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Reactive Extraction of Levulinic Acid by Amberlite LA-2 Extractant

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The production of organic acids at relatively low concentrations in aqueous solutions is typical of both electrochemical and biochemical syntheses. The recovery of these solute species can be achieved by solvent extraction, and the reactive recovery of carboxylic acids from aqueous solutions has received increasing attention. In this study the reactive extraction of levulinic acid was done at 298.15 K, and all experiments were reported on the extraction of levulinic acid by Amberlite LA-2 dissolved in five different esters (dimethyl phthalate, dimethyl adipate, dimethyl succinate, dimethyl glutarate, and diethyl carbonate), five different alcohols (isoamyl alcohol, hexan-1-ol, octan-1-ol, nonan-1-ol, and decan-1-ol) and two different ketones (diisobutyl ketone (DIBK) and methyl isobutyl ketone (MIBK)). Furthermore, single pure solvents (not containing Amberlite LA-2) were used for physical extraction. Experimental results of batch extraction experiments were calculated and reported as distribution coefficients (K_D), loading factors (T_T), stoichiometric loading factors (T_S), separation factors (S_f) and extraction efficiencies (E). The isoamyl alcohol was found to be the most effective solvent with a maximum distribution value (K_D) of 68.017. According to the data determined from the experiments, a linear solvation energy relationship (LSER) model equation was found to calculate loading factors (T_T) for the alcohols with an R^2 value of 0.98.

Introduction

Levulinic acid extraction from the aqueous phase is important in view of a number of its uses. The recovery technique should provide high selectivity and yield. There are many techniques for the recovery of carboxylic acids from aqueous solutions such as distillation, membranes, dialysis, electrodialysis, and reactive extraction. The profound success of reactive extraction has been obtained in the recovery of carboxylic acids from dilute solution. Also, levulinic acid, a carboxylic acid that contains a ketone structure, is a clear to brownish semisolid that melts at 37 °C and is soluble in alcohol, ether, and chloroform. Levulinic acid can be used as an acidulant in foods and beverages. It is used as an intermediate in the manufacturing of synthetic fibers, pharmaceuticals, pesticides, plastics, and rubber. It is used in the manufacturing of perfumery, food additives, fuel additives, herbicides, solder fluxes, stabilizers, and printing inks. Levulinic acid and its esters are used as plasticizers and solvents in polymers, textiles, and coatings.[1]

In the production of carboxylic acids by fermentation, free acid is required for the manufacturing 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 proteinlike impurities, the concentration of salt, the conversion of acid salts to free acids, and the polishing of 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, making fermentation-based chemical technology impractical.[3,4]

Table 1. Results for Physical Extraction of Levulinic Acid with Pure Solvents[a]

			C^*_{lev}		
	solvents	pH_{aq}	$mol \cdot L^{-1}$	K_D	E
esters	dimethylphthalate	2.96	0.065	0.104	9.4339
	dimethyladipat	3.10	0.099	0.167	14.368
	dimethylglutarate	3.15	0.112	0.194	16.255
	dimethylsuccinate	3.20	0.124	0.219	17.997
	dietilkarbonat	3.37	0.167	0.319	24.238
ketones					
	diisobuthylketone	3.36	0.156	0.292	22.640
	methylisobuthylketone	3.42	0.178	0.348	25.834
alcohols					
	isoamylalcohol	3.64	0.234	0.514	33.962
	hexan-1-ol	3.50	0.199	0.406	28.882
	octan-1-ol	3.40	0.175	0.340	25.399
	nonan-1-ol	3.38	0.169	0.325	24.528
	decan-1-ol	3.34	0.160	0.302	23.222

[a] C^*_{lev} is the concentration of levulinic acid in organic phase, K_D is the distribution coefficient, and E is the extraction efficiency.

The extractability of most organic acids by current solvents is very low, and reactive extraction must be considered. Reactive extraction is an important recovery technique that has received increasing attention, over the past decade in particular, for the recovery of carboxylic acids. Reactive extraction employs an extractant in the removal of the acid. There are three categories of extractants that are used in reactive extraction. These are extraction by solvation with carbon-bonded oxygen-bearing extractants, solvation with phosphorus-bonded oxygen-bearing extractants, and proton transfer or ion-pairing formation with high-molecular-weight aliphatic amines and their salts. The long-chain aliphatic amines have been efficiently used in reactive

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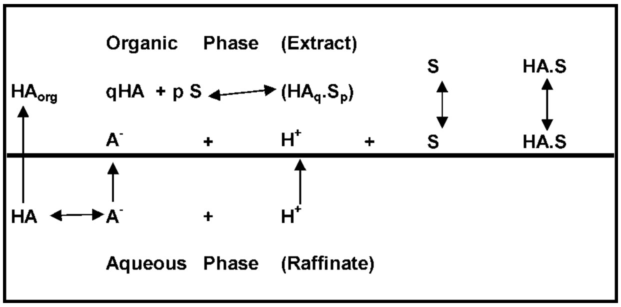

