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Extraction Equilibrium of Dicarboxylic Acids with Tertiary Amine in Single and Binary Diluents

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ABSTRACT

The extraction equilibria of aliphatic dicarboxylic acids with solutions of trialkylamine (TAA) in binary diluents were measured and compared. Oxalic, succinic, DL-malic and D-tartaric acids were used. Trialkylamine with C_7–C_9 carbon atom chains was dissolved in 1-octanol, methylisobutyl ketone (MIBK), and chloroform, or in their binary mixtures with *n*-heptane. Physical extraction with pure active diluents also was measured. The contribution of physical extraction was significant only in the case of succinic and oxalic acids and with octanol-1 and MIBK as diluents. In all systems, formation of the (1 : 1) acid : amine complex was found dominant at low aqueous-phase equilibrium acid concentrations. The values of the respective equilibrium constants grew in the same order

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as the first dissociation constants of these acids. In the region of high acid concentrations, overloading of amine was observed, indicating formation of (2 : 1) and (3 : 1) complexes. Here, the extraction grew with increasing lyophilicity of the acids. Various modifications of a mathematical model, incorporating reactions of formation of these complexes and physical extraction, were used for correlating the equilibrium data.

Key Words: Liquid extraction; Equilibrium; Dicarboxylic acid; Tertiary amine; Diluent; Mathematical model.

INTRODUCTION

Extraction of carboxylic and hydroxy-carboxylic acids from aqueous solutions with long-chain trialkylamines (TAA) was proposed as an effective method of their recovery and refining.[1−4] To decrease the viscosity of the organic phase, solutions of amine in organic diluents were used. The high extraction power of amines is due to the formation of various acid : amine complexes in the organic phase. Active diluents (modifiers), e.g., polar species or solvents with proton or electron donating groups, usually promote the acid extraction by stabilizing simple acid : amine complexes. They also prevent the third phase (second organic phase) formation. Inert diluents, such as higher aliphatic hydrocarbons, have no such effect. The use of binary diluents, composed of an active and an inert diluent,[2,5] allows tuning of the system properties. The "diluent swing" technique also was proposed for facilitating the acid re-extraction into water. It consists in reducing the modifier concentration in the binary diluent before the re-extraction step.

Extraction equilibrium of various carboxylic acids with TAA in active and mixed diluents was often investigated. Acetic, lactic, succinic, malonic, maleic, and fumaric acids were extracted with Alamine 336 in nitrobenzene, chloroform, and methyl-isobutyl ketone (MIBK),[6] aconitic, citric, lactic, malic, and oxalic acids with tri-iso-octylamine in chloroform, 1-octanol and in a 1-hexanol/*n*-heptane mixture.[7] In papers[8−10] on extraction of citric acid with TAA and the effect of various diluents, extraction temperature and co-extraction of water on the equilibrium were studied. As diluents *p*-xylene, toluene, benzene, MIBK, methylene chloride, chloroform, 1-octanol, and 1-octanol/*n*-heptane mixtures were used. A mathematical model was developed based on the simultaneous formation of various acid : amine complexes and their aggregates. The model incorporated nonideality of both aqueous and organic phases, and co-extraction of water. Three hydroxy-carboxylic acids, lactic, malic, and citric acids, were extracted with TAA in mixtures of 1-octanol, chloroform, and MIBK with *n*-heptane.[11,12] The temperature of extraction also was varied. The data were correlated by using various modifications of the above mathematical model. Kirsch and Maurer[13] and Kirsch et al.[14] investigated the extraction of oxalic acid with tri-*n*-octylamine in toluene, chloroform, and MIBK. In the mathematical model used for data correlation, formation of (1 : 2), (1 : 1), (2 : 1), and (2 : 2) acid : amine complexes and their hydrates, and partitioning of amine and modifiers, were included. Tomovska et al.[15] studied the extraction of D-tartaric acid with TAA. They used mixtures of 1-octanol, isodecanol, and MIBK as modifiers, and *n*-heptane and kerosene as inert diluents. The data for systems with alcoholic modifiers were successfully correlated with a mathematical model comprising complexes (1 : 2), (1 : 1), and (2 : 1); in the systems with MIBK complexes, (1 : 1), (2 : 1), (3 : 1), or (1 : 1), (1 : 2), (3 : 1) were used for correlation. In the present work, their results for tartaric acid and MIBK are compared with the other systems studied.

In the present study, the extraction equilibria of four dicarboxylic acids, oxalic, succinic, DL-malic, and D-tartaric acids, with solutions of TAA in various diluents, have been studied and mutually compared. These acids are widely applied in food production, textile industry, production of plastics, and other industrial branches, and the development of new methods of their separation and refining is, therefore, of immediate practical interest. Chloroform, 1-octanol, and MIBK, and their mixtures with *n*-heptane, were used as diluents. The molality of amine in the diluent, as well as the fraction of the modifier in it, were varied; the extraction with the modifier without amine also was included.

EXPERIMENTAL

The TAA used was a mixture of aliphatic amines with C_7–C_9 carbon chains (average molecular weight 363.3 g/mol). Before use, it was successively washed with aqueous hydrochloric acid (1 M), sodium hydroxide (3 M), and water. Other chemicals were of chemical purity grade. The dicarboxylic acids used were oxalic, D-tartaric (Lachema Co., Brno, CR), succinic (Fluka, Riedel-de Haen GmbH, Hanover, Germany), and DL-malic (Sigma, Aldrich Co., Prague, CR); the modifiers were chloroform (Lachema Co.), 1-octanol (Sigma), and MIBK (Sigma), the inert diluent was *n*-heptane (Sigma).

