

<Subscripts>

d	= desorbent
f	= feed
j	= iteration times
k	= components
n	= zone number (=I to IV)
0	= inlet
1	= outlet

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A SIMULATION FOR LIQUID SURFACTANT MEMBRANE PERMEATION IN A CONTINUOUS COUNTERCURRENT COLUMN

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Key Words: Extraction, Liquid Surfactant Membrane, Column Operation, Simulation, Permeation Process, Metal Ion

The continuous permeation of metal ions in a countercurrent column was simulated in order to develop a continuous separation process with the liquid surfactant membrane technique. In the simulation, an axial dispersion model was applied for a continuous phase. For the permeation of metal ion in a dispersed phase, an approximate model was adopted in which the external diffusion around the dispersed phase, the diffusion through a peripheral thin oil layer in the dispersed phase and the extraction reaction at the interface between the continuous and dispersed phases were taken into account. The observed concentration distributions of metal ions in the column reported by Marr *et al.* were satisfactorily simulated by the models applied and by use of the conventional relations for liquid-liquid extraction.

Introduction

The liquid surfactant membrane technique has been noted as a novel separation and concentration method. In the industrial application of this technique, a continuous operation using a mixer-settler or a column is required. A column operation is preferable for treating a large amount of feed solution. However, only one study has been reported, in which continuous permeation tests of some metals were carried out in a countercurrent column by Marr *et al.*⁶⁾

The purpose of our work is to develop a continuous

separation process with the liquid surfactant membrane technique. In the present paper, simulation results for a continuous permeation of metal ions when a countercurrent column is used as liquid membrane contact equipment are presented. The simulation was made on the basis of the column and the experimental results reported by Marr *et al.*⁶⁾ The column has only a stirrer and does not have baffle plates or stators.

1. Simulation Model

Figure 1 shows a model of a continuous countercurrent column operation. The feed, an aqueous phase containing a metal ion, is supplied at a top of column as a continuous phase. The dispersed phase is a (W/O)

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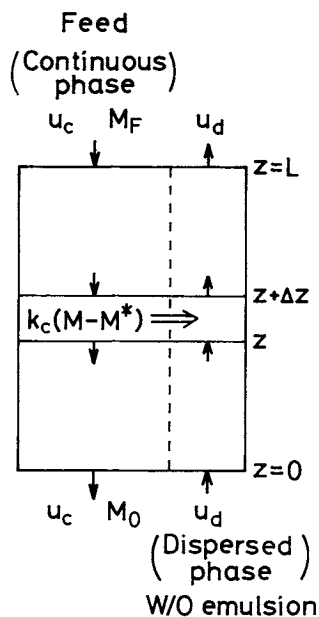


Fig. 1. Modelling of column.

emulsion which consists of another aqueous phase for stripping the metal and an oil phase containing a carrier and a surfactant. It is supplied from the bottom of the column and flows countercurrently with the continuous phase in the column. M is metal ion concentration and u is flow rate. The metal ion permeates from the continuous phase to the dispersed phase.

When an axial dispersion model is applied for the continuous phase, Eq. (1) is obtained from a mass balance of the metal ion.

$$E_c(d^2M/dz^2) + u_c(dM/dz) - k_c a(M - M^*) = 0 \quad (1)$$

where E , k and a are the axial dispersion coefficient, the mass-transfer coefficient and the superficial area of contact of the phases, respectively. The superscript* represents the interface between the continuous and dispersed phases. Using the following dimensionless parameters,

$$\begin{aligned} Pe &= Lu_c/E_c, \quad N_c = 6\phi Lk_c/d_p u_c \\ A &= M/M_F, \quad Z = z/L, \quad a = 6\phi/d_p \end{aligned} \quad (2)$$

Equation (1) is transformed as follows:

$$(1/Pe)(d^2A/dZ^2) + (dA/dZ) - N_c(A - A^*) = 0 \quad (3)$$

where ϕ is the dispersed-phase holdup and d_p is the diameter of (W/O)/W emulsion drop.

