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Liquid−Liquid Equilibria of Butyric Acid in Water + Solvent Systems with Trioctylamine as Extractant

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Liquid−liquid equilibrium data of butyric acid in the systems water + solvent with tri-*n*-octylamine as extractant and *n*-alkanes as diluent, and water + pure *n*-alkanes are presented. The distribution coefficient is a linear function of the aqueous concentration of butyric acid for pure *n*-alkanes. For solvents containing trioctylamine, the dependence of the distribution coefficient of butyric acid goes through a maximum at a concentration of butyric acid of about 0.2 kmol·m^{-3}. An overloading of the extractant reaching the value of almost 6 was observed. The loading is independent of the extractant concentration. The experimental data were interpreted by a chemical reaction mechanism and a related model in which the existence of (1,1) to (7,1) acid−amine complexes and a monomer and a dimer of butyric acid in the solvent was supposed. The equilibrium constants of formation of these complexes and the distribution of individual species in the solvent were estimated. This model fits experimental equilibrium data well. With increasing temperature, the value of the distribution coefficient of butyric acid decreases. Coextraction of water in the solvents is proportional to the concentration of butyric acid, and in the solvent with trioctylamine, it is 10 times higher than that in pure *n*-alkanes.

Introduction

Solvent extraction and pertraction through liquid membranes can be considered for the recovery of carboxylic acids from aqueous solutions as an alternative way to the calcium salt precipitation techniques.[1] Both extraction and pertraction can be employed not only in downstream separations but also integrated with fermentation.[2−5] Membrane-based solvent extraction of carboxylic acids has been studied previously.[6−8] An advantage of the on-line extraction or pertraction in fermentation technologies is the removal of products, which often have an inhibitory effect on the production rate, thereby permitting a continuous or semicontinuous process.

Organic solvents used for extraction can be classified into three major types: (1) conventional oxygen-bearing and hydrocarbon solvents, (2) phosphorus-bonded oxygen-bearing extractants, and (3) higher molecular mass aliphatic amines.[1] The conventional solvents such as ketones and alcohols give rather low distribution coefficients for carboxylic acids, making the extraction inefficient.[9] Solvents with organophosphates, such as tri-*n*-butyl phosphate[10−12] and trioctylphosphine oxide,[13] and aliphatic amines have a larger distribution coefficient for carboxylic acids. Several aliphatic amines have been used in the extraction of carboxylic acids[9,12,14−23] and in their pertraction.[4,7,24,25] The extraction of hydroxycarboxylic acids has been studied in papers,[1,15,26−30] and their pertraction was reported in ref 31. Toxicities of extractants, including amine types, and other components of solvents in fungal and bacterial fermentations were investigated in refs 3, 32, and 33. Several factors have an important influence on the extraction characteristics, such as the nature of the acid extracted, the composition of the aqueous phase, the concentrations of the acid and the extractant, and the type of the diluent used.

A detailed evaluation of solvents for the extraction of butyric acid is not available in the literature. Zigová et al.[20] carried out screening of 14 solvents for the extraction of butyric acid. A tertiary amine in different diluents, C_8 to C_{18} alcohols, dibutyl ether, toluene, and vegetable oils, has been tested. The highest distribution coefficient for butyric acid from these solvents had tertiary amines, which enabled the extraction of acid at a pH above the pK_a value. The influence of pH on the extraction equilibria of butyric acid with tertiary amine (Alamine 336) and quaternary amine chloride (Aliquat 336) in octanol and kerosene has been studied by Yang et al.[16] These authors suggested an equation for the calculation of the distribution coefficient at very low and high pH values. Ingale et al.[11] obtained data for the extraction of carboxylic acids C_2 to C_6 with tributyl phosphate in the presence of mineral acids (H_2SO_4 and HCl) and their sodium salts. The effect of the concentration of tributyl phosphate in hexane on the extraction constant for butyric acid was investigated by Wang.[10] Hano et al.[13] determined the values of the extraction constant for several acids with trioctylphosphine oxide. For butyric acid the value of this constant was 51.9 m^3·kmol^{-1}. Davison and Thompson have found that the distribution coefficients of butyric acid and butanol for oleyl alcohol are nearly the same and are about 3.[34] Hegazi[35] studied the extraction of butyric acid from aqueous solutions by various concentrations of carbonyl-containing compounds dissolved in toluene at 30 °C. A low value of the distribution coefficient of 0.56 was determined for vegetable oils.[36]

The aim of this work was to measure liquid−liquid equilibrium data for the distribution of butyric acid in the systems water + solvent with trioctylamine, as an extractant, and water + pure *n*-alkanes and to formulate and

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evaluate the extraction mechanism and the related model describing these liquid−liquid equilibria.

Theory

In the proposal of a mathematical model for the extraction equilibria of an organic acid in the system solvent containing trioctylamine + water, the following assumptions, similarly as in refs 22 and 23, have been considered:

1. Two types of interactions of acid with the organic solvent, (i) physical dissolving of acid in the solvent in the form of a monomer and a dimer and (ii) chemical reaction of molecules of undissociated acid with one molecule of extractant with formation of various complexes, are possible.
2. Neither extractant nor complexes are soluble in the aqueous phase.
3. The volumes of phases depend on the concentration of acid in the given phase and fulfill the additivity of volumes.
4. Hydration of complexes was not considered in the model.

Physical Extraction. The undissociated carboxylic acid from the aqueous solution is dissolved in the organic solvent without extractant, which can be written formally in form of the following chemical reaction:

$$\mathrm{HA} \Leftrightarrow \overline{\mathrm{HA}} \qquad K'_{\mathrm{M}} = \frac{a_{\overline{\mathrm{HA}}}}{a_{\mathrm{HA}}} \tag{1}$$

where K'_{M} is the extraction constant of the monomer and a is the activity of the species. The overbar designates species in the solvent (organic) phase.

Many carboxylic acids form dimers in nonpolar organic solvents, for example in n-alkanes, which can be expressed by the following chemical reaction

$$2\overline{\mathrm{HA}} \Leftrightarrow \overline{(\mathrm{HA})_2} \qquad K'_{\mathrm{d}} = \frac{a_{\overline{(\mathrm{HA})_2}}}{a^2_{\overline{\mathrm{HA}}}} \tag{2}$$

where K'_{d} is the dimerization constant of the acid monomer in the organic phase.

The organic acid dissociates in the aqueous solution according to the reaction

$$\mathrm{HA} \Leftrightarrow \mathrm{A}^- + \mathrm{H}_+ \qquad K'_{\mathrm{a}} = \frac{a_{\mathrm{A}^-} a_{\mathrm{H}^+}}{a_{\mathrm{HA}}} \tag{3}$$

where K'_{a} are dissociation constants of the carboxylic acid in the aqueous phase. In the first approximation both phases are assumed to be ideal and equilibrium constants are defined by the equation

$$K_{\mathrm{M}} = \frac{[\overline{\mathrm{HA}}\,]}{[\mathrm{HA}]} = \frac{c_{\mathrm{MS}}}{c^*_{\mathrm{F}}} \tag{4}$$

where K_{M} is the extraction constant of the monomer based on molar concentrations of species, the square brackets denote the molar concentrations of species, c_{MS} is the molar concentration of the monomer of butyric acid in the organic phase, and c^*_{F} is the equilibrium concentration of undissociated butyric acid in the aqueous phase.

$$K_{\mathrm{d}} = \frac{\lfloor\overline{(\mathrm{HA})_2}\rfloor}{[\overline{\mathrm{HA}}]^2} = \frac{c_{\mathrm{DS}}}{c^2_{\mathrm{MS}}} \tag{5}$$

K_{d} is the dimerization constant of the acid based on molar concentrations of species, and c_{DS} is the molar concentration of dimer of butyric acid in the solvent.

$$K_{\mathrm{a}} = \frac{[\mathrm{A}^-][\mathrm{H}^+]}{[\mathrm{HA}]} \tag{6}$$

where K_{a} is the dissociation constant of acid based on molar concentrations of species.

