Experimental and Modeling Studies on the Extraction of Glutaric Acid by Trioctylamine

Nil Pehlivanoğlu,[‡] Hasan Uslu,[*,†] and Ş. İsmail Kırbaşlar[‡]

Beykent University, Engineering and Architecture Faculty, Chemical Engineering Department, Ayazağa, İstanbul, Turkey, and Istanbul University, Engineering Faculty, Chemical Engineering Department, 34320, İstanbul, Turkey

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The reactive extraction equilibria for aqueous solutions of glutaric acid, with trioctylamine (TOA) in various diluents, including isoamyl alcohol, octan-1-ol, nonan-1-ol, decan-1-ol, methyl ethyl ketone (MEK), diisobutyl ketone (DIBK), hexan-2-one, toluene, kerosene, and *n*-hexane, were determined at various TOA 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. Kerosene was found to be the most effective diluent with the highest value of K_D (7.88). The complexation constants K_{11} and K_{21} were calculated for each diluent. The results of the liquid−liquid equilibrium measurements were correlated by a linear solvation energy relationship (LSER) model which takes into account physical interactions and modified Freundlich and Langmuir equations. Experimental results of the glutaric acid extraction are compared to model results.

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1. Introduction

Glutaric acid (pentanedioic acid) is a dicarboxylic acid with five carbon atoms, occurring in plant and animal tissues. Glutaric acid is found in the blood and urine. α-Ketoglutaric acid, a derivative of glutaric acid which has a ketone group on the carbon atom next to the acid group, is produced from the amino group of an amino acid (glutamate) and is found as an intermediate in the Krebs cycle in the body. In the industrial field, ketoglutaric acid exhibits typical carboxyl group chemistry useful in a variety of industrial applications. It is a white crystalline solid having the lowest melting point among dicarboxylic acids (98 °C). It is very soluble in water, and the solution is a medium strong acid. Glutaric acid is used in the production of polyester, polyols, polyamides, ester plasticizers, and corrosion inhibitors. It is used in the synthesis of pharmaceuticals, surfactants, and metal finishing compounds. α-Ketoglutaric acid is used in dietary supplements to improve protein synthesis. Therefore, it is essential to purify glutaric acid from aqueous solution.

Solvent extraction is an efficient technology for separation and concentration of solutes from leachates, fermentation broths, industrial wastes, and other industrial streams. Long-chain, aliphatic tertiary amines, e.g., Alamine 336 and phosphorus-bonded oxygen-containing extractants, dissolved in suitable organic solvents are effective extractants for carboxylic acids.[1]

The specific chemical interactions between extractant and acid molecules to form a complex in the extractant phase allow more acids to be extracted from the aqueous phase. Recently, extractive recovery of carboxylic acids by amine systems from aqueous solutions, such as fermentation broth and wastewater, including lower than 10 % (by weight) acid concentrations, has received increasing attention.[2] Reactive extraction is an important separation technique for the recovery of carboxylic acids. Many works have been studied the separation of carbocyclic acids from aqueous solution by reactive extraction.[3−14]

This study examines the LSER, modified Freundlich, and modified Langmuir models on the equilibria of glutaric acid reactive extraction. In this sense, the reactive extraction of glutaric acid from aqueous solutions by TOA in ten different diluents was studied. The above-mentioned models were fit to the results of the batch equilibrium extraction experiments. A survey of the literature showed that there are no available data about this extraction system.

2. Theory

The intent of carboxylic acids is to form dimers in the organic phase because of their intermolecular hydrogen bonding.[5] All results were interpreted as the recovery of glutaric acid using TOA. The formation of a complex via the interfacial reaction can be represented as

$$q\mathrm{HA}_{\mathrm{aq}} + p\mathrm{S}_{\mathrm{org}} \leftrightarrow (\mathrm{HA}_q \cdot \mathrm{S}_p)_{\mathrm{org}} \tag{1}$$

In eq 1, HA is the undissociated acid molecule; S is the amine molecule; and p and q are the stoichiometric coefficients.

As the glutaric acid−TOA complex is formed, it is rapidly extracted into the organic phase. The equilibrium complexation constant is defined as

$$K_{qp} = \frac{[(\mathrm{HA})_q \cdot (\mathrm{S})_p]_{\mathrm{org}}}{[\mathrm{HA}]_{\mathrm{aq}}^q \cdot [\mathrm{S}]_{\mathrm{org}}^p} \tag{2}$$

K_{qp} is expected to depend on the properties of the acid and the solvation efficiency of the diluent used. q and p are the stoichiometric coefficients of acid and amine, respectively.

The distribution coefficient is defined as the ratio of the concentration of organic acid in the organic phase to organic acid in the aqueous phase. The experimentally accessible distribution coefficient (K_D) is given as

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[*] Corresponding author. E-mail: hasanuslu@gmail.com.
[†] Beykent University.
[‡] Istanbul University.

