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Distribution of Butyric Acid between Water and Several Solvents

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Distribution of butyric acid between water and trioctylamine dissolved in 17 solvents (isoamyl alcohol, 1-nonanol, 1-decanol, 1-dodecanol, oleyl alcohol, methyl ethyl ketone, isopropyl methyl ketone, isobutyl methyl ketone, 4-heptanone, ethyl acetate, cyclohexyl acetate, dimethyl phthalate, dibutyl phthalate, *tert*-*b*utyl methyl ether, kerosene, *n*-hexane, toluene) and 4 vegetable oils (haselnut, corn, soybean, olive) have been studied at $T = 298.15$ K. The highest distribution coefficient for butyric acid is shown by trioctylamine dissolved in isoamyl alcohol. As the molar mass of the alcohol increases, the value of the distribution coefficient decreases. In the amine extraction, it was observed that the use of trioctylamine dissolved in alcohol increased the distribution coefficient between 6 and 7 times; dissolving in ketones increased the distribution between 3 and 5 times; dissolving in esters increased it 4 to 9 times; dissolving in *tert*-*b*utyl methyl ether increased it 2.3 times; dissolving in hydrocarbons increased it 10 to 18 times; and dissolving in vegetable oils increased it 12.5 times, all as compared to use of the pure solvents as extractant.

Introduction

The extraction of organic acids from aqueous media and other broth has been investigated in connection with the development of the biotechnology in the last decade. In previous studies, it has been stated that the extractability of most organic acids by conventional solvents is very low and that reactive extraction must be considered.[1−4] Aliphatic amine extractants with high molecular weight, such as trioctylamine and Alamine 336, are proposed for the reactive extraction of carboxylic acids. Due to their physical properties, they must always be used in the form of solutions in organic diluents. It was found that diluents, especially those with functional groups, can affect the extraction behavior of amine significantly.[5]

Butyric acid is employed in the diary or food industries to increase the fragrance of beverages or foodstuffs, in the pharmaceutical industry, and as a raw material for the production of biodegradable polymers based on β-hydroxybutyrate. This makes biotechnological production of butyric acid interesting. In recent years, with the increase in demand for naturally produced butyric acid with its wide use and the development of new biotechnology, the fermentation route for butyric acid production has become of more interest than the organic synthesis methods. Subsequent separation, purification, and concentration of the acid from the fermentation broth are difficult because of the high affinities of the acids for water. Solvent extraction process have been proposed for the recovery of organic acids from the fermented broth, and it has the advantage of continuously removing the acid and keeping the acids concentration in the broth to a low level. This is effective in suppressing product inhibition and increasing reactor efficiency.

A detailed evaluation of solvents for the extraction of butyric acid is not available in the literature. Nevertheless, Zigová et al.[6] carried out screening of 14 solvents for the extraction of butyric acid and a tertiary amine (Hostarex A327) in different diluents, C_8 to C_{18} alcohols (*n*-octanol, isodecanol, isotridecanol, oleyl alcohol), *n*-alkanes (narrow dodecane fraction with C_{10} to C_{13} *n*-alkanes), di-*n*-butyl ether, toluene, and vegetable oils (rapeseed and sunflower).

This study is a part of a research program on the recovery of butyric acid from dilute aqueous solutions using organic solvents. In this work, the extraction of butyric acid with trioctylamine in several solvents (isoamyl alcohol, 1-nonanol, 1-decanol, 1-dodecanol, oleyl alcohol, methyl ethyl ketone (MEK), isopropyl methyl ketone, isobutyl methyl ketone (MIBK), 4-heptanone, ethyl acetate, cyclohexyl acetate, dimethyl phthalate, dibutyl phthalate, *tert*-*b*utyl methyl ether, kerosene, *n*-hexane, toluene) and four vegetable oils (haselnut, corn, soybean, olive) at $T = 298.15$ K have been investigated, for which no such data were available in the literature.

