Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Mok, Young Sun and Lee, Won Kook(1994) 'Water Transport in Water-in-Oil-in-Water Liquid Emulsion Membrane System for the Separation of Lactic Acid', Separation Science and Technology, 29: 6, 743 — 764
To link to this Article: DOI: 10.1080/01496399408005606
URL: http://dx.doi.org/10.1080/01496399408005606

SEPARATION SCIENCE AND TECHNOLOGY, **29**(6), pp. 743–764, 1994

Water Transport in Water-in-Oil-in-Water Liquid Emulsion Membrane System for the Separation of Lactic Acid

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ABSTRACT

Liquid emulsion membranes (LEMs) were applied to the separation of lactic acid from an aqueous feed phase, and water transport (swelling) was investigated during the separation. Considering that as lactic acid was extracted into the internal stripping phase, osmotic pressure difference across the membrane was varied, the water transfer coefficient was evaluated. The water transfer coefficient was larger at higher carrier concentration and initial lactic acid concentration, which means that emulsion swelling can also be mediated by solute/carrier complexes although it is, in general, osmotically induced. The appropriate LEM formulation was given for separation and concentration of lactic acid. If both separation and concentration are desired, evidently emulsion swelling should be considered in conjunction with the transport rate of lactic acid. It was observed that the separated solute concentration in the internal phase was lowered due to swelling during the operation. Nevertheless, lactic acid could be concentrated in the internal phase more than 6 times in specific conditions, indicating that as the volume ratio of external phase to internal phase is increased, a still higher concentration in the internal phase can be obtained. The change in mean internal droplet size with swelling was measured at given intervals to understand the associated interfacial phenomenon. From this experiment it was proved that the amount of swelling cannot be quantitatively determined from the change of mean droplet size.

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INTRODUCTION

Liquid emulsion membranes (LEMs) were invented by Li (1) and have been used for a variety of separations (2–6). The LEM separation technique is a highly selective method of separating organics, inorganics, and metal ions capable of simultaneous extraction and stripping.

Recently, the demand for lactic acid, which is the monomer of polylactic acid, has increased steadily, so that easier and cheaper techniques to separate lactic acid are needed. However, there are a few reports on the separation of lactic acid.

Chaudhuri et al. were the first to apply LEMs to the separation of lactic acid using Alamine 336 as a carrier and Span 80 as a surfactant (7, 8). Their system, however, has several problems. Surfactant Span 80, for example, transports a lot of water and causes the emulsion to be unstable when the stripping reagent concentration is high. Additionally, in their study the lactic acid could not be highly concentrated in the internal phase due to the low treatment ratio (external/emulsion volume = 2).

Interest in LEMs for biochemical separations has focused on their potential for cocurrent product removal in fermentation broths through reduced product inhibition of the fermenting organisms. LEMs, when applied to biochemical separations, are water-in-oil-in-water (W/O/W) systems. The problems associated with a W/O/W LEM system is emulsion swelling. The disadvantages of swelling are the dilution of separated product in the internal phase and the increase of membrane breakage. These phenomena are caused by the osmotic pressure gradient across the membrane phase.

Many studies on emulsion swelling have been reported elsewhere (9–13). However, most of these studies deal with systems which do not possess any transportable solutes. When a system contains solute, the osmotic pressure difference across the membrane varies as the solute is extracted into the internal stripping phase, and the possibility exists that the solute transports water by way of solute hydration and aggregated solute–carrier complexes. Therefore, solute transport should be taken into account when studying emulsion swelling.

In this study the application of LEMs to the separation of lactic acid is discussed using Amberlite LA2 as the carrier, Paranox 100 as the surfactant, and sodium carbonate as the stripping reagent.

This article reports the effect of variables on lactic acid transport and emulsion swelling, and the quantitative and interpretative aspects of the study are discussed. Emulsion swelling indicates that the optimal LEM formulation can be obtained with respect to separation and concentration. An attempt has been made to elucidate how lactic acid and Amberlite

LA2 affect water transport (swelling). In addition, the change of mean internal droplet size (Sauter mean diameter) with swelling was periodically measured during the course of a run, which is important for understanding the interfacial phenomenon and subsequent mathematical modeling.

THEORY

Transport of Lactic Acid

For the aqueous systems considered here, a membrane is defined as a water-immiscible phase which separates two aqueous phases, thus preventing direct contact of the aqueous phases. A water-in-oil (W/O) emulsion is formed and dispersed throughout an aqueous (feed) phase in a reactor. A schematic diagram of an LEM system is presented in Fig. 1.

In this study, sodium carbonate was used as the stripping reagent in the internal aqueous phase to accept lactic acid. The hydrogen gradient provides the driving force for lactic acid transport. Hydrolysis of Na_2CO_3 is chemically and mathematically equated as follows:

$$CO_3^{2-} + H_2O \Leftrightarrow HCO_3^- + OH^- \tag{1}$$

$$K_{b1} = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = 2.1 \times 10^{-4} \tag{2}$$

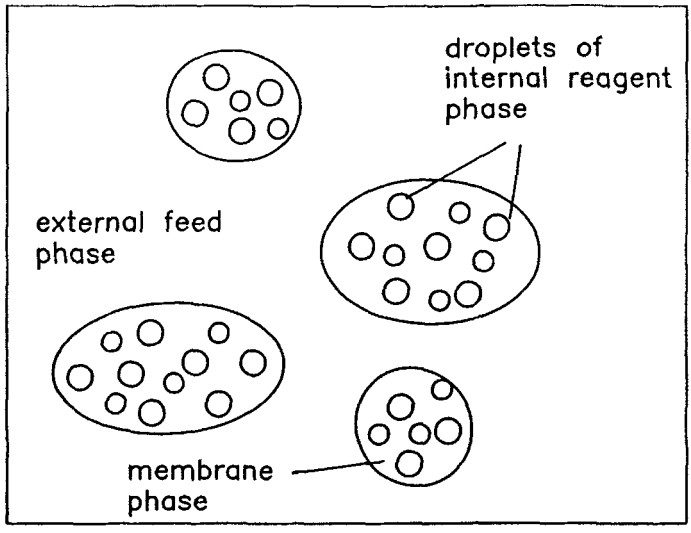

FIG. 1 Schematic diagram of a liquid emulsion membrane system.

