

Purification of L-Malic Acid from Aqueous Solution by a Method of Reactive Extraction

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Malic acid is a C₄-dicarboxylic acid and an intermediate of the tricarboxylic acid cycle. It has been widely used in the polymer, food, and pharmaceutical industries. Malic acid is produced by a fermentation process with a lot of bacteria in about between (8 and 10) % by weight aqueous solution. In this study, malic acid has been extracted from aqueous solution by reactive batch extraction in solvents with and without trioctyl methyl ammonium chloride (TOMAC or Aliquat 336). Five different constant concentrations of TOMAC have been prepared using five different esters (dimethyl phthalate, dimethyl adipate, dimethyl succinate, dimethyl glutarate, diethyl carbonate), five different alcohols (isoamyl alcohol, hexan-1-ol, octan-1-ol, nonan-1-ol, decan-1-ol), and two different ketones (diisobutyl ketone (DIBK), methylisobutyl ketone (MIBK)). The results have been reported as distribution coefficients (K_D), loading factors (T_T), stoichiometric loading factors (T_S), separation factors (S_f), and extraction efficiencies (E). The most effective solvent has been determined to be isoamyl alcohol with a distribution value of 2.674. The maximum values of the overall equilibrium complexation constants in isoamyl alcohol for (acid:amine) (1:1) K_{E1} and (2:1) K_{E2} are 1.580 and 7.250, respectively. The linear solvation energy relationship (LSER) has been accurately regressed to the experimental distribution coefficients.

1. Introduction

Malic acid, a four-carbon dicarboxylic acid, is currently used mainly as an acidulant and taste enhancer in the beverage and food industry. Racemic malic acid is synthesized petrochemically from maleic anhydride. Enantiomerically pure L-malic acid (e.g., for production of pharmaceuticals) is produced from fumarate (synthesized from maleic anhydride) by enantioselective hydration with fumarase, using either immobilized cells or isolated enzymes.^{1,2} Increasing oil prices, concerns about climate change, and advances in the field of metabolic engineering have fueled renewed interest in the production of organic acids by microbial fermentation.³ In 2004, the U.S. Department of Energy included a group of 1,4-dicarboxylic acids, consisting of succinic, fumaric, and malic acids, in the top 12 most interesting chemical building blocks that can be derived from biomass.⁴

In 1924, malic acid was identified as a product of yeast fermentation.⁵ Since then, malic acid production has been observed in a wide range of microorganisms. Fermentative production of malic acid has been most successfully demonstrated with *Aspergillus flavus*, achieving 63 % of the maximum theoretical yield of malic acid on glucose at high production rates and titers.⁶ Since its potential aflatoxin production disqualified *A. flavus* as a producer of food-grade chemicals,⁷ malic acid production has been studied with other organisms, including the yeast *Saccharomyces cerevisiae*, and they are presented in Table 1.^{8–18} The highest reported malic acid concentration obtained with *S. cerevisiae* thus far is 12 g·L⁻¹, which was achieved by overexpression of the cytosolic isoenzyme of malate dehydrogenase (Mdh2p).¹⁷ Recently, another yeast, a natural isolate of *Zygosaccharomyces rouxii*, was shown to produce

up to 75 g·L⁻¹ of malic acid in a complex medium containing 300 g·L⁻¹ of glucose.¹⁸

Tertiary amines and quaternary ammonium salts have been found to be efficient extractants for carboxylic acid which are intended to dimer in the organic phase (Figure 1). Usually, they have been dissolved in inert diluents to improve the physical properties of the organic phase and/or active diluents to prevent third phase formation and to improve the extraction. Extractive recovery of carboxylic acids from dilute aqueous solutions, such as fermentation broth and wastewater, which have acid concentrations lower than 10 % (w/w), has received increasing attention. Solvent extraction with conventional solvents such as alcohols, ketones, ethers, and aliphatic hydrocarbons is not efficient when applied to dilute carboxylic acid solutions because of the low aqueous activity of carboxylic acids resulting in low distribution coefficients.^{19–21} However, carboxylic acid extractions with aliphatic amines have large distribution coefficients. Several aliphatic amines have been used successfully to extract carboxylic acids.^{22–32}

In this study, the reactive extraction of malic acid from aqueous solutions with trioctyl methyl ammonium chloride (TOMAC) in several solvents, five different esters (dimethyl phthalate, dimethyl adipate, dimethyl succinate, dimethyl glutarate, diethyl carbonate), five different alcohols (isoamyl alcohol, hexan-1-ol, octan-1-ol, nonan-1-ol, decan-1-ol), and two different ketones (diisobutyl ketone (DIBK), methylisobutyl ketone (MIBK)) has been investigated. A new LSER model equation has been obtained for the experimental results of the alcohols.

