping NH_3 from solution. Of course, the converse is also true.

In addition, the presence of any other acid in solution, such as HCl, also decreases NH_3 volatility. On the other hand, the presence of any other base in solution, such as NaOH, decreases CO_2 and H_2S volatility. Thus if there is an excess of anions in a wastewater, a portion of the NH_3 will be paired with them as NH_4^+ and this portion of the ammonia will be essentially impossible to strip from solution. An excess of cations has the same effect on CO_2 and H_2S.

Some generalizations may be drawn from various stripper simulations which have been published. As expected, for a given removal efficiency, the number of stages decreases as the steam-to-water ratio increases and vice versa. There are pinches at either end of the spectrum though. Beyond a certain steam rate, the number of stages cannot be reduced significantly by increasing the steam rate. Beyond a certain number of stages, the steam rate cannot be decreased significantly by increasing the number of stages (Melin et. al., 1975; Seufert et. al., 1979).

The acid gases have higher Henry's Law constants than NH_3 and are easier to remove from solution than NH_3 is. This means that NH_3 specifications will generally determine stripper designs (Melin et. al., 1975). For instance, for a feed containing approximately the same weight fractions of CO_2 and NH_3, only 90% of the NH_3 is removed when no measurable amount of CO_2 is left in the solution (steam rate: 0.105 lb steam/lb feed water; 4 theoretical stages) (Seufert et. al., 1979). For a similar feed containing NH_3 and H_2S, 90% of the NH_3 is removed when 96% of the H_2S is removed (steam rate: 0.105 lb steam/lb feed water; 6 theoretical stages) (Seufert et. al., 1979). The latter requires more stages and/or more steam than the former. This reflects the fact that H_2S is less volatile than CO_2 and consequently that CO_2 is easier to strip from solution than H_2S is. The higher steam requirements for the same percent NH_3 removal in the H_2S/NH_3 case are a result of the higher residual acid gas concentration. In order to get higher removal efficiencies for H_2S, the pH must be lowered by the removal of more NH_3. Thus, nearly 98% of the NH_3 must be removed to achieve 99.9% H_2S removal (Seufert et. al., 1979). When H_2S is present in low concentrations it is often necessary to remove more NH_3 than would otherwise be required in order to reach the required H_2S specification. This of course requires more steam and/or more stages. Operation at higher temperatures will help as the relative volatility of H_2S to NH_3 increases with temperature (Seufert et. al., 1979). The presence of CO_2 enhances H_2S volatility due to the decrease in pH which it causes (Darton et. al., 1978).

Columns are usually operated at about 25 psia and temperatures greater than 100°C. Energy requirements for the stripping of these wastewaters range from 0.08 to 0.20 lb steam/lb feed water (Darton et. al., 1978). This represents from 30 to 70% of the total stripping costs of \$2 to \$5/1000 gallons of water treated (Seufert et. al., 1979). Fifteen to 20 actual trays are required. Tray efficiencies are between 35 and 65% (Darton et. al., 1978; Seufert et. al., 1979). Under these conditions up to 20% of the phenols in the wastewater will be stripped with the gases (Seufert et. al., 1979). Refluxing decreases the amount of phenols stripped, but increases stripping costs.

Composition and temperature profiles within a stripper are given by Verhoff and Choi (1979). Figures 1.4 and 1.5 show the concentration profiles for NH_3, CO_2, and H_2S within a column. Figure 1.6 shows the pH profile. These calculations were based on a fixed concentration of the bottom effluent: NH_3, 240 ppm; CO_2, 10 ppm; H_2S, 15 ppm; organics, 880 ppm; Cu^{2+}, 1.1 ppm. The pinch in terms of NH_3 stripping occurs at the top of the column, as seen in Figure 1.4 at a steam rate of 1 lb/gal water and a bottom-tray temperature of 105°C. At the top of the column the pH is lowest, and NH_3 ionization is greatest. The temperature is also at its lowest value at the top of the column. The addition of a non-volatile cation to raise the pH serves to suppress NH_3 ionization and aids NH_3 removal. As seen by the dashed curves in Figure 1.4 the effect is to move the pinch in NH_3 stripping away from the top of the column.

For the acid gases, the pinch appears to occur closer to the bottom of the column, as seen in Figure 1.5 for H_2S at a bottom-tray temperature of 105°C. At the bottom of the column the pH is highest and the acid gases are most ionized. The low temperature at the top of the column does tend to pull the pinch point up the column some. The addition of a non-volatile cation raises the pH at the top of the column and moves the pinch in acid-gas stripping toward the top of the column.

F. ISOLATION OF AMMONIA FROM ACID GASES

Steam stripping of these wastewaters can remove the dissolved gas

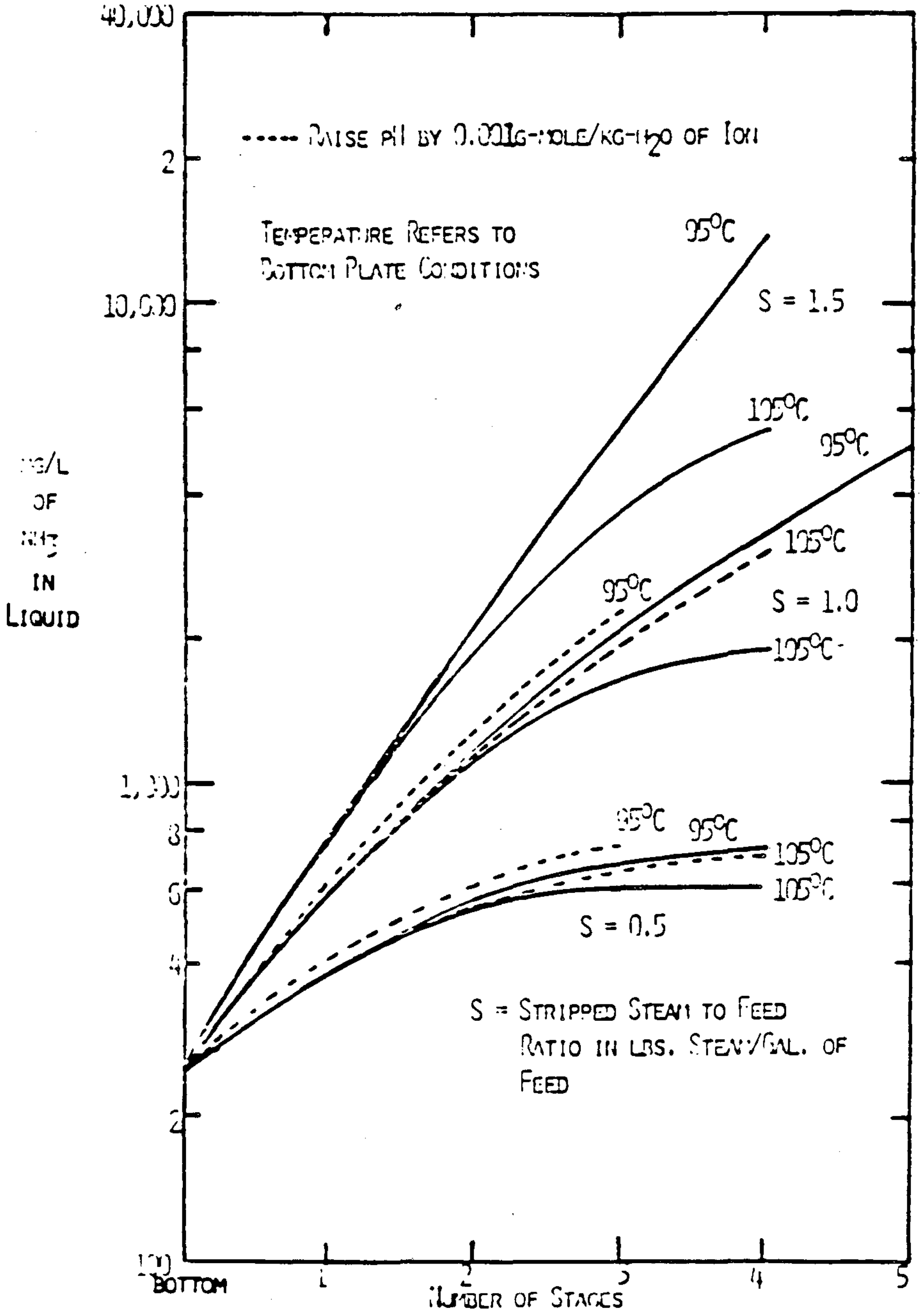

FIGURE 1.4: NH_3 CONCENTRATION PROFILES IN STRIPPER: Effects of pH, steam rate and temperature. Adjusting ion is non-volatile cation in VLE model.

Source: Verhoff and Choi, 1979

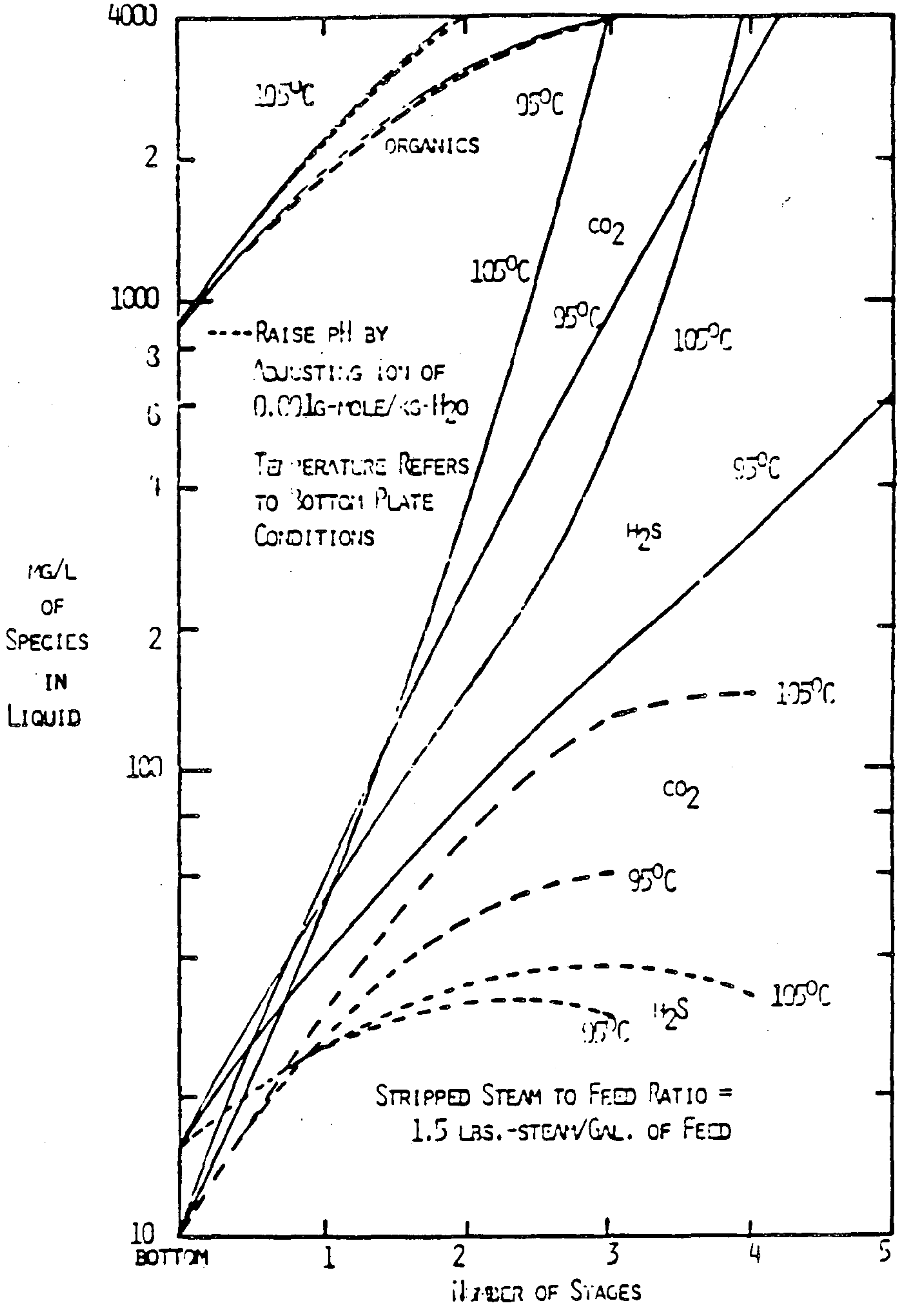

FIGURE 1.5: CO_2 AND H_2S CONCENTRATION PROFILES IN STRIPPER: Effects of pH and temperature. Adjusting ion is non-volatile cation in VLE model.

Source: Verhoff and Choi, 1979

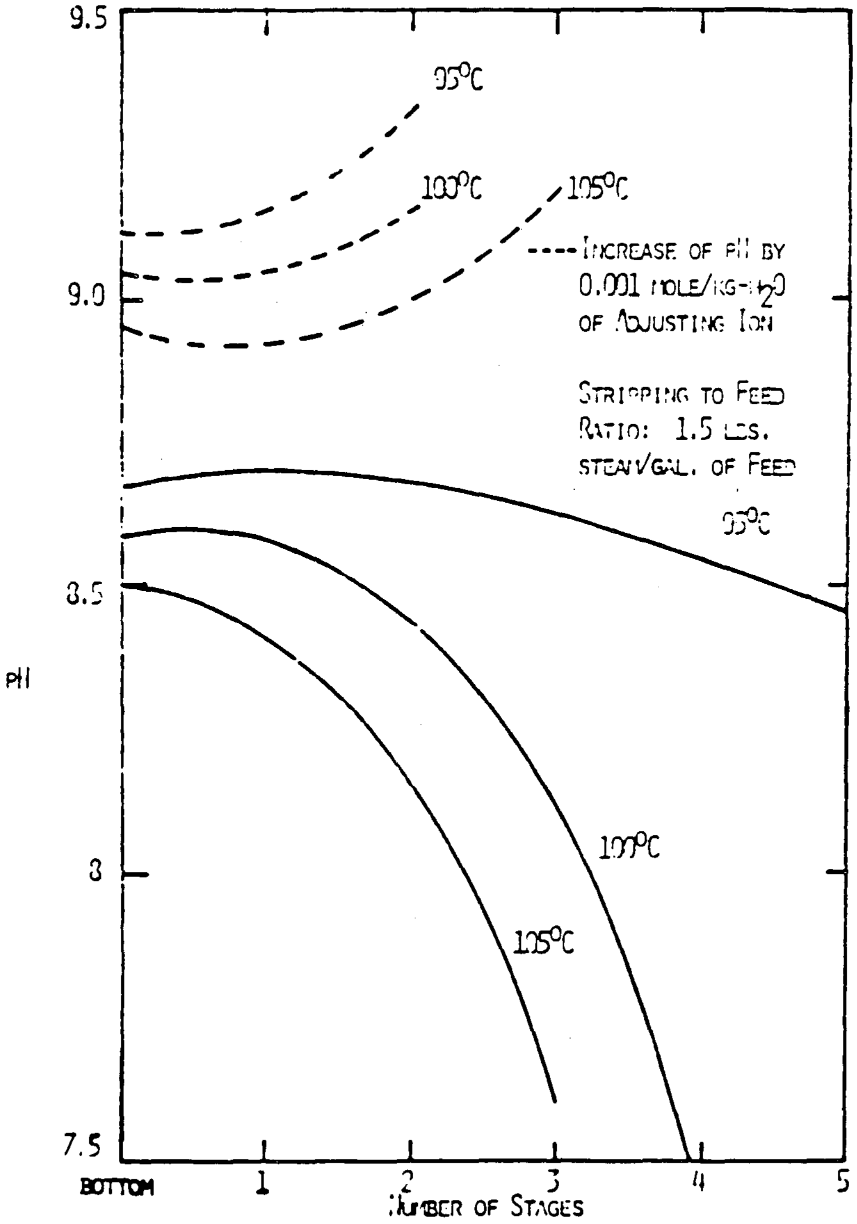

FIGURE 1.6: pH PROFILES IN STRIPPER: Effects of added non-volative cation and temperature. Adjusting ion is non-volatile cation in VLE model.

Source: Verhoff and Choi, 1979

contaminants, but it does not accomplish the oft-desired goal of isolating the NH_3 from the acid gases. Goldstein et. al. (1981) estimate that ammonia recovery is economically desirable for feedwater ammonia concentrations in excess of 1% (w/w), for water flows between 250 and 500 gpm. Two developed processes for isolating NH_3 from acid gases are described below.

1. PHOSAM-W PROCESS (Seufert et. al., 1979)

In this process all of the gases are first stripped from solution. The ammonia is then removed from this stream by selective absorption into an acid-containing solution which can be further processed.

Figure 1.7 is a flow sheet for the Phosam-W process of the U.S. Steel Corporation Engineers and Consultants Incorporated (UEC). Preheated feed enters the bottom section of the superstill and is steam stripped to remove all of the dissolved gases. Clean water exits the bottom of the tower. In the upper section of the superstill the gases are contacted with an aqueous phosphoric acid solution (Phosam solution). The NH_3 is absorbed out of the gas stream, and the acid gases exit the top of the still for further treatment. The ammonia-rich phosphoric acid solution is sent to a stripper in which the ammonia is removed from the solution. The lean solution is recycled back to the superstill. The ammonia leaves the top of this stripper as an aqueous solution. This solution is distilled in the ammonia fractionator to produce NH_3-free water at the bottom and salable anhydrous NH_3 at the top.

The feed to the superstill is preheated by the stripped water and

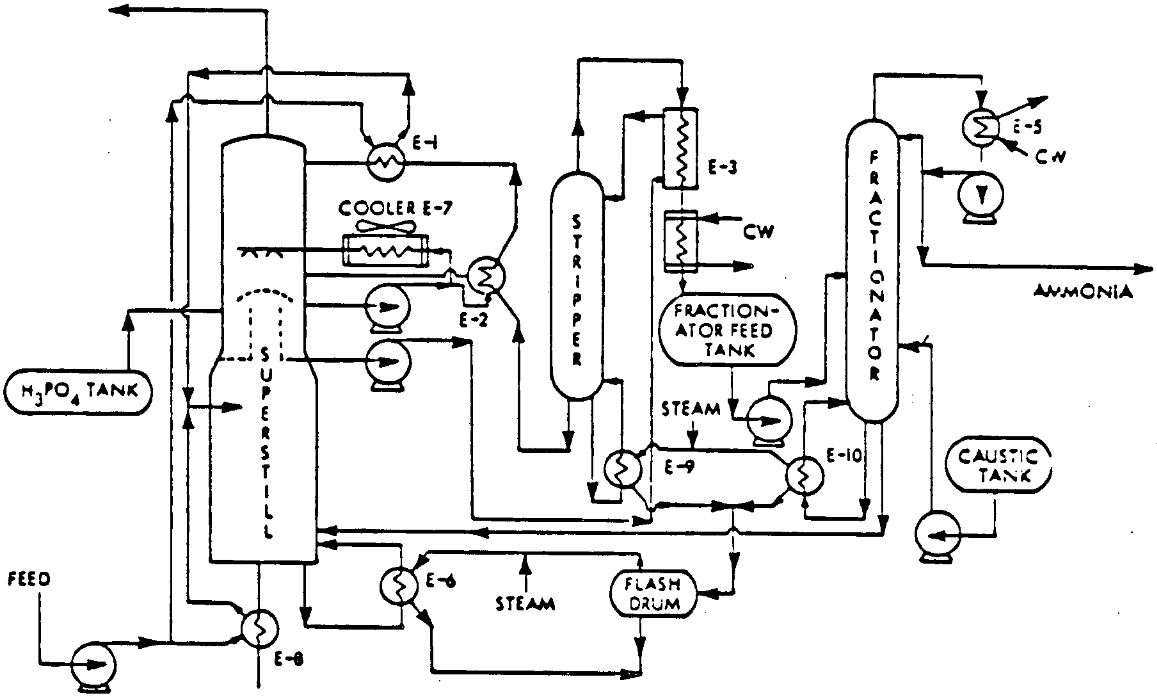

FIGURE 1.7: PHOSAM-W PROCESS.

Source: Water Purification Associates, 1977 the lean Phosam solution. The superstill is operated slightly above atmospheric pressure. A steam rate between 0.11 and 0.13 lb steam/lb water is required for effective ammonia removal. A portion of this steam is provided by flashing the bottoms of the NH_3 fractionator. The make-up steam requirement for the superstill is about 0.06 lb steam/lb feed.

The lean Phosam solution contains ammonia and phosphoric acid at a molar ratio slightly greater than one. In the rich solution this ratio is increased to slightly less than two. In this pH range the ammonia is readily absorbed. The NH_3 absorption is exothermic, so the Phosam solution must be cooled. The cooled solution is sprayed back into the lower part of the absorber section of the superstill. The rich Phosam solution is used to condense the exit vapors from the Phosam stripper partially and then is fed to the Phosam stripper.

The Phosam stripper is operated at elevated pressure and temperature. The required circulation rate of the Phosam solution depends on the feed rate of ammonia to the system, not the feed rate of water. For a Lurgi process-condensate water containing 17,000 ppm NH_3 and 33,000 ppm CO_2, 0.18 lb of 600 psig steam are required per lb of feed water. The regenerated Phosam solution is heat exchanged with the feed wastewater and returned to the superstill. The exit vapor from the Phosam stripper contains between 10 and 20% (w/w) NH_3 and is condensed by the rich Phosam solution plus additional cooling water. This aqua ammonia solution is fed to an NH_3 fractionator.

In the NH_3 fractionator anhydrous NH_3 is produced. This distillation is more favorable at low pressure. However, if the ammonia vapor is to be condensed by cooling water, the column must be operated at about 225 psia. The steam requirement per unit quantity of feed for this fractionation increases as the feed concentration increases. Of course the more concentrated the feed, the smaller the solution flow rate. For the UEC design, 0.05 lb steam at 600 psig are required per lb of feed wastewater. Caustic is added to prevent buildup of acid gases in the fractionator, which would contaminate the NH_3 product. The exit NH_3 vapor is 99.9% pure and is condensed with cooling water. The hot clean water leaving the bottom of the fractionator is used to provide part of the steam requirements to the superstill.

For the UEC design for the Lurgi process-condensate water (17,000 ppm NH_3) steam costs constitute about 60% of the total cost of the process. For a wastewater flow of 950,000 lb/hr, the total cost of the process is $\$7.4 \times 10^6$/yr, or about \$8/1000 gallons of water treated. At \$120/ton, credit for ammonia sale amounts to $\$7.65 \times 10^6$/yr. With the sale of ammonia this process operates at a very slight profit for this feed NH_3 concentration. Profitability would increase as NH_3 throughput increased. For waters containing significant amounts of H_2S, costs are slightly higher (Water Purification Associates, 1977).

An alternative to the Phosam-W process is to use dilute sulfuric acid to absorb NH_3 from the gas stream and thus produce an ammonium sulfate product. This product is less valuable than anhydrous NH_3. Since the absorption solution is not regenerated, a significant steam savings is recognized. However, this is compensated by the chemical costs to supply sulfuric acid, the value of which is not recovered in the sale of the ammonium sulfate fertilizer. Sulfuric acid is the major cost item for this process. For the same feed as that described for the Phosam-W process, this plant has a total cost of $\$13 \times 10^6$/yr and nets only \$7.35 × 10^6/yr from the sale of ammonium sulfate fertilizer. Clearly under most circumstances, the Phosam-W process is preferred.

2. ALL-DISTILLATION PROCESS

This process, known as the CLL (Chemie-Linde-Lurgi) process, effects separation of NH_3 from the acid gases in a first column, the deacidification column. Aqueous NH_3 leaves the bottom of this first column and is concentrated in a second column, the ammonia column.

Chemical additives may be used to keep the NH_3 from leaving with the stripped vapor. Addition of an acid will hold the NH_3 in solution, and consequently the acid gases will be readily stripped. The NH_3 stream must then be treated with alkali to raise the pH and liberate NH_3. The chemical costs will be prohibitive for this approach, and the increase in total dissolved salts in the exit water will be unacceptable. Another approach (Deschamps and Renault, 1969) is to add a non-volatile acid to the feed. This releases the acid gases. The ammonia is then liberated from the non-volatile acid by stripping at high temperature or low pressure. The non-volatile acid is then recycled. This process is not acceptable since it would require vaporization of all of the wastewater, which would be expensive.

The preferred way of holding all of the NH_3 in the liquid is to reflux clean water to the deacidification tower. One design (Water Purification Associates, 1977) for this column requires 24 actual trays, 2 below the feed. The steam rate is 0.08 lb steam/lb feed, and the wash rate is 1.3 lb water wash/lb feed. This column is best operated at high pressure (temperature) as suggested by Chevron (Klett, 1972). The aqueous ammonia leaving the bottom of the column is somewhat below half of the feed concentration. To produce 30% NH_3 in the second column 22 trays are required, 4 above the feed. The steam rate is 0.13 lb/lb feed to the column. In terms of the feed to the process, this is 0.29 lb steam/lb feed water. This process is less energy efficient and more expensive than the Phosam-W process.

Total costs for the treatment of wastewaters from solid-fuel conversion processes, including organics removal etc., are estimated to be between $20 and $50/1000 gal (King et. al., 1981). Costs for isolating NH_3 from the acid gases are a large portion of this cost. It is apparent that any process modification or new process development which can reduce the cost of NH_3 isolation would be welcomed.

G. BASIS FOR PROPOSED PROCESS

As stated earlier, the presence of NH_3 in solution depresses the effective volatility of the acid gases and vice versa. In the stripping of a CO_2/NH_3-containing wastewater, as the more volatile CO_2 is stripped the pH rises and more CO_2 ionizes. CO_2 volatility decreases due to both its lower total concentration and its increased ionization. CO_2 stripping continues and the pH rises until NH_3 volatility becomes comparable to CO_2 volatility. The two gases are then stripped together and the pH levels off. The CO_2 is difficult to remove due to its high degree of ionization and NH_3 is hard to remove due to its low Henry's law constant as well as its significant degree of ionization. This is the source of the high energy requirements to clean these wastewaters.

1. GENERAL PRINCIPLE

Steam requirements for CO_2 removal would be lowered by stripping at a low pH. To keep the pH low, ammonia removal must be simultaneous with CO_2 removal. This requires the inclusion of a second, independent process for the removal of NH_3. The removal of the two species by the two different separation processes should be carried out at the same time so that the processes balance and the pH is maintained within the desired bounds. The combination of these two processes could then increase CO_2 volatility and also isolate NH_3 from the acid gases.

The concept can be reversed and the NH_3 stripped and the acid gases removed by the second separation process. This is a less likely implementation since the acid gases are generally more volatile than NH_3. Further, it may be difficult to define a second process that could effectively remove both CO_2 and H_2S.

The proposed process is to combine two simultaneous separation processes, one for the removal of acid gases, the other for the removal of NH_3.

2. STRIPPING PLUS LIQUID-MEMBRANE EXTRACTION

Li, Cahn and Minday (Cahn et. al., 1978; Li and Cahn, 1975) originally proposed the idea of two simultaneous separation processes. They described a process which combines liquid-membrane extraction with steam stripping, a process they call "extripping". One implementation of their idea is shown in Figure 1.8 and is discussed in detail below. They also suggest the possibility of combining either distillation, extraction, ion exchange or adsorption together with stripping.

For an H_2S/NH_3 wastewater, Cahn et. al. (1978) propose extracting

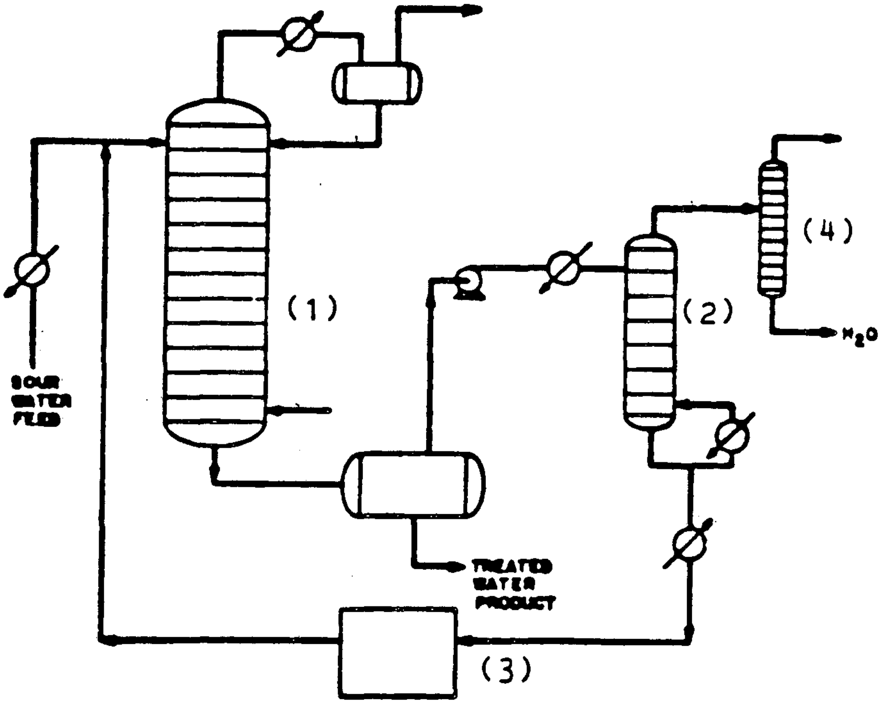

FIGURE 1.8: EXTRIPPING PROCESS.

Source: Li and Cahn, 1975

NH_3 into the liquid membrane while simultaneously stripping the H_2S. The liquid-membrane system consists of drops of water-in-oil emulsion. An aqueous internal phase containing a water-soluble acid is emulsified with an external oil phase, composed of 12 wt% Lubrizol and 88 wt% Solvent 100 Neutral (isoparaffin, Exxon). Lubrizol is a styrene-maleic anhydride co-polymer with 95% of the groups esterified with C_{10}-C_{18} alcohols. It serves as both a surfactant and a stabilizer in the membrane phase. Molecular species are soluble in the external phase but ionic species are not. Transfer agents, including ion exchangers, may be used to facilitate permeability into the membrane (Downs and Li, 1981).

When the liquid-membrane system is contacted with an aqueous H_2S/NH_3 solution, molecular H_2S and NH_3 will permeate through the membrane and into the internal acid solution. The driving force for this transfer is the difference in activity of the molecular species in the wastewater and in the internal acid solution. At the low pH of the internal solution, the H_2S will remain in molecular form, but the NH_3 will ionize to NH_4^+. Thus the driving force for H_2S permeation will quickly approach zero, while that for NH_3 will remain high. However, in a liquid-membrane process with no simultaneous stripping, as more ammonia is removed from the solution by permeation, the pH of the wastewater will drop, ammonia will ionize, and the driving force for NH_3 permeation will fall. This parallels the problem in stripping in which, as a species is removed from solution, its extent of ionization increases and ease of stripping decreases. For the permeation case, if H_2S is stripped from solution simultaneously, the pH will be maintained at a desirable level.

In experiments designed to test this concept Cahn et. al. (1978) examined the removal of NH_3 and H_2S from ammonium sulfide solutions at 85°C. In one experiment stripping the solution for 20 minutes removed 40% of the NH_3 and 90% of the H_2S from the solution. Contacting the solution with the liquid-membrane containing a sulfuric acid internal phase resulted in 50% NH_3 removal and 50% H_2S removal after 20 minutes. However when the two operations were carried out simultaneously solute removal was much more effective. After 10 minutes 92.5% of the ammonia and greater than 95% of the H_2S were removed from the solution.

For the regenerable acid process shown in Figure 1.8 the internal acid phase of the liquid membrane is a 30% solution of the monoammonium salt of succinic acid in water. The sour water is combined with the liquid membrane and sent to a steam stripper (1), operated at 185°F. Steam requirements are projected to be as low as 0.03 lb steam/lb water (Li and Cahn, 1975). An NH_3-free vapor leaves the top of the column and may be sent to a Claus plant for sulfur recovery. The clean water is then separated from the liquid-membrane system. The liquid-membrane system, which now contains mostly the diammonium salt of succinic acid, is sent to a regeneration column (2). The column operates at 400°F and 250 psig and requires from 0.06 to 0.12 lb steam/lb feed water to release the ammonia and convert the internal phase back to the monoammonium salt of succinic acid. In the regenerator, as much as 60% of the emulsion can break and so it is necessary to send the regenerated solution to an emulsion make-up and maintenance system (3). The NH_3/H_2O vapor leaving the top of the column is sent to a conventional ammonia fractionation column (4) to produce anhydrous NH_3.

This process has some characteristics in common with the Phosam-W process. The circulation rates of both the liquid-membrane system and the Phosam solution depend on the ammonia feed rate, not the water feed rate. In both processes the NH_3 enters an acid solution already containing some NH_3. The solution oscillates between a high and a low ammonia content. One distinct advantage of the extripping process over the Phosam-W process is the savings in steam in the sour water stripper. In the Phosam-W process all of the gases are first stripped and then the vapors are treated. In the extripping process a significant savings in steam for removing H_2S results from the simultaneous removal of NH_3 in the stripper.

However, there are some problems in the implementation of the extripping process as described by Cahn et. al. (1978; Li and Cahn, 1975). At the present time no liquid-membrane extraction processes have been commercialized. The technology of breaking and reforming the emulsion is complex and may cause difficulties on a commercial scale. Leakage of the internal solution into the feed water can also be a problem.

A second implementation of the liquid-membrane extripping process is to use a non-regenerable internal acid phase, such as sulfuric acid. In this case no regeneration is necessary. The spent emulsion is broken, the ammonium sulfate released and a new emulsion is formed with fresh sulfuric acid. As with the similar alternative to the Phosam-W process, this implementation is less desirable because of consumption of sulfuric acid and formation of ammonium sulfate rather than anhydrous NH_3 as the product.

H. PROPOSED PROCESS

In view of the problems outlined above that exist for the liquid-membrane extraction technique, the possibility of using one of the other separation techniques was investigated. In the current work, the possibility of combining solvent extraction with simultaneous steam stripping is pursued. This process could offer all of the advantages of the extripping process, yet it also involves more conventional technology. The key to this process is to identify a solvent for the selective extraction of either NH_3 or the acid gases from wastewaters.

Figure 1.9 shows a proposed implementation of the combined stripping/solvent extraction process. Three unit operations are involved: wastewater stripping, solvent extraction, and distillative solvent regeneration. As shown the process is designed to strip the acid gases and extract NH_3.

When the wastewater enters the acid-gas stripper a portion of the volatile acid gases is removed, raising the aqueous phase pH. (This assumes that the ratio of acid gases to ammonia is such that the NH_3 is the least volatile species, which is usually the case). This water is then sent to the solvent extraction part of the process, in which NH_3 is extracted from the wastewater. As will be seen in Chapter 4, a high aqueous-phase pH favors NH_3 extraction. Once some of the NH_3 is extracted, the pH is lowered. This aqueous stream is separated from the solvent and returned to the acid-gas stripper. This transfer between stripping and extraction may be carried out as many times as needed. The net effect is the stripping of the acid gases at a low pH, which enhances their volatility and lowers steam requirements for their removal.

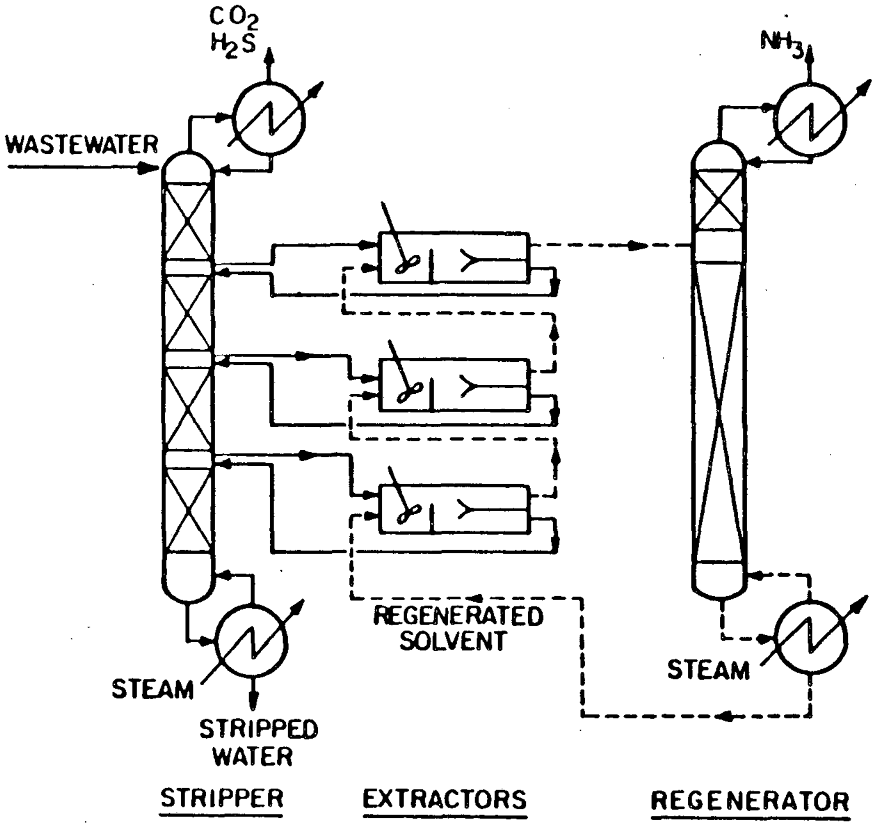

FIGURE 1.9: PROPOSED PROCESS: Simultaneous Solvent Extraction and Steam Stripping.

In the solvent extraction part of the process, the aqueous phase and the solvent phase are contacted countercurrently, which improves the NH_3 removal efficiency. The solvent loaded with NH_3 is sent to the solvent regenerator, in which the NH_3 is removed. The NH_3-free solvent is then returned to the solvent extraction part of the process.

In the solvent regenerator, NH_3 is removed from the solvent by lowering the pressure and/or by raising the temperature. Alternatively, a mass-separating agent can be used to regenerate the solvent.

I. SOLVENT EXTRACTION

In solvent extraction, two immiscible phases are contacted and solutes distribute between them, equilibrating between the two phases. If the standard states are the same, the activity of a solute in each phase (<u>1</u> and <u>2</u>) is the same:

$$x_1 \gamma_1 = x_2 \gamma_2 \tag{1.17}$$

A mole-fraction-based distribution coefficient may be defined as:

$$K_x = \frac{x_1}{x_2} = \frac{\gamma_2}{\gamma_1} \tag{1.18}$$

Here the solvent phase is <u>1</u> and the aqueous phase is <u>2</u>.

Thus the distribution of the solute between the two phases occurs due to solution non-idealities in at least one of the phases. For design purposes, K_c, based on solute concentrations in the two phases, or K_d, based on solute weight fractions in the two phases, is usually more useful. After equilibration, the solvent is referred to as the extract and the aqueous phase is referred to as the raffinate.

If the solute to be removed is polar, then a polar solvent will generally be required, so that γ_1 will be low. This can lead to the use of a solvent that associates or complexes with the solute (Kiezyk and Mackay, 1971; King, 1980). Use of a polar solvent can lead to several problems. First, a polar solvent will tend to have a high solubility in the aqueous phase. This presents economic and environmental problems and would be a particular concern in wastewater treatment (Kiezyk and Mackay, 1971; Grinstead et. al., 1969). In wastewater treatment a raffinate clean-up step is usually required. One solution to this problem is to add a substantial amount of organic weighting to the solvent molecule containing the desired functional group. Second, an amphiphilic solvent will have some tendency to emulsify with the aqueous phase. This could result in additional solvent losses, slower phase-separation rates and lower overall throughputs (Grinstead et. al., 1969). Finally, it should be pointed out that a high value of K is desirable. For efficient solute removal, a general criterion is for K times the flow ratio of solvent to water to be greater than about 1.4 (King, 1980).

In the proposed process, effective solute removal will shift the pH into the range of easier removal of the other solute by stripping. However if the solvent interacts too strongly with the solute, so that K is too large, then regeneration of the solvent will be difficult if not impossible, and the energy savings gained in the wastewater stripper will be negated by energy requirements in the solvent regenerator. Thus K should fall within the range in which it is high enough to give substantial extraction with a reasonable phase ratio, but is low enough to enable economical regeneration of the solvent.

The solvent to be used in the proposed combined stripping/solvent extraction process should meet several requirements. It should have reasonable values of physical properties such as viscosity and density. It should have a sufficiently high K for the solute of interest (either NH_3 or the acid gases), yet should be regenerable by a mass-or-energy separating agent. The solute released from the solvent should be in a salable form. The solvent should be stable under process conditions, exhibit good phase separation properties versus the aqueous phase and have a low solubility in the aqueous phases present in the process.

J. GOALS AND APPROACH

The goals of the current work were to identify potential solvents for the proposed extraction/stripping process, to study experimentally the factors affecting the solvent properties, to assess the overall feasibility of the process and to suggest operating conditions for the process.

Potential solvents will be identified based on the results of batch-extraction experiments. For the more desirable solvents additional experiments will then be performed to quantify the distribution coefficients (K_c), solvent solubility losses to the aqueous phase and solvent-regeneration properties. A qualitative assessment of phase-separation properties will also be made. Finally this information will be used in some preliminary design calculations.

Chapter 2 describes the analytical methods used in this work and Chapter 3 discusses the experimental procedures followed.

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CHAPTER 2

ANALYTICAL METHODS

A. AQUEOUS NH_3, CO_2, AND H_2S CONCENTRATION AND pH MEASUREMENTS

Aqueous concentrations of NH_3, CO_2, and H_2S, were determined with specific-ion and specific-gas electrodes. The ammonia electrode was an Orion Model 95-10 and the carbon dioxide electrode was an Orion Model 95-02 (Orion Research Incorporated). The hydrogen sulfide electrode was an Orion Model 94-16 used in conjunction with an Orion Model 90-02 double-junction reference electrode.

Electrode responses were measured with a Corning Model 12 pH meter and later with an Orion Model 701A digital pH/mV meter. A five-channel electrode switch (Orion Model 605) was used with the latter meter. This allowed for calibrating each electrode separately and for switching between electrodes without having to disconnect the electrode already in use.

Operating characteristics of the electrodes were similar in that in all three cases a buffer solution was added to the sample both to adjust the ionic strength of the solution and to convert the species in solution into the form sensed by the electrode.

1. AMMONIA ELECTRODE

This is a gas-sensing electrode. In this case, the samples and standards were first adjusted to pH 11 or above by adding 10 M NaOH. Generally, 1 ml of this solution was added per 100 ml of sample. This converted all of the ammonia in solution to the NH_3 form, which is the form sensed by the electrode.

A schematic drawing of the ammonia electrode is presented as Figure 2.1. The electrode has a hydrophobic gas-permeable membrane separating the sample from the electrode internal filling solution (Orion # 95-10-02). NH_3 diffuses through the membrane until its activity is equal on both sides of the membrane. The internal filling solution contains ammonium chloride at a sufficiently high level that its ammonium ion activity can be considered fixed. Thus, as NH_3 diffuses into the internal solution, the hydroxide ion activity increases proportionately:

$$a_{OH^-} = a_{NH_3} \times K_b / a_{NH_4^+} \tag{2.1}$$

$$a_{NH_4^+} = \text{constant}$$

where a represents the activity of the species.

Since the electrode sensing element is a pH electrode, the potential difference (E) between it and the internal reference element (E_o) is related to the hydroxide ion concentration by the Nernst equation:

$$E = E_o + S \times \log (a_{OH^-}) \tag{2.2}$$

where S is the electrode slope and is given theoretically by:

$$S = 2.303\ RT/ZF \tag{2.3}$$

and R is the universal gas constant, T is the temperature, Z is the

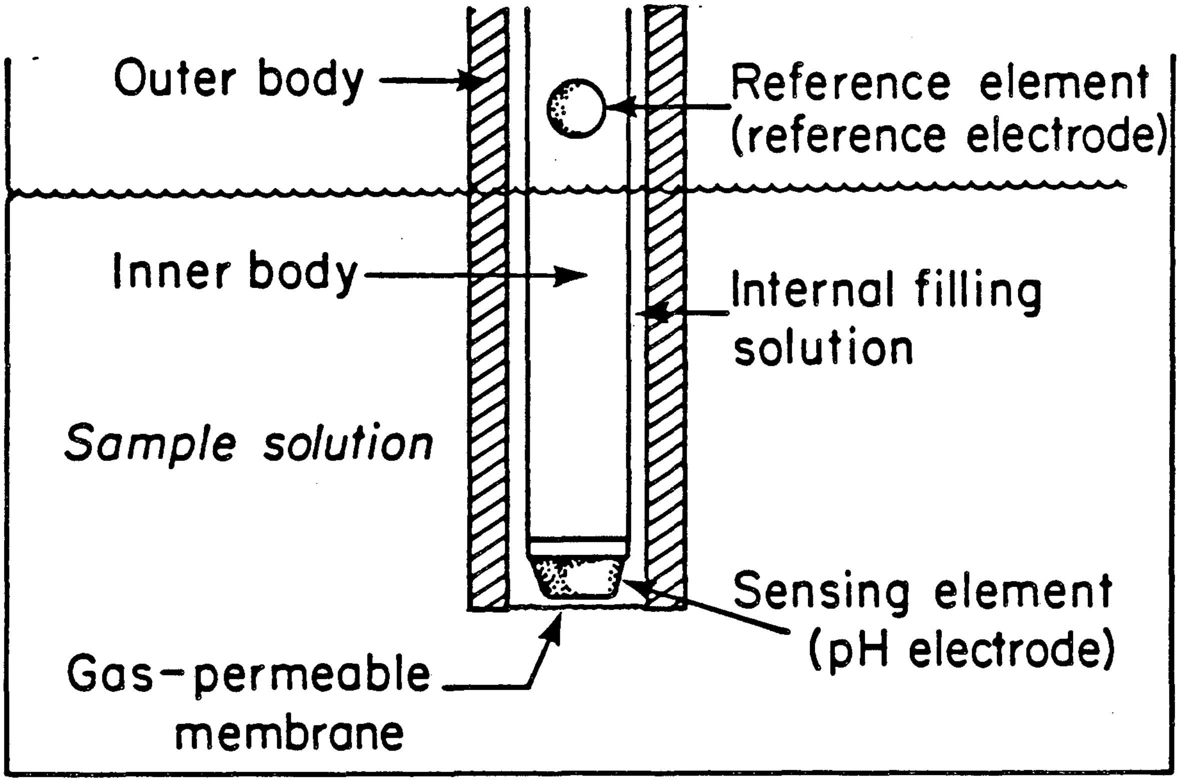

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FIGURE 2.1: GAS-SENSING ELECTRODE.

charge on the ion, and F is Faraday's constant. E_o is determined by the internal reference element, which responds to the fixed level of chloride in the internal filling solution. Combining Equations 2.1 and 2.2 yields:

$$E = E_o' + S \times \log (a_{NH_3}) \qquad (2.4)$$

Therefore, the electrode response to ammonia is also Nernstian. Since ammonia activity is equal on both sides of the membrane, the electrode potential is also Nernstian in ammonia activity in the sample solution.

Electrode slope is determined by the potential change ($E_2 - E_1$) caused by a factor of 10 increase in ammonia activity.

$$E_2 - E_1 = S \times \log (10) = S \qquad (2.5)$$

Values of S range from - 56 to - 58 mV at room temperature.

Direct measurements of sample concentrations can be made by first preparing a calibration curve of electrode potential versus standard solution concentrations. Ammonium chloride solution is used as the standard. With the calibration curve, electrode potential measurements for samples can be converted into sample concentrations. Standards and samples should be at the same temperature and have about the same ionic strength. This keeps activity coefficients nearly constant, and allows replacing activities with concentrations.

A more convenient method for measuring concentrations of unknown solutions is the known addition method. In this procedure a standard of known concentration is added to the sample solution. From the change in electrode potential caused by this addition, the sample concentration can be calculated. If the standard solution does not change the concentration of the sample too dramatically, then activity ratios may be replaced by concentration ratios.

Letting:

C_0 = concentration of sample

V_0 = sample volume

V_b = volume of NaOH or buffer added

V_1 = volume after NaOH or buffer addition ($V_0 + V_b$)

C_1 = concentration after NaOH or buffer added (C_0V_0/V_1)

C_2 = concentration of standard

V_2 = volume of standard added

V = final volume ($V_1 + V_2$)

C = final concentration [$(C_2V_2 + C_0V_0)/V$]

E = potential reading after standard addition

E_1 = potential reading before standard addition

then:

$$\Delta E = E - E_1 = S \times \log C/C_1 \tag{2.6}$$

or:

$$C/C_1 = 10^{\Delta E/S} \equiv K \tag{2.7}$$

Rearranging to solve for C_0 yields:

$$C_0 = \frac{C_2V_2}{V_0(K \times \frac{V}{V_1} - 1)} \tag{2.8}$$

The known addition method was used extensively in this work. Generally, V_2 was 10% of V_0, and for accurate measurements ΔE was between about 10 and 40. This corresponds to C_2 about 10 to 50 times greater than C_0. Samples were usually diluted so that available standard solutions could be used. Occasionally, sample concentrations were checked by the direct measurement method.

A magnetic stirrer was used to assure adequate mixing of the solution, and solutions were kept covered during measurements. Sample requirements were fairly non-restrictive. Total ammonia concentration should be in the range of 6×10^{-5} $\underline{M}$ to 1 $\underline{M}$. This allows for rapid electrode response and yet keeps the rate of ammonia loss from solution low. Only volatile amines interfere with electrode response. However, solutions containing surfactants wet the membrane and cause it to discolor and to deteriorate. This results in leakage of the filling solution into the sample and produces invalid readings.

2. CARBON DIOXIDE ELECTRODE

This is also a gas-sensing electrode, and its operation is similar to that of the NH_3 electrode. The buffer solution was prepared by adding 294 grams of sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) to distilled water to make one liter of solution. Concentrated HCl was then added to acidify the solution to pH 4.5. Generally, 5 ml of this solution were added to 50 ml of sample or standard solution. This buffer lowered the pH of samples and standards to pH 4.8 to 5.2 and adjusted the total level of dissolved species in solution to 0.4 $\underline{M}$. Under these conditions all of the carbon dioxide in solution was converted to the CO_2 form, which is the form sensed by the electrode.

For this electrode the internal filling solution (Orion # 95-02-02) contains a high level of sodium bicarbonate, so that the bicarbonate ion activity can be considered fixed. As CO_2 diffuses from the sample through the membrane and into the internal solution, the hydrogen ion activity of the internal filling solution increases proportionately. In this case Equation 2.1 becomes:

$$a_{H^+} = a_{CO_2} \times K_a / a_{HCO_3^-} \tag{2.9}$$

$$a_{HCO_3^-} = \text{constant}$$

The activity of the hydrogen ion in the internal solution is measured by the sensing element (pH electrode). The electrode response is given by:

$$E = E_o + S \times \log (a_{H^+}) \tag{2.10}$$

or, in terms of CO_2 activity:

$$E = E_o' + S \times \log (a_{CO_2}) \tag{2.11}$$

Here S is between + 55 and + 57 mV at room temperature.

The known addition method was also used for CO_2 measurements. Sodium bicarbonate solutions were used as standards.

Solutions were mixed by swirling rather than by magnetic stirring, and were kept covered during measurements. This minimized CO_2 loss from solution. Again, sample requirements were simple. Total CO_2 concentration should be between 1×10^{-4} $\underline{M}$ and 2×10^{-2} $\underline{M}$. Volatile weak acids are the only potential interfering species. However when a series of measurements was made it was necessary to rewet the sensing element continually by unscrewing the cap of the electrode and gently pumping the inner body up and down several times. If the space between the sensing element and the membrane became dry, electrode response characteristics deteriorated.

3. SULFIDE ELECTRODE

This electrode differs some from the NH_3 and CO_2 electrodes in that it senses ions in solution rather than dissolved gases. The buffer solution (SAOB II) consisted of 200 ml of 10 $\underline{M}$ NaOH, 35 grams ascorbic acid and 67 grams disodium EDTA, diluted to one liter with distilled water. Samples and standards were diluted 1:1 with this buffer. This buffer solution prevented oxidation of sulfide ions to elemental sulfur, adjusted the ionic strength and raised the pH so that all of the sulfur (i.e. H_2S, HS^-, and S^{2-}) in solution existed as S^{2-}, the form sensed by the electrode.

The sulfide electrode, which can also be used as a silver electrode, consists of a solid silver sulfide membrane bonded into an epoxy body (see Figure 2.2). Silver sulfide is extremely insoluble, so these two ions are never present in solution together. Thus when the electrode is placed in a solution containing sulfide ions, silver ions migrate within the membrane, setting up a potential (E) that depends on the activity of sulfide ions in the solution. The reference potential (E_o) is established by a separate reference electrode. The potential

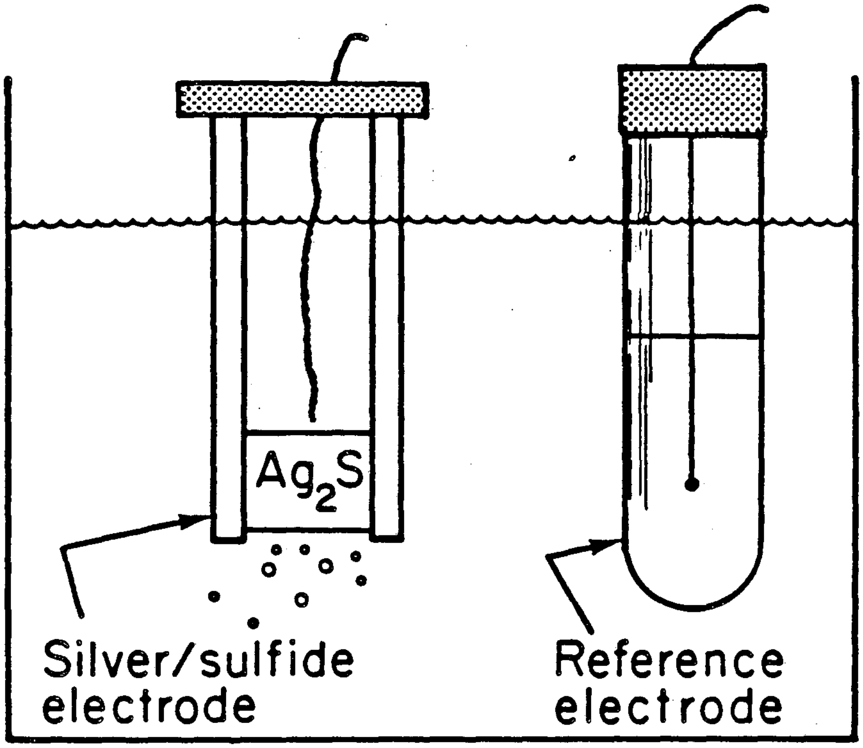

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FIGURE 2.2: SULFIDE ION-SENSING ELECTRODE.

difference is related to the activity of the sulfide ion as:

$$E = E_o + S \times (\log a_{S^{2-}}) \qquad (2.12)$$

Here, S is about -28 mV at room temperature. The SAOB II solution keeps the ionic strength and hence the activity coefficients constant, so that activity is proportional to concentration.

Direct measurements and the known addition method were both occasionally used to measure hydrogen sulfide concentrations. The standard solution was prepared from a saturated sodium sulfide solution. The exact concentration of this standard was determined by titration with a Pb standard. This titration method was also used to measure sample concentrations.

In the titration method, a lead titrant, either $Pb(ClO_4)_2$ or $Pb(NO_3)_2$, about 10 to 20 times as concentrated as the sample is prepared. Magnetic stirring is used throughout the titration. As the titrant is added to the sample (previously diluted 1:1 with SAOB II) PbS precipitates out of solution, and the mV reading of the electrode becomes more positive. A sharp endpoint is reached when the lead added is stoichiometrically equivalent to the sulfide initially present. The sample concentration, before dilution with SAOB II, is:

$$C_s = (V_t/V_s)C_t \qquad (2.13)$$

where:

C_s, V_s = concentration, volume of sample

C_t = concentration of titrant

V_t = endpoint titrant volume.

Sample concentrations for this electrode should be above 10^{-5} M. Since sulfur in solution is converted to the non-volatile sulfide ion, loss of H_2S to the atmosphere is not a problem, even at high concentrations. In addition, it was necessary to protect the SAOB II from oxidation by air.

Orion reports reproducibilities of ±2% for these electrodes. However, in this work somewhat larger variations were found, ranging up to ± 10% for very dilute solutions. Thus, the average concentration of several replicate samples is reported. Additional information on these electrodes is available in the Orion Research Inc. Instruction Manuals and in their Analytical Methods Guide.

4. pH ELECTRODE

The pH of aqueous samples was measured with either a Ag/AgCl pH electrode and a standard reference electrode or a semi-micro combination pH electrode (Orion model 91-03). The latter allowed measurements in small sample volumes. Experimentally, it was found that pH measurements drifted when the ionic strength of the sample was low or when CO_2 was being lost to the atmosphere from the solution. When accurate pH values were required, as in the data used to develop the liquid-liquid equilibria models, ions were added to the solutions to stabilize the pH. For instance, in this case, the feed solution for the extractions consisted of NH_4OH, plus 0.01 M to 0.02 M $(NH_4)_2HPO_4$. Reproducible pH values were thereby obtained. Without the ammonium phosphate present, pH measurements were erratic.

To avoid increases in pH due to CO_2 loss, sample pH was measured as rapidly as possible. For instance, if the sample was a raffinate from an extraction, organic and aqueous phases were centrifuged together, the aqueous phase withdrawn, and the pH measured immediately. This permitted measurement of the equilibrium pH of the raffinate rather than some higher value resulting from CO_2 loss from the solution.

B. ORGANIC-PHASE AMMONIA-CONCENTRATION MEASUREMENTS

Generally, the concentration of ammonia in an organic phase was calculated from a mass balance. When a liquid cation exchanger was used to extract ammonia, the organic phase ammonia concentration was occasionally verified by a back extraction with approximately 4 M H_2SO_4. This back extraction of ammonia out of the organic phase was quantitative and occurred because the distribution coefficient for ammonia into the organic phase was essentially zero at the low pH of 4 M sulfuric acid. The organic-to-aqueous volumetric phase ratio for these back extractions was 1:2. The ammonia electrode was used to measure the ammonia concentration in the sulfuric acid raffinate. To do this the sulfuric acid raffinate had to be diluted, usually either 1/100 or 1/50. Even with these dilution factors it was necessary to add more than the normal amount of 10 M NaOH to the samples in order to raise the pH into the required range for proper operation of the ammonia electrode. The pH of a sample after addition of the 10 M NaOH was checked with pH paper. Organic-phase ammonia concentrations measured in this way agreed very well with those calculated by mass balances.

C. AQUEOUS-PHASE PHOSPHORUS-CONCENTRATION MEASUREMENTS

In order to determine the distribution of di-2-ethylhexyl phosphoric acid (D2EHPA) and its salts between an organic and an aqueous phase, the phosphorus content of the aqueous phase had to be determined. These measurements were performed by the Micro-Analytical Laboratory in the College of Chemistry at the University of California, Berkeley.

The method followed was that described by Pregl and Grant (1951). The organic phosphorus compound in the aqueous phase is destroyed by boiling with a mixture of nitric and sulfuric acids, which oxidize the compound to orthophosphoric acid (H_3PO_4). This acid is then precipitated quantitatively with the Lorenz ammonium molybdate reagent and weighed as ammonium phosphomolybdate. Because the precipitate weighed is 63 times as heavy as the phosphorus which it contains, the error in this method can be rather low. This gravimetric factor is empirical and holds only for the conditions specified.

The results of these tests were reported as mg of elemental phosphorus per ml of solution. These were converted to moles/liter by dividing by the molecular weight of phosphorus (30.9). This was equal to the molar concentration of all phosphorus-containing compounds in the solution, assuming that none contained more than one phosphorus atom. When all of the phosphorus-containing compounds were assumed to be D2EHPA (MW = 322.4), then:

$$\text{ppm, D2EHPA} = \text{mg P/ml} \times 1000 \times \frac{322.4}{30.9} \qquad (2.14)$$

Samples contained between 0.005 mg P/ml and 0.5 mg P/ml. The lower limit of detection was 0.001 mg P/ml. At the lower concentrations, reproducibilities were about ± 20%. At the higher concentrations, reproducibility was better.

The applicability of this method to the determination of D2EHPA in aqueous solutions was ascertained by measuring the solubility of D2EHPA into Milli-Q® water (water purified by the Milli-Q® Water Purification System). The D2EHPA had previously been purified by the copper-salt-precipitation method (See Chapter 3, section B). The D2EHPA and water were well mixed, and then the aqueous phase was removed and centrifuged six times, including once with an ultracentrifuge. Between centrifugations, the aqueous phase was transferred to a fresh centrifuge tube. The measured solubility of D2EHPA was 93 ppm, which compares well with the reported value of 100 ppm (Mobil Chemical Company, 1981). Other researchers have used this method to determine concentrations of tri-octylphosphine oxide and associated compounds in both aqueous and organic solutions (Bixby and King, 1983).

