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Influence of Extractant (TBP and TOA), Diluent, and Modifier on Extraction Equilibrium of Monocarboxylic Acids

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Recently, new processes for recovery of monocarboxylic acids have been studied. Among these processes, liquid−liquid extraction has had special attention. This process of extraction is attractive if an adequate solvent is used, which shows high selectivity and efficiency, does not affect the thermal stability of products, and requires low energy consumption. In the present work, extraction equilibria of the systems tributyl phosphate and trioctylamine in organic diluents (decan-1-ol and dodecane), water, and each of five lower monocarboxylic acids were measured at the temperature (20 ± 1) °C. For each studied acid are obtained different extraction isotherms in dependence on the composition of the organic phase. From the treatment of experimental data it is shown that the estimated values of the equilibrium extraction constant and the apparent number of extractant molecules reacting with one molecule of monoacid depend not only on the organic phase composition but also on how they are determined.

Introduction

The pharmaceutical, food, and biotechnology industries abound with examples where there is a need to remove organic compounds from aqueous effluents or fermentation broth. Organophosphorus compounds and long chain tertiary amines are effective extractants to recover and separate organic acids from dilute solutions.[1−10]

The extractants are dissolved in different types of diluents, which influence the distribution of solutes between the coexisting phases in equilibrium. For the removal and separation of organic acids, it is very important to understand the influence of different parameters on the overall distribution coefficient of each organic acid. For the evaluation of the distribution coefficient, it is necessary to know the values of the constant of extraction and the number of reacting molecules of extractant. Usually for their determination the mass action law, which represents the product of the concentration of reacting species and the concentration of product of the reaction, is applied, according to the general equation of interaction between the extractant and the extracted substance.

There are many papers where the extraction constant and the number of reacting molecules of extractant are estimated from the mass action law but the obtained values are different according to the composition of the solvent for the same extractant and the organic acid.[11−20]

The difference between the estimated values of parameters appears not only because the composition of the organic phase changes but also dependent on the number of measured factors and the way the extraction constant and number of reacting molecules are evaluated.

The aim of this study is to show the influence of inert and active (modifier) diluent concentrations on the determination of the equilibrium extraction constant and the number of extractant reacting molecules, as well as the method for their calculation when monocarboxylic acids are extracted.

Extraction Equilibrium

The extraction equilibrium of a weak monocarboxylic acid (HA) with the extractants tributyl phosphate (TBP) or trioctylamine (TOA) can be presented as follows:

$$\mathrm{HA} + n\overline{\mathrm{E}} \rightleftharpoons \overline{\mathrm{E}_n\cdot\mathrm{HA}} \tag{1}$$

where n is the number of reacting molecules of extractant. According to the literature data,[1,10,12,14,21,22,24] $n = 1$ for monoacids. Equation 1 becomes

$$\mathrm{HA} + \overline{\mathrm{E}} \rightleftharpoons \overline{\mathrm{E}\cdot\mathrm{HA}} \tag{1-a}$$

According to the mass action law, the extraction constant (K_E) of the organic acid (HA) is

$$K_{\mathrm{E}_{(\mathrm{HA})}} = \frac{[\overline{\mathrm{E}\cdot\mathrm{HA}}]}{[\overline{\mathrm{E}}][\mathrm{HA}]} \tag{1-b}$$

where the concentration of species is denoted by square brackets and expressed in molar concentration, an overbar means the species in the organic phase, HA is the organic acid, $\overline{\mathrm{E}}$ is the extractant, $\overline{\mathrm{E}\cdot\mathrm{HA}}$ is the reaction product in the organic phase, and $K_{\mathrm{E}_{(\mathrm{HA})}}$ is the extraction constant of the organic acid (HA).

The overall distribution coefficient of the extracted acid (m_{HA}) represents the ratio of the total acid concentration in the organic phase ($\bar{C}_{\mathrm{HA}}$) to the total acid concentration in the aqueous phase (C_{HA}) in all possible forms. If only

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Table 1. Characteristics of Substances Used in This Study with Their Chemical Abstracts Service (CAS) Registry Numbers[a]

substance	CAS reg. no.	purity[b]/mass %	formula	mol wt/g·mol^{-1}	specific gravity/kg·L^{-1}	pK_a^{25} (25 °C)
formic acid	64-18-6	99	$HCOOH$	48.0	1.22	3.75
acetic acid	64-19-7	99.5	CH_3COOH	60.0	1.05	4.56
lactic acid	50-21-5	80	$CH_3CHOHCOOH$	90.08	1.21	3.66
propionic acid	79-09-4	99	$CH_3\,CH_2COOOH$	74.08	0.99	4.67
butyric acid	107-92-6	99	$CH_3CH_2CH_2COOH$	88.11	0.95	4.63
tri-*n*-butyl phosphate	126-73-8	99	$[CH_3(CH_2)_3O_3]P(O)$	266.32	0.98	
tri-*n*-octylamine	116-76-3	98	$[CH_3(CH_2)_7]_3N$	353.68	0.80	
dodecane	112-40-3	99	$CH_3(CH_2)_{10}CH_3$	170.3	0.75	
decane-1-ol	112-30-1	99	$CH_3(CH_2)_9OH$	158.28	0.83	

[a] Supplied by the authors. [b] Purities are reported and confirmed by the providers.

extraction with chemical reaction takes place according to eq 1-b, the distribution coefficient of the extracted acid (m_{HA}) is

$$m_{HA} = m_R = \frac{[\overline{C_{HA}}]}{[C_{HA}]} = \frac{[\overline{E\cdot HA}]}{(1-\alpha)[HA]} = \frac{K_{E(HA)}[\overline{E}]}{(1-\alpha)} \qquad (2)$$

where $\alpha = K_a/(K_a + [H^+])$ is the part of the dissociated molecules, K_a is a dissociation constant of the monocarboxylic acid, and m_R is the distribution coefficient due to the chemical reaction.

Finally, we can write

$$\log m_R + \log(1/(1-\alpha)) = \log K_{E(HA)} + \log[\overline{E}] \qquad (3)$$

or

$$\log m_R + \log(K_a + [H^+]) + pH = \log K_{E(HA)} + \log[\overline{E}] \qquad (3\text{-a})$$

Equation 3 or 3-a represents a straight line. The intercept allows us to determine the overall extraction constant $K_{E(HA)}$, and the slope corresponds to the number of reacting molecules of extractant (n). In the case of monoacids, $n = 1$ (eq 1-a). This expression must be used only when the organic phase contains 100% of the extractant or when the diluent does not influence the extraction process and also when the solute is not removed by physical extraction.

Usually the diluent removes the species by physical extraction. In this way their concentration in the organic phase increases. On the other hand, the diluent can decrease the concentration of extracted species in the organic phase because it decreases the solubility of these ones in the organic phase or vice versa. In this case, the overall calculated distribution coefficient, which represents the ratio of the total acid concentration in the organic phase to that in the aqueous phase in all possible forms, will include other terms, and the estimation of the equilibrium extraction constant ($K_{E(HA)}$) and the number of extractant molecules which react with one molecule of acid (n) by means of eq 3 will be incorrect.

When an amine is used as extractant in a mixture with an inert diluent and an active diluent (modifier) in a reactive extraction, the solubility of extracted species increases in the organic phase. The influence of diluents on the values of estimated $K_{E(HA)}$ and n depends not only on the concentration of the modifier in the presence of inert diluent but also on the volume phase ratio between modifier and diluent components, as can be seen in this study.

Experimental Section

Reagents. (a) Extractants: Tributyl phosphate (TBP) with 99 mass % purity and trioctylamine (TOA) with 98 mass % purity were supplied by Acros Organics. They were used as extractant without any further purification.

Table 2. Time To Reach the Extraction Equilibrium

	TBP in dodecane (70:30 vol %)			TOA and decane-1-ol in dodecane (20:20:60 vol %)		
	10^2C_{HA}	t		10^2C_{HA}	t	
acid	mol·L^{-1}	min	m	mol·L^{-1}	min	m
butyric	7.95	10	18.9	8.40	14	12.2
propionic	7.79	5	7.86	8.11	4	3.53
formic	4.86	10	2.07	7.20	6	3.18
acetic	2.60	5	1.72	8.46	5	1.42
lactic	7.34	5	1.23	8.03	3	2.29

(b) Diluents: Dodecane, with 99 mass % purity, was utilized as inactive diluent, and decane-1-ol, with 99 mass % purity, as modifier (active diluent). These products are from Acros Organics.

(c) Monocarboxylic Acids: Formic acid (99 mass %), acetic acid (99.5 mass %), propionic acid (99 mass %), butyric acid (99 mass %), and lactic acid (80 mass %) were provided by Sigma Aldrich Co. For lactic acid a distillation with total reflux during 8 h was effected for break up of the dimers.

Aqueous solutions were prepared by dissolving different quantities of the organic acids in the deionized water without pH adjustment (Millipore Milli-Q Water System). The acid concentrations were comprised between 0.026 and 0.250 mol·L^{-1} with an accuracy of ±1%.

The characteristics of the reagents used in this study are shown in Table 1.

Experimental Procedure

The experiments were carried out in 125 mL separatory funnels. The organic and the aqueous phases were shaken for 30 min at ambient temperature (20 ± 1) °C on a shaking machine AGITELEC with frequency 280 rpm. This mixing time was sufficient to reach the liquid−liquid equilibrium, as can be seen in Table 2.

The pH of the aqueous phase before extraction and after phase separations was measured with a WTW microprocessor pH-meter, equipped with a temperature compensating probe. The pH-meter was standardized against standard solutions at pH 4.00 and 7.00, with an allowable error of ±0.01. The volumes of the aqueous and the organic phases were measured before and after extraction. The measurements were generally accurate to within ±0.1 mL for all cases.

The extraction equilibrium time was determined from a batch experiment for each acid, with an organic/aqueous phases volumetric ratio equal to 1. TBP in dodecane and a TOA mixture with decane-1-ol in the volume ratio 1:1 dissolved in dodecane were used as solvents.

