Spandau, H., and F. Klanberg, *Z. Anorg. Chem.*, **295**, 309 (1959), cited by P. Goldfinger and M. Jeunehomme.
Stierwalt, D. L., *Navy Ordnance Lab Report 667*, Corona, CA (1966), cited by W. L. Wolfe, *Handbook of Optics*. Chapter 7, W. G. Driscoll and W. Vaughan, eds., McGraw-Hill, New York (1978).
Veselovskii, B. K., *J. of Appl. Chem.*, USSR, **15**, 422 (1942), cited by P. Goldfinger and M. Juenehomme.
Wilke, C. R., "Viscosity Equation for Gas Mixtures," *J. Chem. Phys.*, **18**, 517 (1950).

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Batch Extraction with Liquid Surfactant Membranes: A Diffusion Controlled Model

A model of diffusion controlled mass transfer in liquid surfactant membranes is developed for uniform emulsion globules having no internal circulation. The solute is assumed to react instantaneously and irreversibly with the internal reagent at a reaction surface which advances into the globule as the reagent is consumed. A perturbation solution to the resulting non-linear equations is presented. In general, the zero-order, or pseudo-steady state solution alone often gives an adequate representation of the process. Experimental data on the batch extraction of phenol from waste water are in good agreement with the model predictions.

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SCOPE

Mathematical models currently available for predicting the mass transfer performance of liquid-surfactant membrane systems are of limited utility, both because they rely on parameters which cannot be estimated independently of the extraction runs themselves, and because the data obtained from batch experiments generally do not extrapolate to continuous flow situations. The reason is that these models do not adequately reflect the actual mass transfer processes occurring within the LM globules, and it is apparent that a more detailed mathematical modelling approach must be adopted if a meaningful interpretation of experimental extraction data is to be made.

In this work, a model is formulated for the calculation of solute extraction rates in the presence of a diffusion-controlled reaction by uniform emulsion globules dispersed in a well-mixed fluid, and a regular perturbation solution to the model equations is developed. The model is tested experimentally using the extraction of phenol from water by aqueous caustic solutions as the test system.

CONCLUSIONS AND SIGNIFICANCE

The development reported here is the first to provide reasonably accurate predictions, without the use of adjustable parameters, of solute extraction rates in batch liquid membrane systems. The only information required, in addition to pertinent equilibrium and transport properties, is the Sauter mean diameter of the suspended globules. This model thus represents a significant improvement over existing design procedures, both for liquid membranes and analogous processes such as extraction by reactive solvents and heat transfer in the presence of phase changes. Examples of current interest include hydrometallurgy, and the removal of trace contaminants from waste streams.

INTRODUCTION

Since their discovery just over a decade ago (Li, 1968), liquid surfactant membranes have demonstrated considerable potential as effective tools for an increasingly wide variety of separations (Maugh, 1976). These include: 1. the fractionation of hydrocarbons (Li, 1971a, 1971b; Shah and Owens, 1972; Cahn and Li, 1976a, 1976b; Alessi et al., 1980; Halwachs et al., 1980); 2. the recovery and enrichment of heavy metal ions (Schiffer et al., 1974; Hochhauser and Cussler, 1975; Martin and Davies, 1976/1977; Kondo et al., 1979; Völkel et al., 1980; Strzelbicki and Charewicz, 1980;

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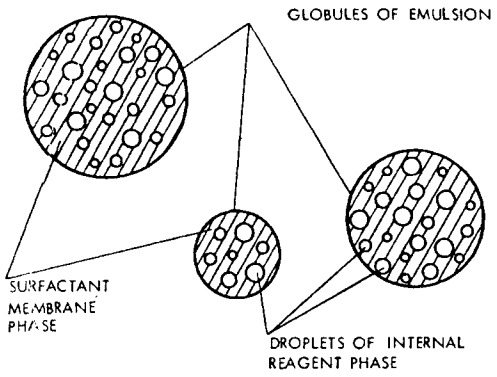

Figure 1. Schematic diagram of a liquid surfactant membrane system.

Frankenfeld et al., 1981); 3. the removal of trace contaminants from waste water (Li and Shrier, 1972; Cahn and Li, 1974; Frankenfeld and Li, 1977; Kitagawa et al., 1977; Halwachs et al., 1980; Terry et al., 1981); and 4. a number of diverse applications in the biochemical and biomedical fields (May and Li, 1972; Li and Asher, 1973, May and Li, 1974; Mohan and Li, 1974, 1975; Asher et al., 1975, 1977; May and Li, 1977; Frankenfeld et al., 1978). Liquid membranes also have potential utility as membrane reactors incorporating simultaneous separation and reaction processes (Ollis et al., 1972; Wolynic and Ollis, 1974; Cussler and Evans, 1980).

Liquid surfactant membranes are usually prepared by first forming an emulsion between two immiscible phases, and then dispersing this emulsion in a third (continuous) phase by agitation. The liquid membrane phase is that which separates the encapsulated drops in the emulsion from the external, continuous phase, as shown schematically in Figure 1. In general, the internal phase droplets are small, having diameters of 1–10 μm, whereas the emulsion globules are usually about 0.1–2 mm in diameter. The separation of a mixture, or removal of a solute from the continuous phase, can occur by the selective transfer of the solute through the membrane phase to the encapsulated internal reagent. Surfactants and additives are normally included in the membrane phase formulation to control the stability, permeability and selectivity of the membrane. At the end of an extraction run the emulsion and aqueous feed phases are separated, and the reacted internal reagent phase can be recovered, if desired, by breaking the emulsion.

The effectiveness of the liquid membrane process can be enhanced by utilizing a facilitated transport mechanism to maximize both the flux through the membrane phase, and the capacity of the receiving phase for the diffusing species. Matulevicius and Li (1975) and Li (1978, 1981) have identified two mechanisms which they call Type 1 and Type 2 facilitations, respectively. In facilitation of the first type, the concentration gradient of the membrane soluble permeate is maximized by irreversibly reacting the solute in the receiving phase, and thereby maintaining the permeate concentration effectively zero in this phase. It is desirable that the reaction products be incapable of diffusing back through the membrane. In Type 2 facilitation, an ion exchange reagent incorporated in the membrane phase "carries" the diffusing species across the membrane to the receiving phase. This is commonly known as "carrier mediated" transport. In both cases, the diffusing species is eventually immobilized at the expense of some consumable reagent. For instance, phenol can be reacted with NaOH to form the oil-insoluble sodium phenolate, whereas extraction of the cupric ion is often balanced by the counter transport of protons.

While a number of investigations on extraction with liquid membranes have been reported in the literature, physical interpretations of the results in terms of existing mathematical models have not been entirely satisfactory. For instance, Cahn and Li (1974) used a very simple approach in which the mass transfer rate is assumed to be directly proportional to the average solute concentration difference between the continuous and the internal reagent phases. However, they found that the effective permeation rate constant varied with time during the batch removal of phenol from waste water. This model was also used by Boyadzhiev et al. (1978). Matulevicius and Li (1975) suggested that the diffusion of phenol in LM globules is limited to the outer layers of the encapsulated droplets only. They formulated and solved the unsteady state equations for the hollow sphere model, in which phenol diffuses from the surface of the globule to some fixed, interior position, where it is removed by reaction with the internal reagent. Their model does not account for the effect of the rate at which the internal reagent is consumed, however. A similar limitation is inherent in the work of Hochhauser and Cussler (1975) in their investigation on the concentration of chromium with liquid membranes. Kopp et al. (1978) recognized this problem, and proposed that the process be described in terms of a boundary at which the reaction occurs, and which moves in towards the globule center as the reagent is consumed. Unfortunately, their use of the solution for the equivalent planar problem to represent the transport in a spherical geometry limits the range of applicability of their work, as does their neglect of changes in the external phase concentration.

Scant attention has been given to the actual design of separations equipment using the models discussed above. In fact, Cahn and Li (1974) appear to be the only authors to have addresseed this problem, albeit only briefly. However, their suggestion that permeation rate constants estimated from batch experiments be used in the design of continuous cocurrent plant-type treating equipment is compromised by the fact that this "constant" is, in fact, not constant at all. The question remains as to what average value of the rate constant should be used.

