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Characteristics of Lactic Acid Transport in Supported Liquid Membranes

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ABSTRACT

Transport of lactic acid in supported liquid membranes containing tertiary amines (Alamine 336, Henkel Corp.) as the carrier was investigated. Both equilibrium extraction constants (K_t) and effective diffusion coefficients (D) of the acid–amine complex were measured for systems with various diluents. Larger K_t values and, thus, more efficient extraction were found when diluents were used, especially with oleyl alcohol which improved the polarity of the oil membrane and led to an approximately sixtyfold increase in the K_t value. Experimental results of D for different supported liquid membranes were found in the range of 2 to 7 $\times 10^{-7}$ cm^2/s. Although much lower than those predicted by the Wilke–Chang equation, the values are consistent in the orders of magnitude with the literature results for other permeates in similar supported liquid membranes.

INTRODUCTION

Lactic acid is a useful commodity with its myriad uses ranging from acidulant and preservatives in the food industries to biodegradable sutures for medical applications (1). Although there are synthetic routes to produce lactic acid, half of the world's requirement of lactic acid is fulfilled by fermentations (1). As the fermentation proceeds, the rate begins to slow because of the accumulation of lactic acid. The growth inhibition of cells by lactic acid has been studied, among others, by Yabannavar and Wang (2). They observed that the major portion of the inhibition was

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caused by undissociated lactic acid. With intermittent removal of the lactic acid by solvent extraction, the productivity of lactic acid was shown to improve by 18%.

Several methods are available for the recovery of lactic acid from the fermentation broth which can be broadly divided into two categories, viz., in situ (e.g., calcium lactate crystallization and electrodialysis) and downstream processes (e.g., distillation and liquid–liquid extraction). In the calcium lactate crystallization method, carbonate is added to the fermentation broth to prevent pH lowering. Calcium carbonate reacts with lactic acid to produce calcium lactate, which complicates the final recovery process by forming clusters which are difficult to wash (1). The recovered product may contain some ash (3). The susceptibility of calcium lactate to fungus infections is also a problem of the finished product (4). With the application of electrodialysis, the continuous removal of lactic acid can be achieved (5). However, microbial cells in the fermentation broth tend to attach to the membrane and cause an increase in electrical resistance, hence a decrease in the efficiency of electrodialysis. Transportation of other mobile ions present in the fermentation broth also poses a problem. Nomura et al. (6) proposed the use of immobilized cells in the lactic acid production by electrodialysis fermentation. This may solve the problems associated with membrane fouling but not those associated with the removal of other mobile ions. As for downstream recovery, liquid–liquid extraction gives an ash-free product which needs additional treatment to remove other impurities from the raw fermentation materials (3). High quality lactic acid can be prepared by the distillation of lactate esters; however, self-esterification and impurities from the crude fermentation liquor can pose significant problems (7).

Several studies have been conducted to utilize liquid membrane technology for the removal of organic acids. Thien and Hatton (8) gave a nice consolidated picture of the application of liquid membrane emulsion (LME) in biochemical processing. O'Brien and Senske (9) used the LME for the separation and recovery of acetic, propionic, and acrylic acids. Attempts by these researchers to remove lactic acid by LME were, however, unsuccessful. The extremely low solubilities of lactic acid in organic solvents (without carriers) were concluded to be the reason for this. Sirman et al. (10) reported the extraction of citric acid using a supported liquid membrane (SLM). Wennersten (11) studied the extraction of citric acid from fermentation broth using a tertiary amine as the carrier in several organic solvents. Nonpolar diluents were found to give better selectivity and phase separation. Chaudhury and Pyle (12) reported the extraction of lactic acid using an LME with a tertiary amine as the carrier and con-

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cluded that facilitated transport by the formation of a lactic acid–amine complex was the dominant mechanism of extraction.

Despite the attempted applications in lactic acid recovery, no thorough studies on the fundamental properties of lactic acid transport in liquid membranes are available. The present work aims at determining the equilibrium extraction constants (K_t) and the effective diffusion coefficients (D) for lactic acid transport in supported liquid membranes with a tertiary amine (Alamine 336, Henkel Corporation, Kankakee, Illinois) as the carrier. The results of the study should prove useful in the design and prediction of the rate of lactic acid recovery by liquid membranes.