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$$K_D = \frac{\bar{C}_{HA}}{C_{HA,total}} = \frac{\bar{C}_{HA_q \cdot S_p}}{C_{HA} + C_{A^-}} \tag{3}$$

In eq 3, $\bar{C}_{HA}$ is the total concentration of the acid in the organic phase; $C_{HA,total}$ is the total concentration of acid in the aqueous phase; and C_{HA} is the undissociated acid in the aqueous phase. The overbar refers to the organic phase for all equations.

The apparent equilibrium constant K_A for the acid dissociation reaction can be written in terms of species concentrations for dilute solutions

$$HA \leftrightarrow H^+ + A^-, \qquad K_A = \frac{C_{H^+} \cdot C_{A^-}}{C_{HA}} \tag{4}$$

From eqs 3 and 4

$$K_D = \frac{\bar{C}_{HA_q \cdot S_p}}{C_{HA} + C_{A^-}} = \frac{K_{qp} \cdot \bar{C}_{HA}^{q} \cdot \bar{C}_{S}^{p}}{C_{HA} + K_A \cdot C_{HA}/C_{H^+}} \tag{5}$$

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 is

$$Z = \frac{\bar{C}_{HA}}{[S]_{org}^{initial}} \tag{6}$$

where $\bar{C}_{HA}$ is the concentration of undissociated glutaric acid in the organic phase and $[S]_{org}^{initial}$ is the initial amine concentration in the organic phase.

$[S]_{org}$ can be expressed as

$$[S]_{org} = [S]_{org}^{initial} - p\bar{C}_{HA} \tag{7}$$

Extraction efficiency is defined by the following equation

$$E = \frac{K_D \cdot 100}{1 + K_D} \tag{8}$$

3. Materials and Method

3.1. Chemicals. Trioctylamine (TOA) (M = 353.67 g·mol^{-1}), glutaric acid, and the diluents were purchased from the Merck Company. All chemicals were used without further purification. Purities of all solvents are over 98 %.

3.2. Analysis Methods. A solution with an initial concentration of 0.606 mol·L^{-1} (8 % by weight) of aqueous glutaric acid was prepared. The initial organic phases were prepared by the dissolution of TOA in the diluents to produce solutions at six concentrations (0.255 mol·L^{-1}, 0.466 mol·L^{-1}, 0.734 mol·L^{-1}, 0.975 mol·L^{-1}, 1.292 mol·L^{-1}, and 1.591 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) Equal volumes of an aqueous glutaric acid solution and an organic solution of TOA were stirred for 2 h in glass flasks immersed in a Nuve ST402 termostatted water Bath shaker with digital thermometer at (25 ± 0.1) °C. (ii) After equilibration, both phases were separated by centrifugation in 7 min and 1200 rpm. (iii) The concentration of the acid in the aqueous phase was determined by titration with 0.1 mol·L^{-1} sodium hydroxide (relative uncertainty: 1 %) in phenolphthalein indicator. 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 1 %. The pH value of the aqueous phase was determined with a pH meter (Hanna pH 211 Microprocessor pH meter) with deviation of ± 0.01.

