# Liquid–Liquid Equilibria of Acetic, Propionic, Butyric, and Valeric Acids with Trioctylamine as Extractant

**3 AUTHORS**, INCLUDING:

Wei Qin

Tsinghua University

**45** PUBLICATIONS **309** CITATIONS

# Liquid−Liquid Equilibria of Acetic, Propionic, Butyric, and Valeric Acids with Trioctylamine as Extractant

## Zhenyu Li, Wei Qin,* and Youyuan Dai

Department of Chemical Engineering, Tsinghua University, Beijing 100084, People's Republic of China

Liquid−liquid equilibria of aqueous solutions of acetic, propionic, butyric, and valeric acids with trioctylamine in various diluents, 1-octanol, chloroform, methyl isobutyl ketone, and tetrachloromethane, were determined at 298 K. An expression of the extraction equilibrium is derived, and the apparent extraction equilibrium constants ($K_{11}$) are evaluated. The predicted loading of trioctylamine agrees well with the experimental values. The relationship between the $K_{11}$ and the hydrophobicities of the acids is discussed.

## Introduction

Many separation processes in chemical industries utilize a reactive extraction system. A reactive extraction process, which exploits reversible chemical complexation in the extractant phase, provides an effective separation, especially for relatively dilute solutions, such as the aqueous solution of carboxylic acids in a fermentation broth.[1] The solutions of long-chain tertiary amines in diluents such as ketones, alcohols, chloroform, and so forth are very effective extractants for carboxylic acids.[2] The specific chemical interactions among the amines and the acid molecules to form acid−amine complexes in the extractant phase allow more acid to be extracted from the aqueous phase.[3]

In recent years, solvent extraction have received attention for the recovery of carboxylic acids from dilute aqueous solutions, notably with hydrophobic tertiary amines dissolved in various organic diluents.[4−10] The specific affinity of long-chain tertiary amines for carboxylic acids gives high selectivity for this type of solute with respect to water and eventually nonacidic species in the mixture.[11] The formation of acid−amine complexes depends on the nature of diluents, which affect the basicity of the amine and the stability of the ion-pair association in the extractant phase, and these diluents may hydrogen bond with the oxygen accessible on the carboxylic acid. Since the presence of the hydroxyl and carboxylic groups increases the solubility of acids in the water phase, the strong interactions of solvent with solutes are necessary to extract carboxylic acids from dilute aqueous solutions. In the present case, 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.[12] Polar diluents that enhance the extraction power of amines are more favorable than nonpolar diluents, as shown in the extraction of citric, lactic, and succinic acids.[1]

It is believed that the strength of the acid, expressed by $pK_a$, and the diluent type are the major factors controlling the degree of extraction. King et al.[13] proposed that the equilibrium constant of a (1, 1) complex decreases about 1 log unit with each unit increase in $pK_a$ for the extraction equilibrium of carboxylic acids with amines, but the results from the experimental data did not fit the above rule well.

* To whom correspondence should be addressed. E-mail: qinw@chemeng.tsinghua.edu.cn.

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

| chemical | $pK_a$ | hydrophobicity ($\log P$) |
|---|---|---|
| acetic acid | 4.75 | −0.313 |
| propionic acid | 4.87 | 0.290 |
| butyric acid | 4.81 | 0.802 |
| valeric acid | 4.82 | 1.352 |

Hano et al.[14] 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 is quite different from that of trioctylphospine oxide.

In the work of Sabolova et al.,[15] butyric acid was selected to be extracted with trioctylamine in *n*-alkanes. The experimental results were interpreted by a chemical reaction mechanism and a related model with the existence of (1, 1) to (7, 1) acid−amine complexes, and a monomer and a dimer of butyric acid in the solvent were proposed.

This work presents the study of the extraction equilibrium of $C_2$−$C_5$ monocarboxylic acids from aqueous solutions with trioctylamine. Equilibrium data are presented for the system of carboxylic acids with trioctylamine in 1-octanol, chloroform, methyl isobutyl ketone, and tetrachloromethane. An equilibrium model is presented and used to determine model parameters and apparent extraction equilibrium constants.

## Theory

On the basis of mass action law, an expression for the extraction equilibrium of carboxylic acid with trioctylamine as extractant can be obtained. When it is assumed that the carboxylic acid is dissociated in water, extracted into the extractant phase through the physical solubility of the solute in the extractant phase, and forms (1:1), (2:1), and (3:1) acid−amine complexes because of the dimer of acid in the extractant phase, the complexes are formed by the

