KINETIC STUDIES ON THE EXTRACTION OF CITRIC ACID FROM AQUEOUS SOLUTIONS WITH TRI-N-OCTYLAMINE

RUEY-SHIN JUANG* AND WEN-TAUR HUANG
Department of Chemical Engineering, Yuan-Ze Institute of Technology, Nei-Li, Taoyuan, Taiwan 32026, R.O.C.

Key words: Extraction, Kinetics, Citric Acid, Tri-n-octylamine, Stirred Membrane-Based Cell.

In this paper, the rates of the extraction of citric acid from aqueous solutions with tri-*n*-octylamine dissolved in xylene were measured using a stirred membrane-based cell in the 298~328 K temperarature range. It was found that, under the conditions studied, both forward extraction and back-extraction processes were mainly controlled by chemical reactions occurring at the interface on the organic side. The intrinsic rate constants for the formation and dissociation of the acid complexes were determined and a possible reaction mechanism was proposed. The effect of temperature on the reaction kinetics was also investigated and the activation energies were thus obtained.

Introdyction

The amine extraction process has been found to be a promising alternative to conventional calcium salt precipitation processes for the recovery of carboxylic acids from aqueous solutions[10, 12, 23]. A significant amount of work has been done on the equilibrium for carboxylic acid extraction with tertiary and quaternary amines like tri-*n*-octylamine (TOA), trilaurylamine, Alamine 336, and Aliquat 336[2-4, 9, 16, 18, 20-22]. Various aspects of this subject were elucidated, such as quantitative description of the influence of amine and acid concentrarions on the complex composition, coextraction of water, the effect of diluent, and the non-ideality of organic phase (the aggregation behavior).

However, until now there have been only a small number of kinetic studies on this subject. For example, Zhou and Zhong[24, 25] studied the kinetics of citric acid extraction from fermentation solution by trialkylamine in butyl acetate and oleic acid using a single drop method. They obtained the rate equations and activation energies for forward extraction and back-extraction processes. In addition, Schugerl and his coworkers[6, 19] examined the kinetics of salicylic acid extraction from aqueous solution with Amberlite LA-2, a secondary amine, in xylene using a stirred Lewis cell. Based on the assumption that interfacial reactions take place instantaneously, they found that the extraction process is diffusion-controlled and can be described by a two-film transfer model.

In our previous paper[8], an easy-to-operate device, a stirred membrance-based cell, has been developed to satisfactorily estimate the effect of diffusional resistance on the extraction process, and hence to obtain the intrinsic rates of chemical reactions occurring at or near the organic-aqueous interface. In this work, the kinetics of the extraction of citric acid from aqueous media with xylene solutions of TOA was investigated using this stirred cell. Finally, the effect of temperature on the reaction kinetics was examined and a possible reaction mechanism was also proposed.

1. Experimental

1.1 Apparatus, membranes, and reagents

The membrane-based cell used in this work was identical to that described in our previous paper[8]. Two chambers separated by a membrane support of area 44.2-cm^2 were stirred at the same rate (300 rpm), but in opposite directions. The entire cell was immersed in a thermostat controlled in the 298~328 K temperaure range. The microporous hydrophobic PVDF membranes used (GVHP, Millipore Co.) had a mean thickness of 125 μm, an average pore size of 0.22μm, and a typical porosity of 75%.

TOA was a product of Tokyo Chemical Industry Co., Ltd., Japan. It had a purity of about 98.5% and was used without furher purification. Citric acid, xylene, and other inorganic chemicals were supplied by Merck Co. as analytical reagent grades. For the forward extraction process, the organic solution was prepared by diluting TOA in xylene and the aqueous solution was prepared by dissolving citric acid in deionized water without pH adjustment. The initial concentrations of citric acid in the aqueous phase and of TOA in the organic phase were varied between 0.1 and 1.5 mol/dm^3, and between 0.1 and 0.4 mol/dm^3, respectively. For the back-extraction process, the aqueous solution was either 0.1 mol/dm^3 Na_2CO_3 or deionized water. In the organic phase, the initial concentrations of the acid-TOA complex and free TOA were varied from 0.01 to 0.05 mol/dm^3 and from 0.4 to 0.8 mol/dm^3, respectively. Deionized water employed in this work was produced by a Millipore Milli-Q Water System.

* Received October 5, 1994. Correspondence concerning this article should be addressed to R. S. Juang.

Table 1. Transport parameters evaluated in the stirred membrane-based cell at 298 K

system (solute/medium)	diffusivity [m²/s][a]	mass transfer coefficient [m/s]
iodine/water	1.39×10^{-9}	$k_a = 7.2\times10^{-5}$
iodine/kerosene	2.76×10^{-9}	$k_o = 9.02\times10^{-5}$
iodine/membrane (kerosene)		$k_m = 7.60\times10^{-6}$
H_3A/water	5.90×10^{-10}	$k_a = 3.95\times10^{-5}$
H_3A/xylene	1.23×10^{-9}	$k_o = 5.91\times10^{-5}$
H_3A/membrane (xylene)		$k_m = 3.39\times10^{-6}$
TOA/xylene	1.04×10^{-9}	$k_o = 5.28\times10^{-5}$
TOA/membrane (xylene)		$k_m = 2.86\times10^{-6}$
complex/xylene	7.07×10^{-10}	$k_o = 4.09\times10^{-5}$
complex/membrane (xylene)		$k_m = 1.95\times10^{-6}$

