EQUILIBRIA AND MATHEMATICAL MODELS OF EXTRACTION OF CITRIC ACID WITH ISODECANOL/*n*-PARAFFINS SOLUTIONS OF TRIOCTYLAMINE

FILIMENA A. POPOSKA, KOSTADIN NIKOLOVSKI and
RADMILA TOMOVSKA

*Faculty of Technology and Metallurgy, The "Sv. Kiril i Metodij"
University, P.O. box 580, 91001 Skopje, Republic of Macedonia*

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Extraction equilibria of citric acid from aqueous solutions with trioctylamine in isodecanol/*n*-paraffins mixtures, were studied as a function of acid, amine and isodecanol concentrations at 25°C. The equilibrium data were interpreted by "chemical modeling" approach in which existence of (1,1) and (1,2) acid-amine complexes in the organic phase, were assumed. The corresponding equilibrium constants, which represent the experimental results the best, were determined.

Simpler mathematical model which refer to modified Langmuir isotherm, was also used for interpretation of the equilibrium data. Extraction constants and overall acid stoichiometric coefficient, which represent the experimental results the best, were determined. This mathematical form could be suitable in the analysis and design of the process in dynamic conditions.

Introduction

When aerobic fermentation processes are used for production of organic acids, they are the most interesting products which can be made from biomass. With the well known tricarboxylic acid cycle, stemming from glucose by way of pyruvic acid, a number of di- and tricarboxylic aliphatic acids of four to six carbon atoms can be produced. Citric acid is manufactured on a large scale by fermentation.

The classical method for recovering non-volatile hydroxycarboxylic acids, as citric acid is, from fermentation solutions (aqueous solutions in general), is common precipitation process. This method of recovery is costly and unfriendly to the environment.

Because of their hydrophilic nature, hydroxycarboxylic acids are poorly extractable by common organic solvents; so, for their recovering from aqueous solutions reactive liquid-liquid extraction has been considered. Aliphatic tertiary amines, with C₇-C₁₀/C₁₂ alkyl groups (TAA), have been proposed as suitable extractants for carboxylic and hydroxycarboxylic acids (Vanura and Kuca, 1976; Wennersten, 1983; Kertes and King, 1986). The amine extractants are dissolved in a diluent that dilutes the extractant to the desired concentration and controls the viscosity and density of the solvent phase. It has been found that, in the systems with the same acid and the same amine, the type of diluent and the composition of extraction mixture influence the extraction equilibrium.

Polar diluents have been shown to be more convenient diluents than inert ones (nonpolar), due to

the higher distributions. (Tamada *et al.*, 1990; Bizek *et al.*, 1993). However, active polar and proton-donating diluents as halogenated hydrocarbons (dichloromethane, chloroform) and alcohols (octanol, decanol) have been shown to be the most suitable diluents for trioctylamine (TAA in general), because they give the highest distributions resulting from the formation of solvates through specific hydrogen bonding between the proton of the diluent and the acid-amine complex (Bizek *et al.*, 1992; Bizek *et al.*, 1993; Tamada and King, 1990). Mixed diluents (binary) composed of an inert diluent and an active "modifier" have been proposed by many researchers (Bauer *et al.*, 1989; Bizek *et al.*, 1992; Prochazka *et al.*, 1994).

Some authors suggest the formation of acid-amine complexes of only one type, (1,1) or (1,2), depending on the diluent (Pyatnitskii *et al.*, 1973; Bolshova *et al.*, 1988), while the others suggest the formation of at least two (Vanura and Kuca, 1976; Bizek *et al.*, 1992; Bizek *et al.*, 1993; Poposka and Nikolovski, 1993; Hauer and Marr, 1993; Prochazka *et al.*, 1994). Some authors pay attention to the mathematical modeling of the amine extraction of citric acid (Bauer *et al.*, 1989; Bizek *et al.*, 1992; Bizek *et al.*, 1993; Poposka and Nikolovski, 1993; Hauer and Marr, 1993; Prochazka *et al.*, 1994).

In this work, equilibrium of the extraction of citric acid from aqueous solutions with isodecanol/*n*-paraffins solutions of trioctylamine was investigated and mathematically formulated. The aim of this work is to evaluate appropriate mathematical model suitable for describing the kinetics and interfacial conditions in dynamic systems.

