Extractive Separation of Glutaric Acid by Aliquat 336 in Different Solvents

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The reactive extraction equilibria for aqueous solutions of glutaric acid, with trioctylmethyl ammonium chloride (Aliquat 336) in various diluents, including 3-methyl-butan-1-ol, octan-1-ol, nonan-1-ol, decan-1-ol, methyl ethyl ketone, 2,6-dimethyl-4-heptanone, hexan-2-one, toluene, kerosene, and hexane, were determined at various Aliquat 336 (A336) concentrations. Experimental results of batch extraction experiments are calculated and reported as distribution coefficients (K_D), loading factors (Z), and extraction efficiency (E). All measurements were carried out at 25 °C. 2,6-Dimethyl-4-heptanone was found to be the most effective diluent with the highest value of K_D (8.51) for the glutaric acid + Aliquat 336 extraction system. The effect of pH has been investigated for octan-1-ol + A336 on glutaric acid extraction in the range of pH 2 to 8. The linear solvation energy relationship (LSER) model has been used to fit the experimental data.

Introduction

Hydroxyl carboxylic acids are important in medical and pharmaceutical applications.[1] Moreover, they are additives in well-known household and industrial cleaners, automotive oil, and cosmetics in perfume industry, as well as oil and water well flow enhancers, and are used in pH control in the food industry.[2]

The specific chemical interactions between extractant and acids to form a complex in the extractant phase allow more acids to be extracted from the aqueous phase. Recently, the extractive recovery of carboxylic acids by amine systems from aqueous solutions, such as fermentation broth and some wastewater streams, including lower than 0.10 mass fraction of acid, has received increasing attention.[3] Reactive extraction is an important separation technique for the recovery of carboxylic acids. The separation of carboxylic acids from aqueous solution by reactive extraction has been studied by many groups.[4−15]

The aim of this study is to investigate the effect of a modifier on the extraction of glutaric acid by using Aliquat 336. The extraction of glutaric acid from aqueous solutions by Aliquat 336 in diluents has been studied over a wide range of amine concentration from (0.22 to 1.31) mol·L^{-1}. Batch extraction experiments have been performed by using Aliquat 336 which is dissolved in four types of solvents: type 1 is ketones (methyl ethyl ketone and 2,6 mimethyl-4-heptanone), type 2 is alcohols (3-methyl-butan-1-ol, octan-1-ol, nonan-1-ol, decan-1-ol), type 3 is aliphatics (hexane, kerosene), and type 4 is aromatic (toluene). The distribution coefficients, the loading factors, and the degree of extraction have been calculated from the experimental results. A survey of the literature showed that there are no available data about this extraction system (glutaric acid + Aliquat 336 + diluent).

Theory

The intent of carboxylic acids is to form dimers in the organic phase, because of their intermolecular hydrogen bonding.[11] Kyuchoukov et al.[16] explained the extraction of carboxylic acid with an quaternary ammonium salt extractant (Aliquat 336) (R_4NCl). The glutarate anions [A^-] are extracted by chemical interaction with the quaternary ammonium chloride [$R_4N^+Cl^-$] according to the reaction

$$\overline{R_4N^+Cl^-} + A^- \leftrightarrow \overline{R_4N^+A^-} + Cl^- \qquad (1)$$

Following Kyuchoukov et al.,[16] we assume that the undissociated molecules are removed by chemical interaction according to

$$\overline{R_4N^+Cl^-} + GA \leftrightarrow \overline{R_4N^+Cl^-{:}GA} \qquad (2)$$

with the extraction equilibrium constant

$$K_E = \frac{\overline{[R_4N^+Cl^-{:}GA]}}{[GA]\cdot\overline{[R_4N^+Cl^-]}} \qquad (3)$$

where GA is the glutaric acid.

