

Extraction Equilibria of Monocarboxylic Acids with Trialkylphosphine Oxide

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Liquid–liquid extraction based on reversible chemical complexation is a novel separation technique that is highly effective and selective for separating polar organic solutes from aqueous solutions. Equilibria of aqueous solutions of formic acid, acetic acid, propionic acid, butyric acid, caproic acid, monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, and lactic acid with trialkylphosphine oxide in kerosene were investigated. Equilibrium concentrations are given at 298 K. An extraction equilibrium model was used to describe the experimental data. Calculated organic acid concentrations in both phases are in good agreement with the experimental values

Introduction

Liquid–liquid extraction is an efficient, economical, and environmentally friendly method for separation of acids. It is, therefore, applicable in recovery of acids from waste streams, facilitating 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. Kertes and King¹ made an excellent review on extraction of carboxylic acids. They categorized organic solvents used for extraction into three types: (a) carbon-bonded, oxygen-containing extractants; (b) phosphorus-bonded, oxygen-containing extractants; and (c) high-molecular-weight aliphatic amines. When a phosphorus-bonded, oxygen-containing extractant is used, the solvation has a higher specificity. In ion-pair extraction, chemical reaction presents. Carbon-bonded, oxygen-containing extractants are not particularly suitable by themselves for the recovery of carboxylic acids, because of the low distribution ratios and high mutual solubilities of the phases. Phosphorus-bonded, oxygen-containing extractants have a phosphoryl group and so have a stronger Lewis basicity than those of carbon-bonded, oxygen-containing extractants. Phosphorus-bonded, oxygen-containing extractants only coextract small amounts of water, and their solubilities in water are very low. For example, 30% (mass) trioctylphosphine oxide in Chevron Solvent 25 (a mixture of primarily C₈ and C₉ alkylated aromatics, Chevron Chemical Co.) was equilibrated with 10% (mass) aqueous acetic acid solution; the solubility of trioctylphosphine oxide in the aqueous phase was <1 ppm². The basicity of the phosphoryl oxygen increases in the order trialkyl phosphate [(RO)₃P=O] < dialkyl phosphate [(R=)₂RP=O] < alkylalkyl phosphinate [(RO)₂P=O] < trialkyl phosphine oxide [R₃P=O]. According to Wardell and King,³ the basicity of the extractant increases with the number of butoxy groups (OCH₂CH₂CH₂CH₃). 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.⁴ and Fesseha⁵ 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,^{6–9} tributyl phosphate,^{10–12} high-molecular-weight alkylamines,^{13–27} trioctylamine and tributyl phosphate,²⁸ and trioctylamine and di(2-ethylhexyl)-phosphoric acid.^{29–31}

Wardell and King³ explored the use of strongly basic organic extractants for acetic acid and found that certain organophosphorus compounds, such as trioctylphosphine oxide, and high-molecular-weight amines, such as trioctylamine, were much more effective extractants than the conventional solvents. Helse⁶ discussed the use of trioctylphosphine oxide as a solvent for acetic acid extraction. Ricker et al.⁴ investigated the properties of these extractants in more detail and measured distribution ratios as high as 160.0 for di-tridecylamine. The trioctylphosphine oxide and amine extractants must be diluted with an organic solvent to provide appropriate physical properties for use in an extraction process. Watson et al.³² developed a liquid phosphine oxide, which is a mixture of four trialkylphosphine oxides R₃P=O in which each R group is either *n*-hexyl or *n*-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 coefficients 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 p*K*_a; the stronger the acid, the stronger the interaction with trioctylphosphine oxide. Another factor is the hydrophobicity of acid molecules.

Hano et al.⁷ 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 p*K*_a value.

Matsumoto et al.⁷ measured the extraction rates of organic acids with trioctylphosphine oxide. They found that the extraction equilibrium of organic acids was established

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Table 1. Physical Properties of Trialkylphosphine Oxide (TRPO) and Kerosene

name	formula	average MW	viscosity, $\eta/\text{Pa}\cdot\text{s}$	density, $\rho/\text{g}\cdot\text{cm}^{-3}$
trialkylphosphine oxide ^a	$[\text{CH}_3(\text{CH}_2)_{7-9}]_3\text{P}=\text{O}$	350	0.04 (at 25 °C), 0.014 (50 °C)	0.88 (25 °C)
kerosene ^b		170–310 °C ^c	0.00168 (at 40 °C)	0.84 (20 °C)

^a Data from Cytec Canada Inc. ^b Data from Sinopec, Beijing. ^c Distillation range.

