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Partitioning of Gluconic Acid between Water and Trioctyl Methylammonium Chloride and Organic Solvents

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Phase equilibria governing the reactive extraction of gluconic acid from aqueous solution into solutions of trioctyl methylammonium chloride in the single solvents cyclohexane, hexane, 2,2,4-trimethyl pentane, 1-butanol, toluene, methyl isobutyl ketone, and ethyl acetate are investigated. All measurements were carried out at 298.15 K. The distribution coefficients, *D*, loading factors, *Z*, and extraction efficiencies, *E*, are derived. The maximum removal of gluconic acid is mass 69% with methyl isobutyl ketone with a 1.71 mol·L^{-1} initial concentration of trioctyl methylammonium chloride.

Introduction

Extractive recovery of carboxylic acids from dilute aqueous solutions, such as fermentation broth and wastewater, which have acid mass fractions lower than 10% has received increasing attention. Solvent extraction with conventional solvents such as alcohols, ketones, ethers, and aliphatic hydrocarbons is not efficient as tertiary amines when applied to dilute, carboxylic acid solutions.[1−3] However, carboxylic acid extractions with aliphatic tertiary amines have large distribution coefficients. Several aliphatic amines have been used successfully to extract carboxylic acids. For gluconic acid, the classical approach for recovery from a fermentation broth has been to add calcium hydroxide to form the calcium salt of the carboxylic acid, to which an acid such as sulfuric acid is added to liberate the free carboxylic acid.[4−6] This approach consumes chemicals (e.g., lime and sulfuric acid) and produces a waste salt stream. Consequently, such methods are falling out of favor. The strong amine interaction with the acid allows the formation of acid−amine complexes and thus provides for high distribution coefficients. In addition, the high affinity of organic base for the acid gives selectivity for the acid over nonacid components in the mixture.[7] However, primary amines are too soluble in water to be used with aqueous solutions. Secondary amines are subject to amide formation upon regeneration by distillation. Consequently, tertiary and quaternary amines have received the most attention. The extraction of carboxylic acids with tertiary amines has been extensively studied.[8]

Inci[9] has studied the extraction of gluconic acid by trioctylamine in different diluting solvents. He found high distribution coefficients for gluconic acid.[9] Several workers have investigated a similiar system.[10] However, to date, the extraction of gluconic acid with quaternary amines has not been documented in the literature. It is essential to understand the effects of different factors on the extraction of gluconic acid with a quaternary amine before the production process can be optimally designed.[10]

In this work, trioctyl methylammonium chloride was studied for its ability to extract gluconic acid at various amine concentrations. Prior to this work, quaternary amines have not been well studied for their abilities to extract organic acid. Also, seven diluents, cyclohexane, 2,2,4-trimethyl pentane, 1-butanol, toluene, methyl isobutyl ketone (MIBK), and ethyl acetate, were investigated for their abilities to increase the extracting power of amine extractant. As a result of extraction experiments, distribution coefficients, extraction efficiencies, and loading factors are also presented in this work.

Theoretical

The extraction of gluconic acid (HA) with trioctyl methylammonium chloride (R_4NCl) can be described by the following reaction.

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

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*

$$K = (a_{\mathrm{HAR_4N^+}})(a_{\mathrm{Cl^-}})/(a_{\mathrm{HA}})(a_{\mathrm{R_4NCl}}) \tag{2}$$

where a denote activities.[5−9] Replacing the activities by the products of molalities and molal activity coefficients, γ, eq 2 takes the form of eq 3.

$$K = \{(m_{\mathrm{HAR_4N^+}}\gamma_{\mathrm{HAR_4N^+}})(m_{\mathrm{Cl^-}}\gamma_{\mathrm{Cl^-}})\}/\{(m_{\mathrm{HA}}\gamma_{\mathrm{HA}})(m_{\mathrm{R_4NCl}}\gamma_{\mathrm{R_4NCl}})\} \tag{3}$$

