Equilibrium Studies of Extraction of Levulinic Acid by (Trioctylamine (TOA) + Ester) Solvents

Hasan Uslu*,†,‡ and Ş. İsmail Kırbaşlar‡

Beykent University, Engineering & Architecture Faculty, Chemical Engineering Department, Ayazağa Köyü, İstanbul, Turkey, and İstanbul University, Engineering Faculty, Chemical Engineering Department, 34320, İstanbul, Turkey

Reactive extraction of levulinic acid has been done at 298.15 K. All experiments are reported on the extraction of levulinic acid by trioctylamine (TOA) dissolved in 11 different ester solvents (ethyl propionate, dimethyl phthalate, hexyl acetate, cyclohexyl acetate, dimethyl adipate, propyl acetate,, dimethyl glutarate, dimethyl fumarate, diethyl sebacate, and diethyl carbonate), as well as single solvents. Experimental results of batch extraction experiments are calculated and reported as distribution coefficients ($K_D = \bar{c}_{HA}/c_{HA,total}$), loading factors ($T_T$), stoichiometric loading factor (T_S), separation factor (S_f), and extraction efficiency (E). The diethyl carbonate was found to be the most effective solvent with a maximum distribution value of 5.75. Maximum values of possible equilibrium complexation constants for (acid + amine) (1:1) K_{11} and (2:1) K_{21} were determined as 3.32 and 32.59 for diethyl carbonate, respectively.

Introduction

Levulinic acid, a carboxylic acid containing a ketone structure, is a clear to brownish semisolid that melts at 37 °C and is soluble in alcohols, ethers, and chloroform. Levulinic acid can be used as an acidulant in foods and beverages. It is used as an intermediate to manufacture synthetic fibers, pharmaceuticals, pesticides, plastics, rubber, and synthetic fibers. It is used to manufacture perfumery, food additives, fuel additives, herbicides, solder flux, stabilizers, and printing inks. Levulinic acid and its esters are also used as platicizers and solvents in polymers, textiles, and coatings. Therefore, it is important to separate and purify levulinic acid.[1]

In the production of carboxylic acids by fermentation, the free acid is required for the manufacture of commodities and specialty chemicals. Moreover, contaminating proteins and cell byproducts need to be removed from the final product. Thus, to be cost-effective, the separation process requires the removal of cells and protein-like impurities, concentration of the salt, conversion of the acid salt into the free acid, and purification of the free acid to its required purity.[2] As such, the costs associated with product recovery, concentration, acidification, and purification have been very high in the past accounting for (60 to 70) % of the product cost and making fermentation-based chemical technology impractical.[3,4]

There are many processes to separate carboxylic acids from aqueous solutions. The oldest method is based on precipitation of the insoluble calcium salts of carboxylic acids with $Ca(OH)_2$ or $CaCO_3$ followed by reacidification with H_2SO_4.[5] Another method is liquid−liquid extraction in which a solute is transferred between an aqueous and water-immiscible organic phase based on the physical contact of the two phases. Some scientists used membranes that involve electrodialysis, nanofiltration, and reverse osmosis. The newest method is reactive extraction which is based on extraction. The extractant in the organic phase reacts with the material in the aqueous phase, and the reaction complexes formed are then solubilized in the organic phase. Extractants such as hydrocarbon, phosphorus, and aliphatic amine extractants are mainly used in the reactive extraction of carboxylic acids. Hong and Hong studied reactive extraction of succinic acid with tripropylamine (TPA) in various diluents and found that the distribution coefficient and the extraction efficiency increase with an increase in TPA concentration.[6] Inci studied the extraction of citric acid and glycolic acid by Alamine 336 and tri-*n*-octylamine in four diluting solvents.[7,8] Uslu has made both equilibrium and kinetic studies of propionic acid and tartaric with Alamine 336.[9,10] Kyuchoukov et al.[11,12] investigated simultaneously the influence of active and inert diluents on the extraction of lactic acid by tri-*n*-octylamine (TOA) and the tri-*iso*-octylamine (TIOA) and separation of tartaric and lactic acids by solvent extraction. Qin et al.[13] studied the extraction equilibria of glycolic acid and glyoxylic acid with trialkylphosphine oxide and trioctylamine. Sabolova et al.[14] reported liquid−liquid equilibria of butyric acid in water plus solvent systems with the reactive extractant trioctylamine. Martak and Schlosser[15] studied liquid−liquid equilibria of dimethylcyclopropane carboxylic acid in water + solvent systems with trioctylamine as an extractant.

