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Separation Science and Technology
Publication details, including instructions for authors and subscription information:
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To cite this Article Mok, Young Sun , Lee, Sang Chul and Lee, Won Kook(1995) 'Synergistic Effect of Surfactant on Transport Rate of Organic Acid in Liquid Emulsion Membranes', Separation Science and Technology, 30: 3, 399 — 417
To link to this Article: DOI: 10.1080/01496399508013879
URL: http://dx.doi.org/10.1080/01496399508013879

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SEPARATION SCIENCE AND TECHNOLOGY, **30**(3), pp. 399–417, 1995

Synergistic Effect of Surfactant on Transport Rate of Organic Acid in Liquid Emulsion Membranes

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ABSTRACT

Liquid emulsion membranes were applied to the separation of penicillin G, and a model was proposed to describe the transport of penicillin G facilitated by two carriers. A polyamine-type surfactant such as ECA 4360J acts not only as carrier but also as surface-stabilizing agent, thus the influence of surfactant on the transport rate should be considered in mathematical modeling when its effect is significant. The proposed model is based on the shrinking core approach (advancing reaction front model) and takes into account the resistances of mass transfer in the water boundary layer, the thin oil film, and the emulsion. An equation expressing the overall mass transfer coefficient is given so as to simplify the model equations. The model shows good agreements with the experimental data. However, the calculated results underestimated the experimental data when the effect of the surfactant on transport rate is ignored. This indicates that the surfactant plays an important role in penicillin G transport. The model considering the contribution of surfactant is able to account for the increase in transport rate with surfactant concentration.

INTRODUCTION

Liquid emulsion membranes (LEMs), in which simultaneous extraction/reextraction occurs, have been applied to a variety of separations, including removal of phenols and amines from wastewater, recovery of metal

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ions, and separation of hydrocarbons (1–5). Lately, a new separation process of organic acids in biotechnology that combines high selectivity for the desired product, high separation rate, and energy efficiency has been of interest. In this context, LEMs present a promising process for the recovery of organic acid from fermentation broth.

LEMs are usually prepared by first forming an emulsion between two immiscible phases (the surfactant-laden organic phase and the aqueous stripping phase) and then dispersing this emulsion in a feed phase by agitation. Two miscible aqueous phases (the feed phase and the stripping phase) can be separated by an organic phase, thus preventing the mixing of the miscible phases.

In conventional solvent extraction processes, penicillin G is extracted with *n*-butyl acetate at low pH. In spite of low temperature and extraction time, losses of penicillin G during recovery are considerable due to decomposition. To reduce these losses, Reschke and Schügerl considered reactive extraction with an amine as a carrier in the pH 5 to 7 range where penicillin G is stable (6–8). However, there are several economic problems connected with extraction methods. First, an organic solvent and a carrier are used in excess. Moreover, a reextraction step is required to recover penicillin G from the organic phase. In addition, the degree of extraction diminishes as the ratio of throughput of the organic phase to that of the aqueous phase is increased in order to concentrate penicillin G. The above disadvantages may be reduced by a liquid emulsion membrane process.

Some studies of potential applications of LEMs in biotechnology have appeared in the recent literature: e.g., separations of amino acid (9–11), lactic acid (12–14), and penicillin G (15, 16). However, few quantitative models have been developed to describe and predict the extraction kinetics of organic acids. There have been no reports on the development of models where LEMs have been used in the separation of penicillin G.

In LEMs for the separation of organic acids, the use of a polyamine-type surfactant can give rise to an increase in separation rate since the species can also facilitate transport. The study of Reisinger et al. showed the surfactant as well as the carrier amine enhances lactic acid transport (12). They used ECA 11522, which is a kind of polyamine type, as the surfactant. Hano et al. made it clear through experiments that the carrier-mediated transport by ECA 4360J contributes considerably to the extraction of penicillin G (15, 16). Thus, the influence of surfactant on the separation rate cannot be neglected when a polyamine such as ECA 4360J or Paranox 100 is used as the surfactant. Nevertheless, none of the modeling studies in the literature include facilitated transport by two carriers (surfactant and carrier).

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In this study, LEMs were applied to the separation of penicillin G from an aqueous solution with Amberlite LA2 as the carrier, ECA 4360J as the surfactant, and sodium carbonate as the stripping reagent. We propose a model for penicillin G transport facilitated by both the surfactant and the carrier. The major objective of this study was to examine the importance of surfactant on penicillin G transport. In order to verify the accuracy of model, experimental data were compared with the calculated results.

THEORY

Transport Mechanism of Penicillin G

The carrier, Amberlite LA2, a secondary amine, has been widely used by others as an ion-complexing agent for the recovery of organic acid by using reactive extraction. It can also be used for LEM separation of organic acid, and good results have been obtained.