[a]The diffusivities of all solutes were estimated by the Hayduk-Minhas correlation[17]

1.2 Experimental procedure

The initial extraction and back-extraction rates were separately measured using the stirred cell by the following procedures. An organic solution with a volume of about 255 cm^3 was first placed in the lower cell. The membrane impregnated with organic solution was clamped and the cell was assembled. An equal volume of aqueous solution was then poured into the upper cell. The timing was started upon addition of aqueous solution. Samples (5-10 cm^3) were withdrawn at certain time intervals from the aqueous phase. In the forward extracrion process, the concentration of citric acid in the aqueous phase was titrated with NaOH using Radiometer Autotitrator Model RTS82. In the back-extraction process, the concentration of citric acid in the aqueous phase was determined by HPLC (Waters Model 501, Millipore Co.). The HPLC consists of a solvent delivery pump (Model 510), an injector (Model U6K), and an UV/Vis detector (Model 484). A Hamilton column PRP-X300 for organic acid analysis was used in this study. The PRP-X300 is a 7-μm, spherical poly (styrene-divinylbenzene) sulfonate ion exclusion column, and has a pore size of 10 nm and an exchange capacity of 0.17 meq/g. The mobile phase was 10^{-3} mol/dm^3 H_2SO_4. The concentrations of citric acid in the organic phase were calculated by mass balance. Each experiment was duplicated under identical conditions.

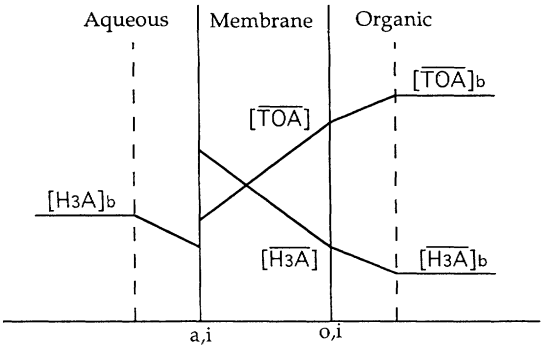
2. Results and Discussion

2.1 Determination of the mass-transfer coefficients

For the stirred cell used here, the individual mass-transfer coefficients of iodine in the aqueous phase, in the bulk organic phase, and in the membrane phase, k_a, k_o, and k_m, have been experimentally determined at a stirring speed of 300 rpm and 298 K[8]. Hence, the individual mass-transfer coefficients of H_3A, TOA, and the acid-TOA complex can be directly correlated from the measured results of iodine on the basis of the relationships $k_m \propto D_j$ and k_a (or k_o) $\propto D_j^{2/3}\,\gamma^{-1/6}$, where γ is the kinematic viscosity of the solvent[13]. The calculated results are compiled in **Table 1**.

In this correlation, the diffusivities of species in the bulk liquid phase are estimated by the Hayduk and Minhas correlation[17]. The kinematic viscosities of kerosene

(1) Forward extraction process



(2) Backward stripping process

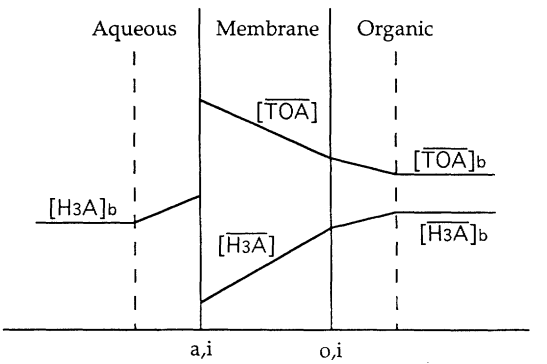


Fig. 1 Concentration profiles of reactive species forward extraction and backward stripping processes in the membrane-based permeation cell

and xylene are 1.52×10^{-6} and 7.67×10^{-7} m^2/s, respectively, at 298 K. The molar volumes of xylene and H_3A at their normal boiling points are estimated to be 141.9 and 202.4 cm^3/mol, respectively, by the Tyn and Calus method[17]. Also, the parachors for xylene, H_3A, TOA, and the acid-TOA complex are estimated to be 285.1, 340.2, 1024, and 2558 $cm^3\cdot g^{1/4}/s^{1/2}$, respectively, by the method of additive group contributions[17]. It should be noted that the parachor of citric acid in xylene should be doubled since the acid exists as dimers.

Although diffusion behavior within the porous membrane may be affected by molecular structure and size of diffusing species[5], the validity of direct correlation between k_m and D_j for the membrane support under consideration has been justified previously from experments[8].

2.2 Detarmination of the initial extraxtion and stripping rates

It was reported that a microporous hydrophobic membrane with high porosity and pore size anywhere between 10^{-3} and 10^2 μm is not readily wetted by water[11]. On the other hand, hydrocarbons and most other organic solvents readily wet it. Hence, the species concentration at both sides of the membrane-organic interface is assumed to be identical since the interface is basically homogeneous

