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Equilibrium of Aqueous Propionic Acid with Trioctylamine in Dodecane

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The equilibrium between propionic acid (HA) in an aqueous solution with trioctylamine ($\overline{B}$) in dodecane was measured at 303 K. Propionic acid was found to be extracted into the organic solution as $\overline{(HA)_n B}$ (n = 1, 2, 3, and 4) complexes when the propionic acid concentration in aqueous solution was less than 1.0 mol·dm^{-3}. However, at concentrations above 1.0 mol·dm^{-3}, the consecutive reaction between complexes proceeded simultaneously with the extraction reaction between the complexes and propionic acid. The concentration of water in the dodecane phase was significantly affected by the concentrations of trioctylamine and propionic acid in the organic phase.

Introduction

Long-chain alkylamines have been used as an extractant of acids and precious metals (*1−8*). Trioctylamine, a tertiary amine, reacts with acids to form oil-soluble complexes. It is expected as an extractant in the separation and the concentration of fatty acids in fermentation engineering (*6*).

For treatment in dilute systems containing a fermented medium and waste water, extractants encapsulated in microcapsules and extractants contained in impregnated resins have been developed (*7−10*). In our study, dodecane was used as a diluent to prepare trioctylamine enclosed in styrene−divinylbenzene copolymer microcapsules by *in-situ* polymerization. Dodecane is representative of poor solvents for polystyrene (*7*, *8*).

In amine extraction systems, many studies have been made using toluene, benzene, 4-methyl-2-pentanone, and hexane as the diluent. However, measurements have not been reported for dodecane.

In the present work, the equilibrium between aqueous propionic acid and dodecane + trioctylamine was measured. The results were analyzed using the extraction model, and they were compared with previous measurements (*2*, *11*).

Experimental Section

Trioctylamine (99.7 mass %) was purchased from Koei Chemical Co., Ltd., and was used without further purification. Propionic acid and dodecane were GR grade of Wako Pure Chemical Industries Ltd. and were used without further purification.

Equal volumes of known concentrations of trioctylamine + dodecane and propionic acid + water, where each initial concentration was known, were shaken in an Erlenmeyer flask at 303 K to attain equilibrium. The temperature was controlled within ±0.2 K. The solutions were shaken for 1 h, and left to settle for 2 h prior to analysis. Trioctylamine concentrations in dodecane were determined by titration with hydrochloric acid in a methanol + butanol (1:1 volume ratio) solution using bromocresol green as the indicator, and propionic acid concentrations in the aqueous phase were determined by titration with aqueous sodium hydroxide solution using phenolphthalein as the indicator.

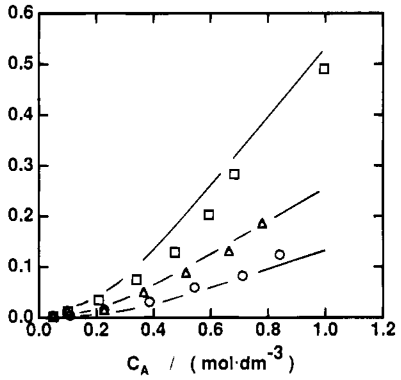

Figure 1. Relation between propionic acid concentration in organic solution, $\overline{C_A}$, and in aqueous solution, C_A, ranging in C_A below 1.0 mol·dm^{-3}, with various concentrations of trioctylamine. The solid lines represent calculated results with the derived equilibrium constants: (○) $\overline{C_{B,0}}$ = 0.050 mol·dm^{-3}, (△) $\overline{C_{B,0}}$ = 0.104 mol·dm^{-3}, (□) $\overline{C_{B,0}}$ = 0.216 mol·dm^{-3}.

The amount of water in the dodecane phase was determined by Karl Fischer titration (HYDRANAL-Composites 5, model MKS-1S, Ridel-de Haën Co., Ltd.)

The titration measurement was carried out in triplicate.

