COPPER EXTRACTION WITH LIQUID SURFACTANT MEMBRANE IN MIXCO EXTRACTOR

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The extraction of copper with a liquid surfactant membrane containing LIX 65N as carrier and glutamic acid dioleylester ribitol as surfactant was carried out in a Mixco column. The copper concentration profile along the column was measured. The experimental results were analyzed by the backflow model, taking account of the interfacial reaction between copper in the continuous phase and carrier in the W/O emulsion phase and of the diffusion of copper in the continuous phase without an adjustable parameter.

Introduction

For the refining of copper, hydrometallurgical alternatives involving sovent extraction to conventional pyrometallurgical processes have been developed from the viewpoints of energy saving and effective utilization of resources. Recently, the liquid surfactant membrane (LSM) process has drawn practical interest as a novel separation technique in treatment of metal-processing waste water, hydrometallurgy, etc., and since 1986 the LSM technique has been applied industrially to the recovery of zinc from spin bath[3] in Austria.

The LSM process was applied to copper extraction from an acid leach solution by Li et al.[8] and Marr et al.[1,10] Li et al.[6] carried out a continuous bench-scale operation using mixer-settlers and concluded that the LSM process is more economical than the conventional solvent extraction process using mixer-settlers. However, they indicate that the design of settlers requires special attention because of the swelling of emulsion and entrainment of water in the settler. Therefore, use of an extraction column should considered because the volume of settled emulsion phase in the column is much smaller than that in mixer-settlers. Marr et al.[1] studied the extraction of copper using a continuous pilot plant with a column of 6 m active height and 0.1 m diameter. They applied the axial-dispersion model, taking account of the swelling due to osmosis in the analysis of their system. Kataoka et al.[6] simulated the experimental results for the copper-LIX 70 system and the zinc-D2EHPA system obtained by Marr et al.,[9] using an axial-dispersion model. In their studies, the reaction rate constant was an adjustable parameter.
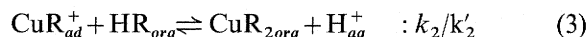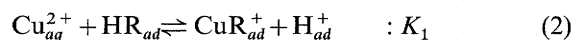
Design of the extractor must be based on a kinetic model of copper permeation and a model of the hydrodynamics in the column. In the above studies, Span 80 or polyamine was used as surfactant. The effect of surfactants on the kinetics of metal permeation has not been clarified.

In work reported in previous papers,[4,5,11] L-glutamic acid dioleylester ribitol (abbreviated as $2C_{18}\Delta$ [9]GE) as a new and excellent surfactant for the LSM process was developed and the kinetics of copper permeation through LSM containing LIX 65N as a carrier and $2C_{18}\Delta$ [9]GE was clarified in a batch reactor. In this work, copper extraction with LSM containing LIX 65N and $2C_{18}\Delta$ [9]GE was carried out in a continuous countercurrent contactor, the Mixco column. The experimental results were analyzed by a backflow model on the basis of a kinetic model of copper permeation.

1. Theory

1.1 Extraction of copper with LSM

As shown in the previous paper,[4] the extraction of copper with LIX 65N at the interface between the external aqueous and W/O emulsion phases is expressed by the following interfacial reaction steps.

$$HR_{org} \rightleftharpoons HR_{ad} \qquad : K_{ad} \qquad (1)$$

$$Cu_{aq}^{2+} + HR_{ad} \rightleftharpoons CuR_{ad}^+ + H_{ad}^+ \qquad : K_1 \qquad (2)$$

$$CuR_{ad}^+ + HR_{org} \rightleftharpoons CuR_{2org} + H_{aq}^+ \qquad : k_2/k_2' \qquad (3)$$

Assuming that Eq. (3) in the above reaction scheme is a rate-determining step, the interfacial reaction rate is written as

$$R = \frac{k_f C_{HR}^{2*} C_M^*/a_H^* - k_2' C_{MR2}^* a_H^*}{1 + K_{ad} C_{HR}^* + K_s C_s} \qquad (4)$$

where $k_f = k_2 K_1 (K_{ad}/S_{HR})$, K_{ad} and K_s are interfacial adsorption equilibrium constants of the extractant and the surfactant respectively, C_s is the surfactant concentration, S_{HR} is the interfacial area occupied by unit mole of the extractant, and superscript * denotes the aqueous or organic solution adjacent to the interface.

