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Modeling of Liquid Emulsion Membrane for Organic Acid Separation

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유기산의 분리를 위한 유화액막의 수학적 모델

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Abstract: A mathematical model was proposed to describe the behavior of the liquid emulsion membrane(LEM) containing sodium carbonate as internal stripping reagent. Experimental results of the batch extraction of lactic acid were compared with computed results by using the model. It was found that the model computations could predict fairly well the effects of parameter variations such as the carrier concentration, the stripping reagent concentration, the stirrer speed and the treatment ratio. An attempt has been made to reduce emulsion swelling which is one of the main problem of LEM. As the additives for swelling control, liquid paraffin, n-decanol, cyclohexanone and Span 85 were used. All the additives that were investigated tend to reduce the quantity of swelling to some extent. Cyclohexanone was found not only to reduce the swelling but also to increase largely the acid transport rate.

요 약 : 내부상의 탈거제로 탄산나트륨을 함유하는 유화액막의 거동을 묘사하기 위하여 수학적 모델이 제시되었다. 젖산의 회분식 추출 실험 결과가 모델의 계산 결과와 비교되었는데, 모델의 계산 결과는 담체농도, 탈거제농도, 교반속도, 처리비와 같은 변수의 영향을 잘 예측할 수 있었다. 유화액막의 주요 문제 중의 하나인 에멀젼의 팽윤을 줄이기 위하여, 액체 파라핀, n-데칸올, 사이클로헥사논, 스판-85 같은 막 첨가제가 사용되었다. 사용된 모든 첨가제는 팽윤 정도를 줄이는데 어느 정도 효과가 있었다. 사이클로헥사논은 팽윤을 줄일 뿐만 아니라, 젖산의 전달 속도를 크게 증가시키는 것으로 관찰되었다.

1. Introduction

Liquid emulsion membrane(LEM) has been widely used in many separation problems such as recovery of metal ions, removal of phenols and separation of hydrocarbons in that the LEM technique possesses a high potential for separation and concentration of various solutes[1-4]. Nowadays, some stud-

ies of application in biotechnology have appeared, including extraction of amino acids and carboxylic acids from fermentation broths[5-9]. Especially, interest is focused on the separation of lactic acid as a result of an increasing demand for this acid which is the monomer of polylactic acid.

Lactic acid is produced by fermentation. When LEM technique is applied to product recovery, demulsification is needed after extraction and settling. As well as demulsification, product recovery involves precipitation and subsequent dissolution using calcium hydroxide and sulphuric acid. Further treatment involves the use of activated carbon to removes impurities and ionic contaminants, multiple effect evaporation and, finally vacuum crystallization[5].

When organic acids are separated by LEM, sodium hydroxide, potassium hydroxide or sodium carbonate can be used as stripping reagent in the internal phase. As pointed out by Boey and Pyle[5], however, sodium hydroxide and potassium hydroxide have several problems. Emulsions containing NaOH solutions have inferior extraction properties to those emulsions containing sodium carbonate solutions, which proved highly satisfactory both in terms of emulsion stability and extraction properties. Moreover, strong NaOH solutions are corrosive and hazardous in handling, and more importantly, if the product were to be used in food processing, possible contamination with hazardous chemicals must be avoided. Thus, sodium carbonate that has no serious problems is suggested as stripping reagent for liquid emulsion membrane system.

When the stripping phase is made of aqueous sodium carbonate, the expression of pH change of stripping phase becomes mathematically complex due to the hydrolysis of sodium carbonate. This study presents a model of LEM which contains sodium carbonate as stripping reagent. The proposed model takes into account the mass transfer resistance in the thin aqueous film at the outside of the emulsion globule and the diffusion resistance through the liquid membrane. The model assumes reaction equilibrium both at the interface between the external phase and the membrane phase, and the interface between the membrane phase and the internal phase.

Emulsion swelling which is one of major disadvantages results in dilution of the separated product and emulsion breakage, thus the swelling control is very important to increase the efficiency of liquid emulsion membranes. The aim of this work is to verify the accuracy of the model and to reduce the emulsion swelling by using several membrane additives.

2. Theory

2. 1. LEM Configuration

A schematic diagram of a LEM system is presented in Fig. 1. Liquid emulsion membranes are prepared by first forming a water-in-oil(W/O) emulsion and then dispersing the emulsion throughout an aqueous(feed) phase by agitation for extraction. For the aqueous system to be considered herein, the liquid membrane refers to the phase between the encapsulated phase in the emulsion and the external continuous phase. The membrane phase is not miscible with the internal encapsulated phase and/or the external phase, thus preventing direct contact of one aqueous phase with the other aqueous phase. The membrane phase may be organic(as

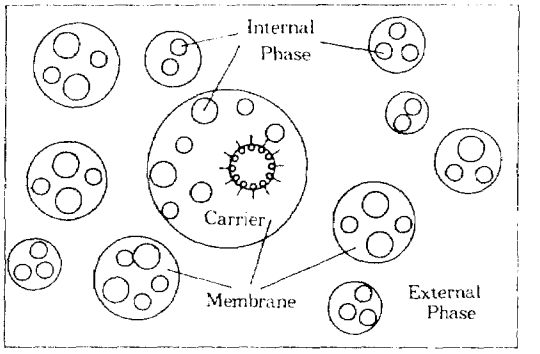

Fig. 1. Schematic diagram of a liquid emulsion membrane system.

in the case of water/oil/water system), and this phase incorporates surfactant as stabilizing agent and carrier. The internal encapsulated phase containing high concentration of sodium carbonate can act as a stripping phase. It can concentrate lactic acid that is extracted from the aqueous feed(external continuous phase) at the outside of the liquid membrane(organic phase).