2. Materials and Experimental Procedure

2.1. Materials. TOMAC (IUPAC name: tricaprilmethylammonium chloride) is a mixture of C₈ (octyl) and C₁₀ (capryl)

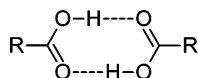
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Table 1. Overview of Production Titrers, Yields, and Rates Presented in Various Studies of Malic Acid Production by Fermentation-Based Methods

organism(s)	year	malic acid (g·L ⁻¹)	yield (mol·mol ⁻¹)	productivity (g·L ⁻¹ ·h ⁻¹)	ref
<i>A. flavus</i>	1962	60	0.84	0.1	Abe et al. ¹⁵
	1988	36	0.51	0.19	Peleg et al. ¹²
	1991	113	1.26	0.59	Battat et al. ⁶
<i>Rhizopus arrhizus</i> and <i>Paecilomyces varioti</i>	1983	48	0.81	0.34	Takao et al. ¹⁰
<i>Monascus araneosus</i>	1993	28	0.50	0.23	Lumyong and Tomita ¹³
<i>Schizophyllum commune</i>	1997	18	0.48	0.16	Kawagoe et al. ¹⁴
<i>Z. rouxii</i>	2007	75	0.52	0.54	Taing and Taing ¹⁸
<i>S. cerevisiae</i>	1984	1		0.01	Fatichenti et al. ¹⁶
	1988	2			Schwartz and Radler ¹¹
	1996	6	0.09	0.18	Pines et al. ¹⁷
	2008	59	0.42	0.19	Rintze et al. ⁸

**Figure 1.** Dimers of carboxylic acid.

chains with C₈ predominating. TOMAC, which is a quaternary ammonium salt, is a clear reddish brown liquid with the molecular mass of 0.404 kg·mol⁻¹. The density of Aliquat 336 is 0.88 kg·L⁻¹. Malic acid (Merck, > 99 %, molecular weight 134.09 g·mol⁻¹, and pK_{a1} = 3.40, pK_{a2} = 5.13), alcohols (hexan-1-ol (Merck, > 99 %), octan-1-ol (Merck, > 99 %), nonan-1-ol (Merck, > 99 %), decan-1-ol (Merck, > 99 %)), ketones (MIBK (Merck, > 99 %), and DIBK (Merck, > 99 %)), and esters (dimethyl phthalate (Merck, > 99 %), dimethyl adipate (Merck, > 99 %), dimethyl succinate (Merck, > 99 %), dimethyl glutarate (Merck, > 99 %), diethyl carbonate (Merck, > 99 %), hexan-1-ol (Merck, > 99 %)) have been supplied from Merck and Fluka and used without further purification.

2.2. Experimental Procedure. The known mass of malic acid was dissolved in distilled water to prepare the solutions with about an initial concentration of acid of 0.800 mol·L⁻¹. The solvents were used to dissolve the amine (TOMAC). The organic phases were prepared by the dissolution of TOMAC in the diluents to produce solutions at five constant concentrations, in the range of (0.464 to 1.692) mol·L⁻¹. Known volumes of aqueous and organic solutions were added to 50 mL Erlenmeyer flasks and equilibrated in a Nuve Shaker ST402 bath at 298.15 K for 2 h, which preliminary tests demonstrated to be a sufficient time for equilibration. Thereafter, the mixture was kept in a bath for another 3 h to reach full separation of phases. After equilibration, both phases were separated by centrifugation at 1200 rpm for about 7 min for better phase separation.

The acid concentration of aqueous phase samples was analyzed by using a titration with 0.1 N sodium hydroxide (relative uncertainty: ± 1 %) by means of phenolphthalein as an indicator, with each measurement being preformed in duplicate. In most cases, the deviation between the amount of acid analyzed and the amount of acid known by preparing the solutions by mass did not exceed ± 3 %. The pH value of the aqueous phase was determined with a pH meter (Hanna pH 211 Microprocessor pH meter) with a deviation of ± 1 %.

3. Results and Discussions

Results of the experimental studies of levulinic acid reactive extraction by TOMAC in various solvents have been investigated in six parts.

3.1. Physical Extraction. The physical extraction of malic acid was studied for a better understanding of the amine effect on extraction of malic acid. Table 2 presents the results of

Table 2. Results for Physical Extraction of Malic Acid with Pure Solvents

	solvents	pH _{aq}	C _{MA} [*]	K _D	E
			(mol·L ⁻¹)		
esters	dimethyl phthalate	1.98	0.082	0.114	10.250
	dimethyl adipate	2.11	0.127	0.188	15.875
	dimethyl glutarate	2.17	0.146	0.223	18.250
	dimethyl succinate	2.22	0.162	0.254	20.250
	diethyl carbonate	2.35	0.207	0.349	25.875
ketones	diisobutyl ketone	2.34	0.204	0.342	25.550
	methyl isobutyl ketone	2.40	0.224	0.389	28.000
alcohols	isoamyl alcohol	2.59	0.287	0.559	35.875
	hexan-1-ol	2.47	0.246	0.444	30.750
	octan-1-ol	2.39	0.219	0.377	27.375
	nonan-1-ol	2.36	0.209	0.354	26.125
	decan-1-ol	2.32	0.198	0.329	24.750

physical extraction of malic acid by pure solvents without TOMAC. Generally, all solvents give very low distribution coefficients. With the help of pure isoamyl alcohol, the highest extraction degree of 35.875 % of malic acid has been raised in the aqueous phase to the organic phase. In the categories of diluents, alcohols are more dominant than esters and ketones because they have higher polarity.

