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Correlation for Prediction of Extraction Characteristics for Separation of Weak Acids/Bases by Liquid Surfactant Membrane

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ABSTRACT

A single parameter model was earlier presented by Bhowal and Datta for prediction of the extraction rate of weak acids/bases by a liquid surfactant membrane. This parameter represents the fraction of solute diffusing into the emulsion globule that will be converted into reaction product by a reversible reaction in the internal droplets and was taken to be a constant for all systems. A useful generalized correlation has been developed in this work for calculation of the said parameter by regression as a function of the physical parameters and experimental conditions of the system. The validity of the correlation has been checked through comparison with the predictions of the reversible reaction approach of Bunge and Noble. The parameter value obtained from this correlation gave better estimations of the extraction profiles than those obtained assuming it to be a constant.

INTRODUCTION

Liquid surfactant membranes (LSM) invented by Li (3) have been applied to a variety of separations, including recovery and purification of metal ions, removal of organic contaminants from wastewater, and various biochemical and biomedical applications. They are usually prepared by first forming an emulsion between two immiscible phases and then dispersing this emulsion in a third (continuous) phase by agitation. The membrane phase is the liquid

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phase that separates the encapsulated internal droplets in the emulsion from the external continuous phase.

This paper considers LSM extraction by solute diffusion through the oil membrane followed by reaction with the reagent present in the internal droplets (type-1 facilitation). Recent mathematical descriptions of this transport mechanism have been formulated in two ways. One approach was described by Ho et al. (4) 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 which are completely depleted of reagent because 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, and this boundary separates the inner region which contains no solute from the outer region which contains no reagent. As the reagent is consumed by the reaction, the reaction front advances into the globule. It is assumed that the reaction products are immobilized and hence are incapable of backdiffusion.

An alternate procedure, taken by Bunge and Noble (2) as well as Teramoto et al. (5), incorporates reaction equilibrium into a description of the rate-controlling membrane transport processes. Reaction reversibility precludes an advancing reaction front since there are no separate reacted and unreacted regions. Prediction of an extraction profile of solutes by the reversible model of Bunge and Noble (2) depends on four dimensionless groups: σ_1, σ_2, σ_3, and σ_4. These can be estimated from physical parameters and experimental conditions.

Several assumptions are common to both the advancing front (4) and reversible reaction approach (2). Chief among them are:

1. The membrane phase is completely immiscible with the aqueous phase
2. The emulsion globule size variation can be lumped into a single Sauter mean diameter
3. Local equilibrium holds between the dispersed and continuous phases of the emulsion
4. Coalescence and redispersion of emulsion globules are neglected
5. Absence of leakage of solute from the internal droplets and swelling of the emulsion globule
6. The external mass transfer resistance is negligible
7. No internal circulation occurs within the globule

The existing literature on extraction models demonstrates the superiority of models which incorporate reaction reversibility over the irreversible reaction assumption of the advancing front approach. Prediction of extraction profiles of solutes using the two above-mentioned models shows that while the advancing front model does an acceptable job of predicting extraction rates for solutes with a high reaction constant for short extraction times, it provides poor predictions for solutes with a low reaction constant, *K*, or for long extraction times. However, a notable feature of the advancing front model is its algebraic solution which permits easy calculations.

According to the reversible reaction model (2), it is conceivable that solute exists even at the center of the emulsion globule. However, as illustrated in Fig. 1 for the extraction of aniline by LSM, beyond a certain radial distance the concentration of solute in the emulsion globule drops to a value which can be considered to be zero. All the extracted solute can thus be assumed to exist within this front which moves toward the center of the globule with time. These profiles have been simulated using the model equations of Bunge and Noble (2).