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1. Mathematical Modeling

All evaluated models up to now, start from the mechanism of extraction which imply parallel or parallel-consecutive reactions of acid-base type, when acid-amine complexes of different stoichiometry are formed.

If "chemical" interactions between the components of the complex (acid and amine) are much stronger compared to the "physical" interactions in the system, the equilibrium can be described by mass action law. This approach is known as "chemical modeling" by means of which, the number, the type and the proportion of possible acid-amine complexes, can be described. This approach has some limitations because of nonidealities of the organic and aqueous phase, however, it is a useful tool for describing data quantitatively, and for deeper understanding of the mechanism of extraction.

The extraction equilibrium of the system can be described by the set of reactions of p acid (citric acid, H_3A) molecules and q amine (TAA, R_3N) molecules to form various (p,q) complexes, with corresponding true equilibrium constants β_{pq} :

$$\beta_{pq} = \frac{\{(H_3A)_p(R_3N)_q\}}{\{H_3A\}^p \cdot \{R_3N\}^q} \quad (2)$$

The chemical modeling approach for extraction equilibrium description, was used, for the first time, by Vanura and Kuca (1976). Interpreting their data on citric acid extraction with toluene solution of triaurylamine, they suggested interaction between nondissociated aqueous acid with amine which results in formation of complexes of a general formula $(acid)_p(amine)_{p+1}(H_2O)_h$, where p was 1,2 or 5 and h was 1,2 or 4. They found the simultaneous formation of at least two acid-amine complexes. Tamada *et al.*, (1990) have performed a systematic study on the influence of diluents on amine extraction of carboxylic acids (acetic acid, lactic acid, succinic acid). Interpreting their data by chemical modeling, they found that the stoichiometry of acid-amine complexes is diluent dependent. These findings were supported by spectroscopic evidence (Tamada and King, 1990).

Bizek *et al.*, (1992) and Bizek *et al.*, (1993) studied the extraction of citric acid with TAA in various diluents. They adopted the chemical modeling to develop the respective mathematical models that include, simultaneously, other effects, *i.e.* the dissociation in the aqueous phase, its nonideality, and the specific and nonspecific interactions in the organic phase. The extraction of citric acid (H_3A) with the amine (R_3N) is described by the set of reactions of formation of the (p,q) complexes. Modeling was made on the assumption of simultaneous formation of at least

two acid-amine complexes, depending on the type of the diluent. In the case of 1-octanol as an active proton-donating diluent, alone or in the mixture with n -heptane, they found existence of (1,1) and (1,2) acid-amine complexes. A mathematical model, with overall numbers of parameters 14, comprising the nonidealities of the aqueous and organic phases and the assumption of three complexes existence, was derived by Prochazka *et al.*, (1994). The investigated systems were aqueous solutions of malic, lactic and citric acid and extraction mixture with TAA and binary diluent composed of an active modifier (1-octanol) and an inert diluent (n -heptane). In the case of citric acid it is confirmed that the existence of (1,1) and (1,2) complexes is essential, but the existence of the (2,3) complex at the low temperatures is significant in the cases with high amine concentration, as well as at the low 1-octanol concentration.

The simpler, but from the practical point of view useful interpretation of the experimental data was evaluated by Bauer *et al.*, (1989). The extraction equilibrium in the systems: aqueous solutions of citric acid and extraction mixture (Hostarex A 324 as a reactive component, isodecanol as a modifier and ShellSolT as a diluent), was investigated. For equilibrium curves estimations, the following model was derived:

$$C_{org} = \frac{D \cdot n \cdot C_{R_3N,org} \cdot C_{aqu}^n}{1 + D \cdot C_{aqu}^n} \quad (3)$$

based on overall reaction according to the stoichiometric equation:

with the equilibrium constant K_c :

$$K_c = \frac{(R_3N(HA)_n)_{org}}{(H^+)_{aqu}^n \cdot (A^-)_{aqu}^n \cdot (R_3N)_{org}} \quad (5)$$

They found that the association number n , which has a meaning of an overall stoichiometric acid coefficient, is mainly independent on the composition of the extraction mixture ($n=0.64-0.72$), and that for one citric acid molecule two amine molecules are required !. On the basis of the equilibrium data, they found that the composition of 30vol% amine, 30vol% isodecanol and 40vol% ShellSol T, was an optimum.