The following approximations are assumed under appropriate experimental conditions: 1) carrier concentration is in considerable excess over copper concentration in feed aqueous solution and the stripping rate at the interface between internal aqueous and organic solutions is extremely fast compared with the extraction rate between the feed aqueous and organic solutions, that is, $C_{MR2} = 0$ and $C_{HR} = C_{HRO}$; 2) the pH is kept constant in the column when a buffer solution is used, that is, $a_H = a_{HO}$.

Equation (4) reduces to

$$R = \frac{k_f C_{HRO}^2 C_M^*/a_{HO}}{1 + K_{ad} C_{HRO} + K_s C_s} \qquad (5)$$

The concentration of copper adjacent to the external interface is obtained from the following relation, in which the interfacial reaction rate equals the mass transfer rate at steady state.

$$R = k_M (C_M - C_M^*) \qquad (6)$$

where k_M is the mass transfer coefficient of copper.

Equation (7) is obtained by eliminating C_M^* from Eqs. (5) and (6).

$$R = k_o C_M \qquad (7)$$

where

$$\frac{1}{k_o} = \frac{1}{k_M} + \frac{1 + K_{ad} C_{HRO} + K_s C_s}{k_f C_{HRO}^2/a_{HO}} \qquad (8)$$

The values of k_f, K_{ad} and K_s in Eq. (8) have been obtained experimentally by measuring the extraction rate of copper in a batch reactor[4] and the interfacial tension.[7]

The mass transfer coefficient of copper in the continuous phase, k_M, can be estimated from the following correlation, obtained by Bibaud and Treybal.[2]

$$k_M = 8.47 \times 10^{-5} \exp\{0.85 v_i^{0.03} [\log(n_R D_R^2/v_c) - 3.504] - (0.550 v_i^{1/3} + 0.7605)\} \qquad (9)$$

where v_i is the volume of i-th stage, n_R is the stirring speed, D_R is impeller diameter and v_c is the kinematic viscosity of the continuous phase.

1.2 Modeling of Mixco column

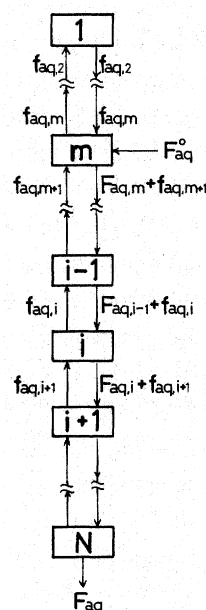It is well known that axial dispersion affects the

Fig. 1. Backflow model

performance of a continuous countercurrent extractor. A backflow model[13] is considered to be preferable for the Mixco extractor. Therefore, the back flow model was applied to the analysis of extraction of copper with LSM.

Mass transfer in emulsion phase can be neglected when the above assumption, which is used in the derivation of Eq. (5), is valid. A schematic diagram of the backflow model composed of N cells for the continuous countercurrent contactor using LSM is shown as **Fig. 1**.

The mass balance of copper ion in the continuous phase of i-th stage is written as

$$(F_{aq,i-1} + f_{aq,i})C_{M,i-1} - (F_{aq,i} + f_{aq,i} + f_{aq,i+1})C_{M,i} + f_{aq,i+1}C_{M,i+1} = v_i \phi_i a_i R_i \qquad (10)$$

where F_{aq} and f_{aq} are volumetric flow rate and backflow respectively, ϕ_i and a_i are holdup of dispersion phase and specific area in i-th stage, respectively.