Theoretical Section

Extraction of weak organic acids from the aqueous phase into the organic phase can occur as a result of physical and/or chemical interactions in the system. When the organic phase contains a complexing agent such as amine or another solvating extractant (S), the complex of the acid is formed according to the following overall reaction:

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

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

$$K_{pq} = \frac{C_{(\mathrm{HA})_p\mathrm{S}_q(\mathrm{org})}}{C^{p}_{\mathrm{HA(aq)}} \cdot C^{q}_{\mathrm{S(org)}}} \tag{2}$$

where C expresses concentration in molar terms. In the case

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

compound	$\rho^{293.15\mathrm{K}}(\mathrm{exp})$ g·cm^{-3}	$\rho^{293.15\mathrm{K}}(\mathrm{lit.})^{8}$ g·cm^{-3}	n(exp)	$n(\mathrm{lit.})^{8}$	source (mass purity)
water	0.9999	0.9982	1.3324	1.3330	bidistilled
butyric acid	$0.9523^{298.15}$	$0.9528^{298.15}$	1.3982	1.3980	Merck (>99 %)
trioctylamine	0.8107	0.8110	$1.4505^{292.15}$	$1.4510^{292.15}$	Merck (>95 %)
isoamyl alcohol	0.8084	0.8104	1.4075	1.4053	Merck (>98 %)
1-nonanol	0.8285	0.8280	1.4327	1.4333	Merck (>98 %)
1-decanol	0.8296	0.8297	1.4374	1.4372	Merck (>99 %)
1-dodecanol	$0.8311^{297.15}$	$0.8309^{297.15}$			Merck (>98 %)
oleyl alcohol	0.8490	0.8489	1.4601	1.4606	Merck (∼75 %)
methyl ethyl ketone	$0.7982^{298.15}$	$0.7999^{298.15}$	1.3793	1.3788	Carlo Erba (>99.8 %)
isopropyl methyl ketone	0.8048	0.8051	1.3884	1.3880	Merck (>98 %)
isobutyl methyl ketone	$0.7961^{298.15}$	$0.7965^{298.15}$	1.3958	1.3962	Merck (>99 %)
4-heptanone	0.8176	0.8174	1.4068	1.4069	Merck (>98 %)
ethyl acetate	0.9001	0.9003	1.3720	1.3723	Merck(>99 %)
cyclohexyl acetate	0.9684	0.9680	1.4421	1.4420	Merck (>98 %)
dimethyl phthalate	1.1904	1.1905	1.5135	1.5138	Merck (>99 %)
dibutyl phthalate	1.0471	1.0465	1.4909	1.4911	Merck (>99 %)
tert-butyl methyl ether	$0.7347^{298.15}$	$0.7353^{298.15}$	$1.3664^{298.15}$	$1.3664^{298.15}$	Merck (≥99 %)
kerosene	$0.7971^{288.15}$	$0.7750-0.8400^{288.15,b}$	$1.4457^{288.15}$	-	TUPRAS^{b}
n-hexane	$0.6604^{298.15}$	$0.6606^{298.15}$	$1.3729^{298.15}$	$1.3727^{298.15}$	Merck (>97 %)
toluene	0.8667	0.8668	1.4960	1.4961	Merck (≥99 %)
haselnut oil	0.9112		$1.460^{313.15}$	$1.461-1.465^{313.15,a}$	commercial
corn oil	$0.9231^{288.15}$	$0.920-0.928^{288.15,a}$	$1.468^{313.15}$	$1.465-1.466^{313.15,a}$	commercial
soybean oil	$0.9227^{288.15}$	$0.922-0.934^{288.15,a}$	$1.467^{313.15}$	$1.465-1.469^{313.15,a}$	commercial
olive oil	$0.9193^{288.15}$	$0.914-0.925^{288.15,a}$	$1.467^{313.15}$	$1.466-1.468^{313.15,a}$	commercial

[a] Ref 10. [b] Kerosene type jet fuel (JET A-1), TUPRAS Code No. 300, tupras.com.tr.

