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# Extraction of Monocarboxylic Acids with Trioctylamine: Equilibria and Correlation of Apparent Reactive Equilibrium Constant

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Liquid–liquid equilibria for aqueous solutions of carboxylic acids, namely formic, acetic, propionic, butyric, valeric, monochloroacetic, dichloroacetic, trichloroacetic, glyoxylic, glycolic, and lactic acids, with trioctylamine (TOA) in various diluents, including 1-octanol, chloroform, methyl isobutyl ketone (MIBK), tetrachloromethane, and hexane, were determined at various TOA concentrations. The loading of TOA for a given carboxylic acid depends on the nature of the solute; the hydrophobicity and  $pK_a$  of the acid; and the nature of solvent, diluent type, and TOA concentration, which can be expressed by the specific basicity of TOA ( $pK'_{a,B}$ ), and increases with increasing acidity and hydrophobicity of the acid. The strength of solvation of the complex by the diluent for the acids studied decreases in the order 1-octanol  $\geq$  chloroform  $>$  MIBK  $>$  tetrachloromethane  $>$  hexane. An equilibrium model is presented that employs the mass action law and is used to determine model parameters and apparent extraction equilibrium constants ( $K_{11}$ ). The apparent extraction equilibrium constants depend on the hydrophobicity and acidity of the carboxylic acid, as well as the specific basicity of TOA, and the quantitative correlation of  $\log K_{11}$  is obtained using  $P$ ,  $pK_a$ , and  $pK'_{a,B}$ .

## Introduction

The production of organic chemicals at relatively low concentrations in aqueous solutions is typical for both electrochemical and biochemical syntheses. Recovery these solute species can be achieved by solvent extraction, and the reactive recovery of carboxylic acids from the diluent aqueous solutions has received increasing attention.

Long-chain aliphatic amines are effective extractants for the separation of carboxylic acids from dilute aqueous solution.<sup>1–5</sup> The specific chemical interactions between the amines and the acid molecules to form acid–amine complexes in the extractant phase allows more acid to be extracted from the aqueous phase.<sup>3</sup> Generally, the amine extractants are dissolved in a diluent such as a ketone, an alcohol, chloroform, etc., that is, an organic solvent that dilutes the extractant to the desired concentration and controls the viscosity and density of the solvent phase. Many factors have been found to influence the equilibrium extraction characteristics of these systems. Three important variables are the nature of the acid extracted, the concentration of the extractant, and the type of diluent.<sup>6,7</sup> These factors have been extensively studied for the extractions by tertiary amines of several carboxylic acids, including acetic acid,<sup>2,8–11</sup> lactic acid,<sup>2,12–14</sup> propionic acid,<sup>2,15</sup> butyric acid,<sup>2,16</sup> and succinic acid.<sup>5</sup>

The important properties of the acids are mainly the strength of the acid ( $pK_a$ )<sup>7,17</sup> and the hydrophobicity of the acid ( $\log P$ ).<sup>18,19</sup> In addition, King et al.<sup>17</sup> proposed that the equilibrium constant of a 1:1 complex decreases by about 1 logarithm unit for each unit increase in  $pK_a$  for the extraction equilibria of carboxylic acids (acetic, lactic, succinic, malonic, fumaric, and maleic acids) with amines, but the results from the experimental data did

not fit the above rule well. Hano et al.<sup>18</sup> investigated the extraction equilibria of organic acids (acetic, glycolic, propionic, lactic, pyruvic, butyric, succinic, fumaric, maleic, itaconic, tartaric, citric, and isocitric) with trioctylphosphine oxide in hexane and concluded that the number of carboxyl groups and the extraction equilibrium were controlled by the hydrophobicity of the acid, not by the  $pK_a$  value. However, the degree of extraction of trioctylamine (TOA) is quite different from that of trioctylphosphine oxide (TRPO).

The nature of the diluent affects the basicity of the amine and the stability of the ion-pair association in the extractant phase. Moreover, these diluents can hydrogen bond with the oxygen accessible on the carboxylic acid. Polar diluents that enhance the extraction power of amines are more favorable than nonpolar diluents, as shown in the extractions of citric, lactic, and succinic acids.<sup>2,6</sup> At low concentration of acid in the aqueous solution (0.5 mass %), the dominant complex corresponds to a stoichiometric association between the acid and the tertiary amine.<sup>5</sup>

Eyal et al.<sup>7</sup> summarized the extraction of acid by amines and proposed that four major mechanisms determine acid extraction by amine-based extractants: anion exchange, ion-pair formation, H-bond formation, and solvation. These four mechanisms depend on the strength of the amine-based extractant. For amines of basicity similar to or higher than that of the anion of the extracted acid, extraction is governed by ion-pair formation. H-bonding of undissociated acid becomes important only for extractions of weak bases. Also, the specific basicity of the extractant ( $pK'_{a,B}$ ), defined as follows, is suggested to express the nature of extractant

$$\overline{R_3NH^+} \xrightleftharpoons{K'_{a,B}} \overline{R_3N} + H^+ \\ K'_{a,B} = \frac{[\overline{R_3N}][H^+]}{[\overline{R_3NH^+}]} \quad (1)$$

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**Table 1. Physical Properties of Carboxylic Acids**

acid	$pK_a^{20}$	$\log P^a$	acid	$pK_a^{20}$	$\log P^a$
formic	3.75	-0.538	chloroacetic	2.87	0.139
acetic	4.75	-0.313	dichloroacetic	1.26	0.705
propionic	4.87	0.290	trichloroacetic	0.52	0.713
butyric	4.81	0.802	glycolic	3.83	-1.097
valeric	4.82	1.352	lactic	3.86	-0.413
			glyoxylic	3.34	-0.780

<sup>a</sup> Hydrophobicity.

where  $R_3N$  represents TOA. The species in the organic phase are marked with an overbar, and all of the concentrations are expressed in molar terms.  $pK_{a,B}$  depends on the amine concentration and diluent type, representing the structure of the amine, multiplied by coefficients for diluent solvation properties and for the properties of the anion of the extracted acid (hydrophobic properties and steric hindrance).

Through systematic investigation of the literature, it was found that the studies of the dependence of the extraction equilibrium on the nature of the acid extracted, diluent type, and extractant concentration have been limited to qualitative discussions, such as the dependence of the degree of extraction on the above factors, or poorly quantitative correlations that do not include the strength of the extractant. To understand the reactive extraction mechanism further, it is essential to quantify the effects of the solute, diluent, and extractant on the extraction equilibrium.