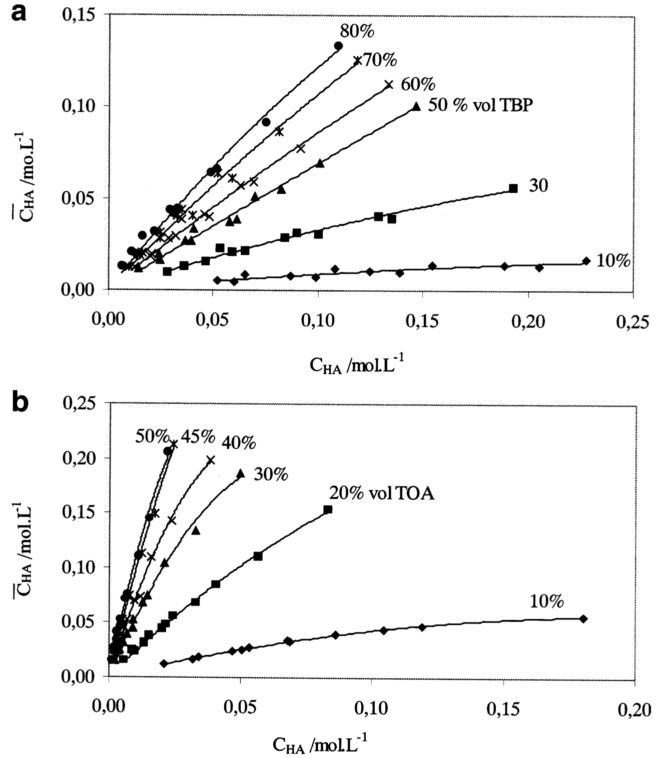

Figure 1. (**a**) Equilibrium isotherms of lactic acid for TBP dissolved in dodecane. Symbols: (◆) 10; (■) 30; (▲) 50; (×) 60; (*) 70; (●) 80 vol %. (**b**) Equilibrium isotherms of lactic acid for TOA/ decane-1-ol (1:1 vol %) in dodecane. Symbols: (◆) 10; (■) 20; (▲) 30; (×) 40; (**b**) 45; (●) 50 vol %.

Four synthetic aqueous solutions containing different concentrations of the organic acid were prepared for batch experiment. For each assay, three volume ratios between the organic and aqueous phases ($\bar{V}/V$) equal to 1, 3, and 5 were examined. Six concentrations of extractant were used (Tables 3 and 4).

The concentration of the organic acid in the aqueous phase was determined by high-performance liquid chromatography (HPLC) using a column for organic acid analyses Aminex HPX-87H (Bio-Rad), 0.005 M H_2SO_4 as mobile phase, and a Spectra 100-UV-vis detector (Spectra-Physics) at 210 nm wavelength. Each sample was (in triplicate) analyzed under identical conditions, and the overage values are reported. The concentration of organic acid in the organic phase was calculated by mass balance with maximum deviation closed to 3%.

$$V_{\text{init}}C_{\text{init}} - VC = \bar{V}\bar{C}$$

where an overbar refers to the organic phase, $V =$ the volume of the phase, $C =$ the total concentration of the acid, and the subscript init refers to the initial solution.

Then, the distribution coefficient (m_{HA}) is calculated with an uncertainty lower than ±4%.

Results and Discussion

In this work, the equilibrium of reactive liquid–liquid extraction of monocarboxylic acids from aqueous solutions with organic extractants (TBP and TOA) was investigated.

First, the time of extraction to equilibrium was evaluated for each acid. The results are presented in Table 2. The variation of equilibrium time was in the range 3 to 14 min. This difference is not significant and cannot be used for kinetic selective extraction.

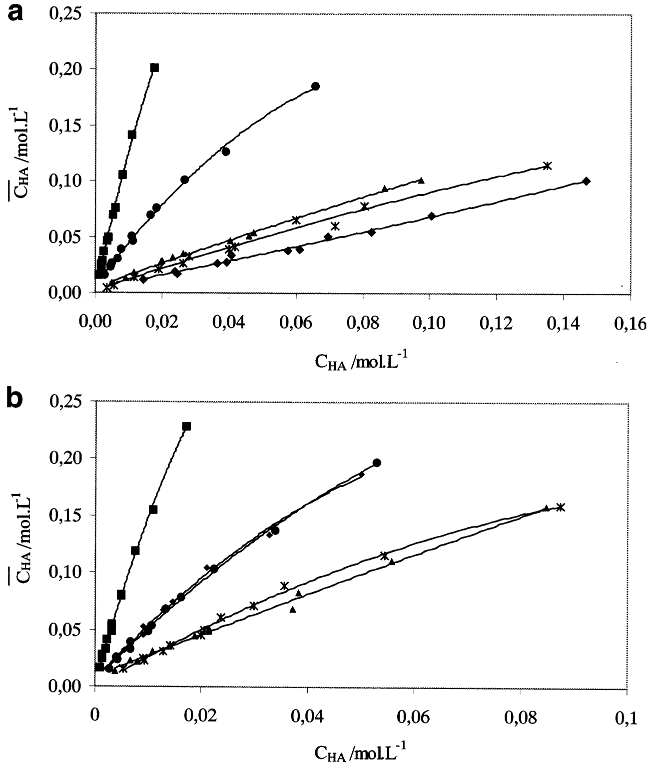

Figure 2. (**a**) Equilibrium isotherms for the extraction of studied acids with TBP in dodecane (1:1 vol %). Symbols: (◆) lactic acid; (■) butyric acid; (▲) formic acid; (*) acetic acid; (●) propionic acid. (**b**) Equilibrium isotherms for the extraction of studied acids by TOA/1-decane-1-ol in dodecane (30, 30, 40 vol %). Symbols: (◆) lactic acid; (■) butyric acid; (▲) formic acid; (*) acetic acid; (●) propionic acid.

The isotherms for each acid were determined from four aqueous solution concentrations, six concentrations of TBP dissolved in dodecane (Tables 3), and six concentrations of a mixture TOA + decane-1-ol (1:1 vol %), added to dodecane (Tables 4). The volume ratios of the organic phase ($\bar{V}/V$) to the aqueous solution were 1, 3, and 5. The concentration of components was expressed in molar units (mol·L^{-1}).

Parts a and b of Figure 1 represent, as an example, the isotherms of lactic acid, when TBP and TOA were used as extractant, respectively. The behavior of both solvents during the extraction process was different. Thus, the experimental data show that when the TBP concentration increases, the overall distribution coefficient (m_{HA}) also rises. In the case of TOA (Figure 1-b), the increase of the distribution coefficient was more significant for a low concentration of TOA, and this coefficient was almost constant at high concentration of extractant. It is important to emphasize the influence of the modifier (decane-1-ol) in the solvent upon the distribution coefficient measured.

Figure 2 shows the isotherms obtained for each acid from the experiments with TBP in dodecane (1:1 vol %) and the mixture TOA/decane-1-ol in dodecane (30:30:40 vol %). In view of this figures, it is obvious that the best solvent behavior corresponds to the isotherms obtained by the second system. According to the results, the extraction efficiencies only for butyric and propionic acids with both solvents were approximately the same.

The extent of extraction by TBP/dodecane as solvent for the studied organic acids can be ordered as follows: butyric acid (BA) > propionic acid (PA) > formic acid (FA) > acetic acid (AA) > lactic acid (LA). When the solvent was composed of TOA + decane-1-ol + dodecane, the order was BA > PA > LA > AA > FA. These results give the

Table 3. Experimental Results, pH, and Equilibrium Concentration (C_{HA}) of the Liquid−Liquid Equilibrium for (A) Formic Acid, (B) Acetic Acid, (C) Lactic Acid, (D) Propionic Acid, and (E) Butyric Acid Using TBP in Dodecane

A. Formic Acid

			$C_{in} = 0.0486\ \mathrm{mol \cdot L^{-1}}$; $\mathrm{pH}_{in} = 2.41$				$C_{in} = 0.102\ \mathrm{mol \cdot L^{-1}}$; $\mathrm{pH}_{in} = 2.28$			
$\bar{V}/V$	[TBP] / $\mathrm{mol \cdot L^{-1}}$	V_{TBP}/V	$10^2 C_{HA}$ / $\mathrm{mol \cdot L^{-1}}$	$10^2 \bar{C}_{HA}$ / $\mathrm{mol \cdot L^{-1}}$	m	pH	$10^2 C_{HA}$ / $\mathrm{mol \cdot L^{-1}}$	$10^2 \bar{C}_{HA}$ / $\mathrm{mol \cdot L^{-1}}$	m	pH
1/1	0.372	0.1	3.64	1.22	0.335	2.44	7.97	2.21	0.277	2.32
	1.12	0.3	2.68	2.18	0.813	2.53	5.81	4.37	0.753	2.38
	1.86	0.5	2.00	2.83	1.42	3.58	4.75	5.38	1.13	2.46
	2.23	0.6	1.75	3.03	1.73	3.64	4.20	5.87	1.40	2.50
	2.60	0.7	1.55	3.21	2.07	3.68	3.82	6.21	1.63	2.52
	2.97	0.8	1.22	3.49	2.86	3.69	3.13	6.81	2.18	2.53
3/1	0.372	0.1	2.12	0.916	0.431	2.51	5.15	1.75	0.341	2.38
	1.12	0.3	1.36	1.17	0.860	2.68	3.18	2.35	0.739	2.52
	1.86	0.5	0.906	1.31	1.45	2.74	1.98	2.70	1.36	2.64
	2.23	0.6	0.776	1.34	1.73	2.79	1.65	2.78	1.69	2.67
	2.60	0.7	0.499	1.40	2.81	2.84	1.28	2.88	2.25	2.71
	2.97	0.8	0.414	1.41	3.47	2.88	1.08	2.91	2.70	2.74
5/1	0.372	0.1	1.82	0.625	0.344	2.56	4.37	1.20	0.276	2.60
	1.12	0.3	0.831	0.807	0.972	2.79	2.02	1.64	0.812	2.72
	1.86	0.5	0.492	0.860	1.75	2.87	1.17	1.78	1.52	2.79
	2.23	0.6	0.385	0.870	2.26	2.97	0.874	1.82	2.09	2.85
	2.60	0.7	0.312	0.873	2.80	2.99	0.739	1.83	2.48	2.94
	2.97	0.8	0.233	0.875	3.76	3.04	0.627	1.83	2.92	3.21

