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Extraction Equilibria of Acetic and Propionic Acids from Dilute Aqueous Solution by Several Solvents

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Abstract

Extraction equilibria of acetic acid and propionic acid with hexane solutions of trioctyl amine, trioctyl phosphine oxide, and tributyl phosphate were studied. The species formed in the systems were estimated, and the distribution coefficients and the equilibrium constants for these species were evaluated.

INTRODUCTION

Though the use of trioctyl amine (TOA), trioctyl phosphine oxide (TOPO), and tributyl phosphate (TBP) for extracting organic acids from aqueous solution has been reported (*1–19*), there is no general agreement on the type of species formed during extraction. Therefore, their kinetics have not been extensively studied, as reported by Lo et al. (*8*).

The purpose of the present work is to identify the complexes formed and to characterize the most efficient solvent to provide a high distribution coefficient for extraction of acetic and propionic acids from water.

Although the species at equilibrium can be described by the law of mass action, there is no generally accepted mathematical description of the whole equilibrium behavior. The analytical equations developed so far to explain the liquid–liquid distribution seem to be inadequate. Different authors have used different stoichiometries of acid-extractant complexes to explain their data. For example, Ricker et al. (*12*) proposed a 1:1 acid amine complex for dilute acid concentrations and aggregations and higher order complexes for higher acid concentrations, whereas Hogfeldt et al. (*3*) proposed 2:1 and 4:1 complexes. A detailed model has been tried in order to prove the equilibrium stoichiometry.

EXPERIMENTAL

The materials used in this work and their properites, together with the supplier's names, are given in Table 1. Ten milliliters of the solvent (extractant + diluent) containing different percentages of the extractant (TOA, TOPO, or TBP) were equilibriated with 75 mL of an aqueous phase of known acid concentration in a shaker for about 2 h. This phase ratio was selected because of its industrial significance. The solution was then left to settle in a thermostated vessel at 25°C to attain equilibrium and for separation of the phases. After thermostating for about 8–10 h, the aqueous phase was centrifuged and the clear aqueous phase was titrated with a known NaOH using Radiometer Autotitrator Model RTS82. The acid content in the organic phase was determined by adding ethyl alcohol and water before titrating with standard alkaline solution. The distribution coefficient (*D*) was calculated as the ratio of molarity of the acid in the organic phase and that in the aqueous phase. Note that in some cases the material balance of the acid does not involve organic- and aqueous-phase titrations; in such instances the data are based on only the aqueous-phase titration values. In such cases the error does not exceed ±5%.

TABLE 1
Chemical Used

Water (H_2O)				
Acetic acid (CH_3COOH), glacial	60.05	99.7	1.049 at 20°C	BDH Chemical Ltd., England
Propionic acid (C_2H_5COOH)	74.08	99.5	0.992 at 20°C	Fluka AG, Switzerland
TOA	353.68	95.0	0.811 at 20°C	Fluka AG, Switzerland
TOPO	386.65	97.0	—	Fluka AG, Switzerland
TBP	266.32	97.0	0.976 at 25°C	Fluka AG, Switzerland
Hexane (C_6H_{14})	86.18	~100	0.662 at 25°C	J. T. Baker Inc., USA
Sodium hydroxide (NaOH)	40.00	~99.9	—	Fluka AG, Switzerland

PHASE EQUILIBRIA

For an (m,n) acid–solvent complex, the reaction and corresponding equilibrium constants are written as

$$m\mathrm{HA}_{\mathrm{aq}} + n\mathrm{S}_0 \leftrightarrow (\mathrm{HA}_m\mathrm{S}_n) \tag{1}$$

$$K_{\mathrm{eq}} = \frac{[\mathrm{HA}_m\mathrm{S}_n]_0}{\{\mathrm{HA}]^m_{\mathrm{aq}}[\mathrm{S}]^n_0} \tag{2}$$

$$[\mathrm{S}]_0 = [\mathrm{S}]_{\mathrm{tot}} - \frac{n}{m}[\mathrm{HA}]_0 \tag{3}$$

By using Eqs. (2) and (3), we get

$$[\mathrm{HA}]_0 = mK_{\mathrm{eq}}[\mathrm{HA}]^m_{\mathrm{aq}}[\mathrm{S}]^n_0 \tag{4}$$