$$HCO_3^- + H_2O \Leftrightarrow H_2CO_3 + OH^- \quad (3)$$

$$K_{b2} = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]} = 2.4 \times 10^{-8} \quad (4)$$

In LEMs, a secondary amine (R_2HN) can be used as a carrier for the separation of lactic acid. When the carrier reaches the interface between the external and membrane phases, it reacts with hydrogen ion and lactate ion to make a complex. The overall reaction for this extraction can be expressed as the forward reaction:

$$H^+(aq) + La^-(aq) + R_2HN(org) \Leftrightarrow R_2HNH^+La^-(org) \quad (5)$$

The complex then diffuses through the membrane to the interface between the membrane and the internal phases. Due to the extremely high pH of the internal phase, the lactate ion is stripped from the membrane phase into the internal phase by the reverse of Eq. (5). This reaction regenerates the carrier, which then diffuses back to the feed side of the membrane. These processes are repeated as long as a difference in hydrogen concentration exists. This uphill transport of lactate ion makes it possible to obtain highly concentrated product solutions from dilute feed streams. Figure 2 illustrates the overall mechanism of lactic acid transport.

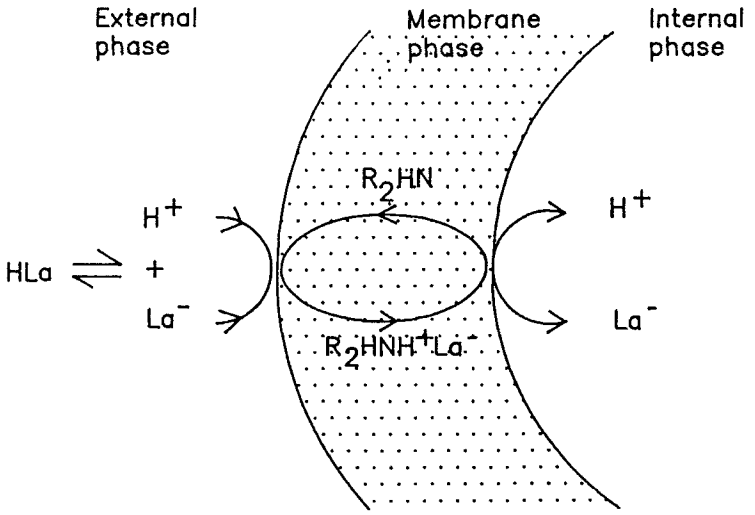

FIG. 2 Overall transport mechanism of lactic acid.

Transport of Water

Generally, water transport into the internal phase (emulsion swelling) is driven by the osmotic pressure difference between the external phase and internal phases, and takes place by way of hydrated surfactant (11) or surfactant aggregates (reversed micelle) (12, 13) to reduce the osmotic pressure difference. Figure 3 shows a schematic representation of the water transport mechanism.

In dilute solution, the osmotic pressure difference between the external and internal phases, $\Delta\Pi$, is given by

$$\Delta\Pi = (C_i - C_e)RT \tag{6}$$

where C_i and C_e are the concentrations of all species (ions + molecules) in the internal and external phases, respectively.

When LEM is applied to the separation of organic acids, swelling can be caused by solute hydration in addition to the osmotically induced one. If a driving force for solute transport exists, emulsion swelling by solute hydration occurs even in the absence of an osmotic pressure difference. Thus, the extent of water transport is related to the coextraction of water along with that of the acid. Then the equation describing the volume flux of water across the membrane is

$$\frac{dV_i}{dt} = k_s A \Delta\Pi + n\overline{V}_{H_2O} + n\overline{V}_{H_2O}\left[-\frac{d(V_e C_e)}{dt}\right] - \epsilon V_i \tag{7}$$

where k_s is the water transfer coefficient, n is the hydration degree of lactic acid, and $\overline{V}_{H_2O}$ is the molar volume of water. If the LEM system is stable during separation, the leakage of internal phase ϵ can be neglected. Assuming each hydrophilic functional group interacts with only one water molecule, the degree of hydration, n, is 2.

If the model is correct, then a plot against $A\Delta\Pi$ should yield a straight line with a slope of k_s, but actually it does not.

Figure 4 shows the effect of the volume fraction of the internal aqueous phase in the emulsion on emulsion viscosity. As the volume fraction of the internal phase is increased by swelling, the emulsion viscosity increases; it increases sharply when the volume fraction of the internal phase is larger than 0.67. This can be explained by the formation of more liquid crystalline structures with an increase in the volume fraction of the internal phase (14). The presence of liquid crystalline structures can lead to water transport resistance, which retards emulsion swelling. Since the increase in emulsion viscosity interferes with the circulation of internal droplets, the transported water primarily dilutes the droplets close to the emulsion glob-