Clearly, a model which more accurately reflects the transport processes controlling the extraction rate will do much to resolve this ambiguity between batch and continuous flow experiments. For this reason, we have developed a more detailed description of transport in liquid membrane systems, without the sacrifice of mathematical tractability. The resulting equations are easy to apply, and enable the prediction of batch extraction rates from first principles, requiring only a knowledge of the diffusion coefficients for the membrane and internal phases, respectively, the partition coefficient for the solute between these phases, and the average globule size. This is a significant improvement over existing models which rely to some extent on parameters which cannot be estimated independently of the extraction runs themselves. Furthermore, the model concepts should carry over directly to continuous flow situations.

ADVANCING FRONT MODEL

In this section we develop a simplified physical model of a typical liquid membrane system, and arrive at an approximate, but useful macroscopic description of LM extraction processes.

Development of a Physical Model

The schematic representation of a typical liquid membrane system shown in Figure 1 indicates two key features which must be adequately described in any realistic model of transport and reaction in such a system. The first is the emulsion heterogeneity resulting from the presence of the droplets of internal reagent dispersed in the emulsion globules, while the second is the nonuniform size distribution of the globules themselves. It is also important to note that the reaction takes place only in the encapsulated droplets, while diffusion occurs in both phases of the emulsion.

The encapsulated internal reagent droplets are considerably smaller in size (1–10 μm in diameter) than the emulsion globules themselves, which usually have diameters in the range 0.1 to 2 mm. Consequently, the droplet time constants are considerably less than those for the emulsion globule as a whole. We can therefore assume

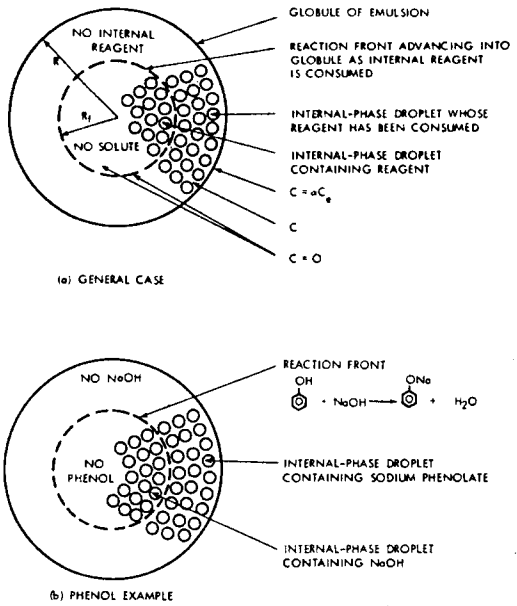

Figure 2. Schematic diagram of the advancing front model.

local equilibrium between the dispersed and continuous phases of the emulsion, and describe the concentration field within the globule in terms of the average local concentration; i.e., we can disregard the composite nature of the emulsion, and treat it as though it were a continuum.

In view of the strong presence of surfactants in the membrane phase, we anticipate no internal circulation within the globules (Rumscheidt and Mason, 1961; Levich, 1962), which condition ensures that the reagent in the encapsulated drops is immobilized. The membrane-soluble solute, however, is free to diffuse into the globule, and this it does until it is depleted by reaction with the internal reagent. This reaction is assumed to be instantaneous and irreversible. Hence the solute is unable to penetrate into the globule beyond those droplets which are completely depleted of reagent, for it is then immediately removed by reaction with the internal reagent. Thus, there must exist a sharp boundary, or reaction front, at which the reaction takes place, and which separates the inner region containing no solute from the outer region which contains no reagent, as depicted in Figure 2. As the reagent is consumed by the reaction, this reaction front advances into the globule. We assume that, on formation, the reaction products are immobilized, and hence that they are incapable of back-diffusion.

While it is almost certain that the dispersion of the emulsion in the continuous phase exhibits a non-uniform globule size distribution, we nevertheless neglect this effect, and assume that the system can be described adequately as being monodisperse with globules of some suitably defined average size (for mass transfer systems, it is customary to use the Sauter mean diameter). We also ignore the possibility of coalescence and redispersion of the emulsion globules, since these processes can be expected to be largely inhibited as a result of the low interfacial tensions produced by the surfactants in the membrane phase (Tavlarides et al., 1970).

For well-agitated systems, the external phase mass transfer resistance can be considered negligible. However, strong agitation may lead to a rupturing of the membranes, with a consequent leakage of the internal reagent (possibly in the form of reaction products) to the external phase (Li and Shrier, 1972). For sufficiently strong membranes, this effect will be negligible (Frankenfeld et al., 1981), and here we will make this simplifying assumption.

In summary, we model the LM system in terms of a monodisperse, non-coalescing collection of spherical globules having no internal circulation. The solute taken up from the external phase diffuses through the globule to a reaction front, where it is removed by an instantaneous and irreversible chemical reaction. The reaction front advances in towards the globule center as the internal reagent is consumed. External phase mass transfer resistance and membrane leakage are assumed to be negligible.

Mathematical Description

The equations describing the concentrations of the solute in the globules and in the external, continuous phase are

Globules:

$$\frac{\partial c}{\partial t} = \frac{\mathcal{D}_{\text{eff}}}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right) \qquad R_f(t) \le r \le R \tag{1}$$

$$t = 0 \qquad c = 0 \qquad (r < R) \tag{2}$$

$$r = R \qquad c = \alpha c_e \qquad (t > 0) \tag{3}$$

$$r = R_f(t) \qquad c = 0 \qquad (t > 0) \tag{4}$$

External Phase:

$$-V_e\frac{dc_e}{dt} = n(4\pi R^2)\mathcal{D}_{\text{eff}}\left.\frac{\partial c}{\partial r}\right|_{r=R} \tag{5}$$

$$= \frac{3}{R}(V_m + V_t)\mathcal{D}_{\text{eff}}\left.\frac{\partial c}{\partial r}\right|_{r=R} \tag{6}$$

$$t = 0 \qquad c_e = c_{e0} \tag{7}$$

A material balance over the reaction front gives

$$-\left(\frac{V_t}{V_m + V_t}\right)c_{t0}\frac{dR_f}{dt} = \mathcal{D}_{\text{eff}}\left.\frac{\partial c}{\partial r}\right|_{r=R_f(t)} \tag{8}$$

$$t = 0 \qquad R_f = R \tag{9}$$

where $c(r)$ is the solute concentration within the globule, averaged over the membrane and internal reagent phases. The external phase, membrane phase and internal reagent volumes are V_e, V_m and V_t, respectively, and the position of the advancing reaction front is denoted by R_f.

The equations can be cast in dimensionless form by defining

$$\eta = \frac{r}{R}; \qquad \chi = \frac{R_f}{R}; \qquad \tau = \frac{\epsilon\mathcal{D}_{\text{eff}}t}{R^2}$$

$$g = \frac{c}{\alpha c_{e0}}; \qquad h = \frac{c_e}{c_{e0}}; \qquad \epsilon = \frac{\alpha c_{e0}}{\left(\frac{V_t}{V_m + V_t}\right)c_{t0}} \tag{10}$$

$$E = 3\left(\frac{c_{t0}V_t}{c_{e0}V_e}\right)$$

The scaled equations are

Globules:

$$\epsilon\frac{\partial g}{\partial \tau} = \frac{1}{\eta^2}\frac{\partial}{\partial \eta}\left(\eta^2\frac{\partial g}{\partial \eta}\right) \qquad \chi \le \eta \le 1 \tag{11}$$

$$\tau = 0 \qquad g = 0 \tag{12}$$

$$\eta = 1 \qquad g = h \tag{13}$$

$$\eta = \chi \qquad g = 0 \tag{14}$$

External Phase:

$$\frac{dh}{d\tau} = -E\left.\frac{\partial g}{\partial \eta}\right|_{\eta=1} \tag{15}$$

$$\tau = 0 \qquad h = 1 \tag{16}$$

Reaction Front:

$$\frac{d\chi}{d\tau} = -\left.\frac{\partial g}{\partial \eta}\right|_{\eta=\chi(\tau)} \tag{17}$$

$$\tau = 0 \qquad \chi = 1 \tag{18}$$

These equations are inherently non-linear, and cannot be solved analytically. However, they are amenable to solution by perturbation methods, as has been demonstrated by Pedroso and Domoto

