J. Chem. Eng. Data **2005,** 50, 1103−1107

Investigation of Diluent Effect on Extraction of Citric Acid by Trioctyl Methyl Ammonium Chloride + Organic Solutions

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Organic solutions of amines are increasingly being used to separate organic acids from aqueous solutions by reactive extraction. This article deals with experimental investigations of the extraction of citric acid using mixtures of trioctyl methylammonium chloride + cyclohexane, 2,2,4-trimethyl pentane, 1-butanol, toluene, methyl isobutyl ketone, and ethyl acetate. All measurements were carried out at 298.15 K. Experimental results of batch extraction experiments are reported as distribution coefficients (D), loading factors (Z), and extraction efficiency (E). The maximum extraction efficiency of citric acid has been found to be 57% with 2,2,4-trimethyl pentane and methyl isobutyl ketone for 1.74 mol·L^{-1} initial concentration of trioctyl methylammonium chloride

Introduction

The recovery of hydroxycarboxylic acids from fermentation broths or aqueous streams is an important process in their manufacture. The separation creates economic and environmental problems and is the determining step in the production. The most common process is still acid precipitation in the form of insoluble calcium salts, which is both costly and unfriendly to the environment.

Reactive liquid−liquid extraction of the acid by a suitable extractant has been found to be a promising alternative to the conventional process.[1−3] Physical extraction using common organic solvents proved to be unsuitable for the recovering of these acids because of their high affinity for water and, consequently, low distribution coefficients. Accordingly, for reactive extraction, extractants with functional groups effective for reversible complexation with acids should be used. Extractants using phosphorus-based oxygen-containing extractants and amine-based extractants have been proposed.[3−5]

Because of their hydrophilic nature, hydroxycarboxylic acids are poorly extractable by common organic solvents, so for their recovery from aqueous solutions, reactive liquid−liquid extraction has been considered. Aliphatic tertiary amines, with C_7−C_{10}/C_{12} alkyl groups (TAA), have been proposed as suitable extractants for carboxylic and hydroxycarboxylic acids.[6,7]

The amine extractants are dissolved in a diluent that dilutes the extractant to the desired concentration and controls the viscosity and density of the solvent phase. It has been found that in systems with the same acid and the same amine the type of diluent and the composition of extraction mixture influence the extraction equilibrium.

Polar diluents have been shown to be more convenient diluents than inert ones (nonpolar) because of their higher distributions.[1−10] However, active polar and proton-donating diluents such as alcohols have been shown to be the most suitable diluents for amines because they give the highest distribution coefficients resulting from the formation of solvates through specific hydrogen bonding between the proton of the diluent and the acid−amine complex.[10,11] Some authors suggest the formation of acid−amine complexes of only one type (one acid, one amine) or (one acid, two amines), depending on the diluent. Others have suggested the formation of at least two.[12,13] It has been found that diluents, especially those with functional groups, can affect the extraction behavior of the amine significantly. The stoichiometry of the solute−amine complex, the loading of amine, and the third phase formation are influenced by the diluent. The effect of the diluent can be understood in terms of its ability to solvate organic-phase species; therefore, it is necessary to distinguish between general solvation from electrostatic, dispersion, or other forces and specific solvation due to hydrogen bonding.

The resulting acid−amine complexes are supposed to be stabilized by hydrogen bonding with the diluent. The structure of acid−amine complexes in diluents was determined by Barrow and Yerger.[8] They proposed 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.[8]

Inci has studied the extraction of citric acid by alamine 336 and tri-n-octylamine in four diluting solvents. He has found high distribution coefficients for citric acid.[9] However, data for citric acid, trioctyl methylammonium chloride, and the diluent system have not been found. The aim of this study is to investigate the extraction of citric acid from aqueous solutions by trioctyl methylammonium chloride extractant in a variety of individual diluents and mixtures over a wide range of amine concentration (from 0.33 to 1.74 mol·L^{-1}).