Results and Discussion

Fatty acids are physically partitioned between organic solvents and water. However, the preliminary experiment reveals that propionic acid concentration in dodecane by physical dissolution was less than 2.0 × 10^{-4} mol·dm^{-3} for C_A up to 1.5 mol·dm^{-3}. The concentration of propionic acid in dodecane + trioctylamine was calculated from the difference between the initial and the equilibrium concentrations of propionic acid in the aqueous solution.

(1) Extraction of Propionic Acid at Concentrations below 1.0 mol·dm^{-3}. The concentration of propionic acid extracted in organic solution, $\overline{C_A}$, was plotted against the equilibrium concentration of propionic acid in aqueous solution, C_A, at various trioctylamine concentrations, $\overline{C_{B0}}$, in Figure 1. The concentration of propionic acid in the organic phase increased with increasing concentration

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Table 1. Equation for Z in Cases Where Respective Complexes Are Formed between Trioctylamine and Propionic Acid

complex	equation for Z
$\overline{\mathrm{HAB}}$ type	$\log(1/Z - 1) = -\log K_{1,1} - p \log C_A$ (2)
$\overline{(\mathrm{HA})_n\mathrm{B}_n}$ type	$\log(1/Z - 1) = -\log(K_{1,1}C_A{}^{p}) + \log f$ (3)
	$f = \dfrac{1}{1 + \sum_{n=2}^{N}\{nK_{1,1}{}^{n-1}\prod_{i=2}^{n}(K_{i,i}C_A{}^{p}\overline{C_B})\}}$
$\overline{(\mathrm{HA})_n\mathrm{B}}$ type	$\log(1/Z - 1) = -\log(K_{1,1}C_A{}^{p}) + \log f$ (4)
	$f = \dfrac{1 - \sum_{n=1}^{N}\{(n-1)\prod_{i=1}^{n}(K_{i,1}C_A{}^{p})\}}{1 + \sum_{n=2}^{N}\{\prod_{i=2}^{n}(K_{i,1}C_A{}^{p})\}}$
$\overline{(\mathrm{HA})\mathrm{B}_n}$ type	$\log(1/Z - 1) = -\log(K_{1,1}C_A{}^{p}) + \log f$ (5)
	$f = \dfrac{1 + \sum_{n=1}^{N}\{(n-1)K_{1,1}C_A{}^{p}\prod_{i=1}^{n}(K_{1,i}\overline{C_B})\}}{1 + \sum_{n=2}^{N}\{\prod_{i=2}^{n}(K_{1,i}\overline{C_B})\}}$

of propionic acid in the aqueous phase and trioctylamine concentration in dodecane.

Kawano et al. proposed the graphical method to predict the chemical species of complexes between trioctylamine and propionic acid in organic solvents (*2*, *11*). In this method, the apparent association number, Z, was introduced to estimate the extraction equilibrium constants. Z is defined as the number of molecules of propionic acid extracted by a molecule of trioctylamine and is given by the following equation:

$$Z = (C_{A,0} - C_A)/\overline{C_{B,0}} \tag{1}$$

The equations of Z, as functions of $\overline{C_{B,0}}$, C_A, and the equilibrium constants, were derived by taking into account the types of complexes and are listed in Table 1.

Figure 2 illustrates the relation between Z and the equilibrium concentration of propionic acid in the aqueous phase. The values of Z increase with the increase in the equilibrium concentration of propionic acid in the aqueous phase regardless of the trioctylamine concentration in dodecane.

From Figures 1 and 2, the type of complex between propionic acid and trioctylamine is likely to be $\overline{(\mathrm{HA})_n\mathrm{B}}$ because the value of Z exceeds unity and is independent of the trioctylamine concentration in dodecane (*2*, *11*). The extraction reaction of propionic acid with trioctylamine in dodecane can, therefore, be described as follows:

$$\mathrm{HA} = \mathrm{H}^+ + \mathrm{A}^- \tag{6}$$

$$\mathrm{H}^+ + \mathrm{A}^- + \overline{\mathrm{B}} = \overline{\mathrm{BHA}} \tag{7}$$

$$\overline{(\mathrm{BHA})(\mathrm{HA})_{n-2}} + \mathrm{HA} = \overline{(\mathrm{BHA})(\mathrm{HA})_{n-1}}\ (n = 2, 3, ..., N) \tag{8}$$

Dissociation equilibrium of propionic acid in the aqueous phase can always be established as shown in eq 6. Propionic acid reacts with trioctylamine at the liquid–liquid interface and forms an ionic-pair species, $\overline{\mathrm{HAB}}$. Subsequently, $\overline{(\mathrm{HA})_{n-1}\mathrm{B}}$ reacts with HA at the interface to form $\overline{(\mathrm{HA})_n\mathrm{B}}$ (n = 2, 3, ..., N) by hydrogen bonding.

