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Equilibria and Kinetics of Extraction of Citric Acid from Aqueous Solutions in Alamine 336–Cyclohexanone System

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Abstract: Equilibria and kinetics for the extraction of citric acid by Alamine 336 in cyclohexanone as diluent are reported. The theory of extraction accompanied by a chemical reaction has been used to obtain the intrinsic kinetics of extraction of citric acid by Alamine 336 in cyclohexanone. The reaction has been found to be first order in both Alamine 336 and citric acid with a rate constant of $8.8 \times 10^{-3}\,\mathrm{m^3\,kmol^{-1}\,s^{-1}}$.

Keywords: Citric acid, Alamine 336, cyclohexanone, reactive extraction, equiilibria, kinetics

INTRODUCTION

Citric acid is one of the most commonly used acids in the food and pharmaceutical industry because of its high solubility, palatability, strong chelating power, and low toxicity. The food industry is the largest consumer of citric acid, using almost 70% of the total production, followed by about 12% by the pharmaceutical industry and 18% for other applications. There is an annual growth of 3.5–4.0% in demand/consumption rate of citric acid (1).

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Although citric acid can be obtained by chemical synthesis, it is produced commercially almost exclusively by fermentation with *Aspergillus niger* because of the much lower cost. The fermentation is carried out by two ways: Surface fermentation, which was the original production method for large-scale manufacture of microbial citric acid, and submerged fermentation, which is more popular nowadays (2, 3).

The separation complexity of the biosynthetic products constitutes a peculiarity of the industrial biotechnologies, especially because of their low concentration in the fermentation broths. Low concentrations of carboxylic acids ($<10\%$) are achieved in fermentations such as those for lactic acid and citric acid from carbohydrates. The challenge is made tougher by their chemical and thermal lability and presence of secondary products in fermentation broth. The classical industrial method for recovering nonvolatile carboxylic acids is precipitation of the calcium salt followed by addition of sulphuric acid to regenerate the product acid while precipitating calcium sulphate. However, this method of recovery is expensive and unfriendly to the environment as it consumes lime and sulphuric acid and also produces a large quantity of calcium sulphate sludge as solid waste (4).

Extraction accompanied by chemical reaction can be considered as an alternative to the conventional calcium salt precipitation techniques for the recovery of carboxylic acids from aqueous stream. Physical extraction with conventional solvents is not an efficient method for the recovery of these acids. Therefore, reactive extraction with specified extractant giving a higher distribution coefficient has been proposed as a promising technique for the recovery of carboxylic and hydroxycarboxylic acids (5, 6). Reactive extraction represents a joint between the chemical phenomena (the reaction between the solute and extractant) and physical phenomena (diffusion and solubilization of the compound resulted from the chemical reaction). Tertiary amines offer advantages over other extractants, on the grounds of lower cost and generally higher equilibrium distribution coefficients (K_D) (7). Alamine 336 (a straight chain tertiary amine containing C_8-C_{10} alkyl groups) diluted with solvent yields a good combination of high K_D, low solubility in water, and good regenerability. These extractants are diluted with an organic solvent to provide suitable physical properties for use in an extraction process. Many factors have important influence on the extraction characteristics: the nature of acid extracted, concentration of the acid, and the extractant and the type of diluent used (8).

Baniel et al. (9) were the first to suggest that acids can be recovered from their aqueous solutions by an extraction process comprising of a first extraction stage in which the aqueous solution is contacted with a water immiscible extractant composing an organic solvent and dissolved therein, at least one secondary or tertiary amine. They suggested that the preferred field of application was the recovery of organic acids produced by fermentation from fermentation broths.

Juang and Huang (10) studied the rate of extraction of citric acid from aqueous solutions with tri-n-octylamine dissolved in xylene using a stirred membrane-based cell. They found that under the conditions studied, both extraction and stripping were mainly controlled by chemical reaction occurring at the interface on the organic side.

