



A new model of batch-extraction in emulsion liquid membrane: Simulation of globule–globule interaction and leakage

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Abstract—The present paper seeks to provide an understanding of the possible effect of interaction between emulsion globules, on batch extraction, utilising emulsion liquid membranes. The conventional reversible model of Bunge and Noble (1984) considers an isolated globule, for explaining type-1, reaction-facilitated transport. Their basic approach has been extended here through Monte Carlo simulation of a system of emulsion globules, interacting via coalescence-redispersion. Collision of such an interacting pair results in internal circulation in membrane phase of globules and causes mixing of solute existing therein. This translates into faster solute penetration inside the globule. Hence, solute depletion rate in the external phase is enhanced, over and above that of a diffusion-limited reaction. In experiments, at high stirring speeds involving extraction of weakly basic amines with a strong internal phase acid (Baird *et al.*, 1987), this trend has been observed during the initial period. A further shortcoming of the reversible model is that it overpredicts the maximum extraction achieved in these experiments, which is corrected by introducing leakage of internal drops during redispersion. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Emulsion liquid membrane; solute extraction; reversible reaction; coalescence-redispersion; leakage; Monte Carlo simulation.

1. INTRODUCTION

Emulsion liquid membranes (ELM) have been used extensively (Ho and Li, 1992) for extraction of diverse kind of solutes and also in multicomponent separation. Of particular interest in these applications is to utilise the large interfacial area for increasing the extraction rates of diffusion-limited systems and to achieve both enrichment and stripping in a single step. To this end, a water-in-oil or oil-in-water emulsion prepared *a priori*, is dispersed in an immiscible external phase under agitation, producing emulsion globules. The resulting ELM system—either of the type W/O/W or O/W/O, thus consists of three phases. A formulation such as above, is designed to extract solutes from the external phase into an internal one. Two general techniques are available for enhancement of mass transfer rate of solutes in these primarily diffusion-controlled systems. One approach in W/O/W systems for example, is to transport the solute from the external aqueous phase across the oil medium of the globule (membrane phase), and then

subsequently react it with a reagent in the internal water drops. This is known as type-I facilitation. On the other hand, for solutes insoluble in oil (e.g. metal ions), an extractant has to be used in the intervening membrane phase, which binds and releases the solute at the external and internal interfaces successively, allowing diffusion of the solute-extractant complex through the liquid membrane. This approach constitutes type-II facilitation.

Predictive studies concerning extraction in either kind of facilitated-transport, so far, have relied on modelling of a single emulsion globule as a representative of the whole system (Ho *et al.*, 1982; Bunge and Noble, 1984; Chan and Lee, 1987; Borwankar *et al.*, 1988). Models with this approach have evolved towards refining the treatment of transport and reaction in an isolated globule; disregarding however the phenomenon of coalescence between globules and their breakage, which results in exchange and mixing of solute content of different globules present in a system. Thus, modelling of solute extraction in ELM by analysing a single globule is perhaps inadequate and therefore requires consideration of a number of such interacting globules together.

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Existing literature on extraction models for type-I facilitation clearly demonstrate the superiority of the reversible reaction model of Bunge and Noble (1984); in comparison to the advancing front treatment of Ho *et al.* (1982), which assumes irreversible reactions, especially towards the end of batch extraction. Both these models are based on diffusion of solute through the membrane. However, the approach in reversible model of depicting the reaction between solute and internal reagent to be reversible is more realistic, and forms our starting point. Further improvements on these models (Kim *et al.*, 1983; Stroeve and Varanasi, 1984; Chan and Lee, 1987) consider extraction to occur through a series of mass transfer resistances in the external and membrane phase. The external phase mass transfer resistance can however be neglected at high stirring speeds, but not frequent coalescence and breakage, which on the contrary are promoted by agitation.

A convenient method towards description of interactions in the dispersed phase is the framework of population balance equations (PBE). However, the reversible model itself requires computation of the solute concentration profile in a globule, which typically being around 0.1–2 mm in diameter, cannot be regarded as well mixed because of slow membrane phase diffusion of solute. A population balance approach therefore has to incorporate both the size distribution of globules as also the existing concentration profile in each of them. Solution of such a multivariate PBE would be too difficult to attempt. Consequently, recourse to Monte Carlo simulation is taken in this study to describe interaction in a system of globules, and in conjunction, the reversible model is solved for each individual globule. A further aspect of importance in membrane extraction is leakage of internal droplets into the external phase, resulting in decreased extraction efficiency. The leakage phenomenon has been incorporated in existing diffusion–reaction models as a continuous flux of internal droplets from a single globule (Chan and Lee, 1987; Borwankar *et al.*, 1988). However, in a model of a single, stable globule, this should be accounted only during intermittent globule break-up. Therefore, the task of the present model is to include the effect of globule–globule interaction; by combining membrane phase mixing and exchange of globule contents along with leakage of internal droplets, in order to interpret batch extraction data in an ELM system.