			$C_{in} = 0.180\ \mathrm{mol \cdot L^{-1}}$; $\mathrm{pH}_{in} = 2.19$				$C_{in} = 0.199\ \mathrm{mol \cdot L^{-1}}$; $\mathrm{pH}_{in} = 2.11$			
$\bar{V}/V$	[TBP] / $\mathrm{mol \cdot L^{-1}}$	V_{TBP}/V	$10^2 C_{HA}$ / $\mathrm{mol \cdot L^{-1}}$	$10^2 \bar{C}_{HA}$ / $\mathrm{mol \cdot L^{-1}}$	m	pH	$10^2 C_{HA}$ / $\mathrm{mol \cdot L^{-1}}$	$10^2 \bar{C}_{HA}$ / $\mathrm{mol \cdot L^{-1}}$	m	pH
1/1	0.37	0.1	14.9	3.09	0.207	2.59	16.6	3.27	0.197	2.13
	1.12	0.3	10.7	7.34	0.687	2.69	12.0	7.95	0.664	2.26
	1.86	0.5	8.66	9.36	1.08	2.80	9.73	10.2	1.05	2.29
	2.23	0.6	8.17	9.75	1.19	2.85	9.22	10.6	1.15	2.30
	2.60	0.7	7.22	10.6	1.47	2.94	8.09	11.6	1.43	2.35
	2.97	0.8	6.37	11.3	1.77	3.00	7.32	12.3	1.67	2.37
3/1	0.37	0.1	10.2	2.59	0.253	2.64	11.6	2.77	0.239	2.17
	1.12	0.3	5.95	4.05	0.680	2.75	6.74	4.41	0.655	2.33
	1.86	0.5	4.05	4.64	1.15	2.86	4.61	5.09	1.10	2.44
	2.23	0.6	3.32	4.87	1.46	2.92	3.81	5.33	1.40	2.52
	2.60	0.7	2.85	4.99	1.75	2.98	3.20	5.49	1.72	2.55
	2.97	0.8	2.23	5.14	2.30	3.02	2.63	5.63	2.14	2.62
5/1	0.37	0.1	8.45	2.00	0.237	3.15	9.58	2.16	0.226	2.24
	1.12	0.3	4.03	2.83	0.701	3.21	4.61	3.09	0.672	2.43
	1.86	0.5	2.34	3.11	1.33	3.29	2.64	3.42	1.30	2.56
	2.23	0.6	2.11	3.13	1.47	3.31	2.34	3.46	1.48	2.62
	2.60	0.7	1.79	3.16	1.77	3.36	1.99	3.48	1.74	2.66
	2.97	0.8	1.27	3.20	2.51	3.42	1.55	3.52	2.27	2.71

B. Acetic Acid

			$C_{in} = 0.026\ \mathrm{mol \cdot L^{-1}}$; $\mathrm{pH}_{in} = 2.93$				$C_{in} = 0.126\ \mathrm{mol \cdot L^{-1}}$; $\mathrm{pH}_{in} = 2.79$			
$\bar{V}/V$	[TBP] / $\mathrm{mol \cdot L^{-1}}$	V_{TBP}/V	$10^2 C_{HA}$ / $\mathrm{mol \cdot L^{-1}}$	$10^2 \bar{C}_{HA}$ / $\mathrm{mol \cdot L^{-1}}$	m	pH	$10^2 C_{HA}$ / $\mathrm{mol \cdot L^{-1}}$	$10^2 \bar{C}_{HA}$ / $\mathrm{mol \cdot L^{-1}}$	m	pH
1/1	0.372	0.1	2.02	0.570	0.281	2.95	10.4	2.19	0.211	2.85
	1.12	0.3	1.49	1.09	0.732	2.97	7.91	4.66	0.589	2.90
	1.86	0.5	1.16	1.42	1.22	3.03	6.00	6.57	1.09	3.02
	2.23	0.6	1.04	1.52	1.46	3.06	5.35	7.15	1.34	3.05
	2.60	0.7	0.933	1.61	1.73	3.08	4.88	7.51	1.54	3.07
	2.97	0.8	0.842	1.69	2.01	3.10	4.39	7.94	1.81	3.09
3/1	0.372	0.1	1.76	0.275	0.158	2.98	8.86	1.24	0.140	2.88
	1.12	0.3	0.853	0.583	0.684	3.11	4.54	2.72	0.597	2.91
	1.86	0.5	0.552	0.674	1.22	3.19	2.82	3.24	1.15	3.01
	2.23	0.6	0.473	0.695	1.47	3.24	2.47	3.33	1.35	3.03
	2.60	0.7	0.421	0.706	1.67	3.26	2.16	3.40	1.58	3.06
	2.97	0.8	0.373	0.715	1.92	3.30	1.94	3.44	1.77	3.10
5/1	0.372	0.1	1.30	0.271	0.209	3.15	6.70	1.25	0.186	2.94
	1.12	0.3	0.620	0.398	0.644	3.21	3.11	1.92	0.618	2.96
	1.86	0.5	0.368	0.441	1.20	3.29	1.88	2.13	1.13	3.05
	2.23	0.6	0.295	0451	1.53	3.31	1.50	2.18	1.45	3.11
	2.60	0.7	0.243	0.456	1.87	3.36	1.26	2.20	1.75	3.15
	2.97	0.8	0.210	0.457	2.18	3.42	1.07	2.22	2.06	3.21

Table 3 (Continued)

B. Acetic Acid (Continued)

			$C_{in} = 0.159$ mol·L^{-1}; pH$_{in} = 2.58$				$C_{in} = 0.250$ mol·L^{-1}; pH$_{in} = 2.46$			
$\bar{V}/V$	[TBP] mol·L^{-1}	V_{TBP}/V	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH
1/1	0.37	0.1	13.2	2.67	0.202	2.67	21.6	3.39	0.157	2.71
	1.12	0.3	10.9	4.96	0.455	2.75	17.6	7.37	0.418	2.96
	1.86	0.5	8.07	7.79	0.966	2.98	13.5	11.5	0.850	3.02
	2.23	0.6	7.42	8.41	1.13	3.02	12.2	12.8	1.05	3.04
	2.60	0.7	6.66	9.04	1.36	3.05	11.1	13.7	1.24	3.05
	2.97	0.8	5.92	9.69	1.64	3.07	9.96	14.7	1.48	3.07
3/1	0.37	0.1	11.5	1.46	0.127	2.97	18.4	2.20	0.119	2.81
	1.12	0.3	5.95	3.36	0.565	3.02	10.6	4.92	0.463	3.02
	1.86	0.5	4.00	3.96	0.988	3.07	7.16	5.98	0.834	3.04
	2.23	0.6	3.26	4.16	1.28	3.10	6.27	6.24	0.994	3.07
	2.60	0.7	3.04	4.21	1.38	3.15	5.44	6.46	1.19	3.15
	2.97	0.8	2.73	4.28	1.57	3.18	4.92	6.58	1.34	3.21
5/1	0.37	0.1	9.19	1.44	0.156	2.98	14.9	2.18	0.146	2.95
	1.12	0.3	4.24	2.37	0.561	3.05	7.12	3.66	0.515	3.04
	1.86	0.5	2.65	2.64	0.999	3.14	4.20	4.16	0.989	3.17
	2.23	0.6	2.31	2.69	1.17	3.18	3.28	4.29	1.31	3.21
	2.60	0.7	1.78	2.75	1.55	3.25	2.81	4.33	1.54	3.27
	2.97	0.8	1.61	2.77	1.71	3.28	2.41	4.37	1.81	3.31

C. Lactic Acid

			$C_{in} = 0.0735$ mol·L^{-1}; pH$_{in} = 2.28$				$C_{in} = 0.119$ mol·L^{-1}; pH$_{in} = 2.03$			
$\bar{V}/V$	[TBP] mol·L^{-1}	V_{TBP}/V	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH
1/1	0.372	0.1	6.53	0.812	0.124	2.30	10.8	1.19	0.110	2.07
	1.12	0.3	5.29	2.25	0.426	2.38	9.00	3.17	0.352	2.08
	1.86	0.5	4.07	3.32	0.818	2.44	6.96	5.09	0.731	2.20
	2.23	0.6	3.47	3.85	1.11	2.50	6.31	5.71	0.905	2.24
	2.60	0.7	3.25	4.05	1.24	2.52	5.88	6.07	1.03	2.27
	2.97	0.8	2.92	4.34	1.48	2.55	5.17	6.61	1.28	2.32
3/1	0.372	0.1	6.01	0.444	0.074	2.34	9.88	0.698	0.070	2.11
	1.12	0.3	3.63	1.32	0.363	2.48	5.87	2.11	0.361	2.26
	1.86	0.5	2.47	1.66	0.671	2.58	3.95	2.70	0.684	2.37
	2.23	0.6	1.98	1.80	0.908	2.64	3.22	2.94	0.912	2.42
	2.60	0.7	1.49	1.92	1.29	2.75	2.46	3.12	1.269	2.48
	2.97	0.8	1.33	1.95	1.46	2.86	2.17	3.20	1.48	2.50
5/1	0.372	0.1	5.18	0.495	0.095	2.36	8.72	0.758	0.087	2.23
	1.12	0.3	2.82	0.954	0.337	2.56	4.61	1.56	0.337	2.40
	1.86	0.5	1.45	1.190	0.820	2.69	2.38	1.94	0.815	2.50
	2.23	0.6	1.24	1.22	0.983	2.75	2.05	1.99	0.971	2.55
	2.60	0.7	0.970	1.26	1.30	2.84	1.60	2.05	1.28	2.15
	2.97	0.8	0.630	1.29	2.04	2.96	1.07	2.10	1.95	2.89

			$C_{in} = 0.168$ mol·L^{-1}; pH$_{in} = 1.98$				$C_{in} = 0.245$ mol·L^{-1}; pH$_{in} = 1.86$			
$\bar{V}/V$	[TBP] mol·L^{-1}	V_{TBP}/V	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH
1/1	0.372	0.1	15.4	1.35	0.087	2.00	22.8	1.69	0.074	1.07
	1.12	0.3	13.5	3.92	0.268	2.01	19.3	5.64	0.290	1.08
	1.86	0.5	10.04	6.94	0.681	2.05	14.7	10.1	0.689	2.20
	2.23	0.6	9.13	7.75	0.849	2.07	13.3	11.3	0.847	2.24
	2.60	0.7	8.10	8.65	1.07	2.13	11.9	12.6	1.06	2.27
	2.97	0.8	7.48	9.19	1.23	2.14	10.9	13.4	1.22	2.32
3/1	0.372	0.1	13.91	0.957	0.069	2.06	20.5	1.31	0.064	2.97
	1.12	0.3	8.43	2.91	0.345	2.15	12.9	4.06	0.316	2.16
	1.86	0.5	5.75	3.77	0.654	2.28	8.26	5.53	0.669	2.31
	2.23	0.6	4.55	4.10	0.901	2.35	6.94	5.89	0.849	2.42
	2.60	0.7	3.46	4.38	1.26	2.38	5.21	6.35	1.22	2.48
	2.97	0.8	3.27	4.43	1.35	2.39	4.88	6.43	1.32	2.50
5/1	0.372	0.1	12.5	1.02	0.082	2.05	19.4	1.16	0.065	1.94
	1.12	0.3	6.54	2.16	0.331	2.21	9.99	3.08	0.308	2.14
	1.86	0.5	3.67	2.66	0.726	2.36	6.11	3.76	0.616	2.32
	2.23	0.6	2.88	2.78	0.968	2.40	4.81	3.97	0.826	2.39
	2.60	0.7	2.48	2.83	1.143	2.46	4.03	4.08	1.013	2.42
	2.97	0.8	1.60	2.93	1.830	2.50	3.11	4.18	1.35	2.45