Table 2. Distribution Coefficients of Butyric Acid for Different Solvents Tested at T = 298.15 K^{a}

solvent type	solvent	D	$C_{\mathrm{BA(aq)}}$	literature
alcohol	isoamyl alcohol	7.81	0.100	this study
	n-octanol	6.31	0.137	ref 6
	1-nonanol	5.75	0.132	this study
	1-decanol	4.81	0.157	this study
	isodecanol	5.60	0.156	ref 6
	isotridecanol	4.82	0.170	ref 6
	1-dodecanol	4.37	0.170	this study
	oleyl alcohol	2.96	0.225	this study
	oleyl alcohol	2.85	0.259	ref 6
ketone	methyl ethyl ketone	4.46	0.185	this study
	isopropyl methyl ketone	7.73	0.108	this study
	isobutyl methyl ketone	6.46	0.126	this study
	4-heptanone	4.42	0.179	this study
ester	ethyl acetate	6.07	0.152	this study
	cyclohexyl acetate	5.08	0.156	this study
	dimethyl phthalate	3.73	0.206	this study
	dibutyl phthalate	2.19	0.307	this study
ether	*tert*-butyl methyl ether	9.57	0.102	this study
	di-*n*-butyl ether	2.96	0.259	ref 6
aromatic	toluene	2.40	0.293	ref 6
	toluene	2.37	0.294	this study
n-alkanes	*n*-alkanes	0.71	0.605	ref 6
	n-hexane	1.15	0.496	this study
	kerosene	0.90	0.531	this study
vegetable oil	haselnut oil	1.08	0.468	this study
	corn oil	1.08	0.462	this study
	soybean oil	1.08	0.469	this study
	olive oil	1.08	0.476	this study
	sunflower oil	0.99	0.523	ref 6
	rape seed oil	1.02	0.510	ref 6

[a] $C_{\mathrm{BA(aq)}}$, butyric acid concentration at equilibrium in aqueous phase.

where there is a single extractant molecule per complex (q = 1), stoichiometry as it is reported for monocarboxylic acids,[7,4] eq 2 can be written as

$$K_{p1} = \frac{C_{(\mathrm{HA})_p\mathrm{S(org)}}}{C^{p}_{\mathrm{HA(aq)}} \cdot C_{\mathrm{S(org)}}} \tag{3}$$

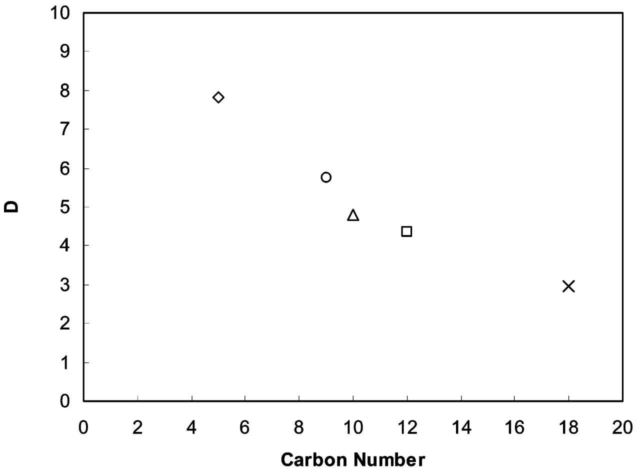

Figure 1. Distribution coefficient of butyric acid vs number of carbon atoms in alcohol molecule for alcohols used in this study: ◇, isoamyl alcohol; ○, 1-nonanol; △, 1-decanol; □, 1-dodecanol; ×, oleyl alcohol.

The distribution coefficient (D) is defined as the equilibrium ratio of total acid concentration in the organic and aqueous phases:

$$D = C_{\mathrm{HA(org)}}/C_{\mathrm{HA(aq)}} \tag{4}$$

where $C_{\mathrm{HA(org)}}$ and $C_{\mathrm{HA(aq)}}$ are the acid concentrations in organic and aqueous phases, respectively. The loading of the extractant (Z) is defined as the total concentration of acid in the organic phase divided by the total concentration of amine in organic phase:[1]

$$Z = C_{\mathrm{HA(org)}}/C_{\mathrm{S(org)}} \tag{5}$$

where $C_{\mathrm{S(org)}}$ is the amine concentration in organic phase.

