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A MODEL FOR THE PREDICTION OF EXTRACTION CHARACTERISTICS OF STRONG ACIDS/BASES BY LIQUID SURFACTANT MEMBRANE

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ABSTRACT

A model has been developed to predict the extraction characteristics of multicomponent solutes with high dissociation constants by Type-I facilitation employing liquid surfactant membrane in a batch separation system. The conventional reversible model of Bunge and Noble (J. Membr. Sci. **1984**, *21*, 55) has been extended incorporating charge balance in the aqueous phases of the extraction system and allowing for hydrolysis of salt in the internal droplets. Model predictions for multicomponent systems are found to be in good agreement with the experimental data available in the literature. Extraction profiles simulated for single component systems using this model have been compared with the reversible model given by Bunge and Noble. The flexibility of the present approach in comparison to the reversible model has been illustrated with examples.

Key Words: Emulsion liquid membrane; Extraction ionic equilibrium; Facilitated transport.

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INTRODUCTION

Liquid surfactant membranes (LSM), first developed by Li (1) for hydrocarbon separation, have since been applied to a variety of separations, including recovery and purification of metal ions, removal of organic contaminants from waste water, and various biochemical and biomedical applications. This is prepared by first forming an emulsion between two immiscible phases and then dispersing this emulsion in a third (continuous) phase, by agitation. The emulsion globules are 0.1–2 mm in diameter, whereas the internal droplets are 1 to 10 μm in diameter. The membrane phase is the liquid phase that separates the encapsulated internal droplets in the emulsion globules from the external continuous phase. The solute is selectively transported from the external continuous phase to the internal encapsulated droplets.

The first models of this type of liquid membrane processes neglected the complex structure of emulsion globules. All the internal droplets were assumed to form one big, homogenous internal drop covered with the membrane. Mass transfer occurs through the stagnant liquid membrane shell into an internal interface where it reacts with the reagent. Some considered an equivalent planer slab of uniform thickness to represent spherical geometry. Later models, such a those of Ho et al. (2), Bunge and Noble (3), and Baird et al. (4), suggested that the droplets of the internal reagent are immobile and are uniformly dispersed in the emulsion globule. In view of the strong presence of surfactants, no internal circulation occurs within the emulsion globule. Globule size variations were lumped into a single effective mean diameter.

Two general mechanisms called Type-I and Type-II facilitation have been identified to maximize the flux through the membrane and the capacity of the receiving phase. In facilitation of the first type, the solute is soluble in the membrane phase. It diffuses through it and reacts with the reagent present in the internal phase. In Type-II facilitation, an extractant incorporated in the membrane phase "carries the solute" through the globule into the internal phase—binding and releasing the solute at the external and internal interfaces respectively.

Several mathematical descriptions of Type-I facilitation have been formulated to describe the transport processes involved. One approach is described by Ho et al. (2) and is referred to as the advancing front approach. Solute removed from the bulk phase diffuses through the globule until it is depleted by an instantaneous and irreversible reaction with the internal reagent. Hence, the solute is unable to penetrate into the globule beyond those droplets that are completely depleted of reagent, as it is immediately removed by reaction with the internal reagent. Thus, there must exist a sharp boundary, or reaction front at which the reaction takes place, which separates the inner region containing no solute from the outer reacted region that contains no reagent. As the reagent is consumed by the reaction, the

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reaction front advances into the globule. It is assumed that the reaction products are immobilized, and hence they are incapable of back diffusion.

An alternate procedure, taken by Bunge and Noble (3) as well as Teramoto et al. (5,6), incorporates reaction equilibrium into a description of the rate-controlling membrane transport processes. Without any adjustable constants, the model of Bunge and Noble (3) predicts batch extraction data from measurable physical parameters. Reaction reversibility precludes the reaction-advancing front, because there is no separate reacted and unreacted regions. Baird et al. (4) extended the reversible reaction model to predict the extraction profiles of multicomponent mixtures. Existing literature on extraction models demonstrate the superiority of models that incorporate reaction reversibility over the irreversible reaction assumption of advancing front approach.

