Separation & Purification Reviews
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597294

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To cite this Article Kremesec, V. J.(1981) 'Modeling of Dispersed-Emulsion Separation Systems', Separation & Purification Reviews, 10: 2, 117 — 157
To link to this Article: DOI: 10.1080/03602548108066010
URL: http://dx.doi.org/10.1080/03602548108066010

SEPARATION AND PURIFICATION METHODS, 10(2), 117-157 (1981)

MODELING OF DISPERSED-EMULSION SEPARATION SYSTEMS

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INTRODUCTION

A dispersed-emulsion separation system is a type or configuration of liquid-membrane separation systems. Such systems are comprised of three liquid phases: two of these liquid phases are miscible with each other but are separated by a third liquid phase (the membrane) which is immiscible with both. The interfaces may be stabilized by a surfactant. Mass is transferred from one of the miscible phases across the liquid membrane to the second miscible phase. These systems were introduced by Li[1,2].

Liquid membranes can be used to cause a highly specific separation by a variety of mechanisms. In the systems introduced by Li[1,2], hydrocarbons were separated because of their widely differing solubilities in a water membrane. The large solubility difference causes large differences in the rates of mass transfer across the membrane.

In other applications, the membrane acts as an encapsulating agent. In waste-water treatment[3] and in the removal of toxic agents from the blood stream[4], a contaminant 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 still another application, a carrier molecule is placed in the liquid-membrane phase. This carrier reacts selectively with a contaminant at one of the interfaces to form a contaminant-carrier complex which diffuses to the opposite interface where the carrier releases the contaminant. Mass transfer across the membrane occurs due to the concentration gradient of the contaminant-carrier complex. In facilitated transport systems, the formation and disintegration of the contaminant-carrier complex occurs simply because of the differing concentration of contaminant on either side of the membrane. Such systems simulate life processes, such as the oxygen-hemoglobin system, but also have been used to separate CO_2, H_2S, and CO[6,7,8]. In carrier-mediated systems, the formation and disintegration of the contaminant-carrier complex is generally driven by a large difference in the pH of the phases on either side of the membrane. Such systems have been used to concentrate contaminants (metal cations) against their concentration gradients[9-12].

There are two primary configurations of liquid membrane systems that have been considered for practical applications -- the dispersed emulsion configuration and the supported membrane configuration. The dispersed-emulsion system is prepared by first emulsifying one of the miscible phases with the membrane phase. For the hydrocarbon separation introduced by Li[1,2], an oil-in-water emulsion is prepared -- the oil dispersed as very fine droplets in the water. This emulsion is dispersed in a continuous phase -- for the example here, a second hydrocarbon phase. The emulsion is kept dispersed in the continuous phase by constant agitation (Figure 1). The second configuration is that of a supported membrane (Figure 1). A mesh or porous material is saturated with a membrane phase and is placed between the solvent and the feed phases. Either of these configurations can be set up in

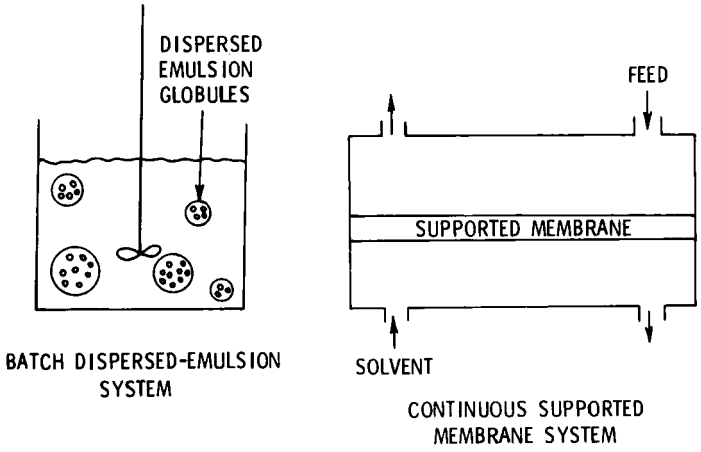

FIGURE 1

Possible processing configurations for liquid membrane systems.

a batch or continuous flow processing scheme. The dispersed-emulsion system could be a series of continuous stirred tanks; the supported membrane in a countercurrent flow scheme.

Each configuration has certain advantages and disadvantages. The dispersed-emulsion configuration has a very high interfacial area and so, theoretically, the mass fluxes could be very high. However, thin membranes can be unstable and rupture and thick membranes might emulsify some of the continuous phase, both of which phenomena give poor separation. The supported membranes, on the other hand, have no stability problems; but they are generally thicker and have considerably less area available for mass transfer, both of which phenomena reduces the total mass flux.

The primary emphasis of this review will be on the modeling of the mass transport in the dispersed-emulsion separation system. However, in what follows, the modeling of supported liquid membranes will be discussed. This is because a large literature exists in this area, and it is natural to attempt to extend this work to dispersed-emulsion systems. The supported membrane models assume that the resistances to mass transfer of the phases on either side of the membrane are negligible, and they use the differential mass balances across the membrane as the basic modeling tool. In extending the supported membrane models to the dispersed emulsion systems, geometrical simplifications are necessary. The extensions to dispersed-emulsion systems will be reviewed. Perhaps the most serious drawback to this approach is that one cannot

necessarily follow at long times the time rate of change of concentration in the encapsulated and external-continuous phases because there is no requirement to satisfy the time dependent mass balances in these phases. One is simply modeling transport within the membrane.