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

	$\bar{C}_s$	$\bar{C}_{HA}$					E
diluent	mol·L^{-1}	mol·L^{-1}	pH$_{aq}$	$K_{D,model}$	K_D	Z	%
isoamyl alcohol	0.255	0.414	5.96	2.458	2.161	1.296	60.135
	0.466	0.416	5.12	2.695	2.199	0.714	60.465
	0.734	0.474	4.53	2.954	3.597	0.516	68.821
	0.975	0.482	3.82	3.238	3.907	0.395	70.031
	1.292	0.488	3.16	3.550	4.160	0.302	70.910
	1.591	0.496	2.78	4.056	4.555	0.249	72.120
octan-1-ol	0.255	0.323	4.99	1.049	1.144	1.012	46.941
	0.466	0.343	4.25	1.326	1.311	0.590	49.909
	0.734	0.370	3.65	1.675	1.572	0.403	53.758
	0.975	0.398	2.98	2.116	1.919	0.326	57.826
	1.292	0.424	2.13	2.673	2.333	0.262	61.564
	1.591	0.459	1.96	3.376	3.123	0.230	66.622
nonan-1-ol	0.255	0.340	4.78	1.189	1.278	1.064	49.360
	0.466	0.367	4.01	1.471	1.539	0.630	53.318
	0.734	0.399	3.12	1.820	1.930	0.434	57.936
	0.975	0.422	2.66	2.252	2.305	0.346	61.344
	1.292	0.444	2.14	2.786	2.755	0.275	64.533
	1.591	0.462	1.75	3.447	3.210	0.232	67.062
decan-1-ol	0.255	0.356	4.66	1.434	1.424	1.113	51.669
	0.466	0.377	4.23	1.720	1.657	0.648	54.857
	0.734	0.406	3.56	2.062	2.041	0.443	59.035
	0.975	0.428	2.86	2.473	2.418	0.351	62.224
	1.292	0.449	2.21	2.966	2.864	0.278	65.193
	1.591	0.468	1.89	3.557	3.419	0.235	68.052
kerosene	0.255	0.434	3.26	-	2.539	1.700	63.104
	0.466	0.458	2.96	-	3.102	0.982	66.512
	0.734	0.482	2.24	-	3.907	0.657	70.031
	0.975	0.499	1.77	-	4.673	0.511	72.450
	1.292	0.513	1.09	-	5.556	0.397	74.539
	1.591	0.537	0.84	-	7.888	0.337	78.057
n-hexane	0.255	0.358	4.12	-	1.446	1.401	51.998
	0.466	0.387	3.83	-	1.777	0.831	56.287
	0.734	0.414	3.56	-	2.161	0.564	60.135
	0.975	0.443	2.82	-	2.720	0.454	64.313
	1.292	0.468	2.06	-	3.395	0.362	67.942
	1.591	0.495	1.65	-	4.478	0.311	71.900
MEK	0.255	0.340	3.89	-	1.285	1.333	49.470
	0.466	0.365	3.42	-	1.515	0.783	52.988
	0.734	0.390	3.06	-	1.816	0.532	56.726
	0.975	0.407	2.71	-	2.053	0.417	59.145
	1.292	0.485	2.23	-	4.030	0.375	70.471
	1.591	0.532	1.83	-	7.246	0.334	77.288
DIBK	0.255	0.243	3.52	-	0.673	0.953	35.396
	0.466	0.259	3.02	-	0.750	0.557	37.705
	0.734	0.313	2.48	-	1.072	0.426	45.511
	0.975	0.376	2.04	-	1.640	0.385	54.637
	1.292	0.412	1.38	-	2.124	0.318	59.805
	1.591	0.472	0.76	-	3.545	0.296	68.602
hexan-2-one	0.255	0.237	3.02	-	0.642	0.927	34.406
	0.466	0.271	2.85	-	0.813	0.583	39.464
	0.734	0.307	2.23	-	1.030	0.418	44.632
	0.975	0.371	1.94	-	1.588	0.381	53.978
	1.292	0.442	1.36	-	2.703	0.342	64.203
	1.591	0.477	0.86	-	3.733	0.300	69.371
toluene	0.255	0.358	5.56	-	1.446	1.121	51.998
	0.466	0.393	4.89	-	1.846	0.674	57.056
	0.734	0.415	4.19	-	2.174	0.452	60.245
	0.975	0.448	3.52	-	2.845	0.367	65.083
	1.292	0.468	2.87	-	3.395	0.289	67.942
	1.591	0.499	2.02	-	4.713	0.251	72.560

[a] $\bar{C}_s$ is the concentration of TOA in the organic phase; $\bar{C}_{HA}$ is the concentration of glutaric acid in the organic phase; $K_{D,model}$ is the distribution coefficient calculated by the LSER model; K_D is the distiribution coefficient, Z is the loading factor; and E is the extraction efficiency.

4. Results and Discussion

4.1. Equilibrium Results. 4.1.1. Complex Formation and Distribution Coefficients. Table 1 presents a survey of the experimental liquid−liquid phase equilibrium investigations for

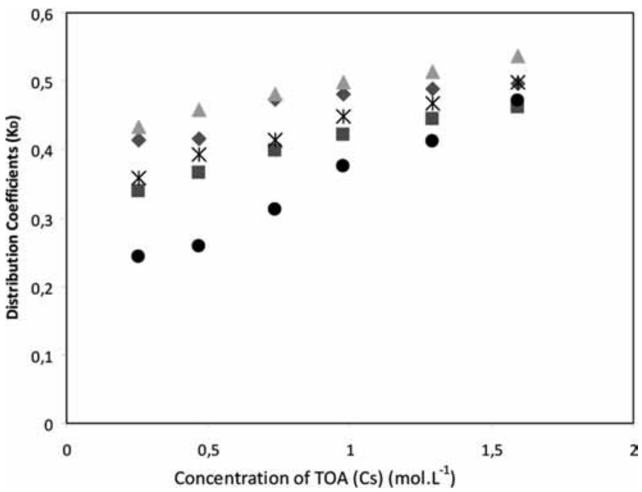

Figure 1. Plot of distribution coefficients, K_D, against the concentration of TOA (C_s). ●, DIBK; ■, Nonanol; ▲, Kerosen; *, Toluene; ♦, Isoamyl alcohol.