In eq 3, m_{HA} is the molality of acid, $m_{\mathrm{R_4NCl}}$ is the molality of amine, γ_{HA} is the molal activity coefficient of acid, $\gamma_{\mathrm{R_4NCl}}$ is the molal activity coefficient of amine, $\gamma_{\mathrm{HAR_4N^+}}$ is the molal activity coefficient of the complex, $m_{\mathrm{Cl^-}}$ is the molality of chloride, and $\gamma_{\mathrm{Cl^-}}$ 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 following form.[9−11]

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

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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 Gluconic Acid with Trioctyl Methylammonium Chloride and Individual Diluting Solvents

	$C_{e,org}$	C_a	$C_{a,org}$			
diluent	$mol \cdot L^{-1}$	$mol \cdot L^{-1}$	$mol \cdot L^{-1}$	D	Z	E
cyclohexane	1.71	0.18	0.31	1.79	0.18	44.18
	1.44	0.18	0.31	1.65	0.21	39.55
	1.15	0.19	0.30	1.55	0.26	35.60
	0.84	0.20	0.29	1.45	0.34	30.96
	0.56	0.20	0.29	1.40	0.51	28.50
	0.28	0.21	0.28	1.38	1.00	27.35
2,2,4-trimethyl pentane	1.75	0.18	0.31	1.78	0.18	43.86
	1.50	0.19	0.30	1.61	0.20	37.85
	1.25	0.19	0.30	1.52	0.24	34.19
	0.86	0.21	0.28	1.33	0.32	25.05
	0.57	0.22	0.27	1.20	0.47	16.98
	0.30	0.23	0.26	1.12	0.87	10.36
MIBK	1.71	0.12	0.37	3.20	0.22	68.79
	1.42	0.13	0.37	2.92	0.26	65.79
	1.23	0.14	0.35	2.55	0.29	60.71
	0.84	0.14	0.35	2.42	0.41	58.66
	0.59	0.15	0.34	2.23	0.58	55.17
	0.27	0.16	0.33	2.10	1.22	52.45
1-butanol	1.71	0.14	0.35	2.50	0.21	60.06
	1.43	0.15	0.34	2.28	0.24	56.09
	1.29	0.16	0.34	2.16	0.26	53.72
	0.70	0.16	0.33	2.02	0.47	50.56
	0.57	0.17	0.32	1.92	0.56	47.88
	0.31	0.18	0.31	1.78	1.00	43.86
hexane	1.64	0.17	0.32	1.83	0.19	45.30
	1.27	0.18	0.31	1.78	0.25	43.71
	0.82	0.19	0.30	1.63	0.37	38.82
	0.68	0.19	0.30	1.52	0.43	34.04
	0.51	0.20	0.29	1.49	0.58	32.82
	0.48	0.20	0.29	1.40	0.60	28.67
toluene	1.72	0.16	0.33	2.08	0.19	51.92
	1.43	0.17	0.32	1.84	0.22	45.52
	1.11	0.18	0.31	1.77	0.28	43.52
	0.85	0.19	0.30	1.60	0.35	37.44
	0.57	0.20	0.29	1.42	0.51	29.82
	0.29	0.22	0.27	1.26	0.93	20.75
ethyl acetate	1.73	0.19	0.30	1.55	0.17	35.33
	1.43	0.20	0.29	1.49	0.21	32.70
	1.15	0.21	0.28	1.35	0.25	25.75
	0.85	0.22	0.27	1.27	0.32	21.02
	0.61	0.22	0.27	1.19	0.43	15.93
	0.32	0.24	0.25	1.05	0.79	4.86

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. The distribution coefficients, D, for gluconic acid extracted from water into the organic phase were determined as

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

where, C_a is the concentration of acid in the aqueous phase after extraction. The efficiency of extraction, E, is expressed as

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

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.