Wennersten (6) found that the distribution coefficient of citric acid was strongly temperature-dependent. That makes it possible to strip the acid into water at a higher temperature. Bizek et al. (11) found that distribution of citric acid between water and amine dissolved in a diluent greatly depended on the diluents. They also correlated the estimated values of overall extraction constants with solvatochromic parameters of the diluents. Prochazka et al. (12) compared the extraction equilibria for lactic, malic, and citric acids and demonstrated the need of applying the temperature and diluent swing principles on the systems investigated.

Kirsch et al. (13) investigated phase equilibria governing the reactive extraction of citric acid from aqueous solution into solutions of tri-n-octylamine in the single solvents toluene, chloroform, and methylisobutylketone. In addition to batch experiments, they also performed spectroscopic measurements, which yielded information about the stoichiometry of complex formation. This is the first publication in which a model describing the partitioning of all components into the coexisting phases is presented. Kirsch and Maurer (14–16) subsequently extended the above approach to study in details the liquid-liquid equilibrium in organic/aqueous two-phase systems containing a tertiary amine (tri-n-octylamine) and two carboxylic acids (acetic and/or oxalic and/or citric acid).

The design of an amine extraction process requires (i) equilibrium and (ii) kinetic data for the acid-amine (solvent) system used. Considerable information on the equilibrium of several acid-amine systems is available in the literature. However, only limited information pertaining to kinetics is available (17). Most of the authors have used empirical rate equations for finding the kinetics of extraction.

The progress of the extraction can be more clearly described by the theory of extraction accompanied by a chemical reaction (18), which is explained later. In this work the same is used to obtain the intrinsic kinetics of extraction of citric acid from aqueous solution in Alamine 336 using cyclohexanone as a diluent, which was reported to give moderate distribution coefficients (6).

THEORY OF EXTRACTION ACCOMPANIED BY A CHEMICAL REACTION

In reactive extraction, the solute reacts with the amine in the organic phase and the resulting acid: amine complexes are supposed to be stabilized due to the hydrogen bonding with the diluent. Because of their hydrophobic nature, the complex formation enhances the extraction of solute from aqueous to organic phase.

The extraction of citric acid with amine can be described by the set of reactions involving the formation of complexes with n acid molecules and one amine molecule.

$$(H_3A)_{org} + (B_o)_{org} \overset{K_{11}}{\longleftrightarrow} (BH_3A)_{org} \tag{1}$$

where H_3A and B_o represent, respectively, the citric acid and the amine.

$$(H_3A)_{org} + (BH_3A)_{org} \overset{K_{21}}{\longleftrightarrow} B(H_3A)_{2,_{org}} \tag{2}$$

$$(H_3A)_{org} + B(H_3A)_{n-1,_{org}} \overset{K_{n1}}{\longleftrightarrow} B(H_3A)_{n,_{org}} \tag{3}$$

The equilibrium complexation constant for the reaction represented by Eq. (3) is

$$K_{En} = \frac{\left[(BH_3A)_n\right]_{org}}{[BH_3A]_{n-1,org}[H_3A]^n_{org}} \tag{4}$$

The extent to which the organic phase (Alamine 336 + cyclohexanone) can be loaded with citric acid is expressed as the loading ratio. The loading of the extractant, z, is defined as the total concentration of acid in the organic phase divided by the total concentration of amine in the organic phase.

$$z = \frac{[H_3A]_{org}}{[B_o]} \tag{5}$$

The value of z depends on the extractability of the acid (strength of the acid-base interaction) and its aqueous concentration and is independent of the amine content in an inert diluent (19).

Doraiswamy and Sharma (18) have given an exhaustive discussion on the theory of extraction accompanied by a chemical reaction. Four regimes of extraction accompanied by reaction have been identified depending upon the physicochemical and hydrodynamic parameters.

Regime 1: Very slow reaction occurring in the bulk liquid phase with practically no reaction in the liquid film. In this case, the characteristic diffusion time is very small compared to the characteristic reaction time. Thus, the entire bulk liquid phase is saturated with the diffusing reactant.

Regime 2: Slow reaction in which the diffusion rate is higher than the rate of homogeneous bulk phase reaction. Therefore, the concentration of the dissolved diffusing solute in the bulk is zero.

