Extraction Equilibria of Propionic and Butyric Acids with Tri-*n*-octylphosphine Oxide/Diluent Systems

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The extraction equilibria of propionic and butyric acids with tri-*n*-octylphosphineoxide (TOPO) dissolved in seven solvents in different chemical structures {isoamyl alcohol, oleyl alcohol, toluene, methyl *tert*-butyl ether (MTBE), cyclohexyl acetate, kerosene, isobutyl methyl ketone (MIBK)} have been measured at 298.15 K. The highest distribution coefficient for both of the acids is obtained by TOPO dissolved in MTBE. It was observed that the use of TOPO dissolved in these diluents has increased the distribution coefficients of propionic and butyric acids between organic and aqueous phases up to 51.22 and 12 times, respectively, compared to the use of pure solvents. The extraction efficiencies with TOPO reached the range of (75.21 to 94.42) % for propionic acid and (90.68 to 96.22) % for butyric acid, depending on the solvent type and concentration.

Introduction

In recent years, several investigations has been carried out on the (liquid−liquid) equilibrium (LLE) measurements of ternary systems including carboxylic acids, to understand and provide further information about the phase behavior of such systems[1−5] and with the aim of developing processes that result in more effective separation of these acids from aqueous fermentation media. These studies stated that the extractability of most organic acids by conventional solvents is very low, and reactive extraction must be considered.[6−11] On the other hand, at most occasions, the fermentation broths are low concentration solutions, and the traditional methods to recover organic acids have obvious drawbacks. For example, the calcium salt precipitation technique consumes sulfuric acid and lime but forms large amounts of byproduct of calcium sulfate.

To get higher recovery, tertiary amines are considered as the most favorable extractants.[7−10] It is a high efficiency process, but these kinds of extractants are easy to form an emulsion or a third phase in the extraction process, which causes extractant loss and damage to the water resource. Also, these types of extractants are somehow toxic to microorganisms and prevent the use of in situ coupling of fermentation and extraction processes. Thus, new alternative methods are highly required.

In this study, we have used a phosphorus compound, tri-*n*-octylphosphine oxide (TOPO), as extractant, which is more environmentally friendly than amines. TOPO, a tertiary alkylphosphine, containing three octyl chains resulting in different conformational structures, is proposed for the reactive extraction of carboxylic acids.[12−15] It can have also some handling advantages since it is a solid chemical. Due to their physical properties, it must always be used in the form of solutions in organic diluents.

Propionic and butyric acids are widely used carboxylic acids in industry. Propionic acid is used in the pharmaceutical industry as a cellulosic solvent and can be used to provide propionates as fungicides. It is also used in the electroplating industry, as an esterifying agent in the production of thermoplastics, and in the manufacture of flavors and perfume bases.[16] It has a potential to replace chemical preservatives and is used as a mold inhibitor in baking, so it is of substantial commercial importance in the sale of "natural" bakery products. The Na^+, Ca^{2+}, and K^+ salts of propionic acid have also been listed as preservatives which are of the category known as "generally recognized as safe" (GRAS) food additives.[17] Also butyric acid is employed in the diary or food industries to increase the fragrance of beverages or foodstuffs, in the pharmaceutical industry, and as a raw material for the production of biodegradable polymers based on β-hydroxy-butyrate. In past decade, with the increase in demand for naturally produced carboxylic acids together with its wide use and the development of new biotechnology, the fermentation routes for propionic and butyric acid production have become of more interest than the organic synthesis methods.

This study is part of a research program on the recovery of carboxylic acids from dilute aqueous solutions using organic solvents. In this work, the extraction of propionic and butyric acids with TOPO solved in several solvents {isoamyl alcohol, oleyl alcohol, toluene, methyl *tert*-butyl ether (MTBE), cyclohexyl acetate, kerosene, isobutyl methyl ketone (MIBK)} has been investigated at $T = 298.15$ K, for which no such data were available in the literature.

