Analysis of the Effect of Internal Phase Leakage on Liquid Membrane Separations

A general physical model of a typical batch extraction system employing liquid surfactant membranes is developed. The model takes into account the continuous-phase resistance and the interfacial resistance along with permeation through a composite emulsion globule. It also quantifies the loss in extraction efficiencies by leakage of the encapsulated phase due to membrane breakage. The physical model is easily adapted to apply to the case of transport facilitation wherein the solute is reacted in the internal phase to yield products incapable of permeating through the membrane phase. Experimental data on o-chlorophenol extraction are satisfactorily correlated with the model.

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Introduction

Liquid surfactant membranes, first developed by Li (1968) in connection with hydrocarbon separation, have since shown tremendous promise in a wide variety of industrial separations. These systems consist of either a water-immiscible emulsion dispersed in water or an oil-immiscible emulsion dispered in oil. In general, the emulsion consists of an encapsulated phase emulsified in the "membrane" phase using surfactants to yield droplets of 1–10 μm dia. The emulsion is then dispersed in the continuous phase by agitation to yield globules of 0.1–2 mm dia. Extraction, usually at the external phase/membrane interface, and stripping at the encapsulated phase/membrane interface, occur simultaneously. At the end of an extraction run the emulsion is separated from the continuous phase and the encapsulated phase is recovered by braking the emulsion.

For hydrocarbon separation, Li (1968, 1971a,b) relied on their widely different solubilities in the aqueous phase. Since then, facilitation mechanisms have been proposed to enhance the effectiveness of liquid membrane separations in a variety of applications. Facilitation can be effected by one of two mechanisms (Matulevicius and Li, 1975; Ho et al., 1982). In one mechanism, called type I facilitation, the concentration gradient of the solute is maximized by reacting the solute in the receiving phase to yield products incapable of permeating through the membrane phase. For instance, phenol can be reacted with sodium hydroxide to yield sodium phenolate, which is insoluble in the oil membrane (Li and Shrier, 1972; Cahn and Li, 1974; Kitigawa et al., 1977; Teramoto et al., 1981, 1983b; Terry et al., 1982; Boyadzhiev et al., 1984). In the second mechanism, called type II facilitation, a carrier is incorporated in the membrane phase to augment the transfer rates. Solvent extraction of metal ions using ion-exchange reagents is an example of carrier-mediated transport (Hochhauser and Cussler, 1975; Strzelbicki and Charewicz, 1978a,b, 1980; Volkel et al., 1980; Cahn et al., 1981; Teramoto et al., 1983a; Wasan et al., 1984).

These and several other applications of liquid surfactant membrane have created an urgent need to develop a thorough understanding of these systems. Consequently, over the last decade or so several models have been developed to describe the transport processes in these systems. The models varied in the degree of sophistication in handling the permeation mechanism. The most sophisticated models have handled the unsteady state permeation through the composite emulsion globule quite correctly (Casamatta et al., 1978; Teramoto et al., 1981, 1983a,b; Ho et al., 1982; Kim et al., 1983; Bunge and Noble, 1984; Fales and Stroeve, 1984).

While considerable modeling effort was directed toward describing the permeation mechanism in a realistic manner, very little attention was paid to accounting for the loss of extraction efficiencies that often occurs in these systems due to the rupture of the membrane. Li and Shrier (1972), Boyadzhiev et al. (1977), Strzelbicki and Charcwicz (1978a,b), Volkel et al. (1980), Cahn et al. (1981), and Terry et al. (1982) have *all* noted that the recovery passes through a maximum beyond which the rate of solute leakage by membrane breakage exceeds its permeation rate. Indeed, the stability of the membrane was cited by Way et al. (1982) as one of the most serious obstacles in

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the successful application of liquid membranes to industrial separations. Boyadzhiev et al. (1977), Cahn et al. (1981), Terry et al. (1982), and Teramoto et al. (1983a) have incorporated leakage in the treatment of their data. However, only Teramoto and coworkers correctly described the permeation step. Their model was for carrier-mediated transport. Despite these studies, our understanding of the mechanisms of membrane rupture is extremely limited.

It is the purpose of this paper to develop a general model of batch extraction with liquid surfactant membranes that combines the realistic description of unsteady state permeation through a composite emulsion globule with a model for the leakage of the solute due to membrane rupture. The rate of leakage by membrane rupture is usually a function of the surfactant concentration and the agitation speed. Strong agitation increases the possibility of membrane rupture and consequent release of the captured solute. Thus, it is often necessary in emulsion liquid membrane extraction to employ only low to moderate agitation. As pointed out by Stroeve and Varanasi (1984) and Fales and Stroeve (1984), then the external phase mass transfer resistance may not be negligible. Thus, we have accounted for the continuous-phase resistance in our model. Furthermore, for the sake of generality, interfacial resistance is also included.

It is clear that no single model will be able to describe all the transport mechanisms utilized in the various applications of liquid membranes without significant modification. Specifically, carrier-mediated transport requires special considerations and in this paper we have excluded this particular application. The treatment can nevertheless be adapted to this end.

We shall first present the general model for physical transport of solute disregarding any chemical reaction effects. In this way we are able to highlight the importance of the various parameters in a more systematic and tractable manner. The model is then adapted to systems employing the type I facilitation mechanism. The model is shown to successfully correlate with experimental data on extraction of o-chlorophenol using liquid surfactant membranes with sodium hydroxide as the internal reagent.

Theoretical Analysis

In this section we develop a physical model of a typical batch emulsion liquid membrane system. The assumptions involved in the mathematical development are discussed below.

When agitation is employed to disperse the emulsion in the continuous phase, a nonuniform globule size distribution is invariably obtained. We nevertheless assume that the system is monodispersed with globules having a diameter equal to the Sauter mean diameter of the polydisperse system. Teramoto et al. (1983a,b) have shown that such a representation causes only a slight discrepancy at large times. We further assume that such monodispersed globules are formed instantaneously as stirring is begun and that no coalescence and redispersion of the globules occur.