An alternative modeling approach is to use the integral mass balances to describe the mass flux in the dispersed-emulsion system. By an integral approach is meant that the time rate of change of the bulk or mixing cup concentration of the phases is the focal point of the model rather than the point concentration changes along the diffusion path, as is the case with the differential mass balances. With the integral approach, it is not necessary to simplify the geometry of the dispersed-emulsion system or to neglect the resistances to mass transfer in the inner and outer phases. There is one instance where the resistances of the external phase might be controlling[13], and it has been estimated that geometrical simplifications can lead to errors of 20%[14,15]. Further, because the interfaces are stabilized by a surfactant, it is reasonable to assume that there is little convection within the inner encapsulated phase droplets and hence its resistance to mass transfer might be significant.

An example of the integral modeling approach as applied to the separation of hydrocarbons in a dispersed-emulsion system will be given. Apparently, the only information one loses, in applying this integral approach instead of the differential balance, is the

nature of the dependence of the process upon the diffusion coefficient in the membrane; or in other words, an expression for the mass transfer coefficient in terms of the diffusion coefficient is not obtained. Although this information can be critical, it can easily be determined by matching experiment and theory. An example will be shown. Matching procedures must also be carried out with the extended differential balances because the value of the product of an effective length and/or area and the effective diffusion coefficient in the supported structure must be determined.

MODELS USING DIFFERENTIAL BALANCES

Supported Membranes

Models of transport across flat or supported liquid membranes generally assume:

(1) The phases on either side of the membrane are well mixed; and hence, the concentration gradient of the permeating species on either side of the membrane is zero.

(2) The liquid membrane is stagnant.

(3) The system is at steady state.

(4) The diffusivities are constant.

(5) Chemical equilibrium exists at each interface.

The assumed physical situation is depicted in Figure 2 for a facilitated transport system.

Schultz, Goddard, and Suchedo[17] have given a comprehensive review of the modeling of the flat liquid membrane systems. The brief descriptions below have been drawn primarily from Smith, Meldon, and Colton[5] and Smith, Lander, and Quinn[18].

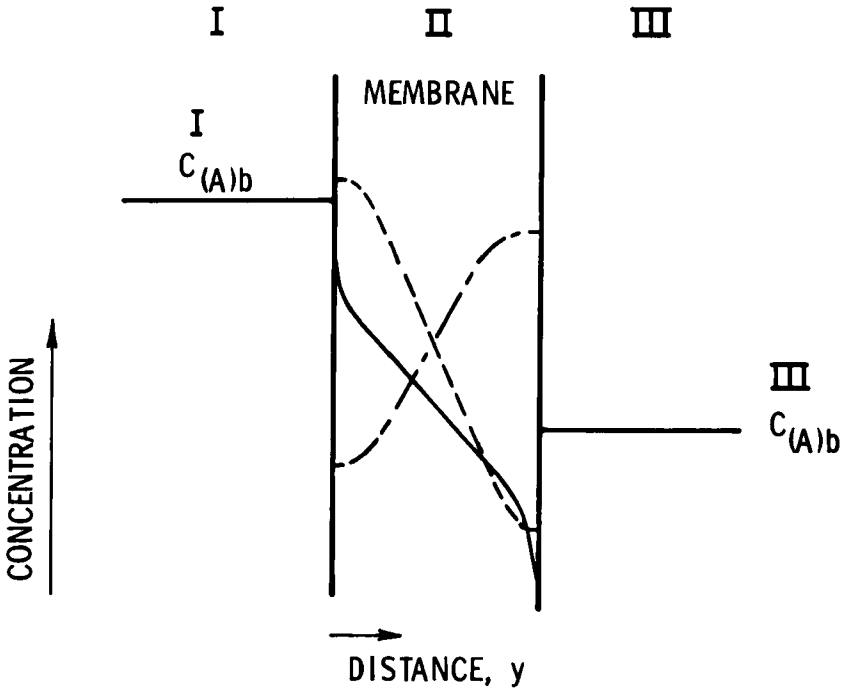

FIGURE 2

Schematic of concentration distribution during facilitated transport through a membrane by concentration difference of pure A and the formation of a contaminant-carrier complex. In the membrane, — denotes concentration of permanent A, --- denotes concentration of contaminant-carrier complex, and — - — denotes concentration of carrier B.

Concentration Differences of Pure A: When no carrier has been added to the membrane, separation occurs because of the concentration difference on either side of the membrane. The molar flux of species A in the membrane is given by:

$$N^{II}_{(A)} = \frac{D^{II}_{(Am)} c^{II} A}{L} (x^{II}_{(A)1} - x^{II}_{(A)2}) \quad (1)$$

in which the superscripts I, II, and III, refer to the three phases identified in Figure 2, subscripts 1 and 2 refer to the I-II and II-III interfaces, respectively, $N_{(A)}$ is the molar flux of species A, $D_{(Am)}$ is the pseudo-binary diffusion coefficient, A is the effective area, L is the thickness of the membrane, c is the molar density, and $x_{(A)}$ is the mole fraction.

Facilitated Transport: As an example of the modeling of facilitated transport and carrier-mediated transport that has been carried out, let us consider the simplest case of a carrier molecule, B, which undergoes a first order reversible reaction with the permeant species A to form the contaminant-carrier complex AB:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AB \quad (2)$$

For the facilitated transport system, the complex is formed at the interface where the concentration of A is greater and dissociates at the opposite interface where the concentration of A is

considerably less. The association and dissociation are governed by the equilibrium coefficient defined as

$$K = \frac{k_1}{k_{-1}} = \frac{c^{II}_{(AB)}}{c^{II}_{(A)}\, c^{II}_{(B)}} \tag{3}$$

For the carrier-mediated system, a reaction, such as (2), is driven by pH differences in the phases bounding the interfaces, but the equilibrium relation can still be expressed in the form of equation (3).