Theoretical

A reactive extractant dissolved in active diluents, i.e., solvents that contain functional groups, interacts strongly with the formed acid−extractant complex. If the chemical interactions are strong compared to the physical interactions in the system, the equilibrium behavior can be modeled by postulating the formation of various stoichiometric complexes of acid and extractant.[9]

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Table 1. Physical Properties of the Chemicals Used in the Experiments at (293 ± 0.20) K

compound	$\rho^{293.15\mathrm{K}}$ (g·cm^{-3}) (exptl)	$\rho^{293.15\mathrm{K}}$ (g·cm^{-3}) (lit.)[18]	n (exptl)	n (lit.)[18]	source (mass purity)
water	0.9999	0.9982	1.3324	1.3330	bidistilled
propionic acid	$0.9884^{298.15}$	$0.9882^{298.15}$	1.3810	1.3809	Merck (> 99 %)
butyric acid	$0.9523^{298.15}$	$0.9528^{298.15}$	1.3982	1.3980	Merck (> 99 %)
kerosene	$0.7971^{288.15}$	0.7750 to $0.8400^{288.15a}$	$1.4457^{288.15}$	–	TUPRAS[a]
toluene	0.8667	0.8668	1.4960	1.4961	Merck (≥ 99 %)
oleyl alcohol	0.8490	0.8489	1.4601	1.4606	Merck (~ 85 %)
isoamyl alcohol	0.8084	0.8104	1.4075	1.4053	Merck (> 98 %)
cyclohexyl acetate	0.9684	0.9680	1.4421	1.4420	Merck (> 98 %)
methyl *tert*-butyl ether	$0.7347^{298.15}$	$0.7353^{298.15}$	$1.3664^{298.15}$	$1.3664^{298.15}$	Merck (≥ 99 %)
isobutyl methyl ketone	$0.7961^{298.15}$	$0.7965^{298.15}$	1.3958	1.3962	Merck (> 99 %)

[a] Kerosene type Jet Fuel (JET A-1), TUPRAS Code No. 300, www.tupras.com.tr.

Table 2. Distribution Coefficients of Acids (D_2) and Water (D_1) and Separation Factors (S) for Different Pure Solvents Tested at T = 298.15 K

acid	solvent	D_2	D_1	S
propionic acid	kerosene	0.09	0.0002	450.00
	toluene	0.35	0.0010	350.00
	oleyl alcohol	0.58	0.0141	41.13
	isoamyl alcohol	2.05	0.0721	28.43
	cyclohexyl acetate	1.28	0.0151	84.77
	methyl *tert*-butyl ether	2.10	0.0176	119.32
	isobutyl methyl ketone	2.13	0.0161	132.30
butyric acid	kerosene	0.94	0.0003	3133.33
	toluene	2.57	0.0010	2570.00
	oleyl alcohol	2.94	0.0165	178.18
	isoamyl alcohol	8.03	0.0779	103.08
	cyclohexyl acetate	4.88	0.0152	321.05
	methyl *tert*-butyl ether	9.84	0.0258	381.40
	isobutyl methyl ketone	6.59	0.0159	490.57

Extraction of weak organic acids from the aqueous phase into the organic phase by strong solvating extractant, TOPO, is represented according to the following overall reaction[9,12]

$$p\mathrm{HA}_{(\mathrm{aq})} + q\mathrm{TOPO}_{\mathrm{org}} \leftrightarrow (\mathrm{HA})_p\mathrm{TOPO}_{q(\mathrm{org})} \qquad (1)$$

where p and q are the molecule number of acid, HA, and TOPO, respectively (aq, aqueous phase; org, organic phase). Here, the related equilibrium-extraction constant, K_{pq}, is

$$K_{pq} = \frac{C_{\mathrm{HA,org}}}{C^{p}_{\mathrm{HA,aq}} \cdot C^{q}_{\mathrm{TOPO,org}}} \qquad (2)$$

where $C_{\mathrm{HA,org}}$ and $C_{\mathrm{HA,aq}}$ are the acid concentrations in organic and aqueous phases, respectively, and $C_{\mathrm{TOPO,org}}$ is the TOPO concentration in the organic phase. In the case where there is a single extractant molecule per complex ($q = 1$), stoichiometry as it is reported for monocarboxylic acids eq 2 can be written as

$$K_{p1} = \frac{C_{\mathrm{HA,org}}}{C^{p}_{\mathrm{HA,aq}} \cdot C_{\mathrm{TOPO,org}}} \qquad (3)$$

It is well-known that a carboxylic acid dissociates in aqueous solution and dimerizes in a nonpolar solvent. However, previous studies have shown that the equilibrium terms relating to these cases can be neglected under the present experimental conditions.[13] Therefore, only the species $(\mathrm{HA})_p\mathrm{TOPO}_q$ are presumed to exist in organic solution.