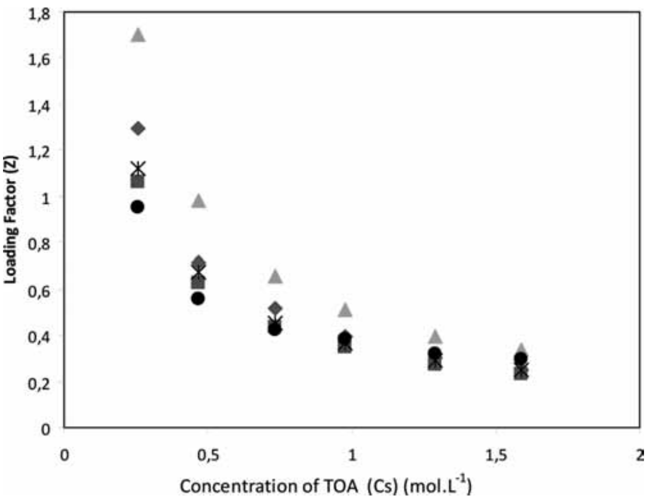

Figure 2. Plot of loading factors, Z, against the concentration of TOA (C_s). ●, DIBK; ■, Nonanol; ▲, Kerosen; *, Toluene; ♦, Isoamyl alcohol.

the distribution of glutaric acid. The amine (TOA) concentrations in the initial organic solution were prepared in the range of 0.255 mol·L^{-1}, 0.466 mol·L^{-1}, 0.734 mol·L^{-1}, 0.975 mol·L^{-1}, 1.292 mol·L^{-1}, and 1.591 mol·L^{-1} by using isoamyl alcohol, octan-1-ol, nonan-1-ol, decan-1-ol, methyl ethyl ketone (MEK), diisobutyl ketone (DIBK), hexan-2-one, toluene, kerosene, and *n*-hexane. The glutaric acid concentration in the initial aqueous phase was 0.606 mol·L^{-1}. The experimental results are given in Table 1. Figure 1 demonstrates the influence of TOA in the organic phase on the distribution ratio of glutaric acid. It was observed from the experiments that the ratio of the glutaric acid concentration in the organic phase varied between (0.237 and 0.537) mol·L^{-1}. The distribution coefficient of glutaric acid in that range is between about (7.888 and 0.642) mol·L^{-1} in the ten diluents. Preliminary experiments showed that 1.591 mol·L^{-1} of TOA gave maximum distribution coefficients. Synergistic effects of TOA + solvents give lower K_D above this concentration.

Extraction of carboxylic acids with tertiary amine + solvent systems 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 diluent can be divided into general solvation and specific

Table 2. Values of the Equilibrium Complexation (K_{11} and K_{21}) Constants of Glutaric Acid for Various Diluents + TOA^a

diluent	$\bar{C}_s$ mol·L^{-1}	K_{11} L^{-1}·mol^{-1}	K_{21} L^{-2}·mol^{-2}	diluent	K_{11} L^{-1}·mol^{-1}	K_{21} L^{-2}·mol^{-2}
isoamyl alcohol	0.255	6.764	35.292	kerosene	9.932	58.015
	0.466	3.774	19.927		6.653	45.038
	0.734	3.918	29.726		5.320	43.086
	0.975	3.204	25.953		4.791	44.853
	1.292	2.576	21.940		4.300	46.534
	1.591	2.289	20.988		4.956	72.693
octan-1-ol	0.255	3.581	12.674	*n*-hexane	5.656	22.834
	0.466	2.250	8.587		3.812	17.473
	0.734	1.712	7.268		2.943	15.357
	0.975	1.574	7.584		2.789	17.124
	1.292	1.444	7.945		2.627	19.059
	1.591	1.570	10.682		2.814	25.444
nonan-1-ol	0.255	4.002	15.050	MEK	5.028	18.962
	0.466	2.641	11.068		3.250	13.491
	0.734	2.102	10.165		2.473	11.496
	0.975	1.890	10.314		2.104	10.605
	1.292	1.706	10.573		3.119	25.901
	1.591	1.613	11.210		4.553	61.963
decan-1-ol	0.255	4.455	17.823	DIBK	2.634	7.274
	0.466	2.844	12.472		1.609	4.648
	0.734	2.223	11.161		1.460	4.993
	0.975	1.983	11.189		1.681	7.324
	1.292	1.773	11.309		1.644	8.479
	1.591	1.718	12.535		2.227	16.706
toluene	0.255	4.525	18.267	heptan-2-one	2.513	6.812
	0.466	3.168	14.884		1.745	5.224
	0.734	2.368	12.406		1.402	4.699
	0.975	2.334	14.812		1.628	6.958
	1.292	2.102	15.247		2.092	12.786
	1.591	2.369	22.340		2.345	18.321

^{a} $\bar{C}_s$ is the concentration of TOA in the organic phase. K_{11} is the complexation constant for 1 acid + 1 amine. K_{21} is the complexation constant for 2 acids + 1 amine.