In this study, we have investigated the extraction of levulinic acid from aqueous solutions with trioctylamine (TOA) in several solvents. Eleven esters (ethyl propionate, dimethyl phthalate, hexyl acetate, cyclohexyl acetate, dimethyl adipate, propyl acetate,, dimethyl glutarate, dimethyl fumarate, diethyl sebacate, diethyl carbonate) have been used as solvents to dilute TOA. Experiments have been made also with the single solvents.

The survey of the literature shows that the reactive extraction of levulinic acid has not been reported for these extraction systems.

Theory of Complex Formation

As Young et al. explained, the carboxylic acids tend to form dimers in the organic phase because of intermolecular hydrogen bonding. The following three assumptions must be taken into account in the reactive extraction to explain the mechanism of the acid + amine complex in monocarboxylic acids:[16]

* Corresponding author. E-mail: hasanuslu@gmail.com.
† Beykent University.
‡ Istanbul University.

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(1) The solubility of trioctlyamine (TOA) in the aqueous phase is negligible.

(2) TOA reacts only with the undissociated form of the acid.

(3) The solubility of esters in the aqueous phase is negligible.

Reactive extraction of carboxylic acids with an amine-based extractant can be described by the following equations:

$$\mathrm{HA(1)} + \overline{\mathrm{R_3N}}\mathrm{(2)} \leftrightarrow \overline{\mathrm{HA-R_3N}}\mathrm{(3)}, \qquad K_{11} = \frac{a_3^1}{a_1^1 \cdot a_2^1} \quad (1)$$

$$2\mathrm{HA(1)} + \overline{\mathrm{R_3N}}\mathrm{(2)} \leftrightarrow \overline{\mathrm{(HA)_2-R_3N}}\mathrm{(4)}, \qquad K_{21} = \frac{a_4^1}{a_1^2 \cdot a_2^1} \quad (2)$$

In eqs 1 and 2, a_1 is the activity of the undissociated part of the acid in the aqueous phase; a_2 is the activity of amine in the organic phase; a_3 is activity of the acid + amine (1:1) complex in the organic phase; and a_4 is the activity of the acid + amine (2:1) complex in the organic phase.

Equations 1 and 2 could be written in terms of dissociated species, hydrogen ions, and acid radical anions, as it is used in the literature on amine extraction of acids.[17] Taking into account the dissociation equilibrium, one can show that both concepts are equivalent, the only difference being the values of equilibrium constants. Replacing the activities by the products of molalities and molal activity coefficients, eq 2 takes the form

$$K = (m_{(\mathrm{HA})\cdot(\mathrm{R_3N})}\gamma_{(\mathrm{HA})\cdot(\mathrm{R_3N})})/(m_{(\mathrm{HA})} \cdot \gamma_{(\mathrm{HA})})\cdot(m_{(\mathrm{R_3N})} \cdot \gamma_{(\mathrm{R_3N})})^* \quad (3)$$

where $m_{(\mathrm{HA}).(\mathrm{R_3N})}$ is the molality of the complex and $\gamma_{(\mathrm{HA})\cdot(\mathrm{R_3N})}$ is the molal activity coefficient of the complex.

The concentration of undissociated monocarboxylic acid is given by

$$C_{\mathrm{HA}} = \frac{C_{\mathrm{HA,total}}}{1 + 10^{\mathrm{pH} - \mathrm{p}K_{\mathrm{A}}}} \quad (4)$$

The total equilibrium concentration of monocarboxylic acid in the organic phase is obtained by the following equation

$$\bar{C}_{\mathrm{HA}} = \bar{C}_{\mathrm{HA-R_3N}} + 2\bar{C}_{\mathrm{(HA)_2-R_3N}} = K_{11} \cdot C_{\mathrm{HA}} \cdot \bar{C}_{\mathrm{R_3N}} + 2K_{21} \cdot C_{\mathrm{HA}}^2 \cdot \bar{C}_{\mathrm{R_3N}} \quad (5)$$

Free trioctylamine concentration in the organic phase can be calculated as

$$\bar{C}_{\mathrm{R_3N}} = C_{\mathrm{R_3N}}^0 - \bar{C}_{\mathrm{HA-R_3N}} - \bar{C}_{\mathrm{(HA)_2-R_3N}} = C_{\mathrm{R_3N}}^0 - K_{11} \cdot C_{\mathrm{HA}} \cdot \bar{C}_{\mathrm{R_3N}} - K_{21} \cdot C_{\mathrm{HA}}^2 \cdot \bar{C}_{\mathrm{R_3N}} \quad (6)$$