To show the selectivity and the extraction strength of the solvent to extract acid from aqueous solution, the distribution coefficients D_i for water ($i = 1$) and acid ($i = 2$) and the separation factors S were determined as follows

$$D_i = C_{i,\mathrm{org}}/C_{i,\mathrm{aq}} \qquad (4)$$

$$S = D_2/D_1 \qquad (5)$$

where D_1 and D_2 are the distribution coefficients of water and acid, respectively, and $C_{i,\mathrm{org}}$ and $C_{i,\mathrm{aq}}$ are the mole concentrations of component i in solvent-rich and water-rich phases, respectively.

The loading of the extractant (Z) is defined as the total concentration of acid in the organic phase divided by the total concentration of TOPO in the organic phase.[6]

$$Z = C_{\mathrm{HA,org}}/C_{\mathrm{TOPO,org}} \qquad (6)$$

Experimental Section

Chemicals. The purity of the chemicals was checked on the basis of their densities and refractive indexes at T = (293 ± 0.20) K. The measured values of water, propionic acid, butyric acid, and solvents used in this study are listed in Table 1, along with sources and true densities given in the literature.[18] All chemicals were used without further purification. Gas chromatographic analysis did not detect any appreciable peaks of impurities. A gas chromatograph (Hewlett-Packard GC, model 6890 Series), equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID), was used for determination of water and organics used in the experiments. A 15 m HP-Plot Q column (320 μm diameter with a 20 μm film thickness) was taken with a temperature programmed analysis. The analysis conditions were as follows: column temperature, from (323.15 to 563.15) K at 20 K·min^{-1}, at 563.15 K (10 min) injection mode, split ratio 100:1; injector temperature, 563.15 K; and detector temperature, 583.15 K; carrier gas, nitrogen 1 cm^3·min^{-1}; injected volume of 0.3 μL of liquid sample. Deionized water was further distilled before use. Densities and refractive indexes were measured with an Anton Paar densimeter (DMA 4500 model) equipped with a refractometer (RXA 170 model) in an accuracy of ± 1·10^{-4} g·cm^{-3} and ± 1·10^{-4}, respectively. The physical properties measured are in good agreement with published values.

Apparatus and Procedure. Aqueous propionic and butyric acid solutions were prepared from distilled water with initial concentrations of (0.987 and 0.996) mol·L^{-1}, respectively. Organic phases were taken first as pure solvents shown in Table 2 and then by mixing TOPO with these solvents to produce solutions in different concentrations, approximately in the range of (0.02 to 1) mol·L^{-1}, as shown in Table 3. Experiments were performed by shaking equal volumes (10 mL) of initial aqueous and organic phases, placed in glass flasks, in a shaker bath at T = 298.15 K for 5 h, which preliminary tests show to be a sufficient time for equilibrium. Thereafter, the phases were separated after (5 to 8) h settling at T = 298.15 K. Temperature