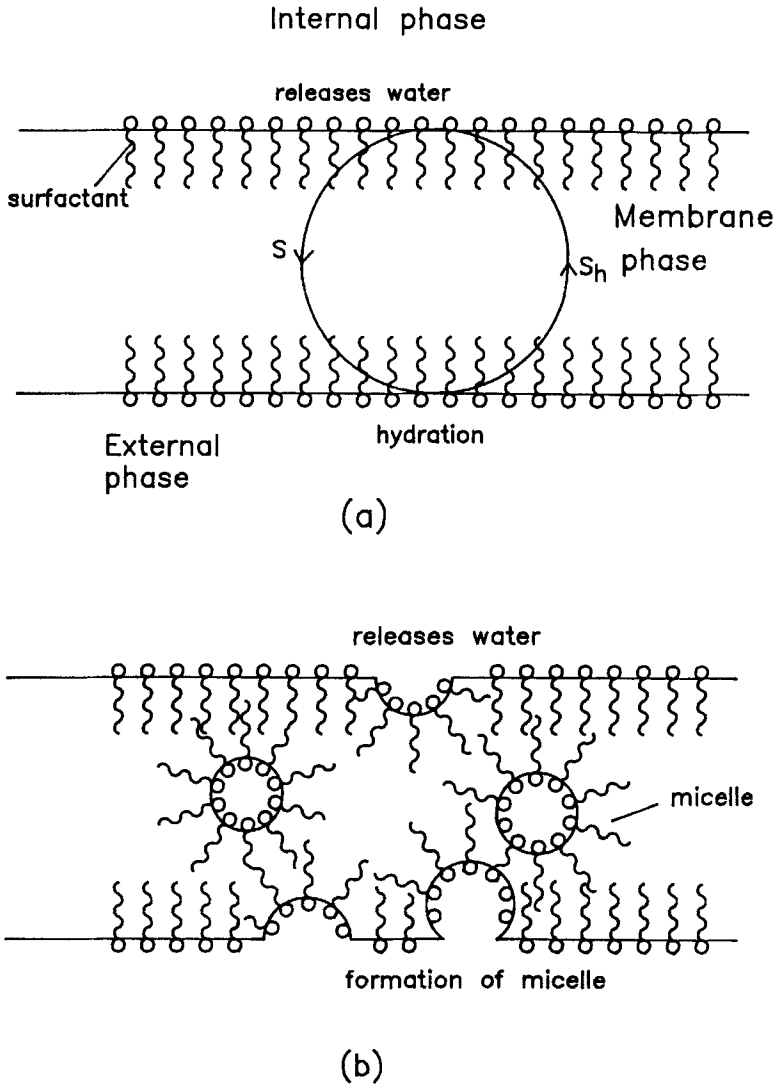

FIG. 3 Schematic representation of water transport. (a) Hydrated surfactant mechanism. (b) Reversed micelle mechanism. S: Non- (or poorly-) hydrated surfactant. S_h: Hydrated surfactant.

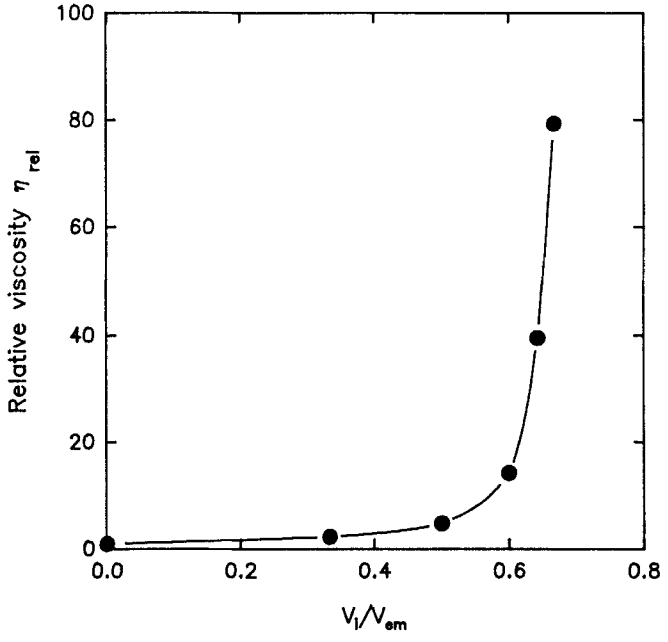

FIG. 4 The change in relative emulsion viscosity as a function of internal phase volume fraction in the emulsion.

ule surface, which reduces osmotic pressure difference, so that the diffusion distance for water becomes increasingly longer. That is, swelling does not penetrate far into the emulsion globule. Therefore, the volume flux of water transport is inversely proportional to the increasing internal phase volume. Equation (7) should be rewritten

$$\frac{dV_i}{dt} = k_{sw}A(C_i - C_e)\left(\frac{V_{i,0}}{V_i}\right)^{\beta} + n\overline{V}_{H_2O}\left[-\frac{d(V_eC_e)}{dt}\right] \tag{8}$$

where k_{sw} is equal to k_sRT.

In the present system the total concentration in the internal phase which influences the osmotic pressure is equated as follows:

$$C_i = [Na^+]_i + [CO_3^{2-}]_i + [HCO_3^-]_i + [H_2CO_3]_i + [La^-]_i \tag{9}$$

The mass balance equations are as follows:

$$[Na^+]/2 = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3] \tag{10}$$

$$\begin{aligned} V_{e,0}C_{e,0} &= V_eC_e + V_mC_m + V_i[La]_i \\ &\cong V_eC_e + V_i[La^-]_i \end{aligned} \tag{11}$$

Using Eqs. (10) and (11), Eq. (9) can be rewritten as

$$C_i = \frac{3}{2}[Na^+]_i + \left(C_{e,0}\frac{V_{e,0}}{V_e} - C_e\right)\frac{V_e}{V_i} \tag{12}$$

Since the membrane is the water-immiscible phase, another mass balances hold, and Eq. (12) can be written in terms of only C_e and V_i:

$$[Na^+]_{i,0}V_{i,0} = [Na^+]_iV_i \tag{13}$$

$$V_{e,0} + V_{i,0} = V_e + V_i \tag{14}$$

It is necessary to obtain an expression for the interfacial area A before we can solve Eq. (8). The number of emulsion globules can be determined from the initial mean radius, $R_0 = D_{32}/2$ ($D_{32} = \sum n_iD_i^3/\sum n_iD_i^2$: Sauter mean diameter):

$$N_{em} = V_{em,0}\Big/\frac{4}{3}\pi R_0^3 \tag{15}$$

where $V_{em,0}$ is the initial emulsion volume ($V_m + V_{i,0}$).

