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Comparative Equilibrium Studies for Citric Acid by Amberlite LA-2 or Tridodecylamine (TDA)

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Carboxylic acids like citric acid are produced by fermentation. They have been used in many industrial fields as intermediate and starting materials, and their importance is still growing. It is important to separate them from the fermentation broth. In this sense, comparison of different types of solvents and amines for extraction of carboxylic acids from the fermentation broth and the most effective amine-solvent composition is sought. Studies have been performed on the extraction of citric acid from fermentation broth by tridodecylamine (TDA) (a long chain tertiary amine), and Amberlite LA-2 (a secondary amine mixture). These extractants were dissolved in different solvents having different chemical structures. The extractions were carried out at 298 K. Comparison of the results were made using the distribution coefficient, loading factor, separation factor, and the percentage of extraction yield. The most effective solvent was determined as 1-octanol for both TDA and Amberlite LA-2 with a distribution value of 29.63 and 103.80, respectively. The maximum value of the extraction efficiency was found to be 99.05 % with Amberlite LA-2 in 1-octanol.

Introduction

The purification of organic acids is very important when they are used as starting materials for food additions, pharmaceuticals, biodegradable plastics and other products. The purity of organic acids affects the quality of the final products.[1,2]

Citric acid is an important commercial product with a global production more than one million tons per year.[3] Almost the entire quantity of citric acid is produced by fermentation, mainly through submerged fermentation of starch or sucrose based media, using the filamentous fungus *Aspergillus niger*. The food industry is the largest consumer of citric acid. They use almost 70 % of the total production. Other usage is about 12 % by the pharmaceutical industry and 18 % in other applications.[4] There is also an annual growth of (3.5 to 4.0) % in the demand/consumption rate of citric acid.

Because this acid is produced by fermentation, its solutions contain many impurities, such as microorganisms, other organic acids, and residual raw material compounds. Organic acids purification from fermentation broth is a very difficult procedure. The choice of purification method is determined based on cost, environmental limitations, and facility.[5,6]

Citric acid is conventionally purified by precipitation and acidification steps. In citric acid purification, lime is added to the fermentation broth and calcium citrate is precipitated, and then calcium citrate is acidified with H_2SO_4. After these steps citric acid is purified. This method has a lot of disadvantages. It is a batch purification method. After the acidification step, a large quantity of calcium sulfate is generated, and organic impurities are retained so it cannot be released to the environment. After the precipitation step, the acid salts have some impurities. These impurities (acid salts) are removed by washing with an excess of water. This causes loss of product. The advantage of this method is the cheaper unit cost than other methods.[5]

Alternatively, distillation, adsorption, membrane separation, and electrodialysis can be used for removing organic acids from the fermentation broth continuously. Reactive extraction of organic acids with an amine extractant has been found to be a promising alternative to the conventional process. In reactive extraction, a reaction occurs between the amine extractant and extracted acid. In this reaction, acid-amine complex formation occurs. This complex is solubilized into the organic phase, and the organic acid is recovered from the organic phase by stripping. For economic recovery, the extractant should provide a high equilibrium distribution coefficient. For this purpose, the extractant selection is very important. The extractant should also have low water solubility. It has been reported that secondary and long chain tertiary amines are suitable for the extraction of organic acids from aqueous solution. Amine extractants are solubilized in organic solvents. Thus, extractant concentration, viscosity, and density can be controlled.[5,7]

The recovery of carboxylic acids by reactive extraction has been studied by several research groups. Wasewar et al. reported that Alamine 336 in oleyl alcohol has the highest distribution coefficient and is the ideal extraction system for lactic acid.[8] The same researchers studied the equilibria and kinetics for the reactive extraction of lactic acid using Alamine 336 in decanol.[9] Martak and Schlosser[10] studied the liquid−liquid equilibria of dimethylcyclopropane carboxylic acid in water + solvent systems with trioctylamine as the extractant. Uslu and Kirbaşlar recently have studied the reactive extraction of levulinic acid by trioctyl amine.[11,12]

In this study, two different amines were chosen because of their high affinity for carboxylic acids. The extractability of citric acid by a secondery amine (Amberlite LA-2) and tertiary amine (TDA) was investigated in different diluents. MIBK, toluene,

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cyclohexane, isooctane, and 1-octanol were chosen to investigate their solvation capacity of the amines.

Theoretical

The complex formation, during the extraction of hydroxycarboxylic acids by the long chain aliphatic amines can be generally described by the following reaction

$$p[A] + q[B]_{org} \leftrightarrow [A_pB_q]_{org} \qquad (1)$$

The complex formation is an equilibrium reaction. In this reaction, A is the acid molecule and B is the amine molecule. If a diluent interacts with the complex strongly, it can be represented as

$$p[A] + q[B] + r[F]_{org} \leftrightarrow [A_pB_qF_r]_{org} \qquad (2)$$

where F is the diluent molecule. The diluents used in the extraction can be classified as "active" and "inert" diluents. Active diluents contain functional groups that interact strongly with the complex, for example, 1-octanol, MIBK, as shown in reaction 2. Inert diluents do not interact with the complex, for example, cyclohexane, isooctane. Aliphatic hydrocarbons are generally inert diluents.[5]