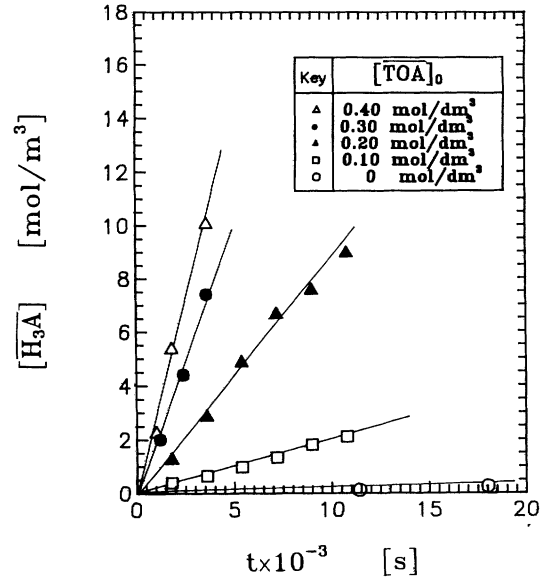


Fig. 2 Variation of the concentration of citric acid-TOA complex in the organic phase with contact time at 298 K. $[H_3A]_0 = 0.1$ mol/dm^3

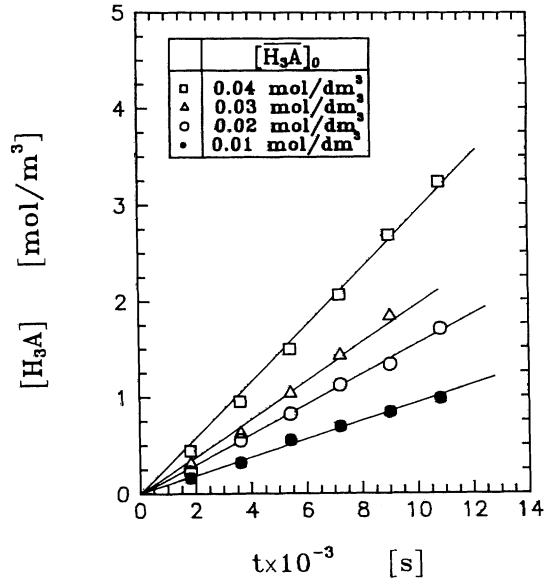


Fig. 3 Variation of the concentration of citric acid in the aqueous phase with contact time at 298 K. Strip phase: $[Na_2CO_3] = 0.1$ mol/dm^3, $[\overline{TOA}]_0 = 0.4$ mol/dm^3

due to high porosity of the membrane used[5]. The concentration profiles of the species across the membrane-based cell for the extraction and back-extraction processes are illustrated in **Fig. 1**.

Figures 2 and **3** show the variation of the amount of citric acid in the initially acidfree phase and contact time for extraction and back-extraction processes, respectively. It is found that all data points lie on straight lines passing through the origin. Initial extraction and back-extraction rates, R_f and R_b, are calculated from the slope of each straight line according to

$$R_f = (V_o / S)(d[\overline{H_3A}] / dt) \quad (1)$$

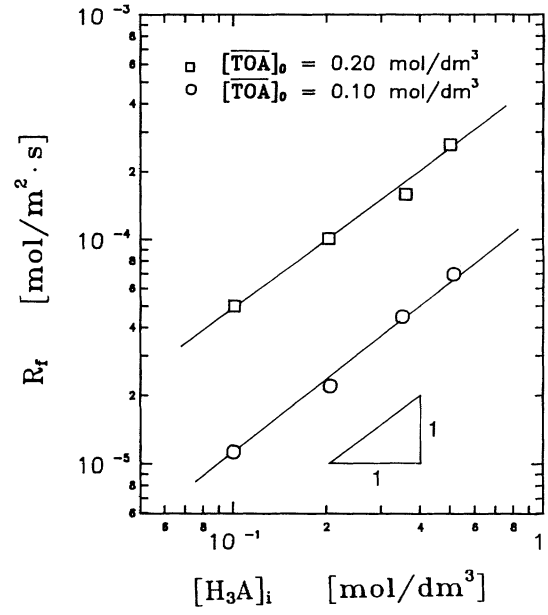


Fig. 4 Effect of citric acid concentration in the aqueous phase on the rate of forward reaction at 298 K

$$R_b = (V_a / S)(d[H_3A] / dt) \quad (2)$$

where V and S are the volume of bulk solution and the membrane cross-section area, respectively. $[\overline{H_3A}]$ repesents the concentration of acid-TOA complex in the organic phase for simplicity. This is due to the fact that the contribution of citric acid extracted physically is negligibly small, compared with that extracted with TOA[9], as also shown in Fig. 2.

2.3 Initial extraction and stripping rates

As reported by Playne and Smith[15], the solubility of TOA and xylene in water are only 0.0012 and 0.19 dm^3/m^3, respectively. The reaction between citric acid and TOA is thus expected to take place at the interface on the organic side to form the complexes[1]. In all real processes, the apparent extraction rate (and back-extraction) is determined not only by the interfacial chemical kinetics, but also by the diffusion of species toward and away from the interface[7]. In order to eliminate the contribution of diffusional resistance to the overall process, an attempt was made to estimate the species concentrations at or adjacent to the aqueous-organic interface and to correlate them with the kinetic data.