2. MODEL DEVELOPMENT

2.1. Simulation scheme

We now proceed to elucidate the technique of Monte Carlo simulation followed in the present work. Essentially, we have utilised the concept of quiescence interval, developed by Shah *et al.* (1977) for a particulate system. Their implementation involves generation of the random time instants, when an evolving multiphase system undergoes an abrupt change in the

dispersed phase attributes, due to such events as for example, coalescence and breakage. In the present context, these discrete birth–death mechanisms alter the state of the participating globules, which being subject to turbulent agitation interact randomly. Thus, volume and solute content of these globules may change by a discrete amount. These processes in turn affect all the globules but at different times. Furthermore, internal phase hold-up of a globule is also altered if leakage occurs during its break-up. Apart from these intermittent changes, all the globules are further subject to smooth alterations in their respective solute concentration profile due to diffusion and reaction.

The effect of polydispersity of globules on batch extraction has been investigated by Lorbach and Hatton (1988), and shown to be not significant. Accordingly, the extracting system is simulated by following the temporal evolution of N monodisperse emulsion globules, along with the associated external phase containing the solute. In order to preserve the monodisperse condition, we have treated the disparate coalescence and breakage steps as a unified coalescence–redispersion event, first proposed by Curl (1963) for dispersed drops.

We, therefore, use a binary coalescence frequency, assuming redistribution of coalesced globules into two equal halves to be instantaneous. To this end, we generate the coalescence time intervals (quiescence intervals) for the simulated system, denoted by T_Q ; assuming that any pair of globules has a volume-average binary coalescence frequency q , independent of their volume and physical properties. One then has to identify the pair of globules which undergoes the designated coalescence redispersion at the end of this time interval, and recalculate their concentration profile and hold-up, after accounting for leakage. Thus, number and volume of globules remain constant. The system is updated after each coalescence redispersion by keeping track of hold-up and solute concentration profile in each globule, till the simulation clock reaches the desired extraction time. Simulation runs can be replicated until the ensemble-averaged extraction profile shows no further change.

Now, if we follow a single globule in time, it can undergo coalescence with surrounding globules in the reactor at a frequency of qN_g , where N_g is the number density of globules. However, due to randomness of pairwise interactions, this frequency would be maintained only on an average for each globule. For the simulated system of N globules, this implies that on an average, a total of $\frac{1}{2}qN_gN$ coalescence events occur per unit time. The factor $\frac{1}{2}$ appears, since, each coalescence involves selection of two globules from the system of N such globules. This would preserve, independent of system size N , the requirement that any globule should be interacting at a frequency of qN_g .

The quiescence time interval T_Q is a random variable and is known to follow an exponential distribution with mean $1/q_T$, where q_T is the total coalescence

frequency for N globules, given by

$$q_T = \frac{1}{2} q N_g N. \tag{1}$$

Therefore, the probability that none of the N globules undergo any coalescence in time t_Q (a sample value of T_Q) is given by

$$\Pr(0 \leq T_Q \leq t_Q) = 1 - \exp[-q_T t_Q]. \tag{2}$$

Inverting the cumulative distribution we get the random, quiescence time intervals as

$$t_Q = -\frac{\ln(1-u)}{q_T} \tag{3}$$

where u is obtained from an uniform random number generator between 0 and 1.

Now, the total number of possible collision pair c is given by, $\frac{1}{2} N(N-1)$. Hence, the probability that any j th and k th globules coalesce, given that a coalescence event is due, is

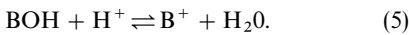
$$\Pr[x = (j, k) | T_Q = t_Q] = \frac{1}{c}, \quad 1 \leq j, k \leq N \tag{4}$$

since each pair has equal coalescence probability.

To identify this pair (j, k) , we generate a second random value of u , and compare with the above probability to obtain x . The relevant globules are then allowed to undergo coalescence-redispersion. In the following section, we describe the model equations solved in the above simulation format.