By combining eqs 5 and 6, the loading factor T_{T} can be written in the form

$$T_{\mathrm{T}} = \frac{\bar{C}_{\mathrm{HA}}}{C_{\mathrm{R_3N}}^0} = \frac{K_{11} \cdot C_{\mathrm{HA}} + 2K_{21} \cdot C_{\mathrm{HA}}^2}{1 + K_{11} \cdot C_{\mathrm{HA}} + K_{21} \cdot C_{\mathrm{HA}}^2} \quad (7)$$

The stoichiometric loading factor, T_{s}, is the ratio of the overall complexed acid to total amine in the organic phase. This factor includes a correction term ($vC_{\mathrm{lev}}^{*\mathrm{s}}$) ($C_{\mathrm{lev}}^{*\mathrm{s}}$ is the concentration of acid in the aqueous phase after extraction by single pure solvents) for the amount of acid extracted by the diluent in the solvent mixture ($C_{\mathrm{TOA}}^* = C_{\mathrm{R_3N}}^0$).

$$T_{\mathrm{s}} = \frac{(C_{\mathrm{lev}}^* - v \cdot C_{\mathrm{lev}}^{*\mathrm{s}})}{C_{\mathrm{TOA}}^*} \quad (8)$$

In eq 13, v is the volume fraction of diluent in mixture and $C_{\mathrm{lev}}^{*\mathrm{s}}$ is the concentration of acid extracted by the pure diluent alone not containing amine.

Distribution coefficients for levulinic acid extracted from water into the organic phase were determined as

$$K_{\mathrm{D}} = \frac{\bar{C}_{\mathrm{HA}}}{C_{\mathrm{HA,total}}} \quad (9)$$

The degree of extraction is defined as the following equation

$$E = \left(1 - \frac{C_{\mathrm{HA}}}{C_{\mathrm{HA,total}}}\right) \cdot 100 \quad (10)$$

The relative proportion between physical interaction and chemical reaction was evaluated with respect to a modified separation factor which is expressed by the ratio of the complexed acid to overall extracted acid

$$s_{\mathrm{f}} = \frac{C_{\mathrm{lev}}^*}{C_{\mathrm{lev}}^* + C_{\mathrm{A^-}}^*} \quad (11)$$

Material and Experimental Procedure

Materials. TOA, which is a synonymous name to *N*,*N*-dioctyl-1-octanamine ((Merck Co.) > 99 %), is an anion exchange extractant and a colorless liquid with a molecular weight of 353.67. Levulinic acid (Merck, > 99 %, molecular weight: 116.12, and pK_{a} 4.59) and ethyl propionate, dimethyl phthalate, hexyl acetate, cyclohexyl acetate, dimethyl adipate, propyl acetate,, dimethyl glutarate, dimethyl fumarate, diethyl sebacate, and diethyl carbonate were supplied from MERCK and Fluka. All chemicals were used without further purification.

Experimental Procedure. The known masses of levulinic acid were dissolved in distilled water to prepare the solutions with about initial concentrations of acid of 0.689 mol·L^{-1}. The solvents were used to dissolve amine. The organic phases were prepared by the dissolution of TOA in the diluents to produce solutions with approximately five constant concentrations, in the range of (0.590 to 1.731) mol·L^{-1}. Known volumes of aqueous and organic solutions of known concentration were added to 50 mL Erlenmeyer flasks and equilibrated in a Nuve Shaker ST402 bath at 298.15 K for 2 h, which preliminary tests demonstrated to be a sufficient time for equilibration. Thereafter, the mixture was kept in a bath for another 3 h to reach full separation of phases. After equilibration, both phases were separated by centrifugation at 1200 rpm for about 7 min for better phase separation.

The aqueous phase samples were analyzed for solute concentration by using titration with sodium hydroxide (relative uncertainty: 1 + %) as a standard solution and phenolphthalein as the indicator, with each measurement being preformed in duplicate. In most cases, the deviation between the amount of acid analyzed and the amount of acid known by preparing the solutions by mass did not exceed 3 + %. The solubilities of amine salts and diluents in the aqueous phase were negligible in the range of variables investigated.

The pH value of the aqueous phase was determined with a pH meter (Hanna pH 211 Microprocessor pH meter) with a deviation ± 0.01.