In this work equilibrium data will be interpreted with chemical modeling and with the approach of the overall reaction of acid-base type.

2. Experimental

Aqueous solutions of citric acid: all solutions were prepared by diluting the citric acid monohydrate of

analytical purity, (Merck) into distilled water. The initial concentration of the acid, c_{AA}^0 , was varied from 0.15 to 0.79 mol/l.

Extraction mixture: The reactive component was a trioctylamine (TOA) ($M=353.7$, $d=812 \text{ kg/m}^3$) (Merck), and the diluent was a mixture of an active and an inert component, *e.g.* isodecanol as a modifier ($M=158.29$, $d=840 \text{ kg/m}^3$), (Riedel-DE-Haen), and C_{10} – C_{12} *n*-paraffins as a diluent ($M_{\text{average}}=150$, $d_{\text{average}}=745 \text{ kg/m}^3$), (Riedel-De-Haen). The concentration of the components of extraction mixture were ranged as follows: initial concentration of the amine, c_B^0 , (0.1–0.7 mol/l) or (0.153–0.120 mol/kg¹), and mass fraction of isodecanol in the mixed diluent, x_M , (0.08–0.6 kg/kg¹).

Procedure: The same volumes of aqueous and organic phases of known concentrations were equilibrated in a temperature-controlled shaker bath at 25°C for 1h, for which preliminary tests showed that it was a sufficient time for equilibration. Citric acid concentrations in aqueous phase were determined by potentiometric titration with aqueous NaOH solutions using phenolphthalein as an indicator. The concentrations of citric acid in the organic phase were calculated by mass balances.

3. Results and Discussion

Some experimental equilibrium data are presented in the **Figs. 1 and 2**, as extraction isotherms. In **Fig. 1** the effect of the concentration of the amine is evident: the amount of extracted acid from aqueous solutions of any initial concentration, increases with increasing the amine concentration; the obvious plateaus of the curves ($c_{AA} \rightarrow \infty$), for all initial concentrations of the amine, show a maximum loading, Z_{max} :

$$Z_{\text{max}} = \frac{c_{AO, \text{max}}}{c_B^0} \quad (6)$$

where $c_{AO, \text{max}}$ is the concentration of the acid in the organic phase corresponding to the plateau of the curves.

In **Fig. 2** the effect of the modifier concentration, isodecanol, is demonstrated: the increase of isodecanol content in the extraction mixture promote the extraction in the area of lower acid concentrations in the aqueous phase; the convergence of the curves as the loading approaches maximum value, shows that the dependence of the maximum loading on modifier content is no discernible throughout the entire investigated modifier concentration range.

The evaluated values of the ratio Z_{max} , corresponding to the plateau of the extraction isotherms,

¹denoto kg mixed diluent (isodecanol + *n*-paraffins)

Fig 1 Extraction of citric acid by trioctylamine in isodecanol/*n*-paraffins mixtures. Equilibrium isotherms. Dependence on amine concentration

Fig 2 Extraction of citric acid by trioctylamine in isodecanol/*n*-paraffins mixtures. Equilibrium isotherms. Dependence on modifier content

as a function of amine concentration, c_B^0 are presented in **Table 1** and **Fig. 3**. All the obtained values lie between 0.67–0.74, *e.g.* they are smaller than one. Increasing the amine concentration has little effect upon maximum loading.

According to the Z_{max} values and dependence of Z_{max} on amine concentration a suggestion can be made that complexes with more than one molecule of the amine are present. So, the overall stoichiometry of the

Table 1 Extraction of citric acid by trioctylamine in isodecanol/*n* – paraffins mixtures. Values of the model parameters from Eq. (8)