MATERIALS AND METHODS

In this study, Alamine 336 (tricaprylamine or tri—C8 to C10 alkyl amines) was used as the carrier. Tertiary amines have traditionally been used in hydrometallurgical processes. The capacity of amines to act as extractants is related to their basicity, i.e., to the fact that their nitrogen atom has a mobile lone electron pair capable of forming coordinate bonds with molecules of other compounds (13). Smith and Page (14) found the suitability of long–chain aliphatic amines for the extraction of strong as well as weak acids, and proposed their use in the recovery of organic acids from biological materials and fermentation broths. The efficacy of tertiary amines in the recovery of various organic acids has since been proposed and proved in many works (e.g., Refs. 2, 8, 11, 12, 15, 16).

The amines can be dissolved in various solvents such as aliphatics, aromatics, C4 or higher alcohols, and combinations of these. Aliphatic hydrocarbons are the most hydrophobic and alcohols the most hydrophilic. The use of diluents is desirable (17) because they help in reducing the viscosity of the tertiary amines and in controlling both the density difference and the interfacial tension between the aqueous and membrane phases.

For an SLM, the liquid membrane is held in the pore structure by capillary forces. According to the Young and Laplace equation,

$$P_c = (2\gamma/a) \cos \theta \tag{1}$$

where P_c is the capillary pressure, γ is the oil–water (O/W) interfacial tension, a is the radius of the membrane pores, and θ is the contact angle between the oil and the walls of the pores (18). Therefore, interfacial tension plays an important role in determining the stability of an SLM; diluents with higher O–W interfacial tensions are expected to help stabilize the SLM. In general, aliphatic hydrocarbons have higher interfacial

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tensions than aromatic solvents (19). This, coupled with the observations made by Wennersten (11) that nonpolar diluents give better selectivity and phase separation, led us to include *n*-hexadecane as a diluent in the present study.

When a small amount of alcohol is added to hydrocarbon–amine systems, the solubilities of complexed amines in low-polar, nonsolvating solvents such as aliphatic hydrocarbons markedly increase (13). The additive may also increase the mutual solubility of hydrocarbon and amine, if it is soluble in both (20). Weiser and Geankoplis (21) reported the effectiveness of isoamyl alcohol for the purification of lactic acid by extraction. Guided by the work of other researchers, Yabannavar and Wang (2) chose oleyl alcohol as a suitable solvent for lactic acid extraction from a fermentation broth. Taking all these factors into consideration, oleyl alcohol was studied in this work both as an additive and a diluent.

In summary, the following oil phases were selected for the study of equilibrium extraction constants: (a) 100% Alamine 336; (b) 15% Alamine 336/*n*-hexadecane; (c) 15% Alamine 336/15% oleyl alcohol/*n*-hexadecane; and (d) 15% Alamine 336/oleyl alcohol.

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Determination of Equilibrium Extraction Constant

The aqueous lactic acid solution (4 or 40 mM) and the oil phase were mixed at a known volume ratio for about 15 hours in a tightly stoppered flask. The two phases were then separated by centrifugation. The oil phase was next contacted with a 0.1 N NaOH solution for 2 hours to extract the complexed lactic acid from the oil phase to the base. Centrifugation was again done to separate the two phases. The two aqueous solutions, i.e., the equilibrated lactic acid solution and the stripping base, were then colorimetrically analyzed (22) for their total lactate concentrations. The concentration of complexed lactic acid in the oil phase was calculated from the analyzed lactate concentration in the base. A material balance was made to check the accuracy of the results, which normally agreed within $\pm 5\%$.

In the colorimetric method, lactic acid was converted into acetaldehyde by treatment with concentrated sulfuric acid, and the acetaldehyde concentration was determined by its color reaction with *p*-hydroxyphenyl in the presence of cupric ions. The color was read in a spectrophotometer at 560 nm. Sufficiently consistent and accurate results were found. Analyses by enzymatic assay and titration were also investigated. The commonly used enzymatic colorimetric assay using the lactate diagnostic kit from Sigma Chemical Co. (Catalog No. 735-10) gave erroneous results in this study. Here, lactic acid is converted to pyruvate and hydrogen perox-

ide by oxidase. In the presence of the formed hydrogen peroxide, peroxidase catalyzes the oxidative condensation of chromogen precursors to produce a colored dye with an absorption maximum at 540 nm. The errors were probably caused by interference from the amine–lactic acid salts present in the equilibrated aqueous solution. The titration method was found to work well for higher concentrations (~20 mM or higher) of lactic acid but unsuitable for lower concentrations.

These equilibrium studies were made in varying volume ratios of oil phase to aqueous phase.