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

total aqueous conc/mol·L ⁻¹			total organic conc/mol·L ⁻¹	
init formic acid	equil formic acid	init/equil pH	init TRPO	equil formic acid
0.0191	0.0075	2.88/3.33	0.2514	0.0116
0.0373	0.0152	2.73/3.09	0.2514	0.0221
0.0872	0.0403	2.50/2.73	0.2514	0.0469
0.1718	0.0925	2.32/2.42	0.2514	0.0793
0.1900	0.0889	2.18/2.37	0.2514	0.1011
0.2400	0.1162	2.13/2.27	0.2514	0.1238
0.2820	0.1484	2.11/2.21	0.2514	0.1336
0.3526	0.2097	2.14/2.23	0.2514	0.1429
0.4601	0.2919	1.95/2.04	0.2514	0.1682
0.6381	0.4430	1.85/1.92	0.2514	0.1951
0.7401	0.5421	1.81/1.87	0.2514	0.1980
0.8262	0.6165	1.80/1.84	0.2514	0.2097
0.0191	0.0042	2.88/3.42	0.7542	0.0149
0.0373	0.0081	2.73/3.25	0.7542	0.0292
0.0872	0.0201	2.50/2.97	0.7542	0.0671
0.1718	0.0429	2.32/2.66	0.7542	0.1289
0.3526	0.1037	2.14/2.40	0.7542	0.2489
0.4601	0.1313	1.95/2.22	0.7542	0.3288
0.6381	0.2099	1.85/2.11	0.7542	0.4282
0.7401	0.2710	1.81/2.05	0.7542	0.4691
0.8262	0.3231	1.80/2.00	0.7542	0.5021
1.0862	0.5253	1.69/1.88	0.7542	0.5609
1.2440	0.6510	1.65/1.82	0.7542	0.5930
1.4463	0.8300	1.59/1.76	0.7542	0.6163
1.6663	1.0035	1.56/1.67	0.7542	0.6628
1.8023	1.1451	1.51/1.65	0.7542	0.6572
0.0191	0.0031	2.88/3.68	1.2570	0.0160
0.0373	0.0056	2.73/3.47	1.2570	0.0317
0.0872	0.0126	2.50/3.13	1.2570	0.0746
0.1718	0.0273	2.32/2.83	1.2570	0.1445
0.3526	0.0612	2.14/2.58	1.2570	0.2914
0.0191	0.0028	2.88/3.71	1.7598	0.0163
0.0373	0.0047	2.73/3.54	1.7598	0.0326
0.0872	0.0105	2.50/3.20	1.7598	0.0767
0.1718	0.0209	2.32/2.91	1.7598	0.1509
0.3526	0.0449	2.14/2.67	1.7598	0.3077
0.0191	0.0028	2.88/3.72	2.2626	0.0163
0.0872	0.0090	2.50/3.27	2.2626	0.0782
0.1718	0.0180	2.32/2.92	2.2626	0.1538
0.3526	0.0377	2.14/2.70	2.2626	0.3149
0.0191	0.0030	2.88/3.81	2.5140	0.0188
0.0373	0.0043	2.73/3.60	2.5140	0.0330
0.0872	0.0093	2.50/3.30	2.5140	0.0779
0.1718	0.0181	2.32/2.97	2.5140	0.1537
0.3526	0.0373	2.14/2.71	2.5140	0.3153

at the interface and the extraction rates were limited by the mass transfer, except for crotonic acid. In crotonic acid, the observed rates were well explained by considering the film diffusion of the acid and the reaction between the acid and trioctylphosphine oxide in organic solution.

Fahim et al.⁹ studied extraction equilibrium 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.

Siebold et al.³³ used trialkylphosphine oxide (mixture of trioctylphosphine oxide and triheptylphosphine oxide), secondary and tertiary amines, and two quaternary ammonium salts as extractants to extract lactic acid from cultivation media. Kerosene, butyl acetate, or oleyl alcohol was used as a diluent. Long-chain alcohols (isodecanol), alkyl phosphates (tributyl phosphate), and acidic organic compounds (4-nonylphenol) were used as modifiers if a third phase was formed during the extraction because of the low solubility of the lactic-extractant complex in the diluent. The recovery of free lactic acid with re-extraction of lactate by HCl and H₂SO₄ was also discussed.

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

total aqueous conc/mol·L ⁻¹			total organic conc/mol·L ⁻¹	
init acetic acid	equil acetic acid	init/equil pH	init TRPO	equil acetic acid
0.0165	0.0067	3.50/4.10	0.2514	0.0098
0.0322	0.0125	3.32/3.90	0.2514	0.0197
0.0824	0.0350	3.12/3.51	0.2514	0.0474
0.1681	0.0840	2.88/3.21	0.2514	0.0841
0.2252	0.1271	2.64/2.86	0.2514	0.0981
0.2741	0.1601	2.58/2.77	0.2514	0.1140
0.3335	0.2010	2.71/2.92	0.2514	0.1325
0.4067	0.2693	2.48/2.66	0.2514	0.1374
0.5011	0.3520	2.43/2.57	0.2514	0.1491
0.6042	0.4444	2.37/2.51	0.2514	0.1598
0.7004	0.5342	2.33/2.47	0.2514	0.1662
0.0175	0.0046	3.78/4.25	0.7542	0.0129
0.0322	0.0081	3.32/3.75	0.7542	0.0241
0.0824	0.0210	3.12/3.54	0.7542	0.0614
0.1681	0.0444	2.88/3.38	0.7542	0.1237
0.3335	0.0962	2.71/3.20	0.7542	0.2373
0.4067	0.1301	2.48/2.78	0.7542	0.2766
0.5006	0.1761	2.43/2.73	0.7542	0.3245
0.6041	0.2240	2.37/2.67	0.7542	0.3801
0.7004	0.2799	2.33/2.61	0.7542	0.4205
0.7533	0.3142	2.30/2.58	0.7542	0.4391
0.8047	0.3469	2.28/2.56	0.7542	0.4578
1.0068	0.4844	2.22/2.48	0.7542	0.5224
1.1978	0.6393	2.17/2.43	0.7542	0.5586
1.4039	0.8121	2.12/2.35	0.7542	0.5918
0.0175	0.0039	3.78/4.22	1.2570	0.0136
0.0322	0.0064	3.32/4.00	1.2570	0.0258
0.0824	0.0160	3.12/3.69	1.2570	0.0664
0.1681	0.0331	2.88/3.46	1.2570	0.1350
0.3335	0.0688	2.71/3.24	1.2570	0.2647
0.0175	0.0036	3.78/4.09	1.7598	0.0139
0.0322	0.0059	3.32/3.87	1.7598	0.0263
0.0824	0.0137	3.12/3.64	1.7598	0.0705
0.1681	0.0272	2.88/3.48	1.7598	0.1409
0.3335	0.0573	2.71/3.27	1.7598	0.2762
0.0175	0.0037	3.78/4.23	2.2626	0.0138
0.0322	0.0056	3.32/4.06	2.2626	0.0266
0.0824	0.0129	3.12/3.80	2.2626	0.0713
0.1681	0.0246	2.88/3.62	2.2626	0.1435
0.3335	0.0478	2.71/3.44	2.2626	0.2857
0.0175	0.0030	3.78/4.06	2.5140	0.0145
0.0322	0.0050	3.32/3.93	2.5140	0.0272
0.0824	0.0120	3.12/3.71	2.5140	0.0722
0.1681	0.0224	2.88/3.52	2.5140	0.1457
0.3335	0.0477	2.71/3.31	2.5140	0.2858