The distribution coefficient is defined as

$$D = \frac{[\mathrm{HA}]_0}{[\mathrm{HA}]_{\mathrm{aq}}} = \frac{mK_{\mathrm{eq}}[\mathrm{HA}]^m_{\mathrm{aq}}[\mathrm{S}]^n_0}{[\mathrm{HA}]_{\mathrm{aq}}}$$

$$= \frac{mK_{\mathrm{eq}}[\mathrm{HA}]^m_{\mathrm{aq}}\left([\mathrm{S}]_{\mathrm{tot}} - \frac{n}{m}[\mathrm{HA}]_0\right)}{[\mathrm{HA}]_{\mathrm{aq}}} \tag{5}$$

thus

$$\log D = \log mK_{\mathrm{eq}} + \log\left(([\mathrm{SA}]_{\mathrm{tot}} - \frac{n}{m}[\mathrm{HA}]_0)^n[\mathrm{HA}]^{m-1}_{\mathrm{aq}}\right) \tag{6}$$

A plot of

$$\log \mathrm{D} \text{ versus } \log\left(\{[\mathrm{S}]_{\mathrm{tot}} - \frac{n}{m}[\mathrm{HA}]_0\}^n[\mathrm{HA}]^{m-1}_{\mathrm{aq}}\right)$$

should give a straight line with a slope equal to unity and an intercept of ($\log mK_{\mathrm{eq}}$). For different values of m and n, the slope and intercept were calculated by using the least-squares regression for all the data points (N).

The loading Z is defined as $Z_{\text{exp}} = [\text{HA}]_0/[\text{S}]_{\text{tot}}$ and can be predicted as

$$Z_{\text{pred}} = \frac{mK_{\text{eq}}[\text{HA}]_{\text{aq}}^m[\text{S}]_0^n}{[\text{S}]_0 + nK_{\text{eq}}[\text{HA}]_{\text{aq}}^m[\text{S}]_0^n} \tag{7}$$

The free extractant in the organic phase is defined as

$$[\text{S}]_0 = [\text{S}]_{\text{tot}} - nK_{\text{eq}}[\text{HA}]_{\text{aq}}^m[\text{S}]_0^n$$

The error involved in such prediction is calculated by

$$\%\ \text{Error} = \frac{1}{N}\sum_{i=1}^{N}\frac{Z_{\text{exp}_i} - Z_{\text{pred}_i}}{Z_{\text{exp}_i}} \times 100 \tag{8}$$

Different values of m and n are selected and the actual complex should give a slope equal to unity and a minimum percent error when calculating loading and the distribution coefficient.

RESULTS AND DISCUSSIONS

Figures 1 to 6 show experimental curves of the distribution coefficients versus molarity of acetic and propionic acids in the aqueous phase at equilibrium with TOA, TOPO, and TBP as extractants. The data for only one acid concentration are given in Table 2. It is evident that the distribution coefficients for propionic acid are much higher than those for acetic acid. But considering the effect of the different extractants on each acid, it is

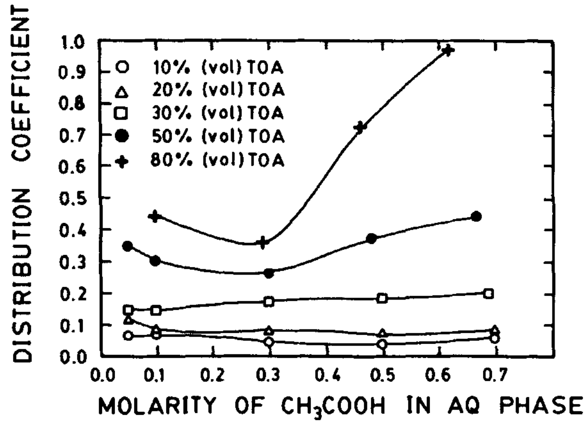


FIG. 1. Distribution coefficients of acetic acid from water at 25°C to TOA in hexane.

