# Extraction with Double Emulsions in a Batch Reactor: Effect of Continuous-Phase Resistance

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The extraction of solutes with double emulsions is a new separation process which has received considerable attention for treating waste water and enriching heavy metal ions. The use of double emulsions in separation processes was demonstrated by Li and Shrier (1972) with liquid surfactant membranes. The liquid surfactant membranes are essentially double emulsions of either the water/oil/water or oil/water/oil type. The drops are made up of the liquid surfactant phase (membrane phase) which contains small subdrops of a reagent phase which serves to sequester chemical species. The double emulsion drops are usually from 50 $\mu$m to several mm and the subdrops are usually 1 to 10 $\mu$m. A solute to be extracted from the continuous phase diffuses through the membrane phase of the double emulsion drops and then reacts with an appropriate reagent in the reagent phase. The transformed solute remains trapped in the subdrops if its permeability properties in the membrane phase are poor.

Because of the high surface area to volume ratio, short diffusion distances, and the good permeability characteristics of liquid membranes, extraction with a double emulsion is an attractive separation system. Double emulsions have been studied in a wide variety of separation processes, for example, waste water treatment (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 extraction of metal ions (Shiffer et al., 1974; Hochhauser and Cussler, 1975; Martin and Davies, 1976/1977; Lee et al., 1978; Kondo et al., 1979; Boyadzhiev and Kyuchoukov, 1980; Völkel et al., 1980; Kondo et al., 1981). These separation processes have been reviewed in the literature (Marr and Kopp, 1982; Stroeve and Varanasi, 1982).

A number of theoretical treatments on extraction with double emulsions have been presented in the literature. In general, the double emulsion drop has been modelled in three different ways: 1) planar geometry with the liquid membrane phase presenting a flat layer separating the continuous and reagent phases (Cahn and Li, 1974); 2) the spherical shell model in which the subdrops are assumed to form one large coalesced subdrop of reagent phase within the spherical membrane phase (Matulevicius and Li, 1975); 3) the integral mass balance technique (Kremesec, 1981; Kremesec and Slattery, 1982); and 4) homogeneous drops with effective transport parameters and an average reagent concentration throughout the drop (Ho et al., 1982). The model by Ho et al. (1982) is based on an advancing front approach and gives good results in predicting batch extraction of phenol from waste water. Earlier, Kopp et al. (1978) used an advancing front model to describe extraction, but their approach was limited because they used planar geometry and they neglected the change of the solute concentration in the continuous-phase concentration.

Ho et al. (1982) improved upon the work of Kopp et al. (1978) by developing a model of diffusion-controlled mass transfer in double emulsions for uniform and homogeneous emulsion globules. The solute was assumed to react irreversibly and instantaneously with the reagent at a sharp reaction front which advances into the emulsion drop as reagent is consumed. A solution of the nonlinear differential equations was obtained by perturbation analysis. Ho et al. (1982) showed for practically all extraction situations that the zero-order perturbation solution was sufficient, and that the solution was akin to the pseudosteady-state solution.

Ho et al. (1982) considered the case of extraction in well-agitated systems where the continuous-phase mass transfer resistance is negligible. However, for many double emulsion extraction systems, strong agitation may lead to rupture of the double emulsion drops and the release of captured solute and reagent to the continuous phase (Li and Shrier, 1972; Hochhauser and Cussler, 1975; Maugh, 1976). To avoid this undesirable condition, agitation rates may have to be sufficiently low to avoid rupture of the drops. In a poorly agitated batch extractor, the continuous-phase mass transfer resistance will no longer be negligible. We have incorporated the external mass transfer resistance for extraction with double emulsions in poorly stirred fluids. Our approach is somewhat similar to the model of Ho et al. (1982), the main difference being that we make the pseudosteady-state assumption early in our advancing front model. The double emulsion dispersion is modelled as an ensemble of uniform, homogeneous drops which do not coalesce or rupture.