Penicillin G is transported from the feed to the internal phase as follows. First, penicillin G in the external phase diffuses through the external boundary layer. Second, penicillin G anion and proton react with the secondary amine at the interface between the external phase and the membrane phase to form a complex. This reaction equilibrium can be expressed as follows (7):

$$K_{eq,1} = \frac{C_{m1}}{C_H C_p C_{B1}} \qquad \text{for Amberlite LA2} \tag{1}$$

where C_{m1} is the penicillin/carrier complex concentration, C_H is the proton concentration, C_p is the penicillin G anion concentration, and C_{B1} is the carrier concentration.

Similarly, the equilibrium of penicillin G with ECA 4360J is equated as

$$K_{eq,2} = \frac{C_{m2}}{C_H C_p C_{B2}} \qquad \text{for ECA 4360J} \tag{2}$$

where C_{m2} is the concentration of the complex made of penicillin and ECA 4360J.

The two complexes formed at the external interface diffuse through the membrane to the interface between the membrane and internal phases. At this interface, the penicillin G anion is stripped from the complex by a strong base and the carrier diffuses back to the feed side of the membrane. Since the stripping reaction is an acid/base reaction, the reverse reaction can be successfully ignored.

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Model Formulation

A shrinking core model is depicted in Fig. 1. It describes the increase in diffusion distance with the increase in degree of extraction. The complexes formed at the external interface primarily neutralize the droplets close to the emulsion globule surface, so that the diffusion distance becomes increasingly longer to reach unreacted droplets. If so, a sharp chemical reaction front is formed during the diffusion of complexes, as shown in Fig. 1. This front will gradually advance toward the center of the globule as the stripping reagent in the droplets is consumed. Diffusion will take place between the external aqueous phase and the advancing reaction front at any time. We assume that the concentration profiles are linear in the external boundary layer, the thin oil film, and the emulsion phase. Figure 2 represents concentration profiles of components in an emulsion globule. In this model the resistance of the stripping reaction is assumed to be negligible since the surface area of the internal phase is very large and the acid/base reaction is very fast.

The following assumptions are additionally made in the mathematical development.

1. Globule size variations can be lumped into a single effective diameter (Sauter mean diameter d_{32}).
2. The external and membrane phases, as well as the membrane and internal phases, are totally immiscible.
3. No internal circulation occurs in the emulsion globule.
4. Emulsion breakage is neglected.

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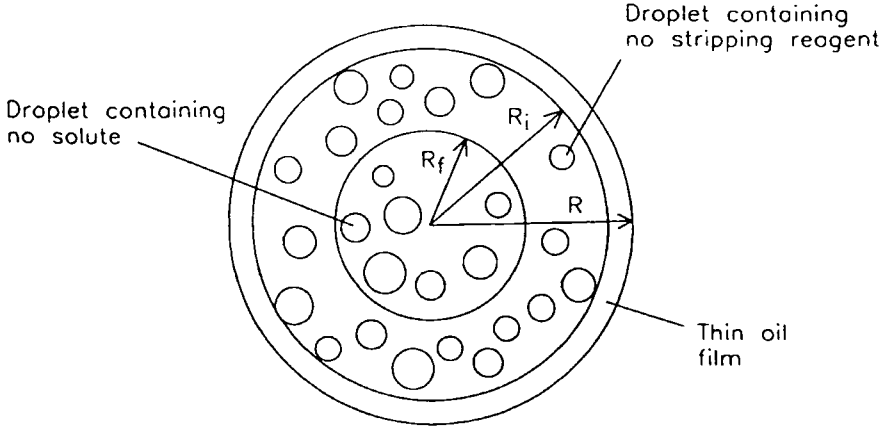

FIG. 1 Schematic representation of an emulsion globule.

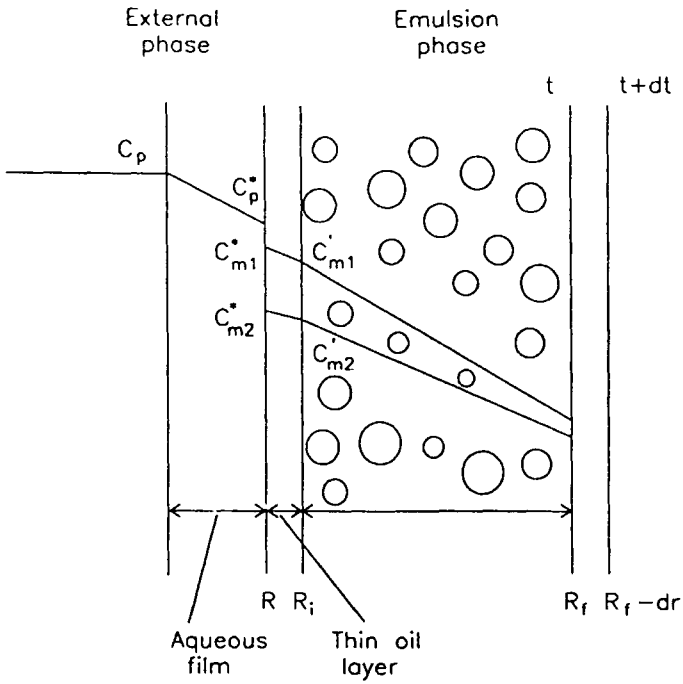

FIG. 2 Concentration profile of each component, assuming quasi-steady state.