The overall (analytical) concentration of the acid in physical extraction into the solvent without extractant, in all possible forms of the acid in the organic phase and taking into account eqs 4 and 5, can be expressed as

$$c^*_{\mathrm{aS}} = c_{\mathrm{MS}} + 2c_{\mathrm{DS}} = K_{\mathrm{M}} c^*_{\mathrm{F}} + 2K^2_{\mathrm{M}} K_{\mathrm{d}} (c^*_{\mathrm{F}})^2 \tag{7}$$

For the concentration of the undissociated acid in the aqueous phase the following relation can be derived

$$c^*_{\mathrm{F}} = \frac{c^*_{\mathrm{aF}}}{1 + 10^{(\mathrm{pH^*-pKa})}} \tag{8}$$

where c^*_{aF} is the overall concentration of the acid in the aqueous solution. For butyric acid pK_{a} = 4.83 at 25 °C.[37]

The distribution coefficient is defined by the equation

$$\mathrm{D} = c^*_{\mathrm{aS}}/c^*_{\mathrm{F}} \tag{9}$$

By combining eqs 7 and 9, one gets

$$D = K_{\mathrm{M}} + 2K^2_{\mathrm{M}} K_{\mathrm{d}} c^*_{\mathrm{F}} \tag{10}$$

From eq 10 it follows that the distribution coefficient is a linear function of the concentration of the undissociated acid in the aqueous phase.

Reactive Extraction of the Acid by an Extractant. In the case of alkylamine extractants, the extraction process is based on the acid−base reaction of alkylamine P and carboxylic acid HA. In many cases the organic phase is able to dissolve a higher amount of acid than corresponds to the molar ratio acid/carrier = 1:1. The loading of the carrier, z, is defined as the ratio of the overall concentration of acid in the organic phase in the form of complexes, that is, the difference between the overall acid concentration in the organic phase and the concentration of acid in the form of a monomer and a dimer (physical extraction), to the overall (analytical) concentration of amine in the organic phase, c_{aP}[15]

$$z = \frac{c^*_{\mathrm{aS}} - c^*_{\mathrm{aSphys}}}{c_{\mathrm{aP}}} \tag{11}$$

The concentration of the physically dissolved acid in monomer and dimer forms in the solvent with extractant c^*_{aSphys} was determined as follows: In the solvent with reactive extractant and supposing the additivity of volumes, the sum of volumes of n-alkanes, $V_{\mathrm{n-alk}}$, and the physically extracted organic acid, V_{Fphys}, is represented by the symbol V_{Sphys}. The following relation will give this sum:

$$V_{\mathrm{Sphys}} = V_{\mathrm{n-alk}} + V_{\mathrm{Aphys}} = V_{\mathrm{So}}\left(1 - \frac{c_{\mathrm{aPo}} \mathrm{M_P}}{\rho_{\mathrm{P}}}\right) + \frac{n_{\mathrm{Sphys}} \mathrm{M_A}}{\rho_{\mathrm{A}}} \tag{12}$$

where the term in parentheses accounts for the correction of the volume of extractant in the solvent, V_{So} is the initial volume of the organic phase, c_{aPo} is the initial analytical concentration of extractant, $\mathrm{M_P}$ and $\mathrm{M_A}$ are the molar masses of the extractant and acid, respectively, and ρ_P and ρ_A are the densities of the extractant and acid, respectively. The molar amount of the physically extracted acid in the solvent, n_Sphys, is

$$n_\mathrm{Sphys} = n_\mathrm{MS} + 2n_\mathrm{DS} = (K_\mathrm{M}c_\mathrm{F}^* + 2K_\mathrm{M}^2K_\mathrm{d}(c_\mathrm{F}^*)^2)V_\mathrm{Sphys} \qquad (13)$$

Supposing the additivity of volumes for the ratio of volumes of the pure solvent and the solvent with the extracted acid

$$\frac{V_\mathrm{So}}{V_\mathrm{S}} = 1 - \frac{c_\mathrm{aS}^*\mathrm{M_A}}{\rho_\mathrm{A}} \qquad (14)$$

where c_aS^* is the equilibrium total concentration of acid in the solvent. Combining eqs 13 and 14 for the concentration of the physically extracted acid, the following relationship can be derived

$$c_\mathrm{aSphys}^* = \frac{n_\mathrm{Sphys}}{V_\mathrm{S}} = \left(1 - \frac{c_\mathrm{aS}^*\mathrm{M_A}}{\rho_\mathrm{A}}\right)\left(1 - \frac{c_\mathrm{aPo}\mathrm{M_P}}{\rho_\mathrm{P}}\right)\frac{K_\mathrm{M}c_\mathrm{F}^* + 2K_\mathrm{M}^2K_\mathrm{d}(c_\mathrm{F}^*)^2}{1 - [K_\mathrm{M}c_\mathrm{F}^* + 2K_\mathrm{M}^2K_\mathrm{d}(c_\mathrm{F}^*)^2]\dfrac{\mathrm{M_A}}{\rho_\mathrm{A}}} \qquad (15)$$

The existence of more types of complexes containing one or more acid molecules and only one molecule of amine, as is characteristic for monocarboxylic acids, can be expressed by the following reaction scheme

$$\overline{\mathrm{P}} + p\mathrm{HA} \leftrightarrow \overline{(\mathrm{HA})_p\mathrm{P}} \qquad K'_{p,1} = \frac{a_{\overline{(\mathrm{HA})p\mathrm{P}}}}{a_{\overline{\mathrm{P}}}a_\mathrm{HA}^p} \qquad (16)$$

where $K'_{p,1}$ is the extraction constant of acid–extractant complexes with (p,1) stoichiometry and species in the organic phase are marked with an overbar.