Table 3. Extraction Results with TOPO/Diluent Systems

acid	diluent	$C_{\mathrm{TOPO,org}}$ (mol·L^{-1})	$C_{\mathrm{HA,aq}}$ (mol·L^{-1})	$C_{\mathrm{HA,org}}$ (mol·L^{-1})	D	Z	E %
propionic acid	kerosene	0.0221	0.8559	0.1221	0.14	5.52	13.28
		0.2070	0.6715	0.3175	0.47	1.53	31.97
		0.4023	0.5026	0.4898	0.97	1.22	49.08
		0.5272	0.3867	0.6060	1.57	1.15	60.82
		0.6889	0.2651	0.7011	2.64	1.02	73.14
		0.8961	0.1727	0.8117	4.70	0.91	82.50
	toluene	0.0239	0.7018	0.2875	0.41	12.03	28.90
		0.1130	0.6112	0.3780	0.62	3.35	38.07
		0.2252	0.5288	0.4604	0.87	2.04	46.42
		0.4541	0.2834	0.7000	2.47	1.54	71.29
		0.6897	0.2020	0.8633	4.27	1.25	79.53
		0.9682	0.1205	0.8665	7.19	0.89	87.79
	oleyl alcohol	0.0323	0.5021	0.4739	0.94	14.67	49.13
		0.2059	0.4488	0.5399	1.20	2.62	54.53
		0.3755	0.3933	0.5858	1.49	1.56	60.15
		0.5239	0.3377	0.6316	1.87	1.21	65.79
		0.7108	0.2912	0.6704	2.30	0.94	70.50
		0.9009	0.2447	0.7091	2.90	0.79	75.21
	isoamyl alcohol	0.0216	0.2537	0.7374	2.91	34.14	74.30
		0.2195	0.2410	0.7502	3.11	3.42	75.58
		0.4098	0.2297	0.7603	3.31	1.86	76.73
		0.6003	0.2183	0.7703	3.53	1.28	77.88
		0.7911	0.2035	0.7868	3.87	0.99	79.38
		0.9593	0.1887	0.8032	4.26	0.84	80.88
	cyclohexyl acetate	0.0252	0.4051	0.5754	1.42	22.83	58.96
		0.2465	0.3186	0.6692	2.10	2.72	67.72
		0.4322	0.2615	0.7511	2.87	1.74	73.51
		0.6195	0.1985	0.7922	3.99	1.28	79.89
		0.8113	0.1514	0.8402	5.55	1.04	84.66
		1.0608	0.1063	0.8827	8.30	0.83	89.23
	tert-butyl methyl ether	0.0190	0.3071	0.6764	2.20	35.60	68.89
		0.1916	0.2377	0.7404	3.11	3.86	75.92
		0.3915	0.1950	0.8352	4.28	2.13	80.24
		0.5593	0.1500	0.8345	5.56	1.49	84.80
		0.6998	0.1021	0.6698	6.56	0.96	89.66
		0.8412	0.0551	0.4250	7.71	0.51	94.42
	isobutyl methyl ketone	0.0238	0.3132	0.6722	2.15	28.24	68.27
		0.2092	0.2601	0.7289	2.80	3.48	73.65
		0.3897	0.2455	0.8611	3.51	2.21	75.13
		0.5217	0.1801	0.8036	4.46	1.54	81.75
		0.7781	0.1459	0.8522	5.84	1.10	85.22
		0.8912	0.1175	0.8641	7.35	0.97	88.10
butyric acid	kerosene	0.0651	0.4750	0.5112	1.08	7.85	52.31
		0.2341	0.3575	0.6323	1.77	2.70	64.11
		0.3743	0.2807	0.7068	2.52	1.89	71.82
		0.5293	0.2025	0.7842	3.87	1.48	79.67
		0.7521	0.1066	0.8133	7.63	1.08	89.30
		0.9065	0.0745	0.9102	12.22	1.00	92.52
	toluene	0.0719	0.2678	0.7254	2.71	10.1	73.11
		0.2525	0.2136	0.7785	3.64	3.08	78.55
		0.4003	0.1753	0.8187	4.67	2.05	82.40
		0.5643	0.1258	0.8620	6.85	1.53	87.37
		0.7985	0.0746	0.8931	11.97	1.12	92.51
		0.9717	0.0497	0.9363	18.84	0.96	95.01
	oleyl alcohol	0.0635	0.1960	0.7941	4.05	12.51	80.32
		0.2412	0.1652	0.8203	4.97	3.40	83.41
		0.3935	0.1504	0.8362	5.56	2.13	84.90
		0.5338	0.1340	0.8532	6.37	1.60	86.55
		0.7201	0.1121	0.8871	7.91	1.23	88.74
		0.9110	0.0928	0.8974	9.67	0.99	90.68
	isoamyl alcohol	0.0663	0.0872	0.9024	10.35	13.61	91.24
		0.2462	0.0825	0.9027	10.94	3.67	91.72
		0.3890	0.0788	0.9058	11.49	2.33	92.09
		0.5567	0.0759	0.9092	11.98	1.63	92.38
		0.7581	0.0711	0.9138	12.85	1.21	92.86
		0.9490	0.0668	0.9171	13.73	0.97	93.29
	cyclohexyl acetate	0.0748	0.1429	0.8475	5.93	11.33	85.65
		0.2748	0.1103	0.8724	7.91	3.17	88.93
		0.4366	0.0877	0.8978	10.24	2.06	91.19
		0.6173	0.0726	0.9149	12.60	1.48	92.71
		0.8950	0.0486	0.9302	19.14	1.04	95.12
		1.0616	0.0376	0.9486	25.23	0.89	96.22

