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Modeling of Amine-Facilitated Liquid Membrane Transport of Binary Organic Acids

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ABSTRACT

The transport rates of lactic and citric acids from binary solutions across supported liquid membranes containing tri-*n*-ocytylamine are measured. A mass transfer model is proposed which considers aqueous film diffusion, interfacial chemical reaction, and membrane diffusion. It is shown that the difference between the measured and modeled rates was more significant at high total acid and amine concentrations. This could be partly due to the ignorance of mutual interactions between the acids in the aqueous phase and the complexes in the membrane phase in this model (chemical effect), and to limited validity of "fixed" transport properties over a rather wide concentration range (mechanical effect).

Key Words. Mass transfer modeling; Supported liquid membrane; Tri-*n*-octylamine; Citric acid; Lactic acid

INTRODUCTION

The amine-based extraction process has been found to be a prospective alternative to conventional calcium salt precipitation procedures for recovering organic acids from aqueous streams (1, 2). The liquid membrane is a promising technology for this purpose because it combines extraction and stripping processes in one unit (3–5). A supported liquid membrane (SLM)

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which uses a porous membrane support impregnated with complexing carriers to separate the feed and strip phases represents one of the feasible types of liquid membranes (3, 4).

Although much experimental work was done on the recovery and separation of organic acids from single-acid solutions (6–11) and multi-acid mixtures (12–15) using amine-based liquid membranes, there have been few studies on mass transfer modeling, especially for multi-acid systems. For example, Sirman et al. (12) separated citric acid and lactic acid by SLMs containing Alamine 336 (a tertiary amine) and qualitatively indicated that membrane diffusion and reaction at the feed–membrane interface play an important role in the transport mechanism when the two acids compete for extraction. Also, Reisinger and Marr (15) separated organic acids from fermentation broths by a liquid surfactant membrane, another type of liquid membrane, containing Amberlite LA-2 (a secondary amine). They found from experiments that monocarboxylic acids such as lactic acid can be separated.

The chemistry involved in SLM transport is essentially the same as that involved in solvent extraction, but the overall process is governed by kinetic rather than equilibrium properties (16). Thus, a good knowledge of transport properties of the relevant geometry (mass-transfer coefficients) and chemistry of solvent extraction (mainly, kinetics) allow the SLM transport of single solutes to be modeled (7, 16, 17). The aim of this paper is to compare the measured and predicted rates of binary lactic and citric acids across SLMs containing tri-*n*-octylamine (TOA). The proposed model involves all possible transport resistances but ignores mutual interactions between the two acids in the aqueous phase and the complexes in the membrane phase. Experiments were carried out as a function of the total concentration of the acids and their concentration ratio in the feed phase.

MODELING OF THE TRANSPORT RATE

Chemistry of Solvent Extraction

The extraction of single organic acid (HA) from aqueous solutions with tertiary amines such as TOA can be expressed by the following stoichiometric reaction (18, 19):

$$p\text{HA} + q\overline{\text{TOA}} \Leftrightarrow \overline{(\text{HA})_p(\text{TOA})_q}; \qquad K_{pq} \tag{1}$$

where the overbar refers to the organic phase and HA is citric acid (HC) or lactic acid (HL). Although citric acid is a tricarboxylic acid, the symbol is acceptable because here the pH is far less than its pK_{a2} (= 4.76). The equilibrium constant K_{pq} is given by

$$K_{pq} = [\overline{(\text{HA})_p(\text{TOA})_q}]/[\text{HA}]^p[\overline{\text{TOA}}]^q \tag{2}$$

In xylene, the HC–TOA complexes have the compositions (p,q) of (1,1), (1,2), and (2,3). The values of K_{pq} are $K_{11} = 4.1 \times 10^{-4}$ m^3/mol, $K_{12} = 1.43 \times 10^{-6}$ (m^3/mol)^2, and $K_{23} = 3.79 \times 10^{-10}$ (m^3/mol)^4 at 303 K (18). On the other hand, the compositions of HL–TOA complexes are (1,1), (1,2), and (3,1). The equilibrium constants are $K_{11} = 3.41 \times 10^{-4}$ m^3/mol, $K_{12} = 3.18 \times 10^{-8}$ (m^3/mol)^2, and $K_{31} = 5.48 \times 10^{-10}$ (m^3/mol)^3 at 303 K (19).