Equations (12) to (15) are obtained by defining the dimensionless terms as Eq. (11) and substituting these into Eqs. (7), (8) and (10):

$$Q_{aq} = \frac{F_{aq}}{F_{aq}^0}, \quad q_{aq} = \frac{f_{aq}}{F_{aq}^0}, \quad X_M = \frac{C_M}{C_M^0},$$

$$N_{ox} = \frac{v_i \phi_i a_i k_o}{F_{aq}^0} \qquad (11)$$

For $i = 1$:

$$-(q_{aq,2} + N_{ox})X_{M,1} + q_{aq,2}X_{M,2} = 0 \qquad (12)$$

For $1 < i < m$:

$$q_{aq,i}X_{M,i-1} - (q_{aq,i} + q_{aq,i+1} + N_{ox})X_{M,i} + q_{aq,i+1}X_{M,i+1} = 0 \qquad (13)$$

For $i = m$ (feed stage):

$$q_{aq,m}X_{M,m-1}-(Q_{aq,m}+q_{aq,m}+q_{aq,m+1}+N_{ox})X_{M,m}$$
$$+q_{aq,m+1}X_{M,m+1}+Q_{aq}X_M^0=0 \qquad (14)$$

For $m<i<N$:

$$(Q_{aq,i-1}+q_{aq,i})X_{M,i-1}-(Q_{aq,i}+q_{aq,i}+q_{aq,i+1}$$
$$+N_{ox})X_{M,i}+q_{aq,i+1}X_{M,i+1}=0 \qquad (15)$$

The dimensionless volumetric backflow q_{aq} is correlated with the Peclet number, Pe $(=u_cL/E_c)^{10)}$:

$$q_{aq,i}=(Pe\cdot h_i\cdot(1-\phi_i))^{-1}-Q_{aq}/(2(1-\phi_i)) \qquad (16)$$

where h_i is the dimensionless height of i-th stage.

The Peclet number can be estimated by using the following correlation of the axial dispersion coefficient,[2] E_c, for the Mixco column.

$$E_c=\frac{u_cz_c}{1-\phi}\left\{0.0268\frac{n_RD_R(1-\phi)}{u_c}-0.14\right\} \qquad (17)$$

where u_c is mean superficial velocity of the continuous phase and z_c is height of compartment.

Holdup of dispersion phase can be calculated from the following correlation for liquid-liquid extraction in the Mixco column:[2]

$$(u_d/\phi)+(u_c/1-\phi)=(u_k/1-\phi) \qquad (18)$$

with the characteristic velocity, u_k:

$$\frac{u_k\mu_c}{\gamma}=1.77\times10^{-4}\left(\frac{g}{n_RD_R}\right)\left(\frac{\Delta\rho}{\rho_c}\right)^{0.9} \qquad (19)$$

where μ_c and ρ_c are viscosity and density of the continuous phase, respectively, and $\Delta\rho$ and γ are the difference in density and interfacial tension between continuous and emulsion phases respectively.

2. Experimental

2.1 Reagents

The surfactant, $2C_{18}\Delta$ [9]GE, was synthesized according to the procedure mentioned previously.[5] E-2-hydroxy-5-nonylbenzophenoneoxime (henceforth E-HNBPO and denoted as HR), the active component of the commercial extractant LIX 65N, was used as a carrier in LSM. E-HNBPO was purified from commercial LIX 65N by the method described in the previous paper.[4] Heptane of G.R. grade was used as a diluent. The other inorganic reagents were of reagent grade.

