Extraction Equilibria of Glycolic and Glyoxylic Acids with Trialkylphosphine Oxide and Trioctylamine as Extractant

Wei Qin,* Yaohong Zhang, Zhenyu Li, and Youyuan Dai

Department of Chemical Engineering, Tsinghua University, Beijing 100084, P. R. China

Extraction of glycolic acid and glyoxylic acid from aqueous solution by trialkylphosphine oxide in methyl isobutyl ketone and trioctylamine in 1-octanol was studied under various extractant and acid concentrations. Glycolic acid can be extracted into the organic phase better by trialkylphosphine oxide than glyoxylic acid, whereas glyoxylic acid can be extracted into the organic phase better by trioctylamine than glycolic acid. Trialkylphosphine oxide could be used to remove glycolic acid from the mixture of glycolic acid and glyoxylic acid. A mathematical model was developed to describe the above liquid−liquid equilibrium. The reactive extraction mechanism of glycolic and glyoxylic acids with trialkylphosphine oxide and trioctylamine is also discussed.

Introduction

The production of organic chemicals at relatively low concentration in aqueous solutions is typical when using electrochemical and biochemical synthetic methods. Recovery of these solute species can be achieved by solvent extraction, and the reactive recovery of carboxylic acid from the diluent aqueous solutions has received increasing attention.[1]

Extractants such as phosphorus-bonded, oxygen-containing extractants, tributyl phosphate and trialkylphosphine oxide, and long-chain, aliphatic amines, trioctylamine and trialkyl(mono)methylammonium chloride, are more effective for the extraction of carboxylic acids and have been used in the separation of acetic acid,[2−6] lactic acid,[7−10] propionic acid,[8,11] butyric acid,[8,12] succinic acid,[13] and so forth. The strong interaction between the acid and extractant allows for the formation of acid−extractant complexes and thus provides for high equilibrium distribution ratios. Additionally, the high affinity of the organic base and phosphorus oxygen extractants for the acid gives selectivity for the acid over other nonacidic components in the mixture. This reaction is reversible, enabling recovery of the acid and recycling of the solvent.

Glyoxylic acid is an important chemical and can be used as the substrate for the production of pharmaceutical intermediates such as *p*-hydroxyphenylacetic acid, allantoin, vanillin, and *p*-hydroxyphenylglycine. Recently, there has been increasing interest in using an electroreduction method for glyoxylic acid production from oxalic acid[14,15] instead of using an oxidation method from glyoxal with nitric acid. Because glyoxylic acid can be further reduced to glycolic acid by the electroreduction method, the glyoxylic acid product refined by the annealed method is a mixture solution with about 3 mass % oxalic acid, 3−4 mass % glycolic acid, and about 35 mass % glyoxylic acid. It is clear that the purity of the glyoxylic acid produced is unsatisfactory, and it is necessary to remove the impurity, oxalic acid and glycolic acid, and to improve the product purity.

Reactive extraction with trioctylamine as extractant has been used successfully to remove oxalic acid from the mixture of oxalic acid and glyoxylic acid.[17] However, the removal of glycolic acid from the mixture of glyoxylic acid and glycolic acid is difficult, because glyoxylic acid has a slightly larger acidity and hydrophobicity than glycolic acid (as shown in Table 1); thus, it is extracted more easily into the organic phase than glycolic acid.

Table 1. Physical Properties of Carboxylic Acids

chemical	formula	avg MW	pK_a[16]	hydrophobicity (log P [a])[16]
glycolic acid	$HO-CH_2-COOH$	76.05	3.83	−1.097
glyoxylic acid	$HOC-COOH$	74.04	3.34	−0.413

[a] log P is the distribution coefficient with 1-octanol as the extractant log form suggested by Hansch.

In this work, the extraction of glyoxylic acid and glycolic acid from aqueous solution by trialkylphosphine oxide and trioctylamine was examined. Equilibrium data are presented for the system of carboxylic acid with trialkylphosphine oxide in methyl isobutyl ketone and trioctylamine in 1-octanol. A mathematical model based on mass action law has been developed to describe the liquid−liquid equilibrium.

