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Extraction of Citric Acid from Aqueous Solution by Means of a Long Chain Aliphatic Quaternary Amine/Diluent System

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Studies are reported on the extraction of citric acid by trioctyl methyl ammonium chloride dissolved in 1-propanol, 1-octanol, 1-decanol (active solvents), and their mixtures (1:1 volume ratio). The aim of this study was to investigate the extraction of citric acid from water by a long-chain aliphatic quaternary amine. Experimental results of batch extraction experiments are calculated and reported as distribution coefficients, loading factors, and extraction efficiency. All measurements were carried out at two different temperatures 298.15 K and 303.15 K. The results of the liquid−liquid equilibrium measurements were correlated by a linear solvation energy relationship model, which takes into account physical interactions. Solvatochromic parameters of the model were obtained from the literature. The remaining parameters were fitted to the experimental results. Experimental results for the liquid−liquid equilibrium are compared to the model.

1. Introduction

Citric acid is used as a flavoring and preservative in food and beverages, especially soft drinks. Citrate salts of various metals are used to deliver those minerals in a biologically available form in many dietary supplements. The buffering properties of citrates are used to control pH in household cleaners and pharmaceuticals. It is used in the biotechnology and pharmaceutical industries to passivate high-purity process piping in lieu of using nitric acid, because nitric acid is a hazardous disposal issue once it is used for this purpose, while citric acid is not. Therefore, purification of the citric acid is very important for industrial processes.

Physical extraction using common organic solvents has proved to be unsuitable for the recovery of organic acids because of their high affinity to water, and consequently low distribution coefficients. The pure diluent does not extract the solute, while the modifier influences the extracting power of the amine. Because amine salts with carboxylic acids are slightly soluble in the aqueous phase, a pertinent role of the modifier is to improve the solubility of the salts in the extract phase.[1] Reactive liquid−liquid extraction of the acid by a suitable extractant has been found to be a promising alternative to conventional processes.

The recovery of carboxylic acids by liquid−liquid extraction with aliphatic tertiary amines and quaternary amines dissolved in organic diluents has been studied by several authors.[2−4]

Gringstead[5] investigated the behavior and base strength of various amine types and classes in the reactive extraction of hydrochloric acid in a toluene diluent. He reported that the base strength decreased in the order primary > secondary > tertiary.

In our earlier studies, we investigated the reactive extraction of glycolic acid, gluconic acid, and propionic acid using the quaternary amine (trioctyl methyl ammonium chloride, TOMAC).[6−8] Furthermore, Uslu studied the extraction of propionic acid and tartaric acid with a tertiary amine (Alamine 336) and showed formation of an acid−amine complex with high distribution coefficients.[9−10] Bilgin et al. used corn oil, sunflower oil, olive oil, rape seed oil, soybean oil, and hazelnut oil as an another alternative to dilute trioctylamine for butyric acid extraction.[11] Furthermore, Inci investigated extraction of a lot of carboxylic acids, gluconic acid, salicylic acid, acetic acid, citric acid, and succinic acid using tertiary amines, and their overall extraction constants were determined.[12−16]

In the present work, the extraction of citric acid from aqueous solutions by TOMAC (0.362 to 1.775 mol·L^{-1}) was studied. Extraction experiments were carried out with TOMAC dissolved in the diluents 1-propanol, 1-octanol, 1-decanol, and their mixtures. As a result of the batch extraction experiments, partitioning coefficients were calculated. In addition to partitioning coefficients, the extraction efficiencies and variation of loading factors were obtained.