Under steady-state conditions, the concentration of each species adjecent to the interface is obtained from the experimental R_f values, in which the interfacial reaction rate equals the mass-transfer rate[8]. Consequently, we have

$$R_f = k_{H_3A}([H_3A]_b - [H_3A]_i) = (4/5) K_{\overline{TOA}}([\overline{TOA}]_b - [\overline{TOA}]_i) \quad (3)$$

where the subscripts "i" and "b" refer to the aqueous-membrane (organic) interface and bulk phase, respecitively. $K_{\overline{TOA}}$ is the overall mass-transfer coefficent of TOA across the membrane and organic stagnant layer, which equals $1/[(1/k_m)+(1/k_o)]$. The stoichiometric ratio (4/5) is

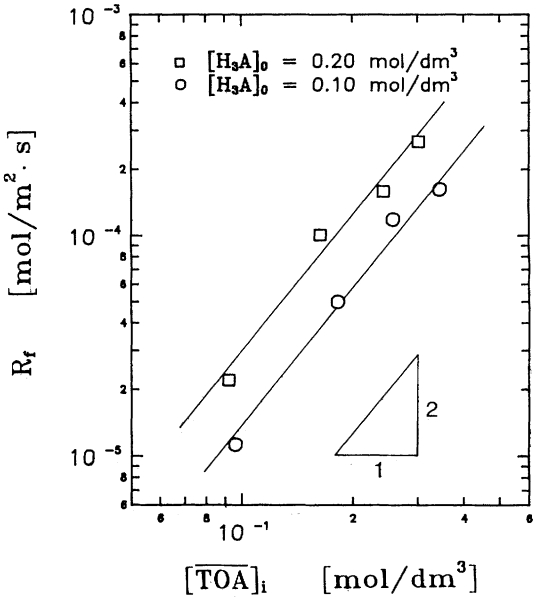


Fig. 5 Effect of TOA concentration in the organic phase on the rate of forward reaction at 298 K

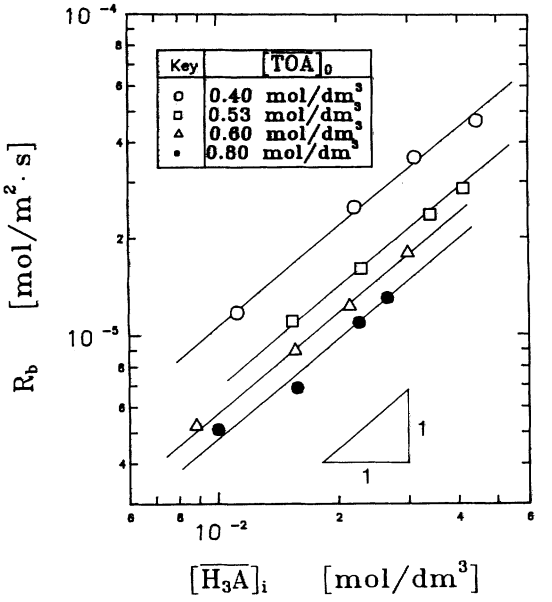


Fig. 6 Effect of the concentration of citric acid-TOA complex in the organic phase on the rate of backward reaction at 298 K. Strip phase: $[Na_2CO_3]$ = 0.1 mol/dm^3

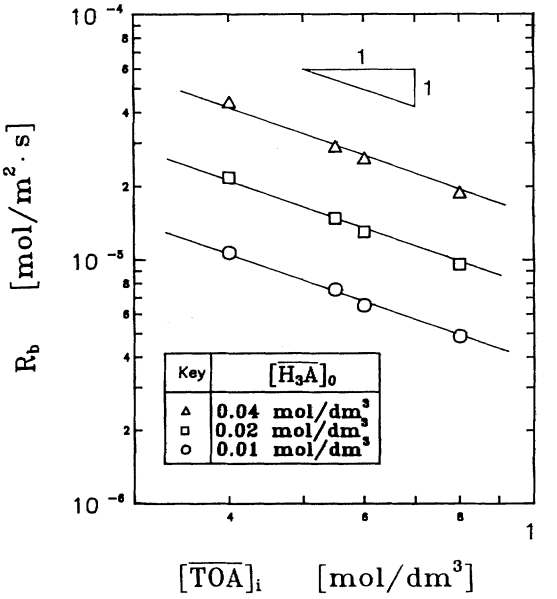


Fig. 7 Effect of free TOA concentration in the organic phase on the rate of backward reaction at 298 K. Strip phase: $[Na_2CO_3]$ = 0.1 mol/dm^3

obtained from extraction equilibrium results[9], which means that there is, on average, (5/4) TOA reacted with one acid per complex under the conditions studied.

Figures 4 and **5** are log-log plots for forward reaction rates under various interfacial concentrations of citric acid and TOA, respectively. Figure 4 shows that the slope of these lines is one under the conditions examined. It follows from Fig. 5 that the forward reaction rate is second order with respect to TOA concentration. Based on the above findings, the initial rates of complex formation between citric acid and TOA can be expressed as

$$R_f = k_f [H_3A]_b [\overline{TOA}]^2 \tag{4}$$

The rate constant k_f is found to be $(1.54 \pm 0.30) \times 10^{-11}$ (m^7 / mol^2·s) at 298 K.

On the other hand, the influence of interfacial concentrations of the acid-TOA complex and free TOA on backward reaction rates are illustrated in **Figs. 6** and **7**, respectively. In this stage, the strip phase is 0.1 mol/dm^3 Na_2CO_3. The interfacial concentrations of species are obtained similarly by

$$\begin{aligned} R_b &= k_{H_3A}([H_3A]_i - [H_3A]_b) \\ &= (4/5)\, K_{\overline{TOA}}([\overline{TOA}]_i - [\overline{TOA}]_b) \\ &= K_{\overline{H_3A}}([\overline{H_3A}]_b - [\overline{H_3A}]_i) \end{aligned} \tag{5}$$

where $K_{\overline{H_3A}}$ is the overall mass-transfer coefficient of acid-*TOA* complex across the membrane and organic stagnant layer.