Determination of Effective Diffusion Coefficient

Experiments were made with a supported liquid membrane system where two aqueous phases were contained in two Plexiglas chambers separated by a porous hydrophobic polymeric membrane. The polymeric membrane had been carefully soaked in the oil (liquid membrane) phase. Figure 1 shows the schematic diagram of the experimental setup. The transport rate of lactic acid through the liquid membrane was assessed by following the decrease of total lactate concentration in the source solution. The chamber for the source solution was therefore made smaller in volume, i.e., 60 vs 120 mL, so as to make the change of lactate concentration more pronounced. The whole setup was placed on an electromagnetic stirrer with 15 stirring positions so that the aqueous solutions in both chambers could be agitated to minimize the mass transfer resistances in the aqueous films adjacent to the membrane. An agitation rate of 350 rpm was used throughout the study. Up to four sets of the chambers can be run simultaneously on the stirrer. Experiments were made at the room temperature, ~23°C.

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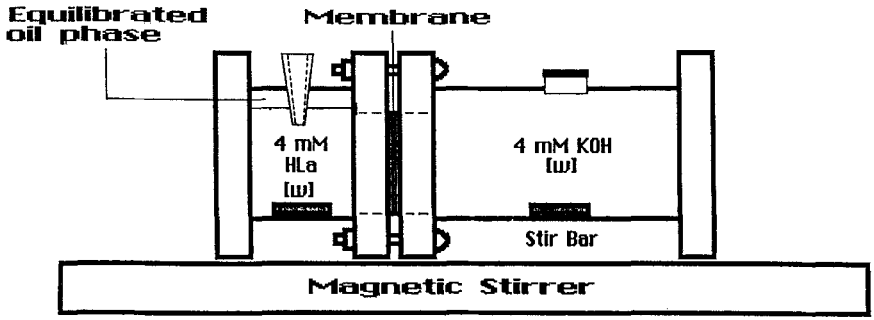

FIG. 1 Schematic of the experimental setup for determination of effective diffusion coefficients in supported liquid membranes.

Polymeric Membrane

Two different membranes were used to support the oil phase. The thinner membrane (TEFLO, Gelman Sciences Inc., Ann Arbor, Michigan) is made of polytetrafluoroethylene (PTFE) with a polymethylpentene (PMP) support ring around it. It has a thickness of 25 μm and an effective pore size of 2 μm. The thicker membrane (Tefsep PTFE Membrane, Micron Separations Inc., Westboro, Massachusetts) has a thickness of 130 μm and an effective pore size of 0.22 μm. It is made of PTFE laminated to a polypropylene woven support.

In order to determine the porosity of the TEFLO membrane, a support ring taken from a sacrificed membrane and an intact membrane were separately weighed and then soaked in *n*-hexadecane for 2 hours. After removing any excess oil sticking to their surfaces, the support ring and the membrane were weighed and resoaked. This process was repeated until two consecutive results were almost equal. From the known density of *n*-hexadecane [0.7733 g/cm^3 (23)], the total pore volume was calculated from the weight difference between the soaked and dry membranes. The porosity was then assessed as the volume fraction of the pores in the total membrane. A similar procedure was adopted to determine the porosity of the thicker membrane. The porosities were found to be 0.67 and 0.77 for the thinner and thicker membranes, respectively.

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Oil Phase

The following oil phases were used in the study: 1) 15% Alamine 336/*n*-hexadecane; 2) 15% Alamine 336/15% oleyl alcohol/70% *n*-hexadecane; and 3) 15% Alamine 336/oleyl alcohol. All concentrations are in w/w units.

Aqueous Phase

Lactic acid solutions of two different concentrations (4 and 40 mM) were used in the study as the source (or feed) aqueous phase. Although the solubility of Alamine 336 in water is negligible [less than 10 ppm (24)], the solubility of the lactic acid–Alamine 336 complex is comparatively high. In fact, when studying the extraction of acetic acid from water by chloroform containing various concentrations of trioctylamine, Wardell and King (25) clearly identified the presence of a salt of acetic acid–trioctylamine in the equilibrated aqueous phase. In order to avert possible dissolution of Alamine 336 from the membrane phase into the lactic acid solution in the form of a complexed salt, the feed aqueous phase was preequilibrated with the oil phase (60:1 volume ratio). After it had been

poured into the smaller chamber of the setup, a measured amount (~1 mL) of the equilibrated oil phase was also added to the surface of the feed solution (a procedure that had been found necessary). Several earlier runs made without considering the solubility of the complex in the lactic acid solution failed, mainly because there was only a minute amount (<15 mg) of Alamine 336 in the oil membrane phase initially.