Table 3.. Continued

acid	diluent	$C_{\mathrm{TOPO,org}}$ (mol·L^{-1})	$C_{\mathrm{HA,aq}}$ (mol·L^{-1})	$C_{\mathrm{HA,org}}$ (mol·L^{-1})	D	Z	E %
	tert-butyl methyl ether	0.0586	0.0903	0.8998	9.96	15.35	90.93
		0.2129	0.0777	0.9125	11.74	4.29	92.20
		0.3380	0.0661	0.9204	13.92	2.72	93.36
		0.4790	0.0606	0.9269	15.30	1.94	93.92
		0.7102	0.0463	0.9371	20.24	1.32	95.35
		0.8245	0.0393	0.9466	24.09	1.15	96.05
	isobutyl methyl ketone	0.0622	0.1095	0.8768	8.01	14.1	89.01
		0.2285	0.0928	0.8924	9.62	3.91	90.68
		0.3666	0.0785	0.9067	11.55	2.47	92.12
		0.5206	0.0642	0.9183	14.30	1.76	93.55
		0.7481	0.0487	0.9303	19.10	1.24	95.11
		0.8831	0.0420	0.9415	22.42	1.07	95.78

was controlled using an electronic controller with a precision of 0.1 K. All mixtures were prepared by weighing with a Mettler scale precision of ± 0.0001 g.

Acid concentrations in aqueous solutions were determined by volumetric NaOH titration with a relative uncertainty of 1 %.[19] Acid analysis was checked against a material balance. It was seen that the deviation between the amount of acid analyzed and the amount of acid known by preparing the solutions by weighing did not exceed 3 %. The mutual solubilities of organic and aqueous phases were minimized by the preliminary saturation of diluent in water, and so the mutual solubilities are taken as negligible in the range of variables investigated.

Results and Discussion

Distributions of propionic and butyric acids between water and pure solvents used in this study are presented in terms of distribution coefficients of acids and water and separation factors at $T = 298.15$ K in Table 2. Among the solvents used in this study, the highest distribution coefficient for propionic acid was observed with isobutyl methyl ketone (2.13), MTBE (2.10), and isoamyl alcohol (2.05), and the lowest with kerosene (0.09). The highest distribution coefficient for butyric acid was obtained with MTBE (9.84) and the lowest also with kerosene (0.94). For both of the acids, isoamyl alcohol gives higher distribution coefficients than oleyl alcohol because of the fact that increasing molecular weight of alcohols results with decreasing distribution.[5,11] A plot of the distribution coefficients for both of the acids vs the individual solvents used in this study are shown in Figure 1.

Figures 2 and 3 demonstrate the influence of the organic solvents on propionic and butyric acid distribution between water and the TOPO−diluent system, respectively. The plots of propionic acid and butyric acid extraction efficiencies, E, against initial TOPO concentration in different individual diluting solvents are shown in Figures 4 and 5, respectively, with respect to the following formula

$$E = \left(1 - \left(\frac{C_{\mathrm{HA,aq}}}{C^{0}_{\mathrm{HA,aq}}}\right)\right) \cdot 100 \qquad (7)$$

where $C^{0}_{\mathrm{HA,aq}}$ is the initial acid concentration in the aqueous phase.

