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ANALYSIS OF LEAKAGE EFFECT IN COUPLED TRANSPORT THROUGH LIQUID SURFACTANT MEMBRANE

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ABSTRACT

Considerable effort has been directed toward describing, through analysis of mass-transfer resistances for solute diffusion and reaction in an emulsion drop, the permeation mechanism in liquid membrane systems based on the advancing reaction front model. However, very little attention has been paid to the loss of extraction efficiency often encountered in these systems due to rupture of the emulsion globules. In the present study, an unsteady-state mathematical model for batch extraction of monovalent $HCrO_4^-$ and divalent CrO_4^{2-} from aqueous solution, through the use of Aliquat 336 as extractant and sodium hydroxide as stripping reagent, is reported. The rate of change of internal-phase volume due to membrane breakage was assumed to be independent of time, and an instantaneous and irreversible reaction between the solute and the internal reagent at the membrane–internal droplet interface was presumed to create a reaction front within the emulsion globule. The leakage coefficient was determined experimentally and was found to be dependent on internal-phase volume fraction. Batch experiments were

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performed for separation of Cr(VI) from aqueous potassium dichromate solution and the validity of the model was tested through the comparisons of model predictions with experimental data for different internal-phase volume fractions. The effect of external-phase pH on overall extraction in presence of leakage was also studied with semiempirical equations of the solute distribution coefficient that were obtained through experiments.

INTRODUCTION

Since their development in 1968 (1), liquid surfactant membranes (LSMs) have shown tremendous promise in a wide variety of industrial separations, such as those involved in the removal of weak acids/bases from wastewater, extraction of metal ions from metal-industry effluents, and several biochemical and biomedical applications. A number of mathematical models have been developed to describe the mechanism of solute transfer through the LSMs based on either the reversible reaction model (2–5) or the advancing reaction front model (6–9). However, the loss of extraction efficiencies that often occur in these systems, due to lack of stability of the emulsion globules, creates problems that inhibit the use of either model in industrial equipment. Rupture of the thin membrane film causes the internal phase within the emulsion drops to leak out into the external phase and can have a detrimental effect on the ultimate extraction performance. A number of researchers like Li and Shrier (10), Cahn et al. (11), and Terry, Li, and Ho (12) noted that the fractional solute recovery passes through a maximum beyond which the rate of solute leakage due to membrane rupture exceeds its permeation rate. Therefore, the incorporation of this breakage effect in the mathematical descriptions of liquid membrane transport is needed. While considerable modeling effort has been directed toward describing the permeation mechanism in a realistic manner, very little attention has been paid to extraction efficiency losses due to membrane rupture.

A number of researchers, such as Hochchauser and Cussler (13), Martin and Davies (14), Kita, Matsumoto, and Yonezawa (15), Kondo et al. (16), Takahasi, Ohtsubo, and Takeuchi (17), Shere and Cheung (18), have performed experimental studies on emulsion stability. Their studies revealed that the emulsion breakup was dependent on factors such as agitation speed, nature and concentration of the surfactant, volume fraction of the internal phase, and viscosity of the membrane solution. These studies have limited applicability as they are useful only to the specific conditions under which the experiments were performed.

The first mass-transfer model incorporating the effects of solute leakage was suggested by Boyadzhiev, Sapundzhiev, and Bezenshek (19) for separation of 2 hydrocarbons by simple permeation through an aqueous membrane phase. Ho

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and Li (20) extended the model of Boyadzhiev, Sapundzhiev, and Bezenshek to continuous multistage operations and extraction in mechanically agitated columns. They also accomplished minimization of adverse leakage effects on the extraction efficiency. They added a chemical reagent to the continuous phase to convert the leaked reaction products to an extractable form that could be reextracted by the liquid membrane emulsion. Terry, Li, and Ho (12) analyzed the extraction of phenolic compounds and organic acid by liquid membranes. Without considering breakage effects, they generated theoretical extraction curves using the advancing reaction front model. They then used the breakage model together with experimental extraction results to estimate the effects of breakage on the extraction efficiency of the membrane system. Frankenfeld and Cahn (21) presented a leakage model, based on the membrane film model of Cahn and Li (22), in which a constant leakage rate was considered. Shere and Cheung (23) developed a model, based on a droplet formation model, for leakage of internal reagent into the bulk phase. They assumed the diffusivity of the internal phase to be negligible so that the macrodroplet breakup was the main mechanism responsible for microdroplet release. A mass-transfer model that was based on the assumption that internal-phase leakage effects were due to membrane rupture was also proposed by Chan and Lee (24). Their model was based on the reversible reaction model, and at a constant stirring speed, the volumetric leakage rate was assumed to be the product of a time-dependent leakage function and the volume of the internal phase. Borwankar et al. (25) developed a general model for the physical transport of solute that combined the realistic description of unsteady-state permeation through a composite emulsion globule with a mechanism for solute leakage due to membrane rupture. The leakage coefficient in their study was assumed to be a function of time at a constant agitation speed unlike in the work of Terry, Li, and Ho (12) and Boyadzhiev, Sapundzhiev, and Bezenshek (19). However, their model showed some discrepancies in the predictions of the pH versus time data. Lee and Chan (26) also proposed a reversible-reaction model that incorporated the solute leakage in a time-varying leakage function. Although the model predicted the general trends of the extraction phenomena fairly well, a deviation was observed between the theoretical predictions and experimental data. The discrepancy may have been due to the time-varying correlation of the leakage rate. Bhowal and Datta (27) also incorporated the effect of time-varying leakage of the internal phase, due to membrane-phase rupture, in their mathematical model for analyzing experimental data of batch extraction of weak acids by a strong base as the internal reagent. Liu and Zhang (28) proposed a pseudo–steady state, advancing reaction front model that accounted for membrane breakage but failed to allow for predictions on the leakage effects on the reaction-front movement.

