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Solvent Extraction Equilibria of Acids. VI. The Extraction of Several Mono- and Dicarboxylic Acids with Trioctylphosphine Oxide in Hexane

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The solvent extraction equilibria of acetic, propionic, and butyric acid and mono-, di-, and trichloroacetic acid (HA), as well as those of oxalic, malonic, succinic, glutaric, and adipic acid (H_2A), have been determined in liquid-liquid systems of hexane containing none or a certain amount of trioctylphosphine oxide (E) and an aqueous 1 mol dm^{-3} chloride solution at 25 °C. The constants, $K_d=[HA]_{org}/[HA]$, $K_{dim}=[(HA)_2]_{org}/[HA]_{org}^2$, $K_{ex1}'=[HAE]_{org}/[HA][E]_{org}$, $K_{ex2}'=[H_2AE_2]_{org}/[H_2A][E]_{org}^2$, and $\beta_{1(org)}=[HAE]_{org}/[HA]_{org}[E]_{org}$, have then been determined from the data. It was found that, among the three fatty acids, the value of K_{ex1}' was higher as the chain length increased, but the values of $\beta_{1(org)}$ were nearly all the same, while among the chloroacetic acids they were higher as the number of chloride atom increased. The extraction of the dicarboxylic acids with E was not very different, although the number of the $-CH_2-$ between the two carboxyl groups changed from zero to four.

In this series of reports, we have reported on the solvent extraction behavior of various inorganic acids with trioctylphosphine oxide (TOPO) in organic solvents.[1-5] In the present paper, we will study the extraction equilibria of acetic, propionic, and butyric acid, mono-, di-, and trichloroacetic acid, and oxalic, malonic, succinic, glutaric, and adipic acid, in 1 mol·dm^{-3} chloride solutions with TOPO in hexane at 25 °C.

Experimental

The experiments were performed much as has previously been described.[1-5] All the reagents were of an analytical grade. The acid was dissolved in 1 mol dm^{-3} hydrochloric acid or 1 mol dm^{-3} (H, Na)Cl ionic media, placed in contact with the same volume of hexane containing none or a certain amount of TOPO in a stoppered glass tube by means of a mechanical shaker, and centrifuged. A certain amount of the organic phase was then pipetted off and titrated with a standard barium hydroxide solution, using phenolphthalein as the indicator.

Statistical

Here the subscript "org" and the lack of subscript denote the species in the organic and aqueous phases respectively. The mono- and dicarboxylic acids are represented by HA and H_2A respectively, while TOPO is represented by E. Since the extraction of dicarboxylic acid species containing no E was negligible, and that of the HAE_2 and H_2AE species was also found to be negligible, the following equilibrium constants were employed for the data analysis:

$$K_d = [HA]_{org}[HA]^{-1}, \tag{1}$$

$$K_{dim} = [(HA)_2]_{org}[HA]_{org}^{-2}, \tag{2}$$

$$K_{ex1}' = [HAE]_{org}[HA]^{-1}[E]_{org}^{-1}, \tag{3}$$

$$K_{ex2}' = [H_2AE_2]_{org}[H_2A]^{-1}[E]_{org}^{-2}. \tag{4}$$

The distribution ratio, D, was defined by the ratio of total acid concentrations in the organic and aqueous phases. The latter was calculated from the initial acid concentration in the aqueous phase and the equilibrium acid concentration in the organic phase. The dissociation in 1 mol dm^{-3} hydrochloric acid was negligible except for trichloroacetic acid, and the observed distribution ratio of the dicarboxylic acids was found to be

$$D = [H_2AE_2]_{org}[H_2A]^{-1} = K_{ex2}'[E]_{org}^2. \tag{5}$$

The distribution ratio for the monocarboxylic acids should generally be written as

$$D = ([HA]_{org}+2[(HA)_2]_{org}+[HAE]_{org})([HA]+[A^-])^{-1} = (K_d+2K_d^2K_{dim}[HA]+K_{ex1}'[E]_{org})(1+K_a[H^+]^{-1})^{-1}. \tag{6}$$

The $[A^-]$ or $K_a[H^+]^{-1}$ term was found to be negligible except for trichloroacetic acid; furthermore, the $[HA]_{org}$ and $[(HA)_2]_{org}$ terms or the K_d and $2K_d^2K_{dim}$ [HA] terms were found to be negligible in the presence of TOPO except for the case of butyric acid.

The free TOPO concentration at equilibrium was calculated by subtracting the fraction combined with acid, which could be written as $[HAE]_{org}$ or $2[H_2AE_2]_{org}$. In the case of butyric acid, however, the extraction of the HA and $(HA)_2$ species was corrected by using the data obtained in the absence of TOPO.