5. Carrier concentration is uniform in the emulsion globule and equal to the initial concentration.

By the mass balance, the following equation can be obtained in the external phase:

$$-V_e\frac{dC_p}{dt}(1 + 10^{pK_a - pH}) = kA(C_p - C_p^*) \tag{3}$$

where k is mass transfer coefficient in the external boundary layer, A is the surface area available for mass transfer, and the superscript * indicates the interface between the external and membrane phases.

If quasi-steady-state is assumed, the flux of carrier/solute complex is expressed as

$$J_1 = \frac{D_{m1}}{\delta}\frac{R_i}{R}(C_{m1}^* - C'_{m1}) \qquad \text{in the thin oil film } (R_i < r < R) \tag{4}$$

where D_{m1} is the diffusivity of the carrier/solute complex in the oil phase

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and δ is the thickness of the thin oil layer. From the above assumption (quasi-steady-state), J_1 is also equated as

$$J_1 = \frac{D_{\text{eff},1}}{R_i - R_f}\frac{R_f}{R_i}C'_{m1} \qquad \text{in the emulsion phase } (< R_i) \tag{5}$$

where $D_{\text{eff},1}$ is the effective diffusivity of the carrier/solute complex in the emulsion phase and R_f is the radius of the advancing front. It should be noted that the concentration of each component in the membrane phase is zero at the advancing front.

When the series resistances are considered, the flux can be expressed as

$$J_1 = K_{ov,1}C^*_{m1} \tag{6}$$

where

$$\frac{1}{K_{ov,1}} = \frac{\delta}{D_{m1}}\frac{R}{R_i} + \frac{R_i - R_f}{D_{\text{eff},1}}\frac{R_i}{R_f} \tag{7}$$

For the ECA 4360J/penicillin complex, similar equations are obtained:

$$J_2 = K_{ov,2}C^*_{m2} \tag{8}$$

where

$$\frac{1}{K_{ov,2}} = \frac{\delta}{D_{m2}}\frac{R}{R_i} + \frac{R_i - R_f}{D_{\text{eff},2}}\frac{R_i}{R_f} \tag{9}$$

In the above equations, the subscript "2" indicates the ECA 4360J/penicillin G complex.

The flux in the external boundary layer is given as

$$J_e = k(C_p - C^*_p) \tag{10}$$

Equation (10) can be rewritten using the equilibrium constant:

$$J_e = k\left(C_p - \frac{C^*_{m1}}{K_{eq,1}C_H C_{B1}}\right) \tag{11}$$

From mass balance, the flux J_e is equal to the sum of the two fluxes, thus

$$J_e = J_1 + J_2 \tag{12}$$

Substituting Eqs. (6), (8), and (11) into Eq. (12) gives

$$k\left(C_p - \frac{C^*_{m1}}{K_{eq,1}C_H C_{B1}}\right) = K_{ov,1}C^*_{m1} + K_{ov,2}C^*_{m2} \tag{13}$$

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From Eqs. (1) and (2):

$$C_{m2} = \frac{K_{eq,2}}{K_{eq,1}} \frac{C_{B2}}{C_{B1}} C_{m1} \tag{14}$$

Equation (13) can be rewritten by substitution of Eq. (14) as follows:

$$J = k\left(C_p - \frac{C_p^*}{K_{eq,1} C_H C_{B1}}\right) = \left(K_{ov,1} + K_{ov,2} \frac{K_{eq,2}}{K_{eq,1}} \frac{C_{B2}}{C_{B1}}\right) C_{m1}^* \tag{15}$$

Rewriting Eq. (15) in terms of the overall mass transfer coefficient:

$$J_e = J = K_{tot} C_p \tag{16}$$

In Eq. (16) the overall mass transfer coefficient is expressed as

$$\frac{1}{K_{tot}} = \frac{1}{k} + \frac{1}{K_{eq,1} C_H C_{B1}} \frac{1}{\left(K_{ov,1} + K_{ov,2} \dfrac{K_{eq,2}}{K_{eq,1}} \dfrac{C_{B2}}{C_{B1}}\right)} \tag{17}$$

Consequently, the equation expressing concentration change in the external phase can be rewritten as

$$-V_e \frac{dC_p}{dt} (1 + 10^{pK_a - pH}) = J_e A = K_{tot} A C_p \tag{18}$$

As we know, mass transfer area A can be estimated from the emulsion volume and the number of emulsion globules as follows:

$$A = 4\pi R^2 N_{em} = 4\pi R^2 \left(\frac{V_{em}}{4\pi R^3/3}\right) = \frac{3V_{em}}{R} \tag{19}$$

It should be noted that the concentration of the penicillin G anion in a reacted internal droplet is equal to the concentration of sodium ion. Thus, from the material balance, the radius of the reaction front is given by

$$V_e(C_{e,0} - C_e) = \frac{4\pi}{3} (R_i^3 - R_f^3) \phi_i N_{em} (2C_{i,0}) \tag{20}$$

Here, C_e is the total concentration of penicillin G, that is, undissociated penicillin G and penicillin G anion, ϕ_i is the volume fraction of the internal phase in the emulsion globule which does not include the volume of thin oil film ($0 < r < R_i$), and $C_{i,0}$ is the initial stripping reagent concentration.