The overall distribution coefficient expresses the ratio between the total concentration of extracted substance in all of its possible forms in the organic and the aqueous phase

$$K_D = \frac{\bar{C}_{GA}}{C_{GA,total}} \qquad (4)$$

In eq 4 $\bar{C}_{GA}$ is the total concentration of the glutaric acid in the organic phase, and $C_{GAtotal}$ is the total concentration of glutaric acid in the aqueous phase. The overbar refers to the organic phase for all equations.

The loading of the extractant, Z, is defined as the total concentration of acid in the organic phase, divided by the total concentration of extractant in the organic phase

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$$Z = \frac{\bar{C}_{\mathrm{GA}}}{C_{\mathrm{A336}}} \tag{5}$$

where $\bar{C}_{\mathrm{GA}}$ is the concentration of undissociated glutaric acid in the organic phase and C_{A336} is the initial amine concentration in the organic phase.

Extraction efficiency is defined by the following equation:

$$E = \frac{K_{\mathrm{D}} \cdot 100}{1 + K_{\mathrm{D}}} \tag{6}$$

Materials and Method

Chemicals. Aliquat 336 (IUPAC name: methyltrialkyl ammonium chloride), which is a mixture of C_8 (octyl) and C_{10} (capryl) chains with C_8 predominating, was purchased from Merck Company. Aliquat 336, which is quaternary ammonium salt, is a clear reddish brown liquid with the molecular weight of 404.17 $\mathrm{g \cdot mol^{-1}}$. The density of Aliquat 336 is 0.88 $\mathrm{g \cdot cm^{-3}}$. Glutaric acid and the diluents were purchased from the Merck Company. All chemicals were used without further purification. Purities of all diluents are over 98 %.

Analysis Methods. An 0.830 $\mathrm{mol \cdot L^{-1}}$ of initial glutaric acid aqueous solution was prepared. The initial organic phases were prepared by the dissolution of Aliquat 336 in the diluents to produce solutions at six concentrations [(0.22, 0.44, 0.66, 0.88, 1.09, and 1.31) $\mathrm{mol \cdot L^{-1}}$]. In general, an amine extractant must always be used in the form of a solution in organic diluents due to its high viscosity and corrosive properties. Equal volumes (15 mL) of an aqueous glutaric acid solution and an organic solution of Aliquat 336 were stirred for 2 h in glass flasks immersed in Nuve ST402 thermostatted bath. The speed of the shaker in the horizontal axis is 30 rpm for all of the experiments. The bath shaker with a digital thermometer was at (25 ± 0.1) °C. After equilibration, both phases were separated by centrifuged for 7 min at 1200 rpm for a better separation of phases. The concentration of the acid in the aqueous phase was determined by titration with 0.1 $\mathrm{mol \cdot L^{-1}}$ sodium hydroxide (relative uncertainty: 1 %) with phenolphthalein indicator. The acid concentration in the organic phase was determined by the material balance. In most cases the relative deviation between the amount of acid analyzed and the amount of acid known from preparing the solutions by mass did not exceed 1 %. The pH value of the aqueous phase was determined with a pH meter (Hanna pH 211 Microprocessor pH meter) with an uncertainty of 1 %. UV−visible spectroscopy was used to analyze the glutaric acid amount in effect of pH studies. The calibration curve was drawn with prepared standard solutions of glutaric acid before the sample analysis. One milliliter aqueous samples after the extraction were taken for analysis and were used for UV−visible spectroscopy.[17,18]

