

# Solvent Equilibria for Extraction of Carboxylic Acids from Water

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Phosphoryl and tertiary amine solvents and solvent mixtures have been investigated for extraction of acetic and formic acids from water. Among phosphoryl compounds, equilibrium distribution coefficients ( $K_D$ ) increase in the order phosphate < phosphonate < phosphine oxide. Tributyl- and trioctylphosphine oxides give higher values of  $K_D$  than the corresponding triphenyl compound. Trioctylamines give higher values of  $K_D$  than tributylamine, apparently because of higher solubility of the reaction product in the solvent phase.  $K_D$  for acetic acid exhibits a maximum value at intermediate solvent compositions of trioctylamines or phosphine oxides and a diluent.

## Introduction

Low-molecular-weight carboxylic acids appear in a number of industrially important waste waters for which acid recovery could be economically advantageous. Solvent extraction is a potentially attractive process for solute recovery but is deterred by the high affinity of these acids for water. The purpose of the present work was to identify and characterize solvents and solvent mixtures which provide a relatively high equilibrium distribution coefficient for extraction of acetic and formic acids from water. Higher equilibrium distribution coefficients allow use of lower solvent-to-water flow ratios.

Equilibrium distribution coefficients for acetic acid at low concentrations in systems of various conventional solvents and water are reported by Treybal (7) and Won (9), among others. General agreement with these previously reported values was found during preliminary experiments in the present work (8). For dilute acetic acid solutions, equilibrium distribution coefficients ( $K_D$  = weight fraction of acetic acid in solvent phase/weight fraction of acetic acid in aqueous phase, at equilibrium) covered the following  $K_D$  ranges for the indicated solvents: ethers ( $C_4$ - $C_6$ ), 0.63-0.14; acetates ( $C_4$ - $C_{10}$ ), 0.89-0.17; ketones ( $C_4$ - $C_{10}$ ), 1.20-0.61; alcohols ( $C_4$ - $C_6$ ), 1.68-0.64. In contrast, tributyl phosphate (TBP) was found in the present work and other previous studies to give  $K_D$  of approximately 2.3. The relatively high  $K_D$  of TBP is probably related to the high polarity of the phosphoryl bond ( $\text{>P}\rightarrow\text{O}$ ), which enables it to act as a Lewis base.

Values of  $K_D$  found for compounds containing the carbonyl group ( $\text{>C=O}$ ) are shown in Table IA. Substituents are either ethoxy groups ( $C_2H_5O-$ ) or ethyl groups ( $C_2H_5-$ ). The more electronegative ethoxy groups serve to decrease  $K_D$ , because they decrease the electron-donating ability of the carbonyl oxygen and diminish its Lewis basicity. Similar behavior for phosphoryl compounds would lead to an increase of  $K_D$  by substituting alkyl groups for the alkoxy groups in TBP, leading successively to phosphonates, phosphinates, and phosphine oxides. This prediction was reinforced by recent indications that a mixture of trioctylphosphine oxide (TOPO) and an undisclosed diluent is an effective solvent for extraction of acetic acid (2-4).

Extending the argument of Lewis basicity for extraction of acetic acid leads to long-chain amines as solvents. These compounds can react with organic or mineral acids and form ammonium salts or ion pairs (1, 5, 6). Experiments were therefore performed to characterize the effectiveness of solvent

mixtures containing alkylamines or phosphine oxides.

## Experimental Procedure

Fifty milliliters of standard acid (0.5 wt % acetic acid or 0.4 wt % formic acid) solution in water was shaken for 5 min with 50 mL of the organic phase in a separatory funnel. After the two layers had separated for 1 h, 25 mL of the aqueous phase was removed and titrated with 0.05 N NaOH. A Corning Model 12 pH meter was used to monitor pH changes during the titration. Twenty-five milliliters of the organic layer was removed and washed with an excess amount of 0.1 N NaOH in another separatory funnel. After the two layers had separated for 1 h, 25 mL of the aqueous phase was back-titrated with 0.05 N HCl. From the endpoints of these two titrations, the aqueous layer and organic layer acetic acid concentrations were calculated.

