

Perturbation analysis of facilitated mass transport through batch liquid membranes

A Chatterjee† and R Nagarajan

Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802, USA

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Abstract. The general equations describing facilitated mass transport of metal ions through batch liquid membranes are non-linear and demand complex numerical solution procedures. We show that under certain conditions the problem can be cast in a moving boundary formalism and we present the associated transport equations. By exploiting the smallness of a parameter naturally appearing in these equations, we derive a perturbation solution to the problem. Our analytical solution, which contains no fitted parameters, correctly displays all the qualitative features of available experimental data. Furthermore, it provides an easy calculation of the asymptotic limit to the transport rate computed from the general equations. We conclude by showing that the perturbation technique is versatile enough to handle an arbitrary form of the rate expression for the metal-organic complexation reaction, which is the primary source of non-linearity in the general governing equations.

Nomenclature

a	Interfacial area per unit volume of external phase (cm^{-1})
C	Concentration of species (moles cm^{-3})
B	$(1 - 2/E)^{1/3}$, dimensionless
D	Effective species diffusivity ($\text{cm}^2 \text{s}^{-1}$)
Da	Damkohler number for reaction-diffusion process, dimensionless
E	$(V_i C_{io}) / (V_e C_{co})$, dimensionless
k	Effective rate constant for complexation (cm s^{-1})
k_f	True rate constant for complexation (cm s^{-1})
p, q	Exponents in the rate expression for the complexation reaction, dimensionless
r	Radial position (cm)
R	Radius of emulsion globule (cm)
R_f	Position of moving boundary (cm)
t	Time (s)
V	Volume of a phase (cm^3)
$\alpha_1, \alpha_2, \alpha_3$	Functions introduced in equations (24), (25) and (26)
β	C_{10}/C_{co} , dimensionless
χ	Position of moving boundary, dimensionless
$\delta(\)$	Delta distribution
ϵ	Perturbation parameter, dimensionless

φ	Concentration of the free carrier in the emulsion globule, dimensionless
η	Radial position, dimensionless
θ	External phase species concentration, dimensionless
ψ	Concentration of the complexed carrier in the emulsion globule, dimensionless
Ψ	Function employed in equation (37)
τ	Time, dimensionless
ξ	$(1 - \eta)/(1 - \chi)$

Subscripts

1; 2	Free carrier; complexed carrier
e; i	External phase; internal phase
0	Initial value
r, χ, ξ	Partial derivative
t	Total emulsion phase

1. Introduction

A novel chemical separation process based on the concept of liquid membranes was described by Li (1968). The process utilizes either aqueous or non-aqueous liquid membranes depending on the nature of the separation involved. An aqueous liquid membrane is used when mass transfer between two organic phases is to be realized, while a non-aqueous liquid membrane is

† To whom all correspondence should be addressed at: Intel Corporation, MS: SC9-62, 2250 Mission College Blvd., PO Box 58125, Santa Clara, CA 95052-8125, USA.

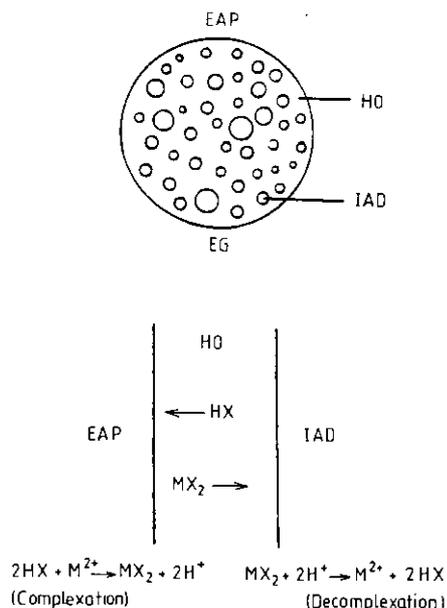


Figure 1. Schematic of facilitated mass transport through liquid membranes: EAP, external aqueous phase; HO, hydrocarbon oil; IAD, internal aqueous droplet; EG, emulsion globule.