Table 1. Results for Extraction of Levulinic Acid with the TOA + Ester System[a]

solvents (esters)	C_{TOA} / mol·L^{-1}	pH_{aq}	C^*_{lev} / mol· L^{-1}	K_D	T_T	T_S	S_f	E
diethylsebacate	0.590	3.39	0.172	0.332	0.291	0.286	0.974	24.963
	0.861	3.63	0.231	0.504	0.268	0.261	0.967	33.526
	1.158	3.86	0.288	0.718	0.248	0.240	0.956	41.799
	1.431	4.06	0.338	0.963	0.236	0.227	0.941	49.056
	1.731	4.25	0.387	1.281	0.223	0.214	0.922	56.168
dimethyl phthalate	0.590	3.48	0.194	0.392	0.328	0.319	0.972	28.156
	0.861	3.65	0.236	0.521	0.274	0.261	0.966	34.252
	1.158	3.95	0.312	0.827	0.269	0.255	0.949	45.283
	1.431	4.15	0.361	1.100	0.252	0.237	0.933	52.394
	1.731	4.34	0.409	1.461	0.236	0.220	0.910	59.361
hexyl acetate	0.590	3.56	0.215	0.453	0.364	0.351	0.969	31.204
	0.861	3.80	0.274	0.660	0.318	0.300	0.959	39.767
	1.158	4.06	0.339	0.968	0.292	0.273	0.941	49.202
	1.431	4.25	0.387	1.281	0.270	0.249	0.921	56.168
	1.731	4.46	0.438	1.745	0.253	0.231	0.893	63.570
cyclohexyl acetate	0.590	3.55	0.212	0.444	0.359	0.347	0.970	30.769
	0.861	3.79	0.271	0.648	0.314	0.298	0.960	39.332
	1.158	4.03	0.333	0.935	0.287	0.268	0.943	48.330
	1.431	4.23	0.381	1.237	0.266	0.246	0.924	55.297
	1.731	4.43	0.432	1.681	0.249	0.228	0.896	62.699
dimethyladipate	0.590	3.61	0.226	0.488	0.383	0.369	0.968	32.801
	0.861	3.84	0.284	0.701	0.329	0.310	0.957	41.219
	1.158	4.12	0.353	1.050	0.304	0.283	0.936	51.233
	1.431	4.28	0.393	1.327	0.274	0.251	0.918	57.039
	1.731	4.54	0.458	1.982	0.264	0.240	0.878	66.473
dimethyl glutarate	0.590	3.66	0.238	0.528	0.403	0.387	0.966	34.542
	0.861	3.89	0.296	0.753	0.343	0.322	0.954	42.960
	1.158	4.16	0.364	1.120	0.314	0.290	0.932	52.830
	1.431	4.34	0.409	1.461	0.285	0.259	0.910	59.361
	1.731	4.58	0.469	2.132	0.270	0.243	0.870	68.069
dimethyl succinate	0.590	3.69	0.247	0.559	0.418	0.401	0.964	35.849
	0.861	3.93	0.305	0.794	0.354	0.330	0.951	44.267
	1.158	4.21	0.376	1.201	0.324	0.297	0.926	54.571
	1.431	4.42	0.428	1.639	0.299	0.270	0.899	62.119
	1.731	4.65	0.485	2.377	0.280	0.250	0.857	70.392
dimethyl fumarate	0.590	3.75	0.262	0.613	0.444	0.424	0.961	38.026
	0.861	4.04	0.333	0.935	0.386	0.360	0.943	48.330
	1.158	4.31	0.400	1.384	0.345	0.315	0.915	58.055
	1.431	4.57	0.466	2.089	0.325	0.293	0.872	67.634
	1.731	4.84	0.533	3.416	0.307	0.274	0.808	77.358
isopropyl acetate	0.590	3.85	0.285	0.705	0.483	0.461	0.956	41.364
	0.861	4.15	0.360	1.094	0.418	0.388	0.933	52.249
	1.158	4.39	0.422	1.580	0.364	0.331	0.903	61.248
	1.431	4.67	0.490	2.462	0.342	0.306	0.852	71.117
	1.731	4.95	0.561	4.382	0.324	0.286	0.774	81.422
ethyl propionate	0.590	3.87	0.291	0.731	0.493	0.470	0.955	42.235
	0.861	4.17	0.366	1.133	0.425	0.394	0.931	53.120
	1.158	4.03	0.330	0.919	0.285	0.250	0.944	47.895
	1.431	4.72	0.503	2.704	0.351	0.314	0.840	73.004
	1.731	4.99	0.573	4.939	0.331	0.292	0.758	83.164
diethyl carbonate	0.590	3.90	0.298	0.762	0.505	0.481	0.953	43.251
	0.861	4.21	0.375	1.194	0.435	0.403	0.927	54.426
	1.158	4.48	0.443	1.800	0.382	0.346	0.889	64.296
	1.431	4.69	0.496	2.569	0.346	0.307	0.847	71.988
	1.731	5.05	0.587	5.754	0.339	0.298	0.739	85.195

[a] C_{TOA} is the concentration of TOA in the organic phase; C^*_{lev} is the concentration of levulinic acid in the organic phase; K_D is the distribution coefficient; T_T is the loading factor; T_s is the stoichiometric loading factor; S_f is the separation factor; and E is the extraction efficiency.