A tertiary amine and a secondary amine were chosen as extractants in this study. Complex formation reactions of these extractants with carboxylic acids based on reaction 1 are shown below. For TDA, a tertiary amine[13] was chosen

$$[H_pA]_{aq} + i[R_3N]_{org} \leftrightarrow [R_3NH]_iH_{p-i}A \quad p = 1, 2, 3 \quad i = 1, 2, 3 \qquad (3)$$

For Amberlite LA-2, a secondary amine[14] was chosen

$$[H_pA]_{aq} + i[R_2NH]_{org} \leftrightarrow [R_2NH_2]_iH_{p-i}A \quad p = 1, 2, 3 \quad i = 1, 2, 3 \qquad (4)$$

If the interaction between the acid and amine is strong, the reactive extraction is more effective.

The distribution coefficient (D), loading factor (Z), and extraction yield (E) are calculated for the comparison of the extraction results for both amine extractants.

The distribution coefficient is defined as ratio of the concentration of organic acid in the organic phase to the concentration of organic acid in the aqueous phase

$$D = \frac{C_{A,org}}{C_{A,aq}} \qquad (5)$$

The loading factor (Z) of extractant is defined as the total concentration of acid in the organic phase, $C_{A,org}$, divided by the total concentration of amine in the organic phase, C_B

$$Z_t = \frac{C_{A,org}}{C_{B,org}} \qquad (6)$$

The stoichiometric loading factor, Z_s, is the ratio of the overall complexed acid to total amine in the organic phase. This factor includes a correction term ($\upsilon \cdot C^{s}_{A,org}$) for the amount of acid extracted by the diluents in the solvent mixture

$$Z_s = \frac{(C_{A,org} - \upsilon \cdot C^{*s}_{A,org})}{C_B} \qquad (7)$$

Extraction yield is determined as the percentage of extracted acid

$$E = \left(1 - \frac{(C_{A,aq})}{C_{Ao}}\right) \cdot 100 \qquad (8)$$

In eq 8, $C_{A,aq}$ is the concentration of acid in aqueous phase after extraction; C_{Ao} is the initial acid concentration in the aqueous phase.[15]

If an extractant is suitable for the chosen acid, the distribution coefficient should be larger than 1. Furthermore, complexes with more than one acid per amine should be formed for more economic extraction. In other words, loading factors have high values.

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

$$S_f = \frac{C_{A,org}}{C_{A,org} + C_{A^-}} \qquad (9)$$

Experimental Section

Two types of amines, tridodecylamine (TDA) and Amberlite LA-2, five types of solvents were purchased from Merck and Fluka and they were used in the extraction of citric acid. TDA (purity >99 %) is a long chain tertiary amine, and Amberlite LA-2 (purity >99 %) is a normal and isododecyl secondary amine mixture. TDA is a colorless liquid extractant. Its melting point, density, and molecular weight are 16 °C, 0.82 $g \cdot cm^{-3}$, and 522.01 $g \cdot mol^{-1}$, respectively. Amberlite LA-2 is a yellow liquid, its acid binding capacity, viscosity, and density are 2.6 $meq \cdot g^{-1}$ to 2.9 $meq \cdot g^{-1}$, 18 cP at 25 °C, and 0.83 $g.cm^{-3}$, respectively. The molecular weight of Amberlite LA-2 is between (353 and 395) $g \cdot mol^{-1}$, but its mean molar mass of 374 has been offered.[16] Methyl isobutylketone (MIBK) (purity >99 %), 1-octanol (purity >98 %), toluene (purity >99 %), cyclohexane (purity >98 %), and iso-octane (purity >98 %) were used for diluting the amine extractants.

Citric acid (Merck Co., number 1.00244) was diluted by distilled water to prepare approximately a 10 % (w/w) solution. The organic phase was prepared by diluting the amine extractants in five diluents. Aqueous and organic solutions were added to Erlenmeyer flasks and shaken in a thermostatted shaker bath (Nüve ST402) at 25 °C for 4 h. This equilibrium period was found in preliminary experiments. After achieving the equilibrium state, the aqueous phase acid concentrations were determined by titration using 0.1 N NaOH solution with phenolphthalein as indicator (relative uncertainty: 1 %). 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 1 %. Aqueous phase pH measurements were performed with a Hanna Instruments pH 211 Microprocessor pH meter.

Result and Discussion

Table 1a,b shows the results of the extraction experiments when TDA and Amberlite LA-2 were used, respectively. The concentration of TDA in the solvents was between 0.22 $mol \cdot L^{-1}$ and 2.62 $mol \cdot L^{-1}$. The Amberlite LA-2 concentration was changed in the range of 0.32 $mol \cdot L^{-1}$ to 3.60 $mol \cdot L^{-1}$. The initial citric acid concentration was 1.11 $mol \cdot L^{-1}$ (= 10 % w/w) and the initial pH value of the acid was 1.52.

