0273-2289/04/114/0671–0688/$25.00

A Hollow-Fiber Membrane Extraction Process for Recovery and Separation of Lactic Acid from Aqueous Solution

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Abstract

An energy-efficient hollow-fiber membrane extraction process was successfully developed to separate and recover lactic acid produced in fermentation. Although many fermentation processes have been developed for lactic acid production, an economical method for lactic acid recovery from the fermentation broth is still needed. Continuous extraction of lactic acid from a simulated aqueous stream was achieved by using Alamine 336 in 2-octanol contained in a hollow-fiber membrane extractor. In this process, the extractant was simultaneously regenerated by stripping with NaOH in a second membrane extractor, and the final product is a concentrated lactate salt solution. The extraction rate increased linearly with an increase in the Alamine 336 content in the solvent (from 5 to 40%). Increasing the concentration of the undissociated lactic acid in the feed solution by either increasing the lactate concentration (from 5 to 40 g/L) or decreasing the solution pH (from 5.0 to 4.0) also increased the extraction rate. Based on these observations, a reactive extraction model with a first-order reaction mechanism for both lactic acid and amine concentrations was proposed. The extraction rate also increased with an increase in the feed flow rate, but not the flow rates of solvent and the stripping solution, suggesting that the process was not limited by diffusion in the liquid films or membrane pores. A mathematical model considering both diffusion and chemical reaction in the extractor and back extractor was developed to simulate the process. The model fits the experimental data well and can be used in scale up design of the process.

Index Entries: Reactive extraction; hollow-fiber membrane; lactic acid; mass transfer; Alamine 336.

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Introduction

Lactic acid is an important chemical that has wide applications in food, pharmaceutical, cosmetic, and chemical industries. There are increasing interests in production of lactate esters and biodegradable polylactic acid (PLA) from lactic acid. Lactate esters are a relatively new family of solvents with specific properties. They are considered safe and are biodegradable *(1)*. In many situations they can replace toxic solvents. Their functions vary from that of intermediates in chemical reactions to solvents in ink formulations and cleaning applications *(2)*. PLA has been widely used in medical implants, sutures, and drug-delivery systems because of its capacity to dissolve over time *(3–5)*. PLA also can be used in products such as plant pots, disposable diapers, and textile fabrics.

Lactic acid can be produced from a petrochemical route or from fermentation *(6,7)*. The petrochemical route can only produce racemic mixtures of lactic acid, whereas fermentation can produce optically pure isomer. D(–)-Lactic acid is toxic and must be limited in animal feeds *(8)*, and an optically pure lactic acid is required to produce a specific PLA *(9)*. In addition, fermentation utilizes renewable resources that make fermentation more attractive than the petrochemical route. Extractive fermentation, which couples fermentation with on-line product removal, can eliminate end product inhibition and increase product yield, final product concentration, and reactor productivity. A number of extractive fermentation methods have been reported in the literature, including solvent extraction *(10–12)*, precipitation *(13)*, electrodialysis *(14,15)*, adsorption by ion-exchange resin *(16–18)*, and an aqueous two-phase system *(19–20)*.

Reactive extraction is a promising technology for the recovery of lactic acid because it provides a high distribution coefficient and the extractant can be readily regenerated by back extraction with an alkaline solution *(10,11)*. Aliphatic amines are effective and relatively inexpensive extractants that have been used successfully to extract carboxylic acids *(21)*. Primary amines are too soluble in water to be used with aqueous solutions. Quaternary amines such as Aliquat 336 and secondary amines such as Adogen 283 are more toxic to microorganisms than tertiary amine such as Alamine 336, which is an ideal extractant for use in extractive lactic acid fermentation *(12)*. Emulsion has been a problem in the solvent extractive fermentation process because emulsion causes toxicity to cells *(22)*. To overcome this problem, a solvent extraction approach called hollow-fiber membrane-based extraction has been proposed that can provide nondispersive phase contact. With the membrane-immobilized-phase contact, cells can be protected from direct contact with solvents, and the emulsions, which would otherwise be produced in most cases, can be avoided. The additional advantages of hollow-fiber membranes are ease of separation of two phases and high efficiency owing to high specific surface area per unit reactor volume.

In the present work, continuous extraction of lactic acid from an aqueous solution with a solvent consisting of Alamine 336 and 2-octanol in a hollow-fiber membrane extractor was studied. The lactic acid in the solvent

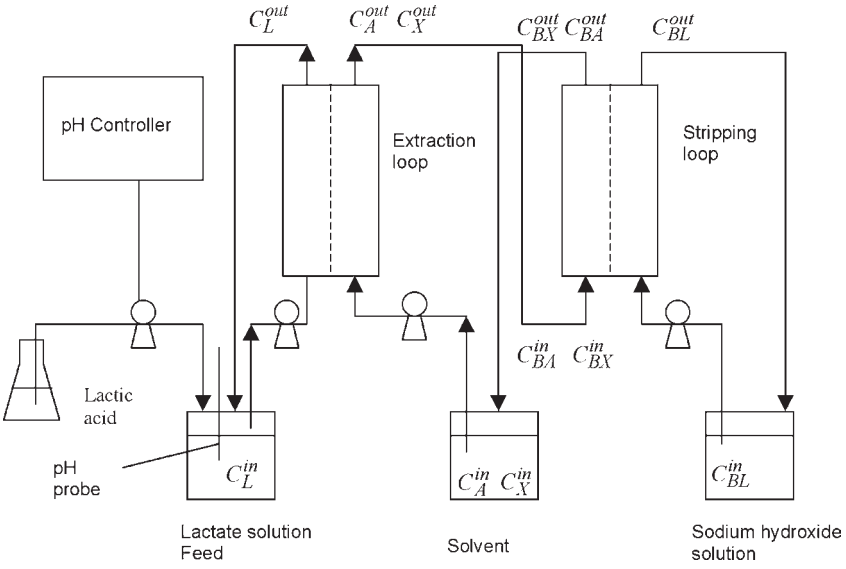

Fig. 1. Experimental setup for extraction and stripping using two hollow-fiber membrane modules.