2. 2. Transport of Lactic Acid

Fig. 2 illustrates the overall transport mechanism of lactic acid. In LEMs secondary amine(R_2HN) can be used as a carrier for the separation of lactic acid. When the carrier reaches the interface between the aqueous external phase and the liquid membrane phase, it reacts with proton and lactate anion to form a complex($R_2HNH^+La^-$) which is soluble in the organic membrane phase. The reaction for the extraction can be expressed as follows:

$$H^+(aq)+La^-(aq)+R_2HN(org) = R_2HNH^+La^-(org) \quad (1)$$

$$K_{eq}=\frac{C_m}{C_H C_{La} C_B} \quad (2)$$

where C_B is the concentration of the carrier(R_2HN), and C_m is the concentration of the complex($R_2HNH^+La^-$).

The complex then diffuses through the membrane to the interface between the membrane and internal phases. Due to extremely high concentration of hydroxyl ion in the internal phase, the lactate anion is stripped from the membrane phase into the internal phase, the high pH of the internal phase preventing lactate anion from reacting again with the carrier. The stripping reaction can be expressed as the reverse of eqn.(1)

The stripping 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 proton concentration exists. This uphill transport of lactate anion makes it possible to obtain highly concentrated product solution from dilute feed solution.

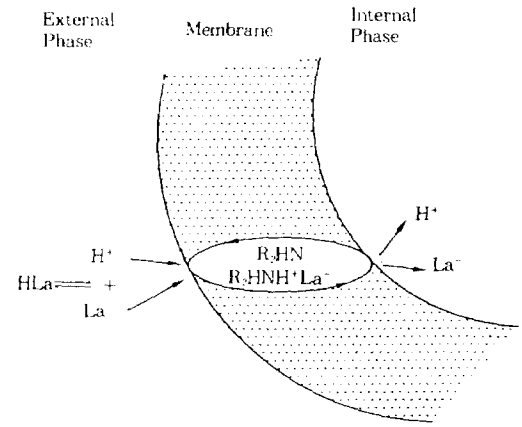

Fig. 2. Overall transport mechanism of lactic acid.

2. 3. Internal Phase pH

In this study, sodium carbonate was used as the internal stripping reagent to give driving force for lactic acid transport. When sodium carbonate is used as a stripping reagent, the pH change in the internal phase according to the accumulation of solute becomes somewhat complex. The pH expression can be obtained from the hydrolysis of sodium carbonate and the charge balance in the internal phase.

Equilibrium equations for the hydrolysis of Na_2CO_3 can be written as follows[10]

$$CO_3^{2-}+H_2O=HCO_3^-+OH^- \quad (3)$$

$$K_H=\frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]}=2.1\times10^{-4} \quad (4)$$

$$HCO_3^-+H_2O=H_2CO_3+OH^- \quad (5)$$

$$K_H=\frac{[H_2CO_3][OH^-]}{[HCO_3^-]}=2.4\times10^{-8} \quad (6)$$

The electroneutrality condition and the mass balance in the internal phase can be written as follows:

$$[Na^+]+[H^+] = 2[CO_3^{2-}]+[HCO_3^-]+[La^-]+[OH] \quad (7)$$

$$\frac{[Na^+]}{2}=[CO_3^{2-}]+[HCO_3^-]+[H_2CO_3] \quad (8)$$

From ion product Kw and, eqns.(4), (6), (7) and

(8), the expression of proton concentration in the internal phase can be obtained

$$C_H^4+C_1C_H^3+C_2C_H^2-C_3C_H-C_4=0 \quad (9)$$

where

$$C_1=\frac{K_w}{K_{b2}}+C_{Na}-C_{La}$$

$$C_2=\frac{C_{Na}}{2}\frac{K_w}{K_{b2}}+\frac{K_w^2}{K_{b1}+K_{b2}}-K_w-\frac{K_w}{K_{b2}}C_{La}$$

$$C_3=\frac{K_w^2}{K_{b2}}+\frac{K_w^2}{K_{b1}K_{b2}}C_{La}$$

$$C_4=\frac{K_w^3}{K_{b1}K_{b2}}$$

2.4. Model Formulation

Followings are assumed for the mathematical development:

(1) Although emulsion globules have a non-uniform distribution, the system is characterized in terms of mean globule diameter. It is also assumed that the internal droplets are immobile because of the presence of surfactant.

(2) No coalescence and redispersion occur between all emulsion globules.

(3) The external phase is well mixed.

(4) Chemical equilibrium holds in each interface, i.e., no interfacial resistances are considered.

(5) Emulsion breakage and swelling are neglected.

(6) The carrier concentration is much higher than the concentration of solute/carrier complex since the complex is constantly removed by the stripping reagent(the calculated results are not presented in this paper, however it is shown from the calculation that the carrier concentration is $10^3\sim10^9$ times higher that the complex concentration during extraction). Thus, the carrier concentration can be assumed to be equal to its initial value at all positions.

Fig. 3 presents the schematic picture of the present model based on the above assumptions. When

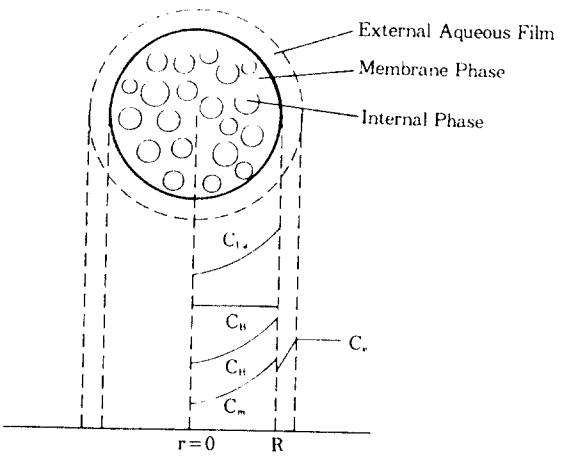

Fig. 3. Concentration profiles of components in an emulsion globule.

the film theory is applied to the diffusion in the external aqueous film, the following equation can be derived in the external phase

$$\frac{dC_e}{dt}=-\frac{1}{V_e}kA(C_e-C_e^*) \quad (10)$$

where C_e is the lactic acid concentration in the external phase, C_e^* is the lactic acid concentration at the interface between the external phase and the membrane phase, V_e is the volume of external phase, t is the stirring time, k is the mass transfer coefficient, and A is the surface area of emulsion globules.

