Extraction of Glyoxylic Acid, Glycolic Acid, Acrylic Acid, and Benzoic Acid with Trialkylphosphine Oxide

Yi Li, Yundong Wang,* Yuxin Li, and Youyuan Dai

The State Key Laboratory of Chemical Engineering (Tsinghua University), Department of Chemical Engineering, Tsinghua University, Beijing 100084, People's Republic of China

Liquid−liquid extraction based on reversible chemical complexation is a novel separation technique that is highly effective and selective for separation of polar organic solutes from aqueous solutions. Equilibria of aqueous solutions of glyoxylic acid, glycolic acid, acrylic acid, and benzoic acid with trialkylphosphine oxide (TRPO) in kerosene were investigated. Equilibrium concentrations are given at 298 K. An extraction equilibrium model was used to describe the experimental data. The equilibrium constants were evaluated. Loading of TRPO was calculated.

Introduction

Liquid−liquid extraction is an efficient, economical, and environmentally friendly method for separation of organic acid. It is, therefore, applicable in recovery of acids from waste streams, facilitation of processes through separating of acidic products or byproducts, recovery of acidic products, and so forth. Extractive recovery of carboxylic acids from dilute aqueous solutions has received increasing attention. Phosphorus-bonded, oxygen-containing extractants have a phosphoryl group and so have a stronger Lewis basicity than carbon-bonded, oxygen-containing extractants. Phosphorus-bonded, oxygen-containing extractants only coextract small amounts of water, and their solubilities in water are very low. The distribution ratios of the acids are substantially higher with phosphorus-bonded, oxygen-containing extractants than with carbon-bonded, oxygen-containing extractants. Ricker et al.[1] and Fesseha[2] found that distribution ratios are also affected by the diluent and the concentration of acids; the higher the concentration of acid, the lower the distribution ratio.

Extraction of organic acids has long been studied using trioctylphosphine oxide[3−6] and tributyl phosphate.[7−10] Watson et al.[11] developed a liquid phosphine oxide, which is a mixture of four trialkylphosphine oxides $R_3P{=}O$ in which each R group is either hexyl or octyl. The commercial product is named CYANEX 923 extractant. They used trialkylphosphine oxide to extract phenol, acetic acid, and ethanol and made a comparison with trioctylphosphine oxide. The results showed that distribution ratios were increased by 2^m, where m is related to moles of phosphoryl in the extracting complex. The value of m is 1.6 for phenol, 1.0 for acetic acid, and 0.9 for ethanol.

It is believed that two effects controlled the degree of extraction. One is the strength of the acid, expressed by pK_a; the stronger the acid, the stronger the interaction with trioctylphosphine oxide. Another factor is the hydrophobicity of acid molecules. Fahim et al.[6] studied extraction equilibria of acetic acid and propionic acid with hexane solutions of trioctylamine, trioctylphosphine oxide, and tributyl phosphate. The complexes formed during the extraction were proposed, and the extraction efficiencies with the three types of extractants were compared.

* Corresponding author.

The main objective of the research described in this paper is to go further into the study of the extraction of monocarboxylic acids from aqueous solutions with trialkylphosphine oxide (TRPO) to gain a better understanding of the extraction equilibra of the acids. Extraction equilibria of glyoxylic acid, glycolic acid, acrylic acid, and benzoic acid with trialkylphosphine oxide in kerosene were investigated. An equilibrium model based on mass action law is presented and used to describe the data. The equilibrium constants were evaluated. Loading of TRPO was calculated.

Experimental Section

Reagents. All monocarboxylic acids used were of reagent grade. The extractant trialkylphosphine oxide was kindly supplied by Cytec Canada Inc. free of charge and used without further purification. Hydrogenated kerosene was used as the diluent. Table 1 lists the physiochemical properties of trialkylphosphine oxide and kerosene. The mixed solvent has trialkylphosphine oxide molar concentrations from 0.2514 mol/L (10% (volume) trialkylphosphine oxide + 90% (volume) kerosene) to 2.514 mol/L (100% (volume) trialkylphosphine oxide).