2.2 Extraction of copper by LSM in a Mixco column

The countercurrent Mixco column used for copper extraction with LSM is shown in **Fig. 2** and the column geometry is listed in **Table 1**. Seven sampling glass tubes are fitted to the side of the column for measuring the concentration profile along the column. The continuous aqueous solution was prepared by dissolving copper nitrate in acetic acid-sodium acetate or nitric acid buffer solution. The dispersion phase,
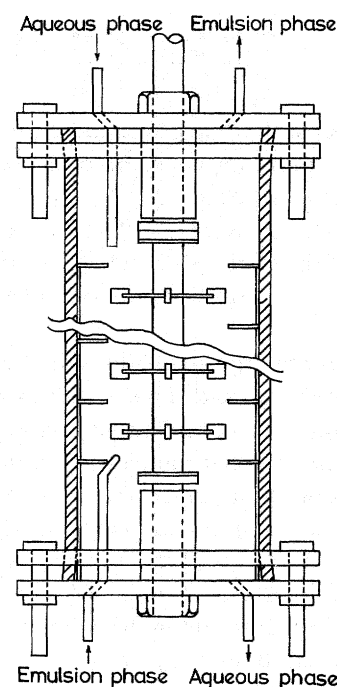

Aqueous phase Emulsion phase

Emulsion phase Aqueous phase

Fig. 2. Mixco extractor

Table 1. Geometry of Mixco column

Column length	$L=0.6$ m	Column diameter	0.05 m
Height of each stage	$z_c=0.025$ m	Impeller diameter	$D_R=0.028$ m
Number of turbines	13		

W/O emulsion containing nickel nitrate as a break-up tracer in internal aqueous solution, was prepared in the same way as described previously.[4] The continuous and emulsion phases were fed from nozzles in the upper and lower flanges respectively. The emulsion drops rose to the top of the column and coalesced. At steady state, the continuous solution was sampled and the concentrations of copper and nickel in the solution were determined by atomic absorption spectrochemical analysis. The diameter of emulsion globules in each stage of the Mixco extractor was measured by a photographic method to obtain the Sauter mean diameter, which is useful for the calculation of the interfacial area. The volume of the internal aqueous solution in the emulsion phase was determined by the Karl-Fischer method. Holdup of dispersion phase was determined by measuring the volume of W/O emulsion phase in the column after inlet and outlet cocks for the feed solutions were simultaneously stopped. the experimental conditions are listed in **Table 2**.

3. Results and Discussion

3.1 Effect of pH on extraction of copper

Figure 3 shows the effect of pH on the extent of

Table 2. Experimental conditions

Flow rate of continuous phase	$F_{aq}^0 = (0.5-2.0) \times 10^{-6} \, \text{m}^3/\text{s}$
Flow rate of emulsion phase	$F_E^0 = 0.1 \times 10^{-6} \, \text{m}^3/\text{s}$
Concentration of extractant	$C_{HR} = 50, \, 100 \, \text{mol}/\text{m}^3$
Concentration of surfactant	$C_s = 8 \, \text{mol}/\text{m}^3$
Concentration of copper	$C_M^0 = 0.2-1 \, \text{mol}/\text{m}^3$
pH of continuous phase	$\text{pH} = 2.5-5.5$
Volume ratio in emulsion phase	$V_{aq}^{i0}/V_{org} = 1$
Concentration of sulfuric acid in internal aqueous solution	$C_{H_2SO_4} = 500 \, \text{mol}/\text{m}^3$
Stirring speed	$n_R = 8.33 \, \text{s}^{-1} \, (500 \, \text{rpm})$

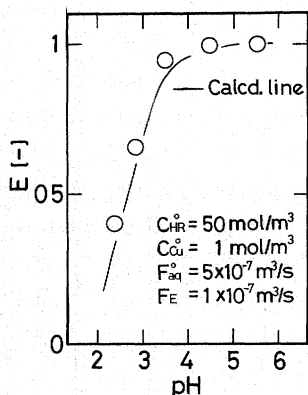**Fig. 4.** Concentration profile of copper in column

Fig. 3. Effect of pH on extent of copper extracted

copper extracted at the outlet of the continuous phase, $E(=(C_{Cu}^0 - C_{Cu})/C_{Cu}^0)$. As expected from the previous paper,[4] E increases with pH.