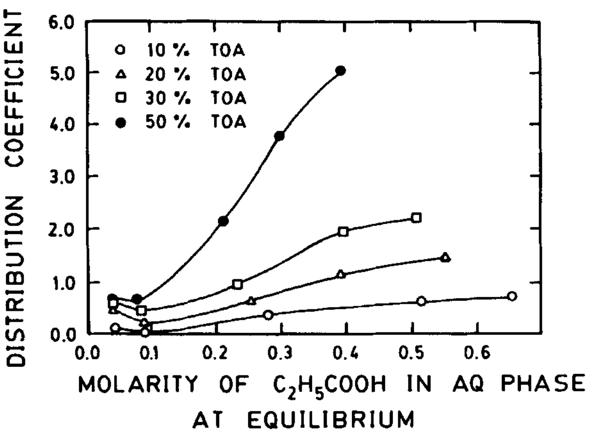


FIG. 2. Distribution coefficients of propionic acid extracted from water at 25°C to TOA in hexane.

obvious that TOPO gives the highest distribution coefficients for acetic acid while TOA does the same for propionic acid. However, TBP also produces reasonably high distribution coefficient values for both acids.

The results are in complete agreement with the theoretical background of the extracting power of these extractants. Among the phosphoryl compounds, tributyl phosphate (TBP) has been chosen for the high polarity of its phosphoryl bond (>P—O), which enables it to act as a Lewis base.

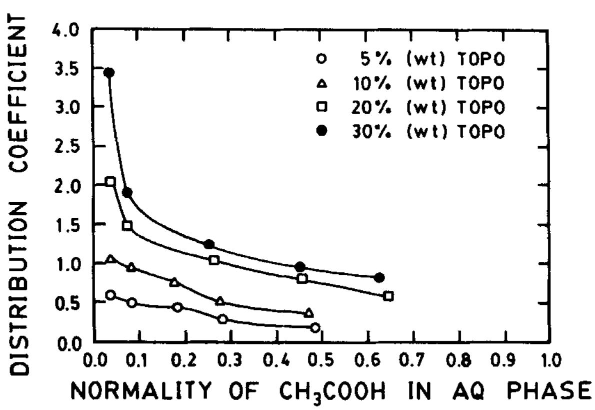


FIG. 3. Distribution coefficients of acetic acid extracted from water at 25°C to TOPO in hexane.

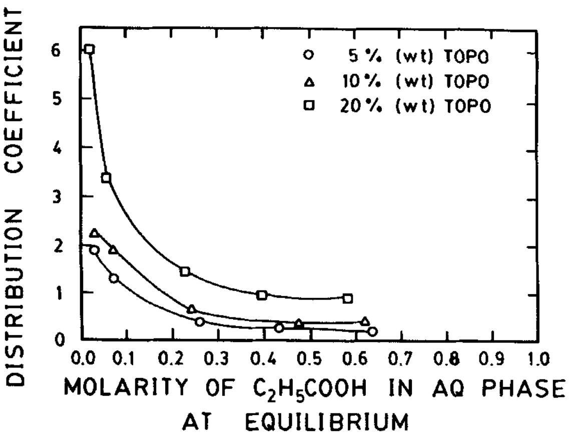


FIG. 4. Distribution coefficients of propionic acid extracted from water at 25°C to TOPO in hexane.

If the alkoxy groups in TBP are substituted for by alkyl groups, then the Lewis basicity is increased through inductive effects. This is the case with trioctyl phosphine oxide (TOPO). Due to its higher basicity, it should give higher distribution coefficients (*17*). In this case the phosphoryl oxygen becomes a still stronger electron donor with the removal of oxygen from the other linkages to the phosphorus atom.

Trioctyl amine is a choice for another kind of Lewis base.

The results for the distribution coefficients are in good agreement with published data, especially for acetic acid (as in Table 3).

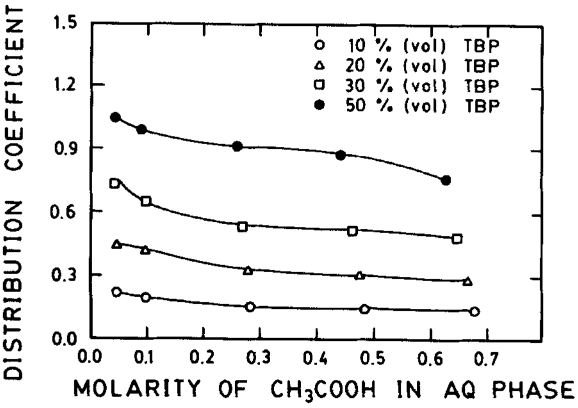


FIG. 5. Distribution coefficients of acetic acid extracted from water at 25°C to TBP in hexane.