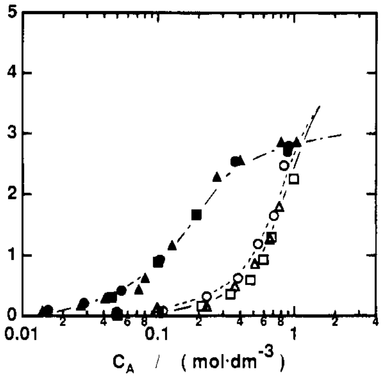

Figure 2. Z against propionic acid concentration in aqueous solution, C_A, ranging in C_A below 1.0 mol·dm^{-3}, with various concentration of trioctyl amine. The open symbols and closed symbols are the data for dodecane and for benzene, respectively. The solid line represents the calculated results with the derived equilibrium constants in dodecane. The broken and the one-dotted lines represent extraction equilibria calculated with equilibrium constants in hexane and benzene, respectively: for dodecane, (○) $\overline{C_{B,0}}$ = 0.050 mol·dm^{-3} (△) $\overline{C_{B,0}}$ = 0.104 mol·dm^{-3}, (□) $\overline{C_{B,0}}$ = 0.216 mol·dm^{-3}; for benzene, (●) $\overline{C_{B,0}}$ = 0.050 mol·dm^{-3}, (▲) $\overline{C_{B,0}}$ = 0.10 mol·dm^{-3}, (■) $\overline{C_{B,0}}$ = 0.20 mol·dm^{-3}.

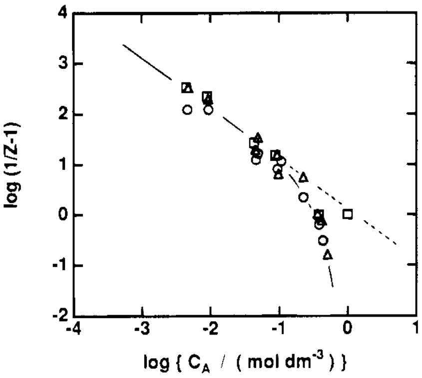

Figure 3. log(1/Z − 1) vs log C_A plots for the extraction equilibrium between dodecane solutions of trioctylamine and aqueous solutions of propionic acid. The tangent line at low C_A indicates k = 1.0. The solid line is calculated by the use of the derived equilibrium constants: (○) $\overline{C_{B,0}}$ = 0.050 mol·dm^{-3}, (△) $\overline{C_{B,0}}$ = 0.102 mol·dm^{-3}, (□) $\overline{C_{B,0}}$ = 0.198 mol·dm^{-3}.

Figure 3 shows the plots of log(1/Z − 1) against the equilibrium concentration of propionic acid in the aqueous phase, C_A. At low C_A, the C_A approaches a straight line, being independent of the trioctylamine concentration in dodecane. Equation 4 has been simplified to the following equation at low C_A (*2*, *11*):

$$\log(1/Z - 1) = -\log K_{1,1} - k \log C_A \tag{2}$$

The slope and the intercept of the straight line in Figure 3 provide the dissociation coefficient of propionic acid in the aqueous solution (k) and the equilibrium constant ($K_{1,1}$) of eq 2, respectively. In the range of C_A below 1.0 mol·dm^{-3}, it is assumed that only the complexes $\overline{\mathrm{HAB}}$, $\overline{(\mathrm{HA})_2\mathrm{B}}$, $\overline{(\mathrm{HA})_3\mathrm{B}}$, and $\overline{(\mathrm{HA})_4\mathrm{B}}$ are formed in the organic phase. Equations 2 and 4 with N = 4 were adopted in the determination of the equilibrium constants. The results are summarized in Table 2. Graphical analysis can be