From the equilibrium constant K_{eq} and acidic dissociation constant($k_a=C_HC_{La}/C_e$), C_e^* is expressed as

$$C_e^*=\frac{C_m^*}{K_{eq}K_aC_B^0} \quad (11)$$

where C_m^* is the concentration of carrier/solute complex at the interface between the external and membrane phases.

The diffusion in the emulsion phase can be expressed by using the effective diffusivity D_e as follows

$$\phi\frac{\partial C_{La}}{\partial t}+(1-\phi)\frac{\partial C_m}{\partial t}=\frac{D_e}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_m}{\partial r}\right) \quad (0\le r\le R) \quad (12)$$

The derivative of C_{La} in eqn.(12) can be obtained from the equilibrium constant [eqn.(2)] and the pH expression[eqn.(9)] as follows(see Appendix)

$$\frac{\partial C_{La}}{\partial t} = \frac{(4C_H^3+3C_1C_H^2+2C_2C_H-C_3)C_H/C_m}{(4C_H^3+3C_1C_H^2+2C_2C_H-C_3)\dfrac{K_aC_mC_H^2}{C_m}+(C_H^3+\dfrac{K_a}{K_{b1}}C_H^2+\dfrac{K_a^2}{K_{b1}K_{b2}}C_H)}\frac{\partial C_m}{\partial t} \quad (13)$$

Initial and boundary conditions are as follows:

$$t=0,\ C_e=C_{e,\infty},\ C_m=C_{La}=0 (0\le r\le R) \quad (14)$$

We use boundary condition at the center of emulsion globule to have no flux making the problem symmetric about the origin.

$$r=0,\ \frac{\partial C_m}{\partial r}=0 (t\le 0) \quad (15)$$

At the interface between the external phase and the membrane phase, we use the boundary condition of the third kind. Thus,

$$r=R,\ D_e\frac{\partial C_m}{\partial r}=k(C_e-C_e^*) (t\le 0) \quad (16)$$

To solve the above equations, the following relations are required:

(i) The number of emulsion globules can be determined from the mean radius, $R=D_{32}/2$,($D_{32}=\sum n_i D_i^3/\sum n_i D_i^2$: Sauter-mean diameter)

$$N_{em}=\frac{V_m+V_i}{(4/3)\pi R^3} \quad (17)$$

(iii) The surface area of emulsion globules is

$$A=\frac{3(V_m+V_i)}{R} \quad (18)$$

The eqns.(9)-(18) may be simultaneously solved numerically by using the method of line(MOL)(a combination of the finite difference method and the Gear's algorithm in the subroutine IVPAG of IMSL MATH library)[11, 12].

3. Experimental

3. 1. Materials

The membrane phase was prepared by mixing kerosene as the diluent, Amberlite LA2 as the carrier, and Paranox 100 as the surfactant. Amberlite LA2 is a secondary amine purchased from Sigma Chemical Company in USA and Paranox 100 is a polyamine-type surfactant made by Exxon Chemical Company in USA. The main component of the membrane phase, kerosene was obtained from Kanto Chemical Company in Japan.

Cosurfactant Span 85(sorbitan trioleate) was supplied from Sigma Chemical Company. Span 85 which is a surfactant having a low HLB(hydrophilic /lipophilic balance) value will transport water less than other surfactants having high HLB value.

Sodium carbonate(extra pure), purchased from Junsei Chemical Company, was used as the stripping reagent.

Lactic acid was supplied in concentration form (90 wt%) by Katayama Chemical Company. The concentrated lactic acid solution also contained dimers(lactic anhydride) which can be hydrolyzed to lactic acid by heating a dilute aqueous solution for several hours.

For the purpose of swelling control, cyclohexanone, liquid paraffin and long chain aliphatic alcohol(n-decanol) were used as the additives. Cyclohexanone and liquid paraffin were obtained from Junsei Chemical Company, and n-decanol was obtained from Fluka Chemical Company.

3. 2. Methods

A stable water-in-oil(W/O) emulsion was prepared by initially dissolving 5wt% surfactant and carrier in kerosene and then adding 50cm3 of 0.6M Na_2CO_3 solution to make volume of 100cm^3 under high shear(12000rpm) provided by a homogenizer (Tekmar company, Germany).

The W/O emulsion was then dispersed by a six-bladed stirrer(4.3cm diameter) into a four-baffled vessel(10cm diameter) containing 400cm^3 of 0.1 M feed solution to give a W/O/W system. The extraction of 0.1 M lactic acid was carried out at initial pH 2.5(the pH of feed phase was 2.5 when 0.1 M

lactic acid was dissolved). The stirrer speed was measured by a tachometer and was maintained at a desired speed. All experiments were carried out at 25℃.

At given intervals, samples of about 7cm^3 were withdrawn by a pipette, filtered to remove the W/O emulsion drops, and the residual lactic acid concentration in the filtrate was determined by colorimetric method[13] or by high-performance liquid chromatography(Waters) using a YMC-Pack C8 column with refractive index detector. In HPLC analysis, the flow rate of mobile phase(0.005 N H_2SO_4) was 0.3cm^3/min. The color reagent was prepared by dissolving 3g of $FeCl_3$(Kanto Chem. Co.)in 12.5cm^3 of 1 N HCl. This solution was freshly diluted 1:5 with water and used as the color reagent. A 0.5cm^3 sample of the lactic acid solution was added to 5cm^3 of water in a test tube. 0.5cm^3 of the color reagent was added to the test tube and the absorbance at 360nm was measured using a spectrophotometer (PU 8715, Philips).

Water content in the collected emulsion was determined by Karl-Fisher method[14] and then the internal phase volume was calculated from the volume ratio to initial value of the internal aqueous phase.