The species mole balances of the diffusing-reacting species in the stagnant membrane are:

$$D^{II}_{(Am)} \frac{d^2 c^{II}_{(A)}}{dy^2} = r$$

$$D^{II}_{(Bm)} \frac{d^2 c^{II}_{(B)}}{dy^2} = r \tag{4}$$

$$D^{II}_{(ABm)} \frac{d^2 c^{II}_{(AB)}}{dy^2} = -r$$

where

$$r = k_1 c^{II}_{(A)} c^{II}_{(B)} - k_{-1} c^{II}_{(AB)} \tag{5}$$

In general, one assumes that $D^{II}_{(Bm)} = D^{II}_{(ABm)}$ because the carrier molecule is usually significantly larger than the permeant molecule.

The boundary conditions are:

$$\text{at } y = 0: \quad c^{II}_{(A)} = c^{II}_{(A)1}$$

$$\text{at } y = L: \quad c^{II}_{(A)} = c^{II}_{(A)2} \tag{6}$$

and

$$\text{at } y = 0, L: \quad \frac{d\, c^{II}_{(AB)}}{dy} = \frac{d\, c^{II}_{(B)}}{dy} = 0 \,. \tag{7}$$

Goddard et al.[19] have pointed out that of the four conditions expressed by (6) and (7) only three are independent. As a last constraint, conservation of the carrier in the membrane is required:

$$\frac{1}{L} \int_0^L (c^{II}_{(AB)} + c^{II}_{(B)})dy = c^{II}_{(B)0} \,. \tag{8}$$

Useful approximate analytical solutions for this problem have been developed for cases where the Damkohler number,

$$N_{Da} = \frac{k_{-1} L^2}{D^{II}_{(Am)}} \,, \tag{9}$$

is either very large or very small. The Damkohler number is the ratio of reaction time to diffusion time. For cases of slow reaction where diffusion time predominates (or for very thin membranes), the approximate solution of (4) through (8) is a power series of the form[5]

$$\frac{N^T_{(A)}}{N_{(A)}} = 1 + \frac{1}{12} N_{Da} \frac{K c^{II}_{(B)0}}{K \bar{c}^{II}_{(A)} + 1} + 0(N^2_{Da}) \qquad (10)$$

in which

$$\bar{c}^{II}_{(A)} = \frac{c^{II}_{(A)1} + c^{II}_{(A)2}}{2},$$

$N^T_{(A)}$ is the mass flux due to both facilitated or carrier-mediated transport and diffusion of pure A, and $N_{(A)}$ is the mass flux due strictly to diffusion of pure species A which is given by equation (1).

For large Damkohler numbers (fast reaction or thick membranes), the approximate solution consists of three simultaneous equations which must be solved by trial and error. Smith et al.[5] show a very favorable comparison of the predictions of the approximate solutions with the numerical results of Kutchai et al.[20] for an oxygen-hemoglobin system.

However, the most common assumption is that the Damkohler number is infinite. In this case, the reaction is very fast and the per-

meant and carrier are at equilibrium everywhere within the membrane and at its boundaries. The solution is easily obtained[19,18]:

$$\frac{N^{T}_{(A)}}{N_{(A)}} = 1 + \frac{D^{II}_{(Am)}\, K\, c^{II}_{(B)0}}{D^{II}_{(Am)}\,(1 + K\, c^{II}_{(A)1})(1 + K\, c^{II}_{(A)2})} \qquad (11)$$

Solutions have also been given for more complex reactions[16,21,22].

In supported systems, the diffusion coefficient is an effective diffusion coefficient because of the tortuous path through the porous support. Equation (11) is generally multiplied by an effective area to obtain the total mass flux across the membrane. The product of the area and the effective diffusion coefficient may be determined by curve fitting of the theory to experiment. The equilibrium coefficient is determined by separate experiment. In most applications, if the mass flux data can be fit to (11) or one developed for more complex reactions, it is assumed that the kinetics have been modeled correctly.

Dispersed Emulsions

The models for the dispersed-emulsion configuration which employ the differential balances can be characterized as describing mass transport between concentric spherical shells. In the most brute force approach, one simply assumes that all of the fine droplets

are coalesced into a single large droplet, and the process consists of diffusion across a stagnant membrane of length δ (see Figure 3). Furthermore, in addition to the previous assumptions, it is also assumed that:

(6) Any effects of surfactants can be neglected.

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

It is common to neglect the spherical geometry of Figure 3 and analyze the data of a dispersed-emulsion separation by simply applying the equations for steady state transport (for example, equation (11)) across the supported membrane[16]. A fit of theory

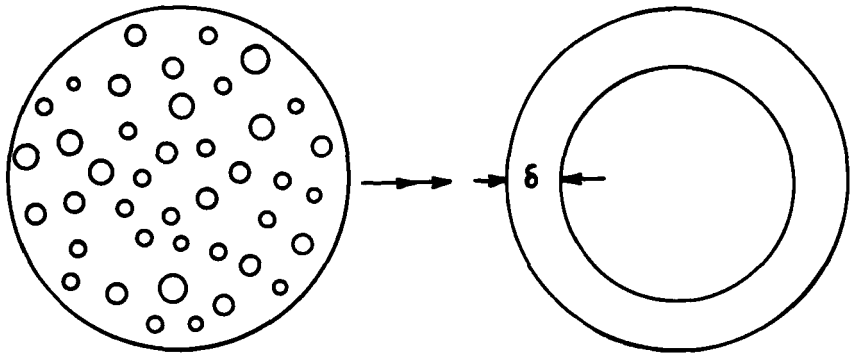

FIGURE 3

Standard geometrical simplification of a dispersed-emulsion globule.

to experiment is taken to imply that the kinetics are modeled correctly and that the simplifications are justified.

