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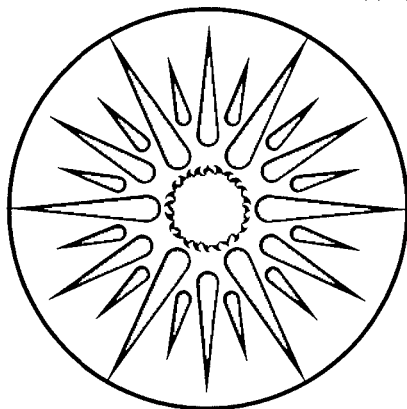
COMBINED SOLVENT EXTRACTION AND STRIPPING FOR
REMOVAL AND ISOLATION OF AMMONIA FROM SOUR WATERS

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COMBINED SOLVENT EXTRACTION AND STRIPPING FOR REMOVAL
AND ISOLATION OF AMMONIA FROM SOUR WATERS

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ABSTRACT

Simultaneous stripping and solvent extraction offer the possibility of removing and isolating ammonia from sour waters with less steam consumption. Liquid cation exchangers were found to be effective for extraction of ammonia under those conditions. Among the liquid cation exchangers considered, di-2-ethylhexyl phosphoric acid (D2EHPA) appeared to have the most favorable properties. Addition of modifiers to diluents for D2EHPA profoundly affects a number of important solvent properties and affords an avenue toward solvent improvement. Acid modifiers, such as alcohols, phenols, and carboxylic acids, solvate the D2EHPA-ammonium ion pair and thereby increase the degree of extraction of ammonia, reduce aqueous-solubility losses of D2EHPA, improve phase-separation properties, and decrease the volatility of ammonia upon solvent regeneration. Basic amine modifiers complex with D2EHPA, and thereby decrease the degree of ammonia extraction, reduce aqueous-solubility losses of D2EHPA, and increase the volatility of ammonia upon solvent regeneration. These effects have been demonstrated and interpreted through complexation models. Preliminary cost analyses indicate that the dominant factors are steam costs for solvent regeneration and costs of replacing extractant lost by aqueous solubility.

INTRODUCTION

In many industrial applications volatile weak acids, such as CO_2 and H_2S, and weak bases, such as NH_3, are present in significant quantities in waste-waters. Condensate waters from coal-conversion processes can contain all three of these components at a pH around 7.5 to 9.5 (King, et al, 1981). Petroleum-refinery sour waters typically contain NH_3 and H_2S at pH about 7.5 (Darton, et al, 1978). Energy requirements for removing these contaminants by ordinary steam stripping can be large, requiring a boil-up of 10 to 20% of the feed water, depending on the degree of ammonia removal required. It is often desired to isolate the individual components, in order to sell the ammonia

and/or to send the H_2S to a Claus plant. This is even more energy inten-
sive. For example, the Phosam-W and the "all-distillation" processes require
boil-ups of between 25 and 35% of the feed water (Seufert, et al, 1979).
These high steam requirements result from the interaction between the acidic
and basic components, suppressing the volatilitites. At the pH of the waste-
waters, NH_3, CO_2 and H_2S are largely ionized. Only the un-ionized form is
volatile, so the presence of the base serves to decrease the volatility of the
acid and vice versa.

To save energy in the treatment of these wastewaters it would be desir-
able to strip the acid gases from solution at low pH. But in order to do this
a second mechanism, or separation process, must be employed to remove ammonia
under these conditions. Cahn, et al. (1978) originally proposed such a com-
bined process. They suggest using liquid-membrane extraction to remove ammon-
ia and steam stripping to remove the acid gases, a combined process which they
call "extripping."

In the current work combining solvent extraction with steam stripping is
investigated. One possible implementation of this process is shown in Figure
1. The wastewater enters the stripper, and a fraction of the acid gases is
removed. As a result the pH rises. The partially stripped water is then sent
to an extractor in which ammonia is extracted. This lowers the pH. This
water is then returned to the stripper for further CO_2 and H_2S removal. This
stripping/extraction may be repeated as often as needed. The net effect is
that desired; the acid gases are stripped from solution at a low pH. The sol-
vent which leaves the extractor loaded with ammonia is regenerated by strip-
ping at elevated temperature and/or low pressure. Ammonia is thus isolated
from the acid gases. Other flow configurations for implementing this approach
are also possible.

The key to this process is to identify a suitable solvent. The solvent should (1) have a high capacity and selectivity for either the basic or acidic components, (2) result in low solvent losses to the aqueous phase through solubility losses and/or incomplete phase separation, (3) be easily regenerable and release the extracted solute in salable form, (4) have reasonable viscosity and density, and (5) be inexpensive and commercially available.

The goals of the current work were (1) to identify solvents that meet the above requirements and to study experimentally the factors that affect these solvent properties, (2) to identify potential problem areas in the implementation of this approach, and (3) to suggest reasonable operating conditions.

Simple batch extractions were performed to assess the capacities of solvents for CO_2, H_2S, and NH_3. The properties (aqueous solubility, phase separation, and regenerability) of the more likely solvents were studied in greater detail.

<div align="center">EXPERIMENTAL METHODS</div>

Reagents

Table 1 lists the sources of the less conventional compounds used in this work. All compounds were used as received, with the exception of di-2-ethylhexyl phosphoric acid (D2EHPA) and octylphenyl phosphoric acid (OPAP). Mono-2-ethylhexyl phosphoric acid was removed from D2EHPA by the copper-salt-precipitation method described by McDowell, et al (1976). Titration of the purified product produced one endpoint of the strong acid type, indicating that the mono-2-ethylhexyl phosphoric acid had been largely removed from the D2EHPA. Mono-octylphenyl phosphoric acid was removed from OPAP by successive washings with sodium hydroxide solution, followed by a contacting with HCl and then water.

Analytical Methods

Concentrations of CO_2 and NH_3 in aqueous solutions were determined with specific-gas electrodes (Models 95-02 and 95-10, Orion Research Inc.) Concentrations of H_2S in aqueous solutions were determined with a specific-ion electrode (Orion Model 94-16) used in conjunction with an Orion Model 90-02 double-junction reference electrode.

Electrode responses were measured with an Orion Model 701A digital pH/mV meter with a five-channel electrode switch (Orion Model 605).

The pH of aqueous solutions was measured with either a Ag/AgCl pH electrode or a semi-micro combination pH electrode (Orion Model 91-03).

The concentration of solutes in organic phases was generally determined by mass balance. Occasionally, however, the concentration of ammonia in the organic phase was verified by back extraction of the ammonia into approximately 4 $\underline{M}$ H_2SO_4.

The concentration of water in the organic phase was determined by Karl Fischer titration.

Experimental Methods

Extractions: All extractions were performed in 125-mL separatory funnels. Normal procedure was to mix the two phases on a Labline Junior Orbit Shaker operated at about 250 RPM. In later work (NH_3 extractions) the aqueous phase (raffinate) was centrifuged after the extraction in an International Clinical Centrifuge (1200 RCM). In all cases concentration-based distribution coefficients (K_c) were calculated as:

$$K_c = \frac{C_F - C_R}{C_R} \left(\frac{W}{S} \right) \tag{1}$$

where C_F is the feed concentration (mol/L), C_R is the raffinate concentration (mol/L), W is the volume of aqueous phase, and S is the volume of solvent phase. This equation assumes total immiscibility of the phases.

D2EHPA Solubility Measurements: Raffinates generated in extractions using D2EHPA or OPAP extractant were twice centifuged, and then the concentration of phosphorus in the aqueous phase was determined. The method used was a standard decompostion and precipitation method described by Pregl and Grant (1951). This analysis gave the mg P/mL solvent. This was converted to molarity or to ppm D2EHPA as follows:

$$\text{ppm D2EHPA} = \text{mg P/mL} \times 1000 \times 322/30.9 \qquad (2)$$

Only purified D2EHPA or OPAP was used when making these measurements, since the high aqueous solubilities of the mono-esters would have distorted calculated values for D2EHPA or OPAP solubility. The solubility of D2EHPA in water as measured by this technique was 93 ppm, which compares well with the reported value of 100 ppm (Mobil Chemical Co., 1981).

Solvent Regeneration Studies: 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 the solvent was followed.

Qualitative Studies: In these studies the stripping medium was either vaporized solvent and nitrogen, or steam which was bubbled through the solvent.

Quantitative Studies: The apparatus used for these studies is shown in Figure 2. A relatively non-volatile diluent was used, and nitrogen was the sole stripping medium. After passing through the solvent, the NH_3-

containing nitrogen passed through a sulfuric acid solution which absorbed ammonia. The nitrogen then passed through a wet test meter. Measurement of the NH_3 concentration in the sulfuric acid solution after a given number of moles of nitrogen had passed through gave the number of moles of NH_3 stripped by that amount of nitrogen. This was converted to the partial pressure of NH_3 (P_{NH_3}) as follows:

$$P_{NH_3} = \frac{\text{moles } NH_3}{\text{moles } NH_3 + \text{moles } N_2} \times \text{Pressure} \qquad (3)$$

It was not confirmed that this apparatus indeed provides equilibrium vapor.

Extraction/Stripping Experiments: These experiments were designed to compare the ease of CO_2 removal from an aqueous solution, in the presence of a solvent which extracted NH_3 and in the absence of such a solvent. The apparatus used was similar to that pictured in Figure 2, except that the experiments were conducted at room temperature, and an extra set of absorbers (for removal of CO_2 from the nitrogen stripping gas) was placed in series after the ammonia absorbers. The aqueous phase contained approximately 0.6 M NH_3 and CO_2. The solvent contained 0.48 M D2EHPA in either toluene, 50% (v/v) Alfol 10/toluene, or 0.53 M Adogen 364 in toluene. In one of the stripping cases no D2EHPA was present in toluene. In all cases the solvent-to-water volumetric phase ratio (S/W) was 2.5.

Further information on experimental procedures is available elsewhere (Mackenzie & King, 1984).

RESULTS AND DISCUSSION

Solvent Selection

Methyl isobutyl ketone (MIBK), 3 wt % TOPO in kerosene, ethyl acetate, dimethylaniline, 9% (v/v) Alamine 336 in kerosene and 9% (v/v) Adogen 283 in kerosene, at S/W = 1, and TBP, at S/W = 0.3, did not extract a measurable amount of CO_2 from an aqueous ammonium carbonate solution (initial concentration of CO_2 = 0.15 $\underline{M}$).