Regime 3: Fast reaction occurring in the film. In this case, both diffusion and the reaction occur simultaneously in the diffusion film.

Regime 4: Instantaneous reaction in which the reaction is so fast that the two reactants cannot coexist and a reaction plane is formed in the diffusion film. At this reaction plane, both reactants are instantaneously and completely consumed.

When the reaction is reversible, the solute has a finite equilibrium concentration in the bulk and the driving force needs to be modified by incorporating the same. The guidelines for discerning the mechanism in stirred cell are given in Table 1. The extraction involves the partitioning of the solute A available in the aqueous phase to the organic phase:

$$\mathrm{A_{aq}} \longrightarrow \mathrm{A_{org}} \tag{6}$$

The solute A present in the organic phase combines with the organic reactant (amine), B according to

$$\mathrm{mA} + n\mathrm{B} \Longleftrightarrow \mathrm{Complex} \tag{7}$$

The hydrodynamic factors (as signified by the speed of agitation in a stirred cell) are unimportant in regimes 1 and 3 whereas the same affect the rate of extraction in regimes 2 and 4. The expressions for the rate of extraction are given by Doraiswamy and Sharma (18). The expression for regime 1, extraction accompanied by a slow general order chemical reaction is

$$R_A = lK_{mn}[A^*]^m[B_0]^n \tag{8}$$

where l is the liquid volume holdup of B phase, based on total liquid volume.

Table 1. Procedure for discerning reaction mechanism: stirred cell

	Effect on the specific rate of absorption ($\mathrm{kmol\,m^{-2}\,s^{-1}}$)			
Regime	$[A^*]$	$[B_o]$	Speed of agitation	Volume of liquid (B phase)
1	$\propto [A^*]^m$	$\propto [B_o]^n$	None	$\propto$ Volume
2	$\propto [A^*]$	None	Increases with increase in the speed of stirring	None
3	$\propto [A^*]^{(m+1)/2}$	$\propto [B_o]^{n/2}$	None	None
4	None[a]	$\propto [B_o]$	Increases with increase in the speed of stirring in the same manner as in Regime 2	None

[a] Provided that $[B_o] \gg z[A^*]$.

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EXPERIMENTAL

Reagents

All the chemicals used (citric acid, cyclohexanone, sodium hydroxide) were of reagent grade. Alamine 336 (Henkel Co., USA), a C_8–C_{10} saturated straight-chain tertiary amine mixture, is a pale yellow liquid practically insoluble in water (<5 ppm), with an average molecular weight $M = 392$ g/mol and a density of 0.81 g/cm^3 at 20°C. Cyclohexanone ($M = 98.15$ g/mol, density $= 0.95$ g/cm^3 at 20°C) was supplied by S. D. Fine Chemicals Ltd., Mumbai, India. All the chemicals were used without further purification. All solutions were prepared by dissolving citric acid monohydrate of analytical purity in distilled water. The initial concentration of citric acid was varied from 0.05 to 0.50 kmol m^{-3}. This comparatively low concentration range was used because in the practical case of acid recovery from fermentation broths, the acid concentrations are not expected to be high. (The maximum concentration which can be obtained in the fermentation broth is 0.83 kmol m^{-3}) (6).

Procedures

Equilibrium

All the experiments were carried out at room temperature (30°C). Equilibrium isotherms were determined by contacting equal volumes (50 mL) of organic and aqueous solutions of known concentrations in a temperature-controled shaker bath for 12 h. The two phases were allowed to settle for 2 h. To determine the concentration of citric acid, the aqueous phase was titrated with NaOH. The corresponding acid concentrations in the organic phase were calculated by mass balance.