**Table 2. Equilibrium Data for the System Acetic Acid + Trioctylamine in Diluent**

| $S_0$/mol·L$^{-1}$ | equil pH in aq phase | total equil conc of acetic acid/mol·L$^{-1}$ | |
|---|---|---|---|
| | | aq conc | org conc |
| *1-Octanol as the Diluent* | | | |
| 0.500 | 5.16 | 0.0019 | 0.0120 |
| 0.500 | 4.79 | 0.0060 | 0.0871 |
| 0.500 | 4.51 | 0.0130 | 0.1350 |
| 0.500 | 4.23 | 0.0230 | 0.2090 |
| 0.500 | 3.97 | 0.0480 | 0.3472 |
| 0.500 | 3.71 | 0.0870 | 0.4320 |
| 0.500 | 3.45 | 0.1250 | 0.4860 |
| 0.500 | 3.4 | 0.1860 | 0.5530 |
| 0.500 | 3.29 | 0.2550 | 0.6318 |
| 0.500 | 3.18 | 0.3400 | 0.7020 |
| 1.000 | 3.09 | 0.4190 | 0.7690 |
| 1.000 | 5.31 | 0.0020 | 0.0101 |
| 1.000 | 5.11 | 0.0060 | 0.0571 |
| 1.000 | 4.81 | 0.0140 | 0.1840 |
| 1.000 | 4.33 | 0.0430 | 0.3520 |
| 1.000 | 4.02 | 0.0850 | 0.5260 |
| 1.000 | 3.89 | 0.1180 | 0.6210 |
| 1.000 | 3.59 | 0.2370 | 0.9500 |
| 1.000 | 3.5 | 0.2910 | 1.0050 |
| 1.000 | 3.34 | 0.6330 | 1.2560 |
| 1.000 | 3.12 | 1.0890 | 1.5720 |
| *Chloroform as the Diluent* | | | |
| 0.500 | 4.75 | 0.0077 | 0.0560 |
| 0.500 | 4.51 | 0.0180 | 0.1050 |
| 0.500 | 4.36 | 0.0290 | 0.1690 |
| 0.500 | 4.16 | 0.0430 | 0.2280 |
| 0.500 | 4.02 | 0.0720 | 0.3230 |
| 0.500 | 3.79 | 0.1069 | 0.4116 |
| 0.500 | 3.57 | 0.1570 | 0.4540 |
| 0.500 | 3.53 | 0.1990 | 0.5400 |
| 0.500 | 3.41 | 0.2610 | 0.6260 |
| 0.500 | 3.26 | 0.3530 | 0.6890 |
| 1.000 | 4.89 | 0.0058 | 0.0580 |
| 1.000 | 4.70 | 0.0120 | 0.1110 |
| 1.000 | 4.58 | 0.0180 | 0.1800 |
| 1.000 | 4.32 | 0.0420 | 0.3530 |
| 1.000 | 4.06 | 0.0700 | 0.5410 |
| 1.000 | 3.86 | 0.1110 | 0.7750 |
| 1.000 | 3.69 | 0.1680 | 0.9210 |
| 1.000 | 3.60 | 0.2070 | 1.0210 |
| *Methyl Isobutyl Ketone as the Diluent* | | | |
| 0.500 | 4.12 | 0.0320 | 0.0320 |
| 0.500 | 3.86 | 0.0570 | 0.0660 |
| 0.500 | 3.71 | 0.0850 | 0.1130 |
| 0.500 | 3.53 | 0.1110 | 0.1610 |
| 0.500 | 3.41 | 0.1550 | 0.2410 |
| 0.500 | 3.19 | 0.2040 | 0.3150 |
| 0.500 | 3.14 | 0.2410 | 0.3690 |
| 0.500 | 3.03 | 0.2990 | 0.4400 |
| 0.500 | 2.95 | 0.3710 | 0.5160 |
| 0.500 | 2.86 | 0.4530 | 0.5890 |
| 0.500 | 2.93 | 0.5340 | 0.6540 |
| 1.000 | 4.93 | 0.0190 | 0.0450 |
| 1.000 | 4.61 | 0.0400 | 0.0830 |
| 1.000 | 4.38 | 0.0630 | 0.1350 |
| 1.000 | 4.09 | 0.1170 | 0.2780 |
| 1.000 | 3.95 | 0.1700 | 0.4400 |
| 1.000 | 3.85 | 0.1910 | 0.5480 |
| 1.000 | 3.67 | 0.2780 | 0.9090 |
| 1.000 | 3.60 | 0.2990 | 1.0270 |
| 1.000 | 3.52 | 0.3680 | 1.3180 |
| 1.000 | 3.34 | 0.5420 | 1.7440 |
| *Tetrachloromethane as the Diluent* | | | |
| 0.500 | 3.55 | 0.0501 | 0.0140 |
| 0.500 | 3.39 | 0.0940 | 0.0302 |
| 0.500 | 3.32 | 0.1480 | 0.0501 |
| 0.500 | 3.19 | 0.1990 | 0.0730 |
| 0.500 | 3.20 | 0.2830 | 0.1120 |
| 0.500 | 3.06 | 0.3600 | 0.1590 |
| 0.500 | 3.00 | 0.4120 | 0.1990 |
| 0.500 | 2.90 | 0.5590 | 0.3270 |
| 0.500 | 2.86 | 0.6390 | 0.4030 |
| 0.500 | 2.79 | 0.7380 | 0.4490 |