Gentry et al.³⁴ reported a method for recovering short-chain carboxylic acids having from 1 to 10 carbon atoms, and particularly formic acid and acetic acid and mixtures thereof, from dilute solutions of such acids. Typical concentrations of aqueous solutions were 1–3% by weight acids. The solvent extractant for use in their invention was a mixture of four trialkylphosphine oxides: R₃P=O, R₂R'P=O, RR'₂P=O, and R'₃P=O, where R refers to CH₃(CH₂)₇ and R' refers to CH₃(CH₂)₅, respectively.

The main objective of the research described in this paper is to study the extraction of monocarboxylic acids from aqueous solutions with trialkylphosphine oxide to provide a better understanding of the extraction equilibria of the acids. Equilibrium data are presented for the system monocarboxylic acids with trialkylphosphine oxide in kerosene. An equilibrium model based on mass action law is presented and used to describe the data. The calculated equilibrium concentrations in all cases are in a good agreement with the experimental values.

Experimental Section

Reagents. All monocarboxylic acids used were of reagent grade. The extractant trialkylphosphine oxide was kindly supplied by CYTEC Canada Incorporation free of charge

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

total aqueous conc/mol·L ⁻¹			total organic conc/mol·L ⁻¹	
init propionic acid	equil propionic acid	init/equil pH	init TRPO	equil propionic acid
0.0179	0.0029	3.44/3.83	0.2514	0.0150
0.0288	0.0045	3.35/3.70	0.2514	0.0243
0.0529	0.0086	3.15/3.57	0.2514	0.0443
0.1125	0.0218	2.95/3.34	0.2514	0.0907
0.2412	0.0789	2.72/3.02	0.2514	0.1623
0.2938	0.1067	2.69/2.92	0.2514	0.1871
0.3895	0.1578	2.62/2.90	0.2514	0.2317
0.4830	0.2477	2.56/2.71	0.2514	0.2353
0.5945	0.3370	2.49/2.65	0.2514	0.2575
0.7002	0.4193	2.42/2.59	0.2514	0.2809
0.0179	0.0017	3.44/3.55	0.7542	0.0162
0.0288	0.0025	3.35/3.46	0.7542	0.0263
0.0529	0.0048	3.15/3.37	0.7542	0.0481
0.1125	0.0104	2.95/3.25	0.7542	0.1021
0.2412	0.0263	2.72/3.12	0.7542	0.2149
0.2938	0.0331	2.69/3.11	0.7542	0.2607
0.3895	0.0520	2.62/3.01	0.7542	0.3375
0.4830	0.0786	2.56/2.92	0.7542	0.4044
0.5945	0.1241	2.49/2.81	0.7542	0.4704
0.7002	0.1614	2.42/2.75	0.7542	0.5388
0.8336	0.2479	2.34/2.64	0.7542	0.5857
0.9712	0.3346	2.27/2.56	0.7542	0.6366
0.0179	0.0017	3.44/3.70	1.2570	0.0162
0.0288	0.0023	3.35/3.65	1.2570	0.0265
0.0529	0.0036	3.15/3.59	1.2570	0.0493
0.1125	0.0070	2.95/3.51	1.2570	0.1055
0.2412	0.0148	2.72/3.45	1.2570	0.2264
0.0179	0.0017	3.44/3.66	1.7598	0.0162
0.0288	0.0023	3.35/3.60	1.7598	0.0265
0.0529	0.0031	3.15/3.53	1.7598	0.0498
0.1125	0.0059	2.95/3.41	1.7598	0.1066
0.2412	0.0121	2.72/3.36	1.7598	0.2291
0.0179	0.0021	3.44/3.46	2.5140	0.0158
0.0288	0.0024	3.35/3.45	2.5140	0.0264
0.0529	0.0033	3.15/3.44	2.5140	0.0496
0.1125	0.0056	2.95/3.41	2.5140	0.1069
0.2412	0.0099	2.72/3.34	2.5140	0.2313
0.4644	0.0204	2.52/3.11	2.5140	0.4440
0.6635	0.0301	2.43/3.03	2.5140	0.6333
0.8536	0.0424	2.37/2.98	2.5140	0.8112

and used without further purification. Hydrogenated kerosene was used as diluent. Table 1 lists the physicochemical 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 (25 mL) of acids was contacted with 25 mL of solvent. The mixture was shaken for 1 h. It was observed that this time was sufficient to establish the equilibrium between two phases. The mixture was then transferred in a separating funnel and allowed to settle for at least 30 min, which previous experiments showed was sufficient time 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 the amount of acid in the organic phase was obtained by a mass balance.