D. ORGANIC-PHASE WATER-CONCENTRATION MEASUREMENTS

The water content of an organic phase was determined by the standard Karl Fischer analysis. The indicator endpoint was used to signal the end of the titration.

E. ORGANIC-PHASE PHENOL-CONCENTRATION MEASUREMENTS

The amount of phenol extracted from aqueous solutions into various organic phases was determined by gas chromatographic analyses of the organic phases. The gas chromatograph was a Varian 3700 equipped with a flame ionization detector. A 20 inch by 1/8 inch stainless steel column packed with 100 - 200 mesh 5% OV-101 HP Chrom G was used. The column temperature was 70°C, the injector temperature 240°C, and the detector temperature 320°C. After the phenol eluted, the column temperature was programmed to increase to 300°C at 25°C/min in order to remove heavy components that had deposited onto the column from the organic solvent.

F. REFERENCES

Bixby, J. L.; King, C. J. "The Regeneration of Tri-octyl Phosphine Oxide Solutions Used to Extract Phenol From Water", Lawrence Berkeley Laboratory, Aug. 1983, LBL-16577.

Mobil Chemical Company, Industrial Chemicals Group, Phosphorus Division, Richmond, VA, 1981, Bulletin #081201.

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CHAPTER 3

EXPERIMENTAL PROCEDURES AND APPARATUS

A. REAGENTS

The reagents used in this work and their sources are listed in Table 3.1. All reagents were used as received, with the exception of di-2-ethylhexyl phosphoric acid (D2EHPA).

B. D2EHPA PURIFICATION PROCEDURE

Commerical D2EHPA typically contains several percent of impurities such as mono-2-ethylhexyl phosphoric acid, pyrophosphates, phosphoric acid and 2-ethyl hexanol. In addition, some metallic impurities are present. Fe(III) is the most common of these and is responsible for the amber color of the as-received product (Partridge and Jensen, 1969).

In an actual process most of these impurities would be washed out of the D2EHPA after several circulations. In order to study the properties of D2EHPA as it would exist in an actual process, much of the D2EHPA used in this work was purified before use. The method followed was originally proposed by Partridge and Jensen (1969) and further developed by McDowell, Perdue and Case (1976).

In this procedure, an organic phase containing 0.5 M D2EHPA in toluene was contacted with half its volume of a saturated sodium sulfate solution containing NaOH. The NaOH was present in an amount 10% in stoichiometric excess of the D2EHPA. This converted all of the D2EHPA to the sodium form, which can effectively extract copper. McDowell et. al. (1976) state that, if too much NaOH is added, precipitation of basic

TABLE 3.1

SOURCE AND DESCRIPTION OF CHEMICALS USED

COMPOUND	SUPPLIER	DESCRIPTION
Adogen 283	Ashland Chemicals	2° amine, C_{13} branched
Adogen 364	Ashland Chemicals	3° amine, C_8-C_{10} straight-chain
Alamine 336	General Mills	3° amine, C_8-C_{10} straight-chain
Alfol 10	Conoco Chemical	1-decanol
Amberlite LA-2	Rohm and Haas	2° amine, highly branched
BAMBP	Frinton Laboratories	4-sec-butyl-2-(α-methyl benzyl) phenol
Chevron 25	Chevron Chemical Co.	C_8-C_9 alkylated aromatics
Decalin	Aldrich	Decahydronaphthalene, reagent grade
Di-2-ethyl hexyl phosphoric acid (D2EHPA)	Mobil Chemical Co.	technical grade
1-Decanoic acid	Eastman Organic Chemicals	reagent grade
1-Decanol	Calbiochem	reagent grade
Dimethyl aniline	not available	
2,4-Dimethyl phenol	Aldrich	reagent grade
Dinonyl naphthalene sulfonic acid (DNNSA)	King Industries	DN-052:50% in Norpar 12 DN-040:40% in heptane
Ethyl acetate	Mallinckrodt	reagent grade

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Table 3.1, continued

COMPOUND	SUPPLIER	DESCRIPTION
2-Ethyl-1-hexanol	Matheson, Coleman and Bell	technical grade
Hexyl ether	Alfa Products	reagent grade
Hi-Sol 4-2	Ashland Chemicals	Hydrocarbon mixture, mostly alkylbenzenes, technical grade
Isobutyl-heptyl ketone (IBHK)	Union Carbide	2-methyl-4-decanone technical grade
Isodecyl alcohol	USS Chemicals	branched-chain primary aliphatic alcohol
Methylene chloride	Mallinckrodt	reagent grade
Methyl-isobutyl ketone (MIBK)	Mallinckrodt	1-methyl-2-pentanone reagent grade
Neodecanoic acid	Exxon Chemicals	branched, technical grade
Nitrobenzene	Aldrich	reagent grade
Nonyl phenol (NP)	ICN Pharmaceuticals	reagent grade
Norpar 12	King Industries	n-C_{10}-C_{13} paraffins
1-Octanol	Aldrich	reagent grade
Octyl phenyl acid phospate (OPAP)	Mobil Chemical Co.	50% mixture of mono- and di-esters
Tributyl phosphate (TBP)	Mobil Chemical Co.	technical grade
1,1,2,2-Tetra chloro ethane	Aldrich	reagent grade
Toluene	Mallinckrodt	reagent grade
Tri-n-octyl phosphine oxide (TOPO)	American Cyanamid	technical grade

metal compounds can occur. In this work, even under the conditions suggested, a golden precipitate often formed, which presumably was iron hydroxide. Care was taken to avoid entraining this precipitate in the organic phase. The sodium sulfate was added to the aqueous phase as a salting agent to prevent the highly surface-active sodium salt of D2EHPA from emulsifying the aqueous and organic phases.

After the two phases were well mixed and then separated, the organic phase was removed and contacted with enough 0.5 M copper sulfate to provide an equivalent amount of copper plus a 15% excess. Again the phases were well mixed and separated and the organic phase was removed.

At this point, all of the D2EHPA had been converted into the copper salt form, and as a result the organic phase was a characteristic blue color. The volume of the organic phase was then reduced by about 40% in a rotary vacuum evaporator.

Next, the copper/D2EHPA salt was precipitated. Per liter of original organic phase, 2 liters of acetone were placed in a vessel and the contents well stirred by a magnetic stirrer. The concentrated organic phase was then added to the acetone, and the copper/D2EHPA salt precipitated immediately. After the precipitate settled, the supernate was removed and the precipitate was washed once with about three times its volume of fresh acetone. It was then slurried with additional acetone, filtered and air dried overnight.

To convert the copper/D2EHPA back to the acid form, the precipitate was contacted simultaneously with 2 liters of approximately 4 M H_2SO_4 and 1 liter of toluene per mole of D2EHPA. Two additional H_2SO_4 washes were required to complete the conversion of all of the copper in the organic phase back into hydrogen.

The organic solution was then clear and colorless and contained D2EHPA in toluene. It was washed three to five times with water to remove entrained sulfuric acid. Finally, the toluene and entrained water were removed in the rotary vacuum evaporator. The final product was nearly pure D2EHPA, as verified by titration.

D2EHPA was titrated as suggested in the Mobil literature (1981). To 1.5 ml of D2EHPA were added 100 ml acetone, 33 ml water and 5 drops phenolphthalein indicator (1% in ethanol). This solution was titrated with 0.1 N NaOH.

A sample result of such titrations for as-received D2EHPA is shown in Figure 3.1, and for purified D2EHPA in Figure 3.2. The absence of a second endpoint in the latter indicates that all of the mono-2-ethylhexyl phosphoric acid had been removed by the purification procedure. Analysis of several of these titrations showed that the as-received D2EHPA contained 86.7% (w/w) D2EHPA and 1.94% (w/w) mono-2-ethylhexyl phosphoric acid. The purified samples contained 91.6% (w/w) D2EHPA and no measurable mono-2-ethylhexyl phosphoric acid. The remainder of the solutions was assumed to be non-acidic impurities, which are known to be not as effectively removed by this purification procedure as the acidic impurities are. Thus they are probably not very water soluble.

C. PRELIMINARY EXTRACTIONS

These extractions were designed to screen possible solvents for CO_2, H_2S, and NH_3.

For CO_2 the aqueous feed for the extractions was an ammonium carbonate solution. The pH of the feed was sometimes lowered with

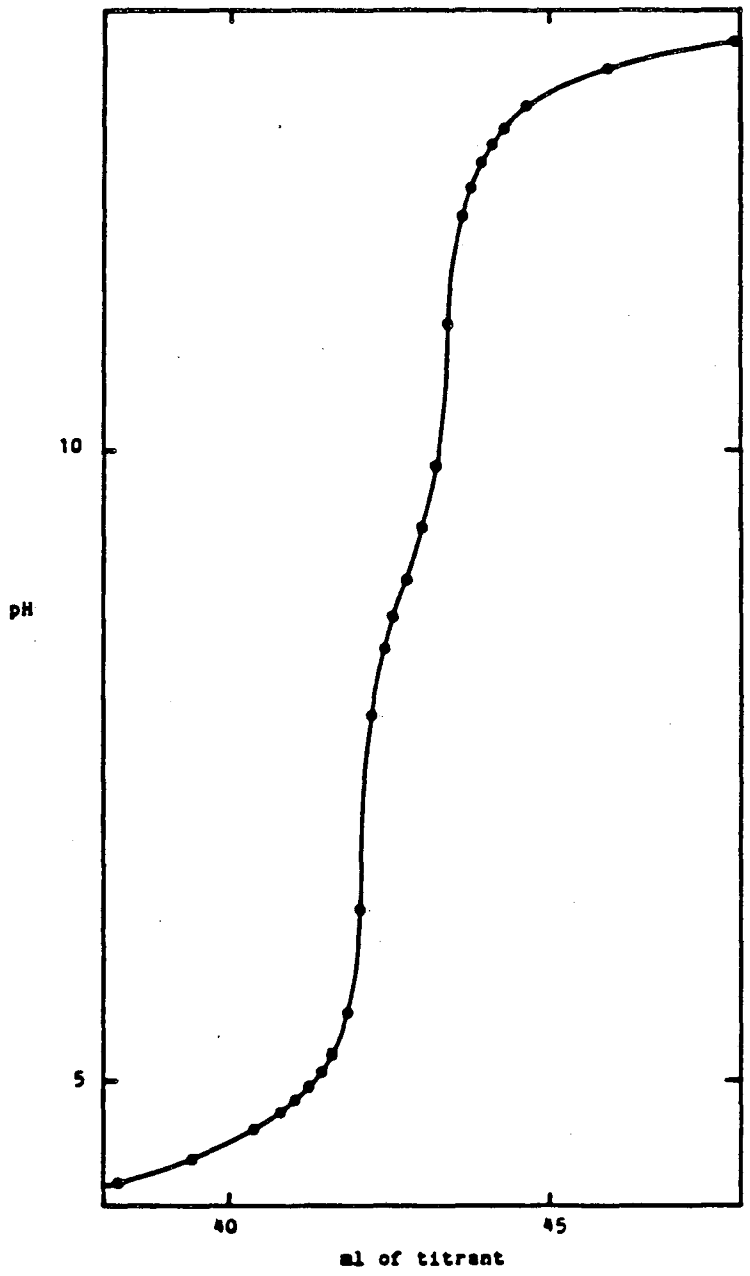

FIGURE 3.1: TITRATION OF AS-RECEIVED D2EHPA.

Titrant = 0.1 N NaOH; 1.5 ml D2EHPA

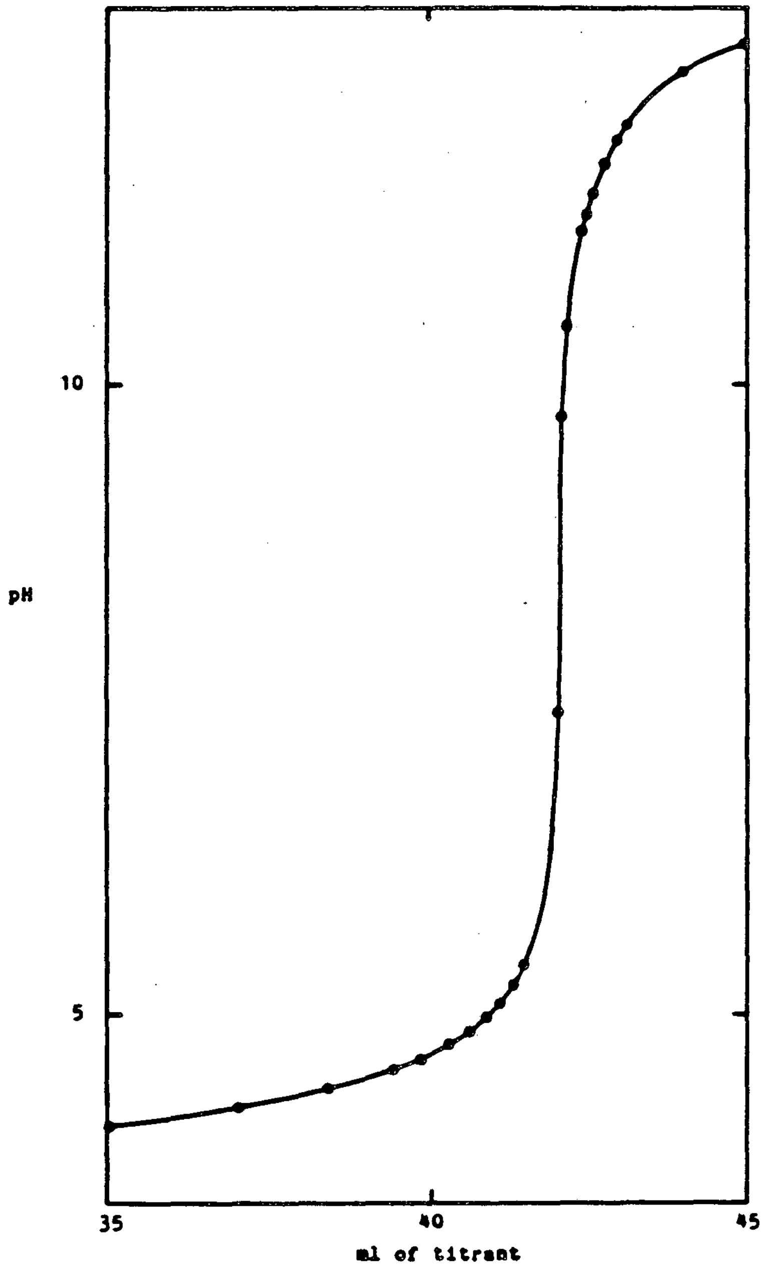

FIGURE 3.2: TITRATION OF PURIFIED D2EHPA.

Titrant = 0.1 N NaOH; 1.5 ml D2EHPA, purified by copper-salt-precipitation method either H_2SO_4 or HCl. Extractions were performed in 125-ml separatory funnels, and mixing of the two phases was mostly by hand, although in later experiments the mixing was by a Labline Junior Orbit Shaker, operated at 250 RPM. After the phases separated, the concentrations of CO_2 in the feed and the raffinate were measured with the CO_2 electrode, and the amount of CO_2 extracted was calculated by mass balance.

For H_2S the feed was an ammonium sulfide solution. The pH was sometimes varied with KH_2PO_4/NaOH buffers of varying ionic strength. Extractions were performed in 125-ml separatory funnels. As before, mixing techniques varied. Some mixing was by hand; however for many of the extractions, mixing was by the Junior Orbit Shaker, operated at 300 RPM. The concentrations of H_2S in the feed and the raffinate were measured with the sulfide electrode, and the amount of H_2S extracted was calculated by mass balance.

For NH_3 the aqueous feed was either an ammonium carbonate, an ammonium bicarbonate, an ammonium hydroxide, or an ammonium chloride solution. Extractions were performed in 125-ml separatory funnels, and for almost all of the extractions mixing was by the Junior Orbit Shaker, operated at 250 RPM. Concentrations of NH_3 in the feed and the raffinate were measured with the ammonia electrode, and the amount of ammonia extracted was calculated by mass balance. The temperature dependence of NH_3 distribution coefficients into D2EHPA-containing solvents was studied by performing extractions at temperatures above room temperature. A Precision Shaking Water Bath was used for these experiments and was operated between 50 and 150 oscillations/minute.

For all of these extractions and other extractions in this work, the concentration-based distribution coefficient, K_C, was calculated as:

$$K_C = \frac{(C_F - C_R)}{C_R} \frac{W}{S} \tag{3.1}$$

where:

C_F = concentration of feed ($\underline{M}$)

C_R = concentration of raffinate ($\underline{M}$)

W/S = aqueous-to-organic volumetric phase ratio.

D. COMPARISON OF D2EHPA AND DNNSA AS EXTRACTANTS FOR AMMONIA

A comparison between D2EHPA and DNNSA as solvents for ammonia was made by measuring the distribution coefficients for ammonia into these solvents as a function of the raffinate equilibrium pH. In these experiments, both solvents were used as received and therefore contained acidic impurities. To achieve a high raffinate pH a $NaOH/NaHCO_3$ buffer solution was used as part of the feed for the extractions.

The aqueous feed for these extractions was 0.48 $\underline{M}$ NaOH, 0.36 $\underline{M}$ $NaHCO_3$, and 0.15 $\underline{M}$ NH_3, added as ammonium carbonate. The pH of this solution was about 10.5. To achieve a range of raffinate pH values, the feed pH was varied by adding concentrated HCl. The organic phases were 0.2 $\underline{M}$ D2EHPA in kerosene and 0.18 $\underline{M}$ DNNSA in heptane/kerosene. The aqueous-to-organic volumetric phase ratio was 0.75. The phases were mixed for more than one hour at 250 RPM on the Junior Orbit Shaker. After the phases separated, the pH of the raffinate was measured, and its NH_3 concentration determined with the ammonia electrode. Above a pH of about 6, extractions with the D2EHPA-containing solvent resulted in the formation of three equilibrium phases. Measurements were made on the bottom phase of the three.

E. SCREENING OF DILUENTS FOR D2EHPA

Several different compounds were screened as potential diluents for D2EHPA. These compounds were either used alone or added as a modifier to another diluent. The purpose of these tests was to determine how the diluent affected D2EHPA capacity for ammonia, D2EHPA losses from the organic into the aqueous phase, and aqueous/organic phase-separation properties.

The aqueous phase for these extractions was an ammonium bicarbonate solution, at about pH 8. The organic phase was purified D2EHPA in the chosen diluent. The phases were added in the desired proportions to a 125-ml separatory funnel and mixed for one hour on the Junior Orbit Shaker at 250 RPM. The phases were allowed to settle overnight. Phase-separation properties were observed before and after the settling period. After the settling period the aqueous raffinate was centrifuged for 30 minutes at 3300 RPM (about 1200 RCF) in an International Clinical Centrifuge. The bottom portion of the aqueous phase was removed with a syringe, care being taken to leave behind any trace organic phase that may have collected on the top of the aqueous phase during centrifugation. The aqueous phase was then recentrifuged for an additional 30 minutes. Again, the bottom portion of the aqueous phase was removed, and this time it was prepared for the desired measurements. The pH of the raffinate was estimated with pH paper. A portion of the sample was diluted for ammonia-concentration measurements and subsequent calculation of percent of ammonia extracted. The remainder of the sample was sent to the Micro-Analytical Laboratory for aqueous-phase phosphorus-concentration measurements.

F. LIQUID-LIQUID EXTRACTION EQUILIBRIA FOR D2EHPA-CONTAINING SOLVENTS

The development of a model for the liquid-liquid extraction equilibria for these types of solvents required accurate knowledge of the ammonia distribution between the two phases and the equilibrium pH of the raffinate as a function of the organic-phase D2EHPA concentration, the system stoichiometry, and the diluent. The system stoichiometry is the ratio of the concentration of the ammonium/D2EHPA complex in the organic phase to the total, or initial, concentration of D2EHPA.

The aqueous phase for these extractions was ammonium hydroxide diluted to the desired concentration plus between 0.01 M and 0.02 M $(NH_4)_2HPO_4$ added to stabilize pH readings. The organic phase was purified D2EHPA at the desired concentration in the diluent under study. The diluents were toluene, 50% (v/v) Alfol 10 in toluene, and Adogen 364 in toluene. The organic phases were pre-equilibrated with an approximately equal volume of distilled water. For a given D2EHPA concentration and solvent-to-water ratio, system stoichiometry could be increased by increasing the feed concentration of ammonium hydroxide.

As for other extractions, the two phases were mixed together in a 125-ml separatory funnel for one hour on the Junior Orbit Shaker, operated at 250 RPM and at room temperature. They were allowed to settle overnight. After phase-separation properties had been noted, the raffinate was removed, centrifuged at 3300 RPM for 30 minutes, transferred to a fresh centrifuge tube and recentrifuged another 30 minutes. The pH of the raffinate was then measured with the semi-micro pH electrode, and a portion of the raffinate was diluted for ammonia-concentration measurements. The organic phase was also centrifuged, usually for one hour at 1700 RPM, to remove entrained water. Subsequently, the water content of the organic phase was determined.

G. REGENERATION OF SOLVENTS FOR AMMONIA

The ease of ammonia removal from solvents was determined by batch stripping experiments. The NH_3-laden solvent was stripped at elevated temperatures and the course of ammonia removal from solution followed.

1. QUALITATIVE STUDIES

In preliminary qualitative studies, heating was via a heating mantle, and the solvent temperature was controlled by refluxing the diluent and/or by boiling water through the solvent. In the former case, the diluent served as part of the stripping medium, and nitrogen was used as a supplemental stripping medium. After passing through the vertical diluent condenser, the nitrogen entered a vessel containing dilute H_2SO_4 provided to remove any stripped ammonia from the nitrogen. In the latter case, water vapor provided the stripping medium, and after it had bubbled through the solvent it was condensed in a side arm condenser. The ammonia content of this aqueous condensate was then determined. These experiments simply indicated whether or not ammonia could be liberated from the solvents by stripping at elevated temperatures. They were used as screening estimates for the relative regenerability of D2EHPA and DNNSA-containing solvents.

2. QUANTITATIVE STUDIES

Later experiments were designed to give the quantitative information needed to calculate partial pressure of ammonia (P_{NH_3}) above D2EHPA-containing solvents as a function of the ammonium/D2EHPA complex concentration in the solvent. In these experiments solvent heating was provided by an oil bath, the diluent was relatively non-volatile at the experimental conditions, and nitrogen was used as the sole stripping medium. In this way, the total number of moles of stripping medium used to remove a given number of moles of ammonia from the solvent was known simply by measuring the nitrogen flow.

The oil bath used in these experiments was about six liters of Ucon Oil 550 (Union Carbide Corporation) in an insulated metal bucket. A contact thermometer connected through a relay box controlled the power to a 500-Watt blade heater, thus regulating the temperature. To help heat the oil to the desired temperature, additional heating was provided by a 750-W plate heater. This was disconnected when the bath approached the set-point temperature. As a safety feature, a thermoswitch (Fenwal Incorporated) set at 150°C was wired into the power side of the circuit. If a temperature excursion occurred due to the relay switch becoming stuck in the "on" position, this thermoswitch would break the circuit providing power to the blade heater.

The basic solvent used in these experiments was 0.48 M D2EHPA in Norpar 12 or in 50% (v/v) isodecyl alcohol in Norpar 12. The D2EHPA used was the as-received product, as it was assumed that the impurities present in the commercial product would not affect solvent regeneration properties. However some of the impurities were removed by washing the D2EHPA-containing solvents three times with an approximately equal volume of distilled water. The solvents were loaded with ammonia in batch extractions. The alcohol-containing solvent was contacted with an ammonium bicarbonate solution containing a 10% molar excess of ammonia over D2EHPA, at an aqueous-to-organic volumetric phase ratio of 0.9. Measurements of organic-phase ammonia concentrations showed nearly 100% loading of D2EHPA with ammonia. The Norpar 12 solvent could not be loaded to near 100% with ammonia, as this would result in third-phase formation. Instead it was contacted with an ammonium bicarbonate solution containing enough ammonia to load the D2EHPA to 50%. The aqueous-to-organic volumetric phase ratio was 0.2. Organic-phase ammonia-concentration measurements showed that nearly all of the ammonia had been extracted. In the preparation of both solvents, centrifugation was often required to obtain clear organic phases. Amine-containing solvents and TOPO-containing solvents were prepared by adding these modifiers to the NH_3-laden D2EHPA-in-Norpar-12 solvent. Likewise, solvents with higher D2EHPA concentrations were prepared by adding more D2EHPA to these NH_3-laden solvents. In all cases after such additions, volumes were additive. However, when additional D2EHPA was added to the solvents, the solvents became cloudy. This cloudiness disappeared after several days.

The stripping apparatus is shown in Figure 3.3. The stripping vessel was a 250-ml heart-shaped flask, used to increase the liquid height-to-volume ratio. In each experiment, 100 ml of solvent were stripped in this flask. The middle opening of the flask held a fritted-glass gas sparger. The height of the liquid above the sparger was about 2 inches. A side opening of the flask held a thermometer which extended down into the liquid. The other side opening of the flask was the exit port, through which nitrogen and any stripped NH_3 left the stripping flask. The gases then entered a defoaming flask in which any

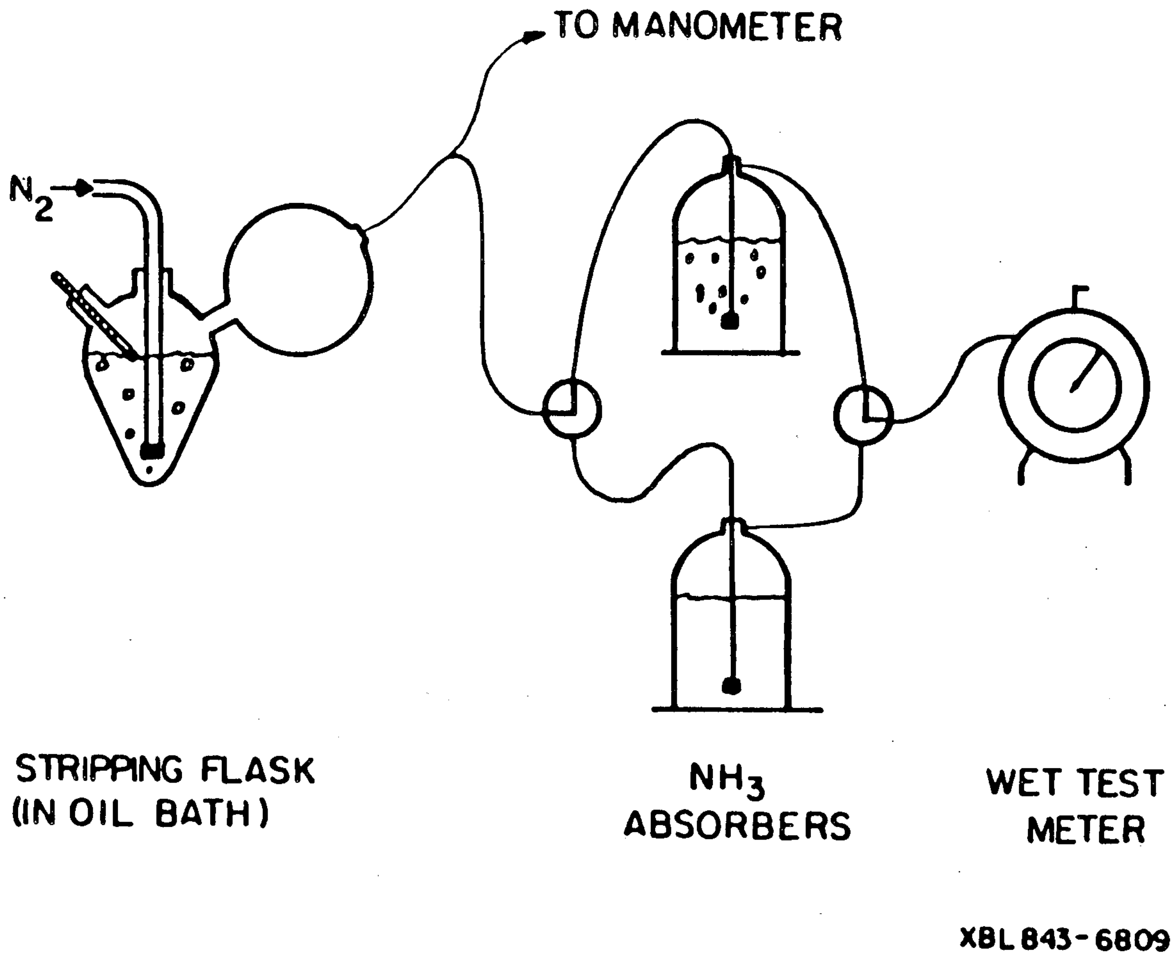

FIGURE 3.3: STRIPPING APPARATUS FOR SOLVENT-REGENERATION STUDIES.

volatilized diluent condensed and drained back into the stripping vessel, providing a source of reflux and, potentially, extra enrichment. The effect of diluent volatility on the calculation of P_{NH_3} is discussed later. Downstream of the defoaming flask, a side port led to a mercury manometer for pressure measurements. Pressure ranged from 1.4 to 2 inches of mercury above atmospheric. Special steps were taken to maintain this pressure. Hose clamps were used on all of the glass-to-tubing connections. All of the glassware had "ears" on both sides of all connections, to which springs were attached. In addition, glass joints were greased and insulated to prevent condensate from lubricating the joint and facilitating leakage.

The main line leaving the defoaming flask led to another flask fitted with a fritted-glass gas sparger. This flask contained 300 ml of dilute sulfuric acid, and the height of the liquid above the sparger was 2 inches. The amount of sulfuric acid present corresponded stoichiometrically to between 5 and 10% of the ammonia initially present in the solvent. Methyl red was added as an indicator to signal when this amount of ammonia had been absorbed. The color change was from red to yellow. When this occurred, the nitrogen stream was diverted to another NH_3 absorber. The contents of the first absorber were stored, and the absorber was refilled with fresh dilute sulfuric acid.

The nitrogen exiting the ammonia absorber flowed through a Labline wet test meter and into the surroundings. The nitrogen flow rate through the wet test meter was between 0.01 and 0.02 ft^3/min, corresponding to between 0.0115 and 0.023 moles/min.

The ammonia concentration in the absorber solutions was measured with the ammonia electrode. The concentration of ammonia in the solvent during stripping was determined by mass balance. At the end of an experiment, the concentration of NH_3 in the organic solvent was determined by the back-extraction method. These results agreed very well with those calculated by mass balance. This indicated that all of the ammonia stripped from solution by the nitrogen stripping gas was absorbed by the sulfuric acid in the absorbers and that leakage was negligible.

With these data ammonia partial pressure could be calculated. First the data were plotted as concentration of ammonia in the solvent as a function of the moles of nitrogen passed through the solvent. For a given change in solvent concentration the number of moles of ammonia removed from solution was calculated, and the number of moles of nitrogen required to effect this change was determined. The system pressure was also known. The partial pressure of ammonia (P_{NH_3}) was calculated as:

$$P_{NH_3} = \frac{\text{moles } NH_3}{\text{moles } NH_3 + \text{moles } N_2} \times \text{Pressure} \qquad (3.2)$$

This P_{NH_3} was assumed to hold at the average of the NH_3 concentration in the solvent before and after the given amount of ammonia had been stripped from solution.

The presence of diluent vapor in the gas phase was neglected. At the highest temperature at which experiments were conducted, 143°C, the vapor pressure of dodecane is about 0.13 atm. Since the total pressure of the system was only slightly greater than one atmosphere, the maximum vapor-phase mole fraction of the diluent was 0.13. Under these conditions the mole fraction of NH_3 plus nitrogen sums to (1-0.13) or

0.87. The actual partial pressure of ammonia should be that calculated by Equation 3.2 multiplied by 0.87. At 127°C the vapor pressure of dodecane is about 0.05 atm, so that the correction factor is 0.95. These corrections are relatively small and are worst-case estimates, since the diluent mole fraction was less than one. As such, they were not included in the calculation of ammonia partial pressure. Ammonia partial pressure was calculated as indicated in Equation 3.2.

H. STRIPPING AND EXTRACTION/STRIPPING

In these experiments, the amount of CO_2 and NH_3 stripped from solution was to be determined as a function of the cubic feet of nitrogen passed through the solution. The aqueous phase was an ammonium bicarbonate solution, and the organic phase, when one was present, was purified D2EHPA in the diluent under study. All solvents were pre-equilibrated with an approximately equal volume of distilled water.

A schematic drawing of the apparatus is presented in Figure 3.4. The procedure followed was similar to that followed for the solvent-regeneration experiments. The solution to be stripped was added to a 250-ml heart-shaped flask. For the stripping experiments without a D2EHPA-containing solvent present two different methods were used. In the first, 75 ml of the aqueous solution were added to the stripping vessel. In the second experiment, designed to simulate more closely the conditions of the extraction/stripping experiments, 50 ml of the aqueous solution plus 125 ml of toluene were added to the vessel. For the experiments with a D2EHPA-containing solvent present, 50 ml of the aqueous solution plus 125 ml of the solvent were added to the vessel. For the toluene-diluent case, only 40 ml of the aqueous feed solution

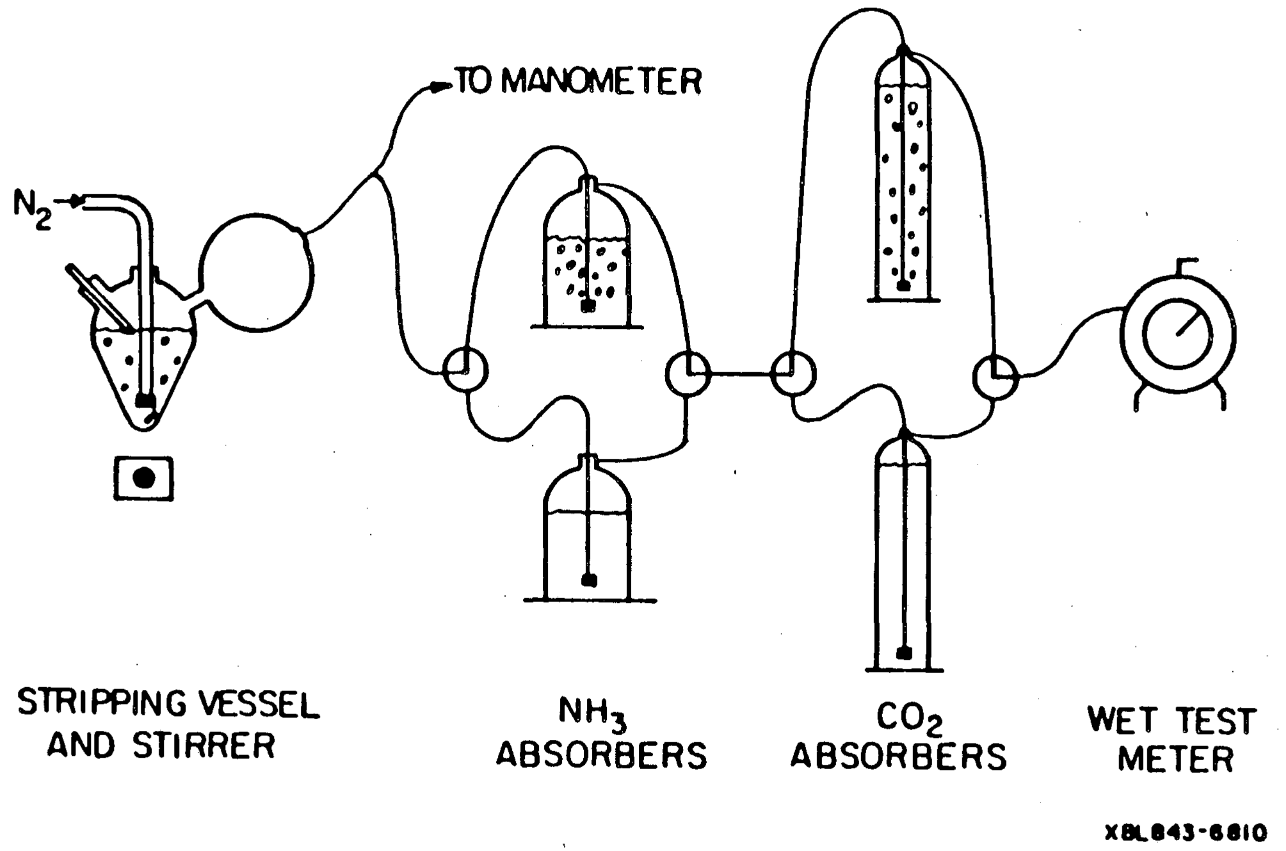

FIGURE 3.4: STRIPPING APPARATUS FOR STRIPPING AND EXTRACTION/STRIPPING STUDIES.

remained and so the phase volumes were reduced to 40 ml and 100 ml, respectively. The stripping flask held a 1/2-inch by 1/8-inch magnetic stir bar. A magnetic stirrer was used to help mix the two phases.

Before entering the stripping vessel the nitrogen was pre-equilibrated with water. The nitrogen stripping gas then entered the stripping vessel through a fritted-glass gas sparger. For the first stripping case the liquid level above the sparger was about 1.7 inches. For the second stripping case and the cases with a D2EHPA-containing solvent present, the aqueous-phase liquid level was 1.5 inches above the sparger. When the phases were mixed, the height of the two phases together was 3 inches above the sparger. The gas exited the stripping vessel through a defoaming flask. This flask was needed for the cases with a D2EHPA-containing solvent present because these solutions foamed significantly, particularly the D2EHPA-in-toluene solvent. The foam collected and broke in the defoaming flask and fell back into the stripping vessel. At the exit of the defoaming flask, a side port led to a mercury manometer. Pressure ranged from 4.6 to 5 inches of mercury above atmospheric. As in the solvent-regeneration experiments, special steps were taken to maintain this pressure. Springs were used on all connections, and all joints were greased properly. When these precautions were taken no gas leaks were detected in the system.

The main line leaving the defoaming flask led to a series of absorbers. First there were two parallel vessels fitted with fritted-glass gas spargers and containing dilute sulfuric acid plus methyl red indicator. These were for the absorption of NH_3 from the stripping gas. Only one absorber was on line at a time. When the stoichiometric amount of ammonia had been absorbed, the absorber was taken off line and the other absorber brought on line. The contents of the first absorber were removed and stored, and the absorber was refilled with fresh solution. After the NH_3 absorbers came two more vessels in parallel. These were also fitted with fritted-glass gas spargers, but contained dilute NaOH solution plus phenolphthalein for absorption of CO_2 from the stripping gas. As with the NH_3 absorbers, when one absorber had reached its stoichiometric limit, signalled by the change in indicator color from pink to colorless, it was taken off line and the other brought on line. After exiting the CO_2 absorber, the nitrogen flowed through a wet test meter and into the surroundings. The nitrogen flow rate was between 0.005 and 0.02 ft^3/min, corresponding to 0.006 to 0.023 moles/min.

The 500 ml of dilute sulfuric acid solution in the ammonia absorber contained a stoichiometric equivalent of about 5% of the ammonia initially present in the solution. The liquid level above the sparger was 3.5 inches. The ammonia concentration in these absorber solutions was measured with the NH_3 electrode. The 900 ml of dilute NaOH solution in the CO_2 absorber contained a stoichiometric equivalent of between 5 and 20% of the CO_2 initially present in the solution. The higher percentage was required when a D2EHPA-containing solvent was present. In these cases, the CO_2 was removed from solution so quickly that the time for switching between absorbers was rather short. CO_2 absorption is a slow (liquid-phase controlled) process, so liquid levels above the spargers were higher in these absorbers than in the ammonia absorbers. The liquid level was 20 inches above the sparger. Also, about 0.1 <u>M</u> NaCl was added to the absorber solution to keep the bubble size small and thus facilitate mass transfer. The concentration of CO_2 in these solutions was measured with the CO_2 electrode.

Immediately after the stripping ended, the pH of the aqueous solution was measured. For the cases with a D2EHPA-containing solvent present, the two phases were first centrifuged together. Then the aqueous phase was withdrawn and the pH measured immediately. All solutions were also diluted for CO_2- and NH_3-concentration measurements as quickly as possible after an experiment ended. For cases with a D2EHPA-containing solvent present, the aqueous phase was centrifuged an additional time and sent to the Micro-Analytical Laboratory for aqueous-phase phosphorus-concentration measurements. Also, the organic-phase ammonia concentration was measured by the back-extraction technique. In all cases mass balance closures for both CO_2 and NH_3 were very good. This indicated that there were no leaks in the system and that essentially all of the NH_3 and CO_2 stripped from solution had been absorbed in the appropriate absorbers.

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CHAPTER 4

SCREENING OF SOLVENTS FOR CO_2, H_2S, and NH_3

A. INTRODUCTION

The solutes to be removed are all somewhat polar and can ionize in water. A solvent to remove one of them from water must interact with it to a significant degree so that the activity coefficient of the solute in the organic solvent is low. The interaction may be due to solvent polarity or may be as strong as a hydrogen bond, or stronger. The interaction may even lead to the formation of an acid-base complex (Kiezyk and Mackay, 1971). To aid in the selection of a solvent, available data for the solubility of these gases (solutes) in various compounds were examined. Many of these compounds are water-soluble and hence are unsuitable for use here. However by analysis of such solubility data some insight may be gained into the type of functional groups that are useful in a solvent.

Solubility data are usually presented as cm^3 of gas dissolved per cm^3 of solvent, usually at one atmosphere partial pressure of gas (Bunsen or Ostwald coefficient). This information can be converted into an estimate of a distribution coefficient by envisioning an equilibrium situation between water, the solvent and the vapor. For the vapor and the solvent:

$$f^v = f^s \qquad (4.1)$$

For the vapor and water:

$$f^V = f^W \qquad (4.2)$$

Since the vapor phases are the same, the solubility of the gas in the solvent divided by the solubility of the gas in water gives an estimate of the distribution coefficient.

The distribution coefficients thus obtained are for the unionized species ($K_{c,un}$). The distribution coefficient of interest is that for the total species, both ionized and unionized (K_c). K_c is equal to $K_{c,un}$ times the fraction of the gas that is unionized in the aqueous phase (Treybal, 1963). As seen in the previous chapter, for acid gases this fraction decreases as pH increases, so K_c also decreases as pH increases. At a pH well below the pK_a of the acid, K_c is constant and is equal to $K_{c,un}$, as long as activity coefficients do not change. The opposite is true for ammonia; K_c increases as pH increases. At a pH well above the pK_a of the ammonium ion, K_c is constant and equal to $K_{c,un}$.

In order to assure complete and efficient removal by a solvent at reasonable solvent-to-water flow rates, K_c for a gas should be high throughout the pH range encountered in the process. Thus, for the acid gases K_c should be high even at a pH of about 9, where the fraction of CO_2 unionized is 2×10^{-3} and the fraction of H_2S unionized is 0.01. For ammonia, K_c should be high even at a pH of 7, where the fraction of NH_3 unionized is 6×10^{-3}. Therefore, the required K_c based on "physical" extraction is probably hopelessly high.

B. SOLVENTS FOR CO_2

Table 4.1 lists $K_{c,un}$ [(cm^3 CO_2 in solvent/cm^3 solvent)/(cm^3 CO_2 in water/cm^3 water)] values for extraction of CO_2 into various solvents, All values are estimated from gas-solubility data at about 298K (Kohl and Riesenfeld, 1979; Seidell, 1940). CO_2 is very soluble in polar solvents, particularly those containing C=O groups (Hildebrand and Scott, 1964), probably due to its quadrupole. Solvents containing this Lewis-base functional group yield high $K_{c,un}$ values. However, as mentioned above, many of the compounds listed are water-soluble. As the molecular weight is increased to reduce water solubility, the concentration of the functional groups decreases and $K_{c,un}$ will also decrease. Clearly, none of the solvents listed will give a high K_c at pH 9.

To verify this prediction, extractions into related solvents were performed. The solvent-to-water ratio (v/v) was about 1, except where noted and the feed concentration was about 0.15 M CO_2. Methyl isobutyl ketone (MIBK) did not extract a detectable amount of CO_2 even at a raffinate pH of 7.6. The phosphoryl group, P=O, is even more basic than the carbonyl group and therefore might extract an acid better. However, tributyl phosphate (TBP) did not extract CO_2 at a raffinate pH of 9 (S/W = 0.3). Tri-n-octyl phosphine oxide (TOPO) is more basic than TBP, but a solution of 3% (w/v) TOPO in kerosene also did not extract CO_2 at this pH. Ethyl acetate is a weaker base than a ketone, but it did extract a small amount of CO_2. At a pH of 8 K_c was about 0.4, but it was essentially zero at pH 9. This is consistent with predicted results for methyl acetate. Finally, dimethylaniline also did not extract CO_2 appreciably.

TABLE 4.1

ESTIMATES OF $K_{c,\,un}$ FOR CO_2

SOLVENT	$K_{c,un}$ (298K)	Source
Selexol (a)	10.9	b
Methyl acetate	7.9	c
Acetone	7.8	c
Acetic acid	5.9	c
N-methyl-2-pyrrolidone	4.8	b
Pyridine	4.3	c
Methanol	4.3	c
Chloroform	4.3	c
Tributyl phosphate	3.3	b
Benzene	2.9	c
Aniline	1.6	c

(a): dimethyl ether of polyethylene glycol

Sources: (b): Kohl and Riesenfeld, 1979

(c): Seidell, 1940

A likely choice of a solvent to extract an acid from solution is an organic amine, as evidenced by the use of organic and aqueous solutions of monoethanolamines to absorb CO_2 from gas streams (Kohl and Riesenfeld, 1979). Amines are stronger Lewis bases than the other compounds tested, including phosphine oxides (Bailes et. al., 1976). This is due partially to the lower electronegativity of N compared with O. Also the presence of a multiple bond at the basic site reduces the basicity of that site. A multiple bond has more s character and s electrons are bound more firmly to the nucleus than p electrons, making them relatively less available for bonding. (Hendrickson et. al., 1970). Gutmann (1977) reports donor numbers for several compounds measured by various techniques. The donor number is a measure of the ability of a compound to donate its electrons. Gutmann (1977) gives a donor number of 40 for tri-ethyl phosphine oxide. That for tri-ethyl amine is less well established but is estimated by Gutmann to be about 61, supporting the idea that amines are stronger bases than phosphine oxides.

Amines generally extract stronger acids better than weaker ones (Diamond, 1967; Ricker et. al., 1979). This is attributed to the increased hydration of the anion of the weak acid, relative to that of the strong acid, making it more hydrophilic and less organophilic than the strong acid. Primary amines usually extract better than secondary amines which usually extract better than tertiary amines (Diamond, 1967; Ricker er. al., 1979). Tertiary amines are the poorest extractors due to the steric hindrance around the nitrogen which blocks the approach of the acid, and also because of the lesser number of hydrogens available to interact with the acid to help stabilize the acid-base complex

(Diamond, 1967; Wardell and King, 1978).

In this work it was found that a 9% (v/v) solution of Alamine 336 (a tertiary amine, General Mills) in kerosene did not extract CO_2, even at a pH of about 5. A 9% (v/v) solution of Adogen 283 (a secondary amine, Ashland Chemicals) in kerosene also did not extract CO_2, at a raffinate pH of 9.1.

These results indicated that extraction of CO_2 from wastewater was not a likely implementation of the combined stripping/solvent extraction process.

C. SOLVENTS FOR H_2S

Table 4.2 summarizes available solubility data for H_2S, converted into $K_{c,un}$ at 298K (Kohl and Riesenfeld, 1979; Seidell, 1940). No real trend is discernible other than that polar solvents are better solvents for H_2S than non-polar ones. None of the solvents listed would give a high K_c at pH 9.

As for CO_2, the extraction of H_2S by Lewis bases was examined. The feed cocnetration was about 0.02 $\underline{M}$ H_2S. Extraction with 10% (w/v) TOPO in MIBK (S/W = 0.4) resulted in poor phase separation, and the data were not quantified. The stronger Lewis-base amines also did not extract H_2S. Specifically, 7.4% (v/v) Alamine 336 in kerosene and 7.4% (v/v) Adogen 283 in kerosene did not extract an appreciable amount of H_2S even at a raffinate pH of about 6 (S/W = 0.8).

Data for extraction of H_2S into MIBK (S/W = 0.4) indicated that this may be a potential solvent for H_2S. However, the data did not give the predicted trend in K_c versus pH. The measured K_c ranged from 0.3 to 0.55 in the raffinate pH range of 4.5 to 12. At a pH greater than 14,

TABLE 4.2

ESTIMATES OF $K_{c,un}$ For H_2S

SOLVENT	$K_{c,un}$ (298K)	Source
Selexol (a)	17.3	b
N-methyl-2-pyrrolidone	16.8	b
Chloroform	6.7	c
Benzene	6.7	c
Aniline	6.1	c
Toluene	5.6	c
Tributyl phosphate	5.5	b
Ethanol	2.9	c
Dodecane	2.3	c
Carbon tetrachloride	2.1	c

(a): dimethyl ether of polyethylene glycol

Sources: (b): Kohl and Riesenfeld, 1979

(c): Seidell, 1940

K_c was essentially zero. At a raffinate pH of 3.9, K_c was calculated to be 8.3. The pH was varied by addition of NaOH or a buffer solution of KH_2PO_4/NaOH to an ammonium sulfide solution. Variations in contact time or settling time did not affect K_c. Since these values of K_c were calculated from aqueous-phase concentration measurements and a mass balance, the effect of H_2S loss due to volatilization is not included. Some stripping of H_2S did occur. A feed solution at pH 7.9 was shaken in a separatory funnel alone and with MIBK present. A 6% reduction in H_2S concentration was measured for the case without the solvent present, while a 23% reduction was measured with the solvent present. Apparently MIBK extracts some H_2S, but in most cases, particularly those at low pH, some H_2S was lost by volatilization. Thus, the K_c values are overestimated.

H_2S was not back-extracted out of MIBK with water, but a 0.1 M NaOH solution contacted with MIBK containing H_2S did recover between 5 and 8% of the H_2S calculated to be in the MIBK. Apparent K_c values for this back extraction ranged from 15 to 26. However, at the high pH of the NaOH raffinate, the K_c value should be very low. The apparent high K_c values indicate that the extraction of H_2S by MIBK may be irreversible.

The K_c of H_2S into MIBK appears to be too low to warrant use of MIBK as a solvent for H_2S. The possibility that this extraction is irreversible further serves to eliminate MIBK as a potential solvent for the proposed process.

No suitable solvents were found for CO_2 or H_2S. Stronger-base extractants such as liquid anion exchangers may extract these gases out of an aqueous solution. However there are indications that these compounds, such as quaternary amines, would be too soluble in the aqueous phases likely to be encountered here to be of commercial interest (Kunin and Winger, 1962). Liquid ion exchangers are discussed at greater length below. Efforts for the remainder of the work concentrated on finding a suitable solvent for NH_3.

D. SOLVENTS FOR NH_3

As for the acid gases, available solubility data for NH_3 were converted into $K_{c,un}$ (Seidell, 1940). As seen in Table 4.3, the values are generally quite low. The acidic compound chloroform exhibits the highest $K_{c,un}$ for ammonia, consistent with the concepts of Lewis acids and Lewis bases (Jensen, 1980). However, even this compound would not exhibit a high enough K_c to extract NH_3 efficiently throughout the pH range encountered in the proposed process. These predictions were verified by extractions of NH_3 into several solvents similar to those listed in Table 4.3. No ammonia was extracted from an ammonium sulfide solution into MIBK (feed concentration = 0.2 $\underline{M}$, S/W = 0.4). Likewise no NH_3 was extracted from an ammonium bicarbonate solution into toluene, 1-octanol, or a 50% (v/v) 1-decanol/toluene mixture (feed concentration = 0.58 $\underline{M}$, S/W = 5).

In light of these results it is apparent that stronger acids are required to remove NH_3 from an aqueous solution containing a weak acid such a CO_2 or H_2S. In particular, an acid which ionizes in the pH range of interest would offer the possibility of forming an ion pair with the ammonium cation. Since at the pH of the wastewater most of the NH_3 is in the ammonium form, the driving force for ion-pairing will be large.

TABLE 4.3

ESTIMATED $K_{c,un}$ FOR NH_3

SOLVENT	$K_{c,un}$ (298K)
Chloroform	0.04
Dimethylforamide	0.023
Cyclohexanol	0.02
Nitrobenzene	0.01
Benzene	0.007
Carbon tetrachloride	0.005

Source: Seidell, 1940

1. PRINCIPLES OF LIQUID-CATION-EXCHANGE EXTRACTION

Acidic extractants of the type of interest include carboxylic acids, organic phosphoric acids and sulfonic acids. These acids are capable of extracting cations from aqueous solutions by an ion-exchange mechanism and are referred to as liquid cation exchangers. They have been used to extract uranium, copper, nickel, rare earths and a host of other metals from leach solutions generated in the hydrometallurgical industry. Consequently, much has been written about the use of these acids in solvent extraction (Ashbrook, 1973; Bailes et. al., 1976; Dyrssen et. al., 1967; Jenkins, 1979; Kunin and Winger, 1962; Marcus and Kertes, 1969; Markovits and Choppin, 1973; Rice, 1978; Ritcey and Ashbrook, 1979). They are usually quite viscous so they are almost always used in diluted form. The solvent then is a solution of the organic acid (extractant) in an organic diluent.

The basic mechanism for extraction of a monovalent cation by a liquid cation exchanger may be expressed as:

$$M^+ + \overline{HA} \rightleftarrows \overline{M^+A^-} + H^+ \qquad (4.3)$$

where an overbar indicates an organic-phase species. The organic acid, HA, ionizes at the interface and exchanges its H^+ for the cation M^+, forming an ion pair in the organic phase. The expression written above is a simplified one as it ignores possible dimerization of the extractant, complexing of the ion pair with additional acid molecules or diluent, and polymerization of the ion pairs (Ashbrook, 1973; Bailes et. al., 1976; McDowell, 1971; Rice, 1978). However this simplified expression is acceptable in most practical situations.

The equilibrium constant for the the above reaction, K_r, is:

$$K_r = \frac{[M^+A^-](H^+)}{[HA](M^+)} \tag{4.4}$$

where square brackets denote organic-phase concentrations and parentheses denote aqueous-phase concentrations. The distribution coefficient, K_{c,M^+}, is the ratio of the organic-phase concentration of species containing M^+ to the aqueous-phase concentration of M^+ and may be written:

$$K_{c,M^+} = \frac{[M^+A^-]}{(M^+)} = \frac{K_r\,[HA]}{(H^+)} \tag{4.5}$$

The value of K_r depends on the cation extracted, the organic extractant used, and the diluent. Consequently, at a given pH, one cation will exhibit a higher K_{c,M^+} than another cation, so that a separation of two cations can be effected by pH adjustment.

Examination of Equation 4.5 shows that, at constant concentration of HA, log K_{c,M^+} will increase linearly with pH. At high pH values, significant aqueous solubility of the acid or the ion pair, or competition from another cation, may result in a decrease in the apparent value of K_{c,M^+} (Rice, 1978).

A distribution isotherm, or plot of organic-phase cation concentration versus aqueous-phase concentration, is useful for design purposes. A distribution isotherm would be drawn for an organic phase containing a constant amount of acid, $[HA]_0$, and for an aqueous phase at a constant pH. As the concentration of the ion pair in the organic phase increases, the concentration of free acid, HA, decreases. This corresponds to a decrease in K_{c,M^+}. Consequently the distribution isotherm will not be linear and will level off at some maximum organic-phase ion-pair concentration. This asymptotic value is determined by the initial concentration of HA and the aqueous-phase pH. Once this value is reached, further increases in aqueous-phase concentration will not measurably increase the organic-phase concentration of the ion pair, and K_{c,M^+} will decrease rapidly. This type of extraction behavior is common in systems in which the solvent interacts specifically with the solute (Ricker et. al., 1979).

In a process application with a given feed composition, if nearly complete extraction of the solute is assumed, then the exit concentration of M^+A^- in the solvent will increase as the solvent-to-water ratio decreases. For a given $[HA]_0$ this corresponds to a lower K_{c,M^+} at the solvent exit. Thus, K_{c,M^+} and the solvent-to-water ratio are coupled, and the effect on K_{c,M^+} of the solvent-to-water flow ratio (through the exit solvent composition) must be considered if the extraction is to be accomplished in a reasonable number of stages.

Equation 4.5 also indicates the behavior to be expected in a series of extractions if the phase ratio and feed composition are held constant and the pH varied independently, without the addition of other cations. K_{c,M^+} will increase with increasing pH, but the effect will be damped by the increase in the concentration of M^+A^-, reducing the concentration of HA. Eventually, no significant increase in M^+A^- will occur, and K_{c,M^+} will be essentially constant. Further decreases in the concentration of H^+ will result in a proportional decrease in the concentration of HA, with the effect on $[M^+A^-]$ not discernible.

If the cation can exist in some other form in the aqueous phase, then the distribution coefficient based on the total concentration of the cation will be less than K_{c,M^+} (Ashbrook, 1972; Rice et. al., 1978). If α represents the fraction of the cation that exists as M^+, then the total distribution coefficient, K_c, is:

$$K_c = K_{c,M^+} \alpha = \frac{K_r [HA]}{(H^+)} \alpha \qquad (4.6)$$

where K_b is given by Equation 1.1.

When NH_4^+ is the cation to be extracted, α is given by:

$$\alpha = \frac{(NH_4^+)}{(NH_4^+) + (NH_3)} = \frac{1}{[\frac{K_w}{K_b (H^+)} + 1]} \qquad (4.7)$$

At a pH substanially greater than the pK_a of ammonium ion:

$$\alpha = \frac{K_b (H^+)}{K_w}, \text{ high pH} \qquad (4.8)$$

Consequently, K_c becomes:

$$K_c = \frac{K_r [HA] K_b}{K_w}, \text{ high pH} \qquad (4.9)$$

At low pH, α is 1 and:

$$K_c = K_{c,NH_4^+}, \text{ low pH} \qquad (4.10)$$

For the extraction of ammonia by a liquid cation exchanger, at a constant $[HA]$, log K_c will increase linearly with increasing pH until the point at which ammonium conversion to ammonia becomes important.

Once the concentration of ammonia far exceeds that of ammonium, K_c will be independent of pH. This pH dependence of K_c is the phenomenon which is used in the measurement of organic-phase ammonia concentrations by back extraction at very low pH (Chapter 2, section B).

2. LIQUID CATION EXCHANGERS AS EXTRACTANTS FOR AMMONIA

In Table 4.4, the data of Flett and Melling (1979) for ammonia extraction into less conventional liquid cation exchangers are presented. These compounds were developed for copper extraction. In the table, the concentration of the extractant in an aliphatic diluent, MSB 210 (Shell) and the system stoichiometry (s) are given. The system stoichiometry is defined as the ratio of the concentration of the ion pair in the organic phase to the total concentration of organic acid, in all forms. For a given organic-phase composition, as s increases, the concentration of HA decreases. The pH of the raffinate and the values of K_{c,NH_4^+} and K_c are also given in the table. While these three compounds all extract ammonia to a small extent, the value of K_c in the pH range of interest, 7 to 9, will be too small for these solvents to extract ammonia effectively under process conditions.

The results for the phenol compound were verified in this work. Neither a 13% (w/w) solution of nonylphenol in toluene nor a 13% (w/w) solution of 4-sec-butyl-2-(α-methylbenzyl) phenol (BAMBP) in toluene extracted ammonia effectively from an ammonium bicarbonate solution at pH about 8 (feed concentration = 0.58 M, S/W = 5).

It is well established in the literature that carboxylic acids, organic phosphoric acids and sulfonic acids can be converted to the ammonium salt form (Ashbrook, 1973; Cook and Szmokaluk, 1971; King

TABLE 4.4

EXTRACTION OF NH_3 BY LIX REAGENTS AND NONYLPHENOL

EXTRACTANT	[EXTRACTANT] (M)	$s^{(a)}$	pH_{raf}	K_{c,NH_4^+}	K_c
Nonyl phenol	1.2	0.16	10	0.46	0.07
LIX 65N (b)	0.8	0.17	9.2	0.09	0.04
LIX 63 (c)	0.4	0.019	10	0.02	0.003

(a): stoichiometry, ratio of concentration of ammonia in organic phase to total concentration of extractant

(b): an aromatic hydroxyoxime; General Mills

(c): an α-hydroxyoxime; General Mills

Source: Flett and Melling, 1979

Industries, 1978; Rice, 1978; Ritcey and Ashbrook, 1969). These acids are often used in this form to extract metals. This is done to control the aqueous phase pH in order to keep it in the range required for optimum extraction and separation of the metals in question. The extraction equilibria and other relevant solvent properties for these acids as extractants for ammonia are not well quantified, however.

In this work five liquid cation exchangers were examined as potential extractants for ammonia. In order of decreasing pK_a (increasing acid strength) they are: neodecanoic acid (pK_a about 7; Ashbrook, 1972), decanoic acid (pK_a about 5), di-2-ethylhexyl phosphoric acid (D2EHPA, pK_a about 3; Kunin and Winger, 1962), octylphenyl phosphoric acid (OPAP), and dinonylnaphthalene sulfonic acid (DNNSA). Tunick et. al. (1979) found that NH_3 extractibility increased in the order oleic acid < D2EHPA < OPAP. Thus NH_3 extractibility increases with the acid strength of the extractant.

a. Carboxylic acids and D2EHPA

A comparison of ammonia extraction by the two carboxylic acids and D2EHPA, as measured in the present work, is shown in Table 4.5. For these extractions, the aqueous-to-organic phase ratio was 0.2. As expected, K_c increases with increasing acid strength. Also K_c is higher in the alcohol-containing diluent than in the aromatic diluent. This fact will be amplified in later chapters.