**Table 3. Equilibrium Data for the System Propionic Acid + Trioctylamine in Diluent**

| $S_0$/mol·L$^{-1}$ | equil pH in aq phase | total equil conc of acetic acid/mol·L$^{-1}$ | |
|---|---|---|---|
| | | aq conc | org conc |
| *1-Octanol as the Diluent* | | | |
| 0.500 | 5.53 | 0.0011 | 0.0310 |
| 0.500 | 5.25 | 0.0024 | 0.0810 |
| 0.500 | 5.00 | 0.0049 | 0.1400 |
| 0.500 | 4.81 | 0.0076 | 0.1870 |
| 0.500 | 4.55 | 0.0140 | 0.2700 |
| 0.500 | 4.23 | 0.0290 | 0.3810 |
| 0.500 | 4.02 | 0.0500 | 0.4780 |
| 0.500 | 3.77 | 0.0790 | 0.5940 |
| 0.500 | 3.62 | 0.1100 | 0.7200 |
| 0.500 | 3.48 | 0.1600 | 0.8360 |
| 0.500 | 3.35 | 0.2100 | 0.9790 |
| 0.500 | 3.24 | 0.2690 | 1.1220 |
| 1.000 | 5.53 | 0.0013 | 0.0530 |
| 1.000 | 5.19 | 0.0027 | 0.1140 |
| 1.000 | 4.91 | 0.0050 | 0.1660 |
| 1.000 | 4.69 | 0.0070 | 0.2240 |
| 1.000 | 4.44 | 0.0130 | 0.3180 |
| 1.000 | 4.18 | 0.0220 | 0.4400 |
| 1.000 | 4.06 | 0.0290 | 0.5030 |
| 1.000 | 3.94 | 0.0330 | 0.5990 |
| 1.000 | 3.74 | 0.0650 | 0.8520 |
| 1.000 | 3.65 | 0.0990 | 1.1040 |
| 1.000 | 3.55 | 0.1901 | 1.5440 |
| *Chloroform as the Diluent* | | | |
| 0.500 | 5.09 | 0.0015 | 0.0520 |
| 0.500 | 4.90 | 0.0025 | 0.0920 |
| 0.500 | 4.75 | 0.0050 | 0.1430 |
| 0.500 | 4.64 | 0.0064 | 0.1940 |
| 0.500 | 4.47 | 0.0110 | 0.2850 |
| 0.500 | 4.25 | 0.0210 | 0.4180 |
| 0.500 | 4.09 | 0.0350 | 0.5390 |
| 0.500 | 3.90 | 0.0560 | 0.6790 |
| 0.500 | 3.73 | 0.0860 | 0.8210 |
| 0.500 | 3.55 | 0.1330 | 0.9400 |
| 0.500 | 3.38 | 0.1940 | 1.0530 |
| 0.500 | 3.25 | 0.2710 | 1.1490 |
| *Methyl Isobutyl Ketone as the Diluent* | | | |
| 0.500 | 4.70 | 0.0110 | 0.0430 |
| 0.500 | 4.51 | 0.0180 | 0.0760 |
| 0.500 | 4.36 | 0.0250 | 0.1220 |
| 0.500 | 4.26 | 0.0330 | 0.1680 |
| 0.500 | 4.12 | 0.0440 | 0.2520 |
| 0.500 | 3.98 | 0.0600 | 0.3790 |
| 0.500 | 3.89 | 0.0720 | 0.4930 |
| 0.500 | 3.78 | 0.0920 | 0.6110 |
| 0.500 | 3.71 | 0.1120 | 0.7450 |
| 0.500 | 3.62 | 0.1360 | 0.8950 |
| 0.500 | 3.53 | 0.1680 | 1.0550 |
| 0.500 | 3.43 | 0.2120 | 1.2130 |
| *Tetrachloromethane as the Diluent* | | | |
| 0.500 | 4.07 | 0.0180 | 0.0350 |
| 0.500 | 3.93 | 0.0320 | 0.0630 |
| 0.500 | 3.80 | 0.0490 | 0.0990 |
| 0.500 | 3.71 | 0.0630 | 0.1370 |
| 0.500 | 3.55 | 0.0900 | 0.2060 |
| 0.500 | 3.49 | 0.1230 | 0.3150 |
| 0.500 | 3.25 | 0.1580 | 0.4930 |
| 0.500 | 3.21 | 0.1960 | 0.6110 |
| 0.500 | 3.16 | 0.2340 | 0.7450 |
| 0.500 | 3.11 | 0.2790 | 0.8950 |
| 0.500 | 3.08 | 0.3350 | 1.0550 |
| 0.500 | 3.01 | 0.4080 | 1.2130 |

stepwise reaction as follows

$$R_3N \cdot (HA)_{p-1(\text{org})} + HA_{\text{aq}} \Leftrightarrow R_3N \cdot (HA)_{p(\text{org})}$$

$$p = 1, 2, 3 \quad (1)$$
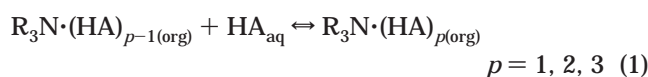
$$K_{p1} = \frac{[R_3N \cdot (HA)_p]_{\text{org}}}{[R_3N \cdot (HA)_{p-1}]_{\text{org}}[HA]_{\text{aq}}} \quad (2)$$

And the material balance for the solute and trioctylamine was involved

$$C_{org} - [HA]_{org} = [R_3N \cdot (HA)]_{org} + 2[R_3N \cdot (HA)_2]_{org} + 3[R_3N \cdot (HA)_3]_{org} = K_{11}[R_3N]_{org}[HA]_{aq} + 2K_{11}K_{21}[R_3N]_{org}[HA]_{aq}^2 + 3K_{11}K_{21}K_{31}[R_3N]_{org}[HA]_{aq}^3 \quad (3)$$

$$S_0 - [R_3N]_{org} = [R_3N \cdot HA]_{org} + [R_3N \cdot (HA)_2]_{org} + [R_3N \cdot (HA)_3]_{org} = K_{11}[R_3N]_{org}[HA]_{aq} + K_{11}K_{21}[R_3N]_{org}[HA]_{aq}^2 + K_{11}K_{21}K_{31}[R_3N]_{org}[HA]_{aq}^3 \quad (4)$$

where $pK_a$ is the dissociation constant of acid in the aqueous phase, $m$ is the physical extraction constant of the acid for the pure diluent, $\phi$ is the volume fraction of diluent in the extractant phase, $S_0$ is the initial concentration of trioctylamine in the extractant phase, $C_{org}$ is the total carboxylic acid concentration in the extractant phase, $K_{p1}$ is the apparent equilibrium constant of the $p$-rank extraction reaction, the square brackets represent the concentrations, and all of the concentrations are expressed in molar terms.