Model. Using the mass action law,¹ 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 solubility of 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

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

total aqueous conc/mol·L ⁻¹			total organic conc/mol·L ⁻¹	
init butyric acid	equil butyric acid	init/equil pH	init TRPO	equil butyric acid
0.0194	0.0011	3.32/4.03	0.2514	0.0183
0.0390	0.0018	3.08/4.07	0.2514	0.0372
0.0590	0.0028	2.98/3.78	0.2514	0.0562
0.0982	0.0052	2.88/3.63	0.2514	0.0930
0.1929	0.0261	2.78/3.29	0.2514	0.1668
0.2827	0.0388	2.64/3.21	0.2514	0.2439
0.3041	0.0423	2.65/3.12	0.2514	0.2618
0.3896	0.0793	2.53/3.15	0.2514	0.3103
0.4589	0.1167	2.56/2.88	0.2514	0.3422
0.4728	0.1187	2.50/2.94	0.2514	0.3541
0.5479	0.1516	2.46/2.89	0.2514	0.3963
0.6097	0.1859	2.49/2.77	0.2514	0.4238
0.6634	0.1966	2.52/2.83	0.2514	0.4668
0.0194	0.0011	3.32/3.68	0.7542	0.0183
0.0390	0.0015	3.08/3.60	0.7542	0.0375
0.0590	0.0019	2.98/3.52	0.7542	0.0571
0.0982	0.0028	2.88/3.53	0.7542	0.0954
0.1929	0.0051	2.78/3.66	0.7542	0.1878
0.2827	0.0082	2.64/3.51	0.7542	0.2745
0.3896	0.0142	2.53/3.26	0.7542	0.3754
0.4728	0.0218	2.50/3.16	0.7542	0.4510
0.5479	0.0308	2.46/3.10	0.7542	0.5171
0.6634	0.0510	2.52/3.00	0.7542	0.6124
0.7493	0.0967	2.50/2.99	0.7542	0.6526
0.8767	0.1316	2.46/2.80	0.7542	0.7451
1.1273	0.1512	2.40/2.85	0.7542	0.9761
1.2638	0.2243	2.27/2.74	0.7542	1.0395
1.5526	0.3157	2.23/2.60	0.7542	1.2369
1.8655	0.3551	2.27/2.65	0.7542	1.5104
2.0852	0.4668	2.17/2.56	0.7542	1.6184
0.0194	0.0013	3.32/3.53	1.2570	0.0181
0.0390	0.0016	3.08/3.52	1.2570	0.0374
0.0590	0.0019	2.98/3.50	1.2570	0.0571
0.0982	0.0025	2.88/3.48	1.2570	0.0957
0.1929	0.0047	2.78/3.46	1.2570	0.1882
0.0194	0.0014	3.32/3.46	1.7598	0.0180
0.0390	0.0017	3.08/3.40	1.7598	0.0373
0.0590	0.0020	2.98/3.39	1.7598	0.0570
0.0982	0.0026	2.88/3.37	1.7598	0.0956
0.1929	0.0038	2.78/3.34	1.7598	0.1891
0.0194	0.0017	3.32/3.33	2.5140	0.0177
0.0390	0.0020	3.08/3.26	2.5140	0.0370
0.0590	0.0022	2.98/3.25	2.5140	0.0568
0.0982	0.0027	2.88/3.26	2.5140	0.0955
0.1929	0.0036	2.78/3.30	2.5140	0.1893
0.4190	0.0066	2.54/3.22	2.5140	0.4124
0.6151	0.0094	2.45/3.18	2.5140	0.6057
0.7763	0.0119	2.36/3.15	2.5140	0.7644

organic–aqueous interface. The distribution ratio can be derived as

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

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. D is the distribution ratio between organic and 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

The equilibrium data at different trialkylphosphine oxide concentrations are given in Tables 2–10. 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

Table 6. Equilibrium Data for the System Caproic Acid + Trialkylphosphine Oxide in Kerosene

total aqueous conc/mol·L ⁻¹			total organic conc/mol·L ⁻¹	
init caproic acid	equil caproic acid	init/equil pH	init TRPO	equil caproic acid
0.0044	0.0017	3.57/4.25	0.0000	0.0027
0.0089	0.0031	3.40/4.05	0.0000	0.0058
0.0165	0.0038	3.26/3.80	0.0000	0.0127
0.0248	0.0050	3.17/3.66	0.0000	0.0198
0.0323	0.0062	3.10/3.59	0.0000	0.0261
0.0044	0.0005	3.57/4.06	0.2514	0.0039
0.0089	0.0003	3.40/4.14	0.2514	0.0086
0.0165	0.0004	3.26/3.99	0.2514	0.0161
0.0248	0.0005	3.17/3.86	0.2514	0.0243
0.0323	0.0006	3.10/3.85	0.2514	0.0317
0.0044	0.0009	3.57/3.66	0.7542	0.0035
0.0089	0.0008	3.40/3.76	0.7542	0.0081
0.0165	0.0009	3.26/3.58	0.7542	0.0156
0.0248	0.0009	3.17/3.53	0.7542	0.0239
0.0323	0.0009	3.10/3.55	0.7542	0.0314
0.0044	0.0012	3.57/3.63	1.2570	0.0032
0.0089	0.0012	3.40/3.53	1.2570	0.0077
0.0165	0.0011	3.26/3.44	1.2570	0.0154
0.0248	0.0012	3.17/3.35	1.2570	0.0236
0.0323	0.0011	3.10/3.46	1.2570	0.0312
0.0044	0.0015	3.57/3.68	1.7598	0.0029
0.0089	0.0016	3.40/3.58	1.7598	0.0073
0.0165	0.0015	3.26/3.58	1.7598	0.0150
0.0248	0.0021	3.17/3.11	1.7598	0.0227
0.0323	0.0015	3.10/3.30	1.7598	0.0308
0.0044	0.0020	3.57/3.63	2.5140	0.0024
0.0089	0.0019	3.40/3.54	2.5140	0.0070
0.0165	0.0017	3.26/3.47	2.5140	0.0148
0.0248	0.0019	3.17/3.38	2.5140	0.0229
0.0323	0.0017	3.10/3.28	2.5140	0.0306