2. Theory

2.1. Equilibrium Theory. Yang et al.[17] showed that quaternary amines can extract both undissociated and dissociated acids. The extraction of citric acid (HA) with trioctyl methyl ammonium chloride (R_4NCl) can be described by the reaction

$$\mathrm{HA} + {}^*\mathrm{R_4NCl} \leftrightarrow {}^*(\mathrm{HA})\cdot(\mathrm{R_4N})^+ + \mathrm{Cl}^- \qquad (1)$$

where HA represents the acid present in the aqueous phase, and organic phase species are marked with an asterisk (*). Reaction 1 can be characterized by the overall thermodynamic extraction constant K

$$K = (a_{(\mathrm{HA})\cdot(\mathrm{R_4N})^+})^*\cdot(a_{\mathrm{Cl}^-})/(a_{(\mathrm{HA})})\cdot(a_{(\mathrm{R_4NCl})})^* \qquad (2)$$

Equation 2 can be written in terms of dissociated species, hydrogen ions and citrate anions, as it is used in the literature for amine extraction of acids. Taking into account the dissociation equilibrium, one can show that both concepts are equivalent

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with the only difference being in the values of equilibrium constants, replacing the activities by the products of molalities and molal activity coefficients. Equation 2 takes the form

$$K = (m_{(\mathrm{HA})\cdot(\mathrm{R_4N})^+}\, \gamma_{(\mathrm{HA})\cdot(\mathrm{R_4N})^+})^* \cdot (m_{\mathrm{Cl}^-} \cdot \gamma_{\mathrm{Cl}^-})/(m_{(\mathrm{HA})} \cdot \gamma_{(\mathrm{HA})}) \cdot (m_{(\mathrm{R_4NCl})} \cdot \gamma_{(\mathrm{R_4NCl})})^* \quad (3)$$

where m_i is the molality of component i, and γ_i, the molal activity coefficient of component i. Water and diluents are the solvents for the aqueous or organic 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 the organic phase. The expression for Z, can be written in the form

$$Z = C^{\mathrm{l}}_1/C^{\mathrm{l}}_2 \quad (4)$$

In eq 4, C^{l}_1 is total concentration of acid in the organic phase, mol·L^{-1}. C^{l}_2 is the total concentration of amine in the organic phase. The partitioning coefficients, D, for citric acid extracted from water into the organic phase were determined as

$$D = C^{\mathrm{l}}_1/C_1 \quad (5)$$

The efficiency of extraction, E, is expressed as

$$E = [1 - (C_1/C^0_{\mathrm{a}})]\cdot 100 \quad (6)$$

where C_1 is the concentration of acid in the aqueous phase after extraction and C^0_{a} is initial concentration of acid in the aqueous phase.

2.1. LSER Model Theory. According to Kamlet[18] the linear solvation energy relationship (LSER) that measures the property, XYZ, in terms of solvent properties is

$$\mathrm{XYZ} = \mathrm{XYZ}^0 + p(\delta_{\mathrm{h}})^2/100 + s(\pi^* + d\delta) + b\beta + a\alpha \quad (7)$$

In eq 7, δ_{h} is the Hildebrand's solubility parameter, π^* and δ are the solvatochromic parameters that measure solute + solvent, dipole + dipole, and dipole + induced dipole interactions, respectively. The solvatochromic parameter α scale of solvent hydrogen-bond donor acidities describes the ability of the solvent to donate a proton in a solvent to solute hydrogen bond. The β scale of 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. The coefficients p, s, d, a, and b include the properties of the solute and with p, s, d, and a determined by least sequares regression analysis. The values of solvatochromic parameters π^*, δ, α, β have been found for several hundreds of compounds.[18] Equation 7 can be adapted to describe the effect of diluents on the values of partitioning coefficients D in the form

$$\ln D = \ln D^0 + p(\delta_{\mathrm{h}})^2/100 + s(\pi^* + d\delta) + b\beta + a\alpha \quad (8)$$

In eq 8, analysis of the parameters π^*, δ, α, and β refer to the diluent, ln D^0 is determined by regression analysis, and D represents the partitioning coefficients for an ideal inert diluent. The second term of eq 8, which contains the solubility parameter δ_{h}, does not affect the values of the objective function significantly. Thus, eq 8 reduces to

$$\ln D = \ln D^0 + s(\pi^* + d\delta) + b\beta + a\alpha \quad (9)$$

The LSER model has been previously used in extraction systems (amine + diluent) acid extraction by Senol.[19−20]

3. Materials and Methods

3.1. Chemicals. TOMAC (M = 442 g·mol^{-1}), citric acid, and solvents were purchased from Merck. All chemicals were used without further purification. Purities of 1-propanol, 1-octanol, and 1-decanol were > 99.7 %, > 99.6 %, > 99.0 % respectively.