The encapsulated droplets are much smaller (1–10 μm dia.) than the emulsion globules (0.1–2 mm dia.). Consequently, the droplet time constants are much smaller than those for the emulsion globule as a whole. Furthermore, the area of the encapsulated phase/membrane interface is much larger than the continuous phase/membrane interface. Thus, while the interfacial resistance may be important at the continuous phase/membrane interface, it is negligible at the encapsulated phase/membrane interface. Therefore, local equilibrium between the dispersed and the continuous phases of the emulsion can be assumed and we can describe the concentration field in the globule in terms of the average local composition; i.e., we can disregard the composite nature of the emulsion globule and treat it as a continuum (Ho, et al., 1982).

As surfactants are used to form the emulsion and are added in large enough amounts to form strong membranes, it is anticipated that internal circulation in the emulsion globule is minimal. Thus, permeation is described in terms of an effective diffusion coefficient.

The solute leakage from the encapsulated phase to the continuous phase due to membrane breakage is considered by assuming that at a given speed of agitation the instantaneous volumetric rate of leakage is proportional to the volume of the encapsulated phase. Unlike the case in the work of Boyadzhiev et al. (1977) and Terry et al. (1982), the constant of proportionality is assumed to be a time-dependent function. It is assumed that only moderate agitation is employed to ensure that leakage is moderately small, so that fractional volume changes of the encapsulated and continuous phases during an extraction run are small. In view of only moderate agitation being employed, continuous-phase mass transfer resistance is taken into account.

Mathematical description

The equation describing the permeation of the solute in an emulsion globule of the type shown in Figure 1 is

$$\frac{\partial C}{\partial t} = \frac{D_e}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C}{\partial r}\right), \quad o \le r \le R, t > o \tag{1}$$

were C is the solute concentration in the emulsion globule averaged over the membrane and the encapsulated phases; i.e.,

$$\begin{aligned} C &= (1-\phi)C_m + \phi C_i \\ &= (1-\phi+\phi/\alpha_2)C_m \end{aligned} \tag{2}$$

Here ϕ is the volume fraction of the encapsulated phase in the emulsion and α_2 is the equilibrium constant relating the solute concentration in the membrane and the internal phase by the condition

$$C_m = \alpha_2 C_i \tag{3}$$

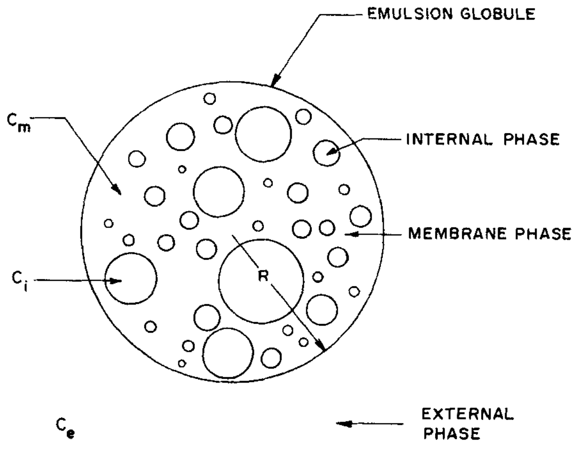

Figure 1. Emulsion liquid membrane system.

The initial condition is

$$C = C_m = C_i = 0 \quad \text{at } t = 0, r < R \tag{4}$$

Taking the interfacial resistance and the continuous-phase mass transfer resistance into account, the boundary condition at the surface of the emulsion globule can be written as

$$D_e \frac{\partial C}{\partial r}\bigg|_{r=R} = k_I\left[C_{ei} - \frac{C_m(R,t)}{\alpha_1}\right] \tag{5}$$

$$= k_e(C_e - C_{ei}) \tag{6}$$

where α_1 is the equilibrium partition coefficient $C_m^{\mathrm{HA}}/C_o^{\mathrm{HA}}|_{eq.}$ between the membrane and the aqueous phase; where k_I is the rate constant for transfer across the interface or $1/k_I$ is the interfacial resistance; and where k_e is the mass transfer coefficient in the external phase and C_{ei} is the concentration on the external side of the membrane/external phase interface. Using Eq. 2, Eq. 5 can be written as

$$D_e \frac{\partial C}{\partial r}\bigg|_{r=R} = k_I\left[C_{ei} - \frac{C(R,t)}{\alpha_1(1 - \phi + \phi/\alpha_2)}\right] \tag{7}$$

Equations 6 and 7 can be combined to yield

$$D_e \frac{\partial C}{\partial r}\bigg|_{r=R} = k\left[C_e - \frac{C(R,t)}{\alpha_1(1 - \phi + \phi/\alpha_2)}\right] \tag{8}$$

where

$$k = \left(\frac{1}{k_I} + \frac{1}{k_e}\right)^{-1} \tag{9}$$

is the overall mass transfer coefficient, or $1/k$ represents the sum of the external-phase mass transfer resistance and the interfacial resistance.

In order to write the solute conservation equation for the external phase, leakage of the solute by membrane breakage must be considered. Due to the leakage of the encapsulated phase, not only the solute conservation equation for the external phase is affected, but V_i, the internal phase volume (and consequently ϕ, its volume fraction), as well as V_e, the volume of the external phase, also change with time. As mentioned above, it is assumed that the leakage is small enough so that changes in V_i and V_e can be neglected. The solute conservation equation for the external phase can then be written as

$$V_e \frac{dC_e}{dt} = -\frac{3}{R}(V_i + V_m)\, D_e \frac{\partial C}{\partial r}\bigg|_{r=R} + J_\psi \tag{10}$$

where J_ψ is the flux of the solute to the external phase due to leakage of the encapsulated phase. At a given stirring speed the volumetric rate of leakage is proportional to the volume of the internal phase. Then, the leakage of the solute is assigned to be given by

$$J_\psi = \psi(t) V_i C_i \tag{11}$$

where $\psi(t)$ is the leakage coefficient which, unlike in the work of Boyadzhiev et al. (1977) and Terry et al. (1982), is assumed here to be a function of time; and $\overline{C}_i$ is the solute concentration in the internal phase averaged over the emulsion globule. Note that following these authors we have used the average concentration $\overline{C}_i$ instead of $C_i(r = R)$ used by Teramoto et al. (1983a).