In the present system, the contribution of diffusional resistance to the overall process seems comparatively insignificant, since the concentration differences of species between those in the bulk phase and at the interface as shown in Eqs. (3) and (5) are small. Under the conditions investigated, the maximum differences for H_3A, TOA (forward extraction process), and the acid-*TOA* complex (back-extraction process) are 15%, 20%, and 25%, respectively, based on the bulk phase concentration.

Figure 6 reveals first-order dependence of the reaction rate on the concentration of acid-*TOA* complex. Moreover, Figure 7 shows that the slopes of the lines are one for the effect of free *TOA* concentration. The dependence of the reverse reaction rate and the concentration of citric acid in the aqueous phase is shown in **Fig. 8**. It is found that the rates of reverse reaction are almost unaffected under the conditions investigated.The initial rates of complex dissociation can thus be expressed as

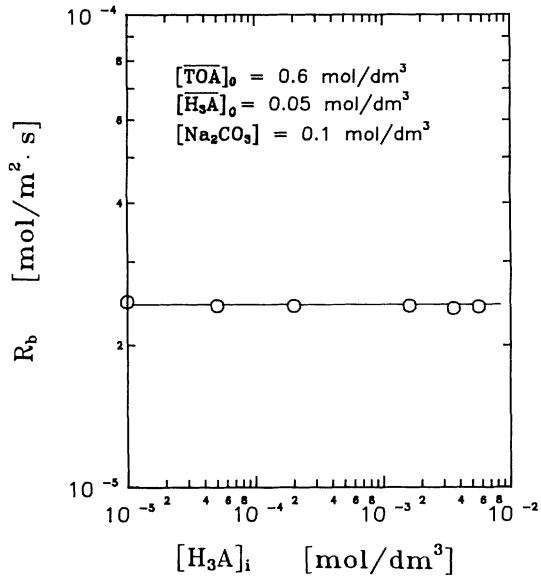


Fig. 8 Effect of citric acid concentration in the aqueous phase on the rate of backward reaction at 298 K. Strip phase: $[Na_2CO_3] = 0.1$ mol/dm³

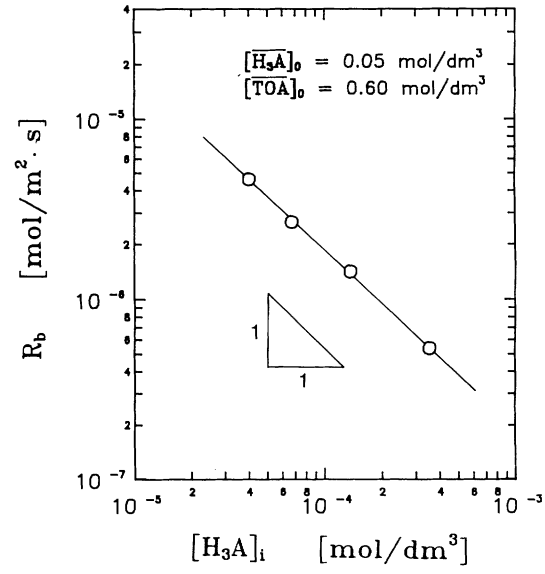


Fig. 9 Effect of citric acid concentration in the aqueous phase on the rate of backward reaction at 298 K. Strip phase: deionized water

$$R_b = k_b [\overline{TOA}]^{-1} [\overline{H_3A}] \quad (6)$$

The rate constant k_b is found to be $(3.90 \pm 0.60) \times 10^{-4}$ (mol/m²·s) at 298 K.

2.4 Proposed reaction mechanism

According to our previous study[9], the stoichiometry of citric acid extraction with TOA dissolved in xylene can be expressesd by

$$pH_3A + q\,\overline{TOA} \Leftrightarrow \overline{(H_3A)_p (TOA)_q};\ K_{pq} \quad (7)$$

The extraction equilibrium constant, K_{pq}, of Eq. (7) is given by

$$K_{pq} = \frac{[\overline{(H_3A)_p (TOA)_q}]}{[H_3A]^p [\overline{TOA}]^q} \quad (8)$$

The best-fit formulations for the acid-*TOA* complex (p, q) are obtained as (1, 1), (1, 2), and (2, 3). The calculated equilibrium constants are $K_{11} = 0.68$ dm³/mol, $K_{12} = 1.68$ (dm³/mol)², and $K_{23} = 4.15 \times 10^2$ (dm³/mol)⁴, respectively, at 298 K. Over the ranges investigated, the mole fraction of (1, 2) complex is always less than 0.2. With increasing $[H_3A]_0$, the mole fraction gradually decreases for (1, 1) complex but gradually increases for (2, 3) complex. For the whole $[H_3A]_0$ range considered, the (1, 1) complex dominates for $[\overline{TOA}]_0 < 0.1$ mol/dm³ and the (2, 3) complex becomes dominant at higher $[\overline{TOA}]_0$.