In two-phase system, dissociation of the acid in the aqueous phase has to be taken into account. For butyric acid, it is stated that the dissociation of the acid is negligeble at pH lower than 2.7. Undissociated acid concentration under this pH is more than 99 % of total acid concentration.[6]

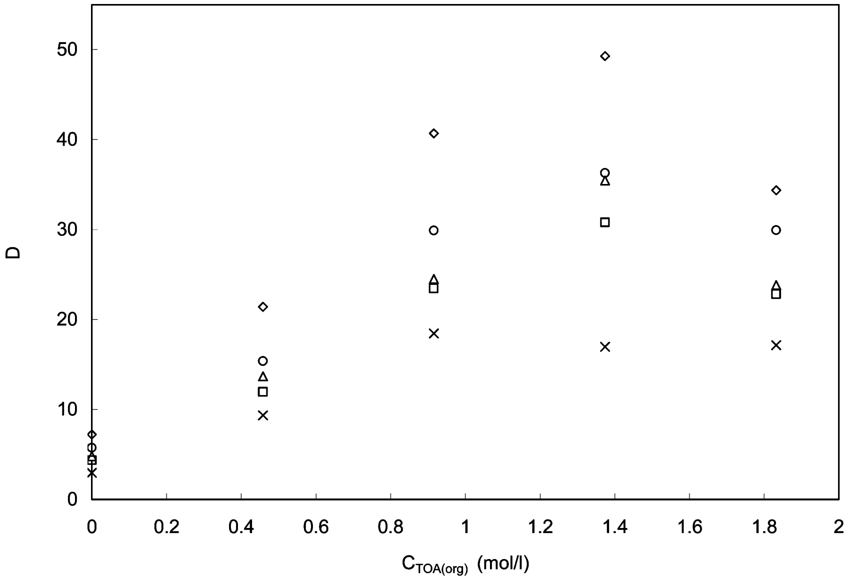

Figure 2. Change of distribution coefficients along with initial trioctylamine concentration in organic phase, $C_{TOA(org)}$, by using alcohol as diluent: ◇, isoamyl alcohol; ○, 1-nonanol; △, 1-decanol; □, 1-dodecanol; ×, oleyl alcohol.

Experimental Section

Chemicals. The purity of the chemicals was checked on the basis of their densities and refractive indexes at $T = (293 \pm 0.20)$ K. The measured values and the purity of water, butyric acid, trioctylamine, and solvents used in this study are listed in Table 1 along with sources and true densities given in the literature.[8] All chemicals were used without further purification. GC analysis did not detect any appreciable peaks of impurities. Deionized water was further distilled before use. Refractive indexes and densities were measured with Anton Paar (model 4500) apparatus. The estimated uncertainties in the measurements were in ± 0.0001 units. The physical properties measured are in good agreement with published values.

Apparatus and Procedure. Aqueous butyric acid solution was prepared from distilled water with an initial concentration about 1 $\text{mol}\cdot\text{L}^{-1}$. Organic phases are prepared either by pure solvents shown in Table 1 or by mixing trioctylamine with these solvents to produce solutions in different concentrations, in the range of (0.45 to 1.8) $\text{mol}\cdot\text{L}^{-1}$. Experiments were performed by shaking equal volumes (10 mL) of initial aqueous and organic phases, placed in glass flasks, in a shaker bath at $T = 298.15$ K for 5 h, which preliminary tests have shown to be a sufficient time for equilibrium. Thereafter the phases were separated after (5 to 8) h settling at $T = 298.15$ K. Temperature was controlled using an electronic controller with a precision of 0.1 K. All mixtures were prepared by weighing with a Mettler scale precision of ± 0.0001 g.