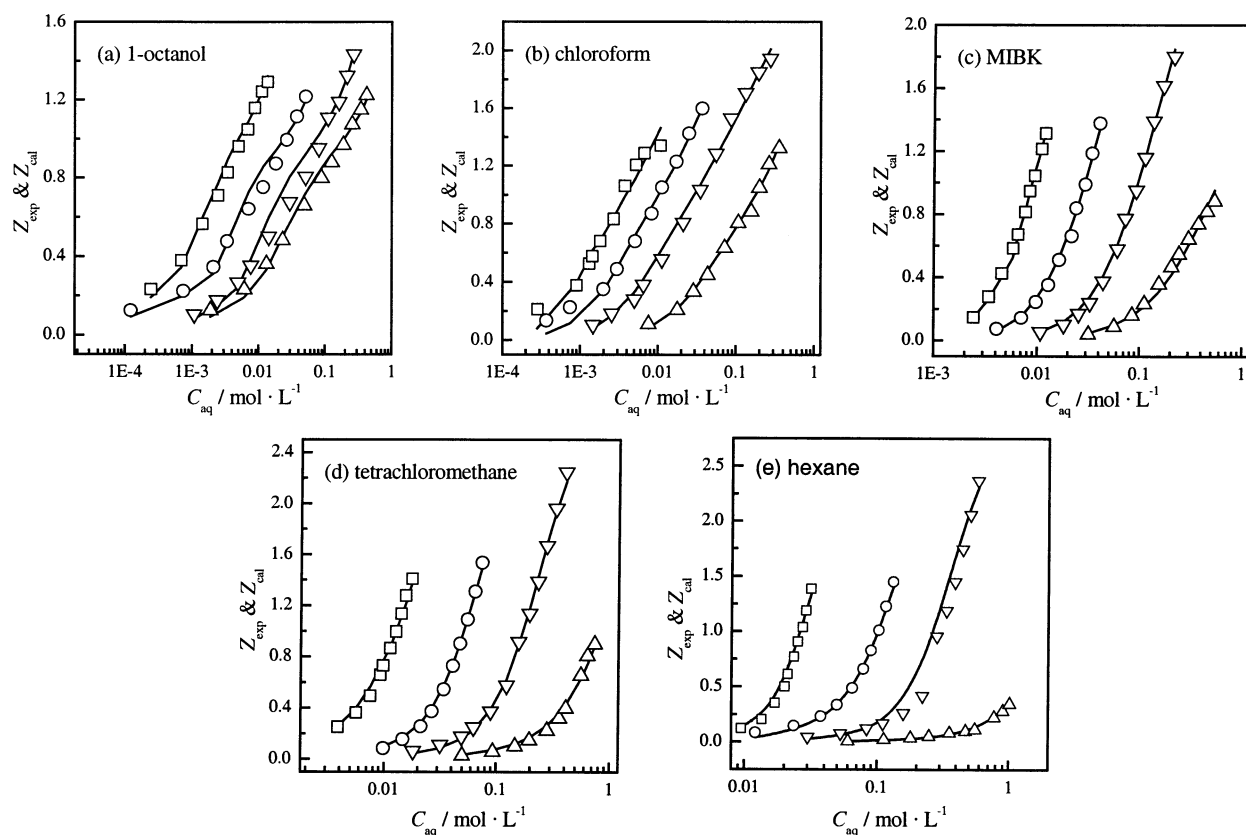
In this work, the extraction of several carboxylic acids by a tertiary amine extractant in a variety of diluents was examined so as to ascertain and compare the equilibrium behaviors of different system. Batch extraction experiments were performed with formic, acetic, propionic, butyric, valeric, monochloroacetic, dichloro-

acetic, trichloroacetic, glycolic, glyoxylic, and lactic acids. The extractant used was trioctylamine (TOA). 1-Octanol, chloroform, methyl isobutyl ketone (MIBK), tetrachloromethane, and hexane were selected as the diluents. Also, the specific basicity of TOA was measured at various TOA concentrations and in various diluents. An equilibrium model is presented and used to determine model parameters and apparent extraction equilibrium constants. Finally, the apparent extraction equilibrium constants were correlated with the nature of the carboxylic acids and extractants used.

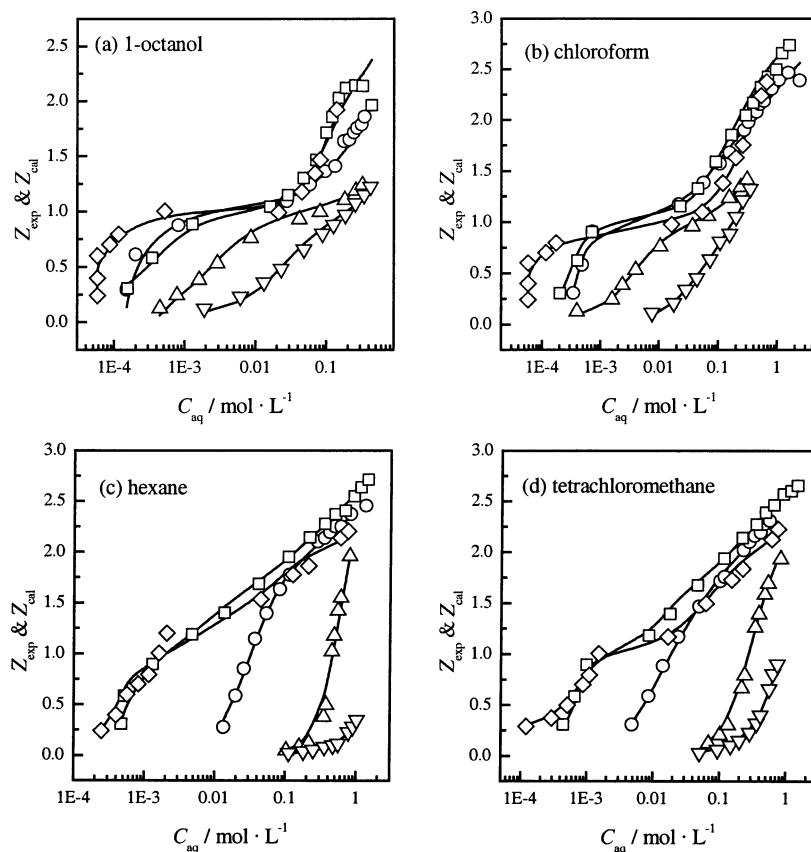
## Materials and Methods

**Chemicals.** All of the carboxylic acids were analytical reagents and were used to prepare organic acid solutions of various concentrations. Characteristics of carboxylic acids are presented in Table 1. Trioctylamine with purity > 99 mass % (Fluka) was used as the extractant. Five diluents, namely, 1-octanol, chloroform, MIBK, tetrachloromethane, and hexane (analytical reagent), were used in this work. Hexane and tetrachloromethane are nonpolar species, whereas 1-octanol and chloroform are protic diluents, and methyl isobutyl ketone is a polar, water-insoluble ketone.