The data for the distribution of citric acid between water and TDA or Amberlite LA-2 dissolved in toluene, 1-octanol, MIBK, cyclohexane, and isooctane are shown in Tables 1 and 2 and are illustrated in Figure 1a,b. The tables show that TDA and

Table 1[a]

(a) Results for Extraction of Citric Acid by TDA with Individual Solvents

diluent	$C_{\mathrm{B,org}}$ ($\mathrm{mol \cdot L^{-1}}$)	C_{A} ($\mathrm{mol \cdot L^{-1}}$)	$C_{\mathrm{A,org}}$ ($\mathrm{mol \cdot L^{-1}}$)	pH	D	Z_{t}	Z_{s}	S_{f}	E (%)
toluene	0.220	0.440	0.070	1.70	0.170	0.320	0.306	0.009	13.730
	0.520	0.270	0.240	1.80	0.900	0.460	0.451	0.040	47.060
	0.940	0.160	0.350	1.99	2.250	0.370	0.364	0.087	68.630
	1.570	0.080	0.430	2.24	5.830	0.270	0.267	0.173	84.310
	2.620	0.040	0.470	2.45	11.800	0.180	0.174	0.271	92.160
1-octanol	0.220	0.360	0.150	1.76	0.430	0.680	0.666	0.023	29.410
	0.520	0.190	0.320	1.87	1.660	0.620	0.602	0.062	62.750
	0.940	0.150	0.360	2.21	2.500	0.380	0.372	0.141	71.370
	1.570	0.070	0.430	2.32	5.660	0.270	0.265	0.202	85.100
	2.620	0.020	0.490	2.78	29.630	0.180	0.180	0.454	96.860
MIBK	0.220	0.370	0.140	1.75	0.390	0.640	0.625	0.021	27.450
	0.520	0.220	0.290	1.88	1.360	0.560	0.548	0.058	56.860
	0.940	0.110	0.400	2.16	3.880	0.430	0.417	0.140	78.430
	1.570	0.050	0.470	2.49	10.200	0.290	0.293	0.290	91.170
	2.620	0.020	0.480	2.81	22.300	0.180	0.178	0.466	95.680
isooctane	0.220	0.410	0.100	1.72	0.250	0.450	0.435	0.014	19.600
	0.520	0.290	0.220	1.82	0.730	0.420	0.407	0.039	43.140
	0.940	0.190	0.320	1.90	1.640	0.340	0.327	0.066	62.750
	1.570	0.125	0.385	2.15	3.100	0.250	0.234	0.132	75.500
	2.620	0.050	0.460	2.28	8.240	0.180	0.167	0.198	90.190
cyclohexane	0.220	0.480	0.030	1.65	0.060	0.140	0.128	0.003	5.880
	0.520	0.410	0.100	1.70	0.240	0.190	0.185	0.013	19.600
	0.940	0.290	0.220	1.82	0.760	0.230	0.228	0.039	43.140
	1.570	0.170	0.340	1.96	1.980	0.220	0.212	0.080	66.600
	2.620	0.100	0.410	2.13	4.030	0.160	0.153	0.134	80.400

(b) Results for Extraction of Citric Acid by Amberlite LA-2 with Individual Solvents

diluent	$C_{\mathrm{B,org}}$ ($\mathrm{mol \cdot L^{-1}}$)	C_{A} ($\mathrm{mol \cdot L^{-1}}$)	$C_{\mathrm{A,org}}$ ($\mathrm{mol \cdot L^{-1}}$)	pH	D	Z_{t}	Z_{s}	S_{f}	E (%)
toluene	0.320	0.420	0.090	1.83	0.200	0.280	0.273	0.017	17.650
	0.740	0.130	0.390	2.24	3.080	0.530	0.520	0.160	75.490
	1.330	0.030	0.480	3.57	15.190	0.360	0.355	0.834	93.730
	2.220	0.030	0.480	4.44	18.030	0.220	0.211	0.973	94.700
	3.700	0.010	0.490	4.89	43.500	0.130	0.129	0.990	97.650
1-octanol	0.320	0.280	0.230	2.02	0.810	0.720	0.708	0.063	45.100
	0.740	0.110	0.400	2.42	3.760	0.540	0.531	0.228	78.430
	1.330	0.030	0.480	3.34	18.030	0.360	0.353	0.747	94.710
	2.220	0.010	0.480	4.62	39.800	0.220	0.210	0.982	97.450
	3.700	0.004	0.510	5.20	103.800	0.140	0.133	0.995	99.050
MIBK	0.320	0.280	0.230	2.01	0.820	0.720	0.711	0.062	45.100
	0.740	0.080	0.430	2.69	5.160	0.580	0.574	0.372	83.730
	1.330	0.030	0.480	3.59	15.890	0.360	0.355	0.840	94.120
	2.220	0.010	0.490	4.61	44.600	0.220	0.216	0.982	97.840
	3.700	0.005	0.510	5.06	92.300	0.140	0.134	0.993	98.930
isooctane	0.320	0.300	0.210	2.04	0.700	0.660	0.643	0.060	41.170
	0.740	0.130	0.380	2.48	2.800	0.520	0.502	0.244	74.510
	1.330	0.030	0.480	3.23	14.300	0.360	0.351	0.696	94.120
	2.220	0.020	0.490	4.11	26.200	0.220	0.213	0.946	96.470
	3.700	0.010	0.490	4.62	40.700	0.130	0.126	0.982	97.650
cyclohexane	0.320	0.300	0.210	2.06	0.700	0.660	0.651	0.063	41.170
	0.740	0.140	0.370	2.46	2.720	0.500	0.495	0.231	72.550
	1.330	0.050	0.450	3.17	8.200	0.340	0.334	0.652	89.220
	2.220	0.030	0.480	4.08	17.850	0.220	0.213	0.942	94.710
	3.700	0.020	0.490	4.56	25.130	0.130	0.130	0.980	96.270