One of the applications of the Emulsion Liquid Membrane (ELM) technique is the extraction of organic acids and bases such as phenol, acetic acid, carboxylic acids, aniline, and *p*- and *m*-toluidiene. These solutes dissociate into ions in the aqueous phase to a greater or lesser extent depending on their dissociation constant. The advancing front model assumes these electrolytes remain in undissociated form in the external phase while being completely dissociated in the internal phase, irrespective of the relative concentrations of the solute and internal reagent or dissociation constant. Though the former assumption would be justified for solute having low dissociation constant, the latter would be valid only for solutes having high dissociations constants.

The reversible model formulation (3) also neglected solute dissociation in the external phase. A chemical equilibrium constant characterizes the reversible reaction of these electrolytes in the internal droplets instead of the more appropriate ionic equilibrium coupled with the condition of electroneutrality. Borowankar et al. (7) took into account the dissociating nature of the solute (*o*-chlorophenol) in the external phase in modeling the effect of internal phase leakage on extraction profiles in a batch system. The solute was considered to reside only in its dissociated form in the internal phase whereas the internal reagent concentration remained constant at its initial value for all extraction times. Such a condition would exist if the original solute to internal reagent mole ratio is small.

Bhowal and Datta (8) presented a single parameter model based on pseudosteady state approximation to predict the experimental extraction data. Though the reversible model predicts a finite solute concentration even at the center of the globule, the model states that beyond a certain distance from the surface of the globule, the concentration of unreacted solute within the emulsion globule can be considered to be zero. The assumption was justified based on the fact that the reaction between weak acid with strong base or vice versa can be considered to be irreversible at low solute to internal reagent concentration, a condition that would prevail in the interior of the emulsion globule. The parameter was later

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related to the physical and experimental conditions of the extraction system (9). Bandyopadhyaya et al. (10) incorporated the effect of globule–globule interaction and leakage in the transport mechanism for extraction of weak organic bases with strong acids. While retaining the equations of the reversible model (3) to describe the concentration profile of the solute in the membrane phase, they took into account the dissociation of the solute in the external phase. Chan and Lee (11) also used the same approach in incorporating the leakage effect due to internal phase for extraction of weak acids by LSM.

The assumptions made by these models add unnecessary complexity to modeling of the system. They could be of limited usefulness in predicting the experimental data of a wide variety of experimental conditions. In this paper, we have developed generalized equations for extraction of multicomponent mixtures of organic acids/bases using LSM in a batch extraction system incorporating the charge balance for both the aqueous phases. The predictions have been compared with the experimental extraction data available in the literature. Simulation of the model equations for single component batch extraction by LSM has been done to demonstrate the advantages associated with the present approach. The results have been compared with the reversible model (3).

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MATHEMATICAL MODELING

The geometry of the emulsion globules is the same as considered by the later models described previously. The external phase resistance has been neglected as has been coalescence and redispersion of globules. We consider the extraction of bases B_jOH where $j = 1, 2, \ldots, n$ from the external phase using a strong internal reagent (HA) that is completely dissociated in the internal droplets. In the external phase, the undissociated solute is in equilibrium with the ions. The undissociated solute from the external phase diffuses through the oil (membrane) phase and partly dissociates in the internal droplets yielding B_j^+ ions. The solute partition coefficient between the internal and membrane phase has been taken to be the same as between the external and membrane phase. The dissociation constant for the *j*th solute in the aqueous phases is given by

$$K_{\mathrm{bj}} = \frac{[\mathrm{B_j^+}][\mathrm{OH^-}]}{[\mathrm{B_jOH}]} \tag{1}$$

The equations describing the solute concentration of B_jOH in the membrane portion of the globule are obtained by adapting the reversible model:

$$\frac{\partial}{\partial t}[\mathrm{B_jOH}]_{\mathrm{m}} = D_{\mathrm{eff_j}} \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}[\mathrm{B_jOH}]_{\mathrm{m}}\right) - \frac{1 - f_{\mathrm{m}}}{f_{\mathrm{m}}}\left(\frac{\partial}{\partial t}[\mathrm{B_jOH}]_{\mathrm{i}} + \frac{\partial}{\partial t}[\mathrm{B_j^+}]_{\mathrm{i}}\right) \quad j = 1, 2, \ldots, n \tag{2}$$