3.2. Analysis Methods. Citric acid is dissolved in water to prepare the solutions with initial mass factors of acid 8 % (0.42 mol·L^{-1}). The initial organic phases were prepared by the dissolution of TOMAC in the diluents to produce solutions with approximately six constant concentrations (1.775 mol·L^{-1}, 1.423 mol·L^{-1}, 1.204 mol·L^{-1}, 0.901 mol·L^{-1}, 0.653 mol·L^{-1}, 0.362 mol·L^{-1}). In general, an amine extractant must always be used in the form of a solution in organic diluents due to its high viscous and corrosive properties. Distribution experiments were carried out as follows: (i) For distribution experiments, equal volumes of an aqueous citric acid solution and an organic solution of TOMAC were stirred for 2 h in glass flasks immersed in a water bath at (25 ± 0.1) °C. (ii) After equilibration, both phases were separated. (iii) The concentration of the acid in the aqueous phase was determined by titration with aqueous 0.1 mol·L^{-1} sodium hydroxide (relative uncertainty: 1 %).[21] Acid analysis was checked against a material balance. In most cases, the deviation between the amount of acid analyzed and the amount of acid known from preparing the solutions by mass did not exceed 3 %.

4. Results and Discussion

4.1. Equilibrium Results. The dissociation constants and pK_{a} values for citric acid in aqueous solution are $K_{\mathrm{a1}} = 1.742\cdot10^{-3}$ and pK_{a1} = 2.759, $K_{\mathrm{a2}} = 8.892\cdot10^{-5}$ and pK_{a2} = 4.051, $K_{\mathrm{a3}} = 7.551\cdot10^{-6}$ and pK_{a3} = 5.122. Recovery of citric acid between water and solvents used in this study is presented in terms of distribution coefficients in Tables 1 and 2 at two different temperatures, 298.15 K and 303.15 K. Tables 1 and 2 show a survey of the experimental liquid−liquid-phase equilibrium investigations for the partitioning of citric acid. The amine concentration in the initial organic solution amounted to up to 0.362 mol·L^{-1}, 0.653 mol·L^{-1}, 0.901 mol·L^{-1}, 1.204 mol·L^{-1}, 1.423 mol·L^{-1}, and 1.775 mol·L^{-1} in 1-propanol, 1-octanol, and their mixture (1-propanol + 1-octanol) (50−50 v/v %). The citric acid concentration in the initial aqueous phase was 0.420 mol/L (8 %).

It can be seen from Tables 1 and 2 that similar results are observed at both temperatures (298.15 K and 303.15 K), and there is only small change in the partitioning coefficients and loading factors over this temperature interval. A considerable amount of citric acid is removed by TOMAC from aqueous solution. The amount of acid removed strongly depends on the concentration of TOMAC and the diluting solvents. The maximum removals of citric acid are 70.000 % with 1-propanol and 61.905 % with the 1-propanol + 1-octanol mixture at 298.15 K for a 1.775 mol·L^{-1} initial concentration of TOMAC. The acid concentration of water at equilibrium (C_1) decreases from 0.293 mol·L^{-1} to 0.172 mol·L^{-1} with an increasing TOMAC concentration from 0.362 mol·L^{-1} to 1.775 mol·L^{-1} with 1-propanol at 298.15 K. Distribution coefficients increase from 0.707 to 2.303 and 0.597 to 1.625 with increasing TOMAC concentration (0.362 mol·L^{-1} to 1.775 mol·L^{-1}) for 1-propanol and the (1-propanol + 1-octanol) mixture, respectively.