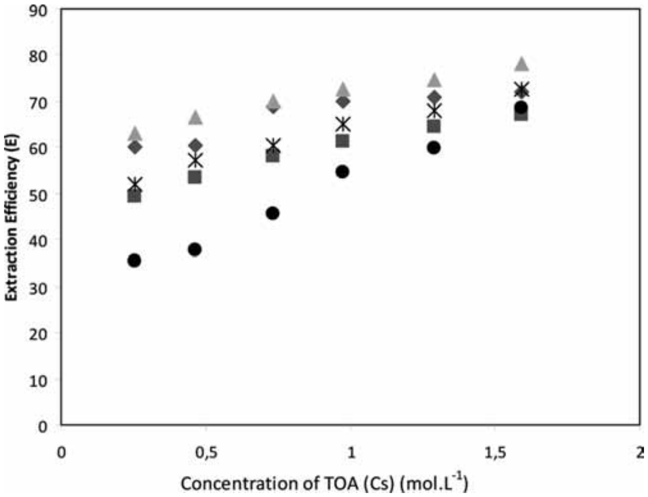

Figure 3. Plot of extraction efficiencies, E, against the concentration of TOA (C_s). ●, DIBK; ■, Nonanol; ▲, Kerosen; *, Toluene; ♦, Isoamyl alcohol.

Table 3. Solvatohromic 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 4. LSER, Modified Freundlich, and Langmuir Equation Parameters of Glutaric Acid Extraction by TOA

LSER	ln D^0	s	d	a	b	R^2
	0.630	−56.775	0	31.081	−4.520	0.940

Freundlich	K_F	n	R^2
isoamyl alcohol	$173 \cdot 10^4$	0.107	0.96
ocantan-1-ol	$264 \cdot 10^3$	0.171	0.99
nonan-1-ol	$168 \cdot 10^3$	0.198	0.95
decan-1-ol	$414 \cdot 10^3$	0.154	0.98

Langmuir	K_L	Q_0	R^2
isoamyl alcohol	−209	−0.0093	0.99
ocantan-1-ol	−823	−0.0024	0.88
nonan-1-ol	−643	−0.0030	0.97
decan-1-ol	−588	−0.0033	0.95

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 the overall extraction constants, K_{11} and K_{21}, for each solvent are given in Table 2. The resulting acid + amine complexes were supposed to be stabilized due to the hydrogen bonding with the modifiers.[15] The values K_{11} and K_{21} for the three most effective diluents at 1.591 mol·L^{-1} of TOA increase in the following trend: TOA + kerosene (4.956 and 72.693) > TOA + MEK (4.553 and 61.963) > TOA + n-hexane (2.814, and 25.444), respectively, where K_{11} and K_{21} have been given in parentheses. The large difference among complexation constant values for the extraction of glutaric acid by TOA + different diluents indicates that solvation of the complex in different diluents is a critical factor in acid extraction.

4.1.2. Loading Factors and Extraction Efficiency. Table 1 shows the effect of TOA concentration on loading. In Figure 2, the loading curve is a plot of the loading factor (Z) vs amine concentration. In this work, the loading factor of all solvent mixtures increases with decreasing concentration of trioctyl amine (TOA).

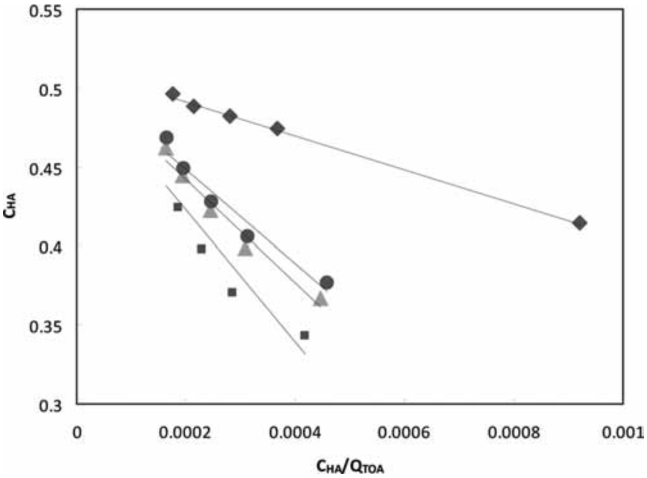

Figure 4. Plot of modified Langmuir equation on glutaric acid extraction by TOA: ●, Decanol; ■, Octanol; ▲, Nonanol; ♦, Isoamyl alcohol.

Overloading, 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 0.255 mol·L^{-1} for all diluents except DIBK and hexan-2-one 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.[16] 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 pKa_1 = 4.31 and pKa_2 = 5.41. In this study, the pH values of the aqueous phase changed in the range of 0.76 to 5.96 when TOA was used.

It will be seen from Table 1 and Figure 3 that a considerable amount of glutaric is removed by trioctylamine from aqueous solutions. The amount of removed acid strongly depends on the concentration of trioctyl amine and diluting solvents. The maximum removal of glutaric acid is 78.057 % with kerosene at a 1.591 mol·L^{-1} initial concentration of TOA. The acid concentration of the organic phase at equilibrium $\bar{C}_{HA}$ increased from 0.059 mol·L^{-1} to 0.225 mol·L^{-1} with an increasing amount of trioctylamine from 0.096 mol·L^{-1} to 0.673 mol·L^{-1} with kerosene. For the other diluents, the removal of glutaric acid changes between 66.622 % and 77.288 % at a 1.591 mol·L^{-1} initial concentration of trioctylamine.