The aforesaid volume ratio (60:1) during pre-equilibration was the same as that in the transport study. Equilibrium was therefore established between the feed and the oil phase from the very beginning of the transport study, fixing the initial condition for more accurate mathematical modeling. Arrangements were made to avoid direct contact of the added oil phase with the support membrane and the removal of oil droplets from the chamber during sample collection (Fig. 1).

A KOH solution with a concentration equivalent to that of the feed was used as the stripping (or sink) aqueous phase. The osmotic pressures were therefore balanced initially in the two aqueous solutions. Samples were collected periodically, and the pH values were measured. The samples were frozen and analyzed later for total lactate concentrations by using the colorimetric method (22) described earlier.

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RESULTS AND DISCUSSION

Equilibrium Extraction Constant

Being bases, tertiary amines (R_3N) can extract acids by neutralization reactions, resulting in the formation of a salt. The following equation emphasizes the acid–base nature of the reaction:

$$(R_3N)_o + (H^+)_w \rightleftharpoons (R_3NH^+)_w \quad (2)$$

The $(R_3NH^+)_w$ ions pair with the lactate ions (La^-) present in the aqueous phase and form the complex $(R_3NH^+)La^-$, henceforth referred to as (R_3NHLa).

A striking behavior of the acid–amine extraction reaction is that the organic phase is, in at least some cases, capable of taking up acid in excess of the amount necessary for stoichiometric neutralization of the amine base (13). Nevertheless, an 1:1 stoichiometry was found to prevail for the extraction of lactic acid by tripentylamine (26) or trioctylamine (27) in chloroform, and by Alamine 336 in a solvent of 70% (v/v) *n*-heptane and 30% (v/v) paraffin (12). Hence, the proposed reaction for the extraction of lactic acid (HLa) by Alamine 336 is

$$(R_3N)_o + (H^+)_w + (La^-)_w \rightleftharpoons ((R_3NH^+)La^-)_o \quad (3)$$

The equilibrium extraction constant, K_t, is accordingly defined as

$$K_t = \frac{[(R_3NH^+)La^-]_o}{[R_3N]_o[H^+]_w[La^-]_w} \quad (4)$$

If the proposed stoichiometry and the law of mass action (Eq. 4) are valid, the log-log plot of $[R_3NHLa]_o$ vs $([R_3N]_o[H^+]_w[La^-]_w)$ must be rectilinear. Data obtained from equilibrium studies with 100% R_3N and 15% R_3N/*n*-hexadecane as the oils were plotted, and the slopes of the best-fit straight lines were found to be reasonably close to 1, i.e., about 1.2 for both cases (Fig. 2). The 1:1 stoichiometry was therefore used in the study to describe the extraction of lactic acid.

K_t's for the oil phases studied are summarized in Table 1. Larger K_t values and, thus, more efficient extraction were found in systems where diluents were used. This finding is consistent with literature reports, such as the facilitated extraction of acetic acid with trioctylamine (25). The effect is much more significant with oleyl alcohol which increases the polarity of the oil phase and improves the solubilities (or stabilities) of the amine–acid complexes in the oil phase (17). The use of a diluent is

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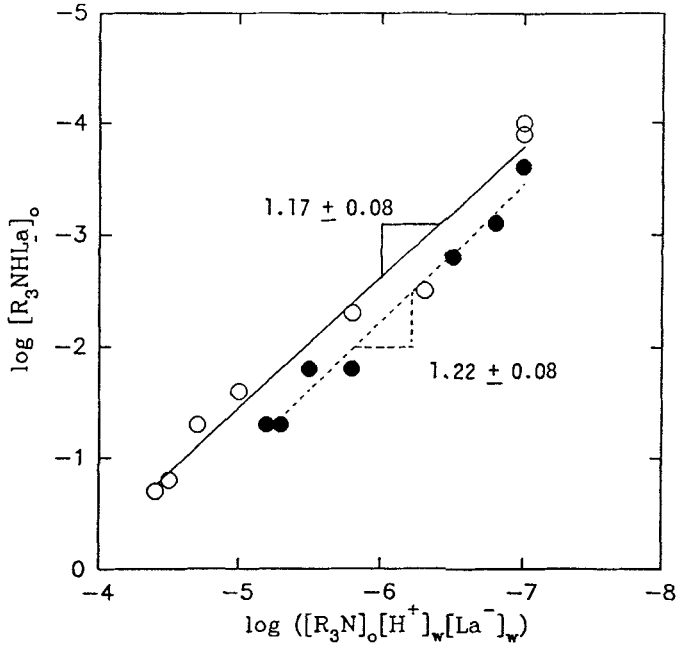

FIG. 2 The least-square linear fit of log ($[R_3NHLa]_o$) with log($[R_3N]_o[H^+]_w[La^-]w$); (○) pure R_3N and (●) 15% R_3N in *n*-hexadecane.