Materials and Methods

Chemicals. Glycolic acid, from Beijing Xizhong Chemical Co, was a chemically pure aqueous solution with concentration > 35 mass % and purity > 99.9%, and glyoxylic acid, from Merck, was an analytical reagent with purity > 97 mass %. The characteristics of the acids are presented in Table 1. Trialkylphosphine oxide was kindly supplied by CYTEC Canada Incorporation free of charge, and trioctylamine with purity > 99 mass % was from Fluka. The two diluents, 1-octanol and methyl isobutyl ketone, from Beijing Chemical Plant, were analytical reagents with purity > 99 mass %. The physical properties of the solvents obtained from the manufactures are list in Table 2.

Extraction Experiments. All extraction experiments were conducted with 50 mL flasks at (25 ± 2) °C. Solvent (15 mL) and 15 mL of the carboxylic acid aqueous solution were added to each flask without adjusting the solution pH. The flask containing the mixture was shaken for about

---

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

10.1021/je025624u CCC: $25.00

Table 2. Physical Properties of Extractants and Diluents

chemical	formula	avg MW	ρ/g·cm^{-3}
trialkylphosphine oxide	$[CH_3(CH_2)_{7-9}]_3P{=}O$	350	0.88
trioctylamine	$[CH_3(CH_2)_7]_3N$	353.67	0.82
methyl isobutyl ketone	$[CH_3]_2CHCH_2COCH_3$	100.16	0.80
1-octanol	$CH_3(CH_2)_7OH$	130.23	0.83

3 h in a shaker bath with a vibrating rate of 200 rpm, and then it was left to equilibrate for (1 to 2) h, followed by separation of the two phases. An aqueous-phase sample was taken from the bottom layer (aqueous phase) using a syringe with a long needle for pH and solute concentration analyses at (25 ± 2) °C.

Sample Analysis. The aqueous samples were analyzed for acid concentration by using a high-pressure liquid chromatography (HPLC) system with an organic acid analysis column (RSpak KC-811) and a UV spectrophotometer (Waters 2487 at 210 nm wavelength). The eluent was 0.1% phosphoric acid, at a flow rate of 1.0 mL·min^{-1}. The concentration of carboxylic acid in the organic phase (C_{org}) was calculated by material balance. The preliminary experiment of stripping of the organic phase indicated that the deviation of calculated values of carboxylic acid concentrations was within ±3%. The pH value of the aqueous phase was determined with a pH meter (Hanna pH 201 model) with a deviation of ±0.02.

Theory

The reactive extraction equilibrium for polar dilute solution of organic solutes could be described by the mass action law in which the equilibrium behavior can be modeled by postulating the formation of various stoichiometric complexes of acid and amine.[18] A reactive equilibrium description of the system can be written as a set of equilibria involving the dissociation equilibrium of the acid in water and the formation of a complex with acid and extractant by ion-pair association or hydrogen bonding,[19] $-COO^-\ {}^+HNR_3$, $-COH\cdots NR_3$, $-CH_2OH\cdots NR_3$, $-COH\cdots O{=}PR_3'$, $-COOH\cdots O{=}PR_3'$, and $-CH_2OH\cdots O{=}PR_3'$, where R_3N and $R_3'P{=}O$ stand for trioctylamine and trialkylphosphine oxide, respectively. It assumes that the reactive extraction between carboxylic acid and extractant takes place at the organic−aqueous interface and two types of complexes, (1, 1) and (1, 2), like HA·S and HA·S$_2$ were formed in the stepwise manner.