Figure 1. Mechanism for the reactive extraction of levulinic acid (HA) by Amberlite LA-2 (S).

extraction because phosphorus and amine extractants are mainly used in the recovery of carboxylic acids. The extractant (amine) in the organic phase reacts with the material in the aqueous phase, and the reaction complexes formed are then solubilized in the organic phase.[4] In this sense, many workers have mainly studied the recovery of carboxylic acid from aqueous solution using secondary, tertiary, and quaternary amines. (i) For secondary amines, in general, extractions of penicillin G have been studied up to now.[5,6] Furthermore, simultaneous physical and reactive extractions of salicylic acid in aqueous solution were performed using Amberlite LA-2 in xylene by Schugerl et al.[7] Kawano et al.[8] studied the extraction equilibria of acetic acid and propionic acid with Amberlite LA-2 in hexane. (ii) For tertiary amines, Hong and Hong studied the reactive extraction of succinic acid with tripropylamine (TPA) in various diluents, and they found that the distribution coefficient and the extraction efficiency increased with an increase in TPA concentration.[9] Inci studied the extraction of citric acid and glycolic acid by alamine 336 and tri-*n*-octylamine in four diluting solvents.[10,11] Wasewar et al.[12,13] reported that the equilibria and the kinetics of the reactive extraction of lactic acid by alamine 336 extractant in decanol and MIBK diluents, and in light of experimental studies, they suggested an extraction mechanism. Martak and Schlosser studied liquid−liquid equilibria of dimethyl cyclopropane carboxylic acid in water−solvent systems with trioctylamine as an extractant.[14] (iii) For quaternary amines, Uslu and Inci investigated the extraction of glycolic and propionic acids using aliquat 336 (as a quaternary amine).[15,16] Kyuchoukov et al.[17] suggested the mechanism of lactic acid extraction with quaternary ammonium chloride (aliquat 336).

The objective of this study was to investigate the extraction of levulinic acid from aqueous solutions with Amberlite LA-2 in several solvents. In this sense, five different esters (dimethyl phthalate, dimethyl adipate, dimethyl succinate, dimethyl glutarate, and diethyl carbonate), five different alcohols (isoamyl alcohol, hexan-1-ol, octan-1-ol, nonan-1-ol, and decan-1-ol) and two different ketones (diisobutyl ketone (DIBK) and methyl isobutyl ketone (MIBK)) have been used as solvents for the dilution of amine Amberlite LA-2. Furthermore, experiments have also been carried out with single pure solvents for physical extraction. The linear solvation energy relationship (LSER) model was applied to the results to calculate loading factors. A survey of the literature shows that the reactive extraction of levulinic acid is not available for these extraction systems.

Materials and Methods

Materials. Amberlite LA-2, (*N*-lauryltrialkyl-methyl amine of 24 to 28 carbon atoms, Merck, > 99 %), an ion exchange extractant, is a yellow liquid with a molecular weight of 353.67. Levulinic acid (Merck, > 99 %), esters (dimethyl phthalate > 98 %, dimethyl adipate > 98 %, dimethyl succinate > 99 %, dimethyl glutarate > 98 %, and diethyl carbonate > 97 %), alcohols (isoamyl alcohol > 99 %, hexan-1-ol > 98 %, octan-1-ol > 99 %, nonan-1-ol > 99 %, and decan-1-ol > 98 %), and ketones (DIBK > 98 % and MIBK > 99 %) were supplied by Merck and Fluka to dilute Amberlite LA-2. All chemicals were used without further purification.

Experimental Studies. Levulinic acid was dissolved in distilled water to prepare a 0.789 mol·L^{-1} acid solution. The pK_a of the levulinic acid was 4.59. We prepared the organic phases by mixing Amberlite LA-2 with the diluents at five

Table 2. Results for the Extraction of Levulinic Acid with Amberlite LA-2 + Ester System[a]