Table 7. Equilibrium Data for the System Monochloroacetic Acid (MCAA) + Trialkylphosphine Oxide in Kerosene

total aqueous conc/mol·L ⁻¹			total organic conc/mol·L ⁻¹	
init MCAA	equil MCAA	init/equil pH	init TRPO	equil MCAA
0.0267	0.0027	2.25/3.01	0.2514	0.0240
0.0556	0.0056	2.08/2.77	0.2514	0.0500
0.1081	0.0118	1.95/2.50	0.2514	0.0963
0.2188	0.0432	1.79/2.14	0.2514	0.1756
0.3239	0.1102	1.70/1.89	0.2514	0.2137
0.3641	0.1402	1.65/1.80	0.2514	0.2239
0.4201	0.1894	1.63/1.73	0.2514	0.2307
0.6401	0.3604	1.52/1.57	0.2514	0.2797
0.0267	0.0023	2.25/3.00	0.7542	0.0244
0.0556	0.0030	2.08/2.88	0.7542	0.0526
0.1081	0.0043	1.95/2.84	0.7542	0.1038
0.2188	0.0095	1.79/2.57	0.7542	0.2093
0.3641	0.0192	1.65/2.34	0.7542	0.3449
0.4201	0.0248	1.63/2.26	0.7542	0.3953
0.6401	0.0631	1.52/2.09	0.7542	0.5770
0.8022	0.1399	1.45/1.88	0.7542	0.6633
0.8982	0.2014	1.42/1.79	0.7542	0.6968
0.9202	0.2119	1.40/1.78	0.7542	0.7083
0.0267	0.0015	2.25/3.13	1.2570	0.0252
0.0556	0.0022	2.08/2.98	1.2570	0.0534
0.1081	0.0032	1.95/2.90	1.2570	0.1049
0.2188	0.0060	1.79/2.61	1.2570	0.2128
0.3641	0.0108	1.65/2.38	1.2570	0.3533
0.0267	0.0018	2.25/2.98	1.7598	0.0249
0.0556	0.0021	2.08/2.89	1.7598	0.0535
0.1081	0.0029	1.95/2.94	1.7598	0.1052
0.2188	0.0051	1.79/2.68	1.7598	0.2137
0.3641	0.0083	1.65/2.48	1.7598	0.3558
0.0267	0.0018	2.25/3.10	2.2626	0.0249
0.0556	0.0022	2.08/3.02	2.2626	0.0534
0.1081	0.0029	1.95/3.09	2.2626	0.1052
0.2188	0.0046	1.79/2.85	2.2626	0.2142
0.3641	0.0072	1.65/2.67	2.2626	0.3569
0.0267	0.0020	2.25/3.06	2.5140	0.0247
0.0556	0.0022	2.08/3.05	2.5140	0.0534
0.1081	0.0027	1.95/3.03	2.5140	0.1054
0.2188	0.0042	1.79/2.92	2.5140	0.2146
0.3641	0.0066	1.65/2.73	2.5140	0.3575

differed for each experimental point. For example, for a 55% (mole) acetic acid extraction with a trialkylphosphine oxide concentration of 0.2514 mol/L and at a starting pH

Table 8. Equilibrium Data for the System Dichloroacetic Acid (DCAA) + Trialkylphosphine Oxide in Kerosene

total aqueous conc/mol·L ⁻¹			total organic conc/mol·L ⁻¹	
init DCAA	equil DCAA	init/equil pH	init TRPO	equil DCAA
0.0162	0.0014	1.81/3.03	0.2514	0.0148
0.0387	0.0021	1.52/2.66	0.2514	0.0366
0.0774	0.0036	1.38/2.43	0.2514	0.0738
0.1510	0.0082	1.11/2.19	0.2514	0.1428
0.2268	0.0212	1.07/1.73	0.2514	0.2056
0.3017	0.0622	0.99/1.53	0.2514	0.2395
0.3963	0.1374	0.88/1.24	0.2514	0.2589
0.4698	0.2184	0.85/1.09	0.2514	0.2514
0.5899	0.3012	0.78/0.95	0.2514	0.2887
0.0162	0.0011	1.81/3.09	0.7542	0.0151
0.0387	0.0016	1.52/2.92	0.7542	0.0371
0.0774	0.0023	1.38/2.72	0.7542	0.0751
0.1510	0.0033	1.11/2.53	0.7542	0.1477
0.2268	0.0045	1.07/2.39	0.7542	0.2223
0.3017	0.0055	0.99/2.30	0.7542	0.2962
0.3963	0.0078	0.88/2.17	0.7542	0.3885
0.4698	0.0115	0.85/1.98	0.7542	0.4583
0.5899	0.0175	0.78/1.81	0.7542	0.5724
0.6960	0.0335	0.73/1.60	0.7542	0.6625
0.7835	0.0689	0.70/1.34	0.7542	0.7146
0.8810	0.1203	0.67/1.18	0.7542	0.7607
0.9726	0.1779	0.63/1.08	0.7542	0.7947
0.0162	0.0011	1.81/3.13	1.2570	0.0151
0.0387	0.0015	1.52/2.96	1.2570	0.0372
0.0774	0.0020	1.38/2.85	1.2570	0.0754
0.1510	0.0026	1.11/2.68	1.2570	0.1484
0.2268	0.0034	1.07/2.52	1.2570	0.2234
0.0162	0.0013	1.81/3.12	1.7598	0.0149
0.0387	0.0015	1.52/3.09	1.7598	0.0372
0.0774	0.0019	1.38/2.92	1.7598	0.0755
0.1510	0.0026	1.11/2.67	1.7598	0.1484
0.2268	0.0030	1.07/2.60	1.7598	0.2238
0.0162	0.0016	1.81/3.06	2.2626	0.0146
0.0387	0.0018	1.52/3.04	2.2626	0.0369
0.0774	0.0025	1.38/2.91	2.2626	0.0749
0.1510	0.0026	1.11/2.74	2.2626	0.1484
0.2268	0.0030	1.07/2.64	2.2626	0.2238
0.0162	0.0018	1.81/3.05	2.5140	0.0144
0.0387	0.0019	1.52/3.02	2.5140	0.0368
0.0774	0.0020	1.38/2.92	2.5140	0.0754
0.1510	0.0028	1.11/2.76	2.5140	0.1482
0.2268	0.0031	1.07/2.65	2.5140	0.2237