c_{AA}^o (mol/l)	c_B^o (mol/l) (mol/kg)	χ_M (kg/kg)	$c_{AO,max}$ (mol/l)	Z_{max}	a	K
0.12-0.58	0.110 (0.155)	0.06 0.231 0.41 0.452	0.076	0.680	0.678	1.86 6.45 9.98 10.22
0.12-0.65	0.213 (0.312)	0.06 0.243 0.41 0.476	0.158	0.710	0.700	2.85 10.23 13.68 14.37
0.15-0.71	0.456 (0.728)	0.07 0.273 0.41 0.533	0.325	0.730	0.730	4.37 11.18 15.07 16.83
0.15-0.79	0.670 (1.210)	0.08 0.162 0.313 0.410 0.460 0.603	0.491	0.735	0.738	5.52 12.84 14.05 16.82 17.26 20.21
Bizek <i>et al.</i> , (1992)						
0.06-0.68	0.465 (0.807)	0.217	0.352	0.756	0.750	10.28
0.13-0.63	0.459 (0.772)	0.354	0.352	0.756	0.729	18.01
Wennersten (1983)						
0.20-0.90	0.688	Shellsol A alone	0.497	0.726	0.805	11.28

Fig 3 Extraction of citric acid by trioctylamine in isodecanol/*n*-paraffins mixtures. Maximum loading of the extractant, Z_{max}

reaction of complexes formation can be established in the form:

or

Since the values of Z_{max} are neither 1.0 (which is expected value for existence of (1,1) complex only) nor 0.5 (which is expected value for existence of (1,2) complex only), it means that the complexes of various stoichiometry are formed. They can be of the type (1,1), (1,2) or aggregates of the type (2,3). In this work, in the case of maximum amine concentration (0.67 mol/l) and minimum modifier content (0.08 kg/kg), the third phase formation was observed, but the effect was not particularly significant. This phenomenon is

characteristic for the systems showing aggregation which is significant in extraction mixtures with high amine concentration, and in the case of inert diluent (Tamada *et al.*, 1990; Tamada and King, 1990; Bizek *et al.*, 1992; Bizek *et al.*, 1993). Isodecanol is an active diluent (proton donating one) which has ability to solvate the complex by the formation of complex-modifier hydrogen bond; by this way the modifier prevents complexes from interacting strongly with one another.

According to the facts that: isodecanol is strong solvating diluent; that the entire investigated amine molality range is below 1.2 mol/kg; that maximum loading has the values higher than 0.5 but smaller than one; that from the literature data (Bizek *et al.*, 1992; Bizek *et al.*, 1993), assumption of (1,1) and (1,2) complexes formation is good approximation in the systems with TAA (0.157–1.324 mol/kg) and 1-octanol (0.144–1.0 kg/kg), it seems that, for the purposes of mathematical modeling of the equilibrium on the basis of experimental data, in this work, the assumption that only these two complexes exist could be acceptable.

4. Mathematical Modeling of the Equilibria

4.1. Langmuir type of the extraction isotherm

The shape of the extraction isotherms, $c_{AO} = f(c_{AA})$, demonstrated at the Figs. 1 and 2, suggest mathematical description of the curves by modified Langmuir isotherm in the following form:

$$\frac{c_{AO}}{c_{AO,max}} = \frac{K \cdot c_{AA}^a}{(1 + K \cdot c_{AA}^a)} \quad (8)$$

By this expression, the distribution of the undissociated² acid between aqueous and organic phase, where the acid is bond to the amine molecule/molecules, is equivalent to the adsorption of the species H_3A like “adsorbat” from the aqueous phase on the “active sites”, amine molecules on the interface, according to the stoichiometric equation:

In the last two Eqs. (8) and (9), the notation is as follows:

— c_{AO} is the equilibrium concentration of the distributed acid in the organic phase where it exist as a complexes with amine molecules,

— c_{AA} is the equilibrium concentration of the acid in the aqueous phase,

— a is the power of c_{AA} or overall acid/amine stoichiometric ratio,

— K is the equilibrium constant for the overall reaction according to the Eq. (9), which have a meaning of an apparent extraction equilibrium constant based on the molarity scale:

$$K = \frac{c_{complex}}{c_{AA}^a \cdot c_B} \quad (10)$$

The values of the model parameters, K and a , are presented in Table 1.

The obtained values for a confirm: the assumption that they are equivalent to the maximum loading, $a = Z_{max}$; the fact that amine concentration has a little effect on the maximum loading; and that their dependence on the concentration of isodecanol in the extraction mixture is negligible.

The apparent equilibrium extraction constant, K , as it is expected, depends on the concentration of both amine and modifier. The changes of K with amine concentration can be explained by both the “apparent” character of this constant (*i.e.*, the incorporation of the ratio of activity coefficient) and the stoichiometry of complex formation. The influence of the concentration of isodecanol on K can be explained by its solvating ability (“physical” interrelations among the individual complexes and modifier, Prochazka *et al.*, 1994).