Matulevicius and Li[23] have relaxed the steady-state assumption (assumption 3) and modeled time dependent transport in the membrane of the concentric spherical shell system. They assume, however, the concentration of the permeating species in the encapsulated phase to be zero for all time and require that all the other previous assumptions hold. The concentration requirement is justified on the basis that in their example the contaminant reacts with a species in the encapsulated phase which reduces its concentration to effectively zero. Details of their derivation are not given, but their results indicate that they must integrate the solution of their partial differential equation over the membrane-continuous phase interface of all the dispersed-emulsion globules. They give an exponential expression for the concentration in the external continuous phase as a function of an unknown constant ϕ, time, the diffusion coefficient, and the membrane thickness. The constant ϕ is dependent upon drop size distribution, volume ratio, solubility, and membrane thickness. The model does an excellent job of correlating some data on phenol extraction from water. For each experiment, both ϕ and the group, $D^{II}_{(Am)}/\delta^2$, must be determined by curve fitting.

Kondo et al.[13] and Marr et al.[24] contend (Matulevicius and Li might disagree) that the concentric spherical model is only applicable if all of the fine droplets have nearly the same concentra-

tion; that is, the fine droplets inside of the large emulsion droplet are well mixed. They have worried independently that the fine droplets are not well mixed and all possess different concentrations. To model this case, Marr et al.[24] have assumed that all of the droplets are fixed and that a "front" of concentration $c_{(A)}$ advances through the large emulsion globule; that is, the membrane thickness having a concentration $c_{(A)}$ is increasing with time. This is modeled as a problem of absorption with first order chemical reaction in a semi-infinite medium for which the molar flux is given as

$$N_{(A)} = \alpha \sqrt{D^{II}_{(Am)}\, t} \tag{12}$$

in which α is a constant. They have found that their copper extraction data has a $\sqrt{t}$ dependence.

Casamatta et al.[25] have attempted what might be viewed as a combination of the two above approaches. For the case of a hydrocarbon separation, they have fixed the fine droplets but have a layer of water of thickness δ at the outer boundary of the emulsion globule. They attempt to determine the overall mass transfer coefficient in the membrane by summing the contributions of the parallel resistances through the fixed droplets and the interstitial water and the series resistance through the water layer at the boundary of the emulsion droplet. By order of magnitude arguments, they conclude that the water layer is controlling and the overall mass transfer coefficient is given by

$$k_{(A)} = \frac{D^{II}_{(Am)}}{\delta} \qquad (13)$$

where δ is the thickness of the water layer.

The extended differential balance models imply that the dependency of the mass transfer rate upon the power to which the diffusion coefficient in the membrane is raised is between one-half and unity.

A serious drawback to the extension of the differential balance to dispersed-emulsion configurations is that they do not require that the species balances in and across all of the phases be satisfied.

At long times the properties of the internal and external phases -- pH, concentration, or volume -- must change, especially when using the batch type of operation which is commonly employed. These changes must decrease the reaction and mass transfer rates. This slowing down of the rates and their effects would be seen in the model if it was required that the time dependent species mole balances be satisfied. With the possible exception of the Matulevicius and Li[23] model who integrated their results, these species balances are not required to be satisfied by any of the above models. Hence, one may expect that the models resulting from the differential balance approach are only applicable to dispersed-emulsion systems at short times.

MODELS USING INTEGRAL BALANCES

There have been three attempts to apply integral balances to the dispersed-emulsion separation. Kondo et al.[13] used an integral balance approach to analyze the results of a copper extraction. Their previous work[26], in a simplified two-phase system, had indicated that the mass transfer in the external aqueous phase would be controlling. They derived a model which emphasized this fact and analyzed their data. The model deals with a specific problem and rate controlling resistance which has not been commonly observed; so it will not be discussed further. However, it is the only known application of the integral approach to a carrier-mediated system.

The model of Kremesec and Slattery[27] describes a batch separation of a hydrocarbon feed by solubility and diffusion coefficient differences in an aqueous membrane with a mixing configuration as shown in Figure 1. A general model was developed in which the dependencies upon the mass transfer coefficients in each phase, the distribution coefficients at each interface, the interfacial areas, and the individual phase compositions are explicit. This is perhaps the most comprehensive model developed. From the general model, simpler special cases applicable to a set of experiments can be identified. This model will be described in some detail.

Boyadzhiev et al.[28] have also developed a model of the dispersed-emulsion separation process, but it is less general than the model of Kremesec and Slattery[27] and is applied to a carrier-mediated separation without any consideration of the kinetics. However, the model incorporates the rate of membrane breakup. The model is curve fit to the data to determine an overall permeation coefficient and rate coefficient for membrane breakup.

As an example of the integral balance approach to modeling of a dispersed-emulsion separation system, the model of Kremesec and Slattery[27] will be briefly presented. The analysis of data required to correlate the mass transfer coefficients with diffusion coefficients is also discussed.

Theoretical Development

The following assumptions are required:

(a) No chemical reactions occur.

(b) All mass transfer coefficients are constant, independent of concentration and of the rate of mass transfer.

(c) Chemical equilibrium exists at each interface.

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

(e) Any effects of surfactants can be neglected.

(f) The mass fractions of the permeating species of the membrane are very small and their concentration gradients are also very small.

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

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

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

Following Bird et al.[29], the integral mole balance for species A in the continuous-external phase may be written as

$$\frac{d}{dt}\left(x^{III}_{(A)b}\, C^{III}\right) = x^{III}_{(A)2}\,\frac{dC^{III}}{dt} + k^{III}_{(A)2}\, A_2\left(x^{III}_{(A)2} - x^{III}_{(A)b}\right) \qquad (14)$$

in which the term on the left-hand side is the time rate of change of the total moles of A in the continuous-external phase, the first term on the right-hand side is the rate of mole transfer across the membrane-external phase interface resulting from diffusion-induced convection, and the second term is the rate of transfer relative to the molar-averaged velocity. In (14) and

what follows the superscripts I, II, III will denote respectively the encapsulated phase, the membrane phase, and the external-continuous phase; subscripts 1 and 2 denote the encapsulated phase-membrane interface and the membrane-external phase interface, respectively. By C we mean the total moles of a phase; $x_{(A)b}$ is the bulk or mixing cup mole fraction of a species A, $k^{III}_{(A)2}$ is the mass transfer coefficient, and A_2 is the area of the membrane-external phase interface.