Extraction experiments were carried out with trioctyl methylammonium chloride dissolved in diluents of various types—ketone (methyl isobutyl ketone), aromatic (toluene), different alkanes (2,2,4-trimethyl pentane, cyclohexane), different alcohols (1-butanol), and ester (ethyl acetate). From the results of the batch extraction experiments, distribution coefficients were calculated. In addition to distribution coefficients, extraction efficiency and variation of loading factors were obtained. Furthermore, they were used to draw conclusions about the stoichiometry of complex formation.

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10.1021/je0500680 CCC: $30.25

Table 1. Molar Concentration of Amine in the Organic Phase $C_{e,org}$, Molar Concentration of Acid in the Aqueous Phase C_a, Molar Concentration of Acid in the Organic Phase $C_{a,org}$, Distribution Coefficient *D*, Loading Factor *Z*, and Extraction Efficiency *E* for the Extraction of Citric Acid with Trioctyl Methyl Ammonium Chloride and Individual Diluting Solvents

diluent	$C_{e,org}$ / mol·L^{-1}	C_a / mol·L^{-1}	$C_{a,org}$ / mol·L^{-1}	*D*	*Z*	*E*	$C_{e,org}$ / mol·L^{-1}	C_a / mol·L^{-1}	$C_{a,org}$ / mol·L^{-1}	*D*	*Z*	*E*
cyclohexane	0.33	0.34	0.08	0.23	1.03	19.05	1.14	0.26	0.16	0.61	0.23	38.09
	0.59	0.32	0.10	0.31	0.54	23.81	1.42	0.23	0.19	0.82	0.16	45.24
	0.89	0.29	0.13W	0.44	0.33	30.95	1.74	0.19	0.23	1.21	0.11	54.76
2,2,4-trimethyl pentane	0.33	0.31	0.11	0.35	0.90	26.19	1.14	0.24	0.21	0.75	0.21	42.86
	0.59	0.30	0.15	0.40	0.49	28.57	1.42	0.22	0.23	0.90	0.15	47.62
	0.89	0.27	0.19	0.55	0.31	35.71	1.74	0.18	0.24	1.33	0.11	57.14
methyl isobutyl ketone	0.33	0.31	0.11	0.35	0.96	26.19	1.14	0.21	0.21	1.00	0.18	50.00
	0.59	0.27	0.15	0.55	0.47	35.71	1.42	0.19	0.23	1.21	0.14	54.76
	0.89	0.23	0.19	0.82	0.26	45.24	1.74	0.18	0.24	1.33	0.11	57.14
1-butanol	0.33	0.31	0.11	0.35	0.82	26.19	1.14	0.26	0.16	0.61	0.22	38.09
	0.59	0.30	0.12	0.40	0.46	28.57	1.42	0.23	0.19	0.82	0.16	45.24
	0.89	0.28	0.14	0.50	0.30	33.33	1.74	0.20	0.22	110	0.11	52.38
ethyl acetate	0.33	0.37	0.05	0.13	1.00	11.90	1.14	0.31	0.11	0.35	0.26	26.19
	0.59	0.35	0.07	0.20	0.57	16.66	1.42	0.30	0.12	0.40	0.20	28.57
	0.89	0.33	0.09	0.27	0.38	21.43	1.74	0.28	0.14	0.50	0.16	33.33
toluene	0.33	0.34	0.08	0.23	1.36	19.05	1.14	0.24	0.18	0.75	0.21	42.86
	0.59	0.32	0.10	0.31	0.59	23.81	1.42	0.22	0.20	0.90	0.15	47.62
	0.89	0.28	0.14	0.50	0.32	33.33	1.74	0.19	0.23	1.21	0.11	54.76

Theoretical Section

The extraction of citric acid (HA*)* with trioctyl methylammonium chloride (R_4NCl*)* can be described by the reaction

$$HA + {}^*R_4NCl = {}^*(HA)\cdot(R_4N)^+ + Cl^- \tag{1}$$

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 equilibrium constant *K*.