No appreciable amount of H_2S was extracted from an ammonium sulfide solution (initial concentration of H_2S = 0.02 $\underline{M}$) by 7.4% (v/v) Alamine 336 in kerosene or 7.4% (v/v) Adogen 283 in kerosene (S/W = 0.8). MIBK (S/W = 0.4) appeared to extract a small amount of H_2S, but the results were not reproducible.

No ammonia was extracted from the ammonium sulfide solution by MIBK. Likewise no NH_3 was extracted from an ammonium bicarbonate solution by toluene, 1-octanol, 50% (v/v) 1-decanol in toluene, 13% (w/w) nonylphenol in toluene, or 13% (w/w) 4-sec-butyl-2-(α-methylbenzyl) phenol in toluene (S/W = 5, initial concentration of ammonia = 0.58 $\underline{M}$).

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 as 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 NH_4^+ form, the driving force for ion pairing will be large. Extraction of NH_3 is preferable over that of acid gases because of the lower volatility of NH_3.

Liquid Cation Exchangers as Extractants for NH_3

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-exchanging mechanism and are known as liquid cation exchangers.

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

$$M^+ + \overline{HA} = \overline{M^+A^-} + H^+ \tag{4}$$
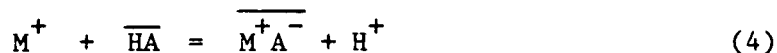
where an overbar indicates organic-phase species. The organic acid, HA, ionizes at or near the aqueous/organic interface and exchanges its H^+ for the cation, M^+, forming an ion pair in the organic phase. This is a simplified expression which ignores possible dimerization of the extractant, complexing of the ion pair with additional acid molecules or diluent, and polymerization of the ion pair (Ashbrook, 1973).

The concentration-based distribution coefficient for NH_4^+, K_{c,NH_4^+}, is the ratio of the organic phase concentration of species containing ammonia to the aqueous phase concentration of NH_4^+. It may be expressed in terms of the activity-based equilibrium constant for Equation 4, K_r:

$$K_{c,NH_4^+} = \frac{[NH_4^+A^-]}{(NH_4^+)} = \frac{K_r [HA] \gamma_{HA}^o \gamma_{NH_4^+}^a}{(H^+) \gamma_{H^+}^a \gamma_{NH_4^+A^-}^o} \tag{5}$$

where square brackets and the superscript o denote organic-phase properties and parentheses and the superscript a denote aqueous-phase properties. γ is the activity coefficient.

From Equation 5 it is seen that K_{c,NH_4^+} increases with increasing pH. For the proposed process K_c for ammonia must be high in the pH range of interest, 7 to 9. At pH = 7 nearly all of the ammonia is in the ammonium form and $K_c = K_{c,NH_4^+}$. Consequently K_{c,NH_4^+} must be large enough at a pH of about 7.

Liquid cation exchangers 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.

Table 2 presents the results of the extraction of ammonium bicarbonate solutions containing 0.58 $\underline{M}$ ammonia with solvents containing either carboxylic acids or organic phosphoric acids, at S/W = 5. The values of pH were not determined but were estimated by pH paper to decrease from about 8 to about 5, going downward in the table. In light of this trend it is apparent that, as the acid strength of the extractant increases, NH_3 extractability increases. Only the last two extractants appear to exhibit sufficient K_c values for effective extraction of ammonia.

D2EHPA is preferred over OPAP because it gives lower measured solubility losses. The raffinate from the OPAP extraction contained 0.009 $\underline{M}$ phosphorus, while that from the D2EHPA extraction contained 0.001 $\underline{M}$ phosphorus.

DNNSA was also considered as an extractant for ammonia. DNNSA is a stronger acid than D2EHPA. When 0.2 $\underline{M}$ D2EHPA (unpurified) in kerosene was contacted with an aqueous ammonium carbonate solution containing 0.17 $\underline{M}$ NH_3 at S/W = 1.25, the raffinate concentration was 0.036 $\underline{M}$ and the pH was about 5. When 0.18 $\underline{M}$ DNNSA was contacted with a similar feed at S/W = 1, the raffinate concentration was 0.0069 $\underline{M}$ and the pH was about 4. Phase-separation properties were slightly better with the DNNSA system, although both solvents showed some tendency to emulsify with the aqueous phase.

A qualitative assessment was made of the relative regenerabilities of D2EHPA and DNNSA. The solvents used in the regeneration studies were 0.19 $\underline{M}$ DNNSA in Norpar 12 containing 0.07 $\underline{M}$ NH_3, and 0.2 $\underline{M}$ D2EHPA in Norpar 12 containing 0.1 $\underline{M}$ NH_3. First water was boiled through the solvents at atmospheric pressure and at a cumulative water-to-solvent volumetric ratio of 1.0 for DNNSA and 0.5 for D2EHPA. For DNNSA no reduction in organic-phase ammonia concentration occurred, and no NH_3 was found in the aqueous distillate. For D2EHPA, a 32% reduction in organic-phase NH_3 concentration occurred, and 80% of the NH_3 stripped from the organic phase was collected in the aqueous distillate.

Solvent-regeneration experiments at 200°C used the diluent as part of the stripping medium. For DNNSA, 100 mL of solvent were held at 200°C for 2 hours with a nitrogen flow rate of 500 ml/min. For D2EHPA, 150 mL of solvent were held at 200°C for 2 hours with a nitrogen flow rate of 220 ml/min. The nitrogen was passed through a sulfuric acid solution to absorb NH_3 stripped from the solvent.

For the D2EHPA system, the NH_3 concentration in the organic phase was reduced to essentially zero, and 72% of the NH_3 lost from the organic phase was found in the sulfuric acid trap.

For the sulfonic acid system, a solid precipitated out of the solvent during the experiments, and the ammonia concentration of the solvent was reduced by at least 87%. No ammonia was found in the sulfuric acid trap. The solid was collected under various conditions, such as excluding light and/or oxygen, and was analyzed. There was no significant difference in the composition of the solids generated from NH_3-containing solvents. These solids had a molar ratio C:H:S of about 2:8:1, which is very different from that of DNNSA, 28:47:1. In addition the solids had a molar ratio of N to S between 0.8 and 0.9. These results indicate that a large portion of the alkyl part of the molecule was not incorporated into the solid decomposition product but that the ammonia was. Further, the ammonium salt of DNNSA appears to be preferentially decomposed.

No specific 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 summary, the results of solvent screenings indicated that of the extractants studied, D2EHPA was the preferred extractant for ammonia.

Screening of Diluents for D2EHPA

The effects of diluent choice on the solvent properties of D2EHPA were examined—particularly capacity to extract NH_3 (K_c), aqueous solubility of D2EHPA, and phase-separation properties.

As can be seen from Equation 5, any diluent which decreases 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 it solvates the free acid will increase K_{c,NH_4}^+ (Blumberg and Gai, 1977). Conversely, a diluent which preferentially solvates the free acid over the ion pair will decrease K_{c,NH_4}^+.

Diluting an extractant will decrease its aqueous solubility losses since the reduction in concentration should decrease its activity. If the diluent can interact with the extractant and/or the ion pair, then solubility losses should also be less (Baes, 1962). For acidic extractants aqueous-phase solubility increases with increasing pH (Ashbrook, 1972).

All liquid cation exchangers possess some surface activity as a result of the presence of a hydrophilic group (the acid functionality) and a hydrophobic group (the hydrocarbon part). Conversion of the acid to the salt form generally, but not always, increases its surface activity (Cox and Flett, 1977). The salt form is usually more interfacially active than the acid because it is an ion pair and thus more hydrophilic. McDowell's (1977) observations suggest that the alkali salts of D2EHPA are more interfacially active than D2EHPA itself. A diluent which can interact with D2EHPA and especially the ion pair will reduce their activity. This can result in an increase in surface tension and a reduction in emulsification tendencies. The addition of a few percent of TBP or a higher alcohol to an organic phase to improve phase-separation tendencies is well known (Cox and Flett, 1977; Kunin and Winger, 1962).

In this work, 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.

A comparison of diluents was made based on the results of batch extractions in which the feed contained approximately 0.58 $\underline{M}$ ammonia in an ammonium bicarbonate solution, S/W = 5, and the total concentration of D2EHPA in the organic phase was 0.2 $\underline{M}$.

One-Diluent Systems

The use of Norpar 12 as a diluent resulted in high D2EHPA aqueous solubility losses (0.013 $\underline{M}$). IBHK also produced comparatively high solubility losses (0.009 $\underline{M}$). Toluene gave lower solubility losses (0.006 $\underline{M}$). Phase-separation properties were slightly better in the latter case. These results suggest that the π electrons of the aromatic offer some solvation to the ion pair and probably also to D2EHPA.

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 assess their effects on D2EHPA solvent properties.

In these experiments the solvent contained 0.2 $\underline{M}$ D2EHPA in toluene plus various volume percents of the modifier. Some of the results for the effects on NH_3 extraction are presented as Figure 3. Results for aqueous extractant losses are presented as Figure 4. Specific observations of phase-settling properties are given elsewhere.

The weak Lewis bases hexyl ether and IBHK and the weak Lewis acid 1,1,2,2-tetrachloroethane had little effect on the capacity of D2EHPA for NH_3, greatly increased extractant losses, and gave rather poor phase-separation properties. Apparently toluene interacts with both the ion pair and free D2EHPA more strongly than do these compounds.

Strong Lewis bases did affect D2EHPA capacity for NH_3. D2EHPA capacity for NH_3 decreased as the Lewis base modifier was changed from TOPO to A364 to LA2, which is the order of increasing basicity. D2EHPA extractant losses to the aqueous phase were also reduced by the addition of these modifiers to toluene. This occurred despite a higher estimated pH of the raffinate from extractions using these modifiers. These effects indicate that the activity of free D2EHPA is reduced by these modifiers. This effect increases as the molar ratio of modifier to D2EHPA increases. Phase-separation properties also improved when these modifiers were added to the solvent. This is attributed to three possible effects--the reduction in D2EHPA activity, the reduction in concentration and hence activity of the ion pair, and the relatively high raffinate concentrations, resulting in higher ionic strengths.