Emulsion globule sizes were measured photographically, and expressed in terms of the Sauter mean diameter.

The equilibrium constant was determined from equilibrium data using the usual two phase experiments.

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

Table 1. Typical Experimental Conditions

Membrane phase carrier: 5wt%(0.11M)
surfactant: 5wt%
Internal phase Na_2CO_3: 0.6M
External phase lactic acid: 0.1M
Volume ratio external phase/emulsion: 4
Stirrer speed: 250rpm

4. Results and Discussion

So as to investigate the validity of the proposed model, experimental data for the lactic acid transport were compared with computed results. In the other aspect, the reduction of emulsion swelling was performed by using several membrane additives.

4. 1. Effective Diffusivity and Mass Transfer Coefficient

The effective diffusivity of the complex in the heterogeneous emulsion globule can be estimated by the Jefferson-Witzell-Sibbit equation[15]. Molecular diffusivity required for the Jefferson-Witzell-Sibbit equation was obtained from Wilke-Chang correlation[16].

The external phase mass transfer coefficient k was estimated from a correlation for mass transfer in stirred vessel. Although Levins and Glastonbury [17] developed their correlation to describe rigid particles suspended in a stirred vessel, their correlation is still valid to calculate the convective mass transfer coefficient of the external phase strirring in the batch system. Since sufficient surfactant concentration is contained in the membrane phase, the emulsion globule may be treated as a rigid sphere, and so external phase mass transfer coefficient can be determined by such a correlation.

The parameter values used for modeling are listed in Table 2.

4. 2. Comparison between Model and Experimental Data

Lactic acid does not almost partition into the membrane phase so that it can be transported only by the way of solute/carrier complex. Thus, the solute transport rate is fairly strong function of the carrier concentration, that is, its content determines how fast the separation proceeds. Batch extraction of 0.1 M lactic acid is carried out with concentration of Amberlite LA2 in the range 2~8wt%, and with 5wt% surfactant and 0.6 M sodium carbonate. The carrier concentrations used for computation are

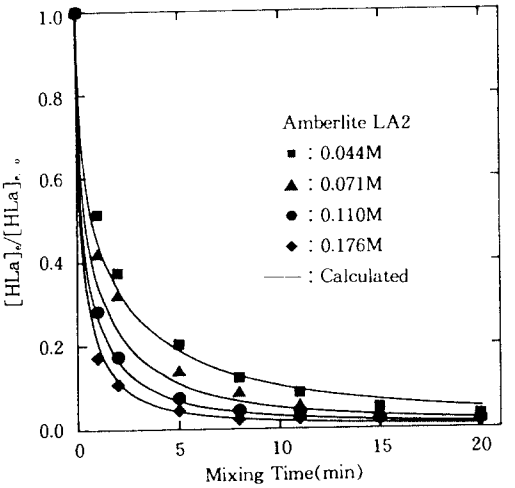

Fig. 4. Effect of carrier concentration on lactic acid transport.

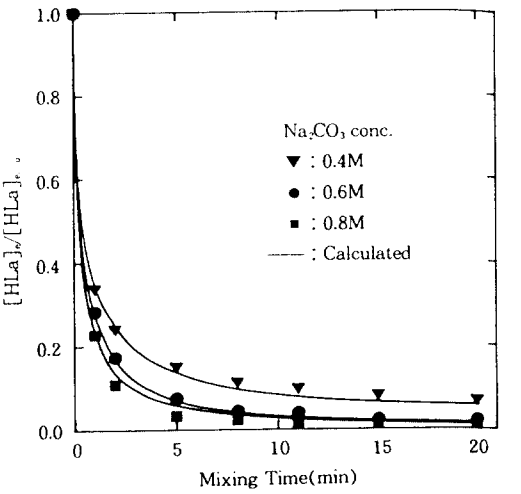

Fig. 5. Effect of stripping reagent concentration on lactic acid transport.

Table 2. Parameters Used

Dissociation constant of lactic acid, pk_a: 3.86	
Equilibrium constant, K_{eq}: $19\times10^4 dm^6/mol^2$	
Effective diffusivity*, D_e: $3.16\times10^{-6} dm^2/min$	
Mass transfer coefficient in the external phase**, k	
3.85×10^{-2}dm/min	for 180rpm
5.03×10^{-2}dm/min	for 250rpm
5.73×10^{-2}dm/min	for 300rpm
6.47×10^{-2}dm/min	for 350rpm
Emulsion globule diameter, R	
0.00277dm	for 180rpm
0.00195dm	for 250rpm
0.00175dm	for 300rpm
0.00150dm	for 350rpm

* Jefferson-Witzell-Sibbit equation[15]
** Levins and Glastonbury[17]

0.044M, 0.071M, 0.110M and 0.176M, corresponding to 2wt%, 3.5wt%, 5wt% and 8wt%. Fig. 4 shows the influence of carrier concentration on lactic acid transport rate where the predicted profiles using the model are also presented. The increases in solute transport rates with increases in Amberlite LA2 concentration represent the increased interfacial solute/carrier complex concentrations, and hence the increased ability of the solute to diffuse the membrane phase via the solute carrier/complex. The solid curves represent the computed results by using the model and agree well with the experimental data.