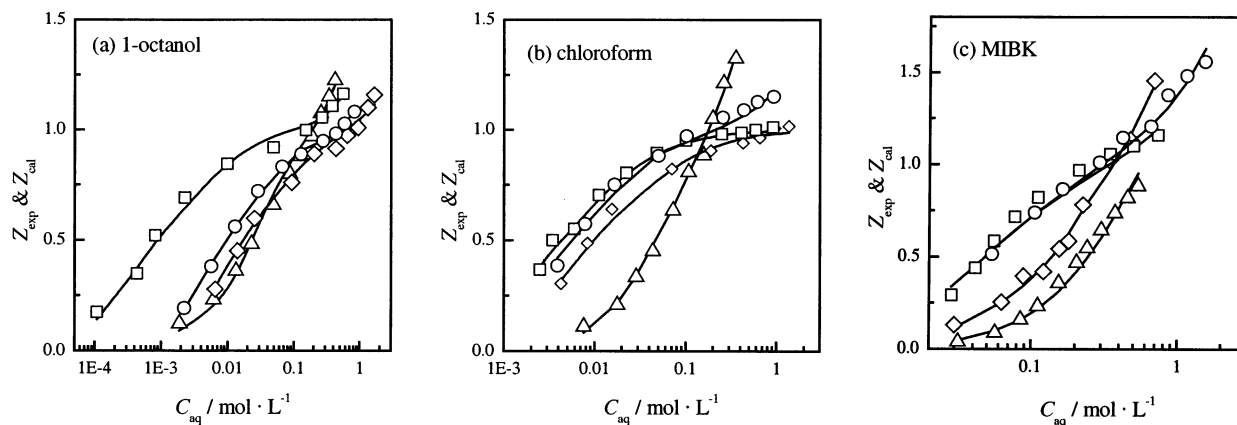
**Extraction Experiments.** The solvents used were amine–diluent mixtures. All extraction experiments were conducted in 100-mL flasks at  $25 \pm 0.5$  °C. Twenty milliliters of the mixture solvent and 20 mL of the carboxylic acid solution were added to a flask without adjustment of the solution pH. The flask containing the mixture was shaken for about 6 h in a shaker bath with a vibration rate of 200 rpm and then was left to equilibrate for 1–2 h, during which the two phases separated. The upper layer (extractant phase) was



**Figure 1.** Loading curves of carboxylic acid in 0.500 mol·L<sup>-1</sup> trioctylamine–diluent systems:  $\Delta$ , acetic acid;  $\nabla$ , propionic acid;  $\circ$ , butyric acid;  $\square$ , valeric acid; —, predicted curve.



**Figure 2.** Loading curves of carboxylic acid in 0.500 mol·L<sup>-1</sup> trioctylamine–diluent systems:  $\Delta$ , formic acid;  $\nabla$ , acetic acid;  $\circ$ , monochloroacetic acid;  $\square$ , dichloroacetic acid;  $\diamond$ , trichloroacetic acid; —, predicted curve.



**Figure 3.** Loading curves of carboxylic acid in 0.500 mol·L<sup>-1</sup> trioctylamine–diluent systems:  $\Delta$ , acetic acid;  $\circ$ , glycolic acid;  $\square$ , glyoxylic acid;  $\diamond$ , lactic acid; —, predicted curve.

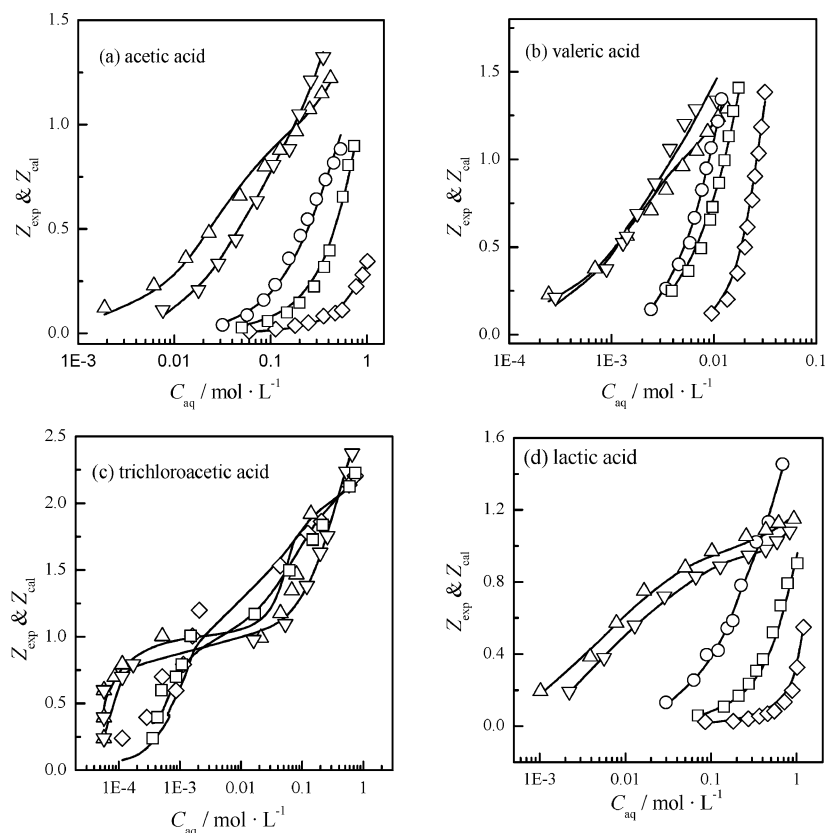
removed and its volume measured, and an aqueous-phase sample was taken from the bottom layer (aqueous phase) for pH and solute concentration analyses.

It was noted that, after extraction, slight changes in the phase volume were observed for all extractions performed with 1-octanol as the diluent. The organic-phase volume increased by about 5%, with a corresponding decrease in the aqueous-phase volume, which could be due to the water transfer into the organic phase to solvate the complex.<sup>21</sup> No significant volume change was observed in the other diluent systems. For extractions with the TOA–hexane system and the pure TOA system, a third emulsion phase was observed at the interface between the aqueous and organic phases for a high initial concentration of carboxylic acid, which

consists of a complex between TOA and carboxylic acid according to FT-IR analyses.

It is known that the equilibrium pH is different from the initial pH because of the removal of acid and extractant, amine, dissolved in the aqueous phase. The solution pH tended to increase in this work, and the difference in pH was  $<2$  because of the pH only from the acid; therefore, the pH dependence on the extractant is not obvious, especially for the cases of higher initial acid concentrations.

**Specific Basicity of TOA Determination.** According to eq 1,  $pK'_{a,B}$  is almost equal to the solution pH value if  $[R_3N] \approx [R_3NH^+]$  and  $[R_3N] \gg [H^+]$ . Thus,  $pK'_{a,B}$  in various diluents and TOA concentrations is determined by a method similar to that used in ref 7. A



**Figure 4.** Loading curves of carboxylic acid in 0.500 mol·L<sup>-1</sup> trioctylamine-diluent systems:  $\Delta$ , 1-octanol;  $\nabla$ , chloroform;  $\circ$ , MIBK;  $\square$ , CCl<sub>4</sub>;  $\diamond$ , hexane; —, predicted curve.

sample of 10 mL of the organic phase was mixed with 10 mL of HCl solution with one-half the molar concentration of the sample. The two phases were mixed for 4 h under the same conditions as used for the extraction equilibrium experiments and then separated, and the pH of the aqueous phase was determined.

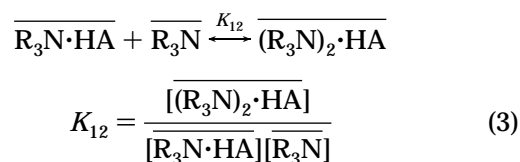
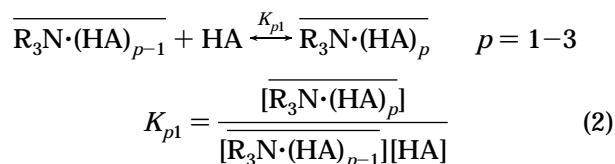
**Sample Analysis.** The aqueous samples were analyzed for solute concentration ( $C_{aq}$ ) by using titration with NaOH as the standard solution and phenolphthalein as the indicator, with each measurement being performed in duplicate. The carboxylic acid concentration in the extractant phase ( $C_{org}$ ) was calculated by material balance based on the volumes of the two phases and  $C_{aq}$  at equilibrium. However, the solute concentration in the organic phase was also determined by first stripping the organic phase with a small amount of a NaOH solution (0.02 mol·L<sup>-1</sup>). The alkaline solution containing the organic salt was then analyzed using a high-performance liquid chromatography (HPLC) system (Waters). The results from these two methods agreed well within a deviation of 3%, which probably resulted from the volume changing for each phase and the error of the analysis method.