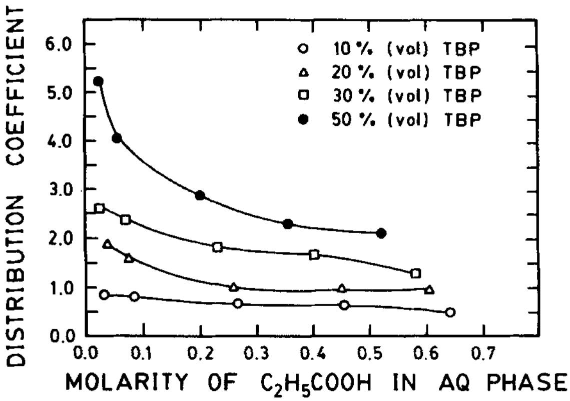


FIG. 6. Distribution coefficients of propionic acid extracted from water at 25°C to TBP in hexane.

TABLE 2
Distribution Coefficients (*D*) for Acetic Acid and Propionic Acid (at 0.4 *M* concentration at equilibrium)

		D	
Extractant	Diluent	For acetic acid	For propionic acid
TOA:	Hexane:		
10 vol%	90 vol%	0.039	0.521
20	80	0.075	1.158
30	70	0.181	1.958
50	50	0.323	5.132
80	20	0.575	—
TOPO:	Hexane:		
5 wt%	95 wt%	0.231	0.313
10	90	0.404	0.426
20	80	0.865	0.975
30	70	1.019	—
TBP:	Hexane:		
10 vol%	90 vol%	0.152	0.674
20	80	0.314	0.949
30	70	0.529	1.670
50	50	0.891	2.200

TABLE 3
Comparison of Distribution Coefficients with Published Data

System in reference, extractant + diluent	Distribution coefficient: Published	Distribution coefficient: This work	Reference
Acetic acid			
TiOA + —	0.505	0.457	*14*
TOA + hexane	0.010	0.020	*5*
TOPO + chevron	3.120	3.250	*12*
TOPO + 2-ethylhexanol	1.120	1.160	*13*
TOPO + kerosene	1.460	1.030	*18*
TOPO + chloroform	0.800	0.785	*16*
TBP + —	1.730	1.680	*10*
TBP + hydrocarbon	2.300	1.740	*13*
TBP + chloroform	0.280	0.290	*16*
Propionic acid			
TiOA + —	6.200	5.660	*14*
TBP + —	8.360	12.40	*9*

Investigations were carried out to determine the association numbers (*m* and *n*) in an acid–extractant complex.

Based on the phase equilibria model, different pairs of complexes were assumed and the slope was calculated by a least-squares fit to all data points. As an example, Table 4 lists trials for the acetic acid–TOPO system along with the percent deviation in loading and in predicted distribution coefficients based on *m* and *n* assumed values. It is obvious that the best complex is that with a slope equal to unity and the lowest percent error. For the acetic acid–TOPO complex, the best was (0.7, 0.5) with a slope of 1.068 and a 5.4% deviation in loading and a 10% deviation in the distribution coefficient. Higher complexes deviate a lot from the real complex satisfying the model equation. For this reason, fractional values less than 1 were tried to fit the data. Results in the final form are given in Tables 5 and 6 for all the systems studied and are also compared with the published data. Note that the aqueous phase acidity used for the analysis of association numbers was kept less than 0.3 *M* to avoid the effect of activities.

