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Unsteady-State Modeling and Analysis for Liquid Surfactant Membrane Hydrocarbon Separation Processes

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The design of separation equipment using emulsion liquid membranes (ELM) requires independent predictive methods for the estimation of solute extraction rates. In this paper an analytical solution for the unsteady-state diffusion equations in a sphere with a time-dependent external-phase concentration as given by Vorstmann and Thijssen for liquid–liquid extraction has been adapted to model ELM hydrocarbon separations. This solution is based on approximating the concentration profile in the external phase by an asymptotic Sherwood number. It is seen that, at extraction factors and Biot numbers typical of hydrocarbon systems, the model gives a unique solution. This solution has been used to predict both batch and continuous countercurrent column ELM separation of benzene from mixtures with *n*-heptane. The model does not require any adjustable parameter, is easily programmable, and should be a useful tool in simulation/design calculations of ELM hydrocarbon separations.

Introduction

Since its discovery by Li in 1971 interest on the separation of hydrocarbons by liquid surfactant membranes had been waning until recently, when during the past 5 years, several research groups (Ulbrich et al., 1991; Garti and Kovacs, 1991; Sharma et al., 1987) have reexamined the process. These investigations show that the liquid surfactant membrane process offers potential for dearomatization of petroleum streams like naphtha and kerosene to meet product specifications for naphtha cracker feedstock and aviation kerosene, respectively. In this context, mathematical modeling of the hydrocarbon transfer through the aqueous surfactant membrane becomes important for formulating accurate and reliable design and scale-up procedures. However, very little attention has been paid so far to rigorous modeling in this area with major research efforts being directed at modeling of liquid membrane wastewater cleanup or metal recovery operations (Ho et al. 1982; Teramoto et al., 1983). In the latter case the separation is based on some type of facilitated transport mechanism either through chemical reaction of solute with reagent in the internal phase as in phenol/ammonia (Lee and Chan, 1990) removal from wastewater or through use of carriers in membrane phase as in recovery of metal ions. The diffusional mass transfer in such systems is complicated by chemical reaction, and the complex mathematical models that have been built up generally require numerical solutions (Bunge and Noble, 1984; Borwanker et al., 1988). Such complications are not present in liquid membrane hydrocarbon separations where separation is based simply on differences in solubility and/or diffusivity of the permeating component in the aqueous membrane phase. The models that have been proposed so far (Krishna et al., 1987; Ulbrich et al., 1991; Gupta et al., 1990) to describe the liquid membrane hydrocarbon transfer have generally developed from the steady-state membrane film model of Cahn and Li (1974). Transient diffusion was modeled by Casamatta et al. (1978), but they made the simplifying assumptions of constant external-phase/surface concentration. Prediction of mass-transfer coefficients using this type of approach requires an estimate of diffusivity in the composite macrodrop as well as effective thickness of the liquid membrane. The latter is very often a fitting parameter or has to be determined from geometric approximations (Casamatta et al., 1978; Gupta et al., 1990). There is thus an element of uncertainty in using these transfer coefficients for scale-up. Moreover, most of the work reported so far has been on batch-scale equipment. In the present investigation an analytical solution to unsteady-state diffusion equation in a sphere with a time-dependant external-phase concentration as given by Vorstman and Thijssen (1971) for liquid–liquid extraction processes has been adapted to model the hydrocarbon transfer in a liquid surfactant membrane macrodrop.

Model Development

The liquid surfactant membrane macrodrop is depicted in Figure 1. The following assumptions are made.

1. All microdrops (hydrocarbon feed) are of uniform size, rigid, immobile, and initially of uniform composition.
2. Local phase equilibrium is established instantaneously between hydrocarbon and aqueous phases.
3. All macrodrops are of uniform size, rigid, and noncoalescing.
4. There is an external film resistance at the macrodrop–external phase interface.

The differential mass balance for solute diffusion from the liquid surfactant membrane macrodrop keeping its composite nature in mind may be written as

$$[1-\phi_1+m\phi_1]\left(\frac{\partial C_d}{\partial t}\right)=\frac{1}{r^2}\left[\frac{\partial}{\partial r}r^2D_e\frac{\partial C_d}{\partial r}\right] \qquad (1)$$

where the dispersed-phase concentrations, C_d, are based on the aqueous (membrane phase). For constant effective diffusivity, D_e, and defining a macrodrop diffusivity, D_M, as

$$D_M=\frac{D_e}{1-\phi_1+m\phi_1} \qquad (2)$$

we get

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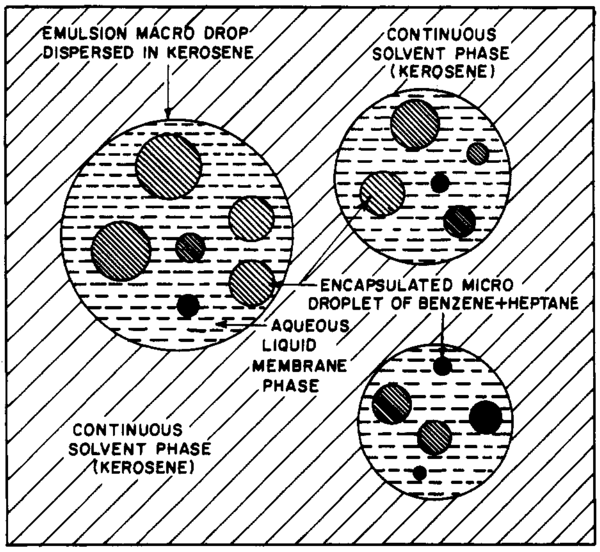