A mass balance gives the expression of ϕ_i in terms of the internal phase volume fraction in the emulsion globule ($0 < r < R$), ϕ:

$$\phi_i = \frac{4\pi R^3 \phi/3}{4\pi R_i^3/3} = \left(\frac{R}{R_i}\right)^3 \phi \tag{21}$$

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Equation (18) may be solved numerically by using Gear's algorithm in the subroutine IVPAG of the IMSL MATH library.

EXPERIMENTAL

Reagent Preparation

Kerosene used as the membrane phase was obtained from Junsei Chemical Company. The carrier, Amberlite LA2, a secondary amine, and the surfactant ECA 4360J were purchased from Sigma Chemical Company. Sodium carbonate was used as the stripping reagent and supplied from Junsei Chemical Company. Penicillin G was obtained as its potassium salt from Sigma Chemical Company.

Citrate buffer solution, used as the external aqueous phase, was prepared to maintain constant pH. It was composed of a mixture of citric acid and trisodium citrate. The total concentration of the buffer solution was 0.408 mol/dm^3. In this system, emulsion swelling by osmotic pressure, which is the most serious problem in LEMs, can hardly occur during separation due to the presence of the buffer solution.

The organic solution (membrane phase) was prepared by dissolving Amberlite LA2 and ECA 4360J in kerosene, and the internal stripping phase was prepared by dissolving sodium carbonate in deionized water. Although the solute flux depends strongly on the stripping reagent concentration, a high concentration should be avoided because penicillin G decomposes at high pH. In a preliminary experiment, the stripping reagent concentration was optimized with respect to the transport rate and the stability of penicillin G, and the appropriate concentration was found to be 0.1 M.

Methods

A water-in-oil emulsion was made by slow addition of the internal aqueous phase to the organic solution with vigorous mixing by an emulsifier (homogenizer, Tekmar). The W/O emulsion (70 cm^3) so prepared was dispersed in the vessel containing feed solution and stirred at a constant speed.

At given intervals, samples were taken from the vessel, filtered to remove the W/O emulsion phase, and the residual penicillin G concentration was immediately analyzed by high-performance liquid chromatography (Waters) using 70 parts of 0.1 mol/dm^3 phosphate buffer solution (a mixture of sodium dihydrogenphosphate dihydrate and disodium hydrogenphosphate dodecahydrate) at pH 7.8 to 30 parts of methanol as the mobile

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phase and a μ-Bondapak C_{18} column with a UV photometric detector (254 nm).

The emulsion globule sizes were measured photographically, and the Sauter mean diameter was calculated. The mean internal droplet size was measured by a centrifugal particle size analyzer (SA-CP3, Shimadzu).

The reaction equilibrium constant of penicillin G with Amberlite LA2 or ECA 4360J was obtained by using the usual two-phase experiments as follows. The organic solution was prepared by dissolving 0.015–0.14 M Amberlite LA2 or ECA 4360J in kerosene, and 0.408 M citrate buffer solutions were prepared at pH 4.8–6.0, and 0.005–0.25 M penicillin G potassium salt was dissolved in the buffer solutions. Equal volumes (30 cm^3) of the prepared organic and aqueous solutions were shaken in a flask for 4 hours, and the penicillin G concentration was measured. $K_{eq,1}$ and $K_{eq,2}$ obtained were 3.0×10^6 and 1.01×10^6 dm^6/mol^2, respectively.

The molecular weight of ECA 4360J was determined by cryoscopy, a technique for determining the molecular weight of a substance by dissolving it and measuring the freezing point of the solution (17).

Experiments involving changing several variables were carried out. When one variable was studied, all the other variables were kept constant at the values listed in Table 1.

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Parameter Estimation

Since sufficient surfactant is contained in the membrane phase in the liquid emulsion membrane system, the emulsion globules may be treated as rigid spherical particles existing in the agitated vessel. Therefore, the

TABLE 1
Typical Experimental Conditions

External phase:
Penicillin G: 0.02 M
Citrate buffer: 0.408 M, pH 5.0
Membrane phase:
ECA 4360J: 5 wt%
Amberlite LA2: 0.01 M
Internal phase:
Sodium carbonate: 0.1 M
Volume ratios of each phase:
Internal/membrane: 1/1
Emulsion/external: 1/6
Stirrer speed: 250 rpm
Emulsifier speed: 12,000 rpm

mass transfer coefficient in the external phase, k, was estimated from a correlation for mass transfer in an agitated vessel (18):

$$\frac{k}{(ND_{ex})^{1/2}} = 2.932 \times 10^{-7}\phi_e^{-0.508}\left(\frac{D}{T}\right)^{0.548} R_e^{1.37} \qquad (22)$$

where D_{ex} is the molecular diffusivity of the solute in the external aqueous phase, cm^2/s; D is the diameter of the propeller, cm; T is the diameter of the vessel, cm; N is the stirring speed, rps; $R_e = \rho_c ND^2/\mu_c$; ρ_c is the density of the external aqueous phase, g/cm^3; and μ_c is the viscosity of the external aqueous phase, g/(cm·s).