[a] $C_{\mathrm{B,org}}$ is the concentration of TDA in the organic phase; C_{A} is the concentration of citric acid in the aqueous phase; $C_{\mathrm{A,org}}$ is the concentration of citric acid in the organic phase; D is the distribution coefficient; Z_{t} is the loading factor; Z_{s} is the stoichiometric loading factor; S_{f} is the separation factor; and E is the extraction efficiency.

Table 2

(a) Results for Extraction of Citric Acid by TDA with Solvent Mixture

diluent mixtures	$C_{\mathrm{B,org}}$ ($\mathrm{mol \cdot L^{-1}}$)	C_{A} ($\mathrm{mol \cdot L^{-1}}$)	$C_{\mathrm{A,org}}$ ($\mathrm{mol \cdot L^{-1}}$)	pH	D	Z_{t}	Z_{s}	S_{f}	E (%)
1-octanol-toluene	2.620	0.020	0.490	2.86	30.600	0.180	0.177	0.500	96.860
1-octanol-MIBK	2.620	0.010	0.490	2.96	38.200	0.190	0.180	0.557	97.450
MIBK-Toluene	2.620	0.020	0.480	2.77	20.500	0.190	0.181	0.443	95.300

(b) Results for Extraction of Citric Acid by Amberlite LA-2 with Solvents Mixture

diluent mixtures	$C_{\mathrm{B,org}}$ ($\mathrm{mol \cdot L^{-1}}$)	C_{A} ($\mathrm{mol \cdot L^{-1}}$)	$C_{\mathrm{A,org}}$ ($\mathrm{mol \cdot L^{-1}}$)	pH	D	Z_{t}	Z_{s}	S_{f}	E (%)
1-octanol-toluene	3.700	0.0052	0.510	3.75	97.000	0.137	0.131	0.889	98.980
1-octanol-MIBK	3.700	0.0059	0.500	4.22	84.200	0.135	0.130	0.958	98.830
MIBK-Toluene	3.700	0.0073	0.500	4.01	69.000	0.135	0.134	0.935	98.570

Amberlite LA-2 are very effective extractants. The maximum extracted citric acid was 96.86 % with TDA dissolved in 1-octanol and 99.05 % with Amberlite LA-2 in a 1-octanol solution. This result was achieved when the amine concentration