2.2. Model equations

The model equations have been written for extraction of a weak base (BOH), using a strong acid (HA) as the internal reagent, for monodisperse globules. In the reversible model, the emulsion globule has been pictured as a spherical oil drop with micron-sized aqueous droplets dispersed uniformly throughout the globule. The solute from the external phase diffuses through the oil (membrane) phase and reacts with the internal reagent present in the internal drops, via a reversible reaction. This may be written as



As a result, a solute concentration gradient develops in the membrane phase of all the globules. Due to incompleteness of the reversible reaction, unreacted solute can be present right upto the globule centre. The equation describing the concentration profile of BOH in the membrane phase of j th emulsion globule is obtained by adapting the reversible model (Bunge and Noble, 1984):

$$\begin{aligned} & \frac{\partial}{\partial t} [\text{BOH}]_{m,j} \\ &= \frac{D_{\text{eff}}}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} [\text{BOH}]_{m,j} \right) \\ & - \left(\frac{1-f_{m,j}}{f_{m,j}} \right) \left(\frac{\partial}{\partial t} [\text{BOH}]_{i,j} + \frac{\partial}{\partial t} [\text{B}^+]_{i,j} \right), \\ & j = 1, N. \end{aligned} \tag{6}$$

Now charge balance in the internal phase requires

$$[\text{H}^+]_{i,j} + [\text{B}^+]_{i,j} = [\text{OH}^-]_{i,j} + [\text{A}^-]_{i,j}. \tag{7}$$

Since extraction is generally carried out using a strong mineral acid (e.g. HCl) in the internal phase, dissociation of water is suppressed by the former and therefore,

$$[\text{OH}^-]_{i,j} \ll [\text{A}^-]_{i,j}.$$

So eq. (7) reduces to

$$[\text{H}^+]_{i,j} + [\text{B}^+]_{i,j} = [\text{A}^-]_{i,j} = [\text{A}^-]_i^0 \tag{8}$$

there being no change in the concentration of inert species, A^- , either due to extraction or leakage, and remains same for all globules.

Furthermore, equilibrium constant for reaction (5) is

$$K = \frac{K_b}{K_w} = \frac{[\text{B}^+]_{i,j}}{[\text{BOH}]_{i,j} [\text{H}^+]_{i,j}}. \tag{9}$$

Combining eqs (8) and (9) we have

$$[\text{B}^+]_{i,j} = \frac{K[\text{BOH}]_{i,j} [\text{A}^-]_i^0}{1 + K[\text{BOH}]_{i,j}}. \tag{10}$$

The high interfacial area of the globules and also that of internal drops results in instantaneous transfer of BOH across interfaces. In each globule, the dispersed aqueous drops would hence be in local equilibrium with the corresponding spatially varying membrane phase solute concentration. We therefore use the following equilibrium partition constant to relate BOH concentration at membrane-drop interfaces throughout the globule:

$$K_{im} = \frac{[\text{BOH}]_{m,j}}{[\text{BOH}]_{i,j}}. \tag{11}$$

Therefore eq. (6) on using eqs (10) and (11), reduces to

$$\begin{aligned} & \frac{\partial}{\partial t} [\text{BOH}]_{m,j} \left[1 + \frac{1}{K_{i,m}} \left(\frac{1-f_{m,j}}{f_{m,j}} \right) \right. \\ & \left. \times \left(1 + \frac{K[\text{A}^-]_i^0}{\left\{ 1 + K \frac{[\text{BOH}]_{m,j}}{K_{i,m}} \right\}^2} \right) \right] \\ &= \frac{D_{\text{eff}}}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} [\text{BOH}]_{m,j} \right), \quad j = 1, N. \end{aligned} \tag{12}$$

The above equation is same as that of the reversible model. The relevant initial and boundary conditions for eq. (12) are

$$t = 0, \quad [\text{BOH}]_{m,j} = 0 \quad (0 \leq r < R) \tag{13}$$

$$r = 0, \quad \frac{\partial}{\partial r} [\text{BOH}]_{m,j} = 0 \quad (t \geq 0) \tag{14}$$

$$r = R, \quad [\text{BOH}]_{m,j} = K_{bm} [\text{BOH}]_e \quad (t \geq 0). \tag{15}$$

For all the globules $f_{m,j}|_{t=0} = f_m^0$, given in Table 2, and for monodisperse globules $R = R_{32}$ which represents the radius of a characteristic globule having same ratio of volume to surface area as that of the whole globule population.

In order to obtain external phase solute concentration we consider the following additional mass balance equation, comprising of the N globules:

$$\begin{aligned} & V_e^0([\text{BOH}]_e^0 + [\text{B}^+]_e^0) \\ &= V_e([\text{BOH}]_e + [\text{B}^+]_e) + \sum_{j=1}^N \int_0^R [([\text{BOH}]_{i,j} \\ &+ [\text{B}^+]_{i,j})(1 - f_{m,j}) + [\text{BOH}]_{m,j} f_{m,j}] 4\pi r^2 dr \end{aligned} \quad (16)$$