Table 3 (Continued)

D. Propionic Acid

			$C_{in} = 0.0860$ mol·L^{-1}; pH$_{in} = 2.92$				$C_{in} = 0.128$ mol·L^{-1}; pH$_{in} = 2.81$			
$\bar{V}/V$	[TBP] mol·L^{-1}	V_{TBP}/V	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH
1/1	0.372	0.1	4.42	4.12	0.932	3.34	6.95	5.81	0.835	2.93
	1.12	0.3	2.93	5.62	1.92	3.47	4.98	7.78	1.56	3.06
	1.86	0.5	1.66	6.89	4.16	3.54	2.65	10.1	3.80	3.16
	2.23	0.6	1.11	7.39	6.38	3.64	1.77	10.9	6.20	3.21
	2.60	0.7	0.899	7.04	7.86	3.71	1.45	10.4	8.16	3.25
	2.97	0.8	0.796	7.12	8.98	3.82	1.29	10.5	9.57	3.32
3/1	0.372	0.1	2.08	2.15	1.03	3.39	3.54	3.07	0.866	3.08
	1.12	0.3	0.913	2.52	2.75	3.41	1.65	3.67	2.22	3.15
	1.86	0.5	0.504	2.61	5.17	3.49	0.778	3.89	4.99	3.27
	2.23	0.6	0.434	2.56	5.90	3.52	0.674	3.82	5.66	3.39
	2.60	0.7	0.284	2.60	9.13	3.66	0.433	3.88	8.96	3.41
	2.97	0.8	0.247	2.61	10.5	3.77	0.419	3.89	9.26	3.45
5/1	0.37	0.1	1.41	1.43	1.01	3.50	2.12	2.13	1.00	3.16
	1.12	0.3	0.463	1.57	3.40	3.59	0.834	2.32	2.79	3.22
	1.86	0.5	0.288	1.58	5.50	3.62	0.460	2.36	5.14	3.36
	2.23	0.6	0.264	1.58	5.97	3.69	0.411	2.35	5.72	3.39
	2.60	0.7	0.187	1.56	8.33	3.72	0.288	2.33	8.08	3.42
	2.97	0.8	0.151	1.57	10.4	3.81	0.244	2.34	9.57	3.51

			$C_{in} = 0.166$ mol·L^{-1}; pH$_{in} = 2.74$				$C_{in} = 0.251$ mol·L^{-1}; pH$_{in} = 2.71$			
$\bar{V}/V$	[TBP] mol·L^{-1}	V_{TBP}/V	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH
1/1	0.37	0.1	9.60	7.00	0.729	3.00	15.01	10.08	0.672	2.80
	1.12	0.3	7.13	9.46	1.33	3.12	12.4	12.7	1.02	2.94
	1.86	0.5	3.89	12.7	3.26	3.19	6.56	18.5	2.82	3.08
	2.23	0.6	2.40	14.2	5.92	3.26	3.94	21.2	5.38	3.11
	2.60	0.7	1.97	13.5	6.85	3.35	3.16	20.2	6.40	3.20
	2.97	0.8	1.73	13.7	7.92	3.41	2.72	20.5	7.54	3.29
3/1	0.37	0.1	4.75	3.94	0.829	3.18	7.08	6.00	0.847	2.89
	1.12	0.3	2.39	4.69	1.96	3.25	4.53	6.81	1.50	3.12
	1.86	0.5	1.09	5.03	4.61	3.36	1.82	7.56	4.15	3.26
	2.23	0.6	0.899	4.96	5.52	3.41	1.43	7.48	5.23	3.32
	2.60	0.7	0.612	5.03	8.22	3.46	0.961	7.60	7.91	3.41
	2.97	0.8	0.585	5.04	8.61	3.52	0.938	7.60	8.11	3.49
5/1	0.37	0.1	2.77	2.76	0.996	3.07	4.21	4.17	0.99	2.88
	1.12	0.3	2.74	2.77	1.01	3.28	2.74	4.40	1.60	3.11
	1.86	0.5	0.656	3.06	4.66	3.41	1.13	4.62	4.08	3.23
	2.23	0.6	0.564	3.05	5.41	3.48	0.912	4.61	5.06	3.31
	2.60	0.7	0.387	3.03	7.83	3.56	0.608	4.58	7.53	3.37
	2.97	0.8	0.332	3.03	9.13	3.65	0.542	4.59	8.46	3.44

E. Butyric Acid

			$C_{in} = 0.0795$ mol·L^{-1}; pH$_{in} = 3.03$				$C_{in} = 0.117$ mol·L^{-1}; pH$_{in} = 2.92$			
$\bar{V}/V$	[TBP] mol·L^{-1}	V_{TBP}/V	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH
1/1	0.372	0.1	2.41	5.53	2.29	3.33	3.74	7.94	2.12	3.53
	1.12	0.3	0.796	7.15	8.99	3.53	1.43	10.2	7.13	3.57
	1.86	0.5	0.530	6.99	13.2	3.63	0.801	10.6	12.8	3.87
	2.23	0.6	0.418	7.08	16.9	3.65	0.685	10.4	15.2	4.00
	2.60	0.7	0.377	7.12	18.9	3.67	0.645	10.4	16.1	4.04
	2.97	0.8	0.340	7.15	21.0	3.68	0.500	10.5	21.0	4.09
3/1	0.372	0.1	0.814	2.37	2.92	3.55	1.31	3.46	2.65	4.12
	1.12	0.3	0.289	2.50	8.65	3.73	0.469	3.66	7.80	4.47
	1.86	0.5	0.177	2.53	14.3	3.82	0.260	3.73	14.3	4.50
	2.23	0.6	0.147	2.52	17.0	3.87	0.250	3.69	14.7	4.55
	2.60	0.7	0.130	2.50	19.2	3.90	0.229	3.67	15.9	4.64
	2.97	0.8	0.113	2.50	22.0	3.92	0.188	3.60	19.1	4.69
5/1	0.372	0.1	0.486	1.47	3.04	3.68	0.814	2.15	2.65	4.52
	1.12	0.3	0.155	1.53	9.87	3.90	0.276	2.24	8.12	4.69
	1.86	0.5	0.0989	1.53	15.5	3.95	0.175	2.25	12.8	4.71
	2.23	0.6	0.0848	1.51	17.9	3.97	0.147	2.23	15.1	4.77
	2.60	0.7	0.0779	1.49	19.1	3.98	0.109	2.20	20.1	4.80
	2.97	0.8	0.0624	1.48	23.7	4.04	0.102	2.17	21.3	4.89

Table 3 (Continued)

E. Butyric Acid (Continued)

			C_{in} = 0.161 mol·L^{-1}; pH$_{in}$ = 2.81				C_{in} = 0.226 mol·L^{-1}; pH$_{in}$ = 2.76			
$\bar{V}/V$	[TBP] mol·L^{-1}	V_{TBP}/V	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH
1/1	0.37	0.1	5.19	10.9	2.09	3.02	9.05	13.5	1.49	3.32
	1.12	0.3	1.98	14.0	7.10	3.19	2.98	19.6	6.56	3.61
	1.86	0.5	1.10	14.1	12.8	3.27	1.76	20.2	11.5	3.78
	2.23	0.6	0.945	14.2	15.0	3.28	1.56	19.8	12.7	3.87
	2.60	0.7	0.896	14.3	15.9	3.32	1.27	20.0	15.7	3.89
	2.97	0.8	0.774	14.4	18.6	3.34	1.13	20.2	17.9	3.95
3/1	0.37	0.1	1.85	4.73	2.55	3.25	3.21	6.44	2.00	3.14
	1.12	0.3	0.695	5.07	7.30	3.41	1.11	7.15	6.44	3.30
	1.86	0.5	0.378	5.12	13.5	3.49	0.597	7.24	12.1	3.39
	2.23	0.6	0.332	5.08	15.3	3.50	0.540	7.19	13.3	3.43
	2.60	0.7	0.323	5.03	15.6	3.53	0.515	7.20	13.9	3.45
	2.97	0.8	0.273	4.94	18.1	3.57	0.422	7.16	16.9	3.46
5/1	0.37	0.1	1.14	2.95	2.59	3.36	1.87	4.11	2.19	3.24
	1.12	0.3	0.358	3.06	8.55	3.53	0.589	4.32	7.33	3.39
	1.86	0.5	0.226	3.07	13.6	3.60	0.366	4.33	11.8	3.48
	2.23	0.6	0.193	3.04	15.7	3.62	0.313	4.31	13.8	3.51
	2.60	0.7	0.156	3.01	19.2	3.64	0.258	4.22	16.3	3.57
	2.97	0.8	0.145	2.97	20.4	3.66	0.236	4.17	17.6	3.59