For the dispersed phase, the permeation model shown in Fig. 2 is generally applied. That is, the metal

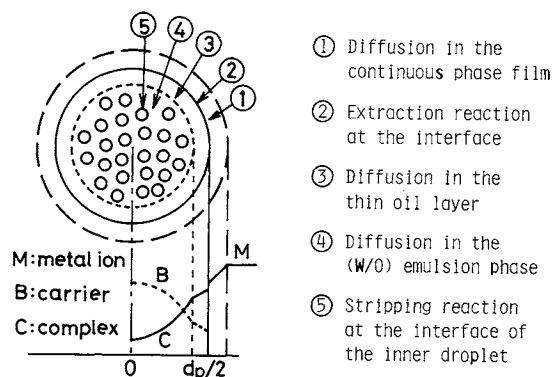


Fig. 2. Permeation model for (W/O)/W emulsion drop.

ion permeates from the continuous phase into the inner aqueous droplets in the dispersed phase by proceeding along the five steps shown in the figure. In column operation, however, the residence time of the dispersed phase is generally short. In addition, when the concentration of metal ion in the continuous phase is low, a metal-carrier complex formed by the extraction reaction at step ② may be stripped in the inner aqueous droplets present near the surface of the (W/O)/W emulsion drop. Therefore, steps ④ and ⑤ were not taken into account and an approximate model for the permeation shown in Fig. 3 was applied in the present analysis. Namely, the overall mass-transfer resistance ($1/K$) is presumed to be expressed as a sum of the resistances of the continuous-phase film diffusion ($1/k_c$), extraction reaction ($1/k_s$) and diffusion in the peripheral thin layer of the oil phase ($1/mk_i$).

$$\frac{1}{K} = \frac{1}{k_c} + \left(\frac{1}{k_s} + \frac{1}{mk_i} \right) = \frac{1}{k_c} + \frac{1}{k_d} \quad (4)$$

where m is the distribution coefficient of metal ion.

Equation (3) therefore reduces to

$$(1/Pe)(d^2A/dZ^2) + (dA/dZ) - N_{oc}A = 0 \quad (5)$$

where

$$N_{oc} = 6\phi LK/d_p u_c.$$

Equation (5) can be analytically solved under the following boundary conditions:⁷⁾

$$\begin{aligned} Z=1; \quad 1 &= (A)_{Z=1-} + (1/Pe)(dA/dZ)_{Z=1-} \\ Z=0; \quad (1/Pe)(dA/dZ)_{Z=0+} &= 0 \end{aligned} \quad (6)$$

and the concentration distribution of the metal ion in the column is given by

$$A = \frac{2(1+q)\exp\{-(1/2)Pe(1-q)Z\} - 2(1-q)\exp\{-(1/2)Pe(1+q)Z\}}{(1+q)^2\exp\{-(1/2)Pe(1-q)\} - (1-q)^2\exp\{-(1/2)Pe(1+q)\}} \quad (7)$$

where

$$q = \{1 + (4N_{oc}/Pe)\}^{1/2}.$$

The values of Pe and N_{oc} are needed to calculate the concentration distribution from Eq. (7).

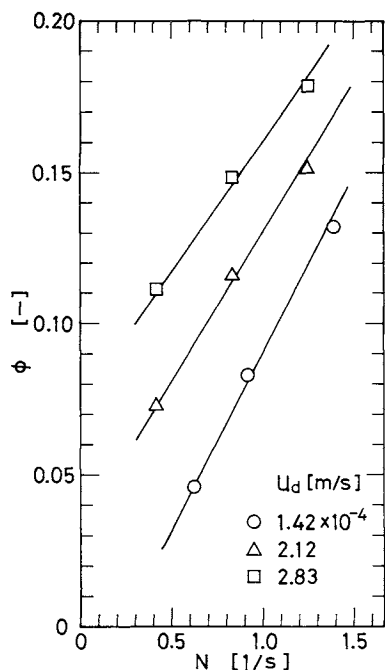


Fig. 6. Relation between ϕ and N .

N in the region of low stirring speed, as shown in Table 1, carried out by Marr *et al.*⁶⁾ and to be constant at 1.05 mm obtained for $N=0$.