In an earlier study we conducted (29), an unsteady-state mathematical model for the batch extraction of Cr(VI) ions from aqueous solution by LSMs with a quaternary ammonium salt (Aliquat 336) as carrier and NaOH as the stripping

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reagent was proposed. The model had been derived from the advancing reaction front model of Ho et al. (6) and neglects the external-phase mass-transfer resistance and the effect of membrane breakage.

In the present study, we modified the unsteady-state advancing reaction front model developed earlier (29) by incorporating into it the leakage effect of the internal phase due to membrane rupture. A schematic diagram of the present system was included in the previous publication (29). The emulsion breakup rate was assumed to be proportional to the internal-phase volume as suggested by Boyadzhiev, Sapundzhiev, and Bezenshek (19). This assumption has been validated by experimental leakage data that shows that the internal-phase volume decreases linearly with time. The effect of internal-phase leakage on reaction front movement has also been incorporated in the present model. The leakage coefficient, which is a model parameter, was determined from experimental leakage data and was found to vary with volume fraction of the internal phase. Therefore, the effect of leakage on solute transfer, as well as reaction front movement, was studied for 3 different internal-phase volume fractions. Attempts were also made to investigate the effect of the external-phase pH on solute extraction in presence of internal-phase leakage. The model was tested against the performance of the earlier study, (29) which had neglected internal-phase leakage as well as against experimental results in a batch system.

MATHEMATICAL MODEL

In the present study, an unsteady-state mathematical model based on the advancing reaction front model, as described in a previous study (29), was proposed for facilitated carrier-mediated batch extraction of monovalent Cr(VI) ($HCrO_4^-$) and divalent Cr(VI) (CrO_4^{2-}). The model accounts for the internal-phase leakage effect due to membrane rupture. A quaternary ammonium chloride (Aliquat 336) was used as the extractant and NaOH was the stripping reagent. The reactions are described as follows:

At the globule-external phase interface

$$HCrO_4^- + \underset{\displaystyle CH_3}{\underset{|}{R_3N - X}} \quad \leftrightarrow \quad \underset{\displaystyle CH_3}{\underset{|}{R_3NHCrO_4}} + X^- \tag{1}$$

$$CrO_4^{2-} + \underset{\displaystyle CH_3}{\underset{|}{2R_3N - X}} \quad \leftrightarrow \quad \underset{\displaystyle CH_3}{\underset{|}{[R_3N]_2CrO_4}} + 2X^- \tag{2}$$

where, $R = (CH_2)_6CH_3$ and X = Cl or OH

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At the reaction front:

$$R_3NHCrO_4 + NaOH = R3N - OH + Na^+ + HCrO_4^- \quad (3)$$
$$\quad\;\; | \qquad\qquad\qquad\quad\;\; |$$
$$\quad CH_3 \qquad\qquad\quad CH_3$$

$$[R_3N]_2\,CrO_4 + 2NaOH = 2R_3N - OH + 2Na^+ + CrO_4^{2-} \quad (4)$$
$$\quad\;\; | \qquad\qquad\qquad\quad\;\; |$$
$$\quad CH_3 \qquad\qquad\quad CH_3$$

Due to breakage of emulsion globules with time, some solute leaks, as does internal reagent from the reacted and unreacted parts of the emulsion globules, into the external phase. The model also takes into account the influence of leakage rate on the reaction front progress. We made the following assumptions in developing the present model:

1. The batch system operates under complete mixing and constant temperature conditions.
2. The physical properties of all the phases and the diffusion coefficient of the solute-carrier complex through the membrane phase are constant throughout the extraction process.
3. The membrane and the external phases, as well as the membrane and the internal phase, are totally immiscible.
4. The ionic form of the solute existing in the external phase is insoluble in the membrane phase so that extraction by nonfacilitated transport can be neglected.
5. The droplets inside the emulsion globules are immobile and uniformly distributed due to the considerable viscosity difference between the aqueous internal phase and the membrane phase and the presence of surfactant in the membrane phase.
6. The concentration gradient within the internal droplets can be neglected.
7. The polydispersed-character effects of the emulsion globules in the continuous phase can be neglected, and the system is monodisperse with globules of average size.
8. The hydrodynamic conditions inside the vessel (the stirrer geometry, the stirrer speed, and the ratio of impeller to vessel diameter) are such that the system is well mixed, and therefore, the mass-transfer resistance around the emulsion globule can be neglected.
9. The main mechanism of leakage is the mechanical rupture of emulsion drops because the diffusion of internal reagent through the membrane is negligible.
10. At a given speed of agitation, the rate of change of internal-phase volume due to leakage is independent of time and proportional to the internal-phase volume.

11. Volume change of emulsion and external phase due to leakage can be neglected.
12. When external-phase pH is low (≤ 6.0), Cr(VI) exists predominantly in the form of $HCrO_4^-$ in the aqueous phase, and 1 mole of the solute-carrier complex reacts with 1 mole of the internal reagent at the reaction front. For higher external phase pH (≥ 6.0), $CrO_4^{2-}$is the predominant ion such that 1 mole of the complex reacts with 2 moles of the internal reagent at the reaction front.