The distribution coefficient, D, is defined as the total molar concentration of carboxylic acid (all forms) in the organic phase, divided by that in the aqueous phase. With appropriate material balance, D can be derived as

$$D = \frac{C_{org}}{C_{aq}} = \frac{[HA]_{org} + [HA\cdot S]_{org} + [HA\cdot S_2]_{org}}{[HA]_{aq} + [A^-]_{aq}} = \frac{\Phi m + K_{11}[S]_{org} + K_{11}K_{12}[S]_{org}^{\ 2}}{1 + 10^{pH-pK_a}} \quad (1)$$

$$[S]_{org} = \frac{\sqrt{(1 + K_{11}[HA]_{aq})^2 + 8S_0K_{11}K_{12}[HA]_{aq}} - (1 + K_{11}[HA]_{aq})}{4K_{11}K_{12}[HA]_{aq}} \quad (2)$$

and

$$[HA]_{aq} = \frac{C_{aq}}{1 + 10^{pH-pK_a}} \quad (3)$$

where HA and S present the carboxylic acid and extractant, respectively. The species concentrations are denoted by square brackets and are expressed in molar terms. A$^-$ stands for the anion of the carboxylic acid. D is the distribution coefficient of the acid between the extractant and aqueous phases. C_{org} and C_{aq} are the total carboxylic acid concentrations in the organic and aqueous phases at the equilibrium conditions, respectively. pK_a is the dissociation constant of the acid in the aqueous phase. m is the physical extraction constant of the acid between pure diluent and water. Φ is the volume fraction of diluent in the organic phase. S_0 is the initial concentration of extractant in the organic phase. K_{11} and K_{12} are the apparent equilibrium constants of the (1, 1) and (1, 2) complexes, respectively. The subscripts aq and org stand for the species in the aqueous phase and the organic phase.

Results and Discussion

The equilibrium data in various systems are given in Tables 3 and 4. K_{11} and K_{12} were determined by fitting the equilibrium data to eqs 1−3 using a least-squares regression method, and the results were listed in Table 5. As shown in Figures 1 and 2, the predicted curves superimpose the experimental data very well. Thus, the model is valid for representing the equilibrium behavior for carboxylic acid with trialkylphosphine oxide and trioctylamine.

Trialkylphosphine Oxide in Methyl Isobutyl Ketone. As shown by the value of the equilibrium data at various concentrations of trialkylphosphine oxide in Table 3, the degree of extraction for both acids is directly proportional to the extractant concentration at the same equilibrium acid concentration in the aqueous phase. This phenomenon indicates that the high extractant concentration benefits the recovery of the acid, and the diluent, methyl isobutyl ketone does not provide additional solvating power that allows higher levels of polar-extractant complexes to stay in the organic phase. Therefore, the degree of extraction for the carboxylic acids can be expressed with the simple additive of the physical extraction from the diluent and the reactive extraction from the extractant, and K_{11} is insensitive to the extractant concentration. This is similar to the equilibrium behavior of other carboxylic acids with phosphorus-bonded, oxygen-containing extractants.[20,21]

As indicated by the values of K_{11} and K_{12} for both acids, glycolic acid has two forms, complexes (1, 1) and (1, 2), with trialkylphosphine oxide, while glyoxylic acid only has one complex, (1, 1). Comparing the experimental data for both acids, the degree of extraction for glycolic acid with trialkylphosphine oxide is higher than that for glyoxylic acid. This phenomenon is in contrast to the extraction rules that the more hydrophobic and acidic the acid, the larger the degree of extraction.[3,22] Maybe this results from the extra association with extractant and glycolic acid (complex (1, 2)) or less steric hindrance of phosphorus-bonded, oxygen-containing extractants. Trialkylphosphine oxide can be used to remove glycolic acid from the mixture of glycolic acid and glyoxylic acid.

Trioctylamine in 1-Octanol. Similar to the case of trialkylphosphine oxide as the extractant, the degree of extraction of trioctylamine for both acids increases with an increase of the extractant concentration but is not directly proportional to the extractant concentration at the same equilibrium acid concentration in the aqueous phase, as shown by the equilibrium data in Table 4. This fact ascertains that the polar diluent, 1-octanol, provides additional solvating power that allows higher levels of polar