Table 1. Molar Concentration of Amine in the Organic Phase, C^{l}_{2}, Molar Concentration of Acid in the Aqueous Phase, C_1, Molar Concentration of Acid in the Organic Phase, C^{l}_{1}, Partitioning Coefficient, *D*, Loading Factor, *Z*, and Extraction Efficiency, *E*, for the Extraction of Citric Acid with TOMAC and Diluting Solvents[a]

	C^{l}_{2} mol·L^{-1}	C_1 mol·L^{-1}		C^{l}_{1} ml·L^{-1}		*D*		*Z*		*E* %	
diluents		*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
1-propanol	0.362	0.246	0.248	0.174	0.172	0.707	0.694	0.481	0.475	41.428	40.952
	0.653	0.224	0.227	0.196	0.193	0.875	0.850	0.300	0.295	46.667	45.952
	0.901	0.214	0.216	0.206	0.204	0.962	0.944	0.229	0.226	49.047	48.571
	1.204	0.172	0.175	0.248	0.245	1.441	1.400	0.206	0.203	59.048	58.333
	1.423	0.154	0.156	0.266	0.264	1.727	1.692	0.187	0.185	63.333	62.857
	1.775	0.126	0.127	0.294	0.293	2.333	2.307	0.166	0.165	70.000	69.761
1-octanol	0.362	0.296	0.298	0.124	0.122	0.419	0.409	0.342	0.337	29.521	29.047
	0.653	0.277	0.280	0.143	0.140	0.516	0.500	0.219	0.214	34.048	33.333
	0.901	0.258	0.259	0.162	0.161	0.628	0.622	0.179	0.178	38.571	38.333
	1.204	0.222	0.224	0.198	0.196	0.892	0.875	0.164	0.163	47.143	46.666
	1.423	0.216	0.217	0.204	0.203	0.944	0.935	0.143	0.142	48.571	48.333
	1.775	0.195	0.197	0.225	0.223	1.154	1.132	0.127	0.125	53.571	53.095
1-decanol	0.362	0.334	0.335	0.086	0.085	0.257	0.254	0.237	0.234	20.476	20.238
	0.653	0.313	0.315	0.107	0.105	0.342	0.333	0.164	0.161	25.476	25.000
	0.901	0.311	0.314	0.109	0.106	0.350	0.337	0.121	0.117	25.952	25.238
	1.204	0.285	0.286	0.135	0.134	0.474	0.468	0.112	0.111	32.143	31.904
	1.423	0.275	0.276	0.145	0.144	0.527	0.522	0.102	0.101	34.523	34.285
	1.775	0.246	0.248	0.174	0.172	0.707	0.693	0.098	0.096	41.428	40.952

[a] *A* and *B* refer to temperatures 298.15 K and 303.15 K, respectively.

Table 2. Molar Concentration of Amine in the Organic Phase, C^{l}_{2}, Molar Concentration of Acid in the Aqueous Phase, C_1, Molar Concentration of Acid in the Organic Phase, C^{l}_{1}, Partitioning Coefficient, *D*, Loading Factor, *Z*, and Extraction Efficiency, *E*, for the Extraction of Citric Acid with TOMAC and Diluting Solvents[a]

	C^{l}_{2} mol·L^{-1}	C_1 mol·L^{-1}		C^{l}_{1} mol·L^{-1}		*D*		*Z*		*E* %	
diluents		*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
1-propanol + 1-octanol	0.362	0.263	0.265	0.157	0.155	0.597	0.585	0.434	0.428	37.381	36.904
	0.653	0.244	0.246	0.176	0.174	0.721	0.707	0.269	0.266	41.905	41.428
	0.901	0.223	0.225	0.197	0.195	0.883	0.866	0.219	0.216	46.905	46.428
	1.204	0.195	0.196	0.225	0.224	1.154	1.143	0.187	0.186	53.571	53.333
	1.423	0.183	0.185	0.237	0.235	1.295	1.270	0.167	0.165	56.428	55.952
	1.775	0.160	0.163	0.260	0.257	1.625	1.577	0.146	0.144	61.905	61.190
1-propanol + 1-decanol	0.362	0.291	0.292	0.129	0.128	0.443	0.438	0.356	0.353	30.714	30.476
	0.653	0.273	0.276	0.147	0.144	0.538	0.521	0.225	0.220	35.000	34.285
	0.901	0.264	0.265	0.156	0.155	0.591	0.584	0.173	0.172	37.142	36.904
	1.204	0.241	0.243	0.179	0.177	0.743	0.728	0.149	0.147	42.619	42.143
	1.423	0.232	0.233	0.188	0.187	0.810	0.802	0.132	0.131	44.762	44.523
	1.775	0.222	0.224	0.198	0.196	0.892	0.875	0.111	0.110	47.143	46.666
1-octanol + 1-decanol	0.362	0.310	0.312	0.110	0.108	0.355	0.346	0.304	0.298	26.190	25.714
	0.653	0.292	0.293	0.128	0.127	0.438	0.433	0.196	0.194	30.476	30.238
	0.901	0.281	0.284	0.139	0.136	0.495	0.478	0.154	0.151	33.095	32.380
	1.204	0.271	0.273	0.149	0.147	0.549	0.538	0.124	0.122	35.476	35.000
	1.423	0.253	0.255	0.167	0.165	0.660	0.647	0.117	0.115	39.762	39.285
	1.775	0.242	0.243	0.178	0.177	0.735	0.728	0.100	0.099	42.381	42.142