3.2. Distribution Coefficients. 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

$$K_D = \frac{[\text{HA}]_{\text{org}}}{[\text{HA}]_{\text{aq}}} = \frac{[\text{HA}_q \cdot \text{S}_p]_{\text{org}}}{[\text{HA}]_{\text{aq}} + [\text{A}^-]_{\text{aq}}} \quad (1)$$

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

$$\text{HA} \leftrightarrow \text{H}^+ + \text{A}^-, \quad K_A = \frac{C_{\text{H}^+} \cdot C_{\text{A}^-}}{C_{\text{HA}}} \quad (2)$$

From eqs 1 and 2, the distribution coefficients for extracted malic acid were determined as

$$K_D = \frac{[\text{HA}_q \cdot \text{S}_p]_{\text{org}}}{[\text{HA}]_{\text{aq}} + [\text{A}^-]_{\text{aq}}} = \frac{K_{qp} \cdot [\text{HA}]_{\text{aq}}^q \cdot [\text{S}]_{\text{org}}^p}{[\text{HA}]_{\text{aq}} + K_A \cdot [\text{HA}]_{\text{aq}} / [\text{H}^+]_{\text{aq}}} = \frac{K_S \cdot [\text{S}]_{\text{org}}^p}{1 + K_A / [\text{H}^+]_{\text{aq}}} \quad (3)$$

$$K_S = K_{qp} \cdot [\text{HA}]_{\text{aq}}^{(q-1)} \quad (4)$$

The extraction of malic acid by TOMAC dissolved in esters (dimethyl phthalate, dimethyl adipate, dimethyl succinate, dimethyl glutarate, diethyl carbonate), alcohols (isoamyl alcohol,

Table 3. Results for Extraction of Malic Acid with the TOMAC + Ester System

solvents (esters)	C_{TOA}^*		C_{MA}^*		K_D	T_T	T_S	S_f	E
	(mol·L ⁻¹)	pH _{aq}	(mol·L ⁻¹)						
dimethyl phthalate	0.464	2.43	0.236	0.420	0.509	0.493	0.541	29.577	
	0.763	2.53	0.267	0.503	0.350	0.331	0.627	33.466	
	1.101	2.59	0.289	0.568	0.263	0.243	0.676	36.224	
	1.393	2.69	0.321	0.673	0.231	0.210	0.745	40.227	
	1.692	2.76	0.345	0.759	0.204	0.183	0.787	43.149	
dimethyl adipate	0.464	2.46	0.245	0.444	0.530	0.505	0.568	30.747	
	0.763	2.54	0.272	0.516	0.356	0.328	0.637	34.036	
	1.101	2.63	0.300	0.603	0.273	0.243	0.704	37.616	
	1.393	2.73	0.335	0.722	0.240	0.210	0.770	41.927	
	1.692	2.83	0.367	0.848	0.216	0.185	0.822	45.887	
dimethyl glutarate	0.464	2.49	0.255	0.468	0.549	0.523	0.594	31.880	
	0.763	2.56	0.279	0.537	0.366	0.333	0.653	34.938	
	1.101	2.68	0.318	0.662	0.289	0.255	0.739	39.831	
	1.393	2.77	0.348	0.771	0.250	0.214	0.792	43.534	
	1.692	2.87	0.380	0.906	0.224	0.188	0.839	47.534	
dimethyl succinate	0.464	2.52	0.266	0.499	0.573	0.544	0.621	33.288	
	0.763	2.59	0.287	0.562	0.377	0.340	0.672	35.979	
	1.101	2.74	0.337	0.73	0.306	0.269	0.775	42.196	
	1.393	2.85	0.374	0.88	0.268	0.229	0.831	46.808	
	1.692	2.94	0.405	1.027	0.239	0.199	0.867	50.666	
diethyl carbonate	0.464	2.58	0.284	0.553	0.613	0.575	0.667	35.608	
	0.763	2.73	0.336	0.726	0.441	0.395	0.770	42.062	
	1.101	2.85	0.375	0.884	0.340	0.293	0.831	46.921	
	1.393	2.97	0.413	1.071	0.296	0.246	0.877	51.714	
	1.692	3.13	0.467	1.406	0.276	0.224	0.921	58.437	