Methods. Liquid−liquid extraction equilibrium experiments were conducted by contacting measured volumes of aqueous and organic solutions of known concentrations in a stoppered flask with a volume of 100 mL in a thermostated bath shaker maintained at a temperature of 25 °C. An aqueous solution (20 mL) of acids was contacted with 20 mL of solvent. The mixture was shaken for 40 min. It was observed that this time was sufficient to establish the equilibrium between two phases. The mixture was then transferred to a separating funnel and allowed to settle for at least 30 min, which was shown in previous experiments to be sufficient for a complete phase separation. After separation of the phases, the equilibrium pH of the aqueous phase was measured, the acid concentration of the aqueous phase was determined by titration with NaOH (0.1 mol/L and 0.05 mol/L), and the amount of acid in the organic phase was obtained by a mass balance.

Model. Using the mass action law, the extraction equilibrium of monocarboxylic acids by trialkylphosphine oxide can be described by a set of equilibria involving the dissociation equilibrium of the acid in water, the physical

10.1021/je020174r CCC: $25.00 © 2003 American Chemical Society
Published on Web 04/23/2003

Table 1. Physical Properties of Trialkylphosphine Oxide and Kerosene

name	formula	average MW	viscosity, η/Pa·s	density, ρ/g·cm^{-3}
trialkylphosphine oxide[a]	$[CH_3(CH_2)_{7-9}]_3P{=}O$	350	0.04 (at 25 °C), 0.014 (50 °C)	0.88 (25 °C)
kerosene[b]			0.00168 (at 40 °C)	0.84 (20 °C)

[a] Data from Cytec Canada Inc. [b] Data from Sinopec, Beijing; distillation range, 170 to 310 °C.

Table 2. Equilibrium Data for the System Glyoxylic Acid + Trialkylphosphine Oxide in Kerosene

total aqueous concentration/mol·L^{-1}			total organic concentration/mol·L^{-1}	
initial glyoxylic acid	equilibrium glyoxylic acid	initial/ equil pH	initial trialkylphosphine oxide	equilibrium glyoxylic acid
0.0215	0.0211	2.54/2.61	0.2514	0.0004
0.0432	0.0411	2.37/2.42	0.2514	0.0021
0.0630	0.0601	2.23/2.31	0.2514	0.0029
0.0853	0.0805	2.23/2.24	0.2514	0.0048
0.1114	0.1044	2.07/2.17	0.2514	0.0070
0.1674	0.1567	1.97/2.08	0.2514	0.0107
0.2983	0.2792	1.83/1.92	0.2514	0.0191
0.4796	0.4558	1.70/1.79	0.2514	0.0238
0.6273	0.5962	1.55/1.55	0.2514	0.0311
0.8968	0.8495	1.42/1.43	0.2514	0.0473
0.0215	0.0176	2.54/2.58	0.7542	0.0039
0.0432	0.0338	2.37/2.44	0.7542	0.0094
0.0630	0.0493	2.23/2.34	0.7542	0.0137
0.0853	0.0687	2.23/2.27	0.7542	0.0166
0.1114	0.0848	2.07/2.20	0.7542	0.0266
0.1674	0.1332	1.97/2.08	0.7542	0.0342
0.2983	0.2349	1.83/1.96	0.7542	0.0634
0.4796	0.3819	1.70/1.83	0.7542	0.0977
0.6273	0.5105	1.55/1.59	0.7542	0.1168
0.8968	0.7478	1.42/1.47	0.7542	0.1490
0.0215	0.0145	2.54/2.59	1.2570	0.0070
0.0432	0.0289	2.37/2.44	1.2570	0.0143
0.0630	0.0412	2.23/2.35	1.2570	0.0218
0.0853	0.0558	2.23/2.29	1.2570	0.0295
0.1114	0.0690	2.07/2.21	1.2570	0.0424
0.1674	0.1087	1.97/2.11	1.2570	0.0587
0.2983	0.1905	1.83/1.97	1.2570	0.1078
0.4796	0.3213	1.70/1.83	1.2570	0.1583
0.0215	0.0125	2.54/2.63	1.7598	0.0090
0.0432	0.0237	2.37/2.46	1.7598	0.0195
0.0630	0.0337	2.23/2.35	1.7598	0.0293
0.0853	0.0451	2.23/2.31	1.7598	0.0402
0.1114	0.0575	2.07/2.21	1.7598	0.0539
0.1674	0.0881	1.97/2.14	1.7598	0.0793
0.2983	0.1612	1.83/1.97	1.7598	0.1371
0.4796	0.2684	1.70/1.83	1.7598	0.2112
0.0215	0.0118	2.54/2.68	2.5140	0.0097
0.0432	0.0215	2.37/2.52	2.5140	0.0217
0.0630	0.0256	2.23/2.39	2.5140	0.0374
0.0853	0.0353	2.23/2.36	2.5140	0.0500
0.1114	0.0434	2.07/2.27	2.5140	0.0680
0.1674	0.0763	1.97/2.19	2.5140	0.0911
0.2983	0.1202	1.83/2.02	2.5140	0.1781
0.4796	0.2037	1.70/1.90	2.5140	0.2759