The effects of adding alcohols, phenols and carboxylic acids as modifiers to toluene were also studied. The results shown in Figures 3 and 4 for 1-decanol are representative of the results for these compounds. These compounds increased D2EHPA capacity for NH_3, lowered aqueous extractant losses, and improved phase-separation properties. The effects were greater for the phenols and carboxylic acids than for the alcohols. The former are stronger acids than the latter. However compounds which are sterically hindered around the -OH group (BAMBP, neodecanoic acid) did not show these effects to as great an extent as the sterically unhindered compounds. These results suggest that these acid modifiers solvate the ion pair more than they solvate free

D2EHPA. This solvation may occur via H-bonding with the phosphoryl group. This type of solvation may also make the ammonium cation of the ion pair more amenable to solvation by the basic functional groups of these modifiers, either the O in the –OH group or the carbonyl of the acids.

From these studies two types of useful modifier behavior were discerned. First are the modifiers which increase K_c and decrease extractant losses, mostly through solvation of the ion pair. Second are the modifiers which decrease K_c and decrease extractant losses mostly through solvation of free D2EHPA. The properties of solvents representing these two classes were examined in more detail. Specifically the properties of D2EHPA in the following diluents were 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.

Characterization of D2EHPA-containing Solvents

$\underline{K_{c,NH_4^+}}$. Distribution coefficients were measured as a function of aqueous-phase pH at three D2EHPA concentrations (0.48 $\underline{M}$, 0.37 $\underline{M}$, and 0.25 $\underline{M}$) in each of the above-mentioned diluents. The feed for these extractions was an ammonium hydroxide/ammonium phosphate solution. The concentration of the ammonium/D2EHPA ion pair in the organic phase was varied by changing the concentration of ammonium hydroxide in the feed. The results are presented in Figures 5 and 6 as (pH − log K_{c,NH_4^+}) versus stoichiometry (s), which is the concentration of the ammonium/D2EHPA ion pair in the organic phase divided by the total concentration of D2EHPA ($[HA]_o$).

From Equation 5, at constant [HA], (pH − log K_{c,NH_4^+}) is proportional to log $(\gamma^o_{NH_4^+A^-}/\gamma^o_{HA})$, if aqueous phase activity coefficients are neglected. At constant s and total D2EHPA concentration, [HA] is approximately constant. Therefore as the value of (pH − log K_{c,NH_4^+}) decreases, $\gamma^o_{NH_4^+A^-}/\gamma^o_{HA}$ decreases,

indicating preferential solvation of the ion pair over D2EHPA. This value is lowest in the alcohol diluent and highest in the amine diluent. This again indicates that the alcohol preferentially solvates the ion pair and that the amine preferentially solvates free D2EHPA. This latter effect increases as the molar ratio of amine to D2EHPA increases.

K_{c,NH_4}^+ at a given pH and total D2EHPA concentration decreases as stoichiometry increases, reflecting the decrease in the concentration of free D2EHPA. Also, at a given pH and stoichiometry, K_{c,NH_4}^+ increases as the total concentration of D2EHPA increases, reflecting the increase in concentration of free D2EHPA.

No attempt was made to determine the composition of the species present in the organic phase. Instead a simplified approach suggested by McDowell was pursued. Since the composition of the complexes in the organic phase can depend on stoichiometry McDowell suggests plotting (log K_{c,NH_4}^+ − pH) versus log $[HA]_o$ at constant stoichiometry. The slope of these plots (n) should be a reflection of the degree of complexation of the ion pair by additional D2EHPA. Sample plots are shown in Figures 7 and 8. Tables 3 and 4 give the values of the slopes and intercepts as 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 higher at low stoichiometry. This is consistent with McDowell's work on the extraction of alkali metals into D2EHPA in benzene and suggests that additional complexation of the ion pair by D2EHPA occurs at low stoichiometry, when additonal D2EHPA is available for such solvation.

For the amine diluent a more mechanistic model was pursued. The inter-action of the amine (B) with D2EHPA (HA) to form an amine/D2EHPA complex was

written as:

$$B: + HA \;\rightleftharpoons\; B:HA \tag{6}$$

The equilibrium constant of this reaction, $K_{B:HA}$, was calculated. At a given stoichiometry the concentration of D2EHPA not associated with amine or ammonium was calculated by multiplying the ratio of K_{c,NH_4^+} value for the amine diluent to that for the toluene diluent, at the same pH, by the concentration of D2EHPA not associated with ammonium. Mass balances for the amine and for D2EHPA provided the other values needed to calculate $K_{B:HA}$. For cases in which the (amine plus ammonium)-to-D2EHPA molar ratio was greater than one, the calculated values of $K_{B:HA}$ were all about 2000 liter/mole. For cases in which this ratio was less than one it was necessary to include an additional equilibrium between the amine/D2EHPA complex and additional D2EHPA (Mackenzie and King, 1984).

Phase-separation properties. Several factors can affect the phase-separation properties of the systems under study. In general the alcohol diluent systems gave better phase-separation properties than either the toluene diluent or the amine-containing diluent. Other factors which appeared to cause phase-separation problems were high D2EHPA concentration, high concentration of the ammonium/D2EHPA ion pair, low raffinate concentrations, and low S/W and high stoichiometry, especially for the toluene diluent.

Aqueous-phase extractant losses. Table 5 presents results for measured concentration of phosphorus in the aqueous raffinate after an extraction. All of the measured phosphorus was assumed to be D2EHPA, since purified D2EHPA was used in these studies. Further it was assumed that all of the D2EHPA was ionized since the pH values are significantly greater than the pK_a of D2EHPA, which is about 3.

From the first two entries in Table 5 it is seen that at the same pH and approximately the same concentration of free D2EHPA the alcohol diluent gave lower D2EHPA solubility losses than the toluene diluent, indicating that it solvates D2EHPA better than toluene. A similar though less strong conclusion can be drawn from the data in lines 4 and 5. The amine modifier solvates D2EHPA very strongly, as evidenced by the low D2EHPA solubility losses it produced despite the higher pH (lines 3 and 6). As the amine-to-D2EHPA molar ratio increases, the effect of this solvation increases, and solubility losses at a given pH become very low.

Table 6 gives results for measured concentrations of phosphorus in raffinates after back-extraction of the raffinates with fresh (NH_3-free) organic phase. Again the alcohol appears to solvate D2EHPA better than toluene. Also, as the molar ratio of amine to D2EHPA increases solubility losses at a given pH become lower.

Water Coextraction. In general, the moles of water coextracted per mole of ammonium/D2EHPA ion pair increased as stoichiometry increased, as can be seen in Table 7. The amount of water coextracted by the solvent alone leads to artificially high values of this ratio at low stoichiometry. However, in a general sense, it can be stated that at a stoichiometry below 0.5 the lowest water coextraction occurred into the toluene-diluent systems. Above this stoichiometry water coextraction was lowest into the alcohol-diluent systems. At high stoichiometry water coextraction was greatest into the toluene-diluent systems.

If the amount of water coextracted by the diluent alone is subtracted from the total measured water concentrations, the the moles of water coextracted per mole ammonium/D2EHPA ion pair were less for the alcohol diluent than for the other diluents, suggesting that the alcohol replaces part

of the water as the solvating medium for the ammonium/D2EHPA ion pair, making it more organophilic and thus more extractable.

Removing the ammonia from the D2EHPA-containing solvent resulted in a reduction in the amount of water in the solvent. This indicates that a large portion of the water coextracted into the organic phase is associated with the ammonium/D2EHPA ion pair.

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

$$NH_4^{+}A^{-} \rightleftharpoons HA + NH_3\uparrow \tag{7}$$

The partial pressure of ammonia above the solvent, P_{NH_3}, may be expressed in terms of the NH_3 concentration in the organic phase and a Henry's law constant, H. Combining this with an equilibrium constant for the above reaction (K') yields:

$$P_{NH_3} = \frac{H \left[NH_4^{+}A^{-}\right] \gamma_{NH_4^{+}A^{-}}}{K' \left[HA\right] \gamma_{HA} \gamma_{NH_3}} = \frac{K \left[NH_4^{+}A^{-}\right]}{\left[HA\right]} \tag{8}$$

High P_{NH_3} will result from high concentration of the ammonium/D2EHPA ion pair, from low concentration of free D2EHPA, and in solvents in which the ammonium/D2EHPA ion pair is not well solvated (high γ for the ammonium/D2EHPA ion pair) or free D2EHPA is well solvated (low γ for D2EHPA). The results as P_{NH_3} versus concentration of the ammonium/D2EHPA ion pair for the different solvents are presented in Figures 9 and 10 and can be interpreted in terms of Equation 8.

Figure 9 summarizes the effects of temperature and diluent on P_{NH_3}. As expected, for a given diluent P_{NH_3} increases with increasing temperature. At

a given temperature P_{NH_3} was greater for the inert diluent than for the alcohol diluent. The lower P_{NH_3} values for the alcohol diluent are apparently due to the solvation of the ammonium/D2EHPA ion pair by the alcohol.

In Figure 10 the effect of increasing the total concentration of D2EHPA is seen. At the same concentration of ammonium/D2EHPA ion pair, P_{NH_3} is less for the more concentrated diluent due to the higher concentration of free D2EHPA.

The effect of adding Lewis bases to the solvent is to increase P_{NH_3}, as seen in Figure 10. These compounds low the activity of free D2EHPA. Adding A364 produced a greater effect than adding the weaker base TOPO. The effect increased as the molar ratio of amine to D2EHPA increased.

The values of K in Equation 8 were calculated for the alcohol and Norpar 12 diluents. In these calculations [HA] was set equal to the total concentration of D2EHPA minus the concentration of the ammonium/D2EHPA ion pair. For the alcohol diluent values of K were fairly constant between the low- and high-concentration solvents and in general decreased some with decreases in stoichiometry, indicating a reduction in the activity coefficient of the ammonium/D2EHPA ion pair. At 127°C the average K value in the stoichiometry range 0.75 to 0.5 was 8.6×10^{-3} atm. For the range 0.5 to 0.25 it was 7×10^{-3} atm, and below 0.25 it was 3.1×10^{-3} atm. At 143°C the first two values were 1.7×10^{-2} atm and 1.4×10^{-2} atm, respectively. This model indicates that for the alcohol diluent P_{NH_3} is determined solely by stoichiometry.

For the Norpar 12 diluent, K was not constant between the low- and high-concentration solvents. Allowing for additional complexation by D2EHPA gave more nearly constant K" values. Thus for the inert diluent P_{NH_3} was modelled as:

$$P_{NH_3} = \frac{K'' \left[NH_4^+ A^- \right]}{\left[HA \right]^2} \tag{9}$$

As in the development of the liquid-liquid extraction equilbrium models, this extra solvent dependency is intended only to indicate additional complexation of the ion pair by D2EHPA and does not confirm 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'' was 4.9×10^{-3} atm $\underline{M}$, and below 0.25 it was 3.4×10^{-3} atm $\underline{M}$. At 143°C these values were 1.3×10^{-2} atm $\underline{M}$ and 1.1×10^{-2} atm $\underline{M}$, respectively.