It is expected that the complex formation between the acids and TOA occur near the interface on the organic side (20) since the solubilities of TOA and xylene in water are only 0.0012 and 0.19 dm^3/m^3, respectively (21). The kinetics of extraction and backextraction of single lactic and citric acids with TOA in xylene were separately studied using a membrane-based cell. Rate equations for formation and dissociation of the HC–TOA complexes, R_1 and R_{-1}, between water and xylene solutions are given by (22)

$$R_1 = k_1[\mathrm{HC}][\overline{\mathrm{TOA}}]^2 \tag{3}$$

$$R_{-1} = k_{-1}[\mathrm{HC}]^{-1}[\overline{\mathrm{TOA}}]^{-1}[\overline{\mathrm{HC}}] \tag{4}$$

where k_1 was 1.67×10^{-11} m^7/(mol^2·s) and k_{-1} was 3.73×10^{-4} mol^2/(m^5·s) at 303 K. However, the rate equation for dissociation of the HC–TOA complexes between 100 mol/m^3 Na_2CO_3 and xylene solutions became (22)

$$R_{-1} = k_{-1}[\overline{\mathrm{TOA}}]^{-1}[\overline{\mathrm{HC}}] \tag{5}$$

where k_{-1} was 4.90×10^{-4} mol/(m^2·s) at 303 K.

On the other hand, rate equations for the formation and dissociation of HL–TOA complexes between water and xylene solutions can be expressed as (23)

$$R_1 = k_1[\mathrm{HL}][\overline{\mathrm{TOA}}] \tag{6}$$

$$R_{-1} = k_{-1}[\overline{\mathrm{TOA}}]^{-2}[\overline{\mathrm{HL}}]^2 \tag{7}$$

where k_1 was 5.86×10^{-9} m^4/(mol·s) and k_{-1} was 3.50×10^{-2} mol/(m^2·s) at 303 K. If the aqueous solution contained 100 mol/m^3 Na_2CO_3, the rate equation had the same forms as Eqs. (6) and (7) but k_{-1} became 8.55×10^{-2} mol/(m^2·s) at 303 K (23).

Transport Model in SLM

The concentration profiles of species for the transport of binary acids in a TOA–SLM are shown in Fig. 1. In the present model the transfer steps considered include aqueous film diffusion, membrane diffusion, and interfacial chemical reactions, but the mutual interactions between the acids in the aqueous phase or the complexes in the membrane phase are ignored. If the diffusion

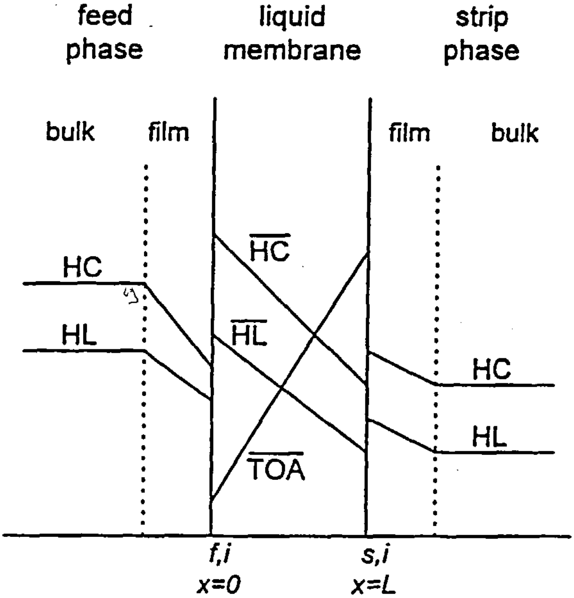

FIG. 1 Concentration profiles of species in the transport of citric and lactic acids across an SLM containing TOA.

processes can be described by Fick's equation, the transport rates of these steps are given as follows (taking the strip phase of Na_2CO_3 as an example).

1–2. Diffusion of the acids in the feed phase toward the membrane:

$$J_1 = k_{HC,f}([HC]_f - [HC]_{f,i}) \tag{8}$$

$$J_2 = k_{HL,f}([HL]_f - [HL]_{f,i}) \tag{9}$$

3–4. Formation of the complexes at the feed–membrane interface:

$$J_3 = (R_1 - R_{-1})_{f,i} \quad \text{for citric acid (Eqs. 3 and 4)} \tag{10}$$

$$J_4 = (R_1 - R_{-1})_{f,i} \quad \text{for lactic acid (Eqs. 6 and 7)} \tag{11}$$

5–7. Diffusion of TOA and the acid complexes through the liquid membrane:

$$J_5 = k_{HC,m}([\overline{HC}]_{f,i} - [\overline{HC}]_{s,i}) \tag{12}$$

$$J_6 = k_{HL,m}([\overline{HL}]_{f,i} - [\overline{HL}]_{s,i}) \tag{13}$$

$$J_7 = k_{TOA,m}([\overline{TOA}]_{s,i} - [\overline{TOA}]_{f,i}) \tag{14}$$

where $\overline{HA}$ represents the acid-TOA complexes for simplicity.