of 3.50, the final pH was 4.10 (Table 3).

The equilibrium acid concentrations in the organic phase increased with an increase of trialkylphosphine oxide concentration and decreased with an increase of the acid concentration in the aqueous phase. At low trialkylphosphine 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 phenomenon confirms the assumption of extraction mechanism; that is, the complex formed between trialkylphosphine oxide and acid is 1:1. At high trialkylphosphine oxide concentration, extraction performance changes on a very small scale.

Except for caproic acid, the 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 lactic acid to 2.99 for caproic acid (Table 11).

The extraction equilibrium constant, K_{11} , is evaluated from eq 1 using a least-squares regression method. Table 11 gives the results for nine monocarboxylic acids studied in this paper. Then, from eq 1, for a known initial acid concentration, the equilibrium pH, and the K_{11} of the acid, the acid concentration in the aqueous phase can be calculated and also the acid concentration in the organic phase. Figure 1 shows the calculated results of organic acid

Table 9. Equilibrium Data for the System Trichloroacetic Acid (TCAA) + Trialkylphosphine Oxide in Kerosene

total aqueous conc/mol·L ⁻¹			total organic conc/mol·L ⁻¹	
init TCAA	equil TCAA	init/equil pH	init TRPO	equil TCAA
0.0040	0.0003	2.44/5.38	0.2514	0.0037
0.0097	0.0004	2.22/4.07	0.2514	0.0093
0.0265	0.0008	1.72/3.40	0.2514	0.0257
0.0567	0.0020	1.50/3.02	0.2514	0.0547
0.1146	0.0047	1.21/2.57	0.2514	0.1099
0.2174	0.0169	0.94/1.97	0.2514	0.2005
0.2751	0.0442	0.84/1.58	0.2514	0.2309
0.3399	0.0968	0.63/1.28	0.2514	0.2431
0.4651	0.2096	0.52/0.99	0.2514	0.2555
0.0097	0.0004	2.22/4.07	0.5028	0.0093
0.0567	0.0013	1.50/3.61	0.5028	0.0554
0.1146	0.0025	1.21/2.73	0.5028	0.1121
0.2174	0.0048	0.94/2.45	0.5028	0.2126
0.3399	0.0097	0.63/2.15	0.5028	0.3302
0.4651	0.0254	0.52/1.77	0.5028	0.4397
0.5963	0.0904	0.41/1.31	0.5028	0.5059
0.6550	0.1899	0.33/1.12	0.5028	0.4651
0.7021	0.2309	0.29/1.07	0.5028	0.4712
0.0097	0.0005	2.22/4.41	0.7542	0.0092
0.0265	0.0006	1.72/3.77	0.7542	0.0259
0.0567	0.0010	1.50/3.25	0.7542	0.0557
0.1146	0.0018	1.21/2.96	0.7542	0.1128
0.2174	0.0035	0.94/2.63	0.7542	0.2139
0.2751	0.0042	0.84/2.58	0.7542	0.2709
0.3399	0.0054	0.63/2.47	0.7542	0.3345
0.4651	0.0090	0.52/2.25	0.7542	0.4561
0.5963	0.0156	0.41/2.00	0.7542	0.5807
0.7021	0.0555	0.29/1.30	0.7542	0.6466
0.7847	0.1086	---/1.22	0.7542	0.6761
0.8332	0.1463	---/1.18	0.7542	0.6869
0.2174	0.0027	0.94/2.82	1.2570	0.2147
0.2751	0.0033	0.84/2.66	1.2570	0.2718
0.3399	0.0039	0.63/2.56	1.2570	0.3360
0.4651	0.0053	0.52/2.39	1.2570	0.4598
0.5963	0.0072	0.41/2.24	1.2570	0.5891
0.2174	0.0026	0.94/2.86	1.7598	0.2148
0.2751	0.0028	0.84/2.82	1.7598	0.2723
0.3399	0.0032	0.63/2.73	1.7598	0.3367
0.4651	0.0041	0.52/2.56	1.7598	0.4610
0.5963	0.0051	0.41/2.44	1.7598	0.5912
0.2174	0.0023	0.94/3.00	2.2626	0.2151
0.2751	0.0025	0.84/2.93	2.2626	0.2726
0.3399	0.0032	0.63/2.82	2.2626	0.3367
0.4651	0.0039	0.52/2.69	2.2626	0.4612
0.5963	0.0042	0.41/2.57	2.2626	0.5921
0.2174	0.0024	0.94/2.99	2.5140	0.2150
0.2751	0.0027	0.84/2.87	2.5140	0.2724
0.3399	0.0031	0.63/2.79	2.5140	0.3368
0.4651	0.0038	0.52/2.65	2.5140	0.4613
0.5963	0.0043	0.41/2.55	2.5140	0.5920