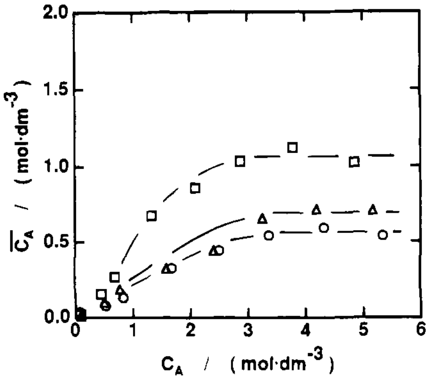

Figure 4. Relation between propionic acid concentration in the dodecane phase, $\overline{C}_A$, and in the aqueous phase, C_A, ranging in C_A above 1.0 mol·dm^{-3}, as a function of trioctylamine concentration, $\overline{C}_{B,0}$: (○) $\overline{C}_{B,0}$ = 0.050 mol·dm^{-3}, (△) $\overline{C}_{B,0}$ = 0.104 mol·dm^{-3}, (□) $\overline{C}_{B,0}$ = 0.216 mol·dm^{-3}.

Table 2. Formation Constants of Complexes between Trioctylamine and Propionic Acid

diluent	k	$K_{1,1}$/ (dm^3· mol^{-1})	$K_{2,1}$/ (dm^3· mol^{-1})	$K_{3,1}$/ (dm^3· mol^{-1})	$K_{4,1}$/ (dm^3· mol^{-1})
dodecane	1.0	0.87	0.91	1.1	2.8
benzene	1.0	5.9	5.6	8.4	
hexane	1.0	0.74	1.3	1.5	1.8

made to two significant figures. The solid lines in Figures 1 and 2 are the results calculated by eq 4 with the equilibrium constants in Table 2. The solid lines in these figures agree well with the observed results. This implies the validity of the reaction model in which four complexes of $\overline{(HA)_nB}$ (n = 1, 2, 3, and 4) are formed.

In order to discuss the diluent effect, equilibrium constants of the extraction reaction between propionic acid and trioctylamine in hexane and benzene are also shown in Table 2 for comparison. The broken line and one-dotted line in Figure 2 represent the results calculated from the equilibrium constants obtained in hexane and benzene, respectively. The closed marks are the data for benzene. In this figure, the data for hexane were not plotted because the data for hexane were close to those for dodecane. From the comparison, the following may be inferred.

When aliphatic solvents like hexane and dodecane were used as the diluent, the aggregation of the complexes was enhanced because of their low solvation properties.

(2) Extraction of Propionic Acid at Concentrations above 1.0 mol·dm^{-3}. Figure 4 presents the relation between the propionic acid concentrations in the organic phase and in the aqueous phase at equilibrium at high C_A. The amount of propionic acid extracted from the aqueous phase into the organic phase increased with increasing $\overline{C}_A$ and approached the value corresponding to $\overline{C}_{B,0}$. The value of Z is plotted against C_A in Figure 5. Z decreased with an increase in $\overline{C}_{B,0}$ at a constant value of C_A. The results in Figures 4 and 5 may offer the following two interpretations. One is the physical dissolution of propionic acid into dodecane for C_A higher than 1.5 mol·dm^{-3}. The other is the formation of complexes like $\overline{(HA)_mB_n}$ (m = 1, 2, ..., M, n = 2, ..., N) which were consecutively formed in the organic phase as the result of aggregation of $\overline{(HA)_nB}$ besides the complex formation of $\overline{(HA)_nB}$. The additional investigation will be required to clarify the results mentioned above.

Distribution Equilibrium of Water. Figure 6 shows the variation of the concentration of water in the organic phase, $\overline{C}_w$, against C_A. $\overline{C}_w$ increases with C_A and trioctylamine concentrations in dodecane. The concentration of water in the dodecane phase becomes constant at concentrations of trioctylamine in dodecane above 3.0 mol·dm^{-3}. These findings suggest that the concentrations of both trioctylamine and propionic acid are the significant determinants of $\overline{C}_w$.