	$C^*_{LA\text{-}2}$		C^*_{lev}					
solvents (esters)	mol·L^{-1}	pH_{aq}	mol·L^{-1}	K_D	T_T	T_S	S_f	E
diethylcarbonate	0.371	5.11	0.670	7.613	1.805	1.656	0.996	88.390
	0.743	5.19	0.691	10.313	0.930	0.774	0.997	91.161
	1.115	5.32	0.724	21.294	0.649	0.486	0.998	95.514
	1.487	5.34	0.729	25.137	0.490	0.326	0.998	96.174
	1.859	5.37	0.736	33.454	0.395	0.230	0.998	97.097
dimethylsuccinate	0.371	5.05	0.655	6.359	1.765	1.618	0.996	86.411
	0.743	5.14	0.677	8.3580	0.911	0.759	0.997	89.313
	1.115	5.28	0.713	15.844	0.639	0.479	0.998	94.063
	1.487	5.31	0.720	18.947	0.484	0.322	0.998	94.986
	1.859	5.33	0.726	22.687	0.390	0.227	0.998	95.778
dimethylglutarate	0.371	5.00	0.643	5.624	1.733	1.589	0.995	84.903
	0.743	5.09	0.667	7.358	0.897	0.747	0.996	88.035
	1.115	5.26	0.708	14.196	0.634	0.476	0.997	93.419
	1.487	5.29	0.715	16.982	0.480	0.320	0.998	94.439
	1.859	5.31	0.720	19.406	0.387	0.225	0.998	95.099
dimethyladipate	0.371	4.12	0.578	1.259	1.557	1.428	0.965	55.751
	0.743	4.97	0.608	5.230	0.818	0.681	0.995	83.950
	1.115	5.07	0.638	6.866	0.572	0.429	0.996	87.287
	1.487	5.18	0.668	9.775	0.449	0.299	0.997	90.719
	1.859	5.27	0.688	15.117	0.370	0.215	0.997	93.795
dimethylphthalate	0.371	4.74	0.422	3.211	1.137	1.043	0.988	76.253
	0.743	4.86	0.636	4.053	0.855	0.713	0.994	80.211
	1.115	4.98	0.661	5.316	0.592	0.444	0.995	84.168
	1.487	5.10	0.687	7.422	0.462	0.308	0.996	88.126
	1.859	5.18	0.711	9.828	0.382	0.222	0.997	90.765

[a] $C^*_{LA\text{-}2}$ is the concentration of Amberlite LA-2 in 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.

Table 3. Results for Extraction of Levulinic Acid with Amberlite LA-2 + Alcohol System and Model Results[a]

solvents (esters)	$C_{\text{LA-2}}$* mol•L−1	pH_{aq}	C_{lev}* mol•L^{-1}	K_D	T_T^{model}	T_T	T_S	S_f	E
isoamylalcohol	0.371	5.22	0.697	11.461	1.483	1.878	1.722	0.997	91.975
	0.743	5.37	0.735	32.155	1.045	0.989	0.824	0.998	96.983
	1.115	5.39	0.741	45.349	0.737	0.664	0.498	0.998	97.842
	1.487	5.41	0.745	57.447	0.519	0.501	0.334	0.998	98.289
	1.859	5.42	0.747	68.017	0.366	0.401	0.234	0.998	98.551
hexan-1-ol	0.371	4.44	0.502	1.9651	1.477	1.353	1.240	0.980	66.275
	0.743	5.25	0.706	13.689	1.036	0.950	0.791	0.997	93.192
	1.115	5.35	0.73	26.860	0.727	0.654	0.491	0.998	96.410
	1.487	5.4	0.743	52.187	0.510	0.499	0.333	0.998	98.119
	1.859	5.41	0.744	56.332	0.358	0.400	0.233	0.998	98.255
octan-1-ol	0.371	4.99	0.642	5.5344	1.483	1.730	1.586	0.995	84.696
	0.743	5.31	0.722	20.055	1.045	0.971	0.809	0.998	95.250
	1.115	5.38	0.738	36.900	0.736	0.661	0.496	0.998	97.361
	1.487	5.39	0.74	41.111	0.518	0.497	0.331	0.998	97.625
	1.859	5.39	0.742	46.375	0.365	0.399	0.232	0.998	97.889
nonan-1-ol	0.371	4.95	0.631	5.0152	1.480	1.700	1.559	0.995	83.375
	0.743	5.29	0.715	16.959	1.040	0.962	0.801	0.998	94.431
	1.115	5.36	0.732	29.013	0.731	0.656	0.492	0.998	96.668
	1.487	5.36	0.734	31.705	0.514	0.493	0.329	0.998	96.942
	1.859	5.37	0.736	33.647	0.361	0.395	0.230	0.998	97.113
decan-1-ol	0.371	4.97	0.637	5.2831	1.475	1.716	1.574	0.995	84.084
	0.743	5.3	0.719	18.580	1.033	0.967	0.806	0.998	94.892
	1.115	5.35	0.73	26.498	0.724	0.654	0.491	0.998	96.363
	1.487	5.36	0.733	11.461	0.507	0.492	0.328	0.998	96.742
	1.859	5.37	0.735	32.155	0.355	0.395	0.230	0.998	97.008

[a] $C_{\text{LA-2}}^*$ is the concentration of Amberlite LA-2 in organic phase, C_{lev}^* is the concentration of levulinic acid in the organic phase, K_D is the distribution coefficient, T_T^{model} is the model value of the loading factor, 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.

constant concentrations in the range of (0.371 to 1.859) mol•L^{-1}. Equal volumes of aqueous and organic solutions of known concentration were added to Erlenmeyer flasks (50 mL) and were shaken 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 acid concentration of aqueous phase samples was analyzed by the use of titration with 0.1 N sodium hydroxide (relative uncertainty ± 1 %) by means of phenolphthalein as an indicator with each measurement being performed 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 pH value of the aqueous phase was determined with a pH meter (Hanna pH 211 microprocessor pH meter) with a deviation of ± 1 %.