To obtain the time rate of change of total moles of species A in the external phase using (14), an expression for the mole fraction of species A at the membrane-external phase interface is required. This can be obtained by solving the following equations: First, the integral mole balance on the membrane phase can be rearranged as (assumptions h and i)

$$x^{II}_{(A)b} = \frac{x^{II}_{(A)1}(k^{II}_{(A)1} A_1 - dC^{I}/dt) + x^{II}_{(A)2}(k^{II}_{(A)2} A_2 - dC^{III}/dt)}{k^{II}_{(A)1} A_1 + k^{II}_{(A)2} A_2} \quad (15)$$

Next, the integral mole balance for A in the entire closed system requires (assumption f)

$$x^{I}_{(A)b} C^{I} + x^{III}_{(A)b} C^{III} = C_{(A)0} . \quad (16)$$

Next, the requirement that the moles of A be conserved at the external phase-membrane interface is expressed as

$$k^{III}_{(A)2}\, A_2\, x^{III}_{(A)b} + k^{II}_{(A)2}\, A_2\, x^{II}_{(A)2}$$

$$= x^{III}_{(A)2}\,(k^{III}_{(A)2}\, A_2 + dC^{III}/dt) \qquad (17)$$

$$+ x^{III}_{(A)2}\,(k^{II}_{(A)2}\, A_2 - dC^{III}/dt)\ ,$$

and at the encapsulated phase-membrane interface is

$$k^{I}_{(A)1}\, A_1\, x^{I}_{(A)b} + k^{II}_{(A)1}\, A_1\, x^{II}_{(A)b}$$

$$= x^{I}_{(A)1}\,(k^{I}_{(A)1}\, A_1 + dC^{I}/dt) \qquad (18)$$

$$+ x^{II}_{(A)1}\,(k^{II}_{(A)1}\, A_1 - dC^{I}/dt)\ .$$

Finally, the expression for the partition coefficients at the phase interfaces (assumption c) are

$$x^{II}_{(A)1} = d_{(A)1}\, x^{I}_{(A)1}$$

and (19)

$$x^{II}_{(A)2} = d_{(A)2}\, x^{III}_{(A)2}\ ,$$

in which

$$d_{(A)1} = \gamma^{I}_{(A)1}/\gamma^{II}_{(A)1}$$

and (20)

$$d_{(A)2} = \gamma^{III}_{(A)2}/\gamma^{II}_{(A)2}$$

where $\gamma_{(A)}$ is the activity coefficient of species A.

From (15) through (19), we find

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

where it is convenient to introduce

$$\begin{aligned} f_{(A)} \equiv\ & (k^{III}_{(A)2}\, A_2 + \frac{dC^{III}}{dt})(k^{I}_{(A)1}\, A_1 + \frac{dC^{I}}{dt})(k^{II}_{(A)1}\, A_1 + k^{II}_{(A)2}\, A_2) \\ & + d_{(A)1}\, k^{II}_{(A)2}\, A_2\, (k^{III}_{(A)2}\, A_2 + \frac{dC^{III}}{dt})(k^{II}_{(A)1}\, A_1 - \frac{dC^{I}}{dt}) \\ & + d_{(A)2}\, k^{II}_{(A)1}\, A_1\, (k^{II}_{(A)2}\, A_2 - \frac{dC^{III}}{dt})(k^{I}_{(A)1}\, A_1 + \frac{dC^{I}}{dt}) \end{aligned} \tag{22}$$

$$\begin{aligned} g_{(A)} \equiv\ & k^{III}_{(A)2}\, A_2\, (k^{I}_{(A)1}\, A_1 + \frac{dC^{I}}{dt})(k^{II}_{(A)1}\, A_1 + k^{II}_{(A)2}\, A_2) \\ & + d_{(A)1}\, k^{III}_{(A)2}\, A_2\, k^{II}_{(A)2}\, A_2\, (k^{II}_{(A)1}\, A_1 - \frac{dC^{I}}{dt}) \\ & - d_{(A)1}\, k^{I}_{(A)1}\, A_1\, k^{II}_{(A)2}\, A_2\, (k^{II}_{(A)1}\, A_1 - \frac{dC^{I}}{dt})\, \frac{C^{III}}{C^{I}} \end{aligned} \tag{23}$$

$$h_{(A)} \equiv d_{(A)1}\, k^{I}_{(A)1}\, A_1\, k^{II}_{(A)2}\, A_2 \left(k^{II}_{(A)1}\, A_1 - \frac{dC^{I}}{dt}\right) \frac{C_{(A)0}}{C^{I}} \tag{24}$$

Eliminating $x^{III}_{(A)2}$ between (14) and (21), we have

$$C^{III} \frac{dx^{III}_{(A)b}}{dt} = \left(k^{III}_{(A)2}\, A_2 + \frac{dC^{III}}{dt}\right)\left(\frac{g_{(A)}}{f_{(A)}} - 1\right) x^{III}_{(A)b}$$

$$+ \left(k^{III}_{(A)2}\, A_2 + \frac{dC^{III}}{dt}\right) \frac{h_{(A)}}{f_{(A)}} \,. \tag{25}$$

Let us assume that we have N species initially present in the external and encapsulated phases. Our objective is to determine the 2N unknowns: $x^{I}_{(A)b}$ (A = 1, ..., N-1), $x^{III}_{(A)b}$ (A = 1, ..., N-1), C^{I}, C^{III}. We might solve for these unknowns using the 2N equations: (16) (A = 1, ..., N-1), (25) (A = 1, ..., N) and the total integral mole balance for the encapsulated and external phases (assumption i)

$$C^{I} + C^{III} = C^{I}_{o} + C^{III}_{o} \tag{26}$$

This is a very general solution in that the dependencies upon all the phase resistances, interfacial areas, and partitioned coefficients are explicit. Along with Boyadzhiev et al.[28], these are the only solutions which require that (16) and (26) be satisfied in a dispersed-emulsion system.