The loading of trioctylamine, $Z$, defined in eq 5 (similar to ref 4), can be expressed with a function of $pK_a$, $\phi$, $m$, $S_0$, $C_{aq}$, pH, $K_{11}$, $K_{21}$, and $K_{31}$, where $C_{aq}$ is the total carboxylic acid concentration in the aqueous phase. Using eqs 3–6, the values of $Z$ of any systems can be predicted if the constants $K_{11}$, $K_{21}$, and $K_{31}$, are known. $K_{11}$, $K_{21}$, and $K_{31}$ as the iterated parameters can be determined by fitting the data $Z$ using nonlinear regression.

$$Z = \frac{C_{org} - [HA]_{org}}{S_0} = \frac{C_{org} - m[HA]_{aq}}{S_0} \quad (5)$$

and

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

## Materials and Methods

**Chemicals.** All of the carboxylic acids were analytical reagents. Trioctylamine with purity > 99 mass % (Fluka) was used as extractant. Four diluents, 1-octanol, chloroform, methyl isobutyl ketone, and tetrachloromethane (analytical reagent), were used in this work. Characteristics of components are presented in Table 1.

**Extraction Experiments.** All extraction experiments were conducted with 50 mL flasks at 25 ± 0.5 °C. Ten milliliters of the extractant and 10 mL of the acid solution were added to each flask. The flask containing the mixture was shaken for about 6 h in a shaker bath with a vibrating rate of 200 rpm and then was left to equilibrate for 1 to 2 h, followed by separating the two phases. The upper layer (extractant phase) was removed, and an aqueous-phase sample was taken from the bottom layer (aqueous phase) for pH and solute concentration analyses.

**Sample Analysis.** The carboxylic acid in the aqueous phase ($C_{aq}$) was titrated by NaOH with a microburet using phenolphthalein as indicator. The carboxylic acid concentrations in the extractant phase ($C_{org}$) were calculated by material balance. The preliminary experiment of stripping of the extractant phase showed that the deviation of the calculation was within 2%, which probably resulted from the volume changing for each phase and the error of the analysis method.

**Table 4. Equilibrium Data for the System Butyric Acid + Trioctylamine in Diluent**

| $S_0$/mol·L$^{-1}$ | equil pH in aq phase | total equil conc of acetic acid/mol·L$^{-1}$ | |
|---|---|---|---|
| | | aq conc | org conc |
| 1-Octanol as the Diluent | | | |
| 0.500 | 5.84 | 0.0001 | 0.0620 |
| 0.500 | 5.62 | 0.0007 | 0.1150 |
| 0.500 | 5.32 | 0.0021 | 0.1820 |
| 0.500 | 5.10 | 0.0033 | 0.2540 |
| 0.500 | 4.82 | 0.0070 | 0.3550 |
| 0.500 | 4.60 | 0.0120 | 0.4320 |
| 0.500 | 4.43 | 0.0180 | 0.5240 |
| 0.500 | 4.26 | 0.0260 | 0.6240 |
| 0.500 | 4.12 | 0.0370 | 0.7380 |
| 0.500 | 3.98 | 0.0500 | 0.8530 |
| 1.000 | 5.65 | 0.0007 | 0.1640 |
| 1.000 | 5.20 | 0.0042 | 0.3610 |
| 1.000 | 4.98 | 0.0076 | 0.5060 |
| 1.000 | 4.70 | 0.0150 | 0.8010 |
| 1.000 | 4.58 | 0.0200 | 0.9580 |
| 1.000 | 4.46 | 0.0250 | 1.1390 |
| 1.000 | 4.36 | 0.0320 | 1.3280 |
| 1.000 | 4.28 | 0.0390 | 1.4820 |
| 1.000 | 4.16 | 0.0510 | 1.7320 |
| 1.000 | 3.86 | 0.0960 | 2.4970 |
| Chloroform as the Diluent | | | |
| 0.500 | 5.63 | 0.0004 | 0.0690 |
| 0.500 | 5.47 | 0.0007 | 0.1150 |
| 0.500 | 5.27 | 0.0020 | 0.1820 |
| 0.500 | 5.15 | 0.0030 | 0.2540 |
| 0.500 | 4.97 | 0.0051 | 0.3570 |
| 0.500 | 4.79 | 0.0083 | 0.4630 |
| 0.500 | 4.65 | 0.0110 | 0.5640 |
| 0.500 | 4.49 | 0.0170 | 0.6730 |
| 0.500 | 4.33 | 0.0250 | 0.7980 |
| 0.500 | 4.17 | 0.0370 | 0.9250 |
| 1.000 | 5.21 | 0.0025 | 0.2590 |
| 1.000 | 4.94 | 0.0052 | 0.5090 |
| 1.000 | 4.84 | 0.0074 | 0.6630 |
| 1.000 | 4.75 | 0.0099 | 0.8080 |
| 1.000 | 4.66 | 0.0130 | 0.9680 |
| 1.000 | 4.56 | 0.0180 | 1.1510 |
| 1.000 | 4.39 | 0.0230 | 1.3410 |
| 1.000 | 4.35 | 0.0300 | 1.4960 |
| 1.000 | 4.31 | 0.0420 | 1.7450 |
| 1.000 | 4.21 | 0.0450 | 1.7990 |
| Methyl Isobutyl Ketone as the Diluent | | | |
| 0.500 | 5.07 | 0.0041 | 0.0576 |
| 0.500 | 4.86 | 0.0070 | 0.1075 |
| 0.500 | 4.70 | 0.0098 | 0.1723 |
| 0.500 | 4.58 | 0.0128 | 0.2416 |
| 0.500 | 4.48 | 0.0163 | 0.3385 |
| 0.500 | 4.35 | 0.0215 | 0.4409 |
| 0.500 | 4.31 | 0.0238 | 0.5405 |
| 0.500 | 4.20 | 0.0289 | 0.6417 |
| 0.500 | 4.14 | 0.0338 | 0.7655 |
| 0.500 | 4.07 | 0.0403 | 0.8939 |
| Tetrachloromethane as the Diluent | | | |
| 0.500 | 3.66 | 0.0099 | 0.0580 |
| 0.500 | 3.61 | 0.0150 | 0.1010 |
| 0.500 | 3.57 | 0.0210 | 0.1630 |
| 0.500 | 3.50 | 0.0270 | 0.2300 |
| 0.500 | 3.46 | 0.0340 | 0.3280 |
| 0.500 | 3.45 | 0.0410 | 0.4300 |
| 0.500 | 3.43 | 0.0470 | 0.5280 |
| 0.500 | 3.42 | 0.0550 | 0.6350 |
| 0.500 | 3.41 | 0.0640 | 0.7590 |
| 0.500 | 3.40 | 0.0740 | 0.8880 |