Butyric acid concentrations in aqueous solutions were determined by volumetric NaOH titration with a relative uncertainty of 1 %.[9] Acid analysis was checked against a material balance. It was seen that the deviation between the amount of acid analyzed and the amount of acid known by preparing the solutions by weighing did not exceed 3 %. The mutual solubilities of organic and aqueous phases were minimized by the preliminary saturation of diluent in water, and so the mutual solubilities are taken as negligible in the range of variables investigated.

Results and Discussion

Distribution of butyric acid between water and pure solvents used in this study at $T = 298.15$ K is presented in terms of distribution coefficients in Table 2. For all of the data listed in Table 2, the pH of the aqueous phase was lower than 2.7 where the dissociation of butyric acid was negligible. Among the solvents used in this study, the highest distribution coefficient is observed with *tert*-buthyl methyl ether, 9.57. Isoamyl alcohol shows the highest distribution value (7.81) between the alcohols used in this study and has a value close to that of isopropyl methyl ketone (7.73). The lowest distribution coefficient is observed with the kerosene (0.90). The distribution coefficient of butyric acid decreases with increasing molecular weight of alcohols. A plot of the distribution coefficient versus the number of carbon atoms in the molecule of alcohols is shown in Figure 1. The distribution coefficient of butyric acid for vegetable oils has a value of about 1, and for pure trioctylamine it reaches the highest value of 25.74.

The distribution coefficient of butyric acid for alcohols with trioctylamine sharply increases with increasing initial concentration of amine in organic phase (Figure 2). The acid + amine complex formation and the high solvation effect of alcohol, because of its polarity, forms a synergetic effect to a certain value of amine concentration (~1.4 $\text{mol}\cdot\text{L}^{-1}$ in general, ~1 $\text{mol}\cdot\text{L}^{-1}$ for oleyl alcohol), and, after this concentration the alcohol becomes trace, so the solvation effect of alcohol loses, and the distribution value tends to decrease. If water insoluble alcohol is present in the solvent, the distribution coefficient of monocarboxylic acids is higher in compared to pure alcohol. This is a consequence of a strong donor−acceptor interaction.

In the case of ketones as diluent for trioctylamine, similar trends are to observe particularly with isopropyl methyl ketone and MIBK, as shown in Figure 3. According to the results for trioctylamine extraction with the help of ketones the order was as follows:

isopropyl methyl ketone ≈ MIBK > MEK > 4-heptanone

Figure 4 demonstrates the influence of the used esters, *tert-b*utyl methyl ether, and vegetable oil (corn oil) on butyric acid distribution between water and organic phase. It can be seen that the extraction power of trioctylamine + diluent mixtures increases generally with increasing initial concentration of trioctylamine in organic phase.

The change of distribution coefficients along with initial trioctylamine concentration in various hydrocarbons are shown

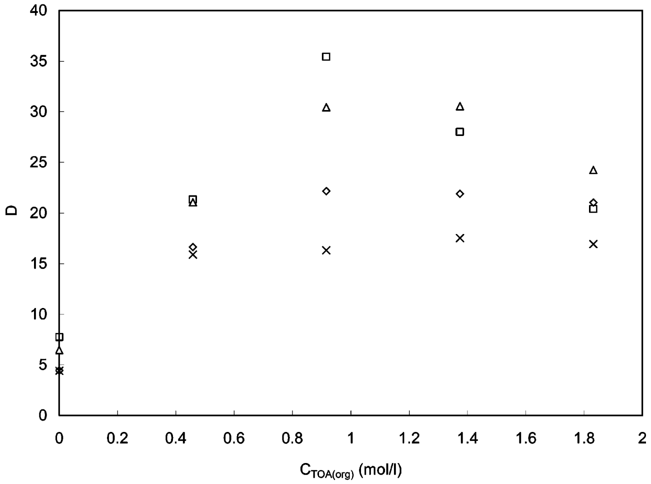

Figure 3. Change of distribution coefficients along with initial trioctylamine concentration in organic phase, $C_{TOA(org)}$, by using ketones as diluent: ◇, methyl ethyl ketone; □, isopropyl methyl ketone; △, isobutyl methyl ketone; ×, 4-heptanone.