A material balance was made by comparing the sum of the amounts of acid found in the aqueous and organic phases with the amount of acid in the original aqueous standard. The percent material balance deviation (% MBD) was computed as

$$\% \text{ MBD} = \frac{[(\text{amount of acid in aqueous phase}) + (\text{amount of acid in organic phase}) - (\text{amount of acid in aqueous standard})]}{(\text{amount of acid in aqueous standard})} \times 100 \quad (1)$$

Generally the amount of acid found in the two product phases was between 1 and 15% higher than the amount in the aqueous standard. From blank runs, in which organic phases were washed with NaOH, it was found that several of the organic constituents interfered with the measurement of acid in the organic phase. By correcting the experimental organic layer acid concentrations through the blank measurements, it was possible to obtain material balances agreeing within 5%.

In these cases where the only significant source of error was found in the organic-phase acid measurement, the distribution coefficient,  $K_D^{\text{aq}}$ , was calculated from the standard feed acid concentration and the final aqueous phase acid concentration,

$$K_D^{\text{aq}} = \frac{[(\text{amount of acid in aqueous standard}) - (\text{amount of acid in aqueous phase})]}{(\text{amount of acid in aqueous phase})} (1/\rho_{\text{org}}) \quad (2)$$

where  $\rho_{\text{org}}$  = initial density of organic phase.

The exception to this procedure came when trioctylphosphine oxide (TOPO) was used as the solvent. Because the higher solubility of this base, or of an impurity present in it, in the aqueous phase interfered with the aqueous-phase analysis, the material balance deviation was from 1 to 15% low. In this case the distribution coefficient,  $K_D^{\text{org}}$ , was calculated from the standard-feed acid concentration and the corrected organic-phase concentration, which was measured as before by washing organic-phase blanks with NaOH to determine the correction term to be added to the experimentally determined organic acid concentration.

$$K_D^{\text{org}} = \frac{\{(\text{corrected amount of acid in the organic phase}) - [(\text{amount of acid in the aqueous standard}) - (\text{corrected amount of acid in the organic phase})]\}}{(1/\rho_{\text{org}})} \quad (3)$$

Table I. Molecular Structure of Some Alkoxy-Substituted Carbonyl and Phosphoryl Solvents, and the Effect of the Substituted Groups on the Acetic Acid Distribution Coefficients

OR   C=O   OR <b>2A</b>	OR   C=O   R <b>3A</b>	R   C=O   R <b>4A</b>	OR   ROP→O   OR <b>1B</b>	OR   ROP→O   R <b>2B</b>	OR   RP→O   R <b>3B</b>	R   RP→O   R <b>4B</b>
A. Carbonyl solvent (with substituted ethoxy groups, -OCH <sub>2</sub> CH <sub>3</sub> )			B. Phosphoryl solvent (with substituted butoxy groups, -OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> )			
Compd	No. of ethoxy groups	K <sub>D</sub> <sup>a</sup>	Compd	No. of butoxy groups	K <sub>D</sub> <sup>a</sup>	
<b>1A.</b> None exists	3		<b>1B.</b> Tributyl phosphate	3	2.3	
<b>2A.</b> Diethyl carbonate	2	0.14	<b>2B.</b> Dibutyl butylphosphonate	2	2.7	
<b>3A.</b> Ethyl propionate	1	0.37	<b>3B.</b> Butyl dibutylphosphinate	1		
<b>4A.</b> 3-Pentanone	0	0.48	<b>4B.</b> Tributylphosphine oxide	0	4.5 <sup>b</sup>	

<sup>a</sup> Aqueous feed = 0.5 wt % acetic acid. <sup>b</sup> 37.3 wt % solution in Chevron Solvent 25. No diluent used for other solvents.