Fig. 5 shows the residual lactic acid concentration in the external phase obtained by changing the stripping reagent concentration. As expected, the separation rate increases with the stripping reagent concentration since the driving force for lactic acid transport is increased. When the stripping reagent concentration is decreased to 0.4M, the separation rate is too low and a significant quantity of lactic acid remains in the external phase because the saturation of internal droplets with lactic acid makes it impossible to transport the acid any longer. When the stripping reagent concentration is increased to 0.8M, the separation rate is only slightly increased. On using higher stripping reagent concentration, the increased osmotic pressure difference must result in greater emulsion swelling, which counteracts the increase in solute transport rate. One of the crucial variables in liquid membrane system is the stripping reagent concentration as the driving force for lactic acid transport. The stripping reagent concentration should be chosen to give not only a sufficiently fast separation rate but also a highly concentrated pro-

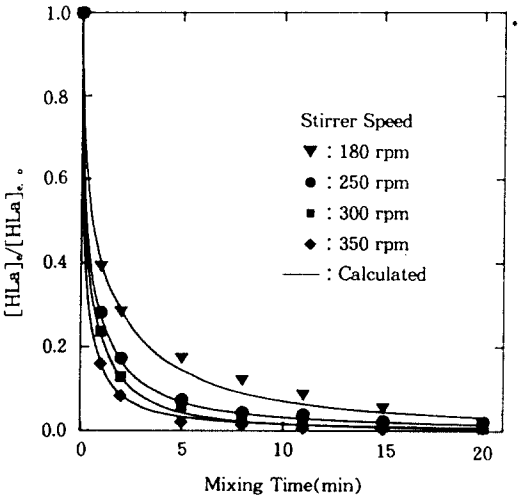

Fig. 6. Effect of stirrer speed on lactic acid transport.

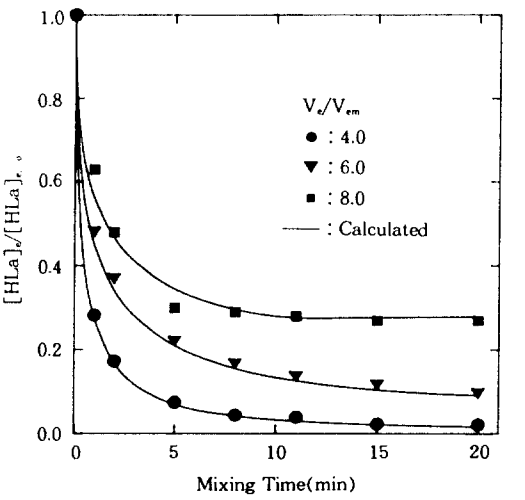

Fig. 7. Effect of treatment ratio on lactic acid transport.

duct. In this context, an appropriate concentration of stripping reagent can be found to be 0.6M.

The stirrer speed affects the emulsion globule size and mass transfer coefficient in the external phase. As the stirrer speed becomes large, the mass transfer resistance in the aqueous film decreases and the interfacial contact area between the external and membrane phases increases because the emulsion disperses as smaller drops. As presented in Fig. 6, therefore, higher solute transport rate(slope) is obtained at higher stirrer speed. The computed results represented by the solid curves in the figure are in satisfactory agreement with the experimental results.

The feed consumes more internal reagent over the course of the separation as the amount of lactic acid in the external phase is increased. The influence of treatment ratio(external/emulsion phase) on lactic acid transport rate is depicted in Fig. 7. As the treatment ratio is increased, the solute transport rate decreases largely due to the relatively reduced capacity of the internal phase to neutralize the transported lactic acid. In case of treatment ratio 8, a reduction in lactic acid concentration of only 72% is achieved and equilibrated in the run, indicating that the stripping reagent concentration is not sufficient to accept all of the lactic acid in the external phase. If the sodium carbonate in the internal phase is completely consumed, the amount of lactic acid that can theoretically be extracted is 75% of the initial value when the treatment ratio is 8. However, it is not possible to attain 75% extraction of the lactic acid from the feed solution because of the reaction reversibility and the emulsion breakage. The present model assumes that there is no breakage of the droplets or globules. Nevertheless, the computed profile never reaches zero even on using excess stripping reagent(see also Fig. 5). The reason is because the reaction equilibrium exists at each interface. The predicted results coincide well with the experimental results.

4. 3. Control of Emulsion Swelling

To be able to apply LEM to the organic acid, emulsion swelling should be controlled because it lowers the efficiency of LEM process. Emulsion swelling occurs in W/O/W LEM system and brings about membrane breakage and product dilution. LEMs are W/O/W system when applied to organic acid separation, thus the effectiveness of LEMs will

depend on the emulsion swelling. Nevertheless, the swelling control of LEMs has not been sufficiently investigated.

Several possible ways to accomplish the swelling control are: (1) decrease osmotic pressure difference by addition of inert species such as glucose to the external phase[6], (2) Increasing membrane viscosity to decrease diffusion rate if the swelling is a diffusional process. However, although the swelling can be decreased by above methods, the addition of inert species to the external phase increases the total separation cost, and increasing membrane viscosity also decreases the solute transport rate. Thus, another method for swelling control is needed in terms of process economics.

Although the reasons and mechanisms of the swelling phenomenon have not been completely elucidated yet, it is well known that surfactant is directly involved in water transport. Significant swelling can be explained as water osmosis that is related to surfactant[18, 19]. Thus the careful choice of surfactant is the most important factor in swelling control. Swelling can also be reduced by formulating membrane phase which is not permeable to water. The species do not have to interfere with the separation, nor change the stability of emulsion.

The formulation of membrane to minimize swelling, as well as to maximize separation rate, should be carefully considered. The effects of several variables which have the possibility to reduce the swelling were investigated. Since some of these variables can affect the solute transport rate, they should be considered simultaneously when studying swelling control. It should be noted that the swelling cannot be avoidable but can be only reduced because the swelling is, of course, caused by coextraction of water along with that of the acid and the influence of surfactant on swelling cannot be perfectly removed.