Kinetics

The stirred cell used for kinetic measurement in this work was a cylindrical glass vessel, 0.07 m in diameter and 0.1 m height, with a flat bottom (20). Aqueous solution of acid (0.1 m^3) was first placed in the vessel. The position of the four-blade paddle stirrers was adjusted to 1 cm below and above the interface. Both the stirrers were mounted on the same shaft and rotated in the same direction. A fixed volume of the organic extractant mixture (Alamine 336 + diluent) was then added and the mixture was stirred. The stirred cell apparatus was provided with an arrangement at the bottom for the removal of the aqueous samples with the help of a syringe. The sample was removed using the syringe without a stoppage in the stirring. Using acid-base titration with NaOH and phenolphthalein as the indicator, acid concentration in aqueous phase was determined (with relative uncertainty 1%). The normality of NaOH solution was standardized using standard oxalic acid solution. The concentration of acid in the organic phase was determined by mass balance. The organic mixture in some selected cases was analyzed by high-performance liquid chromatography. This method yielded the concentration of the complex in the organic phase. This value was used to independently calculate the citric acid transferred which was then checked with value obtained from the decrease in aqueous phase concentration. The experiments (approximately 40%) were repeated in selected cases to check the reproducibility and the results were found to be reproducible within ±3%.

RESULTS AND DISCUSSION

Extraction Equilibria

The equilibrium data on the distribution of citric acid between water and Alamine 336 dissolved in cyclohexanone are presented in Fig. 1. The physical (diluent only) and chemical equilibrium distribution isotherms of 10% ($0.21\,\mathrm{kmol\,m^{-3}}$), 20% ($0.41\,\mathrm{kmol\,m^{-3}}$), and 30% ($0.62\,\mathrm{kmol\,m^{-3}}$) Alamine (v/v) were measured at 30°C. The regression equations for physical equilibria obtained by a statistical analysis of the equilibrium data is

$$C^*_{\mathrm{Aorg}} = 0.19C^*_{\mathrm{Aaq}} + 0.42C^*_{\mathrm{Aaq^2}} \tag{9}$$

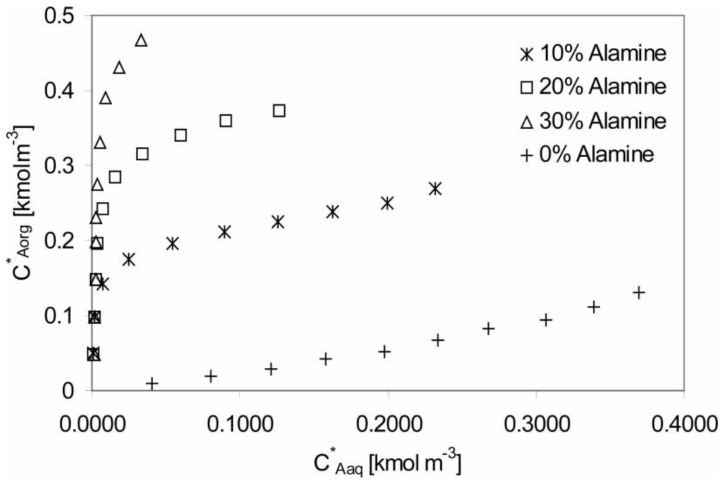

Figure 1. Equilibrium isotherms for reactive extraction of citric acid with various concentrations of Alamine 336 in cyclohexanone.

Table 2. Distribution coefficients (K_D) for the extraction of citric acid at initial concentration of 0.2 kmolm^{-3} with various concentrations of Alamine 336 in cyclohexanone

%Alamine	K_D
0	0.27
10	7.09
20	55.38
30	74.74

In Fig. 1, the effect of the concentration of the Alamine is evident: The amount of acid extracted from aqueous solutions at any initial concentration increases with increasing amine concentration. The values of distribution coefficients at initial acid concentration of 0.2 kmol m^{-3} for various Alamine concentrations are given in Table 2. The distribution coefficients at a particular amine concentration decreases with increasing acid concentration.

In Fig. 2, the equilibrium data are plotted in terms of loading of amine, z. Since there is decrease in loading with increasing alamine concentration, it is clear that complexes involving only one amine are formed (12).