concentrations in the organic phase compared to the experimental ones. The data are in good agreement in most of the cases. When low concentration trialkylphosphine oxide was used to extract a high concentration of a monocarboxylic acid, such as propionic acid, butyric acid, and caproic acid, an overloading of acids was observed. In other words, the acid concentration in the organic phase was larger than the initial trialkylphosphine oxide concentration, which is the maximum acid concentration in the organic phase according to the mass action law model. A possible explanation is that, when the system approaches equilibrium, the acid-trialkylphosphine oxide complex formed may take part in the solvation of the acid and lead to the ratio between trialkylphosphine oxide and acid in the formed complex being greater than 1:1. At high trialkylphosphine oxide concentration, the system is far from a stoichiometric equilibrium; therefore, no overloading happens.

Concluding Remarks

In this work, extraction equilibrium studies for the systems monocarboxylic acids (formic acid, acetic acid,

Table 10. Equilibrium Data for the System Lactic Acid + Trialkylphosphine Oxide in Kerosene

total aqueous conc/mol·L ⁻¹			total organic conc/mol·L ⁻¹	
init lactic acid	equil lactic acid	init/equil pH	init TRPO	equil lactic acid
0.0241	0.0236	2.48/2.51	0.0000	0.0005
0.0658	0.0650	2.30/2.33	0.0000	0.0008
0.1232	0.1222	2.05/2.09	0.0000	0.0010
0.2508	0.2490	1.88/1.91	0.0000	0.0018
0.4716	0.4686	1.79/1.78	0.0000	0.0030
0.7342	0.7276	1.73/1.75	0.0000	0.0066
0.9411	0.9234	1.66/1.68	0.0000	0.0077
1.2270	1.2060	1.60/1.61	0.0000	0.0210
0.0241	0.0158	2.48/2.56	0.2514	0.0083
0.0658	0.0449	2.30/2.46	0.2514	0.0209
0.1232	0.0862	2.05/2.22	0.2514	0.0370
0.2508	0.1840	1.88/2.13	0.2514	0.0668
0.4716	0.3760	1.79/1.97	0.2514	0.0956
0.7342	0.6014	1.73/1.83	0.2514	0.1328
0.9411	0.7899	1.66/1.73	0.2514	0.1512
1.2270	1.0620	1.60/1.68	0.2514	0.1650
0.0241	0.0108	2.48/2.85	0.7542	0.0133
0.0658	0.0282	2.30/2.64	0.7542	0.0376
0.1232	0.0525	2.05/2.47	0.7542	0.0707
0.2508	0.1133	1.88/2.28	0.7542	0.1375
0.4716	0.2464	1.79/2.08	0.7542	0.2252
0.7342	0.4276	1.73/1.98	0.7542	0.3066
0.9411	0.5716	1.66/1.86	0.7542	0.2695
1.2270	0.8196	1.60/1.78	0.7542	0.4074
0.0241	0.0082	2.48/2.90	1.2570	0.0159
0.0658	0.0205	2.30/2.77	1.2570	0.0453
0.1232	0.0378	2.05/2.53	1.2570	0.0854
0.2508	0.0821	1.88/2.36	1.2570	0.1687
0.4716	0.1772	1.79/2.18	1.2570	0.2944
0.7342	0.3088	1.73/2.14	1.2570	0.4254
0.9411	0.4246	1.66/2.01	1.2570	0.5165
1.2270	0.6147	1.60/1.88	1.2570	0.6123
0.0241	0.0064	2.48/2.90	1.7598	0.0177
0.0658	0.0171	2.30/2.77	1.7598	0.0487
0.1232	0.308	2.05/2.53	1.7598	0.0924
0.2508	0.0631	1.88/2.36	1.7598	0.1877
0.4716	0.1362	1.79/2.18	1.7598	0.3354
0.7342	0.2431	1.73/2.14	1.7598	0.4911
0.9411	0.3311	1.66/2.01	1.7598	0.6100
1.2270	0.4900	1.60/1.88	1.7598	0.7370
0.0241	0.0059	2.48/2.90	2.5140	0.0182
0.0658	0.0138	2.30/2.77	2.5140	0.0520
0.1232	0.0233	2.05/2.53	2.5140	0.0999
0.2508	0.0486	1.88/2.36	2.5140	0.2022
0.4716	0.0986	1.79/2.18	2.5140	0.3730
0.7342	0.1619	1.73/2.14	2.5140	0.5723
0.9411	0.2422	1.66/2.01	2.5140	0.6989
1.2270	0.3645	1.60/1.88	2.5140	0.8625