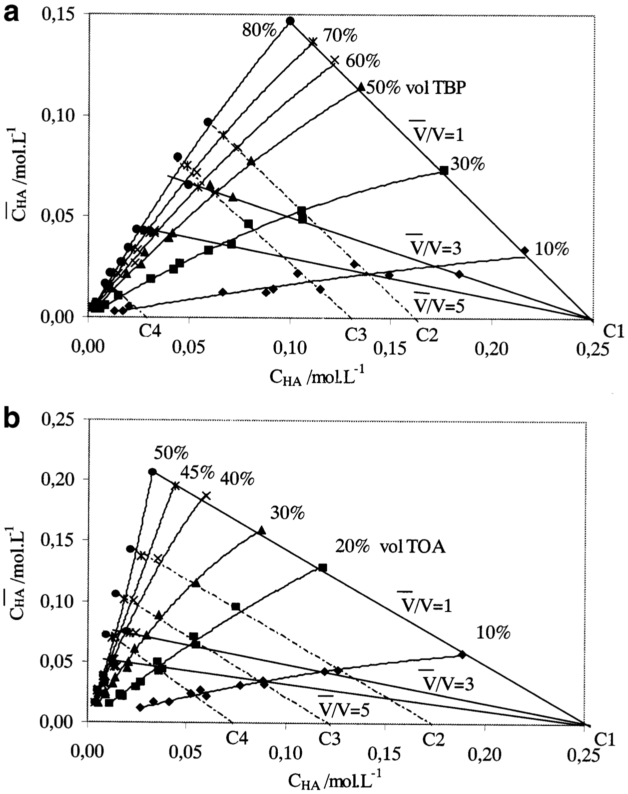

Figure 3. (**a**) Equilibrium concentration of acetic acid versus the initial acid concentration (C1 = 0.25, C2 = 0.159, C3 = 0.126, and C4 = 0.026 mol·L^{-1}) with the volume phase ratio at different volume parts of extractant TBP ($\bar{V}/V$ = 1, 3, 5). Symbols: (◆) 10; (■) 30; (▲) 50; (×) 60; (∗) 70; (●) 80 vol %. (**b**) Equilibrium acetic acid concentration versus initial acid concentration (C1 = 0.247, C2 = 0.170, C3 = 0.124, and C4 = 0.085 mol·L^{-1}) with the volume phase ratio at different volume parts of extractant TOA ($\bar{V}/V$ = 1, 3, 5). Symbols: (◆) 10; (■) 20; (▲) 30; (×) 40; (∗) 45; (●) 50 vol %.

possibility to choose the appropriate solvent for the separation of the organic acids under consideration and to use both solvents consecutively. For example, the lactic acid must be separated from formic acid using TOA as the first extractant, and the extract will contain preferably lactic acid and raffinate formic acid. A second step for extraction of formic acid can be carried out with TBP as extractant.

The liquid–liquid equilibrium depends on the concentration of extractant, the volume phase ratio, and the initial aqueous acid concentration. For example, in view of isotherms (Figure 3), the influence of the preceding factors has been clearly shown for acetic acid with TBP and TOA as extractants.

Table 5 presents the calculated values of K_E and n, when the experiments were carried out with different initial concentrations of organic acid, at different volumes and different concentrations of extractant. The estimated values of n and K_E by this way are not constants for each acid. Different values of extraction constant (K_E) and apparent number of reacting molecules were evaluated in dependence on the initial organic acid concentration and volume phase ratio. This means that if different initial acid concentrations or volume phase ratios are used, the calculated values of extraction constant (K_E) and apparent number of reacting molecules (n) will be different.

To eliminate the influence of the above-mentioned parameters on the estimation of the equilibrium extraction constant (K_E) and the number of apparent reacting extractant molecules (n), another method was utilized. The isotherms of each acid at different concentrations of the extractant were used. Five acid equilibrium concentrations in the aqueous phase were applied. For each concentration, the pH was taken into account. These concentrations were chosen from experimental points corresponding to organic acid concentrations in the solvent for all studied acids. These results are shown in parts a and b of Table 6 for when TBP and TOA were used as extractant, respectively. Figure 4 shows the straight lines obtained for each acid, which represent log m_{HA} + log(1/(1 − α)) as a function of log[$\bar{E}$] (eq 3). The equilibrium acid concentration is equal to 0.015 mol/L in the case of TBP extractant (Figure 3a) and 0.01 mol/L for TOA (Figure 3b). In Figure 4a, almost all lines are parallel, except for that for lactic acid, where the slope is different. In Figure 4b it can be seen that there is a significant difference between the slopes for each acid and, hence, between the apparent calculated values of n (Table 6).

The obtained results of apparent n, for TBP extractant, were close to 1, except for that for lactic acid, where a negative influence was noted, more greatly emphasized by the presence of diluent. Herein, it was found that the acid

Table 4. Experimental Results, pH, and Equilibrium Concentration (C_{HA}) of the Liquid−Liquid Equilibrium for (A) Formic Acid, (B) Acetic Acid, (C) Lactic Acid, (D) Propionic Acid, and (E) Butyric Acid Using TOA−Decane-1-ol (1:1 vol %) in Dodecane

A. Formic Acid

			C_{in} = 0.0721 mol·L^{-1}; pH$_{in}$ = 2.41				C_{in} = 0.124 mol·L^{-1}; pH$_{in}$ = 2.32			
$\bar{V}/V$	[TOA] mol·L^{-1}	$V_{dodecane}/\bar{V}$	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH
1/1	0.226	0.8	3.04	4.18	1.38	2.78	5.22	6.82	1.31	2.52
	0.452	0.6	2.81	4.41	1.57	3.18	4.75	7.29	1.54	2.84
	0.678	0.4	2.16	5.06	2.35	3.61	3.82	8.22	2.15	2.95
	0.904	0.2	1.49	5.73	3.86	3.98	2.63	9.40	3.57	3.19
	1.017	0.1	0.993	6.23	6.27	3.13	1.90	10.2	5.37	3.60
	1.13	0.0	0.940	6.28	6.69	3.22	1.74	10.3	5.91	3.70
3/1	0.226	0.8	1.44	1.93	1.34	3.05	2.46	3.19	1.30	2.90
	0.452	0.6	1.14	2.03	1.79	3.67	2.18	3.29	1.51	3.49
	0.678	0.4	0.798	2.14	2.68	3.80	1.40	3.55	2.53	3.88
	0.904	0.2	0.526	2.23	4.24	4.33	0.978	3.69	3.77	4.18
	1.017	0.1	0.291	2.28	7.81	4.75	0.578	3.77	6.51	4.63
	1.13	0.0	0.259	2.29	8.84	4.83	0.491	3.79	7.72	4.69
5/1	0.226	0.8	0.743	1.29	1.74	3.44	1.53	2.10	1.28	3.14
	0.452	0.6	0.700	1.30	1.86	3.96	1.34	2.14	1.81	3.70
	0.678	0.4	0.378	1.37	3.62	4.31	0.654	2.28	3.52	4.04
	0.904	0.2	0.220	1.38	6.32	4.90	0.404	2.31	5.46	4.55
	1.017	0.1	0.174	1.39	8.03	5.28	0.307	2.33	7.90	5.06
	1.13	0.0	0.152	1.40	9.21	5.33	0.261	2.34	8.95	5.11

			C_{in} = 0.165 mol·L^{-1}; pH$_{in}$ = 2.27				C_{in} = 0.242 mol·L^{-1}; pH$_{in}$ = 2.21			
$\bar{V}/V$	[TOA] mol·L^{-1}	$V_{dodecane}/\bar{V}$	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH
1/1	0.226	0.8	7.39	9.19	1.24	2.43	11.5	12.7	1.10	2.36
	0.452	0.6	6.74	9.85	1.46	2.80	10.0	14.2	1.41	2.60
	0.678	0.4	5.57	11.0	1.98	3.09	8.48	15.8	1.86	2.98
	0.904	0.2	4.08	12.5	3.06	3.50	6.13	18.12	2.96	3.47
	1.017	0.1	2.82	13.7	4.87	3.56	4.33	19.9	4.60	3.49
	1.13	0.0	2.74	13.8	5.04	3.72	4.30	20.0	4.64	3.70
3/1	0.226	0.8	3.61	4.32	1.20	2.74	5.39	6.29	1.17	2.69
	0.452	0.6	3.25	4.44	1.37	3.37	4.92	6.44	1.31	3.30
	0.678	0.4	2.15	4.81	2.23	3.91	3.72	6.84	1.84	3.84
	0.904	0.2	1.61	5.00	3.09	4.30	2.50	7.25	2.89	4.20
	1.017	0.1	1.00	5.13	5.13	4.40	1.72	7.41	4.31	4.32
	1.13	0.0	0.826	5.18	6.27	4.59	1.45	7.50	5.15	4.51
5/1	0.226	0.8	2.39	2.84	1.19	3.02	3.69	4.11	1.11	2.92
	0.452	0.6	1.92	2.93	1.53	3.83	3.08	4.23	1.37	3.69
	0.678	0.4	1.10	3.10	2.84	4.41	1.88	4.47	2.37	4.27
	0.904	0.2	0.800	3.15	4.45	4.83	1.30	4.56	3.50	4.67
	1.017	0.1	0.459	3.20	6.97	4.99	0.800	4.65	5.81	4.63
	1.13	1.0	0.396	3.21	8.11	5.01	0.630	4.68	7.43	4.91

B. Acetic Acid

			C_{in} = 0.0847 mol·L^{-1}; pH$_{in}$ = 2.95				C_{in} = 0.124 mol·L^{-1}; pH$_{in}$ = 2.85			
$\bar{V}/V$	[TOA] mol·L^{-1}	$V_{dodecane}/\bar{V}$	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH
1/1	0.226	0.8	5.73	2.73	0.476	3.08	8.88	3.51	0.395	2.86
	0.452	0.6	3.50	4.96	1.42	3.26	5.36	7.03	1.31	3.07
	0.678	0.4	2.35	6.10	2.59	3.45	3.55	8.83	2.48	2.29
	0.904	0.2	1.37	7.09	5.16	3.72	2.30	10.1	4.37	3.62
	1.017	0.1	1.20	6.97	5.77	3.85	1.83	10.2	5.53	3.55
	1.13	0.0	0.932	7.22	7.75	4.00	1.42	10.5	7.38	3.77
3/1	0.226	0.8	3.33	1.71	0.513	3.21	5.21	2.39	0.459	3.13
	0.452	0.6	1.66	2.26	1.36	3.78	2.67	3.24	1.22	3.46
	0.678	0.4	0.908	2.51	2.77	4.16	1.41	3.65	2.58	3.97
	0.904	0.2	0.517	2.65	5.13	4.52	0.833	3.85	4.62	4.36
	1.017	0.1	0.500	2.62	5.24	4.70	0.800	3.81	4.77	4.51
	1.13	0.0	0.467	2.63	5.64	4.86	0.767	3.82	4.99	4.66
5/1	0.226	0.8	2.66	1.16	0.435	3.52	4.12	1.66	0.402	3.31
	0.452	0.6	1.11	1.47	1.32	4.07	1.73	2.13	1.23	3.90
	0.678	0.4	0.523	1.58	3.04	4.56	0.925	2.29	2.48	4.37
	0.904	0.2	0.383	1.60	4.19	4.94	0.667	2.33	3.49	4.40
	1.017	0.1	0.367	1.61	4.38	5.07	0.617	2.34	3.79	4.96
	1.13	0.0	0.337	1.61	4.79	5.26	0.567	2.35	4.14	5.09