Table 3. Equilibrium Data of Carboxylic Acid between Water and Trialkylphosphine Oxide in Methyl Isobutyl Ketone

init conc of extractant/mol·L^{-1}	equil pH in aq phase	total equil conc of the acid	
		C_{aq}/mol·L^{-1}	C_{org}/mol·L^{-1}
	Glycolic Acid		
0.2568	1.62	2.4655	0.2870
0.2568	1.86	0.9958	0.1438
0.2568	2.05	0.4663	0.0732
0.2568	2.25	0.1869	0.0330
0.2568	2.40	0.0942	0.0174
0.2568	2.75	0.0184	0.0036
0.2568	3.08	0.0075	0.0013
0.5135	1.55	2.3625	0.3900
0.5135	1.89	0.9090	0.2110
0.5135	2.08	0.4212	0.1183
0.5135	2.34	0.1680	0.0519
0.5135	2.43	0.0826	0.0290
0.5135	2.64	0.0400	0.0140
0.5135	2.80	0.0165	0.0055
0.5135	3.13	0.0041	0.0013
0.7702	2.20	0.3733	0.1615
0.7702	2.44	0.1439	0.0774
0.7702	2.67	0.0534	0.0308
0.7702	2.77	0.0346	0.0201
0.7702	2.96	0.0147	0.0081
0.7702	3.09	0.0056	0.0030
1.0270	1.79	2.1042	0.6520
1.0270	2.31	0.3294	0.2068
1.0270	2.41	0.1153	0.0833
1.0270	2.57	0.0530	0.0409
1.0270	2.68	0.0486	0.0396
1.0270	2.73	0.0301	0.0236
1.0270	2.76	0.0299	0.0237
1.0270	2.93	0.0124	0.0093
1.0270	3.13	0.0050	0.0038
1.2838	2.02	0.6657	0.4268
1.2838	2.13	0.3017	0.2378
1.2838	2.28	0.1129	0.1056
1.2838	2.41	0.0546	0.0547
1.2838	2.64	0.0270	0.0270
1.2838	2.77	0.0112	0.0107
1.2838	2.95	0.0057	0.0052
1.7972	1.78	1.8358	0.9605
1.7972	2.11	0.5797	0.5388
1.7972	2.32	0.2598	0.2994
1.7972	2.70	0.0474	0.0644
1.7972	2.81	0.0391	0.0504
1.7972	2.95	0.0246	0.0313
1.7972	3.18	0.0099	0.0124
2.0540	1.68	1.7290	1.0529
2.0540	2.03	0.5392	0.5736
2.0540	2.24	0.2414	0.3149
2.0540	2.51	0.0895	0.1330
2.0540	2.69	0.0437	0.0676
2.0540	2.79	0.0347	0.0543
2.0540	3.13	0.0092	0.0130
2.0540	3.36	0.0049	0.0062
	Glyoxylic Acid		
0.7702	2.52	0.0953	0.0361
0.7702	2.25	0.0615	0.0254
0.7702	2.31	0.0483	0.0166
0.7702	2.49	0.0263	0.0085
0.7702	2.53	0.0195	0.0065
0.7702	2.73	0.0105	0.0034
0.7702	3.15	0.0027	0.0007
0.7702	3.39	0.0015	0.0003
1.2838	2.32	0.0470	0.0400
1.2838	2.36	0.0366	0.0283
1.2838	2.60	0.0147	0.0113
1.2838	2.83	0.0060	0.0044
1.2838	2.99	0.0052	0.0035
1.2838	3.24	0.0023	0.0012
1.2838	3.32	0.0017	0.0009

Table 4. Equilibrium Data of Carboxylic Acid between Water and Trioctylamine in 1-Octanol