Table 4. Results for Extraction of Malic Acid with the TOMAC + Alcohol System and Model Results

solvents (alcohols)	C_{TOA}^*		C_{MA}^*		K_D	K_D^{model}	V	T_T	T_S	S_f	E
	(mol·L ⁻¹)	pH _{aq}	(mol·L ⁻¹)								
isoamyl alcohol	0.464	2.86	0.377	0.894	0.807	0.083	0.813	0.761	0.835	47.201	
	0.763	3.06	0.445	1.255	1.118	0.167	0.583	0.520	0.904	55.654	
	1.101	3.23	0.501	1.676	1.548	0.250	0.455	0.389	0.940	62.630	
	1.393	3.35	0.541	2.094	2.144	0.333	0.388	0.319	0.957	67.679	
	1.692	3.47	0.582	2.674	2.969	0.417	0.344	0.273	0.969	72.781	
hexan-1-ol	0.464	2.77	0.349	0.774	0.768	0.083	0.752	0.708	0.792	43.630	
	0.763	3.02	0.433	1.180	1.012	0.167	0.567	0.513	0.894	54.128	
	1.101	3.16	0.477	1.477	1.333	0.250	0.433	0.377	0.927	59.628	
	1.393	3.24	0.504	1.710	1.756	0.333	0.362	0.303	0.942	63.099	
	1.692	3.35	0.542	2.106	2.314	0.417	0.320	0.259	0.957	67.804	
octan-1-ol	0.464	2.73	0.336	0.725	0.750	0.083	0.724	0.684	0.770	42.028	
	0.763	2.92	0.398	0.992	0.966	0.167	0.522	0.473	0.860	49.799	
	1.101	3.09	0.456	1.327	1.243	0.250	0.414	0.364	0.912	57.026	
	1.393	3.21	0.495	1.626	1.599	0.333	0.355	0.302	0.937	61.919	
	1.692	3.32	0.531	1.981	2.058	0.417	0.314	0.259	0.953	66.454	
nonan-1-ol	0.464	2.70	0.324	0.682	0.732	0.083	0.699	0.660	0.751	40.546	
	0.763	2.84	0.370	0.863	0.919	0.167	0.485	0.439	0.826	46.323	
	1.101	3.02	0.432	1.175	1.153	0.250	0.392	0.344	0.893	54.022	
	1.393	3.16	0.477	1.482	1.447	0.333	0.342	0.292	0.927	59.709	
	1.692	3.27	0.513	1.792	1.817	0.417	0.303	0.251	0.946	64.183	
decan-1-ol	0.464	2.57	0.282	0.547	0.705	0.083	0.609	0.572	0.661	35.358	
	0.763	2.78	0.351	0.784	0.852	0.167	0.460	0.416	0.797	43.946	
	1.101	2.93	0.402	1.014	1.031	0.250	0.365	0.320	0.864	50.347	
	1.393	3.08	0.453	1.307	1.246	0.333	0.325	0.277	0.910	56.653	
	1.692	3.20	0.491	1.596	1.507	0.417	0.290	0.241	0.935	61.479	

hexan-1-ol, octan-1-ol, nonan-1-ol, decan-1-ol), and ketones (diisobutyl ketone (DIBK), methylisobutyl ketone (MIBK)) has been studied. The results of the equilibrium data which were taken from the aqueous phase to the organic phase on the reactive extraction of malic acid have been presented in Tables 3 to 5. The constant concentrations of TOMAC in various solvents were in the range of 0.464 mol·L⁻¹ and 1.692 mol·L⁻¹. The initial concentration of malic acid in the aqueous phase was 0.800 mol·L⁻¹. It can be seen from Figure 2 that the extraction power of the (TOMAC + diluents) mixture changes with increasing initial concentration of TOMAC in the organic phase. According to Tables 3 to 5 and Figure 2 (figures have been drawn for only six solvents so as not to cause any confusion), the distribution coefficients for malic acid extraction by TOMAC have obtained the following orders.

In Alcohols: isoamyl alcohol > hexan-1-ol >> octan-1-ol > nonan-1-ol > decan-1-ol.

In Esters: diethyl carbonate > dimethyl succinate > dimethyl glutarate > dimethyl adipate > dimethyl phthalate.

In Ketones: methyl isobutyl ketone (MIBK) > diisobutyl ketone (DIBK).

The equilibrium data about the distribution of malic acid between water and TOMAC dissolved in diisobutyl ketone and methyl isobutyl ketone have been presented in Table 5. The extraction power of TOMAC is shown to be more effective with MIBK than with DIBK. This situation can be explained by the polarity of MIBK being higher than that of DIBK: the polarity of MIBK is 0.315, whereas the polarity of DIBK is 0.123.