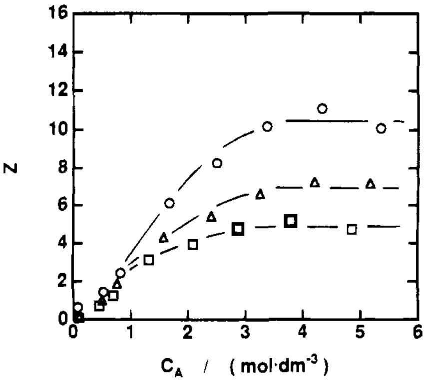

Figure 5. Z against propionic acid concentration in aqueous solution, C_A, ranging in C_A above 1.0 mol·dm^{-3}, as a function of trioctylamine concentration, $\overline{C}_{B,0}$: (○) $\overline{C}_{B,0}$ = 0.050 mol·dm^{-3}, (△) $\overline{C}_{B,0}$ = 0.104 mol·dm^{-3}, (□) $\overline{C}_{B,0}$ = 0.216 mol·dm^{-3}.

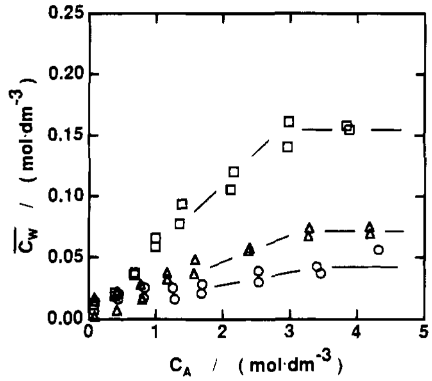

Figure 6. Coextraction of water in dodecane solutions of trioctylamine as a function of trioctylamine concentration, $\overline{C}_{B,0}$: (○) $\overline{C}_{B,0}$ = 0.052 mol·dm^{-3}, (△) $\overline{C}_{B,0}$ = 0.091 mol·dm^{-3}, (□) $\overline{C}_{B,0}$ = 0.191 mol·dm^{-3}.

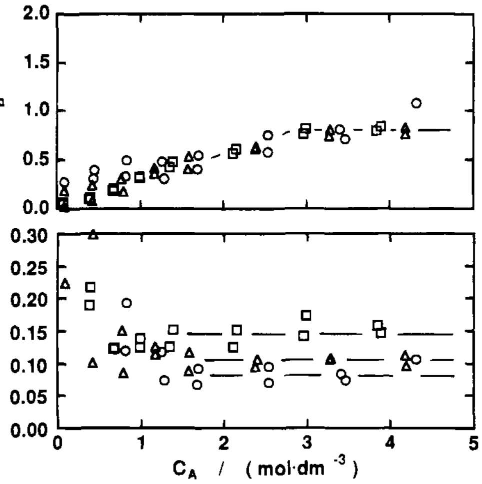

Figure 7. W_A and W_B against propionic acid concentration in aqueous solution, C_A, at various $\overline{C}_{B,0}$: (○) $\overline{C}_{B,0}$ = 0.052 mol·dm^{-3}, (△) $\overline{C}_{B,0}$ = 0.091 mol·dm^{-3}, (□) $\overline{C}_{B,0}$ = 0.191 mol·dm^{-3}.

Figure 7 illustrates the changes of W_A and W_B with C_A. W_A and W_B represent the moles of water extracted in dodecane by 1 mol of propionic acid and trioctylamine, respectively. As shown in Figure 7, W_B was proportional to C_A, being independent of $\overline{C_{B0}}$ above $C_A = 1.0$ mol·dm^{-3}. Furthermore, W_B became constant above $C_A = 3.0$ mol·dm^{-3} where the extraction capacity of propionic acid becomes saturated. W_A depends on $\overline{C_{B0}}$ and gives constant values at each $\overline{C_{B0}}$ at C_A larger than 2.0 mol·dm^{-3}. The representative value of W_A at each $\overline{C_{B0}}$ was increased with increasing $\overline{C_{B0}}$.

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