Results and Discussion

Physical Extraction Results. The physical extraction with carbon-bonded oxygen bearing solvents involves the solvation of acid molecules by donor bonds. Results of the physical extraction of levulinic acid using five alcohols, five esters, and two ketones are presented in Table 1. The extractions showed a very low efficiency for all of the solvents employed.

Distribution Coefficients. The intent of carboxylic acids is to form dimers in the organic phase because of their intermolecular hydrogen bonding.[16] All results were interpreted as the recovery of levulinic acid using Amberlite LA-2. The mechanism of the reactive extraction of levulinic acid by Amberlite LA-2 is shown in Figure 1. The formation of a complex via the interfacial reaction can be represented as

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

In eq 1, HA is the undissociated acid molecule, S is the amine molecule, and p and q are the stoichiometric coefficients.

As the levulinic acid−Amberlite LA-2 complex is formed, it is rapidly extracted into the organic phase. The equilibrium complexation constant is defined as

$$K_{qp} = \frac{[(\text{HA})_q \cdot (\text{S})_p]_{\text{org}}}{[\text{HA}]_{\text{aq}}^q \cdot [\text{S}]_{\text{org}}^p} \tag{2}$$

K_{qp} is expected to depend on the properties of the acid and the solvation efficiency of the diluent used, and q and p are the stoichiometric coefficients of acid and amine, respectively. The experimentally accessible distribution coefficient (K_D) is given as

$$K_D = \frac{[\text{HA}]_{\text{org}}}{[\text{HA}]_{\text{total,aq}}} = \frac{[\text{HA}_q \cdot \text{S}_p]_{\text{org}}}{[\text{HA}]_{\text{aq}} + [\text{A}^-]_{\text{aq}}} \tag{3}$$

In eq 3, $[\text{HA}]_{\text{org}}$ is the total concentration of acid in the organic phase, $[\text{HA}]_{\text{total,aq}}$ is the total concentration of acid in the aqueous phase, and $[\text{HA}]_{\text{aq}}$ is the undissociated acid in the aqueous phase.

The apparent equilibrium constant, K_A, for the acid dissociation reaction can be written in terms of species concentrations for dilute solutions

$$\text{HA} \leftrightarrow \text{H}^+ + \text{A}^-, \quad K_A = \frac{C_{\text{H}^+} {\cdot} C_{\text{A}^-}}{C_{\text{HA}}} \tag{4}$$

From eqs 3 and 4

$$\begin{aligned} K_D &= \frac{[\text{HA}_q \cdot \text{S}_p]_{\text{org}}}{[\text{HA}]_{\text{aq}} + [\text{A}^-]_{\text{aq}}} \\ &= \frac{K_{qp} \cdot [\text{HA}]_{\text{aq}}^q \cdot [\text{S}]_{\text{org}}^p}{[\text{HA}]_{\text{aq}} + K_A \cdot [\text{HA}]_{\text{aq}}/[\text{H}^+]_{\text{aq}}} \\ &= \frac{K_S \cdot [\text{S}]_{\text{org}}^p}{1 + K_A/[\text{H}^+]_{\text{aq}}} \end{aligned} \tag{5}$$

$$K_S = K_{qp} \cdot [\mathrm{HA}]_{\mathrm{aq}}^{(q-1)} \qquad (6)$$

To improve the physical characteristics and extraction efficiency, we chose diluents according to their functional groups (esters, alcohols, ketones). The extraction studies were done with various proportions of Amberlite LA-2 ((0.371 to 1.859) mol·L^{-1}) in the diluents, and results are presented in Tables 2, 3, and 4, and obtained distribution coefficients are demonstrated in Figure 2. (Only six solvents are demonstrated in Figure 2 so as not to cause any confusion.) It is seen from Figure 2 and Tables 2, 3, and 4 that isoamyl alcohol shows the best results in terms of the distribution coefficient value, followed by hexan-1-ol and MIBK. The extraction power of the Amberlite LA-2 + diluent mixture changes with increasing initial concentration of Amberlite LA-2 in the organic phase. The effects of isoamyl alcohol, hexan-1ol, and MIBK are more prominent with Amberlite LA-2 than with other solvents. The maximum extraction (K_D = 65.017) was achieved with 1.859 mol·L^{-1} Amberlite LA-2 in isoamyl alcohol, which was higher than other diluents. According to Table 2, the distribution coefficients for levulinic acid extraction by Amberlite LA-2 in esters leads to the following order: diethyl carbonate > dimethyl succinate > dimethyl glutarate > dimethyl adipate > dimethyl phthalate.