Experimental Section

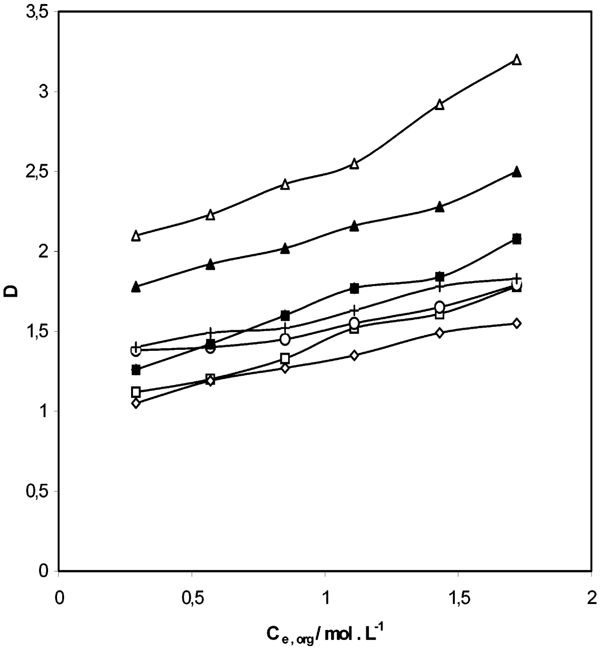

Figure 1. Distribution coefficients, D, with the concentration of trioctyl methylammonium chloride, $C_{e,org}$, in different individual diluting solvents: ■, cyclohexane; □, 2,2,4-trimethyl pentane; ▲, 1-butanol; ◇, ethyl acetate; ○, toluene; △, methyl isobutyl ketone; +, hexane.

Trioctyl methylammonium chloride (Fluka, 91042, >99%), gluconic acid (Merck, 814186, solution 70% mass in water), cyclohexane (Merck, 2817, >99.7%), 2,2,4-trimethyl pentane (Merck, 4727, >99.5%), 1-butanol (Merck, 250220, >99%), toluene (Merck, 8325, >99.5%), methyl isobutyl ketone (Merck, 820820, >99%), hexane (Merck, 822280, >96%), and ethyl acetate (Merck, 822277, >99%) were used without purification.

Gluconic acid was dissolved in water to prepare the solutions with initial concentrations of acid 10% (mass) (=0.49 $mol \cdot L^{-1}$). Equal volumes of an aqueous gluconic acid solution and an organic solution of trioctyl methylammonium chloride were stirred for 2 h, which preliminary tests demonstrated to be a sufficient time for equilibration. The stirring was carried out in glass flasks immersed in a water bath at 298.15 K. After equilibration, both phases were separated and the aqueous phase was analyzed.

The concentration of the acid in the aqueous phase was determined by titration with aqueous 0.1 $mol \cdot L^{-1}$ sodium hydroxide (relative uncertainty 1%).[9,12] 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%. The solubilities of amine salts and diluents in the aqueous phase were negligible in the range of variables investigated.

Results and Discussion

Table 1 demonstrates the influence of organic solvent and the organic phase concentration of trioctyl methylammonium chloride on the distribution coefficients of gluconic acid. The gluconic acid concentration in the initial aqueous phase was 0.49 $mol \cdot L^{-1}$ (mass factor 10%). In the experiments, the concentration of trioctyl methylammonium chloride in the organic phase varied between about 0.27 to 1.75 $mol \cdot L^{-1}$. The distribution coefficient of gluconic acid in that range is between about 3.20 and 2.10 in MIBK, whereas it changes only between about 1.55 and 1.05 in ethyl acetate. It will be seen from Table 1 that considerable amounts of gluconic acid are removed by trioctyl methyl-