$$K = \frac{(a_{\mathrm{HA\ R_4N}}{}^{+})\cdot(a_{\mathrm{Cl}}{}^{-})}{(a_{\mathrm{HA}})\cdot(a_{\mathrm{R_4NCl}})} \tag{2}$$

where *a* denotes the activity.[5-9] Replacing the activities by the products of molalities and molal activity coefficients, γ, gives eq 3.

$$K = \frac{(\mathrm{m}_{\mathrm{HA\ R_4N}}{}^{+}\cdot\gamma_{\mathrm{HA\ R_4N}}{}^{+})\cdot(m_{\mathrm{Cl}}{}^{-}\cdot\gamma_{\mathrm{Cl}}{}^{-})}{(m_{\mathrm{HA}}\cdot\gamma_{\ \mathrm{HA}})\cdot(m_{\mathrm{R_4NCl}}\cdot\gamma_{\mathrm{R_4NCl}})} \tag{3}$$

In eq 3, m_{HA} is the molality of acid, m_{R_4NCl} is the molality of amine, γ_{HA} is the molal activity coefficient of acid, γ_{R_4NCl} is the molal activity coefficient of amine, $\gamma_{\mathrm{HA\ R_4N}}{}^{+}$ is the molal the activity coefficient of the complex, $m_{Cl}{}^{-}$ is the molality of chloride, and $\gamma_{Cl}{}^{-}$ is the molal activity coefficient of chloride.

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.[9,10] The expression for the loading, *Z*, can be written in the form[9-11]

$$Z = \frac{C_{a,org}}{C_{e,org}} \tag{4}$$

In eq 4, $C_{a,org}$ is the total concentration of acid in the organic phase, and $C_{e,org}$ is the total concentration of amine in the organic phase. Distribution coefficients, *D*, for citric acid extracted from water into the organic phase were determined from

$$D = \frac{C_{a,org}}{C_a} \tag{5}$$

where C_a (mol·L^{-1}) is the concentration of acid in the aqueous phase after extraction. The efficiency of extraction, *E*, is expressed as

$$E = \left(1 - \frac{C_a}{C_{ao}}\right)100 \tag{6}$$

where C_{ao} is the initial concentration of acid in the aqueous phase. An *E* value of 100% means that all of the acid in the aqueous phase has been removed and is present in the organic phase.[12-15]

Table 2. Distribution Coefficient *D* for Citric Acid between Solvents and Water, Molar Concentration of Acid in the Aqueous Phase C_a , Molar Concentration of Acid in the Organic Phase $C_{a,org}$, Distribution Coefficient *D*, Loading Factor *Z*, and Extraction Efficiency *E* for the Extraction of Citric Acid

solvent	C_a / mol·L^{-1}	$C_{a,org}$ / mol·L^{-1}	*D*	*E*
cyclohexane	0.41	0.01	0.02	2.38
2,2,4-trimethyl pentane	0.41	0.01	0.02	2.38
methyl isobutyl ketone	0.41	0.01	0.02	2.28
1-butanol	0.33	0.09	0.27	21.43
ethyl acetate	0.40	0.02	0.05	4.76
toluene	0.33	0.09	0.27	21.43

Table 3. Effect of Initial Acid Concentration C_{int} on the Extraction of Citric Acid, Molar Concentration of Amine in the Organic Phase $C_{e,org}$, Molar Concentration of Acid in the Aqueous Phase, C_a, Molar Concentration of Acid in the Organic Phase $C_{a,org}$, Distribution Coefficient *D*, Loading Factor *Z*, and Extraction Efficiency *E* for the Extraction of Citric Acid.

C_{int} / mol·L^{-1}	$C_{e,org}$ / mol·L^{-1}	C_a / mol·L^{-1}	$C_{a,org}$ / mol·L^{-1}	*D*	*Z*	*E*
0.105	0.62	0.09	0.015	0.16	0.14	14.29
0.210	0.59	0.17	0.040	0.23	0.29	19.05
0.315	0.62	0.25	0.065	0.26	0.40	20.63

Experimental Section

Trioctyl methylammonium chloride, citric acid, and solvents were purchased from Merck. The trioctyl methylammonium chloride that was used was a mixture of straight-chain quaternary amine salt (M = 442 g·mol^{-1}). All chemicals were used without further purification.