The acid content in both coexisting phases was analyzed by potentiometric titration with sodium methanolate solution in a methanol/dimethylformamide mixture. The amine in organic phase was titrated with perchloric acid in anhydrous acetic acid, the water content in organic phase was determined by using the Karl–Fischer method. The acid content in the aqueous phase was expressed in molality related to water, the acid and amine molality in organic phase was related to the diluent. The modifier content in the binary diluent was expressed as mass fraction. The content of coextracted water was used for expressing the molality in organic phase on a water-free basis.

Measurements of extraction equilibrium were performed at 25°C. The initial phases were contacted by shaking for 1 hr in separation funnels submerged in a thermostated bath. The equilibrium isotherms for the systems with succinic and tartaric acids were measured at constant values of the initial amine molality $\overline{m_{\mathrm{e}}^{0}} = 0.3;\ 1.0;\ 2.0\,\mathrm{mol/kg}$ diluent and of the modifier mass fraction $\bar{x} = 0.4;\ 0.7;\ 1$. For oxalic and malic acids, the measurements were done at $\overline{m_{\mathrm{e}}^{0}} = 0.3$ and $\bar{x} = 0.4;\ 0.7;\ 1$.

MATHEMATICAL MODEL

The model use in the present work is a modification of that developed in Ref.[11] and used in various variants later,[12,15] for correlation of data on citric and tartaric acids. In the present variant, the following simplifying assumptions have been made: (i) with respect to the absence of strong electrolytes in the aqueous phase and the relatively low dissociation constants of the acids investigated, the aqueous phase is assumed ideal, and the acid dissociation is not included; (ii) the specific bonding of coextracted water and of the modifier molecules to the acid : amine complexes is neglected and these effects are taken as part of the nonspecific interactions expressed by the activity coefficients of species in organic phase; (iii) the solubility of the organic phase components in water is assumed negligible; and (iv) for oxalic and succinic acids, and octanol and MIBK as modifiers, "physical" extraction with the diluent is taken into account.

Dicarboxylic acids can form simple acid : amine complexes (1 : 2) and (1 : 1), associates of the latter with further acid molecules ($i : 1$), $i > 1$, and higher aggregates ($i : j$), with i and $j > 1$. The general form of the respective stoichiometric equation is

$$i\mathrm{H_2A} + j\overline{\mathrm{R_3N}} = \overline{(\mathrm{R_3N})_j(\mathrm{H_2A})_i} \tag{1}$$

H_2A and R_3N are the acid and amine, respectively; the bar denotes a species in organic phase. The equilibrium constants are

$$\beta_{ij} = \frac{\overline{a_{ij}}}{a_{\mathrm{a}}^{i} \cdot \overline{a_{\mathrm{e}}^{j}}} = \frac{\overline{m_{ij}\gamma_{ij}}}{m_{\mathrm{a}}^{i} \cdot \overline{m_{\mathrm{e}}^{j}\gamma_{\mathrm{e}}^{j}}};\quad \beta'_{ij} = \frac{\overline{m_{ij}}}{m_{\mathrm{a}}^{i} \cdot \overline{m_{\mathrm{e}}^{j}}} = \frac{\beta_{ij}\overline{\gamma_{\mathrm{e}}^{j}}}{\overline{\gamma_{ij}}} \tag{2}$$

Here, a is the activity; m, the molality; γ, the activity coefficient; β, β' are the thermodynamic extraction equilibrium constant and the respective quotient based on the mass action law. The subscripts a, e, ij denote the acid, amine, and the ij-complex. In the present work, formation of higher aggregates is not considered. The ratio of activity coefficients in Eq. (2) represents the non-specific interactions among the species in organic phase. In the model, it is expressed as an empirical function of total acid and amine molalities and the modifier mass fraction in the diluent.

$$\beta'_{ij} = \beta_{ij} \exp(A_{ij}\overline{m_{\mathrm{e}}^{0}} + B_{ij}\bar{x} + C_{ij}\overline{m_{\mathrm{a}}}) \tag{3}$$

where β_{ij}, A_{ij}, B_{ij}, C_{ij} are the model parameters. A similar expression has been adopted for the distribution coefficient in physical extraction of the acid. For a binary diluent, the main effect is assumed to be proportional to the modifier fraction in the diluent.

$$\beta'_{\mathrm{d}} = \frac{\overline{m_{\mathrm{ad}}}}{m_{\mathrm{a}}} = \beta_{\mathrm{d}} \cdot \bar{x} \cdot \exp(A_{\mathrm{d}}\overline{m_{\mathrm{e}}^{0}} + B_{\mathrm{d}}\bar{x} + C_{\mathrm{d}}\overline{m_{\mathrm{a}}}) \tag{4}$$

Here $\overline{m_{\mathrm{ad}}}$ is the molality of physically extracted acid in organic phase; β_{d}, A_{d}, B_{d}, C_{d} are the model parameters. In the present work, model variants comprising formation of three acid : amine complexes, or of two complexes and physical extraction, have been used. The system of model equations also includes the balances of total acid and amine molality in organic phase

$$\overline{m_{\mathrm{a}}} = \beta'_{\mathrm{d}} m_{\mathrm{a}} + \sum_{k=1}^{K} i_k (\beta'_{ij} m_{\mathrm{a}}^{i} \overline{m_{\mathrm{e}}^{j}})_k \tag{5}$$

$$\overline{m_{\mathrm{e}}^{0}} = \overline{m_{\mathrm{e}}} + \sum_{k=1}^{K} j_k (\beta'_{ij} m_{\mathrm{a}}^{i} \overline{m_{\mathrm{e}}^{j}})_k \tag{6}$$

where K is the number of complexes taken into account.