(1973a) for the simpler problem of inward spherical solidification with constant surface temperature. Huang and Shih (1975) also considered the freezing problem, but allowed for an external resistance to heat transfer at the surface to ambient surroundings of constant temperature. We follow their lead and simplify the problem statement and solution by using the standard transformation

$$\phi = \eta g \tag{19}$$

and the Landau transformation

$$\delta = \frac{1-\eta}{1-\chi} \tag{20}$$

This latter transformation effectively immobilizes the advancing reaction front, which is now given by $\delta = 1$. At the globule surface $\delta = 0$, and hence δ is seen to represent the fractional distance from the globule surface to the reaction front, and replaces η as the position variable in the analysis. If, in addition, we replace the independent variable time by the normalized reaction front position, the equations transform to

Globules:

$$\frac{\epsilon}{\chi}\left[\delta\frac{\partial\phi}{\partial\delta} + (1-\chi)\frac{\partial\phi}{\partial\chi}\right]\left(\left.\frac{\partial\phi}{\partial\delta}\right|_{\delta=1}\right) = \frac{\partial^2\phi}{\partial\delta^2} \qquad 0 \le \delta \le 1 \tag{21}$$

$$\delta = 0 \qquad \phi(0,\chi) = h(\chi) \tag{22}$$

$$\delta = 1 \qquad \phi(1,\chi) = 0 \tag{23}$$

External Phase:

$$\left(\left.\frac{\partial\phi}{\partial\delta}\right|_{\delta=1}\right)\frac{dh}{d\chi} = E\chi\left[(1-\chi)\phi + \left.\frac{\partial\phi}{\partial\delta}\right|_{\delta=0}\right] \tag{24}$$

$$\chi = 1 \qquad h = 1 \tag{25}$$

Reaction Front:

$$\frac{d\tau}{d\chi} = \chi(1-\chi)\left(\left.\frac{\partial\phi}{\partial\delta}\right|_{\delta=1}\right)^{-1} \tag{26}$$

$$\chi = 1 \qquad \tau = 0 \tag{27}$$

Now, in many liquid membrane operations, the solute in the continuous phase is normally present in small amounts only, whereas the internal reagent concentration is generally high. Thus we anticipate that in a large number of practical applications, ϵ will be considerably less than unity, and therefore serves as an ideal candidate for the perturbation parameter. We assume perturbation solutions, in terms of ϵ, of the form

$$\phi(\delta,\chi;\epsilon) = \phi_0(\delta,\chi) + \epsilon\phi_1(\delta,\chi) + \epsilon^2\phi_2(\delta,\chi) + \ldots \tag{28}$$

$$h(\chi;\epsilon) = h_0(\chi) + \epsilon h_1(\chi) + \epsilon^2 h_2(\chi) + \ldots \tag{29}$$

$$\tau(\chi;\epsilon) = \tau_0(\chi) + \epsilon\tau_1(\chi) + \epsilon^2\tau_2(\chi) + \ldots \tag{30}$$

and substitute these expressions in Eqs. 21 through 27. On expanding, and collecting terms in equal powers of ϵ, the perturbation equations are found to be

Terms of order ϵ^0:

$$\frac{\partial^2\phi_0}{\partial\delta^2} = 0 \tag{31}$$

$$\delta = 0 \qquad \phi_0(0,\chi) = h_0(\chi) \tag{32}$$

$$\delta = 1 \qquad \phi_0(1,\chi) = 0 \tag{33}$$

$$\left(\left.\frac{\partial\phi_0}{\partial\delta}\right|_{\delta=1}\right)\frac{dh_0}{d\chi} = E\chi\left[(1-\chi)\phi_0 + \left.\frac{\partial\phi_0}{\partial\delta}\right|_{\delta=0}\right] \tag{34}$$

$$\chi = 1 \qquad h_0 = 1 \tag{35}$$

$$\frac{d\tau_0}{d\chi} = \chi(1-\chi)\left(\left.\frac{\partial\phi_0}{\partial\delta}\right|_{\delta=1}\right)^{-1} \tag{36}$$

$$\chi = 1 \qquad \tau_0 = 0 \tag{37}$$

Terms of order ϵ^1:

$$\frac{\partial^2\phi_1}{\partial\delta^2} = \frac{1}{\chi}\left[\delta\frac{\partial\phi_0}{\partial\delta} + (1-\chi)\frac{\partial\phi_0}{\partial\chi}\right]\left(\left.\frac{\partial\phi_0}{\partial\delta}\right|_{\delta=1}\right) \tag{38}$$

$$\delta = 0 \qquad \phi_1(0,\chi) = h_1(\chi) \tag{39}$$

$$\delta = 1 \qquad \phi_1(1,\chi) = 0 \tag{40}$$

$$\left(\left.\frac{\partial\phi_0}{\partial\delta}\right|_{\delta=1}\right)\frac{dh_1}{d\chi} = E\chi\left[(1-\chi)\phi_1 + \left.\frac{\partial\phi_1}{\partial\delta}\right|_{\delta=0}\right] - \left(\left.\frac{\partial\phi_1}{\partial\delta}\right|_{\delta=1}\right)\frac{dh_0}{d\chi} \tag{41}$$

$$\chi = 1 \qquad h_1 = 0 \tag{42}$$

$$\frac{d\tau_1}{d\chi} = -\chi(1-\chi)\left(\left.\frac{\partial\phi_1}{\partial\delta}\right|_{\delta=1}\right)\left(\left.\frac{\partial\phi_0}{\partial\delta}\right|_{\delta=1}\right)^{-2} \tag{43}$$

$$\chi = 1 \qquad \tau_1 = 0 \tag{44}$$

Terms of order ϵ^2:

$$\frac{\partial^2\phi_2}{\partial\delta^2} = \frac{1}{\chi}\left\{\left[\delta\frac{\partial\phi_1}{\partial\delta} + (1-\chi)\frac{\partial\phi_1}{\partial\chi}\right]\left(\left.\frac{\partial\phi_0}{\partial\delta}\right|_{\delta=1}\right) + \left[\delta\frac{\partial\phi_0}{\partial\delta} + (1-\chi)\frac{\partial\phi_0}{\partial\chi}\right]\left(\left.\frac{\partial\phi_1}{\partial\delta}\right|_{\delta=1}\right)\right\} \tag{45}$$

$$\delta = 0 \qquad \phi_2(0,\chi) = h_2(\chi) \tag{46}$$

$$\delta = 1 \qquad \phi_2(1,\chi) = 0 \tag{47}$$

$$\left(\left.\frac{\partial\phi_0}{\partial\phi}\right|_{\delta=1}\right)\frac{dh_2}{d\chi} = E\chi\left[(1-\chi)\phi_2 + \left.\frac{\partial\phi_2}{\partial\delta}\right|_{\delta=0}\right] - \left\{\left(\left.\frac{\partial\phi_1}{\partial\delta}\right|_{\delta=1}\right)\frac{dh_1}{d\chi} + \left(\left.\frac{\partial\phi_2}{\partial\delta}\right|_{\delta=1}\right)\frac{dh_0}{d\chi}\right\} \tag{48}$$

$$\chi = 1 \qquad h_2 = 0 \tag{49}$$

$$\frac{d\tau_2}{d\chi} = \chi(1-\chi)\left\{\left(\left.\frac{\partial\phi_1}{\partial\delta}\right|_{\delta=1}\right)^2 - \left(\left.\frac{\partial\phi_2}{\partial\delta}\right|_{\delta=1}\right)\left(\left.\frac{\partial\phi_0}{\partial\delta}\right|_{\delta=1}\right)\right\}\left(\left.\frac{\partial\phi_0}{\partial\delta}\right|_{\delta=1}\right)^{-3} \tag{50}$$

$$\chi = 1 \qquad \tau_2 = 0 \tag{51}$$

The solutions to these systems of equations are

Zero-order solutions:

$$\phi_0 = \frac{E}{3}(\chi^3 - B^3)(1-\delta) \tag{52}$$

$$h_0 = \frac{E}{3}(\chi^3 - B^3) \tag{53}$$

$$\tau_0 = \frac{1}{E}\left[\left(1+\frac{1}{2B}\right)ln\left(\frac{\chi^3-B^3}{1-B^3}\right) - \frac{3}{2B}ln\left(\frac{\chi-B}{1-B}\right)\right] - \frac{\sqrt{3}}{EB}\left[\tan^{-1}\left(\frac{2\chi+B}{\sqrt{3}B}\right) - \tan^{-1}\left(\frac{2+B}{\sqrt{3}B}\right)\right] \tag{54}$$

where

$$B = \left(1 - \frac{3}{E}\right)^{1/3} \tag{55}$$

First-order solutions:

$$\phi_1 = \frac{E^2}{54\chi}[a_0(1-\delta) + a_1(1-\delta) + a_2(1-\delta^2) + a_3(1-\delta^3)] \tag{56}$$

$$h_1 = \frac{E^2}{54\chi}a_1 \tag{57}$$

$$= \frac{E^2}{18}(\chi^3 - B^3)(\chi+2)(\chi-1) \tag{58}$$

$$\tau_1 = \frac{1}{6}\left[\chi^2 - 8\chi + 7 + \left(B + 4 + \frac{1}{B}\right) \times ln\left(\frac{\chi^3-B^3}{1-B^3}\right) - 3\left(B+\frac{1}{B}\right)ln\left(\frac{\chi-B}{1-B}\right)\right] + \frac{1}{\sqrt{3}}\left(B-\frac{1}{B}\right)\left[tan^{-1}\left(\frac{2\chi+B}{\sqrt{3}B}\right) - tan^{-1}\left(\frac{2+B}{\sqrt{3}B}\right)\right] \tag{59}$$

where

$$a_0 = 7\chi^6 - 6\chi^5 - 8B^3\chi^3 + 6B^3\chi^2 + B^6 \quad (60)$$

$$a_1 = 3\chi^6 + 3\chi^5 - 6\chi^4 - 3B^3\chi^3 - 3B^3\chi^2 + 6B^3\chi \quad (61)$$

$$a_2 = -9\chi^6 + 9\chi^5 + 9B^3\chi^3 - 9B^3\chi^2 \quad (62)$$

$$a_3 = 2\chi^6 - 3\chi^5 - B^3\chi^3 + 3B^3\chi^2 - B^6 \quad (63)$$

Second-order solutions:

$$\phi_2 = \frac{E^3}{9{,}720\chi^3}[b_0(1-\delta) + b_1(1-\delta) + b_2(1-\delta^2) + b_3(1-\delta^3) + b_4(1-\delta^4) + b_5(1-\delta^5)] \quad (64)$$

$$h_2 = \frac{E^3}{9{,}720\chi^3} b_1 \quad (65)$$

$$= \frac{E^3}{3{,}240\chi}(\chi^3 - B^3)(\chi - 1)[\chi^4 + 80\chi^3 + 24\chi^2 + (8B^3 - 120)\chi + 7B^3] \quad (66)$$

$$\tau_2 = \frac{E}{540}\left[-7\chi^4 + 40\chi^3 - 100\chi^2 + (144 + 4B^3)\chi - (77 + 8B^3) + 4B^3\frac{1}{\chi} + 6(2B+1)(B+2)(B-1)\ln\left(\frac{\chi^3 - B^3}{1 - B^3}\right) - 54B(B-1)\ln\left(\frac{\chi - B}{1 - B}\right)\right] - \frac{E}{5\sqrt{3}}B(B+1)\left[\tan^{-1}\left(\frac{2\chi + B}{\sqrt{3}\,B}\right) - \tan^{-1}\left(\frac{2 + B}{\sqrt{3}\,B}\right)\right] \quad (67)$$

where

$$b_0 = -(b_2 + b_3 + b_4 + b_5) = (\chi^3 - B^3)(33\chi^7 + 764\chi^6 - 1{,}536\chi^5 + (720 + 87B^3)\chi^4 - 253B^3\chi^3 + 204B^3\chi^2 - 12B^6\chi - 7B^6] \quad (68)$$

$$b_1 = (\chi^3 - B^3)[3\chi^7 + 237\chi^6 - 168\chi^5 + (24B^3 - 432)\chi^4 + (360 - 3B^3)\chi^3 - 21B^3\chi^2] \quad (69)$$

$$b_2 = (\chi^3 - B^3)[-270\chi^7 - 630\chi^6 + 1{,}980\chi^5 - 1{,}080\chi^4 + 90B^3\chi^3 - 90B^3\chi^2] \quad (70)$$

$$b_3 = (\chi^3 - B^3)[360\chi^7 - 410\chi^6 - 300\chi^5 + (360 - 90B^3)\chi^4 + 220B^3\chi^3 - 150B^3\chi^2 + 10B^6] \quad (71)$$

$$b_4 = (\chi^3 - B^3)[-135\chi^7 + 315\chi^6 - 180\chi^5 - 45B^3\chi^3 + 45B^3\chi^2] \quad (72)$$

$$b_5 = (\chi^3 - B^3)[12\chi^7 - 39\chi^6 + 36\chi^5 + 3B^3\chi^4 - 12B^3\chi^3 - 9B^3\chi^2 + 12B^6\chi - 3B^6] \quad (73)$$

Solutions for $E = 3$

From a numerical standpoint, the above solutions break down for $E = 3$ ($B = 0$) where a number of terms became indeterminate. These indeterminacies are readily resolved using L'Hospital's rule. The corresponding results are

Zero-order solutions:

$$\phi_0 = \chi^3(1 - \delta) \quad (74)$$

$$h_0 = \chi^3 \quad (75)$$

$$\tau_0 = \ln\chi + \left(\frac{1}{\chi} - 1\right) \quad (76)$$

First-order solutions:

$$\phi_1 = \frac{1}{6}\chi^3[\chi(7\chi - 6)(1-\delta) + 3(\chi + 2)(\chi - 1)(1-\delta) + 9\chi(1-\chi)(1-\delta^2) + \chi(2\chi - 3)(1-\delta^3)] \quad (77)$$

$$h_1 = \frac{1}{2}\chi^3(\chi + 2)(\chi - 1) \quad (78)$$

$$\tau_1 = \frac{1}{6}[\chi^2 - 8\chi + 7] + 2\ln\chi + \left(\frac{1}{\chi} - 1\right) \quad (79)$$

Second-order solutions:

$$\phi_2 = \frac{1}{360}\chi^3[b_0'(1-\delta) + b_1'(1-\delta) + b_2'(1-\delta^2) + b_3'(1-\delta^3) + b_4'(1-\delta^4) + b_5'(1-\delta^5)] \quad (80)$$

$$h_2 = \frac{1}{120}\chi^3(\chi - 1)(\chi^3 + 80\chi^2 + 24\chi - 120) \quad (81)$$

$$\tau_2 = \frac{1}{180}[-7\chi^4 + 40\chi^3 - 100\chi^2 + 144\chi - 77 - 36\ln\chi] \quad (82)$$

where

$$b_0' = 33\chi^4 + 764\chi^3 - 1536\chi^2 + 720\chi \quad (83)$$

$$b_1' = 3\chi^4 + 237\chi^3 - 168\chi^2 - 432\chi + 360 \quad (84)$$

$$b_2' = -270\chi^4 - 630\chi^3 + 1{,}980\chi^2 - 1{,}080\chi \quad (85)$$

$$b_3' = 360\chi^4 - 410\chi^3 - 300\chi^2 + 360\chi \quad (86)$$

$$b_4' = -135\chi^4 + 315\chi^3 - 180\chi^2 \quad (87)$$

$$b_5' = 12\chi^4 - 39\chi^3 + 36\chi^2 \quad (88)$$

Convergence of Perturbation Sequence

The convergence behavior of the perturbation solutions is closely linked to the values taken on by the parameter E, where $E/3$ is the ratio of the equivalents of internal reagent to moles of solute introduced to the system and, as such, is a measure of the capacity of the system for performing the desired separation. Inspection of the equations shows that the second-order solutions h_2 and τ_2 exhibit singularities at $\chi = 0$, although these singularities can only occur when $E < 3$. For $E \geq 3$, stoichiometric considerations dictate that the minimum possible value that can be attained by χ is B, and it is easy to show that the solutions do not demonstrate singular behavior as $\chi \to B$, even in the limit as $B \to 0$.