Table II. Experimental Results for the Extraction of 0.5 Wt % Acetic Acid with Different Phosphoryl Solvents in Chevron Solvent 25

Solvent concn		% acetic acid removed	K <sub>D</sub>	K <sub>D</sub> /w
Molarity	Wt %			
(A) Tributyl Phosphate (TBP)				
0	0	0.8	0.009	
0.501	15.2	20	0.28	1.8
0.507	44.1	46	0.93	2.1
2.51	71.2	60	1.6	2.2
3.65	100.0	68	2.2	2.2
3.65	100.0	68	2.2	2.2
(B) Dibutyl Butylphosphonate (DBP)				
0.500	13.5	28	0.45	3.3
4.07	100.0	72	2.7	2.7
(C) Tributylphosphine Oxide (TBPO)				
0.507	12.5	64	2.1	17
0.882	22.2	75	3.4	15
1.509	37.3	80	4.5	12
(D) Triphenylphosphine Oxide (TPPO)				
0.201	6.4	12	0.16	2.5

In eq 1-3 no correction was made for the partial miscibilities of the two phases; such corrections would have been quite small.

Relatively unstable emulsions formed on vigorous shaking of the two phases when the solvents contained either the alkylphosphine oxides or the amines. The two phases generally appeared to separate in 1-5 min. A more stable emulsion formed when the organic TOPO phase was stripped with caustic; however, this emulsion could be broken in 30 s to 1 min by addition of a small amount of salt.

Trioctylamine (TOA) and trisooctylamine (TIOA) were obtained from ICN Chemicals. Phosphoryl compounds were supplied by Apache Chemicals, Inc. Seward, Ill. Chevron Solvent 25 was donated by Chevron Chemical Co., Richmond, Calif. Other diluents were chemically pure laboratory reagents from conventional sources.

## Results and Discussion

**Basicity of Solvents.** Table IB gives measured values of  $K_D$  for various pure butyl- and butoxyphosphoryl compounds as solvents. For tributylphosphine oxide (TBPO) the result is for a solvent mixture containing 37.3 wt % TBPO in a diluent of Chevron Solvent 25, a mixture of approximately C<sub>8</sub> alkylaromatics. These results confirm the analogy to carbonyl solvents, wherein exchanging alkyl for alkoxy substituents increases the Lewis basicity through inductive effects, and increases  $K_D$  for acetic acid.

**Diluent Concentrations.** Table II shows values of  $K_D$  for acetic acid measured with solvent mixtures composed of various

Table III. Experimental Results for the Extraction of 0.5 Wt % Acetic Acid with Trioctylphosphine Oxide in Diluent D<sup>a</sup>

Solvent concn			% acetic acid removed	K <sub>D</sub>	K <sub>D</sub> /w
Molarity	Wt %	Mol %			
0.	0	0	18	0.30	
0.201	10.5	3.0	50	1.3	12
0.349	18.1	5.4	70	3.1	17
0.513	25.9	8.4	78	4.7	18
0.898	44.2	17.1	77	4.4	10
1.22	58.6	26.9	74	3.5	6.0

<sup>a</sup> See Table IV for key to diluents.

Table IV. List of Diluents and Measured Values of  $K_D$  for Acetic Acid from Water into Otherwise Pure Diluent

Symbol	Diluent compn	K <sub>D</sub>	Ref
A	Chevron Solvent 25	0.009	8
B	Chloroform	0.028	8
C	<i>n</i> -Hexanol	0.88	8
D	<i>n</i> -Heptane/ <i>n</i> -hexanol 2/1 by vol	0.30	8
E	<i>n</i> -Heptane/ <i>n</i> -hexanol 1/1 by vol		
F	<i>n</i> -Heptane/ <i>n</i> -hexanol 1/2 by vol		
G	Nitrobenzene	0.06	8
H	<i>n</i> -Heptane/chloroform 2/1 by vol <i>n</i> -Heptane	0.02	7

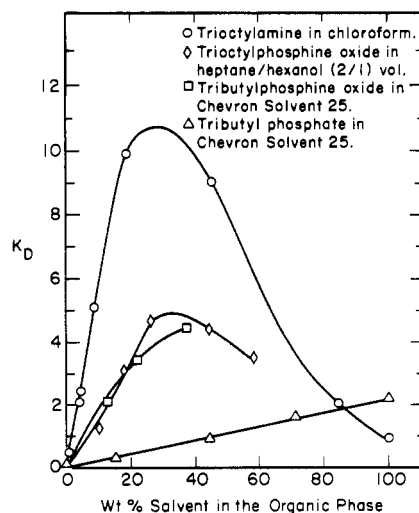


Figure 1. Distribution coefficient,  $K_D$ , as a function of solvent concentration (wt %) in the organic phase.