The system of model equations was solved by using a least squares optimization procedure of Marquardt.[16,17] The objective function was a weighted sum of squares of relative deviations of measured and calculated acid molalities in both coexisting phases

$$S = \frac{\sum_{l=1}^{N} W_l [(1 - m_{\mathrm{a(cal)}}/m_{\mathrm{a(exp)}})^2 + (1 - \overline{m_{\mathrm{a(cal)}}}/\overline{m_{\mathrm{a(exp)}}})^2] N}{\sum_{l=1}^{N} W_l} \tag{7}$$

Here N is the number of experiments, and W_l is the statistical weight of the lth experimental point.

RESULTS AND DISCUSSION

Experimental Results

In the first part of the present work, physical extraction of the individual acids with pure modifiers was investigated. The extraction was significant only for succinic and oxalic acids, and for MIBK and octanol as diluents. This behavior is in accord with the increasing hydrophilic character of the examined acids, succinic $<$ oxalic $<$ tartaric $\approx$ malic, as indicated by their solubility in water (Table 1). The physical extraction isotherms of succinic and oxalic acids, and octanol and MIBK as diluents are compared in Fig. 1. In this figure, as well as in all figures that follow, the solid lines represent results calculated with the mathematical model (see the following). As can be seen, the extraction with both diluents is higher for succinic acid in accord with its more lyophilic character. In Fig. 2, physical extraction of succinic acid with pure 1-octanol is compared with the overall extraction at varying content of TAA in organic phase. The contribution of physical extraction is significant mainly at the high aqueous phase acid molality and at the lowest amine content in organic phase.

In Fig. 3(a) and (b), extraction isotherms of oxalic, succinic, malic, and tartaric acids with TAA solutions in 1-octanol and in MIBK are depicted. The data on extraction of oxalic acid with TAA in MIBK are in good agreement with those presented in Ref.[13]; the data on tartaric acid and MIBK were taken over from Ref.[15]. The acid content in organic phase is expressed as the loading of amine, defined as the total number of acid molecules in organic phase per molecule of amine

$$Z = \frac{\overline{m_a}}{\overline{m_e^0}} \tag{8}$$

Table 1. Acidity constants[18] and solubilities in water[19,20] of acids.

Acid	K_{a1} (25°C)	K_{a2} (25°C)	Solubility (g/100 g water)
Succinic	6.92×10^{-5}	2.45×10^{-6}	6.8; 20°C
Oxalic	5.89×10^{-2}	6.46×10^{-5}	10.6; 25°C
D-Tartaric	6.03×10^{-4}	1.51×10^{-5}	139; 20°C
DL-Malic	3.98×10^{-4}	7.76×10^{-6}	144; 26°C

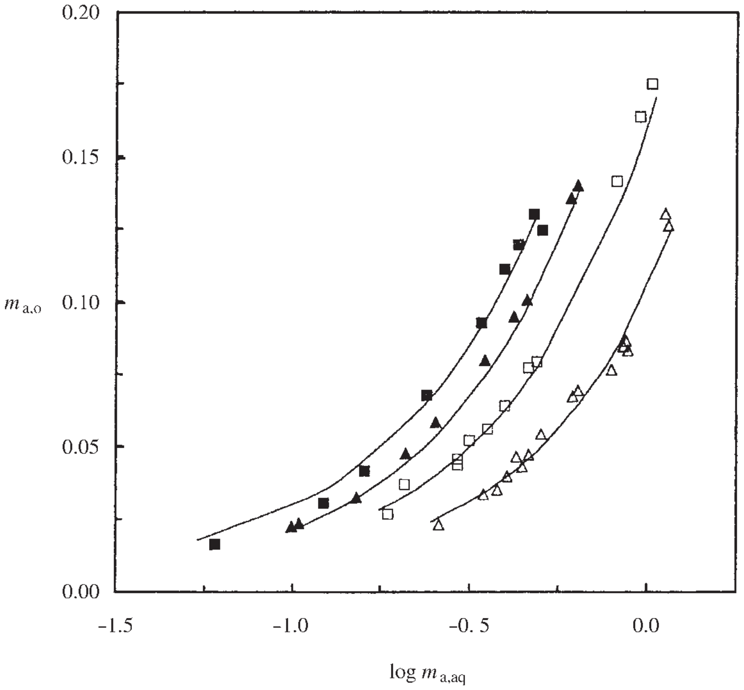

Figure 1. Physical extraction of oxalic (empty points) and succinic (full points) acids. *Key:* Solvent: □—MIBK; Δ—1-octanol.

For oxalic and succinic acids, Z is an apparent value, as it also includes a significant contribution of physical extraction to the overall acid molality in organic phase. The corrected values,

$$Z' = \frac{(\overline{m_a} - \overline{m_{ad}})}{\overline{m_e^0}} \tag{9}$$

calculated by the model are depicted in these and the following figures as dotted lines. In both figures, the order of extraction of individual acids in the low and high ranges of aqueous phase acid concentration are different. Whereas, at low acid concentrations, the loading tends to increase in the order succinic < tartaric < malic < oxalic acid; at high aqueous acid concentrations, it follows the sequence tartaric < malic < oxalic < succinic. The first sequence resembles that of the acid strength; the second sequence approximates the reverse of the acid solubility in water (see Table 1). A plausible explanation of this behavior is that in the low concentration range,