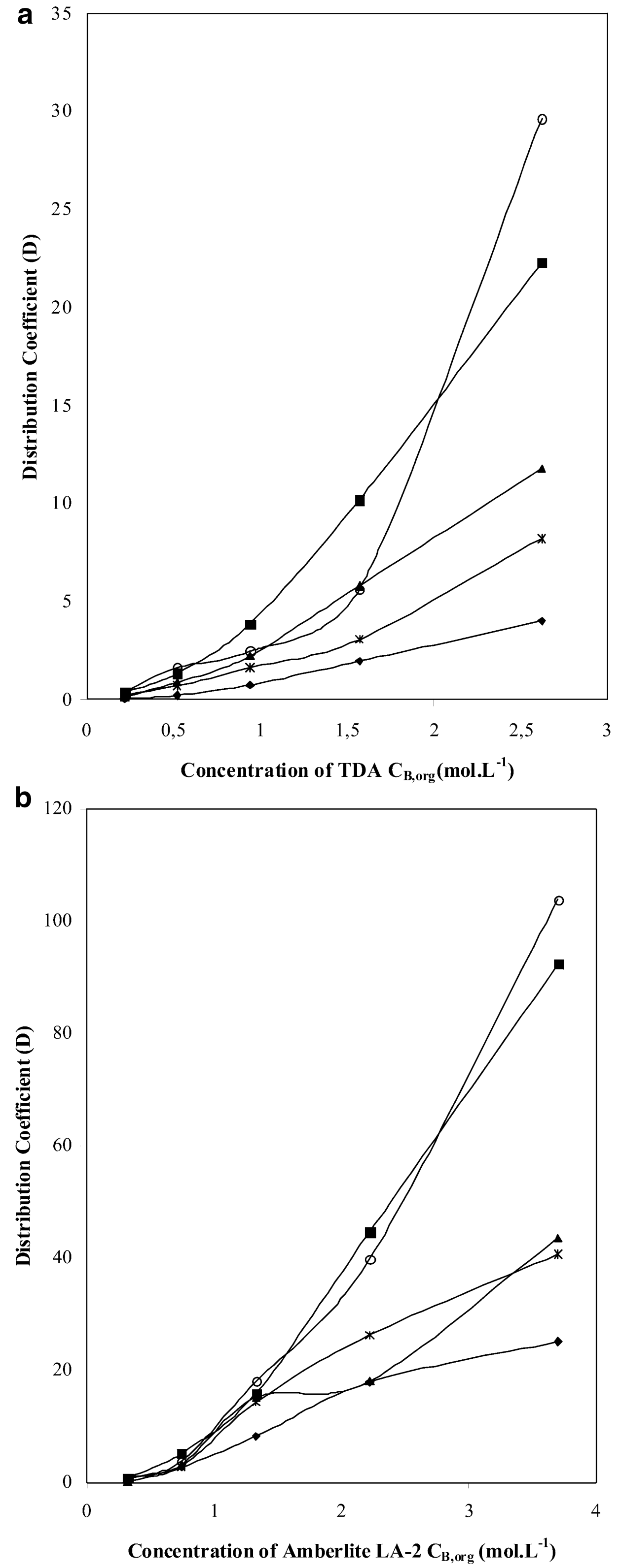

Figure 1. (a) Variation of distribution coefficients with concentration of TDA in different solvents.▲, toluene; ○, 1-octanol; ■, MIBK; *, isooctane; ●, cyclohexane. (b) Variation of distribution coefficients with concentration of Amberlite LA-2 in different solvents. ▲, toluene; ○, 1-octanol; ■, MIBK; *, isooctane; ●, cyclohexane.

was the highest value in the organic phase, 2.62 mol·L^{-1} of TDA and 3.70 mol·L^{-1} of Amberlite LA-2. At the lowest concentration value, the extraction yield was 5.88 % with Amberlite LA-2 dissolved in cyclohexane. This result shows that *D* increased with an increasing amount of amine. Choudhury et al. reported that the distribution coefficient increased with an increasing amount of amine extractant, and they reported that the increasing amine concentration might have a toxic effect on microorganisms in the in situ extractive fermentation. That is why the loading factor is an important expression.

The distribution coefficients increase from 0.06 to 29.63 with increasing concentration of TDA (0.22 mol·L^{-1} to 2.62 mol·L^{-1} with 1-octanol. When using cyclohexane, it was observed that the distribution coefficient changed between 0.06 and 4.03. This comparison shows that 1-octanol was the most effective solvent for citric acid extraction by TDA. On the other hand, the reactive extraction of citric acid by Amberlite LA-2 with 1-octanol gave values of the distribution coefficient between 0.81 and 103.80 with increasing Amberlite LA-2 concentration from (0.32 to 3.70) mol·L^{-1}.

In the extraction of carboxylic acids by TDA or Amberlite LA-2, an acid-amine complex occurs. Solvents interact with the complex. This interaction can be classified as "general solvation" and "specific interaction". Cyclohexane and isooctane are nonpolar diluents, so they affect the complex very slightly. That is why cyclohexane and isooctane gave lower distribution coefficients than 1-octanol and MIBK.[5]

MIBK has a high dielectric constant, 13.1 Debye at 20 °C, and it has a reactive functional group. These properties cause a very effective interaction between the polar complex and MIBK, as an example of general solvation. As Table 1a,b shows, the distribution coefficient changed between 0.39 and 92.30 when MIBK was used as solvent. These values were the second highest distribution coefficients for citric acid extraction by TDA or Amberlite LA-2. The third highest value was obtained by toluene. Toluene has aromatic π-electrons that interact with the complex specifically, and distribution coefficients ranged between 0.17 and 43.50.

Alcohol diluents give unexpected distribution coefficients. Hydrogen bonding occurs between the proton of the diluent and the complex. This characteristic of alcohol provides extra solvation for the complex. For this reason, 1-octanol had the best results for citric acid extraction, even though its dielectric constant is 10.3 Debye at 20 °C.

The maximum distribution coefficients for the diluents are found to be in the following order for both amines: 1-octanol > MIBK > toluene > isooctane > cyclohexane.

The loading curve is a plot of Z versus extractant concentration. In Figure 2a,b, the effect of TDA or Amberlite LA-2 concentration on loading is shown, respectively. As shown in Figure 2a,b, except for cyclohexane the other solvents show loading decreases with increasing amine concentration. For nonaggregating systems in inert diluents, for example, monocarboxylic acids in alkane or aromatic diluents, there was no effect of amine concentration on loading. So, in the present work cyclohexane has no effect on amine concentration loading.

Overloading, loading greater than unity, indicates that complexes with more than one acid per amine have been formed. Overloading was not observed for any of the diluents used in this study. Systems that exhibit aggregation, formation of complexes with large numbers of acid and amine molecules, exhibit an abrupt increase in loading at a critical acid concentration. In this study, toluene showed an abrupt increase in loading after which loading started to decrease.

The pH of the aqueous phase is an important parameter for the reactive extraction of organic acids. Yang et al. reported that lower pH values result in good separation of organic acids by long chain tertiary amines.[17] The most effective extraction is carried out when the pH value is below the pK_a of the acid.