solubility of the solute between aqueous and organic phases, and the formation of a complex with acid and trialkylphosphine oxide. It is assumed that only a 1:1 complex was formed and that the complexation reaction between trialkylphosphine oxide and organic acids took place at the organic−aqueous interface. The distribution ratio can be derived as[12]

$$D = \frac{\overline{[HA{\cdot}TRPO]} + \overline{[HA]}}{[HA] + [A^-]} = \frac{B_0 K_{11}}{(1 + K_{11}[HA])(1 + 10^{pH-pK_a})} + \frac{\phi m}{1 + 10^{pH-pK_a}} \quad (1)$$

where the bars refer to species in the organic phase and the equilibrium species concentrations are denoted by square brackets and are expressed in molar concentrations.

Table 3. Equilibrium Data for the System Glycolic Acid + Trialkylphosphine Oxide in Kerosene

total aqueous concentration/mol·L^{-1}			total organic concentration/mol·L^{-1}	
initial glycolic acid	equilibrium glycolic acid	initial/ equil pH	initial trialkylphosphine oxide	equilibrium glycolic acid
0.0119	0.0097	2.86/2.94	0.2514	0.0022
0.0239	0.0192	2.63/2.80	0.2514	0.0047
0.0476	0.0376	2.46/2.66	0.2514	0.0100
0.0947	0.0768	2.30/2.51	0.2514	0.0179
0.1165	0.0938	2.21/2.40	0.2514	0.0227
0.2335	0.1910	2.03/2.25	0.2514	0.0425
0.3606	0.2881	1.95/2.19	0.2514	0.0725
0.4741	0.3899	1.91/2.09	0.2514	0.0842
0.5763	0.4593	1.87/2.05	0.2514	0.1170
0.6913	0.5560	1.77/2.00	0.2514	0.1353
0.9258	0.7464	1.69/1.94	0.2514	0.1794
1.1729	0.9540	1.66/1.88	0.2514	0.2189
0.0119	0.0079	2.86/3.00	0.5028	0.0040
0.0239	0.0164	2.63/2.82	0.5028	0.0075
0.0476	0.0303	2.46/2.66	0.5028	0.0173
0.0947	0.0644	2.30/2.52	0.5028	0.0303
0.1165	0.0793	2.21/2.45	0.5028	0.0372
0.2335	0.1640	2.03/2.29	0.5028	0.0695
0.3606	0.2478	1.95/2.21	0.5028	0.1128
0.4741	0.3340	1.91/2.12	0.5028	0.1401
0.5763	0.4212	1.87/2.06	0.5028	0.1551
0.6913	0.5205	1.77/1.99	0.5028	0.1708
0.9258	0.7030	1.69/1.89	0.5028	0.2228
1.1729	0.9145	1.66/1.83	0.5028	0.2584
0.0119	0.0075	2.86/3.13	0.7542	0.0044
0.0239	0.0149	2.63/2.93	0.7542	0.0090
0.0476	0.0288	2.46/2.74	0.7542	0.0188
0.0947	0.0581	2.30/2.57	0.7542	0.0366
0.1165	0.0707	2.21/2.52	0.7542	0.0458
0.2335	0.1467	2.03/2.36	0.7542	0.0868
0.3606	0.2254	1.95/2.27	0.7542	0.1352
0.4741	0.3038	1.91/2.16	0.7542	0.1703
0.5763	0.3660	1.87/2.12	0.7542	0.2103
0.6913	0.4566	1.77/2.07	0.7542	0.2347
0.9258	0.6235	1.69/2.00	0.7542	0.3023
1.1729	0.8021	1.66/1.90	0.7542	0.3708