The values of the model parameters, a and K from Eq. (8), are also evaluated from the data regarding citric acid extraction by amines obtained by Bizek *et al.*, (1992) and Wennersten (1983). These results are presented in Table 1, too.

The results of fitting with the Langmuir modified model are presented in Fig. 4. It is evident that a very good fit has obtained.

From the obtained values of the model parameters, for all mathematically treated systems with this model, it results the suitability of the modified Langmuir for describing the equilibrium of the citric acid extraction with tertiary amines. On the other hand, this simple model does not starts with a proposed mechanism for formation of acid-amine complexes and neglects nonidealities of both phases, because of that it may has a practical meaning - it is a suitable mathematical form for description of the kinetics and interfacial conditions in dynamic systems.

4.2. Mathematical model with (1,1) and (1,2) acid-amine complexes

In the case of proton-donating diluents, such as isodecanol, when the concentrations of the amine in the extraction mixture are not so high to promote aggregation, the extraction process can be assumed by the reactions:

²It has been shown that the process can be described as a distribution of non-dissociated portion of the acid as well as a distribution of its dissociated portion, *i.e.* both concepts are equivalent. The only difference is in the values of the equilibrium constants (Bizek *et al.*, 1992).

Fig 4 Extraction of citric acid by trioctylamine in isodecanol/*n*-paraffins mixtures. Correlation of the experimental equilibrium data and calculated results by modified Langmuir isotherm-Eq. (8)

where H_3A represents the undissociated part of the acid, which is present in the aqueous phase (it is assumed that only undissociated acid molecules take part in the reactions), and the overbars denote species in the organic phase.

The reactions between amine and acid molecules take place at/near the interface, on the organic phase side. As a result highly polar acid-amine complexes, (1,1) and (1,2), are formed, and afterwards stabilized due to the hydrogen bonding with the isodecanol molecules. In this way, the complex-diluent solvates can be transported into the bulk organic phase.

Corresponding thermodynamic extraction constants of the reactions (11a) and (11b) are:

$$\overline{K}_{11} = \frac{\{(H_3A)(R_3N)\}}{\{H_3A\} \cdot \{R_3N\}} \quad (12a)$$

$$\overline{K}_{12} = \frac{\{(H_3A)(R_3N)_2\}}{\{H_3A\} \cdot \{R_3N\}^2} \quad (12b)$$

where the species activities are denoted by braces.

For practical application, the activities of the organic phase species are assumed to be proportional to the concentration of the species with the constants of proportionality (the nonidealities) taken up in the equilibrium constant. The activity of the acid is

assumed to be proportional to the concentration of undissociated acid in the equilibrium aqueous phase. However, when the molality of citric acid in the aqueous phase is lower than 0.4 mol/kg, the activity coefficients of undissociated acid are close to unity (Bizek *et al.*, 1992), as it is the case in the present work.

The apparent equilibrium constants, based on a molarity scale, can be given by these equations:

$$K_{11} = \frac{c_{\text{complex}(1,1)}}{c_{AA} \cdot c_B} = \frac{c_{11}}{c_{AA} \cdot c_B} \quad [1/\text{mol}] \quad (13a)$$

$$K_{12} = \frac{c_{\text{complex}(1,2)}}{c_{AA} \cdot c_B^2} = \frac{c_{12}}{c_{AA} \cdot c_B^2} \quad [1/\text{mol}]^2 \quad (13b)$$

where species concentrations are expressed in molar units.

Combining Eqs. (13a) and (13b) with the balance equations of the acid and amine in the organic phase, the mathematical model of equilibrium for (1,1) and (1,2) stoichiometry is obtained in the form:

$$\begin{aligned} c_{AO} &= \sum_i c_{ij} = c_{11} + c_{12} = \sum_j K_{1j} \cdot c_{AA} \cdot c_B^j \\ &= K_{11} \cdot c_{AA} \cdot c_B + K_{12} \cdot c_{AA} \cdot c_B^2 \end{aligned} \quad (14)$$

$$\begin{aligned} c_B &= c_B^o - \sum_j c_{ij} = c_B^o - (c_{11} + 2c_{12}) \\ &= c_B^o - \sum_j K_{1j} \cdot c_{AA} \cdot c_B^j \\ &= c_B^o - (K_{11} \cdot c_{AA} \cdot c_B + 2K_{12} \cdot c_{AA} \cdot c_B^2) \end{aligned} \quad (15)$$

where: $k = 1, 2$ — number of individual reactions,

i — stoichiometric coefficient of acid in the complex and

j — stoichiometric coefficient of amine in the complex

The values of K_{11} and K_{12} are expected to be dependent on the amine concentration, the composition of the solvent (*i.e.* modifier concentration) and the temperature.