These points are illustrated graphically on Figures 3, 4 and 5, where the zero-, first- and second-order solutions for the external phase solute concentration as functions of dimensionless time are shown for selected values of E, and the perturbation parameter ϵ. [The results plotted are h_0 vs. τ_0, $h^{(1)} = h_0 + \epsilon h_1$ vs. $\tau^{(1)} = \tau_0 + \epsilon\tau_1$, $h^{(2)} = h_0 + \epsilon h_1 + \epsilon^2 h_2$ vs. $\tau^{(2)} = \tau_0 + \epsilon\tau_1 + \epsilon^2\tau_2$, and h^* vs. τ^*, where h^* and τ^* are given by Eqs. 89 and 90.] The singularities for $E < 3$ are dramatically obvious for high values of ϵ, where the second-order solutions $h^{(2)}$ fold back on themselves. These effects will always be evident for $E < 3$, although the turn-around points will occur at increasingly larger times τ as ϵ increases. No such

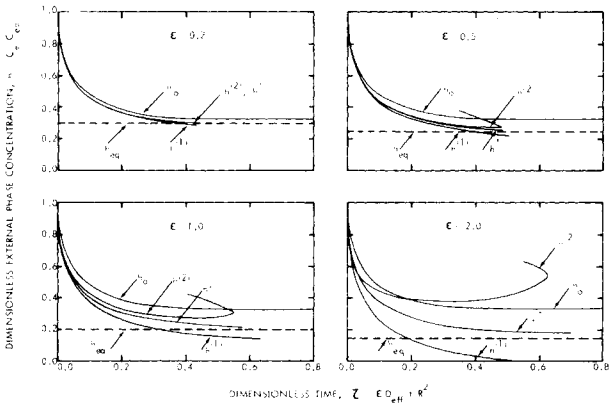

Figure 3. Perturbation solutions for the external phase concentration: $E = 2.0$.

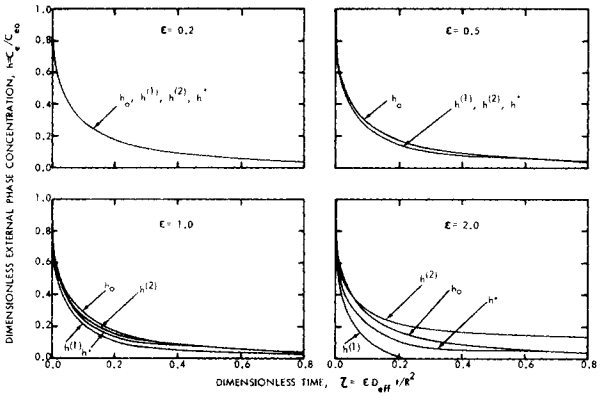

Figure 4. Perturbation solutions for the external phase concentration: E = 3.0.

behavior is exhibited for $E \geq 3$, of course, and the second-order solutions decrease monotonically with increasing τ.

The sequence of solutions $\{h^{(i)}\}$ is not convergent for large values of ϵ. [Although high values of ϵ are unlikely to be encountered in batch experiments, values of ϵ on the order of unity can be anticipated, for example, in the feed section of a countercurrent mixer-settler train. For the sake of generality, we also consider these large values of ϵ here.] Nevertheless, even with only the first three terms of the series expansions, a great deal of information may be culled through application of the non-linear transformations due to Shanks (1955) as discussed by Pedroso and Domoto (1973a, 1973b). These transformations extend the range of applicability of the perturbation solutions, and are particularly useful when the series either converge slowly, or diverge. We have

$$h^*(\chi) = \frac{h_0 h_1 - \epsilon(h_0 h_2 - h_1^2)}{h_1 - \epsilon h_2} \tag{89}$$

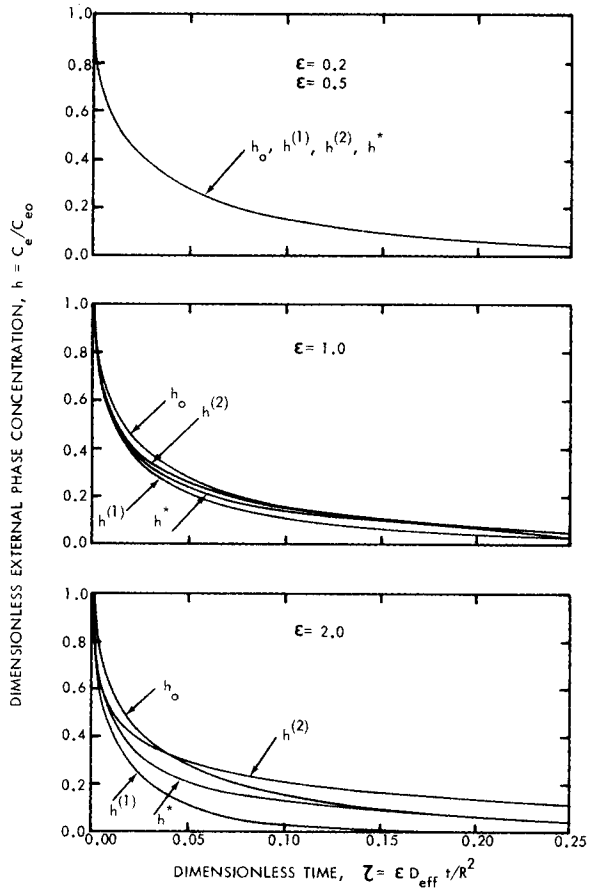

Figure 5. Perturbation solutions for the external phase concentration: E = 4.0.

and

$$\tau^*(\chi) = \frac{\tau_0\tau_1 - \epsilon(\tau_0\tau_2 - \tau_1^2)}{\tau_1 - \epsilon\tau_2} \tag{90}$$

The curves relating h^* to τ^* are shown in Figures 3, 4 and 5 for the values of E and ϵ considered earlier. The success of the non-linear transformations in overcoming the divergent character of the solutions for large ϵ is clearly evident. This is especially true of the results for $E = 2.0$, where the transformed solutions appear to asymptote toward the expected final equilibrium concentration values*—derived from material balance considerations to be

$$h_{eq} = \frac{1 - E/3}{1 + \epsilon E/3} \tag{91}$$

and shown as broken lines in Figure 3.

In most cases of practical interest, where values of ϵ are somewhat less than unity, the zero-order solution alone gives an adequate representation of the mass transfer processes occurring in the system. For instance, the deviations between the zero-order and higher-order solutions for $E = 2.0$ and $\epsilon = 0.2$ (Figure 3) are probably well within the bounds of experimental error, and thus no advantage is to be gained by going beyond the zero-order solution. For higher values of ϵ, however, appreciable errors can be introduced if higher order terms are neglected. The range of ϵ values for which the zero-order solutions alone are adequate appears to increase with increasing E, which corresponds to a decreasing penetration of the reaction front into the globule. This is evidenced by the results for $\epsilon = 0.5$ and E values of 2.0, 3.0 and 4.0 (Figures 3, 4 and 5).

The effect of E on the extraction rate for small values of ϵ is illustrated in Figure 6.

EXPERIMENTAL

Two experiments on the batch extraction of phenol from waste water using a liquid membrane emulsion with an aqueous NaOH solution as the internal reagent were available to test the utility of the mathematical analysis. This LM system has been reported on quite extensively in the literature (Li and Shrier, 1972; Cahn and Li, 1974; Matulevicius and Li,

* For larger values of time τ, however, the concentrations h^* increase again to asymptote toward the zero-order solutions h_0, although for all practical purposes the region where this occurs is beyond the range of interest.