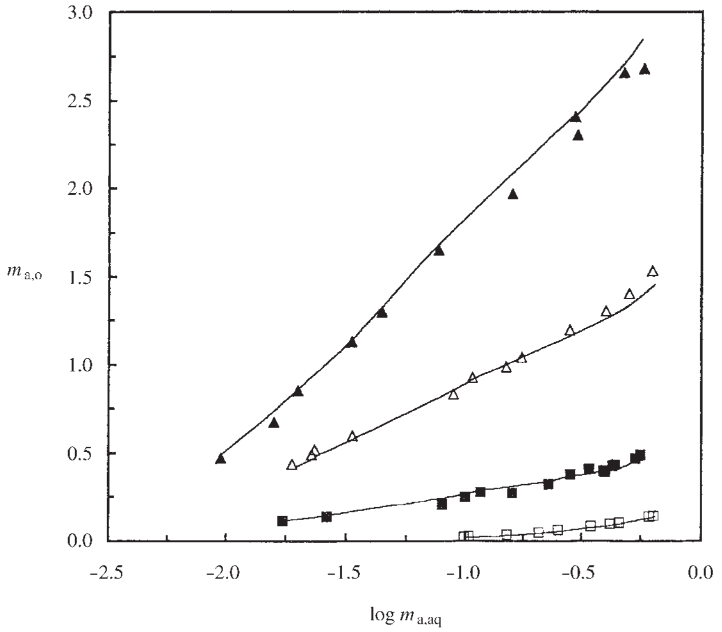

Figure 2. Extraction of succinic acid with solutions of TAA in 1-octanol. *Key:* □—$\overline{m_e^0} = 0\,\text{mol/kg}$; ■—$\overline{m_e^0} = 0.3\,\text{mol/kg}$; Δ—$\overline{m_e^0} = 1.0\,\text{mol/kg}$; ▲—$\overline{m_e^0} = 2.0\,\text{mol/kg}$.

where formation of the (1 : 1) or (1 : 2) complexes by ion pair addition predominates, the increasing acid strength enhances the extraction. In the high concentration range, where (2 : 1) and (3 : 1) complexes form by addition of further acid molecules, the increasing lyophilicity of the acid promotes both the reactive and physical extraction.

Besides this similarity in extractability trends of individual acids in systems with both diluents, Fig. 3(a) and (b) shows also different effects of 1-octanol and MIBK on the extraction of a particular acid. Most striking is the more pronounced tendency of all acids to overloading of amine in the systems with MIBK. Whereas, the alcohol, as proton donor, may compete with free acid in association with the (1 : 1) complex by hydrogen bonding, MIBK, as electron donor, promotes this association. In the case of oxalic acid and MIBK, the region of overloading could not be shown, since at $m_a > 0.18\,\text{mol/kg}$ water formation of the third phase (second organic phase) took place. This difference in amine extraction of carboxylic acids with MIBK and 1-octanol as solvents also was reported in previous works.[6,12]

The effects of different diluents on the extraction of succinic and tartaric acids are compared in Fig. 4(a) and (b). Besides 1-octanol and MIBK,

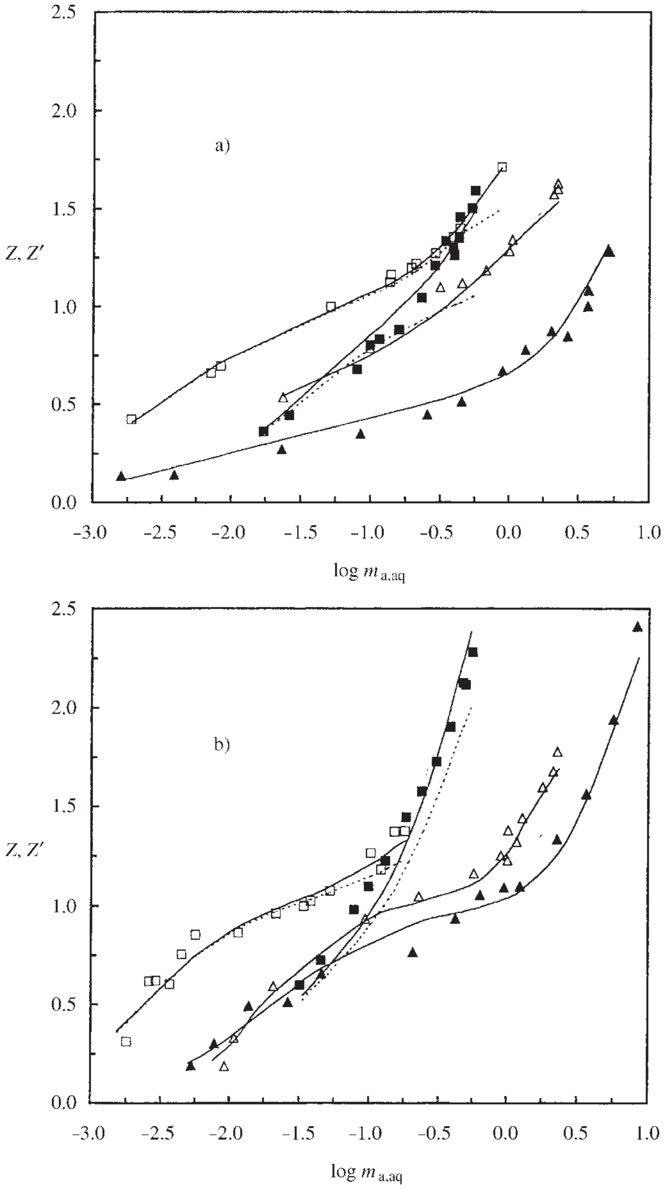

Figure 3. Extraction of oxalic, succinic, malic, and tartaric acids with TAA. Diluent: (a) 1-octanol; (b) MIBK. $\overline{m_e^0} = 0.3\,\text{mol/kg}$; $\bar{x} = 1$. *Key:* Acids: □—oxalic; ■—succinic; △—malic; ▲—tartaric; ....—Z'. *Source:* Data for tartaric acid and MIBK were taken from Tomovska et al.[15]