[a] *A* and *B* refer to temperatures 298.15 K and 303.15 K, respectively.

Table 3. Molar Concentration of Acid in the Aqueous Phase, C_1, Molar Concentration of Acid in the Organic Phase, C^{l}_{1}, Partitioning Coefficient, *D*, and Extraction Efficiency, *E*, for the Extraction of Citric Acid between Solvents and Water[a]

	C_1 mol·L^{-1}		C^{l}_{1} mol·L^{-1}		*D*		*E* %	
diluents	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
1-propanol	0.321	0.323	0.099	0.097	0.308	0.300	23.571	23.095
1-octanol	0.358	0.361	0.062	0.059	0.173	0.163	14.762	14.047
1-decanol	0.389	0.391	0.031	0.029	0.079	0.074	7.381	6.904
1-propanol + 1-octanol	0.327	0.330	0.093	0.090	0.284	0.273	22.143	21.428
1-propanol + 1-decanol	0.351	0.352	0.069	0.068	0.196	0.193	16.428	16.191
1-octanol + 1-decanol	0.377	0.379	0.043	0.041	0.114	0.108	10.238	9.761

[a] *A* and *B* refer to temperatures 298.15 K and 303.15 K, respectively.

Figure 1 demonstrates the influence of TOMAC in the organic phase on the distribution ratio of citric acid. In the experiments, the concentration of citric acid in the aqueous phase varied between about 0.334 mol·L^{-1} and 0.126 mol·L^{-1} for individual solvents. The best distribution ratio of citric acid in that range is between about 2.33 and 0.707 in 1-propanol at 298.15 K.

Figure 2 demonstrates the influence of TOMAC in the organic phase on the distribution ratio of citric acid for solvent mixtures. In the experiments, the concentration of citric acid in the aqueous phase varied between about 0.310 mol·L^{-1} to 0.160 mol·L^{-1}. The distribution ratio of citric acid in that range is between about 1.625 and 0.335 at 298.15 K.

In Figures 3 and 4, the effect of TOMAC concentration on loading is shown for individual solvents and solvent mixtures, respectively. The loading curve is a plot of loading factor (*Z*) versus amine concentration. In this work, the loading factor of

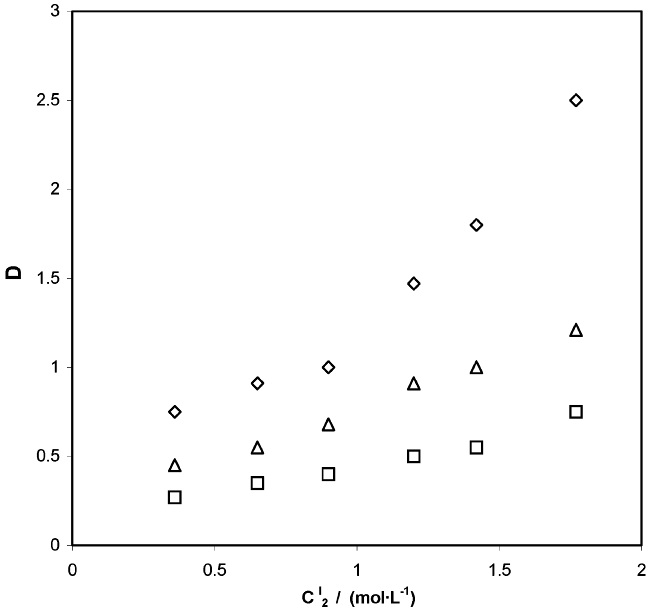

Figure 1. Partitioning coefficients, *D*, with C^l_2, concentration of TOMAC in different diluting solvents: ◇, 1-propanol; △,1-octanol; □, 1-decanol.