Citric acid was dissolved in water to prepare solutions with an initial concentration of acid (mass fraction) of 8%

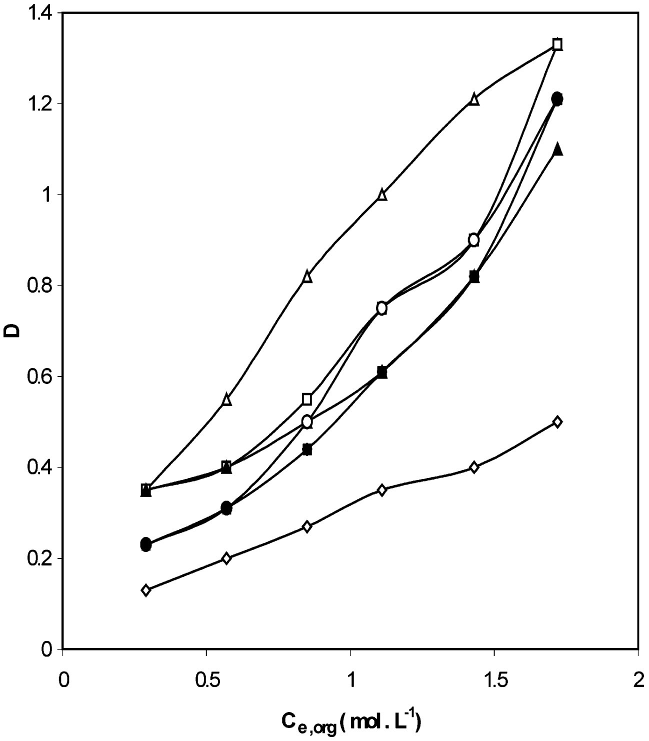

Figure 1. Distribution coefficient D vs concentration of trioctyl methylammonium chloride $C_{e,org}$ in different diluting solvents: ■, cyclohexane; □, 2,2,4-trimethyl pentane; ▲, 1-butanol; ◇, ethyl acetate; ○, toluene; △, methyl isobutyl ketone.

(= 0.42 mol·L^{-1}). The initial organic phases were prepared by the dissolution of trioctyl methylammonium chloride in the diluents to produce solutions with approximately constant concentrations of 1.74 mol·L^{-1}, 1.42 mol·L^{-1}, 1.14 mol·L^{-1}, 0.89 mol·L^{-1}, 0.59 mol·L^{-1}, and 0.33 mol·L^{-1}.

For distribution experiments, equal volumes of an aqueous citric acid solution and an organic solution of trioctyl methylammonium chloride were stirred for 2 h in glass flasks immersed in a water bath at 25 ± 0.1 °C. After equilibration, both phases were separated. 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%).[12] Acid analysis was checked against the material balance. The uncertainty in the results was 3%.

Results and Discussion

Table 1 presents a survey of the experimental liquid−liquid phase equilibrium investigations for the partitioning of citric acid. The amine concentrations in the initial organic solution were ≤0.33 mol·L^{-1}, 0.59 mol·L^{-1}, 0.89 mol·L^{-1}, 1.14 mol·L^{-1}, 1.48 mol·L^{-1}, and 1.74 mol·L^{-1} in cyclohexane, 2,2,4-trimethyl pentane, 1-butanol, toluene, methyl isobutyl ketone, and ethyl acetate, respectively. The citric acid concentration in the initial aqueous phase was 0.42 mol·L^{-1}. The experimental results are given in Table 1. Figure 1 demonstrates the influence of trioctyl methylammonium chloride in the organic phase on the distribution ratio of citric acid. In the experiments, the equilibrium concentration of citric acid in the aqueous phase varied between about 0.37 mol·L^{-1} to 0.18 mol·L^{-1}. The distribution coefficents of citric acid in that range are between about 1.33 to 0.23 in cyclohexane, 2,2,4-trimethyl pentane, 1-butanol, toluene, and methyl isobutyl ketone, whereas they changes only between about 0.50 to 0.13 in ethyl acetate