It is necessary to obtain an expression for C_i before we proceed. From an overall mass balance we have

$$V_e(C_e^o - C_e) = V_m C_m + V_i C_i \tag{12}$$

where C_e^o is the initial concentration of the solute in the external phase and $\overline{C}_m$ is its concentration in the membrane phase averaged over the emulsion globule. Usually in liquid membrane separations, $\alpha_2 \ll 1$ and therefore $C_m \ll C_i$ everywhere in the emulsion globule, which implies $\overline{C}_m \ll \overline{C}_i$. Equation 12 can then be simplified to yield

$$V_e(C_e^o - C_e) = V_i \overline{C}_i \tag{13}$$

From Eqs. 10, 11, and 13 we obtain

$$\frac{dC_e}{dt} - \psi(C_e^o - C_e) = -\frac{3}{R}\frac{(V_i + V_m)}{V_e} D_e \frac{\partial C}{\partial r}\bigg|_{r=R} \tag{14}$$

the initial condition being

$$C_e = C_e^o \quad \text{at } t = 0 \tag{15}$$

Equations 1, 4, 8, 14, and 15 define the system of equations that must be solved. It is convenient to employ the standard transformation

$$y = rC \tag{16}$$

to solve these equations. Before we discuss the method of solution of the resulting equations, it is convenient to cast them in dimensionless form. To this end we define the following dimensionless variables:

$$C^* = \frac{C}{C_e^o};\quad C_e^* = \frac{C_e}{C_e^o};\quad \theta = \frac{D_e t}{R^2};\quad \xi = \frac{r}{R};$$
$$y^* = \frac{y}{RC_e^o};\quad \phi_e = \frac{V_i + V_m}{V_i + V_m + V_e};\quad Bi = \frac{Rk}{D_e};$$
$$\alpha = \mathrm{A}_1(1 - \phi + \phi/\alpha_2);\quad \psi^* = \frac{R^2\psi}{D_e} \tag{17}$$

It should be noted that the parameters α and ϕ_e together determine the "equilibrium" extraction in the absence of leakage. It can be shown that

$$\frac{C_e^{eq}}{C_e^o} = \frac{1}{\left(1 + \dfrac{\alpha\phi_e}{1 - \phi_e}\right)}$$

In the presence of leakage, of course, one would expect zero extraction at long times since all the encapsulated phase would have spilled into the external phase.

After the transformation as per Eq. 16 and nondimensionalization using Eq. 17, Eqs. 1, 8, 14, and 15 become

$$\frac{\partial y^*}{\partial \theta} = \frac{\partial^2 y^*}{\partial \xi^2}, \quad 0 \le \xi \le 1, \quad \theta > 0 \tag{18}$$

$$y^* = 0 \quad \text{at } \theta = 0, \quad \xi < 1 \tag{19}$$

$$\left.\frac{\partial y^*}{\partial \xi}\right|_{\xi=1} - y^*(1,\theta) = Bi\left[C_e^* - \frac{y^*(1,\theta)}{\alpha}\right] \tag{20}$$

$$\frac{dC_e^*}{d\theta} - \psi^*(1 - C_e^*) = -3\left(\frac{\phi_e}{1-\phi_e}\right)\left[\left.\frac{\partial y^*}{\partial \xi}\right|_{\xi=1} - y^*(1,\theta)\right] \tag{21}$$

and

$$C_e^* = 1 \quad \text{at } \theta = 0 \tag{22}$$

respectively. Furthermore, since C is finite, we have

$$y^* = 0 \quad \text{at } \xi = 0, \quad t \ge 0 \tag{23}$$

The above system of equations is linear. However, in anticipation of nonlinear terms entering into the formulation when we apply the model to systems employing the type I facilitation mechanism, we have employed a numerical procedure for the solution of these equations. We first write Eq. 21 as

$$\frac{dC_e^*}{d\theta} + \psi^*(\theta)C_e^* = \psi^*(\theta) - 3\left(\frac{\phi_e}{1-\phi_e}\right)\left[\left.\frac{\partial y^*}{\partial \xi}\right|_{\xi=1} - y^*(1,\theta)\right]$$

or

$$\frac{d}{d\theta}(C_e^*\chi) = \chi\left[\psi^*(\theta) - 3\left(\frac{\phi_e}{1-\phi_e}\right)\left(\left.\frac{\partial y^*}{\partial \xi}\right|_{\xi=1} - y^*(1,\theta)\right)\right]$$

or

$$C_e^*(\theta + \Delta\theta)\chi(\theta + \Delta\theta) - C_e^*(\theta)\chi(\theta) = \int_\theta^{\theta+\Delta\theta} \chi(\theta) \cdot \left[\psi^*(\theta) - 3\left(\frac{\phi_e}{1-\phi_e}\right)\left(\left.\frac{\partial y^*}{\partial \xi}\right|_{\xi=1} - y^*(1,\theta)\right)\right] d\theta \tag{24}$$

Here

$$\chi(\theta) = \exp\left[\int \psi^*(\theta)\, d\theta\right] \tag{25}$$

is the integrating factor. The integral on the righthand side of Eq. 24 was evaluated using the trapezoidal rule and the partial derivative was evaluated using the central difference formula. A Crank-Nicholson scheme was used to put Eq. 18 in finite-difference form and a central difference formula was used to render Eq. 20 in finite-difference form. The resulting set of equations can be used to obtain, by matrix inversion, a solution progressing in time from the initial conditions represented by Eqs. 19 and 22. The matrix inversion can be achieved using the Thomas algorithm (Finlayson, 1981) after the matrix is rendered tridiagonal.

Parametric Study

Computer calculations were performed to highlight the effect of the various parameters of the physical model. We summarize some of these results below, beginning with the limiting case of no leakage.