## THEORY

The solute from the continuous phase diffuses into the emulsion drop to the reaction front, where it is consumed by the reagent in an irreversible and instantaneous reaction. As the reagent is consumed, the reaction front recedes toward the center of the drop. For a homogeneous drop, the flux of solute arriving at the front is given by

$$D_{\text{eff}} \frac{dC}{dr} = \frac{N}{4\pi r^2} \tag{1}$$

(We have adopted the nomenclature of Ho et al., 1982.) Assuming pseudosteady-state diffusion, integration of Eq. 1 from the front to the surface of the drop yields the concentration of solute at the surface of the drop

$$C_s = \frac{N}{4\pi D_{\text{eff}}} \left( \frac{1}{R_f} - \frac{1}{R} \right) \tag{2}$$

The flux of mass from the continuous phase to the surface of the drop is

$$N = k_e 4\pi R^2 (C_e' - C_s') \tag{3}$$

where $C_s = \alpha C'_s$. Combination of Eqs. 2 and 3 leads to

$$C'_e = \frac{N}{4\pi R^2}\left\{\frac{1}{k_e} + \frac{1}{D_{\text{eff}}\alpha}\left[\frac{R(R-R_f)}{R_f}\right]\right\} \tag{4}$$

The rate that the reagent is reacted is given by the solute mass balance

$$-\frac{d}{dt}\left[\frac{4}{3}\pi R_f^3\left(\frac{V_i}{V_i+V_m}\right)C_{io}\right] = N - \frac{d}{dt}\left[\int_{R_f}^{R} C(4\pi r^2)dr\right] \tag{5}$$

The second term on the righthand side accounts for the accumulation of unreacted solute present in the region depleted of reagent. The introduction of the solute accumulation term is a partial correction for ignoring solute accumulation in Eq. 2. The correction is in most cases small, i.e., less than 10%. The introduction of the accumulation term only in Eq. 5 and not in Eq. 2 is similar to the approach used by Spaan (1973) in an advancing front model for oxygen uptake in flat hemoglobin layers. Hoofd and Kreuzer (1977) have reconsidered Spaan's problem and introduced solute accumulation terms in both the concentration profile and the solute mass balance. Their results indicate that if Spaan's accumulation term is multiplied by ⅔, Spaan's correction for flat layers becomes exact. In the case of spherical geometry, Hoofd's approach leads to unwieldy equations so that we have adopted Spaan's approach. Similar to Eq. 2, a solution for C can be obtained and substituted into the above equation. A relationship for the rate of change of the advancing front radius is then obtained

$$\frac{dR_f}{dt} = \frac{N}{\left[-4\pi R_f^2 C_{io}\left(\frac{V_i}{V_i+V_m}\right) + \frac{N}{D_{\text{eff}}}\left(\frac{R_f}{3} - \frac{R^3}{3R_f^2}\right)\right]} \tag{6}$$

The total amount of solute extracted from the continuous phase is

$$-V_e\frac{dC'_e}{dt} = nN \tag{7}$$

where the total number of double emulsion drops is given by

$$n = \frac{V_m + V_i}{\frac{4}{3}\pi R^3} \tag{8}$$

Equations 6 and 7 with the expression for the solute flux (Eq. 4) form the basis of the solution subject to the initial conditions

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

$$t = 0 \qquad C'_e = C'_{eo} \tag{10}$$

Similarly to Ho et al. (1982). the equations can be cast in dimensionless form by defining

$$\chi = \frac{R_f}{R}, \qquad \tau = \frac{\epsilon D_{\text{eff}} t}{R^2}$$

$$h = \frac{C'_e}{C'_{eo}}, \qquad \epsilon = \frac{\alpha C'_{eo}}{\left(\frac{V_i}{V_m+V_i}\right)C_{io}}$$

$$E = 3\left[\frac{V_i C_{io}}{V_e C'_{eo}}\right], \qquad m = \frac{D_{\text{eff}}\alpha}{k_e R} \tag{11}$$