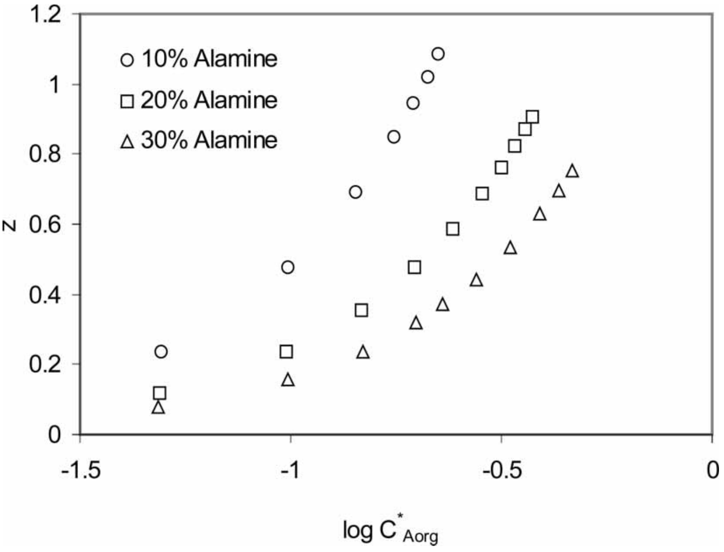

Figure 2. Loading of Alamine 336 with cyclohexanone.

The stoichiometry of the overall extraction reaction depends on the loading ratio in the organic phase, z. If the organic phase is not highly concentrated, i.e., at very low loading ratios, the (1 : 1) complex is formed and a plot of $z/(1-z)$ vs. C^*_{Aaq} is a straight line whose slope gives the complexation constant K_{E1} in equation (10) (20).

$$\frac{z}{1-z} = K_{E1}C_A \tag{10}$$

A plot of Eq. (10) is shown in Fig. 3 with a slope of 194.26. Hence, the equilibrium complexation constant for the (1 : 1) complex at 30°C for the extraction of citric acid with Alamine 336 dissolved in cyclohexanone, for low concentrations of citric acid in the organic phase is

$$K_{E1} = 194.26\,\mathrm{m^3\,kmol^{-1}}$$

This is the case when the moles of acid per moles of Alamine in the organic phase are less than unity (8).

Kinetics

Physical Mass Transfer Coefficient

The value of physical mass transfer coefficient k_L is required for confirming the regime of extraction. This was obtained by conducting physical extraction (diluent only) of citric acid from water. For a batch process a differential mass

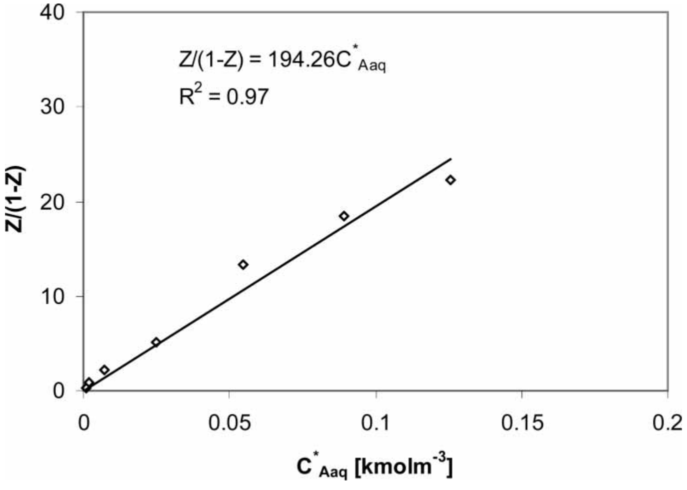

Figure 3. Plot of $z/(1-z)$ vs. C_A for the estimation of (1 : 1) citric acid–Alamine 336 equilibrium complexation constant.

balance yields the following equation (20)

$$V_{\text{org}}\frac{dC_{\text{org}}}{dt} = k_L A_C\left(C^*_{\text{org}} - C_{\text{org}}\right) \tag{11}$$

Integration of this equation yields

$$k_L = \frac{V_{\text{org}}}{A_C t}\int_0^{C_{\text{org}}}\frac{dC_{\text{org}}}{\left(C^*_{\text{org}} - C_{org}\right)} \tag{12}$$