4. 3. 1. Effect of Liquid Paraffin Content

Increasing the membrane viscosity needs to reduce the swelling if the water transport is a kind of

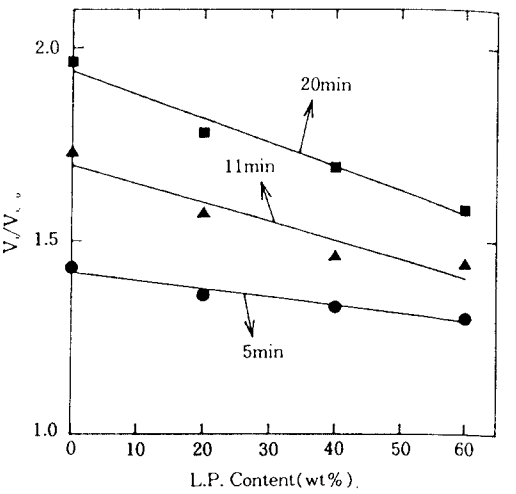

Fig. 8. Effect of liquid paraffin content on emulsion swelling.

diffusional process, thus it is obviously desirable that the membrane phase should be made of viscous oil such as liquid paraffin. In order to examine the effect of membrane viscosity, membrane phases of different viscosity are prepared by changing the liquid paraffin content. Fig. 8 shows the effect of liquid paraffin(L.P.) content on swelling. As the L.P. content increases, the swelling greatly decreases since the diffusion rate of components containing water decreases. As well, since the higher emulsion viscosity results in larger emulsion globule size, the relative amount of surfactant available for water transport is decreased by the increase in globule size(the decrease in surface area).

One of the advantages of LEM is rapid separation rate, however, an increase in L.P. content decreases the transport rate too much(see Fig. 9). In this LEM system, there is an initial fast reduction in the lactic acid concentration, i.e., the maximum transport rates of lactic acid occur at the beginning of extraction and the transport rate largely decreases with the elapsed time. Therefore, the initial transport rate greatly affects the overall separation rate. The initial transport rates in Fig. 9 are calculated from the concentration change in the external phase

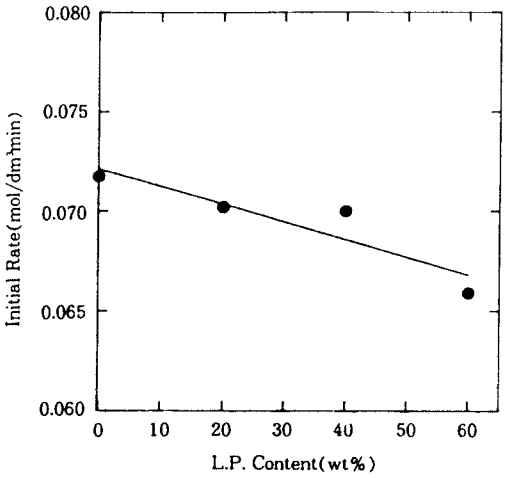

Fig. 9. Initial transport rate of lactic acid as a function of liquid paraffin content.

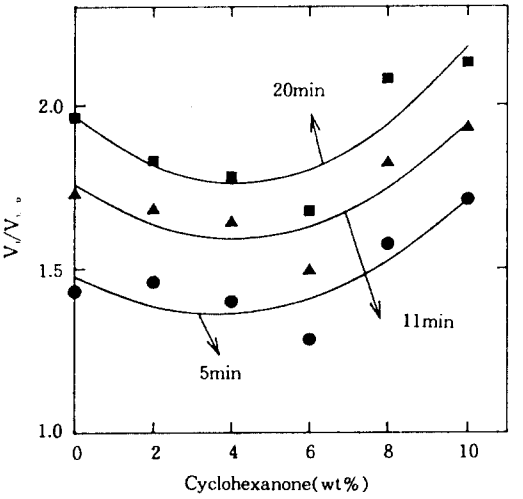

Fig. 10. Effect of cyclohexanone content on emulsion swelling.

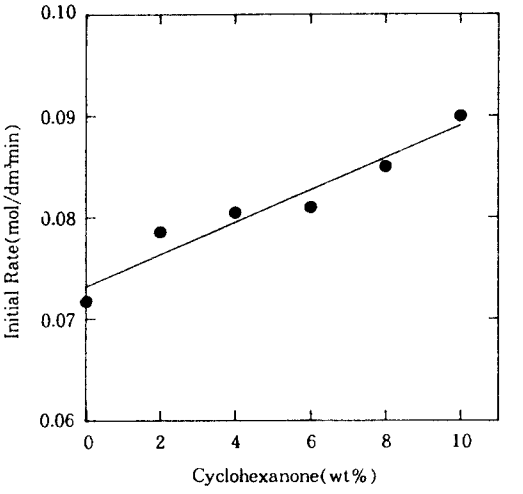

Fig. 11. Initial transport rate of lactic acid as a function of cyclohexanone content.

up to 1 minute. The decrease in lactic acid transport rate must be caused by the increase in membrane viscosity, therefore, other method to reduce the swelling should be used so as not to affect the separation rate.

4. 3. 2. Effect of Cyclohexanone Content

Swelling can be effectively controlled without significant influence on solute transport rate if the membrane phase is formed which is less permeable to water. The membrane capable of reducing swelling may be formulated by the addition of cyclohexanone. Mukkolath et al.(1990) found that the swelling can greatly be reduced by the addition of cyclohexanone to have preferential micellization of Span 80 with the added reagent rather than with water[20]. The cyclohexanone concentration in the membrane to minimize swelling was found to be about unity volume ratio of it to Span 80. As can be seen in Fig. 10, the swelling also decreases in this system by the addition of cyclohexanone when the concentration is below about 6wt%, but at higher concentration, the swelling increases beyond a minimum with cyclohexanone concentration because the decrease in viscosity of emulsion phase overcome the ability of cyclohexanone to reduce swelling. It is observed that cyclohexanone has an additional effect on this system besides the reduction of swelling, i.e., the transport rate of lactic acid increases with cyclohexanone content(Fig. 11). This large increase in transport rate with cyclohexanone content can hardly be explained by only the viscosity change of membrane phase because cyclohexanone has great influence on equilibrium

constant between lactic acid and carrier. The equilibrium constant between lactic acid and Amberlite LA2 in cyclohexanone($4.3\times10^5 dm^6/mol^2$) is much larger than that in kerosene($1.9\times10^4 dm^6/mol^2$). Therefore, the complex concentration formed at the interface between the external phase and the membrane phase increases as the cyclohexanone content in membrane phase increases. As a result, the transport rate of lactic acid increases with the increase in cyclohexanone content.