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The initial and relevant boundary conditions for Equation (2) are

$$\begin{aligned} t &= 0 \quad [\mathrm{B_jOH}]_\mathrm{m} = 0 \\ r &= R \quad [\mathrm{B_jOH}]_\mathrm{m} = K_\mathrm{j}[\mathrm{B_jOH}]_\mathrm{e} \\ r &= 0 \quad \frac{\partial[\mathrm{B_jOH}]_\mathrm{m}}{\partial r} = 0 \end{aligned} \tag{3}$$

The charge balance in the internal phase requires

$$\sum_{\mathrm{k}=1}^{n}[\mathrm{B_k^+}]_\mathrm{i} + [H^+]_\mathrm{i} = [\mathrm{OH^-}]_\mathrm{i} + [\mathrm{A^-}]_\mathrm{i} \tag{4}$$

there being no change in the concentration of the inert species, A^-, due to extraction. The ionization constant of water is

$$[\mathrm{H^+}]_\mathrm{i}[\mathrm{OH^-}]_\mathrm{i} = K_\mathrm{w} \tag{5}$$

Equation (2) has been rewritten in terms of the concentration of solute in the membrane phase. The details of the derivation are given in Appendix B.

$$\left\{1 + \frac{1-f_\mathrm{m}}{f_\mathrm{m}}P_\mathrm{j}\right\}\frac{\partial}{\partial\tau}[\mathrm{B_jOH}]_\mathrm{m} + \frac{1-f_\mathrm{m}}{f_\mathrm{m}}\sum_{\substack{\mathrm{k}=1\\ \mathrm{k}\neq\mathrm{j}}}^{n} Q_\mathrm{k}\frac{\partial}{\partial\tau}[\mathrm{B_kOH}]_\mathrm{m} = \frac{D_{\mathrm{eff_j}}}{D_{\mathrm{eff_{mix}}}}\frac{1}{\eta^2}\frac{\partial}{\partial\eta}\left(\eta^2\frac{\partial}{\partial\eta}[\mathrm{B_jOH}]_\mathrm{m}\right) \tag{6}$$

In order to obtain external phase concentration of the solutes, we consider the following mass balance equation written for the *j*th component

$$[\mathrm{B_jOH}]_\mathrm{eo} + [\mathrm{B_j^+}]_\mathrm{eo} = [\mathrm{B_jOH}]_\mathrm{e} + [\mathrm{B_j^+}]_\mathrm{e} + 3\frac{1-f_\mathrm{b}}{f_\mathrm{b}}\int_0^1 \{(1-f_\mathrm{m})([\mathrm{B_jOH}]_\mathrm{i} + [\mathrm{B_j^+}]_\mathrm{i}) + f_\mathrm{m}[\mathrm{B_jOH}]_\mathrm{m}\}\eta^2\,d\eta \tag{7}$$

for $\tau = 0$ and

$$[\mathrm{B_jOH}]_\mathrm{e} = [\mathrm{B_jOH}]_\mathrm{eo} \tag{8}$$

The charge balance in the external phase is then:

$$\sum_{\mathrm{k}=1}^{n}[\mathrm{B_k^+}]_\mathrm{e} + [\mathrm{H^+}]_\mathrm{e} = [\mathrm{OH^-}]_\mathrm{e} \tag{9}$$

The multicomponent equations are solved numerically. The partial differential Equation (6) are discretised in space coordinate using finite difference. The resulting set of ordinary differential equations has been solved by multidimensional