was then stripped or back extracted with an alkaline solution in a second membrane extractor, which simultaneously regenerated the solvent extractant. The effects of operational variables, including concentrations of lactic acid in the aqueous feed solution and Alamine 336 in the solvent; pH; and flow rates of the feed, solvent, and stripping solution, on the extraction rate were studied. In addition, a theoretical model considering both diffusion and chemical reaction was developed. The model simulated the data well and can be used for optimal design and scale up of the extraction process.

Materials and Methods

Experimental Setup

Figure 1 shows the experimental setup for the simultaneous extraction and stripping process using two hollow-fiber membrane modules. Each hollow fiber membrane extractor (Liqui-Cel Extra Flow, 2.5 in. × 8 in., Celgard, Hoest Celanese) contained about 10,200 polypropylene hollow fibers (15-cm length, 240-µm id, 300 µm o od, 30-µm wall thickness, 0.03-µm membrane pore size, 40% membrane porosity) with an effective membrane surface area of 1.4 m^2. The priming volume of the tube side was 145 mL, and that of the shell side was 195 mL. The feed solution was prepared from 85% lactic acid (pharmaceutical grade; Sigma, St. Louis, MO) diluted with distilled water to a desirable concentration (5–40 g/L). The pH of the feed lactic acid solution was adjusted to the set point (4.0, 4.5, and 5.0) by adding NaOH pellets to the solution. The organic solvent was Alamine 336

(straight-chain tertiary amine containing C_8-C_{10} alkyl groups, with a mol wt of 363.3 and a density of 0.81; Henkel) in 2-octanol (mol wt of 130.23 and a density of 0.822) as a diluent. The Alamine content in the solvent varied from 5 to 40% (v/v). The stripping solution was a 6 *N* NaOH solution.

In the experiments, the lactic acid solution (500 mL) was circulated through the shell side of the extractor, the organic solvent (500 mL) was circulated through the tube side of the extractor and back extractor, and the base solution (500 mL) was circulated through the shell side of the back extractor. The pressure difference across the membrane was adjusted by partially closing a valve at the outlet of the aqueous phase. The pressure difference across the hollow-fiber membrane was kept at ~4 psi, with the aqueous-phase (shell) side being higher than the organic-phase (tube) side to prevent solvent breakthrough. The pH and the concentration of lactic acid in the feed solution were maintained at constant values by automatically adding a concentrated lactic acid solution to the feed reservoir, as lactic acid was being extracted, through the use of a pH controller and a feed pump. The concentration of lactic acid in the stripping base solution was monitored to evaluate the extraction rate. Unless otherwise noted, the experiments were carried out at the same flow rate of 80 mL/min for all three streams (the lactic acid solution, solvent, and stripping solution), at pH 4.5 and ambient temperature (~25°C), with 40 g/L of lactic acid solution and 30% (v/v) Alamine 336 in 2-octanol as the solvent. The effects of amine content in the organic solvent (from 5 to 40%), lactic acid concentration (from 5 to 40 g/L) and pH (4.0, 4.5, and 5.0) of the feed solution, and liquid flow rates (from 20 to 120 mL/min) on the extraction process performance were studied.

Analytical Methods

A high-performance liquid chromatograph (HPLC) was used to analyze the concentration of lactic acid in the base solution. The HPLC system consisted of an automatic injector (Shimadzu SIL-10Ai), a pump (Shimadzu LC-10Ai), an organic acid analysis column (HPX-87H; Bio-Rad, Hercules, CA), a column oven at 45°C (Shimadzu CTO-10A), and a refractive index detector (Shimadzu RID-10A). The eluent was 0.01 *N* H_2SO_4 at a flow rate of 0.6 mL/min. The viscosity of the organic phase was measured using a digital viscometer (Brookfield Model DV.II).

Mathematical Model

Extraction

The reactive extraction of lactic acid by the amine solvent follows a reversible reaction and can be represented by the following reaction mechanism:

$$\text{Lactic Acid} + \text{Amine} \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} \left[\text{Lactic acid} - \text{Amine}\right]$$