init conc of extractant/mol·L^{-1}	equil pH in aq phase	total equil conc of the acid	
		C_{aq}/mol·L^{-1}	C_{org}/mol·L^{-1}
	Glycolic Acid		
0.2000	4.05	0.0033	0.0620
0.2000	3.64	0.0095	0.1100
0.2000	3.12	0.0370	0.1610
0.2000	2.79	0.0960	0.1730
0.2000	2.49	0.2370	0.1730
0.2000	2.33	0.3770	0.1650
0.2000	2.17	0.6350	0.1570
0.2000	2.06	0.8790	0.1390
0.2000	1.94	1.2590	0.0830
0.2000	1.79	1.7480	0.0410
0.5000	3.98	0.0064	0.1390
0.5000	3.64	0.0140	0.2260
0.5000	3.38	0.0250	0.3000
0.5000	2.86	0.0920	0.3850
0.5000	2.57	0.2010	0.4070
0.5000	2.30	0.4330	0.4840
0.5000	2.17	0.6420	0.5260
0.5000	2.05	0.9310	0.5620
0.5000	1.92	1.3190	0.6310
0.5000	1.83	1.6480	0.6810
1.0000	4.33	0.0081	0.1300
1.0000	4.09	0.0120	0.2190
1.0000	3.93	0.0170	0.2950
1.0000	3.69	0.0300	0.4410
1.0000	3.49	0.0490	0.5600
1.0000	3.12	0.1180	0.7280
1.0000	2.85	0.2380	0.8330
1.0000	2.56	0.4690	0.9130
1.0000	2.33	0.8080	1.0320
1.0000	2.18	1.1150	1.1220
	Glyoxylic Acid		
0.5000	4.61	0.0004	0.1730
0.5000	4.24	0.0008	0.2600
0.5000	3.88	0.0023	0.3450
0.5000	3.32	0.0100	0.4250
0.5000	2.68	0.0490	0.4730
0.5000	2.28	0.1510	0.5440
0.5000	2.10	0.2630	0.6050
0.5000	1.97	0.3770	0.6650
0.5000	1.83	0.5570	0.7460
1.0000	5.01	0.0006	0.1300
1.0000	4.52	0.0011	0.2590
1.0000	4.08	0.0018	0.4320
1.0000	3.74	0.0052	0.6030
1.0000	3.31	0.0140	0.7670
1.0000	2.70	0.0540	0.9010
1.0000	2.31	0.1340	0.9950
1.0000	2.09	0.2280	1.0750
1.0000	1.95	0.3320	1.1450
1.0000	1.81	0.5010	1.2360

acid−amine complexes to stay in the organic phase. Therefore, there is an optimum composition for diluent−amine mixture solvent, and K_{11} is dependent on the extractant concentration. In this case, K_{11} decreased with the amine concentration.

Two complexes (1, 1) and (1, 2) are formed with not only glycolic acid but also glyoxylic acid and trioctylamine, and both K_{11} and K_{12} for glyoxylic acid are larger than those for glycolic acid. It is apparent that the degree of extraction for glycolic acid with amine is lower than that for glyoxylic acid. This phenomenon accords with the reactive extraction rule, and it should be taken into account that the solvent should be regenerated with undissociated acid if amine is used to separate glycolic and glyoxylic acid with glyoxylic acid as the product.

Conclusions

In this work, the equilibrium data of glycolic acid and glyoxylic acid extracted by trialkylphosphine oxide in methyl isobutyl ketone and trioctylamine in 1-octanol were

Table 5. Model Parameters for Extractant−Carboxylic Acid Systems

solute	$S_0{}^a$/mol·L^{-1}	$K_{11}{}^b$/L·mol^{-1}	$K_{12}{}^c$/L·mol^{-1}	m^d
Trialkylphosphine Oxide in Methyl Isobutyl Ketone as Extractant				
glycolic acid	0.2568	0.593	0	0.0536
	0.5135	0.593	0.159	0.0536
	0.7702	0.593	0.400	0.0536
	1.0270	0.593	0.387	0.0536
	1.2838	0.593	0.272	0.0536
	1.7972	0.593	0.233	0.0536
	2.0540	0.593	0.206	0.0536
glyoxylic acid	0.7702	0.448	0	0.0886
	1.2838	0.695	0	0.0886
Trioctylamine in 1-Octanol as Extractant				
glycolic acid	0.2000	145	20.0	0.0798
	0.5000	90	4.1	0.0798
	1.0000	40	2.1	0.0798
glyoxylic acid	0.5000	2345	26.0	0.3860
	1.0000	1004	9.0	0.3860

[a] Initial concentration of extractant. [b] Apparent equilibrium constant of the (1, 1) complex. [c] Apparent equilibrium constant of the (1, 2) complex. [d] Physical extraction constant of the acid with pure diluent.