4. 3. 3. Effect of Span 85 Content in Surfactant Mixture

The surfactant is one of the most important variables in swelling control since it plays an important role in water transport. The hydrophilic part of surfactant is responsible for swelling, so that the use of surfactant having low HLB value such as Span 85 (HLB=1.8) can decrease the swelling. While Span 85 has less hydrophilic part than Paranox 100, its molecular weight(956g/mol) is much smaller than that of Paranox 100(2000g/mol), and thus the diffusivity of Span 85 is larger than that of Paranox 100. To investigate the effect of the amount of hydrophilic part, mixture of Paranox 100 and Span 85 is used as surface active agent and experiments are carried out by varying the Span 85 content. Span 85 is sorbitan trioleate, and Paranox 100 is a polyamine-type surfactant.

Fig. 12 shows the effect of Span 85 content in the surfactant mixture on swelling. The decrease of hydrophilic part in the surfactant mixture can cause the decrease of water solubility and of water transport rate, i.e., surfactant hydration and reversed micelle decrease with decrease of hydrophilic part in the surfactant mixture. On the other hand, the diffusivity of surfactant mixture increases with the Span 85 fraction because the average molecular weight of surfactant mixture decreases with the increase in the Span 85 fraction. Therefore, the decrease in hydrophilic part by using Span 85 as cosurfactant is canceled by the increase in diffusivity. This is the reason why the increase in Span 85 fraction has only a little influence on swelling.

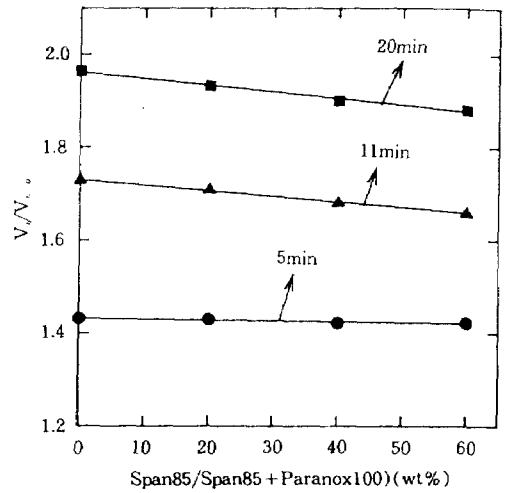

Fig. 12. Effect of Span 85 content in surfactant mixture.

4. 3. 4. Long Chain Aliphatic Alcohol Content

In liquid extraction of organic acids, the presence of amine shows a tendency to the aggregation of the polar acid-amine complexes. With few exceptions, the complexes of most of organic acids are cationic aggregation colloids that form micelles of a variety of sizes, shapes, and properties[21]. The process of micellar aggregation in organic solvents used as diluents for amines is a stepwise formation of oligomers, where the extent(number of aggregated units) and the degree(size of aggregated units) of aggregation depend on the characteristics of amine, acid radicals, and the organic solvent. Analogously, the acid-amine complexes may tend to aggregate in LEM system, but since liquid emulsion membrane is a dynamic process that the complex is constantly stripped, the aggregated complex cannot maintain its micellar form. An alternative possibility is that the swelling can be mediated by way of the aggregated acid-amine complexes containing water. The complexes formed may aggregate at the external interface, which then diffuses to be stripped. Therefore, a modifier needs to prevent the acid-amine complex from aggregating. In this study, n-decanol was used as the modifier, and it would be expected that the portion of swelling via

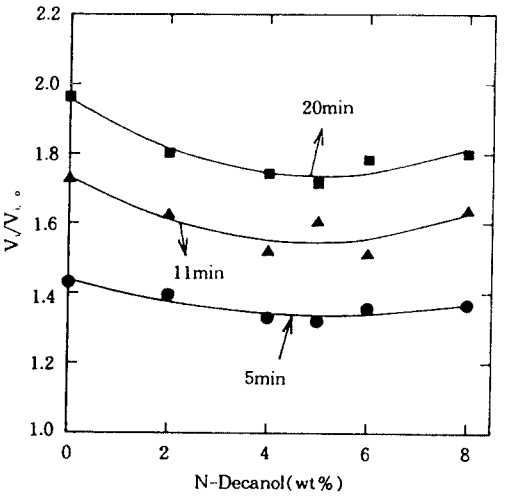

Fig. 13. Effect of n-decanol content on emulsion swelling.

these aggregated acid-amine complexes can be reduced by the addition of the modifier.

Fig. 13 represents the effect of long chain aliphatic alcohol concentration on swelling, where it was shown that n-decanol was somewhat effective for swelling control. When reactive extraction was performed with only Amberlite LA2, much more third phase was formed than with the addition of n-decanol. This may explain that n-decanol was effective for swelling control.

As n-decanol concentration was increased, a minimum value of the internal phase volume was observed, followed by increase in the internal phase volume. N-decanol has a hydrophilic group that can transport water, thus the excess of n-decanol will increase the swelling rather than decreasing it. Thus, the swelling was getting increased as the n-decanol concentration was increased more than 5wt%.

5. Conclusions

A mathematical model considering the pH variation in the internal phase was proposed to describe the behavior of liquid emulsion membrane containing sodium carbonate as the stripping reagent. The proposed model considers the mass transfer resistance in the external aqueous boundary layer and the diffusion resistance in the emulsion phase, and assumes the reaction equilibrium at each interface. Although all the resistances can affect the separation rate, the controlling step is the diffusion of lactic acid-carrier complex in the emulsion phase. The model predictions were examined by comparison with the experimental data on the batch extraction of lactic acid, and found to predict well the variations of feed concentration in the external phase. This good agreement of the experimental data to the predicted results supports the model used for facilitated transport in LEM system. The experimental and predicted results in Fig. 4 to Fig. 7 show that the concentration profiles are steep, which is the feature of diffusion-controlling system.