Discussion of Results

The extraction of levulinic acid by TOA dissolved in 11 different esters (ethyl propionate, dimethyl phthalate, hexyl acetate, cyclohexyl acetate, dimethyl adipate, propyl acetate, dimethyl succinate, dimethyl glutarate, dimethyl fumarate, diethyl sebacate, diethyl carbonate) was studied. The results of the equilibrium data on the reactive extraction of levulinic acid from the aqueous phase to the organic phase were presented in Table 1 and Figure 1. The prepared constant concentrations of TOA in various solvents were in the range of (0.590 to 1.741) mol·L^{-1}. The initial concentration of levulinic acid in the aqueous phase was 0.689 mol·L^{-1}. As can be seen from Figure 1, the extraction power of the TOA + diluent mixture changes with the increasing initial concentrations of TOA in the organic phase. According to Table 1 and Figure 1 (figures were drawn for only six solvents so as not to cause any confusion), the distribution coefficients for levulinic acid extractions by TOA were obtained from the following obvious orders which were found for the respective: diethyl carbonate > ethyl propionate > isopropyl acetate > dimethyl fumarate > dimethyl succinate > dimetyl glutarate > dimethyl adipate > cyclohexylacetate > hexylacetate > dimethyl phthalate > diethylsebacate. The highest extraction efficiency of levulinic acid that has been found is 85.195 % using diethyl carbonate in the vicinity of 1.731

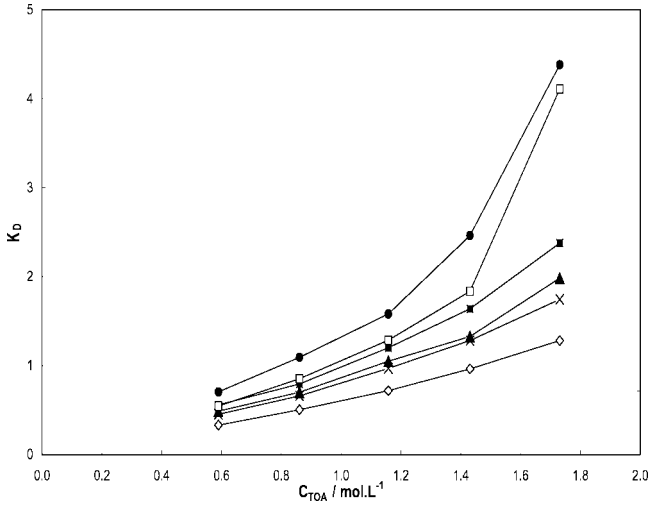

Figure 1. Plot of distribution coefficients K_D against concentration of TOA (C_{TOA}): ●, diethyl carbonate; □, isopropyl acetate; ■, dimethyl succinate; ▼, dimethyladipate; ×, hexyl acetate; ◇, diethylsebacate.

Table 2. Results for Physical Extraction of Levulinic Acid with Pure Solvents[a]

	solvents	pH_{aq}	C^*_{lev} / mol·L^{-1}	K_D	E
esters	diethylsebacate	2.85	0.036	0.055	5.2249
	dimethyl phthalate	2.96	0.065	0.104	9.4339
	hexylacetate	3.06	0.090	0.150	13.062
	cyclohexylacetate	3.05	0.086	0.142	12.481
	dimethyladipate	3.10	0.099	0.167	14.368
	dimetylglutarate	3.15	0.112	0.194	16.255
	dimethylsuccinate	3.20	0.124	0.219	17.997
	dimethylfumarate	3.25	0.137	0.248	19.883
	isopropylacetate	3.32	0.154	0.287	22.351
	ethylpropionate	3.34	0.159	0.300	23.076
	diethylcarbonate	3.37	0.167	0.319	24.238

[a] C_{lev} is the concentration of levulinic acid in the organic phase; K_D is the distribution coefficient; and E is the extraction efficiency.

mol·L^{-1} concentration value of TOA. The acid concentration in the organic phase at equilibrium C_{HA} increases from (0.172 to 0.587) mol·L^{-1} with increasing concentration of TOA from (0.590 to 1.731) mol·L^{-1}. Distribution coefficientsincrease from 0.332 to 5.754 with decreasing initial TOA concentration among all the esters used in this study. It can be obviously seen from Tables 1 and 2 that the increase of amine concentration brings about a gradual increase of extraction efficiency.