The data for the amine-containing diluents were found to be independent of the concentration of free D2EHPA.

Some insight into the effect of temperature on K_c can be discerned by consideration of the ratios of P_{NH_3} values in different diluents. At a given concentration of the ammonium/D2EHPA ion pair, the ratio of P_{NH_3} values in two different solvents is inversely proportional to the ratio of their K_c values. This ratio can be compared to the ratio of K_c values at room temperature. These values were estimated by calculating $K_{c,NH_4}{}^+$ values from Figures 5 and 6 at pH equal to 9.25. At this pH K_c is equal to $K_{c,NH_4}{}^+$.

The effect of raising temperature is to bring K_{c,NH_3} values for the different diluents closer together. The ratio of the P_{NH_3} value at 127°C for the amine diluent to that for the Norpar 12 diluent at an amine-to-D2EHPA molar ratio of 1:2 is about 4, while the ratio of K_c values at 25°C (toluene to amine diluent) is on the order of 100. At an amine-to-D2EHPA molar ratio of 1:1 these values are about 5 and 300, respectively. This suggests that the amine/D2EHPA complex is weaker at higher temperatures, which would be expected.

A similar effect is seen with the alcohol diluent. The ratio the of P_{NH_3} value at 127°C for the Norpar 12 diluent to that for the alcohol diluent is

about 3. The ratio of K_c values at 25°C (alcohol to toluene diluent) is about 6. This indicates that the alcohol is less effective at solvating the ammonium/D2EHPA ion pair at higher temperatures than it is at lower temperatures.

Comparison of Extraction/Stripping with Stripping Alone

The results for CO_2 removal from aqueous solutions are presented in Figure 11. The data are plotted as the fraction of CO_2 left in the solution as a function of the cubic feet of nitrogen passed through 50 mL of aqueous solution.

The data indicate that CO_2 is much more readily stripped from solution in the presence of a solvent containing D2EHPA. Specifically CO_2 removal is highest when the diluent for D2EHPA is an alcohol, followed by toluene, and then the amine-containing diluent. This is the order of decreasing K_{c,NH_4^+} values. Thus the solvent which is most effective in extracting ammonia from the aqueous solution results in highest CO_2 volatility. This is a result of the lower aqueous-phase pH, due to removal of the base, NH_3.

For the stripping in the absence of a solvent, at the end of the experiment 20 % of the ammonia initially present in the aqueous phase had been stripped from the solution along with the CO_2. For the cases with a D2EHPA-containing solvent present, the amount of the ammonia initially present in the aqueous phase and stripped with the CO_2 ranged from 0.06% (alcohol diluent) to 1.5% (amine diluent).

These experiments demonstrate that the combination of stripping and solvent extraction serves to enhance CO_2 volatility and reduce NH_3 volatility, thereby making the CO_2 easier to strip and enabling isolation of the ammonia from the CO_2.

Design Considerations

Some preliminary calculations were performed to estimate the costs for the proposed extraction/stripping process (Mackenzie and King, 1984). The costs considered were steam costs for the acid-gas stripper, steam costs for the solvent regeneration column and the cost for replenishing D2EHPA lost through aqueous solubility. The latter two costs appear to be dominant.

With D2EHPA-containing solvents, the upper limit on regeneration temperature appears to be about 130 °C. Higher temperatures cause significant thermal degradation of D2EHPA (Mackenzie and King, 1984). With this temperature and a diluent giving a pressure of 0.4 atm, the costs for regenerating the solvent ranged from $2.30/1000 gal water (inert diluent) to $9.40/1000 gal water (alcohol diluent). In these cases the solvent is only partially regenerated and then recycled. Costs for replacing D2EHPA ranged from $4/1000 gal (alcohol diluent) to $19/1000 gal (amine diluent), at a D2EHPA cost of $2.60/lb. These costs are higher than ones that have been cited for the Phosam-W process.

Energy requirements for solvent regeneration could be reduced by using a more thermally stable solvent, so that the regeneration could be carried out at higher temperatues. Alternatively the use of a weaker extractant could be considered. This would have the potential advantage of the complexation being more readily reversible and thus requiring less energy or a lower temperature for regeneration. However this would be at the expense of higher S/W in the extraction part of the process and/or less effective ammonia removal.

Solvent replenishment costs could be reduced if D2EHPA could be recovered from the aqueous phase, perhaps by adsorption or acidification. Alternatively a less-water-soluble extractant could be considered.

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TABLE 1. SOURCES 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
Di-2-ethyl hexyl phosphoric acid (D2EHPA)	Mobil Chemical Co.	technical grade
Dinonyl naphthalene sulfonic acid (DNNSA)	King Industries	DN-052:50% in Norpar 12 DN-040:40% in heptane
Isobutyl-heptyl ketone (IBHK)	Union Carbide	2-methyl-4-decanone, technical grade
Isodecyl alcohol	USS Chemicals	branched-chain primary aliphatic alcohol
Neodecanoic acid	Exxon Chemicals	branched, technical grade
Nonyl phenol (NP)	ICN Pharmaceuticals	reagent grade
Norpar 12	King Industries	$n-C_{10}-C_{13}$ paraffins
Octyl phenyl acid phosphate (OPAP)	Mobil Chemical Co.	50% mixture of mono- and di-esters
Tributyl phosphate (TBP)	Mobil Chemical Co.	technical grade
Tri-n-octyl phosphine oxide (TOPO)	American Cyanamid	technical grade

TABLE 2. COMPARISON OF LIQUID CATION EXCHANGERS AS EXTRACTANTS FOR AMMONIA. Diluent: 50% decanol in toluene. S/W (v/v) = 5.

Extractant (mol/L)	[Extractant] (mol/L)	$(N)^{(a)}$ (mol/L)	K_c	pK_a
neodecanoic acid	0.27	0.47	0.034	$7^{(b)}$
decanoic acid	0.27	0.35	0.12	5
D2EHPA	0.21	0.017	6.1	$3^{(c)}$
OPAP	0.18	0.012	7.5	<3

(a): Measured total concentration of ammonia in raffinate.

(b): Ashbrook, 1972.

(c) Kunin and Winger, 1962.

TABLE 3: PARAMETERS FOR LIQUID-LIQUID EXTRACTION MODEL FOR TOLUENE DILUENT[a]

s[b]	n	-I	correlation coefficient
0.15	3.36	3.75	0.985
0.26	2.18	4.46	-
0.53	1.29	5.09	1
0.78	1.24	5.31	0.96
0.94	0.64	5.79	-

(a): Parameters defined in Equation: $\log K_{c,NH_4^+} - pH = n \log \{D2EHPA\}_o + I$

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

TABLE 4: 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	1.14	4.25	0.98
0.79	1.21	4.56	0.92
0.92	1.4	4.84	0.97

(a): Parameters defined in Equation: $\log K_{c,NH_4^+} - pH = n \log \{D2EHPA\}_o + I$

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

TABLE 5: D2EHPA LOSSES BY AQUEOUS-PHASE SOLUBILITY

Diluent	[D2EHPA] (mol/L)	pH	P[a] (mol/L)	$[NH_4^+A^-]$ (mol/L)
50% (v/v) 1-decanol/toluene	0.2	6[b]	0.0009	0.1
Toluene	0.2	6[b]	0.0058	0.1
0.08 M A364/toluene	0.2	7.2[b]	0.0023	0.08
50% (v/v) Alfol 10/toluene	0.48	6.2	0.004	0.25
Toluene	0.48	6.57	0.0125	0.23
0.52 M A364/toluene	0.48	8.7	0.006	0.21

(a): Measured aqueous-phase phosphorus concentration

(b): Estimated from liquid-liquid equilibrium data

TABLE 6: D2EHPA SOLUBILITY LOSSES IN THE BACK EXTRACTION OF RAFFINATES

Diluent	[D2EHPA] (mol/L)	(N)[a]	pH	P[b] (mol/L)
50% Alfol/toluene	0.48	0.004[c]	6[c]	0.00055
Toluene	0.48	0.005	4.6	0.0015
0.52 M A364/toluene	0.48	0.02	8	0.003
0.52 M A364/toluene	0.45	0.0086	6[d]	0.0028

(a): Measured total concentration of ammonia in raffinate

(b): Measured concentration of phosphorus in raffinate

(c): Values not stable

(d): Estimated from liquid-liquid equilibrium data

TABLE 7: WATER COEXTRACTION

[D2EHPA] (mol/L)	$[NH_4^+A^-]$ (mol/L)	Toluene $[H_2O]^{(a)}$ (mol/L)	50% Alfol 10/ Toluene $[H_2O]^{(a)}$ (mol/L)	1:2 A364/D2EHPA in Toluene $[H_2O]^{(a)}$ (mol/L)	1:1 A364/D2EHPA in Toluene $[H_2O]^{(a)}$ (mol/L)
0.25	0.035	0.08	0.60	0.14	0.58[b]
0.25	0.23	2.04	1.53	1.9	1.6[c]
0.48	0.07	0.12	0.70	0.41	0.51[d]
0.48	0.46	5.06	2.84	4.2	3.1[e]