employed for transferring species between two aqueous phases. In practice, liquid membranes are formed by preparing multiple emulsions. An oil in water in oil (owo) multiple emulsion generated by dispersing an oil in water emulsion in an external oil phase gives rise to an aqueous liquid membrane. Similarly, a water in oil in water (wow) multiple emulsion formed by dispersing a water in oil emulsion in an external aqueous phase yields a non-aqueous liquid membrane. Li's pioneering work demonstrated the application of liquid membranes to the separation of hydrocarbons. During the last two decades, the use of liquid membranes to remove trace organic compounds from waste water has interested many workers in the area of separation science (Matulevicius and Li 1975, Halwachs *et al* 1980). Other researchers have utilized liquid membranes to investigate the removal and subsequent enrichment of heavy metal ions (such as Cu^{2+}) from dilute aqueous solutions (Martin and Davies 1976–1977, Kondo *et al* 1979, Strzelbicki and Charewicz 1980, Danesi *et al* 1981).

A schematic representation of a wow liquid membrane system and the transport processes occurring within it are shown in figure 1. Transport of metal ions through liquid membranes as sketched in figure 1 is referred to as facilitated transport because of the presence of an organic molecule (the 'carrier') in the liquid membrane. This molecule reacts with the metal ion in the external aqueous solution to form an organo-metallic complex which diffuses easily through the hydrocarbon phase constituting the liquid membrane. When the complex reaches the internal aqueous droplets within the emulsion globule, the decomplexation reaction occurs leading to the release of the metal ion and regeneration of the organic carrier. In this manner

the carrier molecule facilitates transport of the metal ion across the liquid membrane.

In order to describe quantitatively the transport processes occurring inside an emulsion globule it is necessary to develop a physical view of an emulsion globule. In reality, an emulsion globule consists of many small internal aqueous droplets surrounded by the hydrocarbon oil. Two idealizations of this true picture are possible, namely, the shell and core model and the continuum model. The first assumes that every spherical globule consists of a single internal aqueous droplet surrounded by the oil layer (the liquid membrane) whose thickness is determined by the relative volumes of the two phases used in preparing the emulsion (Matulevicius and Li 1975). While this model is relatively simple to analyse, it is limited in its ability to describe experimental data quantitatively. Kopp *et al* (1978) note that with the shell and core model values of physical parameters do not remain invariant when they are used to fit different sets of experimental data. The second model treats an emulsion globule as a continuum which is ascribed effective physical properties, such as species diffusivity, whose values reflect the nature of the dispersion of the internal aqueous droplets within the emulsion globule. This approach was suggested by Kopp *et al* (1978) and employed very successfully by Ho and coworkers (Ho *et al* 1982) to model phenol removal from dilute aqueous solutions.

A general description of facilitated transport through liquid membranes involves solution of the coupled parabolic reaction–diffusion equations, one each for the free and complexed forms of the carrier. These equations, along with appropriate initial and boundary data, are non-linear and thus extensive numerical computations are required for their solution (Teramoto *et al* 1983). Given the complexity of the equations involved such an approach is computationally expensive. In this paper we show that under certain conditions the transport problem can be cast in a moving boundary formalism which admits a perturbation solution. The perturbation technique we employ is similar to that used by Ho *et al* (1982) and it is based on the work of Pedroso and Domoto (1973a, b) on the inward solidification of a sphere. However, unlike these two works which dealt with a single equation, we are here concerned with a set of coupled conservation equations and this presents an extension of the scope of applicability of the technique. Apart from these interesting mathematical aspects, our analytical solution (which does not contain any adjustable parameters) provides an asymptotic limit to the maximum transport rate computed from the general governing equations. Such a limit can be very useful when one is interested primarily in the qualitative behaviour of the transport process under altered parameter values, particularly when the use of a given carrier molecule (or metal ion) necessitates the use of an algebraically complicated constitutive equation for the rate of the complexation reaction. Complete numerical solution of the full governing equations in

these instances can be both time consuming and expensive.