Figure 1. Schematic representation of ELM macrodrop.

$$\frac{\partial C_\mathrm{d}}{\partial t} = D_\mathrm{M}\frac{1}{r^2}\left[\frac{\partial}{\partial r}r^2\left(\frac{\partial C_\mathrm{d}}{\partial r}\right)\right] \tag{3}$$

subject to the initial and boundary conditions

$$t = 0 \quad 0 < r < R \quad C_\mathrm{d} = C_\mathrm{d}^\circ \tag{4}$$

$$r = 0 \quad t > 0 \quad \frac{\partial C_\mathrm{d}}{\partial r} = 0 \tag{5}$$

$$r = R \quad t > 0 \quad -D_\mathrm{M}\frac{\partial C_\mathrm{d}}{\partial r} = k_\mathrm{c}[C_\mathrm{c,i} - C_\mathrm{c}(t)] \tag{6}$$

For the external phase we have

$$V_\mathrm{c}\frac{\mathrm{d}C_\mathrm{c}}{\mathrm{d}t} = \frac{3}{R}(V_\mathrm{i} + V_\mathrm{m})k_\mathrm{c}[C_\mathrm{c,i} - C_\mathrm{c}(t)] \tag{7}$$

with the initial condition at $t = 0$:

$$C_\mathrm{c} = 0 \tag{8}$$

The development of the analytical solution to this set of equations based on asymptotic Sherwood numbers as given by Vorstman and Thijssen (1971) is described briefly in the Appendix. The expression for fractional solute extracted from the ELM macrodrop which results is given as

$$F = \frac{C_\mathrm{d} - C_\mathrm{d}^\circ}{(C_\mathrm{c}^\circ/m) - C_\mathrm{d}^\circ} = \frac{6Bi^2}{\epsilon - 1}\sum_{n=1}^{\infty}\frac{\frac{\epsilon A}{\mu_n^{\,2}} + \epsilon + \left(1 - \frac{\epsilon A}{\mu_n^{\,2}} - \epsilon\right)\mathrm{e}^{-\mu_n^2 Fo} - \mathrm{e}^{A(Fo)}}{\beta_n} \tag{9}$$

where

$$A = \frac{3(1 - \epsilon)\overline{Sh}_\mathrm{od,a}}{2\epsilon} \tag{10}$$

$$\beta_n = (A + \mu_n^{\,2})(\mu_n^{\,2} + Bi(Bi - 1)) \tag{11}$$

and μ_n are roots of the equation

$$\tan \mu_n = \mu_n/(-Bi + 1) \tag{12}$$

In the present study this expression was used to predict the fractional solute extraction in the batch and continuous column experiments on liquid membrane separation of benzene from mixtures of benzene and *n*-heptane.

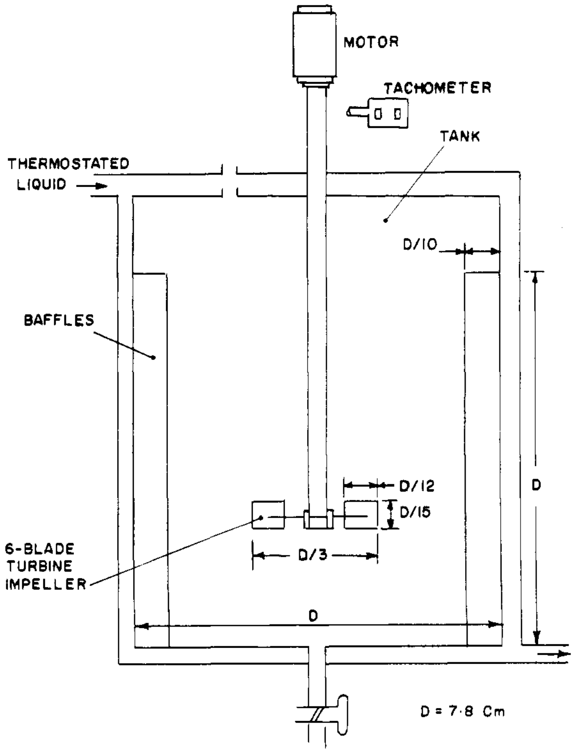

Figure 2. Diagram of mixer unit in permeation experiments.