The rate of change of volume of the internal phase due to breakage is

$$\frac{dV_i}{dt} = -\psi V_i \tag{5}$$

Because volume change of emulsion and external phase due to leakage can be neglected, V_i can be replaced by $\phi_t V$ so that Eq. (5) becomes

$$\frac{d\phi_t}{dt} = -\psi \phi_t \tag{6}$$

Integrating Eq. (6), one obtains

$$\text{or, } \phi_t = \phi^{-\psi_t} \tag{7}$$

The material balance of the solute ions contained in the external phase is

$$-V_0 \frac{d(C_0)}{dt} = n \cdot 4\pi \cdot R_2^0 \cdot D_{\text{eff}} \cdot \frac{\partial C_m}{\partial r} \Big|_{r = R_0} - J_L \tag{8}$$

where J_L = volumetric leakage rate of solute from the reacted region of the globules ($R_0 > r > R_f$) to the external phase.

$$J_L = \psi \cdot \phi_t \cdot n \cdot \frac{4}{3}\pi (R_0^3 - R_f^3) \cdot C_i/m \tag{9}$$

where $m = 1$ or 2 depending upon the pH of the external phase.

By substituting ϕ_t from Eq. (7) into Eq. (9), the following is obtained:

$$J_L = \psi \cdot \phi \cdot e^{-\psi t} \cdot n \cdot \frac{4}{3}\pi (R_0^3 - R_f^3) \cdot C_i/m \tag{10}$$

By substituting J_L from Eq. (10) into Eq. (8) and simplifying, the following is obtained:

$$-\frac{dC_0}{dt} = \frac{3V}{V_0}\left[\frac{D_{\text{eff}}}{R_0}\frac{\partial C_m}{\partial r}\Big|_{r = R_0} - \frac{\psi}{3m}\phi\, e^{-\psi t}(1 - R_f^3/R_0^3)C_i\right] \tag{11}$$

The initial condition for Eq. (11) is

$$C_0 = C_0^* \qquad \text{at} \qquad t = 0 \tag{12}$$

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The material balance of the solute in the reacted region of the globules ($R_0 > r > R_f$) is

$$\frac{\partial C_m}{\partial t} = \frac{D_{\text{eff}}}{(1-\phi)}\left[\frac{\partial^2 C_{\text{m}}}{\partial r^2} + \frac{2}{r}\frac{\partial C_{\text{m}}}{\partial r}\right] \tag{13}$$

The initial and boundary conditions of Eq. (13) are

$$C_{\text{m}}(0, r) = 0 \tag{14}$$

$$C_{\text{m}}(t, R_0) = C_{\text{m}}\big|_{r = R_0} = C_{\text{D}} \cdot C_0 \tag{15}$$

$$C_{\text{m}}(t, R_{\text{f}}) = 0 \tag{16}$$

$$\frac{\partial C_m}{\partial r}\Big|_{r = R_{\text{t}} = 0} = 0 \tag{17}$$

The rate of consumption of internal reagent is

$$-\frac{\text{d}}{\text{dt}}\left(\frac{4}{3}\pi R_{\text{f}}^3 \phi_t C_{\text{i}}\right) = m\, 4\, \pi\, R_{\text{f}}^2\, D_{\text{eff}} \frac{\partial C_{\text{m}}}{\partial r}\Big|_{r = R_{\text{t}}} \tag{18}$$

Substituting ϕ_t from Eq. (7) into Eq. (18), one obtains

$$-\frac{\text{d}}{\text{dt}}\left(\frac{4}{3}\pi R_{\text{f}}^3 \phi\, \text{e}^{-\psi t} C_{\text{i}}\right) = m\, 4\, \pi\, R_{\text{f}}^2\, D_{\text{eff}} \frac{\partial C_{\text{m}}}{\partial r}\Big|_{r = R_{\text{t}}} \tag{19}$$

$$\text{or } -\frac{\text{d}R_{\text{f}}}{\text{dt}} = \frac{m\, D_{\text{eff}}}{C_{\text{i}}\, \phi\, \text{e}^{-\psi t}} \frac{\partial C_{\text{m}}}{\partial r}\Big|_{r = R_{\text{f}}} - \frac{R_{\text{f}}\, \psi}{3} \tag{20}$$

The initial condition for this reaction is

$$R_{\text{f}} = R_0 \quad \text{at} \quad t = 0 \tag{21}$$

The above equations can be represented in dimensionless form through the introduction of the following dimensionless variables:

$$\begin{array}{lll} \tau = D_{\text{eff}}\text{t}/R_0^2 & X = r/R_0 & X_{\text{f}} = R_{\text{f}}/R_0 \\ \theta_0 = C_0/C_0^* & \theta_{\text{m}} = C_{\text{m}}/C_0^* & \theta_{\text{i}} = C_{\text{i}}/C_0^* \\ E = 3V/V_0 & S = \psi R_0^2/D_{\text{eff}} & \end{array} \tag{22}$$