We adopt the continuum picture of an emulsion globule and assume that the decomplexation reaction inside the globules leading to the release of the metal ion is rapid compared to species diffusion within the emulsion globule continuum, and furthermore, that the metal ion once free, is immobilized, say by the formation of a precipitate, so that it cannot participate in any subsequent reaction. The moving boundary then divides the globules into an outer shell containing precipitated metal ions and an inner core containing the internal reagent at its initial concentration. Assuming that the external aqueous phase is well mixed, the transport rate is governed by the time scales of species diffusion within the emulsion globule continuum and the complexation reaction. In addition, the diffusion path length is the smallest in this description and so the diffusion resistance is the least possible. When the decomplexation reaction is not rapid it not only adds to the overall resistance, but also enlarges the diffusion field for the complexed carrier which then extends all the way to the centre of the globule. For these reasons, when the decomplexation reaction is rapid the driving force for separation is at a maximum while the overall resistance is at a minimum, hence the predicted separation rate represents an upper limit. In many experiments the diffusion time scale is larger than the complexation reaction time scale and so it tends to dominate the separation rate. Kopp *et al* (1978) also attempted an analysis of facilitated transport in terms of a moving boundary, but their analysis is too approximate to be of general value.

2. Formulation of equations

We consider a batch system comprising of a well mixed external aqueous phase of volume V_e in which an emulsion phase of volume V_i (containing internal aqueous droplets of total volume V_j) has been dispersed, giving rise to emulsion globules of radius R .

The species continuity equations for the free and complexed forms of the carrier in the emulsion globule continuum are, respectively

$$\frac{D}{r^2} \frac{\partial r^2 C_{1r}}{\partial r} + 2DC_{2r} \delta(r - R_t) = \frac{\partial C_1}{\partial t} \quad 0 < r < R \quad (1)$$

$$\frac{D}{r^2} \frac{\partial r^2 C_{2r}}{\partial r} = \frac{\partial C_2}{\partial t} \quad R_t(t) < r < R. \quad (2)$$

In these equations $C_{1r} = \partial C_1 / \partial r$, $C_{2r} = \partial C_2 / \partial r$ and $\delta(\)$ is the delta distribution. C_1 and C_2 are the molar concentrations of the free and complexed carrier, respectively; $R_t(t)$ is the position of the moving boundary; D is the effective binary diffusion coefficient of each species and t represents time. The second term on the left-hand side of the first equation containing the delta distribution represents regeneration of free

carrier at the moving boundary due to the fast decomplexation reaction, the factor two reflecting its stoichiometry.

Initial and boundary data on these equations are as follows

(i) Uniform free carrier concentration in the globules at $t = 0$

$$C_1(r, t = 0) = C_{10}. \quad (3)$$

(ii) No complexed carrier in the globule at $t = 0$

$$C_2(r, t = 0) = 0. \quad (4)$$

(iii) Rapid decomplexation of the carrier at the moving boundary

$$C_2(r = R_t, t) = 0. \quad (5)$$

(iv) Stoichiometric relation between the fluxes of free and complexed carrier at the interface $r = R$ dictated by the complexation reaction

$$D \frac{\partial C_1}{\partial r} = -2D \frac{\partial C_2}{\partial r} \quad \text{at } r = R. \quad (6)$$