Table 4. Results for Extraction of Levulinic Acid with Amberlite LA-2 + Ketone System[a]

solvents (ketones)	$C^*_{\mathrm{LA\text{-}2}}$ mol·L^{-1}	pH$_{\mathrm{aq}}$	C^*_{lev} mol·L^{-1}	K_D	T_T	T_S	S_f	E
DIBK	0.371	4.67	0.560	2.832	1.509	1.384	0.989	73.905
	0.743	4.97	0.635	5.173	0.854	0.712	0.995	83.801
	1.115	5.03	0.652	6.157	0.584	0.438	0.996	86.029
	1.487	5.13	0.675	8.209	0.453	0.302	0.997	89.142
	1.859	5.15	0.681	8.825	0.366	0.213	0.997	89.822
MIBK	0.371	5.02	0.648	5.890	1.746	1.602	0.996	85.488
	0.743	5.16	0.684	9.243	0.920	0.766	0.997	90.237
	1.115	5.29	0.716	17.047	0.642	0.481	0.998	94.459
	1.487	5.35	0.731	27.074	0.491	0.327	0.998	96.437
	1.859	5.40	0.743	49.533	0.399	0.233	0.998	98.021

[a] $C^*_{\mathrm{LA\text{-}2}}$ is the concentration of Amberlite LA-2 in 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.

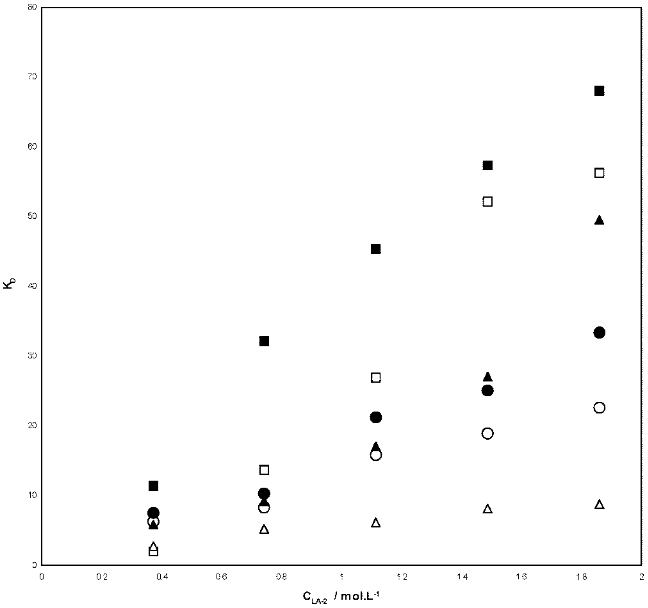

Figure 2. Plot of distribution coefficients (K_D) against concentration of Amberlite LA-2 ($C^*_{\mathrm{LA\text{-}2}}$): ●, diethyl carbonate; ○, diethyl succinate; □, hexan-1-ol; ■, isoamyl alcohol; ▲, MIBK; △, DIBK.

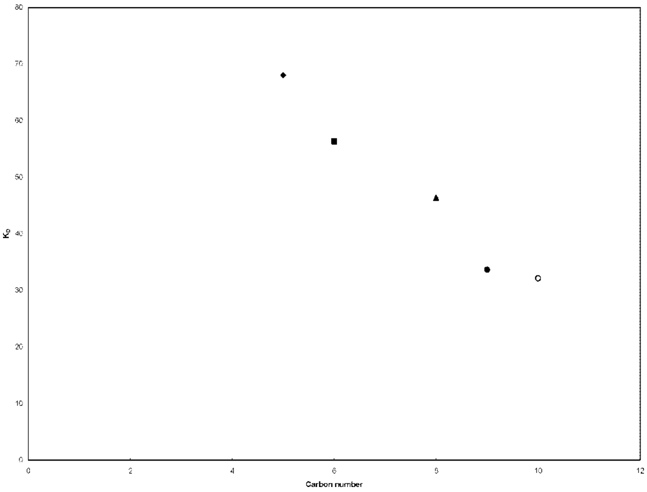

Figure 3. Distribution coefficients (K_D) of extraction of levulinic acid according to carbon number of alcohols at 1.859 mol·L^{-1} Amberlite LA-2 concentration: ◆, isoamyl alcohol; ■, hexan-1-ol; ▲, octan-1-ol; ●, nonan-1-ol; ○, decan-1-ol.