Figure 2 shows the effect of the Biot number B_i on extraction in the absence of leakage. Recall that the Biot number is the ratio of diffusional resistance to the sum of the continuous-phase mass transfer resistance and the interfacial resistance. A Biot number greater than 10^5 signifies the limiting diffusion-controlled case for this set of parameters ($\alpha = 250$, $\phi_e = 0.16$, and $\psi^* = 0$). As the Biot number is decreased or the external phase resistance and/or the interfacial resistance is increased at constant diffusional resistance, the extraction rate is decreased as expected.

It is interesting to examine the effect of globule radius on the time for a given percent extraction, for the limiting cases of Biot number tending to zero and infinity. In the diffusion-controlled case ($Bi \longrightarrow \infty$ or $>10^5$ in this case), increasing R increases the diffusional resistance proportionally; furthermore, the interfacial area decreases as $1/R$. Consequently, the time for a given extent of extraction increases as R^2. This is evident from the fact that a unique curve of C_e^* vs. θ is obtained in the diffusion-controlled case so that for a given extent of extraction, the time t increases as R^2 since θ is the same. On the other hand, in the limiting case when the external phase resistance and/or the interfacial resistance is controlling ($B_i \longleftarrow 0$), increasing R decreases the interfacial area as $1/R$ again, but the controlling resistance is not affected. As a result, the time for a given extent of extraction increases linearly with R. For the set of parameters

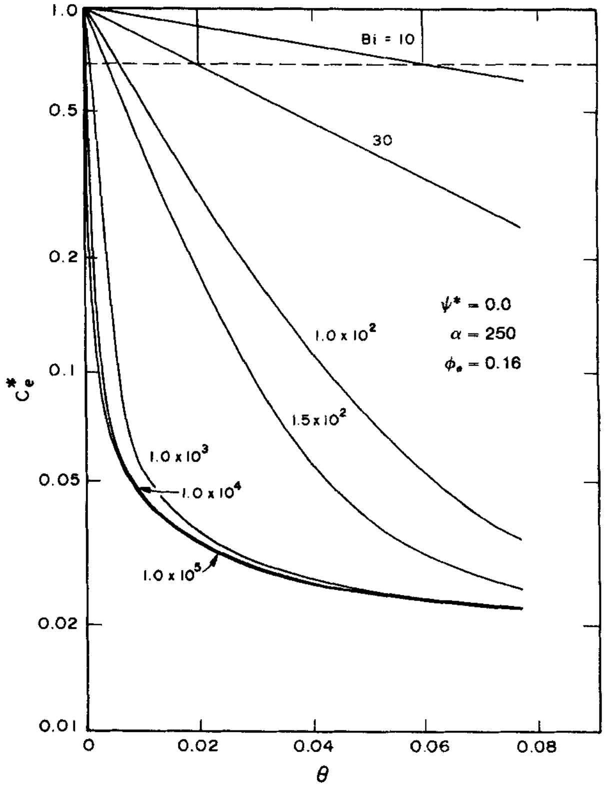

Figure 2. Effect of Biot number on extraction in the absence of leakage.

chosen here ($\alpha = 250$, $\phi_e = 0.16$, $\psi^* = 0$) this is seen to be the case $B_i < 30$. The broken line in Figure 2 is a line for a constant extent of extraction. It is seen that it intersects the $B_i = 10$ and 30 curves at $\theta = 0.06$ and 0.02, respectively. If the change in Biot number is due to change in the radius R, then a threefold increase in R from $Bi = 10$ to $Bi = 30$ reduces θ from 0.06 to 0.02 (threefold) and hence increases t ($= \theta R^2/D$) threefold. Thus, for $Bi < 30$, the time for a given extent of extraction varies linearly with R, implying that for $Bi < 30$, diffusional resistance is negligible compared to the external phase resistance and/or the interfacial resistance.

In the intermediate case, for $30 < Bi < 10^5$, diffusional as well as external phase resistance and/or interfacial resistance is important, and the time for a given extent of extraction changes as R^a where a lies between 1 and 2.

The effect of leakage on extraction, which indeed is the focus of this paper, is shown in Figure 3 for the case of constant leakage coefficient. It is seen that in the presence of leakage the extraction efficiency passes through a maximum. Initially, the driving force for permeation is high and the concentration of the solute in the external phase decreases with time. The driving force continuously decreases as extraction proceeds and at the time the extraction is maximum, or C_e^* is minimum, the rate of solute transport from the external phase to the encapsulated phase equals its rate of leakage. After this time the net transport is outward. The maximum value of extraction efficiency, or the minimum value of C_e^*, and the time at which it occurs are both functions of the leakage coefficient, at constant transport resistances—as the leakage coefficient increases, the minimum C_e^* increases and the time of its occurrence decreases.

Finally, in Figure 4 we show the effect of the Biot number Bi on extraction in the presence of leakage for a constant leakage coefficient. At constant diffusional resistance, decreasing the Biot number increases the total resistance to solute transport from the external phase to the encapsulated phase. Thus, as the Biot number is decreased, the extraction rate decreases. Also, the minimum value of C_e^* and the time of the minimum are both seen to increase with decreasing Biot number. As the Biot number decreases, the inward solute flux decreases, and thus the leakage flux of the solute can equal the inward flux at higher C_e^* (or lower $\overline{C}_i$, see Eqs. 11 and 13). Thus, the minimum C_e^* increases. Furthermore, the overall time-scale of the process is increased due to the lower transport rates, which explains why the time of maximum extraction or minimum C_e^* increases as the Biot number is increased.