The pH value of the aqueous phase was determined with a pH meter, Hanna pH 201 models.
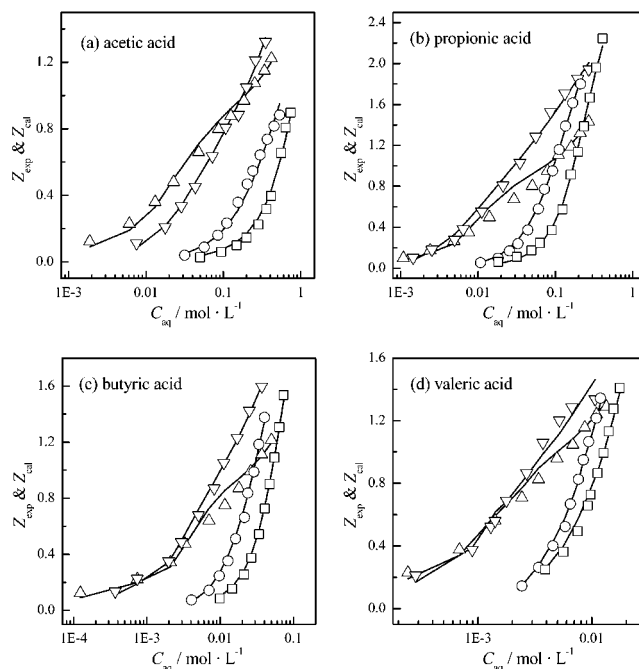
## Results and Discussion

The equilibrium data in various trioctylamine-diluent systems are given in Tables 2–5. According to eqs 3–5,