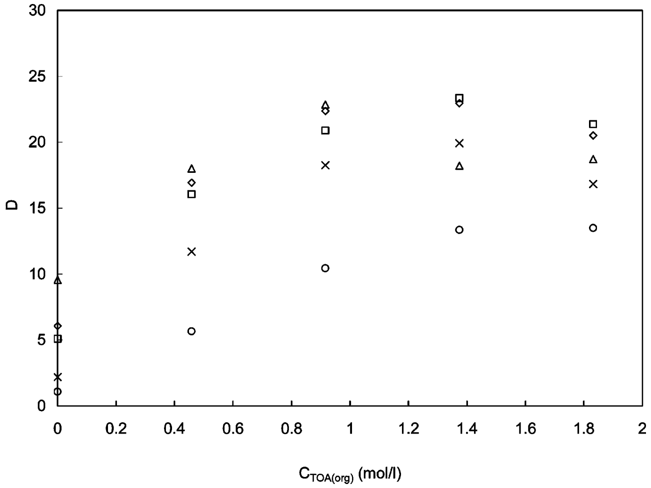

Figure 4. Change of distribution coefficients along with initial trioctylamine concentration in organic phase, $C_{TOA(org)}$, by using of various esters or *tert*-butyl methyl ether or corn oil as diluent: △, *tert*-butyl methyl ether; ○, corn oil; ◇, ethyl acetate; □, cyclohexyl acetate; ×, dibutyl phthalate.

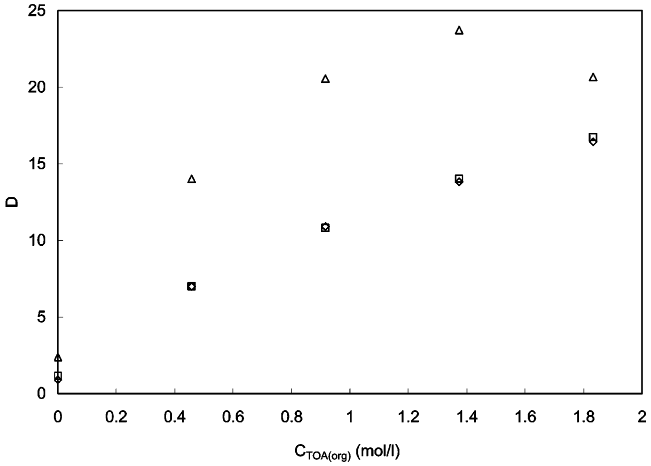

Figure 5. Change of distribution coefficients along with initial trioctylamine concentration in organic phase, $C_{TOA(org)}$, by using of various hydrocarbons as diluent: △, toluene; ◇, kerosene; □, *n*-hexane.

in Figure 5. It was observed that toluene, an aromatic diluent, shows higher distribution trend than *n*-hexane and kerosene, which has been rationalized as solvation due to interaction of the aromatic π electrons with acid−amine complex. Kerosene and *n*-hexane, being nonpolar diluents, give nearly the same distribution inclination.

