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Analysis of Batch, Dispersed-Emulsion, Separation Systems

An analysis of a batch, dispersed-emulsion (liquid membrane), separation system results in simple models that describe the concentrations and masses of each phase as functions of time. Comparisons with a limited set of experimental data are offered. One of these models allows a set of pilot studies to be extended to performance predictions and comparative studies of different feed-membrane-solvent combinations, which could lead to an optimally designed separation process.

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SCOPE

A liquid membrane separation system is comprised of three liquid phases. Two miscible phases are separated from each other by a third membrane phase that is insoluble with both. The interfaces are stabilized by a surfactant. The rate of mass transfer between the two miscible phases is controlled by the rate of mass transfer across the liquid membrane phase. Such systems were introduced by Li (1971a and b), who separated hydrocarbons by taking advantage of the differences among their solubilities in an aqueous membrane.

In waste water treatment (Li and Shrier, 1972) and in the removal of toxic agents from blood streams (Asher et al., 1975), a compound is transferred from one aqueous phase, across an oil membrane, into another aqueous phase where it undergoes a chemical reaction. The product of the reaction cannot cross the oil membrane because of solubility limitations.

In facilitated transport systems, a carrier molecule is placed in the liquid membrane phase (Caracciolo et al., 1975). This carrier reacts selectively with an ionic species at an interface and diffuses to the opposite interface where it releases the ion. Such a system has been demonstrated in concentrating chromium against its concentration gradient (Hochhauser and Cussler, 1975).

Two configurations of liquid membrane systems have been considered for application.

In one configuration, a mesh or porous material is saturated with the membrane phase and is placed between the solvent and feed phases. This configuration has been studied extensively and analyses have been developed to the point where data correlations and comparative studies are possible (Caracciolo et al., 1975; Schultz et al., 1974; Lee et al., 1978).

A second configuration employs a dispersed emulsion in a stirred tank (Li, 1971b; Li and Shrier, 1972; Hochhauser and Cussler, 1975). The first step is to emulsify the feed and membrane phases. This emulsion is then dispersed in the continuous solvent phase. Although experimental results indicate that this scheme is feasible (Lee et al., 1978), an analysis has not been developed that is adequate for data correlations or comparative studies. Boyadzhiev et al. (1977) have recognized in their analysis that the volumes of the phases change with time, but they assumed that the mass densities of the phases are independent of time. This would not be justified generally even for the heptane-toluene-kerosene system they studied.

Our objective is to construct an analysis for a batch, dispersed-emulsion (liquid-membrane), separation system that is adequate for data correlations or comparative studies. The components of the feed separate, because their solubilities and diffusion coefficients in the membrane differ, resulting in different rates of mass transfer across the membrane. Interphase mass transfer is described in terms of mass transfer coefficients. The masses of the feed and of the solvent phases are allowed to vary with time. The concentrations of a species on either side of an interface are related by distribution coefficients. The use of this analysis is illustrated with a limited set of experimental data.

CONCLUSIONS AND SIGNIFICANCE

An approximate analysis of a batch, dispersed-emulsion (liquid-membrane), separation system results in two simple models that describe the concentrations and masses of each phase as functions of time. The simplified variable mass model allows the masses of the feed and solvent phases to vary with time; the simplified fixed mass model assumes that the masses of the phases are independent of time. Both of these simplified models assume that the initial concentrations and masses are known and that the distribution coefficients appearing in the models can be calculated independently as functions of the concentrations.

For an N component system, the simplified variable mass

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model involves N parameters $k^{II}_{(A)}A_2$ ($A = 1, \ldots, N$) that must be determined empirically. Here $k^{II}_{(A)}$ is the film coefficient for mass transfer of species A ($A = 1, \ldots, N$) within the membrane (phase II); A_2 is the area of the membrane-solvent interface. For any given system, $N-1$ of these parameters can be identified by equating the first term of a power series solution for the simplified variable mass model with the initial experimental slope of mass fraction as a function of time for $N-1$ species. The remaining parameter can be determined by interpolation from a plot of $k^{II}_{(A)}A_2$ as a function of the pseudo-binary diffusion coefficient $\mathcal{D}\vartheta^{II}_{(Am)}$ ($A = 1, \ldots, N$) for a dilute solution of species A in the multicomponent membrane. The agreement with a limited set of experimental data is good.

This suggests that, so long as all conditions controlling mixing are held nearly constant, a limited set of pilot scale studies could be used to form a data correlation for $k^{II}_{(A)}A_2$ as a function of $\mathcal{D}^{II}_{(Am)}$. This data correlation could then be used together with the simplified variable mass model in making comparative studies and performance predictions leading to an optimally designed separation process.

For an N component system, the simplified fixed mass model involves $N-1$ parameters $k^{II}_{(A)}A_2$ ($A = 2, \ldots, N$) that must be determined empirically; $k^{II}_{(1)}A_2$ is not a free parameter, because the sum of the mass fractions is required to be unity. For any given system, these $N-1$ parameters can be identified by fitting the model to the initial experimental slope of mass fraction as a function of time for $N-1$ species. Depending upon which set of species is chosen to determine these parameters, the agreement with experimental data can be good or bad.

In the context of the simplified fixed mass model, no correlation for $k^{II}_{(A)}A_2$ as a function of $\mathcal{D}^{II}_{(Am)}$ is possible. There is no basis for using the simplified fixed mass model in making comparative studies or performance predictions.

We recommend using the simplified variable mass model.

STATEMENT OF PROBLEM

In preparing a batch, dispersed-emulsion (liquid-membrane), separation system, the feed and membrane phases are mixed to form an emulsion, and this emulsion is dispersed in a continuous solvent phase. The various species present are transferred between the feed and solvent phases. The difference in the rates at which each species is transferred across the membrane produces the separation. Our initial objective is to determine the concentration of each species in the continuous solvent phase as a function of time. We begin with a general discussion from which two special cases are identified.

GENERAL THEORY

We require the following assumptions:

i) The dispersed-emulsion system is closed. We consider only batch and not continuous processes.

ii) No chemical reactions occur.

iii) All mass transfer coefficients are constants, independent of concentration and of the rate of mass transfer.

iv) Chemical equilibrium exists at each interface.

v) The interfacial compositions are independent of position at each interface.

vi) Any effects of surfactants can be neglected.

vii) The mass fractions of the permeating species in the membrane are very small. Their concentration gradients are also very small.

viii) The mass fractions of membrane components in the feed and solvent phases are very small and they may be neglected.

ix) The mass fractions of the permeating species in the membrane phase are independent of time.

x) The total mass of the membrane phase is independent of time.

The integral overall mass balance for the solvent phase is

$$\frac{dm^{III}}{dt} = \int_{S_2} \rho^{III}(\underline{v}^{III} - \underline{u}_2) \cdot \xi_2^{III}\, dA \tag{1}$$

Since the system is closed, the time rate of change of the mass of the solvent is equal to the rate at which mass is transferred into the solvent at the moving membrane-solvent interface S_2. The superscripts I, II, III will denote respectively the encapsulated feed phase, the membrane phase, and the continuous solvent phase; subscript 1, the feed-membrane interface; subscript 2, the membrane-solvent interface. By m^{III} we mean the mass of the solvent phase; ρ^{III} is the overall mass density of the solvent; $\underline{v}^{III}$ the mass-averaged velocity of the solvent; $\underline{u}_2$ the velocity of the interface S_2; ξ_2^{III} the unit vector normal to the interface S_2 and pointing into the solvent phase; dA denotes that an area integration is to be performed. Similarly, for the feed

$$\frac{dm^{I}}{dt} = \int_{S_1} \rho^{I}(\underline{v}^{I} - \underline{u}_1) \cdot \xi_1^{I}\, dA \tag{2}$$

The integral mass balance for the feed and solvent phases requires (assumption x)

$$m^{I} + m^{III} = m_0^{I} + m_0^{III} \tag{3}$$

where the subscript 0 denotes the initial mass of each phase.