Table 4 (Continued)

B. Acetic Acid (Continued)

			$C_{\text{in}} = 0.170$ mol·L^{-1}; pH$_{\text{in}} = 2.80$				$C_{\text{in}} = 0.247$ mol·L^{-1}; pH$_{\text{in}} = 2.60$			
$\bar{V}/V$	[TOA] mol·L^{-1}	$V_{\text{dodecane}}/\bar{V}$	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{\text{HA}}$ mol·L^{-1}	m	pH	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{\text{HA}}$ mol·L^{-1}	m	pH
1/1	0.226	0.8	12.6	4.36	0.345	2.90	18.9	5.76	0.31	2.83
	0.452	0.6	7.46	9.53	1.28	3.03	11.8	12.8	1.08	2.93
	0.678	0.4	5.45	11.5	2.12	3.23	8.73	15.9	1.82	3.14
	0.904	0.2	3.50	13.5	3.86	3.46	5.92	18.8	3.17	3.32
	1.017	0.1	2.69	13.8	5.11	3.56	4.36	19.5	4.48	3.40
	1.13	0.0	2.12	14.3	6.71	3.70	3.21	20.6	6.43	3.57
3/1	0.226	0.8	7.72	3.09	0.400	3.06	12.0	4.23	0.35	2.95
	0.452	0.6	3.73	4.42	1.18	3.45	5.46	6.40	1.17	3.30
	0.678	0.4	2.05	4.98	2.43	3.85	2.98	7.15	2.40	3.70
	0.904	0.2	1.31	5.22	3.97	4.22	2.41	7.33	3.04	4.08
	1.017	0.1	1.25	5.18	4.15	4.37	2.15	7.41	3.45	4.22
	1.13	0.0	1.18	5.20	4.40	4.56	1.96	7.50	3.80	4.42
5/1	0.226	0.8	6.00	2.20	0.366	3.23	8.94	3.15	0.35	3.14
	0.452	0.6	2.41	2.92	1.21	3.77	3.57	4.22	1.18	3.65
	0.678	0.4	1.27	3.15	2.47	4.25	2.00	4.50	2.25	4.13
	0.904	0.2	0.917	3.19	3.48	4.51	1.48	4.60	3.10	4.53
	1.017	0.1	0.867	3.20	3.70	4.79	1.35	4.63	3.44	4.70
	1.13	0.0	0.850	3.20	3.77	4.96	1.33	4.63	3.48	4.88

C. Lactic Acid

			$C_{\text{in}} = 0.0803$ mol·L^{-1}; pH$_{\text{in}} = 2.43$				$C_{\text{in}} = 0.125$ mol·L^{-1}; pH$_{\text{in}} = 2.38$			
$\bar{V}/V$	[TOA] mol·L^{-1}	$V_{\text{dodecane}}/\bar{V}$	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{\text{HA}}$ mol·L^{-1}	m	pH	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{\text{HA}}$ mol·L^{-1}	m	pH
1/1	0.226	0.8	5.33	2.70	0.51	2.59	8.61	3.93	0.46	2.47
	0.452	0.6	2.44	5.60	2.29	2.83	4.05	8.49	2.10	2.66
	0.678	0.4	1.28	6.76	5.30	3.07	2.11	10.4	4.95	2.94
	0.904	0.2	0.976	7.06	7.23	3.41	1.61	10.9	6.79	3.20
	1.017	0.1	0.743	7.29	9.81	3.63	1.22	11.3	9.28	3.26
	1.13	0.0	0.610	7.10	11.6	3.53	1.08	10.9	10.1	3.46
3/1	0.226	0.8	3.18	1.62	0.51	2.82	5.05	2.50	0.49	2.61
	0.452	0.6	0.888	2.38	2.68	3.32	1.50	3.68	2.46	3.05
	0.678	0.4	0.394	2.55	6.46	3.36	0.670	3.96	5.94	3.48
	0.904	0.2	0.277	2.55	9.18	4.20	0.466	3.97	8.51	3.88
	1.017	0.1	0.191	2.58	13.5	4.40	0.333	4.01	12.04	4.01
	1.13	0.0	0.166	2.58	15.5	4.59	0.277	4.03	14.5	4.24
5/1	0.226	0.8	2.10	1.19	0.56	3.00	3.44	1.82	0.53	2.76
	0.452	0.6	0.555	1.50	2.70	3.68	0.950	2.32	2.44	3.28
	0.678	0.4	0.222	1.56	7.04	4.19	0.387	2.43	6.28	3.87
	0.904	0.2	0.161	1.56	9.70	4.68	0.267	2.43	9.10	3.91
	1.017	0.1	0.127	1.57	12.3	4.74	0.207	2.44	11.7	3.98
	1.13	0.0	0.111	1.57	14.2	4.97	0.177	2.45	13.8	4.54

			$C_{\text{in}} = 0.166$ mol·L^{-1}; pH$_{\text{in}} = 2.32$				$C_{\text{in}} = 0.236$ mol·L^{-1}; pH$_{\text{in}} = 2.25$			
$\bar{V}/V$	[TOA] mol·L^{-1}	$V_{\text{dodecane}}/\bar{V}$	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{\text{HA}}$ mol·L^{-1}	m	pH	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{\text{HA}}$ mol·L^{-1}	m	pH
1/1	0.226	0.8	11.9	4.69	0.390	2.42	18.04	5.62	0.310	2.60
	0.452	0.6	5.67	11.1	1.93	2.69	8.33	15.3	1.84	2.73
	0.678	0.4	3.27	13.3	4.07	2.83	4.99	18.7	3.74	2.78
	0.904	0.2	2.39	14.2	5.95	3.11	3.82	19.8	5.20	2.85
	1.017	0.1	1.72	14.8	8.65	3.26	2.40	21.3	8.85	2.96
	1.13	0.0	1.50	14.4	9.64	3.37	2.21	20.5	9.29	3.12
3/1	0.226	0.8	6.88	3.24	0.470	2.64	10.4	4.41	0.420	2.57
	0.452	0.6	2.13	4.82	2.26	3.22	3.31	6.78	2.05	2.78
	0.678	0.4	0.910	5.23	5.75	3.46	1.45	7.40	5.09	3.08
	0.904	0.2	0.693	5.23	7.53	3.68	1.17	7.39	6.31	3.39
	1.017	0.1	0.488	5.29	10.8	3.97	0.790	7.51	9.50	3.60
	1.13	0.0	0.410	5.31	12.9	4.17	0.670	7.54	11.3	3.76
5/1	0.226	0.8	4.72	2.38	0.500	2.97	6.79	3.37	0.50	2.78
	0.452	0.6	1.33	3.05	2.29	3.26	2.00	4.33	2.17	3.00
	0.678	0.4	0.555	3.21	5.78	3.66	0.915	4.55	4.97	3.42
	0.904	0.2	0.377	3.20	8.52	4.17	0.550	4.58	8.34	3.82
	1.017	0.1	0.288	3.30	11.2	4.37	0.440	4.60	10.4	3.99
	1.13	0.0	0.266	3.40	12.4	4.57	0.388	4.61	11.9	4.19

Table 4 (Continued)

D. Propionic Acid

			C_{in} = 0.081 mol·L^{-1}; pH$_{in}$ = 2.95				C_{in} = 0.125 mol·L^{-1}; pH$_{in}$ = 2.83			
$\bar{V}/V$	[TOA] mol·L^{-1}	$V_{dodecane}/\bar{V}$	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH
1/1	0.226	0.8	3.06	5.08	1.66	3.22	5.07	7.48	1.48	3.11
	0.452	0.6	1.91	6.22	3.25	3.53	3.16	9.39	2.97	3.40
	0.678	0.4	1.33	6.81	5.09	3.87	2.22	10.3	4.63	3.70
	0.904	0.2	1.01	7.13	7.04	4.14	1.69	10.9	6.43	4.02
	1.017	0.1	0.866	6.97	8.05	4.35	1.38	10.7	7.77	4.18
	1.13	0.0	0.770	7.06	9.17	4.41	1.28	10.8	8.41	4.31
3/1	0.226	0.8	1.24	2.30	1.86	3.63	2.13	3.47	1.63	3.5
	0.452	0.6	0.597	2.51	4.21	4.27	0.975	3.86	3.96	4.05
	0.678	0.4	0.405	2.58	6.37	4.76	0.669	3.96	5.92	4.60
	0.904	0.2	0.315	2.57	8.17	5.16	0.512	3.96	7.73	4.89
	1.017	0.1	0.270	2.58	9.57	5.28	0.436	3.98	9.12	4.98
	1.13	0.0	0.246	2.59	10.5	5.45	0.405	4.00	9.84	5.29
5/1	0.226	0.8	0.743	1.48	1.99	3.98	1.23	2.26	1.83	3.76
	0.452	0.6	0.344	1.56	4.53	4.70	0.574	2.39	4.17	4.48
	0.678	0.4	0.259	1.58	6.08	5.20	0.417	2.42	5.81	4.98
	0.904	0.2	0.186	1.58	8.46	5.59	0.310	2.43	7.81	5.39
	1.017	0.1	0.148	1.58	10.7	5.70	0.242	2.44	10.1	5.53
	1.13	0.0	0.135	1.59	11.8	5.79	0.236	2.44	10.3	5.67