Neodecanoic acid does not have the acid strength to extract ammonia effectively. Decanoic acid does extract NH_3 to an appreciable extent. However, even in the alcohol diluent, K_c is too low over the potential pH range of 7 to 9 to permit efficient removal of ammonia at reasonable

TABLE 4.5

EXTRACTION OF AMMONIA BY CARBOXYLIC ACIDS AND D2EHPA

FEED = 0.58 M NH_4HCO_3 solution   S/W (v/v) = 5

EXTRACTANT	[EXTRACTANT] (M)	DILUENT	(N)$^{(a)}$ (M)	s	$pH_{raf}^{(b)}$	K_c	NH_3 EXTRACTED (%)
Neodecanoic acid	0.27	toluene	0.54	0.01	8-9	0.005	2.6
"	0.27	50% (v/v) iso-decyl alcohol/toluene	0.47	0.06	8-9	0.034	14.4
Decanoic acid	0.27	toluene		←poor phase separation→			
"	0.27	50% (v/v) iso-decyl alcohol/toluene	0.35	0.15	8-9	0.12	36.8
D2EHPA	0.21	toluene	0.038	0.5	6	2.6	93.3
"	0.21	50% (v/v) iso-decyl alcohol/toluene	0.014	0.5	6	7.6	97.5

(a): total concentration of ammonia in raffinate, moles/liter
(b): pH_{raf} estimated with pH paper

solvent flow rates. The equilibrium raffinate pH was not measured in this case, but was estimated by pH paper to be about 8. Thus at a pH of 7, K_c would be about 0.01. This K_c value could be increased by keeping the stoichiometry the same and increasing the concentration of decanoic acid in the solvent. However, even a four-fold increase in concentration would still result in a low K_c. A process designed with this solvent would require a high solvent-to-water flow ratio to achieve nearly complete NH_3 removal. If the solvent-to-water flow ratio were reduced, the concentration of ammonia in the exit solvent would increase. As seen earlier, this decreases K_c. Consequently, the degree of extraction of ammonia would become less, or more stages would be required. The extractibility of ammonia by carboxylic acids is probably too low for these extractants to be considered for use in the proposed process.

In addition, the phase-separation properties were poor for decanoic acid in either toluene or Norpar 12 (aliphatic diluent) contacted with an ammonium bicarbonate solution. After the mixing of these two phases, a foamy white emulsion resulted. Eventually, a clear organic phase settled out, but the bottom phase remained creamy white, with a white solid dispersed in it. Such a suspension would be unacceptable in an actual process.

In applications for metals extraction D2EHPA is usually preferred over carboxylic acids as an extractant because D2EHPA exhibits faster mass transfer rates and lower aqueous solubility losses. In extractions involving D2EHPA equilibration is very fast; often less than 1 minute is required to reach equilibrium. By contrast, equilibration times when carboxylic acids are used as extractants can be 10 times as long (Ashbrook, 1973). This difference in mass-transfer rates was observed here also. When a D2EHPA-containing solvent was mixed with an ammonium bicarbonate solution, it was necessary to vent the separatory funnel immediately in order to release the CO_2 that had been liberated from the solution due to ammonia extraction. For the carboxylic acid system, the gas evolution was less intense and was not required until at least fifteen minutes after contacting the two phases.

Solubility losses for carboxylic acids were not measured in this work. However Ashbrook (1973) reports solubility losses for carboxylic acids about 30 times greater (weight basis) than those for D2EHPA under similar conditions. This could impose a great strain on a raffinate clean-up system. In addition, the economic value of the losses would be higher in the carboxylic acid system, as the carboxlic acid cost is only about $\frac{1}{4}$ that of D2EHPA (weight basis).

Due to their low extraction capacities, their higher aqueous solubility losses and their lower equilibration rates, carboxylic acids have not found much use in the hydrometallurgical industry, other than in the extraction of rare earths and Co/Ni from ammoniacal media. They are used only under conditions in which solvent losses can be kept low, either due to low pH or high salt concentrations. For these same reasons, carboxylic acids were not considered further here as extractants for NH_3.

b. OPAP and D2EHPA

Two organic phosphoric acids, D2EHPA and OPAP, were considered as extractants for ammonia. OPAP is a stronger acid than D2EHPA due to the electron-withdrawing property of its aryl substituents. OPAP comes as a 50% mixture of mono- and di-esters. The mono-ester is much more water soluble than the di-ester, so it was removed from the as-received product. To do this 40 grams of the as-received product were dissolved in toluene. This solution was contacted with 120 ml of approximately 1 M NaOH. After separation, the pH of the NaOH solution was found to have been lowered, presumably due to the solubility of the mono-ester of OPAP. The organic phase was then contacted 8 times with 100 ml of approximately 0.5 M NaOH. The pH values of these additional caustic washes were in the basic range. At this point all of the mono-ester was assumed to have been removed from the organic phase. The OPAP left in the organic phase was in the sodium-salt form. This was converted back to the acid form by contacting the organic phase with 100 ml of 36% HCl. Entrained HCl was removed by washing the organic phase with 100 ml of distilled water. Next the toluene and entrained water and HCl were removed in a rotary evaporator. Twenty-eight grams of OPAP were recovered. This was the OPAP used in the subsequent extractions.

Table 4.6 compares results of extractions using D2EHPA and OPAP. The aqueous feed was approximately 0.58 M ammonium bicarbonate, and the organic-to-aqueous phase ratio was 5 (v/v). Phase separation was satisfactory in all cases. The pH of the raffinates was estimated with pH paper to be about 5 for the OPAP extractions and 6 or more for the D2EHPA extractions. Under the same conditions, OPAP exhibits a higher K_c for NH_3 than D2EHPA, particularly in light of the lower pH values of the raffinates from the extractions with OPAP. This is expected, since OPAP is a stronger acid than D2EHPA. Also, increasing the concentration of the extractant increased K_c, as expected. Use of an alcohol-containing diluent also increased K_c, as seen previously. The most important difference between the two extractants is the higher aqueous

TABLE 4.6

EXTRACTION OF AMMONIA BY D2EHPA AND OPAP

FEED = 0.58 M NH_4HCO_3 S/W (v/v) = 5

EXTRACTANT	[EXTRACTANT] (M)	DILUENT	K_c	$(P)^{(a)}$ (M)
OPAP	0.18	toluene	4.2	0.017
"	0.58	toluene	5.2	0.02
"	0.18	50% (v/v) 1-decanol/ toluene	7.5	0.009
D2EHPA	0.21	toluene	2.9	0.007
"	0.54	toluene	8.8	0.007
"	0.21	50% (v/v) 1-decanol/ toluene	6.1	0.001

(a): measured concentration of phosphorus in the aqueous raffinate solubility losses when OPAP was the extractant. This occurred despite the higher molecular weight of OPAP and the lower raffinate pH and may be due to the higher acidity of OPAP (Kunin and Winger, 1962).

OPAP shows no real advantage over D2EHPA as an extractant for NH_3 and results in higher aqueous solubility losses. Therefore, it was not considered further as an extractant for NH_3.

c. DNNSA and D2EHPA

The final extractant considered was dinonylnaphthalene sulfonic acid (DNNSA). It is a stronger acid than D2EHPA, and therefore should extract NH_3 better. When 0.2 $\underline{M}$ D2EHPA (as-received) in kerosene was used to extract ammonia from a 0.17 $\underline{M}$ ammonium carbonate solution at an aqueous-to-organic phase ratio of 0.8, the raffinate concentration was 0.036 $\underline{M}$ and the pH was about 5. K_c was 3. In a similar extraction, at an aqueous-to-organic phase ratio of one, 0.18 $\underline{M}$ DNNSA gave a raffinate concentration of 0.0069 $\underline{M}$ at a pH of about 4. K_c was about 21. Phase separation was slightly better with the DNNSA system, although both solvents showed a tendency to emulsify with the aqueous phase.

Figure 4.1 shows the results of a comparison of D2EHPA and DNNSA as extractants for NH_3. The conditions are described in Chapter 3, section D. The feed concentrations of sodium and ammonia were constant and the pH was varied by adding HCl. At pH below 3, the pK_a of D2EHPA, K_c for ammonia in the D2EHPA system is essentially zero. The H^+ concentration in the aqueous phase is high and H^+ is preferred over the other cations in solution by D2EHPA. DNNSA, being a stronger acid, does extract even at the low pH values. Above a certain pH (2 for DNNSA and 6 for D2EHPA)

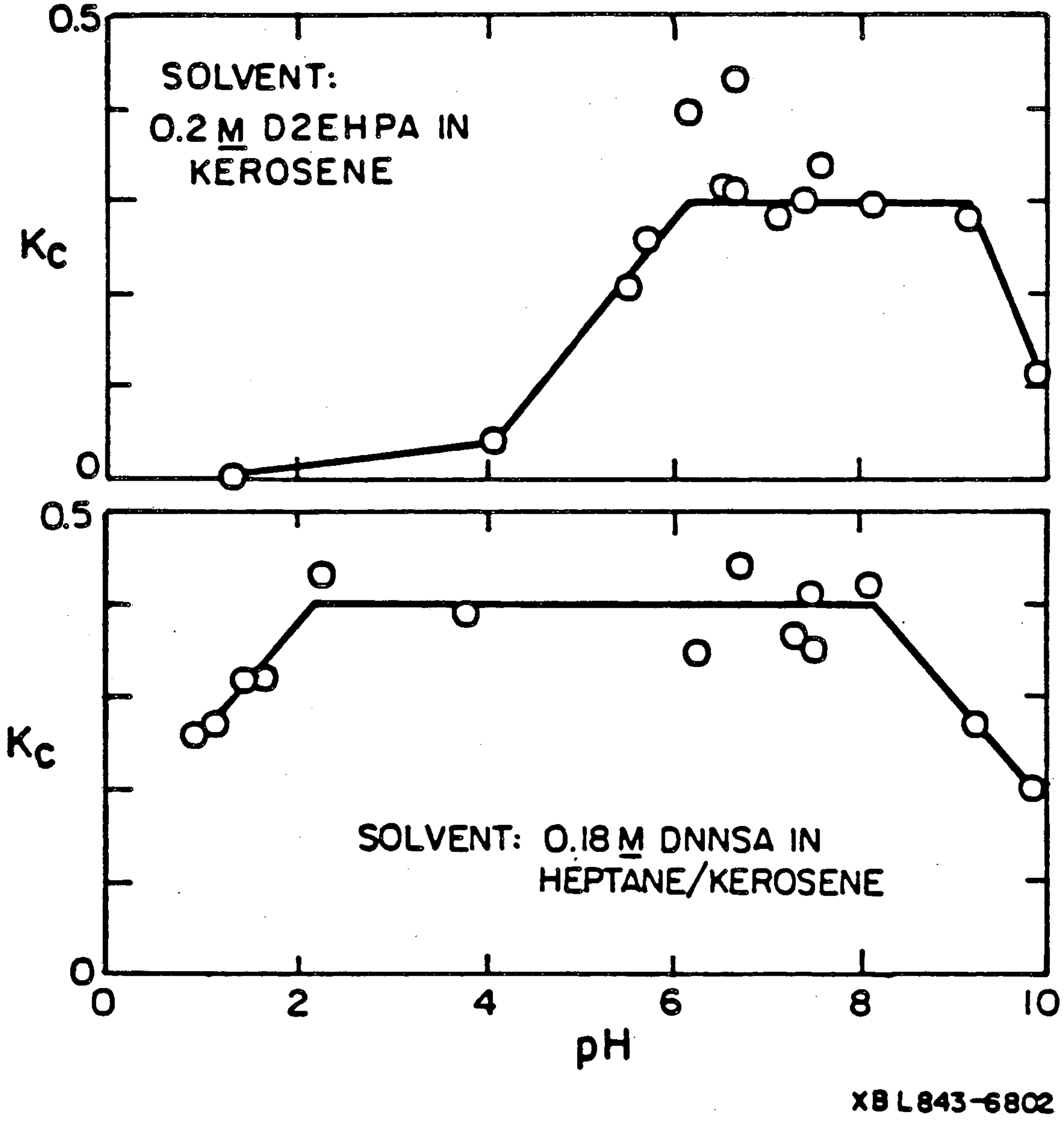


FIGURE 4.1: COMPARISON OF D2EHPA AND DNNSA AS EXTRACTANTS FOR AMMONIA. Feed = 0.48 M NaOH, 0.36 M $NaHCO_3$, 0.15 M NH_3; pH varied by HCl addition; W/S = 0.75.

K_c levels off. This corresponds to loading of the extractant with ammonium and sodium cations. As pH is increased an imperceptible increase in organic-phase ion-pair concentrations occurs along with a lowering of the already low concentration of unused acid.

For DNNSA, K_c for ammonia levels off at about 0.4. Assuming all of the acid not paired with ammonium is paired with sodium, then the K_c for sodium is 0.2. Thus DNNSA prefers ammonium slightly over sodium. Khophar and Narayanankutty (1968) found this to be true for a chloroform diluent (K_c ratio of 2.2), but not a hexane diluent (K_c ratio of 0.9). For D2EHPA, K_c for ammonia levels off at about 0.3. However the meaning of this value is questionable since three equilibrium phases were present above a pH of about 6. The phenomenon of third-phase formation in D2EHPA systems is well known and is discussed in Chapter 6.

For both the solvents at a pH above about 9, K_c for ammonia falls off, due to the decrease in α, the fraction of ammonia in the ammonium form.

A second comparison between D2EHPA and DNNSA was made by determining their ability to extract ammonia from ammonium chloride solutions. The conditions were the same as for the above-mentioned experiments, except that the feed was a 0.14 $\underline{M}$ NH_4Cl solution (pH about 6.9). A negligible amount of NH_3 was extracted by D2EHPA, just enough to lower the pH to 2.5. The DNNSA system gave a K_c of 1.1 at a raffinate pH of 1.36. In subsequent extractions the raffinate pH was raised by replacing some of the ammonium chloride with ammonium hydroxide, thus keeping the feed concentration of NH_3 the same. As more NH_4OH was added, phase separation in the D2EHPA system became worse, resulting in a white emulsion. The phase-separation problems in the

DNNSA system were not nearly so bad. Figure 4.2 shows the results for the DNNSA system.

For these data, the concentration of unused acid, [HA], is nearly constant. Therefore from Equation 4.5 log K_c versus pH should be linear with slope equal to 1. A least-squares fit to the data gives a slope of 1.02, supporting the extraction mechanism proposed. More rigorous analyses of DNNSA extraction systems, taking into account organic-phase micelle formation, are available elsewhere (Markovits and Choppin, 1973; van Dalen and Gerritsma, 1971; van Dalen et. al., 1974).

Both DNNSA and D2EHPA appeared to be useful extractants for NH_3. A qualitative assessment of relative regenerability was then made. The solvents used in the regeneration studies were 0.19 M DNNSA in Norpar 12, containing 0.07 M ammonia, and 0.2 M D2EHPA in Norpar 12, containing 0.1 M ammonia. These experiments are discussed in Chapter 3, section G.

In the first type of regeneration experiment, water was boiled underneath the organic phase at atmospheric pressure. For DNNSA the aqueous-to-organic phase ratio was 1; for D2EHPA it was 0.5. After the water had boiled through the solvent it was condensed in a side arm condenser, and its composition was measured. The organic-phase ammonia concentration was also measured. For DNNSA, no reduction in organic-phase NH_3 concentration occurred, and no ammonia was found in the aqueous distillate. For D2EHPA, a 32% reduction in organic-phase NH_3 concentration occurred, and 80% of the ammonia stripped from the organic phase was collected in the aqueous distillate. DNNSA is harder to regenerate than D2EHPA, as expected from its higher acid strength.

The regenerabilities of the solvents were also compared at temperatures up to 200°C. The diluent boiled at this temperature and

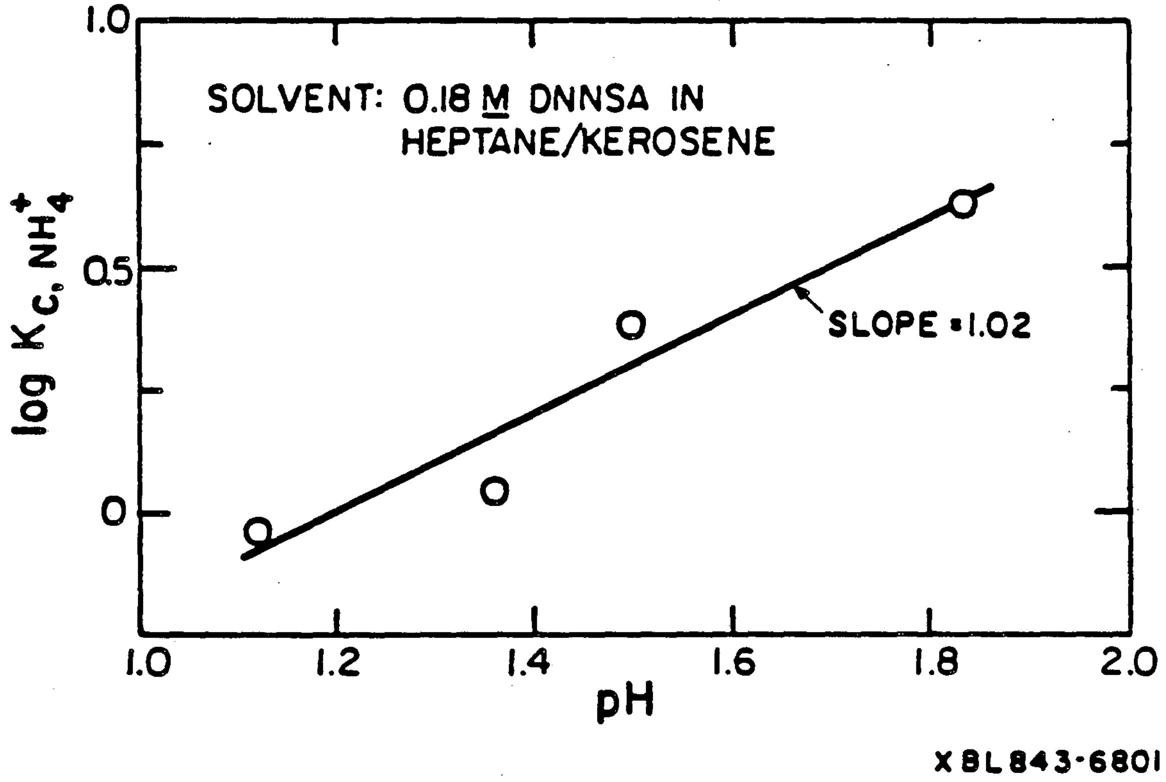


FIGURE 4.2: EXTRACTION OF AMMONIA BY DNNSA AT LOW pH.

Feed = 0.14 M NH_4Cl/NH_4OH; W/S = 0.75.

thus provided the stripping medium. In addition, nitrogen was introduced into the vapor space to aid in carrying the vapor through a sulfuric acid solution used to trap NH_3. Under the experimental conditions the diluent flowed back as reflux, so the solvent composition did not change drastically. For DNNSA, 100 ml of the above-mentioned solvent were held at 200°C for two hours. The nitrogen flow rate was 500 ml/min. For D2EHPA, 150 ml of the above-mentioned solvent were held at 200°C for two hours, and the nitrogen flow rate was 220 ml/min.

For the DNNSA system, a solid precipitated out of the solvent during the experiments. It was first detected at a temperature below 200°C. Measurements of ammonia concentration in an uncentrifuged organic phase showed that 81% of the NH_3 was lost from the organic phase. A centrifuged organic phase showed an 87% reduction in NH_3 concentration. This difference due to centrifuging was larger in other experiments. Apparently the solid contained NH_3, and this NH_3 could be detected to some extent by the analytical method used. This was confirmed as discussed below. No ammonia was found in the sulfuric acid trap.

For the D2EHPA system, the ammonia concentration in the organic phase was reduced to essentially zero and 72% of the ammonia lost from the organic phase was found in the sulfuric acid trap.

In order to assess the thermal stabilities of these extractants, the extracting power of a solvent that had been heated was compared to that for the unheated solvent. For DNNSA, three organic phases were compared. There were (1) 0.19 $\underline{M}$ DNNSA in Norpar 12, (2) 0.19 $\underline{M}$ DNNSA in Norpar 12, heated to 200°C and then centrifuged to remove the solid that had formed, and (3) 0.19 $\underline{M}$ DNNSA originally containing 0.07 $\underline{M}$ NH_3, heated to greater than 130°C. The NH_3 concentration of the last solvent was essentially zero after the heating process, and some solid was present in this solvent. These solvents were used to extract NH_3 from a 0.13 M ammonium chloride solution at an aqueous-to-organic phase ratio of 3. The K_c values measured for the three solvents were 1.5, 0.5, and 0.5, respectively. This indicated that heating DNNSA-containing solvents caused significant thermal degradation of DNNSA.

For D2EHPA the solvent regenerated at 200°C was contacted with a 0.56 M ammonium carbonate solution at an aqueous-to-organic phase ratio of 0.19. The K_c value was 3 and was essentially the same as that for a fresh D2EHPA solvent. Apparently no significant loss of D2EHPA occurred during the heating process. D2EHPA appears to be much more thermally stable than DNNSA. The thermal stability of D2EHPA is considered again in Chapter 6, section E.

The solid formed during heating of DNNSA was analyzed for elemental C, H, N, and S by the Micro-Analytical Laboratory of the College of Chemistry. The solid was generated in four different ways. (1) A solvent containing 0.19 M DNNSA was heated to 200°C. (2) A solvent of the same composition but containing 0.07 M NH_3 was heated to 200°C. (3) A solvent like that in (2) was heated to 200°C, but in this case, the solvent was first sparged for two hours with nitrogen at a flow rate of 200 ml/min, and during the heating process the vapor space was sparged with nitrogen at a rate of 330 ml/min. (4) A solvent was treated as in (3), except that the experiment was performed in darkness. Case (3) was designed to show the effect of eliminating oxygen from the environment. Case (4) was designed to show the effect of eliminating both oxygen and light. All solids were dried in a vacuum oven before analysis.

Table 4.7 compares the results for the four cases. No significant variation in the amount of solid formed in the different experiments was observed. The results are given as both the measured weight percent of each element in the solid (oxygen determined by difference) and the molar ratio of each element to sulfur. The expected compositions for DNNSA and for the ammonium salt of DNNSA are also given. There is no significant difference in the composition of the solids generated from an NH_3-containing solvent (cases 2,3, and 4). Hence neither oxygen nor light appears to be the culprit in the solid formation. The molar ratio of N to S is nearly one for these cases, indicating the incorporation of the ammonia nitrogen into the solid. This may also indicate that the ammonium salt of DNNSA is preferentially decomposed. The O content of the solids is high, while the C and H contents are low. This indicates that a significant portion of the alkyl part of the molecule is not incorporated into the solid decomposition product. The solids were all hygroscopic and lost weight while being weighed.

For the conditions in case (4), if all of the NH_3 lost from the solvent had been incorporated into the solid, then 1.1 grams of solid would have been produced. Solid collection was difficult, but 0.45 grams were collected. Therefore it appears that the loss of NH_3 from the solvent is due largely to solid formation.

No decomposition reaction was deduced, but it does appear that NH_3 cannot be stripped from a DNNSA-containing solvent without massive thermal decomposition of the extractant.

In addition to its non-regenerability, DNNSA is expected to have a high enough water solubility under process conditions to make it

TABLE 4.7

ELEMENTAL ANALYSES OF SOLIDS FORMED ON HEATING DNNSA

	CASE #					
ELEMENT	1	2	3	4	DNNSA	NH_4^+ SALT
			WEIGHT PERCENT			
C	53.12	10.22	18.17	24.92	73	70.4
H	5.34	4.73	6.01	5.86	9.6	9.9
N	0.13	7.29	7.80	7.85	0	2.9
S	9.24	20.78	19.03	22.44	7	6.7
O(a)	32.17	56.98	48.99	38.93	10.4	10.0
			MOLAR RATIO RELATIVE TO S = 1			
C	15.3	1.3	2.5	3	28	28
H	18.5	7.3	10.1	8.4	44	47
N	0.03	0.8	0.94	0.8	0	1
S	1	1	1	1	1	1
O	7	5.5	5.2	3.5	3	3

(a): determined by difference

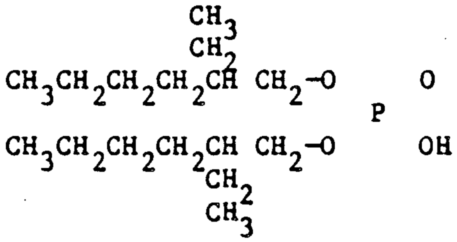
economically and environmentally unattractive (Kunin and Winger, 1962). For these reasons, DNNSA was not considered further as an extractant for NH_3 in this process.

The above results indicated that D2EHPA was the preferred extractant for NH_3. The remainder of this work concentrated on modifying and quantifying D2EHPA-solvent properties.

E. USES AND PHYSICAL PROPERTIES OF D2EHPA

D2EHPA is commonly used in the hydrometallurgical industry. It is used to extract uranium, vanadium, beryllium, zinc, nickel, cobalt and molybdenum on a commercial scale (Mobil Chemical Company, 1981; Ritcey and Ashbrook, 1979). In addition D2EHPA has been used on a research scale to extract numerous other metals (Peppard, 1966). In these processes the metal is stripped from the loaded D2EHPA solvent by reducing the metal to a lower oxidation state, making it less extractable, or by back-extracting the metal into an acidic or basic solution. Specific references to these works will be made as they become relevant.

The structure of D2EHPA is:



$$\begin{array}{llll}
\qquad\qquad\quad \mathrm{CH_3} & & & \\
\qquad\qquad\quad \mathrm{CH_2} & & & \\
\mathrm{CH_3CH_2CH_2CH_2CH} & \mathrm{CH_2{-}O} & & \mathrm{O} \\
 & & \mathrm{P} & \\
\mathrm{CH_3CH_2CH_2CH_2CH} & \mathrm{CH_2{-}O} & & \mathrm{OH} \\
\qquad\qquad\quad \mathrm{CH_2} & & & \\
\qquad\qquad\quad \mathrm{CH_3} & & &
\end{array}$$

Its physical properties are given in Table 4.8.

D2EHPA is considered a moderate toxin via oral and dermal routes. The LD_{50} for rats is 4940 mg/kg body weight (Sax, 1979). The LD_{50} for

TABLE 4.8

PHYSICAL PROPERTIES OF D2EHPA

Molecular weight	322.4
Appearance	Clear, colorless liquid
Density (20°C) (g/cc)	0.974
Viscosity, Brookfield (20°C) (cps)	56
Solubility (20°C): in water (wt %)	0.01
water in (wt %)	2.4
Cost (2/84) ($/lb)	2.60

Source: Mobil Chemical Company, 1981

rainbow trout is 49 - 56 ppm (Dave and Lidman, 1978). D2EHPA did not demonstrate mutagenic activity either directly or in the presnce of liver microsomal enzymes employing Salmonella indicator organisms (Mobil Chemical Company, 1981). D2EHPA is a skin irritant.

D2EHPA should be hydrolytically stable under the conditions of the proposed process. Its long, branched alkyl groups increase its resistance to hydrolysis, as does the steric hindrance provided by the ethyl group on the number-two carbon of the alkyl radical (Gamrath et. al., 1954). Alkaline hydrolysis should occur only in the presence of a strong base, at elevated temperatures, over a long period of time (McDowell, 1982). However, aqueous solutions of lower alkyl phosphoric acids do hydrolyze at elevated temperatures (Hooker, 1979). Salts of the alkylphosphoric acids are much less susceptible to hydrolysis (Hochwalt et. al., 1942).

The thermal degradation of alkyl phosphoric acids is acid-catalyzed (Gamrath et. al., 1954) and results in the formation of alkyl ethers and olefins as well as mono-alkyl phosphoric acids and orthophosphoric acids (Gamrath et. al., 1954; Hooker, 1979). Neutralizing the acid with NH_3 may increase its thermal stability (Gamrath et. al., 1954). Organic phosphoric acids containing branched alkyl radicals are less thermally stable than those containing straight-chain ones. However, if the H's on the number-two carbon are replaced with alkyl groups, the thermal stability of the compound increases (Gamrath et. al., 1954). Increase in molecular weight also increases thermal stability (Gamrath et. al., 1954). Acids containing straight-chain C_{12} radicals are reasonably stable at 100°C, but show measurable decomposition if held at 150°C for one hour. Significant decomposition occurs at about 200°C (Hooker, 1979).

The choice of diluent is known to affect solvent properties. In the next chapter results are given for the screening of several diluents for their effects on the solvent properties of D2EHPA.

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CHAPTER 5

SCREENING OF DILUENTS FOR D2EHPA

D2EHPA, being somewhat viscous, is almost always used in diluted form. In this chapter results are given for the screening of several diluents for D2EHPA. The effects of these diluents on the solvent properties of D2EHPA, particularly capacity of D2EHPA to extract NH_3 (K_c), aqueous solubility losses of D2EHPA and phase-separation properties, are examined.

A. EFFECT OF DILUENT ON DISTRIBUTION COEFFICIENT

The distribution coefficient for NH_4^+ into a D2EHPA-containing solvent as given by Equation 4.5 is properly written in terms of activities. In this case, K_{c,NH_4^+} may be expressed:

$$K_{c,NH_4^+} = \frac{[NH_4^+A^-]}{(NH_4^+)} = K_r \frac{[HA]\ \gamma^o_{HA}\ \gamma^a_{NH_4^+}}{a_{H^+}\ \gamma^o_{NH_4^+A^-}} \qquad (5.1)$$

where square brackets denote organic-phase concentrations, parentheses denote aqueous-phase concentrations and superscripts o and a denote organic and aqueous phase, respectively.

K_{c,NH_4^+} may be decreased by decreasing the activity of the free acid, either through reducing its concentration or its organic-phase activity coefficient. K_{c,NH_4^+} may be increased by decreasing the organic-phase activity coefficient of the ammonium/D2EHPA ion pair. Consequently any diluent which reduces the activity coefficient of the ion pair relative to that of the free acid will increase K_{c,NH_4^+}. This suggests that a diluent which solvates the ion pair better than the free acid will increase K_{c,NH_4^+} (Blumberg and Gai, 1977).

The effects of diluents on K_{c,NH_4^+} for D2EHPA-containing solvents are much discussed in the literature (Blumberg and Gai, 1977; Healy, 1967, 1968; Irving, 1967; Kolarik, 1967). These effects are very system-dependent, but some generalizations can be made.

The addition of basic compounds, such as tributyl phosphate (TBP) or trioctyl phosphine oxide (TOPO), as well as the addition of alcohols and phenols, to a solvent containing D2EHPA in some relatively inert diluent is often described in terms of synergism and antagonism. Synergism results when the observed K_c is larger than that predicted on the basis of data for extraction by each of the two components separately. In this case the two compounds are D2EHPA and the additive, or modifier. Synergism occurs when the modifier solvates or forms a complex with the cation/D2EHPA ion pair, resulting in a species which is more organophilic. The decrease in activity coefficient for the complex due to the solvation exceeds the decrease in activity coefficient of D2EHPA due to its interaction with the modifier. Antagonism is the opposite of synergism. In this case the modifier preferentially interacts with D2EHPA, rather than the ion pair, and K_c is less than expected. A synergistic coefficient, SC, may be defined as (Healy, 1968):

$$SC = \log \frac{K_{c,1+2}}{K_{c,1} + K_{c,2}} \qquad (5.2)$$

where:

$K_{c,1}$ = K_c for D2EHPA in diluent

$K_{c,2}$ = K_c for modifier in diluent

$K_{c,1+2}$ = K_c for D2EHPA plus modifier in diluent.

This definition implies that $K_{c,1+2}$ is determined at the same concentrations of D2EHPA and modifier used to determine $K_{c,1}$ and $K_{c,2}$, respectively. Alternatively, $K_{c,1}$ and $K_{c,2}$ must be weighted according to the relative amount of each component in the combined solvent.

For synergism, SC is positive and for antagonism, SC is negative. Often, both synergism and antagonism occur in the same system. For low concentrations of the modifier, SC is positive. But, as the modifier concentration increases, SC decreases and may become negative (Duyckaerts and Desreux, 1977).

In the extraction of trivalent metals, the highest K_c usually occurs into a non-polar diluent. K_c into aromatic diluents tends to be lower (Kolarik, 1967). The lowest K_c for both divalent and trivalent metals occurs into H-donor type diluents, especially alcohols (Blumberg and Gai, 1977; Kolarik, 1967). The very basic phosphoryl group of D2EHPA forms a strong complex with the alcohol, reducing the activity of D2EHPA and in at least one case, lowering K_c by six orders on magnitude (Kolarik, 1967). On the other hand, the addition of alcohols and phenols into D2EHPA-containing solvents produces a synergism for monovalent cations. Thus, Muir et. al. (1980) found that phenols increase K_c for Ag(I) and Cu(I), but not for Cu(II), Zn(II) nor Fe(II). Healy (1968) also reports this synergistic effect for the alkali metals, particularly Cs. In these cases, it is envisioned that the alcohol competes with water in the solvation sphere of the metal. If the metal is solvated by the alcohol or phenol it is more organophilic and thus should have a lower organic-phase activity coefficient. This effect is seen with monovalent cations but not with multivalent cations because the latter, having a smaller size-to-charge ratio, are more strongly hydrated (Muir et. al., 1980). Among the alkali metals, the synergism is greatest for the least hydrated metal, Cs.

Liem (1967) and Zangen (1963) both saw an increase in K_c for UO_2^{2+} and Am^{3+} as TBP was added to a solvent system containing di-n-butyl phosphoric acid. But above a certain concentration of TBP K_c declined, due to the formation of a complex between the acid and the ester. On the other hand, Navratil (1967) saw only a decrease in K_c for Hf^{4+} as TBP was added to the system. McDowell (1968) reports that TBP interacts with both the sodium and strontium salts of D2EHPA, but not much with the free acid alone.

Amines have also been used as modifiers in D2EHPA-containing solvents. Deptula (1971) reported a strong interaction between tri-n-octyl amine (TOA) and dialkyl phosphoric acids, resulting in antagonistic effects in the extraction of UO_2^{2+} and Cr^{6+}. However, if strong mineral acids were present in the aqueous phase, then the amine interacted with them to a certain extent and the antagonistic effect decreased. For the extraction of uranium from sulfuric acid solutions by TOA and a dialkyl phosphoric acid, a synergistic effect occurred at high sulfuric acid concentrations. This was attributed to the formation of a complex involving the metal, sulfuric acid, the amine and the dialkyl phosphoric acid. This synergistic effect was not observed when orthophosphoric acid was the mineral acid in the aqueous phase, because orthophosphoric acid is not effectively extracted by TOA. Gogia et. al.

(1983) report a synergism in the extraction of Zn(II) and Cd(II) by the addition of aliphatic and heterocyclic amines to solvents containing lower fatty acids. They attribute this effect to the organic bases replacing water molecules in the coordination sphere of the metal.

An additional effect on extraction occurs when the acid itself is capable of solvating the ion pair. This is known to occur in both carboxylic acid systems (Ashbrook, 1973) and D2EHPA systems (McDowell, 1971). If the acid can complex with the ion pair the extractibility of the ion pair is markedly higher (Hanson, 1971). However the overall effect on K_c will depend on the relative effects of the lowering of the activity of the acid versus the lowering of the activity of the ion pair as a result of such solvation.

Most of the large effects of diluents on K_c occur due to chemical interactions such as H-bonding, rather than through physical effects, such as polarity and dielectric constants (Kolarik, 1967).

In the extraction of NH_3 with D2EHPA, diluents or modifiers which interact preferentially with the ion pair, either through H-bonding with the phosphoryl group of the D2EHPA or through solvation of the ammonium cation, will increase K_c. Diluents which interact preferentially with D2EHPA will decrease K_c.

B. EFFECT OF DILUENT ON AQUEOUS EXTRACTANT LOSSES

Not much information is available on factors that affect solubility losses in systems containing liquid cation exchangers. The reason for this is two-fold. First, in the usual applications for these compounds the species being extracted are rather valuable and hence a substantial cost for solvent replacement can be tolerated. Second, most of these extractions are performed under conditions in which solubility losses are low, due to either low pH or high salt concentrations.

The solubility of a liquid cation exchanger into water is not a particularly useful value since it does not indicate the effect of diluents, pH or aqueous-phase salt concentrations.

Diluting the extractant will decrease its solubility into the aqueous phase due to its reduced organic-phase concentration. Gindin (1960) observed this effect. In addition, if the diluent can interact with the extractant, then extractant solubility losses will be less. Thus increasing solvent polarity or H-bonding power should lower solubility losses of the extractant (Baes, 1962). Hardy and Scargill (1959) found that adding TBP to an organic phase containing di-n-butyl phosphoric acid reduced extractant losses to the aqueous phase.

For acidic extractants, aqueous-phase solubility is found to increase with increasing pH, a rapid rise occurring above the pK_a of the acid (Ashbrook, 1972). However the salt concentration of the aqueous phase also has a large effect. Salts act to salt out the acid from the aqueous phase, thus lowering its aqueous solubility. In one case Ashbrook (1972) found a factor-of-ten decrease in aqueous solubility by increasing the salt concentration of the aqueous phase from 0.5 M to 4 M. Grinstead and Davis (1970) also saw a lowering of solubility losses with increases in salt concentration.

A generalized equation for expressing solubility losses can be derived as follows. The distribution of D2EHPA not in the ion pair, i.e. HA, between the organic and aqueous phases may be represented by:

$$[HA] \rightleftarrows (HA) \rightleftarrows (H^{+}) + (A^{-}) \qquad (5.3)$$

The equilibrium constant for this reaction is:

$$K_a = \frac{a_{H^+} (A^-) \gamma^a_{A^-}}{[HA] \gamma^o_{HA}} \tag{5.4}$$

Written in this way K_a depends on the solvent. A small K_a implies good solvation of free D2EHPA by the solvent. The activity coefficient for HA accounts for solution non-idealities such as complexation of D2EHPA with the ion pair. In the following equations all organic-phase effects are lumped into γ^o_{HA} and K_a is taken to be independent of the solvent.

The total concentration of acid in the aqueous phase, P, is:

$$P = (A^-) + (HA) + (NH_4^+A^-) \tag{5.5}$$

If it is assumed that all of the ion pair is dissociated in the aqueous phase due to the high dielectric constant of water, then the last term in Equation 5.5 is negligible. If it is further assumed that the pH is significantly greater than the pK_a of D2EHPA then (HA) is small compared to (A^-) and:

$$P = (A^-) , \quad \text{high pH} \tag{5.6}$$

Using Equation 5.6 in Equation 5.4 yields the desired relationship:

$$P = \frac{K_a [HA] \gamma^o_{HA}}{a_{H^+} \gamma^a_{A^-}} , \quad \text{high pH} \tag{5.7}$$

Thus, the total aqueous solubility of the extractant is dependent on the concentration of the extractant in the organic phase and inversely proportional to the activity of hydrogen ions in the aqueous phase. The salt concentration of the aqueous phase will affect the aqueous-phase activity coefficients. In Equation 5.5 the effect will be to change the pH at which the second term becomes small. In Equation 5.7 an increase in $\gamma^a_{A^-}$ will decrease aqueous extractant losses, thus producing the observed salting-out effect.

These equations must be considered only as approximations to the real case. They neglect organic-phase dimerization of the extractant and additional complexing of the ion pair by the acid. These effects as well as solvent effects are broadly lumped into the activity coefficient of the acid.

A related expression may be derived by combining Equations 5.1 and 5.7:

$$P = \frac{K_a \, [NH_4{}^+A^-] \, \gamma^o_{NH_4{}^+A^-}}{K_r \, (NH_4{}^+) \, \gamma^a_{NH_4{}^+} \, \gamma^a_{A^-}} \tag{5.8}$$

Again, Equation 5.8 is a simplification in that it neglects the organic-phase composition of species containing the ion pair. These effects as well as solvent effects are broadly lumped into the organic-phase activity coefficient of the ion pair.

Equations 5.7 and 5.8 are useful in that they can provide some insight into the effects of various diluents on aqueous solubility losses. Equation 5.8 may be expressed in terms of $K_{c,NH_4{}^+}$:

$$\frac{K_{c,NH_4^+}}{P} = \frac{K_r \gamma^a_{A^-} \gamma^a_{NH_4^+}}{K_a \gamma^o_{NH_4^+A^-}} \tag{5.9}$$

Similarly, Equation 5.7 may be expressed in terms of a distribution coefficient for H^+, K_{c,H^+}:

$$\frac{K_{c,H^+}}{P} = \frac{\gamma^a_{A^-}}{K_a \gamma^o_{HA}} \tag{5.10}$$

In this case, K_{c,H^+} is expressed in terms of the activity of the hydrogen ion, since this is the quantity usually measured.

For nearly similar aqueous phases, the quantities $K_{c,NH_4^+}/P$ and $K_{c,H^+}/P$ for different diluents give some insights into the effects of these diluents on organic-phase activity coefficients. Thus, if a diluent produces a relatively high $K_{c,NH_4^+}/P$ value, then γ for the ion pair in the organic phase is relatively low either due to diluent or complexation effects. The same can be said of $K_{c,H^+}/P$ and the free acid. It must be remembered however that only qualitative statements can be made based on such considerations.

From the above it is apparent that aqueous solubility losses can be affected by aqueous-phase pH, salt concentration and organic-phase reagent concentration. Diluent choice is also critical. A diluent which interacts with either D2EHPA or the ion pair will decrease aqueous solubility losses. A diluent which interacts with both of these will decrease losses even further. The availability of additional free acid to solvate the ion pair should also help to lower solubility losses.

D2EHPA costs \$2.60/lb (2/84, Mobil Chemical Company). A loss of 100 ppm will cost \$2.20/1000 gal of water treated. The total costs for this process in order for it to be competitive with similar processes, such as the Phosam-W process, should be between \$8 and \$11/1000 gal (Seufert et. al., 1979; King et. al., 1981). The portion of this cost that can be allotted to solvent-replacement costs will depend on the steam savings that this process can generate.

C. EFFECTS OF DILUENT ON PHASE-SEPARATION PROPERTIES

All liquid cation exchangers possess some surface activity (Kunin and Winger, 1962). This is a result of the presence of a hydrophilic group (the acid functionality) and a hydrophobic group (the hydrocarbon part). This interfacial activity increases with increasing pH as the acid group ionizes (Cox and Flett, 1977), at least for pH values below the pK_a of the acid. Inoue et. al. (1980) found that the fractional coverage of an aqueous/organic interface with the anion of Versatic 10 (a branched carboxylic acid) increased with increasing pH in the pH range less than 6, which is the approximate pK_a of Versatic 10.

Conversion of the acid to the salt form generally, although not always, increases its interfacial activity (Cox and Flett, 1977). The salt form would be expected to be more interfacially active than the acid because it is an ion pair and thus more hydrophilic. McDowell's observations suggest that the alkali salts of D2EHPA are more interfacially active than D2EHPA itself (McDowell, 1971).

1. EMULSION FORMATION

The presence in the organic phase of a species with significant surface activity results in a tendency for the organic phase to emulsify with the aqueous phase. Monovalent cations generally stabilize oil-in-water type emulsions (Adamson, 1982). These emulsions may be broken by increasing the oil-to-water phase ratio or by adding salts to the aqueous phase. Wu et. al. (1980) noted the effect of volumetric phase ratio on the phase-separation properties of D2EHPA in an octanol/kerosene diluent and an ammonium hydroxide solution. At a given concentration of D2EHPA and the ammonium/D2EHPA ion pair, decreasing the amount of the aqueous phase resulted in breaking of an oil-in-water emulsion and the formation of a clear aqueous phase.

Some qualitative experiments were performed to determine the nature of the phase-separation problems encountered in this work. Generally, after using a D2EHPA-containing solvent to extract NH_3, phase-separation problems manifested themselves in the formation of white emulsions. These emulsions either encompassed all of the contents of the system or existed as a white emulsion zone at the interface of the two phases. Various amounts of organic and aqueous phases existed above and below the emulsion zone respectively. When a white emulsion was centrifuged, the results were generally the same. The top organic phase was clear, the bottom phase was a little cloudy and a white zone existed at the interface. The size of this zone depended on the intensity and duration of centrifugation, but usually the zone could not be made to disappear entirely.

The effect of altering the solvent-to-water volumetric phase ratio (S/W) was also determined. To an emulsion formed when D2EHPA in Norpar 12 was used to extract NH_3, more water and more Norpar 12 were added. The addition of water served only to increase the volume of the emulsion. It centrifuged to a top clear phase, a white middle zone and a cloudy bottom phase. The addition of more Norpar 12 to the system broke the emulsion. Two phases formed and became clear on centrifugation. Similarly, when 25 ml of an emulsion formed in a system of D2EHPA/NH_3 in 50% (v/v) isodecyl alcohol/toluene was contacted with 25 ml of water, one white phase resulted. This eventually settled to a top white phase and a cloudy bottom phase. However, when 25 ml of Norpar 12 were added to 25 ml of the original emulsion, the emulsion broke to form a clear top phase, a slightly cloudy bottom phase and a small amount of white at the interface. When enough D2EHPA was added to this latter system to make the total addition of organic equal to 0.5 M D2EHPA in Norpar 12, the same phase-separation properties resulted. Also, when 4 ml of approximately 0.1 M NaCl were added to 4 ml of the emulsion, the emulsion broke and yielded two phases which cleared upon centrifugation. Finally, when the aqueous phase contained an amount of NH_3 in stoichiometric excess of the D2EHPA present in the solvent, phase-separation properties were generally excellent, except in the case of an aliphatic diluent. This case resulted in third-phase formation, which is discussed below. These results taken together indicate that D2EHPA-containing solvents, when partially converted to the ammonium salt, have a tendency to form oil-in-water type emulsions. These emulsions may be avoided by operating at low W/S and high raffinate concentrations.

Another way to reduce the tendency to form emulsions is by reducing the activity of the surface-active species in the organic phase. This may be accomplished through a judicious choice of diluent. For instance, Cox and Flett (1977) report an increase in interfacial tension in a D2EHPA-containing system when TBP was added. TBP interacted with D2EHPA in the bulk organic phase and decreased its interfacial activity. This increased the interfacial tension and would reduce emulsification tendencies. The addition of a few percent of alcohol to an organic phase to improve phase-separation properties is also well known (Cox and Flett, 1977; Kunin and Winger, 1962; Ritcey and Ashbrook, 1979).

McDowell (1971) reported increased phase-separation problems when a large fraction of D2EHPA in the organic phase was converted to the alkali salt form. This suggests that the complex formed when additional D2EHPA is available to solvate the ion pair is less interfacially active than the unsolvated complex.

2. ADDITIONAL PHASE-SEPARATION PROBLEMS

Two other phase-separation properties of D2EHPA-containing solvents are worth mentioning. The first is the tendency to form stable third phases. This occurs when the limiting solubility of a solute in the organic phase is reached. At this point the organic phase splits into two distinct and immiscible phases which are also immiscible with the aqueous phase (Mills and Logan, 1967). The heavier organic phase is generally gelatinous and richer in the solute. This phase also contains some diluent and some water (Brown and Healy, 1978; Ritcey and Ashbrook, 1979). Third-phase formation can be avoided by operating below the saturation level of the extractant or by using a diluent which can better solvate the solute or ion pair (Koch, 1968). Even weak interactions with the ion pair can eliminate the problem (Rozen, 1967). Modifiers, such as TBP or alcohols, added to the solvent can serve the same purpose.

In the present work third-phase formation was observed only with an aliphatic diluent. The nature of the middle phase was determined by adding more water and more Norpar 12 to it. The water caused the phase to become cloudy, while the Norpar 12 did not mix with it at all.

Third-phase formation was a problem in the experiments reported in Chapter 4, section D in which 0.2 M D2EHPA in kerosene was used to extract ammonium and sodium from aqueous phases containing large excesses of these species. It occurred when the pH was high enough to permit loading of the D2EHPA. However, when 0.48 M D2EHPA in Norpar 12 was loaded to 0.22 M NH_3 (for solvent-regeneration studies) only two phases resulted. Apparently the presence of additional free acid to solvate the ion pair can prevent third-phase formation.

The organic diluent also affects the tendency toward third-phase formation. When 19 ml of 0.48 M D2EHPA in Norpar 12 were contacted with 1.2 M NH_4HCO_3 at a S/W of 2, three phases resulted. When 2 ml of isodecyl alcohol were added, two phases resulted. Likewise, when 19 ml of a similar solvent were contacted with 0.58 M NH_4HCO_3 at a S/W of 0.9, three phases resulted. Adding 1 ml of Adogen 364 (a tertiary amine) produced two phases. Even the addition of 10 ml more of aqueous feed did not result in the formation of a third phase. To confirm the diluent effect further it was observed that 0.48 M D2EHPA in 50% (v/v) isodecyl alcohol/Norpar 12 could be loaded to near 100% NH_3 (as was done for the solvent-regeneration studies) without the formation of a third phase. Finally, attempts to load 0.2 M D2EHPA in Norpar 12 to 100% NH_3 resulted in third-phase formation, while only two phases resulted when the diluent was toluene.

Occasionally when the Norpar 12 diluent was used, systems on the verge of third-phase formation resulted. For instance, 0.2 M D2EHPA in

Norpar 12 contacted at a S/W of 1.4 with approximately 0.3 M NH_3 as ammonium carbonate produced a clear top phase and a cloudy bottom phase of a gel-like consistency. When the experiment was repeated, three phases resulted. Also, when 0.2 M D2EHPA in Norpar 12 was contacted with 0.5 M NH_3 as ammonium carbonate at a S/W of 2.8, two clear phases resulted. However, when attempts were made to measure the concentration of the bottom phase, the solution attacked the membrane of the NH_3 electrode, indicating the presence of a surface-active species. Back extraction of the top phase with sulfuric acid indicated that there was no measurable amount of ammonia in the organic phase. Attempts to use this top phase to extract NH_3 from a 0.56 M ammonium carbonate solution at S/W of 5 resulted in no NH_3 extraction. These results suggest that there was no D2EHPA in the top phase and that all of the D2EHPA was in the bottom phase. This system was apparently on the verge of third-phase formation.

As pointed out above, third-phase formation is a problem only at high conversion of D2EHPA to the ion pair in an aliphatic diluent.

Another interesting phenomenon in these systems is the formation of a single phase when the S/W ratio is very high. Ritcey and Ashbrook (1979) report that an organic phase containing 26% (v/v) D2EHPA (about 0.8 M) and 6% (v/v) TBP in undecane contacted with a stoichiometric equivalent of 27 wt % NH_4OH (about 14 M) yields one clear phase. The S/W is about 20. This was confirmed here. Decreasing the S/W to 10 by adding more 27 wt % NH_4OH still produced one phase. Similar results were obtained with MIBK as the diluent. However if the aqueous phase were instead 0.5 M NH_4OH at a stoichiometric amount (S/W of 0.72), only two phases resulted. The top phase was cloudy and the bottom phase was white. Conversion of a large fraction of D2EHPA to the salt form generally increases the amount of water coextracted (McDowell and Coleman, 1965).

These experiments point out the importance of coextracted water in these systems. Variables affecting the amount of water coextracted will be discussed Chapter 6, section D.

In summary, the most important phase-separation problem in these systems is that of emulsion formation. In an actual process this is undesirable because the phase-separation rate may limit the throughput of the process. In addition emulsion formation may represent additional losses of reagent.

Emulsion-formation tendency will be affected by diluent, the degree of conversion of D2EHPA to the ion pair and aqueous-phase composition. A diluent which interacts with either D2EHPA, or preferably with the more interfacially active ion pair, will reduce the activity of these species and thus reduce their interfacial activity. This will increase interfacial tension and hinder emulsion formation. The presence of additional D2EHPA to solvate the ion pair will also reduce emulsification tendencies. Finally, a high salt concentration in the aqueous phase will improve phase-separation properties.

Experimental results for the effects of various diluents on the capacity of D2EHPA to extract NH_3, D2EHPA solvent losses and aqueous/organic phase-separation properties are described below.

D. RESULTS OF DILUENT SCREENINGS

The procedures followed here are given in Chapter 3, section E. In all cases described below, the pH was low enough (between about 6 and 8) that K_{c,NH_4^+} was essentially equal to K_c and was calculated as the concentration of the ammonium/D2EHPA ion pair in the organic phase divided by the concentration of ammonia in the aqueous raffinate, both expressed as moles/liter; see Equation 3.1. $K_{c,NH_4^+}/P$ is equal to the measured value of K_{c,NH_4^+} divided by the concentration of phosphorus in the aqueous raffinate, expressed as moles/liter.

1. ONE-DILUENT SYSTEMS

Table 5.1 presents results of extractions using various diluents for D2EHPA. Nitrobenzene is an unsatisfactory diluent. It formed a soapy white aqueous phase, which contained a gel-like substance. Of the remaining solvents, Norpar 12 appears to offer the least solvation to the ion pair, based on the low $K_{c,NH_4^+}/P$ value. It produced the highest extractant losses, but note that this value represents only about 1.5% of the D2EHPA in the system, which is unimportant in terms of extraction properties. Relative to Norpar 12 isobutyl heptyl ketone (IBHK) offers some weak solvation as seen through the reduced extractant losses. The aromatic compounds offer significantly more solvation. Phase-separation properties were also slightly better in the latter cases, further suggesting that the Π electrons of the aromatic are solvating the ion pair and probably also D2EHPA. From the standpoints discussed so far the best diluent listed is 12% (v/v) 1-decanol in toluene. This diluent gave a high $K_{c,NH_4^+}/P$ value and excellent phase-separation properties, indicating a strong interaction between the alcohol and the ion pair.

Increasing the concentration of D2EHPA in the solvent while keeping the ion-pair concentration constant increased the value of $K_{c,NH_4^+}/P$ and

TABLE 5.1

EFFECT OF SINGLE DILUENT ON D2EHPA SOLVENT PROPERTIES

SOLVENT: 0.2 M D2EHPA IN DILUENT   S/W (v/v) = 5

DILUENT	(N)(a)	(P)(b)	K_c	$K_{c,NH_4^+}/P$	PHASE SEPARATION(e)		
	(M)	(M)			O	A	I
Nitrobenzene(c)	-	-	-	-	-	-	-
Norpar 12	0.031	0.013	3.3	2.5×10^2	1	4	4
IBHK	-	0.009	-	-	1	3	4
Toluene	0.034	0.0058	2.9	5.0×10^2	-	(d)	-
Chevron 25	0.032	0.0057	3.1	5.4×10^2	1	3	4
Methylene chloride	-	0.004	-	-	1	4	4
12% (v/v) 1-Decanol in toluene	0.021	0.0027	4.3	1.6×10^3	1	1	2

continued on next page

TABLE 5.1, continued

SOLVENT: 0.5 $\underline{M}$ D2EHPA IN DILUENT   S/W (v/v) = 5

DILUENT	$(N)^{(a)}$	$(P)^{(b)}$	K_c	$K_{c,NH_4^+/P}$	PHASE SEPARATION$^{(e)}$		
	$(\underline{M})$	$(\underline{M})$			O	A	I
Nitrobenzene	-	0.0083	-	-	1	2	2
IBHK	-	0.0043	-	-	1	1	2
Toluene	0.01	0.0055	9.0	1.6×10^3	1	2	2
Methylene chloride	-	0.0037	-	-	1	1	2
12% (v/v) 1-Decanol in toluene	0.0081	0.0033	9.9	3.0×10^3	1	1	2

(a): total concentration of ammonia in raffinate
(b): measured concentration of phosphorus in raffinate
(c): aqueous phase was soapy white with gel-like material in it - no measurements were made
(d): phase-separation properties varied from a white emulsion zone at interface to a single white emulsion
(e): Key to Phase-Separation Properties:

O = Organic Phase:
1 = clear
2 = white

A = Aqueous Phase:
1 = clear
2 = cloudy
3 = cloudy white
4 = white

I = Interface:
1 = clear
2 = white dot on interface
3 = white line at interface
4 = white zone at interface
(if A = 4, then I = 4)

improved phase-separation properties for the toluene diluent. This indicates that additional D2EHPA solvates the ion pair, lowering its activity coefficient and making it less interfacially active. For the alcohol diluent, the effect on $K_{c,NH_4^+/P}$ is similar, although not as large. Apparently, the alcohol offers significant solvation to the ion pair, so that the effect of additional solvation by D2EHPA is not as important as in the toluene-diluent case.

The pH values were estimated by pH paper to be lower for the more concentrated D2EHPA solvents. The higher K_c values in these cases are due to the higher D2EHPA concentration. The comparable solubility losses between the low and high D2EHPA concentration cases despite the higher concentration of D2EHPA in the latter case also reflect the lower pH values. It does not appear to be possible to make a meaningful statement about the relative values of the activity coefficients of D2EHPA in the different diluents.

2. MODIFIER-PLUS-DILUENT SYSTEMS

Using a mixed diluent of some relatively inert diluent plus a modifier takes advantage of the chemical nature of a modifier which might be too viscous to be used alone. Several Lewis acids and bases were added as modifiers to toluene in a mixed diluent in order to examine their effects on D2EHPA-solvent properties.

a. Weak Lewis Bases and Acids added as Modifiers to Toluene

In these and subsequent experiments, 0.58 $\underline{M}$ NH_4HCO_3 was contacted with approximately 0.2 $\underline{M}$ D2EHPA in toluene plus various amounts of modifier. The S/W was approximately 5. Results for NH_3 extraction are presented in Figure 5.1. Results for aqueous extractant losses are presented in Figure 5.2. Table 5.2 summarizes the data for the weak Lewis bases hexyl ether (HE) and IBHK and for the weak Lewis acid 1,1,2,2-tetrachloroethane. Phase-separation tendencies are also indicated. These three compounds all have little effect on D2EHPA capacity for NH_3, but greatly increase extractant losses. They offer little solvation to the ion pair as seen through the decrease in $K_{c,NH_4^+/P}$ values as more modifier is added to the solvent. Phase-separation properties were also rather poor. Apparently, toluene interacts with the ion pair better than does any of these compounds. The relative constancy of K_c values suggests that toluene must also interact more strongly with D2EHPA than these compounds do. These particular Lewis bases and acid are too weak to exhibit any specific interaction with D2EHPA.

Baes (1962) reports that the solvating power of these diluents for dialkyl phosphoric acids increases from aliphatics to ethers to toluene to MIBK. The higher molecular weight of IBHK compared to MIBK will dilute the functionality of the IBHK and reduce its solvating powers. The results here are consistent with this ordering of solvating power.

b. Strong Lewis Bases added as Modifiers to Toluene

The experimental conditions were the same as those described above. Results for percent NH_3 extracted are presented in Figure 5.1 and for aqueous extractant losses in Figure 5.2. Table 5.3 summarizes the results.

Base strength for the compounds studied increases from TOPO to the tertiary amine, Adogen 364 (A364) to the secondary amine, Amberlite LA2

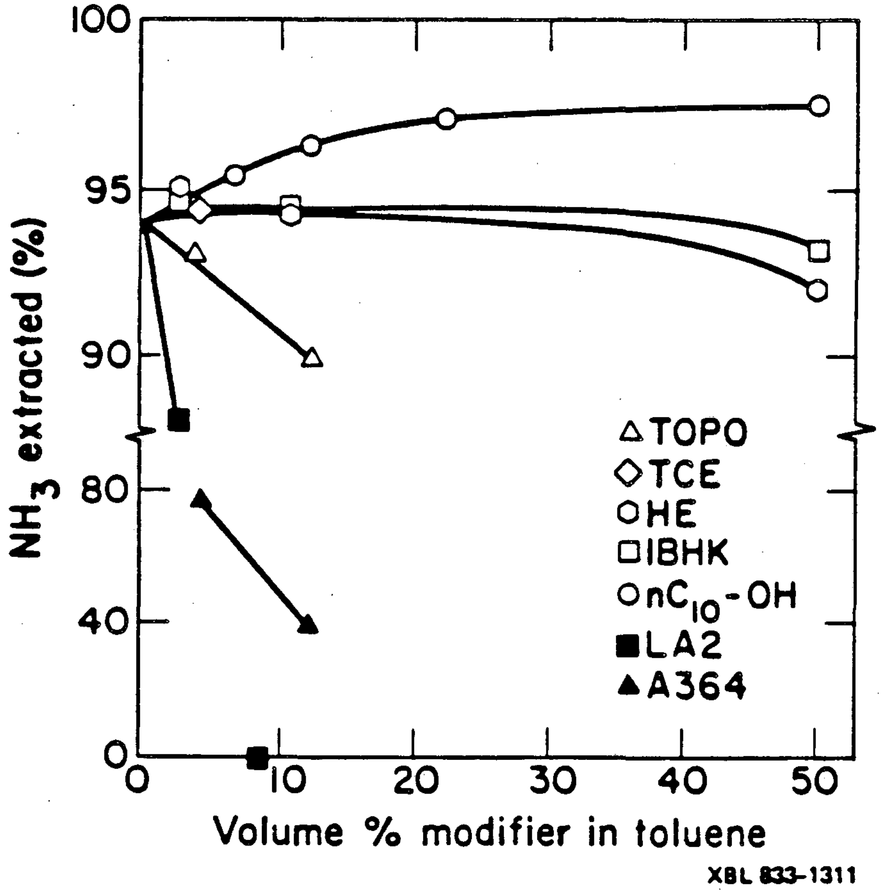

FIGURE 5.1: EFFECT ON D2EHPA EXTRACTION OF AMMONIA OF ADDING VARIOUS LEWIS ACIDS AND BASES AS MODIFIERS TO A TOLUENE DILUENT. Aqueous feed = 0.58 M NH_4HCO_3; 0.2 M D2EHPA in organic phase; S/W (v/v) = 5. Modifiers: TOPO = Tri-n-octyl phosphine oxide; TCE = 1,1,2,2-Tetra chloroethane; HE = Hexyl ether; IBHK = Isobutyl-heptyl ketone; nC_{10}-OH = 1-Decanol; LA2 = Amberlite LA-2; A364 = Adogen 364.