where

$$V_e^0 = N \frac{4}{3} \pi R^3 \frac{f_b}{(1 - f_b)}. \quad (17)$$

After the (j, k) pair coalesces, at the time given by eq. (3), the membrane phase constituents of the two coalescing globules mix during the fusion step. However, the internal drops are not subjected to any collision with each other and therefore remain physically isolated. As a first step we assume the membrane phase mixing to be completed in the fused globule. Hence, the pre-existing solute concentration profiles in the membrane phase of the individual, interacting globules are abolished, resulting in a uniform membrane phase concentration throughout the transient, bigger globule. Furthermore, as required by the instantaneous nature of the reversible extraction reaction and BOH partition coefficients, membrane phase BOH concentration in this new globule achieves rapid equilibrium with the internal phase BOH and B^+ concentrations. As a consequence, we allow all the internal drops to achieve a solute concentration in equilibrium with the surrounding, uniform, membrane phase solute concentration. Mixing of the membrane phase solute and its equilibrium-redistribution with the internal phase is assumed to be instantaneous and no mass transfer from the external phase occurs during that period. This uniform membrane concentration in the transient globule, called $[\text{BOH}]_{m,t}$, is obtained from the following equation:

$$\begin{aligned} & [([\text{BOH}]_{i,t} + [\text{B}^+]_{i,t})(1 - f_{m,t}) + [\text{BOH}]_{m,t} f_{m,t}] V_t \\ &= T = \int_0^R [([\text{BOH}]_{i,j} + [\text{B}^+]_{i,j}) \\ &\quad \times (1 - f_{m,j}) + [\text{BOH}]_{m,j} f_{m,j}] 4\pi r^2 dr \\ &\quad + \int_0^R [([\text{BOH}]_{i,k} + [\text{B}^+]_{i,k})(1 - f_{m,k}) \\ &\quad + [\text{BOH}]_{m,k} f_{m,k}] 4\pi r^2 dr \end{aligned}$$

where

$$V_t = 2 \frac{4}{3} \pi R^3 \quad (19)$$

and

$$f_{m,t} = \frac{(f_{m,j} + f_{m,k})}{2}. \quad (20)$$

According to previous assumption, leakage occurs when the transient globule redisperses into two equal halves. In absence of any suitable hydrodynamic estimate, we have assumed that a fixed volume fraction of the internal phase v , leaks out during redispersion of the coalesced globule. The volume of internal phase leaked out is given by

$$V_l = v(1 - f_{m,t}) V_t, \quad (21)$$

with an associated amount of solute,

$$L = V_l([\text{BOH}]_{i,t} + [\text{B}^+]_{i,t}). \quad (22)$$

Fractional change in volume of daughter globules due to leakage will be $vqN_g(1 - f_m)t$, which will generally be small, and change in radius will be even smaller. The radius of redispersed globules therefore is assumed to remain unchanged by leakage. The external phase volume after leakage V_e^l , however is updated by adding the leaked volume V_l , to the prior-leakage external phase volume V_e . The new concentrations in the external phase are also recalculated, taking the leaked components into account, on satisfying eqs. (23)–(26).

Mass balance of solute:

$$V_e^l([\text{BOH}]_e^l + [\text{B}^+]_e^l) = V_e([\text{BOH}]_e + [\text{B}^+]_e) + L. \quad (23)$$

Charge balance:

$$[\text{OH}^-]_e^l + [\text{A}^-]_e^l = [\text{H}^+]_e^l + [\text{B}^+]_e^l \quad (24)$$

where

$$V_e^l[\text{A}^-]_e^l = V_e[\text{A}^-]_e + V_l[\text{A}^-]_e^0 \quad (25)$$

along with dissociation constant for the base and water,

$$K_b = \frac{[\text{B}^+]_e^l [\text{OH}^-]_e^l}{[\text{BOH}]_e^l}, \quad K_w = [\text{H}^+]_e^l [\text{OH}^-]_e^l. \quad (26)$$

The daughter globules also emerge with identical solute concentration in the membrane phase and an equilibrated solute content in the drops, with no gradient in either phase. However, the new uniform concentration is different from the transient, parent globule due to leakage. This is obtained as follows:

$$\begin{aligned} & [([\text{BOH}]_{i,d} + [\text{B}^+]_{i,d})(1 - f_{m,d}) \\ &+ [\text{BOH}]_{m,d} f_{m,d}] V_d = \frac{T - L}{2} \end{aligned} \quad (27)$$

where

$$f_{m,d} = \frac{(V_t - (1 - f_{m,j})V_j - (1 - f_{m,k})V_k)}{(V_t - V_l)} \quad (28)$$

and

$$V_d = \frac{V_l}{2}. \quad (29)$$

Of course, subsequently, mass transfer from external phase allows gradients to be set up in each of these globules, until they encounter any further collision.

Thus, we do not allow intermixing of the internal drops in a globule, during coalescence. Rather it is only through the above postulated mechanism that all the internal drops attain the same uniform concentration after redispersion.