The distribution ratio of the fatty acids in the absence of TOPO was plotted as a function of [HA]:

$$\log D = \log(K_d+2K_d^2K_{dim}[HA]), \tag{7}$$

and the constants were obtained by a curve-fitting method.[6]

The other equilibrium constants were obtained by introducing the experimental data into Eq. 5 or 6. Since the acid dissociation was not negligible for trichloroacetic acid, the distribution ratio was obtained at a certain $[E]_{org,initial}$ value as a function of $[H^+]$ in 1 mol dm^{-3} (H, Na)Cl solutions. Then, from these experimental data and a certain assumed value of K_a, the values of K_{ex1}' in Eq. 6 were calculated. Trials were repeated by introducing other assumed values of K_a and the standard deviation of the K_{ex1}' was calculated from each set of values of K_{ex1}'. Then, the values of the standard deviation were plotted against the K_a value. The K_a value which gave the minimum standard deviation was estimated from the plot and was subsequently employed for the data analysis of trichloroacetic acid.

Results

In the present work, a 1 mol dm^{-3} chloride solution was always employed as the aqueous phase. How-

Table 1. Distribution data of mono-, di-, and trichloroacetic acid between hexane containing no TOPO and 1 mol dm^{-3} HCl
The concentrations are in the mol dm^{-3} units.

(a) Monochloroacetic acid

$[HA]_{org,total}\times10^4$ [a]	$[HA]_{total}\times10$	$[HA]\times10$	$[A^-]$ [b]	$[HA]_{org}\times10^4$	$[(HA)_2]_{org}\times10^5$
7.99	8.01	8.01	—	5.80	21.8
4.97	5.34	5.34	—	3.87	9.69
3.89	4.45	4.45	—	3.22	6.73
3.02	3.56	3.56	—	2.58	4.30

(b) Dichloroacetic acid

$[HA]_{org,total}\times10^4$ [a]	$[HA]_{total}\times10$	$[HA]\times10$	$[A^-]$ [b]	$[HA]_{org}\times10^4$	$[(HA)_2]_{org}\times10^4$
21.2	7.45	7.45	—	14.2	5.87
12.1	4.97	4.97	—	9.49	2.61
9.50	4.14	4.14	—	7.91	1.81
7.34	3.31	3.31	—	6.32	1.16
5.40	2.48	2.48	—	4.74	0.651

(c) Trichloroacetic acid

$[HA]_{org,total}\times10^3$ [a]	$[HA]_{total}\times10$	$[HA]\times10$	$[A^-]\times10^2$	$[HA]_{org}\times10^4$	$[(HA)_2]_{org}\times10^3$
5.01	7.86	6.49	13.7	15.2	3.58
2.59	5.24	4.30	9.4	10.1	1.57
1.94	4.37	3.58	7.9	8.38	1.09
1.38	3.50	2.86	6.4	6.69	0.695
0.886	2.63	2.14	4.9	5.01	0.389

a) Experimentally observed values; the other values were calculated from these as in the text. b) The dissociation of mono- and dichloroacetic acid in 1 mol dm^{-3} HCl was negligible.

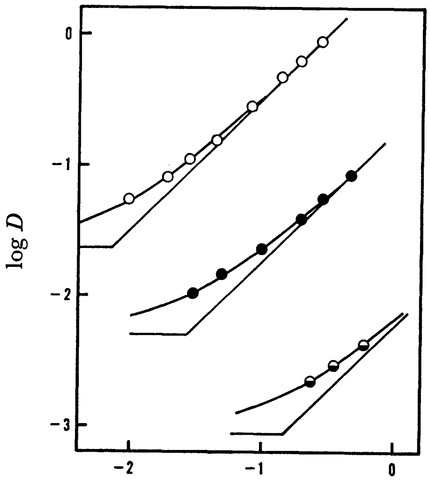


Fig. 1. Distribution ratio of acetic (◒), propionic (●), and butyric (○) acid between hexane and 1 mol·dm^{-3} HCl as a function of the acid concentration in the aqueous phase at equilibrium. The solid curves were obtained by introducing the constants K_d and K_{dim} into Eq. 7.