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TABLE 1
Experimental Results of Equilibrium Extraction Constants and Effective Diffusion Coefficients

Oil phase[a]	K_t (M^{-2})	D (cm^2/s)		
		Experimental results		Wilke–Chang prediction
		Straight line[b]	Exponential[b]	
1	2.8×10^3	—	—	—
2	5.9×10^3	$(3.619 \pm 0.260) \times 10^{-7}$	$(4.130 \pm 0.764) \times 10^{-7}$	2.096×10^{-6}
3	1.7×10^5	$(2.160 \pm 0.541) \times 10^{-7}$	$(2.125 \pm 0.442) \times 10^{-7}$	6.839×10^{-6}
4	1.6×10^4	$(6.644 \pm 0.791) \times 10^{-7}$	$(6.531 \pm 0.794) \times 10^{-7}$	2.453×10^{-6}

[a] 1: 100% R_3N.
2: 15% R_3N/*n*-hexadecane.
3: 15% R_3N/oleyl alcohol.
4: 15% R_3N/15% oleyl alcohol/*n*-hexadecane.
[b] Results obtained with the best-fit linear or exponential correlation between $[H^+]_w$ and $[LA]_w$.

also desirable from the operational perspective because it offers more flexibility for manipulating the various aspects (e.g., selectivity, capacity, cost, etc.) of the system.

Effective Diffusion Coefficient

For the study conducted on two-chamber systems for lactic acid transport through an SLM, the proposed overall transfer mechanism is given in Fig. 3. As soon as the complex R_3NHLa reaches the interface of the membrane phase and the stripping medium, H^+ reacts with OH^- to form water molecules. The unloading of H^+ nullifies the ion-pair association and results in the release of La^- into the stripping medium. Thus, both hydrogen and lactate ions are transferred from the feed to the stripping medium, and R_3N is again available for further transport of hydrogen and lactate ions.

With the proposed transfer mechanism, the mass transfer rate of lactic acid in the supported liquid membrane is affected by three factors:

1. The rates of mass transfer to and from the membrane phase through boundary layers at the interface between the membrane and the two aqueous solutions
2. The diffusion rate of the complex across the membrane phase
3. The reaction rates of extraction and stripping at the two interfaces

The first factor may be neglected in the system studied because adequate agitation was provided in both aqueous phases to minimize the resistances in the boundary layers. Furthermore, it is generally assumed that the reactions are fast compared with the diffusion of the complex in the membrane phase and are confined to the interfaces (13, 15). Because of the extremely low solubility of lactic acid in the organic phases used

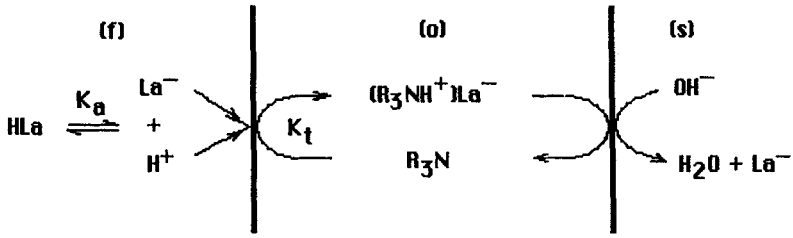

FIG. 3 Proposed mechanism for the facilitated transport of lactic acid.

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in the study (9), the contribution of the unfacilitated transport of lactic acid in the overall removal process is assumed to be negligible.

With these assumptions, the rate-limiting step of lactic acid transport is diffusion of the complex across the liquid membrane. Accordingly, a material balance based on the total lactate in the source chamber, including both the aqueous feed and the added oil phase on its surface, can be established as

$$V_1 \frac{d[\mathrm{LA}]_1}{dt} + V_2 \frac{d[\mathrm{LA}]_2}{dt} = -\frac{DA\epsilon}{L}[\mathrm{R_3NHLa}]_{3,i} \tag{5}$$

where V_1 = volume of the equilibrated oil phase added to the surface of aqueous feed
V_2 = volume of the equilibrated aqueous feed
[LA] = total lactate concentration, i.e., $[\mathrm{La}^-]$ + [HLa] in the feed and $[\mathrm{R_3NHLa}]$ in the oil
A = cross-sectional area of the polymeric membrane in contact with the aqueous feed
L = thickness of the membrane
ϵ = membrane porosity

Subscripts 1, 2, and 3 represent the equilibrated oil phase added to the surface of the feed solution, the source aqueous phase, and the liquid membrane phase, respectively. $[\mathrm{R_3NHLa}]_{3,i}$ stands for the membrane-phase concentration of the complex at the feed–membrane interface.