Now, all the globules start with same volume fraction of membrane phase. Interestingly, however, due to the random nature of the coalescence-redispersion process, any globule would undergo different number of such events and at different times, and hence would loose variable amount of internal phase via associated leakage. Correspondingly, membrane volume fraction in a globule increases and thus a distribution in volume fraction develops with time. Equation (28) implies that any two interacting globules j and k , with different membrane phase volume fractions, emerge with the same membrane volume fraction $f_{m,d}$, of daughter globules, which is reassigned after redispersion to the indices j and k . Therefore, a distribution in membrane volume fraction would exist in the extractor.

The partial differential equation (12) has been non-dimensionalised and discretised using finite difference. The resulting initial value problem has been solved by Runge-Kutta method with a time step of 0.1 s for monodisperse globules. Simultaneously, eq. (16) was satisfied as a mass balance constraint at each time step, to obtain the external phase solute concentration ($[\text{BOH}]_e + [\text{B}^+]_e$) with time. The changes in the interacting globules and the external phase, due to coalescence and leakage occurring at time intervals given by eq. (3), were calculated by using eqs (18), and (22)–(27).

3. RESULTS AND DISCUSSION

The new model has been used to compute the extraction profiles of weak organic bases like amines for the experimental conditions of Baird *et al.* (1987). HCl was used as the internal reagent for facilitating the solute transport. These predicted profiles have been compared with the reversible model predictions of Baird *et al.* (1987) in Figs 1–3. The coalescence frequency q and leakage fraction ν , appearing in the present model, are treated as adjustable parameters. These and other relevant parameters for simulation are given in Tables 1 and 2. An estimate of q obtained from the empirical equation of Laso *et al.* (1987), for the enlisted experimental conditions is of the same order. The leakage coefficient ν , presently used, on

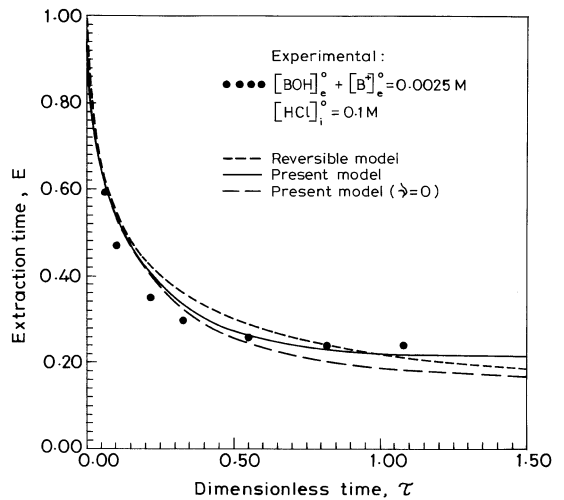


Fig. 1. Comparison of present model and reversible model for experimental data of 4-chloroaniline extraction.

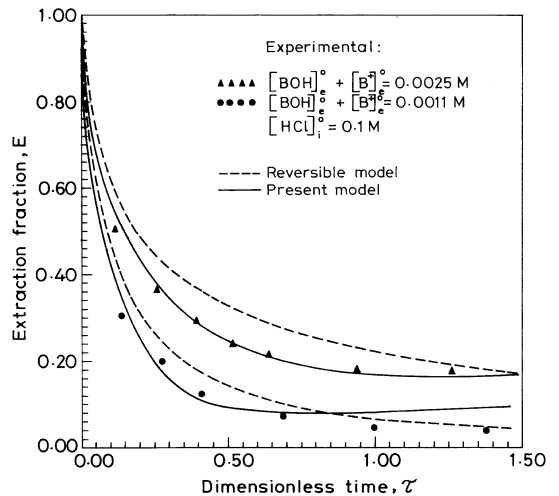


Fig. 2. Comparison of present model and reversible model for experimental data of *p*-toluidiene extraction.

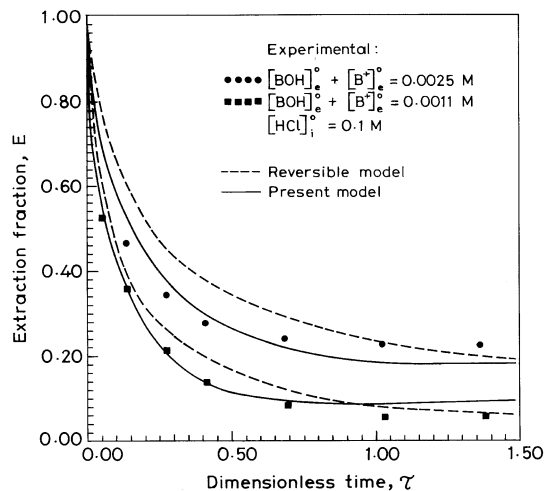


Fig. 3. Comparison of present model and reversible model for experimental data of *m*-toluidiene extraction.