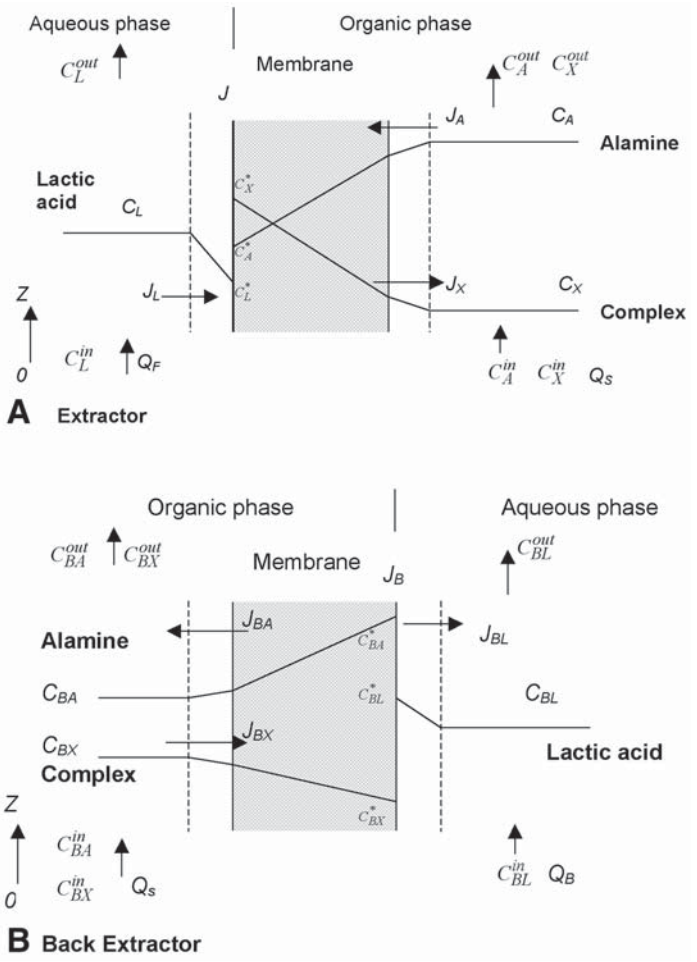

Fig. 2. Concentration profiles of various species in aqueous and organic phases and membrane: **(A)** extractor, **(B)** back extractor.

Figure 2 illustrates the concentration profiles of various species (lactic acid, amine, and lactic acid–amine complex) in the extraction system. Both reactive and physical extractions of lactic acid take place at the interface between the aqueous and organic phases or at the outer membrane surface of the hollow fiber, and the solute flux owing to the extraction, *J*, can be described by Eq. 1:

$$J = k_1 C_L^* C_A^* - k_{-1} C_X^* + k_2 C_L^* \quad (1)$$

In Eq. 1, a first-order reaction kinetics between lactic acid and amine is assumed. The second term is the reverse reaction and the last term is attributed to physical extraction.

The fluxes for lactic acid (J_L) through the aqueous-phase liquid film, and amine (J_A) and the complex (J_X) through the organic-phase liquid film and the membrane, can be expressed, respectively, as follows:

$$J_L = k_L\left(C_L - C_L^*\right) \tag{2}$$

$$J_A = k_{AO}\left(C_A - C_A^*\right) \tag{3}$$

$$J_X = k_{XO}\left(C_X^* - C_X\right) \tag{4}$$

At steady state, all fluxes are equal and $J = J_L = J_A = J_X$. After substituting for C_L^*, C_A^*, and C_X^* using the expressions given in Eqs. 2–4, Eq. 1 becomes

$$J = k_1\left(C_L - J/k_L\right)\left(C_A - J/k_{AO}\right) - k_{-1}\left(J/k_X + C_X\right) + k_2\left(C_L - J/k_L\right) \tag{5}$$

Back Extraction

Back extraction with a strong alkaline (NaOH) solution is an irreversible reaction that simultaneously regenerates the amine and produces sodium lactate and water:

$$\left[\text{Lactic Acid} + \text{Amine}\right] + \text{NaOH} \overset{k_{-1}}{\leftrightarrow} \text{Na} \cdot \text{Lactate} + \text{water} + \text{Amine}$$

The flux of the stripping reaction, J_B, can be described by the following equation when there is an excessive amount of NaOH in the stripping solution (pH >> 10.0):

$$J_B = k_{-1} C_{BX}^* \tag{6}$$

The fluxes for lactic acid (J_{BL}) to move across the aqueous-phase film to the stripping solution, and amine (J_{BA}) and the complex (J_{BX}) through the organic-phase liquid film and the membrane, are, respectively, as follows:

$$J_{BL} = k_L\left(C_{BL}^* - C_{BL}\right) \tag{7}$$

$$J_{BA} = k_{AO}\left(C_{BA}^* - C_{BA}\right) \tag{8}$$

$$J_{BX} = k_{XO}\left(C_{BX} - C_{BX}^*\right) \tag{9}$$

At steady state, all fluxes are equal and thus

$$J_B = J_{BX} = J_{BA} = J_{BL} = k_{-1} k_{XO} C_{BX} / \left(k_{-1} + k_{XO}\right) \tag{10}$$