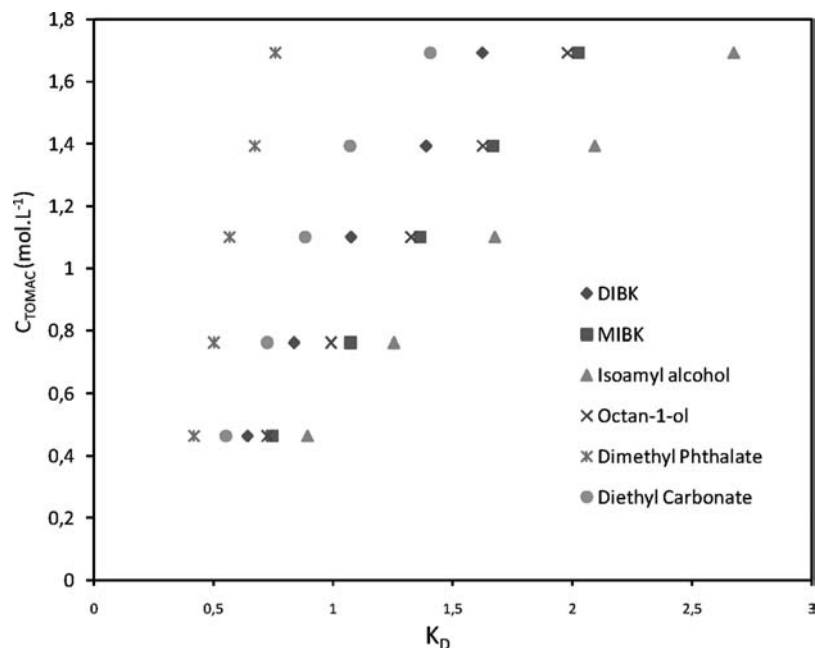


Figure 2. Plot of distribution coefficients K_D against concentration of TOMAC (C_{TOMAC}).

3.3. Extraction Efficiency and Separation Factor. Extraction efficiency shows the percentage of extracted acid from the aqueous phase to the organic phase and is expressed by eq 5.

$$E = \frac{K_D \cdot 100}{1 + K_D} \quad (5)$$

The highest extraction efficiency of malic acid that has been found is 72.781 % using isoamyl alcohol at a $1.694 \text{ mol} \cdot \text{L}^{-1}$ initial concentration of TOMAC. The acid concentration in the organic phase, C_{MA}^* , increases from $0.236 \text{ mol} \cdot \text{L}^{-1}$ to $0.582 \text{ mol} \cdot \text{L}^{-1}$ with increasing concentration of TOMAC from $0.464 \text{ mol} \cdot \text{L}^{-1}$ to $1.694 \text{ mol} \cdot \text{L}^{-1}$. It can be seen from Tables 3 to 5 that the increase of amine concentration brings about a gradual increase of extraction efficiency. The maximum values of 72.781 %, 67.804 %, and 58.437 % of the malic acid have been extracted in the vicinity of $1.694 \text{ mol} \cdot \text{L}^{-1}$ of TOMAC concentration with isoamyl alcohol, hexan-1-ol, and diethyl carbonate, respectively.

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

$$S_f = \frac{C_{MA}^*}{C_{MA}^* + C_{A^-}^*} \quad (6)$$

The effects of the modified separation factor (S_f) on the concentration of TOMAC have been presented in Tables 3 to 5 and shown in Figure 4 (figures have been drawn for only six solvents so as not to cause any confusion). The separation factor (S_f) shows the relative proportion between physical interaction and chemical reaction. For all solvents (esters), with increasing concentration of TOMAC, increases in separation factors have been observed. At the TOMAC concentration range (0.464 to 1.692) $\text{mol} \cdot \text{L}^{-1}$, the separation factor showed a gradual increase in all diluents.

3.4. Loading Factors T_T and T_S . The extent to which the organic phase can be loaded with malic acid is expressed as the overall loading factor (T_T) as

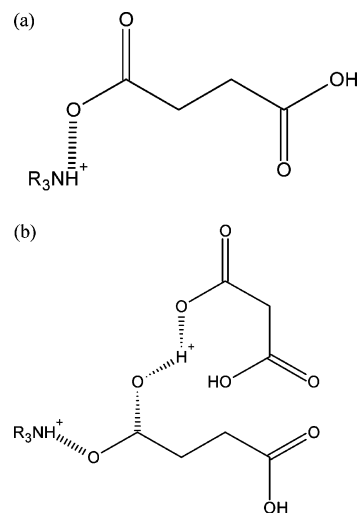


Figure 3. Possible acid-amine complex forms. (a) Acid-amine complex (1:1). (b) Acid-amine complex (2:1).

$$T_T = \frac{C_{MA}^*}{[S]_{org}} \quad (7)$$

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

$$[S]_{org} = [S]_{org}^{initial} - pC_{MA}^* \quad (8)$$

The stoichiometric loading factor, T_S , is the ratio of the overall complexed acid to total amine in the organic phase. This factor includes a correction term, ($v \cdot C_{MA}^*$) (C_{MA}^* is the concentration of acid in the aqueous phase after extraction by single pure solvents), for the amount of acid extracted by the diluents in the solvent mixture ($C_{TOA}^* = C_{R_3N}^0$)

$$T_S = \frac{(C_{MA}^* - v \cdot C_{MA}^*)}{C_{TOA}^*} \quad (9)$$

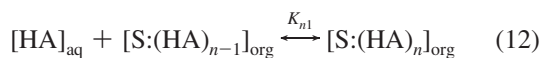
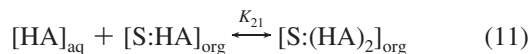
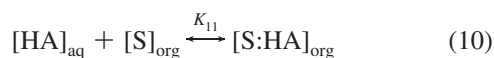
In eq 9, v is the volume fraction of diluents in extractant mixture, and C_{MA}^* is the extracted acid concentration by pure diluents alone not containing amine.