8–9. Dissociation of the complexes at the membrane–strip interface:

$$J_8 = (R_{-1} - R_1)_{s,i} \qquad \text{for citric acid (Eqs. 3 and 5)} \tag{15}$$

$$J_9 = (R_{-1} - R_1)_{s,i} \qquad \text{for lactic acid (Eqs. 6 and 7)} \tag{16}$$

10–11. Diffusion of the acids in the strip phase outside the membrane:

$$J_{10} = k_{\mathrm{HC,s}}([\mathrm{HC}]_{s,i} - [\mathrm{HC}]_s) \tag{17}$$

$$J_{11} = k_{\mathrm{HL,s}}([\mathrm{HL}]_{s,i} - [\mathrm{HL}]_s) \tag{18}$$

Because the solubility of TOA in the aqueous phase is negligibly small (8, 20), the total amount of TOA in the membrane phase is kept constant.

$$[\overline{\mathrm{TOA}}]_0 = (1/\delta) \int_0^\delta ([\overline{\mathrm{TOA}}] + (5/4)[\overline{\mathrm{HC}}] + [\overline{\mathrm{HL}}])dx \tag{19}$$

The stoichiometric ratios 5/4 for HC and 1 for HL in Eq. (19) are found from extraction equilibrium results (18, 19). If the concentration profiles of the species in the membrane phase are linear, we have

$$[\overline{\mathrm{TOA}}]_0 = (1/2)([\overline{\mathrm{TOA}}]_{f,i} + [\overline{\mathrm{TOA}}]_{s,i}) + (5/8)([\overline{\mathrm{HC}}]_{f,i} + [\overline{\mathrm{HC}}]_{s,i}) + (1/2)([\overline{\mathrm{HL}}]_{f,i} + [\overline{\mathrm{HL}}]_{s,i}) \tag{20}$$

Since counterdiffusion of TOA and its complexes occurs in the membrane phase, the continuity of the total flux of TOA is held.

$$(5/4)J_5 + J_6 = J_7 \tag{21}$$

Furthermore, at steady state the following equalities hold:

$$J_1 = J_3 = J_5 = J_8 = J_{10} = J_{\mathrm{HC}} \tag{22}$$

$$J_2 = J_4 = J_6 = J_9 = J_{11} = J_{\mathrm{HL}} \tag{23}$$

Provided that the mass-transfer coefficients and rate constants in Eqs. (8)–(18) are known, we can calculate the transport rates, J_{HC} and J_{HL}, by solving the system of Eqs. (8)–(18) with the additional conditions of Eqs. (20)–(23) using a trial-and-error method.

EXPERIMENTAL

Apparatus, Membrane, and Solutions

The cell used in this work was identical to that employed earlier (7). Two chambers were stirred at the same rate (300 rpm) but in opposite directions. This stirring strength was sufficient to keep the aqueous-film thickness minimum. The entire cell was immersed in a thermostat at 303 K. The hydrophobic

PVDF microporous membrane (Millipore, GVHP) had a mean thickness of 125 μm, an average pore size of 0.22 μm, and a typical porosity of 75%.

The water used was deionized by a Millipore Milli-Q system. TOA was a product of Tokyo Chemical Industry Co., Ltd., Japan. It had a purity of about 98.5% and was used as received. Xylene, lactic acid, citric acid, and other inorganic chemicals were supplied by Merck Co. as analytical reagent grade. The membrane phase was prepared by diluting TOA with xylene and presaturating with acid-free aqueous phase. The pores in the membrane support were filled with TOA under vacuum as reported previously (7), and the resulting liquid membranes were immersed in the membrane phase before use.

The feed phase was prepared by dissolving acids in water without pH adjustment. The strip phase was either water or 100 mol/m^3 Na_2CO_3. All aqueous phases were presaturated with xylene. The initial concentrations of total acids in the feed phase and of TOA in the membrane phase ranged from 100 to 500 and from 100 to 400 mol/m^3, respectively.

Procedure

The membrane soaked with TOA was clamped and the apparatus was assembled. The feed and strip phases (255 cm^3 each) were introduced into the lower and upper chambers, respectively, and the mixing was started. When steady state was reached (about 30 minutes), samples (3 cm^3) were taken from the strip phase at preset time intervals. The concentrations of the acids were determined by HPLC (Jasco, Japan) with a UV detector at 210 nm. A Hamilton ion exclusion column PRP-X300 (7 μm) for organic acid analysis was used; it has a pore size of 10 nm and an exchange capacity of 0.17 meq/g. The mobile phase was 1 mol/m^3 H_2SO_4. Each experiment was duplicated under identical conditions.