Table 1. System parameters of Baird *et al.* (1987)

System parameters	p-Toluidiene	m-Toluidiene	4-chloro aniline
K_{bm}	3.9	3.9	5.8
K_{im}	3.9	3.9	5.8
$K (\times 10^{-4} \text{ mol}^{-1} l)$	12.02	5.37	1.4
$D_{cfr}^* (\times 10^{10} \text{ m}^2 \text{ s}^{-1})$			
(At $2.5 \times 10^{-3} \text{ M}$)	0.875	1.025	1.327
(At $1.1 \times 10^{-3} \text{ M}$)	1.2	1.35	–
E^∞			
(At $2.5 \times 10^{-3} \text{ M}$)	0.0755	0.098	0.155
(At $1.1 \times 10^{-3} \text{ M}$)	0.0065	0.014	–

*Calculated according to Bunge and Noble (1984), using aqueous and organic-phase diffusivities reported by Baird *et al.* (1987).

Table 2. Experimental and simulation parameters

Parameters	Values
N_s	500 rpm
f_m^0	0.64
f_b	0.94
N_g	$5.47 \times 10^8 \text{ m}^{-3}$
$[A^-]_i^0$	0.1 M
$([\text{BOH}] + [\text{B}^+])^0$	$2.5 \times 10^{-3}, 1.1 \times 10^{-3} \text{ M}$
R_{32}	$3 \times 10^{-4} \text{ m}$
q	$7 \times 10^{-12} \text{ m}^3 \text{ s}^{-1}$
v	0.02
N	100

multiplying with q , and number density of globules N_g , provide an equivalent estimate of continuous leakage coefficient of a single globule used in previous models (Chan and Lee, 1987; Borwankar *et al.*, 1988). The resulting coefficient, vqN_g , for our case is of the order of 10^{-5} s^{-1} .

Tracer experiments have been carried out (Nakashio, 1993), to directly measure the extent of leakage for different surfactants. For an almost similar membrane type and composition (nature and concentration of surfactant), as that used by Braid *et al.* (1987). Nakashio (1993) report a value of the same order as obtained from the current model. We, however, cannot utilise the exact value of Nakashio (1993) due to differences in membrane composition (e.g. solvent oil) and in operating variables. Borwankar *et al.* (1987), on the other hand, had to devise a time dependent leakage parameter, for explaining their experimental data. Their leakage coefficient was increasing with time, which was not properly substantiated from a physical standpoint. Furthermore, they performed experiments at a much lower stirrer speed of 150 r.p.m., resulting in a significantly lower fitted value. Contrary to this Braid *et al.* (1987), did experiments at 500 r.p.m., where one expects more leakage, as the globules experience increasing shear with increase in agitation. This trend of leakage with r.p.m.

has been verified by Terry *et al.* (1982), while reporting leakage rate fitted to their own experimental data. For an agitator speed in the range of 520 to 535 r.p.m., it is of the same order as found from the present model. In fact, no model exists to predict the leakage coefficient *a priori*. However, our estimated parametric value compares favourably with the above mentioned experimental data of previous workers.

For all the dimensionless solute concentration–time plots (E vs τ) of different amines shown (Figs 1–3), the reversible model underpredicts the extraction at small residence time but overpredicts towards the end. However, the simulated curves from the present model, are able to represent the experimental data more closely, throughout the whole extraction period. Such an improvement is due to the incorporation of interaction and leakage in the reversible model. This has been explained below.

The sole effect of coalescence-redispersion on ELM extraction can be seen from Fig. 1, on comparing the reversible model results with the simulated curve in absence of leakage ($v = 0$). This comparison shows that the above phenomena improves prediction at small extraction times but diverges subsequently from the experimental points. This is true for all the systems considered here and the improvement can be explained as follows. Globules undergoing interaction attain a uniform value of $[\text{BOH}]_m$ temporarily, due to complete mixing of globule's membrane contents through internal circulation. The net effect is that the solute penetrates faster inside the globule and reacts therein. As a result the effective reaction rate, otherwise limited by slow membrane-phase diffusion, is considerably enhanced. Effect of this enhanced solute penetration is seen to be quite significant for big emulsion globules ($R = R_{32} = 3 \times 10^{-4} \text{ m}$) in consideration here. Furthermore, the post-coalescence average $[\text{BOH}]_m$ in the coalescing globules will be less than the pre-coalescence value of $[\text{BOH}]_{mlr=R}$. This would have been true even in absence of any internal reaction. Both these effects combine to give a steep concentration gradient at the globule-external phase boundary, increasing subsequent solute flux. Thus,

faster extraction results, compared to the isolated globule considered in the reversible model. Interaction thus causes a quicker approach towards the equilibrium-limited final extraction E^∞ . This value is same as that obtained from the reversible model for a single globule.