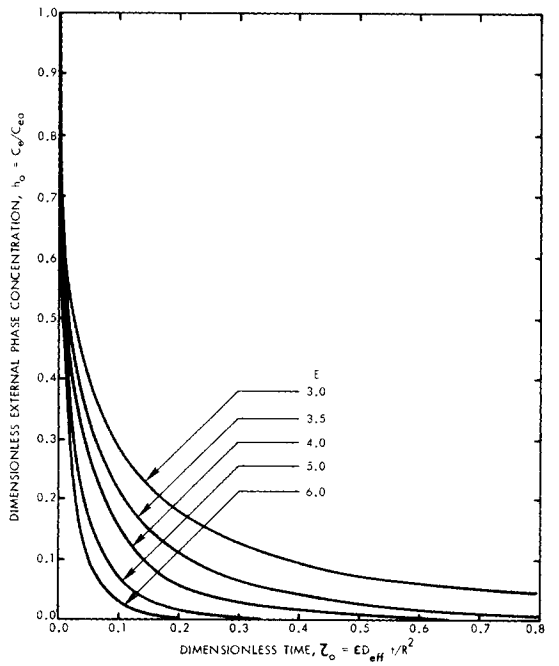

Figure 6. Zero-order, or pseudo-steady state, solutions for the external phase concentration.

TABLE 1. EXPERIMENTAL CONDITIONS AND PHYSICAL PROPERTIES

$V_i/(V_m + V_i) = 0.363$
$c_{i0} = 0.375$ N
$\alpha' = 0.52$
$E = 3.32$
$\mathcal{D}_{eff} = 1.23 \times 10^{-10} m^2/s$

$V_e/(V_m + V_i) = 15.0$
$c_{e0} = 8.19 \times 10^{-3}$N
$\alpha = 0.694$
$\epsilon = 0.0418$
$T = 296.15$ K

N (rpm)	R (mm)
400	0.5
600	0.3

1975; Halwachs et al., 1980; Marr and Kopp, 1980; Terry et al., 1981), and is characterized by a simple extraction chemistry: the phenol diffuses through the membrane (oil) phase of the emulsion, and reacts instantaneously and irreversibly with the internal reagent (NaOH) to form the oil-insoluble sodium phenolate.

Liquid Membrane Emulsion Preparation

The LM emulsion used in this study was one of the typical formulations reported previously by Li and Shrier (1972), Li et al. (1973), Cahn and Li (1974), May and Li (1972, 1974), Mohan and Li (1974, 1975), Matulevicius and Li (1975) and Kitagawa et al. (1977). The membrane (oil) phase was 1% by weight Span 80, 3% ENJ 3029, and 96% S100N. Span 80 (sorbiton monooleate, manufactured by ICI America) is a surfactant, whereas ENJ 3029, a nonionic polyamine, made by Exxon Chemical Company, was added for its membrane strengthening properties. S100N, dewaxed Solvent 100 Neutral, also made by Exxon, is a middle distillate and an isoparaffinic solvent having an average molecular weight of 386.5, a cloud point of 33.9°C, a pour point of 32.2°C, and a specific gravity of 0.85 at 25°C. The resulting oil phase had an average molecular weight of 433 and a viscosity of 43.9×10^{-3} Ns/m^2 at 23°C. In the laboratory preparation of the emulsion, 175.5 ml oil and 100 ml aqueous NaOH solution (1.5% of weight, 0.375 N) were mixed in a Waring blender at a stirring speed of 12,000 rpm for 2 min. The emulsion, with a dispersed aqueous phase volume of 36.3%, had an average droplet size of about 1 μm.

Experimental Apparatus and Procedure

For the extraction experiments, 52 ml prepared emulsion was dispersed in 780 ml aqueous feed solution, giving a feed to emulsion volume ratio of 15. The phenol concentration of the feed was 0.77 g/L (8.19×10^{-3}N). The two phases were mixed in a 102 mm diameter standard mixer with four vertical baffles and a 50.8 mm diameter marine propeller. Samples of the external phase were removed periodically during the course of a run and analyzed for phenol by UV absorbance at a peak wave length of 271 nm.

Two extraction runs were conducted, one at a mixing rate of 400 rpm, and the other at 600 rpm. The temperature was 23°C in both cases. Emulsion globule sizes were determined photographically, and expressed in terms of the Sauter mean diameter. The mean diameters were found to be 1.0 mm at 400 rpm, and 0.6 mm at 600 rpm. The distribution coefficient, α, for phenol between the oil and the external aqueous phase was determined at equilibrium to be 0.52.

All pertinent operating variables are recorded in Table 1. It may be seen from this table that ϵ is small relative to unity, and that E is large enough that not all the NaOH can be consumed. Under these conditions h_0, $h^{(1)}$, $h^{(2)}$ and h^* should be indistinguishable.

ESTIMATION OF PHYSICAL PROPERTIES

The phenol equilibrium distribution coefficient for the aqueous feed/emulsion system and the effective diffusivity of phenol in the emulsion phase are required if model predictions are to be compared with the experimental results. Below, we discuss the estimation of these parameters.

Equilibrium Distribution Coefficient α

The average concentration of the diffusing solute in the exhausted region of the emulsion ($r > R_f$) is

$$c = \left(\frac{V_i c_i + V_m c_m}{V_i + V_m}\right) = \left(\frac{V_i/\alpha' + V_m}{V_i + V_m}\right) c_m \qquad (92)$$

where we have assumed local equilibrium between the membrane phase and the internal reagent droplets. This can be justified on the grounds that the diffusion time constant for the encapsulated droplets is considerably smaller than that for the emulsion globules. Here, α' is the distribution coefficient for phenol between the membrane phase and the depleted internal reagent phase. Because the initial concentration of the internal reagent (and hence of the reaction products) is relatively low, we assume α' is the same as that obtained for the oil/external phase system, i.e., $\alpha' = 0.52$.

At the globule surface, assuming no external phase mass transfer resistance, we have equilibrium between the external aqueous phase and the *membrane* phase. Thus

$$c_m = \alpha' c_e \qquad \text{at } r = R. \qquad (93)$$

But, we have also assumed equilibrium between the external phase and the *emulsion* at the globule surface. Hence,

$$c = \left(\frac{V_i/\alpha' + V_m}{V_i + V_m}\right) c_m = \alpha c_e \qquad \text{at } r = R \qquad (94)$$

On combining Eqs. 93 and 94, we determine

$$\alpha = \left(\frac{V_i + \alpha' V_m}{V_i + V_m}\right) \qquad (95)$$

For the conditions given in Table 1, we find $\alpha = 0.694$.

Effective Diffusivity

The effective diffusivity $\mathcal{D}'_{eff}$ of phenol in the emulsion mixture, based on a concentration driving force defined in terms of the membrane phase concentration, c_m, can be estimated from the Jefferson-Witzell-Sibbett equation (Crank, 1975) which, in our notation, reads

$$\mathcal{D}'_{eff} = \mathcal{D}_m \left[\frac{4(1+2p)^2 - \pi}{4(1+2p)^2}\right] + \frac{\pi}{4(1+2p)^2}\left[\frac{(1+2p)\mathcal{D}_A \mathcal{D}_m}{\mathcal{D}_m + 2p\mathcal{D}_A}\right] \qquad (96)$$

where

$$\mathcal{D}_A = \frac{2(\mathcal{D}_i/\alpha')\mathcal{D}_m}{(\mathcal{D}_i/\alpha') - \mathcal{D}_m}\left[\frac{\mathcal{D}_i/\alpha'}{(\mathcal{D}_i/\alpha') - \mathcal{D}_m} ln \frac{(\mathcal{D}_i/\alpha')}{\mathcal{D}_m} - 1\right]$$

$$p = 0.403\left(\frac{V_i}{V_m + V_i}\right)^{-1/3} - 0.5$$

The effective diffusivity $\mathcal{D}_{eff}$ based on the average concentration, c, in the emulsion mixture can be related to $\mathcal{D}'_{eff}$ through the equation

$$\mathcal{D}_{eff}\frac{dc}{dr} = \mathcal{D}'_{eff}\frac{dc_m}{dr} \qquad (97)$$

On substituting Eq. 92 into Eq. 97, and using Eq. 95, we obtain

$$\mathcal{D}_{eff} = \left(\frac{\alpha'}{\alpha}\right)\mathcal{D}'_{eff} \qquad (98)$$