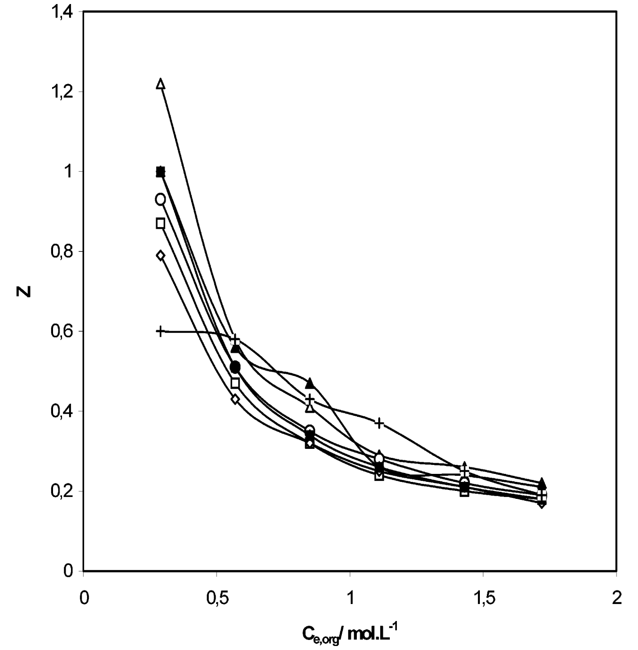

Figure 2. Loading factors, Z, with the concentration of trioctyl methylammonium chloride, $C_{e,org}$, in different individual diluting solvents: ■, cyclohexane; □, 2,2,4-trimethyl pentane; ▲, 1-butanol; ◇, ethyl acetate; ○, toluene; △, methyl isobutyl ketone; +, hexane.

Table 2. 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, Extraction Efficiency, E, for the Extraction of Gluconic Acid with Trioctyl Methylammonium Chloride and Diluting Solvent Mixtures (50% + 50%)

diluent solvent mixture	$C_{e,org}$ mol·L^{-1}	C_a mol·L^{-1}	$C_{a,org}$ mol·L^{-1}	D	Z	E
MIBK + toluene	0.29	0.13	0.36	1.70	1.08	41.11
	0.57	0.14	0.35	1.82	0.56	45.01
	0.85	0.15	0.34	1.92	0.38	47.90
	1.14	0.17	0.32	2.20	0.30	54.49
	1.42	0.17	0.32	2.43	0.24	59.25
	1.72	0.18	0.31	2.64	0.21	62.17
1-butanol + MIBK	0.29	0.20	0.29	1.44	1.20	30.77
	0.58	0.18	0.31	1.66	0.57	39.92
	0.86	0.18	0.31	1.79	0.38	44.03
	1.15	0.17	0.32	1.94	0.27	48.43
	1.44	0.16	0.33	2.07	0.21	51.67
	1.72	0.14	0.35	2.43	0.17	58.85
toluene + 1-butanol	0.31	0.17	0.32	1.90	1.09	47.32
	0.58	0.17	0.32	1.92	0.56	47.94
	0.86	0.17	0.33	1.97	0.38	49.12
	1.14	0.16	0.33	1.99	0.28	49.85
	1.42	0.16	0.33	2.00	0.23	50.05
	1.71	0.15	0.34	2.18	0.19	54.13

ammonium chloride from the aqueous solutions. The amount of acid removed strongly depends on the trioctyl methylammonium chloride concentration and diluting solvent. The maximum removal of gluconic acid is 69% mass with methyl isobutyl ketone and a 1.72 mol·L^{-1} concentration of trioctyl methylammonium chloride. The acid concentration in water at equilibrium, C_a, increases from 0.12 mol·L^{-1} to 0.16 mol·L^{-1} with an increase in the amount of trioctyl methylammonium chloride from 0.27 mol·L^{-1} to 1.71 mol·L^{-1} for MIBK.

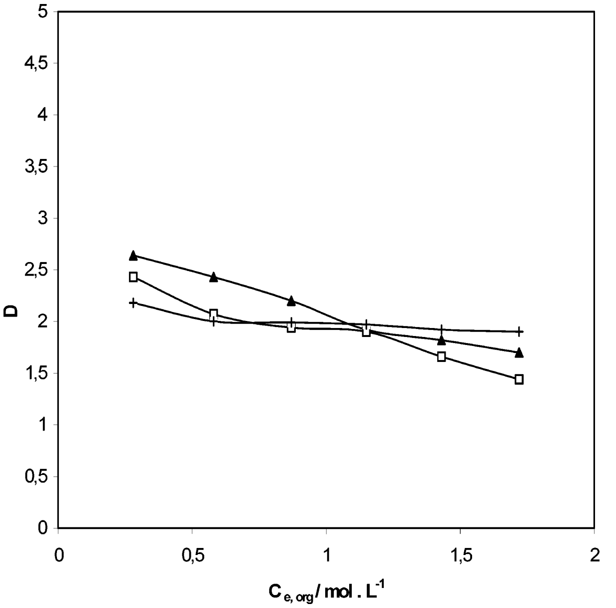

Figure 3. Distribution coefficients, D, with the concentration of trioctyl methylammonium chloride, $C_{e,org}$, in different solvent mixtures: □, 1-butanol + toluene; ▲, methyl isobutyl ketone + toluene; +, 1-butanol + methyl isobutyl ketone.