D is the distribution ratio between the organic and the aqueous phase. K_{11} is the extraction equilibrium constant. m is the physical distribution ratio of acids between kerosene and water. B_0 is the initial concentration of trialkylphosphine oxide. ϕ is the volume fraction of kerosene in the organic phase.

Results and Discussion

The equilibrium data at different trialkylphosphine oxide concentrations are given in Tables 2−5. The equilibrium concentrations of the two phases were determined at different initial solute concentrations (initial pH), and the pH changed as the acid extraction proceeded. The equilibrium pH was always higher than the initial pH, and its value depended on the extent of acid extraction and hence differed for each experimental point. For example, for a 0.0215 mol/L glyoxylic acid extraction with a trialkylphosphine oxide concentration of 0.2514 mol/L and at a starting pH of 2.54, the final pH was 2.61 (Table 2).

The equilibrium acid concentrations in the organic phase increased with an increase of trialkylphosphine oxide concentration and increased with an increase of the acid concentration in the aqueous phase. At low trialkylphos-

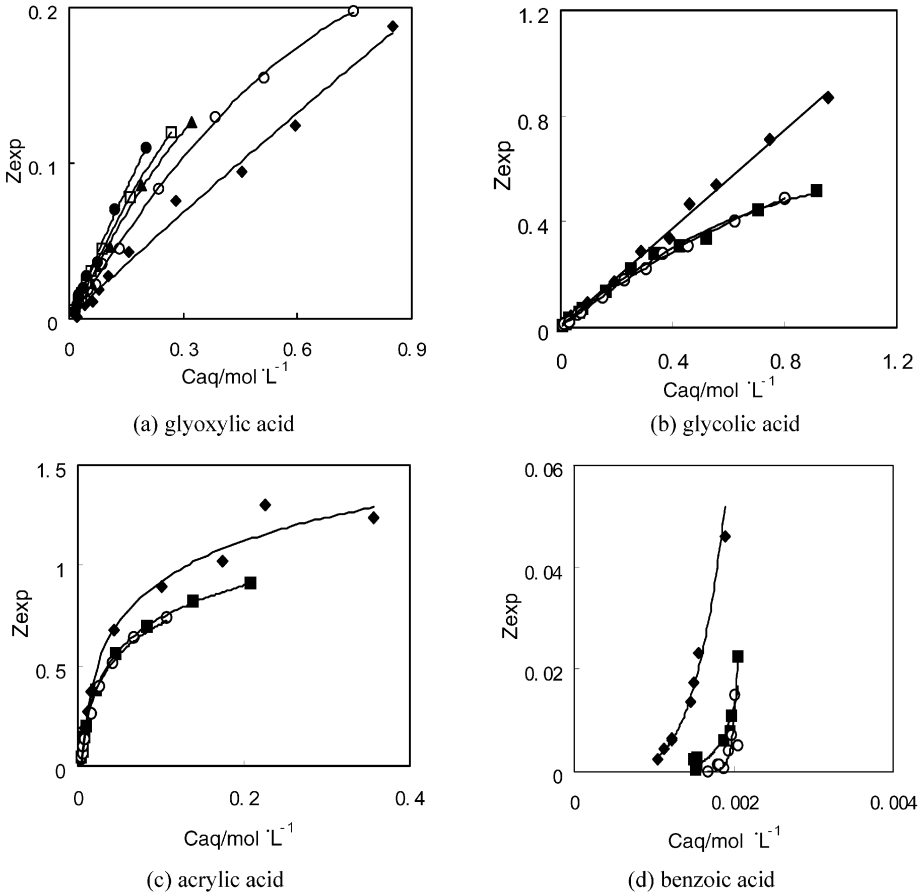

Figure 1. Loading factor versus equilibrium concentration of acid in the aqueous phase: ◆, $B_0 = 0.2514$ mol·L^{-1}; ■, $B_0 = 0.5028$ mol·L^{-1}; ○, $B_0 = 0.7542$ mol·L^{-1}; ▲, $B_0 = 1.2570$ mol·L^{-1}; □, $B_0 = 1.7598$ mol·L^{-1}; ●, $B_0 = 2.514$ mol·L^{-1}.