These results can depend on two properties of solvent. One of them is the molecular size of the solvent which is regarding its molecular diameter, as if its molecules were spherical. This diameter characterizes the "cavity" occupied by a solvent molecule in the liquid solvent. At the same time, this can be described as the mean distance between the centers of mass of two adjacent molecules in the liquid. As the diameter of the solvent molecules increases, the solvation powers of the solvents decrease.[18]

Another property is polarity of solvent. Polarity is a function of transition energy, E_T or Z. Kosower[19,20] defined the polarity parameter, Z, as the molar transition energy, E_T, which is expressed in kcal·mol^{-1}, for the CT absorption band of 1-ethyl-4-(methoxycarbonyl)pyridinium iodide in the appropriate solvent. The stronger the stabilizing effect of the solvent on the ground-state ion pair as compared with the less dipolar radical pair in the excited state, the higher this transition energy and, thus, the Z value. A high Z value corresponds to high solvent polarity. Dimroth and Reichardt[21] have proposed a solvent polarity parameter, $E_T(30)$, based on the transition energy for the longest-wavelength solvatochromic absorption band of the pyridinium *N*-phenolate betaine dye. Owing to this exceptionally large displacement of the solvatochromic absorption band, the $E_T(30)$ values provide an excellent and very sensitive characterization of the polarity of solvents, high $E_T(30)$ values corresponding to high solvent polarity.[19] Molecular weight is an affective property on polarity of esters. Long chain esters have higher polarity than short chain esters. It has been observed that because the chain length in the esters increases their polarity decreases, and as a result, the complex dissolving capacity which is formed in the organic phase decreases.

In addition to levulinic acid reactive extraction, the physical extraction of levulinic acid was studied for a better understanding of the amine effect on levulinic acid. Table 2 presents the extraction of levulinic acid by pure solvents. Generaly, all solvents gave low distribution coefficients. With the help of pure diethylcarbonate, the highest extraction degree of 24.238 % of

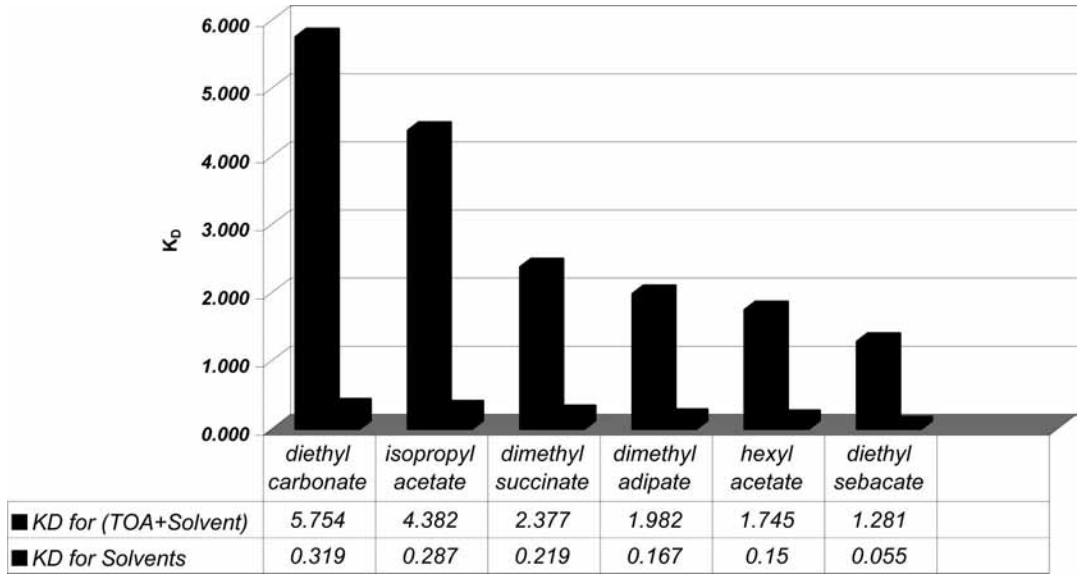

Figure 2. Comparison of distribution coefficients K_D between pure solvent and TOA + solvent (ester) for extraction of levulinic acid.

Table 3. Values of the Complexation Constant of Levulinic Acid for Various Diluents + TOA[a]