(v) Assumption of a bimolecular complexation reaction between the free carrier and the metal ion at the interface $r = R$ implies that

$$D \frac{\partial C_2}{\partial r} = k C_1(R, t) \frac{C_c(t)}{C_{co}} \quad \text{at } r = R \quad (7)$$

where $C_c(t)$ is the concentration of the metal ion in the external aqueous solution, $C_{co} = C_c(t = 0)$ and k is an effective complexation reaction rate constant (see Teramoto *et al* (1983), k is equal to $k_f C_{co}$ divided by the hydrogen ion concentration in the external aqueous phase). Also, we are assuming that the reverse (decomplexation) reaction is suppressed at this interface because of the low value of the external aqueous phase hydrogen ion concentration. A brief comment is needed here: because the complexation reaction generates hydrogen ions, as time proceeds their build-up at the interface may invalidate the assumption just mentioned. We neglect this effect by disallowing a local build-up in the hydrogen ion concentration since the external aqueous phase is considered to be well mixed. In practice this is achieved by maintaining high stirring rates in the experimental system, which also has the advantage of producing emulsion globules with large surface to volume ratios for efficient mass transfer. Furthermore, note that an increase in the external aqueous phase hydrogen ion concentration would actually make the effective rate constant k a function of time. We simplify our model and subsequent analysis by ignoring this effect.

(vi) The conservation equation for the metal ion in the external aqueous phase is

$$-\frac{dC_c}{dt} = a k C_1(R, t) \frac{C_c(t)}{C_{co}} \quad (8)$$

subject to $C_c(t = 0) = C_{co}$, where a is the total inter-

facial area per unit volume of the external aqueous phase.

(vii) At the moving boundary, the conservation equation for the internal reagent (hydrogen ions) reads

$$-\frac{V_i}{V_t} C_{i0} \frac{dR_t}{dt} = 2D \frac{\partial C_2}{\partial r} \quad \text{at } r = R_t \quad (9)$$

subject to $R_t(t=0) = R$, where V_i , V_t are the volumes of the internal aqueous phase and the total emulsion phase, respectively, and C_{i0} is the concentration of the internal reagent in the internal aqueous phase. The factor two once again reflects the stoichiometry of the decomplexation reaction.

(viii) Finally, since the organic part of the carrier never leaves the emulsion globules its total number of moles must be conserved, thus

$$\int_0^R C_1 r^2 dr + \int_{R_t(t)}^R 2C_2 r^2 dr = C_{i0} \frac{R^3}{3}. \quad (10)$$

These equations may be non-dimensionalized by setting

$$\begin{aligned} \eta &= \frac{r}{R} & \chi &= \frac{R_t}{R} \\ \varphi &= \eta \frac{C_1}{C_{e0}} & \psi &= \eta \frac{C_2}{C_{e0}} & \theta &= \frac{C_c}{C_{e0}} \\ \varepsilon &= \frac{V_t C_{e0}}{V_i C_{i0}} & \tau &= \varepsilon \frac{Dt}{R^2}. \end{aligned}$$

In order to freeze the moving boundary we introduce the additional transformation (Ho *et al* 1982)

$$\xi = \frac{1 - \eta}{1 - \chi}$$

so that $\xi = 1$ now represents the location of the moving boundary. Using ξ and χ as the independent variables we can rewrite the equations governing the transport process as described below. In what follows, subscripts χ and ξ denote partial derivatives. Species continuity equations for the free and complexed carrier

$$\begin{aligned} \varphi_{\xi\xi} - 2\left(\psi_{\xi} + \frac{1 - \chi}{1 - \xi(1 - \chi)} \psi\right) \delta(\xi - 1) \\ = \left(\frac{\varepsilon}{\chi}\right) [\xi \varphi_{\xi} + (1 - \chi) \varphi_{\chi}] [2\psi_{\xi}(\xi = 1)] \quad 0 \leq \xi \leq \frac{1}{1 - \chi} \end{aligned} \quad (11)$$

$$\psi_{\xi\xi} = \left(\frac{\varepsilon}{\chi}\right) [\xi \psi_{\xi} + (1 - \chi) \psi_{\chi}] [2\psi_{\xi}(\xi = 1)] \quad 0 \leq \xi \leq 1 \quad (12)$$

subject to the boundary conditions

$$\varphi = 0 \quad \text{at } \xi = \frac{1}{(1 - \chi)} \quad (13)$$

$$\psi = 0 \quad \text{at } \xi = 1 \quad (14)$$

$$-\frac{\varphi_{\xi}}{1 - \chi} - \varphi = 2\left(\frac{\psi_{\xi}}{1 - \chi} + \psi\right) \quad \text{at } \xi = 0. \quad (15)$$