Experimental Section

A mixture of benzene and *n*-heptane has been used as a model hydrocarbon feed. The surfactant used was HYOXYD × 200, an alkylphenol polyoxyethylene ether manufactured by M/S HICO Products Pvt. Ltd, Bombay. A kerosene distillate of boiling range 150–240 °C was used as the external phase. Liquid membrane separation experiments were carried out in a batch stirred cell as well as in a continuous column.

Batch Permeation Experiments

The batch permeation experiments were carried out in the glass stirred vessel shown in Figure 2. In the mass-transfer measurements the oil/water (O/W) emulsions were prepared by agitation of the model hydrocarbon feed with aqueous 0.2 wt % surfactant solution at a preselected rate of 2000–3000 rpm in this vessel at 30 °C. The emulsion was then dispersed in the external phase by agitation in the same vessel at a preselected rpm for a specified time. The phases were then allowed to settle and were separately withdrawn. Experimental details on the analysis of the phases, measurements of the microdrop diameter d_{32}^{mic}, and measurements of the macrodrop diameter d_{32}^{mac} have been reported in an earlier publication (Gupta et al., 1990). The experiments were designed to cover a range of parameters like permeation time, emulsification rpm, microdrop holdup in the emulsion, and emulsion/external-phase ratio or macrodrop holdup.

Continuous Countercurrent Permeation Experiments

A glass 51-mm-diameter Oldshue-Rushton type stirred column has been used in these continuous-scale studies and is depicted in Figure 3. Metering pumps were used to deliver feed emulsion and kerosene (external) phases

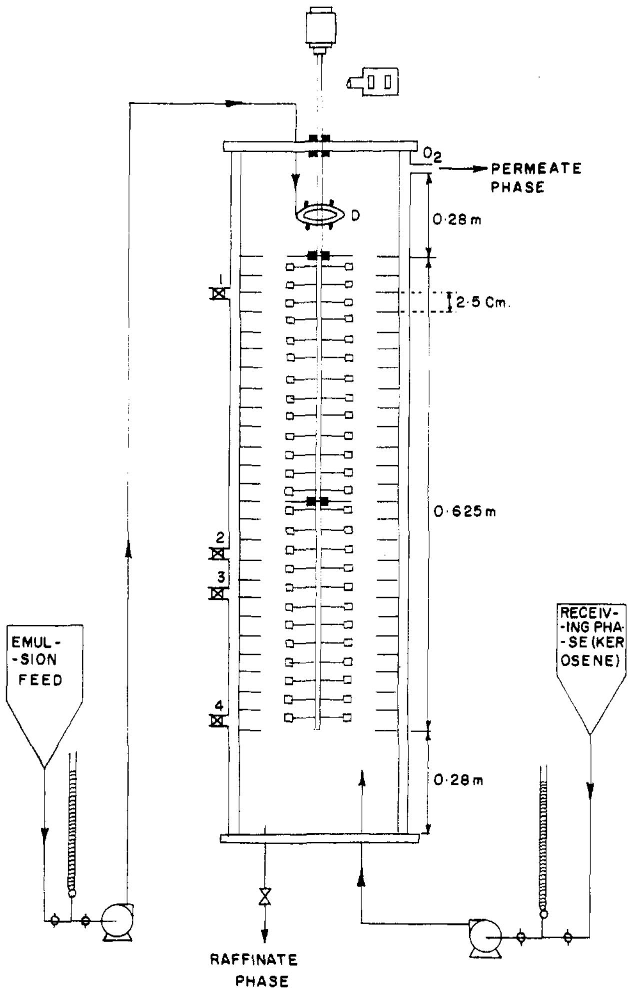

Figure 3. Diagram of Oldshue-Rushton column used in continuous-scale experiments.

from their respective storage vessels to the column. The rotor rpm was monitored continuously by a digital tachometer.

The column has provisions for sampling the dispersion at any of four locations through the sampling ports shown using a three-way liquid paraffin filled sampler. During sampling the liquid paraffin mixed with the external kerosene phase in the dispersion and increased its viscosity so that coalescence of the dispersed liquid membrane macrodrops was prevented. This enabled microscopic measurement of the macrodrop diameters. Holdup of dispersed liquid membrane macrodrops in the column was measured by instantaneous shutdown of all entry and exit valves and noting of the volume of dispersed phase collected. Mass-transfer measurements were made over a range of flow rates of dispersed (emulsion) and continuous (kerosene) phases at a stirrer rpm of 500. The holdup of microdrop phase in the emulsion was 0.56 while benzene concentration in the feed was varied from 25 to 75% by weight. The experiments were carried out at ambient temperatures which varied from 28 to 31 °C. Samples of exit emulsion and kerosene phases were collected for analysis after the column had reached steady state (a minimum operation period of 1 h was necessary for steady-state conditions to be attained as established from trial experiments).