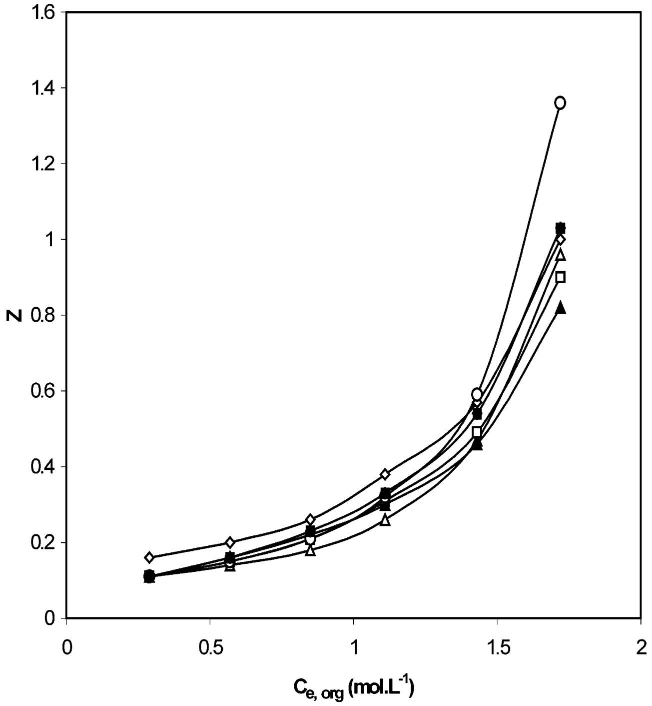

Figure 2. Loading factor Z vs concentration of trioctyl methylammonium chloride $C_{e,org}$ in different diluting solvents: ■, cyclohexane; □, 2,2,4-trimethyl pentane; ▲, 1-butanol; ◇, ethyl acetate; ○, toluene; △, methyl isobutyl ketone.

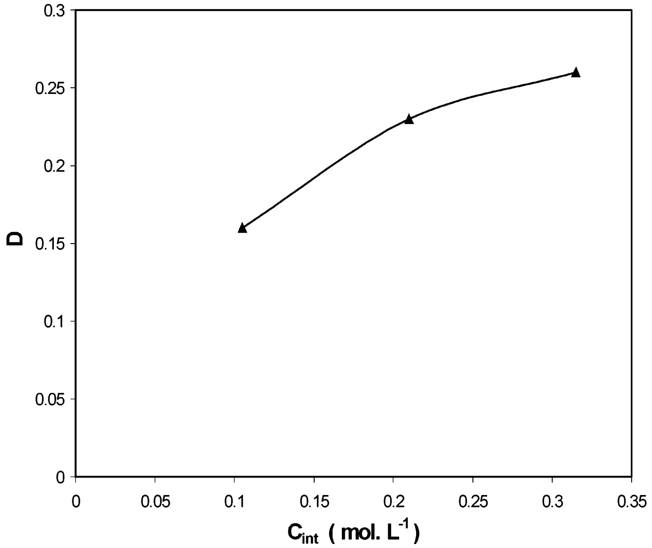

Figure 3. Effect of the initial acid concentration C_{int} on the citric acid distribution D between water and an organic solution of trioctyl methylammonium chloride.

It will be seen from Table 1 that a considerable amount of citric acid is removed by trioctyl methylammonium chloride from aqueous solutions. The amount of acid removed strongly depends on the trioctyl methylammonium chloride concentration and diluting solvent. The maximum removal of citric acid is 57% with 2,2,4-trimethyl pentane and methyl isobutyl ketone for a 1.74 mol·L^{-1} initial concentration of trioctyl methylammonium chloride. The acid concentration in water at equilibrium (C_a) decreases from 0.31 mol·L^{-1} to 0.18 mol·L^{-1}, increasing the amount of trioctyl methylammonium chloride from 0.33 mol·L^{-1} to 1.74 mol·L^{-1} with 2,2,4-trimethyl pentane. The distribution coefficient increases from 0.35 to 1.33 with increases in the amount of trioctyl methylammonium chloride from 0.33 mol·L^{-1} to 1.74 mol·L^{-1} for 2,2,4-trimethyl pentane. The