For estimation of the axial dispersion coefficient E_c , the results reported for the Mixco column, which is relatively similar to the stirred column, were utilized because there is no available result for liquid-liquid extraction in the stirred column. The values of ϕ and E_c were calculated at different N values by using Eqs. (12) and (13)²⁾ correlated for the Mixco column in addition to Eq. (9).

$$\frac{u_k \mu_c}{\sigma} = 1.77 \times 10^{-4} \left(\frac{g}{d_i N^2} \right) \left(\frac{\Delta \rho}{\rho_c} \right)^{0.9} \quad (12)$$

$$E_c = \frac{u_c z_c}{1 - \phi} \left\{ 0.0268 \frac{d_i N (1 - \phi)}{u_c} - 0.14 \right\} \quad (13)$$

where d_i is the impeller diameter and z_c is the compartment height in the Mixco column.

In Fig. 7, the calculated values of ϕ are plotted against N , and E_c is plotted against ϕ as a parameter z_c . The relation between ϕ and N at $u_d = 1.42 \times 10^{-4}$ m/s for the stirred column presented in Fig. 6 is also shown in Fig. 7. In both columns, the N dependency of ϕ is approximately similar although the range of N used is different. Therefore, to evaluate the E_c value for the stirred column, the relations of Fig. 7 were used by assuming that the ϕ dependency of E_c is the same in both columns. From both the results of the permeation test shown in Fig. 5 and the relations of Fig. 7, it was found by a trial-and-error method (see Appendix) that the relation between E_c and ϕ at $z_c = 0.2$ m can be utilized to estimate the E_c value. The

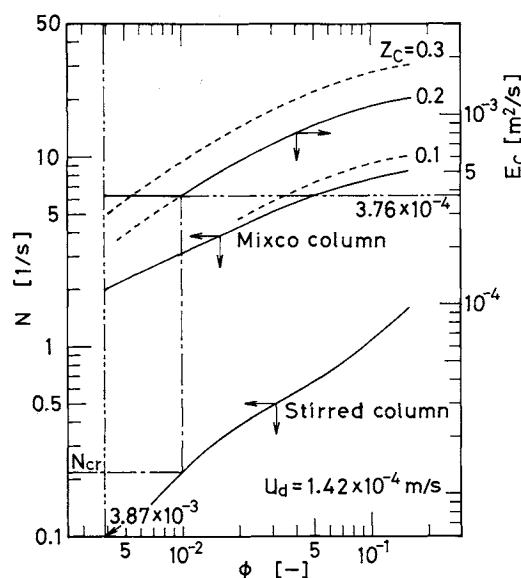


Fig. 7. Plots of N vs. ϕ and E_c vs. ϕ .

values of E_c and N_{oc} determined in this way are represented in Fig. 5. The k_c values were calculated from the N_{oc} values and are plotted against N in Fig. 8. The k_c is proportional to 0.67 power of N in the region above N_{cr} . This N dependency of k_c agrees with the result obtained for the dissolution of solid spheres in the stirred tank without baffle plates by Nagata *et al.*⁸⁾

3. Simulation Results

The concentration distribution of metal ion in the column was simulated for the copper-LIX 70 system and zinc-D2EHPA system, respectively, carried out by Marr *et al.*⁶⁾ 1.25 kmol/m³ and 2.5 kmol/m³ sulfuric acid solutions were respectively used as the inner aqueous phase. The results are shown in Figs. 9 and 10. In the simulation, the values of ϕ , E_c and k_c used for $N=0$ were the same as for the vanadium-Aliquat 336 system, and those for other values of N were estimated by the above method. The value of k_c depends on the diffusivity of metal ion in the continuous phase, but it was assumed to be independent of the metal ion here.* That is, the values of ϕ and E_c were determined using the relations of Fig. 7 and k_c was obtained from the relation of Fig. 8. Furthermore, the dispersed-phase mass-transfer coefficient k_d is necessary to simulate, because the extraction reaction in these systems is slow. The value of k_d involving k_s , which is dependent on the concentration of hydrogen ion, may be expected to vary with axial distance in the column. The column was therefore

* Diffusivities of Cu^{2+} and Zn^{2+} in the continuous phase are estimated as 0.74×10^{-9} and 0.71×10^{-9} m²/s, respectively, from the Nernst-Einstein equation and their respective mobilities. There is a little difference between these diffusivities and the value for vanadium adopted before.