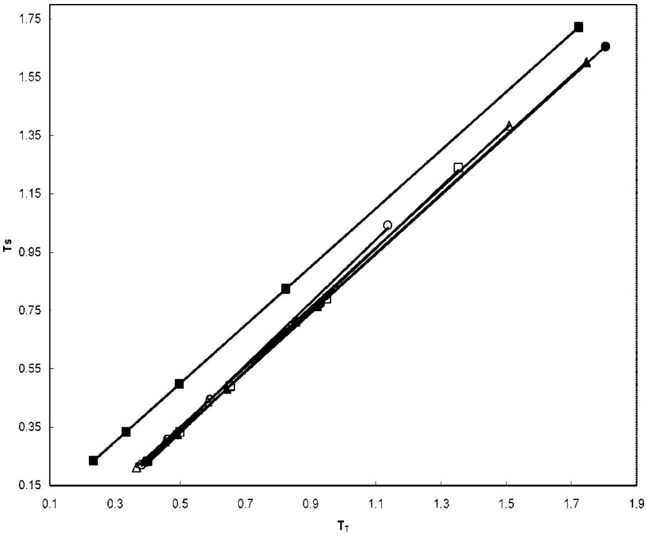

Figure 4. Plot of loading factor (T_T) against stoichiometric loading factor (T_S): ●, diethyl carbonate ($y = 1.0117x - 0.1694$); ○, diethyl succinate ($y = 1.0792x - 0.1939$); □, hexan-1-ol ($y = 1.0539x - 0.1951$); ■, isoamyl alcohol ($y = x$); ▲, MIBK ($y = 1.0163x - 0.1714$); △, DIBK ($y = 1.0241 - 0.1616$).

In terms of alcohols, a plot of the distribution coefficient of levulinic acid against the carbon number of the alcohols used in this study is shown in Figure 3. It can be seen that with an increasing carbon number of the alcohol, which depends on its molecular weight, the distribution coefficient of levulinic acid decreases.

For all of the results mentioned above, the polarity is the most important factor. Among the diluents, isoamyl alcohol has the highest dipole moment. Polarity is a function of the transition energy, E_T, or Z. Kosower[18,19] defined the polarity parameter, Z, as the molar transition energy, $E_{T,}$ which is expressed in kJ·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 higher the Z value. A high Z value

Table 5. Values of the Complexation Constants of Levulinic Acid for Various Diluents + Amberlite LA-2[a]

solvents	K_{11} / $\text{L}\cdot\text{mol}^{-1}$	K_{21} / $\text{L}^2\cdot\text{mol}^{-2}$	K_{31} / $\text{L}^3\cdot\text{mol}^{-3}$	$C^*_{\text{LA-2}}$ / $\text{mol}\cdot\text{L}^{-1}$	solvents	K_{11} / $\text{L}\cdot\text{mol}^{-1}$	K_{21} / $\text{L}^2\cdot\text{mol}^{-2}$	K_{31} / $\text{L}^3\cdot\text{mol}^{-3}$
diethylcarbonate	20	23	2650	0.371	isoamylalcohol	30	504	8276
	13	207	3092	0.743		43	1870	81 304
	19	561	16 520	1.115		39	2299	135 268
	16	582	20 101	1.487		38	2964	228 042
	17	817	37 181	1.859		36	3320	301 900
dimethylsuccinate	17	166	1615	0.371	hexan-1-ol	5	20	80
	11	138	1714	0.743		18	351	6757
	14	315	7017	1.115		23	835	29 824
	12	335	8824	1.487		33	2220	148 048
	12	381	11 918	1.859		28	2041	145 851
dimethylglutarate	15	131	1139	0.371	octan-1-ol	14	128	1108
	9	108	1191	0.743		26	749	20 827
	12	253	5079	1.115		33	1654	82 735
	11	260	6047	1.487		27	1535	85 330
	10	268	7058	1.859		24	1559	97 446
dimethyladipate	8	48	267	0.371	nonan-1-ol	13	105	830
	5	36	242	0.743		22	520	12 103
	4	39	331	1.115		25	971	37 352
	5	55	616	1.487		20	856	35 706
	5	75	1078	1.859		17	817	37 181
dimethylphthalate	3	10	29	0.371	decan-1-ol	14	117	969
	7	57	471	0.743		24	636	16 313
	6	63	649	1.115		23	835	29 824
	6	91	1290	1.487		19	788	31 548
	8	173	3683	1.859		17	747	32 495
DIBK	7	38	194	0.371	MIBK	15	144	1312
	6	56	459	0.743		12	168	2271
	5	52	490	1.115		15	364	8667
	5	65	793	1.487		18	674	24 975
	4	61	802	1.859		26	1776	11 8422