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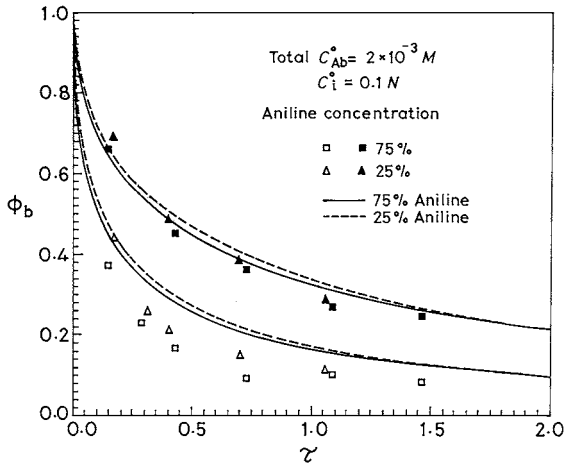

Figure 1. Comparison of present model with the experimental data (symbols) for mixtures of aniline and *p*-toluidiene of Baird et al. (5).

Runge-Kutta method for monodisperse globules. Simultaneously Equation (7) was satisfied for all the components as a mass constraint at each time step.

RESULTS AND DISCUSSION

Baird et al. (4) have reported binary extraction experimental data for aniline ($K_b = 4.274 \times 10^{-10}, K = 1.7$) and *p*-toluidiene ($K_b = 12.02 \times 10^{-10}, K = 3.9$) for initial total amine concentrations of 0.002 M and 0.001 M using LSM. The present model equations have been simulated to compute the extraction profiles of these amines for the given experimental conditions. Figures 1 and 2 compare the model prediction with the experimental extraction data. Identical symbols are used to plot experimental aniline and *p*-toluidiene concentrations of the same mixture; open symbols designate the concentration of *p*-toluidinene, whereas solid symbols specify aniline. The solid squares represent 75% aniline concentration, and the solid triangles represent 25% aniline concentration. The effective diffusion coefficients, D_{eff_j} and $D_{\text{eff}_{\text{mix}}}$ have been calculated according to the approach outlined by Baird et al. (4). The model satisfactorily predicts the experimental extraction performance at both concentrations. The conventional reversible model (3) results have been found to agree closely with those of the extended model. There is no discernable difference in the two models at low dissociation constants of the solute.

The present model equations differ from that of the reversible model in that the charge balance equations have been incorporated for both the phases. One of

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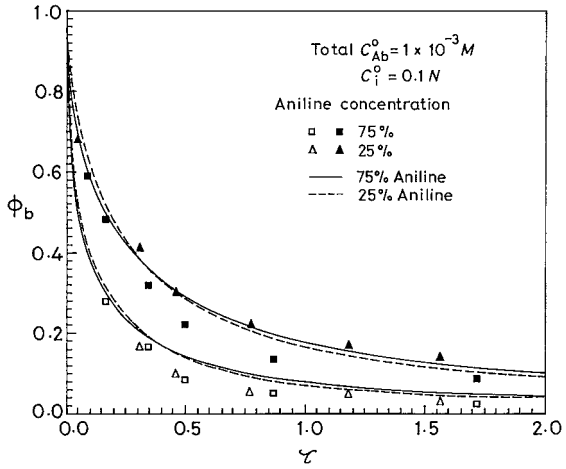

Figure 2. Comparison of present model with the experimental data (symbols) for mixtures of aniline and *p*-toluidiene of Baird et al. (5).

the main differences between the two models lies in the expression relating the concentration of product to initial internal reagent and the solute concentration in the membrane phase. If the hydroxyl concentration in the charge balance equation for the internal phase is considered negligible, Equation (6) for a single solute reduces to the same expression as used by the reversible model. This has been derived in Appendix A. The difference in formulation of the two approaches should reflect on the extraction rate of the solutes. The differences have been demonstrated by comparing the simulated dimensionless external phase concentration versus dimensionless time profiles for hypothetical solutes as depicted in Figures 3 through 6. Simulations have been carried out for the same values of f_m and f_b as in the previous case, that is, 0.64 and 0.94, respectively, whereas the diffusivity has been taken to be same as *p*-toluidiene.