In the first approximation, the activities of the organic phase species are assumed to be proportional to the molar concentrations of species, with the constants of proportionality, or their ratio, lumped into the equilibrium constant. The apparent equilibrium constant for the overall reaction of the complex formation, $K_{p,1}$, can be written as

$$K_{p,1} = \frac{\lfloor\overline{(\mathrm{HA})p\mathrm{P}}\rfloor}{[\overline{\mathrm{P}}][\mathrm{HA}]^p} = \frac{c_{p,1}}{c_\mathrm{P}(c_\mathrm{F}^*)^p} \qquad (17)$$

where c_P is the concentration of the free extractant in the organic phase. From eq 17 it follows that

$$c_{p,1} = K_{p,1}c_\mathrm{P}(c_\mathrm{F}^*)^p \qquad (18)$$

The overall analytical concentration of the extractant in the organic phase is

$$c_\mathrm{aP} = c_\mathrm{aPo}\left(1 - \frac{c_\mathrm{aS}^*\mathrm{M_A}}{\rho_A}\right) \qquad (19)$$

where c_aPo is the initial molar concentration of extractant in the pure solvent. The term in parentheses is the correction expressing the change of the volume of solvent due to the acid extraction, which depends on the overall concentration of the acid in the solvent. The concentration of free extractant in the organic solvent is expressed by the equation

$$c_\mathrm{P} = c_\mathrm{aP} - \sum_p c_{p,1} = c_\mathrm{aP} - \sum_p \lfloor\overline{(\mathrm{HA})_p\mathrm{P}}\rfloor \qquad (20)$$

Combining eqs 18 and 20,

$$c_\mathrm{P} = c_\mathrm{aP} - c_\mathrm{P}\sum_p K_{p,1}(c_\mathrm{F}^*)^p = c_\mathrm{aP} - c_\mathrm{P}X \qquad (21)$$

where

$$X = \sum_p K_{p,1}(c_\mathrm{F}^*)^p \qquad (22)$$

From eq 21 it follows that

$$c_\mathrm{P} = c_\mathrm{aP}/(1 + X) \qquad (23)$$

The overall equilibrium concentration of the acid in the solvent is given by the equation

$$c_\mathrm{aS}^* = c_\mathrm{aSphys}^* + \sum_p pc_{p,1} = c_\mathrm{aSphys}^* + \frac{Bc_\mathrm{aP}}{1 + X} \qquad (24)$$

where

$$B = \sum_p pK_{p,1}(c_\mathrm{F}^*)^p \qquad (25)$$

Combining eqs 15, 19, and 24 gives after rearrangement

$$c_\mathrm{aS}^* = \frac{N}{1 + N\dfrac{\mathrm{M_A}}{\rho_\mathrm{A}}} \qquad (26)$$

Combining eqs 9 and 26 gives the following equation for the distribution coefficient

$$D = \frac{N/c_\mathrm{F}^*}{1 + N\dfrac{\mathrm{M_A}}{\rho_\mathrm{A}}} \qquad (27)$$

where

$$N = \left(1 - \frac{c_\mathrm{aPo}\mathrm{M_P}}{\rho_\mathrm{P}}\right)\frac{K_\mathrm{M}c_\mathrm{F}^* + 2K_\mathrm{M}^2K_\mathrm{d}(c_\mathrm{F}^*)^2}{1 - [K_\mathrm{M}c_\mathrm{F}^* + 2K_\mathrm{M}^2K_\mathrm{d}(c_\mathrm{F}^*)^2]\dfrac{\mathrm{M_A}}{\rho_\mathrm{A}}} + \frac{Bc_\mathrm{aPo}}{1 + X} \qquad (28)$$

It was assumed that the interaction of the butyric acid molecule with free trioctylamine is a rapid reaction resulting in the formation of the complex (1,1). Further, it was supposed that higher complexes with more molecules of butyric acid per one molecule of trioctylamine are formed by hydrogen bonds between the OH group of the acid and the carboxylate group in the complex. For example, considering the chemism with complexes (1,1), (2,1), (3,1), (4,1), (5,1), (6,1), and (7,1), then

$$B = K_{1,1}c_\mathrm{F}^* + 2K_{2,1}(c_\mathrm{F}^*)^2 + 3K_{3,1}(c_\mathrm{F}^*)^3 + 4K_{4,1}(c_\mathrm{F}^*)^4 + 5K_{5,1}(c_\mathrm{F}^*)^5 + 6K_{6,1}(c_\mathrm{F}^*)^6 + 7K_{7,1}(c_\mathrm{F}^*)^7 \qquad (29)$$

$$X = K_{1,1}c_\mathrm{F}^* + K_{2,1}(c_\mathrm{F}^*)^2 + K_{3,1}(c_\mathrm{F}^*)^3 + K_{4,1}(c_\mathrm{F}^*)^4 + K_{5,1}(c_\mathrm{F}^*)^5 + K_{6,1}(c_\mathrm{F}^*)^6 + K_{7,1}(c_\mathrm{F}^*)^7 \qquad (30)$$

The software SCIENTIST did an estimation of the model parameters. As an optimization criterion the sum of

Table 1. Characteristics of Used Chemicals, Solvents, and Solvent Phases

chemical or solvent	t/°C	ρ/kg·m^{-3}	$10^6\nu$/m^2·s^{-1}
butyric acid	20	962.0	
	30	959.0	
	35	945.9	
	40	939.7	
	50	931.1	
trioctylamine	20	809.9	
	30	804.3	
	35	802.6	
	40	800.4	
	50	794.8	
n-alkanes	30	741.4	1.596
0.2 kmol·m^{-3} trioctylamine in *n*-alkanes	30	746.6	1.792
0.4 kmol·m^{-3} trioctylamine in *n*-alkanes	20	758.7	2.477
	30	751.9	2.026
	35	749.6	
	40	748.9	1.753
	50	740.8	
0.6 kmol·m^{-3} trioctylamine in *n*-alkanes	30	758.0	2.297
0.567 kmol·m^{-3} butyric acid in solvent with 0.4 kmol·m^{-3} trioctylamine in *n*-alkanes	30	764.9	
1.022 kmol·m^{-3} butyric acid in solvent with 0.4 kmol·m^{-3} trioctylamine in *n*-alkanes	30	775.7	

squares of deviations has been used. Particular models have been compared according to their fit to experimental data evaluated by the standard deviation

$$\sigma = \left(\frac{\sum [(D_{\mathrm{exp}} - D_{\mathrm{calc}})/D_{\mathrm{exp}}]^2}{N_{\mathrm{e}} - N_{\mathrm{p}}} \right)^{1/2} \tag{31}$$

where N_{e} is the number of experiments and N_{p} is the number of optimized parameters. The correlation coefficient was used as well.

Materials and Methods

Chemicals. (a) n-Alkanes. The dodecane fraction of *n*-alkanes (Slovnaft, Slovakia) was employed as a diluent with the mean molar mass of 166.95 g·mol^{-1}. The composition of *n*-alkanes in mass % was 7.18 C_{10}, 32.39 C_{11}, 33.11 C_{12}, 26.84 C_{13}, 0.28 C_{14}, and higher.

(b) Trioctylamine with purity of >99 mass % (Fluka) was used as received.

(c) Butyric acid with purity > 99 mass % (Merck) was used.

(d) Characteristics of components, solvents, and their solutions are presented in Table 1.

Experimental Methods. The aqueous solution of butyric acid, in most cases with a volume of 20 cm^3, was contacted with 20 cm^3 of organic solvent in 500 cm^3 Erlenmeyer flasks placed in a rotational shaking water bath 1092 (GFL, Germany) at a frequency of shaking of 180 min^{-1} over 5 h. The temperature was set to a selected value and kept within ±0.1 °C. Measurements were performed in the temperature range from 20 °C to 50 °C. After separation of phases, the equilibrium pH of the aqueous phase was measured by Ionmeter 3040 (Jenway, U.K.).

The concentration of butyric acid in the aqueous phases was determined by capillary isotachophoresis with the analyzer EA 100 (Villa, Slovakia) using HCl and a histidine solution with pH = 6.0 as the leading electrolyte. The concentration of butyric acid in the organic phase was also determined by isotachophoresis after stripping the acid into a solution of NaOH.