The values of k_L evaluated using equation (12) for different speeds of agitation are plotted in Fig. 4. The regression relation between mass transfer coefficient and speed of agitation obtained by a statistical analysis of the data is given below:

$$k_L = 1 \times 10^{-5} N^{1.4} \tag{13}$$

Reaction Regime

The reaction between citric acid and Alamine 336 is reversible particularly under conditions of high loading in the organic phase. To avoid problems due to this reversibility, only initial rates were considered for evaluation of the kinetics. The initial rate ($\text{kmol}\,\text{m}^{-3}\,\text{s}^{-1}$) was obtained by fitting the aqueous phase citric acid concentration (C_{Aaq}) vs. time data and obtaining the slope of the curve at time = 0. This value was then divided by the

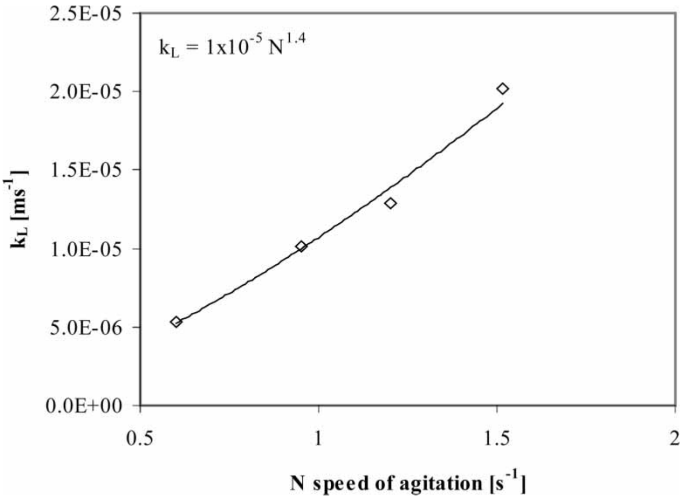

Figure 4. Estimation of physical mass transfer coefficient.

cross-sectional area of the stirred cell to yield the specific rate of extraction, R_A (kmol m^{-2} s^{-1}). Each point of the curve represents a separate experiment.

Effect of Speed of Agitation

To find out the reaction regime, the criterion proposed by Doraiswamy and Sharma (18) was used. The speed of agitation was varied from 0.6 to 1.5 s^{-1}. In this range the liquid-liquid interface was flat and the interfacial area for extraction was equal to the geometric area of the interface. The initial citric acid concentration was 0.2 $kmolm^{-3}$ and the Alamine concentration was 0.21 kmol m^{-3} (10%). Figure 5 shows that there is no effect of speed of agitation on the specific rate of extraction, R_A (kmol m^{-2} s^{-1}). This indicates that reaction occurs either in Regime 1 or 3.

Effect of Phase Volume

To differentiate between Regimes 1 and 3, the effect of organic phase volume on the specific rate of extraction was studied. The speed of agitation was kept constant at 0.95 s^{-1}. Figure 6 shows the plot of R_A vs. phase volume ratio (volume of organic phase/volume of aqueous phase). It is evident that the rate of extraction increases with the volume of organic phase.

From the above experimental results, it can be concluded that the reaction between citric acid and Alamine 336 in cyclohexanone in a stirred cell falls in Regime 1, kinetic-controlled slow reaction occurring in the bulk organic phase.

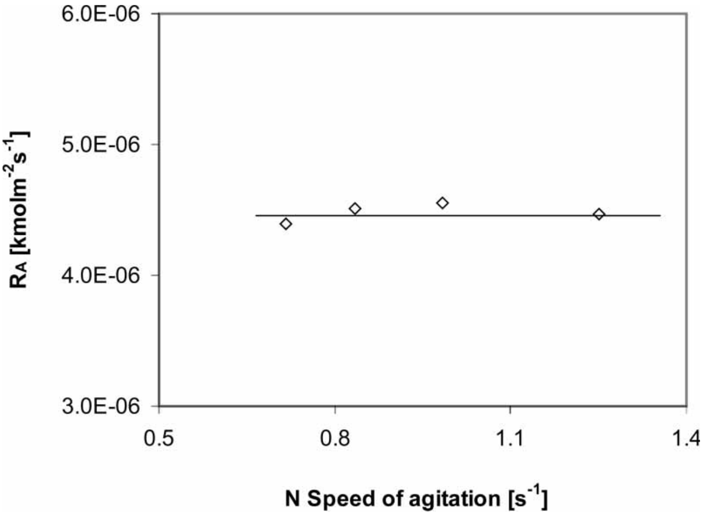

Figure 5. Effect of speed of agitation on the specific rate of extraction for the reactive extraction of citric acid with Alamine 336 in cyclohexanone.