Concentrations of Solutes

The local concentrations of lactic acid in the aqueous feed and stripping solutions inside the extractor and back extractor, respectively, can be obtained from the following equations:

$$-Q_F \int_{C_L^{in}} dC_L = \pi d_o N \int_0 J dz \tag{11}$$

$$Q_B \int_{C_{BL}^{in}} dC_{BL} = \pi d_o N \int_0 J_B dz \tag{12}$$

Similarly, the concentrations of amine and the complex in the organic solvent inside the extractor and back extractor, respectively, can be obtained from the following equations:

$$-Q_S \int_{C_A^{in}} dC_A = \pi d_o N \int_0 J_A dz \tag{13}$$

$$Q_S \int_{C_{BA}^{in}} dC_{BA} = \pi d_o N \int_0 J_{BA} dz \tag{14}$$

$$Q_S \int_{C_X^{in}} dC_X = \pi d_o N \int_0 J_X dz \tag{15}$$

$$-Q_S \int_{C_{BX}^{in}} dC_{BX} = \pi d_o N \int_0 J_{BX} dz \tag{16}$$

However, both C_A and C_X can be found from C_L in the extractor, and C_{BA} and C_{BX} from C_{BL} in the back extractor, by using material balance as follows:

$$Q_S\left(C_A^{in} - C_A\right) = Q_S\left(C_X - C_X^{in}\right) = Q_F\left(C_L^{in} - C_L\right)$$

$$Q_S\left(C_{BA}^{in} - C_{BA}\right) = Q_S\left(C_{BX} - C_{BX}^{in}\right) = Q_B\left(C_{BL}^{in} - C_{BL}\right)$$

The unsteady-state concentrations of lactic acid in the feed reservoir (C_L^{in}), lactic acid in the stripping solution reservoir (C_{BL}^{in}), and amine (C_A^{in}) and the complex (C_X^{in}) in the organic solvent reservoir can be found from the following equations, respectively:

$$V_F \int_{C_{L0}} dC_L^{in} = Q_F \int_0 \left(C_L^{out} - C_L^{in}\right) dt \tag{17}$$

$$V_B \int_0 dC_{BL}^{in} = Q_B \int_0 \left(C_{BL}^{out} - C_{BL}^{in}\right) dt \tag{18}$$

$$V_S \int_{C_{A0}} dC_A^{in} = Q_S \int_0 \left(C_A^{out} - C_{BA}^{in}\right) dt \tag{19}$$

$$V_S \int_0 dC_X^{in} = Q_S \int_0 \left(C_X^{out} - C_{BX}^{in}\right) dt \tag{20}$$

As can be seen in Fig. 1, $C_A^{out} = C_{BA}^{in}$ and $C_X^{out} = C_{BX}^{in}$. In the experiment, the concentration of lactic acid in the feed reservoir was maintained at a constant initial level, C_{L0}. At steady state, the extraction rate in the extractor should be equal to the stripping rate in the back extractor, which can be

determined from the changes in the amount of lactate in the stripping solution reservoir with respect to time using Eq. 18.

Mass Transfer Coefficients

The mass transfer coefficients k_{AO} and k_{XO} in Eqs. 3, 4, 8, and 9 can be calculated from the following equations:

$$k_{AO} = 1/\left(d_o/k_A d_i + d_o/k_M d_m\right) \tag{21}$$

$$k_{XO} = 1/\left(d_o/k_X d_i + d_o/k_M d_m\right) \tag{22}$$

in which d_o and d_i are the outer and inner diameter, respectively; and d_m is the log mean diameter of the hollow-fiber tube.

The mass transfer coefficient in the aqueous phase, $k_{L,}$ can be determined from the liquid velocity, $\nu_{aq,}$ and the diffusivity of lactic acid, $D_{aq} = 8.24 \times 10^{-6}$ cm^2/s, in the aqueous phase as follows *(23)*:

$$\frac{k_L d_o}{D_{aq}} = 1.4\left(\frac{d_o \nu_{aq}}{D_{aq}}\right)^{1/3} \tag{23}$$

For the mass transfer coefficients in the organic liquid film (k_A and k_X) and the porous membrane (k_M), they can be estimated using the following correlations *(23)*:

$$\frac{k_j d_i}{D_{org,j}} = 1.62\left(\frac{d_i^2 \nu_{org}}{L D_{org,j}}\right)^{1/3} \tag{24}$$

$$k_M = \frac{D_{org,j}\varepsilon}{\delta\tau} \tag{25}$$

in which the subscript j indicates either subscript A (for amine) or subscript X (for the complex), and the diffusivity of the amine and the complex in the organic phase can be determined as follows *(24)*:

$$D_{org,j} = 8.2 \times 10^{-8}\left[1 + \left(\frac{3V_o}{V_j}\right)^{0.66}\right] T/\left(\mu_o V_j^{0.33}\right) \tag{26}$$

The estimated mass transfer coefficients for solvents containing various amounts of Alamine 336 are listed in Table 1.

Model Calculation and Parameter Estimation

Numerical integration was applied to the model. The local fluxes in the extractor and back extractor were first calculated from Eqs. 5 and 10, respectively. The solute flux J in Eq. 5 was determined using Fortran IMSL subroutine NEQNJ. The concentrations of lactic acid, amine, and the complex in the extractor and back extractor were then calculated from Eqs. 11–16, which were solved by using the Runge-Kutta method. Equations 17–20

Table 1
Values of μ_O, V_O, $D_{org,A}$, k_A, k_M and k_{AO} for Solvents with Various Alamine 336 Contents