Table 1. Results of Reactive Extraction of Glutaric Acid by Aliquat 336 in Various Diluents[a]

solvent	$\bar{C}_{\mathrm{GA}}$ / $\mathrm{mol \cdot L^{-1}}$	C_{A336} / $\mathrm{mol \cdot L^{-1}}$	K_{D}	$K_{\mathrm{D,model}}$	100 E	Z
3-methyl-butan-1-ol	0.31		0.58	0.64	33.89	
	0.50	0.22	1.49	1.32	61.45	2.29
	0.54	0.44	1.86	1.68	66.43	1.24
	0.58	0.66	2.32	2.38	71.08	0.89
	0.63	0.88	3.11	3.44	76.69	0.72
	0.70	1.09	4.97	4.83	83.94	0.64
	0.74	1.31	7.74	7.98	89.03	0.56
octan-1-ol	0.30		0.55	0.67	35.36	
	0.54	0.22	1.86	1.73	66.52	2.49
	0.57	0.44	2.17	2.41	69.78	1.31
	0.60	0.66	2.54	2.66	72.93	0.92
	0.62	0.88	2.91	2.84	75.50	0.71
	0.64	1.09	3.26	3.44	77.51	0.59
	0.66	1.31	3.79	3.64	79.96	0.50
nonan-1-ol	0.31		0.58	0.63	36.78	
	0.53	0.22	1.69	1.71	64.37	2.40
	0.58	0.44	2.23	2.34	70.34	1.32
	0.60	0.66	2.59	2.74	73.29	0.92
	0.64	0.88	3.21	3.36	77.24	0.73
	0.67	1.09	4.01	4.00	80.87	0.61
	0.70	1.31	4.97	4.89	83.94	0.53
decan-1-ol	0.27		0.48	0.61	32.26	
	0.47	0.22	1.26	1.42	57.65	2.14
	0.53	0.44	1.70	1.79	64.46	1.20
	0.57	0.66	2.14	2.24	69.50	0.87
	0.62	0.88	2.86	2.76	75.13	0.71
	0.67	1.09	4.11	4.08	81.23	0.62
	0.71	1.31	5.81	5.75	85.91	0.54
2,6-dimethyl-4-heptanone	0.36		0.68		40.38	
	0.48	0.22	1.36		59.46	2.21
	0.53	0.44	1.71		64.65	1.21
	0.58	0.66	2.26		70.62	0.88
	0.64	0.88	3.30		77.69	0.73
	0.69	1.09	4.81		83.49	0.63
	0.75	1.31	8.51		89.92	0.57
methyl ethyl ketone	0.28		0.50		33.45	
	0.32	0.22	0.63		41.35	1.49
	0.39	0.44	0.86		48.50	0.89
	0.45	0.66	1.16		55.55	0.68
	0.48	0.88	1.34		58.98	0.55
	0.53	1.09	1.76		65.21	0.49
	0.60	1.31	2.47		72.37	0.45
hexan-2-one	0.27		0.48		32.26	
	0.34	0.22	0.68		43.02	1.55
	0.40	0.44	0.93		50.35	0.92
	0.45	0.66	1.18		56.03	0.69
	0.50	0.88	1.47		61.26	0.57
	0.57	1.09	2.10		69.04	0.52
	0.62	1.31	2.93		75.59	0.48
hexane	0.28		0.50		33.45	
	0.34	0.22	0.69		43.12	1.56
	0.38	0.44	0.84		47.92	0.87
	0.43	0.66	1.07		53.63	0.66
	0.49	0.88	1.42		60.40	0.56
	0.53	1.09	1.69		64.37	0.48
	0.58	1.31	2.29		70.89	0.44
kerosene	0.24		0.39		28.10	
	0.48	0.22	1.36		59.46	2.21
	0.52	0.44	1.64		63.61	1.19
	0.56	0.66	2.03		68.39	0.85
	0.60	0.88	2.60		73.39	0.69
	0.67	1.09	3.90		80.42	0.61
	0.72	1.31	6.37		86.98	0.55
toluene	0.14		0.20		16.73	
	0.19	0.22	0.29		25.78	0.86
	0.30	0.44	0.56		38.57	0.69
	0.43	0.66	1.06		53.53	0.66
	0.50	0.88	1.47		61.16	0.57
	0.58	1.09	2.25		70.52	0.53
	0.65	1.31	3.39		78.15	0.49

[a] C_{A366} is the concentration of Aliquat 336 in the organic phase; $\bar{C}_{\mathrm{GA}}$ is the concentration of glutaric acid in the organic phase; Z is the loading factor; E is the extraction efficiency.