The thickness of the thin oil film, δ, may be evaluated by the equation obtained by Chan et al. (19).

The effective diffusivities in the heterogeneous phase may be calculated with the Maxwell equation (20). It says that diffusion does not depend on the size of internal droplets but only on the volume fraction in the emulsion globule.

$$D_{eff,i} = \frac{2(1 - \phi)}{2 + \phi} D_{mi} \qquad (i = 1 \text{ or } 2) \qquad (23)$$

where 1 and 2 represent the carrier/solute complex and the surfactant/solute complex, respectively. The molecular diffusivity can be estimated by the Wilke–Chang equation (21), and the estimated D_{m1} and D_{m2} are 9.3×10^{-7} and 6.1×10^{-7} dm^2/min, respectively.

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RESULTS AND DISCUSSION

Figure 3 shows the time course of penicillin G separation at the typical experimental conditions; the calculated results are also shown. As can be seen, the model (solid line) satisfactorily predicts the experimental data while the calculation which does not consider the effect of surfactant on transport (dashed line) underpredicts them. These results demonstrate that the role of the second carrier (surfactant) is also important in penicillin G transport and cannot be neglected.

The effect of such variables as the carrier concentration, surfactant concentration, volume fraction of the internal phase in the emulsion, stirrer speed, and volume fraction of emulsion in the system were investigated, and the experimental data for penicillin G transport were compared with the calculated values in order to examine the validity of the model.

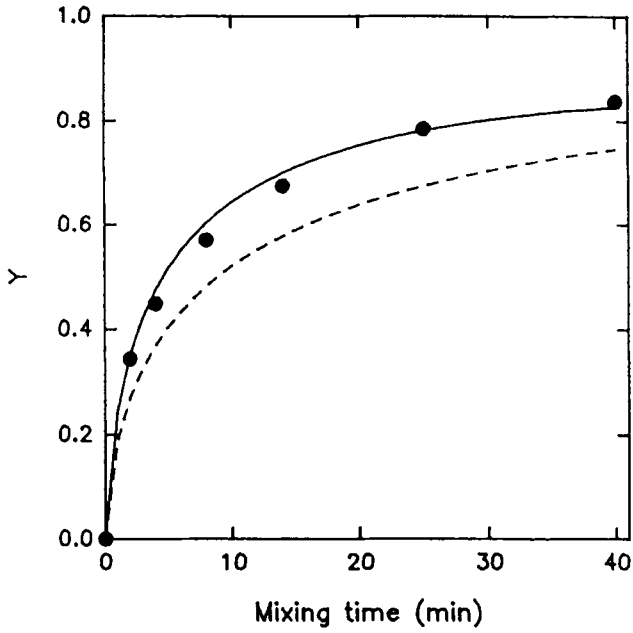

FIG. 3 Comparison of experimental data and calculated results at typical conditions. R = 0.00195 dm, k = 2.08 × 10^{-3} dm/min, $D_{eff,1}$ = 3.7 × 10^{-3} dm^2/min, $D_{eff,2}$ = 2.4 × 10^{-7} dm^2/min.

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Effect of the Carrier Concentration

Penicillin G is transported by way of the solute/carrier complex in this facilitated transport, so that the carrier concentration determines how fast the separation proceeds. The variation of the flux for the three carrier concentrations investigated in this work is presented in Fig. 4. The experiments were performed by varying the carrier concentration from 0.01 to 0.03 M. As expected, the transport rate increased with the carrier concentration whereas the higher carrier concentrations apparently achieve the same final degree of extraction because the total amount of stripping reagent is identical for all of the experiments. Penicillin G is stable in the pH 5 to 7 range. Thus, it is evidently desirable that the transport rate of penicillin G be maintained high since the decomposition of penicillin G can be reduced by fast neutralization of the internal stripping reagent.

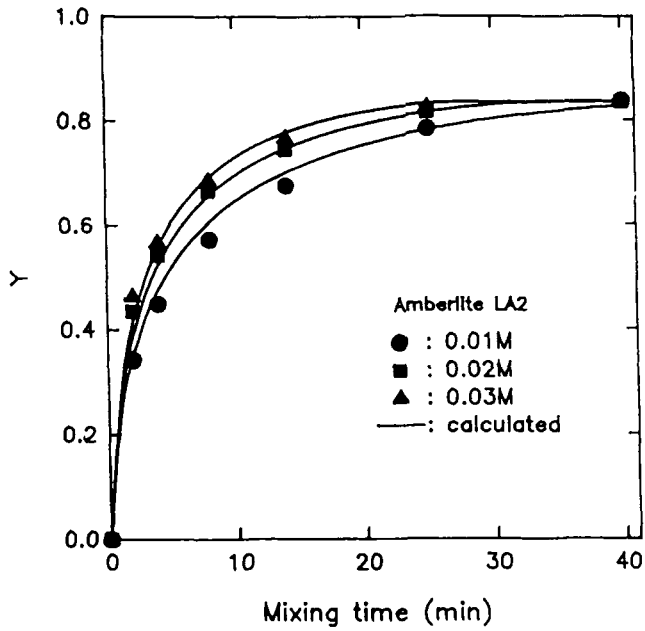

FIG. 4 Effect of carrier concentration on transport rate. R = 0.00195 dm, k = 2.08 × 10^{-3} dm/min, $D_{eff,1}$ = 3.7 × 10^{-3} dm^2/min, $D_{eff,2}$ = 2.4 × 10^{-7} dm^2/min.