Using the stoichiometric equations for individual reactions, (11a) and (11b), as well as the overall stoichiometric equation (11a+11b), stoichiometric tables are evaluated. From the experimentally obtained data, based on the total equilibrium concentration of the acid in the aqueous phase, with application of mass action law, the values of the apparent extraction constants, K_{11} and K_{12} , and the concentrations of individual complexes, c_{11} and c_{12} , were calculated.

The values of the apparent extraction constants, K_{11} and K_{12} , for the studied systems, are presented in **Table 2**.

As it can be seen, the values of K_{12} are more sensitive to both amine and modifier concentration than those of K_{11} . The changes of K_{11} values with amine

Table 2 Extraction of citric acid by trioctylamine in isodecanol/*n*-paraffins mixtures. Calculated values of the apparent equilibrium constants K_{11} and K_{12}

No	c_B^0		χ_M (kg/kg)	K_{11} (1/mol)	K_{12} (1/mol) ²
	(mol/l)	(mol/kg)			
1	0.670	1.210	0.081	6.54	26.28
2	0.670	1.210	0.162	8.77	33.86
3	0.670	1.210	0.313	10.31	75.05
4	0.670	1.210	0.460	13.16	155.95
5	0.670	1.210	0.603	23.13	232.96
6	0.110	0.155	0.410	4.19	1.94
7	0.213	0.321	0.410	5.98	14.72
8	0.456	0.728	0.410	12.77	126.21
4	0.670	1.210	0.410	13.16	155.59
Bizek <i>et al.</i> , (1992)					
9	0.465	0.807	0.217	12.22	76.10
10	0.459	0.772	0.354	21.50	244.42

concentration can be explained by the nonideality of the organic phase (nonspecific interactions among individual complexes, free amine and modifier), while those of K_{12} can be caused by both the nonideality and the reaction stoichiometry (it is assumed stoichiometry described by the Eqs. (11a) and (11b), but, the formation of (1,2) complex could be also assumed as a product of the (1,1) complex and the amine molecule). The influence of isodecanol on K_{11} can be explained by its solvating ability. The higher influence of isodecanol on the K_{12} values can be understood due to the interference with the intramolecular hydrogen bond between adjacent carboxyls which may result in setting free the second carboxyl group to be bonded with amine (Tamada and King, 1990 and Bizek *et al.*, 1992).

The values of K_{11} and K_{12} calculated from the experimental equilibrium data of Bizek *et al.*, (1992), are also presented in Table 2. According to our approach, which is based on a molarity scale, evaluated values of apparent extraction constants are practically the same as those obtained by Bizek *et al.*, (1992). From such results, it is suggested that in the investigated range of concentrations of amine and modifier, the "chemical modeling" with the assumed stoichiometry, as a simpler variant, can be satisfactory.

More information about the participation of the individual reactions in the overall equilibrium is provided by Figs. 5, 6 and 7. Here, the contributions of acid concentration in individual complexes, c_{11} and c_{12} , as well as the overall acid concentration in the organic phase, as a function of the acid concentration in the aqueous phase, are presented.