According to the 1:1 stoichiometry established in the equilibrium extraction study, it is assumed that lactate is present in the oil phase (1) only in the form of the complex $\mathrm{R_3NHLa}$. The presence of the complexed lactate in the aqueous phase can be ignored because of the total dissociation of the salt into $\mathrm{R_3NH^+}$ and $\mathrm{La^-}$. For mathematical simplicity, the effective diffusion coefficients of both $\mathrm{R_3NHLa}$ and $\mathrm{R_3N}$ (free carrier) are assumed to be equal. Denial of this assumption would require the consideration of an uneven distribution of total carrier concentration across the membrane phase. Because the carrier concentration used in the study was in extreme excess, the concentrations of free amine in the oil phases (1) and (3), i.e., $[\mathrm{R_3N}]_o$, are also assumed to be equal and constant with respect to time. Moreover, both the oil phase (1) and the feed–membrane interface (3,*i*) are assumed to be in equilibrium with the aqueous feed solution (2) at any instant. Therefore,

$$[\mathrm{LA}]_1 = [\mathrm{R_3NHLa}]_1 = [\mathrm{R_3NHLa}]_{3,i} = K_t[\mathrm{R_3N}]_o[\mathrm{H^+}]_2[\mathrm{La^-}]_2$$

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With these assumptions, Eq. (5) can be integrated to the following form:

$$\int_0^t \frac{d[\mathrm{LA}]_2}{\left(\dfrac{[\mathrm{LA}]_2}{1+\dfrac{K_a}{[\mathrm{H}^+]_2}}\right)} = -M \ln\left(\frac{[\mathrm{LA}]_2}{1+\dfrac{K_a}{[\mathrm{H}^+]_2}}\right) - DNt \tag{6}$$

where

$$M = \frac{V_1}{V_2} K_t K_a [\mathrm{R_3N}]_o \tag{7}$$

$$N = \frac{A}{V_2 L} K_t K_a [\mathrm{R_3N}]_o \tag{8}$$

and K_a is the dissociation constant of lactic acid in the aqueous phase, i.e.,

$$K_a = \frac{[\mathrm{H}^+]_2[\mathrm{La}^-]_2}{[\mathrm{HLa}]_2} \tag{9}$$

The value of K_a for lactic acid has been reported to be 1.38×10^{-4} M at 25°C (28). Equation (6) needs to be solved to obtain the time profile of the total lactate concentration in the feed solution, which then can be used to determine the effective diffusion coefficient based on the experimental data of $[\mathrm{LA}]_2$.

As is evident from the model, knowledge of the profile of $[\mathrm{H}^+]_2$ is required. Figure 4 depicts our attempts to correlate $[\mathrm{H}^+]_w$ with $[\mathrm{La}^-]_w$. Because hydrogen and lactate ions are co-transferred through the liquid membrane, it is first assumed that at any given instant the concentrations of these two ions in the source aqueous phase are equal. To check the validity of this hypothesis, a 4 mM lactic acid solution was contacted with pure Alamine 336 in varying ratios, and the change in pH of the aqueous solution was measured. The measured values of hydrogen ion concentration versus the predicted values based on this hypothesis (details of the analysis are given in the Appendix) are shown in Fig. 4. For any given volume fraction of Alamine 336, the predicted value is much higher than the experimental datum. It implies that the "missing" hydrogen ions may be present in the aqueous phase in some other forms. One possibility is the presence of $\mathrm{R_3NH}^+$ in the aqueous phase. As mentioned earlier, the presence of a salt of acetic acid–trioctylamine in the aqueous phase has been reported (25). The same has also been observed in this study. When