The effect of the dissociation of acids was found to be negligible. Comparison of the experimental results with published data (Table 5) shows very good agreement with the work of some authors [Kawano et al. (*5*) and Hogfeldt et al. (*3*)]. None of them used our model equations. Kawano's conclusions were based mainly on the loading curves (Z versus log $[HA]_{aq}$),

TABLE 4
Association Numbers (m,n) Trials by the Computer Program System Acetic Acid–TOPO

m	n	Slope	K_{eq}, 1/mol	% error Z	% error D
0.5	0.4	1.2403	2.0283	10.3	23.1
0.7	0.5	1.0684	2.1592	5.4	10.0
0.9	0.6	0.9198	2.4114	5.9	10.5
1.2	0.6	1.0031	2.9476	11.8	18.2
1.4	0.7	0.8598	3.3800	18.5	23.9
1.2	0.8	0.6898	2.8621	28.2	41.4
1.8	0.8	0.7695	4.500	32.0	37.9
1.2	0.9	0.5772	2.8045	39.7	57.1
1.7	0.9	0.6601	3.9085	41.6	50.8
1.3	1.0	0.5110	2.9020	50.2	67.2
2.2	1.0	0.6132	5.3600	55.2	62.4
3.0	1.0	0.0640	10.4747	60.0	64.2
4.0	1.0	0.6560	26.5760	64.4	66.9
1.4	1.1	0.4574	2.9870	59.6	75.0

whereas Hogfeldt's curve shows results different than his predictions. Siebenhofer et al. (*14*) used a different extractant (TiOA), which may be the reason for the deviation of n values. Note that there is not enough data on propionic acid for a comparison to be made. Loading curves for our experimental results with TOA are shown in Fig. 7; the shape of our experimental curves coincide with those of Hogfeldt et al. (*3*) and Sie-

TABLE 5
Results and Comparison for Acetic Acid

System extract and diluent	Recommended complex structures (m,n)	Log (equilibrium constant) for (1,1) (2,1) (3,1), (4,1)	Reference
TOA + hexane	(1,1) (2,1)	−.63 −.199 .37 .98	This work
TOA + hexane	(1,1) (2,1) (3,1) (4,1)	−.85, −1.2, − 2.8 − 2.1	*6*
TLA + heptane	(2,1) (4,1)	−.68 −2	*3*
Amberlite LA-2 + hexane	(1,1) (2,1) (3,1) (4,1)	−2 .42 −.88 −.63	*4*
Alamine 336 + 15% $CHCl_3$ in heptane	(1,) (2,1) (3,1)	.11 .02 −.21	*15*
Alamine 336 + 2 ethyl-l-hexanol	(1,1)	1.83	*12*
Adogen 283 + 2-heptanone	(1,1) (2,1) (3,1)	2.09 2.59 2.52	
Chloroform		2.12	*2*
Trisoctylamine	(3.16,1)		*14*
Tridecylamine + benzene	(1,1) (2,1) (3,1)	.38 .20 .85	*1*
TOPO + hexane	(.7,.5)	For (.7,.5) = .334	This work
TBP + hexane	(1,1)	0.244	This work

TABLE 6
Results and Comparison for Propionic Acid

System extract and diluent	Recommended complex structures (*m*,*n*)	Log (equilibrium constant) for (1,1) (2,1) (3,1) (4,1)	Reference
TOA + hexane	(2.7) (1.7)	For (2.7,1.7) = 1.17	This work
Triisooctylamine	(2.79,1)		*14*
TOA + tridecylamine	(0.62,1)		*14*
TOA + hexane	(1,1) (2,1) (3,1) (4,1)	.13, −.03, 0.14, .40	6
Amberlite LA-2 + hexane	(1,1) (2,) (3,1)	0.18, 1.32, 1.30, 1.55	*4*
Amberlite LA-2 + benzene	(1,1) (2,) (3,1)	.87, 2.35, 3.05	*5*
TOPO + hexane	(0.6,0.4)	For (.6,.4) = 0.492	This work
TOPO + hexane	(1,1)		*7*
TBP + hexane	(0.9,0.9)	For (.9,.9) = 0.345	This work

benhofer et al. (*14*).Figure 8 shows the same trend; however, in this case a very nice loading curve is produced which shows the number of acids per amine to be 2. Here also, the acid concentration was very low.

It is clear from both curves that the amine concentration does not have any effect on the loading, which proves that there is no aggregation.

Equilibrium constants were calculated from the intercept of the slopes as per the model. A comparison with the published values is shown in Tables 5 and 6. The deviation may be explained on the basis that the authors used very high initial acid concentrations.

The pH value of the aqueous phase (2.5–3.1) changes a little after equilibrium is reached, which eliminates the ionization effect in the extraction of these acids.