**Table 5. Equilibrium Data for the System Valeric Acid + Trioctylamine in Diluent**

| $S_0$/mol·L$^{-1}$ | equil pH in aq phase | total equil conc of acetic acid/mol·L$^{-1}$ | |
|---|---|---|---|
| | | aq conc | org conc |
| *1-Octanol as the Diluent* | | | |
| 0.500 | 5.91 | 0.0002 | 0.1150 |
| 0.500 | 5.59 | 0.0007 | 0.1900 |
| 0.500 | 5.27 | 0.0014 | 0.2880 |
| 0.500 | 5.15 | 0.0024 | 0.3680 |
| 0.500 | 4.94 | 0.0034 | 0.4380 |
| 0.500 | 4.76 | 0.0049 | 0.5250 |
| 0.500 | 4.62 | 0.0068 | 0.5950 |
| 0.500 | 4.49 | 0.0087 | 0.6800 |
| 0.500 | 4.37 | 0.0110 | 0.7600 |
| 0.500 | 4.28 | 0.0130 | 0.8250 |
| 1.000 | 5.91 | 0.0003 | 0.2030 |
| 1.000 | 5.54 | 0.0012 | 0.3530 |
| 1.000 | 5.22 | 0.0028 | 0.5880 |
| 1.000 | 5.07 | 0.0045 | 0.7450 |
| 1.000 | 4.98 | 0.0053 | 0.8660 |
| 1.000 | 4.86 | 0.0078 | 0.9830 |
| 1.000 | 4.68 | 0.0110 | 1.1960 |
| 1.000 | 4.55 | 0.0140 | 1.3160 |
| 1.000 | 4.43 | 0.0200 | 1.4930 |
| 1.000 | 4.30 | 0.0240 | 1.6510 |
| *Chloroform as the Diluent* | | | |
| 0.500 | 5.93 | 0.0003 | 0.1100 |
| 0.500 | 5.55 | 0.0009 | 0.2002 |
| 0.500 | 5.39 | 0.0013 | 0.2805 |
| 0.500 | 5.34 | 0.0014 | 0.3080 |
| 0.500 | 5.32 | 0.0018 | 0.3650 |
| 0.500 | 5.17 | 0.0027 | 0.4540 |
| 0.500 | 5.01 | 0.0037 | 0.5830 |
| 0.500 | 4.87 | 0.0052 | 0.6750 |
| 0.500 | 4.73 | 0.0067 | 0.7380 |
| 0.500 | 4.49 | 0.0110 | 0.8200 |
| *Methyl Isobutyl Ketone as the Diluent* | | | |
| 0.500 | 5.26 | 0.0024 | 0.1130 |
| 0.500 | 5.09 | 0.0034 | 0.1880 |
| 0.500 | 4.97 | 0.0045 | 0.2750 |
| 0.500 | 4.88 | 0.0058 | 0.3580 |
| 0.500 | 4.83 | 0.0065 | 0.4400 |
| 0.500 | 4.76 | 0.0076 | 0.5380 |
| 0.500 | 4.68 | 0.0084 | 0.6130 |
| 0.500 | 4.65 | 0.0094 | 0.6880 |
| 0.500 | 4.58 | 0.0110 | 0.7880 |
| 0.500 | 4.54 | 0.0120 | 0.8680 |
| *Tetrachloromethane as the Diluent* | | | |
| 0.500 | 3.96 | 0.0039 | 0.1550 |
| 0.500 | 3.94 | 0.0056 | 0.2250 |
| 0.500 | 3.95 | 0.0075 | 0.3050 |
| 0.500 | 3.96 | 0.0092 | 0.3990 |
| 0.500 | 3.97 | 0.0100 | 0.4350 |
| 0.500 | 4.04 | 0.0110 | 0.5200 |
| 0.500 | 4.05 | 0.0130 | 0.5950 |
| 0.500 | 4.05 | 0.0140 | 0.6750 |
| 0.500 | 4.05 | 0.0150 | 0.7580 |
| 0.500 | 4.03 | 0.0180 | 0.8410 |



**Figure 1.** Loading curve of carboxylic acid in 0.500 mol·L$^{-1}$ trioctylamine−diluent systems: △, 1-octanol; ▽, chloroform; ○, methyl isobutyl ketone; □, tetrachloromethane; −, predicted data.
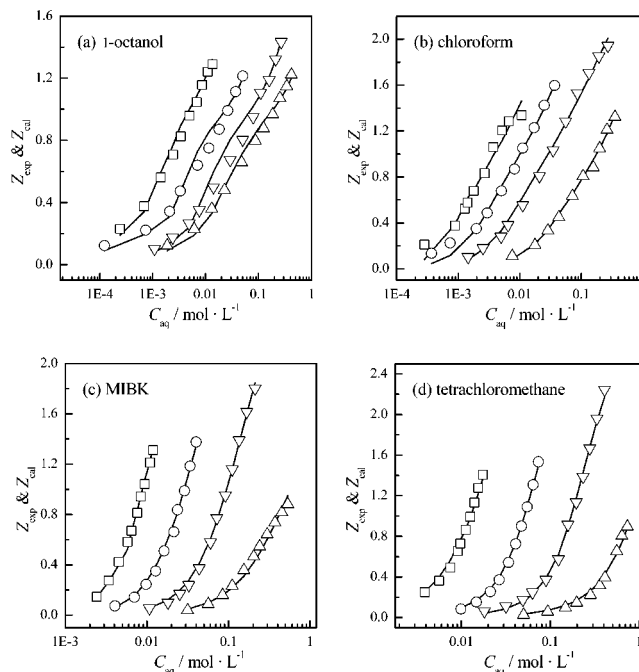


**Figure 2.** Loading curve of carboxylic acid in 0.500 mol·L$^{-1}$ trioctylamine−diluent systems: △, acetic acid; ▽, propionic acid; ○, butyric acid; □, valeric acid; −, predicted data.

$K_{11}$, $K_{21}$, and $K_{31}$ were obtained by fitting the data $Z$ using a least-squares regression method, and the results were listed in Table 6. As shown in Figure 1, the predicted curves superimpose the data very well. Thus, the model is valid for representing the equilibrium behavior of carboxylic acid−trioctylamine systems.

***Diluent.*** In general, the degree of extraction depends on the type of diluent used. A polar diluent increases the extracting ability of relatively low polarity amines by providing additional solvating power that allows higher levels of polar-amine complexes to stay in the extractant phase. On the other hand, a nonpolar diluent does not affect the extraction process with low polarity amines.[17] Similarly, the results obtained in this work (Figure 1) show that polar diluent provides larger loading of trioctylamine

than inert diluent, and the consequence is that 1-octanol ≈ chloroform > methyl isobutyl ketone > tetrachloromethane at $Z < 1$.
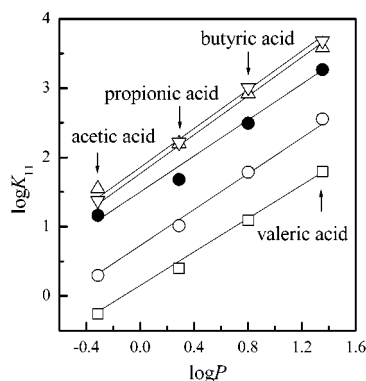
Most complexes exists as the (1, 1) form when the carboxylic acid concentration is low ($Z < 1$).[18] Thus, the apparent equilibrium constant, $K_{11}$, representing the degree of extraction, has the same sequence as $Z$ for the various diluents.