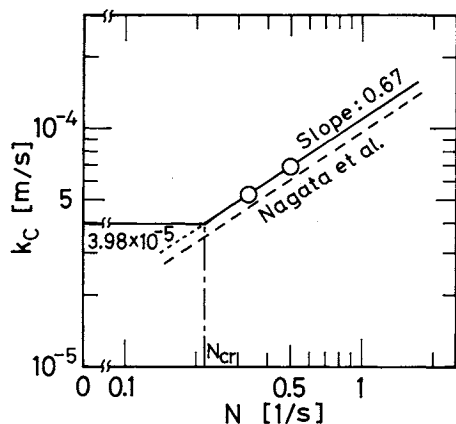


Fig. 8. Relation between k_c and N .

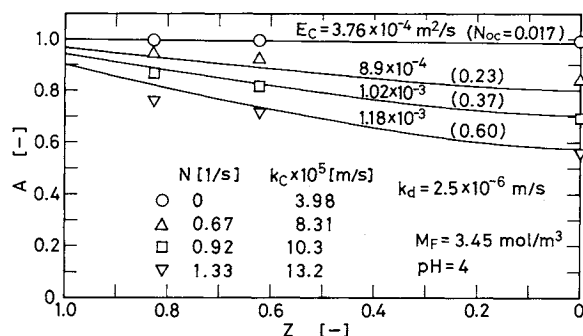


Fig. 9. Simulation result for copper-LIX 70 system.

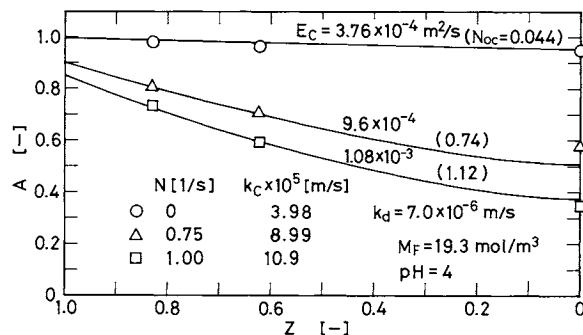


Fig. 10. Simulation result for zinc-D2EHPA system.

divided into three sections in the ratio of 0.4:0.7:1.0 from the bottom of the column, and then the value of K was determined so that the data might be fitted well by Eq. (7) in each section. The smaller K value was obtained for the lower section.* Although it may be considered to be due to the influence of k_d variance, in the present simulation the k_d value was assumed to be constant in the column as a first approximation and adopted the average of values obtained for each N . The effect of hydrogen ion concentration will be studied in the near future. As is clear from Figs. 9 and 10, in both systems the simulation results made by

* For example, the values of k_d obtained from the K values at $N=1.00\text{ s}^{-1}$ for the zinc-D2EHPA system are 7.52×10^{-6} , 7.18×10^{-6} and 6.85×10^{-6} m/s from the top of the column. The average k_d is 7.2×10^{-6} m/s.

using the k_d value represented in the figures satisfy the observed results for every stirring speed.

The value of k_d is about one order smaller than that of k_c . The diffusivities of copper-carrier complex and zinc-carrier complex in the oil phase are estimated from the Wilke-Chang equation¹¹⁾ as 2.35×10^{-10} and 1.92×10^{-10} m²/s, respectively. The k_i value may be predicted to be of magnitude 10^{-4} by using the estimation method proposed by Kim *et al.*⁵⁾ Therefore, it is considered that the permeation process in these two systems is controlled by the resistance of the extraction reaction at the interface between the continuous and dispersed phases.

Conclusion

The continuous permeation of metal ion in the countercurrent column was simulated in order to develop a continuous separation process with the liquid surfactant membrane technique. The experimental results reported by Marr *et al.*⁶⁾ were interpreted satisfactorily by the simulation results, which were made by utilizing the relations reported for the usual liquid-liquid extraction operation.