Type I Facilitation

As discussed in the beginning of this paper, in type I facilitation the concentration gradient of the solute is maximized by reacting the solute in the receiving phase to yield products that are incapable of permeating through the membrane phase. The reaction is by nature reversible and is forced forward by using the reagent in a large excess. The foregoing physical model is applicable to these systems with a minor modification. For instance, the leakage of the solute from the encapsulated phase to the continuous phase is accompanied by the leakage of the internal reagent, which converts some of the solute in the external phase to the impermeable form. Before we discuss the necessary modifications we shall briefly review some of the modeling

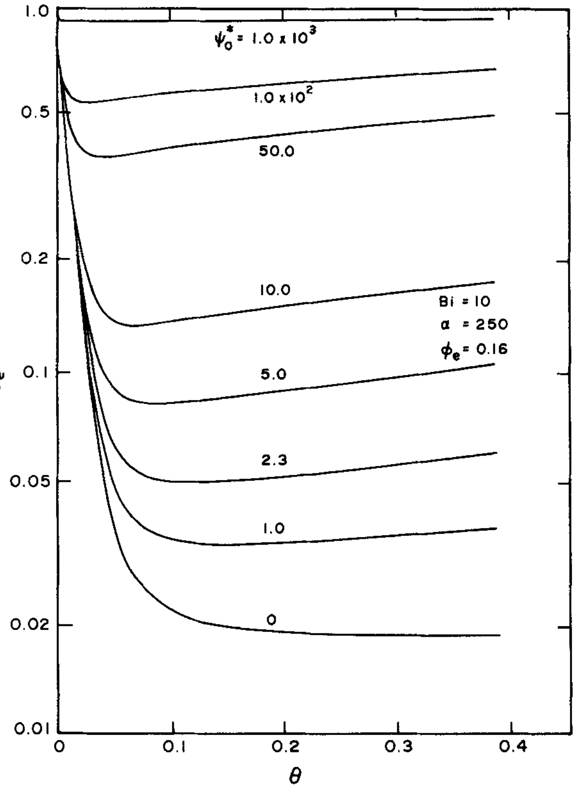

Figure 3. Effect of leakage on extraction-constant leakage coefficient.

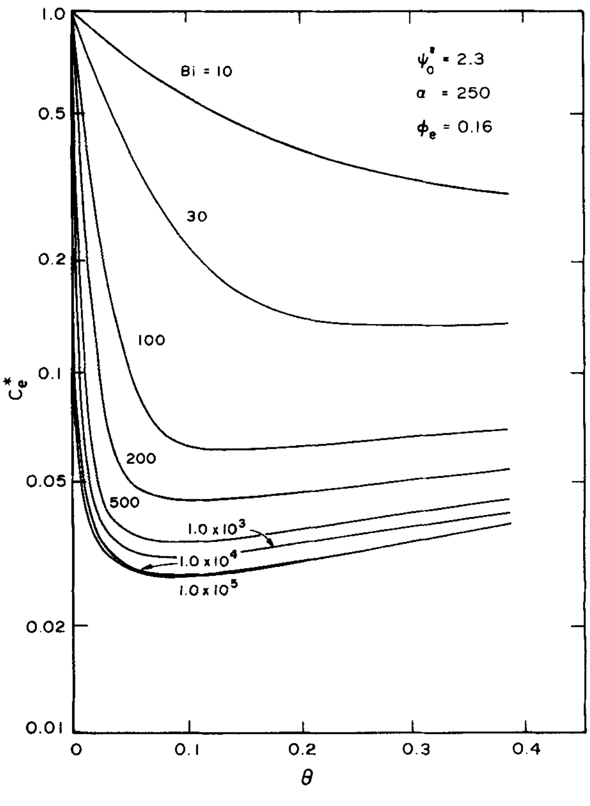

Figure 4. Effect of Biot number of extraction in the presence of leakage.

attempts of previous investigators, beginning with the work of Ho et al. (1982); work prior to that is reviewed therein.

Ho et al. (1982) considered the reaction of the solute with the internal reagent to be irreversible and instantaneous. They developed a diffusion-controlled advancing front model for type I facilitation. Kim et al. (1983) included diffusion through a thin membrane film devoid of the internal phase droplets as an additional resistance, while Stroeve and Varanasi (1984) and Fales and Stroeve (1984) extended the model of Ho et al. by including the continuous-phase resistance. Teramoto et al. (1981, 1983b) and Bunge and Noble (1984) considered correctly that the reaction between the solute and the internal reagent is reversible. Bunge and Noble showed that if the internal reagent is in excess, as is usually the case, the advancing front models overpredict transport rates due to the assumption of reaction irreversibility. Furthermore, Bunge and Noble (1984) predict discontinuous solute concentration profiles in the reacted and the unreacted zone in the emulsion globules at large times. Also, as pointed out by Teramoto et al. (1983b) the equilibrium extraction efficiencies become more than 100%.

None of the above models takes into account the leakage of the encapsulated phase. Only Terry et al. (1982) have considered leakage in connection with phenol extraction by type I facilitation, but they assumed pseudosteady transport and irreversible reaction. We now modify the foregoing physical model for application to a system involving type I facilitation. Clearly, the unsteady transport through a composite emulsion globule and reversible reaction implicit in the model more closely represent the actual situation.

Extraction of phenols

Phenol extraction is an example of type I facilitation and the following discussion applies to all such systems with minor modifications. The system chemistry of phenol extraction with liquid surfactant membranes is shown in Figure 5. Usually in these systems the internal reagent, which is NaOH, is used in very large excess. Thus, phenol can be assumed to be completely dissociated in the internal phase, and the equilibrium constant now defined as

$$\alpha_2 = \frac{C_m^{\mathrm{HA}}}{C_i^{\mathrm{A}^-}}$$

becomes

$$\alpha_2 = \frac{C_m^{\mathrm{HA}}}{C_i^{\mathrm{A}^-}} = \frac{C_m^{\mathrm{HA}}}{C_i^{\mathrm{HA}}} \frac{K_w}{K_a C_i^{\mathrm{OH}^-}} \tag{32}$$

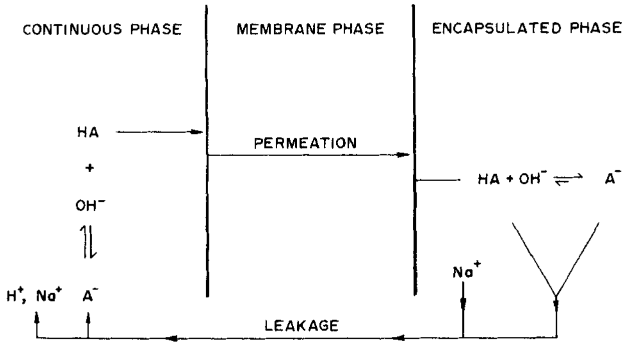

Figure 5. System chemistry of phenol extraction with liquid membrane.

where K_w is the dissociation constant for water and

$$K_a = \frac{C_i^{\mathrm{A}^-} C_i^{\mathrm{H}^+}}{C_i^{\mathrm{HA}}} = \frac{C_e^{\mathrm{A}^-} C_e^{\mathrm{H}^+}}{C_e^{\mathrm{HA}}} \tag{33}$$

is the dissociation constant of phenol in the aqueous phase.