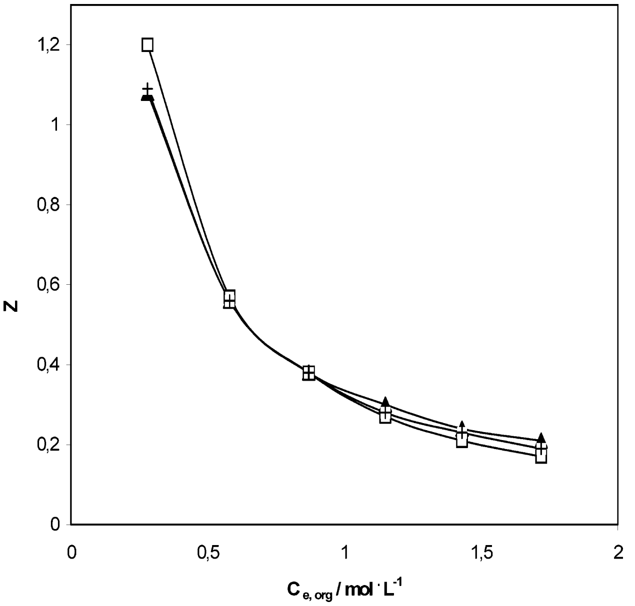

Figure 4. Loading factors, Z, with the concentration of trioctyl methylammonium chloride, $C_{e,org}$, in different solvent mixtures: □, 1-butanol + toluene; ▲, methyl isobutyl ketone + toluene; +, 1-butanol + methyl isobutyl ketone.

The extraction of carboxylic acids with a tertiary amine solvent system can be explained by the formation of acid–amine complexes, which are affected by the diluents in different ways. Solvation of the complex by the diluent is a critical factor in the extraction of acid. The interactions between the complex and the diluent can be divided into general solvation and specific interactions of the diluent with the complex.[12–15] Polar diluents have been shown to be more convenient diluents than inert ones (nonpolar), due to the higher distributions. However, in the extraction of gluconic acid by the 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 gluconic acid by a quaternary amine.[16–19]

Figure 1 shows the effect of organic solvents on the extraction of gluconic acid from aqueous solutions. It can be seen that the extraction power of trioctyl methylammonium chloride and diluent mixture changes with increasing