Table V. Experimental Results for the Extraction of 0.5 Wt % Acetic Acid with Trioctylamines in Chloroform

Solvent <sup>a</sup>	Solvent concn			% acetic acid removed	$K_D$	$K_D/w$
	Molarity	Wt %	Mol %			
None	0.0	0.0	0.0	4	0.028	
I	0.0425	1.0	0.4	39	0.44	40
I	0.170	4.2	1.5	75	2.1	50
I	0.170	4.2	1.5	75	2.1	50
N	0.172	4.2	1.5	78	2.4	57
I	0.340	8.7	3.1	38	5.1	59
N	0.680	18.6	7.2	93	9.9	53
N	1.37	44.7	21.5	91	9.0	20
N	2.06	82.4	61.6	63	2.0	2.4
N	2.31	100.0	100.0	43	0.94	0.94

<sup>a</sup> I = triisooctylamine, N = tri-*n*-octylamine.

Table VI. Experimental Results for the Extraction of 0.5 Wt % Acetic Acid Using Trioctylphosphine Oxide in Various Diluents

Solvent concn		Diluent <sup>a</sup>	% acetic acid removed	$K_D$	$K_D/w$
Molarity	Wt %				
0.201	10.5	D	50	1.3	12
0.203	5.5	B	52	0.8	15
0.513	25.9	D	78	4.7	18
0.496	21.8	A	81	4.8	22
0.496	21.8	A	77	3.8	17

<sup>a</sup> See Table IV for key to diluents.

concentrations of butyl- and butoxyphosphoryl compounds in Chevron Solvent 25; a result is also shown for triphenylphosphine oxide (TPPO) in Chevron Solvent 25. Measured values of  $K_D$  for acetic acid in solvent mixtures of TOPO in a diluent composed of heptane and *n*-hexanol are shown in Table III. These results are plotted in Figure 1.

Table IV lists diluents used in the various experiments in the present work and gives measured values of  $K_D$  for the extraction of acetic acid, at low concentrations from water into otherwise pure diluent. Except for hexyl alcohol, the diluents by themselves give quite low values of  $K_D$ .

Comparison of  $K_D$  for TPPO with those of TBPO and TOPO at similar solvent concentrations shows that  $K_D$  for TPPO is appreciably lower. The electronegative phenyl substituents apparently produce the same effect as alkoxy groups in decreasing the Lewis basicity of the phosphoryl oxygen.

The right-hand columns in Tables II and III show values of the quotient of  $K_D$  divided by the weight fraction ( $w$ ) of the phosphoryl compound in the solvent mixture. For TBP and DBP in Table II the value of  $K_D/w$  is insensitive to the concentration of the phosphoryl compound in the solvent mixture. Such behavior might correspond to simple, stoichiometric interaction of acetic acid with TBP or DBP, with no effect of the diluent on the solvent action, no change in extracted species, and no mass-action effect from consumption of the phosphoryl compound. A more complicated interaction appears to occur in the case of the phosphine oxides, where  $K_D/w$  varies substantially with concentration.  $K_D$  reaches a maximum value at an intermediate solvent-mixture composition for TOPO in the heptane-hexanol diluent.

Table V and Figure 1 show values of  $K_D$  measured for acetic acid with solvent mixtures composed of either triisooctylamine (I) or tri-*n*-octylamine (N) in a chloroform diluent. The two amines behave similarly to one another. The values of  $K_D$  are high compared to those for both phosphoryl solvents and more conventional solvents. This reflects the strong Lewis basicity of the amines. As was the case for the strongly basic phosphine oxides,  $K_D/w$  varies appreciably at higher solvent concentrations, although it varies much less at low amine concentrations in the solvent mixture.