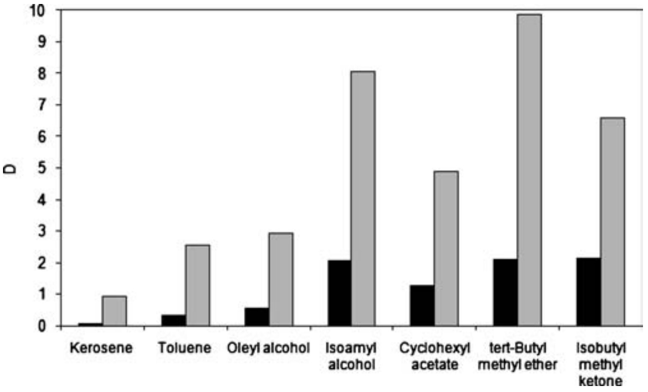

Figure 1. Distribution coefficients, D, of propionic and butyric acids between water and pure solvents: ■, propionic acid; gray □, butyric acid.

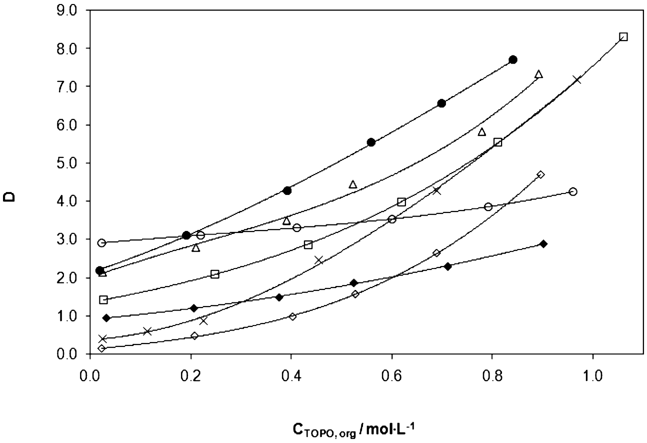

Figure 2. Change of propionic acid distribution coefficients, D, along with initial TOPO concentration, $C_{\mathrm{TOPO,org}}$, in different individual diluting solvents. ◊, kerosene; ×, toluene; ♦, oleyl alcohol; ○, isoamyl alcohol; □, cyclohexyl acetate; ●, methyl *tert*-butyl ether; Δ, isobutyl methyl ketone.

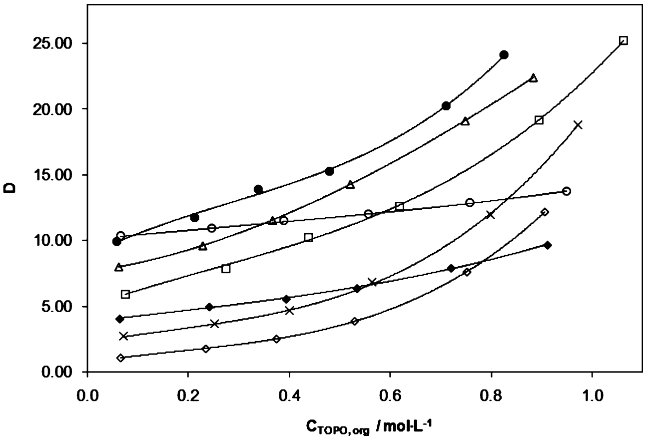

Figure 3. Change of butyric acid distribution coefficients, D, along with initial TOPO concentration, $C_{\mathrm{TOPO,org}}$, in different individual diluting solvents. ◊, kerosene; ×, toluene; ♦, oleyl alcohol; ○, isoamyl alcohol; □, cyclohexyl acetate; ●, methyl *tert*-butyl ether; Δ, isobutyl methyl ketone.