This forms the basis of the single parameter model proposed by Bhowal and Datta (1) which also incorporates the external phase resistance. To identify this reaction front in this model, it was assumed that solute diffusing into the emulsion globule in a time interval is entrapped in a volume. A major fraction of this solute, say ϑ (which has been taken as a parameter), will be converted into reaction product by a reversible reaction in the internal droplets while the unreacted solute distributes itself in the membrane and aqueous phase within this volume. The average concentration of the unreacted solute in the said volume will thus be negligible and can be considered to be zero beyond the boundary of this volume. Further reaction in the volume is assumed to be

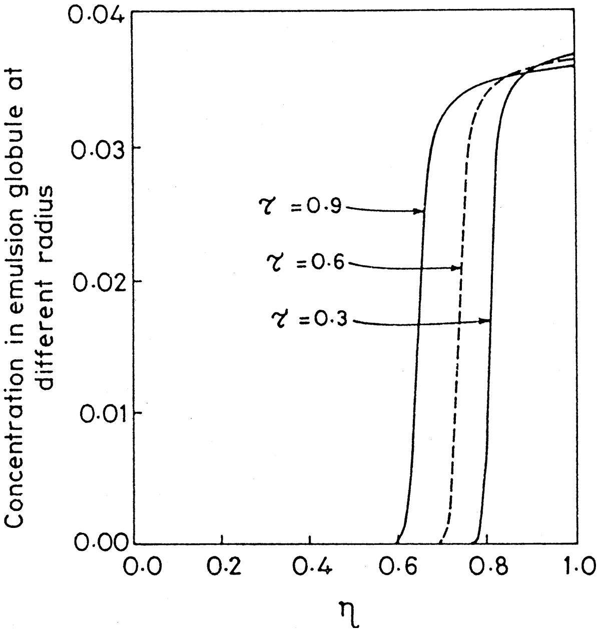

FIG. 1 Concentration profile of solute in the emulsion globule at different extraction times.

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slow. With a parameter value of 0.99, the model fitted the experimental extraction data of various solutes with greater accuracy than the advancing front model. This approach retained the advantages realized in assuming a reaction front while taking into account the realistic approach of reaction reversibility.

The mathematical equations of the reversible model are nonlinear and have no analytical solution. In comparison, simulation of the model equations of Bhowal and Datta (1) is easier from a computational viewpoint. However, the accuracy of predictions using this model (1) has been found to be limited to a narrow range of experimental conditions. This can be attributed to the constant value of ϑ used by Bhowal and Datta (1) for different solutes under all experimental conditions. The parameter ϑ, in fact, is found to be very sensitive because a slight change in the value of the parameter has a significant effect on the simulated extraction profiles.

In this work an attempt has been made to further improve upon the prediction of extraction characteristics of solutes by the model of Bhowal and Datta (1) in order to provide a reliable alternative to the reversible model (2). Accordingly, instead of assuming ϑ to be a constant, in the present study it has been related to the various dimensionless groups which are obtained from the physical and system properties of the extraction system. This dependence of ϑ on the said properties would make the predictions of the model (1) more accurate and generally applicable to all systems. Further, the equations proposed previously (1) have been rearranged and simplified to ensure faster computation. The effects of the experimental conditions on the parameter have also been studied for the prediction of extraction characteristics for the cases of weak acids/bases.

MATHEMATICAL EQUATIONS

The model equations developed by Bhowal and Datta (1) have been rearranged to facilitate computation and are outlined below. The equation, although written for the extraction of a weak base (BOH) by using a strong acid (HA), can also be used for the reverse case without any modification.

Equation (1) described the concentration profile of solute in an emulsion globule:

$$[\mathrm{BOH}]_\mathrm{a} = \frac{A_1}{r} + A_2 \tag{1}$$

where A_1 and A_2 are integration constants.

In this work, in keeping with the assumptions of the advancing front approach and the reversible model, the external phase resistance has been considered negligible.

$$r = R, \qquad [\mathrm{BOH}]_\mathrm{a} = \alpha[\mathrm{BOH}]_\mathrm{e} \tag{2}$$

$$r = R_f, \qquad [\mathrm{BOH}]_a = 0 \tag{3}$$

$$\alpha = (1 - f_m) + K_{mi} f_m \tag{4}$$

The equations related to the concentration of solute in the external phase are

$$T = [\mathrm{BOH}]_e + [\mathrm{B}^+]_e = [\mathrm{BOH}]_e \left(\frac{1 + K_b}{[\mathrm{OH}^-]} \right) \tag{5}$$

$$\frac{d}{dt}(V_e T) = n 4\pi R^2 F \tag{6}$$

where F is the solute flux entering the globule:

$$F = D_{eff} \frac{\alpha [\mathrm{BOH}]_e}{R - R_f} \frac{R_f}{R} \tag{7}$$

If the solute is a weak acid or base, it can be assumed to be remain undissociated in the external phase with negligible error in extraction profile prediction. This obviates the need to use a iterative technique in conjunction with the charge balance equation, as has been done in previous work (1), to obtain the concentration of solute in the external phase.