Figure 4 shows the dimensionless concentration profile of copper along the column. In this figure, Z represents dimensionless height from the bottom of the column. From fig. 4 it is found that this column has greater backmixing than the column utilized by Marr et al.[9] It seems that this is caused by the difference in stirring speed.

Figure 5 shows the effect of pH on (a) the extent of break-up, $\varepsilon(=F_{aq}C_{Ni}/F_{aq}^i C_{Ni}^{i,0})$, (b) the holdup of dispersion phase, ϕ, and (c) the swelling rate of internal aqueous solution, $Y(=V_{aq}^i/V_{aq}^{i0})$. From Fig. 5, the values of ε, ϕ and Y are independent of pH. In all experiments, ε was less than 0.01 and so the influence of break-up of the emulsion on the extraction of copper is negligibly small.

The mean of ϕ at constant flow rate and composition of emulsion phase was 3.5%. The calculated ϕ from Eqs. (18) and (19) was 16%, where the value of interfacial tension ($\gamma = 0.003 \text{N/m}$)[12]* was used because of no data are available concerning the interfacial tension of this system. The large difference between observed and estimated values suggests that the correlation of ϕ for liquid-liquid extraction does

* The value measured by Ohtake et al.[12] is that of interfacial tension between aqueous solution and an emulsion phase composed of kerosene containing Span 80 and $50 \, \text{mol}/\text{m}^3$ nickel sulfate solution.
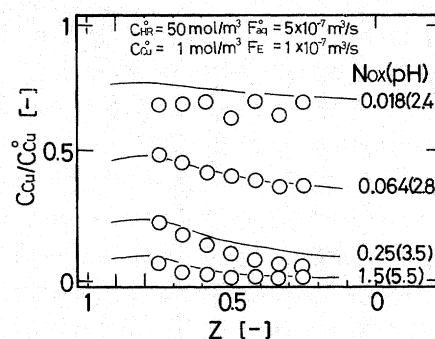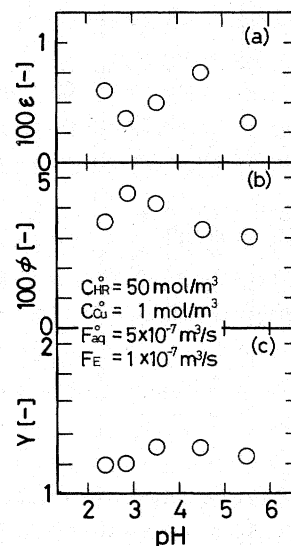

Fig. 5. Effect of pH on extent of break-up of W/O emulsion (a); hold-up of dispersion phase (b); and swelling rate of internal aqueous solution (c)

not apply to the LSM system.

The swelling rate of internal aqueous solution due to osmosis was almost constant at 1.3 regardless of experimental conditions. However, the change of volumetric flow rate of the feed aqueous solution through the column is very small because of low holdup of emulsion phase ($<5\%$).

Distribution curves of the diameter of emulsion globules are shown in **Fig. 6**, which indicates that these are the normal distributions and that the Sauter mean diameter remains almost constant at 0.25 mm through the column.

3.2 Simulation of copper extraction in Mixco column

Kinetic parameters required for the simulation are listed in **Table 3**. As mentioned above, values other than those of k_M were experimentally obtained previously[4,7] and k_M was estimated from Eq. (9).