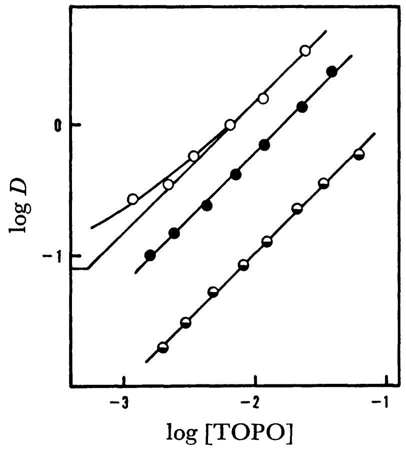


Fig. 2. Distribution ratio of acetic (◒), propionic (●), and butyric (○) acid between hexane containing various amounts of TOPO and 1 mol dm^{-3} HCl initially containing 1×10^{-1}, 3×10^{-2} and 2×10^{-2} mol dm^{-3} of acetic, propionic, and butyric acid, respectively, as a function of the free TOPO concentration. The solid curves were obtained by introducing the extraction constants K_d, K_{dim}, and K_{ex1}' into Eq. 6.

ever, no chloride was ever detected in the organic phase by means of a silver-nitrate-solution test. Thus, the extraction or co-extraction of chloride was concluded to be negligible. This is quite acceptable in view of previous results of this series of reports.[2)]

Figure 1 gives the extraction curves of the three fatty acids in the absence of TOPO as a function of the acid concentration in the aqueous phase, and Fig. 2 shows them as a function of the TOPO concentration. Table 1 lists the distribution data of mono-, di-, and trichloroacetic acid between 1 mol dm^{-3} hydrochloric acid and hexane containing no TOPO, and Fig. 3 shows the extraction curves of mono- and dichloroacetic acid with TOPO, while Table 2 lists the results of the extraction of trichloroacetic acid in 1 mol dm^{-3} (H, Na)Cl solutions with TOPO in hexane. The equilibrium constants obtained from these data by the method described are listed in Table 3. Figure 3 also shows the data of acetic acid in Fig. 2 and the curve for trichloroacetic acid calculated by means of the K_{ex1}' value in Table 3.

TABLE 2. EXTRACTION DATA OF TRICHLOROACETIC ACID
Aq. phase: 1 mol dm^{-3} (H, Na)Cl initially containing 2×10^{-2} mol dm^{-3} of the acid. Org. phase: hexane containing 2×10^{-2} mol dm^{-3} of TOPO. All the concentrations are in mol dm^{-3} units.

$[H^+]\times10^2$	$[HA]_{org}\times10^2$	$[HA]\times10^3$	$[E]_{org}\times10^3$	$\log K_{ex1}'$
100	1.82	1.6	1.78	3.90
60.0	1.79	1.9	2.08	3.80
40.0	1.76	2.2	2.38	3.72
24.0	1.73	2.5	2.68	3.71
16.0	1.70	2.8	2.98	3.71
9.55	1.66	3.2	3.38	3.73
5.75	1.61	3.7	3.88	3.76
3.98	1.55	4.3	4.48	3.77
2.63	1.47	5.1	5.28	3.75
1.95	1.43	5.5	5.68	3.78
1.45	1.35	6.3	6.48	3.76
1.17	1.32	6.6	6.78	3.83
1.00	1.30	6.8	6.98	3.83
0.708	1.19	7.9	8.08	3.81
				(Av. 3.78)

$\log K_{ex1}'$ was calculated by using the value, $K_a=0.24$, which gave the mininum standard deviation of the K_{ex1}'.

Discussion

The extraction and dimerization of fatty acids in liquid–liquid systems have been studied for a long time.$^{7)}$ Most of the previous data have been obtained by employing an aqueous fatty acid solution containing no or only a small amount of an electrolyte as the aqueous phase. In the present study, however, 1 mol dm^{-3} of chloride was always in the aqueous phase; this could cause a salting-out effect, as was found previously.$^{8)}$ However, the K_d values of the fatty acids from the present ionic medium into hexane were still lower than those in the previous study$^{8)}$ from an aqueous solution containing no other salts into carbon tetrachloride (the K_d values were 3.20×10^{-3}, 1.51×10^{-2}, and 3.83×10^{-2} respectively for acetic, propionic, and butyric acid).

There has been a report on the dimerization constant of acetic acid in hexane$^{9)}$ and also one on the distribution and dimerization constants of propionic acid in the hexane–aqueous 0.1 mol dm^{-3} (H, Na)ClO$_4$ system.$^{10)}$ The present dimerization constants of these fatty acids in hexane are very similar to each other. The same tendency, a constancy of the dimerization constants among fatty acids of different chain lengths, was also found in several other organic solvents.$^{10)}$ At the same time, it was also reported that the values increased upon an increase in the chain length of these fatty acids in carbon tetrachloride.$^{8)}$

In Fig. 2, the extracted acid species in the organic phase in the presence of TOPO was, for all practical purposes, monomeric except the butyric acid in the lower TOPO concentration region.