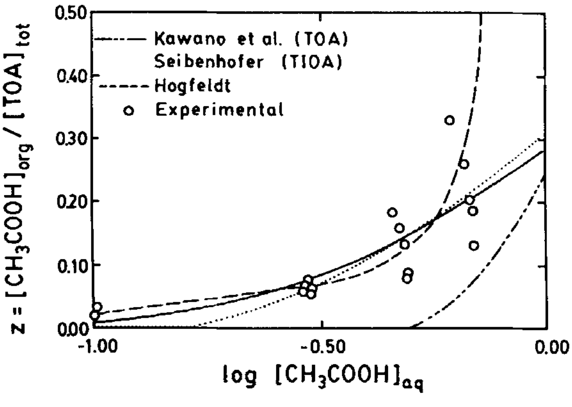


FIG. 7. Loading curves for the system acetic acid–TOA.

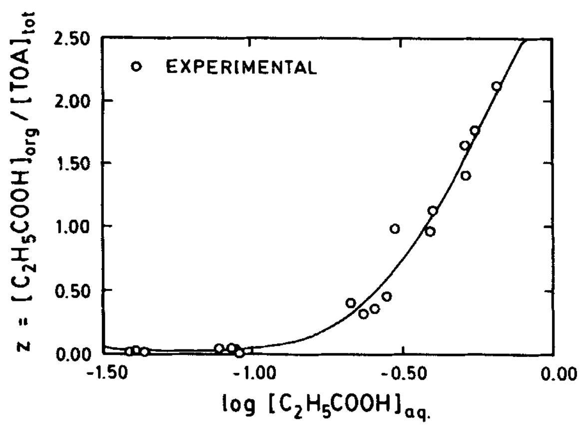
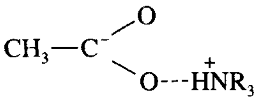


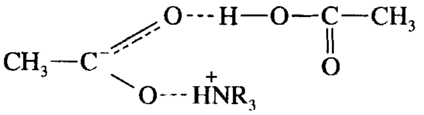
Fig. 8. Loading curve for the system propionic acid–TOA.

The explanation of the structure of the complexes formed should be based on the chemical interactions of the species involved. Spectroscopic studies by different authors revealed that for the (1,1) complex a bond appears in the carboxylate stretching region:



Acetic acid Trialkylamine

and for the (2,1) complex, the first acid forms an ion-pair or hydrogen bond with the amine and the second acid forms a hydrogen bond to the carboxylate in the first acid (also called overloading):



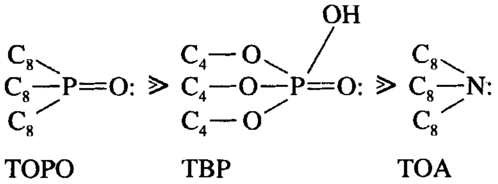
(2,1) Complex

Hence, intramolecular hydrogen bonding is the important determinant information for these complexes.

For monocarboxylic acids in the presence of inert diluents, as in this work, the extractants' concentration does not have any effect on loading because the diluent and the extractant have similar solvating abilities.

Complexes with fractional *m* and *n* values are very difficult to explain. Different complexes may combine to yield fractional values of each species. A hybrid model of this phenomenon is developed in a separate study (*11*).

Different association numbers for different extractants may be explained by looking at the chemical structures of their molecules. Their base strengths decrease in the order (*11*)



TOPO and TBP make complexes through donating electrons, but TOA does it mostly by sharing its ionic strength.

CONCLUSIONS

For dilute acids, the value of *D* decreases in the order TOPO > TBP > TOA. For more concentrated acid solutions, the sequence varies: In the case of CH_3COOH, TOPO > TBP > TOA; in the case of C_2H_5COOH, TOA > TBP > TOPO.

Based on this study it is proposed that the complex $S(HA)_n$ is formed, where $n = 1, 2, 3, 4$, and 5.

GLOSSARY

D	distribution coefficient
HA_{aq}	acid in the aqueous phase at equilibrium
HA_0	acid in the organic phase at equilibrium
K_{eq}	equilibrium constant
m, n	association numbers in the complex
S_0	free extractant in the organic phase
S_{tot}	initial extractant
Z	$[HA]_0/[S_{tot}]$

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