The following equation holds for solute entering an emulsion globule in a time interval, and which is assumed to be entrapped in a volume, ΔV (1):

$$\Delta V([1 - f_m]([\mathrm{BOH}]_i + [\mathrm{B}^+]_i) + f_m[\mathrm{BOH}]_m) = 4\pi R^2 F \Delta t \tag{8}$$

$$K_b = \frac{[\mathrm{B}^+]_i[\mathrm{OH}^-]_i}{[\mathrm{BOH}]_i}, \qquad K_{mi} = \frac{[\mathrm{BOH}]_m}{[\mathrm{BOH}]_i} \tag{9}$$

Instead of the iterative method proposed by Bhowal and Datta for calculating ΔV, the following simplification of Eq. (8) has been carried out in this work.

Substitution of K_b and K_{mi} into Eq. (8) gives the following expression:

$$\Delta V[\mathrm{B}^+]_i \left\{ (1 - f_m) \frac{([\mathrm{OH}^-]}{K_b} + 1) + [\mathrm{OH}^-]_i \frac{f_m K_{mi}}{K_b} \right\} = 4\pi R^2 F \Delta t \tag{10}$$

According to this model:

$$\frac{[\mathrm{B}^+]_i \Delta V}{4\pi R^2 F \Delta t}(1 - f_m) = \vartheta \tag{11}$$

Rearranging Eq. (10) by using Eq. (11), we obtain

$$[\mathrm{OH}^-]_i \left(\frac{1 - f_m}{K_b} + f_m \frac{K_{mi}}{K_b} \right) = (1 - f_m)(\frac{1}{\vartheta} - 1) \tag{12}$$

The hydroxyl concentration obtained from the above equation is substituted in the charge balance equation to obtain the B^+ ion concentration in the internal phase:

$$[B^+]_i = [OH^-]_i + [A^-]_i - [H^+]_i \tag{13}$$

Knowing B_i^+, ΔV is obtained from Eq. (11), and the radius of the reaction front is obtained from

$$\frac{4}{3}\pi R_f^3 = \frac{4}{3}\pi R_{fo}^3 - \Delta V \tag{14}$$

RESULTS AND DISCUSSION

The simulated extraction profiles of *p*-toluidiene at different values of the parameter ϑ, the reversible model predictions, and the experimental data (6) are illustrated in Fig. 2. It is seen from the figure that the reversible model of Bunge and Noble (2), although realistic (as noted by various researchers), still underpredicts the experimental data. This occurs because extraction of solute by LSM is usually accompanied by leakage of solute from the emulsion globules, coalescence, and redispersion of droplets and swelling. Thus, models neglecting these phenomena could use the reversible model (2) as a standard for comparison. Further, it is observed that better prediction of the extraction pro-

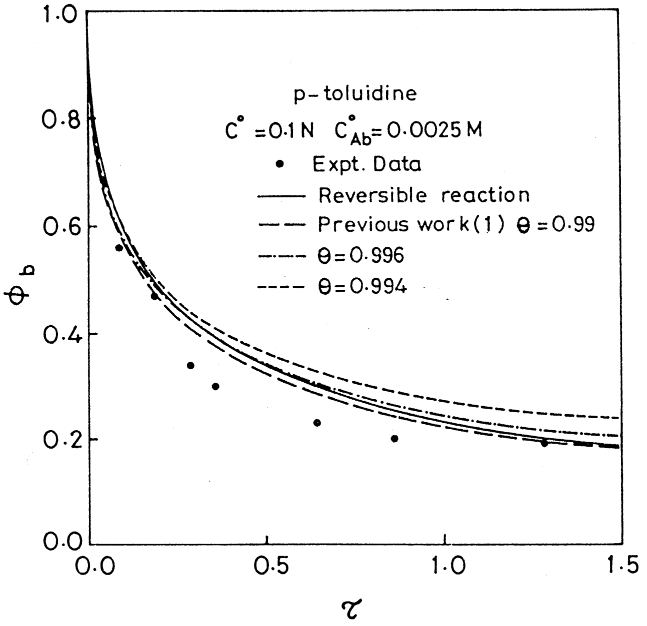

FIG. 2 Extraction profiles with variation of ϑ and the reversible model.

files can be obtained with the model of Bhowal and Datta (1) by taking ϑ different from 0.99.