Results and Discussion

The prediction of fractional solute extraction in a liquid membrane permeation experiment using eq 9 requires knowledge of the extraction factor, distribution coefficient *m*, and Biot number *Bi*. In the present system the partition coefficient for solute (benzene) between hydrocarbon and aqueous phase is around 500 (Gupta et al., 1990), and as the phase ratio of continuous (external) to dispersed (emulsion) phase generally exceeds 3, the extraction factor will exceed 1500. The effect of extraction factor and Biot number on the theoretically predicted fractional solute extraction calculated from eq 9 over a range of Fourier numbers up to 0.5 is shown in Figure 4. It is evident that

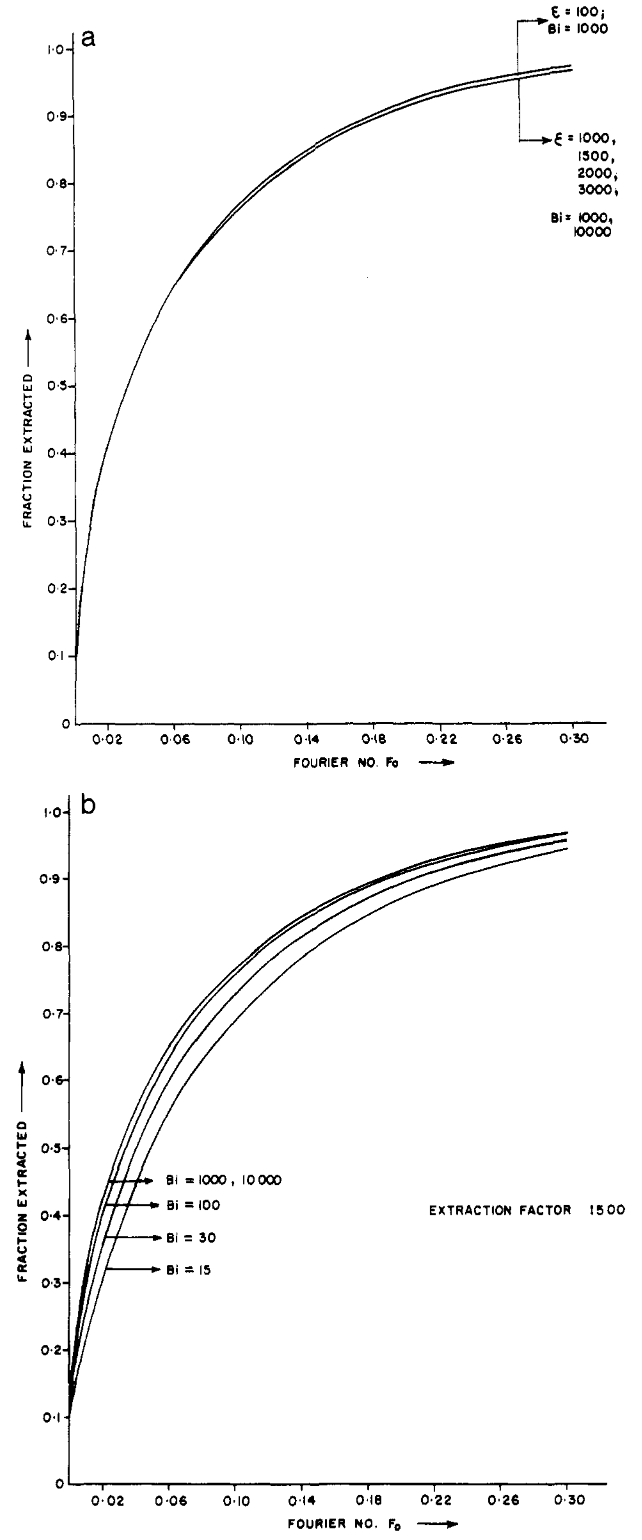

Figure 4. (a) Fraction extracted vs Fourier number with extraction factor variation: model predicted. (b) Fraction extracted vs Fourier number with Biot number variation: model predicted.

Table I. Mass Transfer and Hydrodynamic Data from Batch Liquid Membrane Permeation Experiments (Concentration of Benzene in Feed, C_d° = 387.5 kg/m³; Temperature = 30 °C)