The extraction rate decreases as the original mole ratio of solute to internal reagent ratio increases (3). However, their discussion excludes the effect of solute dissociation; that can be taken into account in this model. The dimensionless external phase concentration obtained by simulation of the reversible and the present model has been plotted in Figure 3 as a function of dimensionless time for two different initial solute concentrations in the external phase. The reversible model approach overestimates the solute extracted for both values of C^0_{Ab}. At large dimensionless times, both the models predict that the system has achieved equilibrium, as indicated by the constant dimensionless concentration. The predicted equilibrium solute concentration in the external phase from these two models is also seen to be different. The same extraction profiles were obtained on using the equations of the reversible model to represent the concentration profiles

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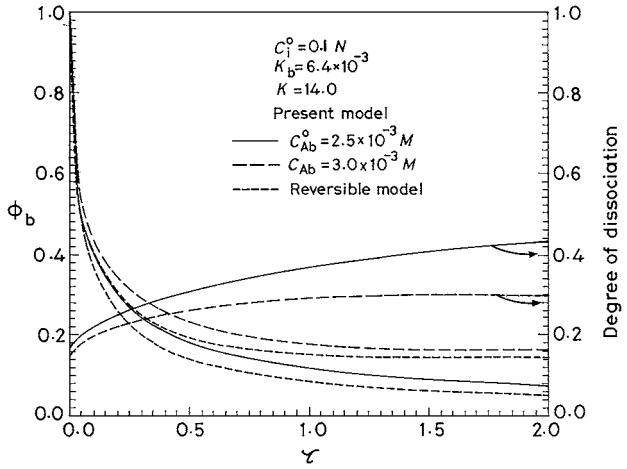

Figure 3. Dimensionless external phase concentration as a function of τ for the present model and the reversible model (3).

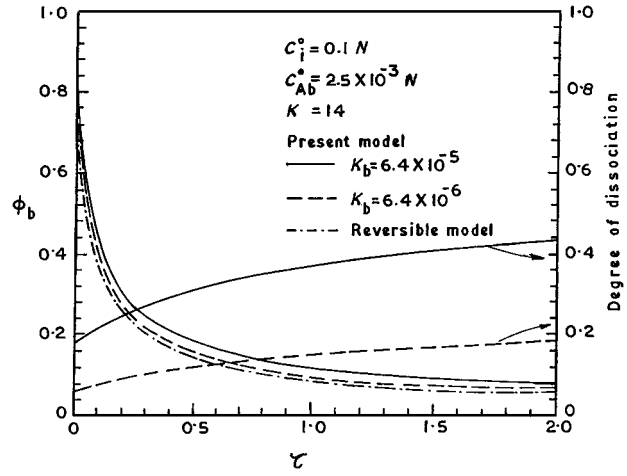

Figure 4. Dimensionless external phase concentration as a function of τ for the present model and the reversible model (3).

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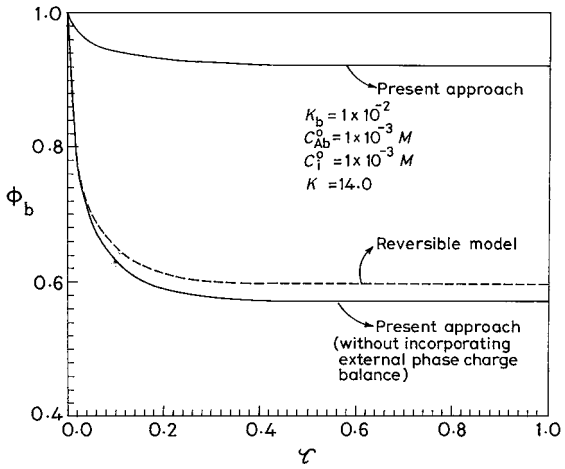

Figure 5. Dimensionless external phase concentration as a function of τ for the present model and the reversible model (3).

within the globule while retaining charge balance equation in the external phase. So the discrepancies arise only due to the exclusion of charge balance equation from the external phase by the reversible model. The ions cannot diffuse into the emulsion globule, and thus constitutes a loss in driving force for solute transfer