RESULTS AND DISCUSSION

Determination of Transport Parameters

For a hydrophobic microporous membrane separating organic and aqueous phases, the individual mass transfer coefficients in the aqueous, organic, and membrane phases, k_a, k_o, and k_m, respectively, can be obtained from flux measurements of one hydrophilic (e.g., acetic acid) and one hydrophobic solutes (e.g., iodine) (24). Because lactic and citric acids are essentially more soluble in water than xylene (18, 19), the value of k_a for HA in the feed phase, $k_{HA,f}$, can be determined in that way from diffusion experiments using the same stirred cell and membrane support (16). The results are listed in

TABLE 1
Values of Parameters Used for the Calculation of Transport Rates at 303 K

Parameter	Citric acid system	Lactic acid system	Reference
Equilibrium constant:			
K_{11}	4.10×10^{-4} m^3/mol	3.41×10^{-4} m^3/mol	18, 19
K_{12}	1.43×10^{-6} (m^3/mol)^2	3.18×10^{-8} (m^3/mol)^2	18, 19
K_{23}	3.79×10^{-10} (m^3/mol)^4		18, 19
K_{31}		5.48×10^{-10} (m^3/mol)^3	18, 19
Rate constant:			
k_1	1.67×10^{-11} m^7/(mol^2·s)	5.89×10^{-9} m^4/(mol^2·s)	22, 23
k_{-1} (water)	3.73×10^{-4} mol^2/(m^5·s)	3.50×10^{-2} mol/(m^2·s)	22, 23
k_{-1} (Na_2CO_3)	4.90×10^{-4} mol/(m^2·s)	8.55×10^{-2} mol/(m^2·s)	22, 23
Mass transfer coefficient:			
$k_{HA,f}$, $k_{HA,s}$	4.08×10^{-5} m/s	6.54×10^{-5} m/s	This work
$k_{HA,m}$	2.05×10^{-6} m/s	2.76×10^{-6} m/s	This work
$k_{TOA,m}$	2.90×10^{-6} m/s	2.90×10^{-6} m/s	This work

Table 1, where the values of k_a in the stripping phase $k_{HA,s}$ are assumed to equal $k_{HA,f}$.

Due to the ease of analysis, mass transfer coefficients of the acid–TOA complexes, rather than TOA itself, in the membrane phase k_m were separately measured in this work. The fluxes were obtained using the same cell, where the complex was transported from a preloaded organic phase (complex concentration 25–40 mol/m^3) through the same membrane support to a fresh organic phase, in which the concentration of the complex was analyzed by HPLC after the acid was completely stripped with 100 mol/m^3 Na_2CO_3. Due to the lack of organic–aqueous interface, k_m is obtained from slope of the plot of concentration versus time which equals $1/[(1/k_m) + (2/k_o)]$. The individual mass transfer coefficients of the complexes in the organic layer k_o are estimated as below.

Here, the values of k_o and k_m for TOA, and of k_o for the complexes, are estimated from k_a for HA and k_m for the complexes based on the relationships that $k_m \propto D_j$ and k_a (or k_o) $\propto D_j^{2/3}\gamma^{-1/6}$, where γ is the kinematic viscosity of the media (25). The estimated results are also listed in Table 1. In this correlation the diffusivities of species D_j are estimated by the Hayduk and Minhas equation (26). The value of γ for xylene at 303 K is 7.67×10^{-7} m^2/s. The molar volumes of xylene, citric acid, and lactic acid at their normal boiling points are found to be 141.9, 202.4, and 98 cm^3/mol, respectively, by the Tyn and Calus method (26). Also, the parachors for xylene, citric acid, lactic acid, TOA, and the citric acid–TOA and lactic acid–TOA complexes are estimated to be 285.1, 340.2, 183.6, 1024, 2558, and 1713 cm^3·g$^{1/4}$/s$^{1/2}$, respectively, by the method of additive group contributions (26). The parachors of citric and lactic acids in xylene should be doubled since they both exist mainly as dimers (18, 19). It is noticed that $k_{\mathrm{HA,m}}$ and $k_{\mathrm{TOA,m}}$ adopted here are on an average basis and assumed to be constant at whole amine concentrations. This effect will be discussed below.

Comparison of the Calculated and Measured Rates

A typical plot of the variation of the strip-phase concentration of lactic acid with contact time is given in Fig. 2, where the initial feed-phase concentration of citric acid is fixed. It is seen that all data points lie on straight lines passing through the origin. The SLM transport rate is thus obtained according to the following initial-rate technique.