Let A be a species initially present in either the solvent or feed phases. The integral mass balance for A in the solvent says

$$\frac{d}{dt}(\omega^{III}_{(A)b}\, m^{III}) = \int_{S_2} \rho^{III}_{(A)}(\underline{v}^{III} - \underline{u}_2) \cdot \xi_2^{III}\, dA + \mathcal{J}^{III}_{(A)} \tag{4}$$

where $\omega^{III}_{(A)b}$ is the bulk or mixing-cup mass fraction of species A in the solvent and

$$\mathcal{J}^{III}_{(A)} \equiv \int_{S_2} \rho^{III}_{(A)}(\underline{v}^{III}_{(A)} - \underline{v}^{III}) \cdot \xi_2^{III}\, dA \tag{5}$$

is the rate at which species A is transferred into the solvent phase at the membrane-solvent interface measured relative to the mass-averaged velocity. We find it convenient to write this in terms of a mass transfer coefficient $k^{III}_{(A)2}$ (Bird et al., 1960):

$$\mathcal{J}^{III}_{(A)} = k^{III}_{(A)2} A_2 (\omega^{III}_{(A)2} - \omega^{III}_{(A)b}) \tag{6}$$

Here A_2 is the area of S_2; $\omega^{III}_{(A)2}$ is the mass fraction of species A in the solvent at S_2. With assumption v and Eq. 1, the first integral on the right of Eq. 4 may be rearranged as

$$\int_{S_2} \rho^{III}_{(A)}(\underline{v}^{III} - \underline{u}_2) \cdot \xi_2^{III}\, dA = \omega^{III}_{(A)2} \int_{S_2} \rho^{III}(\underline{v}^{III} - \underline{u}_2) \cdot \xi_2^{III}\, dA = \omega^{III}_{(A)2} \frac{dm^{III}}{dt} \tag{7}$$

This integral is the contribution to the rate of mass transfer of species A resulting from diffusion-induced convection. Using Eqs. 6 and 7, we can write Eq. 4 as

$$m^{III} \frac{d\omega^{III}_{(A)b}}{dt} = \left(k^{III}_{(A)2} A_2 + \frac{dm^{III}}{dt}\right)\left(\omega^{III}_{(A)2} - \omega^{III}_{(A)b}\right) \tag{8}$$

The integral mass balance for species A in the membrane phase may be written in a similar manner as

$$\frac{d}{dt}(\omega^{II}_{(A)b}\, m^{II}) = \int_{S_1} \rho^{II}_{(A)}(\underline{v}^{II} - \underline{u}_1)\cdot \underline{\xi}^{II}_1\, dA + \int_{S_2} \rho^{II}_{(A)}(\underline{v}^{II} - \underline{u}_2)\cdot \underline{\xi}^{II}_2\, dA + \mathscr{J}^{II}_{(A)1} + \mathscr{J}^{II}_{(A)2}$$
$$= -\omega^{II}_{(A)1}\frac{dm^{I}}{dt} - \omega^{II}_{(A)2}\frac{dm^{III}}{dt} + k^{II}_{(A)1}A_1(\omega^{II}_{(A)1} - \omega^{II}_{(A)b}) + k^{II}_{(A)2}A_2(\omega^{II}_{(A)2} - \omega^{II}_{(A)b}) \quad (9)$$

Neglecting the time rate of change of mass of A in the membrane phase (assumptions ix and x), we may rearrange Eq. 9 to say

$$\omega^{II}_{(A)b} = \frac{\omega^{II}_{(A)1}(k^{II}_{(A)1}A_1 - dm^{I}/dt) + \omega^{II}_{(A)2}(k^{II}_{(A)2}A_2 - dm^{III}/dt)}{k^{II}_{(A)1}A_1 + k^{II}_{(A)2}A_2} \quad (10)$$

The integral mass balance for A in the entire closed system requires (assumption vii)

$$\omega^{I}_{(A)b}\, m^{I} + \omega^{III}_{(A)b}\, m^{III} = m_{(A)0} \quad (11)$$

Here $m_{(A)0}$ is the mass of species A originally charged to the system.

The integral mass balance for species A at the membrane-solvent interface takes the form

$$\int_{S_2} \rho^{III}_{(A)}(\underline{v}^{III}_{(A)} - \underline{u}_2)\cdot \underline{\xi}^{III}_2\, dA + \int_{S_2} \rho^{II}_{(A)}(\underline{v}^{II}_{(A)} - \underline{u}_2)\cdot \underline{\xi}^{II}_2\, dA = 0 \quad (12)$$

In writing this balance, we have ignored any adsorption of A in the interface. By adding and subtracting the area integral of the product of the mass concentration and the mass-averaged velocity, the first integral on the left of Eq. 12 may be rearranged using Eqs. 5 through 7 as

$$\int_{S_2} \rho^{III}_{(A)}(\underline{v}^{III}_{(A)} - \underline{u}_2)\cdot \underline{\xi}^{III}_2\, dA = \omega^{III}_{(A)2}\frac{dm^{III}}{dt} + k^{III}_{(A)2}A_2(\omega^{III}_{(A)2} - \omega^{III}_{(A)b}) \quad (13)$$

In a similar manner, the second integral on the left of Eq. 12 takes the form

$$\int_{S_2} \rho^{II}_{(A)}(\underline{v}^{II}_{(A)} - \underline{u}_2)\cdot \underline{\xi}^{II}_2\, dA = -\omega^{II}_{(A)2}\frac{dm^{III}}{dt} + k^{II}_{(A)2}A_2(\omega^{II}_{(A)2} - \omega^{II}_{(A)b}) \quad (14)$$

Eqs. 13 and 14 permit us to express Eq. 12 as

$$k^{III}_{(A)2}A_2\,\omega^{III}_{(A)b} + k^{II}_{(A)2}A_2\,\omega^{II}_{(A)b} = \omega^{III}_{(A)2}\left(k^{III}_{(A)2}A_2 + \frac{dm^{III}}{dt}\right) + \omega^{II}_{(A)2}\left(k^{II}_{(A)2}A_2 - \frac{dm^{III}}{dt}\right) \quad (15)$$

In a similar manner, we conclude that the integral mass balance for A at the membrane-feed interface says

$$k^{I}_{(A)1}A_1\,\omega^{I}_{(A)b} + k^{II}_{(A)1}A_1\,\omega^{II}_{(A)b} = \omega^{I}_{(A)1}\left(k^{I}_{(A)1}A_1 + \frac{dm^{I}}{dt}\right) + \omega^{II}_{(A)1}\left(k^{II}_{(A)1}A_1 - \frac{dm^{I}}{dt}\right) \quad (16)$$

We assume that we have chemical equilibrium both at the membrane-feed interface (assumption iv)

$$\omega^{II}_{(A)1} = d_{(A)1}\,\omega^{I}_{(A)1} \quad (17)$$

and at the membrane-solvent interface

$$\omega^{II}_{(A)2} = d_{(A)2}\,\omega^{II}_{(A)2} \quad (18)$$

in which

$$d_{(A)1} \equiv \frac{\gamma^{I}_{(A)1}M^{I}_1}{\gamma^{II}_{(A)1}M^{II}_1} \quad (19)$$

$$d_{(A)2} \equiv \frac{\gamma^{III}_{(A)2}M^{III}_2}{\gamma^{II}_{(A)2}M^{II}_2} \quad (20)$$

are the distribution coefficients, $\gamma^{I}_{(A)1}$ is the activity coefficient for species A in the feed evaluated at the membrane-feed interface S_1, and M^{I}_1 is the molar-averaged molecular weight of the feed evaluated at the membrane-feed interface.