The emulsion globule radius is given by

$$R_e = \left(V_{em}\Big/\frac{4}{3}\pi N_{em}\right)^{1/3} \tag{16}$$

From Eqs. (15) and (16), one can obtain the equation for the interfacial area between the external and membrane phases

$$A = N_{em}4\pi R_e^2 = N_{em}4\pi R_0^2\left(\frac{V_{em}}{V_{em,0}}\right)^{2/3} \tag{17}$$

As can be seen in Eq. (17), interfacial area A can be determined from the change of emulsion volume. Since the membrane phase volume V_m is constant, the change of emulsion volume is equal to the change of internal phase volume, V_i.

In order to solve Eq. (8), the profiles of C_e and V_i must be obtained. The change in internal phase volume and lactic acid concentration in the external phase are described by empirical expressions as follows:

$$\frac{V_i}{V_{i,0}} = \frac{a(1 + t)^b}{(a + t)} \tag{18}$$

$$\frac{C_e}{C_{e,0}} = \frac{c + dt}{c + t} \tag{19}$$

The values of a, b, c, and d were obtained by best curve fitting of the experimental data (Figs. 6–8).

Knowing that $-dV_e/dt$ is equal to dV_i/dt, Eq. (8) can be transformed to

$$(1 - n\bar{V}_{H_2O}C_e)\frac{dV_i}{dt} + n\bar{V}_{H_2O}V_e\frac{dC_e}{dt} = k_{sw}A(C_i - C_e)\left(\frac{V_{i,0}}{V_{i,0}}\right)^{\beta} \tag{20}$$

$$Y = k_{sw}X$$

Substituting Eqs. (18) and (19) and the derivatives of Eqs. (18) and (19) into Eq. (20), a graph of Y against X gives the water transfer coefficient k_{sw}.

EXPERIMENTAL

Materials

Kerosene, purchased from Junsei Chemical Co., was used as the membrane phase. The surfactant, Paranox 100, a nonionic polyamine, was obtained from Exxon Chemical Co. Paranox 100 has a high molecular weight, so the use of a bigger surfactant with its smaller diffusivity reduces emulsion swelling if emulsion swelling occurs via the diffusion of hydrated surfactant or reversed micelle.

The carrier, Amberlite LA2, a secondary amine, was purchased from Sigma Chemical Co.

Sodium carbonate, purchased from Junsei Chemical Co., was used as the stripping reagent.

Lactic acid was supplied in concentrated form by Katayama Chemical Co. The concentrated lactic acid solution also contained dimers (lactic anhydride). The lactic anhydride can be hydrolyzed to lactic acid by heating a dilute aqueous solution for several hours.

Methods

A stable emulsion was made by slow addition of the aqueous sodium carbonate solution (internal phase) to the membrane phase. The emulsion consisted of Paranox 100 and Amberlite LA2 dissolved in kerosene under the high shear provided by a homogenizer (Tekmar Company, Germany). The W/O emulsion was then dispersed by a six-bladed turbine into a four-baffled vessel containing the external feed phase to give a W/O/W emulsion system. At given intervals, samples were withdrawn by pipet, filtered to remove the W/O emulsion drops, and the residual lactic acid concentration was analyzed by a colorimetric method (15) or by high-performance liquid chromatography (Waters) using a YMC-Pack C8 column with a refractive index detector.

The emulsion globule sizes were measured photographically, and the Sauter mean diameter was calculated. The emulsion viscosity was measured by a rotational viscometer (Brookfield Model DV-II).

The size distribution of internal droplets and the water content in the removed emulsion were also analyzed. The size of the internal water droplets in the emulsion was measured by using a centrifugal particle size analyzer (SA-CP3, Shimadzu, Japan), and the Sauter mean diameter, d_{32}, was calculated from a specific area as follows:

$$d_{32} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} = \frac{6M}{\rho A_i} \qquad (A_i/M = \text{specific area}) \tag{21}$$

where M and A_i are the total mass and total surface area of internal droplets, respectively.

TABLE 1
Typical Experimental Conditions

Internal phase:
Na_2CO_3: 0.6 M
Membrane phase:
Kerosene: 90 wt%
Amberlite LA2: 5 wt%
Paranox 100: 5 wt%
External phase:
Lactic acid: 0.1 M
Volume ratios of each phase:
Internal/membrane: 1/1
Emulsion/external: 1/4
(emulsion = internal + membrane phases = 0.1 dm^3)
Emulsifier speed: 12,000 rpm
Stirrer speed: 250 rpm

Water content in the W/O emulsion was measured by the Karl-Fisher method, and then the internal phase volume was determined from the volume ratio to initial value of the internal aqueous phase.

The leakage of the internal phase was measured by determination of sodium concentration in the external phase. The sodium concentration was analyzed by an atomic absorption spectrophotometer (AA575). The leakage of the internal phase was less than 0.2% under experimental conditions, so it was ignored.

Typical experimental conditions are summarized in Table 1. When the effect of one variable was studied, all the other variables were kept constant at the values given in Table 1.

RESULTS AND DISCUSSION

Typical Experimental Results

Figure 5 shows the separation results for the typical experimental conditions (Table 1). The effect of swelling on the ability of the membrane to concentrate solute can also be seen in Fig. 5. It is instructive to note that water transport (swelling) occurred during separation, and the separated