At the interface $\xi = 0$ between the globules and the external aqueous solution we have the bimolecular reaction between the metal ion and the free carrier represented by equation (7), which now reads

$$-\frac{1}{1 - \chi} \psi_{\xi}(\xi = 0) - \psi(0, \chi) = Da[\varphi(0, \chi)]\theta(\chi) \quad (16)$$

while the conservation equation for the metal ion in the external aqueous solution transforms to

$$\frac{d\theta}{d\chi} = (3E)Da[\varphi(0, \chi)]\theta(\chi) \frac{\chi(\chi - 1)}{2\psi_{\xi}(\xi = 1)} \quad (17)$$

with the initial condition now being

$$\theta(\chi = 1) = 1. \quad (18)$$

For the moving boundary we find the equation

$$\frac{d\tau}{d\chi} = \frac{\chi(1 - \chi)}{2\psi_{\xi}(\xi = 1)} \quad (19)$$

subject to

$$\tau(\chi = 1) = 0. \quad (20)$$

Finally, (10) modifies to

$$\begin{aligned} (1 - \chi) \int_0^{1/\chi} [\varphi(\xi, \chi)] [1 - \xi(1 - \chi)] d\xi \\ + 2(1 - \chi) \int_0^1 [\psi(\xi, \chi)] [1 - \xi(1 - \chi)] d\xi = \beta/3 \end{aligned} \quad (21)$$

where $\beta = C_{i0}/C_{e0}$.

In these equations Da is the Damkohler number for the reaction-diffusion process ($Da = kR/D$; the ratio of the species diffusion time scale to the complexation reaction time scale) and $E = (V_i C_{i0})/(V_c C_{e0})$ defines the ratio of equivalents of the internal reagent in the internal aqueous droplets to the metal ion in the external aqueous solution. When $E = 2$, the moving boundary extends to the centre of the globules at the end of the separation process when all the metal ions have been removed from the external aqueous solution. For later use we define the parameter B , where $B^3 = 1 - 2/E$.

To solve the above set of rather complicated equations we consider the situation where the parameter ε is small. This is often true since the external aqueous solution is generally very dilute in the metal ion, thus $C_{e0} \ll C_{i0}$ and so $\varepsilon \ll 1$. With ε restricted in this manner it becomes possible to derive a perturbation solution to this reaction-diffusion problem. In what follows we present an outline of the derivation and quote the main results. The calculations, though tedious, are straightforward and the details may be filled in easily at the expense of added algebra.

3. Zero-order perturbation solution

The zero-order equations obtained by letting $\varepsilon \rightarrow 0$ are, in the same notation

$$\varphi_{\xi\xi} - 2\left(\psi_{\xi} + \frac{1-\chi}{1-\xi(1-\chi)}\psi\right)\delta(\xi-1) = 0 \quad (22)$$

$$\psi_{\xi\xi} = 0. \quad (23)$$

All other equations remain unchanged, except that now we interpret the symbols as representing the zero order terms in the perturbation expansion for each dependent variable. Integrating (23) subject to (14) yields

$$\psi(\xi, \chi) = \alpha_1(\chi)[1 - \xi] \quad (24)$$

where α_1 is an unknown function of χ .