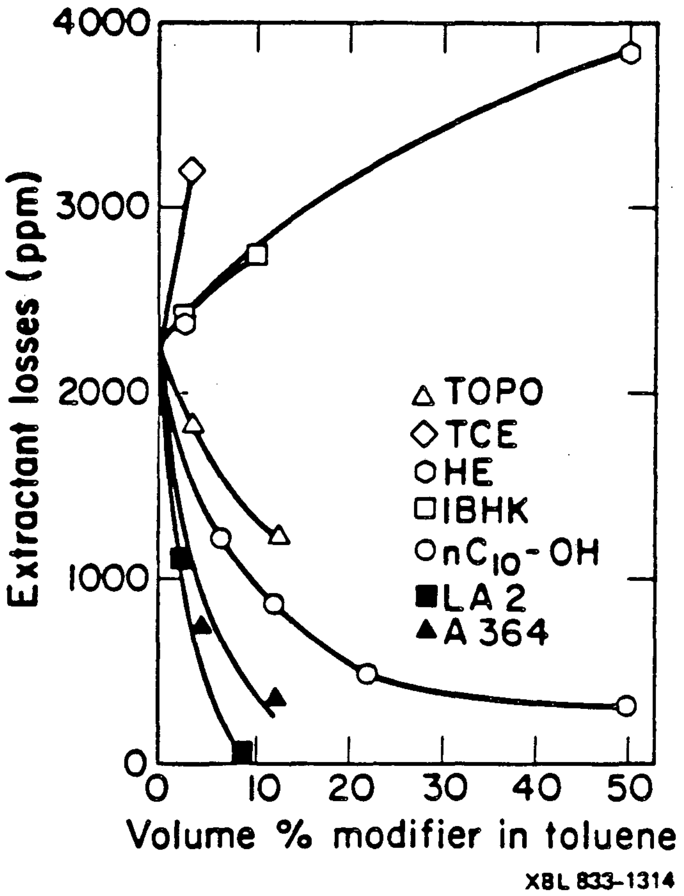

FIGURE 5.2: EFFECT ON D2EHPA AQUEOUS SOLUBILITY LOSSES OF ADDING VARIOUS LEWIS ACIDS AND BASES AS MODIFIERS TO A TOLUENE DILUENT.

Legend: see Figure 5.1.

TABLE 5.2

EFFECTS OF WEAK LEWIS BASES AND ACIDS ON D2EHPA SOLVENT PROPERTIES

SOLVENT: 0.2 M D2EHPA IN TOLUENE PLUS MODIFIER   S/W (v/v) = 5

MODIFIER	VOL % MODIFIER	(N)(a) (M)	K_c	$K_{c,NH_4^+}/P$	PHASE SEPARATION(b) O	A	I
Hexyl ether	2.3	0.028	3.3	4.5×10^2	2	4	4
"	10.4	0.031	2.7	4.4×10^2	2	4	4
"	50	0.045	2.1	1.8×10^2	1	3	4
IBHK	2.3	0.030	3	4.1×10^2	2	4	4
"	10.4	0.030	2.8	3.3×10^2	2	4	4
1,1,2,2-Tetrachloroethane(c)	1.1	-	-	-		←poor→	
"	3.4	0.033	3	3.0×10^2	2	4	4

(a): total concentration of ammonia in raffinate
(b): see Table 5.1 for key to phase-separation properties
(c): poor phase-separation properties prohibited measurements

TABLE 5.3

EFFECTS OF STRONG LEWIS BASES ON D2EHPA SOLVENT PROPERTIES

SOLVENT: 0.2 M D2EHPA IN TOLUENE PLUS MODIFIER S/W (v/v) = 5

MODIFIER	VOL % MODIFIER	MOLAR RATIO: MODIFIER/D2EHPA	(N)[a] (M)	K_c	$K_{c,NH_4^+}/P$	PHASE SEPARATION[b]		
						O	A	I
TOPO	3.4	0.45	0.040	2.4	4.3×10^2	1	3	4
"	12.2	1.8	0.058	1.4	3.8×10^2	1	1	1
Adogen 364	4	0.42	0.13	0.62	2.7×10^2	1	1	1
"	12.2	1.4	0.36	0.11	1.0×10^2	1	1	1
Amberlite LA-2	2.3	0.25	0.068	1.4	3.9×10^2	1	3	3
"	8.4	1.0	0.58	~0	-	1	1	1

(a): total concentration of ammonia in raffinate
(b): see Table 5.1 for key to phase-separation properties

(LA2) as discussed in Chapter 4, section B. These compounds all decrease D2EHPA capacity to extract NH_3 and decrease aqueous extractant losses. The effects are smallest for the weakest base (TOPO) and largest for the strongest base (LA2).

In these cases, the raffinate pH values were estimated by pH paper to be higher than those for the toluene-diluent raffinate. Despite these higher pH values, K_c values were significantly reduced as more Lewis base modifier was added to the system. This suggests that the bases strongly interact with D2EHPA, lowering its activity and lowering K_c. Indeed, when LA2 was present in stoichiometric equivalence with D2EHPA, the K_c value was reduced essentially to zero. The reduction in the activity coefficient of D2EHPA by the Lewis bases is also seen by recognizing that, despite the higher pH values and equal or even greater concentrations of free D2EHPA, extractant losses in these cases were less than for the toluene-diluent case. These arguments indicate that these modifiers produce high $K_{c,H^+/P}$ values.

The reduction in $K_{c,NH_4^+/P}$ as these modifiers are added to the solvent suggests that these bases solvate the ion pair less than toluene does.

The improvement in phase-separation properties when these modifiers are added to the solvent is a result of three possible effects. These are the reduction in D2EHPA activity, the reduction in concentration and hence activity of the ion pair, and the relatively high raffinate concentrations.

It is interesting to compare the 12.2% (v/v) A364 case with that for a toluene diluent that produced a similar raffinate. Contacting 0.2 <u>M</u> D2EHPA in toluene with 0.58 <u>M</u> NH_4HCO_3 at a S/W of 2 resulted in near complete loading of the D2EHPA with NH_3. The raffinate concentration was estimated to be about 0.3 M, making K_c equal to 0.6. The extractant losses were about 320 ppm. Thus $K_{c,NH_4^+/P}$ was 615. The phase-separation properties were the same as for the amine case being considered. In both of these cases, the raffinate pH and aqueous extractant losses were about the same. However for the toluene diluent the concentration of free D2EHPA was very low relative to the amine case. Therefore the activity coefficient for D2EHPA in the amine case must be much lower than in the toluene-diluent case. The relatively large $K_{c,NH_4^+/P}$ value for the toluene case is unexpected. Loading of D2EHPA with NH_3 is expected to lower $K_{c,NH_4^+/P}$. In addition the phase-separation properties for the toluene case were better than expected. These two effects may be due to the high raffinate concentration, and this may be affecting the results for the amine modifier as well.

It may be safely stated however that these Lewis bases interact strongly with D2EHPA, reducing its capacity to extract NH_3 and reducing extractant losses at a given pH and concentration of free acid.

c. Alcohols, Phenols, and Carboxylic Acids added as Modifiers to Toluene

These experiments were performed as described above. The results for D2EHPA capacity to extract NH_3 are given in Figure 5.3. The results for D2EHPA extractant losses are given in Figure 5.4. Results are summarized in Tables 5.4 and 5.5.

The modifiers tested may be divided into two types, those that are sterically unhindered around the OH group and those which are hindered. The sterically unhindered compounds are n-octanol (nC_8OH), n-

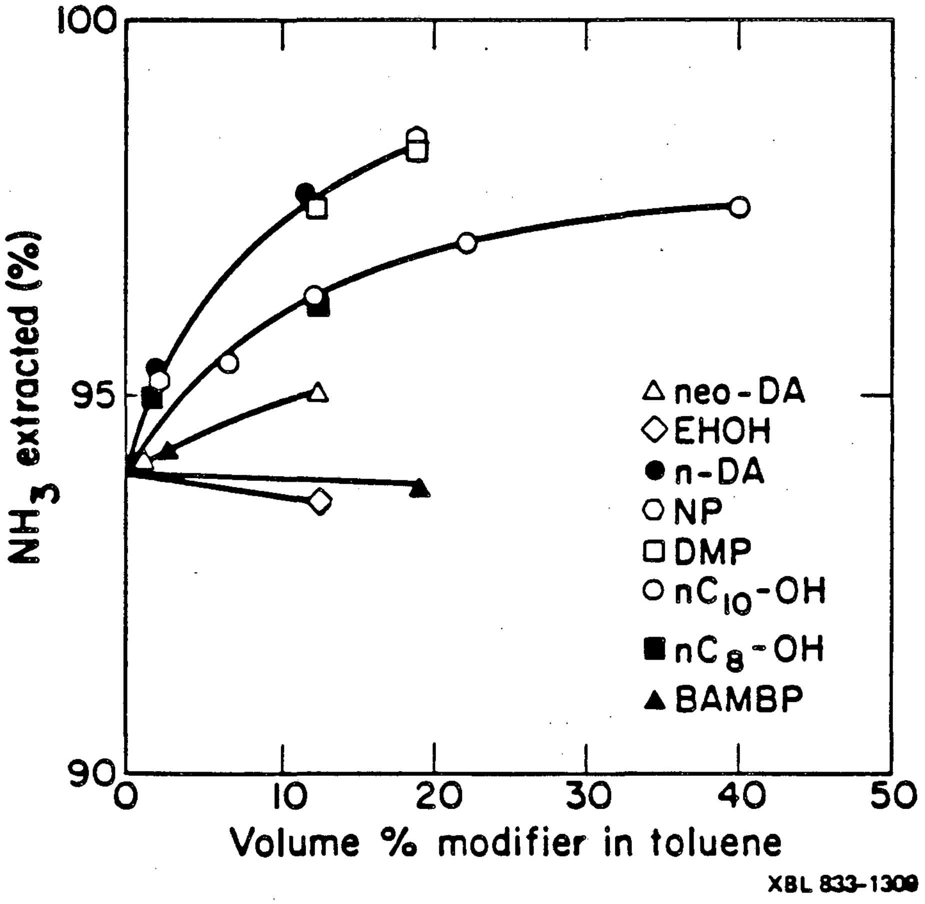

FIGURE 5.3: EFFECT ON D2EHPA EXTRACTION OF AMMONIA OF ADDING VARIOUS ALCOHOLS, PHENOLS, AND CARBOXYLIC ACIDS AS MODIFIERS TO A TOLUENE DILUENT.

Aqueous feed = 0.58 M NH_4HCO_3; 0.2 M D2EHPA in organic phase; S/W (v/v) = 5. Modifiers: n-DA = 1-Decanoic acid; EHOH = 2-Ethyl-1-hexanol; neo-DA = Neodecanoic acid; NP = Nonyl phenol; DMP = 2,4-Dimethyl phenol; nC_{10}-OH = 1-Decanol; nC_8-OH = 1-Octanol; BAMBP = 4-sec-butyl-2-(α-methyl benzyl) phenol.

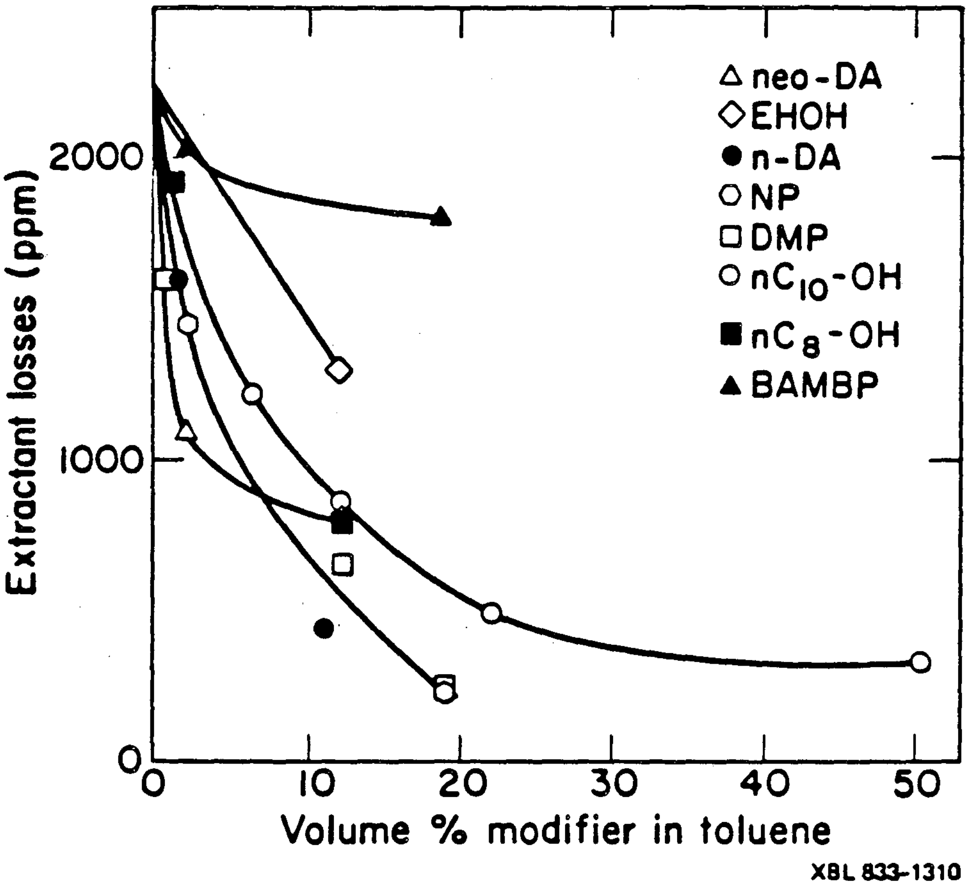

FIGURE 5.4: EFFECT ON D2EHPA AQUEOUS SOLUBILITY LOSSES OF ADDING VARIOUS ALCOHOLS, PHENOLS, AND CARBOXYLIC ACIDS AS MODIFIERS TO A TOLUENE DILUENT.

Legend: see Figure 5.3.

TABLE 5.4

EFFECTS OF ALCOHOLS ON D2EHPA SOLVENT PROPERTIES

SOLVENT: 0.2 M D2EHPA IN TOLUENE PLUS MODIFIER S/W (v/v) = 5

MODIFIER	VOL % MODIFIER	(N)(a)	K_c	$K_{c,NH_4^+}/P$	PHASE SEPARATION(b)		
		(M)			O	A	I
1-Octanol	1.6	0.029	3.5	5.8×10^2	1	2	4
"	12.2	0.022	4.1	1.6×10^3	1	1	2
1-Decanol	1.8	0.027	3.8	4.9×10^2	1	2	4
"	6.4	0.025	3.9	1.1×10^3	1	2	2
"	12.2	0.021	4.3	1.6×10^3	1	1	2
"	22	0.018	4.4	2.9×10^3	1	1	2
"	50	0.015	6.8	7.7×10^3	1	1	2
"	70	0.0098	11	1.2×10^4	1	1	2
"	100	0.0086	12.5	1.8×10^4	1	1	2
2-Ethyl-1-hexanol(c)	1.6	-	-	-	←poor→		
"	12.2	0.037	2.4	7.5×10^2	1	1	2

(a): total concentration of ammonia in raffinate
(b): see Table 5.1 for key to phase-separation properties
(c): poor phase-separation properties prohibited measurements

TABLE 5.5

EFFECTS OF PHENOLS AND CARBOXYLIC ACIDS ON D2EHPA SOLVENT PROPERTIES

SOLVENT: 0.2 $\underline{M}$ D2EHPA IN TOLUENE PLUS MODIFIER   S/W (v/v) = 5

MODIFIER	VOL % MODIFIER	(N)(a) ($\underline{M}$)	K_c	$K_{c,NH_4^+}/P$	PHASE SEPARATION(b)		
					O	A	I
Nonyl phenol	2.2	0.028	3.6	8.0×10^2	1	1	2
"	18.8	0.009	9.5	1.4×10^4	1	1	2
2,4-Dimethyl phenol	1.1	0.034	2.9	5.9×10^2	1	1	2
"	12.2	0.015	6.1	3.1×10^3	1	1	2
"	18.8	0.011	7.9	1.0×10^4	1	1	2
BAMBP	2.2	0.033	3.0	4.8×10^2	1	3	3
"	18.8	0.036	2.3	4.1×10^2	1	3	2
1-Decanoic acid	1.8	0.026	3.8	7.6×10^2	1	1	1
"	11.3	0.013	7.0	5.0×10^3	1	1	1
Neodecanoic acid	1.9	0.034	2.9	8.6×10^2	1	2	4
"	12.2	0.030	3.0	1.2×10^3	1	1	3

(a): total concentration of ammonia in raffinate
(b): see Table 5.1 for key to phase-separation properties

decanol ($nC_{10}OH$), 2,4-dimethyl phenol (DMP), nonyl phenol (NP) and decanoic acid (n-DA). The sterically hindered compounds are 2-ethyl-1-hexanol (EHOH), 4-sec-butyl-2-(α-methylbenzyl) phenol (BAMBP) and neodecanoic acid (neo-DA).

The sterically unhindered compounds increase D2EHPA capacity for NH_3, lower aqueous extractant losses, and improve phase-separation properties. $K_{c,NH_4^+/P}$ values increase with the addition of these modifiers to toluene. These effects all indicate that these compounds strongly solvate the ammonium/D2EHPA ion pair. These effects are larger for the phenols and carboxylic acids than for the alcohols. The former are stronger acids than alcohols. This suggests that these compounds solvate the ion pair via H-bonding with the phosphoryl group. This type of solvation may also make the ammonium cation more amenable to solvation by the basic functional groups of these compounds, either the O in the OH group or the carbonyl of the acid group. The extent of solvation of D2EHPA by these compounds is not readily discernible from the data.

The compounds which are sterically hindered around the OH group do not show these effects to as large an extent as the sterically unhindered compounds. They apparently cannot enter into a complex with the ion pair as readily.

The effects of changing the alcohol and the carrier diluent were also studied. In Table 5.6 results for extractions with different isomers of decanol and different diluents are given. The conditions for these experiments are the same as those given above.

The first two entries compare results for 1-decanol and isodecyl alcohol (a mixture of isomeric trimethyl heptanols, USS Chemicals). The

TABLE 5.6

EFFECTS OF DECANOL ISOMERS AND DILUENTS ON D2EHPA SOLVENT PROPERTIES

SOLVENT: 0.2 M D2EHPA IN 50% (v/v) DECANOL IN DILUENT   S/W (v/v) = 5

$[NH_4^+A^-] = 0.1$ M

DECANOL	DILUENT	(N)[a] (M)	(P)[b] (M)	K_c	$K_{c,NH_4^+/P}$	# of MEASUREMENTS
1-Decanol	Toluene	0.015	0.0009	6.8	7.7×10^3	4
Isodecyl alcohol	Toluene	0.018	0.0013	5.5	4.4×10^3	3
"	Chevron 25	0.017	0.0014	5.8	4.2×10^3	4
"	Hi-Sol 4-2	0.014	0.0020	7.3	3.7×10^3	2
"	Decalin	0.010	0.0018	10.5	5.8×10^3	1
"	Norpar 12	0.018	0.0017	5.6	3.2×10^3	3
Alfol 10	Norpar 12	0.013	0.0013	7.7	5.9×10^3	2

(a): total concentration of ammonia in raffinate
(b): measured concentration of phosphorus in raffinate

NH_3 extraction is about the same but aqueous extractant losses appear higher for the isodecyl alcohol. However part of this is due to the presence of a phosphorus-containing impurity found in the isodecyl alcohol. Contacting water with 50% (v/v) isodecyl alcohol in Chevron 25 at a S/W of 5 produced 6 ppm phosphorus in the aqueous phase. This is about 0.0002 M and could account for the slight difference between the two alcohols. Norpar 12 was also found to contain a phosphorus impurity, also yielding about 6 ppm phosphorus in the aqueous phase in a similar test. Chevron 25, Alfol 10 (commercial n-decanol, Conoco Chemical) toluene and Adogen 364 did not contain phosphorus impurities. Taking this into account, there appears to be no difference between 1-decanol and isodecyl alcohol with respect to effects on D2EHPA-solvent properties. There also appears to be no difference in effect between aromatic diluents, such as toluene, Chevron 25 and Hi-Sol 4-2, and Norpar 12 as diluents for the alcohol. The difference between Alfol 10 and isodecyl alcohol can also be attributed to the phosphorus impurity in isodecyl alcohol. Isodecyl alcohol in decalin appears to be a better diluent for D2EHPA in terms of ion-pair solvation, but this is based on only one data point and may not be significant.

Overall, it appears that the nature of the diluent used for the alcohol modifier is insignificant compared to the effects produced by the alcohol itself. This suggests that the alcohol has strong specific interactions with the ion pair and maybe with D2EHPA which are much larger than the physical effects of the diluent alone.

d. Synergistic Coefficient

Any of these results can be expressed in terms of the synergistic coefficient (SC). Solvent 1 would be D2EHPA at a given concentration in toluene. Solvent 2 would be the modifier in toluene. The combined solvent would be D2EHPA at the given concentration in the modifier plus toluene. For all of the modifiers studied, except decanoic acid, $K_{c,2}$ was essentially zero. Therefore, SC is equal to the log of the ratio of K_c for D2EHPA plus the modifier in toluene to K_c for D2EHPA in toluene. For the alcohols, phenols, and carboxylic acids, SC is positive. For the amines and TOPO, SC is negative.

Two types of useful modifier behavior were discerned by the studies reported in this chapter. First, there are the modifiers which increase K_c and decrease extractant losses, mostly through solvating the ion pair. Second, there are the modifiers which decrease K_c and decrease extractant losses mostly through solvating D2EHPA. In the next chapter, the properties of solvents representing these two classes are examined in more detail. Specifically, the properties of D2EHPA in the following diluents will be studied: (1) 50% (v/v) decanol in toluene or Norpar 12; (2) Adogen 364 in toluene or Norpar 12, and for comparison, (3) toluene or Norpar 12 alone.

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CHAPTER 6

CHARACTERIZATION OF D2EHPA-CONTAINING SOLVENTS

In this chapter the properties of several D2EHPA-containing solvents are reported and discussed. The solvents investigated were D2EHPA in (1) an alcohol-containing diluent, (2) an inert diluent and (3) a tertiary amine-containing diluent. The properties studied were: (1) liquid-liquid extraction equilibria, (2) phase-separation tendencies, (3) aqueous extractant losses, (4) water coextraction, (5) solvent regenerability, (6) temperature dependence of distribution coefficients and (7) solvent thermal stability.

A. LIQUID-LIQUID EXTRACTION EQUILIBRIA

The data discussed in this section were measured as reported in Chapter 3, section F. The feed for these extractions was an ammonium hydroxide/ammonium phosphate solution. The latter was added to help stabilize pH readings. The data for the alcohol-containing diluent (50% (v/v) Alfol 10 in toluene) at D2EHPA concentrations of 0.48 $\underline{M}$, 0.37 $\underline{M}$, and 0.25 $\underline{M}$ are given in Tables 6.1, 6.2, and 6.3, respectively. For the "inert" diluent (toluene) the data are given in Tables 6.4, 6.5 and 6.6. For the amine-containing diluent, the data for 0.48 $\underline{M}$ D2EHPA plus a diluent composed of 0.52 $\underline{M}$ Adogen 364 (A364) in toluene are given in Table 6.7. For 0.48 $\underline{M}$ D2EHPA plus a diluent composed of 0.26 $\underline{M}$ A364 in toluene the data are given in Table 6.8. For 0.25 $\underline{M}$ D2EHPA plus a diluent composed of 0.28 $\underline{M}$ A364 in toluene, the data are given in Table 6.9. For this concentration of D2EHPA in a diluent composed of 0.14 $\underline{M}$

TABLE 6.1

LIQUID-LIQUID EXTRACTION DATA FOR ALCOHOL DILUENT

$[D2EHPA]_o$ = 0.48 M   S/W (v/v) = 2.5

DILUENT = 50% (v/v) Alfol 10 in Toluene

$[NH_4^+A^-]$(a) (M)	(N)(b) (M)	(PO_4^{3-})(c) (M)	pH	K_{c,NH_4^+}(d)	s(e)	PHASE SEPARATION(f) O	A	I
0.072	0.022	0.019	4.75	3.4	0.15	1	1	4
0.266	0.024	0.019	5.68	11.1	0.55	1	1	2
0.39	0.018	0.01	6.34	21.7	0.81	1	1	3
0.45	0.022	0.01	6.64	20.4	0.94	1	1	3

(a): calculated ammonia concentration in the organic phase: mole/liter
(b): measured total concentration of ammonia in raffinate: mole/liter
(c): concentration of phosphate added to feed solution: mole/liter
(d): K_c for ammonium, calculated as concentration of ammonia in organic phase divided by concentration of ammonium ion in aqueous phase, both expressed as mole/liter
(e): stoichiometry, calculated as the concentration of ammonia in organic phase divided by the initial, or total, concentration of D2EHPA, $[D2EHPA]_o$
(f): Key to Phase-Separation Properties:

O = Organic Phase:
  1 = clear
  2 = white

A = Aqueous Phase:
  1 = clear
  2 = cloudy
  3 = cloudy white
  4 = white

I = Interface:
  1 = clear
  2 = white dot on interface
  3 = white line at interface
  4 = white zone at interface
  (if A = 4, then I = 4)

C = After centrifugation, aqueous phase was:
  1 = fine
  2 = cloudy
  (C not always included)

TABLE 6.2

LIQUID-LIQUID EXTRACTION DATA FOR ALCOHOL DILUENT[(a)]

$[D2EHPA]_o = 0.37$ M S/W (v/v) = 2.5

DILUENT = 50% (v/v) Alfol 10 in Toluene

$[NH_4^+A^-]$ (M)	(N) (M)	(PO_4^{3-}) (M)	pH	K_{c,NH_4^+}	s	PHASE SEPARATION O	A	I
0.055	0.013	0.01	5.13	4.3	0.15	1	1	1
0.1	0.014	0.01	5.33	7.2	0.27	1	1	1
0.197	0.014	0.01	5.85	14.2	0.53	1	1	2
0.294	0.017	0.01	6.25	17.8	0.79	1	1	2
0.338	0.017	0.01	6.68	19.7	0.91	1	1	2

(a): see Table 6.1 for explanation of symbols

TABLE 6.3

LIQUID-LIQUID EXTRACTION DATA FOR ALCOHOL DILUENT(a)

$[D2EHPA]_o$ = 0.25 M S/W (v/v) = 2.5

DILUENT = 50% (v/v) Alfol 10 in Toluene

$[NH_4^+A^-]$ (M)	(N) (M)	(PO_4^{3-}) (M)	pH	K_{c,NH_4^+}	s	PHASE SEPARATION		
						O	A	I
0.035	0.013	0.01	5.07	2.7	0.14	1	1	1
0.068	0.013	0.01	5.45	5.4	0.27	1	1	2
0.131	0.015	0.01	5.89	8.7	0.52	1	1	1
0.196	0.017	0.01	6.38	11.5	0.77	1	1	2
0.229	0.017	0.01	6.84	13.7	0.91	1	1	2
0.25	0.030	0.01	8.58	10.2	~1	1	1	2

(a): see Table 6.1 for explanation of symbols

TABLE 6.4

LIQUID-LIQUID EXTRACTION DATA FOR TOLUENE DILUENT(a)

$[\text{D2EHPA}]_o = 0.48\ \underline{M}$ S/W (v/v) = 5

DILUENT = Toluene

$[NH_4^+A^-]$	(N)	(PO_4^{3-})	pH	K_{c,NH_4^+}	s	PHASE SEPARATION			
($\underline{M}$)	($\underline{M}$)	($\underline{M}$)				O	A	I	C
0.069	0.027	0.019	5.18	2.6	0.14	1	1	3	1
0.266	0.045	0.019	6.27	5.9	0.55	2	4	4	2
0.4	0.047	0.019	6.61	8.5	0.83	1	4	4	1
0.46	0.065	0.019	6.85	7.1	0.96	1	2	-	-

(a): see Table 6.1 for explanation of symbols

TABLE 6.5

LIQUID-LIQUID EXTRACTION DATA FOR TOLUENE DILUENT(a)

$[D2EHPA]_o = 0.37$ M   S/W (v/v) = 5

DILUENT = Toluene

$[NH_4^+A^-]$	(N)	(PO_4^{3-})	pH	K_{c,NH_4^+}	s	PHASE SEPARATION			
(M)	(M)	(M)				O	A	I	C
0.054	0.030	0.019	5.55	1.8	0.15	1	2	3	1
0.099	0.032	0.019	5.89	3.1	0.27	1	2	4	1
0.195	0.037	0.019	6.36	5.3	0.53	2	2	4	1
0.24	0.043	0.019	6.57	5.6	0.65	1	4	4	2
0.271	0.045	0.019	6.69	6.0	0.73	1	4	4	2

(a): see Table 6.1 for explanation of symbols

TABLE 6.6

LIQUID-LIQUID EXTRACTION DATA FOR TOLUENE DILUENT(a)

$[D2EHPA]_o$ = 0.25 M   S/W (v/v) = 5

DILUENT = Toluene

$[NH_4^+A^-]$	(N)	(PO_4^{3-})	pH	K_{c,NH_4^+}	s	PHASE SEPARATION			
(M)	(M)	(M)				O	A	I	C
0.035	0.027	0.019	5.85	1.3	0.14	1	1	2	2
0.066	0.030	0.019	6.11	2.2	0.26	2	2	4	2
0.13	0.037	0.019	6.41	3.5	0.51	2	2	4	2
0.195	0.039	0.019	6.74	5.1	0.77	1	4	4	2
0.226	0.045	0.019	6.88	5.0	0.89	1	3	4	2
0.25	0.440	0.019	10.36	8.2	~1	1	1	1	-

(a): see Table 6.1 for explanation of symbols

TABLE 6.7

LIQUID-LIQUID EXTRACTION DATA FOR AMINE DILUENT(a)

$[D2EHPA]_o$ = 0.48 M   S/W (v/v) = 5

DILUENT = 0.52 M Adogen 364 in Toluene

$[NH_4^+A^-]$ (M)	(N) (M)	(PO_4^{3-}) (M)	pH	K_{c,NH_4^+}	s	PHASE SEPARATION O	A	I	C
0.051	0.056	0.019	7.85	0.95	0.11	1	2	3	2
0.106	0.055	0.019	8.24	2.1	0.22	1	2	3	2
0.214	0.066	0.019	8.65	4.1	0.44	1	2	3	2
0.318	0.093	0.019	9.07	5.7	0.66	1	2	3	1
0.366	0.128	0.019	9.34	6.4	0.76	1	2	3	1

(a): see Table 6.1 for explanation of symbols

TABLE 6.8

LIQUID-LIQUID EXTRACTION DATA FOR AMINE DILUENT(a)

$[\text{D2EHPA}]_o$ = 0.48 M   S/W (v/v) = 5

DILUENT = 0.26 M Adogen 364 in Toluene

$[NH_4^+A^-]$ (M)	(N) (M)	(PO_4^{3-}) (M)	pH	K_{c,NH_4^+}	s	PHASE SEPARATION O	A	I	C
0.064	0.045	0.019	6.85	1.4	0.13	1	2	4	2
0.128	0.048	0.019	7.11	2.7	0.26	1	2	4	2
0.255	0.063	0.019	7.93	4.2	0.53	1	3	-	2
0.379	0.087	0.019	8.80	5.9	0.79	1	2	-	1
0.434	0.138	0.019	9.33	6.9	0.90	1	1	1	1

(a): see Table 6.1 for explanation of symbols

TABLE 6.9

LIQUID-LIQUID EXTRACTION DATA FOR AMINE DILUENT[(a)]

$[D2EHPA]_o = 0.25\ \underline{M}$ S/W (v/v) = 2.5

DILUENT = 0.28 M Adogen 364 in Toluene

$[NH_4^+A^-]$ (M)	(N) (M)	(PO_4^{3-}) (M)	pH	K_{c,NH_4^+}	s	PHASE SEPARATION O	A	I	C
0.026	0.036	0.01	8.00	0.75	0.10	2	2	4	1
0.056	0.041	0.01	8.33	1.5	0.22	2	2	4	2
0.118	0.049	0.01	8.78	3.2	0.47	2	4	4	2
0.177	0.064	0.01	9.21	5.3	0.70	2	4	4	2
0.203	0.079	0.01	9.46	6.7	0.81	1	4	4	2

(a): see Table 6.1 for explanation of symbols

A364 in toluene the data are presented in Table 6.10. Finally, additional data for 0.48 M D2EHPA in Alfol 10/toluene are given in Table 6.11. For this last set of data the feed for the extractions was an ammonium hydroxide solution with no phosphate added.

1. pH DEPENDENCE OF K_{c,NH_4^+}

The dependence of K_{c,NH_4^+} on pH was determined by comparing the data in Tables 6.1 and 6.11. For these data the total concentration of D2EHPA was 0.48 M. At a given stoichiometry (ratio of concentration of ammonium/D2EHPA ion pair in the organic phase to that of D2EHPA in all forms in the organic phase) the concentration of free D2EHPA will be constant. Thus, by Equation 4.5 log K_{c,NH_4^+} should be proportional to pH. That is, the difference in log K_{c,NH_4^+} divided by the difference in pH for two data points should be equal to one. For a stoichiometry of 0.14, the ratio was 1.1; for a stoichiometry of 0.54, it was 0.98; for a stoichiometry of 0.81, it was 1.2; and for a stoichiometry of 0.94, it was 0.6. This supports the assumption that log K_{c,NH_4^+} is linear in pH. The deviation from one at high stoichiometry may be due to the sensitivity of K_{c,NH_4^+} to stoichiometry at high stoichiometry, as discussed below. Since log K_{c,NH_4^+} is linearly proportional to pH, then (log K_{c,NH_4^+} - pH) is independent of pH.

2. MODEL FOR K_{c,NH_4^+} FOR THE TOLUENE AND ALCOHOL DILUENTS

Many authors have presented models for distribution coefficients in liquid-cation-exchange systems (Ashbrook, 1972; Mason et. al., 1964; Rice et. al., 1978; van der Zeeuw, 1979a). In the most general case, the extraction of a monovalent cation may be expressed as:

TABLE 6.10

LIQUID-LIQUID EXTRACTION DATA FOR AMINE DILUENT$^{(a)}$

$[\text{D2EHPA}]_o$ = 0.25 <u>M</u>   S/W (v/v) = 5

DILUENT = 0.14 <u>M</u> Adogen 364 in Toluene

$[NH_4{}^+A^-]$ (<u>M</u>)	(N) (<u>M</u>)	$(PO_4{}^{3-})$ (<u>M</u>)	pH	$K_{c,NH_4{}^+}$	s	PHASE SEPARATION O	A	I	C
0.03	0.049	0.019	6.97	0.62	0.12	1	2	3	1
0.063	0.045	0.019	7.24	1.4	0.25	1	3	4	2
0.126	0.056	0.019	7.76	2.3	0.50	1	2	3	2
0.189	0.067	0.019	8.56	3.4	0.75	1	2	-	1
0.219	0.075	0.019	8.96	4.4	0.87	1	2	-	1

(a): see Table 6.1 for explanation of symbols

TABLE 6.11

LIQUID-LIQUID EXTRACTION DATA FOR ALCOHOL DILUENT$^{(a)}$

$[\text{D2EHPA}]_o = 0.48\ \underline{M}$ S/W (v/v) = 2.5

DILUENT = 50% (v/v) Alfol 10 in Toluene

$[NH_4^+A^-]$ ($\underline{M}$)	(N) ($\underline{M}$)	(PO_4^{3-}) ($\underline{M}$)	pH	K_{c,NH_4^+}	s	PHASE SEPARATION O	A	I
0.064	0.0036	0	5.4	18	0.13	2	1	4
0.128	0.0040	0	6.1	32	0.27	1	1	2
0.258	0.0056	0	6.3	46	0.54	1	1	4
0.388	0.0065	0	6.7	60	0.81	1	1	4
0.452	0.0079	0	7.4	58	0.94	1	1	4
0.48	0.0375	0	10.0	89	~1	1	1	4

(a): see Table 6.1 for explanation of symbols

$$M^+ + \frac{m}{y}(HA)_y \rightleftarrows M^+A^-\cdot(m-1)\ HA + H^+ \qquad (6.1)$$

K_{c,M^+} may be expressed as:

$$K_{c,M^+} = \frac{[M^+A^-\cdot\ (m-1)\ HA]}{(M^+)} \qquad (6.2)$$

where square brackets indicate organic phase concentrations and parentheses indicate aqueous phase concentrations. In terms of Equation 6.1 K_{c,M^+} may be expressed:

$$K_{c,M^+} = \frac{K_r\ [(HA)_y]^{m/y}}{(H^+)} \qquad (6.3)$$

where K_r is the reaction equilibrium constant for Equation 6.1 and contains activity coefficients.

These expressions take into account association, probably dimerization, of the organic acid and complexation of the ion pair by additional undissociated acid. To use these models data are usually obtained under fairly rigorous conditions (van der Zeeuw, 1979a). The data are obtained for the extraction of low concentrations of cations into an organic phase containing a large excess of extractant. In this case the concentration of free acid does not change significantly and essentially equals the total concentration. In addition, the aqueous phase ionic strength is tightly controlled. Under these conditions, activity coefficients in both phases are essentially constant.

In these cases at a constant pH a plot of log K_{c,M^+} versus log [HA] will give a slope equal to m/y. If the extent of aggregation of the extractant in the organic phase (y) is known, then the number of acid molecules associated with each cation can be determined.

The above type of analysis gives only an average organic-phase composition. In reality several different species will coexist in equilibrium in the organic phase.

Use of Equation 6.3 is not necessarily limited to cases in which the concentration of free acid is equal to the total concentration. In some cases, the composition of the organic-phase ion pair is known or assumed a priori (Rice et. al., 1978). For instance in the extraction of sodium by D2EHPA, it is known that m is equal to 4 at a stoichiometry less than 0.25 (McDowell, 1971). The concentration of free acid may then be calculated as the initial concentration of acid minus four times the concentration of the cation-containing species in the organic phase. With this information, K_r may be calculated. However, K_r may not be constant throughout the full range of possible stoichiometries since activity coefficients may change. In addition, the composition of the ion-pair complex usually changes with stoichiometry. For sodium, above a stoichiometry of 0.25, the ion pair forms increasing amounts of higher aggregates, or polymers (McDowell, 1971). This tends to increase the amount of water in the organic phase and may cause a decrease in K_{c,M^+} (Healy, 1967, 1968).

Van der Zeeuw (1979a) developed a more rigorous approach for defining the average composition of organic-phase complexes. For the extraction of a monovalent cation, the following equilibrium is considered:

$$M^+ + \frac{m}{y}(HA)_y \rightleftarrows \frac{1}{x}(MA \cdot (m-1)\ HA)_x + H^+ \qquad (6.4)$$

Van der Zeeuw developed a computer program to fit distribution coefficient versus pH data in order to obtain the best values of m, x, y and the equilibrium reaction constant. These best values generally varied with stoichiometry. The degree of solvation of the ion-pair complex with additional acid molecules was often difficult to determine, and van der Zeeuw took this to indicate the coexistence of several complexes with varying degrees of such additional solvation.

In light of the above, it is clear that the equilibrium in liquid-cation-exchange systems at stoichiometries approaching useful values is very complicated. McDowell (1971) suggested an alternate approach for obtaining information about the average composition of organic-phase species. He suggested taking the log of both sides of Equation 6.3:

$$\log K_{c,M^+} - \mathrm{pH} = \log K_r + \frac{m}{y} \log \left[(\mathrm{HA})_y\right] \qquad (6.5)$$

The value of $[(\mathrm{HA})_y]$ was then taken to be a function of the total concentration of the organic acid, $[\mathrm{HA}]_o$; that is

$$\left[(\mathrm{HA})_y\right] = \beta \left[\mathrm{HA}\right]_o \qquad (6.6)$$

where $\beta = (1 - ms)/y$ and s = stoichiometry. In this case β varies with stoichiometry and in the simpliest case of $m = y = 1$, β is equal to $1 - s$. With this substitution for $[(\mathrm{HA})_y]$, Equation 6.5 may be rewritten:

$$\log K_{c,M^+} - \mathrm{pH} = I + n \log \left[\mathrm{HA}\right]_o \qquad (6.7)$$

where $n = m/y$ and β and K_r have been incorporated into I. Values of n will be expected to vary with stoichiometry as the degree of complexation of the ion pair with additional acid molecules varies. McDowell (1971) found that n decreased as stoichiometry increased for the extraction of alkali metals into D2EHPA in benzene. Values of I depend on stoichiometry through β. In addition variations in the activity coefficients of the species involved as well as polymerization of the ion-pair complex will affect I and enhance its dependence on stoichiometry.

McDowell's (1971) proposal based on Equation 6.7 is to plot (log K_{c,NH_4^+} - pH) versus the log of the total D2EHPA concentration at a constant stoichiometry. In his work McDowell obtained straight lines on such plots giving values of n (slope) and I (intercept) dependent on stoichiometry. This suggests that stoichiometry is the primary determinant of the degree of complexation of the ion pair by additional D2EHPA and the degree of polymerization of the ion pair. Total concentration should be expected to affect these properties and to affect organic-phase activity coefficients. Thus the value of the slope should be taken only as an indication of the relative degree of solvation of the ion pair by the undissociated acid. A value of n close to one suggests no additional complexation, while higher values of n indicate such complexation is occurring. If the average aggregation of the extractant in the organic phase is known as a function of system stoichiometry, m can be calculated directly.

This type of analysis presents the same difficulties as that of van der Zeeuw in that the equations are written for only one degree of complexation in the organic phase. While it may be possible to draw some conclusions about the average composition of the organic phase from this type of analysis, this was not the goal of the current work. An accurate representation of organic-phase species would probably require detailed spectroscopic analysis (Rice, 1978).

In the current work an analysis of the type suggested by McDowell (1971) was considered sufficient. The results of these analyses, n and I values from Equation 6.7, were taken only as indications of the extent of complexation of the ammonium/D2EHPA ion pair by additional D2EHPA. No attempt was made to define actual organic-phase species.

Information on the average aggregation of D2EHPA in the system under study is not known. D2EHPA is known to dimerize in toluene and to be monomeric in alcohol diluents (Mason et. al., 1964). It is probably also a monomer in amine-containing diluents. The presence of coextracted water in the organic phase causes a tendency toward monomerization. Thus, in the present study, the slope of the plot suggested by McDowell can give only an indication of the degree of complexation in the organic phase.

Figures 6.1 and 6.2 show plots of (pH - log K_{c,NH_4^+}) versus the log of the total concentration of D2EHPA at various stoichiometries for the toluene diluent and the alcohol-containing diluent respectively. Tables 6.12 and 6.13 give the values of the slope (n) and intercept (I) (as given by Equation 6.7) calculated by a least squares fit to the data. Additional results are also given for cases in which only two data points were available.

For the toluene diluent values of n are highest at low stoichiometry. This is consistent with McDowell's (1971) work on the extraction of alkali metals into D2EHPA in benzene and suggests that additional complexing of the ion pair by undissociated D2EHPA occurs at

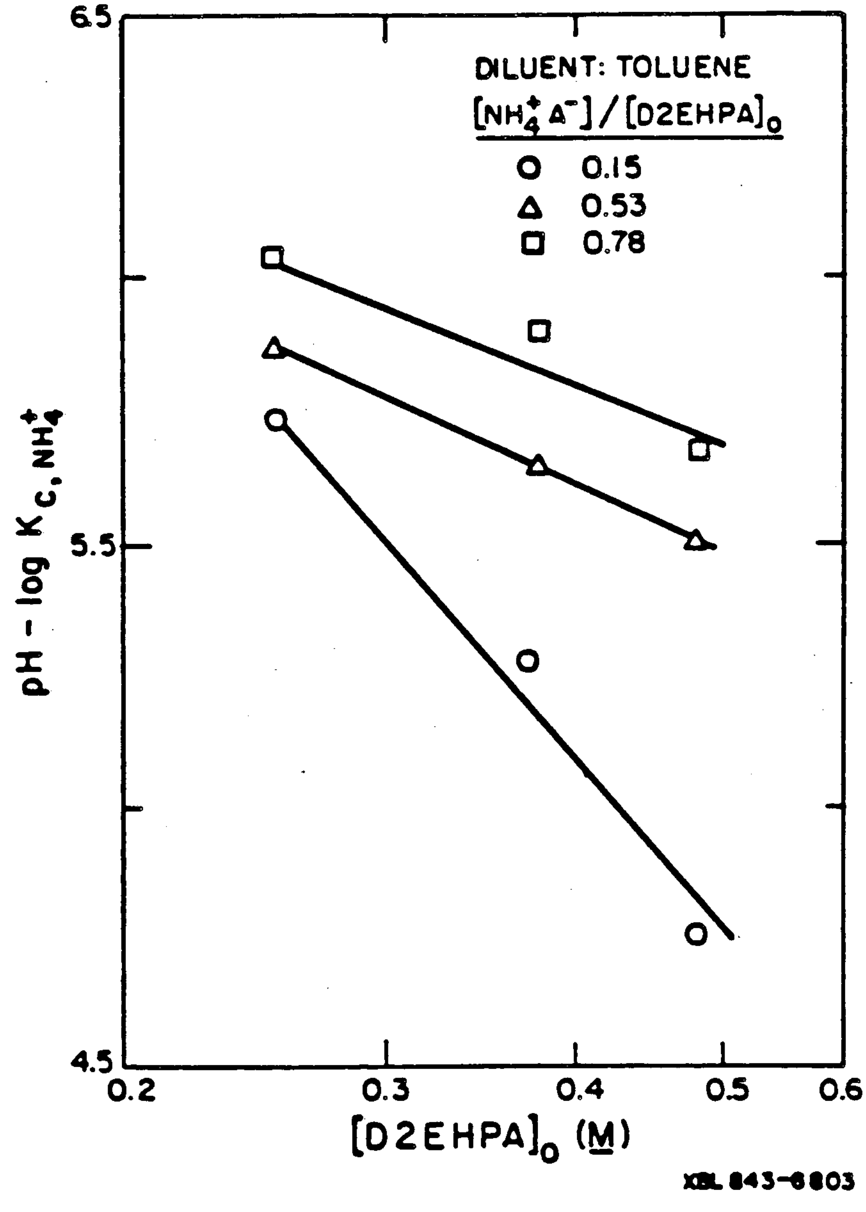

FIGURE 6.1: EFFECT OF D2EHPA CONCENTRATION IN TOLUENE ON K_{c,NH_4^+} AT DIFFERENT STOICHIOMETRIES.

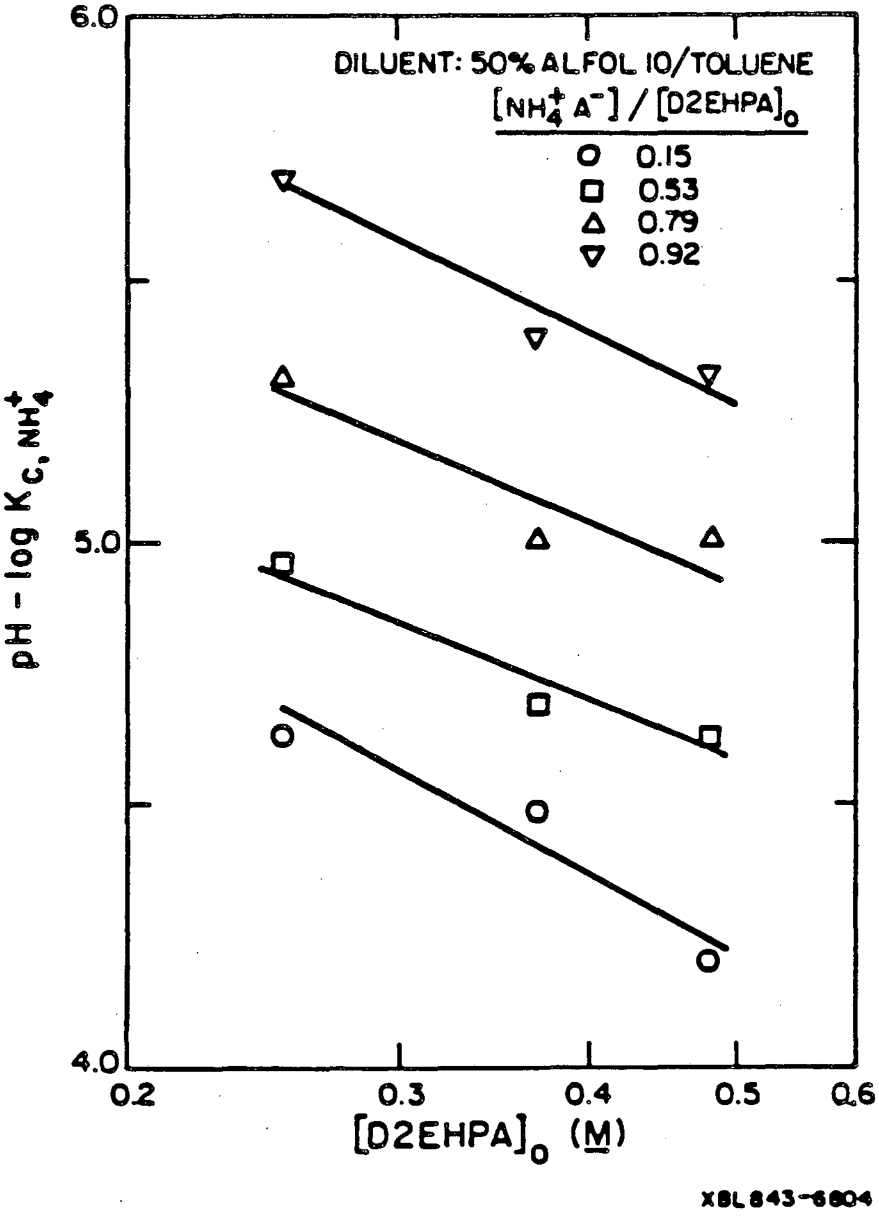

FIGURE 6.2: EFFECT OF D2EHPA CONCENTRATION IN 50% (v/v) ALFOL 10/ TOLUENE ON K_{c,NH_4^+} AT DIFFERENT STOICHIOMETRIES.

TABLE 6.12

PARAMETERS FOR LIQUID-LIQUID EXTRACTION MODEL FOR TOLUENE DILUENT[a]

s[b]	n	-I	correlation coefficient
0.15	3.4	-3.75	0.985
0.26	2.2	-4.46	-
0.53	1.3	-5.09	1
0.78	1.2	-5.31	0.96
0.94	0.64	-5.79	-

(a): parameters defined in Equation 6.7
(b): stoichiometry = $[NH_4^+A^-]/[D2EHPA]_o$

TABLE 6.13

PARAMETERS FOR LIQUID-LIQUID EXTRACTION MODEL FOR ALCOHOL DILUENT[(a)]

$s^{(b)}$	n	-I	correlation coefficient
0.15	1.5	-3.78	0.96
0.27	1.4	-3.86	-
0.54	1.1	-4.25	0.98
0.79	1.2	-4.56	0.92
0.92	1.4	-4.84	0.97

(a): parameters defined in Equation 6.7
(b): stoichiometry: $[NH_4^+A^-]/[D2EHPA]_o$

low stoichiometry, when additional D2EHPA is available for such solvation. This is not seen in the data for the alcohol-containing diluent and suggests that the alcohol itself solvates the ion pair to an extent such that solvation by additional D2EHPA is relatively insignificant.

This same phenomenon may be seen by an alternate plotting of the data in Figures 6.1 and 6.2. If m and y in Equation 6.3 are taken to be 1, then:

$$K_{c,NH_4^+} = \frac{K_r\,[HA]}{(H^+)} \qquad (6.8)$$

and $[HA] = [HA]_o - [NH_4^+A^-]$. Consequently, if the above assumptions hold, then a plot of K_{c,NH_4^+} at a given pH versus [HA] should be a straight line through the origin with a slope equal to $K_r/(H^+)$.

Figure 6.3 presents such a plot for the toluene diluent and the alcohol-containing diluent. For the former, K_{c,NH_4^+} values were calculated at pH 6.5, for the latter the pH value was 6. These calculations were performed assuming log K_{c,NH_4^+} to be linear in pH.

Except for the point at low stoichiometry and high D2EHPA concentration the data for the alcohol-containing diluent appear to fall on a straight line. A linear least squares analysis of the data (including data at an intermediate concentration, not shown, but omitting the one high point) gave: $K_{c,NH_4^+} = 109\ [HA] - 0.264$. The correlation coefficient was 0.975. All concentrations were expressed as mole/liter. The success of this type of fit is a reflection of the values of n in Equation 6.7 and presented in Table 6.13 being close to

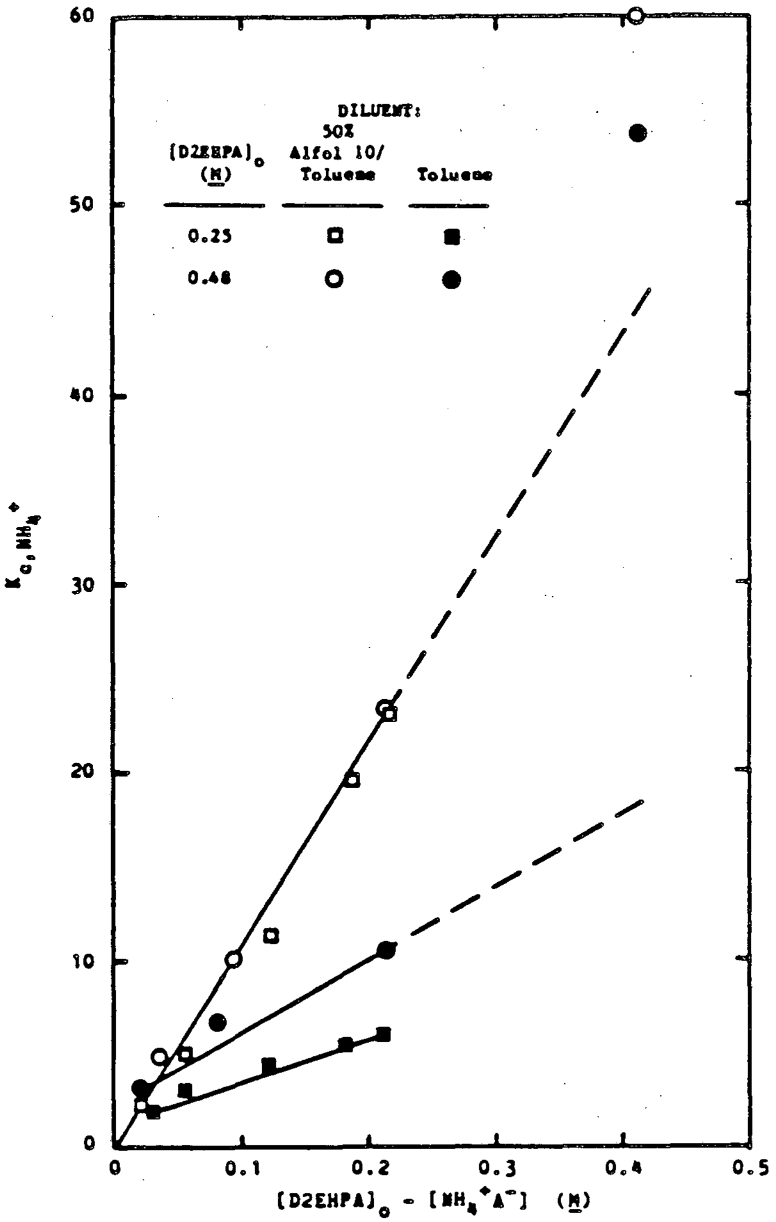

FIGURE 6.3: EFFECT OF CONCENTRATION OF FREE D2EHPA ON K_{c,NH_4^+} FOR TOLUENE AND ALCOHOL-CONTAINING DILUENTS.

K_{c,NH_4^+} calculated at pH = 6 for Alfol 10/toluene diluent, at pH = 6.5 for toluene diluent.

one. Again this indicates that additional complexation of the ammonium/D2EHPA ion pair by D2EHPA is probably small in an alcohol-containing diluent. The success of this type of fit also indicates that the ratio of the activity coefficient for free D2EHPA to that for the ammonium/D2EHPA ion pair is relatively independent of D2EHPA concentration and stoichiometry in this diluent.

For the toluene diluent the data in Figure 6.3 fall on a straight line at a low D2EHPA concentration, but the intercept is greater than zero. At higher D2EHPA concentrations the data do not fall on this same line and the deviations from linearity become significant, reflecting the higher values of n in Equation 6.7 and Table 6.12, especially at low stoichiometry. The curves at both 0.37 $\underline{M}$ D2EHPA (not shown) and 0.48 $\underline{M}$ D2EHPA in toluene are concave upward. Apparently the simplification that m and y are one is not valid for this diluent. The effect on free D2EHPA concentration and its exponent of additional complexation of the ammonium/D2EHPA ion pair by D2EHPA cannot be ignored in this diluent. Additional coordination of the ion pair by free D2EHPA should increase K_{c,NH_4^+} (McDowell, 1971).

The models based on Equation 6.7 may be used to predict K_{c,NH_4^+} values. Given are the total, or inital, concentration of D2EHPA in the organic phase, the total concentration of ammonia in the aqueous feed, the solvent-to-water ratio and the dependence of aqueous phase pH on ammonia concentration. First a plot of (pH - log K_{c,NH_4^+}) versus stoichiometry is constructed, using the models and the D2EHPA concentration. Next, an organic-phase ion-pair concentration is assumed, and by mass balance the concentration of ammonia in the aqueous phase is calculated. This in turn gives K_{c,NH_4^+} and pH. At the stoichiometry assumed and the pH calculated, K_{c,NH_4^+} is determined from the plot. This value is then compared with the previously calculated value and a new ion-pair concentration is assumed. The iteration continues until the K_{c,NH_4^+} values agree.

3. TRENDS IN THE LIQUID-LIQUID EXTRACTION EQUILBRIA DATA FOR THE TOLUENE DILUENT AND THE ALCOHOL-CONTAINING DILUENT

All of the data presented in Tables 6.1 through 6.10 are given in Figures 6.4 and 6.5. These are plots of (pH - log K_{c,NH_4^+}) versus stoichiometry for the three types of diluents considered. The data in Table 6.11 agree well with the curve for the alcohol diluent at 0.48 M D2EHPA.

The highest K_{c,NH_4^+} values occur for the alcohol diluent, followed by the toluene diluent and then the amine-containing diluent. The amine-containing diluent in which the amine-to-D2EHPA molar ratio was 1:2 gives higher K_{c,NH_4^+} values than that for which the ratio is 1:1.

The large K_{c,NH_4^+} values for the alcohol diluent suggest a low activity coefficient for the ion pair in this solvent. This would result from solvation of the ion pair by the alcohol. Such behavior was noted by other authors in the extraction of alkali metals (Healy, 1967, 1968) and other monovalent cations (Muir et. al., 1980) by D2EHPA and was explained in terms of the alcohol replacing water in the solvation sphere of the ion pair (See Chapter 5, section A). These same effects appear to be occurring here (See section D, below). The amine data are discussed at greater length below.