As discussed above, coalescence-redispersion alone cannot explain all the experimental features. The reversible model used by Baird *et al.* (1987), in absence of leakage, expectedly predicts the equilibrium-limited extraction E^∞ to be achieved, if sufficient extraction time is allowed. In contrast, the maximum experimental extraction in figures 1–3 is seen to be much less than E^∞ . For example, for 4-chloroaniline, Table 1 shows the maximum possible theoretical extraction to be 84.5%, for an ELM system with the tabulated concentration and volume fraction. However, in the experiment, only about 76% extraction (Fig. 1) has been achieved. This discrepancy points to the presence of some mechanism attributing to loss in extraction, which becomes dominant than the normal diffusion rate towards the end. Therefore, we have incorporated the leakage model to explain the experimental results particularly towards the end of batch extraction. In this event, previously extracted BOH and B^+ is transferred back to the external medium. Even though leakage occurs intermittently from the beginning, the resulting loss assumes importance only when the internal drops become rich in solute. Thus, the present model which incorporates leakage, provides a more reliable estimate of the final extraction for these experimental data. The extent to which leakage is important is evident from Fig. 1, where it becomes significant at large batch residence time. The combined effects of coalescence and leakage thus provide a significant improvement of results obtained from the present model, in contrast to the basic reversible model. However, in both the Figs 2 and 3, we notice an upward movement of the extraction profile towards the end, for external solute concentration of 1.1×10^{-3} M. This follows from leakage, which in its role of reducing extraction, assumes more significance for lower external concentration.

So far, it has been assumed that every collision leads to coalescence. Furthermore, we have allowed a complete mixing of the membrane phase contents of the fused globule during the dimer life time, so that the redispersed globules emerge with the same and uniform $[BOH]_m$ concentration. Thus, an exchange of solute of the interacting globule occurs implicitly. However, the presence of surfactants may result in partial fusion and smaller dimer life time, due to reduced coalescence efficiency. In the extreme situation, there would be no fusion and exchange at all and the colliding globules would just drift apart with new but different uniform concentrations. Individual internal mixing however, would be possible due to circulation currents set up by the labile surfactant layer during impingement. This possibility prompted us to delineate the separate roles of individual mixing and mutual exchange during globule interactions. We

accordingly, allowed only collision with complete mixing but no fusion and solute exchange. In case of monodisperse globules, we did not observe any discernible effect of exchange added to that of individual mixing. This probably reflects the initial equality of reactant content for monodisperse globules, and the subsequently same diffusion–reaction rate until any interaction. In order to overcome this limitation of the monodisperse population, we sampled same number of globules ($N = 100$), from a symmetric normal distribution of globule volume. The volume of each sampled globule V_g , is obtained by acceptance-rejection technique from a normal probability density function, given by,

$$f(V_g) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-\frac{(V_g - V_{10})^2}{2\sigma^2}\right] \quad (30)$$

where V_{10} is the mean volume of the sample. For preserving the sauter-mean radius of previous monodisperse population (Figs 1–3, $R_{32} = 3 \times 10^{-4}$ m), we have used for the normal distribution a value of $V_{10} = 1.12 \times 10^{-10}$ m³, corresponding to $R_{10} = 2.99 \times 10^{-4}$ m, in the above equation. The resulting sample of 100 globules obtained from eq. (30) then has the same sauter-mean radius of 3×10^{-4} m. For a sample calculation, a value of $\sigma = 3.35 \times 10^{-11}$ m³, was used as the standard deviation of globule volumes in eq. (30). So the sampled normal distribution has a coefficient of variation of 0.3. To simplify the redispersion step, we have preserved the volume of interacting globules, through unequal breakage. As a result, the volume of individual globules do not change during a simulation run; and the previous model equations can be used, by using a variable globule radius and volume.

Figure 4 shows the results for a normally distributed globule volume, without any leakage. Here too, extraction profiles for the two situations of exchange and no-exchange of solute were same, and therefore is

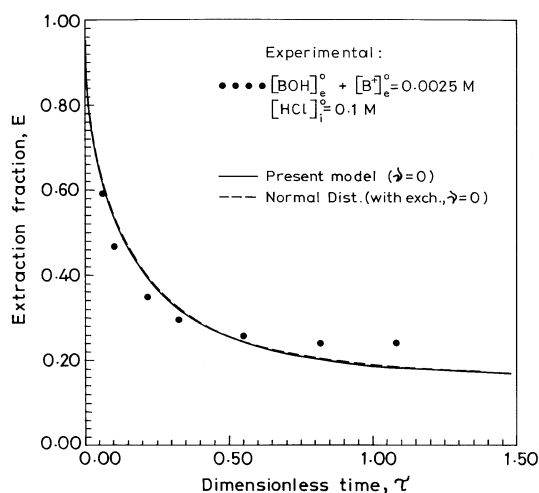


Fig. 4. Effect of a normal globule volume distribution (with exchange) for 4-chloroaniline extraction.