In this work the value of ϑ for a system has been chosen by trial and error. A parameter value was assumed, and the predicted extraction profile was compared with the reversible reaction model predictions of Bunge and Noble (2). That parameter value is selected for a given solute and experimental condition for which the absolute average error in the compared extraction profiles does not exceed 1%. The dimensionless time, τ, up to which the extraction profiles were generated for comparison, was 1.5. Table I summarizes the physical and system parameters of the solutes (2, 4, 6) whose extraction profiles have been simulated.

Two hypothetical solutes were considered such that though they have different values of distribution coefficient, reaction equilibrium constant, initial internal reagent concentration, and initial external phase solute concentration, the magnitudes of the dimensionless groups in the reversible model (2), i.e., σ_1, σ_2, σ_3, and σ_4, are the same. The extraction profiles predicted for the two solutes using the model of Bhowal and Datta (1) was observed to be the same for a given value of ϑ. Other such combinations of σ_1, σ_2, σ_3, and σ_4 also gave the same result. This suggests that ϑ can be related to the dimensionless groups σ_1, σ_2, σ_3, and σ_4 of the reversible model (2). The relation is assumed to be of the form

$$\vartheta = a\sigma_1^b\sigma_2^e\sigma_3^c\sigma_4^d \tag{15}$$

where a, b, c, d, and e are constants.

For a given experimental condition (i.e., f_m and f_b constant):

$$\vartheta = a\sigma_1^b\sigma_3^c\sigma_4^d \tag{16}$$

since K_{mi} and K_{mb} are usually considered to be the same. For a given solute:

$$\vartheta = a\sigma_3^c\sigma_4^d \tag{17}$$

TABLE 1
Physical and System Parameters[a]

Solute	Aniline	Phenol	*m*-Toluidiene	*p*-Toluidiene
D_i ($\times 10^9$)	.932	.998	.835	.835
D_o ($\times 10^9$)	.0583	.065	.0522	.0522
K_{bm}, K_{im}	1.7	.52	3.9	3.9
K ($\times 10^{-4}$)	4.274	1.1	5.37	12.02

[a] $f_m = 0.64, f_b = 0.94$.

TABLE 2
Parameters Obtained by Linear Regression

Solute	Range of C^0_{1G}	Range of $C^0_{Ab} \times 10^3$	$a\ (\times 10^2)$	$b\ (\times 10^3)$	$c\ (\times 10^3)$	$d\ (\times 10^3)$
p-Toluidiene	0.08–0.12	1.5–2.5	−9.207	—	1.4655	−9.285
Aniline	0.08–0.12	1.5–2.5	−6.792	—	9.423	−3.83
Phenol	0.3–0.4	3.0–6.0	−2.049	—	2.463	−5.07
Overall			−5.482	−2.816	6.567	−3.315

Table 2 collects the regression parameters for individual solutes *p*-toluidiene, aniline, and phenol using Eq. (17) as well as all these solutes considered together by using Eq. (16). The variation in the concentrations of the initial internal reagent concentration and bulk concentration studied for developing the correlation are reported in Table 2. In order to ascertain the accuracy in predictions of the extraction profiles using ϑ obtained from the regression parameters of Eq. (16), extraction profiles of *m*-toluidiene, which has not been included in the regression analysis, have been simulated by the model of Bhowal and Datta (1) and compared to the reversible model of Bunge and Noble (Fig. 3). Further, even though regression parameters have been obtained within a certain range of concentrations of C^0_i and C^0_{Ab} (Table 2), experimental conditions outside this range give fairly accurate results as demonstrated in