From Eqs. 1 and 3, the following equation is obtained:

$$K_{ex1}' = K_d\beta_{1(org)}, \tag{8}$$

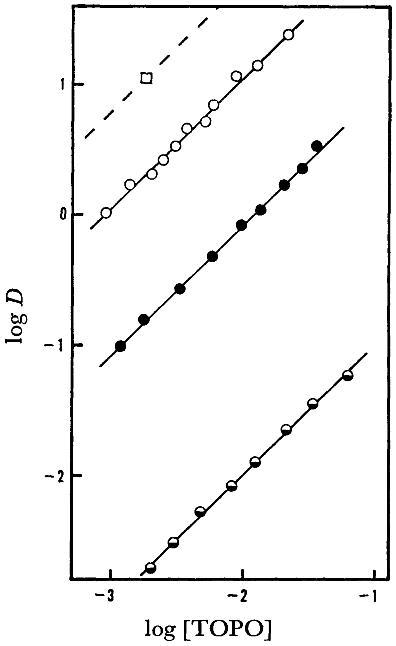
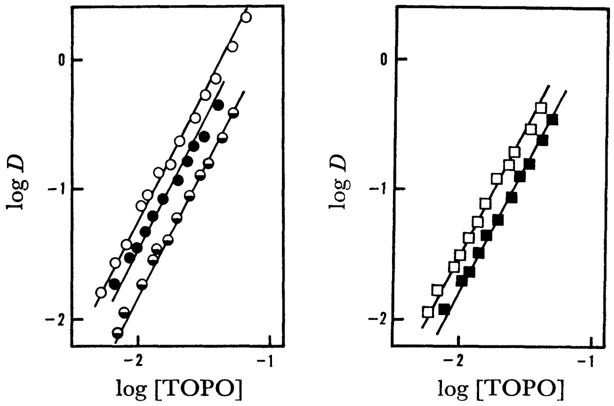


Fig. 3. Distribution ratio of mono- (●), di- (○), and trichloroacetic acid (☐), and acetic acid (◒) between hexane containing various amounts of TOPO and 1 mol dm^{-3} HCl initially containing 3.2×10^{-2} and 3.0×10^{-2} mol dm^{-3} of mono- and dichloroacetic acid, respectively as a function of the free TOPO concentration. The curve for trichloroacetic acid was calculated from K_{ex1}' in Table 3 and for acetic acid was taken from Fig. 2.



Figs. 4 and 5. Distribution ratio of five dicarboxylic acids between hexane containing various amounts of TOPO and 1 mol dm^{-3} HCl initially containing 2.6×10^{-2}, 9.6×10^{-2}, 9.9×10^{-2}, 1.0×10^{-1}, and 1.0×10^{-1} mol dm^{-3} of adipic (○), glutaric (●), succinic (◒), malonic (■), and oxalic (☐) acid, respectively, as a function of the free TOPO concentration.

where $\beta_{1(org)}$ is the association constant of TOPO with monomeric acid in the organic phase. This is written for a monocarboxylic acid as

$$\beta_{1(org)} = [HAE]_{org}[HA]_{org}^{-1}[E]_{org}^{-1}. \tag{9}$$

As may be seen from Table 3, the values of $\beta_{1(org)}$ were nearly the same among all these fatty acids. Furthermore, the association constants of these acids with TOPO

Table 3. Summary of equilibrium constants

(a) Fatty acids					
Acid	$\mathrm{p}K_a$	$\log K_d$	$\log K_{\mathrm{dim}}$	$\log K_{\mathrm{ex1}}'$	$\log \beta_{1(\mathrm{org})}$
CH_3COOH	4.30	−3.06	3.59	1.01	4.07
C_2H_5COOH	4.66***	−2.30	3.56	1.77	4.07
C_3H_7COOH	4.74**	−1.64	3.48	2.17	3.81
(b) Chloroacetic acids					
Acid	$\mathrm{p}K_a$	$\log K_d$	$\log K_{\mathrm{dim}}$	$\log K_{\mathrm{ex1}}'$	$\log \beta_{1(\mathrm{org})}$
$CH_2ClCOOH$	2.66	−3.14	2.51	1.93	5.07
$CHCl_2COOH$	1.30†	−2.72	2.16	3.06	5.78
CCl_3COOH	0.62††	−2.63	2.89	3.78	6.41
(c) Dicarboxylic acids					
Acid	$\mathrm{p}K_{a1}$	$\mathrm{p}K_{a2}$	$\log K_{\mathrm{ex2}}'$		
$(COOH)_2$	1.07	3.57	2.49		
$CH_2(COOH)_2$	2.74	5.11	2.22		
$C_2H_4(COOH)_2$	3.98	5.50	2.18		
$C_3H_6(COOH)_2$	4.09*	4.84*	2.52		
$C_4H_8(COOH)_2$	4.28***	5.00***	2.74		