From Eqs. 10, 11, and 15 through 18, we find

$$\omega^{III}_{(A)2}\,f_{(A)} = g_{(A)}\,\omega^{III}_{(A)b} + h_{(A)} \quad (21)$$

where we have found it convenient to introduce

$$f_{(A)} \equiv \left(k^{III}_{(A)2}A_2 + \frac{dm^{III}}{dt}\right)\left(k^{I}_{(A)1}A_1 + \frac{dm^{I}}{dt}\right)\left(k^{II}_{(A)1}A_1 + k^{II}_{(A)2}A_2\right) + d_{(A)1}\,k^{II}_{(A)2}A_2\left(k^{III}_{(A)2}A_2 + \frac{dm^{III}}{dt}\right)\left(k^{II}_{(A)1}A_1 - \frac{dm^{I}}{dt}\right) + d_{(A)2}\,k^{II}_{(A)1}A_1\left(k^{II}_{(A)2}A_2 - \frac{dm^{III}}{dt}\right)\left(k^{I}_{(A)1}A_1 + \frac{dm^{I}}{dt}\right) \quad (22)$$

$$g_{(A)} \equiv k^{III}_{(A)2}A_2\left(k^{I}_{(A)1}A_1 + \frac{dm^{I}}{dt}\right)\left(k^{II}_{(A)1}A_1 + k^{II}_{(A)2}A_2\right) + d_{(A)1}\,k^{III}_{(A)2}A_2\,k^{II}_{(A)2}A_2\left(k^{II}_{(A)1}A_1 - \frac{dm^{I}}{dt}\right) - d_{(A)1}\,k^{I}_{(A)1}A_1\,k^{II}_{(A)2}A_2\left(k^{II}_{(A)1}A_1 - \frac{dm^{I}}{dt}\right)\frac{m^{III}}{m^{I}} \quad (23)$$

$$h_{(A)} \equiv d_{(A)1}\,k^{I}_{(A)1}A_1\,k^{II}_{(A)2}A_2\left(k^{II}_{(A)1}A_1 - \frac{dm^{I}}{dt}\right)\frac{m_{(A)0}}{m^{I}} \quad (24)$$

Eliminating $\omega^{III}_{(A)2}$ between Eqs. 8 and 21, we have

$$m^{III}\frac{d\omega^{III}_{(A)b}}{dt} = \left(k^{III}_{(A)2}A_2 + \frac{dm^{III}}{dt}\right)\left(\frac{g_{(A)}}{f_{(A)}} - 1\right)\omega^{III}_{(A)b} + \left(k^{III}_{(A)2}A_2 + \frac{dm^{III}}{dt}\right)\frac{h_{(A)}}{f_{(A)}} \quad (25)$$

Let us assume that we have N species initially present in the solvent and feed phases. Our objective is to determine the $2N$ unknowns: $\omega^{I}_{(A)b}\{A = 1, \ldots, N-1\}$, $\omega^{III}_{(A)b}\{A = 1, \ldots, N-1\}$, m^{I}, m^{III}. We might solve for these unknowns using the $2N$ equations: Eqs. 3, 11 $\{A = 1, \ldots, N-1\}$, Eq. 25 $\{A = 1, \ldots, N\}$.

SIMPLIFIED MODELS

Let us continue to identify A as a species initially present in either the solvent or feed phases.

In most cases, we will be able to make several additional assumptions that will considerably simplify our computations.

xi) Species A is relatively insoluble in the membrane phase and

$$d_{(A)1} \ll 1,\ d_{(A)2} \ll 1 \quad (26)$$

xii) Since the feed and membrane phases form a membrane-continuous emulsion that is subsequently dispersed in the solvent,

$$\frac{A_2}{A_1} \ll 1 \quad (27)$$

The diameter of the feed droplets in the membrane phase is much smaller than the diameter of the globules of membrane-feed emulsion dispersed in the solvent phase.

xiii) There is little convection within the membrane phase,

which suggests that the film coefficients for mass transfer on the membrane sides of S_1 and S_2 are nearly equal:

$$k^{II}_{(A)1} = k^{II}_{(A)2} \equiv k^{II}_{(A)} \tag{28}$$

xiv) There is little convection within the feed phase as well, indicating that the film coefficients for mass transfer on either side of S_1 will have the same order of magnitude:

$$\frac{k^{I}_{(A)1}}{k^{II}_{(A)}} \sim 1 \tag{29}$$

xv) There is considerable convection within the solvent:

$$\frac{k^{I}_{(A)1}}{k^{III}_{(A)2}} \ll 1, \frac{k^{II}_{(A)}}{k^{III}_{(A)2}} \ll 1 \tag{30}$$

xvi) For normal operating conditions, it is reasonable to assume that the ratio of the masses of the solvent and feed phases is of the order of unity.

In Eq. 25, we can rewrite the term

$$\frac{g_{(A)}}{f_{(A)}} - 1 = B_{(A)} \left\{ -d_{(A)1} \frac{m^{III}}{m^{I}} - d_{(A)2} + \frac{dm^{III}/dt}{k^{II}_{(A)} A_2} \left[d_{(A)2} - \left(\frac{A_1 + A_2}{A_1} \right) - d_{(A)1} \left(\frac{A_2}{A_1} \right) \frac{m^{III}}{m^{I}} \right] + \frac{dm^{III}/dt}{k^{I}_{(A)1} A_1} \left(d_{(A)2} - d_{(A)1} \right) - \frac{(dm^{III}/dt)^2}{k^{I}_{(A)1} A_1 k^{II}_{(A)} A_2} \left[d_{(A)2} + d_{(A)1} \frac{A_2}{A_1} - \left(\frac{A_1 + A_2}{A_1} \right) \right] \right\} \tag{31}$$

where

$$B_{(A)} \equiv \frac{k^{I}_{(A)1} (k^{II}_{(A)})^2 (A_1)^2 A_2}{f_{(A)}} \tag{32}$$

With Eqs. 26 and 27, and assumption xvi, Eq. (31) can be approximated as

$$\frac{g_{(A)}}{f_{(A)}} - 1 = B_{(A)} \left[-d_{(A)1} \frac{m^{III}}{m^{I}} - d_{(A)2} - \frac{dm^{III}/dt}{k^{II}_{(A)} A_2} + \frac{dm^{III}/dt}{k^{I}_{(A)1} A_1} (d_{(A)2} - d_{(A)1}) + \frac{(dm^{III}/dt)^2}{k^{I}_{(A)1} A_1 k^{II}_{(A)} A_2} \right] \tag{33}$$