The volumes of both phases in equilibrium, which are represent by the symbols V_{F}^* and V_{S}^*, were different from the initial volumes and were calculated according to the following expressions assuming the additivity of volumes, which has been proved experimentally

$$V_{\mathrm{F}}^* = \frac{V_{\mathrm{Fo}}(\rho_{\mathrm{A}} - c_{\mathrm{Fo}}\mathrm{M}_{\mathrm{A}})}{\rho_{\mathrm{A}} - c_{\mathrm{aF}}^*\mathrm{M}_{\mathrm{A}}} \tag{32}$$

$$V_{\mathrm{S}}^* = V_{\mathrm{So}} + V_{\mathrm{Fo}} - V_{\mathrm{F}}^* \tag{33}$$

In each experiment, the mass balance of the acid was checked by the ratio

$$\Delta = \frac{c_{\mathrm{F}}^*\, V_{\mathrm{F}}^* + c_{\mathrm{S}}^*\, V_{\mathrm{S}}^*}{V_{\mathrm{Fo}} c_{\mathrm{Fo}}} \tag{34}$$

In the ideal case, the value of Δ should be 1. In most measurements, the mass balance ratio was within ±3% of this value.

The water content in the organic phases was determined by Karl Fischer titration with reagent Hydranal—Composites (Merck) using an autotitrator DL 50 (Mettler Toledo, CH).

Results and Discussion

Diluent. Higher amines, especially the tertiary types such as trioctylamine, are highly viscous liquids. This is one of the reasons why they are applied dissolved in a diluent for extraction and pertraction. *n*-Alkanes are advantageous also with respect to their low toxicity in comparison with aromatics.[3,32,33] This could be important in the on-line extraction of organic acids from the fermentation broths, which enables us to recover the product and to prevent its inhibition effect for fermentation.[2,3,38,39]

It is well-known that most carboxylic acids, also butyric acid, exist as dimers in the organic phase due to their strong intermolecular hydrogen-bonding, especially in nonpolar solvents, like *n*-alkanes.[1,19,28] The complexes of butyric acid with trioctylamine or butyric acid are well soluble in nonpolar diluents, for example, in *n*-alkanes, and do not require a modifier to prevent the formation of a second organic phase or a precipitate, as it is in the case of hydroxycarboxylic acids.[27,31]

Liquid−Liquid Equilibria for Pure n-Alkanes. Equilibrium data of butyric acid in the pure *n*-alkanes + water system measured at 30 °C are presented in Figure 1 and Table 2. These data were correlated according to eqs 7 to 10 with a good fit, as shown in Figure 1. The following values of the extraction constant of the monomer and the

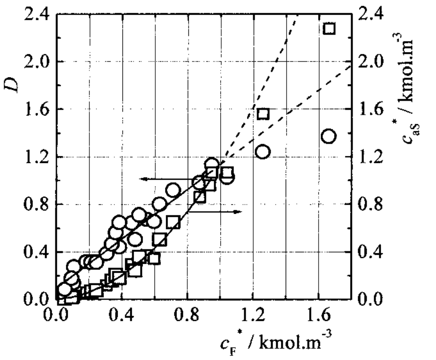

Figure 1. Equilibrium data for physical extraction of butyic acid with pure *n*-alkanes at 30 °C. Lines are correlated according to the presented model considering the acid monomer and dimer in the solvent and experiments up to $c_F^* = 1$ kmol·m^{-3}.

Table 2. Equilibrium Data of Butyric Acid in the System Water + Pure *n*-Alkanes at 30 °C

pH_F^*	c_{aF}^*	c_{aS}^*	$c_{H_2O}^*$	Δ
	kmol·m^{-3}	kmol·m^{-3}	kmol·m^{-3}	
	0		0.00348	
3.13	0.0529	0.0092		0.96
3.06	0.0956	0.0167		1.03
3.12	0.1055	0.0144	0.00633	0.99
3.01	0.1090	0.0299	0.00239	1.02
2.93	0.1856	0.0586	0.00396	0.99
2.73	0.2163	0.0666		1.00
2.69	0.2453	0.0764		1.02
2.65	0.3060	0.1179	0.0030	0.98
2.61	0.3428	0.1582		0.96
2.56	0.3652	0.2047		1.03
2.59	0.3850	0.1697	0.0084	0.98
2.75	0.4594	0.2940	0.0035	0.99
2.59	0.4813	0.2420		0.98
2.56	0.5049	0.2974		0.99
2.61	0.5097	0.3598		1.00
2.77	0.5539	0.3727	0.0055	0.98
2.73	0.5958	0.3402	0.0043	0.98
2.47	0.6324	0.5043		1.03
2.43	0.7143	0.6525	0.0129	0.99
2.52	0.8747	0.8672	0.0179	0.98
2.50	0.9333	0.9600	0.0068	0.98
2.48	0.9486	1.0006	0.0245	0.96
2.38	1.0410	1.0776		0.98
2.22	1.2588	1.5618	0.0195	0.99
2.19	1.6617	2.2767	0.0245	0.99

dimerization constant were obtained: $K_M = 0.0902$ and $K_d = 64.16$ kmol^{-1}·m^3. Moreover, Figure 1 shows that, for the aqueous concentration of butyric acid higher than 1 kmol·m^{-3}, the distribution coefficient is not a linear function of the aqueous acid concentration, as shown in eq 10, and the presented model is not suitable. Another reason might be that, at higher concentrations, activity should be used instead of molar concentration.

For comparison, Juang[9] determined the value of the dimerization constant of acetic acid in xylene, $K_d = 235.0$ kmol^{-1}·m^3, Davies[40] determined that for propionic acid in light petroleum, $K_d = 79.8$ kmol^{-1}·m^3, and Luque[12] calculated this value for valeric acid in toluene, $K_d = 15.4$ kmol^{-1}·m^3. All values were based on the correlation of experimental data. This suggests that with increasing number of C atoms the value of the dimerization constant decreases. The value of the dimerization constant for butyric acid in *n*-alkanes, 64.16 kmol^{-1}·m^3, determined from our equilibrium data, is in good agreement with reported values in succession shown above. Independently, the following values of the dimerization constant for acetic acid in pure toluene at 25 °C were determined from spectral data: $K_d = 314$ kmol^{-1}·m^3 by Ziegenfuss[19] and $K_d = (446 \pm 70)$ kmol^{-1}·m^3 by Fujii.[41]

Table 3. Equilibrium Data of Butyric Acid in the System Water + Pure *n*-Alkanes at 40 °C

pH_F^*	c_{aF}^*	c_{aS}^*	$c_{H_2O}^*$	Δ
	kmol·m^{-3}	kmol·m^{-3}	kmol·m^{-3}	
3.08	0.1944	0.0544	0.0021	1.00
2.84	0.3789	0.1687	0.0025	0.97
2.62	0.4392	0.2257	0.0028	0.98
2.48	0.5808	0.3954	0.0030	0.97
2.39	0.7064	0.5793	0.0041	0.99