On the basis of experimental results of extraction equilibrium and kinetics, the following reaction mechanism is proposed. As the aqueous pH is far less than the first dissociation constant of citric acid ($pK_{a1} = 3.13$), we have:

$$H_3A \Leftrightarrow \overline{H_3A};\ K_1\ (fast) \quad (9)$$

$$\overline{H_3A} + \overline{TOA} \Leftrightarrow \overline{(H_3A)(TOA)};\ K_2\ (fast) \quad (10)$$

$$\overline{(H_3A)(TOA)} + \overline{TOA} \Leftrightarrow \overline{(H_3A)(TOA)_2};\ K_3 / k_{-3}\ (slow) \quad (11)$$

$$\overline{(H_3A)(TOA)} + \overline{(H_3A)(TOA)_2} \Leftrightarrow \overline{(H_3A)_2(TOA)_3};\ K_4\ (fast) \quad (12)$$

If Eq. (11) is assumed to be rate-controlling and the other three reactions be relatively fast, the rate of forward reaction is given by:

$$R_f = k_3[\overline{(H_3A)(TOA)}][\overline{TOA}] = K_1 K_2 k_3 [H_3A][\overline{TOA}]^2 \quad (13)$$

And, the rate of backward reaction is derived as :

$$R_b = k_{-3}[\overline{(H_3A)(TOA)_2}] = K_1^{-1} K_2^{-1} K_4^{-1} k_{-3} [H_3A]^{-1} [\overline{TOA}]^{-1} [\overline{(H_3A)_2(TOA)_3}] \quad (14)$$

The rate-controlling nature of Eq. (11) is just an assumption in this study that can lead to the consistent rate laws as we shall discuss later. However, indirect evidence could be provided by Tamada and King[20] for investigating the complex stoichiometry of carboxylic acid extraction with Alamine 336 from mass action law analysis and infrared spectroscopic studies. They indicated that intramolecular hydrogen bonding of dicarboxylic acids such as fumaric acid impedes the formation of (1, 2) and (2, 2) complexes and the like. This is expected to be more obvious for citric acid, a tricraboxylic acid, in the course of Eq.(11)

Evidently, the derived forward rate equation (Eq. 13) agrees with the experimental one (Eq. 4); however, the derived backward rate equation (Eq.14) is somewhat different from the observed one (Eq. 6), that is, for the order with respect to citric acid in the aqueous phase. The experimental results (Eq. 6) showing that the backward reaction rate is independent of $[H_3A]$ when the strip phase is 0.1 mol/dm³ Na_2CO_3 (pH = 11.36 at 298 K) may be explained as follows. When the acid-TOA complex diffuses and reaches the strip-organic interface, the following reaction occurs immediately :

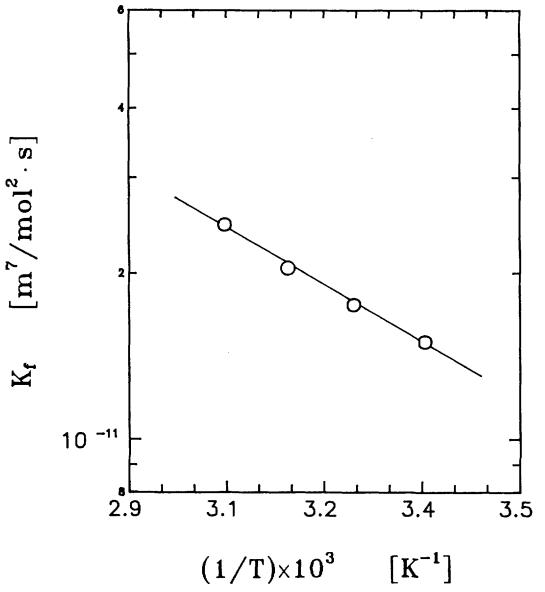


Fig. 10 Dependence of forward rate constant on temperature. $[H_3A]_0 = 0.1$ mol/dm^3, $[\overline{TOA}]_0 = 0.2$ mol/dm^3

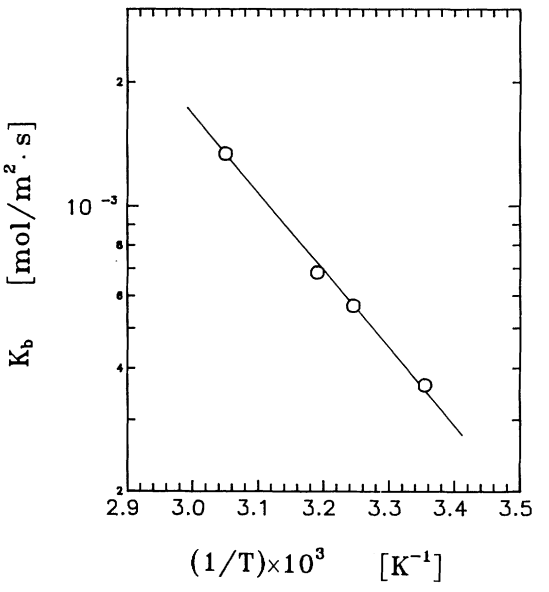


Fig. 11 Dependence of backward rate constant on temperature. Organic phase: $[\overline{H_3A}]_0 = 0.05$ mol/dm^3, $[\overline{TOA}]_0 = 0.6$ mol/dm^3; strip phase: $[Na_2CO_3] = 0.1$ mol/dm^3

$$Na^+ + H_3A \Leftrightarrow NaA^{2-} + 3H^+;\ \beta_1 \qquad (15)$$

The equilibrium constant β_1 is reported to be 1.29×10^{-13} (mol/dm^3)^2 at zero ionic strength and 298 K[14]. In this instance, it is expected that the concentration of the undissociated acid, $[H_3A]$, at the interface on the strip side and in the bulk strip phase will be small, and even zero.