(a): Measured concentration of water in organic phase

(b): $[NH_4^+A^-]$ = 0.026 mol/L

(c): $[NH_4^+A^-]$ = 0.203 mol/L

(d): $[NH_4^+A^-]$ = 0.051 mol/L

(e): $[NH_4^+A^-]$ = 0.37 mol/L
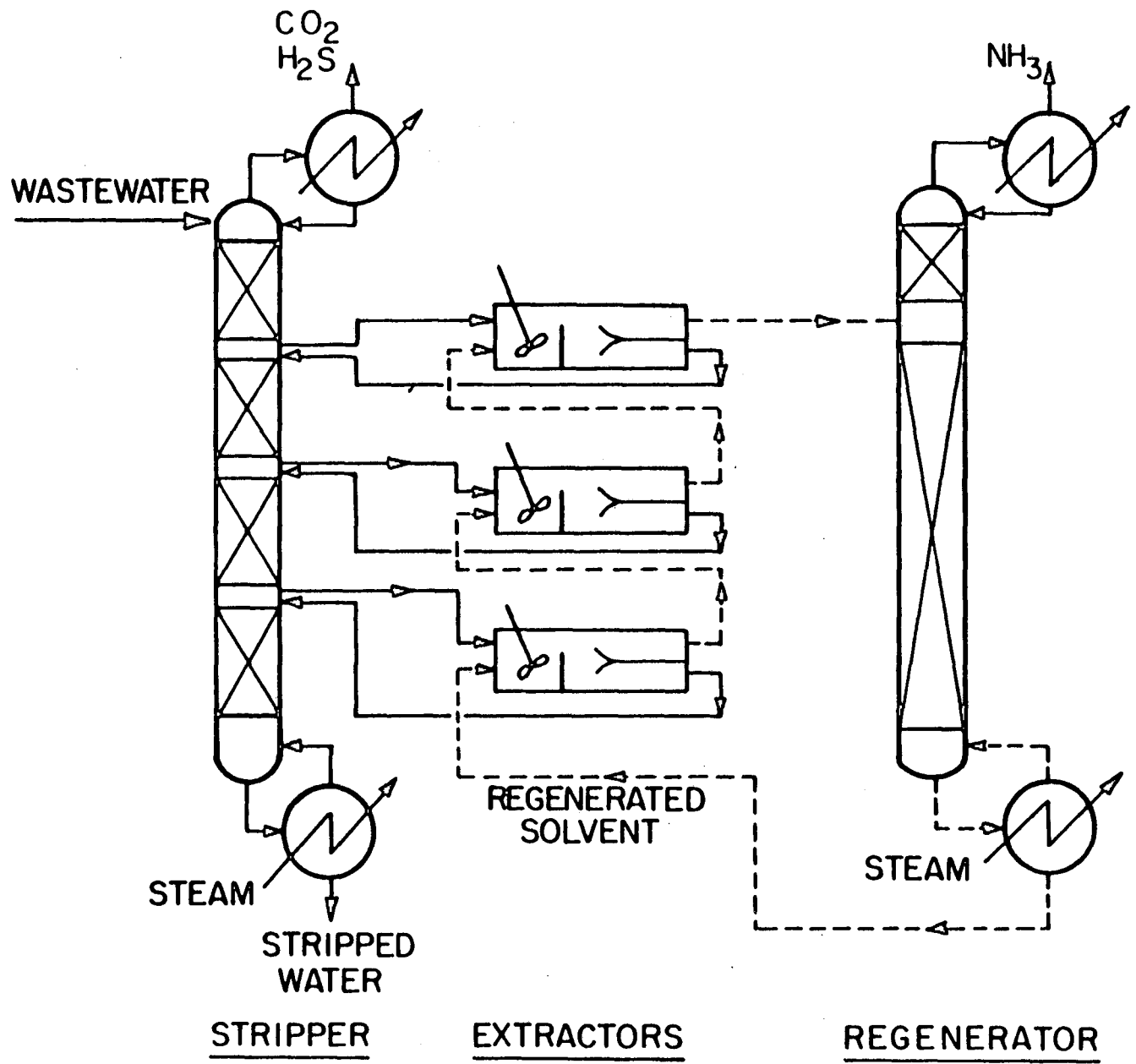
Figure 1. Combined Solvent Extraction and Stripping.
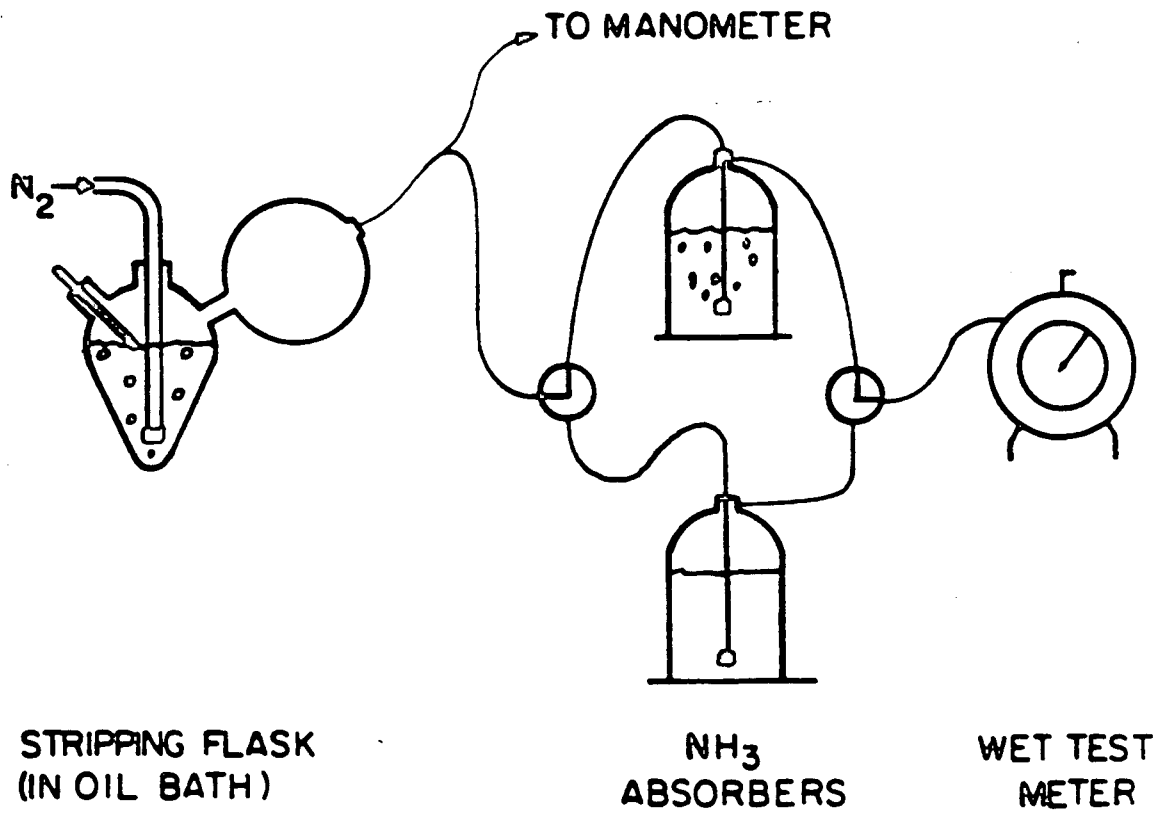
Figure 2. Stripping Apparatus for Solvent-Regeneration Studies.
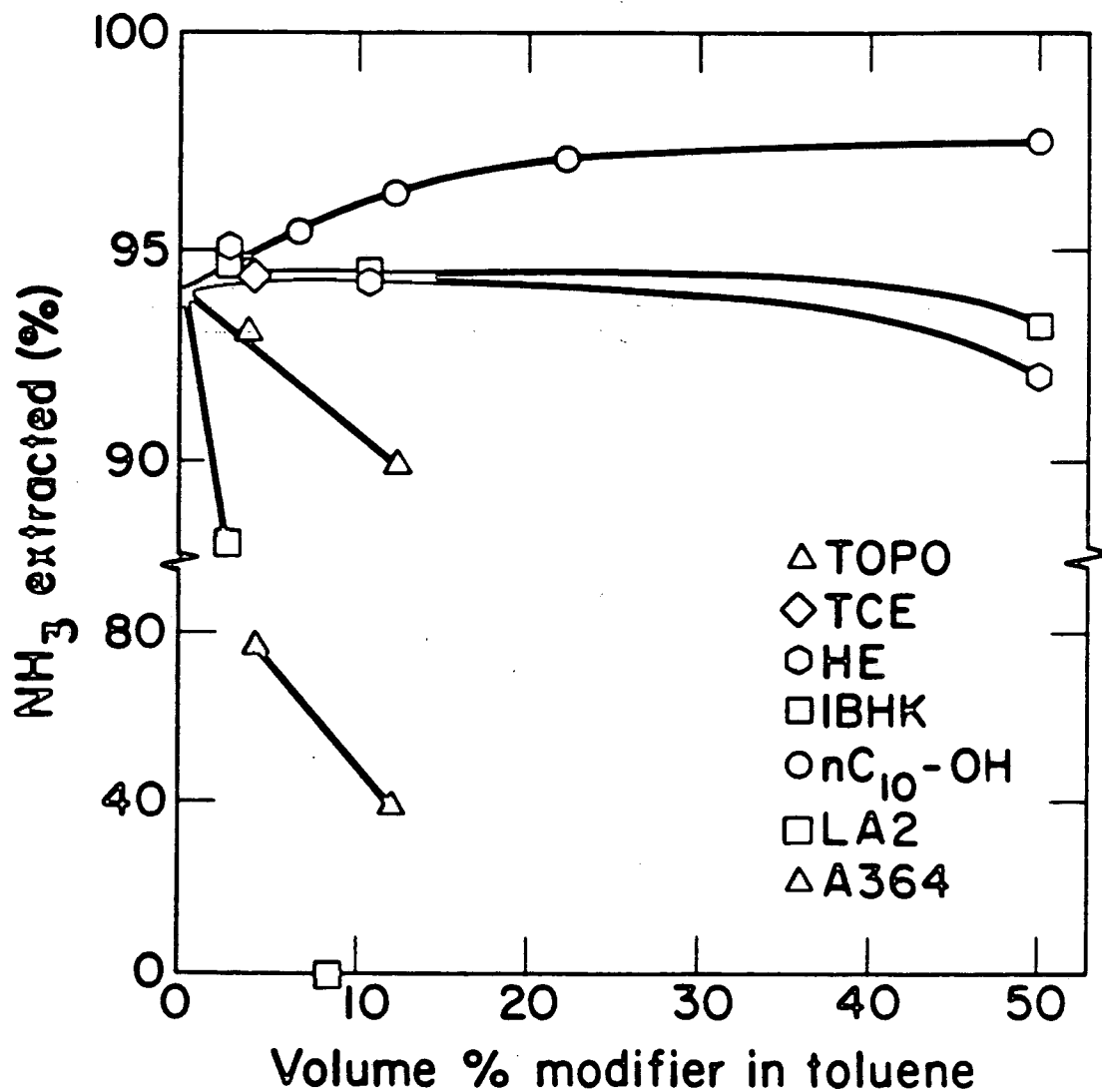
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Figure 3: Effect Upon D2EHPA Extraction of Ammonia From Adding Various Lewis Acids and Bases as Modifiers to a Toluene Diluent. Aqueous feed: 0.58 $\underline{M}$ NH_4HCO_3; 0.2 $\underline{M}$ D2EHPA in organic phase; S/W (v/v) = 5. Modifiers: TOPO = 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.
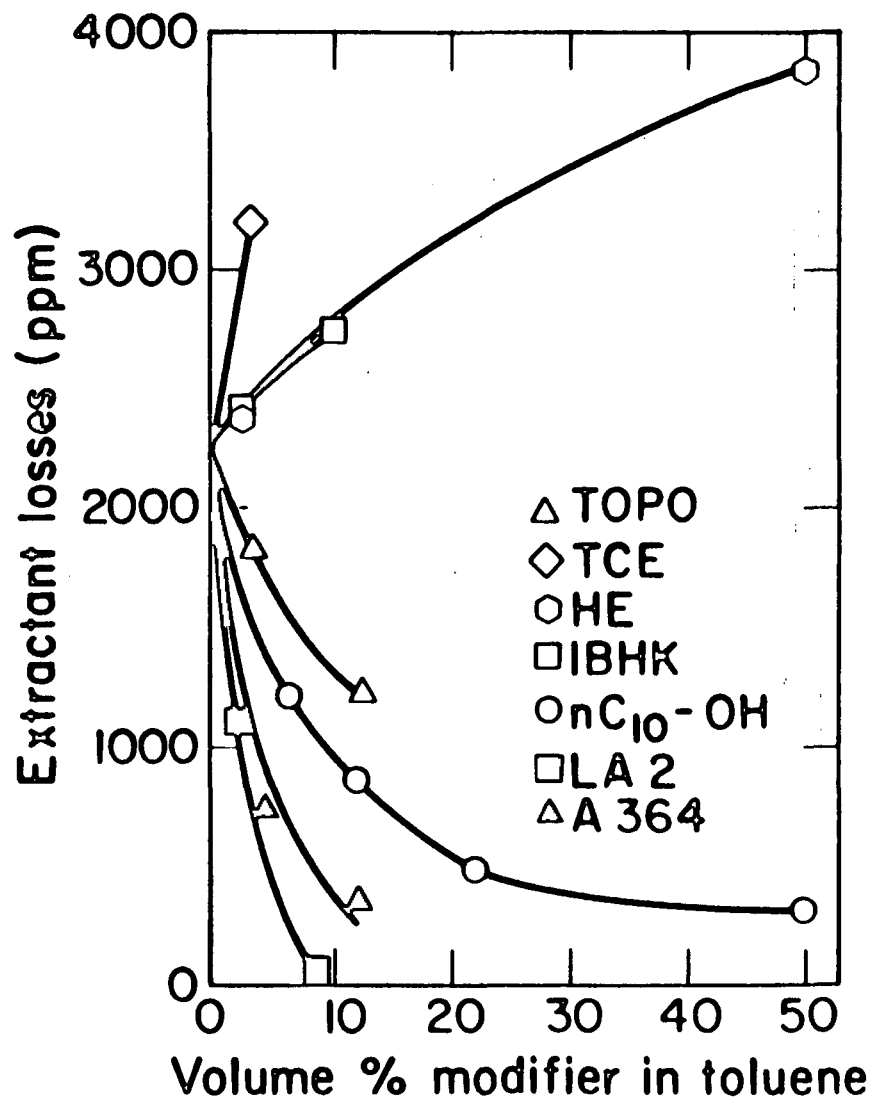
Figure 4. Effect upon D2EHPA Aqueous Solubility Losses from Adding Various Lewis Acids and Bases as Modifiers to a Toluene Diluent. Legend: See Figure 3.