Equations (7), (11–17), (20), and (21) become (in dimensionless form)

$$\phi_{\text{t}} = \phi\, \text{e}^{-S\tau} \tag{23}$$

$$-\frac{\text{d}\theta_0}{\text{d}\tau} = E\left[\frac{\partial \theta_{\text{m}}}{\partial X}\Big|_{X = 1} - \frac{S\, \phi\, \text{e}^{-S\tau}}{3\, m}(1 - X_{\text{f}}^3)\, \theta_{\text{i}}\right] \tag{24}$$

$$\theta_0 = 1.0 \quad \text{at} \quad \tau = 0 \tag{25}$$

$$\frac{\partial \theta_{\text{m}}}{\partial \tau} = \frac{1}{(1-\phi)}\left[\frac{\partial^2 \theta_{\text{m}}}{\partial X^2} + \frac{2}{X}\frac{\partial \theta_{\text{m}}}{\partial X}\right] \tag{26}$$

$$\theta_m(0, X) = 0 \tag{27}$$

$$\theta_m(\tau, X = 1) = \theta_m \big|_{X=1} = C_D \cdot \theta_0 \tag{28}$$

$$\theta_m(\tau, X_f) = 0 \tag{29}$$

$$\frac{\partial \theta_m}{\partial X} \Big|_{X = X_f = 0} = 0 \tag{30}$$

$$-\frac{dX_f}{d\tau} = \frac{m}{\theta_i \phi e^{-S\tau}} \frac{\partial \theta_m}{\partial X} \Big|_{X = X_f} \frac{S}{3} \cdot X_f \tag{31}$$

$$X_f = 0 \quad \text{at} \quad \tau = 0 \tag{32}$$

The coupled Eqs. (24), (26), and (31) were solved by numerical computation with an implicit finite difference technique as discussed in (29). As in the previous study, none of the 3 equations can be solved independently, and therefore, an iterative process was adopted for each time step. The computational procedures for each time step were as follows:

1. Values of θ_0 and X_f were assumed to be equal to those in the previous time step.
2. The assumed values of θ_0 and X_f have been substituted in Eq. (26). Simultaneous linear algebraic equations having a tridiagonal matrix of coefficients, obtained by representing the above equations in finite-difference form, were solved by a matrix inversion and multiplication method to obtain θ_m as a function of X.
3. The values of X_f and θ_m were tested to determine if they satisfied Eq. (31). If they did not, a new estimate for X_f was made and the process from step 2 onward was repeated until the matching was satisfactory.
4. θ_0 was calculated from Eq. (24) and the calculated and assumed values of θ_0 were matched by an iterative process similar to that adopted in step 3 for solving X_f.

EXPERIMENTAL PROCEDURE

The composition of the membrane phase used in this study was as follows: solvent, distilled kerosene of specific gravity 0.798 and boiling range between 145°C and 250°C; extractant, Aliquat 336, 0.5% (vol); surfactant, Paranox 106, 1.5% (vol); stabilizer, decanol, 5% (vol). Double-distilled water was used for preparation of aqueous solutions. Prior to the extraction reaction, the extractant (Aliquat 336), which is commercially available in the chloride form, was converted to the hydroxide form according to the procedure described in (29).

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Experiments were conducted at 2 different values of the external phase pH (~5.5 and ~11.0). In cases where pH ~5.5, the external phase was prepared by dissolving potassium dichromate in double-distilled water; when pH ~ 11.0, the external phase was prepared by dissolving potassium dichromate in 0.001N NaOH solution. The equilibrium experiments to determine the distribution coefficient were performed as described in (29).

For the kinetic studies, batch extractions of chromium with liquid-surfactant membrane were conducted in a baffled glass vessel with a turbine impeller. A constant stirring rate of 150 rpm was maintained to allow the homogeneous dispersion of the organic phase into the aqueous phase, and it was taken as a constant parameter in the present study. Water in oil emulsion was prepared by gradually adding NaOH solution to the organic phase with constant stirring of approximately 5000 rpm for approximately 20 min. The emulsion thus prepared was added to double-distilled water or NaOH solution contained in the baffled glass vessel and stirred for a few minutes to allow the emulsion globules to achieve steady state. Then a small quantity of potassium dichromate solution was added to the vessel. The volume of water or NaOH solution initially taken inside the vessel and the volume and concentration of dichromate solution added were adjusted to obtain the desired volume and concentration of the aqueous phase at the beginning of the extraction process. Samples of the aqueous phase were withdrawn at definite time intervals and were analyzed by a UV spectrophotometer.

In the leakage experiments performed to determine the stability of the emulsion, an aqueous potassium dichromate solution (1000 mg/L) was used as the internal phase. The membrane phase was of the same composition as in extraction experiments. However Aliquat 336 was not added to the membrane phase so that potassium dichromate could only reach the external phase by emulsion globule rupture. Emulsification was carried out under conditions specified previously. The total emulsion volume was 50 cc. The emulsion prepared was mixed with aqueous phase (double-distilled water) in a baffled glass vessel and stirred continuously by a turbine impeller at 150 rpm. Chromium present in the internal phase diffused out of the emulsion globules due to globule rupture and was mixed with the aqueous phase. To determine the concentration of chromium in the external phase, aqueous samples were withdrawn after definite time intervals and analyzed spectrophotometrically as mentioned previously.