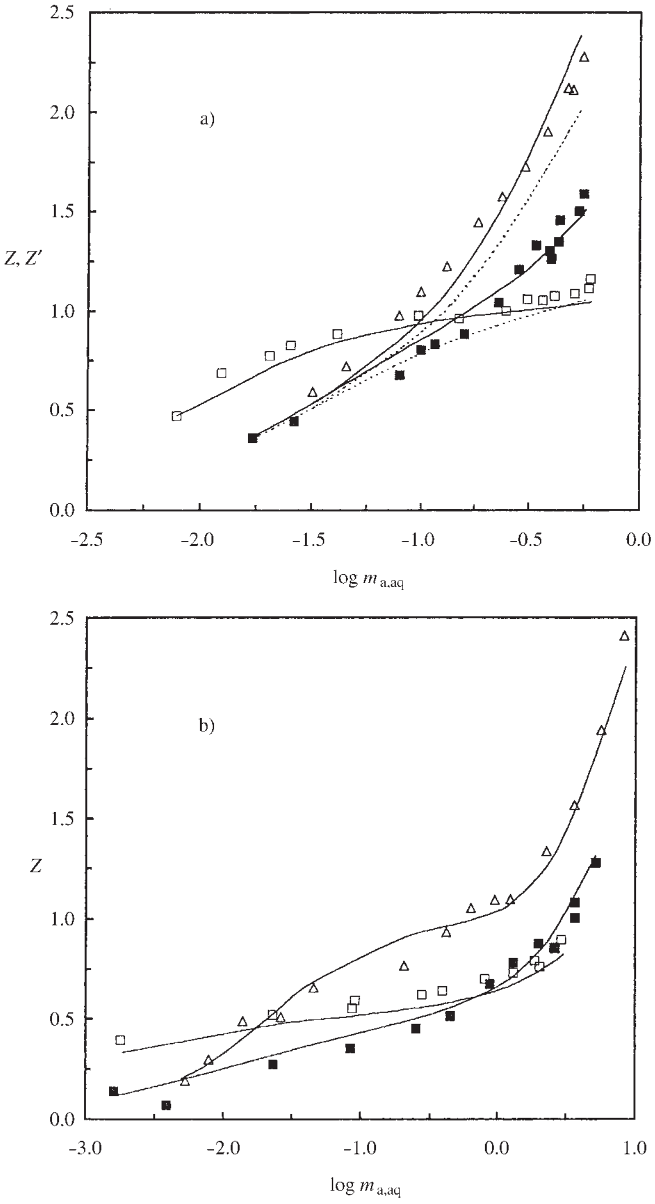

Figure 4. Effect of diluent nature on amine extraction of succinic and tartaric acids: (a) succinic acid; (b) tartaric acid. $\overline{m_e^0} = 0.3\,\text{mol/kg}$; $\bar{x} = 1$. *Key:* Diluent: □—chloroform; ■—1-octanol; △—MIBK; ....—Z'. *Source:* Data for tartaric acid and MIBK were taken from Tomovska et al.[15]

chloroform, another acidic solvent, is included. In the low concentration range, chloroform enhances the acid extraction more than the other two diluents. In the high concentration range, the isotherms in the systems with chloroform show little tendency to overloading, similarly as the corrected isotherms for 1-octanol. Here, the isotherms for MIBK dominate, even when corrected for physical extraction. In the systems with tartaric acid, Fig. 4(b), the most striking difference is that the region of overloading of amine is shifted to almost one order higher aqueous acid concentrations.

Figure 5(a)–(c) shows the effect of the modifier content in the mixed diluent on equilibrium of succinic acid at $\overline{m_e^0} = 0.3\,\mathrm{mol/kg}$ diluent. With all three modifiers, the loading of amine grows strongly with the growing modifier content. In the systems with chloroform [Fig. 5(a)], the isotherms converge to $Z = 1$ at higher acid concentrations and tend to form a plateau. With 1-octanol and MIBK [Fig. 5(b), and (c)], the positive effect of modifier content on the apparent loading persists also at higher acid concentrations, and overloading of amine ($Z > 1$) takes place. In the systems with 1-octanol, it is due mainly to the growing physical extraction; in the systems with MIBK, it also is because of growing formation of $(p:q)$ complexes, with $p > q$.

An important property of the modifier is its ability to prevent formation of the second organic phase at higher acid and amine contents in the organic phase. This process is a result of association of simple acid : amine complexes into higher aggregates and can be prevented by solvation of the complexes with the modifier molecules. With succinic acid and chloroform, third-phase formation was observed at $\overline{m_e^0} = 2.0\,\mathrm{mol/kg}$ diluent, $\bar{x} = 0.4$, and $m_a = 0.14\,\mathrm{mol/kg}$ water. With succinic acid and MIBK it occured at $\overline{m_e^0} = 1.0$ and $2.0\,\mathrm{mol/kg}$ diluent, $\bar{x} = 0.4$ and $m_a = 0.062$ and $0.059\,\mathrm{mol/kg}$ water, respectively. With oxalic acid and MIBK, third phase formed already at $\overline{m_e^0} = 0.3\,\mathrm{mol/kg}$ diluent, with pure modifier ($\bar{x} = 1$), and at $m_a = 0.18\,\mathrm{mol/kg}$ water. In systems with tartaric acid and MIBK,[15] third phase formed at $\bar{x} = 0.4$, $\overline{m_e^0} = 0.3$, 1.0, and $2.0\,\mathrm{mol/kg}$ diluent, and $m_a = 4.8$, 2.4, and $2.0\,\mathrm{mol/kg}$ water, respectively. With 1-octanol as modifier, no third-phase formation was observed with the acids used and in the range of variables examined.