Note from Eqs. 27 and 29 that

$$\frac{k^{II}_{(A)} A_2}{k^{I}_{(A)1} A_1} \ll 1 \tag{34}$$

or

$$\left| \frac{dm^{III}/dt}{k^{I}_{(A)1} A_1} \right| \ll \left| \frac{dm^{III}/dt}{k^{II}_{(A)} A_2} \right| \tag{35}$$

Inequalities (Eqs. 34 and 35) allow us to further reduce Eq. 33 to

$$\frac{g_{(A)}}{f_{(A)}} - 1 = B_{(A)} \left(-d_{(A)1} \frac{m^{III}}{m^{I}} - d_{(A)2} - \frac{dm^{III}/dt}{k^{II}_{(A)} A_2} \right) \tag{36}$$

In Eq. 25, we can rearrange in a similar manner

$$\frac{h_{(A)}}{f_{(A)}} = B_{(A)} d_{(A)1} \left(1 - \frac{dm^{I}/dt}{k^{II}_{(A)} A_1} \right) \frac{m_{(A)0}}{m^{I}} \tag{37}$$

The coefficient $B_{(A)}$ can be expressed in the form

$$B_{(A)} = \left\{ d_{(A)2} + \frac{k^{III}_{(A)2} A_2}{k^{II}_{(A)} A_2} \left(\frac{A_1 + A_2}{A_1} \right) + d_{(A)1} \frac{k^{III}_{(A)2} A_2}{k^{I}_{(A)1} A_1} + \frac{dm^{III}/dt}{k^{I}_{(A)1} A_1} (d_{(A)1} - d_{(A)2}) + \frac{dm^{III}/dt}{k^{II}_{(A)} A_2} \left[\left(\frac{A_1 + A_2}{A_1} \right) - d_{(A)2} \right] + \frac{k^{III}_{(A)2} A_2 \, dm^{III}/dt}{k^{I}_{(A)1} A_1 k^{II}_{(A)} A_2} \left[d_{(A)1} \left(\frac{A_2}{A_1} \right) - \left(\frac{A_1 + A_2}{A_1} \right) \right] + \frac{(dm^{III}/dt)^2}{k^{I}_{(A)1} A_1 k^{II}_{(A)} A_2} \left[d_{(A)2} + d_{(A)1} \frac{A_2}{A_1} - \left(\frac{A_1 + A_2}{A_1} \right) \right] \right\}^{-1} \tag{38}$$

In view of Eqs. 26 through 30, 34 and 35, $B_{(A)}$ collapses to

$$B_{(A)} = k^{II}_{(A)} A_2 \left(k^{III}_{(A)2} A_2 + \frac{dm^{III}}{dt} - \frac{k^{III}_{(A)2} A_2}{k^{I}_{(A)1} A_1} \frac{dm^{III}}{dt} \right)^{-1} \tag{39}$$

From Eq. 3 together with assumption v, we have

$$\frac{dm^{III}}{dt} = -\frac{dm^{I}}{dt} = \frac{1}{\omega^{II}_{(A)1}} \int_{S_1} \rho^{II}_{(A)} (\underline{v}^{II} - \underline{u}_1) \cdot \underline{\xi}^{II}_1 \, dA \tag{40}$$

where the integral on the right denotes the rate at which mass of species A is transferred from S_1 into the membrane phase II as the result of diffusion-induced, convective mass transfer. We can say by analogy with Eqs. 5 and 6 that

$$\mathcal{J}^{II}_{(A)1} \equiv \int_{S_1} \rho^{II}_{(A)} (\underline{v}^{II}_{(A)} - \underline{v}^{II}) \cdot \underline{\xi}^{II}_1 \, dA = k^{II}_{(A)1} A_1 (\omega^{II}_{(A)1} - \omega^{II}_{(A)b}) \tag{41}$$

in which $\mathcal{J}^{II}_{(A)1}$ is the rate at which mass of species A is transferred from S_1 into the membrane phase II by diffusion. Equations 40 and 41 permit us to observe that

$$\frac{dm^{III}/dt}{k^{I}_{(A)1} A_1} = \frac{(\omega^{II}_{(A)1} - \omega^{II}_{(A)b})}{\omega^{II}_{(A)1} \mathcal{J}^{II}_{(A)}} \int_{S_1} \rho^{II}_{(A)} (\underline{v}^{II} - \underline{u}_1) \cdot \underline{\xi}^{II}_1 \, dA \tag{42}$$

By assumption vii, the membrane is a dilute solution of A and the effect of diffusion-induced convection should be negligible with respect to diffusion (Slattery, 1981):

$$\left| \frac{1}{\mathcal{J}^{II}_{(A)}} \int_{S_1} \rho^{II}_{(A)} (\underline{v}^{II} - \underline{u}_1) \cdot \underline{\xi}^{II}_1 \, dA \right| \ll 1 \tag{43}$$

Since the concentration gradients in the membrane are small (assumption vii)

$$\left| \frac{\omega^{II}_{(A)1} - \omega^{II}_{(A)b}}{\omega^{II}_{(A)1}} \right| < 1 \tag{44}$$

we use Eqs. 29 and 42 through 44 to reason

$$\left| \frac{dm^{III}/dt}{k^{I}_{(A)1} A_1} \right| = \left| \frac{dm^{III}/dt}{k^{II}_{(A)} A_1} \right| \ll 1 \tag{45}$$

Returning to Eq. 39, we conclude

$$B_{(A)} = k^{II}_{(A)} A_2 \left(k^{III}_{(A)2} A_2 + \frac{dm^{III}}{dt} \right)^{-1} \tag{46}$$

By Eqs. 3 and 45,

$$\left| \frac{dm^{I}/dt}{k^{II}_{(A)} A_1} \right| \ll 1 \tag{47}$$

and Eq. 37 reduces to

$$\frac{h_{(A)}}{f_{(A)}} = B_{(A)} d_{(A)1} \frac{m_{(A)0}}{m^{I}} \tag{48}$$

As a result of Eqs. 36, 46, and 48, Eq. 25 becomes

$$m^{III} \frac{d\omega^{III}_{(A)b}}{dt} = -k^{II}_{(A)} A_2 \left(d_{(A)2} + d_{(A)1} \frac{m^{III}}{m^{I}} + \frac{dm^{III}/dt}{k^{II}_{(A)} A_2} \right) \omega^{III}_{(A)b} + d_{(A)1} k^{II}_{(A)} A_2 \frac{m_{(A)0}}{m^{I}} \tag{49}$$

which must be integrated consistent with the initial conditions ($A = 1, \ldots, N$)

$$\text{at } t = 0: \ \omega^{III}_{(A)b} = \omega^{III}_{(A)0} \tag{50}$$

We will refer to this as the *simplified variable mass model.*

In order to determine the $N+2$ unknowns $\omega^{III}_{(A)b}$ ($A = 1, \ldots, N$), m^{I}, and m^{III}, we must solve simultaneously Eqs. 3 and 49 ($A = 1, \ldots, N$) and we must require that the sum of the mass fractions equal unity. This set of equations involves N parameters $k^{II}_{(A)} A_2$ ($A = 1, \ldots, N$) that must be determined empirically. (See DETERMINATION of $k^{II}_{(A)} A_2$ for reduction of the number of free parameters to $N-1$.)