solvents (esters)	K_{11}	K_{21}	C_{TOA} / mol·L^{-1}	solvents (esters)	K_{11}	K_{21}
diethylsebacate	0.564	1.091	0.590	dimethyl succinate	0.947	2.143
	0.586	1.279	0.861		0.922	2.402
	0.620	1.547	1.158		1.037	3.314
	0.672	1.917	1.431		1.145	4.390
	0.740	2.451	1.731		1.373	6.732
dimethyl phthalate	0.664	1.342	0.590	dimethyl fumarate	1.039	2.435
	0.605	1.336	0.861		1.086	3.051
	0.715	1.895	1.158		1.195	4.135
	0.769	2.344	1.431		1.460	6.548
	0.843	3.013	1.731		1.973	12.652
hexyl acetate	0.768	1.622	0.590	isopropyl acetate	1.196	2.959
	0.767	1.847	0.861		1.271	3.863
	0.836	2.389	1.158		1.365	5.112
	0.895	2.965	1.431		1.720	8.646
	1.008	4.016	1.731		2.532	19.781
cyclohexyl acetate	0.753	1.579	0.590	ethyl propionate	1.239	3.113
	0.753	1.801	0.861		1.316	4.074
	0.807	2.269	1.158		0.794	2.211
	0.864	2.806	1.431		1.889	10.160
	0.971	3.778	1.731		2.853	24.600
dimethyladipate	0.827	1.786	0.590	diethyl carbonate	1.292	3.304
	0.814	2.011	0.861		1.387	4.417
	0.907	2.700	1.158		1.555	6.321
	0.927	3.134	1.431		1.796	9.305
	1.145	4.958	1.731		3.324	32.594
dimethyl glutarate	0.894	1.983	0.590			
	0.874	2.226	0.861			
	0.967	2.976	1.158			
	1.021	3.645	1.431			
	1.231	5.597	1.731			

[a] C_{TOA} is the concentration of TOA in the organic phase, and K_{11} and K_{21} are the complexation constants for (1 acid + 1 amine) and (2 acids + 1 amine).

levulinic acid was raised in the aqueous phase to the organic phase. Comparison of distribution coefficients of levulinic acid between pure individual esters and TOA + esters is presented in Figure 2. It was observed that the use of TOA dissolved in diethyl carbonate increased the distribution coefficients about 18 times; dissolved in isopropylacetate, it increased about 15 times; dissolved in dimethylsuccinate, it increased about 11 times; dissolved in dimethyladipate, it increased about 12 times; dissolved in hexylacetate it increased about 12 times; and dissolved in diethylsebacate it increased about 23 times, all compared to the use of pure solvents as extractant.

The values of the overall extraction constants, K_{11} and K_{21}, for each concentration of amine were given in Table 3, and the possible complex forms for acid + amine (1:1) and (2:1) were shown in Figure 3. The resulting acid + amine complexes were supposed to be stabilized due to the hydrogen bonding with the diluent.[22,23] Figure 3 shows that the first acid interacts directly with the amine to form an ion pair, and the OH of the carboxyl of the second acid forms a hydrogen bond with the conjugated CO of the carboxylate of the first acid to form a complex.[24,25] The values of K_{11} and K_{21} for the three most effective diluents increase in the following trend: TOA + diethyl carbonate (3.324, 32.594) > TOA + ethyl propionate (2.853, 24.600) > TOA + isopropyl acetate (2.532, 19.781). The large difference among complexation constant values for the extraction of levulinic acid by TOA + different diluents indicates that solvation of the complex in different diluents is a critical factor in acid extraction. Furthermore, Wasewar et al. calculated complexation extraction constants for some caryboxlic acids by a graphical method.[26,27]

The effects of modified separation factors on concentration of TOA were shown in Table 1 and in Figure 4 (figures were

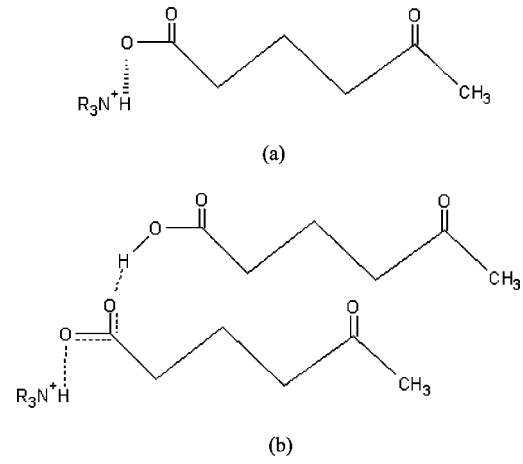

Figure 3. Possible acid−amine complex forms. (a) Acid−amine complex (1:1). (b) Acid−amine complex (2:1).

drawn for only six solvents not to cause any confusion). The separation factor (S_f) shows relative proportion between physical interaction and chemical reaction. For all solvents (esters), with increasing concentration of TOA, decreases in separation factors were observed. At the high TOA concentration range 1.431 to 1.731, the separation factor showed a sharp decrease in diethyl carbonate, ethyl propionate, and isopropyl acetate.

The plot of loading factor T_T againts the ratio of the overall complexed acid to total amine in the organic phase (stoichiometric loading factor), which is marked as T_S, is shown in Figure 5. The slope of the curve of each solvent was given in Figure 5. Diethyl carbonate had a maximum slope with a value of 1.0967. The lowest deviation among all the solvents is dimethyladipate with a slope value of 1 ($y = x$ equation).