4.2. Model Results. 4.2.1. LSER Model Equation. The linear solvation energy relationship (LSER) was initially developed by Kamlet and co-workers.[17] They demonstrated that many types of chemical properties (designated as XYZ), such as aqueous solubility, octanol−water partition coefficient,[18] HPLC capacity factors using a number of mobile and stationary phases,[19] and toxicity to a variety of species,[20] depended on solute−solvent interactions. The model can be expressed by an equation containing three simple and conceptually explicit types of terms

$$\text{XYZ (property)} = \text{cavity term} + \text{dipolar term} + \text{hydrogen-bonding terms} \quad (9)$$

In the LSER model, chemical properties (as XYZ) are related to molecular structure through the energy required to surround a solute with solvent molecules and the energy gained or lost through formation of electrostatic and hydrogen bonds between the chemical and the medium to stabilize this solvent molecule cavity and keep the compound inside it. Chemical properties dependent on this solute−solvent interaction are the result of

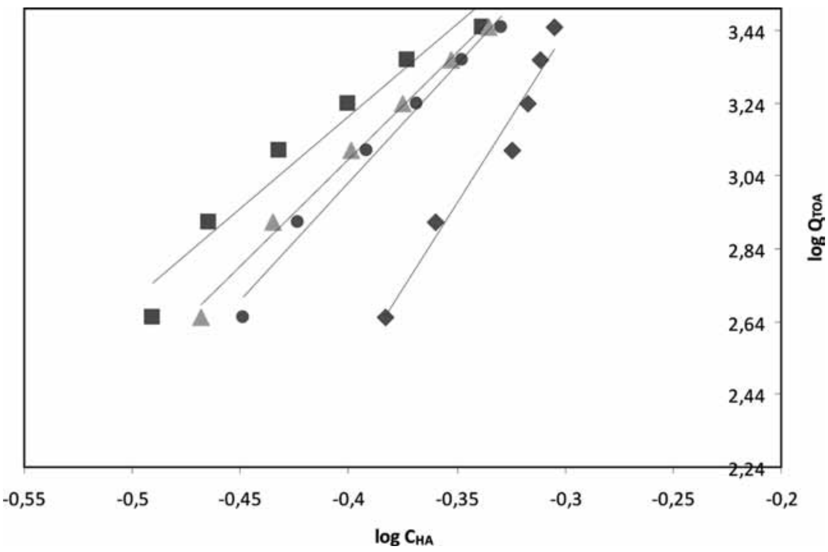

Figure 5. Plot of modified Freundlich equation on glutaric acid extraction by TOA. ●, Decanol; ■, Octanol; ▲, Nonanol; ♦, Isoamyl alcohol.

the contribution from the component groups that form the molecule. The energy terms for component groups then make up the four energy terms for the molecule used in the predictive equation

$$\ln K_{\mathrm{D}} = \ln K_{\mathrm{D}}^{0} + s(v\pi^{*} + v\mathrm{d}\delta) + bv\beta + av\alpha \tag{10}$$

The dipolar−polarizability term, π^*, represents the exoergic effects of solute−solvent dipole−dipole and dipole-induced−dipole interaction, and π^* is a measure of the molecule's ability to stabilize a neighboring charge or dipole through nonspecific dielectric interaction. The hydrogen-bonding terms β and α represent the exoergic effects of hydrogen bonding involving the solvent as a hydrogen bond donor acid (HBD) and the solute as a hydrogen bond acceptor base β (HBA) and the solute as hydrogen bond donor acid α and the solvent as hydrogen bond acceptor base, s, a, and b are regression coefficients, and v is the volume fraction of solvent in the organic phase. The distribution coefficient values can be regressed with the solvatochromic parameters of the solvents from Table 3[17,21] according to eq 10, and results were presented in Table 4. After all the distribution coefficients for each of the alcohols were obtained, they were regressed using computer program SPSS v14.0[22] and LSER parameters as follows

$$\ln K_{\mathrm{D}} = (0.630) + (-56.775)\cdot(v\pi^{*} - 0\cdot v\delta) + 31.081(v\beta) + (-4.520)(v\alpha) \tag{11}$$

For the suitability of the data, the root-mean-square deviation (rmsd) values are calculated from the difference between the experimental data and the predictions of the LSER model, according to the following equation

$$\mathrm{rmsd} = \sqrt{\frac{1}{N}\sum_{i=1}^{n}(K_{\mathrm{D}} - K_{\mathrm{D}}^{\mathrm{model}})} \tag{12}$$

where K_{D} is the experimental distribution coefficient and $K_{\mathrm{D}}^{\mathrm{model}}$ is the calculated distribution coefficient. N is the number of experimental data. The rmsd value of the LSER model is determined to be 0.84.