Hydrodynamic parameters are also listed in Table 3, in which the Peclet number was estimated by using the correlation of the axial dispersion coefficient (Eq. (17)). The observed value was used as ϕ because of the great difference between observed and estimated
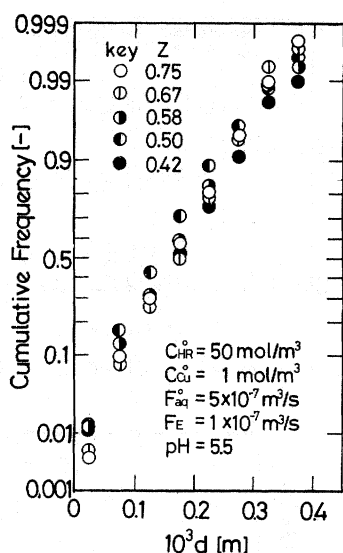
Fig. 6. Distribution curve of diameters of emulsion globules

Table 3. Constants used for analysis

$k_f = 0.9 \times 10^{-6} \, \mathrm{m^{-4}/(mol \cdot s)}$	$K_{ad} = 1/86 \, \mathrm{m^3/mol}$
$K_s = 187 \, \mathrm{m^3/mol}$	$k_M = 4.7 \times 10^{-5} \, \mathrm{m/s}$
$N = 15$	$m = 2$
$Pe = 1$	$d_{32} = 0.25 \times 10^{-3} \, \mathrm{m}$

values.

Because $C_{HRO} \gg C_{CuO}$, the sulfuric acid concentration in the internal aqueous solution is high and the pH of the continuous phase is adjusted by acetate-buffer solution, it is considered that the assumptions used in the derivation of Eq. (5) are satisfied.

Equations (12) to (15) can be solved by assuming that the upper or lower part of the column without turbine corresponds to 1 stage, that is, $N = 15$ and $m = 2$, and that holdup of dispersion phase and the emulsion drop diameter are kept constant through the column.

Solid lines in Figs. 3 and 4 are the results calculated from Eqs. (12) to (15). From Figs. 3 and 4, the calculated results agree approximately with the experimental ones. This indicates that the experimental results are well explained by the backflow model without an adjustable parameter.

Figure 7 shows the relation between dimensionless concentration of copper at the outlet of the continuous phase and N_{ox} as a function of the Peclet number. In Fig. 7, though N_{ox} varied with the experimental conditions, (pH, C_{HRO}, F_{aq}), the experimental data agreed approximately with the results calculated by using $Pe = 1$.

Conclusions

The extraction of copper with a liquid surfactant membrane containing LIX 65N as carrier and glutamic acid dioleylester ribitol as surfactant was
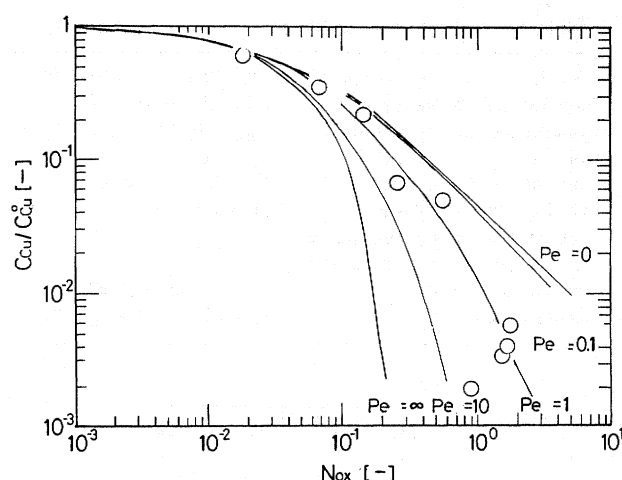

Fig. 7. Relation between copper concentration and N_{ox}

carried out in a Mixco extractor. The experimental results were analyzed by the backflow model, taking account of the interfacial reaction between copper in the continuous phase and the carrier in the W/O emulsion phase and of the diffusion of copper in the continuous phase. It was found that the experimental results are well explained by the backflow model without an adjustable parameter.