**Nature of the Diluent.** Table VI shows values of  $K_D$  measured for acetic acid with solvent mixtures composed of

Table VII. Experimental Results for the Extraction of 0.5 Wt % Acetic Acid Using Triisooctylamine in Various Diluents

Molarity	Wt %	Diluent <sup>a</sup>	$\bar{\delta}$	% acetic acid removed	$K_D$	$K_D/w$
0.170	6.47	H	8.1	34	0.55	8.5
0.179	8.57	D	8.5	53	1.5	18
0.169	5.14	G	9.9	58	1.2	23
0.171	8.00	E	9.0	63	2.3	29
0.178	8.13	F	9.5	72	3.4	42
0.170	4.22	B	9.3	75	2.1	50
0.176	7.57	C	10.4	81	5.3	70

<sup>a</sup> See Table IV for key to diluents.

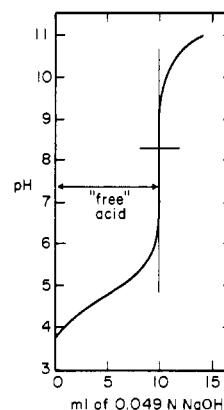


Figure 2. Titration of the aqueous phase after extraction with 0.17 N (4.2 wt %) trioctylamine in chloroform.

TOPO at different concentrations in different diluents. The data are limited, and the effect of the nature of the diluent on  $K_D$  is not apparent.

On the other hand, Table VII shows that  $K_D$  for acetic acid is highly dependent upon the particular diluent used in triisooctylamine solvent systems. The molarity of the base (0.17) in Table VII is about twice the amount corresponding to 1:1 stoichiometric pairing with the acetic acid in the original solution. Extraction of acetic acid appears to increase with increasing solubility parameter [ $\bar{\delta} = (\text{latent energy of vaporization per unit liquid volume})^{1/2}$ ] of the diluent. If acetic acid equilibrates with the amine to form a reaction product which is extracted into the solvent phase, the beneficial effect of higher diluent polarity may reflect a high equilibrium distribution coefficient for this reaction product. There may also be an effect of the diluent on the basicity of the amine in solution or on activity coefficients of reactants and/or the product. For example, one would expect hydrogen bonding of the phosphoryl oxygen with hexyl alcohol.

Yet another important factor relating to the diluent in the amine systems can be inferred from Figures 2-4, which show the measured pH of the aqueous product phase from the extraction as a function of the amount of NaOH added. The two inflection

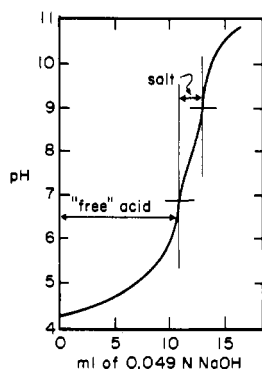


Figure 3. Titration of the aqueous phase after extraction with 2.056 N (82 wt %) trioctylamine in chloroform.

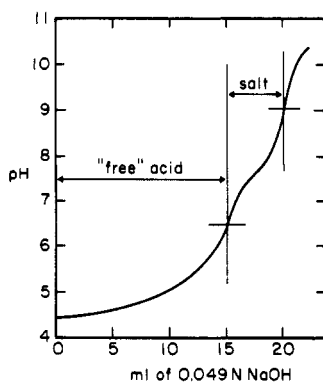


Figure 4. Titration of the aqueous phase after extraction with 100 wt % trioctylamine.

points in Figures 3 and 4 probably mark the  $pK_a$  values of unreacted ("free") acid and of the reaction product ("salt"). If so, the relative amounts of those two species can be taken directly from the titration curves, as shown by the horizontal arrows.

An indication that the second inflection point in the titration curves in Figures 3 and 4 is indeed due to the presence of a salt is that the stirred water phase begins to become cloudy after the free acid has been titrated. This indicates the presence of a second phase, which in these cases would be trioctylamine, a compound which is very insoluble in aqueous solution. Furthermore, an acetic acid material balance including both aqueous and organic phases indicates that acetic acid is also present in the "salt".

Comparison of Figures 2-4 through this interpretation shows that there is no apparent reaction product in the aqueous phase for low amine concentration in the solvent, but that a significant amount develops at higher amine concentrations. Apparently, the diluent is a much better solvent for the reaction product than is the amine itself. As noted above, a more polar diluent may then be a more effective solvent for the reaction product. The competing effects of diluent solvation of reaction product, on the one hand, and of more favorable reaction equilibrium from higher amine concentrations, on the other hand, would then explain the maximum in  $K_D$  for the amine solvents.