Table 4. Equilibrium Data of Butyric Acid in the System Water + 0.2 kmol·m^{-3} of Trioctylamine in *n*-Alkanes at 30 °C

pH_F^*	c_{aF}^*	c_{aS}^*	Δ
	kmol·m^{-3}	kmol·m^{-3}	
3.16	0.0658	0.0522	0.99
3.02	0.1085	0.1329	0.99
2.90	0.1666	0.3031	1.01
3.02	0.2234	0.4624	0.98
2.88	0.2750	0.5822	1.01
2.68	0.3289	0.7149	0.98
2.88	0.3291	0.6805	0.98
2.84	0.4035	0.7944	0.98
2.60	0.5739	1.0103	1.00
2.75	0.5768	1.0646	1.01
2.7	0.6705	1.1628	0.97
2.56	0.8824	1.5669	1.03
2.48	1.0507	1.6650	0.98

Equilibrium data of butyric acid in the system pure *n*-alkanes + water at 40 °C are presented in Table 3, and from their correlation the following values, $K_M = 0.092$ and $K_d = 59.27$ kmol^{-1}·m^3, were obtained. These results, compared with values for 30 °C presented above, show the temperature dependence of the extraction constant of the monomer and the dimerization constant. Values of these constants at 30 °C were used for the correlation of equilibrium data in the system with extractant at the temperatures 20 °C, 30 °C, and 35 °C, and data for *n*-alkanes at 40 °C were used for the correlation of data at 40 °C and 50 °C. The effect of temperature on these two constants for the systems propionic acid in light petroleum and acetic acid in hexane is shown in the paper published by Davies.[40]

Liquid–Liquid Equilibria for the Solvents with Trioctylamine. Equilibrium data of butyric acid in the system water + solvent with trioctylamine as extractant are presented in Tables 4–7 and in Figures 2 and 3. The value of the distribution coefficient strongly depends on the aqueous concentration of butyric acid, especially at lower concentrations, as shown in Figure 3. This dependence goes through a maximum at an aqueous concentration of around 0.2 kmol·m^{-3}, which is sharper for higher extractant concentrations in the solvent. Figure 4 shows the loading of trioctylamine in the organic phase, *z*, defined by eq 11, which represents the average number of butyric acid molecules per one molecule of amine in the solvent. With increasing concentration of butyric acid in the aqueous phase, the loading increases and reaches almost the value 6, which reveals a remarkable overloading of the extractant. This can be achieved only by the formation of molecules or associates with linear or cyclic structure, where acids are associated by hydrogen bonds, as will be discussed below. The loading is practically independent of the extractant concentration, particularly at lower concentrations. From this follows the (*p*,1) stoichiometry of the complexes, where *p* is the number of acid molecules in the complex.

Table 5. Equilibrium Data of Butyric Acid in the System Water + 0.4 kmol·m^{-3} of Trioctylamine in *n*-Alkanes at 30 °C and Coextraction of Water with Acid

pH$^*_F$	c^*_{aF} kmol·m^{-3}	c^*_{aS} kmol·m^{-3}	$c^*_{H_2O}$ kmol·m^{-3}	Δ
	0	0	0.0091	
3.74	0.0571	0.0819		0.99
3.43	0.0742	0.1504		1.01
3.28	0.1150	0.3162		1.00
3.16	0.1353	0.3173		0.98
2.93	0.1370	0.4509	0.0498	0.99
2.96	0.1522	0.5735		1.03
3.03	0.1642	0.6275	0.0793	0.99
3.06	0.2348	0.8607		1.04
2.83	0.2533	1.0759		1.03
3.51	0.2883	0.8290		1.02
2.75	0.3264	1.3348	0.1779	1.01
2.76	0.3878	1.2809		0.99
2.74	0.4572	1.4200		0.99
2.69	0.4734	1.6069		1.00
2.68	0.5209	1.7348	0.2311	0.99
2.65	0.5638	1.5079		1.01
2.57	0.6326	1.8900		0.99
2.59	0.6441	1.8827		1.02
2.61	0.6941	1.6895	0.2502	0.98
2.60	0.8367	2.1215	0.3185	0.99
2.64	1.0270	2.3431		0.99

Table 6. Equilibrium Data of Butyric Acid in the System Water + 0.6 kmol·m^{-3} of Trioctylamine in *n*-Alkanes at 30 °C

pH$^*_F$	c^*_{aF} kmol·m^{-3}	c^*_{aS} kmol·m^{-3}	Δ
3.64	0.0695	0.1584	0.99
3.51	0.0925	0.3638	0.99
2.97	0.1462	0.8905	1.00
2.94	0.2107	1.2096	0.95
3.67	0.2430	1.2920	1.00
2.79	0.2438	1.5120	1.00
3.32	0.2928	1.5087	1.03
2.66	0.4113	1.7049	0.97
2.8	0.6308	2.1519	0.98
2.81	0.7341	2.3760	1.00
2.64	0.8062	2.7264	0.99
3.64	0.0695	0.1584	0.99

Table 7. Equilibrium Data of Butyric Acid in the System Water + 0.4 kmol·m^{-3} of Trioctylamine in *n*-Alkanes at Different Temperatures[a]

t °C	pH$^*_F$	c^*_{aF} kmol·m^{-3}	c^*_{aS} kmol·m^{-3}	$c^*_{H_2O}$ kmol·m^{-3}	Δ
50	3.20	0.1171	0.1546		1.01
50	3.15	0.1855	0.3677	0.0275	0.99
50	3.01	0.2332	0.6424	0.0524	1.01
50	2.85	0.2759	0.8183	0.0484	1.00
50	2.63	0.3215	0.8618	0.0593	0.99
50	2.58	0.4935	1.2732		0.98
50	2.55	0.7654	1.8433	0.1321	0.99
50	2.46	0.9831	2.1269	0.2257	0.98
40	3.18	0.1447	0.3129		1.02
40	3.39	0.1890	0.5133		0.99
40	3.1	0.1942	0.5279		1.00
40	2.91	0.2791	0.8479		1.01
40	2.71	0.3787	0.9927		1.01
40	2.92	0.4711	1.1418		1.01
40	2.73	0.5968	1.4471		0.95
40	2.68	0.8333	2.0009		0.98
40	3.08	0.1310	0.3501		1.01
35	3.21	0.0333	0.0492		0.99
35	2.99	0.0833	0.2091		0.98
35	2.94	0.1866	0.5861		1.04
35	2.99	0.3751	1.3122		0.99
35	2.57	0.4813	1.5718		1.04
35	2.53	0.6847	0.6688		0.99
35	3.05	0.1045	0.3398		0.99
35	2.54	0.6995	1.9552		0.99
35	2.51	0.8850	2.3420		0.99
35	2.48	1.0990	2.6705		0.99
20	2.94	0.1462	0.6080		0.98
20	3.38	0.2321	0.8563		1.01
20	2.82	0.3290	1.1984		0.99
20	2.85	0.3321	1.2961		0.97
20	2.92	0.4677	1.2869		0.98
20	2.57	0.6379	1.7012		1.02
20	2.52	0.65827	1.4989		0.95
20	2.51	0.87697	1.8521		0.96
20	2.71	0.9091	1.7762		0.95
20	3.18	0.97753	2.0416		0.97

[a] Data for 30 °C are in Table 5.