Comparing the results of Figs. 5, 6 and 7, the influence of composition of the extraction mixture on the contribution of the acid in the formed complexes is evident:

Fig 5 Extraction of citric acid by trioctylamine in isodecanol/*n*-paraffins mixtures. Participation of the individual complexes in the citric acid distribution in the organic phase

Fig 6 Extraction of citric acid by trioctylamine in isodecanol/*n*-paraffins mixtures. Participation of the individual complexes in the citric acid distribution in the organic phase

Fig 7 Extraction of citric acid by trioctylamine in isodecanol/*n*-paraffins mixtures. Participation of the individual complexes in the citric acid distribution in the organic phase

*when the concentration of amine is high, the (1,2) complex formation is promoted; increasing the concentration of the acid in aqueous phase, favors the (1,1) complexes, while isotherm for (1,2) complexes passes through its maximum (Fig. 5);

*when in the extraction mixture the concentration of amine is low and the content of isodecanol is high, then it is expected that only (1,1) complexes will be formed-modifier will stabilize them and there will be no competition between modifier and the adjacent carboxyls in the formed complex for the carboxylate site because there will be a small amount of complexes and many isodecanol's molecules (Fig. 6);

*when the concentrations of both the amine and the modifier in the extraction mixture, are medium or high, more uniform distribution of the individual complexes is expected, which means increasing curve for (1,1) complexes and curve with maximum or decreasing one, for (1,2) complexes. For the latter, the acid concentration in the aqueous phase will decide—there will be enough modifier for stabilization of the complexes, while the consumption of the amine will result in an easy formation of the (1,1) complexes towards two amine molecules needed for the complex (1,2) (Fig. 7).

The results of the contribution of the acid in organic phase in the individual complexes, for the system No. 10 in Table 2, obtained in the same manner as those for the system No. 8, are also presented in Fig. 7. The compatibility of the obtained results is obvious. It is confirmed that simpler model can be used in the cases of medium concentration of the amine and higher concentration of the modifier in the extraction mixtures.

Finally, **Fig. 8** shows a very good fit between experimentally obtained data and calculated values of the overall concentration of the acid in the organic phase using model Eq. (14).

Fig 8 Extraction of citric acid by trioctylamine in isodecanol/*n*-paraffins mixtures. Correlation of the experimental equilibrium data and calculated results by the mathematical model presented by the Eqs. (13a), (13b), (14) and (15)

Conclusion

If the mathematical modeling of the equilibrium is, first of all, because of its application in the analysis and design of dynamic systems, then it should answer the following two questions:

* to enable a choice of an extraction mixture which will provide high degree of extraction and easy separation of the phases even in dynamic conditions, and

* to give an appropriate mathematical model (form) which will be easily used for defining interface conditions in design equations.

The comparison of the two evaluated models is made through the Figs. 4 and 8. As it can be seen, both of the models show that there is no significant difference of the goodness of fit between them. The choice of the model, accordingly, can be made on the basis of its further application. If it is for dynamics description of the process or for the practical application, the first model will be preferred because of its simplicity. But if deeper understanding of the process, *i.e.* its mechanism is needed, then the second model will be better.

Nomenclature

$a, b,$	= stoichiometric coefficients, Eqs. (7a) and (7b)	
a, K	= model parameters according to the modified Langmuir isotherm	
c_{aqu}	= acid concentration in aqueous phase, Eq. (3)	[mol/l]
c_{org}	= acid concentration in organic phase, Eq. (3)	[mol/l]
c_{AA}^0, c_{AA}	= citric acid concentration in the aqueous phase, initial and equilibrium respectively	[mol/l]
$c_{AO}, c_{AO, max}$	= citric acid concentration in the organic phase, equilibrium and corresponding to the plateau of the extraction isotherms respectively	[mol/l]
c_{B-CB}^0	= concentration of amine in the organic phase, initial and equilibrium respectively	[mol/l]

$C_{complex}$	= concentration of the various complexes	[mol/l]
c_{11}	= concentration of the complex (1,1)	[mol/l]
c_{12}	= concentration of the complex (1,2)	[mol/l]
D	= equilibrium constant including dissociation constant, Eq. (3)	
H_3A	= tricarboxylic acid	
HA	= organic acid, Eqs.(4) and (5)	
K_c	= equilibrium constant, Eq. (5)	
K_{11}, K_{12}	= thermodynamic extraction constants, Eqs.(12a) and (12b)	
K_{11}, K_{12}	= apparent equilibrium constants, Eqs.(13a) and (13b)	[l/mol], [l/mol] ²
n	= association number, Eqs.(3), (4) and (5)	
R_3N	= tertiary amine	
TAA	= trialkylamine	
TOA	= trioctylamine	
χ_M	= mass fraction of isodecanol in the diluent, (isodecanol + n -paraffins)	[kg/kg]
Z_{max}	= maximum loading of extractant	

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