***Solutes.*** As indicated by the loading of trioctylamine (Figure 2), the degree of extraction of carboxylic acids with trioctylamine is in the order valeric acid > butyric acid >

**Table 6. Model Parameters for Trioctylamine−Carboxylic Acid Systems**

| solute | diluent | $S_0$/mol·L$^{-1}$ | log($K_{11}$/L·mol$^{-1}$) | log($K_{21}$/L·mol$^{-1}$) | log($K_{31}$/L·mol$^{-1}$) | $m$ |
|---|---|---|---|---|---|---|
| acetic acid | 1-octanol | 0.500 | 1.5510 | −0.3979 | −0.0458 | 0.4861 |
| | | 1.000 | 1.1653 | −0.6990 | −0.3010 | 0.4861 |
| | chloroform | 0.500 | 1.3802 | 0 | 0.1761 | 0.0976 |
| | | 1.000 | 1.3010 | 0 | 0 | 0.0976 |
| | methyl isobutyl ketone | 0.500 | 0.2982 | 0.1761 | | 0.5141 |
| | | 1.000 | 0.4482 | 0.4472 | 0.0414 | 0.5141 |
| | tetrachloromethane | 0.500 | −0.1549 | 0 | −0.1549 | 0 |
| propionic acid | 1-octanol | 0.500 | 2.1998 | −0.0458 | 0.5441 | 1.9518 |
| | | 1.000 | 1.6808 | 0.3010 | 0.3424 | 1.9518 |
| | chloroform | 0.500 | 2.2147 | 0.9912 | 0.1761 | 0.8484 |
| | methyl isobutyl ketone | 0.500 | 1.0143 | 0.8129 | 0.7782 | 1.9099 |
| | tetrachloromethane | 0.500 | 0.3979 | 0.6990 | 0.7404 | 0.2858 |
| butyric acid | 1-octanol | 0.500 | 2.9205 | 0.6990 | 0.9031 | 6.3365 |
| | | 1.000 | 2.4933 | 1.1614 | 0.9777 | 6.3365 |
| | chloroform | 0.500 | 3.0095 | 1.4065 | 1.1761 | 4.4079 |
| | | 1.000 | 2.5855 | 1.4914 | 1.0969 | 4.4079 |
| | methyl isobutyl ketone | 0.500 | 1.7876 | 1.2788 | 1.2788 | 6.6106 |
| | tetrachloromethane | 0.500 | 0.9133 | 1.3617 | 1.0969 | 2.1192 |
| valeric acid | 1-octanol | 0.500 | 3.5829 | 1.4472 | 1.3222 | 22.5082 |
| | | 1.000 | 3.2656 | 1.4472 | 1.1461 | 22.5082 |
| | chloroform | 0.500 | 3.6844 | 2.1703 | 1.3424 | 18.3971 |
| | methyl isobutyl ketone | 0.500 | 2.5545 | 2.0212 | 1.7404 | 21.2786 |
| | tetrachloromethane | 0.500 | 1.7944 | 1.8325 | 1.7076 | 10.0733 |



**Figure 3.** Relationship between hydrophobicity (log $P$) and the apparent reactive extraction equilibrium constant log $K_{11}$. $S_0 =$ 0.500 mol·L$^{-1}$: △, 1-octanol; ▽, chloroform; ○, methyl isobutyl ketone; □, tetrachloromethane. $S_0 =$ 1.000 mol·L$^{-1}$: ●, 1-octanol.

propionic acid > acetic acid. It is apparent that the longer chain carboxylic acid has more hydrophobicity and can be extracted better by trioctylamine. Also $K_{11}$ shows the same sequence as $Z$ for the various carboxylic acids.

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 of pH is <2 because of the pH only from the acid; therefore, the pH dependence is not obvious, especially for the higher initial acid concentration cases.

Generally, the degree of extraction depends on three major aspects: (1) the association ability between solute and trioctylamine, p$K_b$ − p$K_a$, (2) the hydrophobicity of the solute, log $P$, which value is the distribution coefficient with 1-octanol as the extractant log form, and (3) the steric effect between solute and extractant. The hydrophobicity of the solute should be the key aspect because of the similar molecular structures and close p$K_a$ values for the present carboxylic acids. A plot of log $K_{11}$ versus log $P$ (based on this work) is shown in Figure 3. log $K_{11}$ is linear with log $P$ of the carboxylic acid, and the slope is about 1.3 for all four diluents. Similarly, the slopes are 1.1 and 1.0 for log $K_{21}$ versus log P and log $K_{31}$ versus log P, respectively.

It should be noted that a polar diluent increases the extracting ability of trioctylamine by providing additional solvating power, but when the trioctylamine concentration in the extractant phase increases, the degree of extraction for carboxylic acid will reduce because of the decrease of the diluent concentration. As indicated by the values of equilibrium data, the degree of extraction for carboxylic acid with trioctylamine, and $K_{11}$, 0.500 mol·L$^{-1}$ trioctylamine + diluent > 1.000 mol·L$^{-1}$ trioctylamine + diluent except for the system of methyl isobutyl ketone as diluent. Therefore, an optimal trioctylamine concentration should be considered in use.