TABLE 1. INITIAL COMPONENT MASSES CHARGED TO EACH PHASE

Run	Feed Components	Initial Mass of Feed Components, g	Membrane Components[a]	Initial Mass of Membrane Components, g	Initial Mass of o-xylene, the Solvent, g
1	toluene	42.73	water	60.01	436.0
	n-heptane	33.53	glycerol	143.6	
2	benzene	44.06	water	60.67	430.1
	toluene	42.45	glycerol	140.1	
3	toluene	43.22	water	60.75	436.5
	n-heptane	33.49	glycerol	140.3	

[a] Initially, the membrane also contained approximately one percent by weight saponin.

The distribution coefficients at each interface must be calculated from Eqs. 19 and 20 using assumptions iv and vi. In integrating Eq. 49, we recommend another assumption for the sake of simplicity:

xvii) The distribution coefficients $d_{(A)1}$ and $d_{(A)2}$ are constants, independent of time.

Support for this assumption will be given later.

The corresponding mass fractions $\omega^{I}_{(A)b}$ $(A = 1, \ldots, N)$ in the feed phase can subsequently be determined from Eq. 11.

A power series solution for the simplified variable mass model is given in the Appendix for use in correlating data. Because convergence of the power series is slow, a numerical solution is preferred for predicting behavior at long times.

In some situations, we may be willing to say

xviii) The masses of the solvent and feed phases are constants, independent of time. This permits Eq. 49 to be immediately integrated consistent with Eq. 50 to obtain the *simplified fixed mass model*

$$\omega^{III}_{(A)b} = \frac{d_{(A)1}m_{(A)0}}{(d_{(A)2}m^{I} + d_{(A)1}m^{III})} + \left[\omega^{III}_{(A)0} - \frac{d_{(A)1}m_{(A)0}}{(d_{(A)2}m^{I} + d_{(A)1}m^{III})}\right] x \exp\left[-\left(d_{(A)2} + d_{(A)1}\frac{m^{III}}{m^{I}}\right)\frac{k^{II}_{(A)}A_2}{m^{III}}t\right] \quad (51)$$

With the simplified fixed mass model, there are only $N-1$ unknowns $\omega^{III}_{(A)b}$ $(A = 1, \ldots, N-1)$ and $N-1$ parameters $k^{II}_{(A)}A_2$ $(A = 1, \ldots, N-1)$ that must be determined empirically, since the sum of the mass fractions is required to be unity.

EXPERIMENTAL STUDIES

The experimental procedure followed that of Li (1971b).

In all cases, a binary hydrocarbon mixture was separated by means of a glycerol-water membrane and o-xylene solvent. Glycerol (~70% by weight) and saponin (a surfactant, ~1% by weight) were added to the water in order to obtain a stable emulsion. All hydrocarbons contained traces of water and other impurities that were ignored. The initial masses are given in Table 1.

The hydrocarbons, glycerol, water, and saponin were agitated in a blender at a low setting for one minute to form a stable emulsion with glycerol-water as the external phase. This emulsion was added to a 1,500 mL beaker containing the o-xylene solvent and dispersed with a two-inch propeller. For the three runs reported in here, there were differences in the speed of the propeller and its height above the bottom of the beaker. This altered the dispersion of the emulsion in the solvent.

The mass fraction of each species in the solvent was followed as a function of time with a gas chromatograph.

DETERMINATION OF DISTRIBUTION COEFFICIENTS

The distribution coefficient, which governs the equilibrium concentration of a species between phases, is a function of the activity coefficient of the component in each phase adjoining the interface. Expressions for the activity coefficient are generally functions of the mole fractions of the species present and a semi-empirical set of constants which represent interactions between molecules. These expressions have limitations as to the type of system they can describe.

The NRTL (non-random two liquid) correlation for activity coefficients (Renon and Prausnitz, 1968) was adopted, since it has been found to be reliable in predicting multicomponent behavior in immiscible systems using only binary coefficients (Renon and Prausnitz, 1968; Joy and Kyle, 1970; Guffey and Wehe, 1972). The binary coefficients for the NRTL equation were obtained from regular solution theory, from mutual solubility data, from activity coefficients at infinite dilution, from vapor-liquid equilibrium data, and from ternary equilibrium data (Kremesec, 1975).

Two sets of distribution coefficients were computed for each experiment. The first set assumes

xix) The mole fractions of the various hydrocarbons are zero in the glycerol-water membrane and the mole fractions of glycerol and of water are zero both in the feed and in the solvent.

Table 2 gives the distribution coefficients calculated on the basis of the initial component masses charged to each phase. Table 3 lists the distribution coefficients computed on the basis of the final compositions predicted by the simplified variable mass model. The small difference supports assumption xvii.

A second set of distribution coefficients assumes that equilibrium was attained at each phase interface. Table 4 shows the distribution coefficients computed on the basis of the initial component masses charged to each phase. Comparison of Tables 2 and 4 supports assumption xix.

DETERMINATION OF $k^{II}_{(A)}A_2$

The experimentally determined mass fractions of hydrocarbons

TABLE 2. INITIAL DISTRIBUTION COEFFICIENTS BASED ON ASSUMPTION XIX

Run	Component	$d_{(A)1}$	$d_{(A)2}$
1	toluene	1.17×10^{-3}	1.18×10^{-3}
	n-heptane	8.41×10^{-5}	1.49×10^{-4}
	o-xylene	5.13×10^{-4}	4.98×10^{-4}
2	benzene	9.94×10^{-4}	1.25×10^{-3}
	toluene	9.13×10^{-4}	1.15×10^{-3}
	o-xylene	3.92×10^{-4}	4.93×10^{-4}
3	toluene	1.14×10^{-3}	1.15×10^{-3}
	n-heptane	7.71×10^{-5}	1.36×10^{-4}
	o-xylene	5.07×10^{-4}	4.93×10^{-4}

TABLE 3. FINAL DISTRIBUTION COEFFICIENTS BASED ON ASSUMPTION XIX

Run	Component	$d_{(A)1}$	$d_{(A)2}$
1	toluene	1.22×10^{-3}	1.17×10^{-3}
	n-heptane	9.06×10^{-5}	1.45×10^{-4}
	o-xylene	5.34×10^{-4}	4.93×10^{-4}
2	benzene	1.20×10^{-3}	1.18×10^{-3}
	toluene	1.10×10^{-3}	1.08×10^{-3}
	o-xylene	4.73×10^{-4}	4.63×10^{-4}

TABLE 4. INITIAL DISTRIBUTION COEFFICIENTS BASED ON EQUILIBRIUM AT INTERFACES

Run	Component	$d_{(A)1}$	$d_{(A)2}$
1	toluene	1.19×10^{-3}	1.19×10^{-3}
	n-heptane	8.55×10^{-5}	1.50×10^{-4}
	o-xylene	5.20×10^{-4}	4.89×10^{-4}
2	benzene	1.02×10^{-3}	1.29×10^{-3}
	toluene	9.37×10^{-4}	1.16×10^{-3}
	o-xylene	4.03×10^{-4}	4.96×10^{-4}
3	toluene	1.16×10^{-3}	1.16×10^{-3}
	n-heptane	7.96×10^{-5}	1.38×10^{-4}
	o-xylene	5.14×10^{-4}	4.96×10^{-4}

in the solvent phase are shown in Figures 1 through 4 for runs 1 and 2.