The amount of internal phase leaked was obtained from the following equation:

$$\% \text{ leakage} = \frac{\begin{array}{r}(\text{solute concentration in external phase}) \\ \times (\text{external phase volume}) \times 100\end{array}}{\begin{array}{r}(\text{initial solute concentration of internal phase}) \\ \times (\text{initial volume of internal phase})\end{array}}$$

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RESULTS AND DISCUSSION

Estimation of Model Parameters

All the parameters used in the present model were determined either experimentally or from standard correlations. The model parameters were emulsion globule Sauter mean diameter (d_{32}), effective diffusivity of solute through the emulsion (D_{eff}), solute distribution between the membrane and external phases (C_D), and the leakage coefficient (Ψ). The method of determination of d_{32}, solute diffusivity through the membrane (D_m), and C_D have been elaborated in (29), and the values of these parameters in the present study are given in Table 1. Equations (1) and (2) show that the distribution coefficient of Cr(VI) between organic and aqueous phases will depend upon the predominant Cr(VI) oxy-anion in the external phase. Because Cr(VI) oxy-anion predominance depends upon the pH value of the solution (30), it is likely to have an influence on the distribution coefficient. Therefore, the distribution coefficient has been determined for the 2 different values of the external phase (pH ~5.5 and ~11.0) considered in the present study. The effective diffusivity of the solute (D_{eff}) was calculated from the value of D_m with the Jefferson-Witzell-Sibbitt correlation (31).

Estimation of Leakage Coefficient

The expression for change in internal-phase volume due to leakage as obtained from Eq. (5) is as follows:

$$V_i = V_i^* \, e^{-\Psi t} \tag{33}$$

where V_i^* = initial internal phase volume (cc); V_i = internal-phase volume at any time (cc); t = time (seconds).

The values of Ψ were obtained for different volume fractions (ϕ) of the internal phase from curve fitting the experimental leakage data. The results are as given in Table 2, which shows that of the 3 different values, Ψ is highest for ϕ equal to 0.5 and lowest for ϕ equal to 0.3.

Table 1. Values of Some Model Parameters of the Present Study

Sauter Mean Emulsion Globule Diameter (d_{32}), cm	Solute Diffusivity Through the Membrane (D_m),cm^2/s	Distribution Coefficient (C_D) for Initial External-Phase pH	
		≈5.5	≈11.0
0.0778	2.54×10^{-6}	$261.235\ C_S^{-0.798}$	$81.238\ C_S^{-0.598}$

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Table 2. Leakage Constants for Different Volume Fractions of Internal Phase

ϕ	ψ	RMS DEV
0.5	2.11×10^{-4}	0.0025
0.4	1.56×10^{-4}	0.0032
0.3	1.05×10^{-4}	0.0024

RMS DEV = Root mean square deviation.

Plots of $-\mathrm{Ln}(V_i/V_i^*)$ vs. time are shown in Fig 1. The slope of the curve indicates values of the leakage coefficients. The results indicate that the leakage rate is independent of time. Initially when the emulsion was introduced in an agitated batch reactor, coalescence and redispersion of emulsion drops occurred in the external continuous phase. For this initial period, leakage rate must be a function of time after which it may be assumed to be constant. However, the experimental data suggest that the leakage rate was independent of time. Therefore, we concluded that the emulsion globules reached stable state within a very short period.

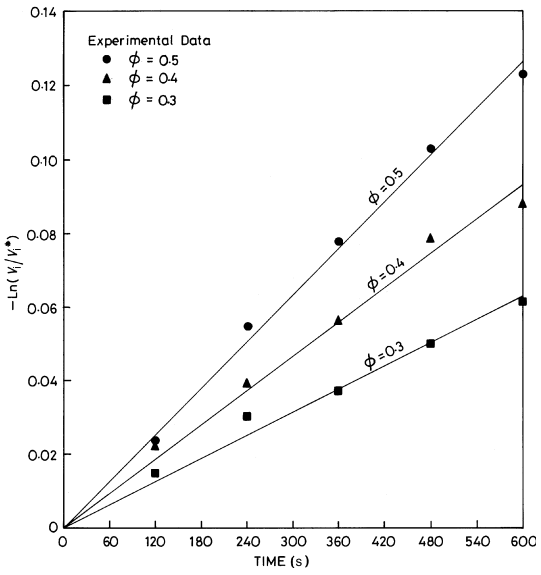

Figure 1. Estimation of leakage coefficient.

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Effect of Volume Fraction of Internal Phase on Leakage Rate

Leakage studies were performed for different values of the dimensionless variable ϕ (volume fraction of internal phase). Figure 2 shows that the percentage leakage of internal phase increased with increases in ϕ. If all the other factors remain constant, the stability of the emulsion decreases with an increase in the fraction of internal phase. The decrease in emulsion stability with increase in internal phase volume fraction in the emulsion can be explained by the decrease in thickness of the membrane phase that encapsulates the microdroplets.

Figure 3 depicts the fractional change in volume of the internal phase as a function of dimensionless time due to leakage. As ϕ increases from 0.3 to 0.5, the emulsion breaks at a faster rate so that the volume change of the internal phase with real time is higher. The effect of internal-phase volume fraction on fractional volume change of the internal phase due to leakage with regard to dimensionless time was expected to be significant. The results are in agreement with data presented in Fig. 2.