Table 4. Equilibrium Data for the System Acrylic Acid + Trialkylphosphine Oxide in Kerosene

total aqueous concentration/mol·L^{-1}			total organic concentration/mol·L^{-1}	
initial acrylic acid	equilibrium acrylic acid	initial/ equil pH	initial trialkylphosphine oxide	equilibrium acrylic acid
0.0281	0.0054	2.87/4.42	0.2514	0.0227
0.0416	0.0068	2.78/4.22	0.2514	0.0348
0.0552	0.0080	2.71/4.08	0.2514	0.0472
0.0793	0.0112	2.62/3.91	0.2514	0.0681
0.1099	0.0158	2.57/3.74	0.2514	0.0941
0.2142	0.0444	2.44/3.30	0.2514	0.1698
0.3270	0.1018	2.34/2.99	0.2514	0.2252
0.4326	0.1749	2.27/2.78	0.2514	0.2577
0.5533	0.2263	2.22/2.69	0.2514	0.3270
0.6668	0.3556	2.17/2.56	0.2514	0.3112
0.0281	0.0045	2.87/4.48	0.5028	0.0236
0.0416	0.0052	2.78/4.29	0.5028	0.0364
0.0552	0.0060	2.71/4.17	0.5028	0.0492
0.0793	0.0085	2.62/4.00	0.5028	0.0708
0.1099	0.0105	2.57/3.85	0.5028	0.0994
0.2142	0.0228	2.44/3.51	0.5028	0.1914
0.3270	0.0453	2.34/3.24	0.5028	0.2817
0.4326	0.0826	2.27/3.03	0.5028	0.3500
0.5533	0.1396	2.22/2.84	0.5028	0.4137
0.6668	0.2077	2.17/2.70	0.5028	0.4591
0.0281	0.0038	2.87/4.43	0.7542	0.0243
0.0416	0.0044	2.78/4.30	0.7542	0.0372
0.0552	0.0051	2.71/4.37	0.7542	0.0501
0.0793	0.0067	2.62/4.03	0.7542	0.0726
0.1099	0.0081	2.57/3.91	0.7542	0.1018
0.2142	0.0161	2.44/3.59	0.7542	0.1981
0.3270	0.0264	2.34/3.40	0.7542	0.3006
0.4326	0.0421	2.27/3.23	0.7542	0.3905
0.5533	0.0668	2.22/3.06	0.7542	0.4865
0.6668	0.1069	2.17/2.91	0.7542	0.5599