In order to compare these data with the predictions of our theory, it is necessary to determine the three free parameters $k^{II}_{(A)}A_2$ ($A = 1, \ldots, 3$). This can be done in either of two ways, depending upon whether the simplified variable mass model or the simplified fixed mass model is adopted.

When the simplified variable mass model is to be used, the first term of the power series solution (A7) in the appendix should be identified with the initial experimental slope of mass fraction as a function of time. In this way, we determined $k^{II}_{(2)}A_2$ and $k^{II}_{(3)}A_2$. Since the three mass fractions are not linearly independent, we could not fix $k^{II}_{(1)}A_2$ in the same manner. With the further assumption (Casamatta et al., 1978)

xx) The mass transfer coefficient $k^{II}_{(A)}$ is proportional to the pseudo-binary diffusion coefficient $\mathcal{D}^{II}_{(Am)}$ for a dilute solution of A in the multicomponent membrane.

we linearly interpolated (or extrapolated) $k^{II}_{(A)}A_2$ as a function of $\mathcal{D}^{II}_{(Am)}$ in order to determine $k^{II}_{(1)}A_2$. The pseudo-binary diffusion coefficients were estimated according to the recommendation of Perkins and Geankoplis (1969; Reid et al., 1977). In each case, we took the solvent, o-xylene, to be species 1. The calculated diffusion coefficients and $k^{II}_{(A)}A_2$ ($A = 1, 2, 3$) are given in Table 5.

Notice that taking advantage of a data correlation between $k^{II}_{(A)}A_2$ and $\mathcal{D}^{II}_{(Am)}$ to determine $k^{II}_{(1)}A_2$ has the effect of reducing the number of free parameters in the simplified variable mass model to $N-1$.

When the simplified fixed mass model is to be used, Eq. 51 should be fit to the initial experimental slope of mass fraction as a function of time for $N-1$ species. The values of $k^{II}_{(A)}A_2$ ($A = 1$, 2, 3) are given in Table 6, any two of which may be used as the free parameters.

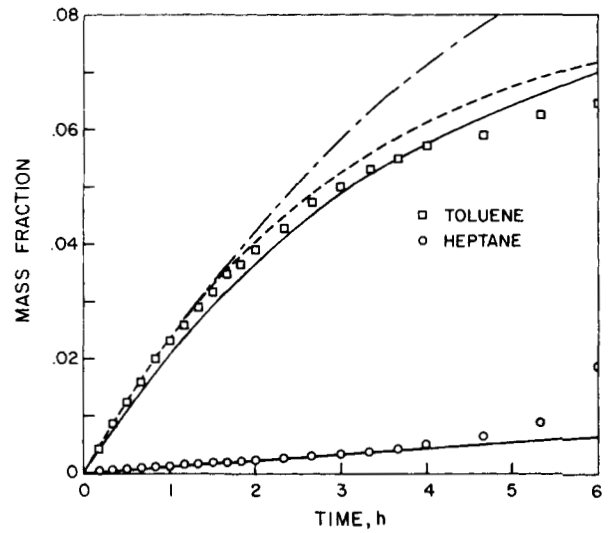

Figure 1. Mass fractions of toluene and heptane in solvent phase as functions of time for run 1; — denotes predictions of the simplified variable mass model, - - - of the simplified fixed mass model for free parameters based upon the initial slopes of the toluene and heptane curves, and - · - of the simplified fixed mass model for free parameters based upon the initial slopes of the heptane and o-xylene curves.

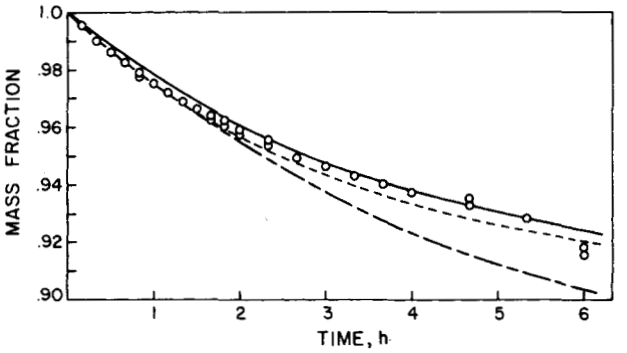

Figure 2. Mass fraction of o-xylene in solvent phase as a function of time for run 1; — denotes predictions of the simplified variable mass model, - - - of the simplified fixed mass model for free parameters based upon the initial slopes of the toluene and heptane curves, and - · - of the simplified fixed mass model for free parameters based upon the initial slopes of the heptane and o-xylene curves.

COMPARISON OF THEORY WITH EXPERIMENT

The results for runs 1 and 2 are given in Figures 1 through 4. All comparisons assume that the initial mass fractions of the feed species in the solvent phase are zero and that the distribution coefficients of Table 2 are applicable.

The predictions made using the simplified fixed mass model may be either good or bad, depending upon which set of species are chosen to determine the two free parameters. If the mass fractions of the feed components are predicted using Eq. 51 and Table 6 and if the solvent mass fraction is determined by requiring the sum of the mass fractions to be unity, the agreement between theory and experiment is good. If the mass fraction of toluene in run 1 or of benzene in run 2 is determined by insuring that the sum of the mass fractions is unity, the agreement is seen to be poor in Figures 1 and 3.

The experiments described here correspond to the special case in which the initial solvent phase contains only species 1. At least for this special case, the predictions of the simplified variable mass model are insensitive to the choice of the two species used in determining the three free parameters. (See appendix for further explanation.) We are encouraged to believe that this may be more

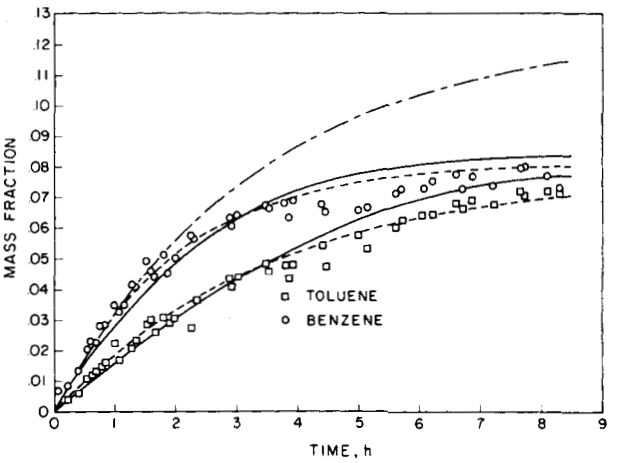

Figure 3. Mass fractions of benzene and toluene in solvent phase as functions of time for run 2; — denotes predictions of the simplified variable mass model, - - - of the simplified fixed mass model for free parameters based upon the initial slopes of the benzene and toluene curves, and - · - of the simplified fixed mass model for free parameters based upon the initial slopes of the toluene and o-xylene curves.