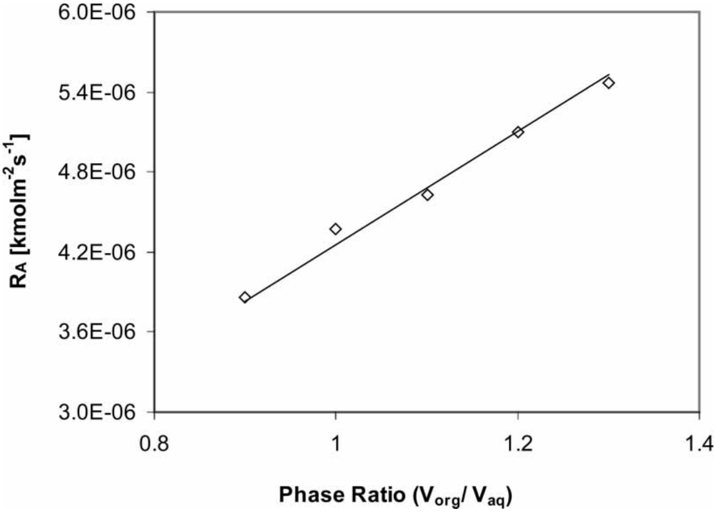

Figure 6. Effect of phase ratio on the specific rate of extraction for the reactive extraction of citric acid with Alamine 336 in cyclohexanone.

Order of Reaction

Order with Respect to Citric Acid

To find out the order of reaction with respect to citric acid, the aqueous phase citric acid concentration was varied from 0.1 to 0.25 kmol m^{-3}. Figure 7 shows the effect of organic phase citric acid concentration on specific rate of extraction, R_A. A regression analysis of the data yielded m = 1 [as per Eq. (1)]. Thus, the reaction is first order with respect to citric acid.

Order with Respect to Alamine 336

Figure 8 shows a plot of the specific rate of extraction of citric acid against initial Alamine 336 concentration in the organic phase. The initial Alamine concentration was varied from 5% to 30%. A regression analysis of the data yielded n = 1 [as per Eq. (1)]. Thus, the reaction is first order with respect to Alamine concentration.

Rate Constant

For m = 1 and n = 1, Eq. (8), the rate expression for the initial part of the extraction is reduced to

$$R_A = lK_{11}\lfloor A^* \rfloor [B_0] \tag{14}$$

Using $l = 0.5$ (the organic phase holdup), the data were fitted to the above equation to obtain the value of rate constant as 8.8×10^{-3} m^3 kmol^{-1} s^{-1}.

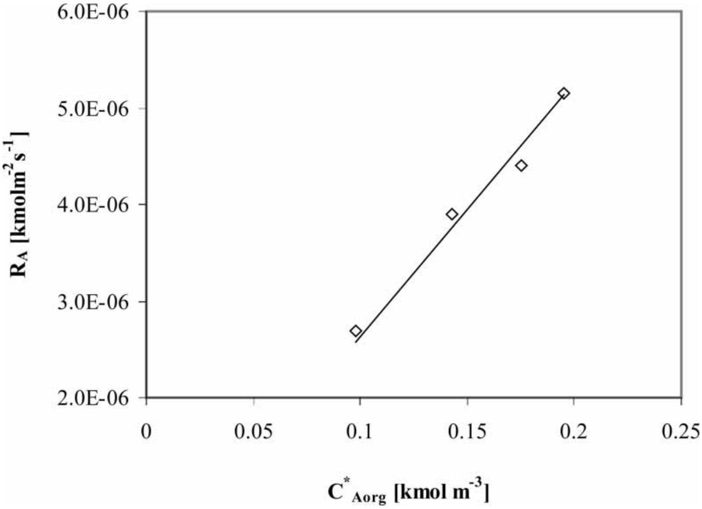

Figure 7. Effect of initial citric acid concentration on the specific rate of extraction for the reactive extraction of citric acid with Alamine 336 in cyclohexanone.