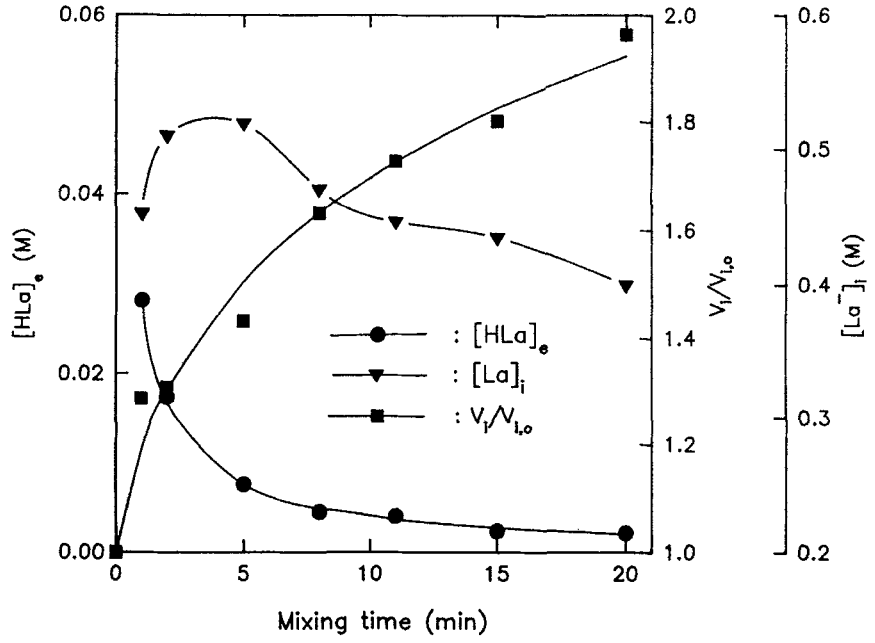

FIG. 5 Typical experimental results.

lactic acid in the internal phase diluted. Since both the separation rate and concentration are important, the effects of LEM formulation on solute transport and emulsion swelling should be examined. As can be seen in Fig. 5, the product concentration in the internal phase reaches a maximum and then gradually decreases, indicating that an optimal operation time exists.

Water Transfer Coefficient

To evaluate the water transfer coefficient, β was repeatedly assumed so that the plot of Eq. (20) was linearly related with the slope of k_{sw}. When β is 3, linear relationships were obtained with the slope of k_{sw}, and the calculated values of $V_i/V_{i,0}$ fit the experimental data well. The water transfer coefficient evaluated at various conditions is given in Table 3 where $k_{sw}/\overline{V}_{H_2O}$ corresponds to the water permeation coefficient in the equation used for lipid bilayer membrane systems (e.g., Ref. 16).

Effects of Variables

The effects of LEM formulation on lactic acid transport and emulsion swelling were investigated, and the variations in the extent of emulsion swelling were interpreted in terms of the water transfer coefficient.

The effect of surfactant concentration on lactic acid transport is shown in Fig. 6(a). Except for extremely low surfactant concentrations, three runs showed similar results after an initial period. However, there are slight differences in the initial transport rate. When the surfactant concentration was decreased to 2 wt%, the initial transport rate slightly increased. On the contrary, when the surfactant concentration was increased to 8 wt%, the initial transport rate slightly decreased. This is easily explained. As the surfactant concentration is increased, the internal droplet size in the emulsion decreases since more internal droplets can be formed at a higher surfactant concentration (see Table 2). The emulsion viscosity increases as the internal droplet size decreases (17). It is readily apparent

TABLE 2
Mean Droplet and Globule Sizes (Sauter mean diameter)

	Paranox 100 concentration (wt%)		
	2	5	8
d_{32} (μm)	4.58	4.29	3.34
D_{32} (dm)	0.0019	0.00195	0.00202

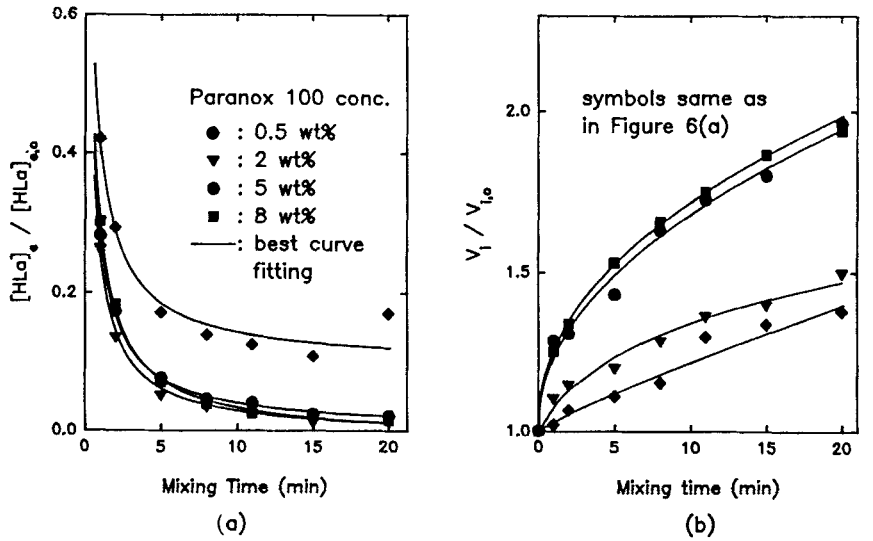

FIG. 6 Effect of Paranox 100 concentration on HLa transport (a) and emulsion swelling (b).

that an increase in emulsion viscosity raises the emulsion globule size. When the emulsion globule size is larger, the mass transfer area becomes smaller.

Figure 6(b) represents the influence of surfactant concentration on emulsion swelling. As the surfactant concentration was increased, the emulsion

TABLE 3
Water Transfer Coefficient

Variables	Concentration	R_0 (dm)	$\frac{k_{sw}}{\bar{V}_{H_2O}} \times 10^3$ (dm/min)
Surfactant (wt%)	2	0.00190	0.52
	5	0.00195	2.13
	8	0.00202	2.53
Carrier (wt%)	2	0.00195	1.87
	5	0.00195	2.13
	8	0.00195	4.58
Initial feed (M)	0.06	0.00211	1.83
	0.10	0.00195	2.13
	0.14	0.00188	2.55

swelling increased. Since the surfactant could be a water carrier, the extent of swelling increased with the surfactant concentration. As noted in many studies, the surfactant plays an important role in water transport. Therefore, as long as the emulsion is stable during separation, a low surfactant concentration is desirable because a high surfactant concentration results in large emulsion swelling and the surfactant is expensive. As expected, a larger water transfer coefficient was obtained at a higher surfactant concentration. Here, it should be noted that in case of 2 wt% surfactant, $V_i/V_{i,0}$ was less than 1.25 at 5 minutes while most of lactic acid was separated.