[a] $C^*_{\text{LA-2}}$ is the concentration of Amberlite LA-2 in the organic phase and K_{11}, K_{21}, and K_{31} are the complexation constants for (one acid + one amine), (two acids + one amine), and (three acids + one amine), respectively.

corresponds to high solvent polarity. Dimroth and Reichardt[20,21] have proposed a solvent polarity parameter, $E_T(30)$, on the basis of the transition energy (Z) 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 correspond to high solvent polarity.[19]

Loading Factors. The extent to which the organic phase can be loaded with levulinic acid is expressed as the overall loading factor (T_T)

$$T_T = \frac{C^*_{\text{lev}}}{[\text{S}]^{\text{initial}}_{\text{org}}} \tag{7}$$

where C^*_{lev} is the concentration of undissociated levulinic acid in the organic phase and $[\text{S}]^{\text{initial}}_{\text{org}}$ is initial amine concentration in the organic phase. $[\text{S}]_{\text{org}}$ can be expressed as

$$[\text{S}]_{\text{org}} = [\text{S}]^{\text{initial}}_{\text{org}} - pC^*_{\text{lev}} \tag{8}$$

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, ($v\cdot C^{*s}_{\text{lev}}$) for the amount of acid extracted by the diluent in the solvent mixture ($[\text{S}]_{\text{org}} = C^*_{\text{LA-2}}$)

$$T_s = \frac{(C^*_{\text{lev}} - v\cdot C^{*s}_{\text{lev}})}{C^*_{\text{LA-2}}} \tag{9}$$

In eq 9, v is the volume fraction of diluent in the mixture and C^{*s}_{lev} is the concentration of acid extracted by the pure diluent alone not containing amine.

A plot of the loading factor, T_T, against the ratio of the overall complexed acid to total amine in the organic phase (stoichiometric loading factor), T_S, is shown in Figure 4. The slopes of the curve of solvents are given in the caption of Figure 4. Diethyl carbonate has the maximum slope with a value of 1.0792. The lowest deviation among the solvents is isoamyl alcohol with a slope value of (one) unity as a result of the $y = x$ equation. For all of the solvents, the loading decreases, indicating that complexes specifically include the diluent, and overloading was observed for all of the solvents in the vicinity of 0.371 and 0.743 $\text{mol}\cdot\text{L}^{-1}$ of Amberlite LA-2 in this study. In this case, there is more than one amine per complex; loading increases with increasing amine concentration. Overloading explains that there is more than one acid in the complex. Wasewar et al.[13] reported the following assumptions about complex formation: $T_T < 0.5$ complex (acid + amine) (1:1), $T_T > 0.5$ complex (acid + amine) (2:1), and $T_T \gg 0.5$ complex (acid + amine) (3:1). According to this assumption, three complex formations were calculated and are presented in Table 5.

Extraction Efficiency and Separation Factors. Extraction efficiency is defined by the following equation

$$E = \frac{K_D\cdot 100}{1 + K_D} \tag{10}$$

The extraction efficiency of levulinic acid extraction with Amberlite LA-2 in isoamyl alcohol was higher than that for the other diluents, as seen from Tables 1, 2, 3, and 4 and Figure 5. (Only six solvents were demonstrated in Figure 5 to not cause any confusion.) The maximum extraction was 98.551 % with a concentration of 1.859 $\text{mol}\cdot\text{L}^{-1}$ of Amberlite LA-2 in isoamyl alcohol. Other effective diluents were hexan-1-ol and MIBK, which had extraction efficiencies of (98.255 and 98.021) %, respectively.

The relative proportion between physical interaction and chemical reaction was evaluated with respect to a modified

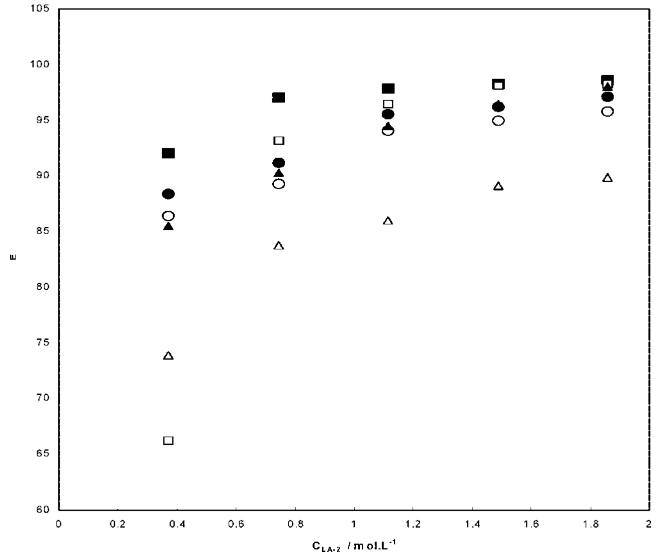

Figure 5. Plot of extraction efficiency (E) against concentration of Amberlite LA-2 ($C_{\text{LA-2}}$): ●, diethyl carbonate; ○, diethyl succinate; □, hexan-1-ol; ■, isoamyl alcohol; ▲, MIBK; △, DIBK.