Table 5. Results for Extraction of Malic Acid with the TOMAC + Ketone System

solvents (ketones)	C_{TOA}^*		C_{MA}^*		K_D	T_T	T_S	S_f	E
	(mol·L ⁻¹)	pH _{aq}	(mol·L ⁻¹)						
DIBK	0.590	2.66	0.312	0.642	0.674	0.635	0.726	39.098	
	0.861	2.82	0.364	0.837	0.477	0.432	0.817	45.563	
	1.158	2.97	0.414	1.075	0.376	0.329	0.877	51.807	
	1.431	3.12	0.465	1.389	0.333	0.285	0.919	58.141	
	1.731	3.21	0.495	1.624	0.292	0.242	0.937	61.890	
MIBK	0.590	2.75	0.342	0.747	0.737	0.697	0.781	42.759	
	0.861	2.97	0.414	1.074	0.542	0.493	0.877	51.783	
	1.158	3.11	0.461	1.365	0.419	0.367	0.917	57.716	
	1.431	3.23	0.500	1.669	0.359	0.305	0.940	62.532	
	1.731	3.33	0.535	2.025	0.316	0.260	0.955	66.942	

The plot of loading factor T_T against the ratio of the overall complexed acid to total amine in the organic phase (stoichiometric loading factor), which is marked as T_S , is shown in Figure 5. The slope of the curve of each solvent has been given in Figure 5. Isoamyl alcohol has a maximum slope with a value of 1.0393. The lowest deviation among all the solvents is dimethyl phthalate with a slope value of 1.0167. The decreases of loading indicate complexes of acid + amine related diluents specifically, and overloading was not observed in all of the solvents (alcohols, esters, ketones) in this study.

3.5. Complex Formation. Tertiary and quaternary amines extract undissociated molecules of carboxylic acid. Keeping in view that the exact chemistry involved in the uptake of acid is unknown, the complex formations can be interpreted by the following set of equations (10 to 12)



The equilibrium complexation constant for the reaction represented by the above equations is (eq 12)

$$K_{\text{En}} = \frac{[\text{S:(HA)}_n]_{\text{org}}}{[\text{S}]_{\text{org}}[\text{HA}]_{\text{aq}}^n} \quad (13)$$

K_{En} is expected to depend on the properties of the acid and the solvation efficiency of the diluent used.

The values of the overall extraction constants, K_{E1} and K_{E2} , for each concentration of amine has been given in Table 6, and the possible complex forms for acid + amine (1:1) and (2:1) are shown in Figure 3. The resulting acid + amine complexes are supposed to be stabilized due to the hydrogen bonding with the diluents.^{33,34} Figure 3 shows 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.^{35,36} The values of K_{E1} and K_{E2} for the three most effective diluents increase in the following trend: TOMAC + isoamyl alcohol (1.580, 7.257) > TOMAC + hexan-1-ol (1.244, 4.832) > TOMAC + MIBK (1.196, 4.525). The large difference among complexation constant values was not observed for the extraction of malic acid by TOMAC + different diluents.

For systems with only one amine per complex, there is no effect of total amine concentration on the loading. If there is more than one amine per complex, loading increases with increasing amine concentration. Systems that exhibit aggregation

and formation of complexes with large numbers of acid and amine molecules exhibit an increase in loading. Solvation of the complex by the diluents is a critical factor in the extraction of acid. The interactions between the complex and diluents can be divided into general solvation and specific interactions of the diluents with the complex. Inert diluents give a very low distribution of the acid into the solvent phase. Alkenes being nonpolar provide very low solvation of the polar complexes. Aromatic diluents give higher distribution which has been rationalized as solvation due to the interaction of the aromatic. They have Π electrons within the complex. Alcohols used in this study are polar and can promote extraction by providing a good solvating media for the ion pair. However, polarity (or polarizability) alone does not completely account for solvating ability. Especially alcohols give unusually high equilibrium constants, higher than would be expected from polarity arguments alone.²⁸

The most effective properties of the solvent, on the extraction, is the polarity. It is a function of transition energy, E_T or Z . Kosower^{37,38} defined the polarity parameter, Z , as the molar transition energy, E_T , which is expressed in kJ·mol⁻¹, for the CT absorption band of 1-ethyl-4-(methoxycarbonyl) pyridinium iodide in the appropriate solvent. The stronger the stabilizing effect of the solvent on the ground-state ion pair as compared with the less dipolar radical pair in the excited state, the higher this transition energy and, thus, the Z value. A high Z value corresponds to high solvent polarity. Dimroth and Reichardt³⁹ have proposed a solvent polarity parameter, $E_T(30)$, based on the transition energy for the longest-wavelength solvatochromic absorption band of the pyridinium *N*-phenolate betaine dye. Owing to this exceptionally large displacement of the solvatochromic absorption band, the $E_T(30)$ values provide an excellent and very sensitive characterization of the polarity of solvents, high $E_T(30)$ values corresponding to high solvent polarity.³⁷ Molecular weight is an effective property on polarity of esters. Long chain esters have higher polarity than short chain esters. It has been observed that because the chain length in the esters increases, their polarity decreases, and as a result, the complex dissolving capacity which is formed in the organic phase decreases.