$$J_{\mathrm{HA}} = (V_s/S)(d[\mathrm{HA}]_s/dt)_{t\to 0} \qquad (24)$$

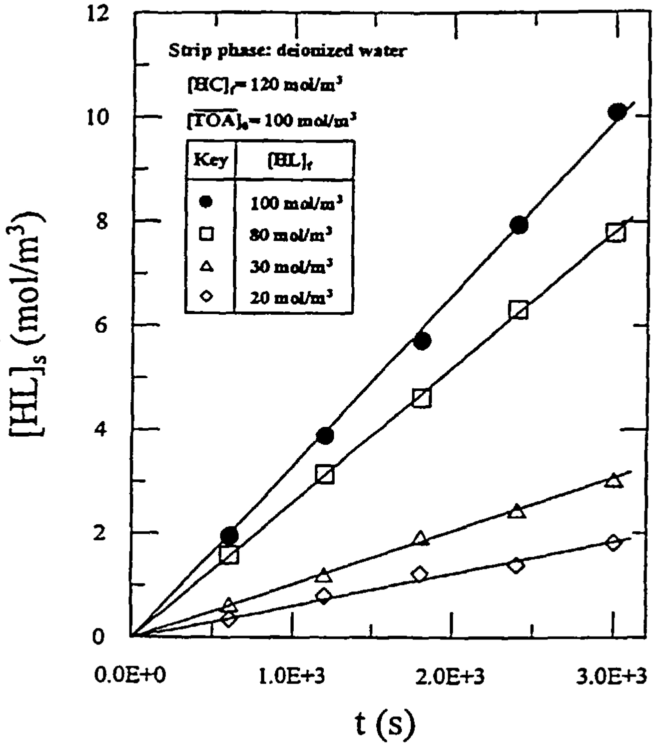

FIG. 2 Variation of strip-phase concentration of lactic acid on contact time.

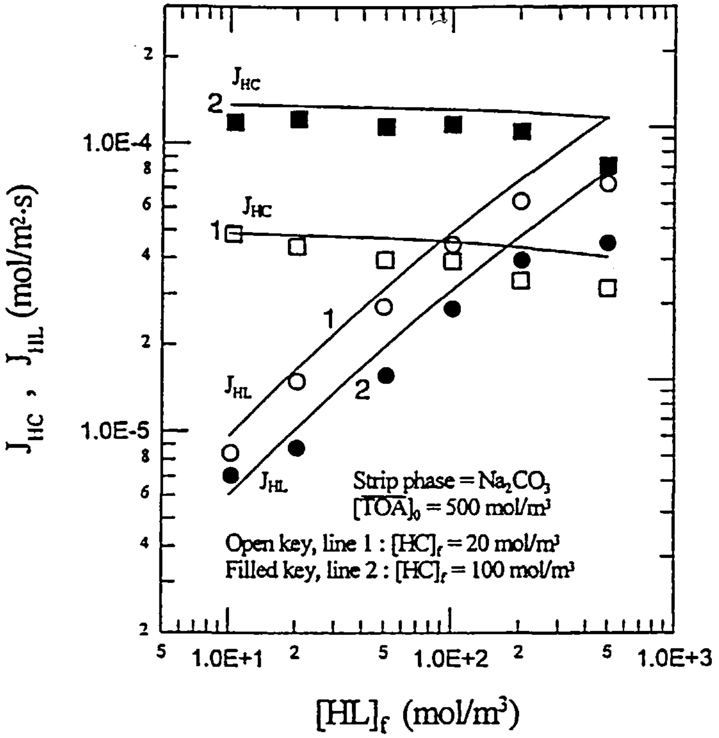

FIG. 3 Comparison of the calculated and measured rates at different initial feed-phase concentrations of lactic acid. Strip phase: 100 mol/m³ Na_2CO_3.

Evidently the "jumping" mechanism, which exists in the transport of Co(II) across an SLM containing about 1800 mol/m³ TOA after a certain period of time (>40 minutes) (27), is not found in the present case. This may be due to a relatively low TOA content, or the short of operation time, or the complicated reaction stoichiometry between the acids and TOA in the membrane phase.

Figures 3–6 show the influences of the initial feed-phase concentration of the acids on the transport rates J_{HA} with 100 mol/m³ Na_2CO_3 and water as a strip phase, respectively, when the initial concentration of one acid is kept constant. It is seen that the transport rate of the acid whose concentration is varied increases with its concentration, but that of the acid whose concentration is fixed reduces. It appears that some extent of interactive effect exists in this binary acid systems. The effects of the initial concentration ratio of the acids in the feed phase on the transport rates are shown in Figs. 7 and 8.