separation factor, which is expressed as the ratio of the complexed acid to overall extracted acid

$$s_f = \frac{C^*_{\text{lev}}}{C^*_{\text{lev}} + C^*_{\text{A}^-}} \tag{11}$$

The effect of the modified separation factor on the concentration of Amberlite LA-2 is shown in Tables 2, 3, and 4. The separation factor (S_f) shows the relative proportion between physical interaction and chemical reaction. For all solvents with increasing concentration of Amberlite LA-2, the separation factors were slightly changed.

Linear Solvation Energy Relationship Model. The properties of an acid−amine system of hydrogen bond formation can be estimated through theoretically based models of the mass action law including the physical interaction terms or by the use of the concept of multiscale association as well as by the application of a generalized solvatochromic approach with an LSER.[22] A modified version of an LSER for predicting the extraction equilibria of an amine−diluent−acid system was given by Bizek et al.[23]

In this study, the LSER model was applied to predict loading factors for Amberlite LA-2 + alcohol systems upon the extraction of levulinic acid. The calculation of distribution coefficients of solvents in amine with the LSER model equation was described in Uslu's earlier work.[24] In brief, the following equation can be used to describe the effect of the diluents on the values of the loading factor (T_T)

$$\ln T_T = \ln T^0_T + s(\pi^* + d\delta) + b\beta + a\alpha \tag{12}$$

In eq 12, π^* and δ are the solvatochromic parameters that measure dipole + dipole and dipole + induced dipole interactions, respectively. The solvatochromic parameter α scale of solvent HBD (hydrogen-bond donor) acidities describes the ability of the solvent to donate a proton in a solvent to a solute hydrogen bond. The β scale of HBA (hydrogen-bond acceptor) basicities provides a measure of the solvent's ability to accept a proton (donate an electron pair) in a solute-to-solvent hydrogen bond, respectively. The coefficients s, d, a and b include the properties of solute coming from regression.[25]

Table 6. Solvatochromic Parameters for Alcohols

solvents	π^*	δ	β	α
isoamylalcohol	0.40	0	0.84	0.84
hexan-1-ol	0.40	0	0.84	0.80
octan-1-ol	0.40	0	0.81	0.77
nonan-1-ol	0.40	0	0.81	0.75
decan-1-ol	0.40	0	0.81	0.72

Table 7. Results of Regression Coefficient for LSER Equation

	$\log K^0_D$	s	d	b	a
coefficients	0.3234	− 3.0794	0	− 1.2758	0.5715

The values of the distribution coefficients can be regressed with the solvatochromic parameters of the solvents from Table 6[26] according to eq 12. All of the obtained loading factors for each alcohol was regressed by the computer program SPSS v14.0. The results of the mutual comparison are shown in Table 3. The LSER model values showed a good regression to the experimental data. The estimated values of parameters of the model are presented in Table 7. It was concluded that by using this model, we can describe distribution coefficients of levulinic acid between water and the amine + solvent system. As a result of regression eq 13, loading factors were calculated.

$$\ln T_T = 0.3234 - 3.0794(\nu\pi^* + 0\nu\delta) - 1.2758(\nu\beta) + 0.5715(\nu\alpha) \tag{13}$$

For the suitability of the data, the root-mean-square deviations (RMSDs) were calculated from the difference between the experimental data and the predictions of the LSER model according to the following equation

$$\text{RMSD} = \sqrt{\frac{1}{N}\sum_{i=1}^{n}\left(T_T - T_T^{\text{model}}\right)} \tag{14}$$

where T_T is the experimental distribution coefficient, and T_T^{model} is the calculated loading factor, and N is the number of experimental data. The RMSD value of the LSER model is found to be 0.083.

The RMSD value shows that all predicted distribution coefficients agree well with the experimental results, and also, the agreements between predictions and measurements are acceptable considering the experimental uncertainty.

Conclusions

The reactive extraction of levulinic acid by the use of Amberlite LA-2 dissolved in five different alcohols, five different esters, and two different ketones was investigated. Among the three diluent categories (alcohols, ketones, esters), alcohols gave the highest K_D value. In particular, isoamyl alcohol has a very high K_D value of 68.017. (Its extraction efficiency is 98.551 %). Complexation constants were calculated for one acid + one amine, two acids + one amine, and three acids + one amine. The LSER model was applied to obtain loading factors. The LSER model values showed a good regression to the experimental data with an R^2 value of 0.98. The estimated values of the parameters of the model were presented.

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