It should be emphasized that although the internal reagent is in large excess, one cannot assume that its consumption locally can be neglected. Indeed, unless $K_a C_e^{\mathrm{HA}} / K_W \ll 1$, consumption of the reagent will occur in the peripheral region at least for a short time at the beginning of the extraction run. At large times the internal reagent is restored in the peripheral region of the emulsion globule by reversal of the reaction. This occurs at the expense of the internal reagent in the core of the droplet. Overall, however, the consumption of the reagent is negligible. In other words, α_2 varies from point to point within the droplet and it is also a function of time. It has the highest value in the peripheral region and decreases monotonically radially inward. Also, it decreases continuously with time until finally it reaches the same limiting value throughout the globule. It must be pointed out that during the extraction experiments cited here the criterion $K_a C_e / K_w < 1$ is met in a very short time (<1 min) and thus α_2 attains the limiting value then. We assume that the variation of α_2 at short times does not affect the extraction results at long times and proceed by treating α_2 to be a constant throughout the emulsion globule at all times. This constant value of α_2 is the limiting value of α_2:

$$\alpha_2 = \frac{\alpha_1 K_w}{K_a C_i^o} \tag{34}$$

Here, C_i^o is the initial concentration of the reagent NaOh in the internal phase and

$$\alpha_1 = \frac{C_m^{\mathrm{HA}}}{C_e^{\mathrm{HA}}} = \frac{C_m^{\mathrm{HA}}}{C_i^{\mathrm{HA}}} \tag{35}$$

is the partition coefficient of undissociated phenol between the oil and aqueous phase.

Before we proceed to apply the model to phenol extraction, we must recognize that in the external phase, phenol exists in both dissociated and undissociated forms in equilibrium, as per Eq. 33. As leakage of the internal phase occurs, OH^- ions are dumped into the external phase along with the phenolate ion A^- and Na^+. As a result of the leakage of OH^- the equilibrium of phenol and phenolate ions shifts towards phenolate ions, these ions being impermeable through the membrane phase. Thus, the leakage affects the extraction of phenols in more than one way. In order to include these considerations we write the total concentration of phenol in the external phase as

$$T = C_e^{\mathrm{HA}} + C_e^{\mathrm{A}^-} \tag{36}$$

The solute conservation equation in the external phase must then be modified to read

$$\frac{dT}{dt} - \psi(T^o - T) = -\frac{3}{R}\left(\frac{V_i + V_m}{V_e}\right) D_e \left.\frac{\partial c}{\partial r}\right|_{r=R}$$

and using Eqs. 35 and 36

$$\frac{d}{dt}\left[C_e^{\mathrm{HA}}\left(1 + \frac{K_a}{C_e^{\mathrm{H^+}}}\right)\right] - \psi\left[T^o - C_e^{\mathrm{HA}}\left(1 + \frac{K_a}{C_e^{\mathrm{H^+}}}\right)\right] = -\frac{3}{R}\left(\frac{V_i + V_m}{V_e}\right) D_e \frac{\partial c}{\partial r}\bigg|_{r=R} \qquad (37)$$

Since $C_e^{\mathrm{H^+}}$ is an unknown we need one additional equation. This is obtained in the form of $\mathrm{Na^+}$ balance:

$$V_e \frac{dC_e^{\mathrm{Na^+}}}{dt} = V_i \psi(t) C_i^{\mathrm{Na^+}} \qquad (38)$$

i.e., the rate of change of $\mathrm{Na^+}$ concentration in the external phase equals its rate of leakage. The charge balance in both internal and external phases dictates that

$$C_e^{\mathrm{Na^+}} = C_e^{\mathrm{OH^-}} + C_e^{\mathrm{A^-}} - C_e^{\mathrm{H^+}} \qquad (39)$$

and

$$C_i^{\mathrm{Na^+}} = C_i^o \qquad (40)$$

Using Eqs. 35, 39, and 40, Eq. 38 may be rewritten as

$$V_e \frac{d}{dt}\left(C_e^{\mathrm{OH^-}} + \frac{K_a C_e^{\mathrm{HA}}}{C_e^{\mathrm{H^+}}} - C_e^{\mathrm{H^+}}\right) = V_i \psi(t) C_i^o \qquad (41)$$

$C_e^{\mathrm{H^+}}$ and $C_e^{\mathrm{OH^-}}$ are, of course, related through K_w, the dissociation constant of water.

We can now identify C_i with $C_i^{\mathrm{A^-}}$, C_m with C_m^{HA}, C_e with C_e^{HA} and treat α_2 as constant as per Eq. 33. We are then able to apply the foregoing model to phenol extraction. We only have to use Eq. 37 in place of Eq. 14 for solute conservation in the external phase, and solve the set of equations simultaneously with Eq. 41. The system is now nonlinear, but can readily be solved using the numerical scheme discused earlier.

Experiments on o-chlorophenol extraction

Kurzeja (1985) has conducted an experimental investigation of o-chlorophenol extraction in our laboratory using liquid surfactant membranes. The equilibrium partition coefficient of o-chlorophenol between the aqueous and organic phase, α_1, was determined from separate experiments. Total concentration of o-chlorophenol (in both dissociated and undissociated forms) in the external phase and the pH of the external phase were measured as functions of time during the liquid membrane extraction experiments. The run was begun by adding the external phase containing phenol to the reactor. The emulsion—internal phase emulsified in the membrane phase—was prepared separately and added to the reactor. Agitation was begun immediately and time zero was marked. Additional details of the experimental set-up and procedure were discussed elsewhere (Kurzeja, 1985). The operating conditions for the extraction runs used here for comparison with the model are given in Table 1.