Table 3. Effect of Trioctylamine Concentration on Loading

solvent	$C_{S(org)}$ / mol·L^{-1}	$C_{HA(org)}$ / mol·L^{-1}	Z	$C_{S(org)}$ / mol·L^{-1}	$C_{HA(org)}$ / mol·L^{-1}	Z
isoamyl alcohol	0.4580	0.9494	2.07	1.3741	0.9716	0.71
	0.9161	0.9677	1.06	1.8322	0.9635	0.53
1-nonanol	0.4580	0.9334	2.04	1.3741	0.9651	0.70
	0.9161	0.9599	1.05	1.8322	0.9588	0.52
1-decanol	0.4580	0.9283	2.03	1.3741	0.9647	0.70
	0.9161	0.9534	1.04	1.8322	0.9516	0.52
1-dodecanol	0.4580	0.9180	2.00	1.3741	0.9600	0.70
	0.9161	0.9537	1.04	1.8322	0.9502	0.52
oleyl alcohol	0.4580	0.8992	1.96	1.3741	0.9359	0.68
	0.9161	0.9421	1.03	1.8322	0.9354	0.51
methyl ethyl ketone	0.4580	0.9231	2.02	1.3741	0.9401	0.68
	0.9161	0.9393	1.03	1.8322	0.9423	0.51
isopropyl methyl ketone	0.4580	0.9464	2.07	1.3741	0.9554	0.70
	0.9161	0.9628	1.05	1.8322	0.9457	0.52
isobutyl methyl ketone	0.4580	0.9459	2.07	1.3741	0.9590	0.70
	0.9161	0.9590	1.05	1.8322	0.9523	0.52
4-heptanone	0.4580	0.9393	2.05	1.3741	0.9390	0.68
	0.9161	0.9350	1.02	1.8322	0.9379	0.51
ethyl acetate	0.4580	0.9240	2.02	1.3741	0.9437	0.69
	0.9161	0.9420	1.03	1.8322	0.9399	0.51
cyclohexyl acetate	0.4580	0.9365	2.04	1.3741	0.9504	0.69
	0.9161	0.9448	1.03	1.8322	0.9430	0.51
dibutyl phthalate	0.4580	0.9161	2.00	1.3741	0.9393	0.68
	0.9161	0.9369	1.02	1.8322	0.9258	0.51
tert-butyl methyl ether	0.4580	0.9255	2.02	1.3741	0.9402	0.68
	0.9161	0.9411	1.03	1.8322	0.9457	0.52
kerosene	0.4580	0.9423	2.06	1.3741	1.0044	0.73
	0.9161	0.9866	1.08	1.8322	1.0152	0.55
n-hexane	0.4580	0.9421	2.06	1.3741	1.0053	0.73
	0.9161	0.9858	1.08	1.8322	1.0163	0.55
toluene	0.4580	1.0054	2.19	1.3741	1.0335	0.75
	0.9161	1.0270	1.12	1.8322	1.0273	0.56
corn oil	0.4580	0.8608	1.88	1.3741	0.9288	0.68
	0.9161	0.9150	1.00	1.8322	0.9275	0.51

The effect of trioctylamine concentration on loading is shown in Table 3. At low amine concentrations overloading have been observed. Overloading (loading greater than unity) indicates the complexes with more than one acid molecule per amine molecule have formed.

As result, it was seen that the use of trioctylamine dissolved in alcohol has increased the distribution coefficient between (6 to 7) times; dissolved in ketones it increased between (3 to 5) times; dissolved in ester it increased between (4 to 9) times; dissolved in *tert-b*utyl methyl ether it increased 2.3 times; dissolved in hydrocarbons it increased between (10 to 18) times; and dissolved in vegetable oils it increased 12.5 times, all as compared to use of the pure solvents as extractant.

Conclusion

The extraction of butyric acid with trioctylamine in several solvents (isoamyl alcohol, 1-nonanol, 1-decanol, 1-dodecanol, oleyl alcohol, methyl ethyl ketone (MEK), isopropyl methyl ketone, isobutyl methyl ketone (MIBK), 4-heptanone, ethyl acetate, cyclohexyl acetate, dimethyl phthalate, dibutyl phthalate, *tert-b*utyl methyl ether, kerosene, *n*-hexane, toluene, and four vegetable oils (haselnut, corn, soybean, olive)) at $T = 298.15$ K have been investigated. It was seen that the use of trioctylamine dissolved in alcohol has increased the distribution coefficient between (6 to 7) times; dissolved in ketones it increased between (3 to 5) times; dissolved in ester it increased between (4 to 9) times; dissolved in *tert-b*utyl methyl ether it increased 2.3 times; dissolved in hydrocarbons it increased between (10 to 18) times; and dissolved in vegetable oils it increased 12.5 times, all as compared to use of the pure solvents as extractant.

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