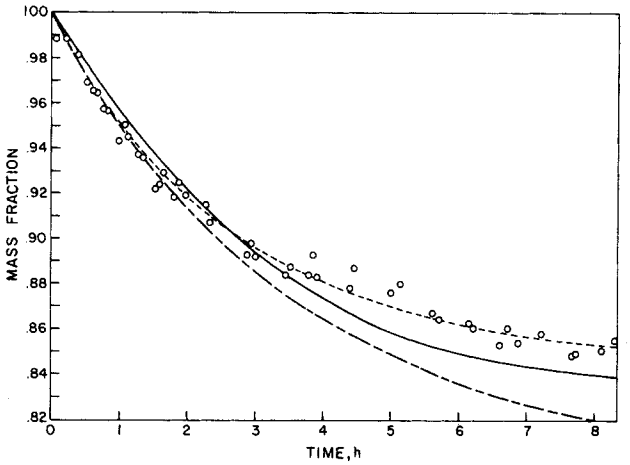

Figure 4. Mass fraction of o-xylene in solvent phase as a function of time for run 2; — denotes predictions of the simplified variable mass model, - - - of the simplified fixed mass model for free parameters based upon the initial slopes of the benzene and toluene curves, and - - - of the simplified fixed mass model for free parameters based upon the initial slopes of the toluene and o-xylene curves.

generally true, in view of the linear correlation that appears to exist between $k^{II}_{(A)}A_2$ and $\mathcal{D}^{II}_{(Am)}$.

A comparison with the theory of Boyadzhiev et al. (1977) is not shown, since that theory involves $N+1$ free parameters that must be determined empirically. The simplified variable and fixed mass models have only $N-1$ free parameters.

SOLVENT EMULSIFICATION

As others have previously reported (Li, 1971b; Hochhauser and Cussler, 1975), the membrane will rupture, if the shear rate used in dispersing the emulsion in the solvent is too large. If the shear rate used in dispersing the emulsion in the solvent is too small, the solvent is emulsified in the same manner as was the feed.

TABLE 5. $k^{II}_{(A)}A_2$ FOR SIMPLIFIED VARIABLE MASS MODEL[b]

Run	Component	Diffusion Coefficient × 10^7, cm^2/s	$k^{II}_{(A)}A_2$, g/s
1	heptane	4.35	3.53
	toluene	5.24	4.34
	o-xylene	4.74	3.89[c]
2	benzene	6.30	7.51
	toluene	5.52	4.42
	o-xylene	5.00	2.31[d]

[b] Values obtained using Eq. A9.
[c] Interpolated value.
[d] Extrapolated value.

TABLE 6. $k^{II}_{(A)}A_2$ FOR SIMPLIFIED FIXED MASS MODEL[e]

Run	Component	$k^{II}_{(A)}A_2$, g/s
1	heptane	4.27
	toluene	5.12
	o-xylene	6.59
2	benzene	9.57
	toluene	5.03
	o-xylene	13.55
3	toluene	9.23
	heptane	9.74
	o-xylene	11.44

[e] Values obtained using Eq. 51 with $\omega^{III}_{(A)0} = 0$. Any two of the three $k^{II}_{(A)}A_2$ ($A = 1, 2, 3$) may be used as the free parameters.

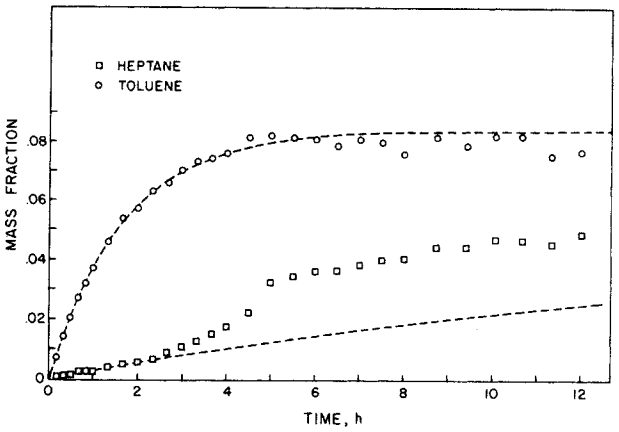

Figure 5. Mass fractions of toluene and heptane in solvent phase as functions of time for run 3; - - - denotes predictions of the simplified fixed mass model for free parameters based upon the initial slopes of the heptane and toluene curves.

The effects of solvent emulsification can be seen in Figure 5. The heptane curve for run 3 deviates considerably from that predicted by the simplified fixed mass model. Figure 6 shows that the volume of the emulsion phase increased sharply as a function of time. (The emulsion volume was determined by stopping the mixing for a few seconds and recording the level in the beaker.) As solvent was emulsified, the membrane thinned and the rate of mass transfer increased. Since heptane was the primary feed component at this point, it quickly permeated into the solvent phase, increasing the heptane concentration and reducing the effectiveness of the separation. Once a steady-state volume of emulsion was achieved, the process appeared to parallel that predicted by the simplified fixed mass model or that expected on the basis of run 1.

In designing the systems studied here, pilot tests were run with a dye, which was insoluble in the aqueous membrane and added to the feed phase. By observing the color of the solvent, we were able to make a judgement about the degree of membrane rupture and direct mixing of the feed and solvent phases. In choosing the systems for runs 1 and 2, emphasis was placed upon the effectiveness of the separation rather than upon the rate at which the separation was achieved. The long times required for the separations reported here reflect our desire to avoid membrane rupture. Less effective separations could have been obtained in shorter periods of time with some membrane rupture (Boyadzhiev et al., 1977).

SUGGESTED APPLICATION

In designing a batch, dispersed emulsion, liquid membrane separation system, we must choose the composition of the mem-

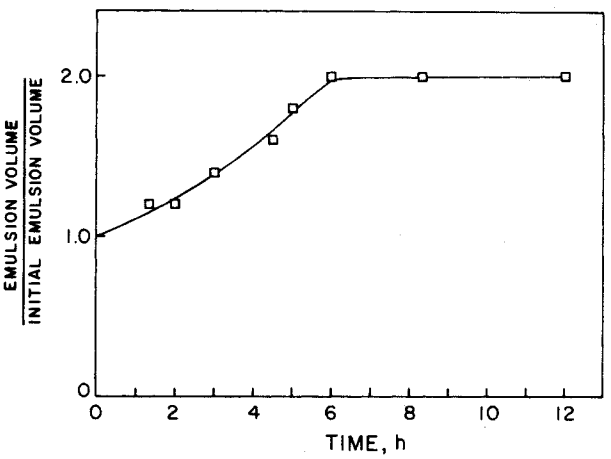

Figure 6. Volume of emulsion phase as a function of time for run 3.

brane and the solvent as well as all of the operating conditions. Pilot-scale experiments are required, but their number can be reduced by employing the theory developed here.

Beginning with tentative choices for the feed, membrane, and solvent compositions based upon a comparison of distribution coefficients, one could experimentally determine a set of mixing parameters that minimizes both solvent emulsification and membrane rupture.

After an initial set of mixing parameters has been determined, a few separation experiments should be carried out in order to construct a correlation of $k^{II}_{(A)}A_2$ as a function of the pseudo-binary diffusion coefficient $\mathcal{D}^{II}_{(Am)}$ for a dilute solution of A in the multicomponent membrane. With this correlation and predictions for the distribution coefficients, the simplified variable mass model may be used to simulate the effects of changes in feed, membrane, or solvent compositions, leading to an optimally designed separation process.