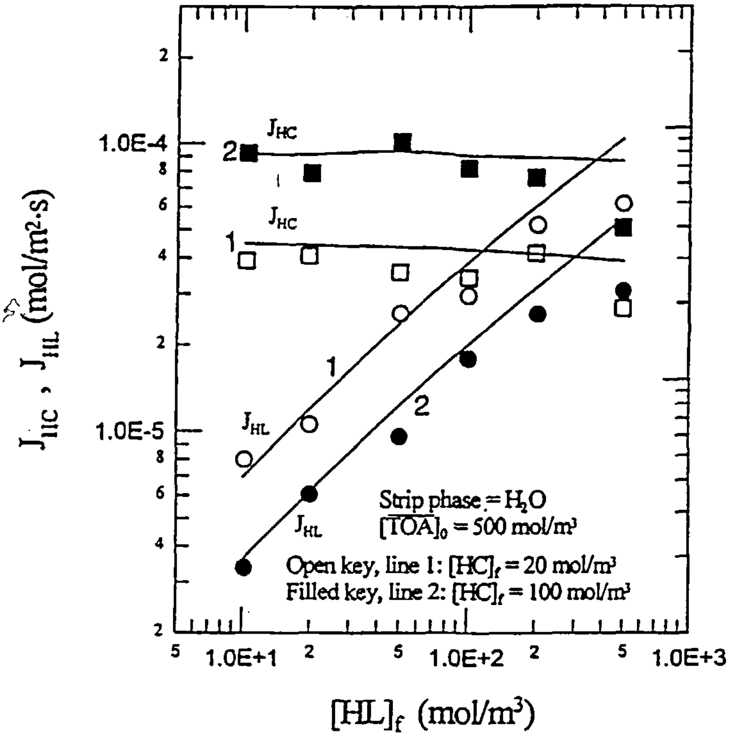

FIG. 4 Comparison of the calculated and measured rates at different initial feed-phase concentrations of lactic acid. Strip phase: deionized water.

It is shown that the transport rates under similar conditions are slightly larger with the use of Na_2CO_3 as a strip phase compared to water (Table 1). The increased transport rate due to the presence of Na_2CO_3 is also explained below. As an organic phase containing the complexes contacts Na_2CO_3, the acids release from the complexes and immediately dissociate to form carboxylate ions via $Na^+ + HA \Leftrightarrow Na^+A^- + H^+$. Thus, the concentration of the undissociated acid, [HA], at the interface and in the bulk phase remains negligibly small, enhancing the transport rate.

The solid curves in Figs. 3–8 were calculated by the present model. Relatively large deviations are generally observed, especially at high concentrations of acids and TOA. The underestimated rates are probably due to oversimplification of the model. First, as indicated above, the membrane-phase mass transfer coefficients k_m for the complexes and TOA carriers are assumed to be concentration-independent for the described ranges. It is recognized that an increase in viscosity of the membrane phase at high concentrations of TOA and the acids, likely due to the aggregation of the acid–TOA complexes, would result in a decrease of $k_{HA,m}$ and $k_{TOA,m}$. In fact, Elhassadi and Do (28) studied the effect of carrier concentration (Alamine 336) on the transport rate. Based on large differences between the viscosity ratios of complexed to uncomplexed carriers calculated from SLM data and measured in the bulk organic phase, they found that the viscosity effect is more pronounced in small membrane pores than in solvent extraction analogy. The previous studies showed that membrane diffusion and chemical reaction at the feed–membrane interface both play an important role in the transport mechanism of single acid systems (7, 29); the effect of the change in k_m appears comparatively significant.

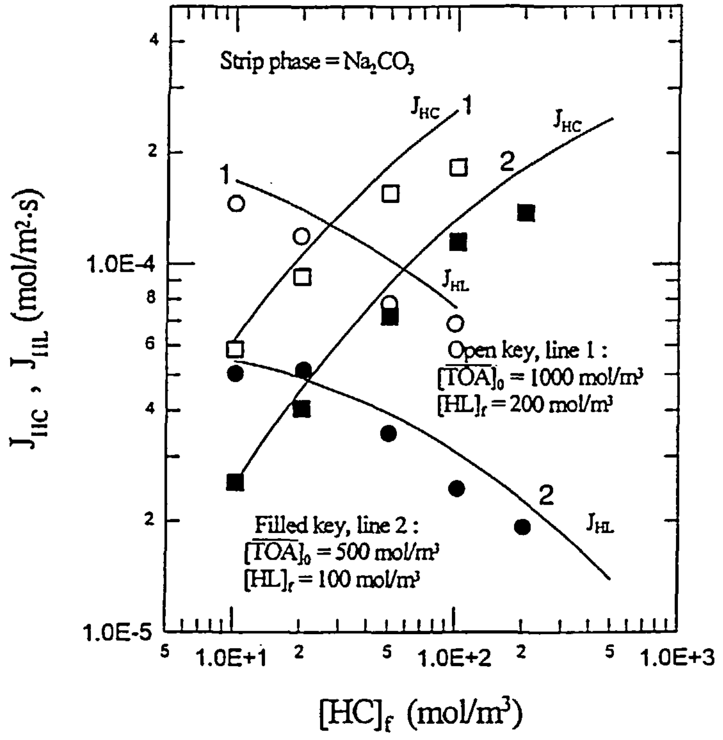

FIG. 5 Comparison of the calculated and measured rates at different initial feed-phase concentrations of citric acid. Strip phase: 100 mol/m³ Na_2CO_3.