The diffusivities of phenol in the individual phases constituting the emulsion were estimated with the aid of the Wilke-Chang correlation (Reid et al., 1977), written here in terms of SI units,

$$\mathcal{D} = 1.17 \times 10^{-16}\frac{T(\psi M)^{0.5}}{\mu V_A^{0.6}} \text{ m}^2/\text{s} \qquad (99)$$

The solvent dissociation factors, ψ, for the aqueous and oil phases were taken to be 2.6 and 1.0, respectively. The viscosities used were 0.936×10^{-3}Ns/m^2 for the aqueous phase, and 43.9×10^{-3}Ns/m^2

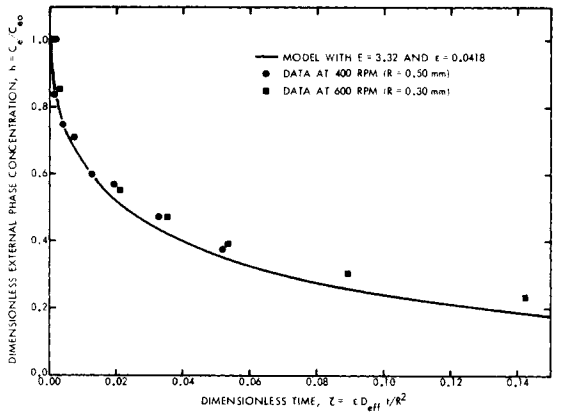

Figure 7. Comparison of model predictions with experimental data for the phenol extraction runs.

for the oil phase. The molar volume of phenol at its normal boiling temperature, V_A, was determined from density data given by Mellan (1977). We find $V_A = 102 \times 10^{-3}$m^3/kg-mol.

The phenol diffusivities at 23°C were calculated to be $\mathcal{D}_i = 9.98 \times 10^{-10}$m^2/s and $\mathcal{D}_m = 0.65 \times 10^{-10}$m^2/s. The effective diffusivity of the emulsion was estimated to be $\mathcal{D}_{\text{eff}} = 1.23 \times 10^{-10}$m^2/s.

TEST OF MODEL PREDICTIONS AGAINST EXPERIMENT

The experimental results, expressed in terms of c_e/c_{e0} and τ, are compared with the perturbation solution predictions in Figure 7. Since $\epsilon \ll 1$ and $E > 3$ in both cases, the higher order solutions are indistinguishable from h_0 in this figure. If one considers that no adjustable parameters were used in making this comparison and that only a single measure of globule size, the Sauter mean diameter, is used, the fit is gratifying.

The differences between the theoretical and experimental results may be due to errors in the estimation of the effective diffusivity, as well as the neglect of the polydisperse character of the dispersed emulsion phase. The deviations cannot be attributed to internal circulation within the globules, nor to coalescence and redispersion phenomena, although both were neglected in the model formulation. These processes would bring fresh, unreacted internal reagent drops from within the globule to the surface, and hence would enhance the extraction rate at the larger times, whereas the observed departures indicate a *decrease* in the extraction rate. It is possible that this is a result of some membrane rupturing, in which the outer layers of encapsulated drops are stripped from the emulsion globules by high shear forces, thereby returning some of the extracted solute to the agitated external phase.

We emphasize that the model formulated in this work contains only parameters that can be estimated independently of the extraction measurements themselves, and that no curve-fitting is required. This is a significant improvement over existing mathematical descriptions of solute removal using liquid membrane technology. The good agreement between the theoretical results and the experimental data instills confidence in the model as a useful prediction method for the analysis and interpretation of batch experimental data.

NOTATION

B = $\left(1 - \frac{3}{E}\right)^{1/3}$, Eq. 55

c = solute concentration in exhausted region of emulsion globules, N

c_e = solute concentration in external, continuous phase, N

c_{e0} = initial solute concentration in external, continuous phase, N

c_i = solute concentration in depleted internal reagent droplets, N

c_{i0} = initial concentration of reagent in the internal phase, N

c_m = solute concentration in membrane phase of emulsion globules, N

$\mathcal{D}_i$ = solute diffusivity in internal phase, m^2/s

$\mathcal{D}_m$ = solute diffusivity in membrane phase, m^2/s

$\mathcal{D}_{\text{eff}}$ = effective solute diffusivity in the emulsion mixture, m^2/s

E = $3\left(\frac{V_i c_{i0}}{V_e c_{e0}}\right)$, $E/3$ = ratio of equivalents internal reagent to equivalents solute in feed

g = $c/\alpha c_{e0}$, normalized solute concentration in emulsion globules

h = c_e/c_{e0}, normalized solute concentration in external, continuous phase

h_0, h_1, h_2 = zero, first and second order terms in perturbation expansion (Eq. 29) for h

$h^{(1)}$ = $h_0 + \epsilon h_1$, first order perturbation solution for h

$h^{(2)}$ = $h_0 + \epsilon h_1 + \epsilon^2 h_2$, second order perturbation solu- for h

h^* = Shanks nonlinear transformation of perturbation solution for h, Eq. 89

h_{eq} = normalized solute concentration in external, continuous phase at equilibrium, Eq. 91

M = solvent molecular weight, kg/kg − mol

n = total number of emulsion globules dispersed in the external, continuous phase

r = radial coordinate, m

R = globule radius, m

R_f = reaction front position, m

t = time, s

T = absolute temperature, K

V_A = molar volume of solute at normal boiling point, m^3/kg − mol

V_e = external phase volume, m^3

V_i = total internal reagent phase volume, m^3

V_m = total membrane phase volume, m^3

Greek Letters

α = distribution coefficient for the solute between the external phase and the exhausted emulsion mixture at equilibrium

α' = distribution coefficient for the solute between the external and membrane phases at equilibrium

δ = $\left(\frac{1-\eta}{1-\chi}\right)$, Eq. 20

ϵ = $\frac{\alpha(V_m + V_i)c_{e0}}{V_i c_{i0}}$, perturbation parameter

η = r/R, normalized radial coordinate

μ = solvent viscosity, Ns/m^2

τ = $\epsilon \mathcal{D}_{\text{eff}} t/R^2$, dimensionless time

τ_0, τ_1, τ_2 = zero, first and second order terms in perturbation expansion (Eq. 30) for τ

$\tau^{(1)}$ = $\tau_0 + \epsilon\tau_1$, first order perturbation solution for τ

$\tau^{(2)}$ = $\tau_0 + \epsilon\tau_1 + \epsilon^2\tau_2$, second order perturbation solution for τ

τ^* = Shanks non-linear transformation of perturbation solution for τ, Eq. 90

ϕ = ηg, Eq. 19

χ = R_f/R, normalized reaction front position

ψ = solvent dissociation factor

LITERATURE CITED

Alessi, P., I. Kikic, and M. Orlandini-Visalberghi, "Liquid Membrane Permeation for the Separation of C_8 Hydrocarbons," *Chem. Eng. J.*, **19**, 221 (1980)

Asher, W. J., K. C. Bovee, J. W. Frankenfeld, R. W. Hamilton, L. W. Henderson, P. G. Holtzapple, and N. N. Li, "Liquid Membrane System Directed toward Chronic Uremia," *Kidney Int.*, **7**, S-409 (1975).

Asher, W. J., T. C. Vogler, K. C. Bovee, P. G. Holtzapple, and R. W. Hamilton, "Liquid Membrane Capsules for Chronic Uremia," *Trans. Am. Soc. Artif. Intern. Organs*, **23**, 673 (1977).

Boyadzhiev, L., T. Sapundzhiev, and E. Bezenshek, "Modelling of Carrier-Mediated Extraction," *Sep. Sci.*, **12**, 541 (1978).

Cahn, R. P. and N. N. Li, "Separation of Phenol from Waste Water by the Liquid Membrane Technique," *Sep. Sci.*, **9**, 505 (1974).

———, "Separations of Organic Compounds by Liquid Membrane Process," *J. Membrane Sci.*, **1**, 129 (1976a).

———, "Hydrocarbon Separation by Liquid Membrane Processes," *Membrane Separation Processes*, P. Meares, ed., Chap. 9, pp. 327–349, Elsevier Scientific Publishing Co., Amsterdam-New York (1976b).