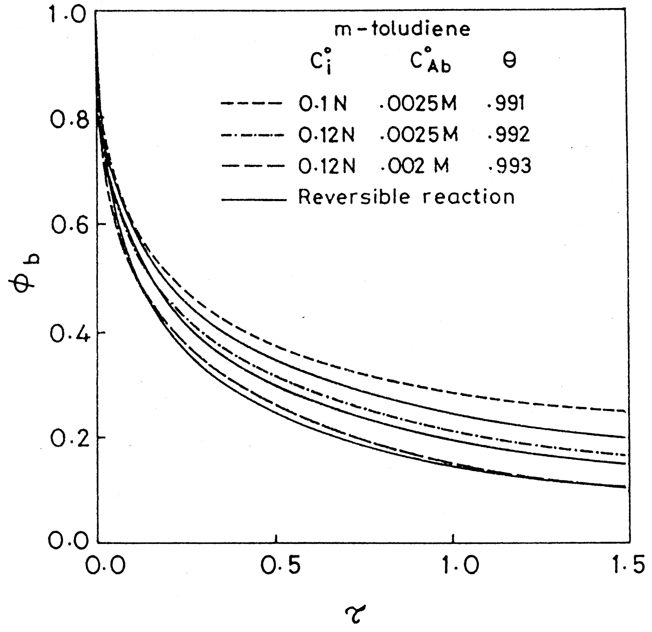

FIG. 3 Comparison of the theoretical model with the reversible model.

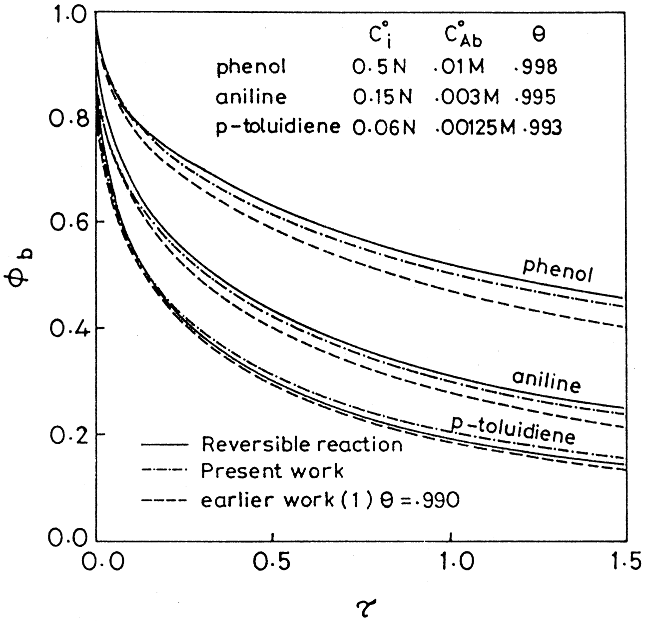

FIG. 4 Comparison of the extraction profile of different models.

Fig. 4. The predictions are also better than those obtained from previous work (1) which assumed the parameter value to be 0.99.

Table 3 lists the effects of changes of various physical parameters and experimental conditions on ϑ. These parameters were obtained by the trial and error procedure mentioned previously. Comparison shows that the parameter value is greater for a decreased initial concentration of solute and a higher internal reagent concentration and reaction equilibrium constant. At a lower initial concentration of reactants or at an increased reaction equilibrium constant, the extraction rate is faster as indicated by the dimensionless concentration in the external phase at the end of the extraction time (Table 3). This indicates

TABLE 3
Values of the Parameters Used[a]

Solute	C_i^0	C_{Ab}^0	σ_3	σ_4	ϕ_b at $\tau = 1.5$	ϑ_{rev}	ϑ
A	0.1	2.5	12,020	300.5	.1865	.973	.992
A	0.1	1.5	12,020	240.4	.127	.985	.998
A	0.12	2.5	14,424	300.5	.1337	.984	.995
B	0.1	2.5	5,370	134.25	.196	.97	.984

[a] A = *p*-toluidiene, B = *m*-toluidiene, $\sigma_1 = .1593$, $\sigma_2 = .023$.

that the magnitude of ϑ will be comparatively greater under those experimental conditions for which σ_3 is high and σ_4 is low, provided σ_1 and σ_2 are the same. Higher values of ϑ thus signify faster extraction under these conditions.