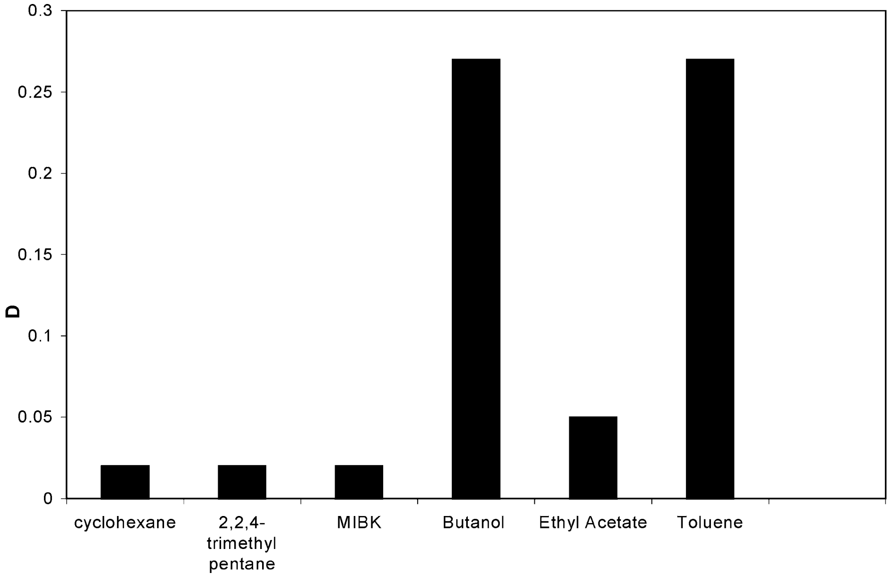

Figure 4. Distribution coefficients *D* of citric acid between water and the solvents used in this study.

removal of citric acid is 54% with cyclohexane, toluene, and a 1.74 mol·L^{-1} initial concentration of trioctyl methylammonium chloride. Ethyl acetate has been found to be the worst diluting solvent for the removal of citric acid (11%) at a 0.33 mol·L^{-1} concentration of trioctyl methylammonium chloride.

The extraction of carboxylic acids with the tertiary amines + solvent system can be explained by the formation of acid−amine complexes, which are affected by the diluents in a different way. The solvation of the complex by the diluent is a critical factor in the extraction of acid. The interactions between the complex and diluent can be divided into general solvation and specific interactions of the diluent with the complex.[16−18] Polar diluents have been shown to be more convenient diluents than inert ones (nonpolar) because of the higher distributions, but in the extraction of citric acid by quaternary amine used in this study, such an effect has not been found. It has been found that the polarity of the diluent is not important in the extraction of citric acid by quaternary amine.[18−22]

Figure 2 shows the effect of trioctyl methylammonium chloride concentration on loading. The loading curve is a plot of Z versus amine concentration.

In this work, the loading of all solvents increases with increasing concentration of trioctyl methylammonium chloride.

Figure 3 shows the effect of the initial concentration of citric acid on the distribution coefficient for the alcohol diluent. The distribution coefficient increases with increasing initial concentration of acid.

Conclusions

The aim of this study is to determine the extractability of citric acid from model aqueous solutions by trioctyl methylammonium chloride + diluent systems. This enables it to function essentially as an anion-exchange reagent. In this study, the maximum removal of citric acid is 57% with methyl isobutyl ketone and 2,2,4-trimethyl pentane and a 1.76 mol·L^{-1} initial concentration of trioctyl methylammonium chloride. The maxiumum extraction abilities for diluents were found to be methyl isobutyl ketone = 2,2,4-trimethyl pentane > cyclohexane = toluene > 1-butanol > ethyl acetate.

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Received for review February 15, 2005. Accepted March 30, 2005.

JE0500680