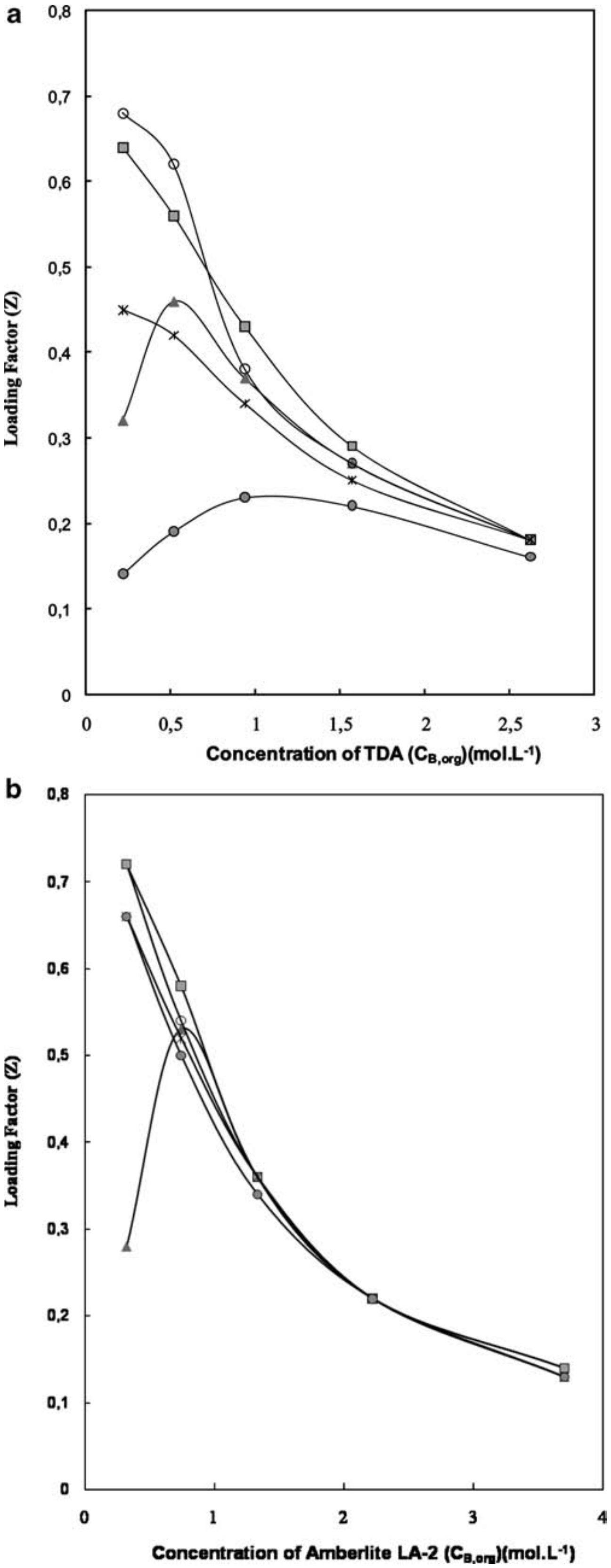

Figure 2. (a) Variation of loading factors with concentration of TDA in different diluting solvents. ▲, toluene; ○, 1-octanol; ■, MIBK; *, isooctane; ●, cyclohexane. (b) Variation of loading factors with concentration of Amberlite LA-2 in different diluting solvents. ▲, toluene; ○, 1-octanol; ■, MIBK; *, isooctane; ●, cyclohexane.

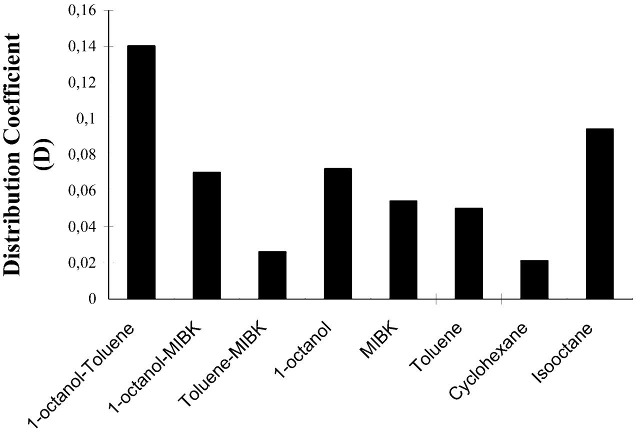

Figure 3. Results of physical extraction of citric acid.

Table 3. Results of Physical Extraction of Citric Acid

diluent	C_A (mol·L^{-1})	$C_{A,org}$ (mol·L^{-1})	pH	D	E (%)
cyclohexane	0.490	0.020	0.02	3.920	0.490
isooctane	0.460	0.050	0.09	9.800	0.460
MIBK	0.480	0.030	0.05	5.880	0.480
1-octanol	0.470	0.040	0.07	7.840	0.470
toluene	0.480	0.030	0.05	5.880	0.480
toluene-1-octanol	0.450	0.060	0.14	11.760	0.450
MIBK-1-octanol	0.470	0.040	0.07	7.840	0.470
MIBK-toluene	0.500	0.010	0.03	1.960	0.500