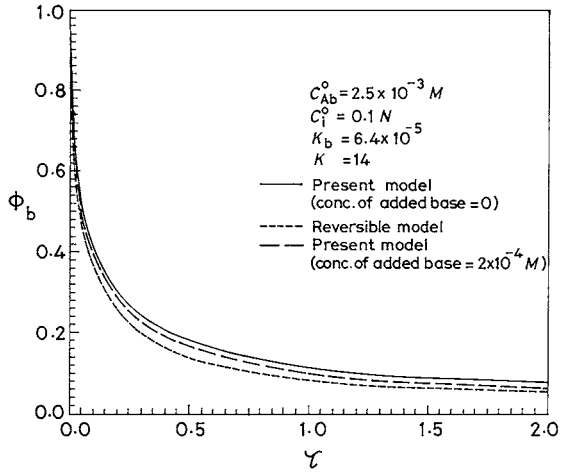

Figure 6. Dimensionless external phase concentration as a function of τ for the present model and the reversible model (3).

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into the emulsion globule. The net result is a lower extraction rate as predicted by this model compared with reversible model that neglects solute dissociation in the external phase.

As extraction proceeds, lowered solute concentration in the external phase results in increased degree of dissociation of solute (defined as the proportion of total number of dissociated molecules to the total number of molecules) as shown in the figure. Degree of dissociation tends towards one as the solution becomes dilute and hence modifies the estimation in the solute extracted obtained from the reversible model. This also gives rise to the increased difference in extraction profiles between the two models at the lower value of the initial solute concentration.

The reversible model suggests that an increased equilibrium constant means a preference of the forward reaction occurring in the internal phase. So the system appears to approach irreversibility and consequently extraction rate is higher. Figure 4 compares the extraction profile of two solutes with identical phase equilibria and varying dissociation constant, K_b. The initial ratio of reagent to solute concentration for both components is same. The predictions of reversible model coincide for the two different values of K_b and are shown by a single dashed curve in the figure. The present model surprisingly predicts that extraction rate increases with decrease with K_b. The profile tends towards the reversible reaction result as K_b decreases. The difference in the extraction characteristics predicted by the two models again lies in not accounting for the dissociation of solute in the external phase. As K_b decreases, the degree of dissociation of solute decreases. As explained earlier, this increases the driving force for extraction and brings the predicted profile by this model closer to the reversible reaction model. Consequently, designing separation equipment using models not considering the effects of solute dissociation could lead to serious errors.

The consequences of neglecting solute dissociation in the external phase on the extraction rate have been stated in the previous paragraphs. The effect of incorporating charge balance in the internal phase on the predicted extraction rates has been examined here. This has been obtained from the comparison between the reversible model results and the present model (shown by a continuous line) simulated, assuming that solute does not dissociate in the external phase and illustrated in Figure 5. Incorporating charge balance in the internal phase indicates an enhanced extraction rate.

To explain the results consider the internal phase charge balance equation

$$[B^+]_i + [H^+]_i = [OH^-]_i + [A^-]_i \tag{10}$$

As shown in Appendix A, the present model reduces to the reversible model if the hydroxyl concentration is assumed to be negligible. As is evident

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from Equation (10), for a given $[A^-]_i$, $[B^+]_i$ is higher on consideration of hydroxyl concentration. So the unreacted solute concentration in the internal phase will be lower. The driving force for mass transfer would be correspondingly increased, and extraction rate is faster. Reversible model neglects the contribution of $[OH^-]_i$ to extraction and hence becomes inadequate to explain the extraction data. This hydroxyl concentration would become negligible when the solute concentration is small compared to reagent concentration in the internal phase. Hydrolysis of the salt would then be negligible and the hydronium concentration is equal to the stoichiometric concentration of unneutralized acid (12).