expt no.	emulsification rpm	ϕ_1	ϕ_2	t^a (s)	d_{32}^{mac} (μm)	F (exptl)	Fo (interpolated)	D_e (m²/s)
1	2000	0.56	0.20	180	560	0.7437	0.091	1.11×10^{-8}
2	2000	0.56	0.20	240	860	0.6675	0.065	1.40×10^{-8}
3	2000	0.56	0.20	300	700	0.7344	0.087	9.96×10^{-9}
4	2000	0.56	0.20	360	700	0.7321	0.086	8.21×10^{-9}
5	2000	0.56	0.11	120	470	0.6527	0.062	8.00×10^{-9}
6	2000	0.56	0.11	180	474	0.7900	0.110	9.63×10^{-9}
7	2000	0.56	0.11	240	472	0.8859	0.172	1.11×10^{-8}
8	2000	0.229	0.20	180	866	0.2220	0.005	6.0×10^{-10}
9	2000	0.302	0.20	180	700	0.3980	0.019	1.96×10^{-9}
10	2000	0.376	0.20	180	700	0.5242	0.035	4.49×10^{-9}
11	2000	0.440	0.20	180	667	0.6807	0.069	9.39×10^{-9}
12	2000	0.500	0.20	180	660	0.7845	0.107	1.58×10^{-8}
13	2000	0.576	0.20	180	627	0.7486	0.092	1.44×10^{-8}
14	2000	0.645	0.20	180	614	0.7884	0.109	1.83×10^{-8}
15	2000	0.72	0.20	180	627	0.7486	0.110	2.16×10^{-8}
16	2000	0.72	0.20	180	614	0.7884	0.077	1.44×10^{-8}
17	2000	0.72	0.20	180	627	0.7917	0.079	1.55×10^{-8}
18	2500	0.72	0.20	180	640	0.7340	0.087	1.78×10^{-8}
19	3000	0.72	0.20	180	600	0.7300	0.085	1.53×10^{-8}
20	1800	0.56	0.11	180	418	0.8874	0.173	1.17×10^{-8}
21	2000	0.56	0.11	180	415	0.8708	0.159	1.06×10^{-8}
22	2500	0.56	0.11	180	428	0.8888	0.174	1.24×10^{-8}

[a] Permeation time.

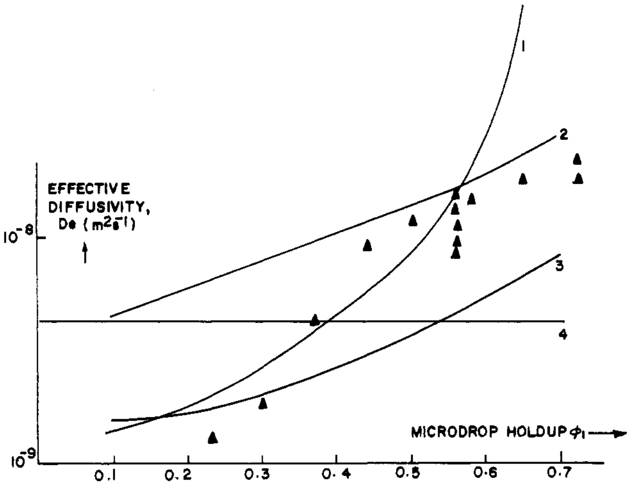

Figure 5. Comparison of experimental effective diffusivities in ELM macrodrops with model predictions. 1, Jefferson-Witzell-Sibbitt model; 2, Maxwell model; 3, Russell model; 4, Casamatta model; ▲, experimental data.

Table II. Correlations for Predicting Effective Diffusivity of Solute in an Emulsion Liquid Membrane Globule

author(s)	correlation
Maxwell	$\frac{D_e}{D_w} = \frac{(2D_w + D_H/m) - 2\phi_1(D_w - D_H/m)}{(2D_w + D_H/m) + \phi_1(D_w - D_H/m)}$
Casamatta et al.	$\frac{D_e}{D_w} = \frac{1 - \phi_1 + 4\phi_1 m}{1 - \phi_1 + \phi_1 m}$
Russell	$\frac{D_e}{D_w} = \frac{\phi_1^{2/3}}{\phi_1^{1/3}\left(\frac{D_w}{D_H m}\right) + 1 - \phi_1^{1/3}} + 1 - \phi_1^{2/3}$
Jefferson et al.	$D_e = \frac{A_A}{A_S}\left[\frac{(0.5 + n)D_A D_w}{0.5D_w + nD_A}\right] + D_w\frac{A_B}{A_S}$ where $D_A = 2mD_H D_w\left[\frac{mD_H}{(D_w - mD_H)^2}\log\left(\frac{mD_H}{D_w}\right) - \frac{1}{(mD_H - D_w)}\right]$ $A_A = \pi/4$; $A_S = (1 + 2n)^2$; $A_B = (1 + 2n)^2 - \pi/4$ and $n = 0.403\phi_1^{-1/3} - 0.5$

at Biot numbers and extraction factors exceeding 1000 a unique fractional extraction vs Fourier number curve exists. Such a unique curve at high *Bi* has also been reported by Borwanker et al. (1988) in modeling phenol separations by W/O/W liquid membranes.