At a constant stoichiometry, as the concentration of D2EHPA decreases the concentration of free acid decreases, and consequently so

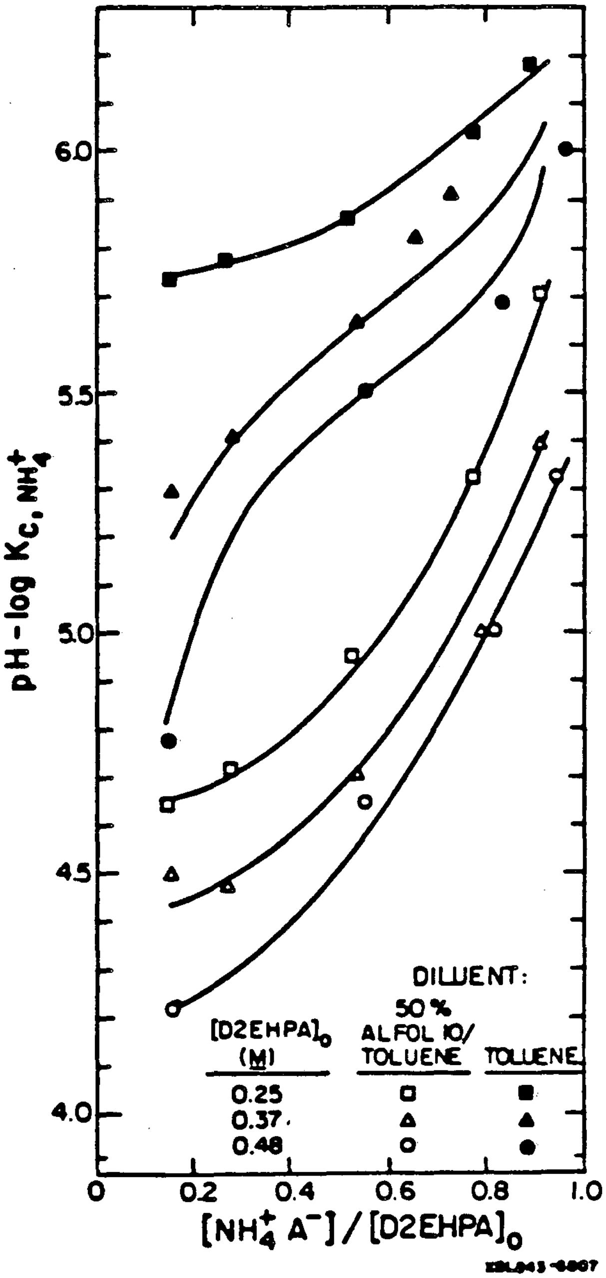

FIGURE 6.4: EFFECT OF STOICHIOMETRY ON K_{c,NH_4^+} FOR TOLUENE AND ALCOHOL-CONTAINING DILUENTS.

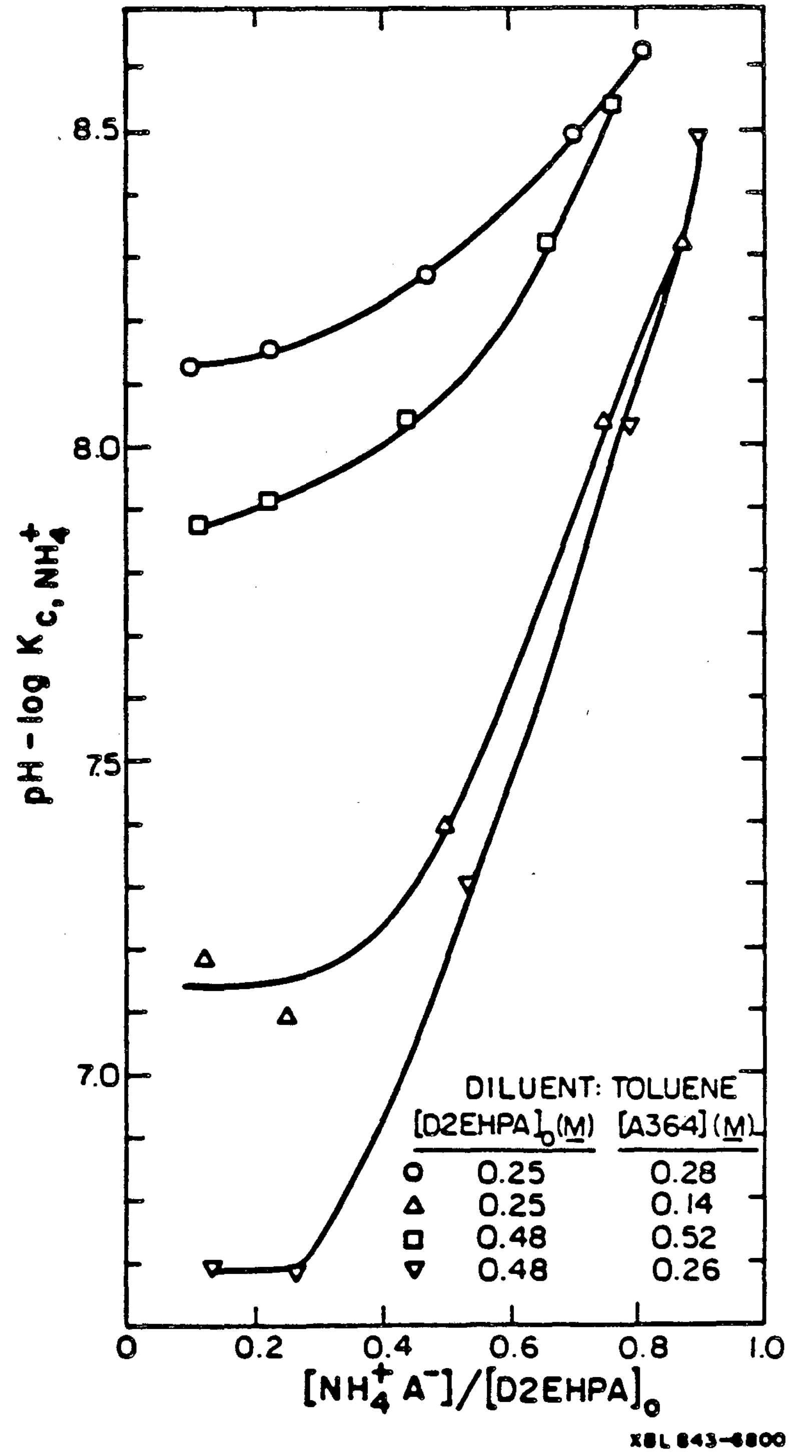

FIGURE 6.5: EFFECT OF STOICHIOMETRY ON K_{c,NH_4^+} FOR AMINE-CONTAINING DILUENTS.

does K_{c,NH_4^+}. At a constant concentration of D2EHPA, as the stoichiometry increases the concentration of free D2EHPA decreases, and K_{c,NH_4^+} decreases also.

If no additional complexation occurs, and y is one, and activity coefficients are ignored, then the ratio of K_{c,NH_4^+} at one stoichiometry to that at another, at a given pH, is given by:

$$\frac{K_{c,NH_4^+,1}}{K_{c,NH_4^+,2}} = \frac{(1-s)_1}{(1-s)_2} \tag{6.9}$$

where 1=lower stoichiometry and 2=higher stoichiometry. Deviations of the ratio of the K_{c,NH_4^+} values from the ratio of the concentrations of the free acid may be explained in terms of activity coefficients and additional complexation of the ion pair by D2EHPA.

In cases where there is additional complexing of the ammonium/D2EHPA ion pair by D2EHPA γ for the ion pair should be less at lower stoichiometry and for higher initial concentrations of D2EHPA.

For the alcohol- and amine-containing diluents the diminished slopes of the curves at low stoichiometry indicate that K_{c,NH_4^+} is relatively independent of stoichiometry in this range. For all of the diluents K_{c,NH_4^+} is very sensitive to stoichiometry at high stoichiometry. This reflects the relative change in the concentration of free acid with stoichiometry. At low stoichiometry, the concentration of free acid is relatively constant, while at high stoichiometry it falls off very rapidly. For instance, ignoring additional complex formation in the organic phase, if the stoichiometry increases from 0.15 to 0.2, the free acid concentration falls by 0.80/0.85, or a factor of 0.94. This would produce a difference of 0.025 in log K_{c,NH_4^+}. On the other hand increasing the stoichiometry from 0.85 to 0.90 causes the free acid concentration to fall by 0.10/0.15 or a factor of 0.67. This would produce a difference of 0.18 in log K_{c,NH_4^+}. Thus the curves are steeper at higher stoichiometry.

This sensitivity of K_{c,NH_4^+} to stoichiometry at high stoichiometry may explain both the low slope of 0.64 at 0.92 stoichiometry for the toluene diluent liquid-liquid extraction data and the low slope (0.6) at high stoichiometry (0.94) of the Δ log K_{c,NH_4^+} versus Δ pH calculation for the alcohol diluent. Slight errors in the value of stoichiometry in this range can greatly affect the position of the curves and subsequent calculations based upon them.

For the alcohol diluent the ratio of K_{c,NH_4^+} values is generally given by Equation 6.9 throughout the range of stoichiometries, as is evidenced by the linearity of the plots in Figure 6.3.

For the toluene diluent the behavior of the curves in Figure 6.3 and 6.4 at low stoichiometry may be explained in terms of additional complexation of the ammonium/D2EHPA ion pair by D2EHPA. The relationship in Equation 6.9 does not hold. The sharp decrease in (pH − log K_{c,NH_4^+}) with decreasing stoichiometry at low stoichiometry in Figure 6.4 indicates that the concentration of free D2EHPA is changing much more rapidly than predicted via Equation 6.9 and that the exponent on the concentration of free D2EHPA exceeds one. A decrease in the activity coefficient for the ion pair at low stoichiometry may also contribute to this effect. This same effect is seen by the deviations from linearity in the plots in Figure 6.3.

Values of the synergistic coefficient (SC) as defined in Chapter 5, section D may be read directly from Figures 6.4 and 6.5. For the alcohol diluent, SC at a given stoichiometry and D2EHPA concentration is given as the difference between (pH − log K_{c,NH_4^+}) for the toluene diluent and that for the alcohol-containing diluent. At a D2EHPA concentration of 0.25 M, SC is about 1 at low stoichiometry and 0.82 at a stoichiometry of 0.7. For 0.48 M D2EHPA these values are 0.57 and 0.84 respectively, and in between the value goes through a maximum. The slight decrease in SC with increasing stoichiometry reflects the non-linearities in the toluene-diluent data (i.e. the curves in Figure 6.3 for the toluene diluent do not go through the origin). SC values go through a maximum at high D2EHPA concentration due to the importance of the above mentioned additional complexation of the ammonium/D2EHPA ion pair by D2EHPA in the toluene diluent at this concentration. This gives higher K_{c,NH_4^+} values for the toluene diluent at low stoichiometry and hence lower SC values.

The effect of temperature on K_{c,NH_4^+} is considered in section E, below.

4. TRENDS IN THE LIQUID-LIQUID EXTRACTION EQUILIBRIA DATA FOR THE AMINE-CONTAINING DILUENTS

The general shape of the curves in Figure 6.5 has already been discussed. K_{c,NH_4^+} values are less for amine-containing diluents than for the other diluents studied. This apparently is due to a strong interaction between D2EHPA and the amine, reducing the activity of free D2EHPA. This interaction can be written as:

$$B: + HA \rightleftarrows B:HA \qquad (6.10)$$

where B: represents the amine and B:HA the amine/D2EHPA complex. At a given concentration of D2EHPA, the higher the concentration of amine, the further the equilibrium expressed by Equation 6.10 will lie to the right.

At a given stoichiometry the effect of the amine is higher the higher the amine-to-D2EHPA molar ratio. At the same molar ratio and at a given stoichiometry, K_{c,NH_4^+} increases with increases in total D2EHPA concentration, reflecting an increase in the free acid concentration.

A plot of K_{c,NH_4^+} versus [HA], expressed as $[D2EHPA]_o - [NH_4^+A^-]$, for the amine-containing diluents is given in Figure 6.6. The pH value for the amine-to-D2EHPA molar ratio of 1:1 is 10, while that for a ratio of 1:2 is 9. At an amine-to-D2EHPA molar ratio of 1:1 the curves are fairly linear, while at an amine-to-D2EHPA molar ratio of 1:2 the curves are concave upward. In the latter case the nonlinear rise in K_{c,NH_4^+} at low stoichiometry (high [HA]), or conversely the nonlinear decrease in K_{c,NH_4^+} values at high stoichiometry (low [HA]) is related to the rise in the ratio of amine to free D2EHPA (that not complexed with ammonium) above one, as discussed below.

The synergistic coefficients for these diluents may be calculated by taking the difference between $(pH - \log K_{c,NH_4^+})$ for toluene and that for the amine-containing diluent. Values at different stoichiometries are presented in Table 6.14. The effect of the amine is greater the larger the absolute value of SC ($|SC|$).

As expected, at a given concentration of D2EHPA $|SC|$ is greater the higher the amine concentration. At low concentration of D2EHPA $|SC|$

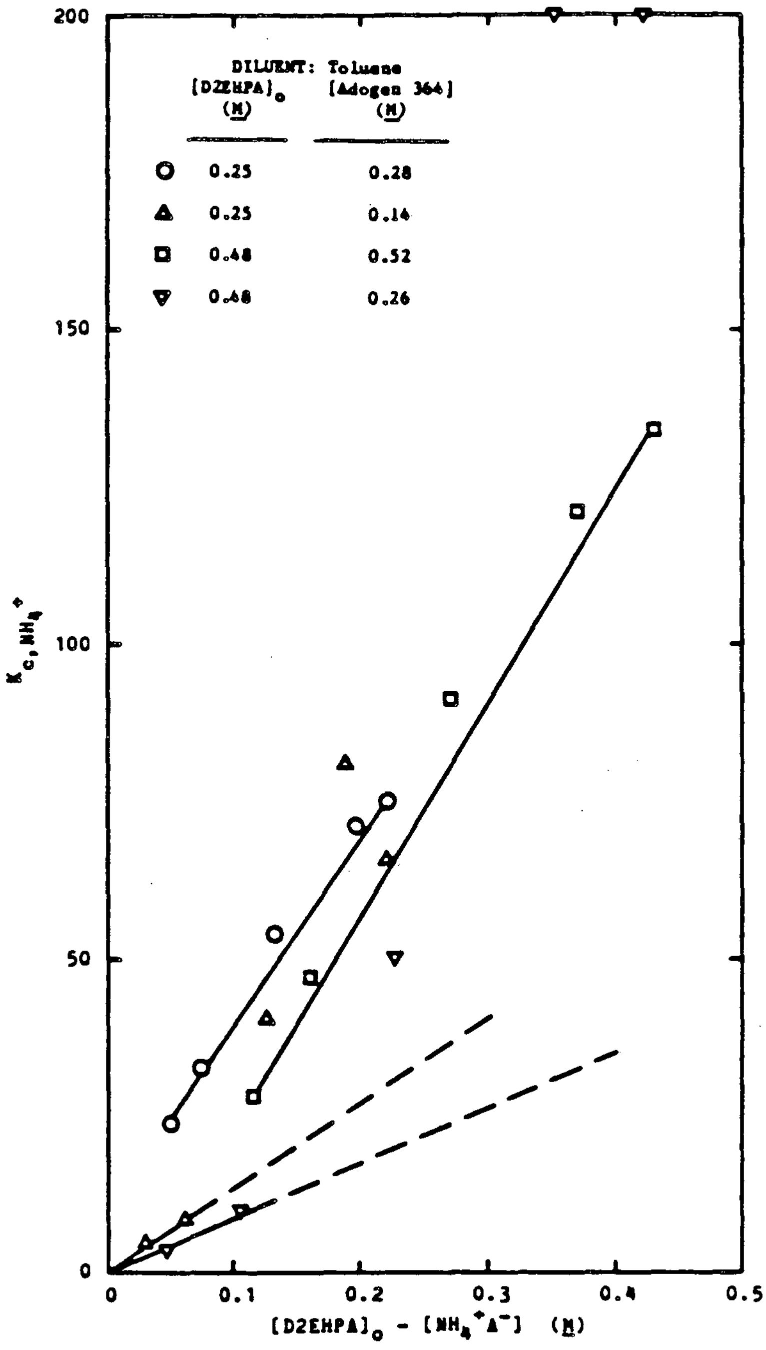

FIGURE 6.6: EFFECT OF CONCENTRATION OF FREE D2EHPA ON K_{c,NH_4^+} FOR AMINE-CONTAINING DILUENTS.

K_{c,NH_4^+} calculated at pH = 9 for 1:2 molar ratio diluents, at pH = 10 for 1:1 molar ratio diluents.

TABLE 6.14

SYNERGISTIC COEFFICIENTS FOR AMINE DILUENTS(a)

$[D2EHPA]_o$ ($\underline{M}$)	[Adogen 364] ($\underline{M}$)	s(b)	SC
0.25	0.28	0.2	-2.38
"	"	0.35	-2.40
"	"	0.50	-2.44
"	"	0.70	-2.49
0.25	0.14	0.20	-1.38
"	"	0.35	-1.39
"	"	0.50	-1.52
"	"	0.70	-1.88
0.48	0.52	0.20	-2.86
"	"	0.35	-2.65
"	"	0.50	-2.62
"	"	0.70	-2.75
0.48	0.26	0.20	-1.65
"	"	0.35	-1.51
"	"	0.50	-1.72
"	"	0.70	-2.12

(a): synergistic coefficient defined in Equation 5.2
(b): stoichiometry: $[NH_4^+A^-]/[D2EHPA]_o$

increases with increasing stoichiometry. This reflects the decrease in the concentration of free D2EHPA (i.e. that not complexed with ammonia) as stoichiometry increases and hence the increase in amine-to-free D2EHPA molar ratio. The variation in $|SC|$ values is greatest for the diluents in which the amine-to-D2EHPA molar ratio is 1:2. In these cases at low stoichiometry even if all of the amine interacted with one D2EHPA there would still be a significant concentration of D2EHPA not associated with either ammonium or amine, and the K_{c,NH_4^+} values reflect this. At higher stoichiometry nearly all of the D2EHPA is associated with either ammonium or amine and the concentration of free D2EHPA is very low. K_{c,NH_4^+} values are also very low and $|SC|$ values become very high. This is seen in the nonlinearities of the plots in Figure 6.6. At an amine-to-D2EHPA molar ratio of 1:1 at all stoichiometries there is enough amine to interact with all of the D2EHPA not associated with ammonium. Consequently K_{c,NH_4^+} values are not as affected by stoichiometry in the way the data for the amine-to-D2EHPA molar ratio of 1:2 are (linear plots in Figure 6.6), and $|SC|$ does not change much with stoichiometry.

At higher D2EHPA concentrations an additional effect is important and $|SC|$ goes through a minimum. The high $|SC|$ at low stoichiometry reflects the higher K_{c,NH_4^+} value for the toluene diluent at low stoichiometry due to the complexation of the ion pair by additional D2EHPA. This is prevented from occurring to as large an extent when the amine is present, since the amine would interact with any available D2EHPA and keep it from solvating the ion pair as extensively. Consequently $|SC|$ is rather high.

It is interesting to consider whether each amine molecule simply interacts with one D2EHPA molecule or if its effect extends beyond that. If the former were true (i.e. the equilibrium reaction constant for Equation 6.10 were infinite) then data for 0.48 M D2EHPA plus 0.26 M A364 in toluene should be approximately superimposable on those for 0.25 M D2EHPA in toluene if the effect of stoichiometry is taken into account. For instance, at a concentration of ammonium/D2EHPA ion pair in the organic phase of 0.14 M the amine case (stoichiometry equal to 0.14/0.48 = 0.29) gives (pH - log K_{c,NH_4^+}) of 6.69 (see Figure 6.5). The toluene case (stoichiometry equal to 0.14/0.25 = 0.56) gives (pH - log K_{c,NH_4^+}) of 5.9 (see Figure 6.4). Likewise for an ammonium/D2EHPA ion pair concentration of 0.2 M the amine case (stoichiometry equal to 0.42) gives (pH - log K_{c,NH_4^+}) equal to 6.97 (Figure 6.5). The toluene case (stoichiometry equal to 0.8) gives (pH - log K_{c,NH_4^+}) equal to 6.08 (Figure 6.4). In both cases K_{c,NH_4^+} for the toluene case is higher than that for the amine case. In other words K_{c,NH_4^+} for the amine case is less than expected. This suggests that the amine is interacting with more than one D2EHPA molecule. Such interactions have been noted in acetic acid extraction by amines, especially at acid-to-amine ratios greater than one (Spala and Ricker, 1982).

5. MODEL FOR K_{c,NH_4^+} FOR THE AMINE DILUENTS

Several attempts were made to model the liquid-liquid equilibrium data for the amine-containing diluents. First, models along the lines of those used for the toluene and alcohol-containing diluents were examined. These were disregarded in favor of a more mechanistic approach.

In this approach the equilibrium constant for the reaction in

Equation 6.10 was determined. The procedure was as follows. For the K_{c,NH_4^+} values to be lower for the amine diluents than for the toluene diluent, the concentration of free D2EHPA must be lower. In order to get an estimate of this concentration it was assumed that the reduction in the concentration of free D2EHPA from the toluene case to the amine case was proportional to the ratio of the respective K_{c,NH_4^+} values, all at the same stoichiometry, D2EHPA concentration, and pH. This approach is not strictly valid, especially at low stoichiometry. In these cases the additional complexing of the ion pair by D2EHPA occurs in the toluene case but to a lesser extent or not at all in the amine case. At higher D2EHPA concentrations the K_{c,NH_4^+} values for toluene will be higher than expected due to the reduction in the activity coefficient of the ammonium/D2EHPA ion pair. Consequently the ratio of K_{c,NH_4^+} for the amine diluent to that for toluene will be low, and the concentration of free acid calculated for the amine diluent will be too low.

With these limitations in mind, the concentration of free D2EHPA in the amine case ($[HA]^a$) was calculated from that in the toluene case ($[HA]^t$) by use of the ratio of K_{c,NH_4^+} values:

$$[HA]^a = [HA]^t \frac{K^a_{c,NH_4^+}}{K^t_{c,NH_4^+}} \qquad (6.11)$$

This model makes the assumption that the activity coefficient of the ammonium/D2EHPA ion pair is the same in both diluents which, as pointed out above, is probably not true. In addition this model assumes that the activity coefficient of free D2EHPA (i.e. that not associated with either ammonium or amine) is the same in both cases.

For this model $[HA]^t$ was calculated as:

$$[HA]^t = [HA]_o - [NH_4^+A^-] \tag{6.12}$$

The concentration of the amine/D2EHPA complex was taken to be:

$$[B{:}HA] = [HA]_o - [NH_4^+A^-] - [HA]^a \tag{6.13}$$

and the concentration of uncomplexed amine ([B]) was taken to be:

$$[B] = [B]_o - [B{:}HA] \tag{6.14}$$

where $[B]_o$ is the total amine concentration.

With this information $K_{B:HA}$ can be calculated as:

$$K_{B:HA} = \frac{[B{:}HA]}{[B]\,[HA]^a} \tag{6.15}$$

The results of such calculations are presented in Table 6.15 for the case of an amine-to-D2EHPA molar ratio of about 1. $K_{B:HA}$ values are fairly constant with the exception of the high values at low stoichiometry. This is due to the erroneously low calculated values of $[HA]^a$, as explained above. In Table 6.16 the results of such calculations are given for the case of an amine-to-D2EHPA molar ratio of 1:2 and for stoichiometries greater than 0.5. $K_{B:HA}$ values calculated here agree well with those presented in Table 6.15.

With this value of $K_{B:HA}$, K_{c,NH_4^+} values for the amine-containing

TABLE 6.15

$K_{B:HA}$ VALUES FOR AMINE DILUENTS(a)

$[D2EHPA]_o = 0.48\ \underline{M}$ $\quad$ $[\text{Adogen } 364] = 0.52\ \underline{M}$

s(b)	K_c^a/K_c^t	$K_{B:HA}$
0.22	1.5×10^{-3}	4.4×10^3
0.44	2.3×10^{-3}	1.7×10^3
0.66	2.0×10^{-3}	1.4×10^3
0.76	1.5×10^{-3}	1.7×10^3

$[D2EHPA]_o = 0.25\ \underline{M}$ $\quad$ $[\text{Adogen } 364] = 0.28\ \underline{M}$

s(b)	K_c^a/K_c^t	$K_{B:HA}$
0.22	4.0×10^{-3}	3.0×10^3
0.47	3.8×10^{-3}	1.8×10^3
0.70	3.2×10^{-3}	1.5×10^3
0.81	2.9×10^{-3}	1.4×10^3

(a): $K_{B:HA}$ defined by Equation 6.15

(b): stoichiometry: $[NH_4{}^+A^-]/[D2EHPA]_o$

TABLE 6.16

$K_{B:HA}$ VALUES FOR AMINE DILUENTS(a)

$[D2EHPA]_o = 0.25$ M [Adogen 364] = 0.14 M

$s^{(b)}$	K_c^a/K_c^t	$K_{B:HA}$
0.50	3.0×10^{-2}	2.5×10^3
0.75	9.5×10^{-3}	1.4×10^3
0.87	7.6×10^{-3}	1.3×10^3

$[D2EHPA]_o = 0.48$ M [Adogen 364] = 0.26 M

$s^{(b)}$	K_c^a/K_c^t	$K_{B:HA}$
0.53	1.7×10^{-2}	1.5×10^3
0.79	4.4×10^{-3}	1.4×10^3
0.90	2.6×10^{-3}	1.7×10^3

(a): $K_{B:HA}$ defined by Equation 6.15
(b): stoichiometry: $[NH_4^+A^-]/[D2EHPA]_o$

diluents can be calculated. Given are the total concentration of D2EHPA in the solvent, the total amine concentration, S/W, the concentration of ammonia in the aqueous feed and the relationship between pH and the aqueous ammonia concentration. A value of the concentration of the ammonium/D2EHPA ion pair, and hence stoichiometry, is assumed. This yields $[HA]^t$ through Equation 6.12. By mass balance the concentration of NH_3 in the aqueous phase is known. This allows calculation of the aqueous phase pH and K_{c,NH_4^+}. At the assumed stoichiometry and calculated pH, K_{c,NH_4^+} for the toluene diluent is calculated from the model presented earlier. Equation 6.11 can then be used to calculate $[HA]^a$. This is used in Equation 6.13 to calculate [B:HA], which in turn is used in Equation 6.14 to calculate [B]. These values are used in Equation 6.15 to calculate a new $[HA]^a$. This is compared with the previously calculated value, and the guess of the ammonium/D2EHPA ion-pair concentration is adjusted. Thus the procedure is iterative.

When data for an amine-to-D2EHPA molar ratio of 1:2 and at stoichiometries less than 0.5 were treated as the data were in Tables 6.15 and 6.16, negative values of [B] resulted. This suggested that the value of [B:HA] was too high. The mass balances in Equations 6.13 and 6.14 could be satisfied if additional D2EHPA were associated with each amine. Thus the following additional equilibrium was considered:

$$B{:}HA + HA \rightleftarrows B{:}(HA)_2 \qquad (6.16)$$

In this case Equation 6.13 becomes:

$$[HA]_o = [B{:}HA] + 2[B{:}(HA)_2] + [NH_4^+A^-] + [HA]^a \qquad (6.17)$$

The equilibrium constant for Equation 6.16 is:

$$K_{B:(HA)_2} = \frac{[B:(HA)_2]}{[B:HA]\ [HA]} \qquad (6.18)$$

Assuming a value of $K_{B:HA}$ of 2000, values of $K_{B:(HA)_2}$ were calculated for the relevant cases. These are given in Table 6.17. The values are not as constant as were those for $K_{B:HA}$, but an important fact is established. For those cases in which the molar ratio of D2EHPA not complexed with ammonia to amine is high, the concentration of $B:(HA)_2$ is relatively high, approximately the same as that for B:HA (see Table 6.18). The concentration of B is relatively low. On the other hand, for the data in Tables 6.15 and 6.16 in which the molar ratio of free D2EHPA to amine is less than one, the concentration of $B:(HA)_2$ is very small and decreases as stoichiometry increases. This complexation of additional D2EHPA by the amine was noted earlier. The complexation of additional D2EHPA by the amine/D2EHPA complex is weaker than the original amine/D2EHPA complexation. This results in K_{c,NH_4^+} values at low stoichiometry for amine-to-D2EHPA molar ratio of 1:2 which are higher than those which would be expected based on K_{c,NH_4^+} values at high stoichiometry. This causes the curves in Figure 6.6 to be concave upward.

Some of the discrepancy in the $K_{B:(HA)_2}$ values may be due to the fact that some of the D2EHPA is complexing with the ammonium/D2EHPA ion pair. This possibility was not considered in these calculations. Thus there is competition between the ammonium/D2EHPA ion pair and the amine/D2EHPA complex for the additional D2EHPA. This model could be

TABLE 6.17

$K_{B:(HA)_2}$ VALUES FOR AMINE DILUENTS(a)

$[D2EHPA]_o = 0.25$ M   [Adogen 364] = 0.14 M

$s^{(b)}$	K_c^a/K_c^t	$K_{B:(HA)_2}$
0.12	4.0×10^{-2}	1.5×10^2
0.25	4.2×10^{-2}	7.8×10^1

$[D2EHPA]_o = 0.48$ M   [Adogen 364] = 0.26 M

$s^{(b)}$	K_c^a/K_c^t	$K_{B:(HA)_2}$
0.13	1.4×10^{-2}	3.0×10^2
0.26	3.0×10^{-2}	5.7×10^1

(a): $K_{B:(HA)_2}$ defined by Equation 6.18

(b): stoichiometry: $[NH_4^+A^-]/[D2EHPA]_o$

TABLE 6.18

RELATIVE AMOUNTS OF FREE AMINE AND AMINE:D2EHPA COMPLEXES

$[\text{D2EHPA}]_o = 0.48\ \underline{M}$

[ADOGEN 364]$^{(a)}$ ($\underline{M}$)	$s^{(b)}$	$\frac{[\text{B:(HA)}_2]}{[\text{Adogen 364}]}$	$\frac{[\text{B}]}{[\text{Adogen 364}]}$	$\frac{[\text{D2EHPA}]_o - [\text{NH}_4{}^+\text{A}^-]}{[\text{Adogen 364}]}$
0.52	0.2	0.06	0.28	0.74
0.52	0.76	0.006	0.78	0.22
0.26	0.13	0.61	0.03	1.61
0.26	0.26	0.38	0.03	1.34
0.26	0.79	0.025	0.60	0.39

(a): total concentration of Adogen 364
(b): stoichiometry: $[\text{NH}_4{}^+\text{A}^-]/[\text{D2EHPA}]_o$

improved by optimizing the values of $K_{B:HA}$ and $K_{B:(HA)_2}$. In addition better values of $[HA]^a$ might be obtained by comparing the K_{c,NH_4^+} values for the amine diluent to that for the toluene diluent under conditions in which the organic-phase activity coefficients for both the ammonium/D2EHPA ion pair and free D2EHPA would be comparable to those in the amine diluent. That is, basing the calculation in Equation 6.11 on K_{c,NH_4^+} values at the same stoichiometry may not have been the best approach. An additional indication of the shortcomings of this model is pointed out by the linearity of the curves in Figure 6.6 at the 1:1 molar ratio. To the extent that these curves are linear and go through the origin then K_{c,NH_4^+} values are proportional to $[HA]^t$ and no additional D2EHPA complexes with the ion pair. This implies that $[HA]^a$ is proportional to $[HA]^t$, which is approximately equal to [B:HA]. Equation 6.15 then suggests that [B] is constant. Thus as stoichiometry increases and the amine is released from D2EHPA the amine must solvate either the ion pair or the amine/D2EHPA complex. Neither of these possibilities was considered in this model.

B. PHASE-SEPARATION PROPERTIES

As pointed out previously, several factors affect the phase-separation properties of the systems under study. These include D2EHPA concentration, ammonium/D2EHPA ion-pair concentration, stoichiometry, raffinate concentration, volumetric phase ratio and pH (at least for pH values less than the pK_a of D2EHPA, which is 3.1 (Ashbrook, 1973)). In this section results are presented for experiments to determine how these variables affect the phase-separation properties for the various diluents studied. The results are interpreted in terms of the factors known to affect phase-separation properties. However it should be noted that the results are qualitative only, and several factors may come into play in each case. For all results reported, mixing was kept as uniform as possible. First solutions were mixed by hand, and then the separatory funnel containing the solution was placed on the Junior Orbit Shaker for one hour at 250 RPM. The solutions were then allowed to settle overnight.

In the results that follow, data are often repeated in different tables to facilitate comparisons. Also it should be noted that when white organic phases resulted these could always be centrifuged to give a clear organic phase and a white emulsion below it.

Data for the alcohol-containing diluent are considered first. The first type of comparison is for systems at the same total concentration of D2EHPA, the same S/W and increasing concentrations of the ammonium/D2EHPA ion pair. In general as this concentration increased the raffinate concentration increased also. This type of comparison would represent several points in a liquid-liquid extraction contacting scheme.

In Table 6.19 results for a D2EHPA concentration of 0.48 $\underline{M}$ and an S/W of 2.5 are presented. As the concentration of the ion pair increases, the quality of the phase-separation properties goes through a minimum. The initial decrease in phase-separation behavior is probably due to the increase in the concentration of the highly interfacially active ammonium/D2EHPA ion pair. The subsequent improvement in behavior may be attributed to an increase in the raffinate concentration, i.e., the higher ionic strength of the aqueous phase. In Tables 6.1, 6.2, 6.3 and 6.11 this improvement in phase-separation behavior is not observed,

TABLE 6.19

PHASE-SEPARATION PROPERTIES FOR ALCOHOL DILUENT AT CONSTANT S/W AND $[D2EHPA]_o$ [a]

S/W (v/v) = 2.5 $[D2EHPA]_o$ = 0.48 M

DILUENT = 50% (v/v) decanol in toluene   FEED = NH_4HCO_3 solution

$[NH_4^+A^-]$ (M)	(N) (M)	s	PHASE SEPARATION O	A	I
~0.004	~0.003	low	1	1	1
0.111	0.01	0.24	2	1	4
0.23	0.017	0.49	1	1	3
0.36	0.045	0.78	1	1	1
0.40	0.17	0.99	1	1	1

(a): see Table 6.1 for explanation of symbols

presumably because the raffinate concentrations never become very high.

In the first set of entries in Table 6.20 (higher initial D2EHPA concentrations), phase-separation properties are poor due to the high concentration of D2EHPA, which increases the viscosity of the organic phase and makes it easier to emulsify. From the next two sets of entries in Table 6.20 it is seen that at high S/W ratios the effect of D2EHPA concentration is not as severe.

By comparing the last set of entries in Table 6.20 with those in Tables 6.1, 6.11 and 6.19 the effect of raffinate concentration can be deduced. All of these data are for 0.48 M D2EHPA in 50% (v/v) alcohol in toluene. The best phase-separation properties are seen for the data in Table 6.20, in which a high concentration of phosphate is present in the aqueous raffinate. Phase-separation properties are about the same for the data in Tables 6.1 and 6.19, with the exception of the improvement observed at high raffinate concentrations in Table 6.19 as noted above. The worst phase-separation properties are exhibited by the data in Table 6.11, in which raffinate concentrations are very low.

A comparison can be made of data at constant stoichiometry. In Table 6.21 the feed concentration was held constant, and the concentration of D2EHPA and S/W were varied to maintain a constant stoichiometry. Phase-separation behavior gets worse as the concentration of D2EHPA increases, but this may also be due to the decrease in S/W and the increase in ammonium/D2EHPA ion-pair concentration. The data in Table 6.22 are for a constant stoichiometry and S/W and increasing concentration of D2EHPA. At all of the stoichiometries studied, increasing the D2EHPA concentration makes the phase-separation properties worse. This is probably due to the increase

TABLE 6.20

PHASE-SEPARATION PROPERTIES FOR ALCOHOL DILUENT
AT CONSTANT S/W AND $[D2EHPA]_o$(a)

DILUENT = 50% (v/v) decanol in toluene FEED = NH_4HCO_3 solution

S/W (v/v)	$[D2EHPA]_o$ (M)	$[NH_4^+A^-]$ (M)	(N) (M)	s	PHASE SEPARATION O	 A	 I
2.5	0.89	0.22	0.009	0.25	2	2	4
"	"	0.44	0.017	0.49	2	2	4
5	0.18	0.055	0.0087	0.31	1	1	3
"	"	0.112	0.02	0.64	1	1	3
5	0.71	0.12	0.0064	0.16	1	1	4
"	"	0.23	0.01	0.33	1	1	3

FEED = ammonium hydroxide/ammonium phosphate solution

S/W (v/v)	$[D2EHPA]_o$ (M)	(PO_4^{3-}) (M)	$[NH_4^+A^-]$ (M)	(N) (M)	s	PHASE SEPARATION O	 A	 I
2.5	0.48	0.3	0.12	0.30	0.25	1	1	1
"	"	0.4	0.17	0.38	0.36	1	1	1

(a): see Table 6.1 for explanation of symbols

TABLE 6.21

PHASE-SEPARATION PROPERTIES FOR ALCOHOL DILUENT

AT CONSTANT STOICHIOMETRY[(a)]

$[NH_4^+A^-]/[D2EHPA]_o = 0.5$

DILUENT = 50% (v/v) decanol in toluene FEED = NH_4HCO_3 solution

$[NH_4^+A^-]$ (M)	(N) (M)	$[D2EHPA]_o$ (M)	S/W (v/v)	PHASE SEPARATION O	A	I
0.1	0.017	0.2	5	1	1	1
0.23	-	0.48	2.5	1	1	3
0.29	-	0.60	2	2	2	4
0.33	0.013	0.69	1.6	2	2	4
0.39	-	0.81	1.4	2	2	4

(a): see Table 6.1 for explanation of symbols

TABLE 6.22

PHASE-SEPARATION PROPERTIES FOR ALCOHOL DILUENT AT CONSTANT STOICHIOMETRY AND S/W[(a)]

DILUENT = 50% (v/v) decanol in toluene FEED = NH_4HCO_3 solution

s	S/W (v/v)	$[NH_4^+A^-]$ (M)	(N) (M)	$[D2EHPA]_o$ (M)	PHASE SEPARATION O	 A	 I
0.33	5	0.055	0.0087	0.18	1	1	2
"	"	0.113	0.01	0.35	1	1	3
"	"	0.233	0.01	0.71	1	1	3
0.24	5	0.05	–	0.20	1	1	1
"	"	0.11	0.01	0.48	1	1	2

FEED = ammonium hydroxide/ammonium phosphate solution

s	S/W (v/v)	(PO_4^{3-}) (M)	$[NH_4^+A^-]$ (M)	(N) (M)	$[D2EHPA]_o$ (M)	PHASE SEPARATION O	 A	 I
0.14	2.5	0.01	0.035	0.013	0.25	1	1	1
"	"	0.01	0.055	0.013	0.37	1	1	1
"	"	0.019	0.072	0.022	0.48	1	1	4

(a): see Table 6.1 for explanation of symbols

in the concentration of the ammonium/D2EHPA ion pair.

In Table 6.23 the effect of varying the concentration of D2EHPA and the stoichiometry at constant S/W and concentration of ammonium/D2EHPA ion pair is studied. Increasing the concentration of D2EHPA decreases stoichiometry and also reduces the raffinate concentration. For the first set of entries in Table 6.23, at the lower concentrations of D2EHPA, phase-separation behavior is not much affected by D2EHPA concentration and stoichiometry. These effects may be offsetting. For all of the entries at higher concentrations of D2EHPA, however, increasing the concentration of D2EHPA causes the phase-separation properties to become worse. This may be due to the high D2EHPA concentration or to the lower raffinate concentrations.

In Table 6.24 the effect of changing S/W at constant concentration of D2EHPA and feed concentration is studied. At both concentrations of D2EHPA studied, phase-separation properties go through a minimum. The phase-separation properties get worse as the concentration of the ion pair and the stoichiometry increase and S/W decreases. Above a certain raffinate concentration, however, phase-separation properties improve, possibly due to the higher raffinate concentrations.

The effect of S/W on phase-separation properties is presented in Table 6.25. At constant concentration of D2EHPA, concentration of ammonium/D2EHPA ion pair and raffinate, decreasing S/W makes the phase-separation properties worse. This was observed in the last chapter and was interpreted in terms of the tendency to form oil-in-water type emulsions.

Data for the toluene diluent are considered next. The data in Tables 6.4, 6.5 and 6.6 parallel those for the alcohol diluent in Tables

TABLE 6.23

PHASE-SEPARATION PROPERTIES FOR ALCOHOL DILUENT AT CONSTANT S/W AND $[NH_4^+A^-]^{(a)}$

DILUENT = 50% (v/v) decanol in toluene FEED = NH_4HCO_3 solution

S/W (v/v)	$[NH_4^+A^-]$ (M)	$[D2EHPA]_o$ (M)	(N) (M)	s	PHASE SEPARATION O	 A	 I
5	0.12	0.18	0.020	0.64	1	1	2
"	"	0.20	0.017	0.54	1	1	1
"	"	0.27	0.013	0.43	1	1	2
"	"	0.35	0.010	0.32	1	1	3
"	"	0.71	0.0064	0.16	1	1	4
2.5	0.22	0.48	-	0.49	1	1	3
"	"	0.89	0.009	0.25	2	2	4
2.5	0.42	0.48	0.17	0.91	1	1	1
"	"	0.89	0.017	0.49	2	2	4

(a): see Table 6.1 for explanation of symbols

TABLE 6.24

PHASE-SEPARATION PROPERTIES FOR ALCOHOL DILUENT

AT CONSTANT $[D2EHPA]_o$ (a)

DILUENT = 50% decanol in toluene   FEED = NH_4HCO_3 solution

$[D2EHPA]_o$	$[NH_4^+A^-]$	(N)	s	S/W	PHASE SEPARATION		
(M)	(M)	(M)		(v/v)	O	A	I
0.48	0.113	0.01	0.24	5	1	1	2
"	0.23	~0.017	0.49	2.5	1	1	3
"	0.305	0.03	0.67	2	2	2	4
"	0.363	0.069	0.87	1.4	1	2	3
0.69	0.115	0.0064	0.16	5	1	1	4
"	0.164	0.01	0.24	3.3	1	1	4
"	0.33	0.013	0.49	1.6	2	2	4
"	0.44	0.027	0.67	1.25	2	2	4
"	0.56	0.046	0.87	0.9	1	2	3

(a): see Table 6.1 for explanation of symbols

TABLE 6.25

PHASE-SEPARATION PROPERTIES FOR ALCOHOL DILUENT AT CONSTANT $[D2EHPA]_o$, $[NH_4{}^+A^-]$, AND $(N)^{(a)}$

DILUENT = 50% (v/v) decanol in toluene FEED = NH_4HCO_3 solution

$[D2EHPA]_o$ (M)	$[NH_4{}^+A^-]$ (M)	(N) (M)	S/W (v/v)	PHASE SEPARATION		
				O	A	I
0.2	0.1	0.017	5	1	1	1
"	"	0.014	2.5	1	1	2
"	"	0.013	1.6	1	1	2
"	"	0.013	1.25	2	2	4
0.48	0.1	0.01	5	1	1	2
"	"	0.01	2.5	1	1	4

(a): see Table 6.1 for explanation of symbols

6.1, 6.2, 6.3, 6.11 and 6.19. For the alcohol diluent phase-separation properties get worse with increases in the concentration of the ammonium/D2EHPA ion pair and then get better at higher raffinate concentrations. For the toluene diluent such a minimum in behavior is seen for the data in Tables 6.4 and 6.6. In Table 6.5 the change in raffinate concentration is not as large, and the improvement in phase separation at high stoichiometry is not observed. This was seen previously when Tables 6.1 and 6.19 were compared. McDowell (1971) observed behavior similar to that reported here at low stoichiometries. He found for extraction of alkali metals by D2EHPA that increasing the stoichiometry above about 0.25 caused a deterioration in phase-separation properties.

Table 6.26 for toluene compares with Table 6.22 for the alcohol diluent. In both cases it is seen that, at constant S/W and stoichiometry, increasing the concentration of D2EHPA causes the phase-separation properties to become worse. This is probably due to the increase in the ammonium/D2EHPA ion-pair concentration. The exceptions are the data at 0.26 stoichiometry. In this case the concentration of D2EHPA was not varied as much as in the other cases.

Table 6.27 for toluene compares with Table 6.23 for the alcohol diluent. There it was found that, at constant S/W and ion-pair concentration, that increasing the concentration of D2EHPA made the phase-separation properties worse, particularly at high concentrations of D2EHPA. For the toluene-diluent case the first two sets of entries in Table 6.27 indicate that increasing the concentration of D2EHPA improves phase-separation properties, probably due to the decrease in stoichiometry. Stoichiometry would be expected to be more important in

TABLE 6.26

PHASE-SEPARATION PROPERTIES FOR TOLUENE DILUENT AT CONSTANT STOICHIOMETRY AND S/W(a)

DILUENT = toluene FEED = ammonium hydroxide/ammonium phosphate solution

s	S/W (v/v)	$(PO_4{}^{3-})$ ($\underline{M}$)	$[NH_4{}^+A^-]$ ($\underline{M}$)	(N) ($\underline{M}$)	$[D2EHPA]_o$ ($\underline{M}$)	PHASE SEPARATION			
						O	A	I	C
0.14	5	0.019	0.035	0.027	0.25	1	1	2	2
"	"	0.019	0.054	0.030	0.37	1	2	3	1
"	"	0.019	0.069	0.027	0.48	1	1	3	1
0.26	5	0.019	0.066	0.030	0.25	2	2	4	2
"	"	0.019	0.099	0.032	0.37	1	2	4	1
0.53	5	0.019	0.13	0.037	0.25	2	2	4	2
"	"	0.019	0.195	0.037	0.37	2	2	4	1
"	"	0.019	0.266	0.045	0.48	2	4	4	2

(a): see Table 6.1 for explanation of symbols

TABLE 6.27

PHASE-SEPARATION PROPERTIES FOR TOLUENE DILUENT AT CONSTANT S/W AND $[NH_4^+A^-]$(a)

DILUENT = toluene FEED = ammonium hydroxide/ammonium phosphate solution

S/W (v/v)	$[NH_4^+A^-]$ (M)	(PO_4^{3-}) (M)	$[D2EHPA]_o$ (M)	(N) (M)	s	PHASE SEPARATION			
						O	A	I	C
5	0.067	0.019	0.25	0.030	0.26	2	2	4	2
"	"	0.019	0.48	0.027	0.14	1	1	3	1
5	0.195	0.019	0.25	0.039	0.77	1	4	4	2
"	"	0.019	0.37	0.037	0.53	2	2	4	1
5	0.25	0.019	0.37	0.045	0.73	1	4	4	2
"	"	0.019	0.48	0.045	0.55	2	4	4	2

(a): see Table 6.1 for explanation of symbols

the toluene-diluent case than in the alcohol case because the complexation of the ammonium/D2EHPA ion pair by additional undissociated D2EHPA is more important in the toluene diluent. Also at high stoichiometry the amount of water coextracted into the organic phase is very high and, especially for the toluene diluent, increases very rapidly with increases in the concentration of the ammonium/D2EHPA ion pair. This may contribute to the phase-separation problems at high stoichiometry. The last set of data in Table 6.27 are for both higher concentrations of D2EHPA and higher stoichiometries. In this case increasing the concentration of D2EHPA makes the phase separation slightly worse.

The phase-separation properties of the amine diluents are considered next. Comparing results in Tables 6.7 and 6.8 suggests that, at constant S/W and concentration of D2EHPA, increasing the concentration of the amine improves phase-separation behavior. This indicates that the extra amine in the system may solvate the ion pair to some extent. The excess amine also interacts to a greater extent with D2EHPA, reducing its interfacial activity.

At the same ratio of amine to D2EHPA, a lower concentration of D2EHPA should give better phase-separation properties at the same stoichiometry. This is true for the case with an amine-to-D2EHPA molar ratio of 1:2 (Tables 6.8 and 6.10), but is not true for the 1:1 case (Tables 6.7 and 6.9). This latter effect may be due to the lower S/W ratio used for the case of lower concentration of D2EHPA.

At an amine-to-D2EHPA molar ratio of 1:1, increasing the concentration of the ammonium/D2EHPA ion pair does not greatly affect phase-separation properties. This is in contrast to the toluene-diluent and alcohol-diluent cases in which phase separation got worse and then improved. The effect here may be due to a balancing of the effects of the higher ammonium/D2EHPA ion pair concentration and the higher raffinate concentration. Solvation by the free amine may also be a factor.

At an amine-to-D2EHPA molar ratio of 1:2, increasing the concentration of the ammonium/D2EHPA ion pair caused a minimum in the phase-separation behavior at low concentrations of D2EHPA (Table 6.10). At the higher concentration of D2EHPA (Table 6.8) the improvement in phase separation at higher concentrations of the ammonium/D2EHPA ion pair is also observed. This may be due to the increase in raffinate concentration. In addition, as the concentration of the ion pair increases the amount of amine per free D2EHPA increases. This would tend to lower the interfacial activity of the D2EHPA. Also, the excess amine may solvate the ion pair some.

The amine diluent phase-separation behavior can be compared with that of the toluene diluent. At a concentration of D2EHPA of 0.48 M, the higher amine concentration (Table 6.7) gives better phase-separation properties than the toluene diluent (Table 6.4). The lower amine concentration (Table 6.8) gives only slightly better phase-separation properties than toluene. However at higher stoichiometries this lower amine concentration gives significantly better phase-separation properties than the toluene diluent. The higher raffinate concentrations for the amine diluent cases may be partially responsible for this behavior. Again solvation of the ion pair by the free amine may also be a factor.

At a D2EHPA concentration of 0.25 M the higher amine concentration

(Table 6.9) gives slightly worse phase-separation behavior than the toluene diluent (Table 6.6). This is probably due to the lower S/W ratio used in the amine-diluent case. At the lower amine concentration (Table 6.10) the above mentioned relative improvement in phase-separation behavior at high stoichiometry is observed.

In summary, it is apparent that many factors affect phase-separation tendencies. The alcohol diluent gives much better phase-separation properties than do either of the other diluents. The amine-containing diluent gives slightly better phase-separation properties than the toluene diluent, especially at high amine-to-D2EHPA molar ratios and higher stoichiometries.

These factors tend to cause phase-separation problems: high concentration of D2EHPA, high concentration of ammonium/D2EHPA ion pair, low raffinate concentrations, low S/W and high stoichiometry (especially for the toluene diluent). For the amine diluent at an amine-to-D2EHPA molar ratio of 1:2 higher stoichiometry appears to improve phase-separation properties.

C. AQUEOUS-PHASE EXTRACTANT LOSSES

In this section results of experiments for determining the aqueous-phase solubility losses of D2EHPA from various solvents are presented. D2EHPA solubility losses were equated to the measured concentration of phosphorus-containing compounds in the aqueous phase (See Chapter 2, section C). Only data for solvents containing D2EHPA which had been purified by the copper-salt-precipitation method are presented (Chapter 3, section B). The water-soluble phosphorus impurities in D2EHPA were assumed to be removed by this procedure. This is based on the results of titrations of purified D2EHPA (Chapter 3, section B) and the results of measuring the water solubility of D2EHPA. The solubility of undiluted, purified D2EHPA was measured at 93 ppm, in agreement with the literature value of 100 ppm (Mobil Chemical Company, 1981). Also the concentration of phosphorus in water after contacting it with 0.2 M purified D2EHPA in toluene, in 50% (v/v) 1-decanol in an aromatic diluent, and in 0.2 M Adogen 364 in toluene was in all cases less than 1 ppm. Several diluents were found to contain phosphorus impurities. Only data for those diluents which did not contain a phosphorus impurity are included. Data comparing aqueous-phase phosphorus concentrations using as-received and purified D2EHPA are presented in Appendix I.

In Table 6.28 data for solutions generated during the extraction/stripping experiments described in Chapter 3, section H are presented. In all of these cases the measured pH value agrees well with that predicted from the vapor-liquid equilibrium model (TIDES) using measured values of the concentrations of CO_2, NH_3 and D2EHPA in the aqueous phase. In addition K_{c,NH_4^+} values agree well with those predicted using Figures 6.4 and 6.5 (see Table 7.10).

Values of $K_{c,NH_4^+}/P$ and $K_{c,H^+}/P$ are given. The latter was calculated based on the concentration of D2EHPA not ion-paired with ammonium. As developed in Chapter 5, section B a high value of the former indicates a low organic-phase activity coefficient for the ammonium/D2EHPA ion pair and a high value of the latter indicates a low activity coefficient for D2EHPA in the organic phase. The results in Table 6.28 indicate that the alcohol diluent produces the lowest organic-phase activity coefficient for the ion pair, supporting the aforementioned concept that the alcohol solvates the ion pair. On the

TABLE 6.28

D2EHPA SOLUBILITY LOSSES

SOLVENT = 0.48 M D2EHPA IN DILUENT

FEED = NH_4HCO_3 solution S/W (v/v) = 2.5

DILUENT	$(NH_4^+)^{(a)}$ (M)	$[NH_4^+A^-]^{(b)}$ (M)	$(P)^{(c)}$ (M)	pH	$K_{c,NH_4^+}/P^{(d)}$	$K_{c,H^+}/P^{(e)}$
50% Alfol 10/ toluene	0.0075	0.25	0.004	6.2	8.2×10^3	8.8×10^7
Toluene	0.0186	0.23	0.0125	6.6	9.9×10^2	7.9×10^7
0.52 M A364/ toluene	0.046	0.21	0.006	8.7	8.0×10^2	2.2×10^{10}

(a): concentration of ammonium ions in raffinate, determined from measured total ammonia concentration and pH: mole/liter
(b): calculated ammonia concentration in the organic phase: mole/liter
(c): measured concentration of phosphorus in raffinate: mole/liter
(d): K_c for ammonium ion divided by concentration of phosphorus in raffinate, expressed as mole/liter
(e): K_c for hydrogen ion divided by concentration of phosphorus in raffinate, expressed as mole/liter

other hand, the amine diluent dramatically lowers the activity coefficient of D2EHPA in the organic phase, supporting the idea that it interacts strongly with D2EHPA.

The fairly constant value of $K_{c,NH_4^+/P}$ between the toluene and amine diluents suggests that the ion pair is solvated about the same in both solvents at this stoichiometry. In the toluene diluent solvation is by D2EHPA and toluene. In the amine-containing diluent solvation is by the free amine and toluene. However this effect was not seen in the results presented in Table 5.3, where increasing the amount of amine in the diluent reduced the value of $K_{c,NH_4^+/P}$.

The fairly constant value of $K_{c,H^+/P}$ between the alcohol and toluene diluents suggests that the activity of D2EHPA is about the same in both solvents at this stoichiometry. Thus the reduction in D2EHPA activity due to solvation by the alcohol is about the same as the reduction by dimerization of D2EHPA and solvation of the ion pair in the toluene diluent.

The ratio of the $K_{c,H^+/P}$ value for the amine diluent to that for the toluene diluent at the same concentration of D2EHPA, same stoichiometry and same pH is proportional to the ratio of the organic-phase activity coefficient for free D2EHPA in the toluene diluent to that in the amine diluent (Equation 5.10). If the organic-phase activity coefficients for the ammonium/D2EHPA ion pair are constant between the two diluents then, the ratio of $K_{c,H^+/P}$ values for the amine diluent versus the toluene diluent is inversely proportional to the respective K_{c,NH_4^+} values. If the same assumptions are made as in deriving Equation 6.11, then the ratio of K_{c,NH_4^+} values is equal to the ratio of the concentration of free D2EHPA in the toluene diluent to the concentration of D2EHPA in the amine diluent not associated with either ammonium or amine, $[HA]^a$. At a constant ratio of $[B:HA]/[B]$, $[HA]^a$ is inversely proportional to $K_{B:HA}$ (Equation 6.15). Thus the ratio of $K_{c,H^+}/P$ in the amine diluent to that in the toluene diluent is inversely proportional to $[HA]^a$ and proportional to $K_{B:HA}$.

To simulate conditions at the raffinate exit of a solvent extraction process, in which a dilute aqueous solution would contact an organic solvent containing very little NH_3, the aqueous solutions described in Table 6.28 were contacted with fresh organic solvents. The results are presented in Table 6.29.

For the data in Table 6.29 the K_{c,NH_4^+} values for the toluene diluent and the amine diluent agree fairly well with those predicted by Figures 6.4 and 6.5. The pH values are also reasonable based on measured NH_3 and D2EHPA concentrations, especially if the effect on aqueous-phase pH of small errors in these concentrations is considered. For the alcohol diluent the NH_3 concentration measurement for the raffinate was not stable. Neither was the pH. The values listed do not agree with those predicted by Figure 6.4. This figure predicts a much higher K_{c,NH_4^+} at a pH of 6. These data are probably in error.

The data in Table 6.29 suggest that at low stoichiometry the amine diluent solvates D2EHPA better than does toluene. For the toluene diluent the reduction in $K_{c,H^+}/P$ as stoichiometry decreases suggests that at high stoichiometry D2EHPA solvates the ion pair and the activity of D2EHPA is lowered. At low stoichiometry this solvation is not as effective in reducing D2EHPA activity. Uncertainties in raffinate concentrations prohibit making useful conclusions about $K_{c,NH_4^+}/P$.

TABLE 6.29

D2EHPA SOLUBILITY LOSSES IN THE BACK EXTRACTION OF RAFFINATES IN TABLE 6.28(a)

SOLVENT = 0.48 M D2EHPA IN DILUENT

FEED = Raffinates from Table 6.28   S/W (v/v) = 2.5

DILUENT	(NH_4^+) (M)	$[NH_4^+A^-]$ (M)	(P) (M)	pH	$K_{c,NH_4^+/P}$	$K_{c,H^+/P}$
50% Alfol 10/ toluene	0.004(b)	0.001	0.00055	6.(b)	5×10^2	1×10^9
Toluene	0.005(b)	0.005	0.0015	4.6	6.7×10^2	1.3×10^7
0.52 M A364/ toluene	0.02	0.016	0.003	8.0	2.9×10^2	1.5×10^{10}

(a): see Table 6.28 for definition of symbols
(b): values not very stable

Table 6.30 presents additional data for extractant losses from a 0.48 M D2EHPA in 50% (v/v) Alfol 10/toluene solvent. These data agree well with the data in Figure 6.4 and the measured concentrations of phosphorus agree well with those expected. Since the only anion present in the aqueous phase is ionized D2EHPA, its concentration must equal that of the ammonium ions, if electroneutrality is to be satisfied. The agreement between the two measured concentrations as presented in Table 6.30 is satisfactory. $K_{c,NH_4^+/P}$ and $K_{c,H^+/P}$ values appear to be independent of stoichiometry as would be expected if no additional complexation of the ion pair occurred. These data also serve to show the effects of uncertainities in the phosphorus-concentration measurements. The values reported in Table 6.28 for the alcohol diluent fall in the range of values given in Table 6.30.

Solubility data for D2EHPA extractant losses from 0.2 M and 0.5 M solvents are presented in Table 6.31. The pH values were not measured but were estimated by pH paper. The values of pH reported were predicted using Figures 6.4 and 6.5 and substantiated the estimates by pH paper. For the toluene diluent, decreasing stoichiometry appears to increase $K_{c,NH_4^+/P}$, suggesting solvation of the ion pair by D2EHPA. In contrast to the effects seen earlier, $K_{c,H^+/P}$ increases with decreasing stoichiometry. Again errors in the aqueous-phase phosphorus-concentration measurements may be responsible, and interpretation of the data is limited to discussing trends.

The results in Table 6.31 again indicate that the alcohol diluent solvates the ion pair the best. On the other hand the amine diluent solvates D2EHPA best, although the value of $K_{c,H^+/P}$ is not as high here as for the case of a 1:1 amine-to-D2EHPA molar ratio. The low $K_{c,NH_4^+/P}$

TABLE 6.30

D2EHPA SOLUBILITY LOSSES(a)

SOLVENT = 0.48 M D2EHPA IN 50% (v/v) Alfol 10/toluene

FEED = NH_4OH solution   S/W (v/v) = 2.5

(NH_4^+) (M)	$[NH_4^+A^-]$ (M)	(P) (M)	pH	$K_{c,NH_4^+/P}$	$K_{c,H^+/P}$
0.0036	0.06	0.0022	5.4	8.0×10^3	4.7×10^7
0.0040	0.13	0.0029	6.1	1.1×10^4	1.5×10^8
0.0056	0.26	0.0082	6.3	5.6×10^3	5.4×10^7
0.0065	0.39	0.0050	6.7	1.2×10^4	9.3×10^7
0.0078	0.45	0.0055	7.4	1.0×10^4	1.4×10^8
0.0056	0.5	0.0053	10.	1.7×10^4	-

(a): see Table 6.28 for definition of symbols

TABLE 6.31

D2EHPA SOLUBILITY LOSSES(a)

SOLVENT = D2EHPA IN DILUENT

FEED = NH_4HCO_3 solution   S/W (v/v) = 5

DILUENT	$[\text{D2EHPA}]_o$(b) (M)	(NH_4^+) (M)	s(c)	(P) (M)	pH(d)	$K_{c,NH_4^+}/P$	$K_{c,H+}/P$
Toluene	0.2	0.034	0.5	0.0058	6.	5×10^2	1.7×10^7
Toluene	0.5	0.01	0.2	0.0055	6.	1.6×10^3	7.3×10^7
50% 1-Decanol/ toluene	0.2	0.015	0.5	0.0009	5.9	7.6×10^3	8.4×10^7
0.08 M A364/ toluene	0.2	0.133	0.4	0.0023	7.2	2.6×10^2	5.3×10^8

(a): see Table 6.28 for definition of symbols
(b): total concentration of D2EHPA, in all forms
(c): stoichiometry, calculated as the concentration of ammonia in-organic phase divided by the initial, or total, concentration of D2EHPA
(d): estimated from Figures 6.4 and 6.5

value for the amine diluent suggests that the ion pair is not well solvated, probably due to the complexation of the D2EHPA by the amine thus preventing it from solvating the ion pair and also due to the lack of free amine.