A route to increasing extraction of organic bases having high dissociation constants using Type-I facilitation could be adding a second base to the external phase with an ion common to the solute. Figure 6 shows the extraction profile of the same solute when a second base is added to the external phase. The added base is assumed to always remain fully dissociated and hence cannot diffuse into the emulsion globule. In the mathematical formulation of the present model, it thus appears as a constant term in the charge balance equation written for the external phase, that is, Equation (9). Analysis of the figure reveals that the solute extraction is enhanced by the presence of this base and approaches the reversible model predictions as the concentration of the added base is progressively increased. This can be explained from the phenomenon of common-ion effect. The presence of the ion $[OH^-]_c$, common with that produced by dissociation of the solute, will depress the degree of dissociation in order to maintain the constant value of K_b. Consequently, the extraction will be faster. This effect can also be utilized in the internal phase to make the extraction rate of solutes more uniform. It clearly demonstrates the flexibility of the present model over the reversible model of Bunge and Noble (3) that cannot represent these extraction characteristics.

CONCLUSION

A model has been formulated for extraction of strong acids/bases by liquid-surfactant membranes by Type-I facilitation. The conventional reversible model equations presented by Bunge and Noble (3) has been modified incorporating the charge balance equations for the aqueous phase of the emulsion globule. The advantages of using this generalised model for extraction of organic acids/bases has been demonstrated. The reversible model formulation can be used to predict the extraction rates if the solutes have low dissociation constants or the ratio of solute to internal reagent concentration is low.

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NOMENCLATURE

C^0_{Ab}	initial concentration of unionised solute in the external phase (mol L^{-1})
C_{Ai}	unreacted solute concentration in the internal phase (mol L^{-1})
C_{Bi}	unreacted regent concentration in the internal phase (mol L^{-1})
C^0_i	initial concentration of internal reagent, same as $[A^-]$ (mol L^{-1})
C_{Pi}	product concentration in the internal phase (mol L^{-1})
D_{eff_j}	effective diffusivity for component j in the mixture of solutes (m^2 s^{-1})
$D_{eff_{mix}}$	concentration averaged effective diffusion coefficient (m^2 s^{-1})
f_b	bulk volume fraction of total volume
f_m	membrane volume fraction of emulsion
K, K_j	distribution coefficient of the undissociated solute between the membrane and aqueous phase
K_b, K_{bj}	dissociation constant for solute j (mol^{-1} L)
K_r	reaction equilibrium constant of Bunge and Noble (1)
K_w	dissociation constant for water (mol^2 L^{-2})
r	radial coordinate (m)
R	radius of the emulsion globules (m)
t	time (s)
$[B_jOH]$	undissociated base j (mol L^{-1})
$[H^+]$	hydronium ion (mol L^{-1})
$[OH^-]$	hydroxyl ion (mol m^{-1})

Subscript

j, k	component number
e	external phase
i	internal phase
m	membrane phase
0	initial

Greek Letters

η	dimensionless radial coordinate, $\frac{r}{R}$
τ	dimensionless time, $\frac{t D_{eff_{mix}}}{R^2}$
ϕ_b	$\frac{[B_jOH]_e+[B_j]^+_e}{[B_jOH]_{eo}+[B_j]}$

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REFERENCES

1. Li, N.N. U.S. Patent 3,410,794, 1968.
2. Ho, W.S.; Hatton, T.A.; Lightfoot, E.N. AlChE J. **1982**, *28*, 662.
3. Bunge, A.L.; Noble, R.D. J. Membr. Sci. **1984**, *21*, 55.
4. Baird, R.S.; Bunge, A.L.; Noble, R.D. AIChE J. **1987**, *33*, 43.
5. Teramoto, M.; Takihana, H.; Sibutani, M.; Yuasa, T.; Miyake, Y.; Teranishi, H. J. Chem. Eng. Jpn. **1981**, *14*, 122.
6. Teramoto, M.; Sakai, T.; Yanagawa, K.; Ohsuga, M.; Miyake, Y. Sep. Sci. Technol. **1983** *18*, 397.
7. Borawankar, R.P.; Chan, C.C.; Wasan, D.T.; Kurzaja, R.M.; Gu, Z.M.; Li, N.N. AIChE J. **1988**, *34*, 753.
8. Bhowal, A.; Datta, S. J. Membr. Sci. **1998**, *139*, 103.
9. Bhowal, A.; Datta, S. Sep. Sci Technol., *in press*.
10. Bandyopadhyaya, R.; Bhowal, A.; Datta, S.; Sanyal, S. K. Chem. Eng. Sci. **1998**, *53*, 2799.
11. Chan, C.C.; Lee, C.J. Chem. Eng. Sci. **1987**, *42*, 83.
12. Glasstone, S. *An Introduction to Electrochemistry*; Affiliated East-West Press Private Ltd.