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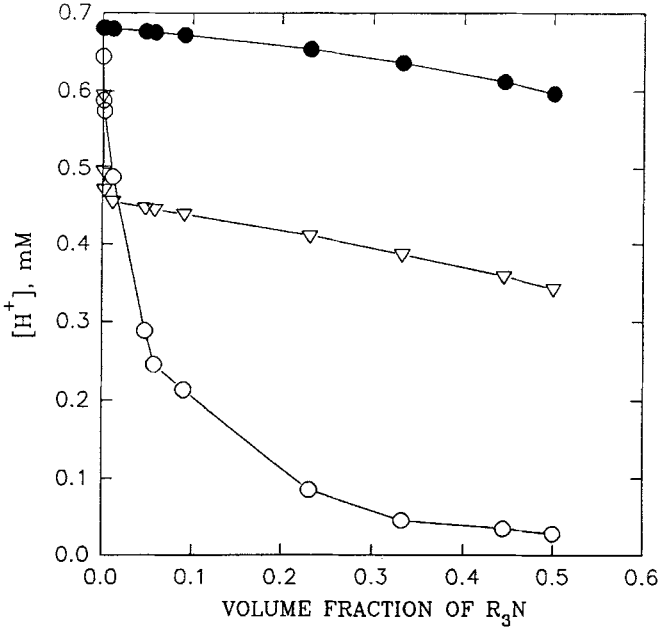

FIG. 4 Changes of the hydrogen ion concentration of a 4 mM lactic acid solution when equilibrated with pure Alamine 336 of varying volume fractions; (○) experimental data, (● and ▽) model predictions assuming $[La^-]_w = [H^+]_w$ and $[La^-]_w = [H^+]_w + [R_3NH^+]_w$, respectively.

a 4 mM lactic acid solution was equilibrated with pure Alamine 336 and the equilibrated aqueous phase was titrated with 0.4 mM NaOH, the titration curve obtained exhibited two inflection points, one corresponding to free lactic acid and the other to R_3NH^+ (Fig. 5). According to this hypothesis, the concentration of lactate ions in the aqueous phase should equal the sum of the concentrations of free hydrogen ions, $[H^+]$, and the protonated amine, $[R_3NH^+]$. Details of the analysis for this hypothesis are again given in the Appendix. As is evident from Fig. 4, this hypothesis only partially succeeded in explaining the experimental observations. The presence of trace amounts of primary and secondary amines, which are more soluble in the acidic solution, may be responsible for the rest.

At this point we resorted to the best-fit method for correlating $[H^+]_2$ with $[LA]_2$. Both experimental and linear fitting of the data were attempted. With these correlations, Eq. (6) was integrated, and the resultant equations were used to determine the effective diffusion coefficient by fitting with the experimental data of total lactate concentration in the aqueous phase. A typical profile is shown in Fig. 6. The effective diffusion

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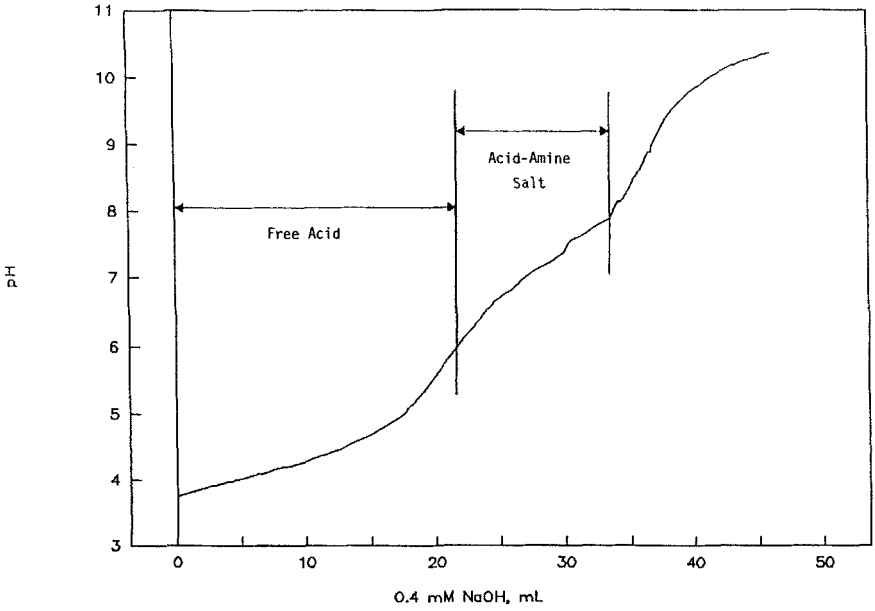

FIG. 5 The titration curve of a 4 mM lactic acid solution after extraction with pure Alamine 336.