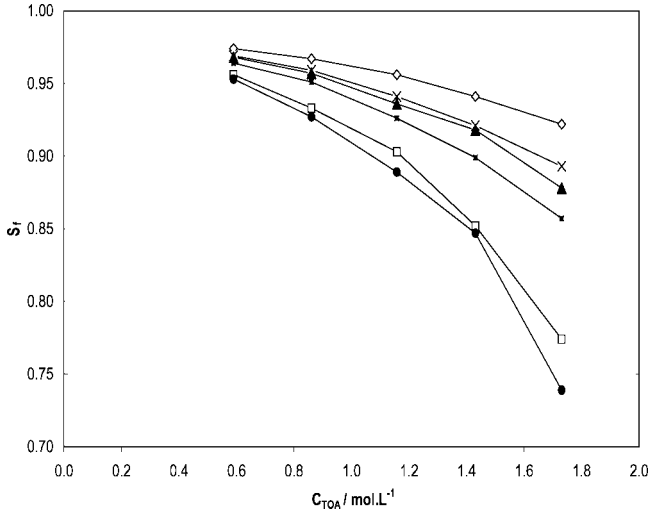

Figure 4. Effect of separation factors S_f on concentration of TOA ($C_{TOA.}$). ●, diethyl carbonate; □, isopropyl acetate; ■, dimethyl succinate; ▼, dimethyladipate; ×, hexyl acetate; ◇, diethylsebacate.

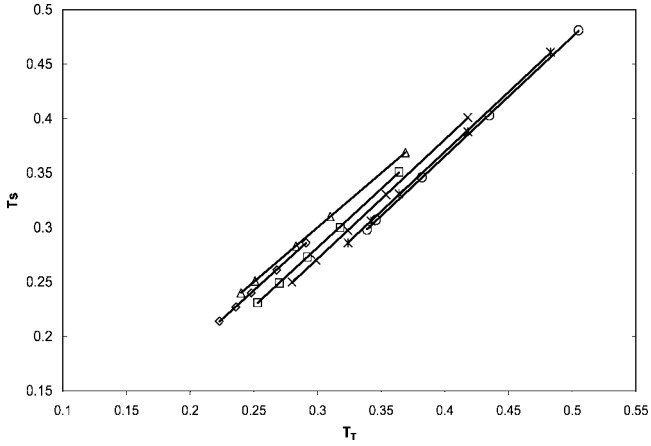

Figure 5. Plot of loading factor T_T against stoichiometric loading factor T_S. ○, diethyl carbonate, $y = 1.0967x - 0.0732$; *, isopropyl acetate, $y = 1.0961x - 0.0689$; ×, dimethyl succinate, $y = 1.0961 - 0.0576$; Δ, dimethyladipate, $y = x$; □, hexyl acetate, $y = 1.0796x - 0.0424$; ◇, diethylsebacate, $y = 1.0609x - 0.023$.

With all of the solvents, the loading decreases, indicating that complexes include the diluent specifically, and overloading was not observed in all of the solvents (esters) in this study. For systems with only one amine per complex, there is no effect of total amine concentration on the loading. If there is more than one amine per complex, loading increases with increasing amine concentration. Systems that exhibit aggregation and formation of complexes with large numbers of acid and amine molecules exhibit an increase in loading. The interactions between the complex and diluent can be divided into general solvation and specific interactions of the diluent with the complex. Inert diluents give a very low distribution of the acid into the solvent phase. Alkanes being nonpolar provide very low solvation of the polar complexes. Aromatic diluent gives higher distribution which has been rationalized as solvation due to the interaction of the aromatic. Π electrons with complex esters used in this study are polar and can promote extraction by providing a good solvating media for the ion pair. However, polarity (or polarizability) alone does not completely account for solvating ability. Especialy alcohols give unusually high equilibrium constants, higher than would be expected from polarity arguments alone.[10]

Conclusion

Extractability of levulinic acid by trioctylamine (TOA) dissolved in seven esters as diluents was investigated. For these extractant systems, distribution coefficients, loading factors, and separation factors were calculated in light of experimental results. The extraction equilibrium was interpreted as a result of consecutive formation of two acid−amine species with stoichiometries of 1:1 and 2:1. Overall thermodynamic extraction constants K_{11} and K_{21} were determinated for each solvent. The highest synergistic extraction efficiency in distribution coefficients was found as a (K_D) value of 5.754 for the TOA + diethyl carbonate extractant system, and maximum values of equilibrium complexation constants were found as 3.324 and 32.594 for K_{11} and K_{21}, respectively.

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