The explanation of the maximum in  $K_D$  is less obvious for TOPO. One potential factor that was identified was that the type of diluent affects TOPO solubility. Although amines were readily miscible with all diluents, more polar diluents were needed to obtain high concentrations of TOPO in the solvent. At high concentrations of phosphine oxides an opalescence sometimes appeared in the solvent after aging for a period of a day or more; this was followed by settling of a cloudy-appearing zone. This suggests that the phosphine oxides may form micelles or other aggregates at higher concentrations, which could in turn reduce their solvent power. There may also be solvating effects of the

Table VIII. Experimental Results for the Extraction of 0.5 Wt % Acetic Acid with Amine Solvents of Different Molecular Weights

Solvent concn		Diluent <sup>a</sup>	% acetic acid removed	$K_D$	$K_D/w$
Molarity	Wt %				
(A) Solvent = Tributylamine					
0.169	3.84	C	22	0.34	8.9
0.168	2.15	B	35	0.38	17
(B) Solvent = Triisooctylamine					
0.175	7.57	C	81	5.3	70
0.170	4.22	B	75	2.1	50

<sup>a</sup> See Table IV for key to diluents.

Table IX. Experimental Results Comparing the Extraction of Acetic Acid and Formic Acid with Phosphoryl Solvents

Acid <sup>a</sup>	Solvent concn		% acid removed	$K_D$	$K_D/w$
	Molarity	Wt %			
(A) Solvent = Tributyl Phosphate (TBP), Diluent = Chevron Solvent 25					
Acetic	1.507	44.1	46	0.93	2.1
Formic	1.507	44.1	48	1.0	2.3
Acetic	3.65	100.0	68	2.2	2.2
Acetic	3.65	100.0	68	2.2	2.2
Formic	3.65	100.0	74	2.9	2.9
Formic	3.65	100.0	74	3.0	3.0
(B) Solvent = Trioctylphosphine Oxide (TOPO), Diluent = (2/1) by Volume Heptane and Hexyl Alcohol					
Acetic	0.513	25.9	78	4.7	18
Formic	0.452	23.0	91	12.7	55

<sup>a</sup> Acid concentrations: (A) formic acid = 0.0857 N or 3940 ppm, (B) acetic acid = 0.0869 N or 5220 ppm.

Table X. Experimental Results Comparing the Extraction of Acetic Acid and Formic Acid with an Amine Solvent

Run	Acid <sup>a</sup>	Solvent concn		% acetic acid removed	$K_D$	$K_D/w$
		Molarity	Wt %			
Solvent = Triisooctylamine, Diluent = Heptane/Hexyl Alcohol (2/1) by Volume						
20	Acetic	0.179	8.57	53	1.5	18
65	Formic	0.179	8.57	80	5.6	65

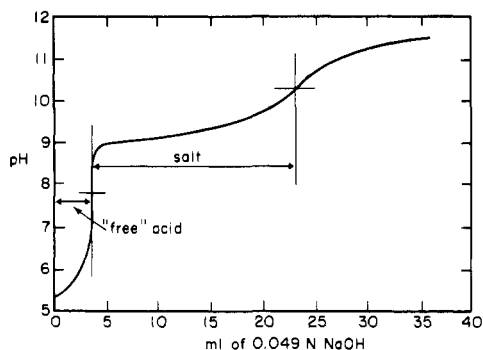
<sup>a</sup> Acid concentrations: acetic acid = 0.0869 N or 5220 ppm, formic acid = 0.0857 N or 3940 ppm.

diluent similar to those found in amine systems, with the data in Table V being too limited to show the effect.

**Molecular Weight of Lewis Base.** Comparison of the results for TBPO and TOPO (Tables II and III and Figure 1) indicates that both are nearly as effective solvents for acetic acid. Apparently there is no significant difference in basicity between the two solvents, and the acetic acid complexes of the two phosphine oxides are comparably insoluble in water.