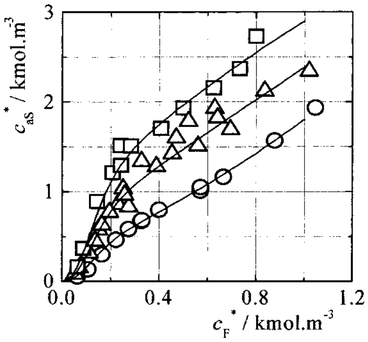

Figure 2. Equilibrium concentration of butyric acid in the solvents with trioctylamine as a carrier versus aqueous concentration of butyric acid at 30 °C: (□) 0.6 kmol·m^{-3} TOA; (△) 0.4 kmol·m^{-3} TOA; (○) 0.2 kmol·m^{-3} TOA. Lines are correlated according to the presented model (mechanism II).

The equilibrium data at 30 °C for the reactive extraction of butyric acid were correlated using the presented model for different values of *p*. The high overloading of the extractant suggests a simultaneous formation of (1,1) to (8,1) complexes. The calculated values of the extraction constants, together with the related correlation coefficient and standard deviation, are listed in Table 8. However, fitting eight chemical reaction constants to the liquid–liquid equilibrium data resulted in a small value of the equilibrium constant for the (8,1) complex. Therefore, this complex was further neglected. From Table 8 it follows that the model with simultaneous formation of (1,1) to (7,1) complexes gives the best fit of the model to experimental data, as shown also in Figures 2–4. The estimated extraction constants have the following values: $K_{1,1}$ = 0.49 kmol^{-1}·m^3, $K_{2,1}$=15.86(kmol·m^{-3})$^{-2}$, $K_{3,1}$=185.6(kmol·m^{-3})$^{-3}$, $K_{4,1}$ = 62.24 (kmol·m^{-3})$^{-4}$, $K_{5,1}$ = 214.9 (kmol·m^{-3})$^{-5}$, $K_{6,1}$ = 295.0 (kmol·m^{-3})$^{-6}$, and $K_{7,1}$ = 109.3 (kmol·m^{-3})$^{-7}$. The values of K_M = 0.0902 and K_d = 64.16 kmol^{-1}·m^3 were used as estimated from measurements with pure *n*-alkanes at 30 °C. In the estimation of all calculated data, presented as lines in Figures 2–6, these values of extraction constants have been used. The model fits experimental data less closely when the concentration of trioctylamine in the solvent or acid in the aqueous phase becomes higher, which can be connected with deviations of these solutions from the supposed ideality. The selection of the extraction mechanism with related structures of complexes is based on fitting the model to data and should be further proved by chemical analysis of the equilibrium solvent phases, which was not possible in this work. This model may be effectively used in modeling mass transfer through liquid membranes or solvent extraction where the concentration dependent distribution coefficient has to be used.

The mechanism of extraction of butyric acid with amines is not available in the literature. For comparison, we refer

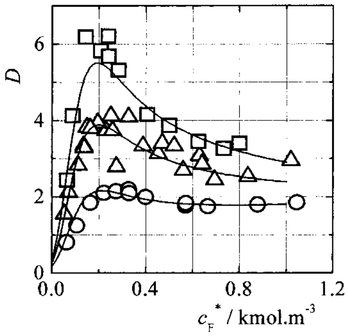

Figure 3. Distribution ratio of butyric acid in water + solvent systems versus aqueous concentration of butyric acid at 30 °C: (□) 0.6 kmol·m^{-3} TOA; (△) 0.4 kmol·m^{-3} TOA; (○) 0.2 kmol·m^{-3} TOA. Lines are correlated according to the presented model (mechanism II).

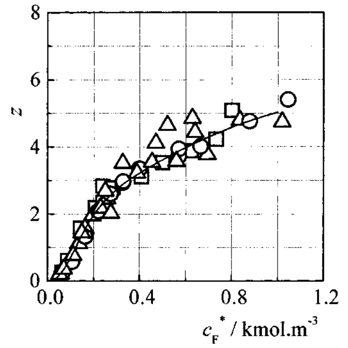

Figure 4. Loading of extractant with butyric acid versus aqueous concentration of butyric acid for different compositions of the solvent: (□) 0.6 kmol·m^{-3} TOA; (△) 0.4 kmol·m^{-3} TOA; (○) 0.2 kmol·m^{-3} TOA. The line is correlated according to the presented model (mechanism II).

Table 8. Extraction Constants, Standard Deviation, and Correlation Coefficients for the Mathematical Model of Liquid–Liquid Equilibrium Involving Different Chemistries of Extraction with Formation of Complexes of Butyric Acid with Trioctylamine with Different Structure $\overline{(HA)_pP}$ at 30 °C

	$K_{p,1}/(m^3·kmol^{-1})^p$		
$(p,1)^a$	mechanism I	mechanism II	mechanism III
(1,1)	0.727	0.488	0.441
(2,1)	14.83	15.86	15.78
(3,1)	199.7	185.6	185.7
(4,1)	12.97	62.24	66.97
(5,1)	304.7	214.9	231.3
(6,1)	378.4	295.0	265.6
(7,1)		109.31	115.0
(8,1)			10.52
r	0.9841	0.9843	0.9843
σ	0.2623	0.2614	0.2614

[a] Structure of the complexes involved in the mechanism.

to results from the extraction of carboxylic acids similar to butyric acid with amines. A simultaneous formation of (p,q) complexes, where p is the number of molecules of the carboxylic acid and q is the number of molecules of the extractant (amine) in the complex, has to be supposed. Ziegenfuss and Maurer[19] suggested (1,1), (2,1), and (3,1) complexes for the extraction of acetic acid with trioctylamine. Yoshizawa et al.[18] proposed that, in the extraction of propionic acid with trioctylamine in dodecane as a diluent, the formed complexes are (1,1), (2,1), (3,1), and (4,1), when the propionic acid concentration in the aqueous solution was less than 1.0 kmol·m^{-3}. Luque[12] showed that valeric acid and the secondary amine Amberlite LA-2 in toluene form (1,1), (2,1), and (3,1) complexes at aqueous acid concentrations up to 0.1 kmol·m^{-3}. Juang[9] suggested (1,1), (2,1), (3,1), and (4,1) complexes for the extraction of acetic acid by trioctylamine in xylene.

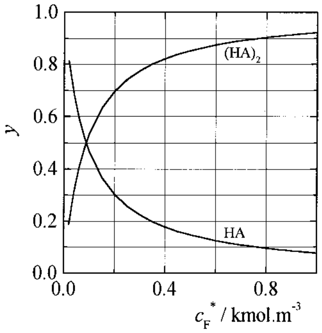

Figure 5. Molar fraction of the monomer and the dimer of butyric acid in pure n-alkanes calculated by eqs 36 and 37 versus aqueous concentration of butyric acid at 30 °C.

Some spectroscopic studies, which support the theory that complexes with more than one acid per amine are formed, can be found in the literature.[14,19,42,43] Chaikhorskii et al.[42] studied IR spectra of complexes of acetic acid and tridecylamine. The authors proposed the complex (3,1), in which an additional acid is hydrogen bonded to the (2,1) complex to form a cyclic arrangement around the amine nitrogen. Tamada and King[14] indicate in their spectroscopic study that the formation of the (1,1) complex involves an ion-pair or hydrogen-bond formation between the acid (succinic, maleic, and fumaric acids) and the amine (Alamine 336), while the (2,1) complex formation involves hydrogen bonding between the carboxyl of the second acid and the carboxylate of the first acid.