The pH value of the aqueous phase was determined with a pH meter (Hanna pH 201 model) with deviation of  $\pm 0.02$ .

## Theory

The reactive extraction equilibrium for polar dilute solutions of organic solutes can be described by the mass action law in which the equilibrium behavior is modeled by postulating the formation of various stoichiometric complexes of acid and amine.<sup>6</sup> In addition, it is assumed that the carboxylic acid is dissociated in water and

extracted into the extractant phase through the physical solubility of the solute in the diluent of the extractant phase and the formation of 1:1, 2:1, 3:1, and 1:2 acid-amine complexes, where the 2:1 and 3:1 complexes result from the dimer and trimer, respectively, of the acid in the extractant phase<sup>22</sup> and the 1:2 complex results from hydrogen-bond association between TOA and the hydroxyl and aldehyde group on carboxylic acid. The physical extraction with diluent and reactive extraction with TOA fit the simple additive model. The complexes are formed by stepwise reactions as follows



where HA represent carboxylic acid.  $K_{p1}$  is the apparent equilibrium constant of the  $p$ -rank extraction reaction, the square brackets indicate concentrations, and all of the concentrations are expressed in molar terms. The overbar signifies species in the organic phase.

The loading of TOA,  $Z$ , is defined as the total concentration of acid (all forms) bonded to TOA in the organic phase divided by the total concentration of TOA (all forms) in the organic phase. With appropriate material balance,  $Z$  is determined for a given set of



**Table 2. Model Parameters for TOA–Carboxylic Acid Systems**

diluent	$C_{\text{TOA}}$ (mol·L <sup>-1</sup> )	$m$	$\log K_{11}$ (L·mol <sup>-1</sup> )	$\log K_{21}$ (L·mol <sup>-1</sup> )	$\log K_{31}$ (L·mol <sup>-1</sup> )	$\log K_{12}$ (L·mol <sup>-1</sup> )	diluent	$C_{\text{TOA}}$ (mol·L <sup>-1</sup> )	$m$	$\log K_{11}$ (L·mol <sup>-1</sup> )	$\log K_{21}$ (L·mol <sup>-1</sup> )	$\log K_{31}$ (L·mol <sup>-1</sup> )	$\log K_{12}$ (L·mol <sup>-1</sup> )
formic acid, $pK_a = 3.75$							butyric acid, $pK_a = 4.81$						
1-octanol	0	0.290	— <sup>a</sup>	—	—	—	1-octanol	0	6.337	—	—	—	—
	0.200	0.290	3.518	-0.403	-0.403	—		0.200	6.337	3.016	0.907	0.460	—
	0.500	0.290	3.412	-0.130	-0.348	—		0.500	6.337	2.920	0.769	0.731	—
	1.000	0.290	2.511	-0.038	-0.158	—		1.000	6.337	2.493	0.840	1.083	—
	1.762	0.290	1.503	0.842	-0.657	—		1.762	6.337	1.579	0.704	1.181	—
chloroform	0	0.007	—	—	—	—	chloroform	0	4.408	—	—	—	—
	0.200	0.007	3.079	0.301	-0.523	—		0.200	4.408	3.001	1.080	0.779	—
	0.500	0.007	3.041	0.176	0	—		0.500	4.408	3.001	1.532	0.930	—
	1.000	0.007	2.477	0.301	-0.638	—		1.000	4.408	2.585	1.557	0.858	—
MIBK	0	0.436	—	—	—	—	MIBK	0	6.611	—	—	—	—
	0.200	0.436	1.960	0.916	0.200	—		0.500	6.611	1.787	1.310	1.252	—
	0.500	0.436	1.732	1.047	-0.010	—	CCl <sub>4</sub>	0	2.119	—	—	—	—
	1.000	0.436	1.462	0.978	-1.323	—		0.500	2.119	0.913	1.293	1.214	—
CCl <sub>4</sub>	0	0	—	—	—	—	hexane	0	1.047	—	—	—	—
	0.200	0	0.255	0.398	-0.222	—		0.500	1.047	0.811	0.167	1.9039	—
	0.500	0	0	1.079	-0.301	—	100% TOA	2.203	—	0.903	0.903	1.398	—
hexane	0	0	—	—	—	—	valeric acid, $pK_a = 4.82$						
	0.200	0	-0.301	0.176	0	—	1-octanol	0	22.058	—	—	—	—
	0.500	0	-0.523	0.477	0.699	—		0.200	22.508	3.758	1.788	1.311	—
100% TOA	2.203	—	0.991	0.602	1.301	—		0.500	22.508	3.582	1.541	1.240	—
acetic acid, $pK_a = 4.75$								1.000	22.508	3.265	1.487	1.089	—
1-octanol	0	0.486	—	—	—	—		1.762	22.508	2.631	1.556	1.130	—
	0.200	0.486	1.875	-0.179	-0.498	—	chloroform	0	18.397	—	—	—	—
	0.500	0.486	1.751	-0.384	0.006	—		0.500	18.397	3.684	2.153	1.153	—
	1.000	0.486	1.165	-0.731	-0.275	—	MIBK	0	21.279	—	—	—	—
	1.762	0.486	0.242	0.066	0.385	—		0.500	21.279	2.558	1.915	1.915	—
chloroform	0	0.098	—	—	—	—	CCl <sub>4</sub>	0	10.073	—	—	—	—
	0.200	0.098	1.462	0	-1.000	—		0.500	10.073	1.794	1.794	1.794	—
	0.500	0.098	1.380	0	0.176	—	hexane	0	5.669	—	—	—	—
	1.000	0.098	1.301	0	0	—		0.500	5.669	1.089	1.721	1.755	—
MIBK	0	0.514	—	—	—	—	100% TOA	2.203	—	1.903	1.699	1.699	—
	0.200	0.514	1.369	0.573	0.670	—	monochloroacetic acid, $pK_a = 2.87$						
	0.500	0.514	0.298	0.201	—	—	1-octanol	0	1.377	—	—	—	—
	1.000	0.514	0.448	0.050	0.624	—		0.200	1.377	5.699	1.052	-0.601	—
CCl <sub>4</sub>	0	0	—	—	—	—		0.500	1.377	6.332	0.872	-0.274	—
	0.500	0	-0.155	0	-0.155	—		1.000	1.377	5.353	0.955	0.353	—
hexane	0	0	—	—	—	—	chloroform	0	0.049	—	—	—	—
	0.200	0	-0.187	—	—	—		0.200	0.049	6.398	1.176	-0.699	—
	0.500	0	-0.886	-0.097	-0.523	—		0.500	0.049	6.255	1.176	-0.222	—
100% TOA	2.203	—	-0.523	-0.301	1.000	—		1.000	0.049	6.079	1.301	-0.097	—
propionic acid, $pK_a = 4.87$							CCl <sub>4</sub>	0	0.023	—	—	—	—
1-octanol	0	1.952	—	—	—	—		0.200	0.023	2.041	1.477	-0.398	—
	0.200	1.952	2.453	0.130	0.118	—		0.500	0.023	2.477	1.477	0	—
	0.400	1.952	2.300	0.203	0.282	—		1.000	0.023	2.903	1.623	0.176	—
	0.500	1.952	2.200	0.133	0.325	—	hexane	0	0.001	—	—	—	—
	0.600	1.952	1.997	0.193	0.407	—		0.200	0.001	1.477	1.477	-0.222	—
	1.000	1.952	1.680	0.328	0.369	—		0.500	0.001	1.699	1.653	-0.097	—
	1.322	1.952	1.494	0.290	0.846	—		1.000	0.001	2.021	1.653	-0.097	—
	1.652	1.952	1.193	0.341	0.840	—	dichloroacetic acid, $pK_a = 1.26$						
	1.982	1.952	0.568	0.289	1.330	—	1-octanol	0	5.075	—	—	—	—
chloroform	0	0.848	—	—	—	—		0.200	5.075	8.743	2.062	1.664	—
	0.200	0.848	2.596	0.790	0.188	—		0.500	5.075	8.522	1.594	1.496	—
	0.500	0.848	2.214	0.993	0.215	—		1.000	5.075	8.287	1.743	0.618	—
MIBK	0	1.910	—	—	—	—	chloroform	0	0.083	—	—	—	—
	0.200	1.910	1.416	0.841	1.018	—		0.200	0.083	8.544	1.477	0.602	—
	0.500	1.910	1.014	0.868	0.646	—		0.500	0.083	6.845	1.342	0.398	—
CCl <sub>4</sub>	0	0.286	—	—	—	—		1.000	0.083	7.845	1.699	0.301	—
	0.500	0.286	0.398	0.699	0.740	—	CCl <sub>4</sub>	0	0.008	—	—	—	—
hexane	0	0.066	—	—	—	—		0.200	0.008	4.477	1.778	0.146	—
	0.500	0.066	0	0.398	1.000	—		0.500	0.008	5.954	2.322	0.204	—
100% TOA	2.203	—	0.398	0.477	0.699	—		1.000	0.008	6.602	2.176	0.146	—
							hexane	0	0.002	—	—	—	—
								0.200	0.002	4.447	2.176	0.255	—
								0.500	0.002	5.845	2.477	0.301	—
								1.000	0.002	5.954	2.398	0.301	—