Figure 7(a) shows the effect of Amberlite LA2 concentration on lactic acid transport. Carrier concentration determines how fast the separation proceeds. As the carrier concentration was increased, the initial lactic acid transport rate (slope) increased. An increase in the initial lactic acid transport rate causes faster lactic acid enrichment in the internal phase, that is, the osmotic pressure gradient in the early stage increases with carrier concentration. Thus, the rate of emulsion swelling increases with carrier concentration, as shown in Fig. 7(b). However, the large differences between the extents of swelling, as in Fig. 7(b), can hardly be explained by only the increase of osmotic pressure difference in the early stage because the lactic acid separation almost reaches equilibrium within a few minutes and then each case has a similar osmotic pressure differ-

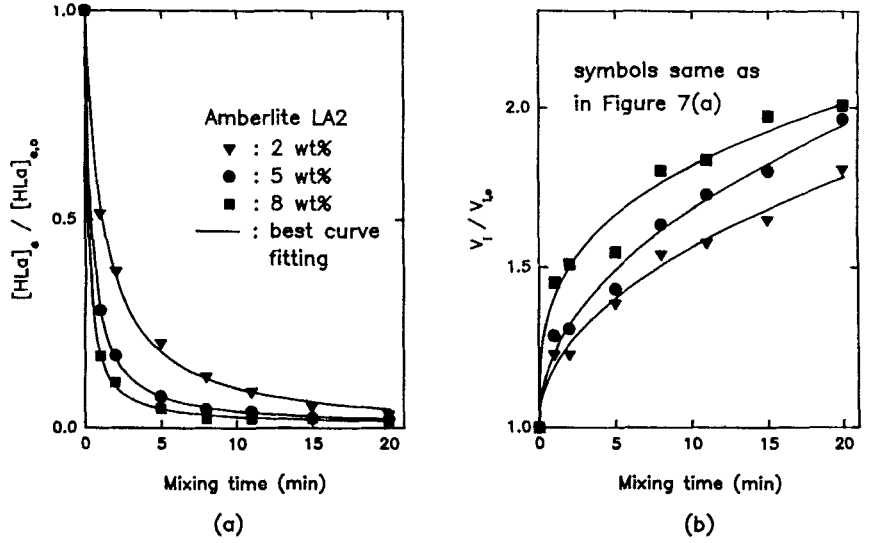

FIG. 7 Effect of carrier concentration on HLa transport (a) and emulsion swelling (b).

ence. This suggests that swelling can be mediated by another scheme. As presented in Table 2, the water transfer coefficient was greatly affected by the carrier concentration, which shows that the carrier molecule is responsible for water transport. A secondary amine, Amberlite LA2 (*N*-lauryl-*N*-trialkyl methyl amine), used as a carrier in this study, does not have any hydrophilic group, so the carrier itself cannot transport water.

$$\text{Amberlite LA2: } C_{12}H_{25}\text{—NH—}CR_1R_2R_3$$

However, since the lactates of secondary amines have the possibility of exhibiting surface-active properties, the lactic acid/Amberlite LA2 complex may enable water to be transported by forming reversed micelle. As can be seen in literature on the liquid extraction of carboxylic acids, the acid–amine complex can form micellar aggregates and transport a lot of water (18–21). Analogously, in the LEM system, the water may be transported as reversed micelles made of lactic acid and Amberlite LA2, and the amount of water transported at higher carrier concentrations appears to be greater than anticipated. Therefore, the carrier concentration which allows a sufficiently fast separation of solute but does not enhance the water transport should be found. At 2 wt% of Amberlite LA2 in the membrane phase, the transport rate is too low. On the other hand, the extent of swelling at 8 wt% is too great. In this context, 5 wt% is proper if the LEM system is to both separate and concentrate.

Figure 8(a) shows the effect of the initial feed concentration on lactic acid transport. It can be seen that when the initial feed concentration is high, lactic acid transport is slow. A higher initial feed concentration, however, results in a greater water transport rate, as shown in Fig. 8(b). This is similar in results to the phenylalanine separation of Itoh et al. (22). Since the internal phase volume is much smaller than the external phase volume, the separated solute concentration in the internal phase when using a higher initial feed concentration is higher than with a lower initial feed concentration. Therefore, while at time zero the osmotic pressure gradient across a membrane decreases with an increase in initial feed concentration, this is inverted during separation due to enrichment of lactic acid in the internal phase. This is the reason why the separation of feed having a higher initial concentration gives a larger extent of swelling. Besides, as shown in Table 3, a higher feed concentration results in a smaller emulsion globule size, i.e., a larger surface area because lactic acid decreases the surface tension of the aqueous feed phase. This decrease of emulsion globule size increases emulsion swelling.

When the water transfer coefficient was investigated, it increased with the initial feed concentration. Since the other conditions were unchanged, this increase in the water transfer coefficient is obviously the influence

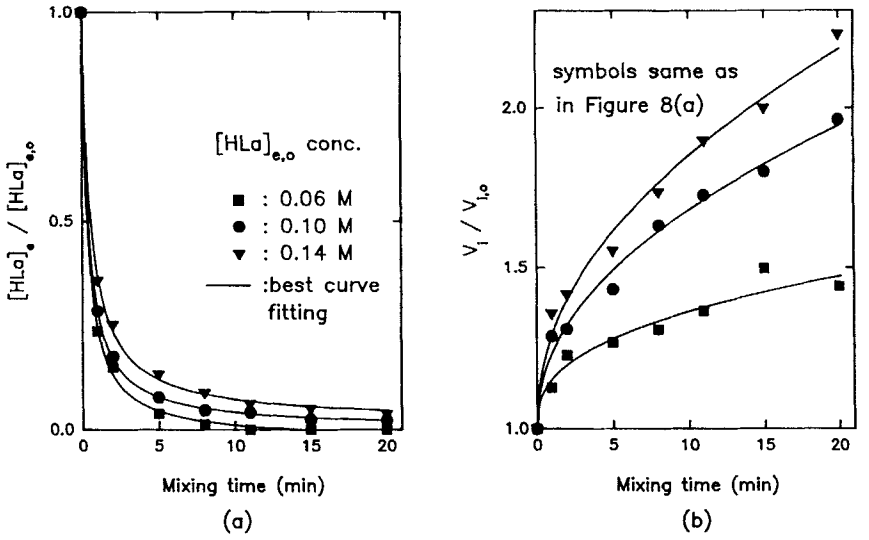

FIG. 8 Effect of initial HLa concentration on transport rate (a) and emulsion swelling (b).