Because one would not normally have all of the information required to use (22) through (25), they are useful only as a

starting point for obtaining simpler models which are applicable to specific experiments. In most cases of hydrocarbon separation in dispersed-emulsion systems, several additional assumptions can be made which will considerably simplify the model. It is further assumed:

(j) Species A is relatively insoluble in the membrane phase and so

$$d_{(A)1} << 1 \; ; \qquad d_{(A)2} << 1 \; . \tag{27}$$

(k) The diameter of the encapsulated droplets in the membrane phase is much smaller than the diameter of the globule of membrane-encapsulated phase emulsion dispersed in the solvent phase, and so

$$\frac{A_2}{A_1} << 1 \; . \tag{28}$$

(l) There is little convection within the membrane phase, which suggests that the film coefficients for mass transfer of the membrane sides of the interface are nearly equal:

$$k^{II}_{(A)1} = k^{II}_{(A)2} = k^{II}_{(A)} \; . \tag{29}$$

(m) There is little convection within the feed phase as well, indicating that the film coefficients for mass transfer on either side of the encapsulated phase-membrane interface will

have the same order of magnitude:

$$\frac{k^{I}_{(A)1}}{k^{II}_{(A)}} \sim 1 \ . \tag{30}$$

This is considerably different from the common assumption of the differential balance approach which says that the ratio is much greater than unity.

(n) There is considerable convection within the solvent:

$$\frac{k^{I}_{(A)1}}{k^{III}_{(A)2}} << 1 \ , \qquad \frac{k^{II}_{(A)}}{k^{III}_{(A)2}} << 1 \ . \tag{31}$$

(o) For normal operating conditions, it is reasonable to assume that the ratio of the masses of the encapsulated and external phases is of the order of unity.

As a result of these assumptions (22) through (25) can be simplified and rearranged to yield[27]

$$C^{III} \frac{dx^{III}_{(A)b}}{dt} = -k^{II}_{(A)} A_2 \left(d_{(A)2} + d_{(A)1} \frac{C^{III}}{C^{I}} + \frac{dC^{III}/dt}{k^{II}_{(A)} A_2}\right) x^{III}_{(A)b}$$

$$+ d_{(A)1} k^{II}_{(A)} A_2 C_{(A)0}/C^{I} \tag{32}$$

which must be integrated consistent with the initial conditions

$$\text{at } t = 0 : \quad x^{III}_{(A)b} = x^{III}_{(A)0} , \qquad A = 1, \ldots, N \tag{33}$$

This will be referred to as the simplified variable mole model because the total number of moles of the phases is allowed to change.

In order to determine the N+2 unknowns $x^{III}_{(A)b}$ (A = 1, ..., N), C^{I}, and C^{III}, (26) and (32) (A = 1, ..., N) must be solved simultaneously and the sum of the mass fractions must equal unity. This set of equations involves N parameters $k^{II}_{(A)}\, A_2$ (A = 1, ..., N) that must be determined empirically. An example of this procedure will be given shortly.

The partition coefficients at each interface must be calculated from (20) using assumptions c and e.

The corresponding mole fractions $x^{I}_{(A)b}$ (A = 1, ..., N) in the encapsulated phase can subsequently be determined from (16).

A power series solution for the simplified variable mole 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 time.

Determination of $k^{II}_{(A)}\ A_2$

As an example of the determination of $k^{II}_{(A)}\ A_2$ the data obtained for a hydrocarbon separation will be analyzed. The experimentally determined mole fractions for two runs by Kremesec and Slattery[27] are shown in Figures 4 and 5. The initial masses charged to each phase are given in Table I. In analyzing this data, it was assumed that:

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

These values are given in Table II.

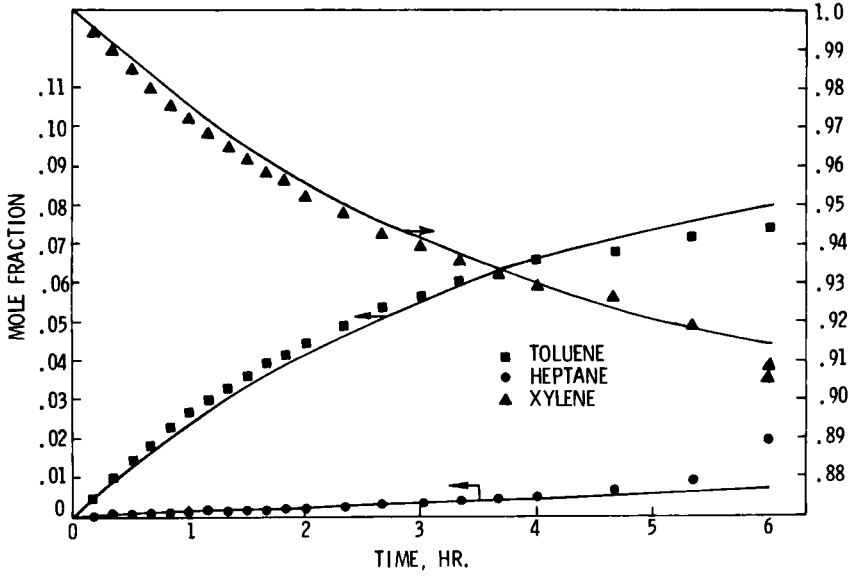

FIGURE 4

Experimental and predicted mole fractions for toluene and heptane in the external phase as a function of time for Run 1.