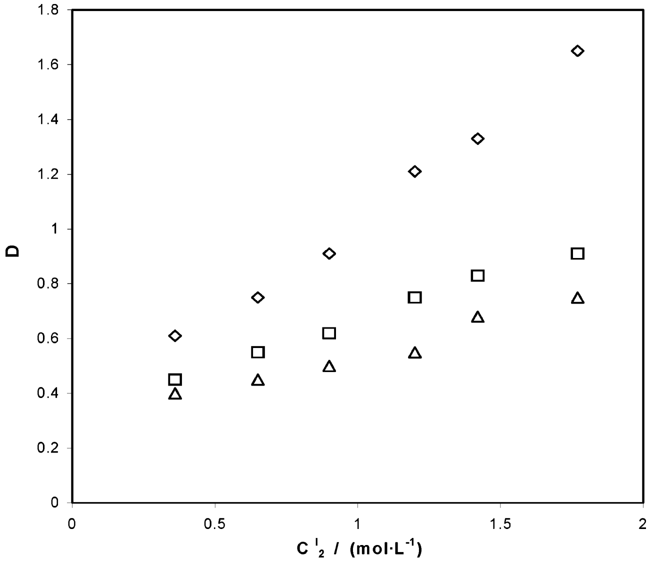

Figure 2. Partitioning coefficients, *D*, with C^l_2, concentration of TOMAC in different diluting solvents: ◇, 1-propanol + 1-octanol; □, 1-propanol + 1-decanol; △, 1-octanol + 1-decanol.

all solvent mixtures increases with decreasing concentration of TOMAC.

The distribution data of citric acid between water and solvents used in this study are presented in Table 3.

4.2. LSER Model Results. Kamlet et al.[18] give the values of solvatochromic parameters for several hundred compounds. By knowing the values of D^0, *s*, *d*, *b*, and *a* parameters for the given extraction system (TOMAC + aqueous citric acid in this case), eq 9 gives an estimation of partitioning coefficients for a wide range of diluents, for which comparatively narrow confidence intervals have been found.

The values of solvatochromic parameters of diluents were taken from Table 4. The remaining parameters were fitted to the experimental results. Experimental results are compared to model predictions in Table 5 and Figure 5. It can be seen that the final correlation gives a good description of the distribution of citric acid over a wide concentration range. The values of the regression parameters D^0, *s*, *d*, *b*, and *a* are presented in Table 6.

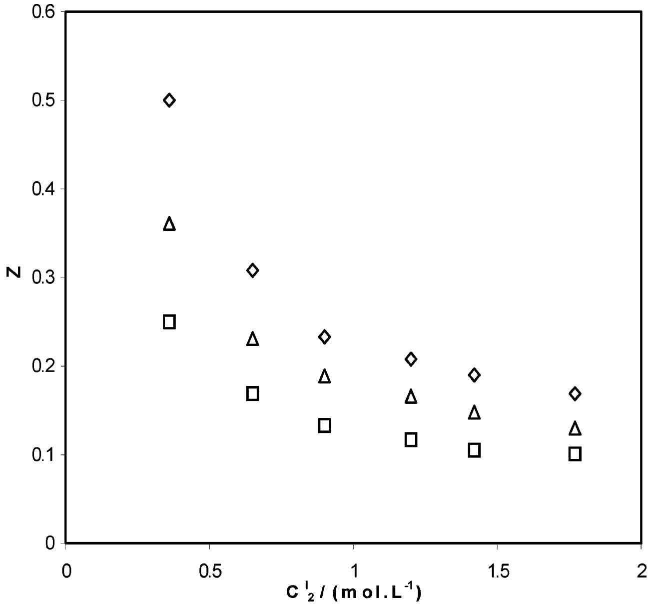

Figure 3. Loading factors, *Z*, with C^l_2, concentration of TOMAC in different diluting solvents: ◇, 1-propanol; △, 1-octanol; □, 1-decanol.