Results of Correlation

The experimental results for the individual systems were correlated by using variants of the above mathematical model. The systems with malic and tartaric acids and with chloroform and 1-octanol were correlated with the variant, including complexes (1 : 1), (2 : 1), and (1 : 2). For oxalic and succinic acids with 1-octanol as diluent, physical extraction was included instead of the (1 : 2) complex formation. In systems with MIBK, where high overloading of

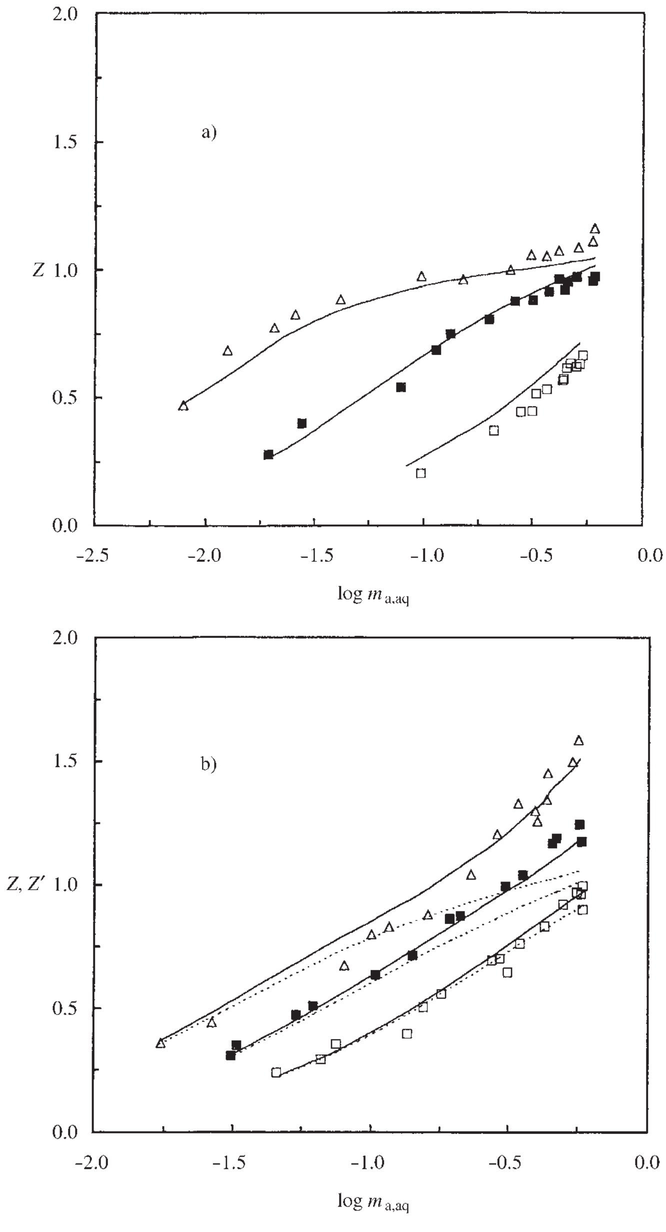

Figure 5. Effect of modifier fraction in binary diluent on extraction of succinic acids with TAA. Modifier: (a) chloroform; (b) 1-octanol; (c) MIBK. $\overline{m_{\mathrm{e}}^{0}} = 0.3\,\mathrm{mol/kg}$; □—$\bar{x} = 0, 4$; ■—$\bar{x} = 0, 7$; △—$\bar{x} = 1$; ....—$Z'$.

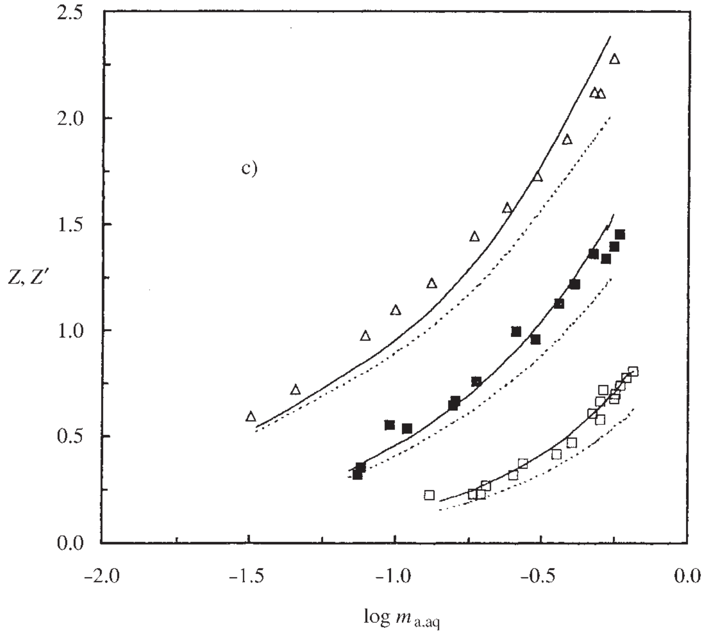

Figure 5. Continued.

amine occurred, models, including formation of the (3 : 1) complex, were used: (1 : 1), (3 : 1), (β_d') for succinic acid; (1 : 1), (2 : 1), (3 : 1) for malic; and tartaric acids. In the case of oxalic acid, where the region of high overloading could not be included because of third-phase formation, the model (1 : 1), (2 : 1), (β_d') was applied. Here ($\beta_d{}'$) means physical extraction.

The optimized parameter values for the systems with chloroform, 1-octanol, and MIBK are shown in Tables 2–4. Here N is the number of experimental points; n, the number of model parameters ($n = 12$); s_r, the standard relative deviation of the particular data set.

$$s_r = \sqrt{\frac{1}{N-n} \cdot \sum_{l=1}^{N} \left[\left(1 - \frac{m_{a(cal)}}{m_{a(exp)}}\right)^2 + \left(1 - \frac{\bar{m}_{a(cal)}}{m_{a(exp)}}\right)^2 \right]_l} \tag{10}$$

The values of the standard relative deviation show a good fit of experimental and calculated data and confirm that the applied models can satisfactorily correlate the data of a number of different acid : amine extraction systems in a large range of concentrations. In general, the parameter values must be considered as mutually dependent and, therefore, are not suited for detailed

Table 2. Parameter values for systems with $CHCl_3/n$-heptane mixtures as diluents.