MDL043-0007
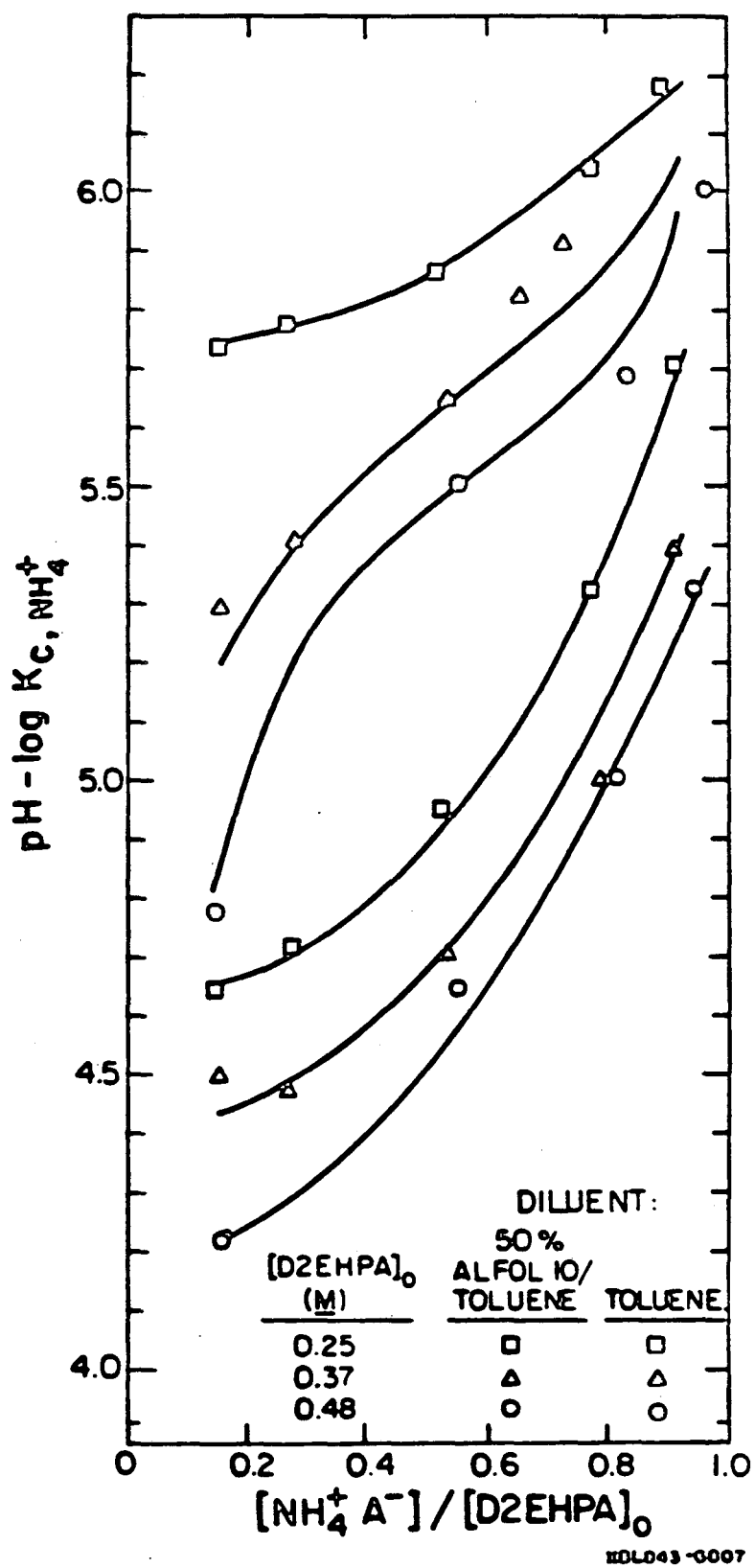
Figure 5. Effect of Stoichiometry on K_{c,NH_4^+} for Toluene + Alcohol-
Containing Diluents.

DILUENT: TOLUENE

	[D2EHPA]$_o$ (M)	[A364] (M)
○	0.25	0.28
△	0.25	0.14
□	0.48	0.52
▽	0.48	0.26
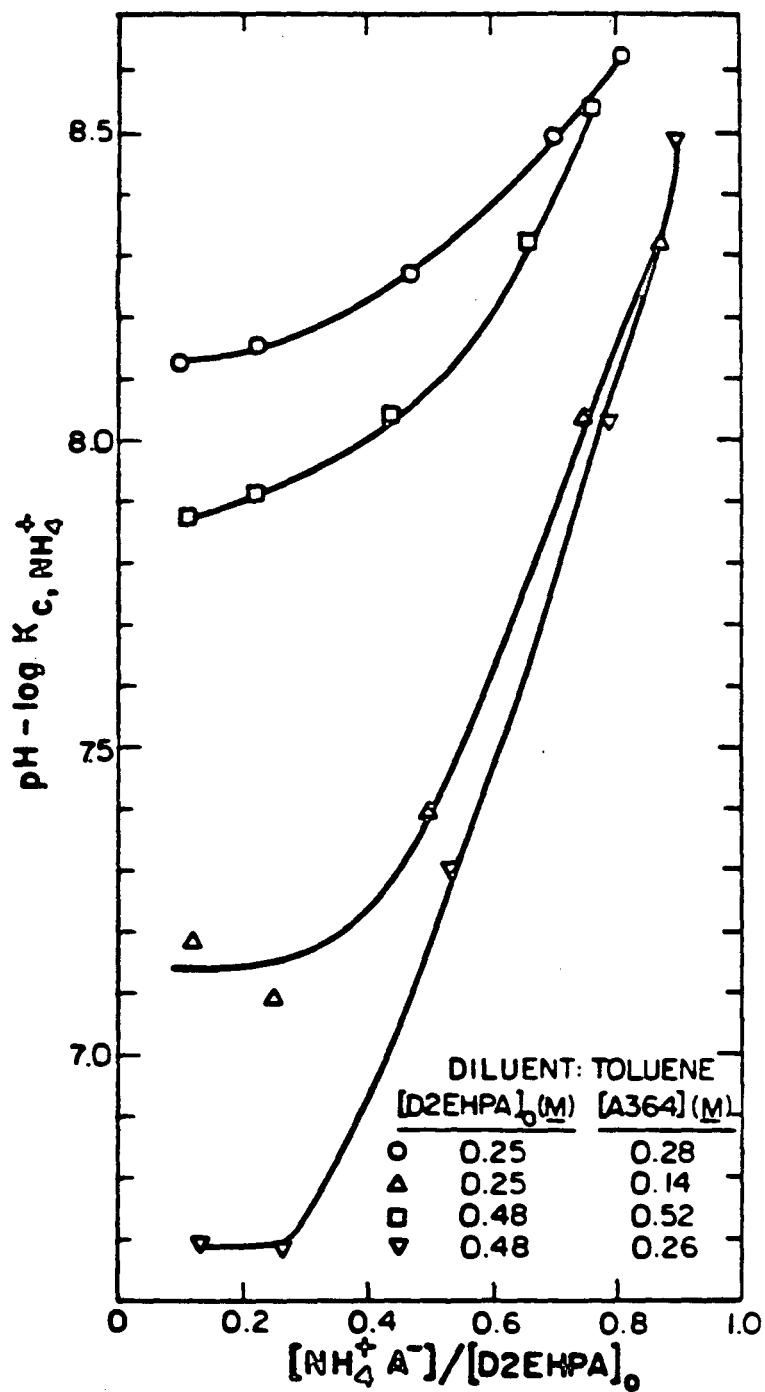
HDL 043-0000