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

4.2.2. Modified Langmuir and Freundlich Equations.

The extraction of liquid molecules or solutes in a solution by reactive extractants and interactions of interfacial area is an important phenomenon in physical chemistry, surface science, and industry. The plotting of isotherms is important to obtain an equation which represents the results and which could be used for design purposes. These isotherms depend on the specific surface area of the extractant mixture, the nature of the extractant, and the acidity of the medium. The Langmuir equation has been modified for an extractant surface containing a finite number of identical complex sites. The model assumes uniform energies of extraction for interaction in both phases. When an extraction process is carried out at a constant temperature, the amount extracted, Q, can be quantitatively described by the Langmuir equation. Poposka et al.[23] have studied the modified Langmuir equation on reactive extraction.

Our modified Langmuir equation is represented by the following equation

$$(\overline{C_{\mathrm{HA}}}/Q_{\mathrm{TOA}}) = (K_1/Q_0) + (\overline{C_{\mathrm{HA}}}/Q_0) \tag{13}$$

In eq 13, Q_{TOA} is the amount of extractant (amine (g)); K_1 is the inverse of the Langmuir constant (K_{L}); and Q_0 is the constant obtained from linear regression.

A plot of $\bar{C}_{\mathrm{HA}}/Q_{\mathrm{TOA}}$ vs $\bar{C}_{\mathrm{HA}}$ gives a straight line showing the applicability of the Langmiur isotherm. The values of Q_0 and K_1 at different concentrations have been determined from the slope and intercept of the plot.[24] The modified Langmuir parameters are very useful in predicting extraction capacities and for incorporating a mass transfer relationship. To verify the Langmuir adsorption isotherm, using a mass based acid concentration ($\bar{C}_{\mathrm{HA}}/Q_{\mathrm{TOA}}$) is plotted against the acid concentration $\bar{C}_{\mathrm{HA}}$ at equilibrium conditions in Figure 4. The values of K_{L} and Q_0 are calculated graphically. The values of the Langmuir parameters are given in Table 4.

The Freundlich equation is used for heterogeneous surface of extractant energies in which the energy term in the Langmuir equation varies as a function of the surface coverage strictly due to variation in the heat of extraction. The modified Freundlich equation is in the form below

$$Q_{\mathrm{TOA}} = K_{\mathrm{F}}\cdot(\overline{C_{\mathrm{HA}}})^{1/n} \tag{14}$$

A logarithmic plot linearizes the equation enabling the exponent n and the constant K_{F} to be determined.[25]

$$\log Q_{\mathrm{TOA}} = \log K_{\mathrm{F}} + (1/n) \log \overline{C_{\mathrm{HA}}} \qquad (15)$$

To verify the validity of the modified Freundlich equation, $\log Q_{\mathrm{TOA}}$ is plotted against $\log \bar{C}_{\mathrm{HA}}$ in Figure 5. The linear plot of $\log Q_{\mathrm{TOA}}$ vs $\log \bar{C}_{\mathrm{HA}}$ indicates the applicability of the modified Freundlich equation. The values of Freundlich parameters are given in Table 4. The results show that all the experimental data for the alcohols obey the modified equations well.

5. Conclusion

The reactive extraction of glutaric acid by using TOA dissolved in ten diluents was investigated. Distribution coefficients, loading factors, and extraction efficiencies for this extraction system were obtained. Complexation constants were calculated for K_{11} (1 acid + 1 amine) and K_{21} (2 acids + 1 amine). The LSER model was applied to obtain distribution coefficients for all diluents. The LSER model values showed a good regression to the experimental data with an R square value of 0.940. Modified Freundlich and Langmuir equations have been fitted to the equilibrium data. All data for alcohols obey these modified equations.

Literature Cited

(1) Kertes, A. S.; King, C. J. Extraction Chemistry of Fermentation Product Carboxylic Acids. *Biotechnol. Bioeng.* **1986**, *28*, 269–282.

(2) Tamada, J. A.; King, C. J. Extraction of carboxylic acids with amine extractants. 2. Chemical interactions and interpretation of data. *Ind. Eng. Chem. Res.* **1990**, *29*, 1327–1333.

(3) Uslu, H. Linear solvation energy relationship (LSER) Modeling and kinetic studies on propionic acid reactive extraction using alamine 336 in a toluene solution. *Ind. Eng. Chem. Res.* **2006**, *45*, 5788.

(4) Uslu, H. Liquid + liquid equilibria of the (water + tartaric acid + Alamine 336 + organic solvents) at 298.15 K. *Fluid Phase Equilib.* **2007**, *253*, 12.