$(i:j)$	β	A	B	C
Succinic acid ($N = 110$; $s_r = 6.98 \times 10^{-2}$)				
$(1:1)$	2.813×10^{-1}	-8.832×10^{-1}	6.125×10^{0}	1.046×10^{0}
$(2:1)$	1.132×10^{-1}	1.582×10^{0}	4.439×10^{0}	-3.197×10^{-1}
$(1:2)$	2.782×10^{0}	-1.125×10^{0}	2.244×10^{0}	-1.337×10^{-2}
Malic acid ($N = 30$; $s_r = 3.42 \times 10^{-2}$)				
$(1:1)$	1.426×10^{0}	-3.850×10^{0}	6.129×10^{0}	-1.100×10^{0}
$(2:1)$	1.244×10^{-1}	2.275×10^{-1}	3.974×10^{-1}	-4.445×10^{-1}
$(1:2)$	3.303×10^{0}	-3.421×10^{1}	3.458×10^{-1}	-4.967×10^{0}
Tartaric acid ($N = 108$; $s_r = 6.45 \times 10^{-2}$)				
$(1:1)$	7.215×10^{-1}	1.066×10^{0}	2.827×10^{0}	-6.018×10^{-2}
$(2:1)$	6.348×10^{-3}	5.205×10^{-1}	5.503×10^{0}	7.881×10^{-1}
$(1:2)$	1.775×10^{0}	-3.797×10^{0}	8.683×10^{0}	4.109×10^{0}

Table 3. Parameter values for systems with 1-octanol/n-heptane mixtures as diluents.

$(i:j)$	β	A	B	C
Oxalic acid ($N = 32$; $s_r = 2.74 \times 10^{-2}$)				
$(1:1)$	3.479×10^{2}	1.056×10^{0}	1.230×10^{-2}	-2.418×10^{0}
$(2:1)$	7.568×10^{0}	2.229×10^{-1}	3.452×10^{0}	-1.999×10^{-1}
(β_d')	6.829×10^{-2}	-4.757×10^{0}	2.913×10^{-1}	1.251×10^{0}
Succinic acid ($N = 134$; $s_r = 4.52 \times 10^{-2}$)				
$(1:1)$	1.978×10^{0}	-3.492×10^{-2}	2.777×10^{0}	1.643×10^{-1}
$(2:1)$	4.732×10^{-1}	8.370×10^{-1}	2.437×10^{0}	5.466×10^{-2}
(β_d')	2.906×10^{-2}	9.012×10^{-2}	1.956×10^{0}	2.997×10^{-1}
Malic acid ($N = 93$; $s_r = 3.94 \times 10^{-2}$)				
$(1:1)$	2.821×10^{0}	1.480×10^{-1}	2.976×10^{0}	-1.815×10^{-1}
$(2:1)$	6.813×10^{-2}	1.027×10^{0}	6.234×10^{0}	-9.708×10^{-1}
$(1:2)$	1.692×10^{0}	-2.423×10^{0}	6.470×10^{0}	1.767×10^{0}
Tartaric acid ($N = 112$; $s_r = 5.70 \times 10^{-2}$)				
$(1:1)$	2.497×10^{0}	2.646×10^{-1}	3.345×10^{-1}	2.375×10^{-1}
$(2:1)$	2.261×10^{-1}	-2.869×10^{0}	9.146×10^{-1}	2.445×10^{0}
$(1:2)$	1.613×10^{2}	1.514×10^{0}	5.968×10^{-1}	-5.425×10^{0}

Table 4. Parameter values for systems with MIBK/*n*-heptane mixtures as diluents.

$(i:j)$	β	A	B	C
Oxalic acid ($N = 34$; $s_r = 5.32 \times 10^{-2}$)				
(1 : 1)	3.688×10^{2}	-1.497×10^{0}	2.131×10^{-1}	2.236×10^{0}
(2 : 1)	1.260×10^{-1}	5.515×10^{-2}	9.193×10^{0}	7.900×10^{-3}
(β_d')	1.510×10^{-1}	-6.464×10^{-3}	-2.810×10^{-3}	3.854×10^{-1}
Succinic acid ($N = 93$; $s_r = 5.84 \times 10^{-2}$)				
(1 : 1)	1.735×10^{-1}	-4.213×10^{-1}	5.134×10^{0}	1.238×10^{0}
(3 : 1)	2.722×10^{-3}	1.421×10^{0}	1.098×10^{1}	-3.425×10^{-2}
(β_d')	3.066×10^{-1}	-8.254×10^{-1}	-3.578×10^{-1}	4.539×10^{-1}
Malic acid ($N = 35$; $s_r = 5.73 \times 10^{-2}$)				
(1 : 1)	4.404×10^{-1}	-8.506×10^{-2}	4.088×10^{0}	5.339×10^{0}
(2 : 1)	1.153×10^{0}	-2.215×10^{-2}	5.929×10^{0}	-3.291×10^{1}
(3 : 1)	5.764×10^{-3}	-9.316×10^{-3}	8.204×10^{0}	1.431×10^{0}
Tartaric acid ($N = 95$; $s_r = 6.17 \times 10^{-2}$)				
(1 : 1)	6.168×10^{-1}	7.177×10^{-1}	4.234×10^{0}	-5.388×10^{-1}
(2 : 1)	1.732×10^{-1}	1.411×10^{-1}	1.004×10^{-2}	3.221×10^{-1}
(3 : 1)	1.021×10^{-4}	1.961×10^{0}	9.238×10^{0}	$-1{,}115 \times 10^{0}$

Note: Data for tartaric acid and MIBK were taken over from Tomovska et al.[15]

analysis. Nevertheless, one can see that β_{11}, the values of equilibrium constants of the most important complex (1 : 1), follow the same sequence as the first dissociation constants of the investigated acids. The values of the parameters B_{ij} expressing the effect of diluent are positive for all acids, diluents, and acid : amine complexes.