Results for additional raffinate back extractions are presented in Table 6.32. In the first two cases the original raffinate was generated from extraction of an NH_4HCO_3 solution with 0.2 $\underline{M}$ D2EHPA in 50% (v/v) 1-decanol/toluene. The raffinate NH_3 concentration was 0.016 $\underline{M}$ and the phosphorus concentration was 0.0008 $\underline{M}$. The original raffinate used for the back extraction represented by the third entry in Table 6.32 was generated by the extraction of an NH_4HCO_3 solution with 0.2 $\underline{M}$ D2EHPA in 6.5% (v/v) 1-decanol in toluene. This raffinate contained 0.032 $\underline{M}$ NH_3 and 0.0034 $\underline{M}$ phosphorus.

In these back extractions it was difficult to get a precise measure of the NH_3 concentration in the second raffinate, and so it was not possible to apply the liquid-liquid extraction models to predict pH. Estimates by pH paper indicated that the pH values of the second raffinates were all lower than those for the original raffinates. This would be consistent with the observation that NH_3 was extracted from the aqueous phases, thus tending to lower pH. Very low extractant solubility losses were measured for the alcohol diluent. The pH values for the first two cases listed in Table 6.32 appeared to be fairly similar and so it can be surmised that the $K_{c,H^+/P}$ value for the alcohol diluent is higher than that for the toluene diluent at this low stoichiometry as might be expected. In addition, $K_{c,NH_4^+/P}$ appears to be higher for the alcohol diluent than for toluene. The 6.5% (v/v) 1-decanol in toluene diluent also appears to give a fairly high $K_{c,H^+/P}$

TABLE 6.32

D2EHPA SOLUBILITY LOSSES IN THE BACK EXTRACTION OF RAFFINATES(a)

SOLVENT = 0.2 M D2EHPA IN DILUENT

FEED = Raffinate 1   S/W (v/v) = 5

	RAFFINATE 1(b)		RAFFINATE 2(c)	
DILUENT	(NH_4+) (M)	(P) (M)	(NH_4+) (M)	(P) (M)
Toluene	0.016	0.0008	0.006(d)	0.0017
50% 1-Decanol/ toluene	0.016	0.0008	0.003(d)	0.00026
6.5% 1-Decanol/ toluene	0.032	0.0034	0.012	0.00036
Toluene	-	0.0051	-	0.0036

(a): see Table 6.28 for definition of symbols
(b): solution used as feed for back extraction
(c): raffinate of back extraction .
(d): values are approximate

value at low stoichiometry. Finally the data in the last line of Table 6.32 also suggest that the activity of D2EHPA is higher in toluene than in the alcohol at low stoichiometry.

The effect of contacting a D2EHPA-free diluent with a raffinate containing 0.017 M NH_3 and 0.001 M D2EHPA was also studied. At an S/W of 4, contacting with toluene did not lower the concentration of either NH_3 or D2EHPA measurably. However 50% (v/v) 1-decanol in toluene lowered the concentration of D2EHPA in the aqueous phase to 0.00016 M, while not significantly changing the NH_3 concentration. This again indicates that at low stoichiometry the alcohol solvates D2EHPA much better than toluene does.

Some additional data for the back extraction of a raffinate are presented in Table 6.33. In this case the original raffinate contained 0.02 M NH_3. Amine-containing diluents were studied. In these cases the NH_3 concentrations of the raffinates were fairly easy to measure, and so Figure 6.5 was used to predict aqueous-phase pH values. These values agreed with the trend in pH values observed by estimation with pH paper.

The results in Table 6.33 support the concept that the activity coefficient of D2EHPA is lowered to a greater extent the higher the molar ratio of amine to D2EHPA. The activity coefficient of the ammonium/D2EHPA ion pair does not appear to be affected appreciably by this ratio, although the data scatter and such an effect would probably be present at higher amine/D2EHPA molar ratios. The very low $K_{c,NH_4^+/P}$ values would suggest that the ion pair is not well solvated by either D2EHPA or the amine. At the lower ratio of amine to D2EHPA this indicates that the amine/D2EHPA complex is solvated by additional D2EHPA making this D2EHPA unavailable for solvating the ion pair. At the

TABLE 6.33

D2EHPA SOLUBILITY LOSSES IN THE BACK EXTRACTION OF RAFFINATES[a]

SOLVENT = D2EHPA IN TOLUENE PLUS AMINE MODIFIER

FEED = solution containing 0.02 M ammonia   S/W (v/v) = 5

[Adogen 364] (M)	$[D2EHPA]_o$[b] (M)	(NH_4^+) (M)	(P) (M)	pH[c]	$K_{c,NH_4^+/P}$	$K_{c,H^+/P}$
0.2	0.45	0.0086	0.0028	6.1	96	2.0×10^8
0.1	0.2	0.0087	0.0039	6.6	68	1.8×10^8
0.2	0.2	0.011	0.0018	7.3	90	2.4×10^9

(a): see Table 6.28 for definition of symbols
(b): total concentration of D2EHPA, in all forms
(c): estimated from Figures 6.4 and 6.5

higher amine-to-D2EHPA ratio, this suggests that the amine does not solvate the ion pair very well. Based on the available $K_{c,NH_4^+/P}$ data for amine-containing diluents no strong conclusion can be drawn about the solvation of the ion pair by the amine.

In summary, high $K_{c,NH_4^+/P}$ values were obtained when the diluent contained an alcohol. High $K_{c,H^+/P}$ values were obtained when the diluent contained an amine. Higher ratios of amine to D2EHPA increased the value of $K_{c,H^+/P}$. In addition at low stoichiometry, the alcohol appears to solvate D2EHPA better than toluene does.

A high value of $K_{c,H^+/P}$ means that at a given D2EHPA concentration and pH D2EHPA extractant losses will be low. On the other hand a high value of $K_{c,NH_4^+/P}$ means that for a situation producing a given K_{c,NH_4^+} D2EHPA extractant losses will be low.

D. WATER COEXTRACTION

Tables 6.34 through 6.37 present results of measurements of the amount of water coextracted by various solvents. Karl Fischer titrations were used to determine these concentrations (see Chapter 2, section D). The measured concentration of water is given, as well as the ratio of the water concentration to that of the ammonium/D2EHPA ion pair. In addition a corrected value of this ratio is also given. For this corrected value the measured solubility of water in the solvent in the absence of NH_3 was subtracted from the measured concentrations when NH_3 was present. This corrected value gives insight into the mechanism of water coextraction, while the non-corrected value is more useful for process design considerations.

On the basis of the corrected ratio the moles of water coextracted

TABLE 6.34

WATER COEXTRACTION, TOLUENE DILUENT

SOLVENT = D2EHPA IN TOLUENE

$[D2EHPA]_o$ ($\underline{M}$)	$[NH_4{}^+A^-]$ ($\underline{M}$)	$s^{(a)}$	$[H_2O]$ weight %	($\underline{M}$)	$[H_2O]/[NH_4{}^+A^-]$ ($\underline{M}/\underline{M}$)	$[H_2O]/[NH_4{}^+A^-]_{corr}{}^{(b)}$ ($\underline{M}/\underline{M}$)
0.25	0	0	0.14	0.07	-	-
"	0.035	0.14	0.15	0.08	2.2	0.25
"	0.13	0.51	0.88	0.43	3.3	2.8
"	0.195	0.77	2.9	1.5	7.4	7.1
"	0.226	0.89	4.1	2.0	9.0	8.8
"	0.25	1	15.4	7.6	30	30
0.48	0	0	0.17	0.09	-	-
"	0.069	0.14	0.24	0.12	1.7	0.49
"	0.266	0.55	2.1	1.1	4.0	3.7
"	0.4	0.83	5.2	2.5	6.4	6.1
"	0.46	0.96	10.5	5.1	11	11

(a): stoichiometry: $[NH_4{}^+A^-]/[D2EHPA]_o$
(b): corrected for amount of water coextracted by diluent, see text

TABLE 6.35

WATER COEXTRACTION, ALCOHOL DILUENT

SOLVENT = D2EHPA IN 50% (v/v) Alfol 10/toluene

$[\text{D2EHPA}]_o$	$[NH_4{}^+A^-]$	$s^{(a)}$	$[H_2O]$		$[H_2O]/[NH_4{}^+A^-]$	$[H_2O]/[NH_4{}^+A^-]_{corr}{}^{(b)}$
(M)	(M)		weight %	(M)	(M/M)	(M/M)
0.25	0	0	1.4	0.66	-	-
"	0.035	0.14	1.3	0.60	17	(-)
"	0.131	0.52	1.9	0.95	7.2	2.2
"	0.229	0.91	3.2	1.5	6.7	3.8
"	0.25	~1	3.5	1.7	6.6	4.0
0.48	0	0	1.3	0.64	-	-
"	0.072	0.15	1.5	0.7	9.7	0.82
"	0.266	0.55	2.7	1.3	4.9	2.6
"	0.454	0.94	5.9	2.8	6.3	4.9

(a): stoichiometry: $[NH_4{}^+A^-]/[\text{D2EHPA}]_o$
(b): corrected for amount of water coextracted by diluent, see text

TABLE 6.36

WATER COEXTRACTION, AMINE-CONTAINING DILUENT

SOLVENT = 0.48 M D2EHPA IN TOLUENE PLUS AMINE MODIFIER

[Adogen 364] (M)	$[NH_4^+A^-]$ (M)	$s^{(a)}$	$[H_2O]$ weight %	$[H_2O]$ (M)	$[H_2O]/[NH_4^+A^-]$ (M/M)	$[H_2O]/[NH_4^+A^-]_{corr}^{(b)}$ (M/M)
0.26	0	0	0.89	0.43	-	-
"	0.064	0.13	0.84	0.41	5.9	(-)
"	0.255	0.53	4.1	1.9	7.6	5.9
"	0.434	0.90	8.7	4.2	9.7	8.7
0.53	0	0	1.8	0.85	-	-
"	0.051	0.11	1.1	0.51	9.9	(-)
"	0.214	0.44	2.9	1.4	6.3	2.4
"	0.366	0.76	6.3	3.1	8.3	6.0

(a): stoichiometry: $[NH_4^+A^-]/[D2EHPA]_o$
(b): corrected for amount of water coextracted by diluent, see text

TABLE 6.37

WATER COEXTRACTION, AMINE-CONTAINING DILUENT

SOLVENT = 0.25 M D2EHPA IN TOLUENE PLUS AMINE MODIFIER

[Adogen 364]	$[NH_4^+A^-]$	s(a)	$[H_2O]$		$[H_2O]/[NH_4^+A^-]$	$[H_2O]/[NH_4^+A^-]_{corr}$ (b)
(M)	(M)		weight %	(M)	(M/M)	(M/M)
0.14	0	0	0.39	0.19	-	-
"	0.03	0.12	0.29	0.14	4.8	(-)
"	0.126	0.50	1.8	0.85	6.7	5.2
"	0.219	0.87	3.9	1.9	8.6	7.8
0.28	0	0	0.7	0.34	-	-
"	0.026	0.10	1.2	0.58	2.2	8.5
"	0.118	0.47	1.7	0.83	7.0	4.2
"	0.203	0.81	3.3	1.6	7.8	6.1

(a): stoichiometry: $[NH_4^+A^-]/[D2EHPA]_0$

(b): corrected for amount of water coextracted by diluent, see text

per mole of NH_3 extracted into a given solvent depends mainly on stoichiometry and is relatively independent of solvent concentration. Water coextraction increases sharply with increasing stoichiometry. The occasional high values of this ratio at low stoichiometries are probably due to errors in measurements of water concentration at low concentrations. The relative change of this ratio with stoichiometry is greatest for the toluene diluent and is approximately the same for the amine and alcohol-containing diluents. At high stoichiometry the alkali metals are known to form polymers in the organic phase (McDowell, 1971), and these have a tendency to extract large amounts of water. This effect would explain the trend seen here for the toluene diluent, where the tendency to polymerize is probably high. At the low concentration of D2EHPA and high stoichiometry the organic phase was cloudy and bluish.

At a given stoichiometry the corrected value of the ratio of moles of water to moles of NH_3 extracted is less for the alcohol diluent than for the other diluents. This supports the idea that the alcohol replaces water as part of the solvating medium for the ammonium/D2EHPA ion pair, making the ion pair more organophilic and thus more extractable. On this same basis more water is extracted when the amine-to-D2EHPA molar ratio is 1:2 than when it is 1:1, at a stoichiometry greater than 0.5. This suggests that the extra amine in the latter case may replace some of the water solvating the ion pair. In general, though, the amine-diluent systems result in more water coextraction than the toluene-diluent systems. If the amine interacts with D2EHPA preventing it from solvating the ammonium/D2EHPA ion pair, then the ion pair may polymerize more readily. Thus at a given concentration of

D2EHPA and a given stoichiometry the extent of ion-pair polymerization may be higher in the amine diluent. This would tend to increase water coextraction. At high stoichiometry in the 1:2 amine to D2EHPA diluent some free amine becomes available to solvate the ion pair and water coextraction into the toluene diluent becomes higher.

In terms of total amount of water coextracted per mole of NH_3, the trends are less discernible. The amount of water coextracted by the solvent alone leads to artifically high values of this ratio at low stoichiometry. However in a general sense it can be said that at a stoichiometry below 0.5, the lowest water coextraction occurs into a toluene-diluent solvent. Above this stoichiometry water coextraction is lowest into the alcohol-diluent solvent. At high stoichiometry water coextraction is highest into the toluene diluent.

Regeneration of a solvent containing D2EHPA plus NH_3 and water serves to decrease the amount of water in the solvent. A solvent containing 0.48 $\underline{M}$ D2EHPA in 50% (v/v) isodecyl alcohol/Norpar 12 and 0.47 $\underline{M}$ NH_3 and 6.3% water was regenerated at 105°C. When 75% of the ammonia had been removed from the solvent the water concentration of the solvent had been reduced to 0.2%. A solvent containing 0.2 $\underline{M}$ D2EHPA in 50% (v/v) isodecyl alcohol/Chevron 25 and 0.1 $\underline{M}$ NH_3 and about 2% water was regenerated at 165°C. When the ammonia concentration was reduced to essentially zero, the water concentration of the organic phase was about 0.5%. Also a solvent containing 0.2 $\underline{M}$ D2EHPA in Norpar 12 and 0.1 $\underline{M}$ NH_3 and about 1.7% water contained less than 0.1% water after it had been regenerated at 200°C. Finally the solvent described above containing 0.48 $\underline{M}$ D2EHPA in 50% (v/v) isodecyl alcohol/Norpar 12 contained less than 1% water after being regenerated by contacting with approximately 4

$\underline{M}$ H_2SO_4. This all indicates that a large portion of the water coextracted into the organic phase is associated with the ammonium/D2EHPA ion pair and will be released from the solvent when the solvent is regenerated.

E. SOLVENT-REGENERATION PROPERTIES

The data discussed in this section were gathered as described in Chapter 3, section G. The raw data are given in Appendix II. In Table 6.38 the initial and final NH_3 concentrations of the solvents studied are given, as well as their final color and the total number of cubic feet of nitrogen passed through the solvent. In all cases 100 ml of solvent were used.

Ammonia is released from the solvent when the ammonium/D2EHPA ion pair breaks apart. This may be viewed as the following reaction:

$$[NH_4^+A^-] \rightleftarrows [NH_3]\uparrow + [HA] \qquad (6.19)$$

where all species are in the organic phase. The reciprocal equilibrium constant for this reaction is:

$$K' = \frac{[NH_4^+A^-]\ \gamma_{NH_4^+A^-}}{[NH_3]\ [HA]\ \gamma_{NH_3}\ \gamma_{HA}} \qquad (6.20)$$

The partial pressure of ammonia above the solvent (P_{NH_3}) may be expressed in terms of the NH_3 concentration and a Henry's law constant:

TABLE 6.38

PROPERTIES OF REGENERATED SOLVENTS

DILUENT	$[D2EHPA]_o$ (M)	$T^{(a)}$ (°C)	$[NH_4^+A^-]_o^{(b)}$ (M)	$[NH_4^+A^-]_f^{(c)}$ (M)	color(d)	Total N_2 (ft^3/100 ml)
50% Isodecyl alcohol/ Norpar 12	0.48	105	0.47	0.065	yellow	49.1
"	"	127	0.47	0.104(e)	yellow	4.91
"	"	143	0.47	0.053	yellow	4.42
"	0.82	127	0.40	0.19	amber	13.3
Norpar 12	0.48	127	0.23	0.097	yellow	3.42
"	"	143	0.23	0.023	amber	3.85
"	0.82	127	0.19	0.11	amber	9.12
0.4 M Adogen 364/ Norpar 12	0.4	127	0.21	0.0037	amber	2.55
0.22 M Adogen 364/ Norpar 12	0.43	127	0.22	0.0065	amber	4.95
0.4 TOPO/ Norpar 12	0.4	127	0.17	0.024	yellow	4.43

(a): temperature of regeneration
(b): measured initial concentration of ammonia in organic phase
(c): measured final concentration of ammonia in organic phase
(d): color of solvent after regeneration
(e): calculated from mass balance

$$P_{NH_3} = [NH_3]\ H \qquad (6.21)$$

Combining Equations 6.20 and 6.21 yields:

$$P_{NH_3} = \frac{H\ [NH_4{}^{+}A^{-}]\ \gamma_{NH_4{}^{+}A^{-}}}{K'\ [HA]\ \gamma_{NH_3}\ \gamma_{HA}} \qquad (6.22)$$

As written the solvent effects on NH_3 in the organic phase are cancelled by the ratio H/γ_{NH_3}.

The activity coefficients and the Henry's law constants can be grouped into a new constant, K:

$$P_{NH_3} = \frac{K\ [NH_4{}^{+}A^{-}]}{[HA]} \qquad (6.23)$$

It is apparent from Equation 6.22 that a higher partial pressure of NH_3 will result above a solvent at high concentrations of the ammonium/D2EHPA ion pair, low concentrations of free D2EHPA and in situations in which the ion pair is not well solvated (high γ for the ion pair) or the free acid is well solvated (low γ for HA). The results obtained for the different solvents can be interpreted by this mechanism.

1. TRENDS IN P_{NH_3} WITH SOLVENT COMPOSITION

Figure 6.7 summarizes the effect of temperature on P_{NH_3} as a

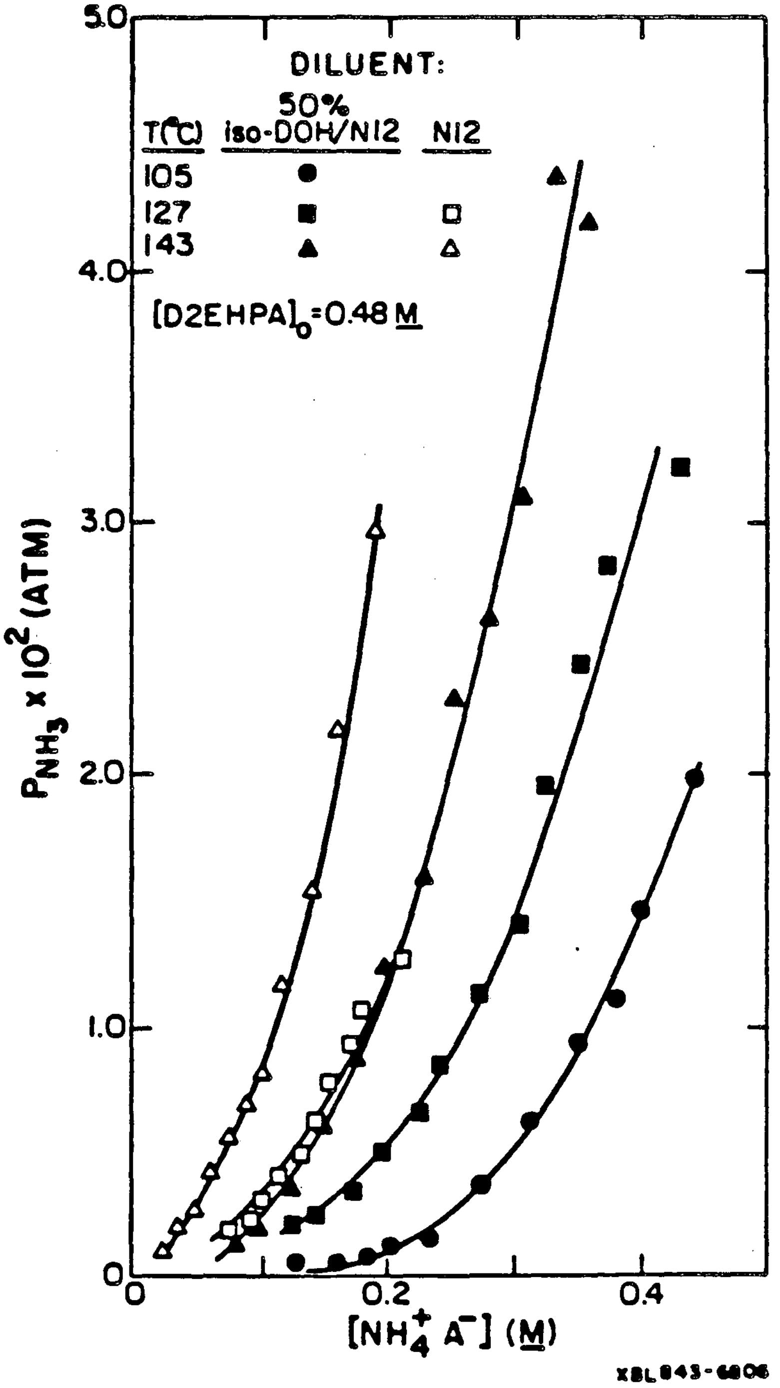

FIGURE 6.7: EFFECTS OF TEMPERATURE AND DILUENT ON SOLVENT-REGENERATION PROPERTIES.

function of the concentration of the ammonium/D2EHPA ion pair in the organic phase. In these results the concentration of the ammonium/D2EHPA ion pair was assumed to be equal to the total concentration of ammonia in the organic phase. This is based on the realization that the solubility of NH_3 in these diluents is rather low, see Table 4.3. As expected, for a given diluent, P_{NH_3} increases with temperature, reflecting at least partially an expected increase in the Henry's law constant in Equation 6.22.

At 127°C P_{NH_3} is greater for the inert diluent than for the alcohol-containing diluent, by a factor of between 2.3 and 2.7. This increase is relatively independent of the concentration of the ammonium/D2EHPA ion pair. At 143°C P_{NH_3} is also greater for the inert diluent than for the alcohol diluent. The ratio increases from about 3 at the highest stoichiometry to 4.2 at the lowest stoichiometry. The lower P_{NH_3} for the alcohol diluent is due to the low ammonium/D2EHPA ion-pair activity coefficient resulting from the solvation of the ammonium/D2EHPA ion pair by the alcohol. The slight increase in the ratio of P_{NH_3} for the two solvents as the concentration of the ion pair decreases at the higher temperature suggests that in this temperature range the solvation of the ion pair by additional D2EHPA in the inert diluent is more temperature sensitive than the solvation by the alcohol.

In Figure 6.8 the effect of increasing the concentration of D2EHPA is seen. At the same ammonium/D2EHPA ion pair concentration P_{NH_3} is less from the more concentrated solvent. This is true for both the inert and the alcohol diluent. As seen from Equations 6.22 or 6.23 this is due to the higher concentration of free D2EHPA in the more concentrated solvents.

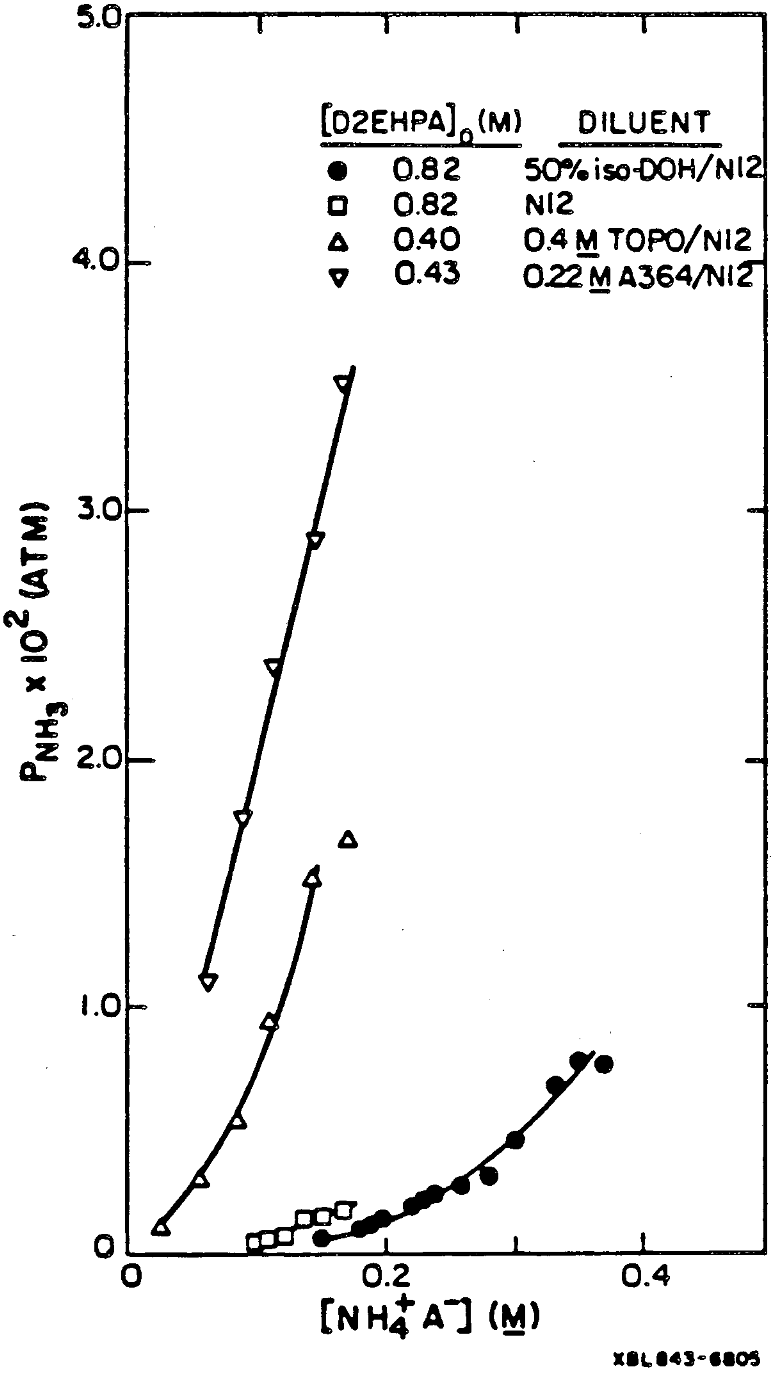

FIGURE 6.8: EFFECTS OF D2EHPA CONCENTRATION AND LEWIS BASE MODIFIERS ON SOLVENT-REGENERATION PROPERTIES.

The effect of adding Lewis bases to the solvents can be seen in Figures 6.8 and 6.9. In Figure 6.8 it is seen that the effect of adding trioctyl phosphine oxide (TOPO) to a solvent is to increase P_{NH_3}, by a factor of between 1.2 and 1.8. The effect of the dilution of the D2EHPA by the addition of the base has been taken into account in reporting this ratio. TOPO complexes with free D2EHPA to a small extent, thus lowering its activity coefficient and increasing P_{NH_3}.

The effect of adding A364 to the solvent at an amine-to-D2EHPA molar ratio of 1:2 is also to increase P_{NH_3}. Here the the enhancement increases from a factor of about 3.2 to one of 5.5 as the concentration of the ammonium/D2EHPA ion pair decreases. The effect of adding the amine to a solvent at a molar ratio of 1:1 is seen in Figure 6.9. Here the ratio of P_{NH_3} increases from 3.5 to 6.4 as the concentration of the ion pair decreases. As proposed earlier when analyzing the effects of amines on K_{c,NH_4^+}, the amine interacts with the D2EHPA, lowering its activity coefficient. This would increase P_{NH_3}.

The dependence of the ratio of P_{NH_3} for the amine diluent to that for the inert diluent on the ion-pair concentration is consistent with the observed change of the absolute value of the synergistic coefficient ($|SC|$) with ion-pair concentration (see Table 6.14). At this concentration of D2EHPA and in this stoichiometry range (less than 0.5) $|SC|$ was largest at low stoichiometry. This was attributed to the amine preventing additional D2EHPA from solvating the ammonia/D2EHPA ion pair. This same mechanism may be applicable here.

2. MODELLING OF P_{NH_3} DATA

It would be most satisfying to model the regeneration data along

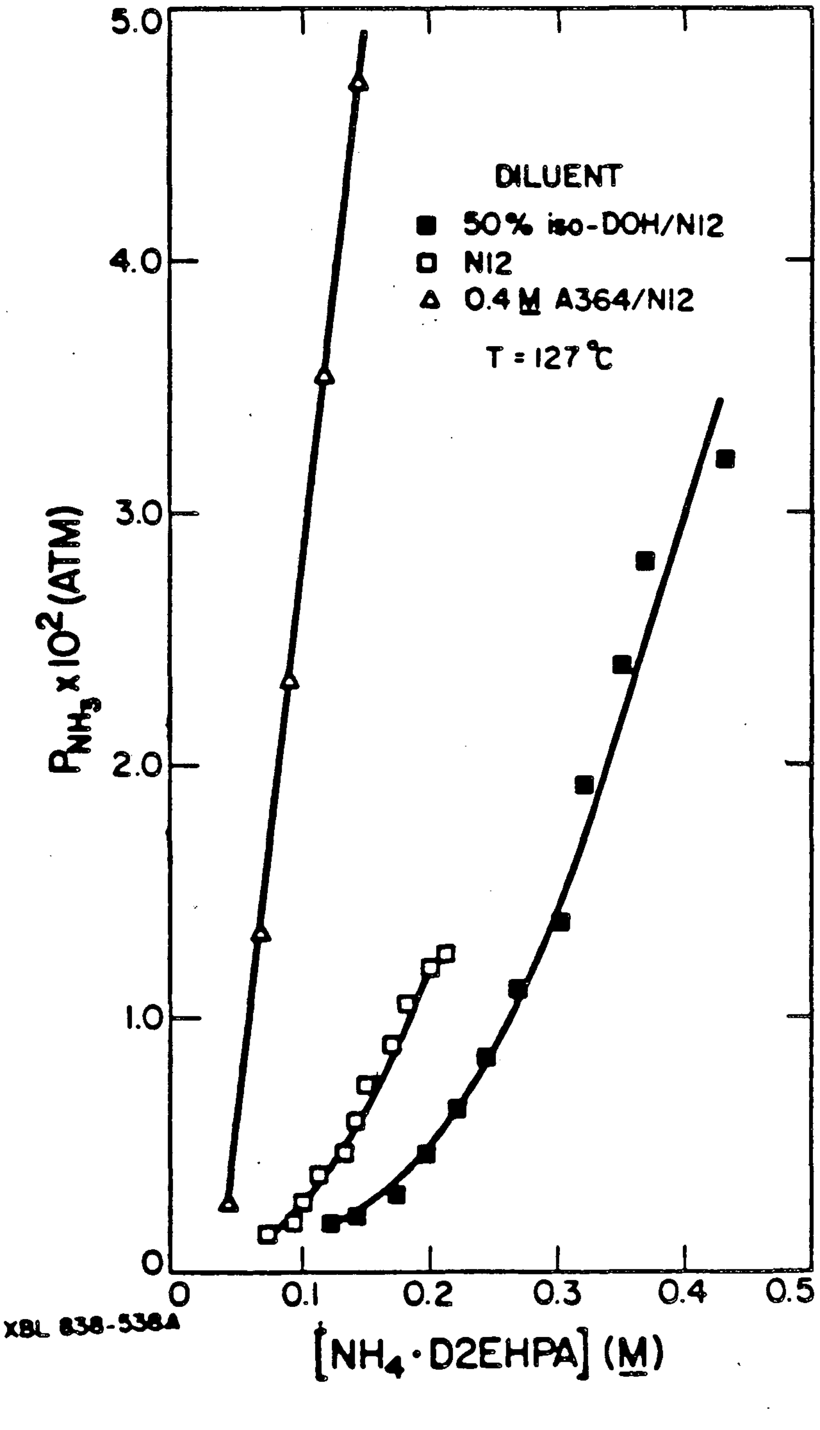

FIGURE 6.9: EFFECT OF DILUENT ON SOLVENT-REGENERATION PROPERTIES.

the same lines as was done for the liquid-liquid equilibrium data. That is, for a given diluent and stoichiometry determine a K from Equation 6.23 (but with total D2EHPA concentration replacing the concentration of the free acid), and also include a solvent-concentration dependence if any. However not enough data are available to permit this type of analysis. In lieu of these data Equation 6.23 was used directly over the whole stoichiometry range. The concentration of free D2EHPA was calculated as the difference between the initial or total concentration of D2EHPA and the concentration of the ammonium/D2EHPA ion pair. This approach has the same limitations as the similar approach for modelling the liquid-liquid equilibrium data. Thus it might be expected that the K values calculated by Equation 6.23 will vary some with stoichiometry, reflecting variations in activity coefficients.

Table 6.39 gives values of K calculated via Equation 6.23 for the alcohol diluent at 127°C. At a given stoichiometry the K values are fairly constant between the low and high concentration solvents. In general, K decreases with decrease in stoichiometry, indicating a reduction in the ion-pair activity coefficient. At 127°C, the average K value in the stoichiometry range 0.75 to 0.5 is 8.6×10^{-3} atm, for the range 0.5 to 0.25, it is 7.0×10^{-3} atm, and below 0.25 it is 3.1×10^{-3} atm. The data at 143°C are presented in Table 6.40. The average K in the stoichiometry range 0.75 to 0.5 is 1.7×10^{-2} atm and from 0.5 to 0.25 it is 1.4×10^{-2} atm. Note that for this model P_{NH_3} is determined solely by stoichiometry.

Table 6.41 summarizes K values calculated by Equation 6.23 for the Norpar 12 diluent. At a given stoichiometry K is not constant between the low and high concentration solvents. Including an additional

TABLE 6.39

CALCULATED K VALUES FOR ALCOHOL DILUENT

T = 127°C [D2EHPA]$_o$ = 0.48 M

DILUENT = 50% (v/v) Isodecyl alcohol in Norpar 12

$[NH_4^+A^-]$ (M)	$P_{NH_3} \times 10^2$ (atm)	$K \times 10^2$ (a) (atm)	s (b)
0.35	2.25	0.84	0.73
0.325	1.93	0.92	0.68
0.3	1.4	0.84	0.63
0.275	1.16	0.87	0.57
0.25	0.91	0.84	0.52
0.225	0.70	0.79	0.47
0.2	0.54	0.76	0.42
0.175	0.37	0.65	0.37
0.15	0.26	0.57	0.31
	[D2EHPA]$_o$ = 0.82 M		
0.35	0.75	1.0	0.43
0.325	0.66	1.0	0.4
0.3	0.44	0.75	0.37
0.275	0.31	0.61	0.34
0.25	0.24	0.56	0.31
0.225	0.18	0.47	0.27
0.2	0.13	0.39	0.24
0.175	0.076	0.28	0.21
0.15	0.054	0.24	0.18

(a): calculated via Equation 6.23

(b): stoichiometry: $[NH_4^+A^-]/[D2EHPA]_o$

TABLE 6.40

CALCULATED K VALUES FOR ALCOHOL DILUENT(a)

T = 143°C $[\text{D2EHPA}]_o$ = 0.48 M

DILUENT = 50% (v/v) Isodecyl alcohol in Norpar 12

$[NH_4^+A^-]$ (M)	$P_{NH_3} \times 10^2$ (atm)	$K \times 10^2$ (atm)	s
0.35	3.96	1.47	0.73
0.325	3.43	1.37	0.68
0.3	2.93	1.76	0.63
0.275	2.51	1.87	0.57
0.25	2.12	1.95	0.52
0.225	1.52	1.72	0.47
0.2	1.19	1.67	0.42
0.175	0.84	1.46	0.37
0.15	0.58	1.28	0.31
0.125	0.33	0.94	0.26

(a): see Table 6.39 for explanation of symbols

TABLE 6.41

CALCULATED K AND K'' VALUES FOR INERT DILUENT$^{(a)}$

T = 127°C [D2EHPA]$_o$ = 0.48 M

DILUENT = Norpar 12

$[NH_4^+A^-]$ (M)	$P_{NH_3} \times 10^2$ (atm)	$K \times 10^2$ (atm)	$K'' \times 10^{2(b)}$ (atm·M)	s
0.2	1.22	1.71	0.48	0.42
0.175	0.97	1.69	0.51	0.37
0.15	0.70	1.54	0.51	0.31
0.125	0.46	1.30	0.46	0.26
0.1	0.28	1.06	0.41	0.21
0.075	0.17	0.89	0.36	0.16
[D2EHPA]$_o$ = 0.82 M				
0.15	0.12	0.54	0.36	0.183
0.125	0.083	0.46	0.32	0.152
0.1	0.053	0.38	0.27	0.122

(a): see Table 6.39 for explanation of symbols
(b): calculated via Equation 6.24

solvent dependency term as was used in modelling the liquid-liquid equilibrium data gives fairly constant K" values. Thus for the inert diluent P_{NH_3} is modelled as:

$$P_{NH_3} = \frac{K'' \left[NH_4^+A^-\right]}{\left[HA\right]^2} \tag{6.24}$$

As in the development of the liquid-liquid extraction equilibrium models, this extra solvent dependency is intended only to indicate additional complexation of the ammonium/D2EHPA ion pair by D2EHPA and does not indicate the presence of a particular species in the organic phase.

At 127°C, in the stoichiometry range 0.5 to 0.25, the average K" is 4.9×10^{-3} atm•<u>M</u> and below 0.25 it is 3.4×10^{-3} atm•<u>M</u>. The data at 143°C are presented in Table 6.42. At this temperature these values are 1.3×10^{-2} atm•<u>M</u> and 1.1×10^{-2} atm•<u>M</u>, respectively. If [HA] is calculated as the difference between the total D2EHPA concentration and twice the ion-pair concentration the K" values increase with decreasing stoichiometry but, at a given stoichiometry, are fairly constant between the high and low concentration solvents. This suggests that some solvent-concentration dependence between one and two is appropriate.

The data for the amine-containing diluent were found to be independent of the concentration of the free acid. Thus for the data at an amine-to-D2EHPA molar ratio of 1:2, P_{NH_3} is given by:

$$P_{NH_3} = 0.2 \left[NH_4^+A^-\right] - 2 \times 10^{-3} \tag{6.25}$$

For the data at an amine-to-D2EHPA molar ratio of 1:1, P_{NH_3} is

TABLE 6.42

CALCULATED K AND K" VALUES FOR INERT DILUENT$^{(a)}$

T = 143°C [D2EHPA]$_o$ = 0.48 M

DILUENT = Norpar 12

$[NH_4^+A^-]$ (M)	$P_{NH_3} \times 10^2$ (atm)	$K \times 10^2$ (atm)	$K" \times 10^2$ (atm·M)	s
0.175	2.49	4.34	1.32	0.37
0.15	1.86	4.09	1.35	0.31
0.125	1.33	3.77	1.34	0.26
0.1	0.8	3.04	1.16	0.21
0.075	0.54	2.91	1.18	0.16
0.05	0.25	2.15	0.92	0.10

(a): see Table 6.41 for explanation of symbols

given by:

$$P_{NH_3} = 0.4\ [NH_4^+A^-] - 1.2 \times 10^{-2} \tag{6.26}$$

This lack of dependence on the concentration of free D2EHPA is curious and may reflect the fact that the data are not necessarily equilibrium data. Note, however, that this type of behavior would correspond to a horizontal line in Figure 6.5 at low stoichiometry, which is reasonably approached. Attempts to model these data in the same way that the data for the amine-containing diluents were modelled in the liquid-liquid equilibrium section met with failure. Due to the nature of the dependence of P_{NH_3} on the concentration of the ammonium/D2EHPA ion pair, $K_{B:HA}$ appeared to decrease with increasing concentration of the ion pair.

3. EFFECT OF TEMPERATURE ON K_c

The solvent regeneration data can be used to determine the effect of temperature on K_c values. This is done by converting P_{NH_3} into K_{c,NH_3}. This approach is similar to that used in Chapter 4 for converting solubility data into distribution coefficients.

A solvent producing a given P_{NH_3} is envisioned as in equilibrium with an aqueous phase producing the same P_{NH_3}. The concentration of NH_3 (in this case undissociated NH_3) in the aqueous phase is given as:

$$(NH_3) = P_{NH_3}/H^{w}_{NH_3} \tag{6.27}$$

where $H^{w}_{NH_3}$ is the Henry's law constant for NH_3 in water at the temperature of the data. For these comparisons the dilute-solution Henry's law constant was used. This is not the same Henry's law constant that appears in Equations 6.21 and 6.22. K_{c,NH_3} is then calculated as the concentration of the ammonium/D2EHPA ion pair in the solvent producing a given P_{NH_3} divided by the concentration of undissociated NH_3 in water producing the same P_{NH_3}. This value is independent of pH, if activity coefficients do not change with pH. Note that at a given concentration of the ammonium/D2EHPA ion pair in two solvents the ratio of the P_{NH_3} values is inversely proportional to the ratio of their K_{c,NH_3} values.

K_{c,NH_3} can be readily calculated from the liquid-liquid equilibrium models for the data at room temperature. As pointed out earlier, (pH - log K_{c,NH_4^+}) is independent of pH. At a pH of 9.25 at room temperature the concentration of ammonium ion is equal to the concentration of undissociated NH_3. Thus log K_{c,NH_3} is equal to log K_{c,NH_4^+}. To calculate K_{c,NH_3} the value of (pH - log K_{c,NH_4^+}) at the appropriate conditions is determined and the value of K_{c,NH_4^+} at pH 9.25 is calculated. In the following discussion K_{c,NH_3} is used as the basis for analyzing temperature effects since it avoids the problem of variations in the dissociation constant of ammonium with temperature. It thus gives a good indication of the relative strength of the ammonium/D2EHPA ion pair and the solvation of D2EHPA and the ion pair as a function of temperature.

The effect of raising temperature is to bring K_{c,NH_3} values for the different diluents closer together. Thus the ratio of P_{NH_3} at 127°C for the amine diluent (at either molar ratio) to that of the Norpar 12 diluent at 127°C is less than the ratio of K_{c,NH_3} for the toluene diluent at 25°C to K_{c,NH_3} for the amine diluent at 25°C. For the diluent containing an amine-to-D2EHPA molar ratio of 1:2 the former ratio is about 4 as pointed out above, while the latter ratio is about 100, as seen from Table 6.14. For an amine-to-D2EHPA molar ratio of 1:1, these values are about 5 and 300 respectively. This suggests that the amine is less effective at higher temperature and that the amine/D2EHPA complex is weaker at higher temperature, as would be expected.

A similar effect is seen with the alcohol diluent. The ratio of P_{NH_3} at 127°C for the Norpar 12 diluent to that of the alcohol diluent at 127°C is about 3 and is less than the ratio of K_{c,NH_3} at 25°C for the alcohol diluent to that for the toluene diluent at 25°C, about 6. This indicates that the alcohol is less effective at higher temperatures and suggests a weakening of the solvation forces between the alcohol and the ammonium/D2EHPA ion pair as temperature increases in this temperature range.

This same effect may also be seen by calculating the ratio of K_{c,NH_3} at 25°C to that at 127°C ($H^{w}_{NH_3} = 0.44$ atm/$\underline{M}$) for the different diluents as presented in Table 6.43. For the alcohol diluent this value is about 3500. For the inert diluent it is about 1000. For the amine diluent it is about 150 at an amine-to-D2EHPA molar ratio of 1:2 and drops to 15 at an amine-to-D2EHPA molar ratio of 1:1. This indicates that for all of the diluents, K_{c,NH_3} decreases with increasing temperature and suggests a weakening of the ammonium/D2EHPA ion pair complex. The stronger temperature dependence for the alcohol diluent relative to the inert diluent suggests that the alcohol is less effective at higher temperatures. This would make K_{c,NH_3} at higher

TABL3 6.43

CALCULATED DEPENDENCE OF K_{c,NH_3} ON TEMPERATURE

$[D2EHPA]_o = 0.48$ M

DILUENT	$[NH_4{}^+A^-]$ (M)	K_{c,NH_3} calculated at:		
		$25°C^{(a)}$	$127°C^{(b)}$	$143°C^{(b)}$
Toluene or Norpar 12	0.175	8.3×10^3	8.0	4.3
"	0.1	1.5×10^4	15.7	7.6
50% (v/v) Decanol in toluene or Norpar 12	0.4	1.8×10^4	5.9	4.6
"	0.2	6.3×10^4	16.3	10.3
0.26 M A364 in toluene or Norpar 12	0.15	3.2×10^2	2.2	-
"	0.1	3.6×10^2	2.2	
0.52 M A364 in toluene or Norpar 12	0.175	1.9×10^1	1.4	-
"	0.1	2.2×10^1	1.6	-

(a): calculated as $K_{c,NH_4{}^+}$ at $pH_w = 9.25$, from Figures 6.4 and 6.5

(b): calculated based on $P_{NH_3}/H^w_{NH_3}$, with $H^w_{NH_3} = 0.44$ atm/M at 127°C, and $H^w_{NH_3} = 0.61$ atm/M at 143°C temperatures lower than expected, approaching that for the inert diluent. The opposite is true for the amine-containing diluents. The weakening of the amine/D2EHPA interaction at higher temperature gives higher K_{c,NH_3} values than expected, again approaching that of the inert diluent. Thus the temperature dependence for the amine-containing diluents is less than for the inert diluent.

For the inert and alcohol-containing diluents, values of K_{c,NH_3} were calculated at different stoichiometries at 25°C, 127°C and also 143°C and are given in Table 6.43. These data were then fit to the van't Hoff equation. That is ln K_{c,NH_3} was plotted versus 1/T. The data fit this equation very well. The slopes were independent of stoichiometry and were determined by a least squares fit. K_{c,NH_3} values were expressed as ratios of molarities in each phase and temperature was expressed in Kelvin. For the inert diluent the slope of this plot, equal to $(-\Delta H/R)$, was 8000 and the correlation coefficient was 0.999. For the alcohol-containing diluent the slope was 9000 and the correlation coefficient was 0.997.

The decrease in K_{c,NH_3} with increase in temperature is an effect commonly observed (van der Zeeuw, 1979b). However for the data given here the temperature dependence is unusually strong. The value of ΔH for the inert diluent would be about -16 kcal/mol, which is high. In addition, extraction experiments to determine the dependence of K_c on temperature indicated that it was nearly independent of temperature up to 60°C, which seems inconsistent with the above results.

Table 6.44 summarizes these results for a solvent containing 0.2 M D2EHPA in Norpar 12. K_c values were measured at room temperature and 60°C. Values of pH were not measured, but they can be assumed to be

TABLE 6.44

TEMPERATURE DEPENDENCE OF K_c FOR NORPAR 12 DILUENT

SOLVENT = 0.2 M D2EHPA IN NORPAR 12

S/W (v/v) = 5 FEED = ammonium carbonate solution

$(N)_{feed}$ (M)	$(N)_{raf,25°C}$ (M)	$(N)_{raf,60°C}$ (M)
0.56	0.043	0.048
0.12	0.028	0.023
0.34	0.033	0.029

comparable between the two cases. It is apparent that K_c did not vary much with temperature. Additional data taken with 0.2 M D2EHPA in various diluents are presented in Table 6.45. Again, K_c does not appear to vary significantly with temperature. However if variations in the pK_a of the ammonium ion with temperature are included, the results here come closer to exhibiting the expected trend.

The reasons for this possible discrepancy are not known. However it may be that either or both ΔH or activity coefficients are not constant with temperature over the range examined, invalidating the use of the van't Hoff equation in this situation. Over the 118°C temperature range examined it seems likely that these values would not be constant. In addition there may be a change in the complexation mechanism at different temperatures causing deviations from the expected dependence on temperature.

4. SOLVENT DEGRADATION DUE TO TEMPERATURE

Some qualitatitive data on the stability of D2EHPA-containing solvents at high temperature were obtained. When D2EHPA thermally degrades the side chain is broken off, and a more water soluble product is formed. Thus a qualitative measure of thermal stability is the change in phosphorus concentration in an aqueous phase contacted with a solvent before and after the solvent is heated. For these tests purified D2EHPA was used in the solvents.

In Table 6.46 results are presented for solvents containing 0.2 M D2EHPA in 50% (v/v) isodecyl alcohol in an aromatic diluent. The solvents initially contained 0.1 M NH_3 and were regenerated at the temperature and for the time indicated. At 110°C the aromatic was

TABLE 6.45

TEMPERATURE DEPENDENCE OF K_c

SOLVENT = 0.2 $\underline{M}$ D2EHPA IN DILUENT

S/W (v/v) = 5 FEED = 0.58 $\underline{M}$ NH_4HCO_3

DILUENT	$(N)_{raf,25°C}$ ($\underline{M}$)	$(N)_{raf,50°C}$ ($\underline{M}$)
Toluene	-	0.024
6.5% Isodecyl alcohol/ toluene	0.018	0.013
50% Isodecyl alcohol/ toluene	0.008	0.0072

TABLE 6.46

SOLVENT DEGRADATION AT 110°C AND 165°C

$[\text{D2EHPA}]_o = 0.2\ \underline{M}$

DILUENT = 50% (v/v) Isodecyl alcohol in aromatic

TEMP (°C) →	25	110	165
TIME (hrs) →	-	7	4
1^{st} Extraction:			
% NH_3 extracted	97	96.5	95.2
Extractant losses, (ppm, D2EHPA)	419	419	5900
2^{nd} Extraction:(a)			
% NH_3 extracted(b)	81	90	63
Extractant losses, (ppm, D2EHPA)	451	450	4390
Distilled water contacting:			
Extractant losses, (ppm, D2EHPA)	100	390	1420
Color:	colorless	colorless	orange

(a): feed was raffinate from first extraction
(b): expressed as % of NH_3 present in first raffinate

toluene. At 165°C the aromatic was Chevron 25. Both of the solvents contained no measurable amount of NH_3 after being regenerated.

For these comparisons the regenerated solvent was contacted with a feed containing 0.58 $\underline{M}$ NH_4HCO_3 at an S/W of 5. Another portion of the solvent was contacted with the raffinate from this extraction, at an S/W of 5. Still another portion of the solvent was contacted with distilled water at an S/W of 5. The latter two experiments were intended to magnify any increase in aqueous-phase phosphorus concentration due to D2EHPA degradation. The values obtained using fresh D2EHPA were fairly low and therefore any increase in these values after heating of the solvent would be significant and easy to determine. Percent NH_3 extracted and the phosphorus content of the aqueous phase (reported as ppm D2EHPA) were measured. As a basis for comparison the same data for a fresh, unheated solvent are also given. The data for the fresh solvent are somewhat misleading, since the isodecyl alcohol used contained a phosphorus impurity. By comparison a solvent containing 1-decanol instead of isodecyl alcohol gave only 260 ppm D2EHPA in the raffinate of the first extraction, 84 ppm D2EHPA in the raffinate of the second extraction and less than 10 ppm D2EHPA for the distilled water contacting. The isodecyl alcohol/ aromatic diluent alone (no D2EHPA) gave the equivalent of about 60 ppm D2EHPA in the distilled water contacting.

Given this complication it is still clear that not much solvent decomposition occurred at 110°C. However a significant amount of decomposition occured at 165°C. This was not due to the impurity in the isodecyl alcohol. A diluent containing 50% (v/v) isodecyl alcohol in Chevron 25 was heated to 160°C and held at that temperature for one hour. When contacted with distilled water at an S/W of 5 it gave the equivalent of only about 30 ppm D2EHPA, which is about the same as the unheated diluent gave.

Data were also obtained at an intermediate temperature of 127°C, and the effect of time was studied. The solvents were 0.2 M D2EHPA in Norpar 12 and 0.2 M D2EHPA in 50% (v/v) Alfol 10/Norpar 12. These solvents were heated to 127°C for the times indicated in Table 6.47. A small amount of water was added to the solvent to allow for any hydrolysis that might occur in an actual process. One ml of water was added per 19 ml of solvent. After the heating period the solvents were contacted with distilled water at an S/W of 5. For the alcohol-containing diluent a portion of this solvent was then contacted with 0.58 M NH_4HCO_3 at an S/W of 5. The remainder of the solvent was contacted with the raffinate from this extraction at an S/W of 5. The results for percent NH_3 extracted and phosphorus concentration in the aqueous phase are given in Table 6.47. Again the same data are given for a fresh, unheated solvent for comparison. Norpar 12 was found to contain a phosphorus impurity giving an equivalent of about 60 ppm D2EHPA in the distilled water contacting.

Solvent decomposition increased with time for both diluents. However, even when held at 127°C for 21 hours, the solvent did not degrade as much as when held at 165°C for only 4 hours.

A quantitative measure of solvent decomposition rates cannot be drawn from these data. However it is apparent that even at 127°C solvent decomposition probably cannot be ignored. The addition to the solvent of a compound that would inhibit this degradation would be desirable. It has been suggested that, since the thermal degradation is

TABLE 6.47

SOLVENT DEGRADATION AT 127°C

$[\text{D2EHPA}]_o = 0.2\ \underline{M}$

DILUENT = 50% (v/v) Alfol 10 in Norpar 12

TEMP (°C) →	25	127	127
TIME (hrs) →	-	7	21
1st Extraction:			
% NH_3 extracted	97.3	97.8	97.9
Extractant losses, (ppm, D2EHPA)	334	681	1054
2nd Extraction:(a)			
% NH_3 extracted (b)	49.4	69.2	70.8
Extractant losses, (ppm, D2EHPA)	< 5	435	547
Distilled water contacting:			
Extractant losses, (ppm, D2EHPA)	< 5	96	216
Color:	colorless	faint yellow	colorless

DILUENT = Norpar 12

Distilled water contacting:			
Extractant losses, (ppm, D2EHPA)	57	495	771
Color:	colorless	colorless	faint yellow

(a): feed was raffinate from first extraction
(b): expressed as % NH_3 present in first raffinate

acid-catalyzed, the addition of a neutralizing compound may hinder the degradation (Gamrath et. al., 1954). The amine compounds may serve this purpose. This possibility was not examined here but does warrant further study.

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CHAPTER 7

DEMONSTRATION OF CONCEPT AND DESIGN CONSIDERATIONS

A. EXTRACTION OF COAL-CONVERSION CONDENSATE WASTEWATERS

The models derived in the previous chapter were based on extraction of synthetic NH_3/CO_2 solutions. In this section the applicability of these models to the extraction of actual coal-conversion wastewaters is examined. The procedure followed for these extractions was similar to that used in obtaining data for the development of the liquid-liquid extraction equilibrium models.

Table 7.1 lists results for extraction of a condensate water from the Morgantown Energy Technology Center (METC) Lurgi, fixed-bed gasifier. The solvent compositions are given, along with measured raffinate NH_3 concentrations and pH values. The initial concentration of NH_3 in the wastewater was 0.25 M, and the pH was about 8. In all of these extractions the organic phase discolored some, presumably due to the oxidation of phenols initially present in the wastewater.

The measured and predicted K_{c,NH_4^+} values are compared in Table 7.1. In these cases the predicted values were obtained from Figures 6.4 and 6.5. Given the solvent composition and the measured system stoichiometry, the value of (pH - log K_{c,NH_4^+}) was obtained from these figures. At the measured pH, K_{c,NH_4^+} was then determined. Agreement between measured and calculated K_{c,NH_4^+} values is very good, with the exception of the extraction results at the higher concentration of D2EHPA in toluene. Even in this case agreement is good enough to conclude that the liquid-liquid extraction equilibrium models developed

TABLE 7.1

EXTRACTION OF MORGANTOWN ENERGY TECHNOLOGY CENTER WASTEWATER

FEED = 0.25 M AMMONIA S/W (v/v) = 2.5

DILUENT	$[D2EHPA]_o$ (M)	$(N)^{(a)}$ (M)	$[NH_4^+A^-]^{(b)}$ (M)	$s^{(c)}$	pH	$K_{c,NH_4^+}^{(d)}$	$K_{c,NH_4^+}^{(e)}$ (model)	PHASE SEPARATION$^{(f)}$		
								O	A	I
Toluene	0.25	0.033	0.09	0.35	6.30	2.6	3.2	1	1	4
"	0.47	0.029	0.09	0.18	5.72	3.1	5.5	1	1	2
50% (v/v) Alfol 10/ toluene	0.25	0.025	0.09	0.36	-	3.6	-	1	1	2
"	0.47	0.023	0.09	0.19	4.80	3.9	3.5	1	1	4
0.28 M A364 in toluene	0.25	0.127	0.05	0.19	-	0.39	-	1	1	1
0.53 M A364 in toluene	0.47	0.055	0.07	0.16	8.06	1.5	1.5	1	1	1

(a): measured total concentration of ammonia in raffinate: mole/liter

(b): calculated ammonia concentration in organic phase: mole/liter

(c): stoichiometry: $[NH_4^+A^-]/[D2EHPA]_o$

(d): K_c for ammonium, calculated as concentration of ammonia in organic phase divided by concentration of ammonium ion in aqueous phasse, both expressed as mole/liter

(e): K_c for ammonium as predicted from data in Figures 6.4 and 6.5

(f): see Table 6.1 for explanation of phase-separation properties notation using synthetic solutions are applicable to actual coal-conversion wastewaters.

The phase-separation tendencies also appear to be consistent with those noted earlier for synthetic solutions. For the toluene diluent at constant S/W and ammonium/D2EHPA ion-pair concentration, increasing the concentration of D2EHPA improved phase-separation properties. This same effect was noted in Table 6.27 and may be due to the reduction in stoichiometry and the consequent increase in the amount of D2EHPA available to solvate the ion pair. The opposite is true for the alcohol diluent system, in which increasing the concentration of D2EHPA worsened the phase-separation properties. This same effect was noted in Table 6.23 and is probably due to the increase in D2EHPA concentration. Stoichiometry is not as important a variable in alcohol-diluent systems as it is in toluene-diluent systems.

Overall, the phase-separation properties were better than expected based on the data presented in Chapter 6, especially for the toluene and amine diluents. This may be due to the presence of other ionic species in the wastewater. The very good phase-separation properties for the amine-diluent cases relative to the other diluents may be due to the higher raffinate concentrations in the amine-diluent cases.

Coextraction of phenol from the wastewater into the solvents was also examined. The wastewater initially contained 1380 mg/l of phenol. The concentrations of phenol in the organic phases after extraction were measured as described in Chapter 2, section E and are reported in Table 7.2. Significant errors are associated with these results because the chromatogram of the solvent contained many peaks close to the phenol peak. Thus the integration of the phenol peak was

TABLE 7.2

PHENOL EXTRACTION FROM METC WASTEWATER

FEED = 1380 mg/l PHENOL S/W (v/v) = 2.5

DILUENT	$[\text{D2EHPA}]_o$ ($\underline{M}$)	[Phenol][(a)] ppm	Phenol extracted[(b)] %
Toluene	0.25	595	94
"	0.47	528	84
50% (v/v) Alfol 10/ toluene	0.25	590	92
"	0.47	585	91
0.28 $\underline{M}$ A364 in toluene	0.25	700	>100
0.53 $\underline{M}$ A364 in toluene	0.48	646	>100

(a): measured organic phase concentration of phenol
(b): calculated % phenol extracted from aqueous phase; values approximate due to uncertainities in [phenol]

not optimal. However from the data in Table 7.2 it is apparent that essentially all of the phenol was extracted into the organic phase. The amine-containing diluent systems may have extracted slightly more phenol than the other solvents. The coextracted phenol was not expected to have much of effect on the equilibrium of the system as measured by the K_{c,NH_4^+} values. A concentration of 700 ppm phenol corresponds to 0.0074 M, which is only 15% of the lowest measured concentration of the ammonium/D2EHPA ion pair (0.049 M).

The high degree of phenol extraction is partially due to the extraction of phenol by the diluents. K_D for phenol extracted from water into toluene is 2.3 mg/l/mg/l (Kiezyk and Mackay, 1971). At the value of S/W used here (2.5) 85% of the phenol would be extracted by toluene. Likewise K_D for phenol extracted from water into n-decanol is 27.4 mg/l/mg/l (Kiezyk and Mackay, 1971). At this value of S/W and accounting for the dilution effect, the alcohol would extract 97% of the phenol. One conclusion that can be drawn from these data is that the presence of D2EHPA and the ammonium/D2EHPA ion pair do not inhibit phenol extraction.