Table 5. Equilibrium Data for the System Benzoic Acid + Trialkylphosphine Oxide in Kerosene

total aqueous concentration/mol·L^{-1}			total organic concentration/mol·L^{-1}	
initial benzoic acid	equilibrium benzoic acid	initial/ equil pH	initial trialkylphosphine oxide	equilibrium benzoic acid
0.0017	0.0011	3.47/6.24	0.2514	0.0006
0.0023	0.0011	3.42/6.18	0.2514	0.0012
0.0028	0.0012	3.38/6.19	0.2514	0.0016
0.0029	0.0013	3.35/6.13	0.2514	0.0016
0.0049	0.0014	3.22/6.04	0.2514	0.0035
0.0059	0.0015	3.18/6.01	0.2514	0.0044
0.0074	0.0016	3.13/5.94	0.2514	0.0058
0.0134	0.0019	3.00/5.82	0.2514	0.0115
0.0017	0.0015	3.47/5.82	0.5028	0.0002
0.0023	0.0016	3.42/5.80	0.5028	0.0007
0.0028	0.0015	3.38/5.85	0.5028	0.0013
0.0029	0.0015	3.35/5.79	0.5028	0.0014
0.0049	0.0019	3.22/5.77	0.5028	0.0030
0.0059	0.0020	3.18/5.76	0.5028	0.0039
0.0074	0.0020	3.13/5.72	0.5028	0.0054
0.0134	0.0021	3.00/5.65	0.5028	0.0113
0.0017	0.00168	3.47/5.56	0.7542	3×10^{-6}
0.0023	0.0019	3.42/5.54	0.7542	0.0004
0.0028	0.0018	3.38/5.58	0.7542	0.0010
0.0029	0.0018	3.35/5.56	0.7542	0.0011
0.0049	0.0019	3.22/5.52	0.7542	0.0030
0.0059	0.0020	3.18/5.44	0.7542	0.0039
0.0074	0.0020	3.13/5.47	0.7542	0.0054
0.0134	0.0020	3.00/5.45	0.7542	0.0114

phine oxide concentration, the acid concentration in the organic phase approaches a maximum value, that is, the initial trialkylphosphine oxide concentration, as the acid concentration in the aqueous phase increases. This phe-

Table 6. Model Parameters for Trialkylphosphine Oxide in Kerosene + Carboxylic Acid Systems

solute	B_0/mol·L^{-1}	pK_a	K_{11}/L·mol^{-1}	m
glyoxylic acid	0.2514−2.5140	3.30	1.00	0.006
glycolic acid	0.2514−0.7542	3.81	1.10	0.008
acrylic acid	0.2514−0.7542	4.26	37.00	0.021
benzoic acid	0.2514−0.7542	4.20	160.80	0.034

nomenon confirms the assumption of the extraction mechanism; that is, the complex formed between trialkylphosphine oxide and acid is 1:1.

The four monocarboxylic acids investigated in this work are very polar organic acids, and their solubilities in a nonpolar solvent such as kerosene are expected to be very low. The extent of these acid extractions by kerosene was determined experimentally. The distribution ratios between kerosene and water ranged from 0.006 for glyoxylic acid to 0.034 for benzoic acid (Table 6). The extraction equilibrium constant, K_{11}, is evaluated from eq 1 using a least-squares regression method. Table 6 gives the results for the four monocarboxylic acids studied in this paper.

Figure 1 shows the extraction equilibrium loading curves of glyoxylic acid, glycolic acid, acrylic acid, and benzoic acid with different trialkylphosphine oxide concentrations in the kerosene. The loading factor, Z, can be derived as $Z = (y - \phi y_{100\%\text{kerosene}})/S_0$, where y refers to the equilibrium acid concentrations in the organic phase and $y_{100\%\text{kerosene}}$ is the equilibrium acid concentrations in the organic phase when the extractant was only composed of the 100% (volume) kerosene. S_0 is the initial concentration of trialkylphosphine oxide. ϕ is the volume fraction of kerosene in the organic phase. The experiments show that the loading factor of trialkylphosphine oxide increases with the decrease of trialkylphosphine oxide concentration, but for the extraction of glyoxylic acid, the situation is the reverse. This phenomenon confirms that the diluent, kerosene, as a nonpolar solvent can provide a favorable condition for extracted compounds whose polarities are very low. So increasing the concentration of kerosene in the complexing agent is highly advantageous for extractions based on reversible chemical complexation. However, the loading factor value increases with an increase of the concentration of trialkylphosphine oxide during the process of the extraction with the glyoxylic acid, because the complex formed by the glyoxylic acid with trialkylphosphine oxide is a very polar organic compound and cannot exist in the nonpolar kerosene steadily.