Estimation of model parameters

Some of the model parameters must be estimated in order to apply the model to experimental data. The equilibrium constant α_2 can easily be calculated from the measured partition coefficient α_1 using Eq. 33. The dissociation constants for o-chlorophenol and water at 25°C were obtained from Weast (1978). The effective diffusivity, D_e, was estimated by the method discussed by Ho et al. (1982) using α_2 as the partition coefficient. It is necessary to know the diffusivities of o-chlorophenol in the membrane phase and phenolate in the internal aqueous phase for this purpose. These were estimated from the Wilke-Chang

Table 1. Experimental Conditions for o-Chlorophenol Extraction

	Run 1	Run 2	Run 3
Type of separation	Batch	Batch	Batch
Agitation speed, rpm	150	150	150
Emulsion globule radius, R, mm	0.208	0.254	0.306
Internal droplet size, μm	<1	<1	<1
External Aqueous Phase			
o-Chlorophenol conc., C_o, ppm	500	500	500
Initial pH	5.7	5.4	5.8
Volume, V_e, cm^3	2,000	2,000	2,000
Membrane Phase (Oil:LOPS*)			
Surfactant: ECA-4360**			
Concentration, wt. %	1	4	6
Volume, V_m, cm^3	100	100	100
Viscosity, cp	2.0	2.37	2.57
Equilib. constant α_1 for undissociated o-chlorophenol between aqueous and membrane phases	0.9	0.9	0.9
Internal Aqueous Phase			
NaOH conc., c_i^o, mol/dm^3	2.5	2.5	2.5
Volume, V_i, cm	100	100	100
Viscosity, cp	1.0	1.0	1.0

*LOPS: low odor paraffin solvent, from Exxon
**ECA-4360: nonionic polyamine, from Exxon

correlation using the measured values of viscosities of the membrane and internal phases reported by Kurzeja (1985). The continuous-phase mass transfer coefficient was estimated from the knowledge of the dimensions of the agitated vessel by using the correlation of Boon-Long et al. (1978) for liquid-solid mass transfer in agitated systems. The emulsion globule may be considered as a solid sphere since it is assumed that internal circulation is absent. The interfacial resistance for the transport of o-chlorophenol across the external phase/membrane interface is assumed negligible. Table 2 summarizes the estimated values of the various parameters.

Correlation of model with o-chlorophenol extraction experiments

The only unknown parameter in the model is the leakage coefficient $\psi(t)$. Preliminary computations indicated that $\psi(t)$ = constant cannot adequately describe the data. Thus, $\psi(t) = \psi_1 \cdot t$, where ψ_1 is a time-independent constant, was used. The correlation of the model with experimental extraction data lies in obtaining the value of ψ_1 that best fits the experimental data. Figure 6 shows the comparison of the model with experimental extraction data for the three different surfactant concentrations in the membrane phase. Note that percent extraction is defined here as $[(T_o - T)/T_o] \times 100$, where T is given by Eq. 36 and T_o is its initial value. The best fit values of ψ_1 are $9.0 \times 10^{-9}\ s^{-2}$ for 1% surfactant, $3.25 \times 10^{-9}\ s^{-2}$ for 4% surfactant, and $3.0 \times 10^{-10}\ s^{-2}$ for 6% surfactant. As expected, the leakage rate decreases with increasing surfactant concentration.

A further test of adequacy of the model in describing o-chlorophenol extraction can be made by comparison of the model predictions with experimental pH vs. time data. Figure 7 shows the comparison of model predictions using the above best fit value of ψ_1 with experimental pH vs. time data for the system containing 1% surfactant. It is seen that there is some discrepancy as noted at the other two surfactant concentrations. We do not believe that the discrepancy could be due to the simplifying assumption of constancy of α_2. Rather, it may be due to the following reasons:

1. The internal circulation may not be completely eliminated so that the transport rates are enhanced, first due to convective diffusion in the emulsion globule, and second since the emulsion globule can no longer be considered to be a solid sphere in estimation of the continuous-phase mass transfer coefficient. As transport rates are increased, ψ_1 would have to be increased to fit the extraction data. Thus, the leakage rate will be higher and the model predictions would more closely match the experimental pH data.

Table 2. Estimated Parameters for o-Chlorophenol Extraction

	Run 1	Run 2	Run 3
Equilib. constant α_2, Eq. 33	1.015×10^{-6}	1.015×10^{-6}	1.015×10^{-6}
Diffusivity in membrane phase, cm^2/s	8.23×10^{-6}	7.05×10^{-6}	6.56×10^{-6}
Diffusivity in internal phase, cm^2/s	1.35×10^{-5}	1.35×10^{-5}	1.35×10^{-5}
Effective diffusivity, D_e, cm^2/s	2.47×10^{-10}	2.13×10^{-10}	1.99×10^{-10}
External phase mass transfer coefficient, k_e, cm/s	9×10^{-3}	8.7×10^{-3}	8.4×10^{-3}

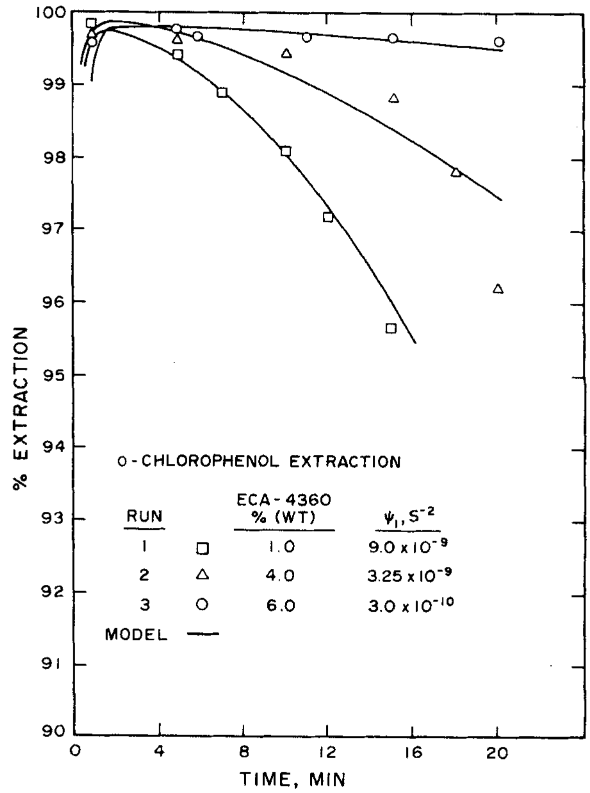

Figure 6. Comparison of model with o-chlorophenol extraction data.