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Effect of the Surfactant Concentration

The effect of ECA 4360 concentration on the transport rate is shown in Fig. 5. The molecular weight of ECA 4360 was determined to be 635 from cryoscopy. Nakashio et al. measured the molecular weight of ECA 4360J by vapor pressure osmometry (22). The value obtained in their study was 706.2, which almost agrees with our result. The surfactant concentrations used in this study were 5, 9, and 12 wt%, corresponding to 0.063, 0.113, and 0.151 M. As mentioned previously, the polyamine-type surfactant acts as a carrier, thus the transport rate increases with the surfactant concentration. The good agreement of calculations with experimental data means that the surfactant as well as the carrier increases the ability of the solute to diffuse the membrane phase by way of the surfactant/carrier complex. If the surfactant contribution is neglected, the increase in transport rate with surfactant concentration cannot be predicted.

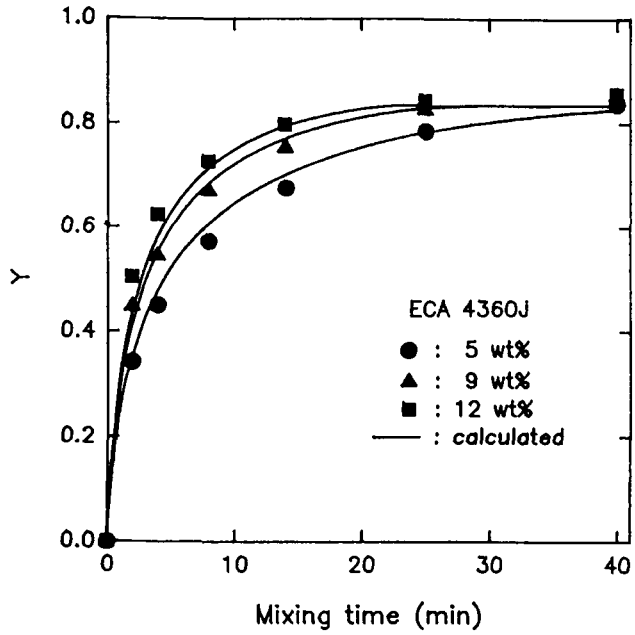

FIG. 5 Effect of surfactant concentration on transport rate. $k = 2.08 \times 10^{-3}$ dm/min, $D_{eff,1} = 3.7 \times 10^{-3}$ dm^2/min, $D_{eff,2} = 2.4 \times 10^{-7}$ dm^2/min. 5 wt%: $R = 0.00195$ dm. 9 wt%: $R = 0.00201$ dm. 12 wt%: $R = 0.00209$ dm.

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Effect of the Internal Phase Volume Fraction in the Emulsion

In Fig. 6 the variation of the transport rate is presented as a function of the internal phase volume fraction in the emulsion. As observed, the transport rate did not increase with the volume fraction of the internal phase despite the increase in the capacity to strip the solute. This can be explained by the decrease in surface area available for mass transfer. The emulsion viscosity increases with the internal phase volume fraction, and the larger emulsion globule size at the larger volume fraction was obviously attributed to the higher emulsion viscosity. This is the reason why the transport rate did not increase with the internal phase volume fraction in spite of the increased capacity for trapping penicillin G.