In summary, it appears that the liquid-liquid extraction equilibrium models developed earlier are applicable to extractions involving actual coal-conversion wastewaters and that trends observed in the extraction of synthetic solutions also apply to the extraction of the wastewaters. See additional data in Appendix III.

B. EXTRACTION/STRIPPING EXPERIMENTS (see also Appendix IV)

These experiments were performed as indicated in Chapter 3, section H. The results for CO_2 removal are presented in Figure 7.1. The

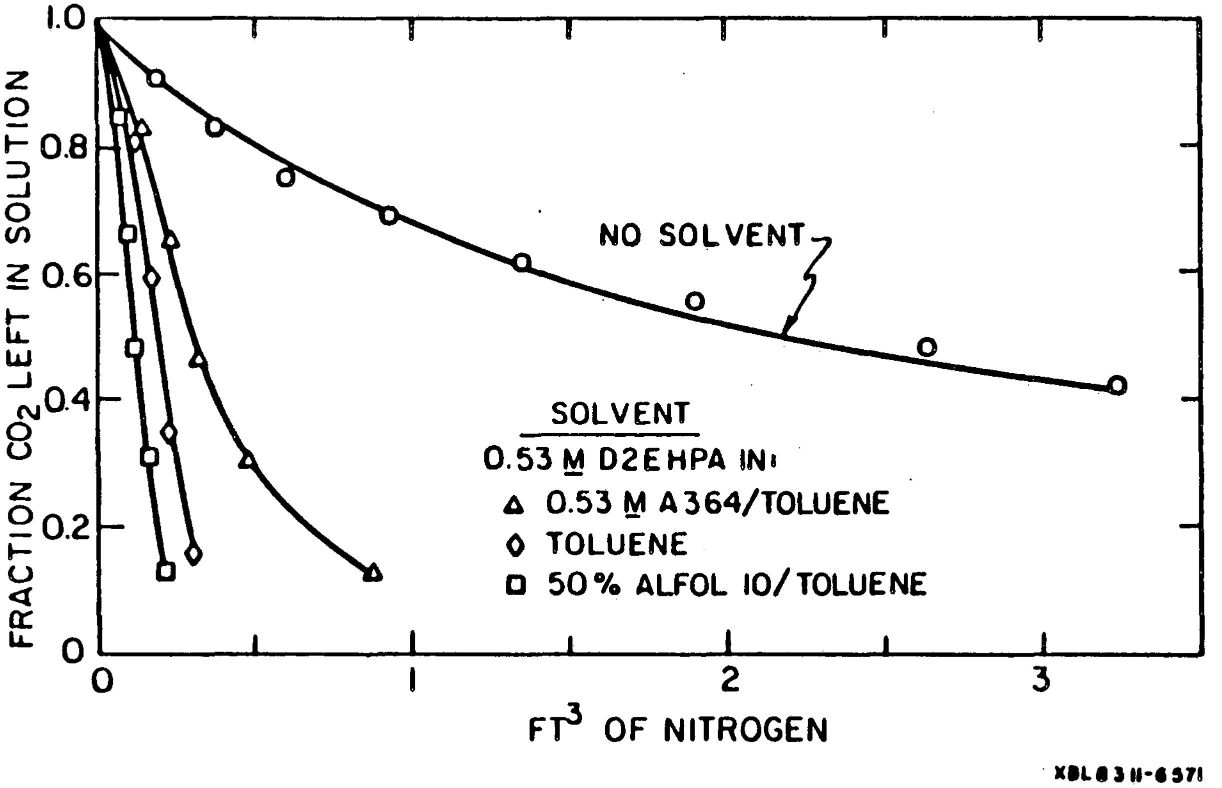


FIGURE 7.1: COMPARISON OF EASE OF REMOVAL OF CO_2 BY STRIPPING WITH THAT BY EXTRACTION/STRIPPING. Stripping: Aqueous phase = 50 ml of 0.64 M CO_2, NH_3. Extraction/Stripping: Aqueous phase = same; organic phase = 0.48 M D2EHPA in diluent; S/W (v/v) = 2.5.

results are plotted as fraction of CO_2 left in the aqueous solution versus the cubic feet of nitrogen passed through the solution. All of the data have been normalized to 50 ml of aqueous solution. For instance, the cubic feet of nitrogen recorded when the solvent was 0.48 M D2EHPA in toluene have been multiplied by 50/40, since only 40 ml of aqueous feed were used in that experiment. The data for the two stripping without D2EHPA extraction cases (i.e. the stripping of 75 ml of aqueous solution and the stripping of 50 ml of aqueous solution in the presence of 125 ml of toluene) were nearly coincident so only the data from the latter experiment are shown in Figure 7.1.

The data for CO_2 removal from solution are also presented in Tables 7.3 and 7.4 for the two cases of stripping with no D2EHPA extractant present. For the extraction/stripping cases the data are presented in Tables 7.5 (alcohol diluent), 7.6 (toluene diluent) and 7.7 (amine diluent). In these tables the calculated partial pressures of CO_2 (P_{CO_2}) are given, as well as the average concentration of CO_2 in the aqueous phase in the interval over which P_{CO_2} was calculated.

Data for NH_3 removal from solution are given in Tables 7.8 and 7.9 for the cases of stripping with no D2EHPA extractant present. The data for the extraction/stripping cases are given in Table 7.10.

For the cases of stripping with no D2EHPA extractant present mass-balance closure was very good. The measured concentrations of CO_2 and NH_3 in the final solution were very close to the values calculated from the initial concentrations and the measured amounts of these gases stripped from solution and absorbed in the absorbers. For the extraction/stripping cases the agreement between calculated and measured CO_2 concentrations was not as good. For the alcohol- and amine-diluent

TABLE 7.3

STRIPPING OF CO_2 FROM SOLVENT-FREE AQUEOUS SOLUTION

$(CO_2)_o$ = 0.63 M (NH$_3$)$_o$ = 0.64 M pH$_o$ = 7.98

P = 1.15 atm

total N_2(a) (ft^3)	Δ N_2 (moles)	CO_2 absorbed(b) (mmoles)	(C)(c) (M)	$(C)_{avg}$(d) (M)	P_{CO_2}(e) (atm)
0	-	-	0.63	-	-
0.08	0.139	2.16	0.60	0.62	1.8×10^{-2}
0.167	0.151	2.70	0.56	0.58	2.0×10^{-2}
0.293	0.220	2.88	0.53	0.55	1.5×10^{-2}
0.48	0.325	2.70	0.49	0.51	9.5×10^{-3}
0.747	0.464	2.70	0.46	0.47	6.7×10^{-3}
1.01	0.452	2.07	0.43	0.44	5.2×10^{-3}
1.42	0.719	2.61	0.39	0.41	4.2×10^{-3}
1.89	0.824	2.34	0.36	0.38	3.3×10^{-3}
2.53	1.10	2.70	0.33	0.34	2.8×10^{-3}
3.27	1.29	2.79	0.29	0.31	2.5×10^{-3}

(a): total cubic feet of nitrogen/ 50 ml solution
(b): total measured concentration of CO_2 in absorber during stripping interval
(c): total concentration of CO_2 in solution; calculated from initial concentration and measured number of mmoles of CO_2 absorbed in absorbers. Final measured (C) = 0.28 M, final pH = 9.35
(d): average total concentration of CO_2 in interval
(e): calculated partial pressure of CO_2; calculated analogous to Equation 3.2

TABLE 7.4

STRIPPING OF CO_2 FROM AQUEOUS SOLUTION IN PRESENCE OF TOLUENE$^{(a)}$

$(CO_2)_o$ = 0.65 M $(NH_3)_o$ = 0.65 M pH_o = 7.98

P = 1.17 atm

total N_2 (ft^3)	Δ N_2 (moles)	CO_2 absorbed (mmoles)	(C) (M)	$(C)_{avg}$ (M)	P_{CO_2} (atm)
0	-	-	0.65	-	-
0.19	0.220	2.63	0.59	0.62	1.4×10^{-2}
0.37	0.209	2.75	0.54	0.57	1.5×10^{-2}
0.60	0.267	2.48	0.49	0.51	1.3×10^{-2}
0.93	0.383	2.38	0.45	0.47	7.2×10^{-3}
1.35	0.487	2.17	0.40	0.42	5.2×10^{-3}
1.90	0.638	2.33	0.36	0.38	4.3×10^{-3}
2.64	0.858	2.35	0.31	0.33	3.2×10^{-3}
3.24	0.696	1.75	0.27	0.29	2.9×10^{-3}

(a): see Table 7.3 for explanation of symbols. Final measured (C) = 0.30 M, final pH = 9.30

TABLE 7.5

EXTRACTION/STRIPPING WITH D2EHPA IN ALCOHOL DILUENT(a)

$(CO_2)_o$ = 0.65 M $(NH_3)_o$ = 0.64 M pH_o = 7.80

P = 1.16 atm

SOLVENT = 0.48 M D2EHPA IN 50% (v/v) Alfol 10/toluene

S/W (v/v) = 2.5

total N_2 (ft^3)	Δ N_2 (moles)	CO_2 absorbed (mmoles)	(C) (M)	$(C)_{avg}$ (M)	P_{CO_2} (atm)
0	-	-	0.65	-	-
0.07	0.081	5.04	0.55	0.60	6.8×10^{-2}
0.10	0.035	5.85	0.43	0.49	1.7×10^{-1}
0.12	0.023	6.12	0.31	0.37	2.4×10^{-1}
0.16	0.047	5.49	0.20	0.25	1.2×10^{-1}
0.22	0.070	5.85	0.083	0.14	9.0×10^{-2}
0.50	0.325	4.41	(-)	0.045	1.6×10^{-2}

(a): see Table 7.3 for explanation of symbols

TABLE 7.6

EXTRACTION/STRIPPING WITH D2EHPA IN TOLUENE DILUENT[(a)]

$(CO_2)_o$ = 0.63 $\underline{M}$ $(NH_3)_o$ = 0.60 $\underline{M}$

P = 1.16 atm

SOLVENT = 0.48 $\underline{M}$ D2EHPA in Toluene

S/W (v/v) = 2.5

total N_2 (ft^3)	Δ N_2 (moles)	CO_2 absorbed (mmoles)	(C) ($\underline{M}$)	$(C)_{avg}$ ($\underline{M}$)	P_{CO_2} (atm)
0	-	-	0.63	-	-
0.125	0.116	4.86	0.51	0.57	4.7×10^{-2}
0.175	0.046	5.67	0.37	0.44	1.3×10^{-1}
0.231	0.052	5.85	0.22	0.29	1.2×10^{-1}
0.294	0.058	4.86	0.099	0.16	9.0×10^{-2}

(a): see Table 7.3 for explanation of symbols

TABLE 7.7

EXTRACTION/STRIPPING WITH D2EHPA IN AMINE DILUENT(a)

$(CO_2)_o$ = 0.63 M $(NH_3)_o$ = 0.60 M pH_o = 8.17

P = 1.16 atm

SOLVENT = 0.48 M D2EHPA in 0.52 M Adogen 364 in toluene

S/W (v/v) = 2.5

total N_2 (ft^3)	Δ N_2 (moles)	CO_2 absorbed (mmoles)	(C) (M)	$(C)_{avg}$ (M)	P_{CO_2} (atm)
0	-	-	0.63	-	-
0.145	0.168	5.71	0.52	0.57	3.8×10^{-2}
0.23	0.099	5.35	0.41	0.46	6.0×10^{-2}
0.32	0.104	5.80	0.29	0.35	6.1×10^{-2}
0.48	0.186	5.15	0.19	0.24	3.1×10^{-2}
0.89	0.476	5.55	0.079	0.13	1.3×10^{-2}
2.02	1.31	4.14	(-)	0.09	3.7×10^{-3}

(a): see Table 7.3 for explanation of symbols

TABLE 7.8

STRIPPING OF NH_3 FROM SOLVENT-FREE AQUEOUS SOLUTION$^{(a)}$

$(CO_2)_o$ = 0.63 M $(NH_3)_o$ = 0.64 M pH_o = 7.98

P = 1.15 atm

total N_2 (ft^3)	Δ N_2 (moles)	NH_3 absorbed (mmoles)	(N) (M)	$(N)_{avg}$ (M)	P_{NH_3} (atm)
0	-	-	0.64	-	-
1.2	2.09	2.35	0.61	0.62	1.3×10^{-3}
1.82	1.08	2.15	0.58	0.59	2.3×10^{-3}
2.35	0.928	2.10	0.55	0.56	2.6×10^{-3}
2.83	0.835	2.10	0.52	0.54	2.9×10^{-3}
3.27	0.754	1.80	0.50	0.51	2.7×10^{-3}

(a): see table 7.3 for explanation of symbols. Here (N) stands for total concentration of ammonia. Final measured (N) = 0.52 M

TABLE 7.9

STRIPPING OF NH_3 FROM AQUEOUS SOLUTION IN PRESENCE OF TOLUENE$^{(a)}$

$(CO_2)_o = 0.65$ M $(NH_3)_o = 0.65$ M $pH_o = 7.98$

$P = 1.17$ atm

total N_2 (ft^3)	ΔN_2 (moles)	NH_3 absorbed (mmoles)	(N) (M)	$(N)_{avg}$ (M)	P_{NH_3} (atm)
0	-	-	0.65	-	-
2.4	2.78	3.25	0.59	0.62	1.4×10^{-3}
3.24	0.974	2.25	0.54	0.56	2.7×10^{-3}

(a): see Table 7.3 for explanation of symbols. Here (N) stands for total concentration of ammonia. Final measured (N) = 0.52 M

TABLE 7.10

PROPERTIES OF FINAL SOLUTIONS FROM EXTRACTION/STRIPPING EXPERIMENTS

SOLVENT = 0.48 M D2EHPA IN DILUENT

	DILUENT:		
	50% (v/v) Alfol 10/ toluene	Toluene	0.52 M Adogen 364 in toluene
(N) (M)	0.0075	0.0186	0.061
(C) (M)	0.0073	0.012	0.049
(P)[a] (M)	0.0041	0.0125	0.006
pH_{meas}	6.2	6.6	8.7
pH_{pred}[b]	6.3	6.3	8.3
$[NH_4^+A^-]$[c] (M)	0.25	0.23	0.22
K_{c,NH_4^+meas}	34	12.5	4.5
K_{c,NH_4^+pred}[d]	41	13.5	4.6
s[e]	0.53	0.48	0.45
% NH_3 stripped	0.064	0.18	1.5
PHASE SEPARATION:[f]			
O	1	1	1
A	1	2	3
I	3	4	4

(a): measured concentration of phosphorus in raffinate: mole/liter
(b): pH predicted using the VLE model TIDES
(c): calculated ammonia concentration in organic phase: mole/liter
(d): K_c for ammonium as predicted from Figures 6.4 and 6.5
(e): stoichiometry, $[NH_4^+A^-]/[D2EHPA]_o$
(f): see Table 6.1 for explanation of phase-separation properties notation

cases the calculated value of CO_2 left in the aqueous solution was negative, indicating that either the initial concentration of CO_2 upon which the calculations were based was too low or the measured absorber concentrations were slightly high. The opposite is true for the toluene-diluent case, in which the calculated final concentration of CO_2 exceeded the measured concentration. These discrepancies are probably due to uncertainities in the measurement of CO_2 concentrations using the CO_2 electrode. Problems in the operation of this electrode were discussed in Chapter 2, section A. The closure of the NH_3 mass balance for the extraction/stripping experiments was satisfactory. The measured concentration of the ammonium/D2EHPA ion pair in the organic phase was within the normal limits of agreement with the calculated value.

In Table 7.11 some measured values of P_{CO_2} from the stripping experiments are compared with equilibrium values. The equilibrium values were calculated by using the data to calculate the approximate concentration of NH_3 in solution at a given concentration of CO_2. The vapor-liquid equilibrium program TIDES was then used to predict the equilibrium partial pressure of CO_2 ($P^e_{CO_2}$). For all of the data presented, the equilibrium values of P_{CO_2} exceed the measured values. The difference decreases at lower concentrations of CO_2.

Table 7.12 presents similar results for NH_3. In this case it was difficult to get a good value of the CO_2 concentration at a given NH_3 concentration since the CO_2 concentration changed more rapidly than the NH_3 concentration. Thus the measured values of P_{NH_3} given are averages over an interval in which, at least initially, the concentration of CO_2 changed significantly. This means that P_{NH_3} changed significantly over the interval. Given this potential variation in P_{NH_3} the data presented

TABLE 7.11

COMPARISON OF MEASURED AND EQUILBRIUM VALUES OF P_{CO_2} FOR STRIPPING IN ABSENCE OF SOLVENT

DATA FROM TABLE 7.3

(C)[a] (M)	(N)[b] (M)	$P_{CO_2,meas}$ (atm)	$P^e_{CO_2}$ [c] (atm)	$P^e_{CO_2}/P_{CO_2,meas}$
0.55	0.61	1.5×10^{-2}	1.6×10^{-1}	11.0
0.51	0.61	9.5×10^{-3}	7.3×10^{-2}	7.7
0.40	0.60	4.2×10^{-3}	2.1×10^{-2}	5.0
0.34	0.55	2.9×10^{-3}	1.4×10^{-2}	4.1
0.30	0.52	2.5×10^{-3}	9.0×10^{-3}	3.6

(a): average total concentration of CO_2
(b): average total concentration of NH_3
(c): equilibrium partial pressure of CO_2 calculated from VLE model TIDES

TABLE 7.12

COMPARISON OF MEASURED AND EQUILIBRIUM VALUES OF P_{NH_3} FOR STRIPPING IN ABSENCE OF SOLVENT(a)

DATA FROM TABLE 7.8

(N) (<u>M</u>)	(C) (<u>M</u>)	$P_{NH_3,meas}$ (atm)	$P^e_{NH_3}$ (atm)	$P^e_{NH_3}/P_{NH_3,meas}$
0.59	0.40	2.3×10^{-3}	1.5×10^{-3}	0.65
0.56	0.35	2.6×10^{-3}	1.7×10^{-3}	0.67
0.54	0.31	2.9×10^{-3}	2.1×10^{-3}	0.71
0.51	0.30	2.7×10^{-3}	1.9×10^{-3}	0.69

(a): see Table 7.11 for explanation of symbols

in Table 7.12 indicate that the equilibrium values of P_{NH_3} and the measured values are close.

The better agreement between the equilibrium and measured values for P_{NH_3} than for P_{CO_2} indicate that the approach to equilibrium is less for CO_2 stripping than for NH_3 stripping. Darton et. al. (1978) suggest that this may be due to the reactions involved. For NH_3 (initially present as NH_4^+) to be stripped from solution only an infinitely fast proton transfer is involved. For CO_2 (initially present as HCO_3^-) to be released, a slower reaction occurs:

$$HCO_3^- \rightleftarrows CO_2 + OH^- \qquad (7.1)$$

This slow reaction could be one of the factors affecting the efficiency (or approach to equilibrium) of CO_2 removal. It should also be recognized that the higher degree of liquid-phase mass-transfer control for CO_2 would lead to a greater departure of the gas-phase partial pressure from the equilibrium value.

The trends in the measured values of P_{NH_3} and P_{CO_2} for the stripping and extraction/stripping experiments are still useful information since the data were obtained under nearly identical conditions.

In the beginning of the stripping experiments P_{CO_2} is much greater than P_{NH_3} (compare Tables 7.3 and 7.4 with Tables 7.8 and 7.9). This reflects the higher Henry's law constant for CO_2. CO_2 is preferentially stripped from solution. This causes the pH to rise from the initial value of about 8. This pH rise results in the formation of more ionized CO_2 and less ionized NH_3. Thus the pH rise serves to decrease P_{CO_2} and increase P_{NH_3}. By the end of the experiment, NH_3 and CO_2 were being removed at comparable rates, and the pH levelled off at about 9.3.

Figure 7.1 indicates that CO_2 is much more readily stripped from solution in the presence of a solvent containing D2EHPA. Specifically, CO_2 removal is easiest when the diluent for D2EHPA is the alcohol diluent, followed by the toluene diluent and then the amine-containing diluent. This same effect may be seen by comparing calculated values of P_{CO_2} in Tables 7.3 through 7.7.

In Table 7.10 the measured final concentrations of NH_3, CO_2 and phosphorus (due to D2EHPA solubility) in the raffinates after the extraction/stripping experiments are given. The final aqueous-phase pH is also given. The pH values predicted using these concentrations in the TIDES model agree well with the measured values. In addition the K_{c,NH_4^+} values predicted via the use of Figures 6.4 and 6.5 agree very well with those measured.

Also included in Table 7.10 is information on the amount of NH_3 stripped from the aqueous solutions during the extraction/stripping experiments, as determined by the amount of NH_3 found in the NH_3 absorbers. The amount of NH_3 stripped increased in going from the alcohol diluent to the toluene diluent to the amine-containing diluent. This trend in NH_3 volatility is a reflection of the observed increase in aqueous-phase NH_3 concentration and pH in going from the alcohol diluent to the toluene diluent to the amine-containing diluent.

The type of behavior expected in the extraction/stripping experiments can be discerned from calculations combining TIDES with the liquid-liquid extraction models given in Chapter 6. These calculations were performed as follows. The initial concentrations of NH_3 and CO_2 in an aqueous solution are known, as are the solvent composition and S/W. A value of the ammonium/D2EHPA ion-pair concentration in the solvent after extraction is assumed, and the stoichiometry determined. From the NH_3 mass balance the concentration of NH_3 in the aqueous phase is known and hence the assumed value of K_{c,NH_4^+} can be calculated. The concentration of CO_2 in the aqueous phase is assumed unchanged. With this information TIDES can be used to calculate the aqueous-phase pH. From knowledge of the organic-phase stoichiometry and the aqueous-phase pH, K_{c,NH_4^+} can be calculated using the models in Chapter 6, or Figures 6.4 and 6.5. This value is compared with the calculated assumed value of K_{c,NH_4^+}, and the assumed concentration of the ammonium/D2EHPA ion pair is adjusted until the values agree. Once the equilibrium conditions have been determined, P_{CO_2}, as calculated from TIDES, is known.

Figure 7.2 presents results for such a series of calculations. The solvents were all 0.48 M D2EHPA in a diluent. The temperature was 298K, and the initial concentrations of both NH_3 and CO_2 were 0.6 M. From this figure it is seen that the use of an alcohol diluent provides the largest enhancement in P_{CO_2}, followed by the toluene diluent and then the amine diluent. Table 7.13 gives more details for these calculations at S/W (v/v) = 2. Results are shown for solutions initially containing 0.6 M NH_3 and either 0.6 M or 0.3 M CO_2. It is seen that the presence of the solvent serves to decrease the NH_3 concentration in the aqueous phase, lowering the pH and increasing P_{CO_2}. The most powerful solvent, D2EHPA in the alcohol diluent, gives the highest K_{c,NH_4^+} and the lowest pH. The weakest solvent, D2EHPA in an amine diluent at a 1:1 molar ratio, gives the lowest K_{c,NH_4^+} and the highest pH.

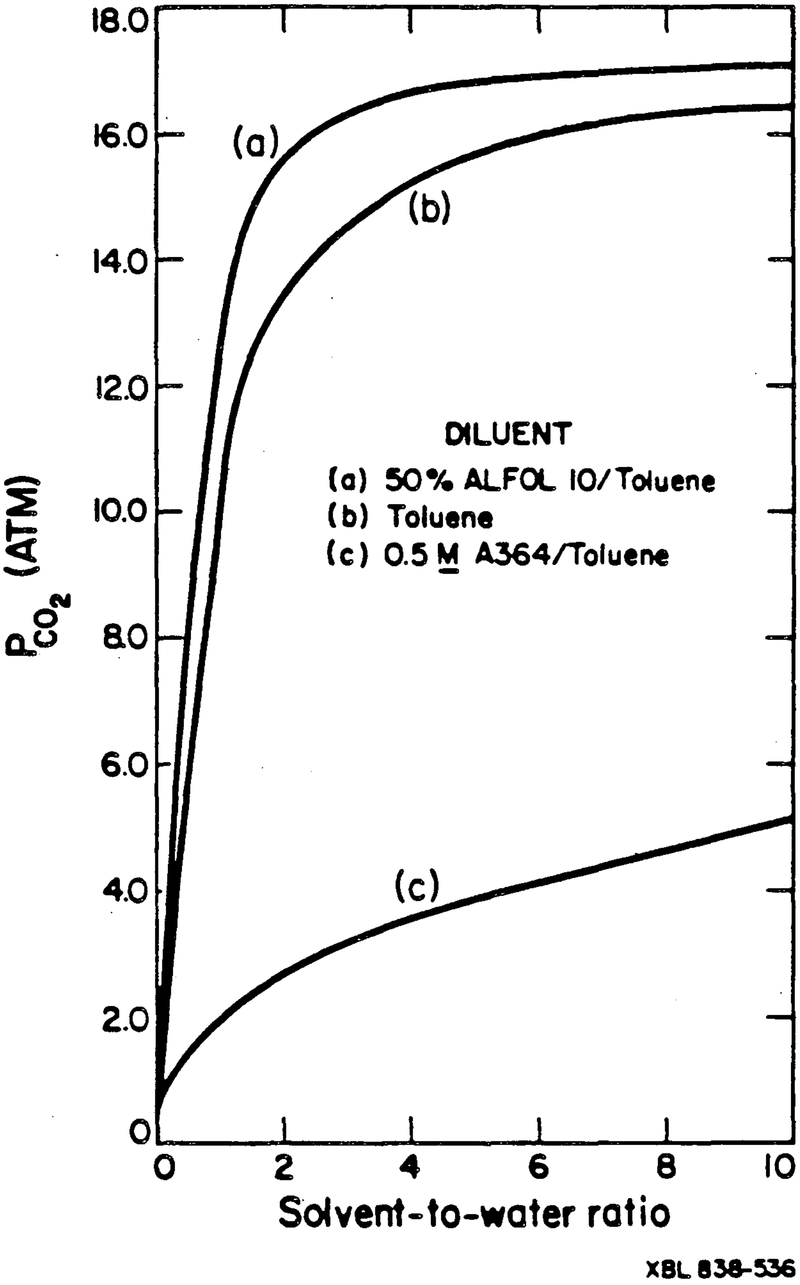


FIGURE 7.2: CALCULATED ENHANCEMENT IN P_{CO_2} DUE TO AMMONIA EXTRACTION. Organic phase = 0.48 M D2EHPA in diluent; Aqueous phase = 0.6 M NH_3, CO_2; T = 298K.

TABLE 7.13

CALCULATED ENHANCEMENT IN P_{CO_2} DUE TO EXTRACTION$^{(a)}$

SOLVENT = 0.48 M D2EHPA IN DILUENT   S/W (v/v) = 2

DILUENT	$(C)_o^{(b)}$ (M)	$(N)_o^{(b)}$ (M)	$(N)_{raf}^{(c)}$ (M)	pH_{raf}	s	K_{c,NH_4^+}	P_{CO_2} (atm)
50% (v/v) Alfol 10/ toluene	0.6	0.6	0.058	5.29	0.57	4.7	15.7
"	0.3	0.6	0.042	5.49	0.59	6.67	7.1
Toluene	0.6	0.6	0.127	5.67	0.50	1.9	13.5
"	0.3	0.6	0.093	5.90	0.53	2.7	5.6
0.26 M A364 in toluene	0.6	0.6	0.342	6.33	0.28	0.38	7.1
"	0.3	0.6	0.237	6.79	0.39	0.77	1.7
0.53 M A364 in toluene	0.6	0.6	0.504	6.89	0.10	0.095	2.7
"	0.3	0.6	0.305	7.73	0.31	0.48	0.23
No solvent	0.6	0.6	0.6	7.54	–	–	0.65
"	0.3	0.6	0.6	9.12	–	–	0.0054

(a): calculated using the VLE model TIDES and Figures 6.4 and 6.5; see Table 7.1 for explanation of symbols
(b): initial total concentrations of NH_3 and CO_2
(c): total concentration of ammonia in raffinate

Higher S/W reduces the concentration of NH_3 in the aqueous phase, lowering the pH further. Above a certain value of S/W, the pH has been lowered to the point at which essentially all of the CO_2 is in the unionized form. Thus no significant increase in P_{CO_2} occurs as S/W is increased further.

Table 7.13 provides some insight into the results of the extraction/stripping experiments. Assume that the initial concentrations of both NH_3 and CO_2 were 0.6 M. If the extraction occurred instantaneously, then the ammonia concentration and the pH would be rapidly lowered and P_{CO_2} would be very high. As CO_2 is stripped from solution (compare the 0.6 M CO_2 case with the 0.3 M CO_2 case) the net effect is a decrease in aqueous-phase NH_3 concentration and an increase in pH. Thus P_{CO_2} decreases and K_{c,NH_4^+} increases.

These trends indicate that P_{CO_2} should decrease throughout the extraction/stripping experiments. As seen in Tables 7.5 through 7.7, P_{CO_2} goes through a maximum. This may be an anomaly in the data or it may indicate that the extraction, although rapid, is not instantaneous. Extraction equilibrium is apparently reached at the end of the extraction/stripping experiments, since the K_{c,NH_4^+} values calculated agree so well with the models derived earlier. Stripping of NH_3 from solution should not affect P_{CO_2} results since, as seen in Table 7.10, very little NH_3 was stripped from solution.

The pH of the solutions at the end of the extraction/stripping experiments are presented in Table 7.10. The final pH value is highest for the amine-diluent system. Thus, at a given concentration of CO_2, P_{CO_2} is lowest for this system than for the other systems examined. For the toluene- and alcohol-diluent systems the final pH value is low enough that the effect of CO_2 ionization on P_{CO_2} is small. For the amine diluent the higher final pH value means that P_{CO_2} is more sensitive to the total concentration of CO_2, since the corresponding pH values result in significant changes in the extent of ionization of the CO_2.

Because of the low extent of CO_2 ionization with the alcohol and toluene diluents, the equilibrium value of P_{CO_2} (from TIDES) is relatively well known. It is apparent that equilibrium values of P_{CO_2} were not reached in these cases. (Compare measured values of P_{CO_2} in Tables 7.5, 7.6 and 7.7 with equilibrium values in Table 7.13.) The low pH values of P_{CO_2} at 0.3 <u>M</u> CO_2 given in Table 7.13 are significantly higher than the values measured and reported in Tables 7.5 and 7.6. For the amine-diluent the effect of pH at this CO_2 concentration is important, since a significant portion of the CO_2 is ionized. The pH value is not known, and so it is difficult to determine if the P_{CO_2} data for the amine diluent are equilibrium data. In light of the fact that the other P_{CO_2} data did not appear to be equilibrium data, it seems likely that these data are not either. However the trends are all as expected. P_{CO_2} increases in the presence of an NH_3-extracting solvent and is greater for the alcohol diluent than for the toluene diluent and is lowest for the amine-containing diluent.

An additional effect which serves to increase P_{CO_2} still further in the presence of the extracting solvents is the lowering of pH due to D2EHPA solubility in the aqueous phase. As D2EHPA dissolves in the aqueous phase it lowers pH and hence enhances CO_2 volatility. However, a comparison of aqueous-phase D2EHPA concentrations reported in Table 7.10 with initial CO_2 concentrations shows that this effect is secondary.

Ammonia volatility is decreased by the presence of the D2EHPA-containing solvents. This is due to the lower aqueous-phase NH_3 concentration and the lower aqueous pH in these systems.

The phase-separation properties of these systems were observed. During the experiments the systems with the D2EHPA-containing solvents foamed significantly. This problem suggests that operation of an actual extraction/stripping process in one vessel is not feasible.

The phase-separation properties at the ends of the extraction/stripping experiments are reported in Table 7.10. The results are those observed after the two phases were centrifuged. Consistent with results presented in Chapter 6, section B, the alcohol diluent gave the best phase-separation properties. In these experiments the amine diluent gave the worst phase-separation properties. Even after an additional centrifugation the raffinate from this case remained cloudy white. The amine-diluent system gave worse phase-separation properties than those reported for similar systems in Chapter 6. For those data S/W was 5 while here it was 2.5. This lower S/W may be responsible for the observed difference in phase-separation properties.

In summary these experiments demonstrate that the combination of stripping and solvent extraction serves to enhance CO_2 volatility and to reduce NH_3 volatility, thereby enabling isolation of NH_3 from CO_2.

C. DESIGN CONSIDERATIONS

This section presents results of preliminary calculations intended to assess the economic viability of the proposed extraction/stripping process, and to identify critical areas for further research. The six main factors addressed are: (1) solvent choice (i.e. D2EHPA concentration and diluent), (2) required solvent-to-water ratio (S/W), (3) D2EHPA solubility losses to the exit aqueous phase, (4) required steam-to-water ratio in the acid-gas stripper (V_s/W), (5) the steam-to-solvent ratio required in the solvent-regeneration column, and (6) other operating costs and capital investments.

1. SOLVENT CHOICE

The choice of solvent will affect the other factors listed above. Therefore several solvents were considered in parallel. The solvents considered were low (0.25 $\underline{M}$) and high (0.48 $\underline{M}$) concentrations of D2EHPA in three diluents — a 50% (v/v) alcohol (probably decanol) in an inert diluent, an inert diluent, and an amine-containing diluent, at two amine-to-D2EHPA molar ratios, 1:1 and 1:2. Data for the inert diluent were taken to be represented by the data for the toluene diluent (K_{c,NH_4^+}, solubility losses) and the Norpar 12 diluent (solvent-regeneration properties). For the following calculations the feed to the extraction/stripping process was taken to be an aqueous solution containing 0.6 $\underline{M}$ CO_2 and 0.6 $\underline{M}$ NH_3.

2. SOLVENT-TO-WATER RATIO (S/W)

In the design of a conventional countercurrent extraction column with straight operating and equilibrium lines, effective solute removal is achievable in a reasonable number of stages if S/W is taken to be such that K_cS/W is about 1.4.

In this process the situation is more complicated. Specifically K_c depends on pH, and even at a constant pH the equilibrium line is not straight. At all points in the extraction process the operating and equilibrium lines should not approach too closely. This can be assured by insisting that K_cS/W be equal to or greater than 1.4 at all points in the extraction process.

For the solvents under consideration K_c at any point in the extraction process can be calculated by using Figures 6.4 and 6.5, as described earlier, and the fraction of ammonia in the ammonium form (Equation 4.6). However this requires that the pH be known or calculable by an independent means (i.e., a vapor-liquid equilibrium model). Note that the use of the data in Figures 6.4 and 6.5 implies that the extraction occurs at about 298K.

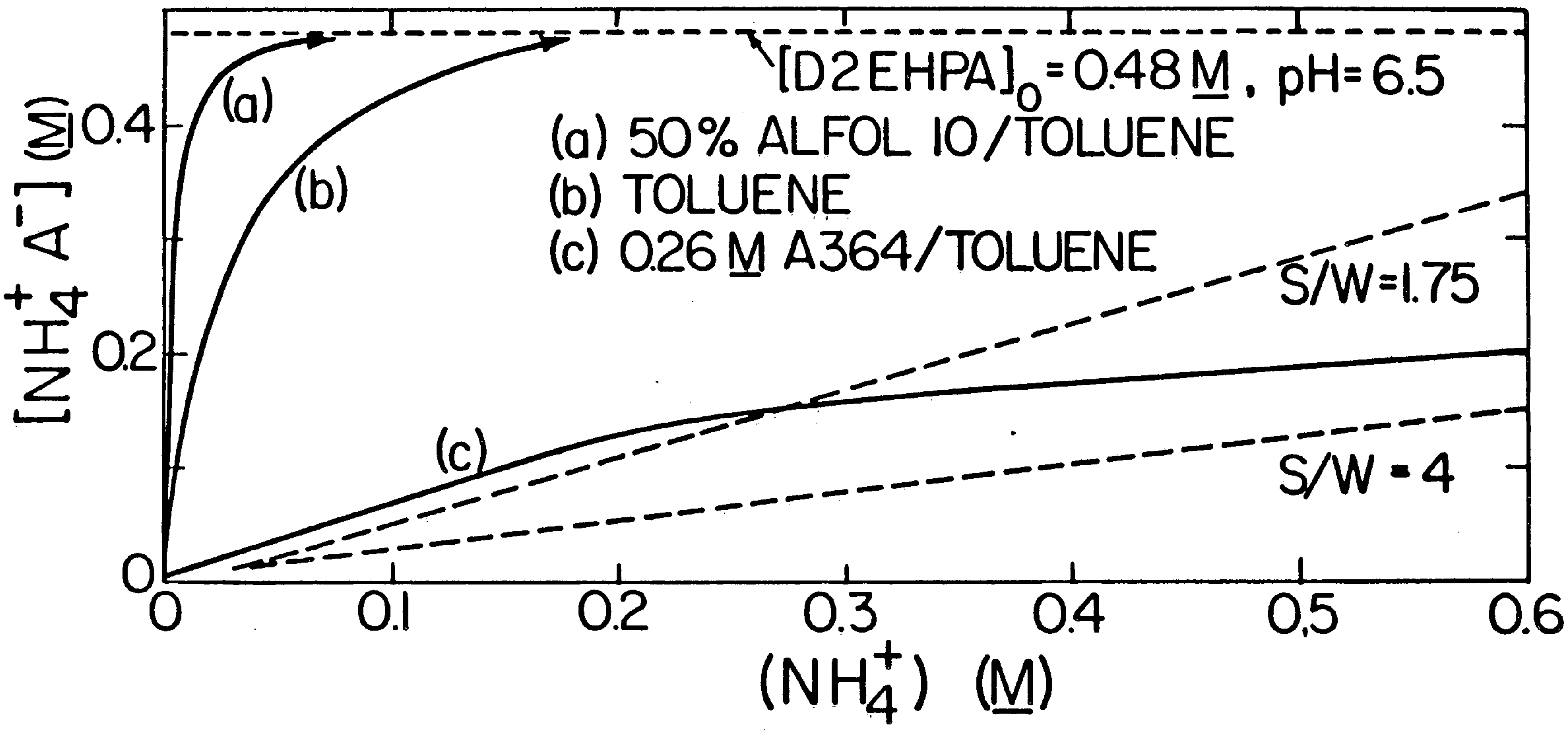
For a given solvent and feed to the extraction process pH on a given stage will depend on the NH_3 and CO_2 concentrations, which in turn will depend on S/W and V_s/W (steam-to-water ratio in the acid-gas stripper). For instance, in the limit of S/W approaching zero (stripping only and no extraction), the pH of the aqueous phase will rise above its initial value owing to the preferential removal of the acid gas CO_2. At the other extreme, as V_s/W approaches zero (extraction only and no stripping), the pH will fall below its initial value due to the preferential removal of the basic gas NH_3.

A precise design of the combined extraction/stripping process would require combining a model for the stripping process with that for the extraction process. Referring to Figure 1.9, for a given S/W and V_s/W the resultant aqueous stream from the first extraction step or steps would be considered as the feed for the stripper. After a number of stripping stages the resultant aqueous phase would be considered as feed to another set of extraction stages. A number of variables would be involved, including the number of extraction stages in any set and the number of stripping stages in any set. This procedure would be very time consuming and probably warranted only in later stages of design.

For the current set of calculations a minimum pH value on all stages was assumed. This gave minimum values of K_c and thus a conservative estimate of S/W. Thus the design criterion was that at this minimum pH value K_cS/W on all stages be at least 1.4. This minimum pH was chosen as 6.5, so that effective removal of CO_2 would occur in the stripping process. At this pH approximately half of the CO_2 will be unionized and readily stripped. At this pH K_c is equal to K_{c,NH_4^+}.

Figure 7.3 presents an extraction distribution isotherm at pH 6.5 for three of the solvents, 0.48 M D2EHPA in the alcohol diluent, in the inert diluent and in the amine diluent (amine-to-D2EHPA molar ratio of 1:2). The data in Figures 6.4 and 6.5 were used to generate these curves. The relative positions of these curves is due to the relative K_c values for the solvents, the highest being for the alcohol diluent and the lowest for the amine diluent. The shapes of the curves are typical of those encountered in extractions with chemical complexing agents. At the dilute end K_c is largest, owing to the high concentration of free D2EHPA.

Since at a constant pH K_c is lowest at the concentrated or solvent exit end of the process, this is the point which determines S/W. At the aqueous feed concentration (0.6 M NH_3) the equilibrium composition of the solvent for the alcohol and inert diluents is essentially 0.48 M. Thus K_c is 0.48/0.6 or 0.8. For a K_cS/W of 1.4, S/W must be 1.75 (v/v). This gives an exit solvent composition of the ammonium/D2EHPA ion pair of 0.33 M and an exit stoichiometry of 0.7. For the amine



XBL843-6808

FIGURE 7.3: EXTRACTION DISTRIBUTION ISOTHERM.

Solvent = 0.48 M D2EHPA in diluent; pH = 6.5.

diluent the concentration of the solvent in equilibrium with the feed is 0.2 M. K_c is 0.2/0.6 or 0.33. For K_cS/W equal to 1.4, S/W must be 4 (v/v). This gives an exit solvent concentration of the ammonium/D2EHPA ion pair of 0.15 M and a stoichiometry of 0.31. Operating lines at these values of S/W are shown in Figure 7.3. These were drawn assuming 95% NH_3 removal from the aqueous feed, and an inlet solvent concentration of the ammonium/D2EHPA ion pair equal to 0.01 M.

A solvent containing a higher molar ratio of amine to D2EHPA would require an S/W ratio greater than 4, which would probably be unacceptable. Therefore the only amine diluent considered further was that containing an amine-to-D2EHPA molar ratio of 1:2. For the lower concentration of D2EHPA (0.25 M) the required S/W for the alcohol and inert diluents was 3.3, while for the amine diluent, at an amine-to-D2EHPA molar ratio of 1:2, S/W was 8.4. This latter value is rather high, and so the lower concentration of D2EHPA in this diluent was not considered further.

The comparison of the inert and amine (1:2) diluents in Table 6.14 revealed that the K_{c,NH_4^+} values for the former were at least 25 times greater than those for the latter at a given organic-phase concentration of the ammonium/D2EHPA ion pair. However no such variation in the required S/W results. As S/W is reduced, the concentration of the ammonium/D2EHPA ion pair in the organic phase increases, the concentration of free D2EHPA decreases and K_c decreases. As stoichiometric equivalence is reached, the concentration of the ammonium/D2EHPA ion pair in the organic phase reaches a limiting value, and K_c decreases rapidly with further increase in the aqueous-phase concentration of NH_3. For a given solvent concentration of D2EHPA and a given concentration of aqueous feed there is an upper limiting value of K_c at the rich end of the extractor, no matter what the diluent is. In this case it would be 0.48/0.6. This value is approached for the inert diluent but not for the amine diluent. Thus for these two diluents the ratio of the K_c values for the solvents in equilibrium with the feed is much smaller than 25 since the K_c values being considered are not at the same concentration of the ammonium/D2EHPA ion pair.

However, the value of the more favorable equilibrium for the inert and alcohol diluents relative to the amine diluent is not completely lost. It influences the shapes of the curves in Figure 7.3 causing the curve for the alcohol diluent to bow more than that for the amine diluent. Due to these shapes, at the S/W values chosen, the number of stages required for effective NH_3 removal will be much less for the alcohol-diluent solvent than for the amine-diluent solvent.

For the alcohol and inert diluents the S/W could be economically reduced below the values chosen. However it could not be reduced below that which would correspond to equilibrium between the entering aqueous phase and the exiting solvent. That is for the solvent containing 0.48 $\underline{M}$ D2EHPA it could not be reduced below 0.6/0.48 or 1.25. At this S/W an infinite number of stages would be required. In addition, very high loading of D2EHPA in an inert aliphatic diluent may lead to third-phase formation. Therefore in subsequent calculations the higher S/W of 1.75 was used.

For the alcohol diluent K_c values are high enough that the use of only one extraction stage is a possibility. If a solution containing 0.6 $\underline{M}$ CO_2 and 0.6 $\underline{M}$ NH_3 were contacted with 0.48 $\underline{M}$ D2EHPA in a 50% alcohol diluent at an S/W of 2 and no CO_2 were stripped from solution, the resultant aqueous phase would contain 0.6 $\underline{M}$ CO_2 and 0.058 $\underline{M}$ NH_3 at a pH of 5.3 (see Table 7.13). This degree of NH_3 removal may be satisfactory in some cases.

If a lower pH value had been assumed, the distribution isotherms in Figure 7.3 would be shifted to the right. If the pH were not much lower, this would not affect the S/W calculated for the inert and alcohol diluents since their equilibrium solvent concentrations of the ammonium/D2EHPA ion pair at the aqueous feed concentration would still be close to stoichiometric loading. But the number of stages required for extraction would increase. For the amine diluent the necessary S/W would increase if the pH were lowered.

The solvents considered for the remainder of the calculations and the S/W ratios used are listed in Table 7.14.

3. SOLVENT SOLUBILITY LOSSES

The most important solvent solubility losses will be those of D2EHPA, which is the most expensive constituent of the solvent. These solvent losses could be estimated by using the calculated $K_{c,H^+}/P$ values given in Chapter 6, section C if the pH of the exit aqueous stream were known. As noted above, the pH value at any stage depends on S/W and V_s/W (steam-to-water ratio in the acid-gas stripper), among other things. Thus it is difficult to estimate the exit aqueous-phase pH.

Thus the approach taken here was to use the D2EHPA solubility losses measured during extraction of raffinates with fresh solvents, which were intended to simulate the aqueous exit end of the extraction process. In these experiments, discussed in Chapter 6, section C, higher final pH values were obtained when the diluent contained an

TABLE 7.14

REQUIRED SOLVENT-TO-WATER RATIOS

DILUENT	$[\mathrm{D2EHPA}]_o$ (M)	S/W (v/v)	$[\mathrm{NH_4}^+\mathrm{A}^-]_{exit}$[a] (M)
Inert	0.25	3.3	0.18
"	0.48	1.8	0.34
50% (v/v) Decanol/ inert	0.25	3.3	0.18
"	0.48	1.8	0.34
0.26 M A364 in inert	0.48	4.0	0.15

(a): concentration of ammonium/D2EHPA ion pair in solvent exiting extractors amine. This is consistent with the expected trend in pH seen in Table 7.13.

The solubility losses of D2EHPA estimated in this way are presented in Table 7.15. Costs are also given based on a February 1984 price for D2EHPA of \$2.60/lb (Mobil Chemical Company, Phosphorus Division).

4.STEAM-TO-WATER RATIO IN ACID-GAS STRIPPER (V_s/W)

Calculation of the required value of V_s/W depends on knowledge of pH (or NH_3 concentration) at a given CO_2 concentration. As pointed out earlier, the pH values on a given stage depend on S/W and V_s/W, and a detailed process design procedure would be necessary to determine the CO_2, NH_3 and pH profiles throughout the column.

In these calculations pH values within the stripping column were assumed and the resultant increase in CO_2 volatility calculated. For a given total concentration of CO_2, decreasing the pH will increase the partial pressure of CO_2 (P_{CO_2}). The steam requirement to strip CO_2 was assumed to be inversely proportional to P_{CO_2}. Therefore the steam requirement after pH lowering by ammonia extraction (V_s/W) was assumed to be related to that without extraction (V_s^o/W) through the ratio of P_{CO_2} values without extraction ($P^o_{CO_2}$) to that with extraction (P_{CO_2}):

$$\left(\frac{V_s}{W}\right) = \left(\frac{V_s^o}{W}\right) \frac{P^o_{CO_2}}{P_{CO_2}} \qquad (7.2)$$

In a conventional stripper the ratio of ammonia to acid gases is generally such that ammonia is the least volatile species, and so pH

TABLE 7.15

ESTIMATED D2EHPA SOLUBILITY LOSSES

DILUENT	$[D2EHPA]_o$ (M)	$(D2EHPA)^{(a)}$ (ppm)	$COST^{(b)}$ ($/1000 gal water)
Inert	0.25	550	12
"	0.48	500	11
50% (v/v) Decanol/ inert	0.25	90	2
"	0.48	180	4
0.26 M A364 in inert	0.48	870	19

(a): estimated concentration of D2EHPA in aqueous raffinate
(b): based on 2/84 price of $2.60/lb (Mobil Chemical Company, Phosphorus Division)

rises downwards in the column due to the preferentially stripping of CO_2. That is, for a feed containing equal amounts of CO_2 and NH_3 (pH equal to 7.6) the exit aqueous phase will have a higher ratio of NH_3 to CO_2 and a higher pH. Thus the pinch in CO_2 stripping occurs at the dilute end of the stripper.

Table 7.16 gives some pH values (at 298K) and associated ratios of CO_2 to NH_3 concentrations, assuming no other acids or bases are present. P_{CO_2} for a total concentration of CO_2 of 0.3 $\underline{M}$ is also given. The P_{CO_2} values are at 373K, the temperature at which stripping is likely to occur.

Decreasing the pH from 8.1 to 6.5 increases P_{CO_2} by a factor of 2. This is the likely pH range to be encountered for the amine-diluent solvent. Lower pH values are likely to be encountered with the alcohol- and inert-diluent solvents, particularly at the dilute end of the column. Decreasing pH from 8.1 to 5.5 increases P_{CO_2} by a factor of four.

A conventional stripper for removing NH_3 and CO_2 from water requires about 0.15 lb steam/lb water to strip the gases effectively (Seufert et. al., 1979). The requirements for effective CO_2 removal are less, so the estimates given below are conservative. Ammonia extraction may reduce this value by the factors given above. Thus for the amine diluent V_s/W was assumed to be 0.07 lb steam/lb water, while for the alcohol and inert diluents it was assumed to be 0.04 lb steam/lb water.

5. STEAM-TO-WATER RATIO IN SOLVENT-REGENERATION COLUMN (V_r/W)

In the solvent-regeneration column solvent loaded with NH_3 is stripped countercurrently with reboiled diluent vapor. The exit gas

TABLE 7.16

P_{CO_2} AT DIFFERENT pH VALUES

TOTAL (CO_2) = 0.3 M

C/N (molar ratio)	pH (298K)	P_{CO_2} (373K) (atm)
7.1	5.5	29.5
1.5	6.5	14.1
0.9	8.1	6.6
0.5	9.1	2.0

stream contains NH_3, diluent and water which was coextracted with the NH_3. These are condensed to form two phases, an aqua NH_3 solution and an organic diluent phase. In the reboiler a portion of the diluent is boiled out of the solvent for use as the stripping medium. After being condensed overhead this diluent is combined with the remainder of the solvent exiting the reboiler and returned to the extraction/stripping part of the process.

To estimate the energy requirements for the solvent-regeneration column, the data obtained in the solvent-regeneration experiments were used (Chapter 6, section E). In the following analysis these data are assumed to be equilibrium data. This assumption is partially based on the observation that in the extraction/stripping experiments (section B, above) the NH_3 stripping did approach equilibrium rather closely. The higher temperature of the solvent-regeneration experiments should have improved the mass transfer coefficients and aided in the approach to equilibrium.

Two energy requirements are considered in this section, the energy to boil the diluent required to provide the stripping medium (V_r/S) and the energy required to boil the coextracted water.

a. Procedure for Determining Stripping-Vapor Requirements

In a typical design of a conventional stripping column the amount of stripping medium required for effective countercurrent stripping is taken to be that needed to give an operating line of slope about 1/1.4 that of the equilibrium line. In the present case the equilibrium relationship is not linear. The criterion here was taken to be that at every place in the column the partial pressure of NH_3 (P_{NH_3}) be no more than 1/1.4 times that which would be in equilibrium with the passing liquid phase ($P^*_{NH_3}$).

In this analysis the temperature was considered constant throughout the column at 127°C. A higher temperature would not be acceptable since it would lead to considerable thermal decomposition of D2EHPA. The column pressure was set at the lowest value that would permit condensation of the aqua NH_3 vapor with cooling water (100°F or 38°C). Note that the column pressure and temperature can be specified independently if the organic diluent is left unspecified at this point. The nature of the organic diluent which is consistent with the specified temperature and pressure is determined later.

The goal of the following calculations was to determine the number of moles of stripping vapor per liter of solvent (V_r/S) required to meet the criterion that P_{NH_3} be equal to or less than $P^*_{NH_3}/1.4$ everywhere in the column. The approach was to determine stripping-vapor requirements at several points subject to the constraint that $P_{NH_3} = P^*_{NH_3}/1.4$. The point requiring the maximum stripping-vapor requirement was the controlling one.

Given the curvature of the $P^*_{NH_3}/[NH_4{}^+A^-]$ relationships in Figures 6.7 and 6.8 it is likely that these solvents will be only partially regenerated. This possibility was considered in the following development. An NH_3 mass balance in the column is:

$$S\left\{[NH_4{}^+\ A^-] - [NH_4{}^+A^-]_{ex}\right\} = y_{NH_3}\ V_t \qquad (7.3)$$

where V_t is the total number of moles in the gas phase, S is the volume of solvent and $[NH_4{}^+A^-]_{ex}$ is the concentration of the ammonium/D2EHPA ion pair in the solvent returned to the extractors.

At a given $[NH_4{}^+A^-]$, the partial pressure of the diluent in the gas phase (P_D) was calculated from the total pressure, P, P_{NH_3} and P_{H_2O}:

$$P_D = P - P_{NH_3} - P_{H_2O} \tag{7.4}$$

where P_{NH_3} was equal to $P^*_{NH_3}/1.4$ and $P^*_{NH_3}$ was evaluated at $[NH_4{}^+A^-]$.

The ratio of the number of moles of stripping vapor to the number of moles of NH_3 is equal to the ratio of their partial pressures. The number of moles of ammonia is given by either side of Equation 7.3. The number of moles of stripping vapor is V_r. Thus,

$$V_r = \frac{P_D}{P_{NH_3}} S \left\{[NH_4{}^+A^-] - [NH_4{}^+A^-]_{ex}\right\} \tag{7.5}$$

The number of moles of stripping vapor per liter of solvent (V_r/S) is:

$$\frac{V_r}{S} = \frac{P_D}{P_{NH_3}} \left\{[NH_4{}^+A^-] - [NH_4{}^+A^-]_{ex}\right\} \tag{7.6}$$

Two sets of calculations were performed, one set ignored the presence of water in the vapor phase ($P_{H_2O} = 0$), and the other considered it. For the latter type of calculation it was assumed that all of the water in the solvent was associated with NH_3 and that as the NH_3 was stripped from the solvent the water associated with the NH_3 was also stripped from the solvent. This assumes that the equilibrium partial pressure of water is equal to the equilibrium partial pressure of NH_3 times the molar ratio of water to NH_3 in the solvent. That is:

$$P_{H_2O} = P_{NH_3} \frac{[H_2O]}{[NH_4^+A^-]} \quad . \tag{7.7}$$

For a given solvent and concentration of ammonium/D2EHPA ion pair the concentration of water in the solvent was estimated from the data given in Chapter 6, section D. These dual calculations were performed because the exact partial pressures of water were not known. Stripping-vapor requirements which ignore water are given as V_{r1}/S, those including water are V_{r2}/S.

As stated earlier, the total pressure in the column was set at that required to condense the aqua ammonia vapor at 100°F. The ratio of ammonia to water in the exit vapor was assumed to be equal to that in the solvent entering the solvent-regeneration column. For the solvents examined the compositions of the exit aqua ammonia are given in Table 7.17. At 0.34 atm the bubble point of a 12 wt% solution of NH_3 in water is 100°F. A 16 wt% solution of NH_3 in water has this bubble point at 0.5 atm (Foust et. al., 1960). The total pressure at each point in the column was therefore taken to be 0.4 atm.

For calculations based on partial regeneration of the solvent it was assumed that the inert-diluent solvents and the alcohol-diluent solvents were regenerated to a stoichiometry of either 0.15 or 0.25. Partial regeneration of the solvent increases the required S/W in the extraction part of the process, at the same NH_3 removal efficiency and the same concentration of solvent exiting the extractors. At a D2EHPA concentration of 0.25 <u>M</u> partial regeneration of the solvent to a stoichiometry of 0.15 increases S/W to 4.1. $[NH_4^+A^-]_{ex}$ in Equation 7.3 is 0.04 <u>M</u>. For regeneration to a stoichiometry of 0.25, these values

TABLE 7.17

COMPOSITION OF EXIT AQUA AMMONIA SOLUTIONS AND ENERGY REQUIREMENTS FOR WATER VAPORIZATION

DILUENT	$[D2EHPA]_o$ (M)	$[NH_4^+A^-]$[(a)] (M)	$[H_2O]$[(b)] (M)	NH_3 in vapor[(c)] (wt %)	V/W[(d)] (lb steam/lb water)
Inert	0.25	0.18	1.1	13.8	0.059
"	0.48	0.34	1.8	15.	0.052
50% (v/v) Decanol/ inert	0.25	0.18	1.3	11.9	0.07
"	0.48	0.34	1.8	15.	0.054
0.26 M A364 in inert	0.48	0.15	1.0	12.4	0.067

(a): concentration of ion pair in solvent feed to regenerator
(b): concentration of water in solvent feed to regenerator, estimated from data in Chapter 6, section D
(c): concentration of ammonia in ammonia/water vapor leaving regenerator
(d): energy required to vaporize water

become 4.9 and 0.063 M, respectively. For a D2EHPA concentration of 0.48 M partial regeneration of the solvent to a stoichiometry of 0.15 increases S/W to 2.1 and $[NH_4^+A^-]_{ex}$ becomes 0.072 M. For regeneration to a stoichiometry of 0.25, these values are 2.6 and 0.12 M, respectively. Partial regeneration of the solvent will also increase the number of extraction stages required.

For the amine-containing diluent (0.48 M D2EHPA/0.26 M A364) the solvent must be regenerated below a stoichiometry of 0.15 if a pinch in the solvent-extraction part of the process is to be avoided. Partial regeneration of this solvent to a stoichiometry of 0.03 was considered. This increases S/W to 4.2 and $[NH_4^+A^-]_{ex}$ is 0.014 M.

The data for $P^*_{NH_3}$ at 0.48 M D2EHPA were taken from Figures 6.7 and 6.8. For the less concentrated D2EHPA solvents $P^*_{NH_3}$ was estimated from the models presented in Chapter 6, section E, using K' and K" values given in Tables 6.39 and 6.41. Table 7.18 presents the results of the calculation of stripping-vapor requirements assuming complete regeneration of the solvent. For each solvent the results of the calculations of V_r/S at different stoichiometries (which would correspond to different points in the column) are given.

Table 7.19 gives the results of the calculations of stripping-vapor requirements assuming partial regeneration of the solvents. In these cases the point in the column which gave the maximum stripping-vapor requirements was determined. This point was established by drawing a line on Figure 6.7 or 6.8 from the point on the x-axis corresponding to $[NH_4^+A^-]_{ex}$. This line was drawn tangent to the equilibrium curve. The values of $P^*_{NH_3}$ and $[NH_4^+A^-]$ at the point of tangency were those used in Equation 7.6.