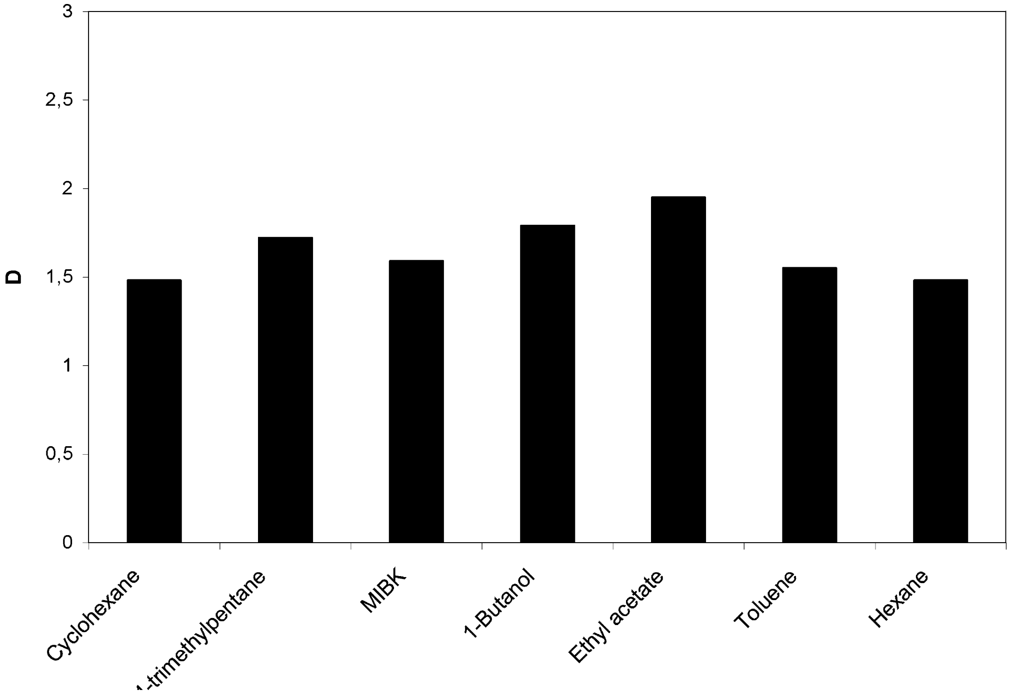

Figure 5. Distribution coefficients, D, for gluconic acid between water and the solvents used in this study.

Table 3. Distribution Coefficients, D, for Gluconic Acid between Solvents and Water

solvent	C_a mol·L^{-1}	$C_{a,org}$ mol·L^{-1}	D	E %
cyclohexane	0.08	0.41	1.48	32.58
2,2,4-trimethyl pentane	0.20	0.29	1.72	41.96
MIBK	0.20	0.29	1.59	36.96
1-butanol	0.19	0.30	1.79	44.11
ethyl acetate	0.17	0.32	1.95	48.60
toluene	0.18	0.31	1.55	35.30
hexane	0.18	0.31	1.48	32.22

initial concentration of trioctyl methylammonium chloride in the organic phase.

In Figure 2, the effect of trioctyl methylammonium chloride concentration on loading is shown. The loading curve is a plot of Z as a function of amine concentration.

For systems with only one amine per complex, there is no effect of total amine concentration on the loading. In this work, the loading of all solvents decreases, indicating that complexes include the diluent specifically complexes include more than one amine per complex.[19−23]

The equilibrium data on the distribution of gluconic acid between water and trioctyl methylammonium chloride dissolved in toluene + MIBK, 1-butanol + MIBK, and toluene + 1-butanol mixtures are presented in Table 2. Figure 3 shows the effect of diluting solvent mixtures on the extraction power of trioctyl methylammonium chloride. The extraction power of trioctyl methylammonium chloride is strongest with the MIBK + toluene mixture. The maximum removal of gluconic acid is mass 62% with MIBK + toluene and a 1.72 mol·L^{-1} initial concentration of trioctyl methylammonium chloride. The acid concentration in water at equilibrium, C_a, increases from 0.13 mol·L^{-1} to 0.18 mol·L^{-1} with an increase in the amount of trioctyl methylammonium chloride from 0.29 mol·L^{-1} to 1.72 mol·L^{-1} for MIBK + toluene. The distribution coefficient increases from 1.70 to 2.64 with an increase in the amount of trioctyl methylammonium chloride. In Figure 4, the effect of solvent mixtures on the loading of trioctyl methylammonium chloride is presented.

The distribution data of gluconic acid between water and solvents used in this study (cyclohexane, 2,2,4-trimethyl pentane, 1-butanol, toluene, methyl isobutyl ketone, hexane, and ethyl acetate) are presented in Table 3 and shown in Figure 5.

Conclusions

The purpose of this study is to determine the extractability of gluconic acid from model aqueous solutions by trioctyl methylammonium chloride and diluent systems. Trioctyl methylammonium chloride is a compound consisting of an organic ion $(\mathbf{Cl})^-$. This enables it to function essentially as an anion exchange reagent. In this study, the maximum removal of gluconic acid is mass 69% with methyl isobutyl ketone with a 1.71 mol·L^{-1} initial concentration of trioctyl methylammonium chloride. The maximum extraction efficiencies for diluents and their mixtures at maximum trioctyl methylammonium chloride concentration are found as:

MIBK > 1-butanol > MIBK + toluene > 1-butanol +
MIBK > toluene − 1-butanol > + toluene >
toluene > cyclohexane > 2,2,4-trimethyl pentane > =
hexane > ethyl acetate

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