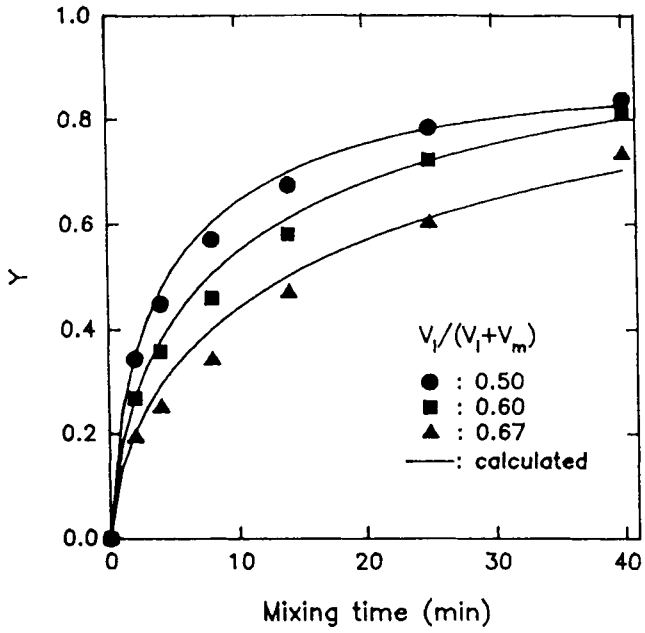

FIG. 6 Effect of volume fraction of the internal phase on transport rate. $k = 2.08 \times 10^{-3}$ dm/min, 0.5: $R = 0.00195$ dm, $D_{eff,1} = 3.7 \times 10^{-3}$ dm^2/min, $D_{eff,2} = 2.4 \times 10^{-7}$ dm^2/min. 0.6: $R = 0.00265$ dm, $D_{eff,1} = 2.84 \times 10^{-3}$ dm^2/min, $D_{eff,2} = 1.85 \times 10^{-7}$ dm^2/min. 0.67: $R = 0.00355$ dm, $D_{eff,1} = 2.31 \times 10^{-3}$ dm^2/min, $D_{eff,2} = 1.5 \times 10^{-7}$ dm^2/min.

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Effect of the Hydrodynamic Condition

The effect of the stirrer speed on the transport rate is presented in Fig. 7. The experiments were carried out by changing the stirrer speed from 250 to 400 rpm. The emulsion globule size decreases with the stirrer speed, that is, the surface area increases with the stirrer speed. As well, the external aqueous boundary layer around emulsion globule becomes thinner as the stirrer speed increases. Thus, the transport rate increased with the stirrer speed due to larger surface area and faster mass transfer in the external boundary layer. This higher transport rate makes it possible to suppress the losses of penicillin G by decomposition since the transported penicillin G neutralizes the internal phase more rapidly.

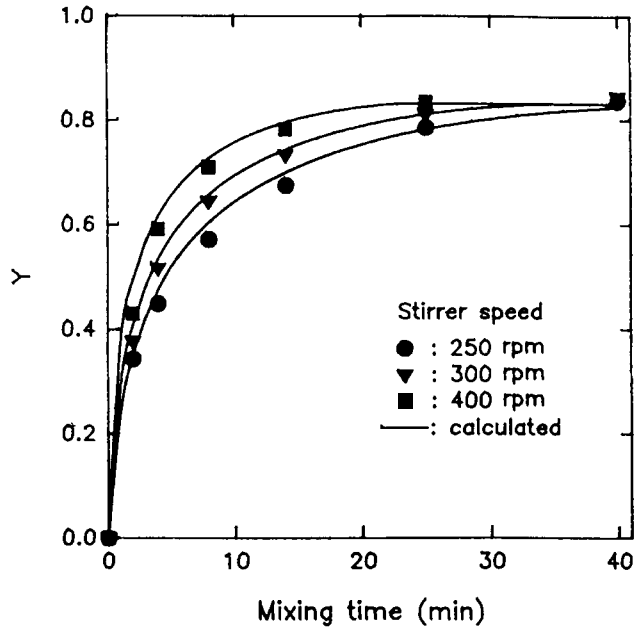

FIG. 7 Effect of stirrer speed on transport rate. $D_{eff,1} = 3.7 \times 10^{-3}$ dm²/min, $D_{eff,2} = 2.4 \times 10^{-7}$ dm²/min. 250 rpm: $R = 0.00195$ dm, $k = 2.08 \times 10^{-3}$ dm/min. 300 rpm: $R = 0.00171$ dm, $k = 2.82 \times 10^{-3}$ dm/min. 400 rpm: $R = 0.00140$ dm, $k = 4.82 \times 10^{-3}$ dm/min.

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Effect of the Volume Fraction of Emulsion in the System

As the amount of penicillin G in the external phase is increased, more stripping reagent is needed to accept all of the acid. The effect of the volume fraction of emulsion on the transport rate is depicted in Fig. 8. When the volume fraction of emulsion in the system is decreased, the solute transport rate is decreased largely due to the relatively reduced capacity of the internal phase to accept the transported penicillin G, that is, increase in the amount of penicillin G per stripping reagent. When the volume fraction of emulsion is 0.1, the transport reaches equilibrium at about 20 minutes and the degree of extraction does not increase any longer with the elapsed time.