Effect of Leakage on Extraction for Different Internal-Phase Volume Fractions

Computer simulation of the model equations (24), (26), and (31) was performed to obtain a concentration profile of the external-phase solute and the re-

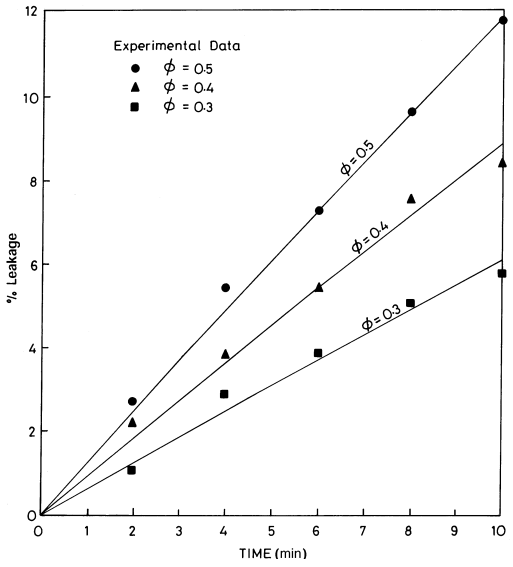

Figure 2. Experimental leakage data.

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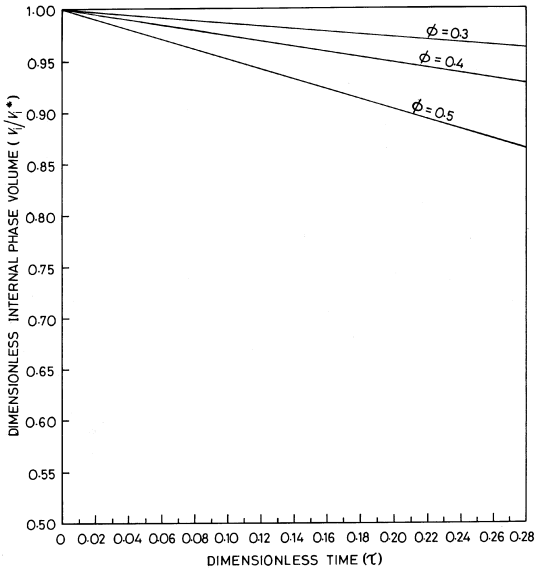

Figure 3. Variation of internal-phase volume due to leakage with regard to dimensionless time.

action front movement. The leakage coefficient Ψ was determined experimentally as discussed previously. The effect of emulsion leakage on concentration profile and reaction front movement for 3 different values of the internal-phase volume fraction (ϕ) is shown in Figs. 4 and 5. The parameters used to generate the curves in Figs. 4 and 5 were $C_0^* = 50$ mg/L; $E = 0.25$; $C_D = 261.235$; $C_S{}^{-0.798}$; $\theta_i = 5.2$; $\phi = 0.5$, 0.4, and 0.3. The figures indicate that extraction was lower and reaction front movement was faster due to leakage of the internal phase. The lower extraction can be attributed to extraction-efficiency loss due to internal-phase leakage. An increase in the internal-phase volume fraction was associated with a further reduction in extraction efficiency due to an increase in the leakage rate (Fig. 4). The internal droplets in the reacted core of the emulsion globules contain solute that was expelled from the internal phase due to leakage. Hence, the overall rate of extraction is the net rate between diffusion of solute into the emulsion drop and the leakage rate of the total solute from the internal phase to the external phase. During the early stage of extraction, when the concentration gradient of the solute is high and the solute diffusion path through the membrane is short, the rate of solute diffusion is much higher than the leakage rate so that the net transport is inward and the overall extraction increases. As time progresses, the diffusion rate decreases due to the lower solute concentration gradient and the higher diffusion path for the solute, and the leakage rate

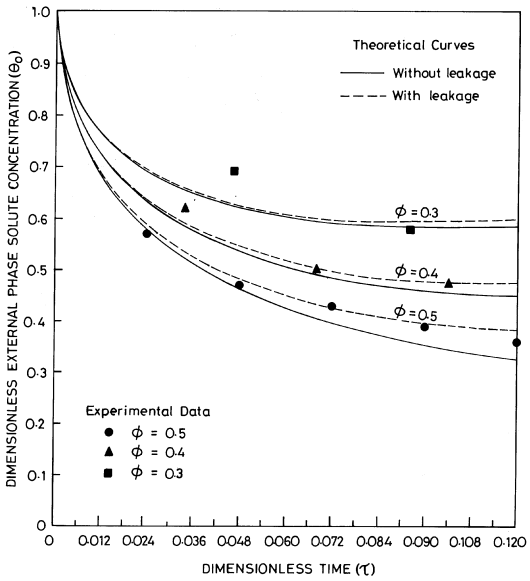

Figure 4. Effect of leakage on external-phase solute concentration profile for different values of volume fraction of internal phase.

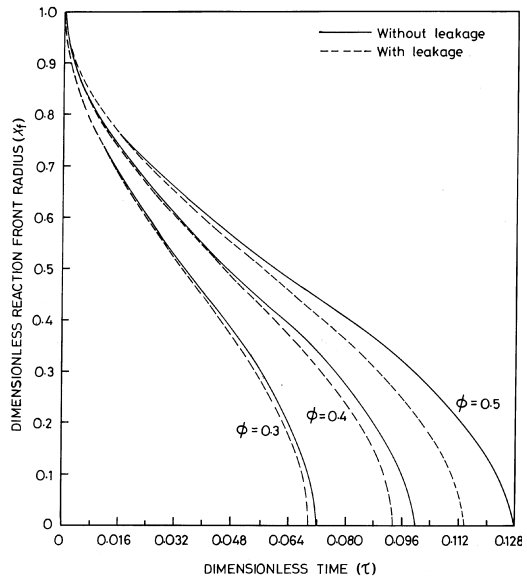

Figure 5. Effect of leakage on reaction front progress for different values of internal-phase volume fraction.