Appendix

When a value of z_c is supposed, the E_c value is obtained for different ϕ and N from Fig. 7. Then the value of N_{oc} is estimated so that the result calculated from Eq. (7) may adequately simulate the observed concentrations at each N value shown in Fig. 5. The k_c values calculated from the resultant N_{oc} are plotted against N as shown in Fig. 8. In Fig. 7, N_{cr} is evaluated as a value of N which is obtained from the E_c value for the case without stirring. On the other hand, in the plot of k_c vs. N , a different N_{cr} is obtained from the k_c value without stirring. The z_c value is determined so that agreement between two values of N_{cr} may be achieved.

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Nomenclature

A	= dimensionless concentration of metal ion, M/M_F	[—]
a	= superficial area of contact of phases	[1/m]
B	= carrier concentration	[mol/m ³]
C	= concentration of metal-carrier complex	[mol/m ³]
D_M	= diffusivity of metal ion	[m ² /s]
D_T	= column diameter	[m]
d_i	= impeller diameter	[m]
d_p	= (W/O)/W emulsion drop diameter	[m]
E	= axial dispersion coefficient	[m ² /s]
g	= gravitational acceleration	[m/s ²]
K	= overall mass-transfer coefficient	[m/s]
k	= mass-transfer coefficient	[m/s]
k_i	= mass-transfer coefficient in peripheral layer of oil phase	[m/s]
k_s	= mass-transfer coefficient at interface	[m/s]
L	= column length	[m]
M	= metal ion concentration	[mol/m ³]
M_F	= feed concentration of metal ion	[mol/m ³]
m	= distribution coefficient of metal ion	[—]

N	= stirring speed	[1/s]
N_c	= $6\phi Lk_c/d_p u_c$	[—]
N_{cr}	= critical stirring speed	[1/s]
N_{oc}	= $6\phi LK/d_p u_c$	[—]
P	= $\rho_c^2 \sigma^3 / \mu_c^4 g \Delta \rho$	[—]
Pe	= Peclet number, Lu_c/E_c	[—]
q	= $\{1 + (4N_{oc}/Pe)\}^{1/2}$	[—]
u	= superficial velocity	[m/s]
u_k	= characteristic velocity	[m/s]
u_s	= slip velocity	[m/s]
Z	= dimensionless axial distance, z/L	[—]
z	= axial distance	[m]
z_c	= compartment height	[m]
μ	= viscosity	[Pa·s]
ρ	= density	[kg/m ³]
$\Delta \rho$	= density difference	[kg/m ³]
σ	= interfacial tension	[N/m]
ϕ	= dispersed phase holdup	[—]
<Subscripts>		
c	= continuous phase	
d	= dispersed phase	

<Superscript>

* = interface

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VAPORIZATION FROM PURE LIQUID SURFACE IN A CENTRIFUGAL MOLECULAR STILL

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Key Words: Evaporation, Vacuum, Mass Transfer, Centrifugal Molecular Still, Liquid Film

The rates of evaporation of pure liquids, EHS (di-2-ethylhexyl sebacate), EHP (di-2-ethylhexyl phthalate) and DBP (dibutyl phthalate), in two centrifugal molecular stills were measured under a pressure of residual inert gas less than 1.3 Pa and compared with the approximate solution derived in our previous paper.⁴⁾

1. Experimental Apparatus and Procedure

A schematic diagram of the experimental apparatus is shown in **Fig. 1**. Two centrifugal molecular stills, MS-150 ($r_i=0.0133$ m, $r_o=0.0798$ m) and MS-380 ($r_i=0.0293$ m, $r_o=0.202$ m), have a conical evaporator-surface with open angle of 140 degrees. The condensing surface is located around the

evaporator-surface and is cooled by water. The feed liquid was supplied to the center of the rotating evaporator-surface through the feed nozzle. The liquid film was heated by a sheathed heater located under the evaporator-surface. A part of the feed liquid was evaporated from the liquid film and the resultant vapor was condensed at the condensing surface to gather into the distillate tank.

The rates of evaporation were determined from the weight of the distillate for a given time interval. The pressures of residual inert gas were measured by a McLeod gauge. The feed temperatures were measured by a thermocouple in the feed pipe near the feed nozzle, and the outlet temperatures by a thermocouple immersed in the liquid jet at the edge of the evaporator-surface. No disturbance or break-up of liquid film on the rotating evaporator-surface was

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