Table 11. Model Parameters for Trialkylphosphine Oxide (in Kerosene)-Carboxylic Acid Systems

solute	B_0 (mol·L ⁻¹)	pK_a	K_{11} (L·mol ⁻¹)	m
formic acid	0.2514-2.514	3.77	6.68	0.050
acetic acid	0.2514-2.514	4.76	4.78	0.010
propionic acid	0.2514-2.514	4.87	12.2	0.017
butyric acid	0.2514-2.514	4.82	35.4	0.077
caproic acid	0.2514-2.514	4.85	6.7	2.990
monochloroacetic acid	0.2514-2.514	2.86	64.93	0.022
dichloroacetic acid	0.2514-2.514	1.26	1300	0.032
trichloroacetic acid	0.2514-2.514	0.64	11800	0.056
lactic acid	0.2514-2.514	3.86	1.0	0.006

propionic acid, butyric acid, caproic acid, monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, and lactic acid) + trialkylphosphine oxide in kerosene were carried out at various trialkylphosphine oxide concentrations and initial acid concentrations. Distribution ratios increase with the increase of trialkylphosphine oxide concentration and decrease with the increase of the acid concentration in the aqueous phase. By using mass action law, and suitable assumptions, the distribution ratio for a acid-trialkylphosphine oxide in kerosene system is derived. In addition, the extraction equilibrium constant, K_{11} , is evaluated by a least-squares regression method. The simulated acid concentration in the organic phase is in good agreement with the experimental values.

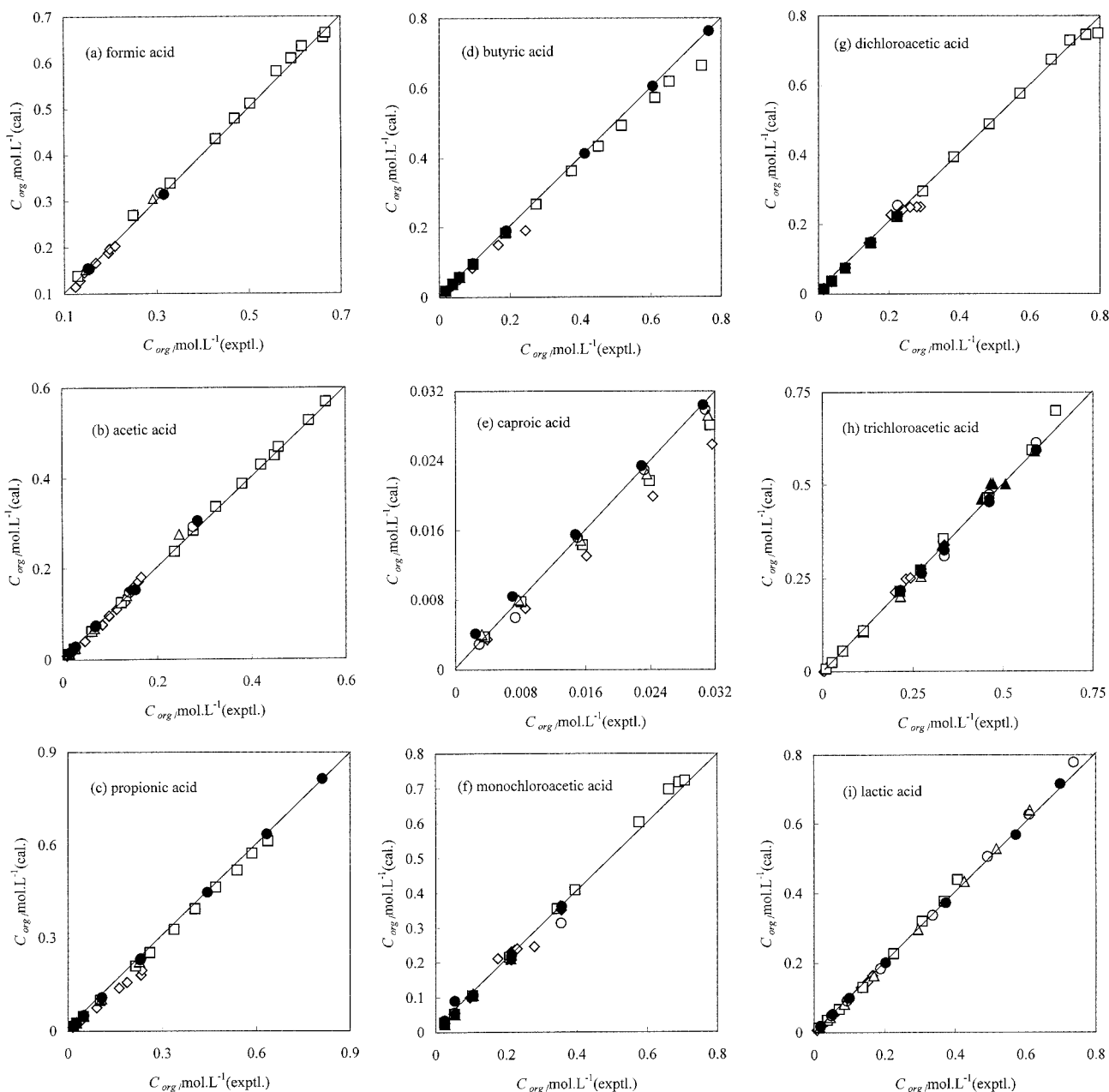


Figure 1. Comparison of experimental and calculated organic acid concentrations in the monocarboxylic acid-trialkylphosphine oxide-kerosene system: \diamond , $B_0 = 0.2514 \text{ mol}\cdot\text{L}^{-1}$; \blacktriangle , $B_0 = 0.5028 \text{ mol}\cdot\text{L}^{-1}$; \square , $B_0 = 0.7542 \text{ mol}\cdot\text{L}^{-1}$; \triangle , $B_0 = 1.257 \text{ mol}\cdot\text{L}^{-1}$; \circ , $B_0 = 1.7598 \text{ mol}\cdot\text{L}^{-1}$; \blacklozenge , $B_0 = 2.2626 \text{ mol}\cdot\text{L}^{-1}$; \bullet , $B_0 = 2.514 \text{ mol}\cdot\text{L}^{-1}$.

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