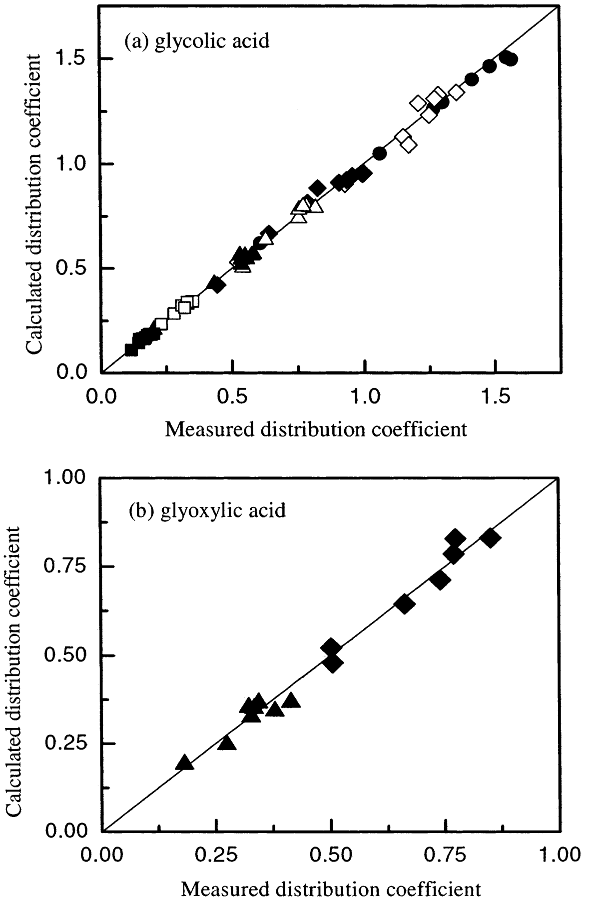

Figure 1. Equilibrium data of carboxylic acid between water and the trialkylphosphine oxide + methyl isobutyl ketone system: ■, 0.2568 mol·L^{-1}; □, 0.5135 mol·L^{-1}; ▲, 0.7702 mol·L^{-1}; △, 1.0270 mol·L^{-1}; ◆, 1.2838 mol·L^{-1}; ◇, 1.7972 mol·L^{-1}; ●, 2.0540 mol·L^{-1}.

presented. The degree of extraction for glycolic acid with trialkylphosphine oxide is higher than that for glyoxylic acid; this is in contrast with the fact that the degree of extraction for glycolic acid with amine is much lower than that for glyoxylic acid. Thus, trialkylphosphine oxide could be used to remove glycolic acid from the mixture of glycolic acid and glyoxylic acid. A mathematical model has been developed to describe the liquid−liquid equilibrium in the system of this paper.

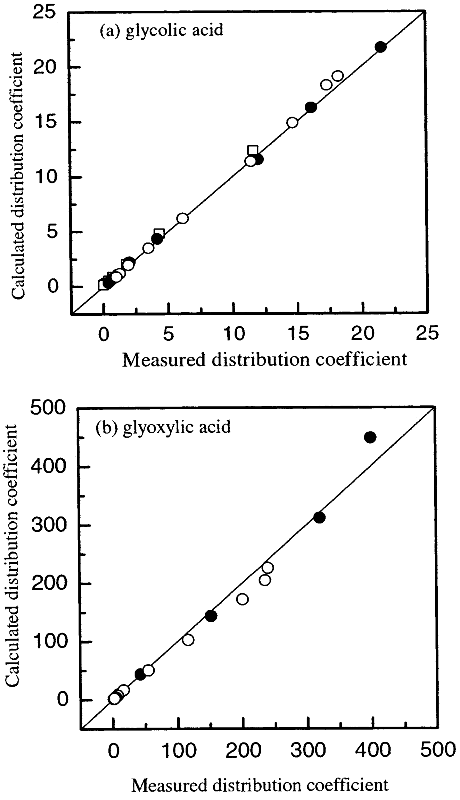

Figure 2. Equilibrium data of carboxylic acid between water and the trioctylamine + 1-octanol system: □, 0.2000 mol·L^{-1}; ●, 0.5000 mol·L^{-1}; ○, 1.0000 mol·L^{-1}.