Table 4

initial acid conc. (mol·L^{-1})	$C_{B,org}$ (mol·L^{-1})	C_A (mol·L^{-1})	$C_{A,org}$ (mol·L^{-1})	D	Z_T	E (%)	
a. Results of Extraction of Citric Acid by TDA at Different Initial Citric Acid Concentration							
1.090	2.620	0.3800	0.710	1.85	0.270	65.140	
0.280	2.620	0.0031	0.270	88.45	0.100	98.840	
0.130	2.620	0.0085	0.130	151.58	0.050	99.340	
b. Results of Extraction of Citric Acid by Amberlte LA-2 at Different Initial Citric Acid Concentration							
1.090	3.700	0.1500	0.940	2.62	6.120	0.250	86.240
0.280	3.700	0.0026	0.280	5.88	108.310	0.080	99.070
0.130	3.700	0.0012	0.130	5.41	110.600	0.040	90.090

The pK_a values of citric acid are pK_{a1}, 3.15; pK_{a2}, 4.77; and pK_{a3}, 5.19. In this study, the pH values of the aqueous phase ranged from 1.65 to 2.81 when TDA was used and from 1.83 to 5.20 when Amberlite LA-2 was used.

Table 2a,b presents D, Z, and E values of the extraction of citric acid by TDA when solvent mixtures were used for diluting the TDA or Amberlite LA-2. The composition of the solvent mixture ratio was 1:1. Solvent mixtures used were 1-octanol + toluene, 1-octanol + MIBK, and toluene + MIBK. As shown in Figure 3, the 1-octanol + MIBK mixture was more effective than the other mixtures, its distribution coefficient was 38.20 and its extraction yield was 97.45 % when TDA was used as an amine extractant. When Amberlite LA-2 was used, its distribution coefficient values increased from 38.20 to 97.00. The most effective mixture is 1-octanol + toluene with Amberlite LA-2. Its distribution coefficient was 97.00 and its extraction yield was 98.98 %.

The physical extraction of citric acid was studied for better understanding of the effect of the amine. Calculated results of extraction of citric acid by pure solvents (not containing amine) (cyclohexane, isooctane, MIBK, 1-octanol, toluene, 1-octanol-toluene, 1-octanol+MIBK, toluene + MIBK) are presented in Table 3 and shown in Figure 3. All pure solvents gave poor distribution coefficient values. 1-Octanol + toluene mixture gave the highest distribution coefficient with a value of 0.06, whereas

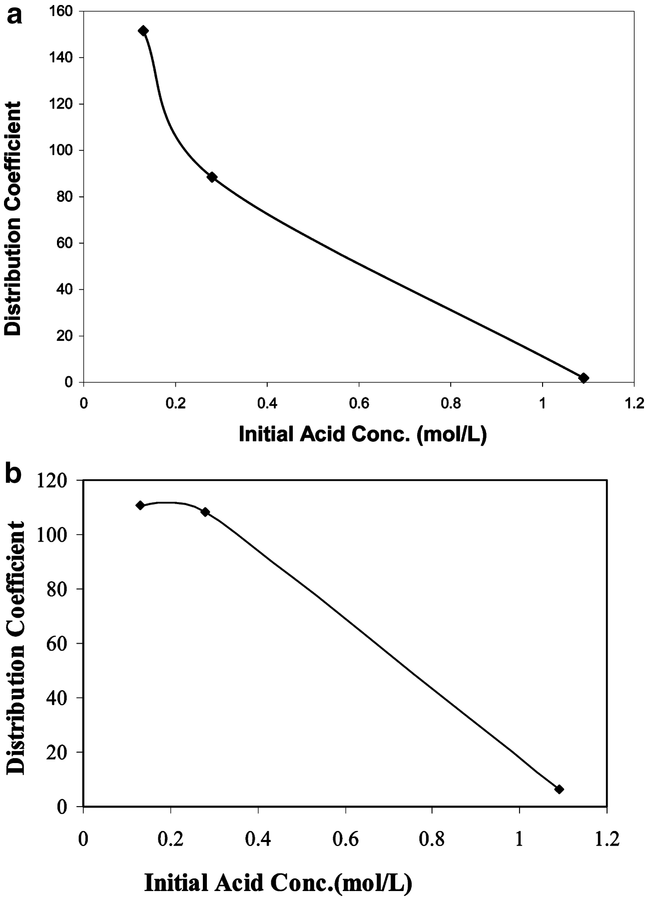

Figure 4. (a) Variation of distribution coefficients in 2.62 mol·L^{-1} concentration of TDA in different initial citric acid concentration. (b) Variation of distribution coefficients in 3.70 mol·L^{-1} concentration of Amberlite LA-2 in different initial citric acid concentration

this solvent mixture gave a 97.00 distribution coefficient value when using Amberlite LA-2.

The effect of modified separation factors on the concentration of TDA and Amberlite LA-2 are presented in Tables 1a,b and 2a,b. The separation factor (S_f) shows the relative proportion between physical interaction and chemical reaction. For all solvents with increasing concentration of amine (TDA and Amberlite LA-2), increasing separation factors were observed. In the amine concentration range (0.32 to 2.22) mol·L^{-1} for Amberlite LA-2 and (0.22 to 0.94) mol·L^{-1} for TDA, the separation factor showed a sharp increase when 1-octanol, MIBK, and toluene were used.

The initial organic acid concentration is also an important parameter for the extraction of organic acids. Yabannavar and Wang investigated acetic acid extraction, and they reported that *D* decreased with increasing initial acid concentration.[18] Similarly, the distribution coefficient decreased with increasing initial acid concentration in this study. This situation is shown in Table 4a,b and Figure 4a,b.