The $\mathrm{p}K_a$ values were taken from Ref. 11. The ionic concentration and temperature were: (no mark) 1 mol dm^{-3} and at 30 °C for acetic acid, 20 °C for monochloroacetic acid and 25 °C for the others; (*) 0.5 mol dm^{-3} and at 25 °C; (**) 0.2 mol dm^{-3} and at 25 °C; (***) 0.1 mol dm^{-3} and at 20 °C for propionic acid and 25 °C for adipic acid; (†) no specification on the ionic medium and at 25 °C; (††) 1 mol dm^{-3} and at 25 °C obtained in the present work.

were larger than the values of K_{dim}. This seems to be reasonable because the phosphoryl-oxygen in TOPO should be a stronger accepter of hydroxyl-hydrogen in the carboxyl group than the carbonyl-oxygen in the carboxyl group; thus, the former can combine with the hydroxyl group more strongly than the latter.

The dissociation of mono- and dichloroacetic acid is negligible in 1 mol dm^{-3} hydrochloric acid. However, that of trichloroacetic acid should be taken into account. A $\mathrm{p}K_a$ value of 0.62 was finally obtained from the data analysis in 1 mol dm^{-3} (H, Na)Cl. The above present value agrees with an estimated value, 0.7, in the literature.[11]

The distribution constant of the monomer, K_d, of monochloroacetic acid was nearly the same as that of acetic acid. However, it was higher as the number of the chlorine atom increased. The replacement of a hydrogen atom with a chlorine atom should change the charge distribution in the molecule, and it could cause an decrease in the K_d by increasing the aquophilic character. However, at the same time, it should cause an increase in the molar volume, which should in turn increase the K_d value by increasing the aquofobic character. The observed value of K_d should be caused by the over-all effect of these two factors.

The extraction of three chloroacetic acids with TOPO was much better than acetic acid, and, among them, the extraction was better when the acid was stronger. The distribution ratio of trichloroacetic acid was too high to measure accurately under the conditions employed for the other two acids; only a calculated extraction curve could be obtained from the data in Table 2, as is given in Fig. 3. The extraction of these chloroacetic acids into hexane containing no TOPO was found to be very poor, as may be seen from Tables 1 and 3. Thus, the good extraction of these acids with TOPO should be attributed to their great tendency to associate with it in the organic phase.

The $\log \beta_{1(\mathrm{org})}$ value between dibutylphosphoric acid and TOPO in hexane was reported to be 4.88;[12] this is lower than chloroacetic acids, but higher than the fatty acids.

It was found that the distribution ratio of all the five dicarboxylic acids studied in the present work was very low in the absence of TOPO; the values of D were estimated to be always lower than 10^{-3}.

These low D values in the absence of TOPO are probably due to a strong hydration of these acids. However, these hydrating water molecules could be replaced by TOPO. Since two TOPO molecules solvated one acid molecule in the organic phase, each carboxyl group should combine with one TOPO by means of a hydrogen-bond; thus, the aquophilic character diminished. It is noticeable that the extraction constants of these dicarboxylic acids are rather similar to each other; this was not observed among the fatty acids which were extracted better when the chain was longer. Among the fatty acids, the values of $\mathrm{p}K_a$ are rather similar to each other; consequently, the abilities to associate with TOPO are probably also similar to each other, as is indicated by the values of $\log \beta_{1(\mathrm{org})}$. Thus, the chain length, in other words, the difference in the molar volume, was the main factor affecting the extraction behavior of the fatty acids. On the other hand, two inverse effects probably determine the degree of extraction of the dicarboxylic acids. The strength of the acid, especially that which dissociates first proton, is greater when the chain is shorter, and, although the values of $\beta_{1(\mathrm{org})}$ could not be determined for these acids, it seems a reasonable guess that the stronger the acids, the stronger the interaction with TOPO. Thus, acids of shorter chains are favorable for the extraction. An increase in the chain length, however, probably increases the aquofobic character of the molecule, and, from this standpoint, longer chains are more favorable for the extraction. The fact that the extraction constants of these dicarboxylic acids are rather similar to each other seems to indicate that two inverse effects are cancelling each other out. We can not yet make a comment on the steric effect of the two TOPO molecules combined with one dicarboxylic acid molecule.

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