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increases as the internal-phase volume in the reacted core increases due to penetration of the reaction front toward the center of the globules. This continues until the leakage rate equals the diffusion rate. At that time, the overall extraction is maximum. After this, the leakage rate exceeds the permeation rate so that the net transport of the solute is outward as depicted in Fig 6. The parameters used to generate the curves in Fig. 6 were $C_0^* = 50$ mg/L; $E = 0.25$; $\phi = 0.5$; $C_D = 261.235$; $C_S{}^{-0.798}$; $\theta_i = 5.2$. Figure 6 also shows that as the value of the leakage coefficient Ψ is increased, the maximum extraction and the time of its occurrence both decreased. The higher the value of Ψ, the faster the leakage, so that the overall extraction is lower and the leakage rate exceeds the diffusion rate relatively quickly. Because the change in dimensionless internal phase volume (V_i/V_{i*}) with dimensionless time (τ) with an increase in ϕ, the quantity of solute leaking out to the external phase from the emulsion was higher for higher volume fractions of the internal phase. Therefore, the higher the volume fraction of the internal phase, the more significant the leakage effect will be on the overall extraction. This is in agreement with the results shown in Fig. 4. The movement of the reaction front is faster as the internal reagent is lost due to leakage, which further reduces the overall extraction rate because the diffusion path for the solute becomes longer.

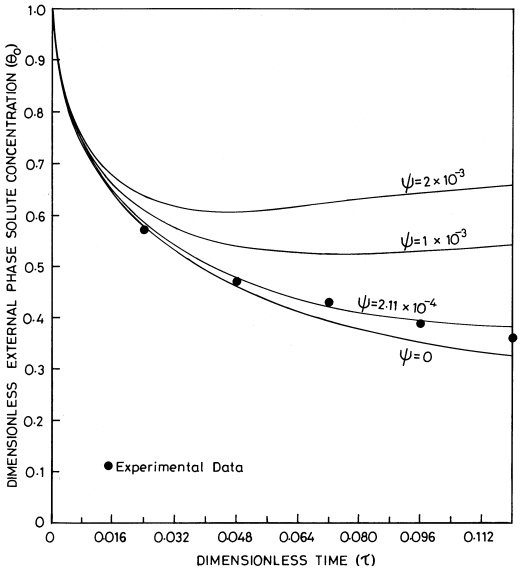

Figure 6. Effect of leakage coefficient on external-phase solute concentration at a constant value of the internal-phase volume fraction ($\phi = 0.5$).

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Effect of Leakage on Extraction for Different External-Phase pH Values

Figure 7 shows the effect of external-phase pH on the net solute extraction in the presence of internal-phase leakage. Studies were conducted for 2 different external-phase pH values (~5.5 and ~11.0). The values of the solute distribution coefficient between organic and aqueous phases (C_D) were determined experimentally as described earlier. The parameters used for computation were $C_0^* = 50$ mg/L; $E = 0.25$; $\theta_i = 5.2$; $\phi = 0.5$. Figure 7 shows that the effect of solute leakage on extraction decreased with an increase in external-phase pH. This may be attributed to the predominance of bivalent CrO_4^{2-} at high pH so that 1 mole of complex reacts with 2 moles of the internal reagent at the reaction front to release only 1 mole of solute as illustrated in Eq. (2). This results in a lower solute concentration in the internal phase in the region of exhausted emulsion globules ($R < r < R_f$). Therefore, for leakage of internal phase due to emulsion-globule rupture, the moles of solute released to the external phase will be much lower when values of external-phase pH are high. As a result, the leakage rate will be lower resulting in a smaller loss in extraction efficiency when the external phase pH is increased.

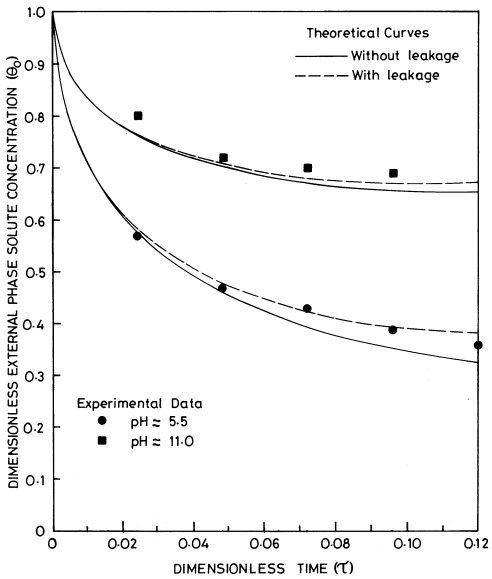

Figure 7. Effect of leakage on external-phase solute concentration profile for different values of external phase pH.