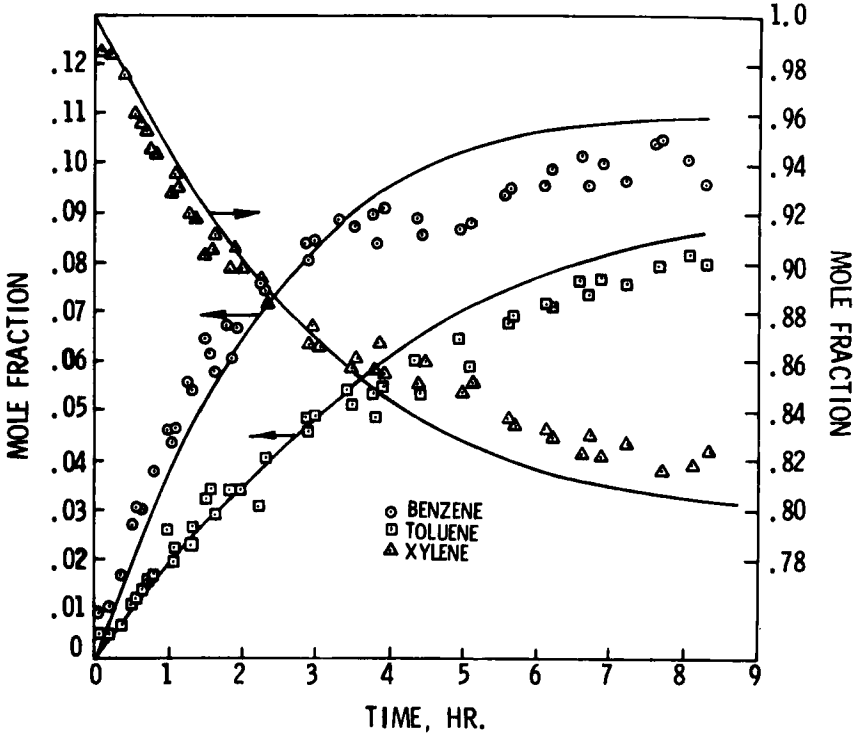

FIGURE 5

Experimental and predicted mole fractions in the external phase as a function of time for Run 2.

When the simplified variable mole model is to be used, the first term of the power series solution (A9) in the appendix should be identified with the initial experimental slope of the mole fraction as a function of time. In this way, $k^{II}_{(2)} A_2$ and $k^{II}_{(3)} A_2$ for the two initial encapsulated feed components were determined. Unfortunately, the three mole fractions are not linearly independent, so $k^{II}_{(1)} A_2$, the coefficient for the

TABLE I

INITIAL COMPONENT MASSES CHARGED TO EACH PHASE

run	encapsulated feed components	initial mass of feed components,g	membrane components[a]	initial mass of membrane components,g	initial mass of o-xylene, external phase
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	

a) The membrane also contained approximately one percent by weight saponin.

TABLE II

PARTITION COEFFICIENTS

run	component	$d_{(A)1}$	$d_{(A)2}$
1	toluene	5.11×10^{-4}	4.63×10^{-4}
	n-heptane	3.66×10^{-5}	5.84×10^{-5}
	o-xylene	2.24×10^{-4}	1.95×10^{-4}
2	benzene	4.85×10^{-4}	4.84×10^{-4}
	toluene	4.44×10^{-4}	4.44×10^{-4}
	o-xylene	1.91×10^{-4}	1.91×10^{-4}

external phase species, could not be fixed in the same manner. Instead, it was assumed that:

(q) The mass transfer coefficient $k^{II}_{(A)}$ is a linear function of the pseudo-binary diffusion coefficient $D_{(Am)}$ for a dilute solution of A in the multicomponent membrane.

Remember that from the extended differential balance approach, it follows that if the encapsulated droplets are well mixed there should be a linear dependence of the mass transfer rate upon the diffusion coefficient. Thus, $k^{II}_{(1)}\ A_2$ for the initial external phase component, always o-xylene, was determined by linear interpolation (or extrapolation). The pseudo-binary diffusion coefficients were estimated according to the recommendations of Perkins and Geankopalis[30]. The calculated diffusion coefficients and $k^{II}_{(A)}\ A_2$ (A = 1, 2, 3) are given in Table III.

The good agreement shown between experiment and theory in Figures 4 and 5 indicates the success of the procedure for correlating the $k^{II}_{(A)}\ A_2$'s and the applicability of the model. For these two runs, there is not much sensitivity of the developed correlation to the power to which the pseudo-binary diffusion coefficient is raised. For these runs, if the mass transfer coefficient is assumed to be a linear function of the square root of the pseudo-binary diffusion coefficient, the calculated values for the o-xylene mass transfer coefficient change by less than 5% and

TABLE III

$k^{II}_{(A)}A_2$ FOR SIMPLIFIED VARIABLE MOLE MODEL

run	component	diffusion coefficient x 10^7, cm^2/sec	$k^{II}_{(A)}A_2$, moles/sec
1	heptane	4.35	.0845
	toluene	5.24	.1039
	o-xylene	4.74	.0930[b]
2	benzene	6.30	.1801
	toluene	5.52	.1062
	o-xylene	5.00	.0569[c]

b) interpolated value

c) extrapolated value

the calculated mole fractions of all species are changed about 1%. This may be because the diffusion coefficients are not very different. However, if one assumes that all the mass transfer coefficients are equal to the average value for that run, then the predicted concentrations are off up to an additional 10% from that shown in Figures 4 and 5. Thus, the slight differences in the values of the mass transfer coefficients have some importance.