The experimental data on batch liquid membrane permeation are reported in Table I. From the experimentally observed values of fractional solute extracted, the corresponding Fourier numbers have been found using the unique theoretically predicted fraction extracted vs Fourier number curve as given in Figure 4 for *Bi* and ϵ exceeding 1000, and these values are also reported in Table I. The effective diffusivity D_e has been calculated from these Fourier numbers using experimental values of macrodrop diameter, real time, microdrop holdup, and distribution coefficient and is given in Table I. The variation of these experimentally derived effective diffusivities with microdrop holdup has been compared in Figure 5 with effective diffusivities predicted theoretically from individual phase solute diffusivities, microholdup, and partition coefficient, m, using the diffusivity models of Casamatta (1978), the Maxwell equation (Crank, 1975), Russell (1954), and Jefferson–Witzell–Sibbitt (JWS) (1958) as summarized in Table II. This comparison shows that the JWS model predicts these effective diffusivities most satisfactorily. Hence by using the JWS model to calculate D_e and experimental values of macrodrop diameter, real time, t, and partition coefficient, m, the theoretical curve for *Bi* and ϵ exceeding 1000 can be used to predict batch liquid surfactant membrane solute extraction. It is noteworthy that these model predictions are not based on any adjustable parameters. Figure 6 shows a comparison of experimental and theoretical solute extraction by this approach for all the batch experiments. As can be seen, the fit between theory and experiment is reasonably satisfactory. The efficacy of the present model in predicting solute extraction in the continuous countercurrent liquid surfactant membrane experiments was next tested. The experimental data on mass transfer and hydrodynamic parameters of drop size and dispersed-phase

Table III. Mass-Transfer and Hydrodynamic Data from Continuous Countercurrent Liquid Membrane Permeation Run

expt no.	Q_d (m³/s)	Q_c (m³/s)	$C_d°$ (kg/m³)	d_{32}^{mac} (μm)	ϕ_2	*Fo*	*F* (exptl)
1	3.27×10^7	1.12×10^6	3.88×10^{-2}	750	0.045	0.1123	0.7816
2	3.50×10^7	1.12×10^6	3.88×10^{-2}	780	0.046	0.0991	0.7687
3	3.83×10^7	1.12×10^6	3.88×10^{-2}	825	0.047	0.0828	0.7515
4	4.68×10^7	1.12×10^6	3.88×10^{-2}	960	0.048	0.0511	0.7068
5	4.19×10^7	1.12×10^6	3.88×10^{-2}	860	0.049	0.0725	0.7230
6	4.43×10^7	1.12×10^6	3.88×10^{-2}	900	0.049	0.0627	0.6676
7	4.61×10^7	1.12×10^6	3.88×10^{-2}	900	0.051	0.0627	0.6240
8	5.84×10^7	1.12×10^6	3.88×10^{-2}	1030	0.055	0.0408	0.6377
9	6.09×10^7	1.12×10^6	3.88×10^{-2}	1020	0.058	0.0421	0.6567
10	8.01×10^7	1.12×10^6	3.88×10^{-2}	1200	0.063	0.0251	0.5370
11	3.35×10^7	1.12×10^6	1.82×10^{-2}	825	0.059	0.1191	0.8581
12	3.91×10^7	1.12×10^6	1.82×10^{-2}	855	0.066	0.1063	0.8199
13	4.17×10^7	1.12×10^6	1.82×10^{-2}	870	0.069	0.1006	0.8391
14	5.51×10^7	1.12×10^6	1.82×10^{-2}	915	0.086	0.0856	0.7996
15	5.99×10^7	1.12×10^6	1.82×10^{-2}	990	0.085	0.0666	0.7858
16	2.98×10^7	1.12×10^6	6.17×10^{-2}	825	0.024	0.0543	0.6421
17	3.50×10^7	1.12×10^6	6.17×10^{-2}	855	0.027	0.0484	0.6652
18	4.41×10^7	1.12×10^6	6.17×10^{-2}	900	0.032	0.0411	0.6355

[a] Concentration of benzene in the feed. [b] Dispersed-phase holdup.

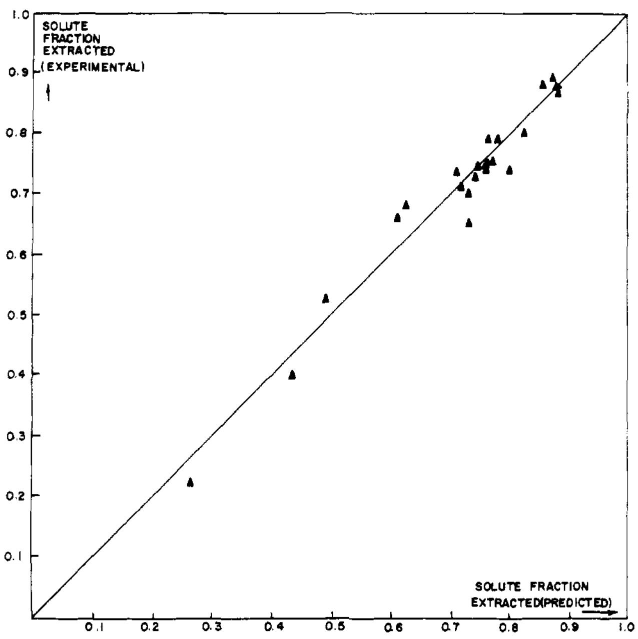

Figure 6. Comparison of fractional solute extracted from batch ELM experiments with model predictions.