stoichiometries as

$$Z_{\text{exp}} = \frac{C_{\text{org}} - [\text{HA}]}{S_0} = \frac{C_{\text{org}} - \phi m [\text{HA}]}{S_0} \quad (4)$$

$$Z_{\text{cal}} = \frac{K_{11}[\text{R}_3\text{N}][\text{HA}](1 + 2K_{21}[\text{HA}] + 3K_{21}K_{31}[\text{HA}]^2 + K_{12}[\text{R}_3\text{N}])}{S_0} \quad (5)$$

In addition,  $[\text{HA}]$  and  $[\text{R}_3\text{N}]$  can be obtained from the

dissociated equilibrium of carboxylic acid (eq 6) and the mass balance of TOA in the organic phase (eq 7), respectively

$$[\text{HA}] = \frac{C_{\text{aq}}}{1 + 10^{\text{pH} - \text{p}K_a}} \quad (6)$$

$$2K_{11}K_{12}[\text{HA}][\text{R}_3\text{N}]^2 + (1 + K_{11}[\text{HA}] + K_{11}K_{21}[\text{HA}]^2 + K_{11}K_{21}K_{31}[\text{HA}]^3)[\text{R}_3\text{N}] - S_0 = 0 \quad (7)$$

where  $\text{p}K_a$  is the dissociation constant of acid in the

Table 2. Continued

diluent	$C_{\text{TOA}}$ (mol·L <sup>-1</sup> )	$m$	$\log K_{11}$ (L·mol <sup>-1</sup> )	$\log K_{21}$ (L·mol <sup>-1</sup> )	$\log K_{31}$ (L·mol <sup>-1</sup> )	$\log K_{12}$ (L·mol <sup>-1</sup> )	diluent	$C_{\text{TOA}}$ (mol·L <sup>-1</sup> )	$m$	$\log K_{11}$ (L·mol <sup>-1</sup> )	$\log K_{21}$ (L·mol <sup>-1</sup> )	$\log K_{31}$ (L·mol <sup>-1</sup> )	$\log K_{12}$ (L·mol <sup>-1</sup> )
trichloroacetic acid, $pK_a = 0.52$							glyoxylic acid, $pK_a = 3.34$						
1-octanol	0	5.169	—	—	—	—	1-octanol	0	0.386	—	—	—	—
	0.200	5.169	9.371	1.973	2.274	—		0.500	0.386	3.826	-0.428	—	0.873
	0.500	5.169	10.407	2.204	2.106	—		1.000	0.386	3.215	-0.472	—	0.276
chloroform	0	0.001	7.447	—	—	—	chloroform	0	0	—	—	—	—
	0.200	0.001	7.447	0.708	0.591	—		0.500	0	2.778	—	—	0.740
	0.500	0.001	9.114	0.716	0.462	—	MIBK	0	0	—	—	—	—
CCl <sub>4</sub>	0	0.001	—	—	—	—		0.500	0	1.389	-0.387	—	—
	0.200	0.001	6.004	1.398	0	—	lactic acid, $pK_a = 3.86$						
	0.500	0.001	6.399	1.602	-0.301	—	1-octanol	0	0.166	—	—	—	—
hexane	0	0	—	—	—	—		0.200	0.166	2.474	-0.592	—	0.699
	0.200	0	6.771	1.813	-0.222	—		0.500	0.166	2.303	-0.886	—	0.778
	0.500	0	7.013	1.903	-0.699	—		1.000	0.166	1.944	-0.456	—	0.477
glycolic acid, $pK_a = 3.83$							chloroform	0	0.025	—	—	—	—
1-octanol	0	0.080	—	—	—	—		0.500	0.025	2.547	-0.611	—	0.602
	0.200	0.080	2.161	-2.886	—	1.301	MIBK	0	0.113	—	—	—	—
	0.500	0.080	1.954	-0.921	—	0.613		0.500	0.113	0.845	0.301	—	—
	1.000	0.080	1.600	-0.959	—	0.322	CCl <sub>4</sub>	0	0	—	—	—	—
chloroform	0	0	—	—	—	—		0.500	0	-0.071	-0.022	—	—
	0.200	0	2.362	-1.745	—	1.176	hexane	0	0	—	—	—	—
	0.500	0	2.352	-1.699	—	0.778		0.500	0	-0.699	-0.097	—	—
MIBK	0	0.050	—	—	—	—							
	0.200	0.050	1.380	-0.060	—	—							
CCl <sub>4</sub>	0	0	—	—	—	—							
	0.200	0	0	-0.602	—	—							

<sup>a</sup> Note: — represents  $K_{mn} = 0$  ( $m = 1-3$  and  $n = 1, 2$ ).

aqueous phase;  $m$  is the physical extraction constant of the acid for the pure diluent, obtained from the partition coefficient with the same initial concentration of carboxylic acid in the TOA–diluent system;  $\Phi$  is the volume fraction of diluent in the extractant phase; and  $S_0$  is the initial concentration of TOA in the extractant phase.  $C_{\text{aq}}$  and  $C_{\text{org}}$  are the total concentrations of carboxylic acid in the aqueous phase and in the organic phase, respectively.