of lactic acid concentration. As mentioned previously, since the aggregated lactic acid/Amberlite LA2 complex is able to transport water, the amount of swelling will be much more due to the formation of more reversed micelles when a higher concentration feed is used.

Figure 9(a) and 9(b) show the effect of sodium carbonate concentration on lactic acid transport and emulsion swelling, respectively. When the sodium carbonate concentration is increased, the lactic acid transport rate increases because the driving force for lactic acid transport increases. However, as the sodium carbonate concentration is increased, water transport (swelling) also increases, which means that the increase in Na_2CO_3 concentration increases the osmotic pressure difference between the external and internal phases. The solid lines in Fig. 9(b) are results calculated with the aid of the best curve fitting of Fig. 9(a). Since sodium carbonate just increased the osmotic pressure difference, the water transfer coefficient will be insensitive to the stripping reagent concentration. Thus, the water transfer coefficient obtained from the typical conditions could be used in this calculation, and good agreement was achieved. One of the crucial variables in lactic acid separation by LEMs is the stripping reagent concentration as the driving force for lactic acid transport. Similarly to other variables, the stripping reagent concentration should be chosen to give a sufficiently fast separation rate but also low emulsion swelling as long as possible. In this respect, 0.6 M of Na_2CO_3 is suitable; this

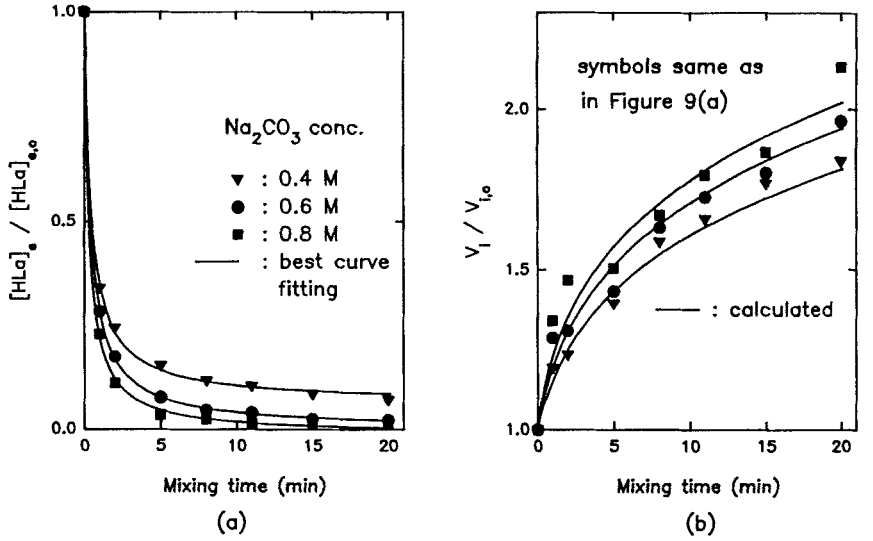

FIG. 9 Effect of Na_2CO_3 concentration on HLa transport (a) and emulsion swelling (b).

corresponds to a 1.5 times excess of the Na_2CO_3 required to neutralize all the lactic acid initially present.

Figure 10 shows the variation of lactic acid concentration in the external and internal phases at an appropriate LEM formulation. The maximum solute concentration in the internal phase was attained at about 5 minutes; however, at longer times it was lowered due to swelling. From this result we can see that the optimal operation time is 5 minutes for then lactic acid could be concentrated more than 6 times.

Mean Internal Droplet Size

An experiment was made to find out whether emulsion swelling leads to a growth of internal droplets or forms new internal droplets. If the internal droplets grow with water transport in the absence of new internal droplet formation, the amount of swelling can be quantitatively measured by means of the droplet size as follows:

$$V_i - V_{i,0} = \frac{\pi}{6}(d_{32}^3 - d_{32,0}^3) \times N_i \tag{22}$$

where N_i is the number of internal droplets.

Table 4 shows that after emulsion swelling, the Sauter mean diameter of internal droplets changed even though the four runs had different fea-

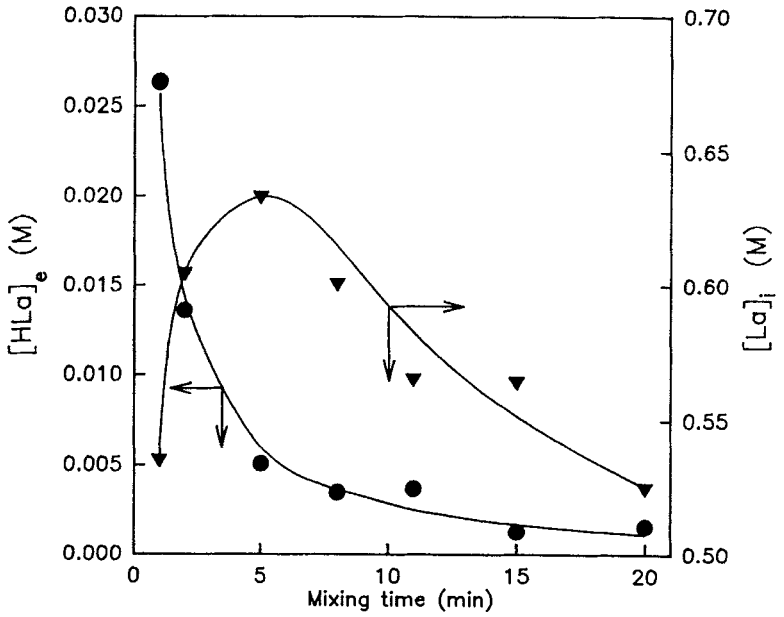

FIG. 10 Separation and concentration at appropriate operating conditions.