———., J. W. Frankenfeld, N. N. Li, D. Naden, and K. N. Subramanian, "Extraction of Metal Ions by Liquid Membranes," *Recent Developments in Separation Science*, N. N. Li, ed., **6**, Chemical Rubber Co., Cleveland, OH (1981).

Crank, J., *The Mathematics of Diffusion*, 2nd ed., Chap 12, Clarendon Press, Oxford (1975).

Cussler, E. L. and D. F. Evans, "Liquid Membranes for Separations and Reactions," *J. Membrane Sci.*, **6**, 113 (1980).

Frankenfeld, J. W. and N. N. Li, "Waste Water Treatment by Liquid Ion Exchange in Liquid Membrane Systems," in *Recent Developments in Separation Science*, N. N. Li, ed., **3**, pp. 285–292, Chemical Rubber Co., Cleveland, OH (1977).

———., W. J. Asher, and N. N. Li, "Biochemical and Biomedical Separations Using Liquid Membranes," in *Recent Developments in Separation Science*, N. N. Li, ed., **4**, pp. 39–50, Chemical Rubber Co., Cleveland, OH (1978).

Halwachs, W., E. Flaschel, and K. Schügerl, "Liquid Membrane Transport—A Highly Selective Separation Process for Organic Solutes," *J. Membrane Sci.*, **6**, 33 (1980).

Hochhauser, A. M. and E. L. Cussler, "Concentrating Chromium with Liquid Surfactant Membranes," *AIChE Symp. Ser.*, **71**, 136 (1975).

Huang, C. L. and Y. P. Shih, "A Perturbation Method for Spherical and Cylindrical Solidification," *Chem. Eng. Sci.*, **30**, 897 (1975).

Kitagawa, T., Y. Nishikawa, J. W. Frankenfeld, and N. N. Li, "Wastewater Treatment by Liquid Membrane Process," *Environ. Sci. Technol.*, **11**, 602 (1977).

Kondo, K., K. Kita, I. Koida, J. Irie and E. Nakashio, "Extraction of Copper with Liquid Surfactant Membranes Containing Benzoylacetone," *J. Chem. Eng. Japan*, **12**, 203 (1979).

Kopp, A. G., R. J. Marr and F. E. Moser, "A New Concept for Mass Transfer in Liquid Surfactant Membranes without Carriers and with Carriers that Pump," *Instn Chem. Eng. Symp. Ser.*, **54**, 279 (1978).

Levich, V. G., *Physicochemical Hydrodynamics*, Prentice-Hall, Englewood Cliffs, NJ (1962).

Li, N. N., "Separating Hydrocarbons with Liquid Membranes," U.S. Patent 3,410,794 (1968).

———, "Permeation through Liquid Surfactant Membranes," *AIChE J.*, **17**, 459 (1971a).

———, "Separation of Hydrocarbons by Liquid Membrane Permeation," *Ind. Eng. Process Des. Develop.*, **10**, 215 (1971b).

———, "Facilitated Transport through Liquid Membranes—An Extended Abstract," *J. Membrane Sci.*, **3**, 265 (1978).

———., "Encapsulation and Separation by Liquid Membranes," *Chemical Engineer*, Inst. of Ch.E. London, (July, 1981).

———., and W. J. Asher, "Blood Oxygenation by Liquid Membrane Permeation," *Chemical Engineering in Medicine*, ACS (Advances in Chemistry Series) pp. 1–14 (1973).

———, and A. L. Shrier, "Liquid Membrane Water Treating," *Recent Developments in Separation Science*, N. N. Li, ed., **1**, p. 163, Chemical Rubber Co., Cleveland, OH (1972).

———, R. P. Cahn and A. L. Shrier, "Liquid Membrane Process for the Separation of Aqueous Mixtures," U.S. Patent 3,779,907 (1973).

Marr, R., and A. Kopp, "Flüssigmembran-Technik-Übersicht über Phänomene, Transportmechanismen und Modellbildungen," *Chem. Ing. Tech.*, **52**, 399 (1980).

Martin, T. P., and G. A. Davies, "The Extraction of Copper from Dilute Aqueous Solutions Using a Liquid Membrane Process," *Hydrometallurgy*, **2**, 315 (1976/1977).

Matulevicius, E. S. and N. N. Li, "Facilitated Transport through Liquid Membranes," *Sep. Purif. Methods*, **4**, 73 (1975).

Maugh, T. H., "Liquid Membranes: New Techniques for Separation, Purification," *Science*, 193, 134 (1976).

May, S. W. and N. N. Li, "The Immobilization of Urease Using Liquid-Surfactant Membranes," *Biochem. Biophys. Res. Commun.*, **47**, 1179 (1972).

———, "Encapsulation of Enzymes in Liquid Membrane Emulsions," *Enzyme Engineering*, E. K. Pye and L. B. Wingaard, eds., **1**, p. 77, Plenum Press, New York (1974).

———, "Liquid-Membrane-Encapsulated Enzymes," *Biomedical Applications of Immobilized Enzymes and Proteins*, T. M. S. Chang, ed., **1**, p. 171, Plenum Press, New York, (1977).

Mellan, I., *Industrial Solvents Handbook*, 2nd ed., p. 306, Noyes Data Corp., NJ (1977).

Mohan, R. R. and N. N. Li, "Reductions and Separation of Nitrate and Nitrite by Liquid Membrane-Encapsulated Enzymes," *Biotechnol. Bioeng.*, **16**, 513 (1974).

———, "Nitrate and Nitrite Reduction by Liquid Membrane-Encapsulated Whole Cells," *ibid.*, **17**, 1137 (1975).

Ollis, D. F., J. B. Thompson, and E. T. Wolynic, "Catalytic Liquid Membrane Reactor: I. Concept and Preliminary Experiments in Acetaldehyde Synthesis," *AIChE J.*, **18**, 457 (1972).

Pedroso, R. I. and G. A. Domoto, "Perturbation Solutions for Spherical Solidification of Saturated Liquids," *Trans. ASME J. Heat Transfer*, **95**, 42 (1973a).

———, "Inward Spherical Solidification-Solution by the Method of Strained Coordinates," *Int. J. Heat Mass Transfer*, **16**, 1037 (1973b).

Reid, R. C., J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids*, 3rd ed., Chap. 11, McGraw-Hill, New York (1977).

Rumscheidt, F. D. and S. G. Mason, "Particle Motions in Sheared Suspensions: XI. Internal Circulation in Fluid Droplets," *J. Colloid Sci.*, **16**, 210 (1961).

Schiffer, D. K., A. Hochhauser, D. F. Evans, and E. L. Cussler, "Concentrating Solutes with Membranes Containing Carriers," *Nature*, **250**, 484 (1974).

Shah, N. D. and T. C. Owens, "Separation of Benzene and Hexane with Liquid Membrane Technique," *Ind. Eng. Chem. Prod. Res. Develop.*, **11**, 58 (1972).

Shanks, D., "Non-Linear Transformations of Divergent and Slowly Convergent Sequences," *J. Math. Phys.*, **34**, 1 (1955).

Strzelbicki, J. and W. Charewicz, "The Liquid Surfactant Membrane Separation of Copper, Cobalt and Nickel from Multicomponent Aqueous Solutions," *Hydrometallurgy*, **5**, 243 (1980).

Tavlarides, L. L., C. A. Coulaloglou, M. A. Zeitlin, G. E. Klinzing, and B. Gal-Or, "Bubble and Drop Phenomena," *Ind. Eng. Chem.*, **62**, 6 (1970).

Terry, R. E., N. N. Li, and W. S. Ho, "Extraction of Phenolic Compounds and Organic Acids by Liquid Membranes," *J. Membrane Sci.* (1981).

Völkel, W., W. Halwachs, and K. Schügerl, "Copper Extraction by Means of a Liquid Surfactant Membrane Process," *J. Membrane Sci.*, **6**, 19 (1980).

Wolynic, E. T. and D. F. Ollis, "The Catalytic Liquid Membrane Reactor Making Acetaldehyde," *CHEMTECH*, 111 (Feb., 1974).

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