The molar fraction of the overall acid extracted in the form of the (p,1) complex in the solvent $y_{p,1}$ is defined by the relation

$$y_{p,1} = p[\overline{(HA)_pP}]/c^*_{aS} \qquad (35)$$

and the molar fractions of butyric acid physically dissolved in the solvent in the form of a monomer, y_M, and a dimer, y_d, are given by the equations

$$y_M = c_{MS}/c^*_{aS} = K_M c^*_F/c^*_{aS} \qquad (36)$$

$$y_d = 2c_d/c^*_{aS} \qquad (37)$$

The distribution of the monomer and the dimer in pure n-alkanes is presented in Figure 5. With increasing concentration of butyric acid in the aqueous phase, the ratio of the monomer decreases and the ratio of the dimer increases. The distributions of individual species in these solvents are given in Figure 6. With increasing concentration of extractant the ratio of the monomer and the dimer in the solvent decreases. At low acid concentrations, most of the butyric acid is in the form of the (1,1) complex. With increasing concentration of butyric acid, the concentration of this complex sharply decreases for all concentrations of trioctylamine. The molar fraction of the (2,1) and (3,1) complexes dramatically increases with the equilibrium aqueous concentration of butyric acid and reaches a maximum at about c^*_F = 0.05 kmol·m^{-3} for the (2,1) complex and at c^*_F = 0.20 kmol·m^{-3} for the (3,1) complex and then gradually decreases (Figure 6). The course of the mole fraction of complexes (4,1), (5,1), and (6,1) is similar for all concentrations of trioctylamine. The concentration

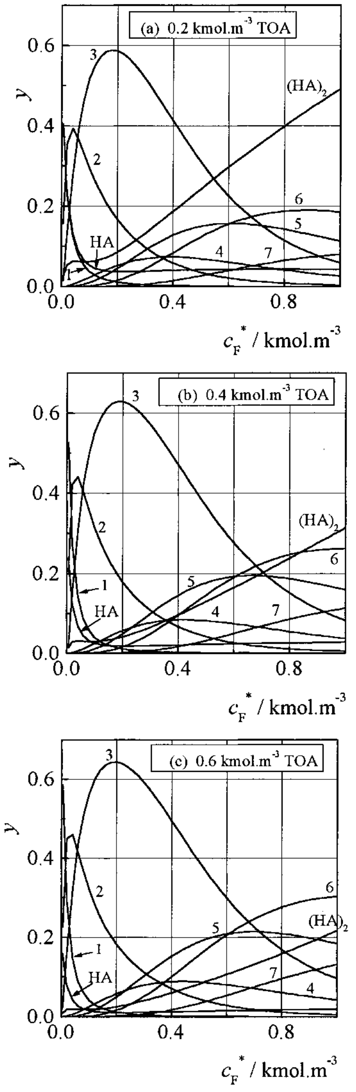

Figure 6. Molar fraction of individual species of butyric acid and complexes of butyric acid with the extractant in the solvents with different concentrations of trioctylamine calculated by eqs 35−37 versus aqueous concentration of butyric acid at 30 °C. Correlated according to the presented model (mechanism II). (1) HAP; (2) $(HA)_2P$; (3) $(HA)_3P$; (4) $(HA)_4P$; (5) $(HA)_5P$; (6) $(HA)_6P$; (7) $(HA)_7P$.

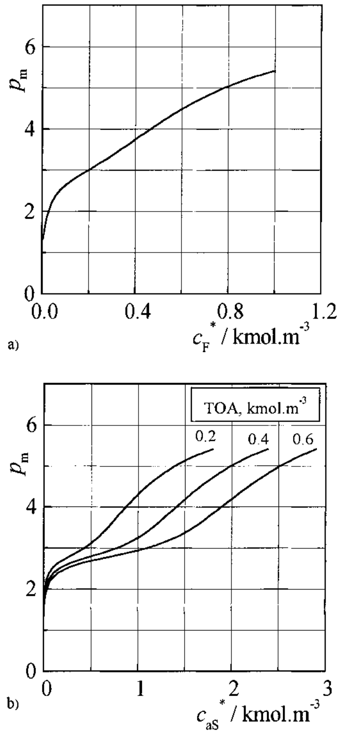

Figure 7. Mean value of the number of acid molecules in the complex, defined by eq 38 versus aqueous concentration of butyric acid (a) or versus equilibrium concentration of butyric acid in the solvent for different concentrations of trioctylamine (b). Correlated according to the presented model for mechanism II.

of these complexes increases with the aqueous concentration of butyric acid and reaches a maximum, whose value depends on the concentration of trioctylamine. The formation of the (7,1) complex monotonically increases with increasing aqueous concentration of butyric acid and the concentration of trioctylamine.

In the solvent with 0.2 kmol·m^{-3} of trioctylamine, it was found that the dominant mechanism at higher aqueous concentrations of butyric acid is the physical extraction in *n*-alkanes. In contradiction to this part, the formation of the (6,1) complex is preferential over other forms for solvents with higher concentration of trioctylamine and at higher aqueous concentrations of butyric acid.

The mean value of the number of acid molecules in the complex, p_m, can be calculated by the relation

$$p_m = \sum p \frac{p\lfloor\overline{(HA)_pP}\rfloor}{c_{aS}^* - c_{aSphys}^*} \qquad (38)$$

and is presented in Figure 7. The mean number of acid molecules in the complex gradually increases with the aqueous concentration of butyric acid, as shown in Figure 7a. The dependence of the size of the mean complex versus aqueous concentration of butyric acid is independent of the extractant concentration for the whole concentration range. On the other hand, the dependence of p_m on the equilibrium concentration of butyric acid in the organic phase depends on the extractant concentration (Figure 7b). With increasing concentration of trioctylamine the number of acid molecules in the mean complex decreases.

Coextraction of Water. In the mathematical model of extraction equilibria of an organic acid in the system solvent containing trioctylamine + water, which is presented in this work, the hydration of complexes was not considered. In the last period of experiments, the concentration of water in the organic phase has been determined. Results from these measurements are presented in Tables 2, 3, 5, and 7. The concentration of coextracted water in the solvent increases with increasing value of the aqueous concentration of butyric acid, as shown in Tables 2, 3, 5, and 7. The concentration of water coextracted with butyric acid in pure *n*-alkanes is about 10 times lower than the concentration of water coextracted with acid−trioctylamine complex. This shows that acid complexes are much more hydrated than the acid itself. The water content slightly decreases with increasing temperature. In the case of the solvent with trioctylamine, the effect of temperature is more pronounced. A decrease in the concentration of coextracted water with increasing temperature is a result of the temperature-dependent distribution coefficient of butyric acid, as Figure 10 reveals.

The hydration ratio of the acid, that is, moles of water extracted into pure *n*-alkanes with 1 mol of butyric acid, is below 0.1 and is decreasing with the concentration of acid to about 0.01, as presented in Figure 8. The concentration of water coextracted into pure *n*-alkanes is low and close to the analytical limit of the method used. This could

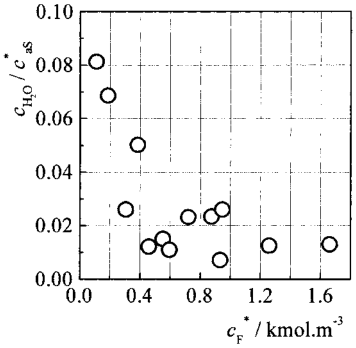

Figure 8. Moles of water coextracted in pure *n*-alkanes with 1 mol of butyric acid versus aqueous concentration of butyric acid at 30 °C.