Literature Cited

(1) Kertes, A. S.; King, C. J. Extraction Chemistry of Fermentation Product Carboxylic Acids. *Biotechnol. Bioeng.* **1986**, *28*, 269−282.

(2) Juang, R. S.; Wu, R. T. Effect of a Water-Insoluble Organic-Acid on Amine Extraction of Acetic Acid from Aqueous-Solutions: Equilibrium Studies. *J. Chem. Technol. Biotechnol.* **1996**, *66*, 160−168.

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

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

(5) Roos, M.; Bart, H.-J. Extraction of Acetic Acid with Tri-*n*-Octylamine: Physical Properties and Phase Equilibria. *J. Chem. Eng. Data* **2001**, *46*, 1198−1202.

(6) Ziegenfuss, H.; Maurer, G. Distribution of Acetic Acid between Water and Organic Solutions of Tri-Octylamine. *Fluid Phase Equilib.* **1994**, *102*, 211−255.

(7) 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.

(8) 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.

(9) Malmary, G.; Albet, J.; Putranto, A.; Hanine, H.; Molinier, J. Recovery of Aconitic and Lactic Acids from Simulated Aqueous Effluents of the Sugar-Cane Industry through Liquid−Liquid Extraction *J. Chem. Technol. Biotechnol.* **2000**, *75* (12), 1169−1173.

(10) Jarvinen, M.; Myllykoski, L.; Keiski, R.; Sohlo, J. Separation of Lactic Acid from Fermented Broth by Reactive Extraction. *Bioseparation* **2000**, *9* (3), 163−166.

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

(12) 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* (3), 735−745.

(13) 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.

(14) Ochoa, J. R.; De Diego, A.; Santa-Olalla, J. Electrosynthesis of Glyoxylic Acid Using a Continuously Electrogenerated Lead Cathode. *J. Appl. Electrochem*. **1993**, *23*, 905−909.

(15) Xia, S. Q.; Chen, S. P.; Sun, S. G. Electrocatalytic Reduction of Oxalic Acid on Platinum Based Pb−Sb Surface Alloy Electrode. *Acta Phys.-Chim. Sin.* **2001**, *17*, 140−143.

(16) John, A. D., Ed. *Lange's Handbook of Chemistry*, XXth ed.; McGraw-Hill Book Co. Inc.: New York, 1972.

(17) Qin, W.; Zhang, Y.; Luo, X.-H.; Dai, Y.-Y. Separation of Oxalic Acid and Glyoxylic Acid by Extraction. *J. Chem. Ind. Eng.* (in Chinese) **2001**, *52* (2), 135−140.

(18) Tamada, J. A.; Kertes, A. S.; King, C. J. Extraction of Carboxylic Acids with Amine Extractants. 1. Equilibrium and Law of Mass Action Modeling. *Ind. Eng. Chem. Res.* **1990**, *29*, 1319−1326.

(19) Li, Z.-Y. Extraction Mechanism of Carboxylic Acid by Trioctylamine. Ph.D. Dissertation, Tsinghua University, Beijing, 2001.

(20) Ingale, M. N.; Mahajani, V. V. Recovery of Carboxylic Acids, C_2-C_6, from an Aqueous Waste Stream Using Tributyl Phosphate (TBP): Effect of Presence of Inorganic Acids and Their Sodium Salts. *Sep. Technol.* **1996**, *6*, 1−7.

(21) Wang, Y.-D.; Li, Y.-X.; Li, Y.; Wang, J.-Y.; Li, Zh.-Y.; Dai, Y.-Y. Extraction Equilibrium of Monocarboxylic Acids with Trialkylphosphine Oxide. *J. Chem. Eng. Data* **2001**, *46*, 831−837.

(22) Tamada, J. A.; Kertes, A. S.; 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.

Received for review October 4, 2002. Accepted January 6, 2003. This work was supported by the National Natural Science Foundation of China (Grant 29836130).

JE025624U