Results and Discussion

Distribution Coefficient (K_D). Table 1 presents a survey of the experimental liquid−liquid phase equilibrium investigations for the distribution of glutaric acid. The amine (Aliquat 336) concentrations in the initial organic solution were prepared in the range of (0.22, 0.44, 0.66, 0.88, 1.09, and 1.31) $\mathrm{mol \cdot L^{-1}}$ by using methyl ethyl ketone and 2,6-dimethyl-4-heptanone, 3-methyl-butan-1-ol, octan-1-ol, nonan-1-ol, decan-1-ol, hexane, kerosene, and toluene. The glutaric acid mass fraction in the initial aqueous phase was 0.08 in mass. The experimental results are given in Table 1. Figure 1 demonstrates the influence of Aliquat 336 in the organic phase on the distribution ratio of glutaric acid. It was observed from the experiments that the

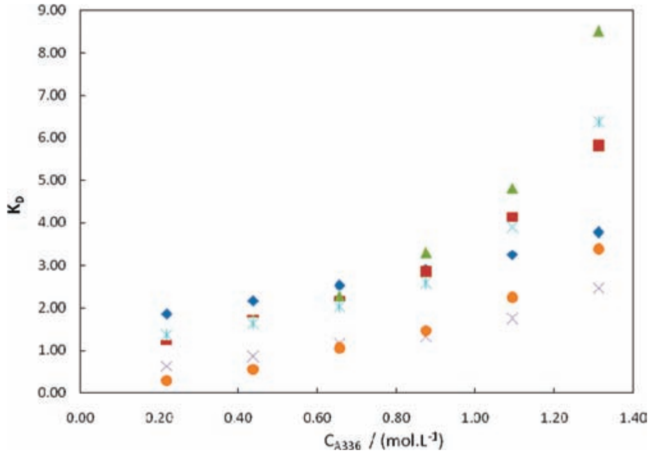

Figure 1. Plot of distribution coefficients, K_D, against the concentration of Aliquat 336 (C_{A336}). ●, toluene; ∗, kerosene; ■, decan-1-ol; ♦, octan-1-ol; ×, 3-methyl-butan-1-ol; ▲, 2,6-dimethyl-4-heptanone.

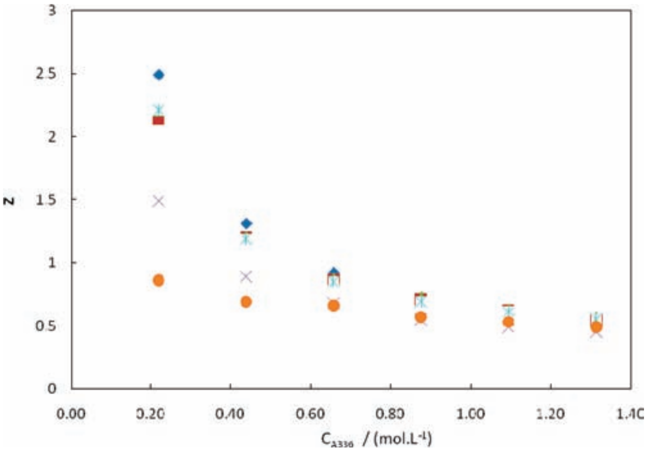

Figure 2. Plot of loading factors, Z, against the concentration of Aliquat 336 (C_{A336}). ●, toluene; ∗, kerosene; ■, decan-1-ol; ♦, octan-1-ol; ×, methyl ethyl ketone; ▲, 2,6-dimethyl-4-heptanone.