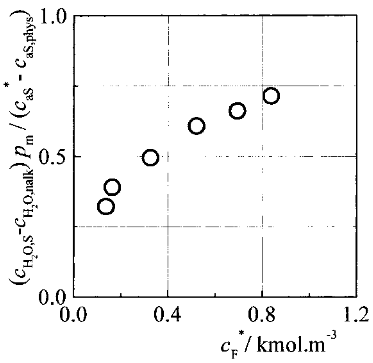

Figure 9. Moles of water coextracted in the organic phase with 1 mol of the complex of butyric acid with extractant versus aqueous concentration of butyric acid at 30 °C. Solvent: 0.4 kmol·m^{-3} of trioctylamine in *n*-alkanes.

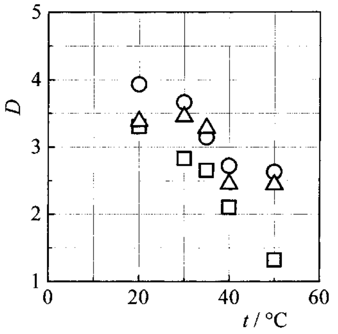

Figure 10. Effect of temperature on the distribution coefficient of butyric acid for the solvent containing 0.4 kmol·m^{-3} of trioctylamine in *n*-alkanes at the equilibrium concentration of butyric acid in the aqueous phase: (△) 0.48; (○) 0.2; (□) 0.1 kmol·m^{-3}.

be the reason for the scatter of the data in Figure 8.

The hydration ratio of the acid−extractant complex, that is, moles of water coextracted into the organic phase per mole of the complex, is shown in Figure 9. The hydration ratio of the complex increases with increasing concentration of butyric acid in the aqueous phase, as can be seen in Figure 9. The hydration ratio of the acid in pure *n*-alkanes and of the complex in the solvent with trioctylamine is around 0.02 and 0.5, respectively. Thus, the stoichiometry cannot be easily estimated and interpreted. Yoshizawa et al.[18] have found in the extraction of propionic acid with trioctylamine that the concentration of water increases with the concentration of acid and the extractant in dodecane, and becomes constant at a concentration of propionic acid in the aqueous phase above 3.0 kmol·m^{-3}, when 0.7 mol of water is extracted per mole of propionic acid. For the aqueous concentration of propionic acid 0.8 kmol·m^{-3}, about 0.35 mol of water per mole of acid is coextracted. At the same concentration of butyric acid, about 0.15 mol of water per mole of acid is coextracted. Vaňura and Kuča[26] have found for the extraction of citric acid with tertiary amine that the values of the hydration number of complexes (2,1), (3,2), and (6,5) are 1, 2, and 4, respectively. In the same system Bízek[28] assumed two amine + citric acid complexes in the organic phase, (1,1) and (2,1), and their hydration numbers 4 and 1, respec-

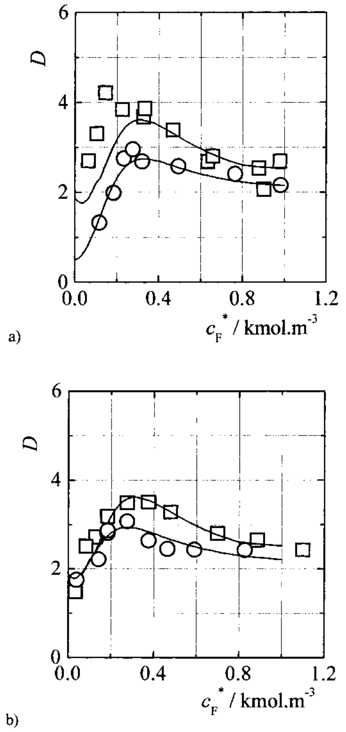

Figure 11. Distribution coefficient of butyric acid for the solvent containing 0.4 kmol·m^{-3} of trioctylamine in *n*-alkanes at various temperatures: (a) (□) 20 °C, (○) 50 °C; (b) (□) 35 °C, (○) 40 °C. Lines are correlated according to the presented model for mechanism II.

Table 9. Equilibrium Constants of the Formation of Complexes of Butyric Acid with Trioctylamine with Different Structures Estimated According to Mechanism II from Equilibrium Data at Various Temperatures[a]

t / °C	$K_{1,1}$ / m^3·kmol^{-1}	$K_{2,1}$ / (m^3·kmol^{-1})^2	$K_{3,1}$ / (m^3·kmol^{-1})^3	$K_{4,1}$ / (m^3·kmol^{-1})^4	$K_{5,1}$ / (m^3·kmol^{-1})^5	$K_{6,1}$ / (m^3·kmol^{-1})^6	$K_{7,1}$ / (m^3·kmol^{-1})^7
20	2.38	10.91	181.7	622.4	74.3	34.32	24.18
30	0.49	15.86	185.6	62.24	214.9	295.0	109.3
35	1.91	28.11	40.15	111.47	403.1	406.2	261.5
40	2.96[b]	15.95[b]	69.67[b]	39.6[b]	23.3[b]	35.0[b]	102.5[b]
	2.99	16.34	64.28	42.7	25.54	34.62	95.21
50	1.37[b]	4.71[b]	39.12[b]	71.93[b]	31.87[b]	20.49[b]	25.77[b]
	1.74	5.26	36.31	77.44	39.73	25.9	19.6

[a] Constants are estimated with values of K_M and K_d based on equilibrium data of butyric acid in pure *n*-alkanes at 30 °C. The value of the dissociation constant of butyric acid, K_a, at 25 °C was used. [b] Calculated with values of K_M and K_d estimated from equilibrium data of butyric acid in pure *n*-alkanes at 40 °C.

tively. This shows that coextraction of water with carboxylic acids is much lower than that with hydroxycarboxylic acids.

Temperature Dependence. The temperature dependence of the equilibrium data of butyric acid is plotted in Figures 10 and 11 and shown in Tables 5 and 7. With increasing temperature, the value of the distribution coefficient of butyric acid decreases, especially at lower acid concentrations (Figure 10), as has been found for several acids also in ref 44. The dependencies of the distribution coefficients of butyric acid at various temperatures versus equilibrium concentration of butyric acid in the aqueous phase are shown in Figure 11. The lines are correlated according to the presented model for mechanism II. This model fits the experimental results well, and the estimated extraction constants for different temperatures are presented in Table 9. The value of K_a was available only at 25 °C and has been used in the correlations for all temperatures. Extraction constants were estimated by the aid of values of K_M and K_d based on the equilibrium data of butyric acid in pure *n*-alkanes at 30 °C. The equilibrium data for the temperatures 40 °C and 50 °C were also correlated with the values of K_M and K_d estimated from data for pure *n*-alkanes at 40 °C. The value of $K_{1,1}$ is more or less independent of temperature, while the values of extraction constants for complexes (2,1), (3,1), and (4,1) slightly decrease with increasing temperature. The temperature dependencies of extraction constants for the higher complexes go through a maximum at about 35 °C, and the values of these constants are decreasing at temperatures above 35 °C, which is unusual and has to be proved by further experiments.

A more detailed thermodynamic analysis of data on temperature dependencies, in terms of apparent enthalpy and entropy of complexation reactions, will require more experimental data and a better understanding of the structure of formed complexes supported by their analytical estimation.

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