The loading of trioctylamine,  $Z_{\text{cal}}$ , is a function of the  $pK_a$  of the carboxylic acid,  $\Phi$ ,  $m$ ,  $S_0$ ,  $C_{\text{aq}}$ , pH,  $K_{11}$ ,  $K_{12}$ ,  $K_{21}$ , and  $K_{31}$ . Using eqs 4–7, the value of  $Z_{\text{cal}}$  can be predicted for any system if the constants  $K_{11}$ ,  $K_{12}$ ,  $K_{21}$ , and  $K_{31}$  are known.  $K_{11}$ ,  $K_{12}$ ,  $K_{21}$ , and  $K_{31}$  as iterated parameters can be determined by fitting the data for  $Z$  using nonlinear regression on the basis of the  $pK_a$  of the carboxylic acid,  $\Phi$ ,  $m$ ,  $S_0$ ,  $C_{\text{aq}}$ , and the pH value.

## Results and Discussion

**Effect of Acids.** Generally, the nature of the extracted acid, that is, its hydrophobicity and acidity, is one of the most important factors affecting the degree of extraction, and extraction is expected to increase with increasing acidity and hydrophobicity of the acid. To examine independently and quantitatively the contributions of the hydrophobicity and acidity of the acid to the extraction equilibrium, organic acids used in this paper were categorized into three types: (1) organic acids with similar  $pK_a$  values (acetic, propionic, butyric, and valeric acids), (2) organic acids with larger differences in their  $pK_a$  values (formic, acetic, monochloroacetic, dichloroacetic, and trichloroacetic acids), and (3) organic acids with other substitute functional group (acetic, glyoxylic, lactic, and glycolic acids).

As indicated in Figure 1, the loadings of TOA for carboxylic acids with similar  $pK_a$  values fall in the order valeric acid > butyric acid > propionic acid > acetic acid. It is apparent that the longer-chain carboxylic acids are more hydrophobic and can be extracted better by TOA.

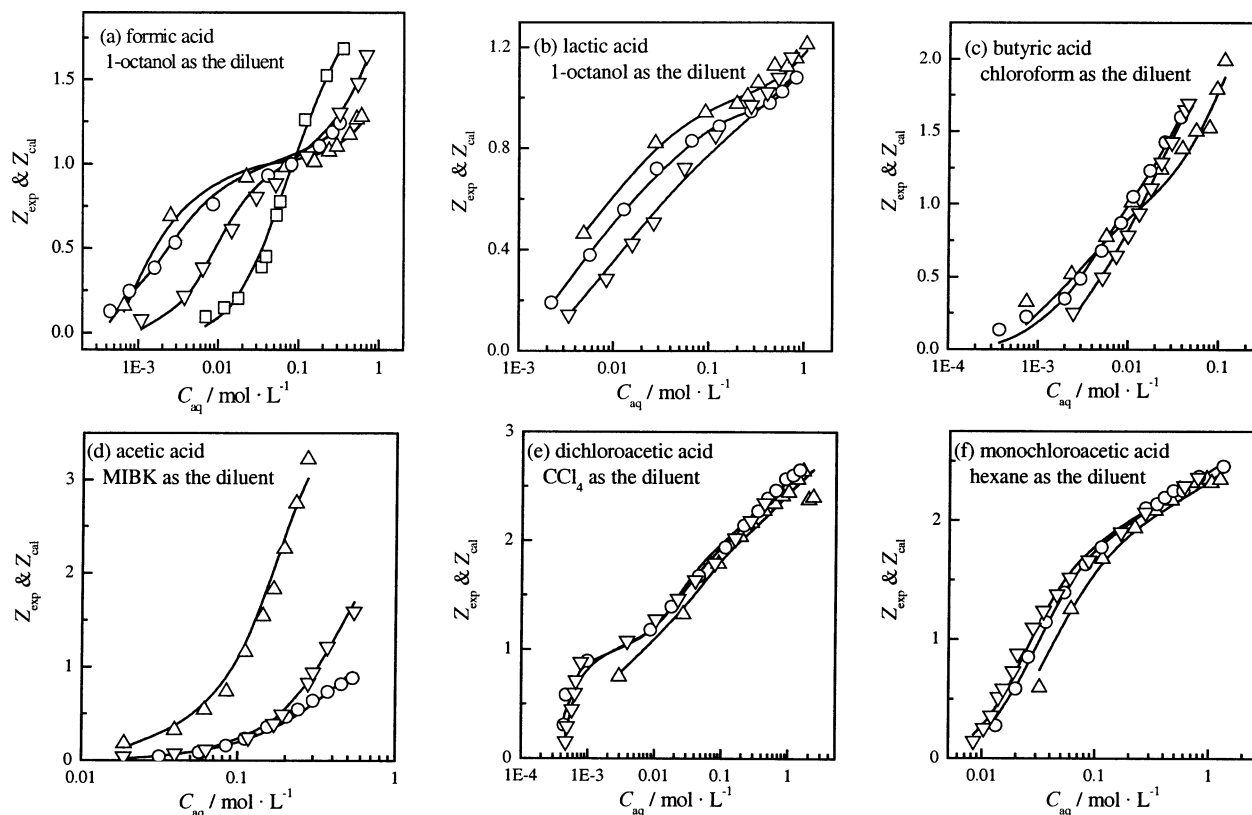
For the acids with larger differences in  $pK_a$ , a strong acid increases the association power between the acid

and an amine, so that the amine can be extracted better into the organic phase. Similarly, the results obtained in this work (Figure 2) show that stronger acids provide larger loadings of trioctylamine than weaker acids, with the order being trichloroacetic acid > dichloroacetic acid > monochloroacetic acid > formic acid > acetic acid.

As shown in Figures 1–3, overloading ( $Z > 1$ ) occurs at relatively high equilibrium aqueous solute concentration. This phenomenon probably occurs for three reasons, namely, co-extraction of water into the organic phase, acid dimerization in the organic phase, and physical extraction of acid by complex in organic phase, all of which are H-bonding mechanisms that depend only on the hydrophobicity of solute and not on the extractant TOA. Therefore, different shapes of the loading curves were observed.

The functional group present on the carboxylic acid, namely, halogen, aldehyde, or hydroxyl, causes the  $pK_a$  and hydrophobicity of the acid to change, thus affecting the extraction equilibrium. As shown in Figure 3, the loading of TOA for carboxylic acids with other substituted functional groups is in the order glyoxylic acid > lactic acid > glycolic acid > acetic acid for  $Z < 1$ . It is clear that the extraction equilibrium for the organic acids with other substituted functional groups also depends on the  $pK_a$  and  $\log P$  of the acid, e.g., the  $pK_a$  of lactic acid is similar to that of glycolic acid, but the longer carbon chain of lactic acid makes this compound more hydrophobic and thus easier to extract than glycolic acid.