2. Since the pH probe in the reactor serves as an obstacle, some breakage of the emulsion globule may occur at the probe. Since the caustic that leaks out is not instantaneously mixed throughout the reactor, the recorded pH may be higher than the actual value.

Of the earlier investigators who had examined the phenol extraction, only Terry et al. (1982) examined the effect of leakage in a quantitative manner. However, they used the simplified (pseudosteady) case of the advancing front model of Ho et al. (1982), which considers the reaction between phenol and hydroxide to be irreversible. Furthermore, they assumed that $Bi \rightarrow \infty$ and fitted the leakage parameter (assumed independent of time) and did not ascertain the adequacy of the model by comparing the pH data. We have demonstrated a reasonably satisfactory agreement of our model with the experimental data by considering both extraction and pH data.

At this stage, it is worth pondering a possible leakage mechanism, and especially to ask whether a time-dependent leakage coefficient is realistic. With the concentrated aqueous phase as the internal phase and a dilute o-chlorophenol solution as the external phase, an osmotic pressure gradient exists in our system. Under this condition, water would be transported from the external phase to the internal phase. (Matsumoto et al., 1980). As the water is pumped in, V_i will increase relative to V_m, making the system unstable and promoting leakage (Florence and Whitehill, 1982; Way et al., 1982). In this mechanism the leakage rate would increase with time as more and more water is

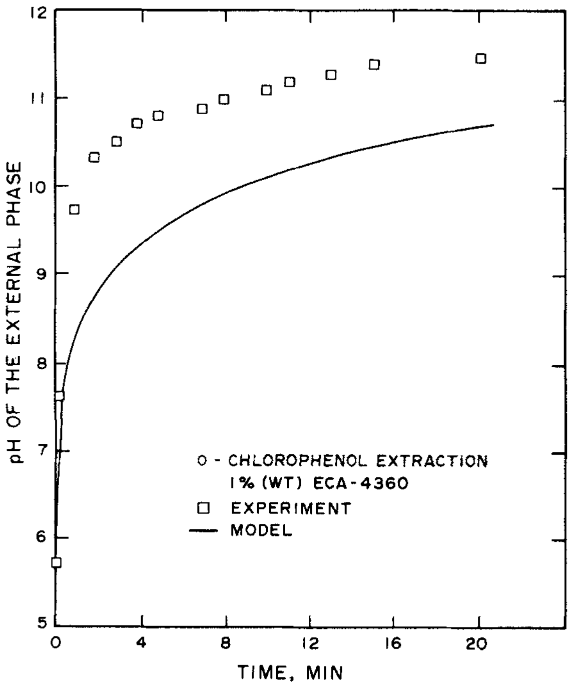

Figure 7. Comparison of model prediction with experimental pH vs. time data.

transported inward. Additional work must be done before one can conclude that this is indeed the operative leakage mechanism.

It must be emphasized that the parameters of the model, with the exception of the leakage coefficient, can be estimated or measured in independent experiments. The Sauter mean diameter must be measured during the extraction run and the data obtained can be used to determine the best fit value of the leakage coefficient. Thus, the model can be used to study quantitatively the effect of various parameters, such as interfacial tension and rheology as well as stirring speeds, on the rate of leakage from *in situ* measurements of a parameter such as the pH during an extraction run. It is hoped that this would provide a better understanding of the mechanism of breakage.

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Notation

Bi = Biot number, Eq. 17
C = solute concentration in emulsion globule, mol/cm^3
C_e = solute concentration in external phase, mol/cm^3
C_{ei} = solute concentration at external phase/membrane phase interface, mol/cm^3
C_i = solute concentration in internal phase, mol/cm^3
$\bar{C}_i$ = average solute concentration in internal phase, mol/cm^3
C_m = solute concentration in membrane phase, mol/cm^3
$\bar{C}_m$ = average solute concentration in membrane phase, mol/cm^3
D_e = effective diffusivity, cm^2/s
J_ψ = solute flux due to membrane leakage, mol/s
k = overall mass transfer coefficient, cm/s
K_a = dissociation constant of phenol, mol/cm^3
k_e = external phase mass transfer coefficient, cm/s
k_l = rate constant for transfer across interface, cm/s
K_W = dissociation constant for water, mol^2/cm^6
R = radius of emulsion globule, cm
r = radial coordinate, cm
t = time, s
T = total concentration of phenol and phenolate in external phase, mol/cm^3
V_e = volume of external phase, cm^3
V_i = volume of internal phase, cm^3
V_m = volume of membrane phase, cm^3
y = parameter, Eq. 16, mol/cm^2

Greek letters

α = constant, Eq. 17
α_1 = equilibrium constant for solute between external and membrane phases
α_2 = equilibrium constant for solute between internal and membrane phases
θ = dimensionless time, Eq. 17
ξ = dimensionless radial coordinate, Eq. 17
ϕ = volume fraction of internal phase in emulsion
ϕ_e = volume fraction, Eq. 17
χ = integration factor, Eq. 25
ψ = leakage coefficient, s^{-1}
ψ_o = leakage constant, s^{-1}
ψ_1 = leakage constant, s^{-2}

Superscripts

A^- = phenolate ion
eq = equilibrium value
H^+ = hydronium ion
HA = undissociated phenol
Na^+ = sodium ion
OH^- = hydroxyl ion
O = initial value
$*$ = dimensionless quantity

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