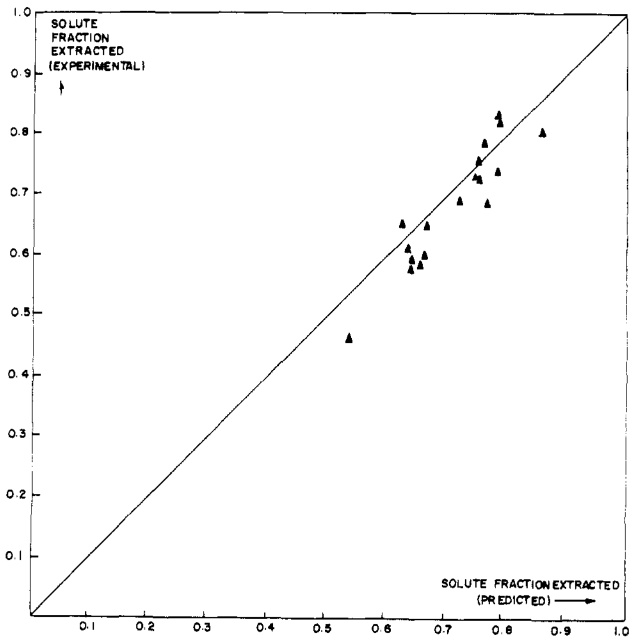

Figure 7. Comparison of fractional solute extracted from continuous countercurrent ELM separations with model-predicted values.

holdup obtained from the continuous column experiments are reported in Table III. The effective diffusivity, D_e, was calculated from the JWS equations. The permeation or contact time of the macrodrop in the column was determined for each run from the relationship $t = Z/(U_d/\phi_2)$ and experimental values of macrodrop diameter were used in the estimation of Fourier number *Fo*. A comparison of the experimental solute fractional extraction with model-predicted values is shown in Figure 7. As is evident, the model predicts the solute fractional extraction fairly well.

In applying the model to predict solute extraction in the countercurrent runs, axial mixing effects have not been considered. However, Vorstmann and Thijssen (1971) have shown that, even for strong mixing effects, no appreciable errors are introduced when asymptotic Sherwood numbers are used in the calculations. Moreover, several workers (Draxler and Marr, 1986; Bart et al., 1988) have noted that axial mixing effects are relatively unimportant in rate-controlled emulsion liquid membrane separations compared to liquid–liquid extraction.

Conclusion

The analytical solution to the transient diffusion equation based on asymptotic Sherwood numbers as developed by Vorstmann and Thijssen (1971) for liquid–liquid extraction processes has been shown to be applicable for predicting hydrocarbon separation from emulsion liquid membrane macrodrops in batch as well as in continuous-scale equipment. The effective diffusivities required in these predictions can be readily estimated from Jefferson–Witzell–Sibbitt equations (Jefferson et al., 1958). The model does not include any adjustable parameters, is easily programmable, and should prove a useful tool in ELM simulations/design calculations.

Nomenclature

A = term defined in eq A8
B = term defined in eq A9
Bi = Biot number ($=mk_cR/D_M$)
C = solute concentration (kg m^{-3})
D = diffusivity (m^2 s^{-1})
d_{32} = Sauter mean diameter (m)

F = fractional solute extracted
Fo = Fourier number ($=4D_\mathrm{M}t/(d_{32}^\mathrm{mac})^2$)
k_c = external mass-transfer coefficient (m s^{-1})
m = solute partition coefficient between hydrocarbon and aqueous phases
N = number of transfer units
Q = volumetric flow rate (m^3 s^{-1})
R = macrodrop radius (m)
r = radial distance (m)
Sh = Sherwood number
t = permeation time (s)
U = superficial velocity (m s^{-1})
V = volume (m^3)
Z = column length (m)

Subscripts

a = asymptotic
c = continuous phase
d = dispersed phase
e = effective
i = internal or interfacial
m = membrane
M = macrodrop
od = overall dispersed

Superscripts

mic = microdrop
mac = macrodrop
0 = initial
— = time averaged

Greek Symbols

β_n = term defined in eq A9
ϵ = extraction factor ($=mQ_\mathrm{c}/Q_\mathrm{d}$)
ξ = dimensionless length ($=r/R$)
μ_n = roots of characteristic equation defined in eq A10
ϕ_1 = microdrop holdup
ϕ_2 = macrodrop holdup