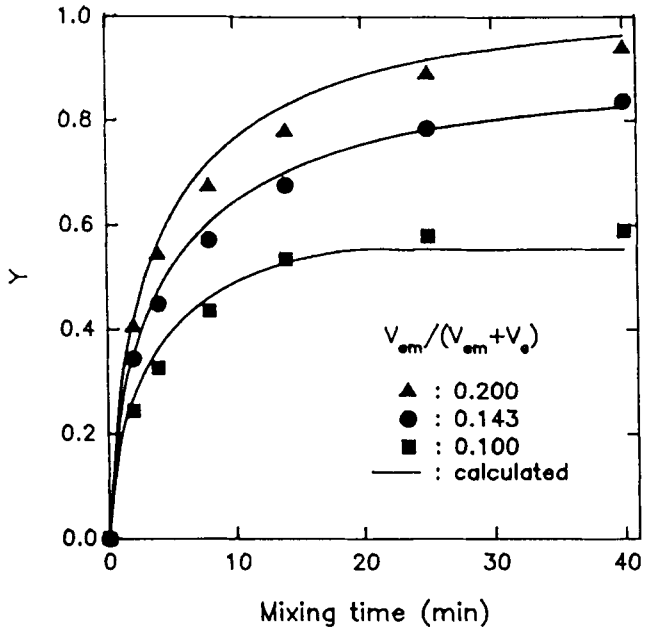

FIG. 8 Effect of volume fraction of the emulsion on transport rate. $D_{eff,1} = 3.7 \times 10^{-3}$ dm²/min, $D_{eff,2} = 2.4 \times 10^{-7}$ dm²/min. 1/4: $R = 0.00230$ dm, $k = 1.69 \times 10^{-3}$ dm/min. 1/6: $R = 0.00195$ dm, $k = 2.08 \times 10^{-3}$ dm/min. 1/9: $R = 0.00181$ dm, $k = 2.08 \times 10^{-3}$ dm/min.

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CONCLUSIONS

Separation of penicillin G by using liquid emulsion membranes was examined with Amberlite LA2 as the carrier and ECA 4360J as the surfactant, and a model for the LEM system facilitated by two carriers was proposed to predict the transport rate of penicillin G. The surfactant, ECA 4360J, a nonionic polyamine, functions not only as carrier but also as surface-stabilizing agent, and the influence on transport is very significant. Therefore, the effect of surfactant should be considered in mathematical modeling when a system contains a polyamine-type surfactant.

The proposed model is based on the shrinking core approach, assuming quasi-steady-state. The model is noble in that the equations are incorporated with the overall mass transfer coefficient and the effect of surfactant on transport is taken into account, which makes it possible to predict the increase in penicillin G transport rate with surfactant concentration.

Although the calculated results slightly overestimate the extraction rates due to the assumption of reaction irreversibility, the model agrees well with the experimental data on the whole. On the other hand, the calculated results underpredict the experimental data significantly when the effect of surfactant on transport is neglected, which supports the model used for this LEM system facilitated by two carriers.

NOMENCLATURE

A	mass transfer area (dm^2)
C_{B1}	carrier concentration in the membrane phase (mol/dm^3)
C_{B2}	surfactant concentration in the membrane phase (mol/dm^3)
C_e	total solute concentration in the external phase (undissociated penicillin G + penicillin G anion) (mol/dm^3)
C_H	proton concentration (mol/dm^3)
$C_{i,0}$	initial concentration of stripping reagent (mol/dm^3)
C_{m1}	concentration of carrier/solute complex (mol/dm^3)
C_{m2}	concentration of surfactant/solute complex (mol/dm^3)
C_p	penicillin G anion concentration in the external phase (mol/dm^3)
D	diameter of the propeller (cm)
$D_{eff,1}$	effective diffusivity of carrier/solute complex (dm^2/min)
$D_{eff,2}$	effective diffusivity of surfactant/solute complex (dm^2/min)
D_{ex}	molecular diffusivity of the solute in the external aqueous phase (cm^2/s)
D_{m1}	diffusivity of carrier/solute complex (dm^2/min)
D_{m2}	diffusivity of surfactant/solute complex (dm^2/min)
J_1	flux of carrier/solute complex ($mol/dm^2 \cdot min$)
J_2	flux of surfactant/solute complex ($mol/dm^2 \cdot min$)
J_e	flux of penicillin G anion in the external phase ($mol/dm^2 \cdot min$)
k	mass transfer coefficient in the external phase (dm/min)
K_a	acidic dissociation constant (mol/dm^3)
$K_{eq\cdot1}$	equilibrium constant of penicillin G with carrier (dm^6/mol^2)
$K_{eq\cdot2}$	equilibrium constant of penicillin G with surfactant (dm^6/mol^2)
$K_{ov,1}$	mass transfer coefficient of carrier/solute complex obtained by considering the series resistances in the thin oil film and the emulsion (dm/min)
$K_{ov,2}$	mass transfer coefficient of carrier/surfactant complex obtained by considering the series resistances in the thin oil film and the emulsion (dm/min)
K_{tot}	overall mass transfer coefficient (dm/min)

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N stirrer speed (rps)
N_{em} number of emulsion globules
R radius of emulsion globule (dm)
R_f radius of advancing front (dm)
R_i radius of inner core of emulsion globule (dm)
t contact time (min)
T diameter of the vessel (cm)
V_e external phase volume (dm^3)
V_{em} emulsion volume (dm^3)
V_i internal phase volume (dm^3)
V_m membrane phase volume (dm^3)
Y degree of extraction, $1 - C_e/C_{e,0}$

Superscript

* interface between the external phase and the membrane phase

Greek Letters

δ thickness of the thin oil film
ϕ volume fraction of the internal phase in the emulsion phase
ϕ_i defined by Eq. (21)
μ_c viscosity of the external aqueous phase [g/(cm·s)]
ρ_c density of the external aqueous phase (g/cm^3)

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Received by editor May 26, 1994

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