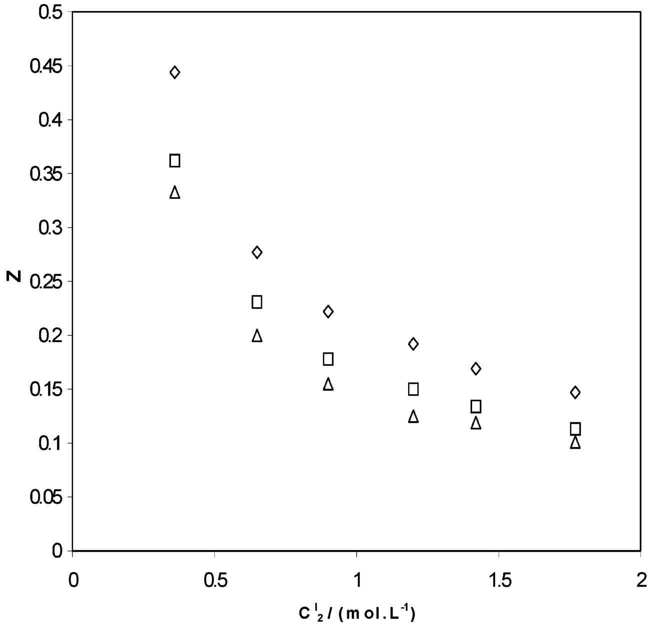

Figure 4. Loading factors, *Z*, with C^l_2, concentration of TOMAC in different diluting solvents: ◇, 1-propanol + 1-octanol; □, 1-propanol + 1-decanol; △, 1-octanol + 1-decanol.

Table 4. Solvatochromic Parameters, Hydrogen-Bond Donor Acidities, π* and δ, Hydrogen-bond Acceptor Basicities, α, β, for 1-propanol, 1-octanol, and 1-decanol

	π^*	*b*	*a*	*d*
1-propanol[18,23]	0.52	0.45	0.78	0
1-octanol[22]	0.40	0.45	0.33	0
1-decanol[24]	0.33	0.36	0.14	0

For the optimal estimation of the model parameters, a regression technique assisted computer program was used to minimize the deviation between the model prediction and experimental data. All predicted partition coefficients agree well with each other, and also the agreements between predictions and measurements are acceptable considering experimental uncertainty. The estimated values of parameters of the model

Table 5. Molar Concentration of Amine in the Organic Phase, C^{l}_{2}, Experimental Results, D, and Model Results, D^{l}, for Comparison of Experimental Results and Model Predictions for 298.15 K

diluents	C^{l}_{2} mol·L^{-1}	D	D^{l}
1-propanol	0.362	0.707	0.732
	0.653	0.875	0.961
	0.901	0.962	0.974
	1.204	1.441	1.442
	1.423	1.727	1.714
	1.775	2.333	2.563
1-octanol	0.362	0.419	0.471
	0.653	0.516	0.540
	0.901	0.628	0.630
	1.204	0.892	0.930
	1.423	0.944	1.022
	1.775	1.154	1.241
1-decanol	0.362	0.257	0.314
	0.653	0.342	0.348
	0.901	0.350	0.385
	1.204	0.474	0.512
	1.423	0.527	0.577
	1.775	0.707	0.762

Table 6. The Values of LSER Model Parameters (*s*, *d*, *b*, *a*), Coefficient of Linear Regression, R^2

	ln D^0	s	d	a	b	R^2
model parameters	0.4372	1.8789	0	2.6531	−1.2316	0.96

are presented in Table 6. The comparison of the model simulation and experimental data for the partitioning coefficient of citric acid is shown in Table 5 and Figure 5. The experimental data shows a good correlation to the calculated values. It has been concluded that by using this model, distribution coefficients of citric acid between water and the amine + diluent system can be described.