**Effect of Diluent.** It is known that a polar diluent increases the extracting ability of relatively low polar amines by providing additional solvating power that allows higher levels of polar–amine complexes to form in the extractant phase. On the other hand, a nonpolar diluent does not affect the extraction process with low polar amines.<sup>17</sup> Similarly, the results obtained in this work (Figure 4) show that polar diluents provide larger loadings of trioctylamine than inert diluents, and the consequence is that the loadings fall in the order 1-octanol > chloroform > methyl isobutyl ketone >



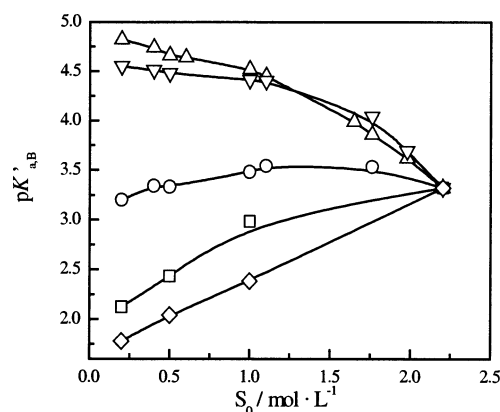
**Figure 5.** Effect of TOA concentration on the extraction equilibrium:  $\Delta$ , 0.20 mol·L<sup>-1</sup>;  $\circ$ , 0.50 mol·L<sup>-1</sup>;  $\nabla$ , 1.0 mol·L<sup>-1</sup>;  $\square$ , 1.76 mol·L<sup>-1</sup>; —, predicted curve.

tetrachloromethane > hexane at  $Z < 1$ . This is the same order as reported in ref 17.

It should be noted that the large differences between the loading of TOA and the polarity of the diluent for the same acid indicate that solvation of the complex by the diluent is a critical factor in the extraction of the acid. The interactions between the complex and solvation can, somewhat arbitrarily, be divided into "general solvation" and "specific interaction" of the diluent with the complex.

Inert diluents, such as hexane and tetrachloromethane, give very low loadings of the amine because, being nonpolar, they provide for very little solvation of the polar complexes. Active diluents, such as 1-octanol and chloroform, have functional groups that enable greater solvation of the complex. In particular, protic halogenated hydrocarbons and alcoholic diluents give unusually high degrees of extraction, higher than would be expected from polarity arguments alone. Specific hydrogen bonding between the proton of the diluent and the acid-amine complex is thought to explain the extra solvation provided by these diluents.

**Effect of Amine Concentration.** As shown in Figure 5, contrasting effects of the amine concentration in protic and polar diluents are observed. This phenomenon can be rationalized by noting that an aliphatic amine, by itself, is a relatively poor solvation medium for polar complexes. Thus, in active diluents with high amine concentrations (e.g., 1-octanol and chloroform), the loading decreases with increasing amine concentration at  $Z < 1$ , as the solvation is occurring in a less favorable solvating medium. In inert diluents, e.g., hexane and tetrachloromethane, there is little observable effect of amine concentration on loading, and loading increases with increasing amine concentration slightly,

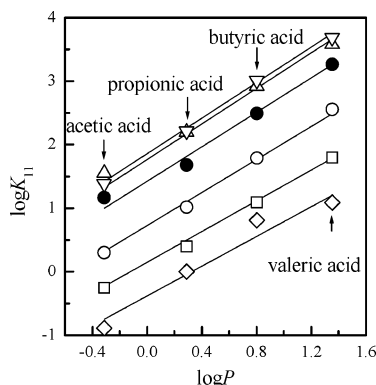


**Figure 6.** Effect of diluent and TOA concentration on the specific basicity of TOA:  $\Delta$ , 1-octanol;  $\nabla$ , chloroform;  $\circ$ , MIBK;  $\square$ , CCl<sub>4</sub>;  $\diamond$ , hexane.

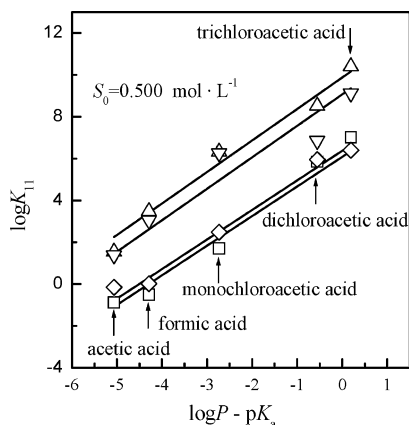
as the inert diluent and the amine have similar solvating abilities. Therefore, an optimal TOA concentration should be considered with an active diluent in use.

**Specific Basicity of TOA.** As shown in Figure 6,  $pK'_{a,B}$  decreases with increasing TOA concentration for the protic and polar diluents chloroform and 1-octanol and increases with increasing TOA concentration for the nonpolar diluents tetrachloromethane and hexane, whereas  $pK'_{a,B}$  is apparently not dependent on the TOA concentration for MIBK as the diluent. For a fixed TOA concentration,  $pK'_{a,B}$  decreases in the order 1-octanol > chloroform > MIBK > CCl<sub>4</sub> > hexane. It is apparent that the loading of TOA and  $pK'_{a,B}$  in various diluents and TOA concentrations fall in the same order; in the other words, the loading of TOA increases with  $pK'_{a,B}$ . Thus, the TOA concentration effect and diluent effect





**Figure 7.** Relationship between the hydrophobicity ( $\log P$ ) and the apparent reactive extraction equilibrium constant  $\log K_{11}$ .  $S_0 = 0.500 \text{ mol} \cdot \text{L}^{-1}$ :  $\Delta$ , 1-octanol;  $\nabla$ , chloroform;  $\circ$ , MIBK;  $\square$ , tetrachloromethane;  $\diamond$ , hexane.  $S_0 = 1.000 \text{ mol} \cdot \text{L}^{-1}$ :  $\bullet$ , 1-octanol.



**Figure 8.** Relationship between  $\log P - pK_a$  and the apparent extraction equilibrium constant  $\log K_{11}$ :  $\Delta$ , 1-octanol;  $\nabla$ , chloroform;  $\square$ , tetrachloromethane;  $\diamond$ , hexane.