3.6. LSER Model Results. The hydrogen bond formation properties of an acid + amine system can be estimated through theoretically based models of the mass action law including the physical interaction terms or using the concept of multiscale association, as well as by applying a generalized solvatochromic approach with a linear solvation energy relationship (LSER).⁴⁰ A modified version of the LSER for predicting the extraction equilibrium of an amine + diluent + acid system has been given by Bizek et al.⁴¹

In this study, the LSER model was applied to predict the distribution coefficient for TOMAC + alcohol systems upon the

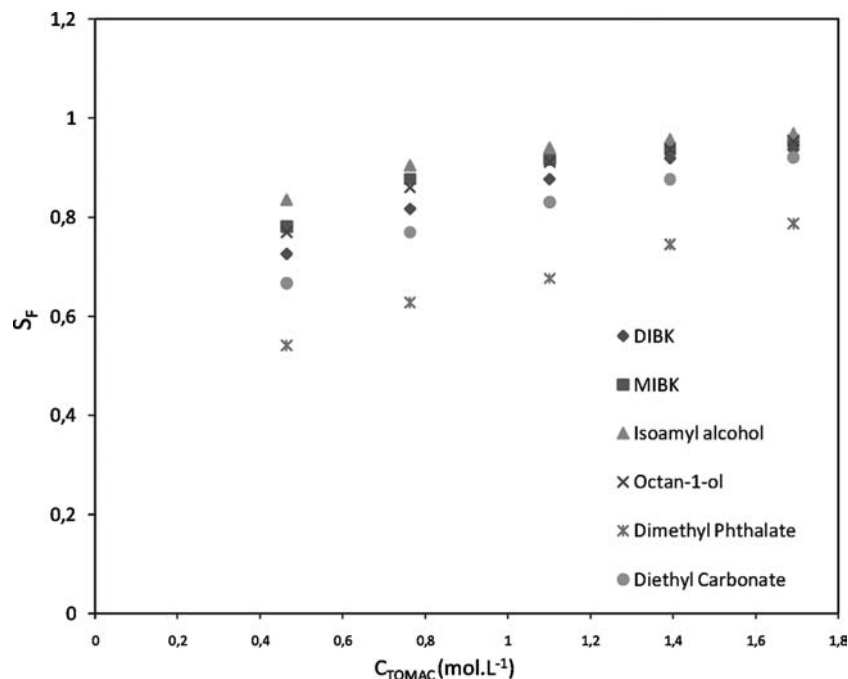


Figure 4. Effect of separation factors S_T on concentration of TOMAC (C_{TOMAC}).

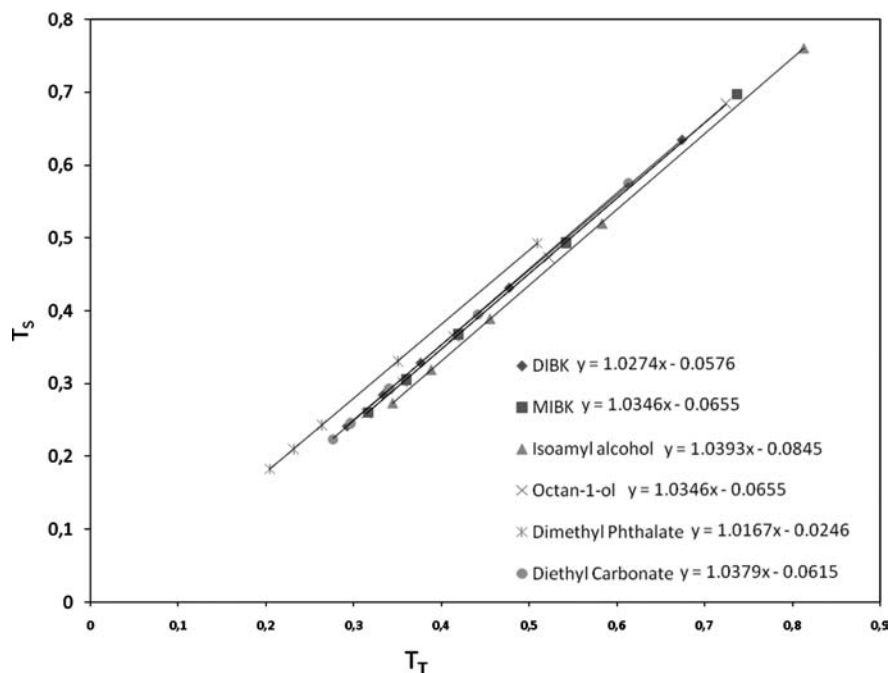


Figure 5. Plot of loading factor T_T against stoichiometric loading factor T_S .