Figure 6. Effect of Stoichiometry on K_{c,NH_4^+} for Amine-Containing Diluents.
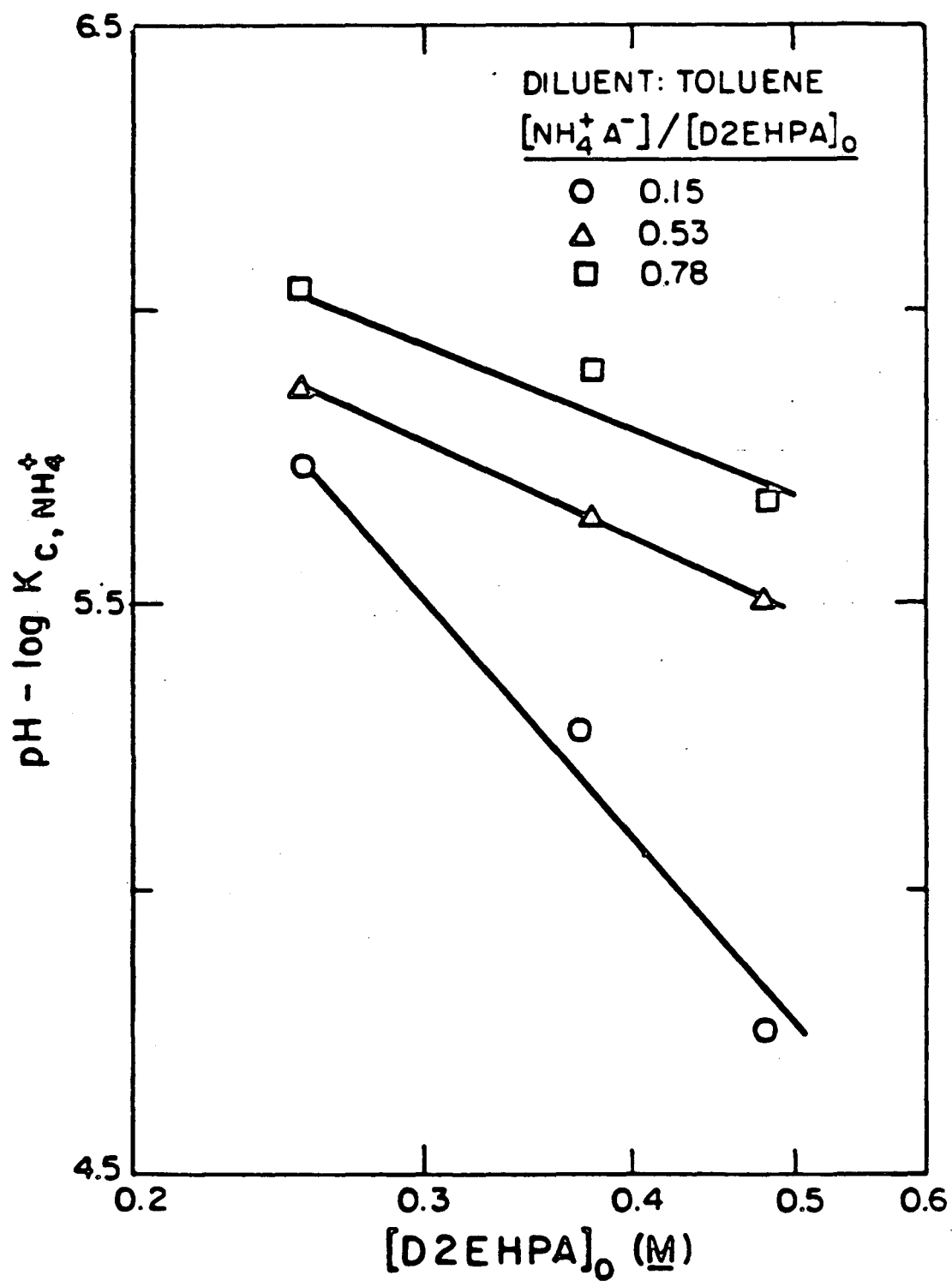
Figure 7. Effect of D2EHPA Concentration on K_{c,NH_4^+} for Toluene Diluent.
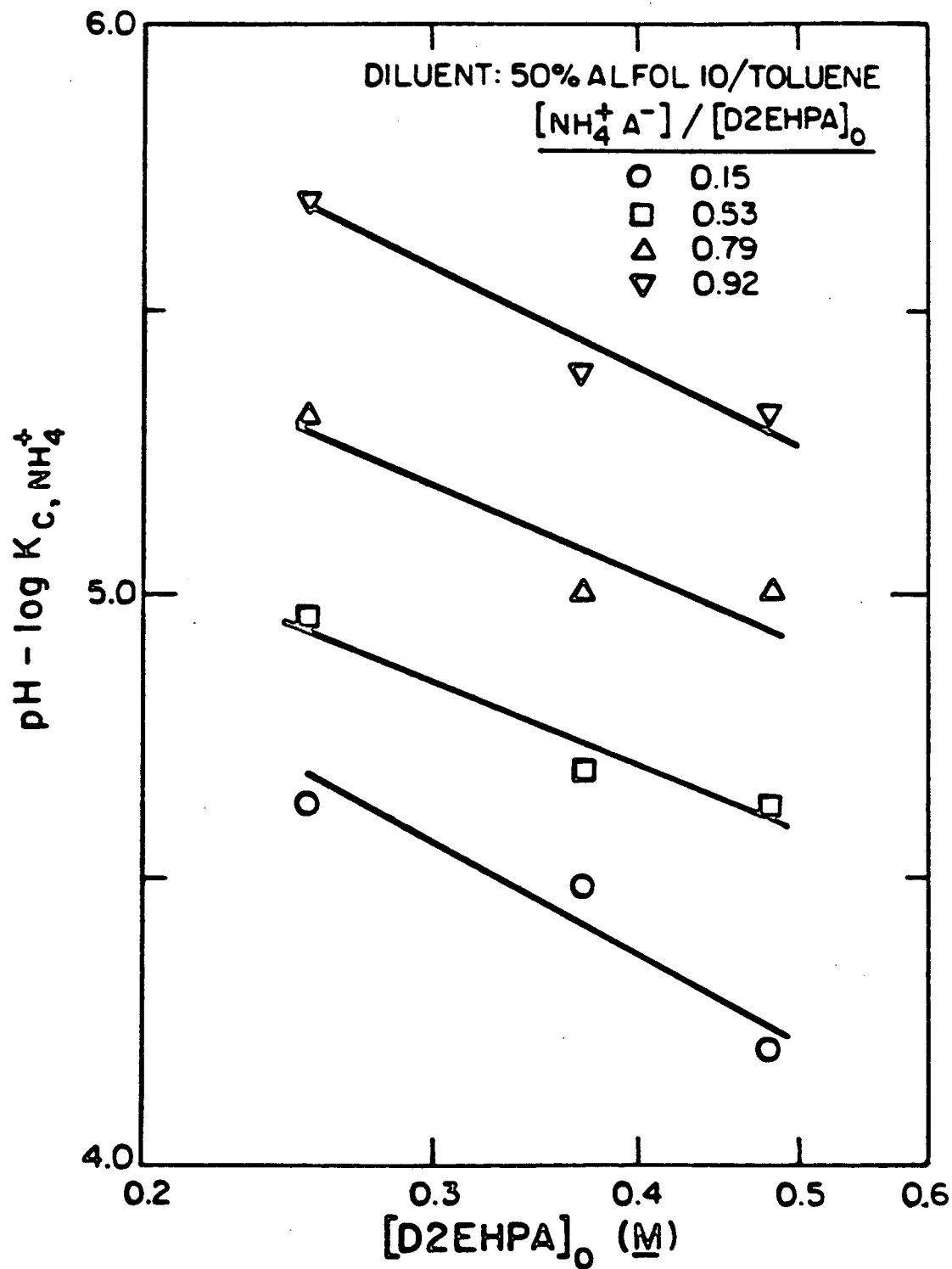
Figure 8. Effect of D2EHPA Concentration on K_{c,NH_4^+} for Alcohol-Containing Diluents.
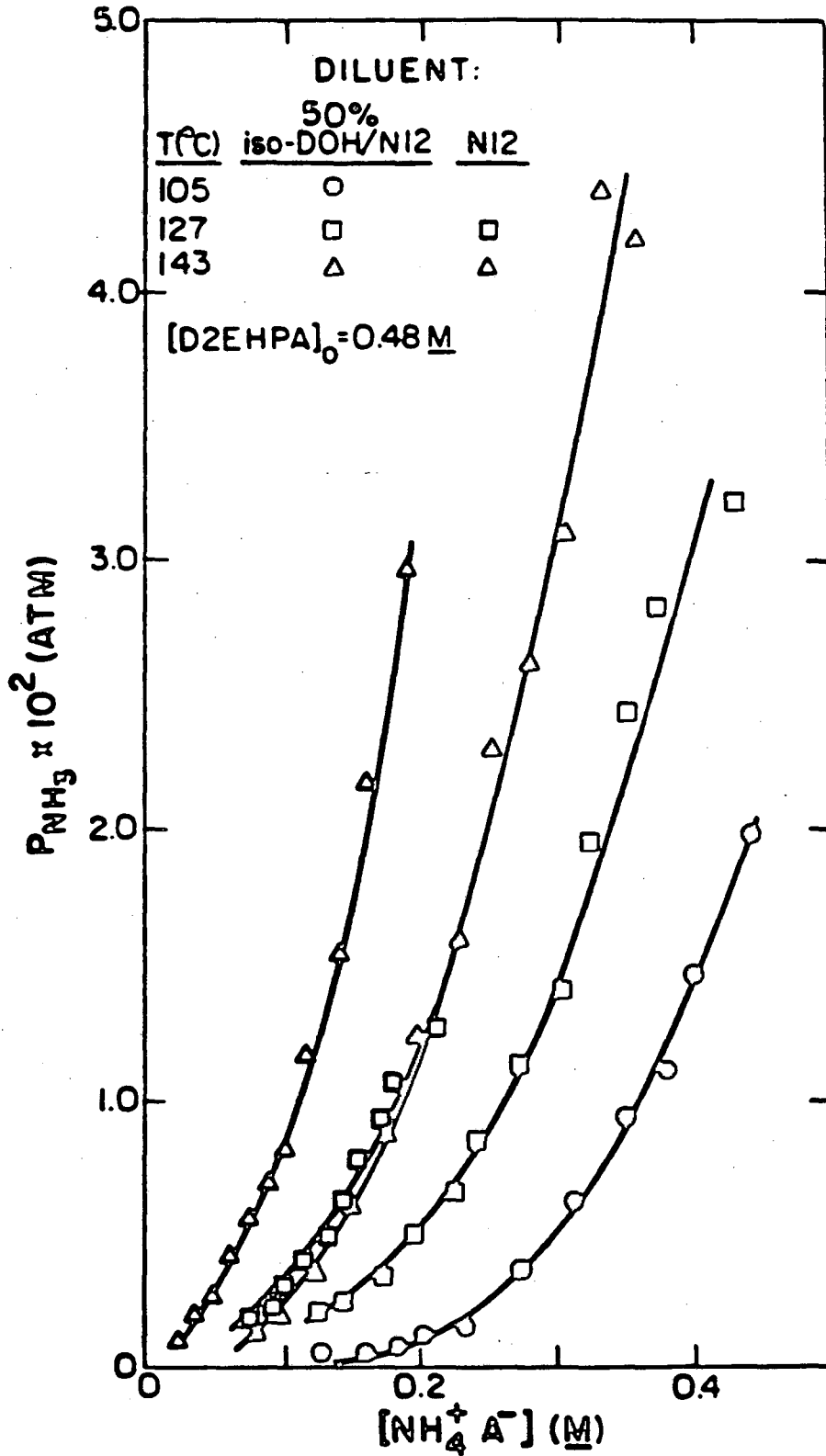
Figure 9. Effects of Temperature and Diluent on Solvent-Regeneration Properties.