The dimensionless equations obtained upon substitution of Eqs. 11 and 4 into Eqs. 6 through 10 are

$$\frac{d\chi}{d\tau} = \frac{3h}{\chi[(1-\chi^{-3})\epsilon h - 3(1-\chi) - 3\chi m]} \tag{12}$$

$$\frac{dh}{d\tau} = -\frac{hE\chi}{\chi m + 1 - \chi} \tag{13}$$

with initial conditions

$$\tau = 0 \qquad \chi = 1 \tag{14}$$

and

$$\tau = 0 \qquad h = 1 \tag{15}$$

The first-order, nonlinear differential equations were solved on the computer with the program DGEAR available from ISML (International Mathematical and Statistical Libraries, Inc., Houston, TX). The program finds approximations to the solutions of a system of first-order ordinary differential equations with initial conditions. The basic methods used by DGEAR are of the implicit linear multistep type (Gear, 1971; Hindmarsch, 1974). Equations 12 through 15 were solved to a tolerance of $1.0 \times 10^{-5}$ for the concentration of species in the continuous phase, $C'_e$. In the case of $\epsilon$ equal to zero, analytical solutions can be obtained for h and $\tau$, which are

$$h = 1 + \frac{E}{3}(\chi^3 - 1) \tag{16}$$

$$\tau = \left(\frac{1-m}{E}\right) ln\left(\frac{a^3+\chi^3}{a^3+1}\right) - \frac{\sqrt{3}}{Ea}\left[\arctan\left(\frac{2\chi-a}{a\sqrt{3}}\right) - \arctan\left(\frac{2-a}{a\sqrt{3}}\right)\right] + \frac{1}{2aE}\left[3\,ln\left(\frac{a+\chi}{a+1}\right) - ln\left(\frac{a^3+\chi^3}{a^3+1}\right)\right] \tag{17}$$

where

$$a = \left(\frac{3-E}{E}\right)^{1/3} \tag{18}$$

## RESULTS AND DISCUSSION

In the extraction of a solute, the desired solution is the dimensionless concentration in the continuous phase vs. dimensionless time, or $h$ vs. $\tau$. Eqs. 12 and 13 show that solutions for $h$ will also be a function of $E$, $\epsilon$, and $m$. The parameter $E$ is three times the ratio of equivalents internal reagent in the reagent phase to equivalents solute in the feed (continuous phase). The parameter $\epsilon$ is the ratio of total solute in the membrane and reagent phase that would be in equilibrium with the initial solute concentration in the feed to the equivalents of reagent in the internal reagent phase. Under normal extraction conditions, $\epsilon$ is smaller than 0.1 (Ho et al., 1982). The parameter m accounts for the ratio of the continuous phase mass transfer resistance to the double emulsion drop resistance and is known as the inverse Biot modulus, $Bi$, where

$$Bi = m^{-1} = \frac{k_e R}{D_{\text{eff}}\alpha}$$

For a given value of $E$, and $\epsilon$ smaller than 0.1, concentration versus time graphs are therefore a function of the inverse Biot modulus which is analogous to the Gurnie-Lurie charts for the nonreactive case of transport from a fluid to a solid body. When the inverse Biot modulus is smaller than 0.01, the continuous-phase resistance can be neglected. For values of $m > 0.01$, the effect of the continuous phase resistance becomes significant. Figure 1 shows the results of