tures. In the case of an extremely low surfactant concentration, the emulsion is unstable and tends to break. When emulsion breakage occurs, unstable larger internal droplets break down sooner than smaller internal droplets. Thus, the mean internal droplet size decreases with time. When the surfactant concentration was increased to 2 wt%, no noticeable change in the average size was found. It seems that the growth and coalescence of internal droplets offsets the formation of new internal droplets. When the surfactant concentration was further increased to 5 wt%, the mean

TABLE 4
Change in Sauter Mean Diameter of Internal Droplet (μm)

Surfactant concentration (wt%)	Mixing time (min)				
	0.0	2	5	8	11
0.5	6.1	5.27	4.69	4.64	4.64
2	4.58	4.55	4.66	4.67	4.67
5	4.29	4.5	4.52	4.76	4.86
8	3.34	3.65	3.57	3.44	3.33

droplet size increased with time because of the growth of internal droplets by large emulsion swelling (see Fig. 6b) overcame the formation of new internal droplets. On the other hand, in the case of 8 wt% surfactant, it was observed that the mean internal droplet size increased in the early stages but then gradually diminished because the excess surfactant formed a lot of new droplets.

In conclusion, we can say the surfactant concentration determines that the mean droplet size will change in some manner with water transport. In addition, it was proved that the amount of transported water could not be determined from a change of mean droplet diameter.

CONCLUSIONS

The LEM process has been applied to the separation of lactic acid from an aqueous feed phase. Experimental results showed that the lactic acid transport rate was increased by an increase in Amberlite LA2 concentration or Na_2CO_3 concentration, and the emulsion swelling was affected by Paranox 100 concentration, Amberlite LA2 concentration, or Na_2CO_3 concentration.

Increases in carrier concentration were shown to result in higher initial solute fluxes and higher swelling rates. With respect to the water transfer coefficient k_{sw}, it is suggested that the increase in emulsion swelling with carrier concentration results from the aggregated solute–carrier complexes as well as from the increase in the osmotic pressure difference in the early stages. Lactic acid concentration in the external phase also has a great influence on emulsion swelling. Since lactic acid in the external phase decreases the surface tension of the external aqueous phase, emulsion globule size decreases with feed concentration, i.e., surface area of emulsion globules increases, and the increase in feed concentration also increases the formation of micellar aggregates which are able to transport water. Therefore, the initial feed concentration is of great importance to emulsion swelling.

A simple model (Eq. 8) originally used to estimate the water transfer coefficient successfully predicted the volume change of internal phase with time when the stripping reagent concentration (initial osmotic pressure difference) was varied, and thus the extent of swelling can be predicted by this equation if carrier and surfactant concentrations capable of transporting water are fixed.

Since the final product concentration in the internal phase and the lactic acid transport rate are also important, both of them should be taken into account. Water transport (emulsion swelling) indicates that the appropriate operating conditions for separation and concentration can be obtained.

The appropriate LEM formulation drawn with respect to the separation and concentration was 2 wt% of surfactant, 5 wt% of carrier, and 0.6 M of Na_2CO_3 for 0.1 M feed, and the optimal operation time was found to be close to 5 minutes. Despite emulsion swelling, lactic acid could be concentrated in the internal phase more than 6 times at the specific LEM formulation.

It was observed that when the surfactant concentration was different, the change in the Sauter mean diameter of internal droplets differed. Therefore, the amount of swelling cannot be quantitatively measured by the mean droplet size.

NOMENCLATURE

A	interfacial area between external and membrane phases (dm^2)
A_i	interfacial area between membrane and internal phases (dm^2)
C_e	total concentration in the external phase (M)
C_i	total concentration of all species (ion and molecule) in the internal phase (M)
d_{32}	Sauter mean diameter of internal droplets (μm)
D_{32}	Sauter mean diameter of emulsion globules (dm)
$[H^+]$	hydrogen ion concentration
$[HLa]_e$	lactic acid concentration in the external phase (M)
$[HLa]_{e,0}$	initial lactic acid concentration in the external phase (M)
K_{b1}	primary basic dissociation constant (mol/dm^3)
K_{b2}	secondary basic dissociation constant (mol/dm^3)
k_{sw}	water transfer coefficient in Eq. (8) ($dm^4/mol \cdot min$)
$[La^-]$	lactate concentration (M)
M	total mass of internal droplets (g)
n	degree of hydration
$[Na^+]$	sodium ion concentration (mol/dm^3)
N_{em}	number of emulsion globules
N_i	number of internal droplets
$[OH^-]$	hydroxyl ion concentration (mol/dm^3)
R	gas constant
R_e	emulsion globule radius (dm)
R_0	initial emulsion globule radius ($D_{32}/2$) (dm)
T	absolute temperature (K)
V_e	external phase volume (dm^3)
V_{em}	emulsion volume (dm^3)

$\overline{V}_{H_2O}$	molar volume of water (dm^3/mol)
V_i	internal phase volume (dm^3)
V_m	membrane phase volume (dm^3)

Subscripts

e	external phase
em	emulsion
i	internal phase
m	membrane phase
0	initial

Greek Letters

β	parameter in Eq. (8)
ϵ	leakage of internal phase volume
η_{rel}	relative viscosity, emulsion/membrane viscosity (η_{em}/η_m)
ρ	density of internal droplets
$\Delta\Pi$	osmotic pressure difference between the external and internal phases

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Received by editor August 2, 1993