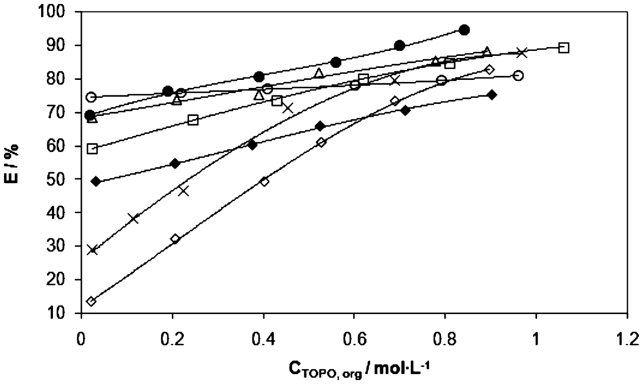

Figure 4. Plot of propionic acid extraction efficiency, *E*, against initial TOPO concentration in different individual diluting solvents, $C_{TOPO,org}$. ◇, kerosene; ×, toluene; ♦, oleyl alcohol; ○, isoamyl alcohol; □, cyclohexyl acetate; ●, methyl *tert*-butyl ether; Δ, isobutyl methyl ketone.

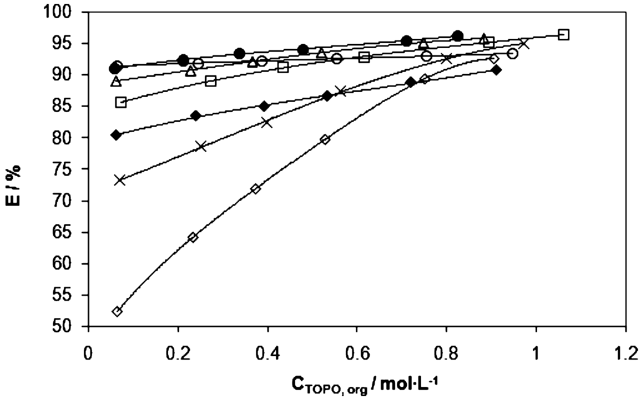

Figure 5. Plot of butyric acid extraction efficiency *E* against initial TOPO concentration in different individual diluting solvents, $C_{TOPO,org}$. ◇, kerosene; ×, toluene; ♦, oleyl alcohol; ○, isoamyl alcohol; □, cyclohexyl acetate; ●, methyl *tert*-butyl ether; Δ, isobutyl methyl ketone.

It can be seen that the extraction power of the TOPO–diluent mixture increases with increasing initial concentration of TOPO in organic phases. For both of the acids, the slopes of the distribution curves for isoamyl alcohol and oleyl alcohol are lower than the others. Except these diluents, the following orders for TOPO extraction were found

MTBE > MIBK > cyclohexyl acetate > toluene > kerosene

The acid–TOPO complex formation and the high solvation effect of MTBE and MIBK, because of their polarity characters, form more synergetic extractive effect than the others. Furthermore, it was observed that toluene, an aromatic diluent, shows higher distribution trend than kerosene, which has been rationalized as solvation due to interaction of the aromatic π electrons with the acid–TOPO complex.

The effect of TOPO concentration on loading, *Z*, is shown in Table 3. At low TOPO concentrations, overloading have been observed. Overloading (loading greater than unity) indicates the complexes with more than one acid molecule per TOPO molecule have formed. In the case of the two type complex formation assumption, the overall extraction constants, K_{11} and K_{21}, are calculated (using eq 3) and presented in Table 4. The resulting complexes are supposed to be stabilized due to hydrogen bonding with the diluents.

Compared to the use of single solvents, TOPO–diluent extractant systems have present a synergetic effect by obtaining up to 51.22 and 12.00 times higher distribution coefficients for propionic and butyric acids, respectively. Also the extraction efficiencies with TOPO reached the range of (75.21 to 94.42) % for propionic acid and (90.68 to 96.22) % for butyric acid, depending on the solvent type and concentration.