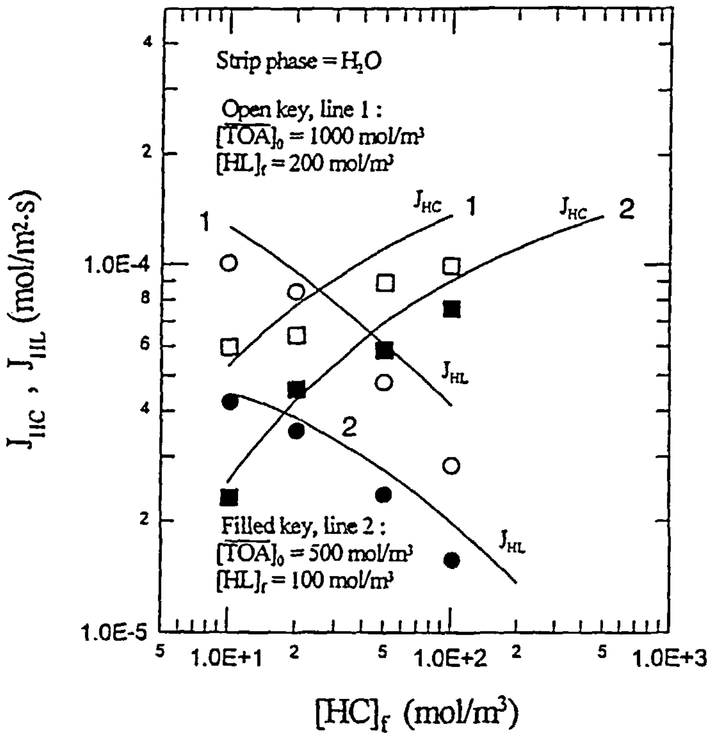

FIG. 6 Comparison of the calculated and measured rates at different initial feed-phase concentrations of citric acid. Strip phase: deionized water.

Second, ignorance of the mutual interactions between acids in the aqueous phase and the complexes in the membrane phase in this model is another possible reason for the underestimated rates. The distribution ratios of solvent extraction of lactic and citric acids in the single and binary systems were measured (29). Compared to single systems, large synergistic effects are obtained in binary systems at an initial concentration ratio α of 1 and 1/4; that is, the distribution ratio of any acid is greatly increased by the addition of the other. At $\alpha = 1/2$ and 1/3, synergistic effects are seen only at high total acid concentration ($>$120 mol/m^3); below that, the distribution of the acid is depressed by the presence of the second acid.

No satisfactory explanation for such a complicated equilibrium behavior can be given at this stage. Because the extraction of organic acids with tertiary amines often involves the formation of ion pairs and hydrogen bonds (30), the decrease in extractability at $\alpha = {}^1/_3 - {}^1/_2$ may be due to primarily intermolecular hydrogen bonding between citric and lactic acids in the aqueous phase. Also, polymerization of the acids or the complexes at these conditions in the organic phase is a logical possibility and may explain the increase in the distribution ratio with increasing total acid concentrations. In fact, the existence of the overloaded (3,1) complex in the single lactic acid system indicates a cyclic arrangement around the amine nitrogen, with the proton associated with the nitrogen atom forming a bond alternately with the two oxygen atoms near it (30). The results obtained in single systems would evidently change due to the presence of the second acid. Detailed equilibrium information of extraction in binary acid systems, including the compositions of adduct complexes, is now being analyzed in our laboratory.

As shown in Figs. 3–6, the presence of citric acid retards the transport of lactic acid, but the presence of lactic acid enhances the transport of citric

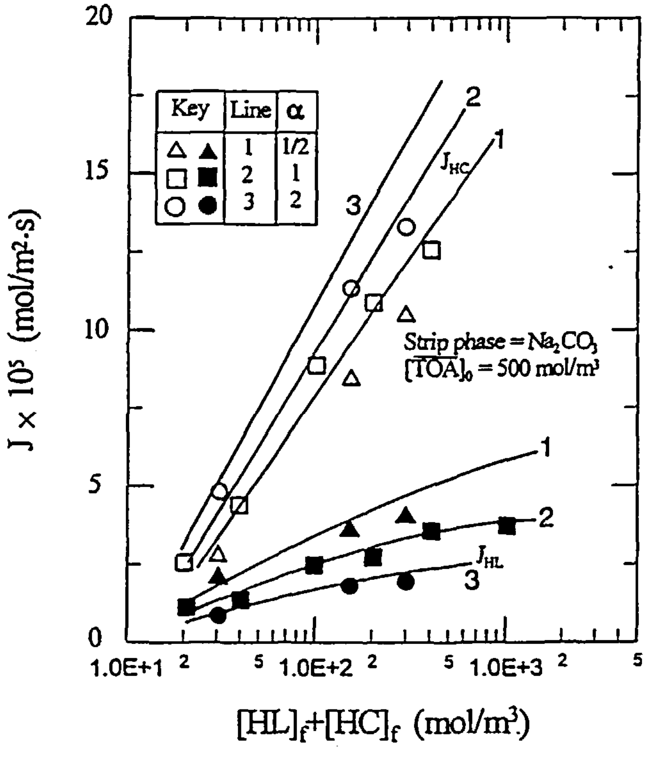

FIG. 7 Comparison of the calculated and measured rates at different concentration ratios of the acids. Strip phase: 100 mol/m^3 Na_2CO_3.