The fraction of solute extracted during the extraction time considered and existing in the internal droplets as the reaction product (ϑ_{rev}) according to the reversible model in the emulsion globules has been calculated and is reported in Table 3. The variation of ϑ obtained for various solutes under our experimental conditions is seen to follow ϑ_{rev} closely. This justifies the values of ϑ obtained.

CONCLUSIONS

A correlation has been developed in this work for calculation of the parameter ϑ of the earlier work of Bhowal and Datta (1) as a function of system parameters and experimental conditions. The present model provides an alternative to the reversible model (2) for predicting the extraction profiles of solutes with less computational effort. Simulation of the external concentration profiles of solutes based on ϑ obtained from the present correlation is seen to give better prediction than the earlier work (1) (which assumed ϑ to be a constant) for extraction of solute by LSM.

NOTATIONS

C_{Ab}^{0}	initial bulk phase solute concentration (M)
C_{i}^{0}	initial internal phase reagent concentration (N)
D_{eff}	effective solute diffusivity in the emulsion globule based on advancing front model ($\mathrm{m}^2 \cdot \mathrm{s}^{-1}$)
f_{b}	bulk volume fraction of total volume
f_{m}	membrane volume fraction of emulsion
K	reaction equilibrium constant ($\mathrm{L} \cdot \mathrm{mol}^{-1}$)
K_{b}	dissociation constant of base ($\mathrm{mol} \cdot \mathrm{L}^{-1}$)
K_{mb}	partition coefficient between membrane and bulk phase
K_{mi}	partition coefficient between membrane and internal phase
n	number of emulsion globules
r	radial coordinate (m)
R	radius of the emulsion globule (m)
R_{f}	radius of reaction front (m)
R_{fo}	radius of reaction front at the previous time step (m)
Δt	time interval (s)
V_{e}	external phase volume (m^3)
$[\mathrm{A}^-]$	concentration of anion ($\mathrm{mol} \cdot \mathrm{m}^{-3}$)
$[\mathrm{B}^+]$	concentration of dissociated base ($\mathrm{mol} \cdot \mathrm{m}^{-3}$)

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[BOH]	concentration of undissociated base ($\mathrm{mol\cdot m^{-3}}$)
$[\mathrm{H^+}]$	hydrogen ion concentration ($\mathrm{mol\cdot m^{-3}}$)
$[\mathrm{OH^-}]$	hydroxyl concentration ($\mathrm{mol\cdot m^{-3}}$)

Greek Symbols

ϕ_b	dimensionless external phase concentration $\left(\frac{C_\mathrm{ib}}{C^0_\mathrm{Ab}}\right)$
σ_1	dimensionless parameter $\left(f_\mathrm{m}\frac{1-f_\mathrm{b}}{f_\mathrm{b}}\right)K_\mathrm{mb}$
σ_2	dimensionless parameter $\left((1-f_\mathrm{m})\frac{1-f_\mathrm{b}}{f_\mathrm{b}}\frac{K_\mathrm{mb}}{K_\mathrm{mi}}\right)$
σ_3	dimensionless reagent concentration (KC^0_i)
σ_4	dimension solute concentration $\left(KC^0_\mathrm{Ab}\frac{K_\mathrm{mb}}{K_\mathrm{mi}}\right)$
ϑ	the model parameter of Bhowal and Datta (1)
τ	dimensionless time $\left(\frac{tD_\mathrm{eff}}{R^2}\right)$

Subscripts

a	reacted region in the emulsion globule
e	external phase
i	internal phase
m	membrane phase

REFERENCES

1. A. Bhowal and S. Datta, *J. Membr. Sci., 139*, 103 (1998).
2. A. L. Bunge and R. D. Noble, *Ibid., 21*, 55 (1984).
3. N. N. Li, US Patent 3,410,794 (1968).
4. W. S. Ho, T. A. Hatton, and E. N. Lightfoot, *AIChE J., 28*, 662 (1982).
5. M. Teramoto, H. Takihana, M. Sibutani, T. Yuasa, Y Miyake, and H. Teranishi, *J. Chem. Eng. Jpn., 14*, 122 (1981).
6. R. S. Braid, A. L. Bunge, and R. D. Noble, *AIChE J., 33*, 43 (1987).

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