Table 4. Overall Extraction Constants

acid	diluent	$C_{TOPO,org}$ (mol·L^{-1})	K_{11} (L·mol^{-1})	K_{21} (L^2·mol^{-2})
propionic acid	kerosene	0.0221	6.46	7.54
		0.2070	2.28	3.40
		0.4023	2.42	4.82
		0.5272	2.97	7.69
		0.6889	3.84	14.48
		0.8961	5.25	30.37
	toluene	0.0239	17.14	24.42
		0.1130	5.47	8.95
		0.2252	3.87	7.31
		0.4541	5.44	19.19
		0.6897	6.20	30.68
		0.9682	7.43	61.64
	oleyl alcohol	0.0323	29.22	58.20
		0.2059	5.84	13.02
		0.3755	3.97	10.09
		0.5239	3.57	10.57
		0.7108	3.24	11.12
		0.9009	3.22	13.15
	isoamyl alcohol	0.0216	134.56	530.41
		0.2195	14.18	58.84
		0.4098	8.08	35.16
		0.6003	5.88	26.93
		0.7911	4.89	24.02
		0.9593	4.44	23.51
	cyclohexyl acetate	0.0252	56.36	139.14
		0.2465	8.52	26.75
		0.4322	6.65	25.41
		0.6195	6.44	32.45
		0.8113	6.84	45.18
		1.0608	7.83	73.64
	tert-butyl methyl ether	0.0190	115.92	377.48
		0.1916	16.26	68.39
		0.3915	10.94	56.10
		0.5593	9.95	66.31
		0.6998	9.37	91.82
		0.8412	9.17	166.41
	isobutyl methyl ketone	0.0238	90.18	287.92
		0.2092	13.40	51.50
		0.3897	9.00	36.66
		0.5217	8.55	47.49
		0.7781	7.51	51.45
		0.8912	8.25	70.23
butyric acid	kerosene	0.0651	16.53	34.80
		0.2341	7.56	21.13
		0.3743	6.73	23.97
		0.5293	7.32	36.13
		0.7521	10.14	95.16
		0.9065	13.48	180.91
	toluene	0.0719	37.67	140.68
		0.2525	14.43	67.58
		0.4003	11.67	66.55
		0.5643	12.14	96.52
		0.7985	14.99	200.98
		0.9717	19.39	390.09
	oleyl alcohol	0.0635	63.80	325.53
		0.2412	20.59	124.62
		0.3935	14.13	93.94
		0.5338	11.93	89.01
		0.7201	10.99	98.03
		0.9110	10.61	114.39
	isoamyl alcohol	0.0663	156.09	1790.00
		0.2462	44.44	538.70
		0.3890	29.55	375.00
		0.5567	21.52	283.50
		0.7581	16.95	238.44
		0.9490	14.47	216.57
	cyclohexyl acetate	0.0748	79.29	554.85
		0.2748	28.78	260.94
		0.4366	23.45	267.36
		0.6173	20.41	281.19
		0.8950	21.39	440.03
		1.0616	23.76	632.04
	tert-butyl methyl ether	0.0586	170.04	1883.10
		0.2129	55.16	709.93
		0.3380	41.20	623.24
		0.4790	31.93	526.93
		0.7102	28.50	615.52
		0.8245	29.21	743.35
	isobutyl methyl ketone	0.0622	128.73	1175.66
		0.2285	42.08	453.50
		0.3666	31.51	401.36
		0.5206	27.48	427.97
		0.7481	25.53	524.33
		0.8831	25.38	604.38

Conclusion

The extraction equilibria of propionic and butyric acids with solvating extractant tri-*n*-octylphosphineoxide (TOPO) dissolved in seven solvents {isoamyl alcohol, oleyl alcohol, toluene, methyl *tert*-butyl ether (MTBE), cyclohexyl acetate, kerosene, isobutyl methyl ketone (MIBK)} have been measured at 298.15 K. The partition of propionic and butyric acids between water and pure solvents is presented in terms of distribution coefficients and separation factors. The results were evaluated on the basis of loading factors, extraction efficiencies, and overall extraction constants.

Butyric acid shows always more distribution in the organic phase than propionic acid. It was seen that *tert*-butyl methyl ether was the best diluent for TOPO to extract both of the acids. The extraction reaction with mixed extractant is reasonably interpreted based on the formation of a complex, which includes more than one acid per TOPO molecule. It is concluded that the used solvents may serve individually as adequate agents to extract the acids from its dilute aqueous solutions; however, the extraction performance can be redounded by using TOPO.

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