Utilizing (24) and integrating (22) for $\xi < 1$ and for $\xi > 1$, matching the two expressions at $\xi = 1$ and using equation (13) allows us to write for $\varphi(\xi, \chi)$

$$\varphi(\xi, \chi) = \alpha_2(\chi)[\xi] + \alpha_3(\chi) \quad \text{for } 0 \leq \xi \leq 1 \quad (25)$$

$$\varphi(\xi, \chi) = [\alpha_2(\chi) + \alpha_3(\chi)] \times \left(\frac{1-\chi}{\chi}(1-\xi) + 1\right) \quad \text{for } \xi \geq 1 \quad (26)$$

where $\alpha_2(\chi)$ and $\alpha_3(\chi)$ again are unknown functions of χ and we have indicated the dependence of the α s on χ which, henceforth, will not be stated explicitly.

Now, equation (15) restricts the α s to obey

$$\alpha_2 = 2\chi\alpha_1 - (1-\chi)\alpha_3. \quad (27)$$

Consequently the expressions for $\varphi(\xi, \chi)$ reduce to

$$\varphi(\xi, \chi) = [2\chi\alpha_1 - (1-\chi)\alpha_3]\xi + \alpha_3 \quad \text{for } \xi \leq 1 \quad (28)$$

$$\varphi(\xi, \chi) = [2\chi\alpha_1 + \chi\alpha_3] \times \left(1 - \frac{1-\chi}{\chi}(\xi-1)\right) \quad \text{for } \xi \geq 1. \quad (29)$$

From equation (16) we can now obtain

$$\frac{\alpha_1}{\alpha_3} = Da[\theta(\chi)] \frac{1-\chi}{\chi} \quad (30)$$

and from (17) we see that

$$\frac{d\theta}{d\chi} = (3E)Da \frac{\alpha_3}{\alpha_1} \theta(\chi) \frac{\chi(1-\chi)}{2}. \quad (31)$$

Combining the last two equations we find an equation for $d\theta/d\chi$ which may be integrated explicitly along with equation (18) to yield

$$\theta(\chi) = 1 + \frac{E}{2}[\chi^3 - 1]. \quad (32)$$

It now remains to solve equation (19) which relates the dimensionless time τ to the variable χ . To proceed we resort to equation (21). We substitute the expressions for $\psi(\xi, \chi)$ and $\varphi(\xi, \chi)$ from equations (24), (28) and (29) into equation (21), and use equation (30) to relate

α_1 and α_3 . Upon carrying out the indicated integrations and after some algebraic simplification we find the relation

$$\alpha_1 = \frac{\beta\chi(1-\chi)}{2\chi(1-\chi) + [2\chi^2/(Da)E(\chi^3 - B^3)]}. \quad (33)$$

When (33) is combined with (19) and the resulting equation integrated subject to the initial condition (equation (20)), there results the simple expression

$$\tau = \frac{1}{2\beta} \left((1-\chi^2) - \frac{3}{2}(1-\chi^3) - \frac{2}{3(Da)E} \ln \frac{\chi^3 - B^3}{1 - B^3} \right) \quad (34)$$

where $B^3 = 1 - 2/E$ as defined earlier.