TABLE 7.18

STRIPPING-VAPOR REQUIREMENTS FOR NEAR COMPLETE REGENERATION OF SOLVENTS

$P = 0.4$ atm T = 127°C

DILUENT	$[\text{D2EHPA}]_o$ (M)	$[NH_4{}^+A^-]^{(a)}$ (M)	$[H_2O]^{(a)}$ (M)	$s^{(a)}$	$P^*_{NH_3}$ (a) (atm)	$V_{r1}/S^{(b)}$ (moles diluent vapor/liter solvent)	$V_{r2}/S^{(b)}$
Inert	0.25	0.125	0.41	0.5	4×10^{-2}	1.6	1.2
"	"	0.063	0.16	0.25	0.8×10^{-2}	4.4	4.2
"	0.48	0.24	0.87	0.5	2×10^{-2}	6.6	5.7
"	"	0.12	0.30	0.25	0.5×10^{-2}	14.8	14.5
50% (v/v) Decanol/ inert	0.25	0.125	0.9	0.5	0.7×10^{-2}	9.9	9.0
"	"	0.063	0.8	0.25	0.2×10^{-2}	17.6	16.8
"	0.48	0.24	1.2	0.5	0.7×10^{-2}	19.0	18.0
"	"	0.12	0.85	0.25	0.2×10^{-2}	33.0	32.0
0.26 M A364 in inert	0.48	0.24	1.8	0.5	4.9×10^{-2}	2.5	0.7
"	"	0.12	0.8	0.25	2.3×10^{-2}	2.8	2.0

(a): conditions at which Equation 7.6 were applied: $[H_2O]$ from Chapter 6, section D; $P^*_{NH_3}$ from Chapter 6, section E; $[NH_4{}^+A^-]_{ex} = 0$; s = stoichiometry

(b): V_{r1}/S calculated neglecting water in vapor phase; V_{r2}/S calculated including water in vapor phase

TABLE 7.19

STRIPPING-VAPOR REQUIREMENTS FOR PARTIAL REGENERATION OF SOLVENTS

$P = 0.4$ atm $T = 127°C$

DILUENT	$[D2EHPA]_o$ ($\underline{M}$)	$[NH_4{}^+A^-]_{ex}^{(a)}$ ($\underline{M}$)	$[NH_4{}^+A^-]^{(b)}$ ($\underline{M}$)	$[H_2O]^{(b)}$ ($\underline{M}$)	$P^*_{NH_3}{}^{(b)}$ (atm)	$V_{r1}/S^{(c)}$ (moles diluent vapor/liter solvent)	$V_{r2}/S^{(c)}$ (moles diluent vapor/liter solvent)
Inert	0.25	0.04	0.06	0.15	0.8×10^{-2}	1.4	1.3
"	"	0.063	0.125	0.45	3.9×10^{-2}	0.8	0.6
"	0.48	0.072	0.15	0.40	0.7×10^{-2}	6.1	5.9
"	"	0.12	0.20	0.65	1.2×10^{-2}	3.7	3.4
50% (v/v) Decanol/ inert	0.25	0.04	0.078	0.90	0.3×10^{-2}	8.1	7.7
"	"	0.063	0.11	0.90	0.5×10^{-2}	4.8	4.4
"	0.48	0.072	0.15	0.95	0.3×10^{-2}	17	16
"	"	0.12	0.20	1.3	0.5×10^{-2}	8.2	7.7
0.26 $\underline{M}$ A364 in inert	0.48	0.014	0.12	0.8	2.3×10^{-2}	2.5	1.8

(a): concentration of the ammonium/D2EHPA ion pair in solvent returned to extractors

(b): conditions at which Equation 7.6 were applied: $[H_2O]$ from Chapter 6, section D; $P^*_{NH_3}$ from Chapter 6, section E

(c): V_{r1}/S calculated neglecting water in vapor phase; V_{r2}/S calculated including water in vapor phase

Table 7.20 converts V_r/S results into the lb steam required to regenerate the solvent per lb of water fed to the process (V_r^s/W). This was done as follows. The V_r/S values for a given solvent were multiplied by S/W for that solvent. A molecular weight of 170 was assumed for the diluent stripping vapor. A water density of 1 kg/l was assumed, so the lb of stripping vapor to be boiled/lb water fed to the process (V_r^w/W) is:

$$\frac{V_r^w}{W} = \frac{V_r}{S} \, \frac{S}{W} \, \frac{170 \text{ g/mol}}{1 \text{ kg/l}} \, \frac{1 \text{ kg}}{1000 \text{ g}} \tag{7.8}$$

To convert (V_r^w/W) into lb steam/lb water it was necessary to multiply by the ratio of the heats of vaporization. As will be seen below, decane (P^v = 0.27 atm at 127°C) is a likely representative diluent choice. For decane at 127°C, ΔH_v is 76 cal/g (Reid et. al., 1977). For water at 155°C (60 psig steam), ΔH_v is 504 cal/g. This ratio gives approximately 0.15 g water/g diluent. Thus:

$$\frac{V_r^s}{W} = \frac{V_r^w}{W} \text{ X } 0.15 = \frac{\text{lb steam}}{\text{lb water}} \tag{7.9}$$

An additional amount of steam was added to this total to account for the energy necessary to boil the water that is stripped from the solvent. These additional requirements are given in Table 7.17. One lb of steam was assumed necessary to boil one lb of water. This amount of steam was added to V_r^s/W to give the total amount of steam required for the solvent regeneration (V_r^t/W). These values are given in Table 7.20. For each solvent, values are given based on the maximum values of V_{r1}/S and V_{r2}/S required for complete solvent regeneration (Table

TABLE 7.20

TOTAL STEAM REQUIREMENTS FOR SOLVENT REGENERATION

DILUENT	$[D2EHPA]_o$ ($\underline{M}$)	$[NH_4^+A^-]_{ex}^{(a)}$ ($\underline{M}$)	S/W (v/v)	$V^t_{r1}/W^{(b)}$ (lb steam/lb water)	$V^t_{r2}/W^{(b)}$ (lb steam/lb water)
Inert	0.25	~0	3.3	0.43	0.41
"	"	0.04	4.1	0.21	0.19
"	"	0.063	4.9	0.16	0.14
"	0.48	~0	1.8	0.71	0.70
"	"	0.072	2.1	0.38	0.37
"	"	0.12	2.6	0.29	0.28
50% (v/v) Decanol/ inert	0.25	~0	3.3	1.6	1.4
"	"	0.04	4.1	0.92	0.88
"	"	0.063	4.9	0.67	0.62
"	0.48	~0	1.8	1.5	1.5
"	"	0.072	2.1	0.96	0.91
"	"	0.12	2.6	0.59	0.56
0.26 $\underline{M}$ A364 in inert	0.48	~0	4.0	0.35	0.27
"	"	0.014	4.2	0.34	0.26

(a): concentration of ammonium/D2EHPA ion pair in solvent returned to extractors

(b): stripping vapor requirements plus that required to vaporize water: V^t_{r1}/W based on V_{r1}/S; V^t_{r2}/W based on V_{r1}/S from Tables 7.18 and 7.19)

7.18). In addition values are given based on V_{r1}/S and V_{r2}/S required for partial regenertion to the stoichiometries considered (Table 7.19). No additional heat effects were included in the calculation of V_r^t/W values.

b. Trends in V_r/S and V_r^t/W

As is seen in Table 7.18 for both the inert and alcohol diluents, V_{r1}/S and V_{r2}/S depend on the point in the column at which they were evaluated. Specifically, for complete regeneration of the solvent V_r/S increases as the concentration of the ammonium/D2EHPA ion pair decreases, that is as stoichiometry decreases. This is due to the relationship between $P^*_{NH_3}$ and $[NH_4{}^+A^-]$, as manifested by the upwards curvature of the plots in Figures 6.7, 6.8, and 6.9. In these cases the slopes of the curves become less at low stoichiometry due to the increase in the concentration of free D2EHPA. The slope of the operating line is therefore less if it is evaluated at low stoichiometry, and this corresponds to higher stripping-vapor requirements. In the regeneration of these solvents at constant temperature the pinch will occur at the bottom, or dilute end, of the column. This type of behavior is observed whenever a chemically complexing solution is being regenerated.

These results in Table 7.18 indicate that, if the solvent is to be regenerated nearly completely, the stripping-vapor requirements must be determined at the lowest stoichiometry to be encountered.

For the amine diluent, $P^*_{NH_3}$ was found to be directly proportional to the concentration of the ammonium/D2EHPA ion pair. Thus, as seen in Table 7.18, V_{r1}/S is relatively independent of stoichiometry. However at lower stoichiometries (below those measured) this may not be true and V_r/S may increase as $[NH_4{}^+A^-]$ decreases.

The results in Table 7.20 indicate that for the inert and alcohol diluents it is advantageous to regenerate the solvent only partially. The savings in stripping-vapor requirements more than compensates for the increased S/W, and V_r^t/W values decrease as the residual concentration of ammonia in the solvent increases. This benefit occurs because of the curvature of the equilibrium relationship between $P^*_{NH_3}$ and $[NH_4{}^+A^-]$. For the amine-containing diluent this relationship is more nearly linear and partial solvent regeneration offers no advantage.

For the alcohol diluent it was found in Chapter 6, section E that $P^*_{NH_3}$ depended only on system stoichiometry. Thus as the concentration of total D2EHPA in the solvent is decreased, the concentration of the ammonium/D2EHPA ion pair which gives a certain $P^*_{NH_3}$ decreases. This produces a higher slope for the equilibrium line and a reduction in V_{r1}/S proportional to the reduction in D2EHPA concentration. Including the presence of water vapor in the calculations gives the same trend in V_{r2}/S, although the relationship between it and D2EHPA concentration is not strictly proportional. However, the use of a lower D2EHPA concentration requires a higher S/W so that the advantage of the lower V_r/S is negated and V_r^t/W values as given in Table 7.20 are relatively independent of D2EHPA concentration.

For the inert diluent the effect of decreasing the concentration of total D2EHPA is different. For the inert diluent it was found in Chapter 6, section E that $P^*_{NH_3}$ depended on both stoichiometry and the concentration of free D2EHPA. Thus, at a constant stoichiometry, decreasing the concentration of D2EHPA results in a decrease in the concentration of free D2EHPA and an increase in $P^*_{NH_3}$. As the concentration of D2EHPA is lowered the equilibrium curve will become steeper and the amount of stripping vapor required less. As seen in Table 7.20 for the inert diluent this reduction in V_r/S is greater than the increase in S/W and the lower concentration of D2EHPA results in lower overall energy requirements for solvent regeneration (V_r^t/W).

Note also that the stripping-vapor requirements are more sensitive to stoichiometry for the inert diluent than for the alcohol diluent (V_{r1}/S values in Table 7.18).

In comparing the three types of diluents it is apparent that at a given concentration of D2EHPA less energy per liter of solvent is required for complete regeneration of the solvent containing the amine modifier than is required for the inert-diluent solvent. The most energy is required for the alcohol-diluent solvent. At 0.48 M D2EHPA the V_{r1}/S values evaluated at a stoichiometry of 0.5 are 2.5, 6.6, and 19 respectively (Table 7.18). When the S/W required to use these solvents is taken into account the total energy requirements for the amine diluent are still less than those for the inert diluent, although the factor is not as large since the amine diluent requires a higher S/W. The difference between the inert and amine diluents is even larger at low stoichiometry. On the other hand it should be remembered that the inert diluent has the advantage of requiring fewer extraction stages. The S/W required for the inert and alcohol diluents is the same, and hence the relative energy requirements will not be affected by including this factor.

The data in Table 7.18 also suggest two ways to increase $P^*_{NH_3}$ and thus decrease V_r/S. Consider a solvent containing 0.48 M D2EHPA in an inert diluent and with an ammonium/D2EHPA ion-pair concentration of 0.12 M. This corresponds to a stoichiometry of 0.25. For this condition V_{rl}/S is 14.8. If the concentration of D2EHPA is decreased at the same ammonium/D2EHPA ion-pair concentration, then, as pointed out above, V_{rl}/S also decreases. For 0.12 M ammonium/D2EHPA ion pair in 0.25 M D2EHPA in an inert diluent, the stoichiometry is 0.5 and V_{rl}/S is 1.6. In other words an effective way to increase $P^*_{NH_3}$ is to decrease the concentration of free D2EHPA. Another way to increase $P^*_{NH_3}$ is to add an amine to the system. In this case 0.48 M D2EHPA in 0.26 M A364 in an inert diluent with 0.12 M ammonia/D2EHPA ion pair gives a stoichiometry of 0.25 and V_{rl}/S of 2.8. The addition of the amine decreases the activity of free D2EHPA.

c. Conclusions for Solvent Regeneration

The energy requirements for solvent regeneration must be calculated to avoid a pinch anywhere in the column. For the isothermal calculations performed here it is apparent that this pinch will occur at the low-concentration or low-stoichiometry end of the column, if the solvent is nearly completely regenerated.

The conclusion of Table 7.20 is that it is best to regenerate the solvent only partially. While this does result in a decrease in energy requirements for solvent regeneration it will tend to increase the number of extraction stages required. In addition, the possibility of phase-separation problems at the solvent entrance to the extraction process exists, since a relatively concentrated solvent would be contacted with a relatively dilute aqueous phase.

Another possibility which was not considered here is to use a split-flow design. In this configuration only a portion of the solvent is regenerated fully. The smaller flow of solvent in the pinch end of the column results in lower stripping-vapor requirements. The application of this design to processes involving equilibria analogous to thus encountered here is an area of current research interest (Thompson, 1985).

Based on Table 7.20 the two most likely solvent candidates, among those considered, in terms of solvent-regeneration requirements are 0.48 M D2EHPA in 0.26 M A364 in an inert diluent, nearly completely regenerated, and 0.25 M D2EHPA in an inert diluent, regenerated to a stoichiometry of 0.25. The other solvents can all be eliminated from consideration because of their high energy requirements for solvent regeneration. In Table 7.21 the compositions of all of the solvents are given. As a basis of calculation the inert diluent is assumed to be a C_{10} alkane. If this Table is compared to Tables 7.18 and 7.19 it can be seen that all of the solvents except for the two listed above require the boil-up of more moles of diluent to provide the stripping medium than are available in the incoming solvent, a situation which has obvious problems. It may be desirable to operate the column at still a lower pressure to reduce stripping-vapor requirements, but this would require refrigeration of the overhead aqua ammonia vapor, which would add to the costs of the process.

If the D2EHPA concentration in the inert diluent were lowered below 0.25 M, the trends discussed above indicate that still lower energy requirements for solvent regeneration would result. This is at the expense of a higher S/W, which would increase other costs in the process. Also the trend of decreasing energy requirements for

TABLE 7.21

SOLVENT COMPOSITIONS

BASIS: 1 LITER OF SOLVENT

DILUENT	$[D2EHPA]_o$ (M)	INERT[(a)] (moles)	ALCOHOL (moles)	AMINE (moles)	D2EHPA (moles)
Inert	0.25	4.8	0	0	0.25
"	0.48	4.4	0	0	0.48
50% (v/v) Decanol/ inert	0.25	2.4	2.4	0	0.25
"	0.48	2.2	2.2	0	0.48
0.26 M A364 in inert	0.48	3.7	0	0.26	0.48

(a): taken to be decane

decreasing D2EHPA concentration in the inert diluent is somewhat tenuous. This trend is based on comparison of measurements of $P^*_{NH_3}$ from 0.48 M D2EHPA and from 0.82 M D2EHPA. Only a small amount of data were gathered at the higher solvent concentration. Thus this result may not be strictly valid. If the inert diluent behaved as the alcohol diluent does, i.e., total energy requirements for solvent regeneration relatively independent of D2EHPA concentration, then the amine diluent solvent might be a better choice. This can be seen by comparing the data for the amine and inert diluents at 0.48 M D2EHPA in Table 7.20.

For the two solvents considered, the vapor pressure of the diluent required to meet the independent specifications of temperature (127°C) and total pressure (0.4 atm) is calculated in Tables 7.22 and 7.23. For the conditions at the solvent entrance to the column (top), the liquid-phase mole fraction of the diluent is given in Table 7.22, assuming a C_{10} alkane diluent. In addition, the mole fraction of diluent in the vapor phase is given, assuming a boil-up of 2 moles diluent/liter solvent and including the presence of water in the exit vapor. With these values and using a total pressure of 0.4 atm the vapor pressure of the diluent (P^v) can be calculated as:

$$P^v = \frac{y\ P}{x} \tag{7.10}$$

The vapor pressure of the diluent based on reboiler conditions is calculated in Table 7.23. For these calculations the solvent at this point is assumed to contain a negligible amount of ammonium/D2EHPA ion pair and water. The mole fraction of diluent in the liquid leaving the reboiler was calculated assuming 2 moles of diluent boiled/liter

TABLE 7.22

REQUIRED VAPOR PRESSURE OF DILUENT

BASED ON SOLVENT ENTRANCE CONDITIONS

V_r/S = 2 moles diluent vapor/liter solvent

DILUENT	$[D2EHPA]_o$ (M)	$[NH_4^+A^-]^{(a)}$ (M)	$[H_2O]^{(a)}$ (M)	$x_D^{(b)}$	$y_D^{(c)}$	P^v (atm)
Inert	0.25	0.18	1.1	0.76	0.63	0.33
0.26 M A364 in inert	0.48	0.15	1.0	0.66	0.63	0.38

(a): concentrations of ammonia and water in solvent entering solvent regenerator
(b): mole fraction of diluent in solvent entering solvent regenerator; D = decane
(c): mole fraction of diluent in vapor exiting solvent regenerator; D = decane

TABLE 7.23

REQUIRED VAPOR PRESSURE OF DILUENT BASED ON REBOILER CONDITIONS

V_r/S = 2 moles diluent vapor/liter solvent

DILUENT	$[D2EHPA]_o$ (M)	$[Diluent]_{in}^{(a)}$ (M)	$x_{D,out}^{(b)}$	P^v (atm)
Inert	0.25	4.8	0.92	0.44
0.26 M A364 in inert	0.48	3.7	0.70	0.57

(a): concentration of diluent in solvent entering reboiler; diluent = decane
(b): mole fraction of diluent in solvent exiting reboiler

solvent. The mole fraction of diluent in the vapor phase was assumed to be essentially one. Equation 7.10 was used to calculate P^v.

The diluent vapor pressure at 127°C corresponds approximately to a C_9-C_{10} alkane, (@127°C, $P^v_{C_9} = 0.53$ atm, $P^v_{C_{10}} = 0.27$ atm). In an actual operation the column would probably not be isothermal. At the top of the column the temperature would be less due to the vaporization of diluent within the column. Thus the amount of stripping vapor present at the top of the column would be greater than that at the bottom of the column. These non-isothermal effects were not considered here.

6. OTHER FACTORS AFFECTING PROCESS DESIGN

Several additional factors need to be considered in estimating the economic viability of this process.

The phase-separation properties of this system are important, as poor phase disengagement would lead to higher solvent loss costs or to extra costs for coalescers or other phase separators. In general the alcohol-diluent solvent gave the best phase-separation properties. It may be possible to minimize the phase-separation difficulties for all of the solvents by using relatively non-intense phase-mixing techniques. The kinetics of the ion-exchange process are generally very fast (Ashbrook, 1973) and so the phases may not need to be mixed as intensely as usually done in solvent-extraction processes. Thus use of contactors such as a centrifugal contactor or a Graesser contactor (Hanson, 1968) should be considered as these provide gentle dispersion of the phases and so reduce the emulsification tendencies of the system. These are more expensive then conventional mixer-settlers and will add to overall capital costs.

Additional D2EHPA losses due to thermal decomposition at the solvent-regeneration temperatures were not considered. These will add to the operating costs for solvent replenishment. The data for D2EHPA thermal decomposition taken in this work were qualitative and do not allow quantification of this additional cost.

Energy requirements for sensible heat effects were not considered. Based on the evidence that K_c decreases with increasing temperature it is envisioned that the solvent-extraction part of the process may operate at a temperature less than the acid-gas stripper, which will be at about 100°C. This will require heating and cooling of the aqueous stream as it passes from the extractors to the stripper and back again. Heat exchange between passing streams will reduce this cost some, but additional operating costs will be incurred for some heating steam and cooling water. Additional capital costs will be associated with the heat exchangers. This need for heating and cooling of the aqueous streams indicates that it is most desirable to use a small number of extraction stages (see Figure 1.9). Alternatively, the acid-gas stripper could be operated at lower pressure and temperature, but this is less efficient.

An additional amount of steam in the diluent reboiler will be required to heat the loaded solvent to the temperature of the solvent-regeneration column. Again heat exchange between the hot lean solvent exiting the regeneration column and the cold loaded solvent entering the column will reduce the steam costs some. This cost will increase as the amount of solvent or S/W increases. These sensible heat effects could be significant.

The cost of operating the solvent-regeneration column at less than atmospheric pressure also has not been calculated, nor has the cost of cooling water to condense the overhead aqua NH_3 and diluent vapors. As mentioned earlier, it may be desirable to operate the column at still a lower pressure, but this would result in additional costs for either compression of the aqua NH_3 vapor in order to condense it with cooling water or the use of refrigeration to condense it at column pressure.

Also no mention has been made of the coextracted organics. It was shown in section A above that the extraction of phenol is not substantially hindered by the presence of D2EHPA or the ammonium/D2EHPA ion pair in the organic phase. Indeed the ammonium/D2EHPA ion pair may enhance phenol extraction since phenol can solvate the ammonium/D2EHPA ion pair. The nature of the organic diluent will also affect phenol coextraction. Phenol has a higher K_c into aromatics (toluene, K_c = 1.97) than aliphatics (n-hexane, K_c = 0.132) (Kiezyk and Mackay, 1971). Liquid-liquid equilibria for extraction of phenol and other organics need to be examined further, but it seems likely that the use of an appropriate diluent for a D2EHPA-based solvent may yield some fractionation of the organics. The organics that are coextracted into the solvent and taken overhead in the solvent regenerator will, when condensed, distribute between the condensed diluent phase and the condensed aqua NH_3. Additional treatment of this aqueous phase will probably be necessary to remove the organics.

One final cost to be considered is that for fractionation of the aqua NH_3 into pure NH_3 and water. This requires about 0.3 lb steam/lb aqua NH_3 (Seufert et. al., 1979). In terms of the amount of water fed to the entire process this becomes about 0.025 lb steam/lb water for the aqua NH_3 solutions generated here. This cost is included in the final cost estimates.

7. CONCLUSIONS AND RECOMMENDATIONS FOR PROCESS DESIGN

In Table 7.24 the costs for various aspects of the process are summarized for the two most likely solvent choices: 0.25 M D2EHPA in an inert diluent, regenerated to a stoichiometry of 0.25, and 0.48 M D2EHPA in 0.26 M A364 in an inert diluent. Information for 0.48 M D2EHPA in a 50% alcohol diluent regenerated to a stoichiometry of 0.25 are also included. The steam requirements for the acid-gas stripper and the solvent-regeneration column are shown as well as the associated energy costs. Steam costs were assumed to be $2/1000 lb. D2EHPA solubility losses are also given, as well as the associated operating costs for solvent replenishment. The February 1984 price of D2EHPA is $2.60/lb (Mobil Chemical Company, Phosphorus Division). A total operating cost for the process is given. This total includes the three costs listed in Table 7.24 plus the cost of steam for the aqua NH_3 fractionation column (0.025 lb steam/lb water or $0.42/1000 gal water). It does not include capital-related expenses, insurances, labor, maintenance, or other costs.

By comparison the Phosam-W process discussed in Chapter 1, section F, requires about 0.29 lb steam/lb water at a cost of $4.80/1000 gal water. The total cost for the Phosam-W process including capital costs amorization is about $8/1000 gal (Seufert et. al., 1979).

It is apparent that the cost of the extraction/stripping process proposed here exceeds that of the Phosam-W process. A savings in steam requirements versus the Phosam-W process is made in the acid-gas stripper. However in both processes it is the cost of the regeneration

TABLE 7.24

COST ESTIMATES

FEED = 0.6 $\underline{M}$ NH_3

	COST ($/1000 gal water)
SOLVENT = 0.25 $\underline{M}$ D2EHPA in inert diluent S/W = 4.9	
V_s/W in acid-gas stripper: 0.04 lb steam/lb water @ $2/1000 lb	0.67
D2EHPA solubility losses: 550 ppm @ $2.60/lb	12.00
V_r^t/W in solvent regenerator: 0.14 lb steam/lb water @ $2/1000 lb	2.30
TOTAL(a)	15.40
SOLVENT = 0.48 $\underline{M}$ D2EHPA plus 0.26 $\underline{M}$ A364 in inert S/W = 4	
V_s/W in acid-gas stripper: 0.07 lb steam/lb water @ $2/1000 lb	1.17
D2EHPA solubility losses: 870 ppm @ $2.60/lb	19.00
V_r^t/W in solvent regenerator: 0.27 lb steam/lb water @ $2/1000 lb	4.50
TOTAL(a)	25.10
SOLVENT = 0.48 $\underline{M}$ D2EHPA in 50%(v/v) Decanol in inert S/W = 2.6	
V_s/W in acid-gas stripper: 0.04 lb steam/lb water @ $2/1000 lb	0.67
D2EHPA solubility losses: 180 ppm @ $2.60/lb	4.00
V_r^t/W in solvent regenerator: 0.56 lb steam/lb water @ $2/1000 lb	9.40
TOTAL(a)	14.50

(a): includes cost of $0.42/1000 gal for 0.025 lb steam/lb water for NH_3 fractionation column part of the process that is the dominant energy cost. For the Phosam-W process steam requirements for the regeneration of the phosam solution make up about 60% of the energy requirements for the process.

In the extraction/stripping process the cost for solvent regeneration would be reduced by operating the regeneration column at a higher temperature. However when D2EHPA is used as the extractant this would lead to significant thermal decomposition of D2EHPA. Thus either an additive must be found that hinders the thermal decomposition reaction for D2EHPA, or a more thermally stable extractant must be used. It was suggested in Chapter 4, section E that the addition of a neutralizing agent to the solvent may hinder the acid-catalyzed decomposition reaction of D2EHPA (Gamrath et. al., 1954). It is possible that an amine may serve this purpose. The addition of an alkyl group to the number-two carbon of the alkyl part of D2EHPA would also enhance its thermal stability (Gamrath et. al., 1954). The weak part of the D2EHPA molecule is the C-O-P linkage and so the use of a phosphinic acid which contains no such linkage may be useful. However such a compound would be less acidic than D2EHPA and a weaker extractant. The commercial availability of these compounds must also be considered. Also, operating the solvent-regeneration column at higher temperature will increase the energy requirements in the diluent reboiler for heating the solvent up to the column temperature.

If the extractant were stronger and more thermally stable than D2EHPA both the extraction and solvent regeneration could be carried out at higher temperatures. This would reduce the sensible heat costs for heating and cooling the aqueous stream passing between the extractors and acid-gas stripper and potentially reduce solvent-regeneration energy requirements, since the regeneration could be carried out at a much higher temperature.

Alternatively a weaker extractant could be considered. This would have the advantage of the complexation being more readily reversible and thus require less energy and/or a lower temperature for solvent regeneration. However the use of a weaker extractant will either increase the required S/W or result in less effective ammonia extraction. Most likely a design based on a weaker extractant would result in some combination of these two effects. Less effective ammonia removal will increase the pH in the acid-gas stripper and increase energy requirements for that stripper. This trade-off between lower energy requirements for the solvent regenerator and higher energy costs for the acid-gas stripper and sensible heat effects (higher S/W and more extraction stages) is probably acceptable however since, for the solvents considered here, the former requirements are the dominant ones.

In the extraction/stripping process the cost for solvent replenishment is also a dominant cost. An important step toward making the process more economical would be either to lower the solubility losses or to recover the lost solvent. For the first two solvents listed in Table 7.24 some treatment of the aqueous phase will be necessary to remove the D2EHPA, based solely on environmental considerations. Such treatment may involve carbon or bubble adsorption or adsorption onto a polymer (Rice, 1978). Solvent-replenishment costs would be reduced if the D2EHPA could be recovered by these processes. A possible way to reduce D2EHPA solubility losses would be to lower the pH of the aqueous phase. But the cost of the acidifying reagent must be considered, as well as the effect this reagent and the lower pH would have on downstream processing of the aqueous phase. Note however that the stream to be acidified would contain very little CO_2 and NH_3 and hence would not be highly buffered -- a situation which prohibits pH adjustment of the aqueous feed to the process.

Of the three solvents listed in Table 7.24, the one with the alcohol diluent offers the advantages of lower S/W and fewer extraction stages (lower sensible heat costs), lower energy costs for the acid-gas stripper, lower D2EHPA solubility-loss costs, and better phase-separation properties. However the energy requirements for solvent regeneration are unacceptably high. An alternate regeneration method is to contact the NH_3-laden solvent with sulfuric acid. The final product of this process would be ammonium sulfate crystals. For proper operation of the ammonium sulfate crystallizer the pH should be about 3.5 (Fluor Corporation, 1959). At a pH of 3.5, 0.48 M D2EHPA in a 50% alcohol diluent gives a maximum K_c (low stoichiometry) of 0.18. This low K_c will result in efficient back extraction of the NH_3 out of the solvent into the sulfuric acid.

Analysis of the analog of the Phosam-W process which would produce ammonium sulfate indicated that the major operating cost for that process was the cost of providing fresh sulfuric acid. This process was less economical than the Phosam-W process (Seufert et. al., 1979).

If the extraction/stripping process proposed here is used to produce ammonium sulfate, some steam savings in the original stripper will be realized. So, it is likely that the cost of sulfuric acid will still dominate the process economics and probably render this implementation of the process uneconomical also.

The first two solvents listed in Table 7.24 do not offer all of the advantages of the alcohol-diluent solvent but they do require lower costs for solvent regeneration.

The additional costs for using these solvents (such as those due to sensible-heat effects and capital costs) will probably be higher for the amine diluent than for the inert diluent, since the amine diluent requires more extraction stages.

Overall, with the solvents considered here, the proposed extraction/stripping process does not appear to offer any advantages over the Phosam-W process. If a more thermally stable, less soluble extractant can be found, then the economics of the process will improve. If the diluent effects on D2EHPA solvent properties delineated in this work apply to other liquid cation exchangers, as is likely, then a potential solvent choice might be an extractant which is a stronger acid than D2EHPA in an alcohol-containing diluent. As pointed out above this would affect sensible heat costs but could reduce overall energy requirements. Alternatively an extractant which is a weaker acid than D2EHPA could also be considered, as discussed above. Either of these alternatives would potentially retain some of the advantages of the alcohol diluent such as lower D2EHPA solubility losses and better phase-separation properties yet also lower solvent-regeneration energy requirements.

It would be interesting to study the properties of a solvent containing D2EHPA in an amine/alcohol diluent. The presence of the alcohol would improve the phase-separation properties and the presence of the amine would improve solvent-regeneration properties. The molar ratio of amine to D2EHPA could be adjusted in an attempt to obtain the desired solvent properties. However, if the amine and alcohol associate preferentially the desired effects might not be produced.

The addition to the solvent of a basic modifier compound that would interact more strongly with D2EHPA at higher temperatures than at lower temperatures would be desirable. However, what such a modifier would be is not obvious.

An alternative approach to improving phase-separation properties would be to use D2EHPA bound to a solid support. Levextrel resins containing D2EHPA on a styrene/divinylbenzene support are available (Kauczor and Meyer, 1978). However the D2EHPA in this form is still susceptible to solubility losses and the capital costs for a process using a solid adsorbent rather than a liquid solvent may be higher.

Finally, one of the most important operating costs for this process is the steam requirements for solvent regeneration. In light of this it is suggested that the equilibrium data for the regeneration of any solvents of interest be quantified more accurately, perhaps through the use of an equilibrium cell.

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CHAPTER 8

SUMMARY OF CONCLUSIONS

1. No suitable non-ionic solvents were found to extract either CO_2 or H_2S out of aqueous solutions containing these gases and NH_3.

2. Liquid cation exchangers were found to be effective solvents for the extraction of NH_3 from aqueous solutions containing NH_3 and acid gases.

3. Di-2-ethylhexyl phosphoric acid (D2EHPA) was chosen as the most desirable liquid cation exchanger, based on its ability to extract NH_3 and its regenerability.

4. D2EHPA extracts NH_3 by an ion-exchange mechanism. K_c depends on the concentration of free D2EHPA and, for a given solvent composition, decreases as the concentration of the ammonium/D2EHPA ion pair in the organic phase increases, at a constant pH. K_c for ammonium increases as pH increases.

5. The diluent used for the D2EHPA-based solvent affects many of the solvent properties, including distribution coefficient, phase-separation properties, aqueous D2EHPA solubility losses and solvent regenerability.

6. When alcohols, phenols and carboxylic acids that are sterically

unhindered around the -OH group are added as modifiers to D2EHPA-based solvents, K_c is increased, phase-separation properties are improved, D2EHPA solubility losses to the aqueous phase are reduced (relative to a situation that produces the same K_c using an inert diluent), but solvent regenerability is less. These factors taken together suggest that these modifiers in a D2EHPA-based solvent solvate the ammonium/D2EHPA ion pair.

7. When Lewis base compounds such as amines and phosphine oxides are added as modifiers to a D2EHPA-based solvent, K_c is decreased, D2EHPA aqueous solubility losses are reduced at a given pH, and solvent regenerability is improved. These factors taken together suggest that Lewis base modifiers interact with D2EHPA, lowering its activity.

8. The combination of solvent extraction of NH_3 and stripping of CO_2 serves to increase the volatility of CO_2 and to isolate NH_3 from the CO_2.

9. The overall economics of the process suggest that the cost for replenishment of D2EHPA due to aqueous solubility losses and the cost for energy to regenerate the solvent dominate. The solvents would most likely be regenerated only partially.

10. The economics of the process could be improved by regeneration of the solvent at higher temperature. To do this a modifier to inhibit D2EHPA thermal decomposition must be found, or another, more thermally stable extractant must be used. Alternatively, a weaker extractant

which would be more readily regenerable could be considered. A likely diluent for this extractant would be an alcohol-containing one. This would include some of the benefits of the alcohol diluent in a more regenerable solvent.

NOMENCLATURE

A^-	Dissociated acid in aqueous phase
B	Free amine
B:HA	Amine/D2EHPA complex
C	Total concentration of carbon dioxide, in all forms ($\underline{M}$)
H	Henry's law constant (atm/$\underline{M}$)
HA	Acidic extractant
K_b	Dissociation constant for ammonia (Equation 1.1)
K_c	Concentration-based distribution coefficient ($\underline{M}/\underline{M}$)
K_{c,H^+}	K_c for hydrogen ion, organic-phase concentration of D2EHPA not associated with ammonia/ aqueous-phase concentration of H^+ ($\underline{M}/\underline{M}$)
K_{c,NH_3}	K_c for ammonia, organic-phase concentration of ammonia/ aqueous-phase concentration of NH_3 ($\underline{M}/\underline{M}$)
K_{c,NH_4}	K_c for ammonium ion, organic-phase concentration of D2EHPA/ aqueous-phase concentration of NH_4^+ ($\underline{M}/\underline{M}$)
$K_{c,un}$	K_c for undissociated species
K_r	Ion-exchange reaction constant, as given in Equation 4.4 (solvent dependent) or Equation 5.1 (solvent independent)
$\underline{M}$	Moles/liter
m	Total number of acid molecules associated with ion pair, undissociated and dissociated (Equations 6.1 and 6.3)
N	Total concentration of ammonia, in all forms ($\underline{M}$)
$NH_4^+A^-$	Ammonium/D2EHPA ion pair
P	Measured concentration of phosphorus in aqueous phase, taken to be D2EHPA ($\underline{M}$)

P_i	Partial pressure of species i (atm)
SC	Synergistic coefficient (Equation 5.2)
S/W	Volumetric solvent-to-water ratio
s	Stoichiometry, concentration of ammonia in organic phase divided by total, or initial, concentration of extractant
V_r/S	Moles stripping vapor in solvent-regeneration column/ liter solvent (Equation 7.6) (1 = ignore water vapor, 2 = include water vapor)
V_r^t/W	Lb steam/lb water required for solvent regeneration, including that for water vaporization (1 = based on V_{r1}/S, 2 = based on V_{r2}/S)
V_s/W	Lb steam/lb water in acid-gas stripper
y	Aggregation of extractant (Equations 6.1 and 6.3)

Subscripts:

ex	To extractors
f	Final
meas	Measured property
o	Initial or total
pred	Predicted property
raf	Raffinate

Superscripts

a	Aqueous-phase property
e,*	Equilibrium
o	Organic-phase property

Other:

γ	Activity coefficient
( )	Aqueous-phase concentration
[ ]	Organic-phase concentration

APPENDIX I

COMPARISON OF AS-RECEIVED AND PURIFIED D2EHPA

A series of extractions were performed using as-received and purified D2EHPA in the solvents. Attention was focused on the measured concentration of phosphorus in the raffinate after these extractions. The solvents contained either 0.2 $\underline{M}$ D2EHPA or 0.5 $\underline{M}$ D2EHPA. The diluents were Norpar 12 or toluene. The aqueous feed contained 0.57 $\underline{M}$ NH_4HCO_3. The S/W (v/v) was 5.

Table I.1 presents the measured concentrations of phosphorus in the raffinates after the extractions. Results are given for solvents containing as-received D2EHPA, which was found by titration to contain 1.9 wt % mono-2-ethylhexyl phosphoric acid. Results are also presented for solvents containing D2EHPA purified by the copper-salt-precipitation method (Chapter 3, section B), in which no measurable amount of mono-2-ethylhexyl phosphoric acid was detected by titration. Finally results are presented for solvents containing D2EHPA which had been purified a second time by this method. This D2EHPA also contained no measurable amount of mono-2-ethylhexyl phosphoric acid.

It is apparent that when mono-2-ethylhexyl phosphoric acid is present in the D2EHPA used in the solvent that the aqueous-phase concentration of phosphorus is higher than when it is absent. This apparently is due to the high water solubility of mono-2-ethylhexyl phosphoric acid and indicates the necessity of removing this impurity from D2EHPA before attempting to base D2EHPA solubility measurements on measured concentrations of phosphorus in raffinates. The agreement of

TABLE I.1

AQUEOUS-PHASE PHOSPHORUS CONCENTRATIONS FROM AS-RECEIVED AND PURIFIED D2EHPA

DILUENT	$[D2EHPA]_o$ (M)	QUALITY	$(P)^{(a)}$ (M)
Norpar 12	0.2	as-received	0.032
"	"	purified once	0.013
"	"	purified twice	0.014
"	0.5	as-received	0.048
Toluene	0.2	as-received	0.029
"	"	purified once	0.0067
"	"	purified twice	0.0069
"	0.5	as-received	0.073
"	"	purified once	0.0043
"	"	purified twice	0.0061

(a): measured concentration of phosphorus in aqueous phase measured phosphorus concentrations between the solvents using D2EHPA purified one time and D2EHPA purified a second time suggests that all of the mono-2-ethylhexyl phosphoric acid is removed by the purification procedure.

If all of the phosphorus in the raffinates from the as-received D2EHPA-based solvents is assumed to be mono-2-ethylhexyl phosphoric acid then the weight fraction of mono-2-ethylhexyl phosphoric acid in D2EHPA can be calculated. The measured concentration of phosphorus in the aqueous phase is divided by S/W and multiplied by the molecular weight of mono-2-ethylhexyl phosphoric acid (210), yielding grams of mono-2-ethylhexyl phosphoric acid/liter solvent. This is divided by the concentration of D2EHPA in the solvent. A 0.2 M D2EHPA solvent contains 72 g D2EHPA/liter and a 0.5 M D2EHPA solvent contains 188 g D2EHPA/liter. From these calculations the weight percent mono-2-ethylhexyl phosphoric acid in D2EHPA was found to be between 1.3 and 1.8, which is close to that measured by titration.

The higher concentration of phosphorus in the raffinates from the as-received D2EHPA-based solvents results in lower aqueous-phase pH values. Consequently, ammonia extraction is hindered. For 0.5 M D2EHPA in toluene the as-received D2EHPA solvent gave an ammonia raffinate concentration of 0.065 M, while the purified D2EHPA solvent gave an ammonia raffinate concentration of 0.01 M. The former concentration is slightly lower than expected based on the requirement of electroneutrality and reflects uncertainties in the measurements of aqueous-phase phosphorus concentrations.

In a related set of experiments the concentrations of NH_3 and CO_2 and the pH of raffinates were measured. The solvents contained either as-received or purified D2EHPA at a concentration of 0.2 M D2EHPA in Norpar 12. The feed contained a total concentration of NH_3 of 0.56 M and a total concentration of CO_2 of 0.57 M at a pH of 7.9. The solvent-to-water ratio (v/v) was 5.

After the extractions the aqueous phases were centrifuged and pH measured. Then CO_2 and NH_3 concentrations were measured. About two hours after these measurements, the pH was measured again. After about one-half hour the CO_2 concentration was remeasured.

The total concentration of NH_3 in the raffinate from the solvent containing as-received D2EHPA was 0.034 M. From the solvent containing purified D2EHPA it was 0.021 M.

The measured values of total CO_2 concentration and pH are presented in Table I.2. For a given concentration of CO_2 the pH value predicted from the vapor-liquid equilibrium model TIDES is given, based on the concentration of NH_3 in the solution. In addition, the expected pH value taking into account the presence of excess anions is given. The values of the concentration of excess anions were taken as the concentration of phosphorus in raffinates from similar extractions reported in Table I.1. All of the mono-2-ethylhexyl phosphoric acid and D2EHPA present in the aqueous phase would be ionized at the pH values encountered here.

Several conclusions can be drawn from Table I.2. First, it is apparent that the concentration of phosphorus (as excess anions) must be taken into account to accurately predict pH values. Second, the concentration of CO_2 decreased when the raffinate was stored. This resulted in a rise in pH for the raffinate from the purified D2EHPA-based solvent, in which the concentration of excess anions was low. In

TABLE I.2

PREDICTED pH VALUES FOR RAFFINATES FROM EXTRACTIONS USING AS-RECEIVED AND PURIFIED D2EHPA[(a)]

SOLVENT = 0.2 $\underline{M}$ D2EHPA IN NORPAR 12

FEED = NH_4HCO_3 solution $(N)_o$ = 0.56 $\underline{M}$ S/W (v/v) = 5

	As-received D2EHPA (N) = 0.034 $\underline{M}$				Purified D2EHPA (N) = 0.02 $\underline{M}$			
			(A^-) = 0	(A^-) = 0.03 $\underline{M}$			(A^-) = 0	(A^-) = 0.01 $\underline{M}$
TIME (hrs)	(C) ($\underline{M}$)	pH	pH_{pred}	pH_{pred}	(C) ($\underline{M}$)	pH	pH_{pred}	pH_{pred}
-	0.02	-	9.0	5.8	0.02	-	8.1	6.4
-	-	6.3	-	-	-	6.5	-	-
+ 2	-	6.6	-	-	-	7.9	-	-
+ $^1/_2$	0.006	-	9.9	7.3	0.013	-	9.2	7.5

(a): (N) and (C) refer to total measured concentrations of ammonia and carbon dioxide, resepctively; (A^-) refers to assumed concentration of excess anions in solution; pH_{pred} refers to pH predicted from TIDES.

this case the pH was greatly affected by the CO_2 concentration. When the concentration of excess anions approached that of NH_3, the pH was relatively independent of CO_2 concentration. In fact more CO_2 was lost from this solution because the pH was maintained at a low value by the presence of the excess anions. In the former case, as CO_2 was lost from solution and the pH rose, the volatility of CO_2 was suppressed. These trends indicate the importance of rapidly measuring CO_2 concentration and pH after an extraction if equilibrium values are to be determined. This motivated the precautions in pH determination discussed in Chapter 2, section A.

APPENDIX II

SOLVENT-REGENERATION DATA

In this appendix the data from the solvent-regeneration experiments are presented. The symbols in the tables are defined below:

total N_2: total cubic feet of nitrogen passed through 100 ml of solvent.

ΔN_2: moles of nitrogen passed through solution in a given interval.

NH_3 absorbed: total number of mmoles of NH_3 collected in absorber during stripping interval.

$[NH_4^+A^-]$: total concentration of ammonium/D2EHPA ion pair in solvent; calculated from initial concentration and measured number of mmoles of NH_3 absorbed in absorbers.

$[NH_4^+A^-]_{avg}$: average concentration of ammonium/D2EHPA ion pair in solvent during interval.

P_{NH_3}: calculated partial pressure of NH_3, using Equation 3.2.

For all of the results the volume of the solvent was assumed to be constant throughout the experiments. The exception to this is for the data taken at 105°C. For that experiment the final volume of the solvent was 79 ml. The volume of the solvent at intermediate values was determined by linear interpolation. The measured final concentration of the ammonium/D2EHPA ion pair ($[NH_4^+A^-]_f$) is also given.

TABLE II.1(a)

SOLVENT-REGENERATION DATA

SOLVENT = 0.48 M D2EHPA in 50% (v/v) Isodecyl alcohol/Norpar 12

T = 105°C P = 1.05 atm

total N_2 (ft^3)	Δ N_2 (moles)	NH_3 absorbed (mmoles)	$[NH_4^+A^-]$ (M)	$[NH_4^+A^-]_{avg}$ (M)	$P_{NH_3} \times 10^2$ (atm)
0	-	-	0.47	-	-
0.13	0.151	2.45	0.45	0.46	1.7
0.27	0.162	3.00	0.42	0.43	1.95
0.46	0.220	3.00	0.39	0.40	1.44
0.70	0.278	2.85	0.36	0.38	1.09
1.00	0.348	3.00	0.33	0.35	0.91
1.68	0.790	4.40	0.29	0.31	0.59
2.85	1.36	4.40	0.25	0.29	0.35
5.36	2.91	4.10	0.21	0.23	0.15
7.88	2.91	2.40	0.19	0.20	0.087
12.22	5.03	2.58	0.17	0.18	0.055
19.28	8.19	2.58	0.14	0.16	0.034
28.65	10.87	1.96	0.12	0.13	0.020
34.34	6.60	0.91	0.11	0.12	0.015
44.86	12.20	1.29	0.10	0.11	0.011
49.13	4.95	0.45	0.097	0.098	0.0097

(a): see text for explanation of symbols; $[NH_4^+A^-]_{f,meas} = 0.065$ M

TABLE II.2(a)

SOLVENT-REGENERATION DATA

SOLVENT = 0.48 M D2EHPA in 50% (v/v) Isodecyl alcohol/Norpar 12

T = 127°C P = 1.05 atm

total N_2 (ft^3)	Δ N_2 (moles)	NH_3 absorbed (mmoles)	$[NH_4^+A^-]$ (M)	$[NH_4^+A^-]_{avg}$ (M)	$P_{NH_3} \times 10^2$ (atm)
0	-	-	0.47	-	-
0.07	0.081	2.88	0.44	0.46	3.6
0.145	0.087	2.70	0.41	0.43	3.16
0.225	0.093	2.70	0.39	0.40	2.97
0.305	0.093	2.58	0.36	0.37	2.84
0.40	0.110	2.58	0.34	0.35	2.40
0.52	0.139	2.61	0.31	0.32	1.93
0.69	0.197	2.73	0.28	0.30	1.37
0.91	0.255	2.70	0.26	0.27	1.10
1.2	0.336	2.70	0.23	0.24	0.836
1.54	0.394	2.40	0.20	0.22	0.635
2.03	0.568	2.61	0.18	0.19	0.480
2.75	0.835	2.49	0.15	0.17	0.312
3.74	1.14	2.46	0.13	0.14	0.226
4.91	1.36	2.43	0.10	0.12	0.187

(a): see text for explanation of symbols

TABLE II.3[a]

SOLVENT-REGENERATION DATA

SOLVENT = 0.48 M D2EHPA in Norpar 12

T = 127°C P = 1.05 atm

total N_2 (ft^3)	Δ N_2 (moles)	NH_3 absorbed (mmoles)	$[NH_4^+A^-]$ (M)	$[NH_4^+A^-]_{avg}$ (M)	$P_{NH_3} \times 10^2$ (atm)
0	-	-	0.23	-	-
0.12	0.139	1.43	0.22	0.22	1.06
0.22	0.116	1.38	0.20	0.21	1.23
0.32	0.116	1.35	0.19	0.20	1.21
0.44	0.139	1.40	0.18	0.18	1.04
0.58	0.162	1.38	0.16	0.17	0.885
0.745	0.191	1.38	0.15	0.15	0.752
0.96	0.249	1.40	0.13	0.14	0.584
1.23	0.313	1.38	0.12	0.13	0.461
1.57	0.394	1.38	0.11	0.11	0.366
2.01	0.505	1.32	0.09	0.10	0.274
2.59	0.679	1.32	0.08	0.09	0.204
3.42	0.963	1.41	0.07	0.07	0.154

(a): see text for explanation of symbols; $[NH_4^+A^-]_{f,meas} = 0.097$ M

TABLE II.4[(a)]

SOLVENT-REGENERATION DATA

SOLVENT = 0.4 M D2EHPA in 0.4 M Adogen 364 in Norpar 12

T = 127°C P = 1.05 atm

total N_2 (ft^3)	Δ N_2 (moles)	NH_3 absorbed (mmoles)	$[NH_4{}^+A^-]$ (M)	$[NH_4{}^+A^-]_{avg}$ (M)	$P_{NH_3} \times 10^2$ (atm)
0	-	-	0.207	-	-
0.05	0.058	2.6	0.181	0.194	4.5
0.09	0.046	2.5	0.156	0.169	5.4
0.14	0.058	2.72	0.129	0.142	4.7
0.205	0.076	2.64	0.102	0.116	3.55
0.3	0.110	2.51	0.077	0.090	2.34
0.46	0.186	2.4	0.053	0.065	1.34
1.19	0.847	1.97	0.034	0.043	0.24
2.55	1.58	0.236	0.031	0.032	0.016

(a): see text for explanation of symbols; $[NH_4{}^+A^-]_{f,meas}$ = 0.0037 M

TABLE II.5(a)

SOLVENT-REGENERATION DATA

SOLVENT = 0.48 M D2EHPA in Norpar 12

T = 143°C P = 1.06 atm

total N_2 (ft^3)	Δ N_2 (moles)	NH_3 absorbed (mmoles)	$[NH_4^+A^-]$ (M)	$[NH_4^+A^-]_{avg}$ (M)	$P_{NH_3} \times 10^2$ (atm)
0	-	-	0.23	-	-
0.09	0.104	2.66	0.20	0.22	2.63
0.175	0.099	2.78	0.18	0.19	2.9
0.285	0.128	2.67	0.15	0.16	2.17
0.445	0.186	2.7	0.12	0.146	1.52
0.55	0.122	1.35	0.11	0.115	1.16
0.70	0.174	1.32	0.095	0.102	0.80
0.88	0.209	1.32	0.082	0.089	0.67
1.11	0.267	1.37	0.068	0.075	0.54
1.425	0.365	1.31	0.055	0.062	0.38
1.885	0.534	1.26	0.043	0.049	0.25
2.6	0.829	1.3	0.03	0.036	0.17
3.85	1.45	1.26	0.017	0.024	0.092

(a): see text for explanation of symbols; $[NH_4^+A^-]_{f,meas}$ = 0.023 M

TABLE II.6[(a)]

SOLVENT-REGENERATION DATA

SOLVENT = 0.48 M D2EHPA in 50% (v/v) Isodecyl alcohol/Norpar 12

T = 143°C P = 1.06 atm

total N_2 (ft^3)	Δ N_2 (moles)	NH_3 absorbed (mmoles)	$[NH_4{}^+A^-]$ (M)	$[NH_4{}^+A^-]_{avg}$ (M)	$P_{NH_3} \times 10^2$ (atm)
0	-	-	0.48	-	-
0.045	0.052	2.6	0.454	0.467	5.03
0.08	0.041	2.56	0.428	0.441	6.29
0.12	0.046	2.64	0.402	0.415	5.7
0.165	0.052	2.64	0.376	0.389	5.1
0.22	0.064	2.61	0.35	0.363	4.17
0.275	0.064	2.74	0.322	0.336	4.36
0.35	0.087	2.63	0.296	0.309	3.11
0.44	0.104	2.62	0.27	0.283	2.6
0.55	0.128	2.8	0.24	0.256	2.28
0.70	0.174	2.61	0.216	0.229	1.57
0.90	0.232	2.7	0.189	0.202	1.22
1.18	0.319	2.58	0.163	0.176	0.85
1.58	0.47	2.58	0.137	0.150	0.58
2.3	0.835	2.6	0.111	0.124	0.33
3.67	1.59	2.65	0.084	0.098	0.18
4.415	0.864	1.08	0.074	0.079	0.13

(a): see text for explanation of symbols; $[NH_4{}^+A^-]_{f,meas}$ = 0.053 M; final measured volume = 86 ml.

TABLE II.7[(a)]

SOLVENT-REGENERATION DATA

SOLVENT = 0.82 M D2EHPA in 50% (v/v) Isodecyl alcohol/Norpar 12

$T = 127°C$ $P = 1.07$ atm

total N_2 (ft^3)	Δ N_2 (moles)	NH_3 absorbed (mmoles)	$[NH_4^+A^-]$ (M)	$[NH_4^+A^-]_{avg}$ (M)	$P_{NH_3} \times 10^2$ (atm)
0	-	-	0.407	-	-
0.40	0.464	2.64	0.38	0.39	0.60
0.71	0.36	2.57	0.355	0.37	0.75
0.88	0.197	1.41	0.341	0.35	0.75
1.07	0.220	1.365	0.327	0.33	0.65
1.29	0.255	1.35	0.314	0.32	0.56
1.815	0.609	2.54	0.288	0.30	0.44
2.58	0.887	2.59	0.262	0.28	0.31
3.07	0.568	1.395	0.249	0.26	0.26
3.63	0.649	1.335	0.235	0.24	0.22
4.3	0.777	1.35	0.222	0.23	0.19
5.155	0.992	1.35	0.208	0.22	0.15
6.13	1.131	1.38	0.194	0.20	0.13
7.48	1.566	1.38	0.181	0.19	0.094
8.7	1.415	1.01	0.170	0.18	0.076
10.66	2.27	1.38	0.157	0.16	0.065
12.17	1.75	0.90	0.148	0.15	0.055
13.29	1.30	0.63	0.141	0.14	0.052

(a): see text for explanation of symbols; $[NH_4^+A^-]_{f,meas} = 0.19$ M; final volume = < 70 ml

TABLE II.8$^{(a)}$

SOLVENT-REGENERATION DATA

SOLVENT = 0.4 M D2EHPA in 0.4 M TOPO in Norpar 12

T = 127°C P = 1.07 atm

total N_2 (ft^3)	Δ N_2 (moles)	NH_3 absorbed (mmoles)	$[NH_4^+A^-]$ (M)	$[NH_4^+A^-]_{avg}$ (M)	$P_{NH_3} \times 10^2$ (atm)
0	-	-	0.183	-	-
0.165	0.191	2.96	0.154	0.168	1.63
0.35	0.185	3.02	0.124	0.139	1.48
0.63	0.325	2.83	0.095	0.109	0.92
1.12	0.568	2.72	0.068	0.082	0.51
2.06	1.09	2.87	0.039	0.054	0.28
4.43	2.75	2.89	0.010	0.025	0.11

(a): see text for explanation of symbols; $[NH_4^+A^-]_{f,meas} = 0.024$ M

TABLE II.9(a)

SOLVENT-REGENERATION DATA

SOLVENT = 0.82 M D2EHPA in Norpar 12

T = 127°C P = 1.07 atm

total N_2 (ft^3)	Δ N_2 (moles)	NH_3 absorbed (mmoles)	$[NH_4^+A^-]$ (M)	$[NH_4^+A^-]_{avg}$ (M)	$P_{NH_3} \times 10^2$ (atm)
0	-	-	0.184	-	-
1.66	1.93	2.53	0.159	0.171	0.14
2.66	1	1.28	0.146	0.152	0.118
3.4	0.86	0.93	0.137	0.141	0.116
4.38	1.14	1.06	0.126	0.131	0.0997
6.21	2.12	1.37	0.113	0.119	0.066
8.48	2.63	1.31	0.100	0.107	0.053
9.12	0.74	0.39	0.096	0.098	0.056

(a): see text for explanation of symbols; $[NH_4^+A^-]_{f,meas}$ = 0.112 M

TABLE II.10[a]

SOLVENT-REGENERATION DATA

SOLVENT = 0.43 M D2EHPA in 0.22 M Adogen 364 in Norpar 12

T = 127°C P = 1.06 atm

total N_2 (ft^3)	Δ N_2 (moles)	NH_3 absorbed (mmoles)	$[NH_4^+A^-]$ (M)	$[NH_4^+A^-]_{avg}$ (M)	$P_{NH_3} \times 10^2$ (atm)
0	-	-	0.21	-	-
0.09	0.104	2.67	0.183	0.197	2.64
0.16	0.081	2.72	0.156	0.169	3.44
0.245	0.099	2.69	0.129	0.143	2.82
0.35	0.122	2.72	0.102	0.116	2.32
0.495	0.168	2.77	0.074	0.088	1.72
0.725	0.267	2.74	0.047	0.061	1.08
1.26	0.621	2.73	0.019	0.033	0.464
3.65	2.77	1.83	0.001	0.010	0.07
4.95	1.51	0.194	(-)	-	-

(a): see text for explanation of symbols; $[NH_4^+A^-]_{f,meas}$ = 0.0065 M

APPENDIX III

ADDITIONAL EXTRACTIONS OF WASTEWATERS

Condensate waters from the Grand Forks Energy Technology Center (GFETC) were extracted with D2EHPA- and DNNSA-based solvents. The wastewater contained 0.37 M NH_3.

When 0.2 M as-received D2EHPA in Norpar 12 was contacted with this water at S/W (v/v) = 5, the raffinate contained 0.04 M NH_3 and the pH, estimated by pH paper, was between 5 and 6. The phase-separation properties were good. Both aqueous and organic phases were clear and there was only a small emulsion at the interface.

When 0.2 M DNNSA in Norpar 12 was contacted with this water at S/W (v/v) = 5, the raffinate contained 0.025 M NH_3 and the pH, estimated by pH paper, was about 2. Phase-separation properties were good.

In both experiments the phases discolored due to the oxidation of phenols.

These results reveal that these solvents do extract NH_3 from wastewaters, as discussed in Chapter 7, section A. In addition they indicate that DNNSA is a stronger extractant than D2EHPA, as pointed out in Chapter 4, section D.

APPENDIX IV

ADDITIONAL EXTRACTION/STRIPPING EXPERIMENT

Experiments similar to those described in Chapter 3, section H are reported here. The aqueous feed contained 0.56 M NH_3 and 0.6 M CO_2 at a pH of 8.9. This high pH indicates that some basic impurity is present in the solution. For the stripping experiments 50 ml of feed were used and the pressure was 1.14 atm. The results for CO_2 removal from solution are given in Figure IV.1. At the end of the stripping experiment the measured concentration of CO_2 was 0.27 M, the measured concentration of NH_3 was 0.45 M and the pH was 9.5. The expected CO_2 concentration (determined from mass balance) was 0.37 M. The expected NH_3 concentration was 0.46 M.

For the extraction/stripping experiments (performed in a 1000 ml round-bottom flask) the aqueous phase was the same as for the stripping experiments and the solvent was 0.2 M as-received D2EHPA in Norpar 12. The S/W was 5 and the pressure was 1.15 atm. Results for CO_2 removal are also presented in Figure IV.1. The pH of the aqueous phase at the end of the extraction/stripping experiments was about 5.8. Less than 0.5% of the NH_3 present in the feed solution was stripped from the solution.

These experiments agree qualitatively with those reported in Chapter 7, section B.

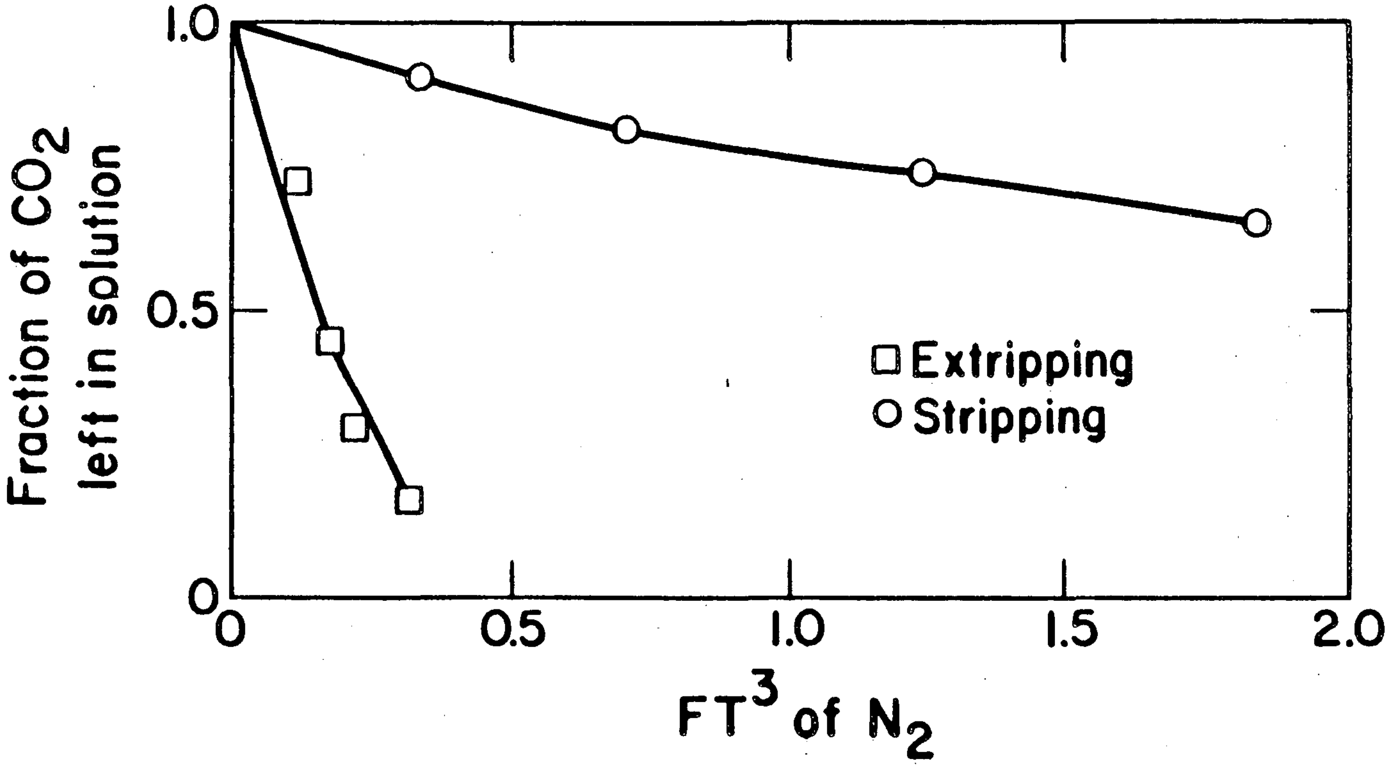

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FIGURE IV.1: COMPARISON OF EASE OF REMOVAL OF CO_2 BY STRIPPING WITH THAT BY EXTRACTION/STRIPPING. Stripping: Aqueous phase = 50 ml of 0.6 M CO_2, NH_3. Extraction/Stripping: Aqueous phase = same; organic phase = 0.2 M D2EHPA in Norpar 12; S/W (v/v) = 5.

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