In all figures, the lines were calculated by using these model variants and the sets of optimum parameter values obtained by correlation. In Fig. 6, the model (1 : 1), (3 : 1), (β_d') was used for simulation of the course of contributions of individual complexes and physical extraction to the overall loading of amine in the system succinic acid–MIBK. It demonstrates the gradual transition between the complexes involved with increasing aqueous phase acid molality. The contribution of physical extraction to overall loading simulated by the respective model variants was depicted in Figs. 3–5 as dotted lines.

CONCLUSIONS

Extraction equilibrium of oxalic, succinic, malic, and tartaric acids with TAA dissolved in chloroform, 1-octanol, MIBK, and in their mixtures

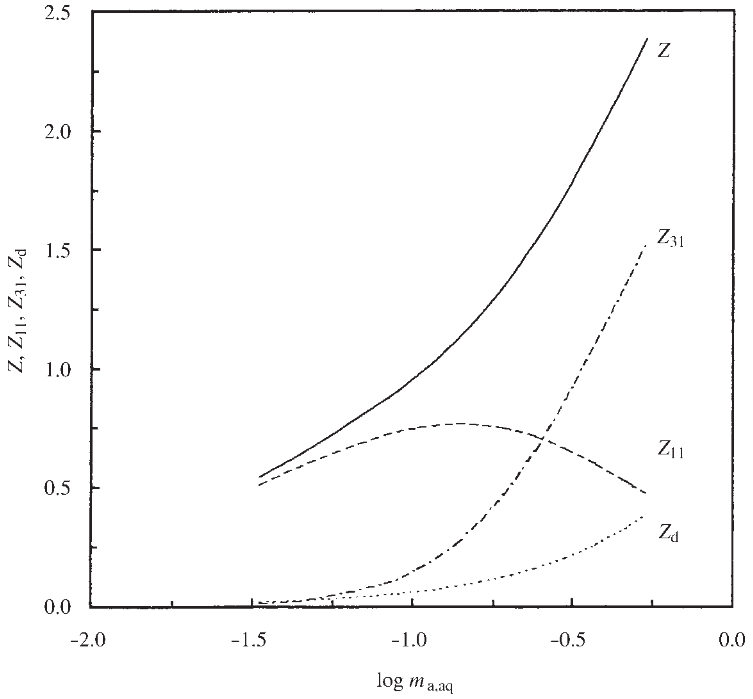

Figure 6. Extraction of succinic acid with TAA in MIBK. Contribution of individual acid : amine complexes and physical extraction with diluent to overall loading of amine. $\overline{m_e^0} = 0.3\,\mathrm{mol/kg}$; $\bar{x} = 1$.

with *n*-heptane, was measured at 25°C. At low aqueous phase acid concentrations, the extraction grew with increasing first dissociation constants of the acids; at high acid concentrations, it increased inversely to the acids' solubility in water. At low aqueous phase acid concentrations, formation of the acid : amine complex (1 : 1) predominated in the organic phase; at high concentrations, overloading of amine took place, indicating formation of (2 : 1) and (3 : 1) complexes. This process was mostly enhanced by MIBK as a modifier. The solvents 1-octanol and chloroform were more effective than MIBK in preventing the third-phase formation. In systems with 1-octanol, no third-phase formation occurred. In the systems with succinic and oxalic acids and with MIBK and 1-octanol, significant physical extraction with the diluent was observed. With malic and tartaric acids, and with all acids and chloroform, this effect was negligible. When mixtures of chloroform, 1-octanol, or MIBK with *n*-heptane were used as diluents, the loading of amine was strongly enhanced with increasing modifier content in the diluent.

The experimental data were correlated with a good fit with mathematical models, including formation of (1 : 1), (1 : 2), (2 : 1), and (3 : 1) acid : amine complexes and physical extraction. With the model, contributions of individual complexes and physical extraction to the overall loading of amine were calculated.

NOTATION

A_d, B_d, C_d	constants in Eq. (4)
A_{ij}, B_{ij}, C_{ij}	constants in Eq. (3)
K	number of acid : amine complexes in the model
K_{a1}, K_{a2}	first and second dissociation constants of dicarboxylic acid
m_a	molality of acid in aqueous phase (mol/kg water)
$\overline{m_a}$	total molality of acid in organic phase (mol/kg diluent)
$\overline{m_{ad}}$	molality of physically extracted acid in organic phase (mol/kg diluent)
$\overline{m_e}$	molality of free TAA in organic phase (mol/kg diluent)
$\overline{m_e^0}$	molality of total TAA in organic phase (mol/kg diluent)
$\overline{m_{ij}}$	molality of complex $(i:j)$ in organic phase (mol/kg diluent)
MIBK	methyl-isobutyl ketone
n	number of model parameters
N	number of experimental points
s_r	relative standard quadratic deviation
S	objective function of optimization algorithm, Eq. (7)
TAA	trialkylamine
W_l	statistical weight of lth experimental point
$\bar{x}$	mass fraction of modifier in diluent
Z	loading of amine
Z'	loading of amine corrected for physical extraction
Z_{ij}, Z_d	contribution of complex $(i:j)$ and physical extraction to overall loading of amine

Greek Letters

β_d, β'_d	distribution coefficient in physical extraction
β_{ij}	thermodynamic extraction equilibrium constant of complex $(i:j)$

β'_{ij}	extraction quotient based on mass action law of complex $(i:j)$
$\overline{\gamma_{\mathrm{e}}}$	activity coefficient of amine in organic phase
$\overline{\gamma_{ij}}$	activity coefficient of complex $(i:j)$ in organic phase

Subscripts

aq	aqueous phase
cal	calculated values
exp	experimental values
l	lth experimental point
o	organic phase

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