## Conclusions

In this work, extraction equilibrium studies for the systems monocarboxylic acid (acetic, propionic, butyric, and valeric acids) + trioctylamine in various diluents (1-octanol, chloroform, methyl isobutyl ketone, and tetrachloromethane) were conducted at various trioctylamine concentrations. The degree of extraction for carboxylic acid with trioctylamine shows that 1-octanol ≈ chloroform > methyl isobutyl ketone > tetrachloromethane, and valeric acid > butyric acid > propionic acid > acetic acid. By using mass action law, and suitable assumptions, an expression of extraction equilibrium is derived, and the apparent extraction equilibrium constants are evaluated. The predicted loading of trioctylamine agrees well with the experimental values. log $K_{11}$ is linear with the hydrophobicity of acids.

## Note Added after ASAP Posting

This article was released ASAP on 6/22/2002 with errors in eq 6 and the paragraph preceding it. The correct version was posted on 7/1/2002.

## Literature Cited

(1) King, C. J. Advances in Separation Techniques: Recovery of Polar Organics from Aqueous Solution. *11th International Congress of Chemical Engineers*, Chisa: Prague, 1993; 2.1 1062−1067.
(2) Kertes, A. S.; King, C. J. Extraction Chemistry of Fermentation Product Carboxylic Acids. *Biotechnol. Bioeng.* **1986**, *28*, 269−282.
(3) Spala, E. E.; Richer, N. L. Thermodynamic Model for Solvating Solutions with Physical Interaction. *Ind. Eng. Chem. Process Des. Dev.* **1982**, *21*, 409−416.
(4) Tamada, J. A.; Kertes, A. S.; King, C. J. Extraction of Carboxylic Acids with Amine Extractants. 1. Equilibria and Law of Mass Action Modeling. *Ind. Eng. Chem. Res.* **1990**, *29*, 1319−1326.
(5) Yang, S. T.; White, S. A.; Hsu, S. T. Extraction of Carboxylic Acids with Tertiary and Quaternary Amines. Effect of pH. *Ind. Eng. Chem. Res.* **1991**, *30*, 1335−1342.

(6) Eyal, A. M.; Canari, R. pH Dependence of Carboxylic and Mineral Acid Extraction by Amine-based Extractants: Effect of p$K_a$, Amine Basicity and Diluent Properties. *Ind. Eng. Chem. Res.* **1995**, *34*, 1067−1075.

(7) Yoshizawa, H. Equilibrium of Aqueous Propionic Acid with Trioctylamine in Dodecane. *J. Chem. Eng. Data* **1994**, *39*, 777−780.

(8) Fahim, A. Extraction Equilibria of Acetic and Propionic acids from Dilute Aqueous Solution by Several Solvents. *Sep. Sci. Technol.* **1992**, *27*, 1809−1821.

(9) King, C. J. Amine-based Systems for Carboxylic Acid Recovery: Tertiary Amines and the Proper Choice of Diluent Allow Extraction and Recovery from Water. *CHEMTECH* **1992**, *5*, 285−291.

(10) Hartl, I.; Marr, R. Extraction Processes for Bioproduct Separation. *Sep. Sci. Technol.* **1993**, *28*, 805−809.

(11) Poole, L. J.; King, C. J. Regeneration of Carboxylic Acid-amine Extracts by Back-extraction with an Aqueous Solution of a Volatile Amine. *Ind. Eng. Chem. Res.* **1991**, *30*, 923−929.

(12) Juang, R. S.; Huang, R. H. Comparison of Extraction Equilibria of Succinic and Tartaric Acids from Aqueous Solutions with Tri-*n*-octylamine. *Ind. Eng. Chem. Res.* **1996**, *35*, 1944−1950.

(13) Tamada, J. A.; King, C. J. Extraction of Carboxylic Acids with Amine Extractants. 2. Chemical Interactions and Interpretation of Data. *Ind. Eng. Chem. Res.* **1990**, *29*, 1327−1333.

(14) Hano, T.; Matsumoto, M.; Ohtake, T.; Sasaki, K.; Kawano, Y. Extraction Equilibria of Organic Acids with Tri-*n*-octylphosphineoxide. *J. Chem. Eng. Jpn.* **1990**, *23*, 734−738.

(15) Sabolova, E.; Schlosser, S.; Martak, J. Liquid−Liquid Equilibria of Butyric Acid in Water + Solvent Systems with Trioctylamine as Extractant. *J. Chem. Eng. Data* **2001**, *46*, 735−745.

(16) Dean, J. A. *Lang's handbook of chemistry*; McGraw-Hill: New York, 1985.

(17) Wen, M.; Yang, Y.; Dai, Y.; Wang, J. Mechanism of extraction of carboxylic acid with tri-o-octylamine. (I) Acetic acid -TOA system. *J. Chem. Ind. Eng. (China, Chin. Ed.)* **1998**, *49*, 303−309.

(18) Juang, R. S.; Huang, R H. Equilibrium studies on reactive extraction of lactic acid with an amine extractant. *Chem. Eng. J.* **1997**, *65*, 47−53.