			C_{in} = 0.170 mol·L^{-1}; pH$_{in}$ = 2.80				C_{in} = 0.250 mol·L^{-1}; pH$_{in}$ = 2.76			
$\bar{V}/V$	[TOA] mol·L^{-1}	$V_{dodecane}/\bar{V}$	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH
1/1	0.226	0.8	7.15	9.91	1.39	3.02	10.9	14.1	1.28	2.97
	0.452	0.6	4.56	12.5	2.74	3.29	7.11	17.9	2.52	3.22
	0.678	0.4	3.37	13.8	4.05	3.66	5.29	19.8	3.73	3.58
	0.904	0.2	2.49	14.6	5.86	3.92	4.00	21.0	5.25	3.80
	1.017	0.1	2.12	14.3	6.73	4.12	3.58	20.6	5.76	3.89
	1.13	0.0	2.02	14.4	7.11	4.24	3.13	21.0	6.72	4.10
3/1	0.226	0.8	3.04	4.67	1.53	3.42	4.79	6.75	1.41	3.30
	0.452	0.6	1.56	5.16	3.31	3.98	2.54	7.49	2.95	3.83
	0.678	0.4	1.05	5.33	5.06	4.12	1.62	7.81	4.82	4.35
	0.904	0.2	0.760	5.35	7.04	4.88	1.15	7.86	6.84	4.69
	1.017	0.1	0.608	5.40	8.89	4.70	0.966	7.91	8.19	4.85
	1.13	0.0	0.590	5.41	9.16	5.18	0.898	7.93	8.83	5.04
5/1	0.226	0.8	1.81	3.05	0.75	1.34	3.05	4.40	1.44	3.65
	0.452	0.6	0.848	3.24	3.82	4.44	1.38	4.73	3.44	4.27
	0.678	0.4	0.655	3.28	5.00	4.90	0.991	4.81	4.85	4.78
	0.904	0.2	0.466	3.29	7.06	5.28	0.746	4.82	6.46	5.14
	1.017	0.1	0.364	3.31	9.07	5.43	0.548	4.86	8.85	5.29
	1.13	0.0	0.335	3.32	9.89	5.55	0.532	4.86	9.13	4.41

E. Butyric Acid

			C_{in} = 0.0841 mol·L^{-1}; pH$_{in}$ = 2.97				C_{in} = 0.126 mol·L^{-1}; pH$_{in}$ = 2.90			
$\bar{V}/V$	[TOA] mol·L^{-1}	$V_{dodecane}/\bar{V}$	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH
1/1	0.226	0.8	1.45	6.95	4.78	3.45	2.49	10.1	4.05	3.36
	0.452	0.6	0.636	7.77	12.2	3.97	1.03	11.6	11.2	3.84
	0.678	0.4	0.477	7.92	16.6	4.31	0.749	11.8	15.8	4.20
	0.904	0.2	0.293	8.11	27.7	4.80	0.465	12.1	26.1	4.57
	1.017	0.1	0.251	7.77	31.0	4.90	0.386	11.6	30.2	4.66
	1.13	0.0	0.227	7.80	34.3	4.98	0.349	11.7	33.4	4.84
3/1	0.226	0.8	0.454	2.65	5.83	4.11	0.772	3.93	5.10	3.98
	0.452	0.6	0.225	2.72	12.1	4.83	0.340	4.08	11.9	4.67
	0.678	0.4	0.138	2.75	19.9	5.27	0.227	4.12	18.1	5.09
	0.904	0.2	0.0919	2.72	29.6	5.67	0.142	4.08	28.7	5.49
	1.017	0.1	0.089	2.72	30.8	5.76	0.136	4.08	29.9	5.58
	1.13	0.0	0.074	2.73	37.0	5.90	0.113	4.09	36.1	5.69
5/1	0.226	0.8	0.284	1.62	5.72	4.51	0.465	2.42	5.21	4.35
	0.452	0.6	0.125	1.66	13.2	5.26	0.204	2.47	12.1	5.09
	0.678	0.4	0.0908	1.66	18.3	5.69	0.142	2.49	17.5	5.46
	0.904	0.2	0.0635	1.65	26.0	6.06	0.0970	2.47	25.5	5.87
	1.017	0.1	0.0510	1.65	32.4	6.15	0.0795	2.48	31.2	5.95
	1.13	0.0	0.0476	1.65	34.7	6.25	0.0743	2.48	33.4	6.06

Table 4 (Continued)

E. Butyric Acid (Continued)

			$C_{in} = 0.166$ mol·L^{-1}; pH$_{in} = 2.79$				$C_{in} = 0.246$ mol·L^{-1}; pH$_{in} = 2.69$			
$\bar{V}/V$	[TOA] mol·L^{-1}	$V_{dodecane}/\bar{V}$	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH	10^2C_{HA} mol·L^{-1}	$10^2\bar{C}_{HA}$ mol·L^{-1}	m	pH
1/1	0.226	0.8	3.65	12.9	3.54	3.34	5.68	18.9	3.32	3.17
	0.452	0.6	1.45	15.1	10.9	3.71	2.25	22.3	9.93	3.55
	0.678	0.4	1.07	15.5	14.4	4.11	1.70	22.9	13.43	3.89
	0.904	0.2	0.636	15.9	25.1	4.47	0.965	23.6	24.5	4.25
	1.017	0.1	0.545	15.3	28.1	4.58	0.827	22.6	27.4	4.36
	1.13	0.0	0.477	15.4	32.3	4.76	0.755	22.7	30.1	4.50
3/1	0.226	0.8	1.11	5.16	4.64	3.88	1.82	7.59	4.17	3.71
	0.452	0.6	0.511	5.36	10.5	4.55	0.794	7.92	9.97	4.37
	0.678	0.4	0.318	5.42	17.1	4.63	0.482	8.02	16.6	4.82
	0.904	0.2	0.199	5.38	27.1	5.36	0.312	7.95	25.5	5.18
	1.017	0.1	0.182	5.38	29.6	5.45	0.281	7.96	28.3	5.29
	1.13	0.0	0.153	5.39	35.2	5.62	0.238	7.97	30.5	5.48
5/1	0.226	0.8	0.658	3.19	4.84	4.28	1.12	4.69	4.17	4.06
	0.452	0.6	0.284	3.26	11.5	5.02	0.454	4.82	10.6	4.81
	0.678	0.4	0.204	3.26	16.1	5.43	0.318	4.85	15.2	5.24
	0.904	0.2	0.134	3.27	24.4	5.78	0.207	4.83	23.4	5.64
	1.017	0.1	0.111	3.26	29.4	5.85	0.173	4.83	28.0	5.70
	1.13	0.0	0.100	3.26	32.7	5.94	0.159	4.83	30.4	5.83

Table 5. Values of the Equilibrium Extraction Constant (K_E) and the Number of Reacting Extractant Molecules with (A) TBP or (B) TOA as Extractant, Calculated for Experimental Data

	formic			acetic			lactic			propionic			butyric		
$\bar{V}/V$	$10C_{HA}$ mol·L^{-1}	n	K_E	$10C_{HA}$ mol·L^{-1}	n	K_E	$10C_{HA}$ mol·L^{-1}	n	K_E	$10C_{HA}$ mol·L^{-1}	n	K_E	$10C_{HA}$ mol·L^{-1}	n	K_E
							(A) TBP as Extractant								
5/1	1.99	1.11	0.769	2.50	1.24	0.561	2.45	1.99	0.172	2.51	0.940	2.86	2.26	0.851	9.34
	1.80	1.22	1.03	1.59	1.17	0.556	1.68	1.47	0.360	1.66	1.06	2.55	1.61	0.911	8.94
	1.02	1.18	0.954	1.26	1.17	0.640	1.19	1.39	0.406	1.28	1.28	3.16	1.17	1.09	18.1
	0.486	1.18	1.15	0.260	1.16	0.670	0.735	1.42	0.416	0.860	1.05	3.23	0.795	0.970	10.9
3/1	1.99	1.10	0.856	2.50	1.25	0.505	2.45	1.64	0.290	2.51	1.10	2.74	2.26	0.872	8.26
	1.80	1.10	0.856	1.59	1.25	0.505	1.68	1.64	0.290	1.66	1.10	2.74	1.61	0.872	8.26
	1.02	1.04	0.919	1.26	1.26	0.548	1.19	1.65	0.292	1.28	1.11	2.82	1.17	1.07	13.3
	0.486	1.02	1.10	0.260	1.24	0.587	0.735	1.41	0.363	0.860	1.07	3.17	0.795	0.970	9.79
1/1	1.99	1.02	0.631	2.50	1.09	0.488	2.45	2.37	0.159	2.51	1.11	2.06	2.26	1.08	7.61
	1.80	1.05	0.700	1.59	1.03	0.552	1.68	1.37	0.322	1.66	1.13	2.21	1.61	0.967	7.83
	1.02	0.969	0.770	1.26	1.06	0.623	1.19	0.950	0.472	1.28	1.09	2.41	1.17	1.09	8.50
	0.486	1.02	0.929	0.260	0.976	0.736	0.735	1.01	0.533	0.860	1.10	2.70	0.795	1.06	8.55
							(B) TOA as Extractant								
5/1	2.42	1.94	63.9	2.47	1.91	11.6	2.36	2.27	40.0	2.50	1.20	30.8	2.46	1.29	373.9
	1.65	2.49	111.9	1.70	2.06	12.3	1.66	2.76	64.3	1.70	1.86	9.28	1.66	1.94	594.5
	1.24	2.62	101.8	1.24	2.20	14.2	1.25	2.65	48.3	1.25	2.47	81.1	1.26	1.37	1395.8
	0.721	2.89	170.3	0.847	2.48	21.6	0.803	3.41	135	0.810	2.23	77.8	0.841	2.63	1145.4
3/1	2.42	1.78	26.3	2.47	1.80	8.68	2.36	2.39	34.0	2.50	1.59	6.27	2.46	1.74	243.9
	1.65	1.78	26.3	1.70	1.80	8.68	1.66	2.39	34.0	1.70	1.59	6.27	1.66	1.74	243.9
	1.24	2.06	35.2	1.24	1.92	10.2	1.25	2.57	38.3	1.25	1.43	25.2	1.26	2.03	339.2
	0.721	2.39	48.4	0.847	2.09	13.2	0.803	3.03	58.1	0.810	1.77	39.8	0.841	2.40	502.20
1/1	2.42	0.888	6.42	2.47	1.73	6.87	2.36	1.97	14.2	2.50	0.77	7.91	2.46	0.83	45.39
	1.65	0.999	6.82	1.70	1.75	7.07	1.66	1.97	13.8	1.70	1.75	6.24	1.66	1.26	60.73
	1.24	1.09	7.20	1.24	1.77	7.36	1.25	1.97	14.3	1.25	0.95	9.12	1.26	1.41	68.16
	0.721	1.66	15.62	0.847	1.76	7.82	0.803	2.08	16.0	0.810	1.16	10.22	0.841	1.63	86.61

that best extracted was butyric acid, which gives, consequently, the largest distribution coefficient.