Alamine 336 content (%)	μ_O (10^{-3} Pa·s)	V_O (cm^3/mol)	$D_{org,A}$ (cm^2/s)	k_A (m/s)	k_M (m/s)	k_{AO} (m/s)
5	6.70	163.7	10.0×10^{-7}	1.20×10^{-6}	5.30×10^{-7}	3.1×10^{-7}
10	7.00	169.4	9.7×10^{-7}	1.15×10^{-6}	5.20×10^{-7}	3.1×10^{-7}
20	7.25	182.0	9.6×10^{-7}	1.14×10^{-6}	5.10×10^{-7}	3.0×10^{-7}
30	7.50	196.6	9.6×10^{-7}	1.13×10^{-6}	5.09×10^{-7}	3.0×10^{-7}
40	8.00	213.7	9.2×10^{-7}	1.10×10^{-6}	4.90×10^{-7}	2.9×10^{-7}

were then used to find the concentrations of lactic acid in the feed reservoir and stripping solution reservoir, and amine and the complex in the solvent reservoir. The calculated values for lactic acid concentration in the stripping solution (C_{BL}^{in}) were then compared with the data to adjust the model parameters. The best values for k_1, k_{-1}, and k_2 in the model were obtained using the Simplex subroutine. In the model calculation, it was assumed that there was no significant change in the liquid volume in all three reservoirs (feed solution, solvent, and stripping solution) and that the system was at steady state. The pk_a value (=3.86) for lactic acid at 25°C and 1 atm was used in estimating the undissociated lactic acid concentration.

Results and Discussion

Effects of Alamine 336 Content

The content of Alamine 336 in the solvent extractant is known to greatly affect lactic acid extraction. San-Martin et al. *(25)* reported that the equilibrium concentration of lactic acid in the solvent increased with an increase in the Alamine 336 content but remained unchanged when the amine content was >40%. Therefore, the amine content in 2-octanol was varied from 5 to 40% (v/v) to study the effect of Alamine 336 content on the extraction rate. As shown in Fig. 3, the lactate concentration in the base solution increased linearly with time, and the extraction rate, as determined from the slope of the linear regression, increased linearly with the Alamine 336 content in the solvent. As can be seen in Fig. 3B, the extraction rate would be greater than zero at 0% Alamine 336 content, indicating physical extraction of lactic acid by 2-octanol. This finding is consistent with the proposed mechanism for the reactive extraction with amine and physical extraction with 2-octanol, as depicted by Eq. 1. It is noted that increasing the amine content had only a minimal effect on the mass transfer coefficients in the organic phase (*see* Table 1), although the viscosity of the organic solvent increased significantly with an increase in the Alamine 336 content, from 6.7×10^{-3} Pa·s at 5% to 8.0×10^{-3} Pa·s at 40%. Table 1 only

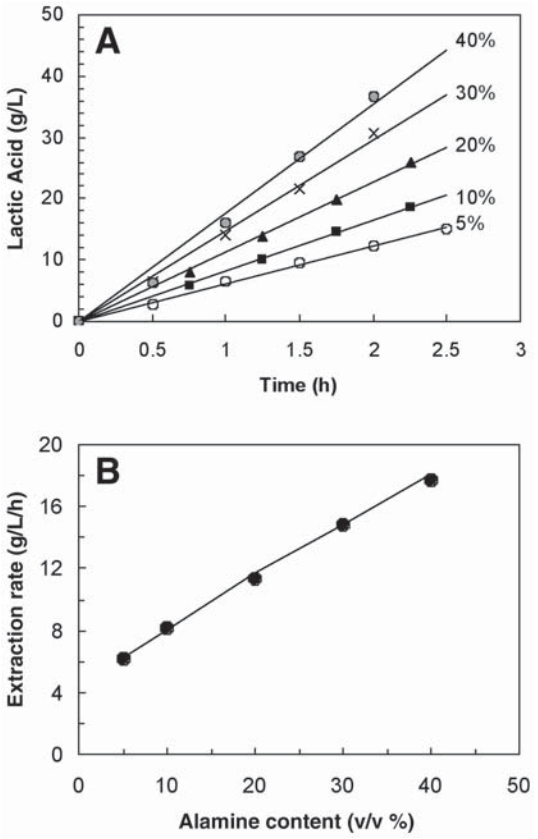

Fig. 3. Effect of Alamine 336 content in solvent on extraction of lactic acid (40 g/L) at pH 4.5 and 80 mL/min flow rate: **(A)** time course of lactate concentration in stripping base solution; **(B)** extraction rate as affected by amine content (the line is the model fit).

lists the values of mass transfer coefficients for amine in the organic phase because the effect on the mass transfer coefficient for the complex is similar. The mass transfer coefficient for the complex is about 10% lower than that for amine because of its larger molecular weight.

Effects of Lactic Acid Concentration and pH

The extraction rate increased with an increase in the lactic acid concentration (Fig. 4) and a decrease in the solution pH (Fig. 5). It is well known that Alamine 336 can only extract the undissociated acid *(26)*. The observed effects of pH and lactic acid were mainly attributed to the undissociated lactic acid concentration in the solution, as illustrated in Fig. 6 with combined data from Figs. 4 and 5. At low acid concentrations, the extraction rate was proportional to the lactic acid concentration, indicating that the reaction was first order with lactic acid concentration. However, at higher acid