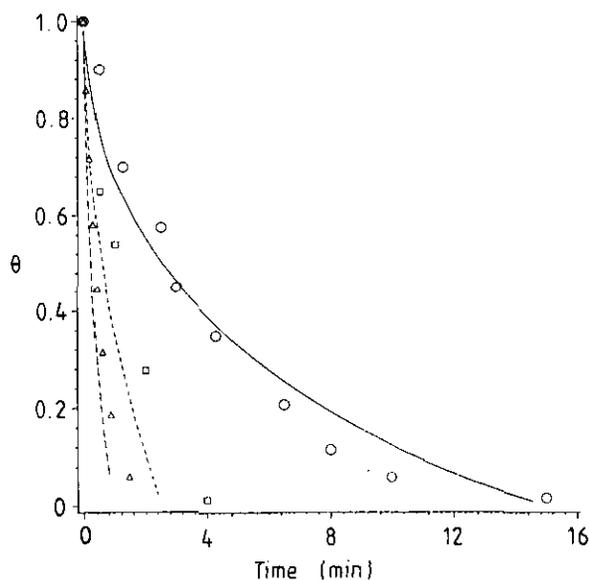
To summarize, equations (32) and (34) determine completely the behaviour of the metal ion concentration in the external aqueous phase as a function of time. We note that if the Damkohler number Da is large (and $E \sim 0(1)$), then τ can be approximated by the first two terms in equation (34) and consequently the time scale of the separation process is dominated by diffusion of the carrier and its complex within the globules. A calculation of the concentration profiles of the free and complexed forms of the carrier within the emulsion globule continuum is easily carried out using equations (24), (28) and (29), with $\alpha_1(\chi)$ and $\alpha_3(\chi)$ given by (33) and (30), respectively. In principle the zero-order solution can be used to derive the higher order terms in the perturbation expansion for each dependent variable, but we do not pursue the matter here. As noted in Ho *et al* (1982), for $\varepsilon < 1$ the zero-order solution alone is adequate for all practical purposes. Finally, we observe that our solution does not show any singular behaviour as $\chi \rightarrow B$, even as $B \rightarrow 0$.

As discussed earlier, our calculations provide an asymptotic upper limit to the actual separation rate observable in a batch experiment. Nevertheless, it would be instructive to obtain some idea of how the calculations compare with representative data. To this end, we examine experimental data on the transport of copper ions reported by Teramoto *et al* (1983) in a comprehensive paper which also presents a very detailed numerical modelling effort. This data set is particularly noteworthy since an attempt has been made to estimate the many parameters (such as k , R , D , etc) needed for a proper characterization of the experimental system. We compare our calculations with data for three different values of the initial concentration of copper in the external aqueous phase.

To estimate the effective physical properties in the emulsion globule continuum we assume that the carrier and its complex do not partition into the internal aqueous droplets of the emulsion, and follow methods given in Ho *et al* (1982). Computed values of relevant parameters are given in table 1 and the comparison is displayed in figure 2. The perturbation calculations represent the qualitative features of the data very well. As noted earlier, from a quantitative viewpoint we do not expect very good agreement, and we certainly do

Table 1. Parameter values for the experimental data of Teramoto *et al* (1983) on the batch separation of copper ions using liquid membranes.

Experimental parameter	Symbol	
Volume of external aqueous phase	V_e	650 cm ³
Volume of total emulsion phase	V_t	99.7 cm ³
Volume of internal aqueous phase	V_i	49.9 cm ³
Initial concentration of free carrier in organic phase of emulsion		0.2 mol cm ⁻³
Initial concentration of free carrier in emulsion globule continuum	C_{10}	0.1 mol cm ⁻³
Concentration of internal reagent (H+) in internal aqueous phase of emulsion	C_{i0}	1.0 mol cm ⁻³
Complexation rate constant	k_f	1.6×10^{-5} cm s ⁻¹
Diffusivity of free and complexed carrier in organic phase of emulsion		2.48×10^{-6} cm ² s ⁻¹
Effective diffusivity in emulsion globule continuum	D	5.9×10^{-7} cm ² s ⁻¹
Radius of emulsion globules	R	3.8×10^{-2} cm
		Value of C_{e0} (mol cm ⁻³)
Dimensionless parameter		8×10^{-3} 1.6×10^{-2} 3.2×10^{-2}
β		12.5 6.25 3.125
Da		82.25 164.5 329
E		9.6 4.8 2.4
ε		0.016 0.032 0.064


Figure 2. Comparison between asymptotic calculations (curves) and experimental data of Teramoto *et al* (1983) (symbols) for three different values of the external aqueous phase initial copper concentration: $C_{e0} = 8.0 \times 10^{-2}$ mol cm⁻³, ———, Δ ; $C_{e0} = 1.6 \times 10^{-2}$ mol cm⁻³, ----, \square ; $C_{e0} = 3.2 \times 10^{-2}$ mol cm⁻³, ———, \circ .