CONCLUSION

Physical and chemical equilibria for the extraction of citric acid by Alamine 336 in cyclohexanone have been determined. The extraction equilibria was interpreted as a result of consecutive formation of acid-amine species with

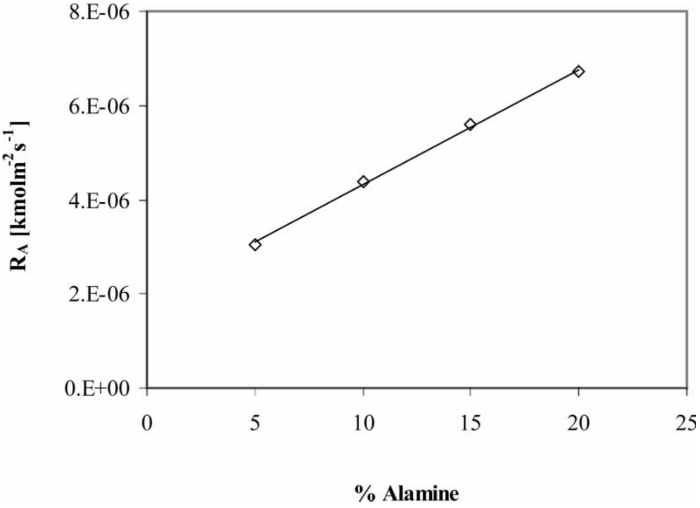

Figure 8. Effect of Alamine 336 concentration on the specific rate of extraction for the reactive extraction of citric acid with Alamine 336 in cyclohexanone.

stoichiometry of 1 : 1 and the equilibrium complexation constant has been estimated.

The theory of extraction accompanied by chemical reaction has been used to obtain kinetics of extraction. The reaction between citric acid and Alamine 336 in cyclohexanone in a stirred cell falls in Regime 1, kinetic-controlled slow reaction occurring in bulk organic phase. The reaction has been found to be first order in both citric acid and Alamine 336 with a rate constant of $8.8 \times 10^{-3}\,m^3\,kmol^{-1}\,s^{-1}$.

NOMENCLATURE

A_c	Cross-sectional area of stirred cell (m^2)
(B_o)	Initial concentration of Alamine 336 in organic phase ($kmol\,m^{-3}$)
C_A, (H_3A)	Citric acid concentration ($kmol\,m^{-3}$)
C^*_{Aaq}	Equilibrium concentration of citric acid in the aqueous phase ($kmol\,m^{-3}$)
C^*_{Aorg}	Equilibrium concentration of citric acid in the organic phase ($kmol\,m^{-3}$)
K_{11}	Second-order reaction rate constant ($m^3\,kmol^{-1}\,s^{-1}$)
K_D	Distribution coefficient (−)
K_{E1}	(1 : 1) citric acid-Alamine equilibrium complexation constant ($m^3\,kmol^{-1}$)
k_L	Physical mass transfer coefficient (ms^{-1})
K_{mn}	Rate constant for a reaction that is mth order in species A and nth order in species B ($(m^3\,kmol^{-1})^{m+n-1}$)
l	Liquid volume holdup of B (organic) phase, based on total liquid volume (−)
m	Order of reaction with respect to the species A
n	Order of reaction with respect to the species B
M	Molecular weight of a compound ($g\,mol^{-1}$)
N	Speed of agitation (s^{-1})
R_A	Specific rate of extraction of species A (i.e., citric acid) ($kmol\,m^{-2}\,s^{-1}$)
V	Phase volume (m^3)
z	Loading ratio (−)

Superscript

*	Equilibrium

Subscripts

aq	Aqueous phase
org	Organic phase

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