The appropriate conditions drawn with respect to the separation rate are 0.6M sodium carbonate, 8wt % carrier and 350rpm stirrer speed for 0.1M feed. However, in real system, the economic aspect should be considered in finding the optimal conditions of the parameters. The carrier is the most expensive agent among the membrane components, and high stirrer speed needs high mechanical energy cost.

Using the liquid emulsion membrane, not only lactic acid can be separated but also concentrated. Emulsion swelling thus determines the concentrated extent of the solute in the internal phase. The extent of swelling depends strongly on membrane viscosity, however, an increase in membrane viscosity greatly decreased the solute transport rate since it is a diffusional process. Thus the method should be avoided although it is effective to reduce swelling.
The aggregation of the acid-amine complexes can be prevented by a long-chain aliphatic alcohol such as n-decanol, and thus the addition of n-decanol as modifier had positive influence on swelling control. The suitable n-decanol concentration was found to be 5wt% in terms of swelling control.

The addition of cyclohexanone was effective for reduction of swelling when its content was below

about 6wt%, and an minimum value of swelling was observed at that concentration. As well, the addition of cyclohexanone increased the acid transport rate due to the shift of chemical equilibrium between lactic acid and Amberlite LA2. Because of this additional effect of cyclohexanone, the additive is proposed to be used as a membrane component.

The swelling is significantly affected by the amount of hydrophilic part in surfactant, but decreasing hydrophilic part in surfactant mixture by Span 85(HLB=1.8) was not effective for this system containing Paranox 100 of high molecular weight.

Nomenclatures

aq	aqueous phase
A	surface area, dm_2
C_B	concentration of carrier, mol/dm^3
C^0_B	initial concentration of carrier, mol/dm^3
C_e	feed concentration in the external phase, mol/dm^3
$C_{e,0}$	initial feed concentration in the external phase, mol/dm^3
C^*_e	concentration of solute at the interface between the external and membrane phases, mol/dm^3
C_H	concentration of proton, mol/dm^3
C_{La}	concentration of lactate anion, mol/dm^3
C_m	concentration of solute/carrier complex, mol/dm^3
C^*_m	concentration of solute/carrier complex at the interface between the external and membrane phases, mol/dm^3
C_{Na}	concentration of sodium ion, mol/dm^3
D_{32}	Sauter mean diameter, dm
D_e	effective diffusivity, dm^2/min
H^+	proton
HLa	lactic acid
k	mass transfer coefficient, dm/min
k_a	acidic dissociation constant of lactic acid, mol/dm^3
K_{b1}	primary basic dissociation constant, mol/dm^3
K_{b2}	secondary basic dissociation constant, mol/dm^3
K_{eq}	equilibrium constant between aqueous and organic phases, dm^6/mol^2
K_w	ion product, mol^2/dm^6
La^-	lactate anion
N_{em}	number of emulsion globules
org	organic phase
r	radius, dm
R	emulsion globule radius, $D_{32}/2$, dm
R_2HN	carrier, secondary amine
$R_2HNH^+La^-$	solute/carrier complex
t	time, min
V_e	volume of external feed phase, dm^3
V_i	volume of internal stripping phase, dm^3
V_m	volume of membrane phase, dm^3
[ ]	molar concentration, mol/dm^3

Subscripts

e	external phase
i	internal phase
m	membrane phase
0	initial condition

Greek letters

ϕ	internal phase volume fraction in emulsion

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Appendix

$$C_4^H + C_1 C_H^3 + C_2 C_H^2 - C_3 C_H - C_4 = 0 \tag{9}$$

where

$$C_1 = \frac{K_w}{K_{b2}} + C_{Na} - C_{La}$$

$$C_2 = \frac{C_{Na}}{2}\frac{K_w}{K_{b2}} + \frac{K_w^2}{K_{b1}+K_{b2}} - K_w - \frac{K_w}{K_{b2}} C_{La}$$

$$C_3 = \frac{K_w^2}{K_{b2}} + \frac{K_w^2}{K_{b1}K_{b2}} C_{La}$$

$$C_4 = \frac{K_w^3}{K_{b1}K_{b2}}$$

Differentiating eqn. (9) with time, t

$$(4C_H^3 + 3C_1 C_H^2 + 2C_2 C_H - C_3)\frac{\partial C_H}{\partial t} -$$

$$(C_H^3 + \frac{K_w}{K_{b2}} C_H^2 + \frac{K_w^2}{K_{b1}K_{b2}} C_H)\frac{\partial C_{La}}{\partial t} = 0 \tag{A-1}$$

Differentiating eqn. (2)(equilibrium constant) with time, t

$$\frac{\partial C_m}{\partial t} = K_{eq} C_H C_B^0 \frac{\partial C_{La}}{\partial t} + K_{eq} C_{La} C_B^0 \frac{\partial C_H}{\partial t} \tag{A-2}$$

Rearranging eqn.(A-2),

$$\frac{\partial C_H}{\partial t} = \frac{1}{K_{eq} C_{La} C_B^0}\frac{\partial C_m}{\partial t} - \frac{C_H}{C_{La}}\frac{\partial C_{La}}{\partial t}$$

$$= \frac{C_H}{C_m}\frac{\partial C_m}{\partial t} - \frac{K_{eq} C_H^2 C_B^0}{C_m}\frac{\partial C_{La}}{\partial t} \tag{A-3}$$

Combining eqns.(A-1) and (A-3).

$$\frac{\partial C_{La}}{\partial t} =$$

$$\frac{(4C_H^3 + 3C_1 C_H^2 + 2C_2 C_H - C_3) C_H / C_m)}{(4C_H^3 + 3C_1 C_H^2 + 2C_2 C_H - C_3)\frac{K_{eq} C_H C_{B1}}{C_m} + (C_H^3 + \frac{K_w}{K_{b2}} C_H^2 + \frac{K_w^2}{K_{b1}K_{b2}} C_H)}\frac{\partial C_m}{\partial t}$$