(5) Uslu, H. Reactive Extraction of Levulinic Acid Using TPA in Toluene Solution: LSER Modeling, Kinetic and Equilibrium Studies. *Sep. Sci. Technol.* **2008**, *43*, 1535–1548.

(6) Keshav, A.; Wasewar, K. L.; Chand, S. Extraction of Acrylic, Propionic, and Butyric Acid Using Aliquat 336 in Oleyl Alcohol: Equilibria and Effect of Temperature. *Ind. Eng. Chem. Res.* **2009**, *48*, 888–893.

(7) Wasewar, K. L.; Heesink, A. B. M.; Versteeg, G. F.; Pangarkar, V. G. Reactive extraction of lactic acid using alamine 336 in MIBK: equilibria and kinetics. *J. Biotechnol.* **1986**, *97*, 59–68.

(8) Kyuchoukov, G.; Labbaci, A.; Albet, J.; Molinier, J. Simultaneous Influence of Active and "Inert" Diluents on the Extraction of Lactic Acid by Means of Tri-*n*-octylamine (TOA) and Tri-*iso*-octylamine (TIOA). *Ind. Eng. Chem. Res.* **2006**, *45*, 503–510.

(9) Marinova, M.; Kyuchoukov, G.; Albet, J.; Molinier, J.; Malmary, G. Separation of tartaric and lactic acids by means of solvent extraction. *Sep. Purif. Technol.* **2004**, *37*, 199–207.

(10) Hong, Y. K.; Hong, W. H. Equilibrium studies on reactive extraction of succinic acid from aqueous solutions with tertiary amines. *Bioprocess Eng.* **2000**, *22*, 477–481.

(11) İnci, İ. Extraction of aqueous solution of gluconic acid with organic solutions of Alamine 336. *Chem. Biochem. Eng. Q.* **2002**, *16*, 185–189.

(12) İnci, İ. Distribution of hydroxy succinic acid between water and organic solutions of aliphatic tertiary amines. *J. Sci. Ind. Res.* **2002**, *61*, 289–293.

(13) Qin, W.; Yaohong, Z.; Zhenyui, L.; Youyuan, D. Extraction Equilibria of Glycolic and Glyoxylic Acids with Trialkylphosphine Oxide and Trioctylamine as Extractant. *J. Chem. Eng. Data* **2002**, *48*, 430–434.

(14) Martak, J.; Schlosser, S. L/L equilibria of dimethylcyclopropanecarboxylic acid in water - Solvent systems with trioctylamine as an extractant. *Chem. Pap.-Chemicke ZVesti.* **2000**, *54*, 413–422.

(15) Senol, A. Effect of Diluent on Amine Extraction of Acetic Acid: Modeling Considerations. *Ind. Eng. Chem. Res.* **2000**, *43*, 6496–6506.

(16) 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.

(17) Kamlet, M. J.; Abboud, M.; Abraham, M. H.; Taft, R. W. Linear Solvation Energy Relationships, 23. A Comprehensive Collection of the Solvatochromic Parameters, $\prod^*$ α β and some Methods for Simplifying the Generalized Solvatochromic Equation. *J. Org. Chem.* **1983**, *48*, 2877–2887.

(18) Kamlet, M. J.; Doberty, R. M.; Abraham, M. H.; Taft, R. W. Linear solvation energy relationships. 46. An improved equation for correlation and prediction of octanol/water partition coefficients of organic nonelectrolytes (including strong hydrogen bond donor solutes). *J. Phys. Chem.* **1988**, *92*, 5244–5255.

(19) Leahy, D. E.; Carr, P. W.; Pearlman, R. S.; Taft, R. W.; Kamlet, M. J. Linear Solva-tion Energy Relation-ships. A Comparison of Molar Volume and Intrinsic Molecular Volume as Measures of the Cavity Term in Reversed Phase Liquid Chroma-tography. *Chromatographia* **1986**, *21*, 473–478.

(20) Kamlet, M. J.; Doherty, R. M.; Taft, R. W.; Abraham, M. H. Solubility properties in polymers and biological media. *Environ. Sci. Technol.* **1986**, *20*, 690–695.

(21) Legget, D. N. Modeling solvent extraction using the solvatochromic parameters α β, and $\prod^*$. *Anal. Chem.* **1993**, *65*, 2907–2909.

(22) http://www.spss.com/,

(23) Poposka, F. A.; Nikolovski, K.; Tomovska, R. Equilibria and Mathematical Models of Extraction of Citric Acid with Isodecanol/*n*-Parrafins Solutions of Trioctylamine. *J. Chem. Eng. Jpn.* **1997**, *30*, 777–785.

(24) Rai, K.; Maheshwari, A. Removal of pollutants from industrial effluents using plastic clay and pyrophyllite. *Asian J. Chem.* **2002**, *14*, 739–745.

(25) Nouri, S. Effect of different treatment on the adsorption of p-cresol by activated carbon. *Asian J. Chem.* **2002**, *14*, 934–942.

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