Appendix

The partial differential equation (3) describing diffusion in the ELM macrodrop can be nondimensionalized by defining the following dimensionless variables, $\xi = r/R$, Fourier number $Fo = D_\mathrm{M}t/R^2$, and Biot number $Bi = mk_\mathrm{c}R/D_\mathrm{M}$, into

$$\frac{\partial C_\mathrm{d}}{\partial Fo} = \frac{1}{\xi^2}\left[\frac{\partial}{\partial \xi}\xi^2\left(\frac{\partial C_\mathrm{d}}{\partial \xi}\right)\right] \tag{A1}$$

with initial and boundary conditions

$$0 < \xi < 1 \qquad Fo = 0 \qquad C_\mathrm{d} = C_\mathrm{d}^\circ \tag{A2}$$

$$\xi = 0 \qquad Fo > \qquad \frac{\partial C_\mathrm{d}}{\partial \xi} = 0 \tag{A3}$$

$$\xi = 1 \qquad Fo > 1 \qquad \frac{\partial C_\mathrm{d}}{\partial \xi} = -Bi[C_\mathrm{d,i} - C_\mathrm{c}(Fo)/m] \tag{A4}$$

Vorstmann and Thijssen (1971) used Mikailov's (1941) solution to this equation:

$$\frac{C_\mathrm{d} - C_\mathrm{d}^\circ}{(C_\mathrm{c}^\circ/m) - C_\mathrm{d}^\circ} = -6Bi^2 \sum_{n=1}^{\infty} \frac{\int_0^{Fo} f(Fo,-\tau)\exp(-\mu_n^2\tau)\,\mathrm{d}\tau}{Bi(-Bi+1) - \mu_n^2} \tag{A5}$$

Here the time dependence of the external-phase concentration is expressed as

$$f(Fo) = \frac{C_\mathrm{c}(Fo) - mC_\mathrm{d}^\circ}{C_\mathrm{c}^\circ - mC_\mathrm{d}^\circ} = \frac{\exp\left[\frac{1-\epsilon}{\epsilon}N_{\mathrm{od},t}\right] - \epsilon}{1-\epsilon} = \frac{\epsilon - \exp\left(\frac{3(1-\epsilon)\overline{Sh}_\mathrm{od}Fo}{2\epsilon}\right)}{\epsilon - 1} \tag{A6}$$

Vorstmann and Thijssen (1971) assumes that a time-independent asymptotic Sherwood number can replace $\overline{Sh}_\mathrm{od}Fo$ in the above equation so that eq A5 can be integrated to give an expression for fractional solute expressed as

$$F = \frac{C_\mathrm{d} - C_\mathrm{d}^\circ}{(C_\mathrm{c}^\circ/m) - C_\mathrm{d}^\circ} = \frac{6Bi^2}{\epsilon - 1}\sum_{n=1}^{\infty}\frac{\frac{\epsilon A}{\mu_n^2} + \epsilon + \left(1 - \frac{\epsilon A}{\mu_n^2} - \epsilon\right)\mathrm{e}^{-\mu_n^2 Fo} - \mathrm{e}^{A(Fo)}}{\beta_n} \tag{A7}$$

where

$$A = \frac{3(1-\epsilon)\overline{Sh}_\mathrm{od,a}}{2\epsilon} \tag{A8}$$

and

$$\beta_n = (A + \mu_n^2)(\mu_n^2 + Bi(Bi - 1)) \tag{A9}$$

with μ_n as roots of the characteristic equation

$$\mu_n = (1 - Bi)\tan \mu_n \tag{A10}$$

To use this expression for fraction solute extracted, knowedge of the asymptotic Sherwood number $\overline{Sh}_\mathrm{od,a}$ is required. The instantaneous Sherwood number $Sh_{\mathrm{od},t}$ is

$$Sh_{\mathrm{od},t} = \left[\frac{2}{3}\left(\frac{6Bi^2}{\epsilon - 1}\right)\sum_{n=1}^{\infty}\frac{\left(\frac{\epsilon A}{\mu_n^2} + \epsilon - 1\right)\mu_n^2\mathrm{e}^{-\mu_n^2 Fo} - A\mathrm{e}^{A(Fo)}}{\beta_n}\right] \Big/ \left[\frac{\epsilon}{\epsilon - 1} - \frac{\mathrm{e}^{A(Fo)}}{\epsilon - 1} - \frac{6Bi^2}{\epsilon - 1}\times \sum_{n=1}^{\infty}\frac{\epsilon\left(\frac{A}{\mu_n^2} + 1\right) + \left(1 - \frac{\epsilon A}{\mu_n^2} - \epsilon\right)\mathrm{e}^{-\mu_n^2 Fo} - \mathrm{e}^{A(Fo)}}{\beta_n}\right] \tag{A11}$$

An iterative solution to this equation gave the instantaneous Sherwood numbers at various times (Fourier numbers). The Sherwood number approached a constant value at Fourier numbers greater than 0.3, and accordingly the Sherwood number at Fourier number of 0.5 was taken as the asymptotic Sherwood number. Using this value and eq A7, the fractional solute extracted from the ELM macrodrop could be calculated.

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