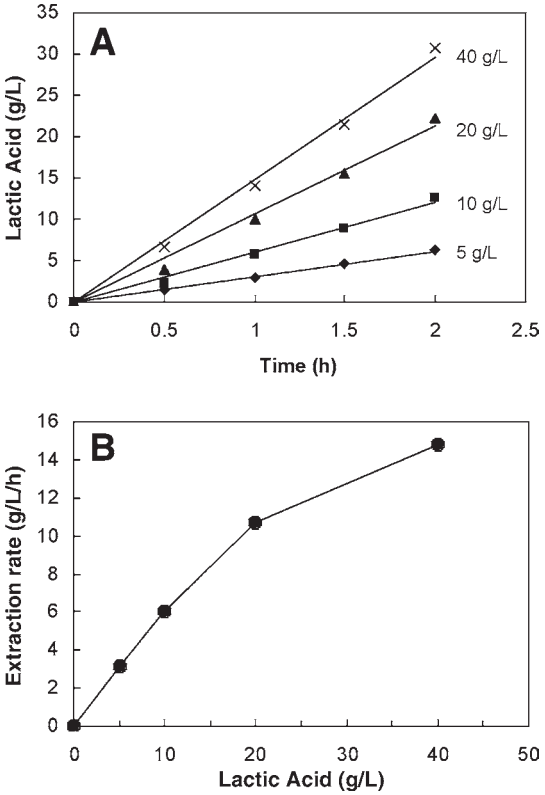

Fig. 4. Effect of lactate concentration on extraction of lactic acid by Alamine 336 (30% [v/v] in 2-octanol) at pH 4.5 and 80 mL/min flow rate: **(A)** time course of lactate concentration in base reservoir; **(B)** extraction rate as affected by concentration of lactic acid in feed solution.

concentrations, the increase in the extraction rate was less than proportional, indicating that the reactive extraction was also affected by the amine concentration at the interface. With more acid molecules in the solution, more amine molecules would be reacted to form the complex, resulting in fewer free amine molecules at the interface. Consequently, the increase in extraction rate would level off at a high lactic acid concentration owing to reduced amine concentration.

Effects of Flow Rate

The liquid velocity in the hollow-fiber membrane extractor affects the thickness of the liquid film on the membrane surface and, thus, may affect the mass transfer rates in the extractor and back extractor. In the present study, one flow rate was varied from 20 to 120 mL/min, whereas the other two flow rates were kept at 80 mL/min. As shown in Fig. 7,

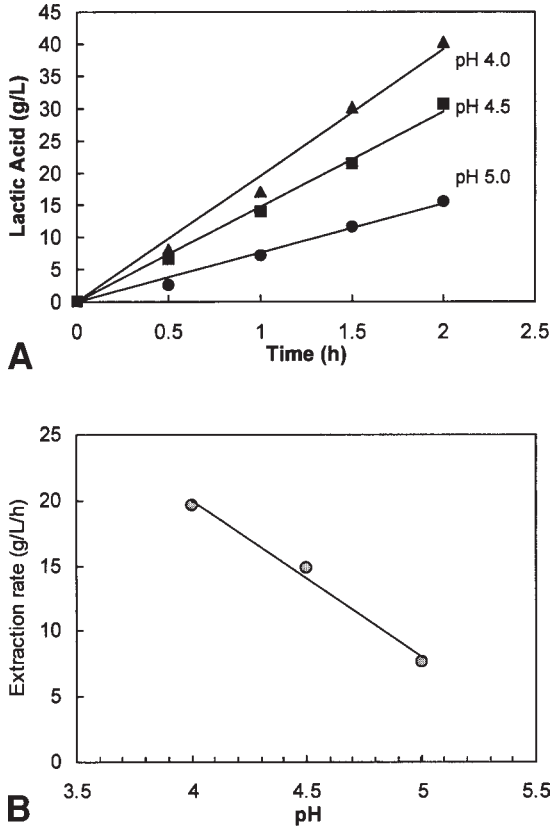

Fig. 5. Effect of pH on extraction of lactic acid (40 g/L) by Alamine 336 (30% [v/v] in 2-octanol) at 80 mL/min flow rate: **(A)** time course of lactate concentration in base reservoir; **(B)** extraction rate as affected by pH of feed solution.

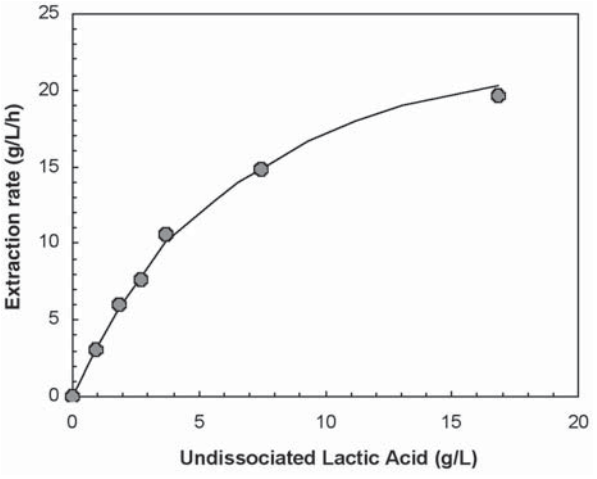

Fig. 6. Effect of undissociated lactic acid concentration on extraction rate with Alamine 336 (30% [v/v] in 2-octanol) at pH 4.5 and 80 mL/min flow rate. The curve is from the model simulation.