Finally, the simplified variable mole model is somewhat more complicated than the previous models presented in the review because the total number of moles in the encapsulated and external phases are allowed to vary with time. If one fixes the total number of

moles in a phase, the model yields a simple exponential function for the concentration versus time, but the mass transfer coefficients cannot be correlated with the diffusion coefficient[27].

SUMMARY

Two paths for modeling of the dispersed-emulsion separation system have been reviewed. Both methods yield expressions which must be curve fit to the data to obtain the effective mass transfer rate parameters. The expressions are vastly different, however.

The most popular approach, that of using a differential mass balance, simplifies the geometry considerably and assumes that all the mass transfer resistance is in the membrane phase. The problem is one of diffusion across a stagnant film possibly with chemical reaction. The model does not require the species mass balances in or across all the phases to be satisfied which may limit the ability of model to correlate data at long times. The proposed models seek to determine the dependence of the process upon the diffusion coefficient in the membrane of the permeating species. Depending upon whether the fine droplets dispersed in the emulsion globules are assumed to have the same or widely different compositions, the approach yields different values for the power to which the diffusion coefficient is to be raised.

The second path, that of an application of the integral mass balances, is somewhat more general in that geometry is not simpli-

fied and the resistances of all the phases may be taken into consideration. In addition, the mass balances in each phase and over the entire system are required to be satisfied. For the example problem analyzed, the final expression shows that the membrane phase resistance is the controlling mass transfer resistance which is in agreement with the initial assumption of the differential balance approach. The final expressions from the two approaches are vastly different, however. The integral approach lumps all of the ignorance of geometry and well-mixed versus fixed droplets into a mass transfer coefficient. A procedure is developed which shows that the mass transfer coefficient can be correlated with the diffusion coefficient. The general integral approach has not been applied in the analysis of facilitated transport or carrier-mediated separation systems. It is probably the only approach which can describe the behavior of batch dispersed-emulsion systems at long times [31].

This review has not addressed the modeling of dispersed-emulsion separation systems which have unstable membranes. Boyadzhiev et al.[28] have made the only -- and a very reasonable -- attempt at incorporating the effects of membrane rupture into an analysis of the process. This may be the only attempt because the modeling of the effects of unstable membranes can only be made within the framework of an integral approach. This is because the rupture of the membrane affects the total concentration of the external phase which is the quantity that the integral approach is focused on.

ACKNOWLEDGEMENTS

I would like to thank C. C. McPheeters of Argonne National Laboratory for providing support and encouragement in the undertaking of this project and to Amoco Production Company for providing secretarial and drafting services.

NOTATION

A_i	area of an interface S_i
c	molar density
C	total moles in a phase
$d_{(A)}$	partition coefficient for species A defined by (20)
$D_{(Am)}$	pseudo-binary diffusion coefficient
$f_{(A)}$	defined by (22)
$g_{(A)}$	defined by (23)
$h_{(A)}$	defined by (24)
k_1, k_{-1}	rate constants
K	equilibrium coefficient
$k_{(A)}$	mass transfer coefficient for species A
L	length
$N_{(A)}$	molar flux of species A
N	number of species present
N_{Da}	Damkohler numbers, Eq. 9
r	rate of reaction
S	surface
t	time

x	mole fraction
y	length coordinate

GREEK LETTERS

$\gamma_{(A)}$	activity coefficient for species A
δ	thickness of the membrane or water layer

SUPERSCRIPTS

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

SUBSCRIPTS

1	denotes the encapsulated phase-membrane interface
2	denotes the membrane-external phase interface
0	denotes an initial condition
b	denotes bulk concentration
(A)	denotes species A (A = 1,...,N)

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APPENDIX: SERIES SOLUTION FOR SIMPLIFIED VARIABLE MOLE MODEL

We can develop a Maclaurin series solution of the form

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

and

$$C^{III} = \sum_{i=0}^{M} b_i\, t^i \qquad \text{(A2)}$$

for (26) and (32) (A = 1,....,N), and requiring that the sum of the mole fractions must be unity. The initial conditions are (33) (A = 1,....,N) and

$$\text{at } t=0 : C^{III} = C_0^{III} \tag{A3}$$

In view of (A3), we see immediately that

$$\alpha_{(A)0} = x^{III}_{(A)0} \quad , \; b_0 = C_0^{III} \tag{A4}$$

Collecting the zero-order terms in (49) and eliminating C^I by means of (26), we find (A = 1,...,N)

$$\alpha_{(A)1} = \frac{k^{II}_{(A)} A_2}{C_0^{III}} \left[\frac{d_{(A)1} C_{(A)0}}{C_0^I} - x^{III}_{(A)0} \left(d_{(A)2} + \frac{d_{(A)1} C_0^{III}}{C_0^I} \right) \right]$$

$$- \frac{b_1 x^{III}_{(A)0}}{C_0^{III}} \tag{A5}$$

Since the sum of the mole fractions must equal unity,

$$b_1 = \sum_{A=1}^{N} k^{II}_{(A)} A_2 \left[\frac{d_{(A)1} C_{(A)0}}{C_0^I} - x^{III}_{(A)0} \left(d_{(A)2} + \frac{d_{(A)1} C_0^{III}}{C_0^I} \right) \right] \tag{A6}$$

The high-order coefficients in (A1) and (A2) can be developed in a similar fashion.

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

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

Since the mole fractions are not linearly independent, (A5) through (A7) permit us to determine N-1 of the coefficients $k^{II}_{(B)}A_2$ (B = 1,...,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 :

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

In this limit, (A5) reduces to

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

$$\alpha_{(B)1} = k^{II}_{(B)}A_2 \ \frac{d_{(B)1}C_{(B)0}}{C^{I}_{0}C^{III}_{0}} \qquad \text{for } B \neq 1 \tag{A9}$$

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