Conclusion

In addition to the physical extraction of citric acid, the reactive extraction of citric acid by both TDA and Amberlite LA-2 with different diluents was studied. The following conclusions can be given:

1. The physical extraction showed the importance of using an amine on the extraction of carboxylic acids. This is because the results of physical extraction are much lower than that of reactive extraction.
2. In light of reactive extraction results, Amberlite LA-2 is a more effective extractant than tridodecyl amine (TDA).
3. Among the diluents used, the most synergistic effect was obtained with 1-octanol + Amberlite LA-2 with a distribution coefficient value of 103.80 and an extraction efficiency of 99.05 %.
4. The 1-octanol + Amberlite LA-2 extractant system is recommended for use as an extractor.

Literature Cited

(1) Takatsuji, W.; Yoshida, H. Adsorption of organic acids on weakly basic ion-exchanger: equilibria. *Chem. Eng. Jpn.* **1997**, *30*, 396.
(2) Lin, J.; Zhou, M.; Zhao, X.; Luo, S.; Lu, Y. Extractive fermentation of L-Lactic acid with immobilized Rhizopus oryzae in a three-phase fluidized bed. *Chem. Eng. Process.* **2007**, *46*, 369.
(3) Papagianni, M. Advances in citric acid fermentation by Aspergillus niger: biochemical aspects, membrane transport and modeling. *Biotechnol. Adv.* **2007**, *25*, 244–263.
(4) Vandenberghe, L. P. S.; Soccol, C. R.; Pandey, A.; Lebeault, J. M. Microbial production of citric acid. *Braz. Arch. Biol. Technol.* **1999**, *42*, 263–276.
(5) Joglerkar, H. G.; Rahman, İ.; Babus, B. D.; Joshi, A. Comparative assessment of downstream processing options for lactic acid. *Sep. Purif. Technol.* **1990**, *52*, 1.
(6) Tamada, J. A.; Kertes, A. S.; King, C. J. Extraction of carboxylic acids with amine extrctants. 1. Equilibria and law of mass action modeling. *Ind. Eng. Chem. Res.* **1990**, *29*, 1319.
(7) Uslu, H.; İnci, İ.; Kirbaslar, S. İ.; Aydin, A. Extraction of Citric Acid from Aqueous Solution by Means of a Long Chain Aliphatic Quaternary Amine/Diluent System. *J. Chem. Eng. Data* **2007**, *52*, 1603–1608.
(8) Wasewar, K. L.; Yawalkar, A. A.; Mouljin, J. A.; Pangarkar, V. G. Fermentation of Glucose to Lactic Acid Coupled with Reactive Extraction: A Review. *Ind. Eng. Chem. Res.* **2004**, *43*, 5969.
(9) Wasewar, K. L.; Heesink, A. B. M.; Versteeg, G. F.; Pangarkar, V. G. Equilibria and kinetics for reactive extraction of lactic acid using Alamine 336 in decanol. *J. Chem. Technol. Biotechnol.* **2002**, *77*, 1068–1075.
(10) Martak, J.; Schlosser, S. L/L equilibria of dimethylcyclopropanecarboxylic acid in water - Solvent systems with trioctylamine as an extractant. *Chem. Pap.* **2000**, *54*, 413–422.
(11) Uslu, H.; Kirbaşlar, Ş. İ. Equilibrium Studies of Extraction of Levulinic Acid by (Trioctylamine (TOA) + Ester) Solvents. *J. Chem. Eng. Data* **2008**, *53*, 1557–1563.
(12) Uslu, H.; Kirbaşlar, Ş. İ. Investigation of Levulinic Acid Distribution from Aqueous phase to Organic phase with TOA Extractant. *Ind. Eng. Chem. Res.* **2008**, *47*, 4598–4606.
(13) İnci, İ.; Aydın, A. Extraction of Hydroxycarboxylic Acids with MIBK/Toluene Solutions of Amines. *J. Sci. Ind. Res.* **2003**, *62*, 926.
(14) Ion transfer technology Amberlite LA-2, Cognis Corporation Mining Chemical, http://www.bsibusiness.com/pdfs/Amberlite_r_LA-2_E.PDF (accessed August 17, 2007).
(15) İnci, İ.; Uslu, H. Extraction of Glycolic Acid from Aqueous Solutions by Trioctyl Methylammonium Chloride and Organic Solvents. *J. Chem. Eng. Data* **2005**, *50*, 536–540.
(16) Juang, R. S.; Lin, Y. S. Investigation on interfacial reaction kinetics of penicilin G and Amberlite LA-2 from membrane flux measurements. *J. Membr. Sci.* **1998**, *141*, 19.
(17) Yang, S. T.; White, S. A.; Hsu, S. T. Extraction of carboxylic acids with tertiary and quaternary amines: effect of pH. *Ind. Eng. Chem. Res.* **1991**, *30*, 1335.
(18) Yabannavar, V. M.; Wang, D. I. C. Strategies for reducing solvent toxicity in extractive fermentations. *Biotechnol. Bioeng.* **1991**, *37*, 716.

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