The system constants in Table 6 reveal that the partition coefficients are strongly correlated to a solute's partition coefficient, which means that the organic solute/amine partitioning equilibrium of a solute is strongly affected by the cavity effect and dispersive solute/amine interactions. The solute hydrogen acidity and basicity, *a* and *b*, also show a significant correlation with the partition coefficient. This confirms that the organic solvent serves as both a hydrogen donor and acceptor. The relative size of the standardized system constants (β), which are the regression coefficients derived from standardized dependent variables, relays information on the relative importance of different types of solute/solvent interactions. This suggests that the strength of the interaction decreases from dispersive interactions, hydrogen bonding, solute/solvent (σ /π) electron pair interaction to solute/solvent dipolarity/ polarizability interaction.

The root-mean-square deviations (rmsd) are calculated from the difference between the experimental data, and the predictions of the LSER model according to the following equation:

$$\text{rmsd} = \sqrt{\frac{1}{N}\sum_{i=1}^{n}(D_{i,\text{exp}} - D_{i,\text{calc}})} \tag{10}$$

where $D_{i,\text{exp}}$, is the experimental distribution coefficient, $D_{i,\text{calc}}$ is the calculated distribution coefficient, and N is the number of experimental data. The rmsd value of the LSER model is found to be 0.076 for 1-propanol, 0.065 for 1-octanol, and 0.061 for 1-decanol.

The rmsd value shows all predicted distribution coefficients agree well with each other, and also the agreements between predictions and measurements is acceptable considering experimental uncertainty.

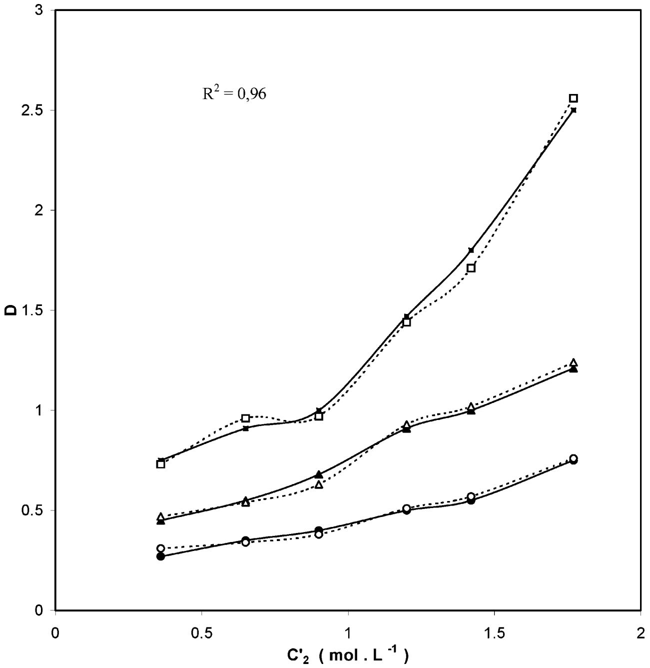

Figure 5. Comparison of variation of distribution coefficients D with concentration of TOMAC C^{l}_{2} and model predictions for individual solvents: ×, 1-propanol, -□- model; ▲, 1-octanol, -△-, model; ●, 1-decanol, -○- model.

5. Conclusions

In this study, the maximum removal of citric acid is 69.761 % with 1-propanol using a 1.775 mol·L^{-1} initial concentration of TOMAC. The maximum extraction efficiencies for diluents at maximum TOMAC are found as: 1-propanol ≫ 1-octanol > 1-decanol > (1-propanol + 1-octanol) > (1-propanol + 1-decanol) > (1-octanol + 1-decanol). This result shows that extractability of the solvents decrease with increasing carbon number of the solvents.

The values of distribution coefficients can be correlated with the solvatochromic parameters of the diluents, π^*, δ, α, β, according to eq 9. The LSER model predicted that distribution coefficients and measurement distribution coefficients agree well with each other considering the experimental uncertainty.

The resulting LSER regression is

$$\ln D = 0.4372 + 1.8789(\pi^* - 0\delta) - 1.2316\beta + 2.6531\alpha$$

This equation was used to predict ln D for the organic solutes.

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