ACKNOWLEDGMENT

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APPENDIX: SERIES SOLUTION FOR SIMPLIFIED VARIABLE MASS MODEL

We can develop a Maclaurin series solution of the form

$$\omega^{III}_{(A)b} = \sum_{i=0}^{M} \alpha_{(A)i}\, t^i \tag{A1}$$

and

$$m^{III} = \sum_{i=0}^{M} b_i\, t^i \tag{A2}$$

for Eqs. 3 and 49 ($A = 1, \ldots, N$), requiring that the sum of the mass fractions must be unity. The initial conditions are Eq. 50 ($A = 1, \ldots, N$) and

$$\text{at } t = 0\text{: } m^{III} = m^{III}_0 \tag{A3}$$

In view of Eq. A3, we see immediately that

$$\alpha_{(A)0} = \omega^{III}_{(A)0},\ b_0 = m^{III}_0 \tag{A4}$$

Collecting the zero-order terms in Eq. 49 and eliminating m^I by means of Eq. 3, we find ($A = 1, \ldots, N$)

$$\alpha_{(A)1} = \frac{k^{II}_{(A)}A_2}{m^{III}_0}\left[\frac{d_{(A)1}m_{(A)0}}{m^I_0} - \omega^{III}_{(A)0}\left(d_{(A)2} + \frac{d_{(A)1}m^{III}_0}{m^I_0}\right)\right] - \frac{b_1\omega^{III}_{(A)0}}{m^{III}_0} \tag{A5}$$

Since the sum of the mass fractions must equal unity,

$$b_1 = \sum_{A=1}^{N} k^{II}_{(A)}A_2\left[\frac{d_{(A)1}m_{(A)0}}{m^I_0} - \omega^{III}_{(A)0}\left(d_{(A)2} + \frac{d_{(A)1}m^{III}_0}{m^I_0}\right)\right] \tag{A6}$$

The higher-order coefficients in Eqs. A1 and A2 can be developed in a similar fashion.

For our present purposes, Eqs. A4 through A6 will be sufficient, since all we require are the initial slopes ($A = 1, \ldots, N$)

$$\text{at } t = 0\text{: } \frac{d\omega^{III}_{(A)b}}{dt} = \alpha_{(A)1} \tag{A7}$$

Since the mass fractions are not linearly independent, Eqs. A5 through A7 permit us to determine $N-1$ of the coefficients $k^{II}_{(B)}A_2$ ($B = 1, \ldots, N$) by measuring $N-1$ of these initial slopes. The experiments described in the text correspond to the special case in which the initial solvent phase contains only species 1:

$$\omega^{III}_{(1)0} = 1,\ \omega^{III}_{(B)0} = 0 \text{ for } B \neq 1 \tag{A8}$$

In this limit, Eq. A5 reduces to

$$\sum_{A=1}^{N} \alpha_{(A)1} = 0$$

$$\alpha_{(B)1} = k^{II}_{(B)}A_2\frac{d_{(B)1}m_{(B)0}}{m^I_0 m^{III}_0} \text{ for } B \neq 1 \tag{A9}$$

No matter which $N-1$ initial slopes are chosen for measurement, $k^{II}_{(1)}A_2$ is the coefficient that can not be determined directly.

NOTATION

A_i = area of surface S_i
dA = denotes area integration to be performed
$B_{(A)}$ = defined by Eq. 32
$d_{(A)}$ = distribution coefficient for species A defined by Eqs. 19 and 20
$f_{(A)}$ = defined by Eq. 22
$g_{(A)}$ = defined by Eq. 23
$h_{(A)}$ = defined by Eq. 24
$\mathcal{J}_{(A)}$ = mass flux of species A with respect to mass averaged velocity
$k_{(A)}$ = mass transfer coefficient for species A
m = mass
M = molar averaged molecular weight
N = number of species present
S = surface
t = time
$\underline{u}_i$ = velocity of surface S_i
$\underline{v}$ = mass averaged velocity
$\underline{v}_{(A)}$ = velocity of species A

Greek Letters

$\gamma_{(A)}$ = activity coefficient for species A
$\underline{\xi}^j_i$ = unit vector normal to the interface i and directed into phase j
ρ = mass density
$\rho_{(A)}$ = mass density of species A
$\omega_{(A)}$ = mass fraction of species A

Superscripts

I, II, or III = denote feed, membrane, or solvent phase respectively

Subscripts

1 = denotes the feed-membrane interface
2 = denotes the membrane-solvent interface
0 = denotes an initial condition
b = denotes bulk concentration
(A) = denotes species A ($A = 1, \ldots, N$)

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Dissolution and Reprecipitation in Porous Solids

When a porous solid dissolves in acid, the dissolved solid can diffuse both into the bulk solution and into the solid's pores. In some cases, these dissolved species can precipitate in the pores, making the solid less permeable to acid. In other cases, the surface dissolution can produce precipitation near the surface and dissolution well below the surface. The results have implications for corrosion, including the demineralization of teeth.

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SCOPE

This work explores how diffusion and chemical reaction affect corrosion of porous ionic solids. It develops an approximate theory for this corrosion, and verifies this theory with qualitative experiments. This work emphasizes a different situation than most studies of the corrosion (Shreir, 1976). In the more common studies, acid attacks an impermeable metal. The rate of this attack depends on the speed of acid diffusion to the metal surface and the kinetics of the acid-metal reaction at this surface. These kinetics are often influenced by fast electron transport in the metal. Because diffusion and chemical reaction occur sequentially, the overall corrosion rate depends on the sum of the resistances of diffusion and of reaction.

In this study, acid attacks a porous ionic solid. Again, the rate of attack is affected by acid and ion diffusion and by any acid-solid chemical reactions. Now, little electron transport occurs in the ionic solid. Now, diffusion and reaction occur within the pores of the solid. The overall rate of reaction now is more analogous to the idea of an effectiveness factor than to the more familiar idea of resistances in series (Carberry, 1976).

This work is limited to cases where much of the corrosion occurs within the solid's pores. It emphasizes cases where the acid-solid reaction is anything but first order. First order cases produce expected and routine results; non-linear examples lead to interesting answers. The basic strategy used in the work is to assume that the reactions are all diffusion controlled, but subject to non-linear chemical equilibria between the various ionic species present. These assumptions are roughly parallel to those used in metallurgy to explain unexpected phase separations (Kirkaldy and Brown, 1963). Their consequences are explored using mathematical approximations developed for membrane transport (Ward, 1970; Cussler, 1971) and for the theory of fog formation (Toor, 1971a,b). These consequences lead to a startling spectrum of surprising results.

CONCLUSIONS AND SIGNIFICANCE

When an acid attacks a porous ionic solid, it often dissolves the material near the solid's surface. When this dissolved material and the acid both diffuse into the solid's pores, they produce a variety of effects. These include:

(1) Further dissolution of the solid when the solid's solubility depends on the acid concentration to less than the first power.
(2) Precipitation of more solid in the pores when the solid's solubility depends on the acid concentration to the second power.
(3) Precipitation of one compound and dissolution of a second compound when the porous solid is a mixture.
(4) Precipitation of the solid in one region and dissolution of this solid in a different region.

These results are predicted from the theory developed below. The theory assumes that the non-linear reactions during the

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