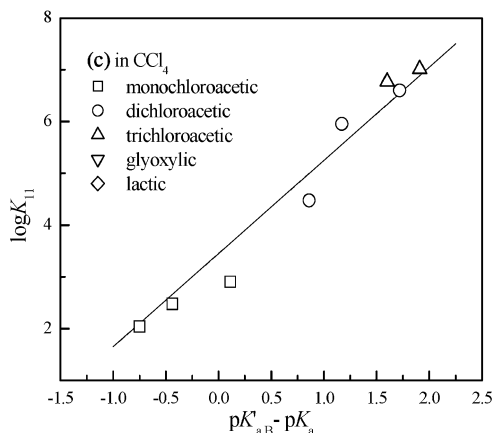
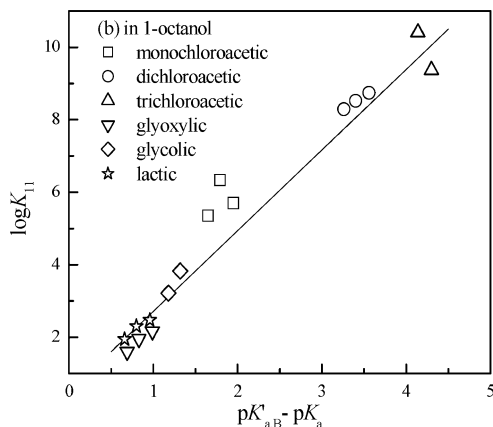
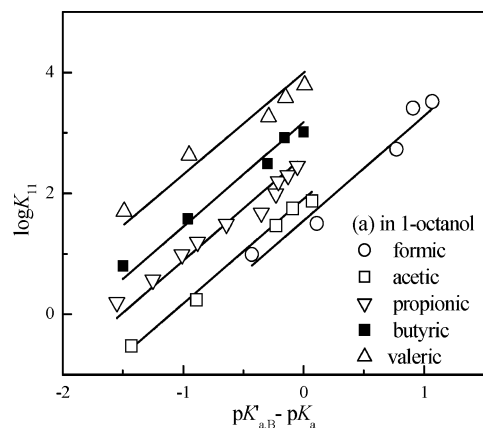
could be explained in terms of the specific basicity of the extractant.

**Correlation of Apparent Reactive Equilibrium Constant** The apparent extraction constants  $K_{11}$ ,  $K_{21}$ ,  $K_{31}$ , and  $K_{12}$  were determined by fitting the experimental data for  $Z$  to eqs 4–7 using a least-squares regression method. The results are listed in Table 2. As shown in Figures 1–5, the predicted curves agree with the experimental data points very well, and most points are within the deviation of  $\pm 10\%$ . Thus, the model is valid in representing the equilibrium behavior of carboxylic acid–triethylamine systems.

It should be noted that the formation of 1:2 complexes of amine and aldehydic or hydroxy acids depends on the diluent types from Table 2, and 1:2 complexes form only in the protic, polar diluents 1-octanol and chloroform. This is because the association style between an amine and an acid depends on the strength of the amine-based extractant,<sup>7</sup> and the basicity of TOA in 1-octanol and chloroform is much higher than that in  $\text{CCl}_4$  and hexane.

Most of complexes exist in the 1:1 form when the carboxylic acid concentration is low ( $Z < 1$ ), which is the typical concentration range for the extraction method.<sup>12</sup> Thus, the apparent equilibrium constant,  $K_{11}$ , can be used to represent the degree of extraction and its correlation was investigated.

Generally, the degree of extraction depends on two major factors: (1) the association ability between the solute and triethylamine,  $pK'_{a,B} - pK_a$ , and (2) the



**Figure 9.**  $\log K_{11}$  vs  $pK'_{a,B} - pK_a$ .

solvation ability of the polar complex in the diluent,  $\log P$ . Thus, the hydrophobicity of the acid should be the key factor for the organic acids with similar  $pK_a$ 's (acetic, propionic, butyric, and valeric acid), and  $\log P - pK_a$  should be key for all of the acids, while the specific basicity of TOA is the parameter for the diluent and TOA concentration. Plots of  $\log K_{11}$  vs  $\log P$ ,  $\log K_{11}$  vs  $\log P - pK_a$ , and  $\log K_{11}$  vs  $pK'_{a,B} - pK_a$  (based on this work) are shown in Figures 7–9, respectively.  $\log K_{11}$  is linear with  $\log P$  and  $\log P - pK_a$  of the carboxylic acid, as well as with  $pK'_{a,B} - pK_a$ , and the slopes are similar for all five diluents. The intercept depends on the diluents used for the acids with similar  $pK_a$  values, and they fall in the order 1-octanol > chloroform > MIBK > tetrachloromethane > hexane.

On the basis of the above analyses and the results of Figures 7–9, which indicate that the extraction equilibrium parameter,  $\log K_{11}$ , mainly depends on the

properties of the organic acid and TOA,  $\log P$ ,  $pK_a$ , and  $pK_{a,B}$ , a correlation equation can be expressed as follows

$$\log K_{11} = C_1(pK_{a,B} - pK_a + \log P) + C_2 \quad (8)$$

The constants  $C_1$  and  $C_2$  in eq 8 can be obtained by fitting a set of 114 data points for  $\log K_{11}$  in Table 2 to eq 8 using a least-squares regression method. Equation 8 then becomes

$$\log K_{11} = 1.3164(pK_{a,B} - pK_a + \log P) + 2.5942$$

$$r = 0.947$$

or

$$\log K_{11} = 1.3164[pK_{a,B} - pK_a + \log (93.47P)] \quad (9)$$

According to the correlation coefficient,  $r = 0.947$ , and the deviation (within  $\pm 20\%$ ) between the calculated  $\log K_{11}$  values and the measured data, the calculated  $\log K_{11}$  values fit the measured data very well. Thus, eq 9 can be used to predict the extraction equilibrium of organic acids with TOA.

## Conclusions

In the present work, extraction equilibrium studies for organic acids (formic, acetic, propionic, butyric, valeric, monochloroacetic, dichloroacetic, trichloroacetic, glyoxylic, glycolic, and lactic acids) with TOA in various diluents (1-octanol, chloroform, MIBK, tetrachloromethane, and hexane) were conducted at various TOA concentrations. The loading of TOA for carboxylic acids with trioctylamine decreases in the order 1-octanol  $\geq$  chloroform  $>$  methyl isobutyl ketone  $>$  tetrachloromethane  $>$  hexane and increases with increasing acidity and hydrophobicity of the acid.

By using the mass action law and suitable assumptions, an expression for extraction equilibrium was derived, and apparent extraction equilibrium constants were evaluated. The apparent extraction equilibrium constants depend on the hydrophobicity and  $pK_a$  of the carboxylic acid, as well as the specific basicity of the extractant, and  $\log K_{11}$  is linear with  $pK_{a,B}$  and  $\log P - pK_a$  with a slope of 1.3164. The predicted loadings of trioctylamine agrees well with the experimental values.

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## Nomenclature

$C_{aq}$  = total concentration of acid in the aqueous phase ( $\text{mol} \cdot \text{L}^{-1}$ )

$C_{org}$  = total concentration of acid in the organic phase ( $\text{mol} \cdot \text{L}^{-1}$ )

$K_{12}$  = apparent equilibrium constant of the 1:2 complex ( $\text{L} \cdot \text{mol}^{-1}$ )

$K_a$  = dissociation constant of the solute ( $\text{mol} \cdot \text{L}^{-1}$ )

$pK_{a,B}$  = the specific basicity of TOA ( $\text{mol} \cdot \text{L}^{-1}$ )

$K_{p1}$  = apparent equilibrium constant of the  $p$ -rank extraction reaction,  $p = 1-3$ , ( $\text{L} \cdot \text{mol}^{-1}$ )

$m$  = physical extraction constant of the acid for the pure diluent

$r$  = correlation coefficient

$[S]$  = concentration of free TOA in the organic phase ( $\text{mol} \cdot \text{L}^{-1}$ )

$S_0$  = initial concentration of TOA in the organic phase ( $\text{mol} \cdot \text{L}^{-1}$ )

$Z$  = loading of TOA

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