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coefficients of the complex R_3NHLa in various supported oil membranes are summarized in Table 1. Evidently, these values were not significantly affected by the choice between the best-fit exponential and linear correlations for $[H^+]_2$ and $[LA]_2$.

The experimental results (Table 1) are consistent in the orders of magnitude with the effective diffusion coefficients reported in the literature for various other permeates in similar liquid membranes (29). The values obtained are, however, far lower than those predicted by the Wilke–Chang equation (30). As faster permeation is one of the proposed key advantages of liquid membranes over their solid counterparts, further experiments are needed to identify and perhaps subdue the factor(s) leading to the lower than expected diffusion coefficients.

APPENDIX

The analysis for the second hypothesis,

$$[La^-]_w = [H^+]_w + [R_3NH^+]_w \tag{10}$$

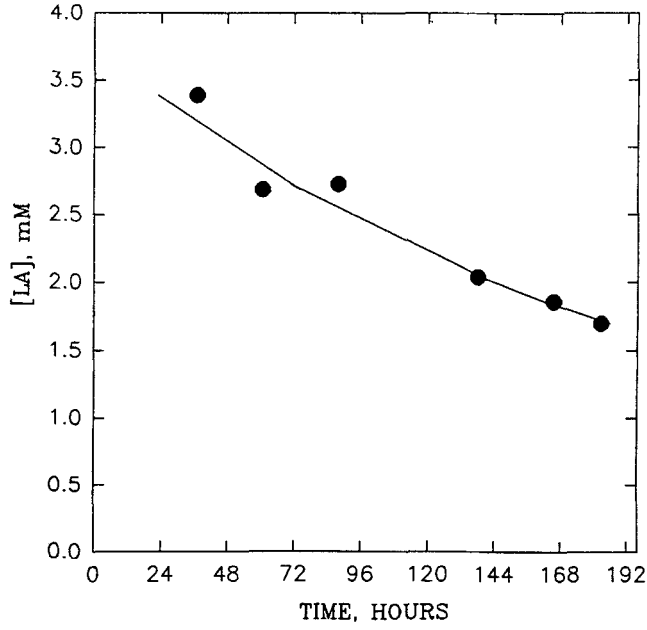

FIG. 6 A typical profile showing the drop of total lactate concentration in the feed aqueous solution; (●) experimental data and (——) the theoretical curve corresponding to the best-fit effective diffusion coefficient, based on Eq. (6).

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is presented here. Results of the first hypothesis, $[La^-]_w = [H^+]_w$, can be easily obtained by equating the concentration of the protonated amine to zero.

Equation (1) describes the formation of $(R_3NH^+)_w$ where the equilibrium constant can be defined as

$$K_1 = \frac{[R_3NH^+]_w}{[H^+]_w[R_3N]_o} \tag{11}$$

Material balances of the total lactate and amine lead to

$$[LA^i]_w = [HLa]_w + [La^-]_w + [R_3NHLa]_o\left(\frac{f_o}{1 - f_o}\right) \tag{12}$$

and

$$[R_3N^i]_o = [R_3N]_o + [R_3NHLa]_o + [R_3NH^+]_w\left(\frac{1 - f_o}{f_o}\right) \tag{13}$$

where the superscript i refers to the initial concentration before contact of the two phases and f_o is the volume fraction of the oil phase.

On substitution with Eqs. (10) and (11) and the expressions for K_a (Eq. 9) and K_t (Eq. 4), Eqs. (12) and (13) become

$$[LA^i]_w = \frac{1}{K_a}[H^+]_w([H^+]_w + [R_3NH^+]_w) + ([H^+]_w + [R_3NH^+]_w) + \frac{K_t}{K_1}[R_3NH^+]_w([H^+]_w + [R_3NH^+]_w)\left(\frac{f_o}{1 - f_o}\right) \quad (14)$$

$$[R_3N^i]_o = \frac{1}{K_1}\frac{[R_3NH^+]_w}{[H^+]_w} + \frac{K_t}{K_1}[R_3NH^+]_w([H^+]_w + [R_3NH^+]_w) + [R_3NH^+]_w\left(\frac{1 - f_o}{f_o}\right) \quad (15)$$

The expression for $[R_3NH^+]_w$ can therefore be obtained by solving Eq. (14) and substituting into Eq. (15). Together, they were used to determine the best-fit value of K_1 based on the experimental data of $[H^+]_w$ for various f_o's. A similar approach was then used to predict $[H^+]_w$ at each f_o with the above best-fit K_1 value. The results are summarized in Fig. 4.

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