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APPENDIX A

The comparing expression leading to the relation between the product concentration (C_{Pi}, $[B^+]_i$) and the unreacted solute in the internal phase in this model and the reversible model (3) for the internal phase is given following

Reversible model (3): Present Work

$$K_r = \frac{C_{Pi}}{C_{Ai}C_{Bi}} \qquad K_b = \frac{[B^+]_i[OH^-]_i}{[BOH]_i}$$
$$K_r = \frac{K_b}{K_w} = \frac{[B^+]_i}{[BOH]_i[H^+]_i} \tag{A-1}$$

$$C^o_{Bi} = C_{Bi} + C_{Pi} \qquad [A^-]_i + [OH^-]_i = [H^+]_i + [B^+]_i \tag{A-2}$$

Neglecting $[OH^-]_i$ and substituting (A-2) in (A-1)

$$C_{Pi} = \frac{K_r C_{Ai} C^o_{Bi}}{1 + K_r C_{Ai}} \qquad [B^+]_i = \frac{K_r[BOH]_i[A^-]_i}{1 + K_r[BOH]_i} \tag{A-3}$$

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The above expressions derived from the two models under the assumption that the hydroxyl concentration can be neglected is the same.

APPENDIX B

Differentiating Equation (4) with respect to t after expressing $[B_j^+]_i$ in terms of $[B_jOH]_m$ using Equation (1) and distribution constant we get:

$$\frac{\partial}{\partial t}[OH^-]_i = \frac{1}{[A^-]_i + 2[OH^-]_i} \sum_{k=1}^{n} \frac{K_{bk}}{K_k} \frac{\partial}{\partial t}[B_kOH]_m \tag{B-1}$$

$$\begin{aligned}\left(\frac{\partial}{\partial t}[B_jOH]_i + \frac{\partial}{\partial t}[B_j^+]_i\right) &= \frac{\partial}{\partial t}\left\{[B_jOH]_i\left(1 + \frac{K_{bj}}{[OH^-]_i}\right)\right\} \\ &= \frac{1}{K_j}\left(1 + \frac{K_{bj}}{[OH^-]_i}\right)\frac{\partial}{\partial t}[B_jOH]_m - \frac{K_{bj}[B_jOH]_m}{K_j[OH^-]_i^2}\frac{\partial}{\partial t}[OH^-]_i \\ &= P_j \frac{\partial}{\partial t}[B_jOH]_m + \sum_{\substack{k=1 \\ k\neq j}}^{n} Q_k \frac{\partial}{\partial t}[B_kOH]_m\end{aligned} \tag{B-2}$$

$$\begin{aligned}P_j &= \frac{1}{K_j}\left\{1 + \frac{K_{bj}}{[OH^-]_i}\right\} - \left(\frac{K_{bj}}{K_j}\right)^2 \frac{1}{[A^-]_i + 2[OH^-]_i} \frac{[B_jOH]_m}{[OH^-]_i^2} \\ Q_k &= -\frac{K_{bk}}{K_k} \frac{1}{[A^-]_i + 2[OH^-]_i} \frac{K_{bj}[B_jOH]_m}{K_j[OH^-]_i^2}\end{aligned} \tag{B-3}$$

Therefore, Equation (2) may be rewritten as

$$\begin{aligned}&\left\{1 + \frac{1 - f_m}{f_m} P_j\right\}\frac{\partial}{\partial t}[B_jOH]_m + \frac{1 - f_m}{f_m} \sum_{\substack{k=1 \\ k\neq j}}^{n} Q_k \frac{\partial}{\partial t}[B_kOH]_m \\ &\quad = D_{eff_j} \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}[B_jOH]_m\right) = Y_j\end{aligned} \tag{B-4}$$

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