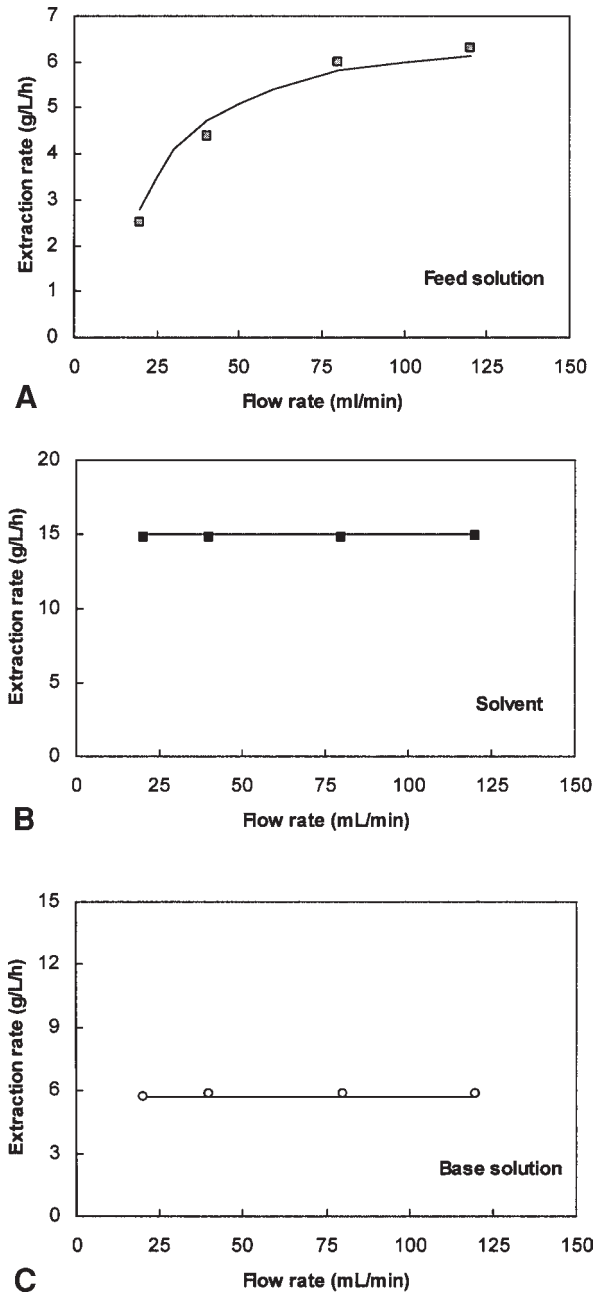

Fig. 7. Effects of flow rates of **(A)** feed solution, **(B)** organic solvent, and **(C)** stripping base solution on extraction of lactic acid by Alamine 336 (30% [v/v] in 2-octanol) at pH 4.5. Only one flow rate was varied in the range studied whereas the other two flow rates were kept at 80 mL/min. The feed contained 10 g/L of lactic acid in (A) and (C), and 40 g/L of lactic acid in (B). The curve and horizontal lines are from the model simulation.

the extraction rate increased with an increase in the flow rate of the feed solution but was not significantly affected by the flow rates of solvent and stripping base solution. The mass transfer coefficient (k_i) in the liquid film should increase with the liquid velocity (v) since k_i is proportional to $v^{1/3}$. However, mass transfer in the system was mainly limited by the membrane resistance since it had a much lower mass transfer coefficient (k_M) than the one in the solvent-phase liquid film (k_A). The overall mass transfer coefficient in the organic phase for amine increased from 2.5×10^{-7} m/s at 20 mL/min to 3.2×10^{-7} m/s at 120 mL/min. However, the increase was not significant and did not affect the overall extraction rate.

The mass transfer coefficient for lactic acid in the aqueous phase was much higher—1.71×10^{-5} m/s at 20 mL/min and 3.1×10^{-5} m/s at 120 mL/min, and thus should not pose any significant resistance to mass transfer in the extraction process. The observed effect of feed flow rate was mainly attributed to the effect of concentration. At a lower feed rate, the lactic acid concentration in the feed solution passing through the extractor would be lowered significantly owing to a longer contact time with the solvent, resulting in a lower mean lactic acid concentration in the extractor and thus a lower extraction rate since the reactive extraction rate is proportional to the lactic acid concentration at the interface. As the feed flow rate continued to increase, the mean concentration of lactic acid in the extractor would approach the feed concentration, and the effect would thus be diminished.

Model

The time course data shown in Fig. 3A were used to determine the model parameters (k_1, k_{-1}, k_2) by fitting the model to the data. The best values for the model parameters are listed in Table 2 and gave excellent fits with the data (*see* Fig. 3B). The model was then used to simulate the remaining data shown in Figs. 6 and 7. As can be seen in Figs. 6 and 7, the model predictions also fit these experimental data very well. Based on the proposed model and experimental observations, the chemical reaction between lactic acid and amine at the interface is the rate-limiting step in the extraction process. For example, in the extraction with 40 g/L of lactic acid at pH 4.5 and 30% Alamine 336, 71.5% of the total resistance is attributed to chemical reaction, whereas mass transfer resistance in the organic phase contributes 26.2% and diffusion resistance in the aqueous phase accounts for only 2.3%. In the back extractor, the reaction resistance is 94.1%, the mass transfer resistance in the organic phase is 5.9%, and there is no significant resistance (0%) in the aqueous phase. It thus can be concluded that the reaction resistance dominates in the reactive extraction carried out in the hollow-fiber membrane extractor. Since the reaction occurs on the interface between the two phases on the membrane surface, the overall reaction or extraction rate is also dependent on the total membrane surface area, as is predicated in Eqs. 11 and 12. Therefore, the extraction process can be scaled up based on the membrane surface area.