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Table 3. Absolute Deviation Between Experimental and Computed Values of External-Phase Solute Concentration

				Previous Model			Present Model		
Run	ϕ	Initial pH	τ	Absolute Deviation	Average Absolute Deviation	Maximum Absolute Deviation	Absolute Deviation	Average Absolute Deviation	Maximum Absolute Deviation
1	0.5	5.5	0.024	0.0089			0.0153		
			0.048	0.0077			0.0009		
			0.072	0.0350	0.0246	0.0374	0.0059	0.0070	0.0153
			0.096	0.0374			0.0053		
			0.120	0.0341			0.0075		
2	0.4	5.5	0.034	0.0363			0.0320		
			0.068	0.0090	0.0229	0.0363	0.0032	0.0118	0.0320
			0.102	0.0234			0.00033		
3	0.3	5.5	0.046	0.0656	0.0357	0.0656	0.0592	0.0368	0.0592
			0.092	0.0057			0.0143		
4	0.5	11.0	0.024	0.0363			0.0346		
			0.048	0.0161	0.0284	0.0363	0.0116	0.0211	0.0346
			0.072	0.0273			0.0191		
			0.096	0.0338			0.0192		

$C_0^* = 50$mg/L; $E = 0.25$; $C_i = 0.01$(N)

COMPARISON OF EXPERIMENTAL DATA WITH COMPUTED RESULTS

To test the validity of the present model, the computed results were compared with those of the previous model (29) as well as with experimental data. Table 3 shows the absolute deviation between experimental data and theoretical predictions of the past and present models for each experimental run. The absolute deviations are based on an initial dimensionless solute concentration (θ_0) of 1.0. Table 3 shows that the computed results of the present model are in agreement with experimental data for run nos. 1, 2, and 4. Although the average deviation between run no. 3 and the model data is slightly increased, the maximum deviation for the present model was reduced. The increase in average deviation in case of $\phi = 0.3$ may be the result of experimental error and the present model may be more reliable for prediction of solute transfer rate through a LSM membrane.

CONCLUSION

The stability of the membrane is an important criterion in liquid membrane extraction as lack of stability causes emulsion globule rupture and leakage of the

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internal reagent to the external phase, which results in a loss of extraction efficiency. This phenomenon was analyzed through an incorporation of leakage effects into the previously developed advancing reaction front model. The overall extraction rate reached a maximum value and then decreased. This result indicates that 2 processes are competing in solute transport: the diffusion of solute through the emulsion globules into the internal phase and the leakage of internal phase due to rupture of emulsion drops. The solute permeation rate decreases and the leakage rate increases with time so that after time, the leakage rate exceeds the solute permeation rate. As a result, the overall extraction decreases. Hence, an optimum extraction time exists when the leakage rate equals the permeation rate. The effect of internal-phase volume fraction was found to be significant to extraction. The fractional reduction in internal-phase volume due to leakage was found to increase with an increase in the internal-phase volume fraction. Hence, we concluded that an increase in the internal-phase volume fraction increases leakage. This conclusion can be explained as the result of the decrease in thickness of the membrane phase encapsulating the internal droplets.

The effect of leakage coefficient on the overall extraction was also studied. The maximum overall extraction and the optimum extraction time are functions of the leakage coefficient, and both decrease with increases in the leakage coefficient. As the leakage coefficient increases, the leakage rate of the solute from the reacted inner core to the external phase increases and the rate of solute diffusion from the external to the internal phase decreases. This is due to longer diffusion paths resulting from higher loss of internal reagent from the unreacted inner core caused by leakage. Therefore, the net rate of solute transport from the external to the internal phase decreases and the leakage rate surpasses the solute diffusion rate relatively early in the process, resulting in low maximum overall extraction as well as a low optimum extraction time.

The effect of external-phase pH on extraction in a model that accounts for leakage was also studied through comparisons of extraction results of 2 different external-phase pH values. At lower pH, leakage has a more detrimental effect to extraction. The predictions of the present model were in better agreement with the experimental data than were those derived from previous model in which leakage indicators were not included. These results thus point out the importance of accommodating the effects of internal-phase leakage due to emulsion rupture in the mathematical model for reliable predictions of mass-transfer rate.

NOMENCLATURE

C_D	distribution coefficient of the solute between membrane and external phase
C_i	concentration of internal reagent (g·moles/cc)
C_m	solute concentration in the membrane phase (g·moles/cc)

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C_0 solute concentration in the external phase (g·moles/cc)
C_0^* initial solute concentration in the external phase (g·moles/cc)
C_S equilibrium aqueous phase solute concentration (mg/L)
D_{eff} effective diffusivity of the solute as complex based on membrane-phase concentration (cm^2/s)
D_m diffusivity of the solute as complex in the membrane phase (cm^2/s)
d_{32} Sauter mean emulsion globule diameter (cm)
E $3V/V_0$ (dimensionless parameter)
J_L leakage rate of solute from the region of reacted emulsion globules (g·moles/sec)
m moles of internal reagent reacting with 1 mole of solute as complex at the reaction front
n number of emulsion globules
R_f reaction front radius (cm)
R_0 Sauter mean emulsion globule radius, $\sum n_j R_j^3 / \sum n_j R_j^2$ (cm)
r Radial position inside an emulsion globule
S $\Psi R_0^2 / D_{eff}$ (dimensionless parameter)
t time (seconds)
V total volume of the emulsion (cc)
V_0 external-phase volume (cc)
V_i volume of internal phase (cc)
V_i^* initial volume of internal phase (cc)
X r/R_0 (dimensionless parameter)
X_f R_f/R_0 = dimensionless reaction front radius

Greek Letters

Ψ leakage coefficient ($second^{-1}$)
ϕ initial volume fraction of internal aqueous phase in the emulsion
ϕ_t volume fraction of internal aqueous phase in the emulsion at any time t
θ_i dimensionless initial concentration of internal reagent = C_i/C_0^*
θ_m dimensionless membrane-phase solute concentration = C_m/C_0^*
θ_0 dimensionless external-phase solute concentration = C_0/C_0^*
τ $D_{eff}t/R_0^2$ (dimensionless time)

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