not claim that our analysis has captured all the details of the separation process. We simply wish to emphasise that our analytical solution (which contains no adjust-

able parameters) predicts the correct qualitative behaviour as a function of the model parameters and provides an easy calculation of the asymptotic separation rate observable in a batch experiment. We believe it can be useful when one is interested primarily in the qualitative features of the transport process under altered parameter values, particularly when the use of a given metal ion or carrier molecule necessitates the use of an algebraically complicated constitutive expression for the rate of the complexation reaction. In such cases, complete numerical solution of the general governing equations for each set of parameter values can be both time consuming and expensive.

In the example considered above, the Damkohler number was large and consequently the diffusion time scale dominated the transport rate. However, when Da is not very large the complexation reaction time scale also becomes important and, if the algebraic form of the rate expression for the complexation reaction is not simple, it adds to the complexity of the general governing equations. We show below that the perturbation technique is versatile enough in that it can handle fairly general polynomial forms of the rate expression for the complexation reaction. Let the kinetic expression for the rate of the complexation reaction, r_s (scaled with the diffusion time scale), between the metal ion in the external aqueous solution and the organic carrier be given by

$$r_s = Da[\varphi(0, \chi)]^p [\theta(\chi)]^q$$

where p and q are arbitrary real numbers. It is a trivial

task to show that (32) remains valid under this generalization. However, (30) now reads

$$\alpha_1 = Da[\theta(\chi)^q] \left(\frac{1-\chi}{\chi} \right) [\alpha_3^p]. \quad (35)$$

When this equation is combined with equation (21) we find for $\alpha_3(\chi)$ the relation

$$2Da[\theta(\chi)^q][\alpha_3(\chi)^p] + \alpha_3(\chi) \frac{\chi}{1-\chi} = \frac{\beta\chi}{1-\chi}. \quad (36)$$

This equation can be differentiated with respect to χ to yield an equation for $d\alpha_3/d\chi$ which can be denoted as

$$\frac{d\alpha_3}{d\chi} = \Psi(\alpha_3, \chi) \quad (37)$$

and which is subject to the initial condition

$$\alpha_3(\chi = 1) = \beta. \quad (38)$$

Finally, (19) can be written in terms of α_3 as follows

$$\frac{d\tau}{d\chi} = -\frac{\chi^2}{2Da} [\theta(\chi)^{-q}][\alpha_3^{-p}] \quad (39)$$

subject to equation (20).

To complete the solution procedure for the general case involving an arbitrary polynomial expression for the rate of the complexation reaction, we must solve (37) and (39) numerically using a standard initial value problem solver. Thus we see that the perturbation scheme is versatile enough to handle fairly general nonlinearities in the metal-organic complexation reaction.

5. Conclusions

The general equations describing facilitated transport of metal ions through batch liquid membranes are non-linear parabolic reaction-diffusion equations requiring numerical methods of solution. In this paper the transport process was modelled as a moving boundary problem. It was shown that a perturbation analysis of the resulting transport equations allows the explicit calculation of an analytical solution. This solution, which contains no adjustable parameters and provides an asymptotic limit to the transport rate given by the general equations, has been compared with experimental data on the transport of copper ions through liquid membranes. The perturbation technique we employed is versatile enough to handle an arbitrary form of the

rate expression for the metal-organic complexation reaction, which is the principal source of non-linearity in the general governing equations. However, in this case the perturbation solution does involve some simple numerical calculations. We suggest that the perturbation solution may be especially useful to model the qualitative features of the transport process, particularly when the use of a certain metal ion or carrier molecule necessitates the use of an algebraically complicated constitutive expression for the rate of the complexation reaction. Complete numerical solution of the general governing equations in these instances can be both time consuming and expensive.

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