It is worth noting that the mass-action constant, (k_f/k_b), is calculated to be 39.5 (dm^3/mol)^3 at 298 K from Eqs. (4) and (6), which lies reasonably between the equilibrium constants K_{12} of 1.68 (dm^3/mol)^2 and K_{23} of 4.15 $\times 10^2$ (dm^3/mol)^4. To verify the accuracy of the derived rate law by Eq. (14), several more back-extraction runs were performed, in which the strip phase was deionized water. These results are shown in **Fig. 9**, which indicates an inverse first-order dependence on the concentration of citric acid in the aqueous phase. In this case, the orders with respect to the acid-TOA complex and free TOA in the organic phase are experimentally found to be unchanged (not shown). Thus, the rate law is given by

$$R_b = k'_b [H_3A]^{-1} [\overline{TOA}]^{-1} [\overline{H_3A}] \qquad (16)$$

The rate constant k'_b is obtained as $(2.12 \pm 0.10) \times 10^{-6}$ (mol^2/m^5·s) at 298 K.

An apparently puzzling thing about the rate law by Eq. (16) is that it seems to predict $R_b = \infty$ at the start of the backward reaction when $[H_3A] = 0$. Actually, Eq. (16) is not valid at the start of the reaction. In deriving Eq. (14) from the mechanism, we use the equilibrium expression by Eq. (12). Thus, Eq. (14) or Eq. (16) is valid only after the equilibrium by Eq. (12) has been established. Since this equilibrium is rapidly established compared with the rate-controlling step, any deviation of the rate from Eq. (16) during the first few instants of the reaction will have no significant effect on the observed kinetics.

As clearly shown in Figs. 8 and 9, the initial rate of back-extraction is practically comparable when the strip phase is either 0.1 mol/dm^3 Na_2CO_3 (2.47×10^{-5} mol/m^2·s) or pure water (1.81×10^{-5} mol/m^2·s). However, the rate of backward reaction abruptly decreses for the latter system as long as citric acid is transfered to the strip phase. In this regard, Na_2CO_3 solution would be preferred.

In fact, different rate laws have been reported for the extraction of citric acid from aqueous solution with trialkyamine (TAA) in oleic acid and butyl acetate using a single drop method[24, 25]. The rates of forward extraction and back-extraction by distilled water are as follows :

$$R_f = k_f [H_3A]^{1/2} [\overline{TAA}] [\overline{oleic\ acid}] \qquad (17)$$

$$R_b = k_b [\overline{H_3A}]^{0.6234} [\overline{TAA}]^{0.8006} [\overline{oleic\ acid}]^{1.898} [\overline{butyl\ acetate}]^{-0.4749} \qquad (18)$$

Obviously, the two rate laws Eqs. 17 and 18 are significantly different from the results obtained in the present work (Eqs. 4 and 16). Such discrepancies may partly be attributed to the presence of additives such as butyl acetate and oleic acid, and partly due to the different contacting device in their work (a single drop column) in which mass-transfer resistance cannot be completely eliminated[7].

2.5 Effect of temperature on the extraction kinetics

Figures 10 and **11** show the effect of temperature on the rates of forward and backward reactions with 0.1 mol/dm^3 Na_2CO_3, respectively. According to Arrhenius law, the preexponential factor and activation energy are found to be 2.46×10^{-9} m^7/ (mol^2·s) and 12.69 kJ/mol, respectively, for the forward reaction, and 6.08×10^2 mol/ (m^2·s) and 35.57 kJ/mol, respectively, for the backward reaction. It should be noted that here, the variation of equilibrium properties, solubility, etc. for each component with

temperature is not considered in evaluating these activation energies.

Evidently, the activation energy for backward reaction is significantly larger than that for forward reaction. These behaviors agree with the quilibium results, that is, forward extraction is favored at low temperature and back-extraction is favored at relatively high temperature[2, 9, 18, 21]. The difference between the above two energies gives an enthalpy of reaction -22.88 kJ/mol, which also lise between those of ΔH_{12} = -35.49 and of ΔH_{23} = -17.39 kJ/mol obtained from equilibrium study[9], as also seen above for the mass-action constant (k_f/k_b).

With regard to the extraction of citric acid with trialkylamine in oleic acid and butyl acetate, the activation energies for forward and backward reactions with distilled water habe also been reported to be 10.84 and 19.88 kJ/mol, respectively[24, 25]. Evidently, a larger activation energy for backward reaction obtained in this study implies that 0.1 mol/dm^3 Na_2CO_3 is more suitable than distilled water to strip citric acid from the organic phase by temperature-swing technique[10, 12, 23].

It is recognized that chemical reaction occurring in the extraction processes, in general, has an activation energy greater than about 42~84 kJ/mol; on the other hand, a process with low activation energy is not necessarily classified to be diffusion-controlled[24]. For example, for the present system both forward extraction and back-extraction processes are proved to be mainly chemical reaction-controlled.

Conclusions

Kinetic studies have been carried out for the extraction of citric acid from aqueous media with xylene solutions of TOA using a stirred membrane-based cell in the temperature range of 298~328 K. The following results are obtained.

(1) For the extraction of citric acid with TOA, an attempt is made to estimate the interfacial concentrations of species and to correlate them with the rate data. Under the conditions studied, the contribution of diffusional resistance to the overall process is comparatively small; that is, the extraction process is mainly controlled by chemical reactions occurring at the interface on the organic side.