Conclusion

In this paper, extraction equilibrium experiments for the systems of monocarboxylic acids (glyoxylic acid, glycolic acid, acrylic acid, and benzoic acid) and trialkylphosphine oxide in kerosene were carried out at different complexing agent concentrations and initial acid concentrations. Models for describing the extraction equilibrium of monocarboxylic acids were proposed. The model parameter, K_{11}, was obtained by experimental data regression. The loading of TRPO was calculated.

Literature Cited

(1) Ricker, N. L.; Michaels, J. N.; King, C. J. Solvent properties of organic bases for extraction of acetic acid from water. *J. Sep. Process Technol.* **1979**, *1* (1), 36−41.

(2) Fesseha, A. Extraction of carboxylic acids by reversible chemical complexation. M.Sc. Thesis, Tsinghua University, Beijing, P. R. China, 1999.

(3) Helsel, R. W. Removing carboxylic acids from aqueous wastes. *Chem. Eng. Prog.* **1977**, *73*, 55−59.

(4) Hano, T.; Matsumoto, M.; Ohtake, T.; Sasaki, K.; Hori, F.; Kawano, Y. Extraction equilibria of organic acids with tri-*n*-octylphosphine oxide. *J. Chem. Eng. Jpn.* **1990**, *23*, 734−738.

(5) Matsumoto, M.; Uenoyama, S.; Hano, T.; Hirata, M.; Miura, S. Extraction kinetics of organic acid with tri-*n*-octylphosphine oxide. *J. Chem. Technol. Biotechnol.* **1996**, *67*, 260−264.

(6) Fahim, M. A.; Qader, A.; Hughes, M. A. Extraction equilibria of acetic and propionic acids from dilute solution by several solvents. *Sep. Sci. Technol.* **1992**, *27*, 1809−1821.

(7) Ingale, M. N.; Mahajani, V. V. Recovery of acetic acid and propionic acid from aqueous waste stream. *Sep. Technol.* **1994**, *4*, 123−126.

(8) Ingale, M. N.; Mahajani, V. V. Recovery of butyric acid, valeric acid and caproic acid (BVC acids) from an aqueous waste stream using tributyl phosphate (TBP) as an extractant. *Sep. Technol.* **1994**, *4*, 252−257.

(9) Ingale, M. N.; Mahajani, V. V. Recovery of carboxylic acids, C_2−C_6 from aqueous waste stream using tributyl phosphate (TBP): Effect of presence of inorganic acids and their sodium salts. *Sep. Technol.* **1996**, *6*, 1−7.

(10) Ricker, N. L.; Pittman, E. F.; King, C. J. Solvent extraction with amines for recovery of acetic acid from dilute aqueous industrial streams. *J. Sep. Process Technol.* **1980**, *1* (2), 23−30.

(11) Watson, E. K.; Ricklton, W. A.; Robertson, A. J.; Brown, T. J. A liquid phosphine oxide: solvent extraction of phenol, acetic acid and ethanol. *Solvent Extr. Ion Exch.* **1988**, *6* (2), 207−220. Erratum: *Solvent Extr. Ion Exch.* **1988**, *6* (6), 1143.

(12) Wang, Y. D.; Li, Y. X.; Li, Y.; Wang, J. Y.; Li, Z. Y.; Dai, Y. Y. Extraction equilibria of monocarboxylic acids with trialkylphosphine oxide. *J. Chem. Eng. Data* **2001**, *46*, 831−837.

Received for review September 4, 2002. Accepted March 26, 2003. This research was carried out under Grant No. 29836130 of the National Natural Science Foundation of China, in the Solvent Extraction Laboratory of the State Key Laboratory of Chemical Engineering of Tsinghua University, Beijing, P. R. China. The authors gratefully acknowledge this grant.

JE020174R