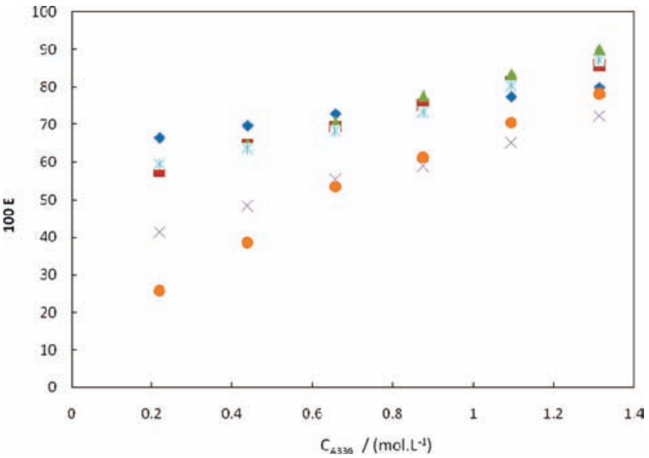

Figure 3. Plot of extraction efficiencies, E, against the concentration of Aliquat 336 (C_{A336}). ●, toluene; ∗, kerosene; ■, decan-1-ol; ♦, octan-1-ol; ×, methyl ethyl ketone; ▲, 2,6-dimethyl-4-heptanone.

ratio of the glutaric acid concentration in the organic phase varied between (0.19 and 0.75) mol·L^{-1}. The distribution coefficient of glutaric acid in that range is between 8.51 and 0.29 in the 10 diluents. Preliminary experiments showed that 1.31 mol·L^{-1} Aliquat 336 gives the maximum distribution coefficients. Synergistic effects of Aliquat 336 + solvents give lower K_D after this concentration.

The extraction of carboxylic acids with tertiary amine + solvent systems can be explained by the formation of acid: amine complexes, which are effected 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 diluent can be divided into general solvation and specific interactions of the diluent with the complex. Polar diluents have been shown to be more convenient diluents than inert ones (nonpolar), due to higher distributions.

The values of distribution coefficients (K_D) for the diluents used at 1.31 mol·L^{-1} of Aliquat 336 increase in following trend: Aliquat 336 + 2,6-dimethyl-4-heptanone (8.51) > Aliquat 336 + 3-methyl-butan-1-ol (7.74) > Aliquat 336 + kerosene (6.37) > Aliquat 336 + decan-1-ol (5.81) > Aliquat 336 + nonan-1-ol (4.97) > Aliquat 336 + octan-1-ol (3.79) > Aliquat 336 + toluene (3.39) > Aliquat 336 + hexan-2-one (2.93) > Aliquat 336 + methyl ethyl ketone (2.47) > Aliquat 336 + hexane (2.29).

Loading Factor (Z). Table 1 shows the effect of Aliquat 336 concentration on loading. In Figure 2 the loading curve is a plot of the loading factor (Z) versus amine concentration. In this work, the loading factor of all solvent mixtures increases with decreasing concentration of Aliquat 336.

Overloading or loading greater than unity indicates that complexes with more than one acid per amine have been formed. Overloading was observed especially in the amine concentration of 0.22 mol·L^{-1} for all diluents except toluene in this study.

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.[19] The most effective extraction is carried out when the pH value is below the pK_a of the acid. The pK_a values of glutaric acid are pK_{a1} 4.31, and pK_{a2} 5.41. In this study the pH values of the aqueous phase changed in the range of 0.76 to 5.96 when was Aliquat 336 used.

Extraction Efficiency (E). It has been seen from Table 1 that a considerable amount of glutaric acid is removed by Aliquat 336 from aqueous solutions. The amount of removed acid strongly depends on the concentration of Aliquat 336 and diluting solvents. The maximum removal of glutaric acid is 89.92 % with 2,6-dimethyl-4-heptanone at a 1.31 mol·L^{-1} initial concentration of Aliquat 336. The acid concentration of the organic phase at equilibrium $\bar{C}_{GA}$ increased from (0.45 to 0.75) mol·L^{-1} with an increasing amount of Aliquat 336 from (0.22 to 1.31) mol·L^{-1} with diisobutyl ketone. For the other diluents, the removal of glutaric acid changes between 70.89 % and 89.03 % at a 1.31 mol·L^{-1} initial concentration of trioctylamine (see Figure 3).