(2) The rate for the formation of acid-TOA complexes can be given as Eq. (4), whereas the rate for the dissociation is expressed by either Eq. (6) or Eq. (16), depending on the strip phase used. The activation energies for forward reaction and backward reaction with 0.1 mol/dm^3 Na_2CO_3 are obtained to be 12.69 and 35.57 kJ/mol, respectively, which reasonably agree with the literature results.

(3) On the basis of the proposed reaction mechanism, the formation and dissociation of the 1:2 acid-TOA complex, $\overline{(H_3A)(TOA)_2}$, according to Eq. (11), is rate-controlling. The derived rate laws are consistent with the experimental results.

Acknowledgments

This work was supported by the ROC National Science Council under Grant No. NSC84-2214-E155-001, which is greatly appreciated.

Nomenclature

D_j	=	diffusivity of species j in bulk liquid phase	[m^2/s]
H_3A	=	citric acid	
K	=	overall mass-transfer coefficient	[m/s]
k	=	individual mass-transfer coefficient	[m/s]
k_b	=	backward reaction rate constant defined in Eq. (6)	[mol/(m^2·s)]
k_f	=	forward reaction rate constant defined in Eq. (4)	[m^7/mol^2·s)]
K_{pq}	=	extraction equilibrium constant defined in Eq. (8)	[dm^3/mol)$^{p+q-1}$]
R_b	=	initial rate of backward reaction defined in Eq. (2)	[mol/(m^2·s)]
R_f	=	initial rate of forward reaction defined in Eq. (1)	[mol/(m^2·s)]
S	=	membrane cross-section area	[m^2]
t	=	time	[s]
T	=	temperature	[K]
TOA	=	tri-n-octylamine	
V	=	volume	[m^3]
[ ]	=	molar concentration of species in the brackets	[mol/dm^3]

<Subscripts>

a = aqueous phase
b = bulk phase
i = adjacent to the aqueous-organic (membrane) interface
m = membrane phase
o = organic phase
0 = initial

<Superscript>

($\overline{overbar}$) = species in the organic (membrane) phase

Literature Cited

1) Basu, R. and K. K. Sirkar: *Solvent Extr. Ion Exch.*, **10**, 119-143 (1992)
2) Bizek, V., J. Horacek, R. Rericha and M. Kousova: *Ind. Eng. Chem. Res.*, **31**, 1554-1562 (1992)
3) Bizek, V., J. Horacek, M. Kousova, A. Heyberger and J. Prochazka: *Chem. Eng. Sci.*, **47**, 1433-1440 (1992)
4) Bizek, V., J. Horacek and M. Kousova: *Chem. Eng. Sci.*, **48**, 1447-1457 (1993)
5) Bohrer, M. P.: *Ind. Eng. Chem. Fundam.*, **22**, 72-78 (1983)
6) Haensel, R., W. Halwachs and K. Schugerl: *Chem. Eng. Sci.*, **41**, 135-141 (1986)
7) Hanna, G. J. and R. D. Noble: *Chem. Rev.*, **85**, 583-598 (1985)
8) Juang, R. S. and R. H. Lo: *Ind. Eng. Chem. Res.*, **33**, 1001-1010 (1994)
9) Juang, R. S. and W. T. Huang: *J. Chem. Eng. Jpn.*, **27**, 498-504 (1994)
10) Kertest, A. S. and C. J. King: *Biotechnol. Bioeng.*, **28**, 269-282 (1986)
11) Kiani, A., R. R. Bhave and K. K. Sirkar: *J. Membr. Sci.*, **20**, 125-145 (1984)
12) King, C. J.: *Chemtech*, **22**, 285-291 (1992)
13) Levich, V. G.: "Physicochemical Hydrodynamics", 2nd ed., p. 60-72, Prentice-Hall, Englewood Cliffs, NJ (1962)
14) Morel, F. M. M.: "Principles of Aquatic Chemistry", p. 242-249, Wiley-Interscience, New York (1983)
15) Playne, M. J. and B. R. Smith: *Biotech. Bioeng.*, **25**, 1251-1265 (1983)
16) Prochazka, J., A. Heyberger, V. Bizek, Kousova and E. Volaufova; *Ind Eng. Chem. Res*, **33**, 1565-1573 (1994)
17) Reid, R. C., J. M. Prausnitz and B. E. Poling: "The Properties of Geses and Liquids", 4th ed., p. 52-55 & p.598-606, McGraw-Hill, New York (1987)

18) Sato, T., H. Watanabe and H. Nakamura: *Bunseki Kagaku*, **34**, 559-563 (1985)
19) Schlichting, E., W. Halwachs and K. Schugerl: *Chem. Eng. Comm.*, **51**, 193-205 (1987)
20) Tamada, J. A. and C. J. King: *Ind. Eng. Chem. Res.*, **29**, 1327-1333 (1990)
21) Tamada, J. A. and C. J. King: *Ind. Eng. Chem. Res.*, **29**, 1333-1338 (1990)
22) Vanura, P. and L. Kuca: *Collect. Czech. Commun.*, **41**, 2857-2877 (1976)
23) Wennersten, R.: *J. Chem. Tech. Biotechnol.*, **33B**, 85-94 (1983)
24) Zhou, C. R. and X. Zhong: *Huaxue Fenying Gongchen Yu Gongyi*, **7**, 46-51 (1991)
25) Zhou, C. R. and X. Zhoug: *Huaxue Fenying Gongchen Yu Gongyi*, **9**, 84-89 (1993)