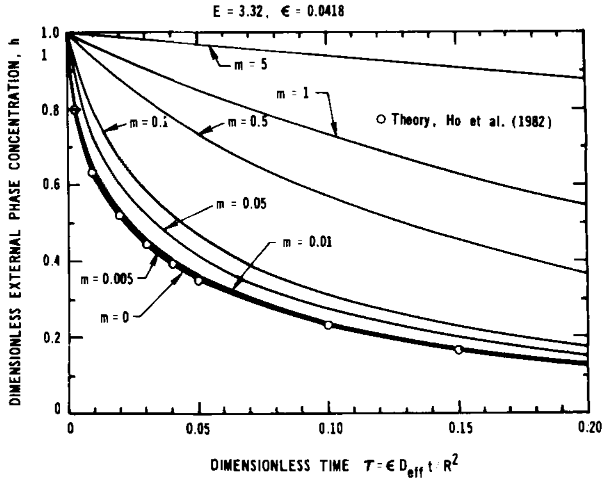

**Figure 1. Theoretical model predictions (solid lines) as a function of the inverse Biot modulus *m*. Theoretical data points (open circles) were obtained from Ho et al. (1982).**

the dimensionless concentration of the continuous phase versus dimensionless time for different values of the inverse Biot modulus. The theoretical lines are compared to the theory of Ho et al. (1982), which is valid for $m = 0$. The comparison of our theory with that of Ho et al. (1982) for $m = 0$ is excellent. For the case of a significant continuous phase mass transfer resistance ($m > 0.01$), our theory takes such an effect into account.

As an example, we calculate the inverse Biot modulus for a typical double emulsion extraction experiment. If the standard mixer has the same dimensions as the vessel used by Ho et al. (1982) than at 60 rpm the impeller Reynolds number is $10^4$ which leads to a value for $k_e$ equal to $7 \times 10^{-6}$ m/s (Skelland and Lee, 1981). For an effective solute diffusivity in the double emulsion phase of $1 \times 10^{-9}$ m$^2$/s, an equlibrium distribution coefficient of 1 and a drop size of 1 mm, the inverse Biot modulus is about $m = 0.14$. As indicated by Figure 1, this value of $m$ would lead to considerably longer extraction times than the case of $m = 0$. The values for the parameters are definitely within the realm of possibilities in double emulsion extraction systems. Good agreement between theory and experimental data where the continuous phase resistance is important has been obtained by Fales and Stroeve (1984). Higher stirring rates may lead to lower values for $m$, but maximum stirring rates may be governed by the drop's resistance to breakup due to hydrodynamic forces (Stroeve and Varanasi, 1982). It should be noted here that the inverse Biot modulus could be considerably larger if the double emulsion drop size is of the order of 100 $\mu$m instead of 1 mm.

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## NOTATION

$C$ = solute concentration in reacted region of double emulsions in equivalents per volume of emulsion
$C'_e$ = solute concentration in external, continuous phase
$C'_s$ = solute concentration in external, continuous phase at the surface of the double emulsion drop
$C'_{eo}$ = initial solute concentration in external, continuous phase
$C_{io}$ = initial concentration of reagent in reagent phase
$D_{\text{eff}}$ = effective solute diffusivity in the double emulsion drop
$E$ $= 3\dfrac{V_i C_{io}}{V_e C'_{eo}}$
$h$ = $C'_e/C'_{eo}$, normalized solute concentration in external, continuous phase
$k_e$ = continuous phase mass transfer coefficient
$m$ = inverse Biot modulus
$n$ = total number of emulsion globules dispersed in the external, continuous phase
$N$ = mass transfer rate of solute
$r$ = radial coordinate
$R$ = double emulsion radius (Sauter mean radius)
$R_f$ = reaction front position
$t$ = time
$V_e$ = external phase volume
$V_i$ = total internal reagent volume
$V_m$ = total membrane phase volume

### Greek Letters

$\alpha$ = distribution coefficient for the solute between the external phase and the reacted (exhausted) double emulsion drop at equilibrium
$\epsilon$ $= \dfrac{\alpha(V_m + V_i)C'_{eo}}{V_i C_{io}}$
$\tau$ = $\epsilon D_{\text{eff}} t/R^2$, dimensionless time
$\sigma$ = $R_f/R$, normalized reaction front

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