Effect of pH. The pH studies have been done at three constant pH values (pH 2 to 8). pH adjustments have been done by adding NaOH or H_2SO_4, and acid analyses have been determined by UV−visible spectroscopy. The effect of pH on the K_D value is illustrated in Figure 4 for only octan-1-ol. At all of the A336 concentrations, the K_D values increased with a decrease in the pH values. A larger fall in the K_D values was observed above pH values of 7.4.

LSER Model. The distribution coefficients (K_D) obtained from experimental results have been modeled by using LSER (linear solvation energy relationship)[20] using a total solvatochromic equation of the form:

$$\log K_D = \log K_0 + s(\pi + d\delta) + a\alpha + b\beta \qquad (7)$$

where π, δ, α, and β are solvatochromic parameters given in Table 2 and log K_0 is the regression values of the solute property

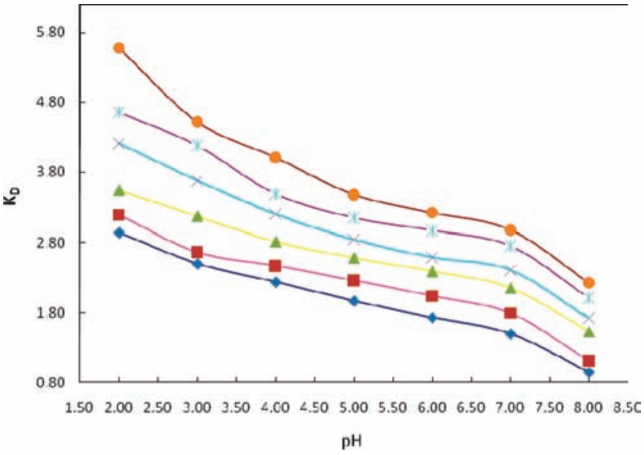

Figure 4. Effect of pH on the K_D value for octan-1-ol. ●, 1.32 mol·L^{-1} A336; ∗, 1.09 mol·L^{-1} A336; ×, 0.88 mol·L^{-1} A336; ▲, 0.66 mol·L^{-1} A336; ■, 0.44 mol·L^{-1} A336; ♦, 0.22 mol·L^{-1} A336.

Table 2. Solvatochromic Parameters, Hydrogen-Bond Donor Acidities, π* and δ, and Hydrogen-Bond Acceptor Basicities, α and β, for Alcohols Used in This Study

solvents	π*	δ	β	α
isoamyl alcohol	0.40	0	0.84	0.84
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 3. LSER Model Parameters[a]

LSER	ln K_D^0	*s*	*d*	*a*	*b*	R^2
	0.417	−42.294	0	24.768	−4.394	0.931

[a] *s*, *d*, *a*, and *b* are coefficients from the correlation. R^2 is the correlation coefficient.

in the reference solvents. *s*, *a*, and *b* are the coefficients from regression. These parameters have been presented in Table 3. The predicted K_D values have been compared with experimental data. It has been clearly seen from Table 1 that correlations between K_D and $K_{D,model}$ are good.

Conclusion

The reactive separation of glutaric acid by using Aliquat 336 dissolved in 10 diluents was investigated. After the extraction of glutaric acid, the following trend has been obtained in terms of extraction efficiency in A336: 2,6-dimethyl-4-heptanone > 3-methyl-butan-1-ol > kerosene > decan-1-ol > nonan-1-ol > octan-1-ol > toluene > hexan-2-one > methyl ethyl ketone > hexane.

The 2,6 dimethyl-4-heptanone has been found to be the most effective solvent with a maximum distribution value of 8.51 at the maximum concentration of Aliquat 336.

The LSER model has shown good trends with close results to experimental data.

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