not shown separately. The obvious conclusion is that fusion and exchange during interactions is not of any importance to predict extraction rates, whereas, internal mixing caused by internal circulation is important. The effect of the theoretical normal distribution is also not significant on extraction rate, when one recognises sauter-mean radius as the characterising globule dimension. The same conclusion has been arrived at by Lorbach and Hatton (1988) for a similar, nearly symmetric, but empirical globule radius distribution.

4. CONCLUSION

Our model focuses on two mechanisms bearing profound influence on ELM extraction, especially at higher agitation speeds. First of all, random coalescence and breakage of emulsion globules which is inevitable in a turbulent field, and hitherto completely relegated in extraction models, has been included for the first time. Instead of modelling a single globule, we simulate a batch system as a collection of emulsion globules interacting via random coalescence-redispersion. Therefore, we have been able to overcome the limitations of existing models, which deal with a single isolated globule. Moreover, accounting of internal phase leakage has been rationalised in this model, which so far was treated as a continuous drainage of droplets from a single globule into the external medium, without citing proper reasons thereof. In contrast to such an ad-hoc description, we have represented leakage from a globule as a discrete process, occurring only at the instant of redispersion. The present approach of Monte Carlo simulation including the above two phenomena has provided a significant advancement over the reversible extraction model of Bunge and Noble (1984). A much better explanation of experimental data of Baird *et al.* (1987) is thus possible with the present model. The model predictions shown are for monodisperse globules undergoing fusion, and solute exchange during interaction. However, the results did not change on relaxing these assumptions. Although we have illustrated the extraction of weak bases, like amines, facilitated with a strong internal phase acid; other systems can be accommodated in the present formulation without any loss of generality.

NOTATION

$[A^-]$	concentration of anion, mol m^{-3}
$[B^+]$	concentration of dissociated base (dissociated solute), mol m^{-3}
$[BOH]$	concentration of undissociated base [undissociated solute], mol m^{-3}
c	total number of collision pairs
D_{eff}	effective diffusivity in globule, $\text{m}^2 \text{s}^{-1}$
E	$([BOH]_e + [B^+]_e)/([BOH]_e + [B^+]_e)^0$, dimensionless external phase solute concentration
f	normal probability density function of globule volume, m^{-3}

f_b	volume fraction of external phase
f_m	volume fraction of globule occupied by the membrane phase
K	reaction equilibrium constant, $\text{mol}^{-1} \text{l}$
K_b	dissociation constant of base, mol l^{-1}
K_{bm}	solute partition coefficient between the membrane and external phases
K_{im}	solute partition coefficient between the membrane and internal phases
K_w	dissociation constant of water, $\text{mol}^2 \text{l}^{-2}$
L	moles of solute leaked, mol
N	total number of globules used in simulation
N_g	number density of globules in the dispersion, m^{-3}
N_s	agitator speed for experiment, rpm
q	volume-average coalescence frequency of a single globule, $\text{m}^3 \text{s}^{-1}$
q_T	total coalescence frequency of N globules, s^{-1}
R_{32}	sauter-mean radius of w/o emulsion globule, m
R_{10}	mean radius of w/o emulsion globule, m
r	radial distance from globule centre, m
T	total mass of solute in transient globule, mol
T_Q	random variable, for quiescence time interval
t	time, s
t_Q	value of random quiescence time interval T_Q , s
u	uniform random number between (0, 1)
V_d	volume of daughter globules, m^3
V_e	volume of external phase associated with N globules, at any time, m^3
V_g	volume of single globule, m^3
V_l	volume of internal phase leaked, m^3
V_t	volume of transient globule, m^3
V_{10}	mean volume of exponentially distributed globules, m^3
x	bi-variate random variable indicating globule indices for collision
$[H^+]$	concentration of hydrogen ion (internal reagent), mol m^{-3}
$[OH^-]$	concentration of hydroxyl ion, mol m^{-3}

Greek letters

ν	volume fraction of internal phase drop leaked
σ	standard deviation in globule volume, m^3
τ	dimensionless time used in Figs (1–4) ($D_{\text{eff}}^b/R_{32}^2$)

Subscripts

d	daughter globules upon redispersion
e	external phase
i	internal phase
j, k	globule index in simulation
m	membrane phase
t	transient globule upon coalescence of pair (j, k)

Superscripts

- l* terms after leakage
 0 initial value
 ∞ final equilibrium value

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