Table 2
Best Values for Model Parameters
Determined from Experimental Data

Parameter	Value
k_1 (m^4/mol·s)	9.5×10^{-10}
k_{-1} (m/s)	1.9×10^{-8}
k_2 (m/s)	2.5×10^{-7}

Basu and Sirkar *(27)* modeled the extraction of citric acid from an aqueous solution with tri-*n*-octylamine (TOA) in methyl isobutyl ketone in hollow-fiber membranes. They assumed that the reaction between TOA and citric acid occurring at the interface was rapid compared to membrane resistance and organic-phase diffusion resistance. In the case of back extraction, they concluded that the interfacial reaction rate was much lower than the extraction rate and cannot be neglected and should be considered in series with the diffusion resistances. However, they did not show the simulation result for back extraction. Coelhoso et al. *(28)* studied the extraction of lactic acid with Aliquat 336, a quaternary amine used as an ion-exchange carrier, in a hollow-fiber membrane and concluded that membrane resistance was the limiting step. They used an equilibrium equation, instead of a constant distribution coefficient, to describe the concentration relationship at interface because the distribution coefficient can vary with the solute concentration. Juang et al. *(29)* studied the extraction of lactic acid from an aqueous solution with TOA in a hollow-fiber membrane and proposed an interfacial chemical reaction mechanism in their model. However, they did not study the simultaneous extraction and stripping of lactate using two hollow-fiber membrane modules. The apparent differences in the extraction mechanism and model proposed between the present study and the aforementioned previous studies may be owing to the different amine solvents used in these studies.

It should be noted that the extraction rate shown in Figs. 3–7 is based on the concentration change in the stripping solution, which can be converted to the extraction rate per unit membrane area commonly used in process scale-up design. With 500 mL of the stripping solution and 1.4 m^2 of the membrane area in the extractor, 1 g/(L·h) is equivalent to 0.357 g/(m^2·h). Thus, the extraction rate at pH 4.0 with 40 g/L of lactic acid and 30% Alamine 336 was ~7.1 g/(m^2·h). A higher extraction rate can be achieved with a more reactive extractant such as Adogen 283, which is a secondary amine.

Conclusion

Simultaneous extraction with solvent containing Alamine 336 and stripping with NaOH in two hollow-fiber membrane extractors from an

aqueous feed of lactic acid solution was demonstrated. The extraction process is effective to continuously recover lactic acid from the aqueous feed containing lactic acid at a concentration as low as 5 g/L and pH between 4.0 and 5.0, which is in the range appropriate for lactic acid fermentation. The process thus can be used to recover and separate lactic acid produced from fermentation. Since the solvent extractant is contained in the hollow fibers and continuously regenerated on-line, the extraction process can be readily integrated with a fermentor for continuous production of lactic acid from sugars. Such an extractive fermentation process will have many advantages over conventional fermentation processes and has been previously demonstrated with propionic acid and butyric acid fermentations *(10,11)*. The process can be used to produce sodium lactate at a high concentration of >30% *(12)* and is more energy efficient compared with other separation methods. The extraction rate increased with an increase in the amine content, the undissociated lactic acid concentration, and the feed flow rate. The proposed reactive extraction model based on a first-order reaction mechanism between lactic acid and amine simulates the experimental data well and can be used in the scale-up design of the process.

Nomenclature

C = solute concentration in bulk solution (mol/m^3)
C^* = solute concentration at interface (mol/m^3)
d_i = inner diameter of hollow fiber, $=2.4 \times 10^{-4}$ (m)
d_m = Log mean diameter of hollow fiber (m)
d_o = outer diameter of hollow fiber, $=3.0 \times 10^{-4}$ (m)
D_{aq} = diffusion coefficient of lactic acid in aqueous phase (cm^2/s)
D_{org} = diffusion coefficient of amine or complex in organic phase (cm^2/s)
J = solute flux (mol/[m^2·s])
k = mass transfer coefficient (m/s)
k_1 = forward reaction rate constant (m^4/mol·s)
k_{-1} = backward reaction rate constant (m/s)
k_2 = physical extraction rate constant (m/s)
N = number of hollow fiber tubes in membrane extractor module, =10,200
Q = volumetric flow rate (m^3/s)
t = time (s)
T = absolute temperature (K)
V = volume of solution in reservoir, $=5 \times 10^{-4}$ (m^3)
V_A = molar volume of amine, =363.3/0.81 (cm^3/mol)
V_O = molar volume of organic solvent (cm^3/mol)
V_X = molar volume of complex, =453.3/0.81 (cm^3/mol)
z = hollow-fiber length coordinate (m)
δ = membrane thickness, $=3.0 \times 10^{-5}$ (m)
ε = membrane porosity, =0.4
μ_O = organic phase viscosity (cP)
ν = liquid velocity (m/s)
τ = tortuosity, =2.5

Subscripts

A = amine
B = back extractor
F = feed
L = lactic acid
M = membrane
O = organic phase
S = solvent
X = complex
0 = initial condition

Superscripts

in = inlet to hollow-fiber module
out = outlet from hollow-fiber module

Acknowledgment

This work was supported in part by the US Department of Agriculture (grant no. 2002-00389).

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