[D2EHPA]$_0$ (M)		DILUENT
○	0.82	50% iso-DOH/N12
□	0.82	N12
△	0.40	0.4 M TOPO/N12
▽	0.43	0.22 M A364/N12

$P_{NH_3} \times 10^2$ (ATM)

$[NH_4^+ A^-]$ (M)
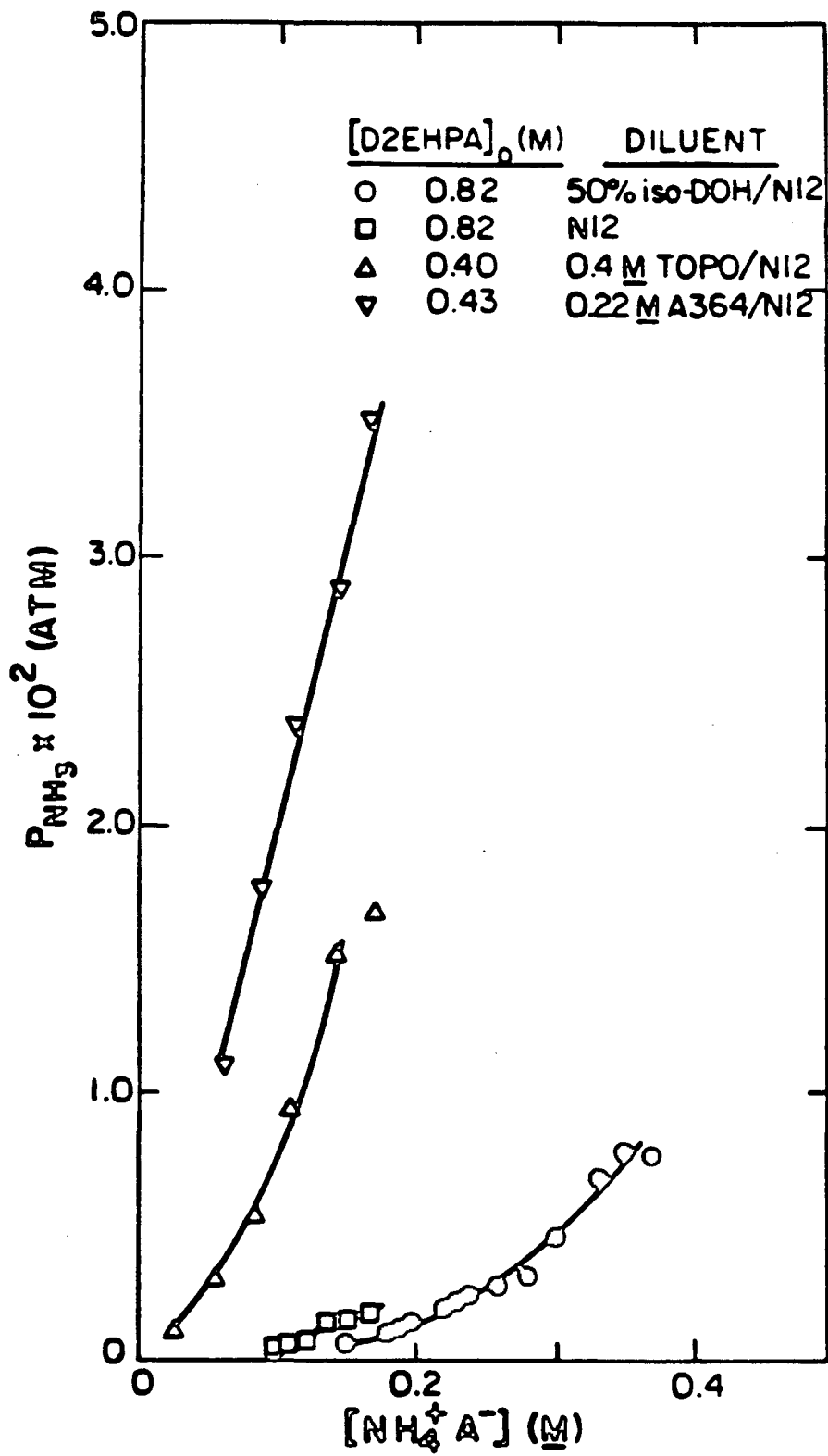
XBL043-0005

Figure 10. Effects of D2EHPA Concentration and Diluent Modifiers on Solvent-Regeneration Properties.
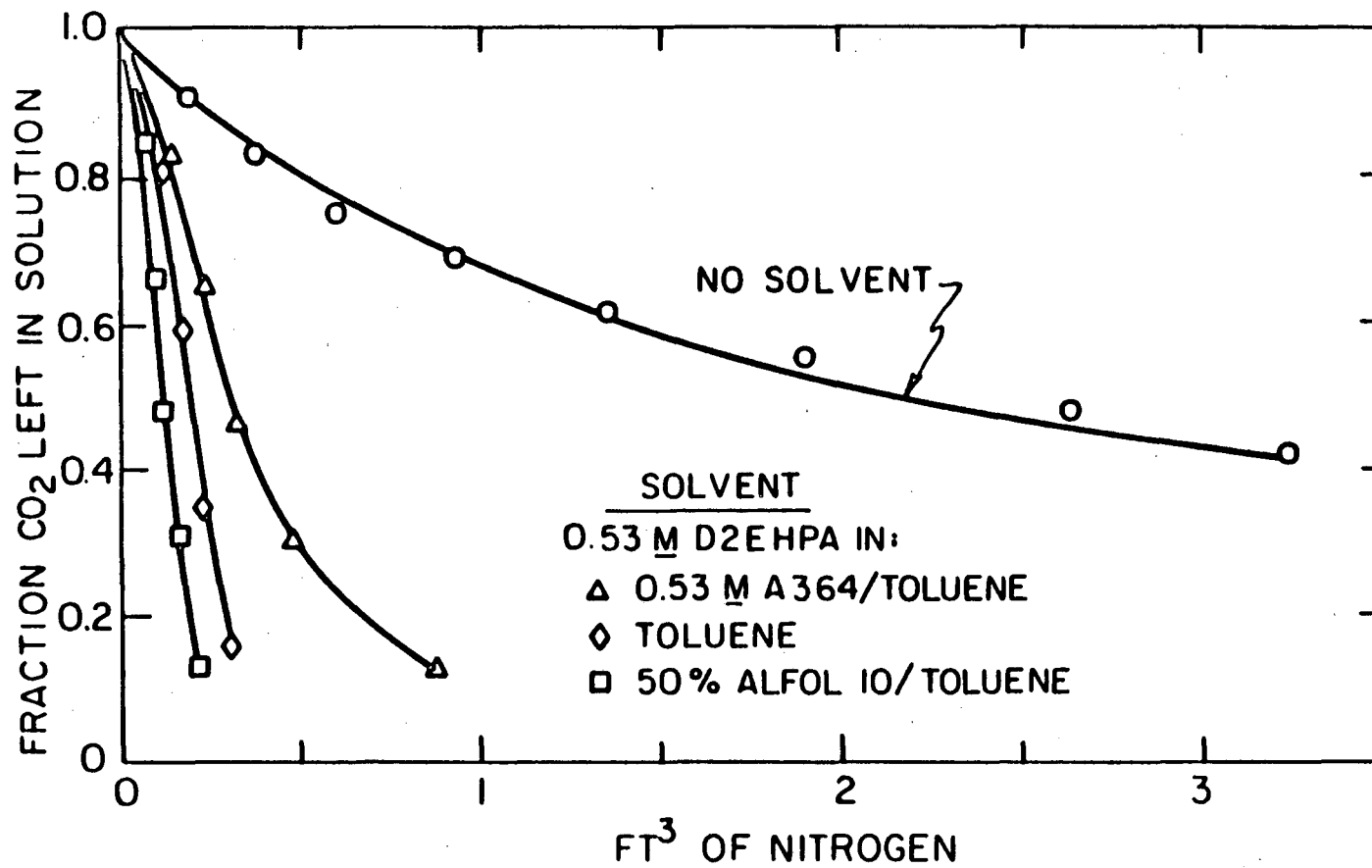
Figure 11. Comparison of Ease of CO_2 Removal by Stripping with that by Extraction/Stripping. Feed = 0.58 $\underline{M}$ NH_4HCO_3; S/W = 2.5; [HA] = 0.48 $\underline{M}$.

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