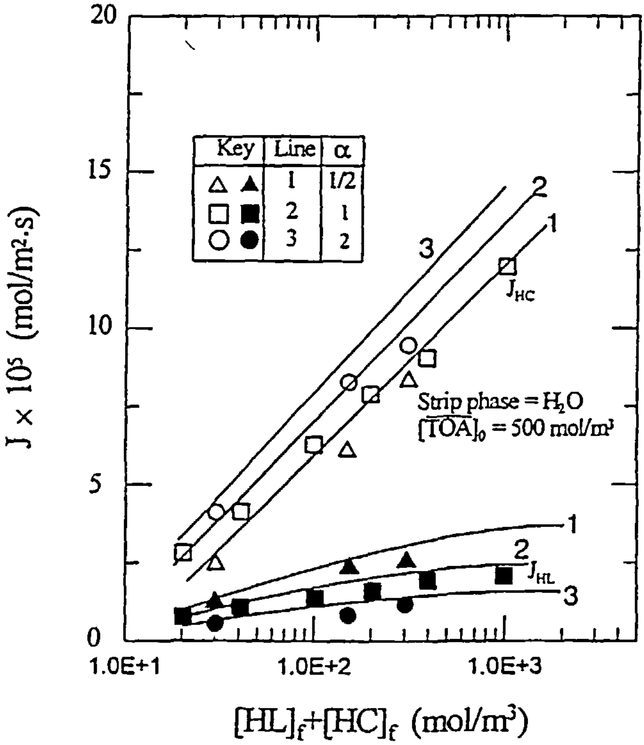

FIG. 8 Comparison of the calculated and measured rates at different concentration ratios of the acids. Strip phase: deionized water.

acid. This is because the acidity of citric acid is stronger (pK_{a1} = 3.13) than that of lactic acid (pK_{a1} = 3.86). It is known that the extraction of organic acids with amine involves formation of intermolecular hydrogen bonds and/or ion pairs (18, 19, 30). The existence of a strong acid would retard dissociation of the weaker acid and reduce the effective concentration of the amine for complexation because the stronger, dissociated acid must compete for the amine. In fact, the addition of a strong acid or base to the feed phase of amine-based SLM processes would lead to a decrease in the transport rate of the weaker acids (11).

CONCLUSIONS

The transport of binary lactic and citric acids by SLMs containing TOA has been experimentally and theoretically studied. When the initial feed concentration of one acid is fixed, the transport rate of the other increases with its concentration, but that of the acid whose concentration is fixed is reduced. This seems that an interactive effect of some extent exists in this binary systems. The transport rates are slightly larger with the use of Na_2CO_3 as a strip phase compared to water under similar conditions. Also, the presence of citric acid retards the transport of lactic acid, but the presence of lactic acid enhances the transport of citric acid. This is because citric acid is a stronger acid than lactic acid. A transport model is presented which takes into account several resistances based on a good knowledge of the chemistry of solvent extraction and the hydrodynamics of stirred cell. Differences between the modeled and measured rates are apparent, especially at high concentrations of the acids and amine. This can be partly due to the limited validity of "fixed" membrane-phase mass transfer coefficients over the whole concentration ranges in the proposed model and to our ignorance of the mutual interactions between the acids in the aqueous phase and the complexes in the membrane phase.

NOMENCLATURE

HC	citric acid
HL	lactic acid
J	transport rate ($mol/m^2 \cdot s$)
k	mass transfer coefficient (m/s)
k_1	reaction rate constant for complex formation
k_{-1}	reaction rate constant for complex dissociation
K_{pq}	extraction equilibrium constant defined in Eq. (2) $(mol/m^3)^{(1-p-q)}$
R_1	rate of complex formation between two immiscible phases ($mol/m^2 \cdot s$)
R_{-1}	rate of complex dissociation between two immiscible phases ($mol/m^2 \cdot s$)
S	membrane cross-sectional area (m^2)
t	time (s)
TOA	tri-*n*-octylamine
V	volume (m^3)
x	distance from the feed–membrane interface (m)
[ ]	molar concentration of species in the brackets (mol/m^3)

Greek Letters

α	initial concentration ratio of citric to lactic acids in the aqueous phase
δ	membrane thickness (m)

Subscripts

f, m, s feed, membrane, and strip phases, respectively
i aqueous–membrane interface
0 initial (total)

Superscript

$\overline{\text{(overbar)}}$ species in membrane or organic phase

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