extraction of malic acid. Calculation of the distribution coefficients of solvents in the amine with the LSER model equation has been described in Uslu's earlier work.²⁷ Briefly, the following equation can be used to describe the effect of diluents on the distribution coefficient (K_D) values

$$\ln K_D = \ln K_D^0 + s(\pi^* + d\delta) + b\beta + a\alpha \quad (14)$$

In eq 13, π^* and δ are the solvatochromic parameters which measure solute-solvent, dipole-dipole, and dipole-induced-dipole interactions, respectively. The solvatochromic parameter α scale of solvent HBD (hydrogen-bond donor) acidities describes the ability of the solvent to donate a proton in a solvent to the solute hydrogen bond. Parameter β of HBA (hydrogen-bond acceptor) basicities provides a measure of the

solvent's ability to accept a proton (donate an electron pair) in a solute-to-solvent hydrogen bond, respectively. The coefficients s , d , a , and b include the solute properties that come from regression.⁴²

The distributions coefficient values can be regressed with the solvatochromic parameters of the solvents from Table 7⁴³ according to eq 14. After all the distribution coefficients for each of the alcohols have been obtained, they were regressed using the computer program SPSS v14.0. The results, with regard to K_D^{model} , are shown in Table 4. The LSER model values showed good regression to the experimental data. The estimated values of parameters of the model have been presented in Table 8. It was concluded that, using this model, the distribution coefficients of malic acid between water and the amine +

Table 6. Values of the Complexation Constant of Malic Acid for Various Diluents + TOMAC

solvents	K_{E1}	K_{E2}	solvents	K_{E1}	K_{E2}
	(L·mol ⁻¹)	(L ² ·mol ⁻²)		(L·mol ⁻¹)	(L ² ·mol ⁻²)
diethyl carbonate	0.830	2.499	isoamyl alcohol	1.580	7.257
dimethyl succinate	0.606	1.537	hexan-1-ol	1.244	4.832
dimethyl glutarate	0.535	1.275	octan-1-ol	1.170	4.362
dimethyl adipate	0.501	1.157	nonan-1-ol	1.059	3.696
dimethyl phthalate	0.448	0.986	decan-1-ol	0.943	3.060
DIBK	0.959	3.148	MIBK	1.196	4.525

Table 7. Solvatochromic Parameters for Alcohols⁴²

solvents	π^*	δ	β	α
isoamyl alcohol	0.40	0	0.84	0.84
hexan-1-ol	0.40	0	0.84	0.80
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 8. Results of Regression Coefficient for the LSER Equation

coefficients	$\log K_D^0$	s	d	b	a	R^2	standard error
	-0.234	-4.309	0	-2.246	6.497	0.955	0.040

solvent system can be described. As a result, the regression equation has been devised to calculate the distribution coefficients

$$\ln K_D = -0.234 + -4.309(v\pi^* + 0\cdot v\delta) + -2.246(v\beta) + 6.497(v\alpha) \quad (15)$$

where v is the volume fraction of solvent in the organic phase.

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

$$\text{rmsd} = \sqrt{\frac{1}{N} \sum_{i=1}^n (K_{D_i} - K_{D_i}^{\text{model}})^2} \quad (16)$$

where K_D is the experimental distribution coefficient and K_D^{model} is the calculated distribution coefficient. N is the number of experimental data. The rmsd value of the LSER model is determined to be 0.093.

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

4. Conclusion

Distribution coefficients, loading factors, and separation factors have been calculated in light of experimental results. The extraction equilibrium was interpreted as a result of consecutive formation of two acid-amine species with stoichiometries of 1:1 and 2:1. Overall thermodynamic extraction constants K_{E1} and K_{E2} have been determined for each of the solvents. The maximum equilibrium complexation constant has been found in isoamyl alcohol solution of TOMAC as values of 1.580 and 7.257 for K_{E1} and K_{E2} , respectively. The highest synergistic extraction efficiency has been found for the TOMAC + isoamyl alcohol extractant system with a K_D value of 2.674. The isoamyl alcohol data can be used to design a reactive extraction process.

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and Modeling" which is pursued in the Institute of Science of Istanbul University.

ABBREVIATIONS

TOA = Trioctyl amine

H₂A = Dicarboxylic acid

R₃N = TOA

p = Molecule number of acid

K_S = Solvation efficiency

K_D = Distribution coefficient

K_A = Apparent equilibrium constant

K_{E1} = Complexation constant for (1 acid + 1 amine)

K_{E2} = Complexation constant for (2 acids + 1 amine).

T_T = Loading factor

T_S = Stoichiometric loading factor

C_{MA} = Malic acid concentration [mol·L⁻¹]

E = Extraction efficiency

S_r = Modified separation factor

LSER = Linear solvation energy relationship

HBD = Hydrogen-bond donor

HBA = Hydrogen-bond acceptor

s , d , a and b = Regression constants

π^* , δ , α , and β = Solvatochromic parameters

v = a volume fraction of solvent related LSER model

q = Molecule number of amine

rmsd = Root mean square deviations

Subscript

aq = Aqueous phase

org = Organic phase

Superscript

* = Organic phase

- = Organic phase

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