When TOA was employed as extractant (Table 6b), the presence of diluent (dodecane) and modifier (decane-1-ol) affected the apparent n values. These values are between 0.99 and 1.94 for all organic acids. This means that the influence of diluent and modifier on the overall distribution coefficient (m_{HA}) is significantly important. The more this influence is important, the higher is the difference between the value of 1 and the calculated apparent n values. Again, the influence of diluent on the lactic acid extraction is more greatly emphasized.

The extraction constant values (K_E) obtained when TOA is utilized as extractant were almost 10 times larger than those in the case where TBP was employed, for example, about 50 times larger for lactic acid.

The influence of diluent and modifier can be observed in Figure 5. The relation of the overall distribution coefficient (m_{HA}) as a function of the extractant concentration of TBP or TOA was studied.

For butyric acid a pronounced positive influence of dodecane concentration on the solubility of the reaction product in the organic phase was observed. This influence on the overall distribution coefficient occurs when TBP is used as extractant. This indicates that the distribution coefficient rises with the concentration of dodecane. The study of the effect of dodecane on the solubility of the reaction product gives values of n smaller than 1.

Table 6. Values of the Apparent Extraction Constant (K_E) and Apparent Number of Reacting Molecules (n) with (A) TBP or (B) TOA as Extractant, Calculated for Different Equilibrium Aqueous Concentrations (C_{HA})

acid	$10^2 C_{HA}$/mol·L^{-1}	pH	n	K_E
	(A) TBP as Extractant			
formic	10.0	2.28	0.806	0.638
	7.50	2.34	0.858	0.690
	5.00	2.42	0.898	0.738
	1.50	2.67	0.942	0.797
	1.00	2.75	0.948	0.804
acetic	10.0	2.97	1.05	0.503
	7.50	2.99	1.06	0.520
	5.00	3.03	1.07	0.536
	1.50	3.14	1.08	0.557
	1.00	3.18	1.08	0.560
lactic	10.0	2.14	1.29	0.329
	7.50	2.22	1.29	0.337
	5.00	2.33	1.28	0.344
	1.50	2.66	1.27	0.354
	1.00	2.78	1.27	0.355
propionic	2.00	3.29	1.06	2.50
	1.50	3.35	1.07	2.53
	1.00	3.43	1.08	2.55
	0.50	3.57	1.08	2.57
	0.10	3.88	1.10	2.58
butyric	1.50	3.51	0.919	7.70
	1.00	3.60	0.941	7.81
	0.75	3.66	0.950	7.85
	0.50	3.76	0.959	7.88
	0.10	4.12	0.973	7.91
	(B) TOA as Extractant			
formic	2.00	3.67	1.57	9.55
	1.50	3.86	1.57	9.46
	1.00	4.13	1.58	9.35
	0.80	4.27	1.58	9.30
	0.50	4.57	1.58	9.22
acetic	2.00	3.80	1.63	6.22
	1.50	3.94	1.59	5.90
	1.00	4.16	1.55	5.63
	0.80	4.27	1.54	5.52
	0.50	4.51	1.52	5.37
lactic	2.00	3.13	1.94	13.9
	1.50	3.26	1.94	13.6
	1.00	3.46	1.93	13.1
	0.80	3.56	1.92	12.9
	0.50	3.78	1.91	12.6
propionic	2.00	3.67	0.99	8.81
	1.50	3.88	1.02	9.02
	1.00	4.17	1.05	9.15
	0.80	4.33	1.06	9.19
	0.50	4.67	1.08	9.22
butyric	1.00	4.09	1.22	70.9
	0.50	4.60	1.24	64.5
	0.40	4.77	1.24	63.1
	0.20	5.27	1.24	60.4
	0.10	5.79	1.24	59.02

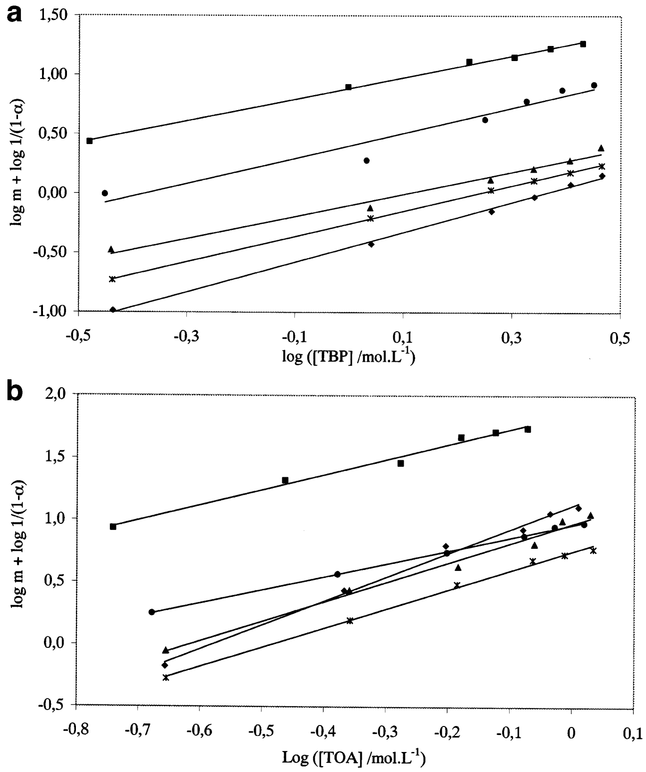

Figure 4. (**a**) Determination of the extraction constant (K_E) and apparent number of reacting molecules (n) when TBP is used as extractant for an equilibrium aqueous acid concentration equal to $C_{HA} = 0.015$ mol·L^{-1}. Symbols: (◆) lactic acid; (■) butyric acid; (▲) formic acid; (∗) acetic acid; (●) propionic acid. (**b**) Determination of the extraction constant (K_E) and apparent number of reacting molecules (n) when TOA is used as extractant for an equilibrium aqueous acid concentration equal to $C_{HA} = 0.015$ mol·L^{-1}. Symbols: (◆) lactic acid; (■) butyric acid; (▲) formic acid; (∗) acetic acid; (●) propionic acid.

The variation of the distribution coefficient as a function of the extractant concentration for acetic acid is shown in Figure 5a. In this case, the influence of dodecane concentration on the solubility of the reaction product is negligible ($n \approx 1$). This means that the overall distribution coefficient (m_{HA}) is equal to the distribution coefficient due to the chemical extraction (m_R).

The dodecane in the solvent causes a change of solubility of the reaction product in the organic phase and, consequently, influences the overall distribution coefficient. This influence was studied when the extraction was carried out with TOA mixed with decane-1-ol (1:1 vol %). The results are shown in Figure 5b. Approximately straight lines were obtained. A positive influence appears for butyric and acetic acids. A negative influence was observed for formic, propionic, and lactic acids. For all examined organic acids, the influence of dodecane is more pronounced when TOA is used than when TBP is employed as extractant. Probably, this significant difference is due to the influence of decane-1-ol (active diluent) on the solubility of the reaction product in the organic phase when reactive liquid−liquid extraction takes place.

Conclusions

From this experimental study and the treatment of obtained results, a conclusion can be drawn that extraction in the presence of chemical reactions is a complex phenomena.

When only chemical interaction between the extractant and the solute is assumed and the mass action law is used for the determination of the equilibrium extraction constant and the number of extractant reacting molecules, the estimated values depend on the applied method. If the experiments are carried out with constant initial aqueous concentration of extracted acid and different concentrations of extractant in the organic phase, the obtained values depend on the initial aqueous acid concentration as well as on the phase ratio. More exact is the method when several extraction isotherms are used. It gives the opportunity for a constant equilibrium acid concentration in the aqueous phase at different equilibrium extractant concentrations to be used. In this case, the estimated values do not differ significantly one from other in dependence on equilibrium acid concentration.

The influence of diluent and modifier on the equilibrium extraction is very important and must be taken quantitatively into account for the treatment of the data.

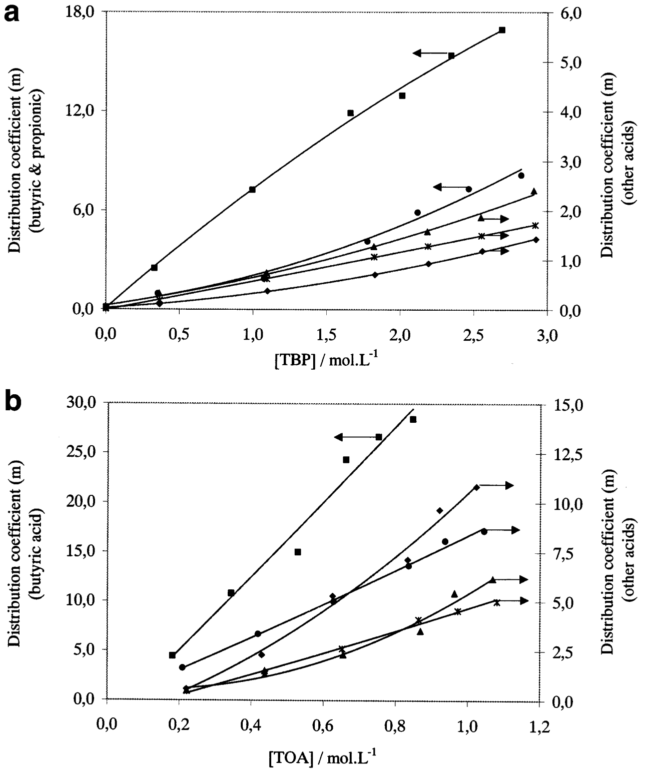

Figure 5. (**a**) Influence of diluent on the overall distribution coefficient (*m*) of the studied acids, for TBP used as extractant. Symbols: (◆) lactic acid; (■) butyric acid; (▲) formic acid; (∗) acetic acid; (●) propionic acid. (**b**) Influence of diluent on the overall distribution coefficient (*m*) of the studied acids, for TOA used as extractant. Symbols: (◆) lactic acid; (■) butyric acid; (▲) formic acid; (∗) acetic acid; (●) propionic acid.

Knowledge of the real mechanisms in the extraction processes is necessary to specify the model, which allows calculations of the values of equilibrium extraction constant and the real number of reacting molecules. These parameters afford the wherewithal for predicting the liquid–liquid equilibrium to achieve particular objectives.

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