By contrast, the results in Table VIII show that tributylamine-diluent mixtures are much less effective solvents than trioctylamine-diluent mixtures. Titration curves for the aqueous phase from tributylamine extraction, such as that shown in Figure 5, suggest very large amounts of reaction product in the aqueous phase. Comparison of Figure 5 with Figure 2 indicates strongly that the lower solvent power of tributylamine is attributable to a high degree of extraction of the reaction product into the aqueous phase and supports the interpretation in terms of that effect.

**Loss of Solvent in the Aqueous Phase.** Because amines and phosphine oxides are relatively expensive, even slight losses in the raffinate product would be economically deleterious to an extraction process for waste waters. Therefore the extent to which the amine-acetate reaction product distributes into the aqueous phase is important, even though it may be small. This



**Figure 5.** Titration of the aqueous phase after extraction with 0.17 N (2.2 wt %) tributylamine in chloroform.

indicates an advantage for higher molecular weight amines. Along this line, the water-soluble base in TOPO solvent mixtures, noted in Experimental Procedure, should be explored and identified as TOPO itself, an impurity in the TOPO and/or a complex of TOPO and acetic acid.

**Formic Acid vs. Acetic Acid.** Tables IX and X compare the extractions of formic acid and acetic acid with various phosphoryl and amine solvents. In all cases the formic acid is more ef-

fectively extracted. The results for the amines agree with other authors (5, 6), who have found that these solvents extract stronger acids more effectively.

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## Infrared Spectroscopic Determination of the Liquid-Vapor Equilibrium in the Ternary System Hexamethyldisiloxane-Chloroform-Carbon Disulfide

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The liquid-vapor equilibrium has been determined in the ternary system hexamethyldisiloxane (HMDS)- $\text{CHCl}_3$ - $\text{CS}_2$  by employing the ebulliometric method under isobaric conditions at an atmospheric pressure of 758 mmHg. The infrared spectroscopic technique has been used for determination of the composition of the liquid and vapor phases. Analytical bands for HMDS,  $\text{CS}_2$ , and  $\text{CHCl}_3$  were 2900, 2160, and 3010  $\text{cm}^{-1}$ , respectively. The system has been found to form one phase and to be zeotropic.

#### Introduction

Studies on liquid-vapor equilibria are important in purification and separation processes in industry. Notwithstanding a large number of publications confined to phase equilibria, experimental data concerning equilibrium parameters ( $x$ ,  $y$ ,  $p$ ,  $T$ ) in binary, ternary, and multicomponent systems are still unsatisfactory to meet commercial needs for high-purity products (4).

The primary objective of this work was to determine the liquid-vapor equilibrium in the ternary system hexamethyldisiloxane (HMDS)- $\text{CHCl}_3$ - $\text{CS}_2$  under isobaric conditions at an atmospheric pressure of 758 mmHg.

HMDS,  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$ , is a hydrophobic liquid that provides an excellent solvent for nonpolar compounds. For this reason, and owing to low cost of its manufacture, HMDS is likely to find a wide application (2). However, prior to employing the solvent in industrial processes, its thermodynamic parameters should be determined including liquid-vapor phase equilibria under

isothermic and isobaric conditions.

This work provides a continuation of our studies on the liquid-liquid and liquid-vapor equilibria in binary and ternary systems comprising HMDS (8-10). These studies may reveal certain hitherto unknown features of HMDS associated with a specific structure of its molecule in which two trimethylsilyl groups are linked through an oxygen atom.

The IR spectroscopy has been used in this work as a rapid and relatively accurate technique for the determination of components of the system.

Quantitative IR spectroscopic determinations have been used by many authors in various branches of chemistry (1, 6, 7, 11, 13), but not in studies of phase equilibria.

Analytical utilization of the IR spectroscopy has been found to be possible when a system meets the following requirements: (i) bands due to characteristic modes of individual components do not overlap; (ii) absorption bands should be strong and well developed, (iii) the system should obey the Beer-Lambert law over a definite concentration range.

The system studied in this work has been found to meet all the aforementioned criteria.

It is worth noting that by employing the Fourier transform IR spectroscopic technique, determinations of high accuracy and sensitivity can be accomplished (5).

#### Experimental Section

All compounds used were of analytical reagent grade purity. They were purified before use by fractional distillation.