Nomenclature

A	=	cross section of column	$[\mathrm{m^2}]$
a	=	specific area	$[\mathrm{m^{-1}}]$
C_j	=	concentration of species j ($j = $ Cu, HR)	$[\mathrm{mol/m^3}]$
C_s	=	concentration of surfactant	$[\mathrm{mol/m^3}]$
C_M^*	=	copper concentration at interface	$[\mathrm{mol/m^3}]$
D_M	=	diffusivity of copper ion	$[\mathrm{m^2/s}]$
D_R	=	impeller diameter	$[\mathrm{m}]$
d_{32}	=	Sauter mean diameter of emulsion drop	$[\mathrm{m}]$
E	=	extent of copper extraction	$[-]$
E_c	=	axial dispersion coefficient	$[\mathrm{m^2/s}]$
F	=	volumetric flow	$[\mathrm{m^3/s}]$
f	=	volumetric backflow	$[\mathrm{m^3/s}]$
h_i	=	dimensionless height of i-th stage	$[-]$
K_{ad}	=	interfacial adsorption equilibrium constant of extractant	$[\mathrm{m^3/mol}]$
K_s	=	interfacial adsorption equilibrium constant of surfactant	$[\mathrm{m^3/mol}]$
k_f	=	overall interfacial reaction rate constant	$[\mathrm{m^4/(mol \cdot s)}]$
k_M	=	mass transfer coefficient of copper	$[\mathrm{m/s}]$
k_o	=	overall mass transfer coefficient of copper	$[\mathrm{m/s}]$
L	=	height of column	$[\mathrm{m}]$
m	=	feed stage	$[-]$
N	=	number of cells	$[-]$
N_{ox}	=	reciprocal dimensionless length per transfer unit based on feed solution defined by Eq. (11)	$[-]$
n_R	=	stirring rate	$[\mathrm{s^{-1}}]$
Pe	=	Peclet number	$[-]$
Q	=	dimensionless volumetric flow	$[-]$
q	=	dimensionless volumetric backflow	$[-]$
R	=	mass transfer rate of copper	$[\mathrm{mol/(m^2 \cdot s)}]$
S_{HR}	=	interfacial area occupied by unit mole	

		of extractant	$[m^2/mol]$
u	=	mean superficial velocity	[m/s]
u_k	=	characteristic velocity	[m/s]
V_{aq}	=	volume of internal aqueous solution	$[m^3]$
v_i	=	volume of i-th stage	$[m^3]$
X_M	=	dimensionless copper concentration	[—]
Y	=	swelling rate of internal aqueous solution	[—]
Z	=	dimensionless height of column	[—]
z_c	=	height of compartment	[m]
γ	=	interfacial tension	[N/m]
ε	=	extent of break-up	[—]
μ	=	viscosity	[Pa·s]
v	=	kinematic viscosity	$[m^2/s]$
ρ	=	density	$[kg/m^3]$
ϕ	=	hld-up of dispersion phase	[—]

⟨Subscripts⟩

aq	=	aqueous solution
c	=	continuous phase
d	=	dispersion phase
E	=	emulsion phase
i	=	i-th stage

⟨Superscript⟩

0	=	initial state
i	=	internal solution
*	=	adjacent to interface

Literature Cited

1) Bart, H. J., R. Wachter, R. Marr and H. J. Muller: *J. Membr. Sci.*, **36**, 413 (1988).
2) Bibaud, R. E. and R. E. Treybal: *AIChE J.*, **12**, 472 (1966).
3) Draxler, J., W. Furst and R. Marr: Proc. ICOM '87, p. 789 (1987).
4) Goto, M., K. Kondo and F. Nakashio: *J.. Chem. Eng. Japan*, **22**, 71 (1989).
5) Goto, M., M. Matsumoto, K. Kondo and F. Nakashio: *J. Chem. Eng. Japan*, **20**, 157 (1987).
6) Kataoka, T., T. Nishiki, M. Yamauchi and Y. Zhong: *J. Chem. Eng. Japan*, **20**, 410 (1987).
7) Kondo, K., K. Funatsu and F. Nakashio: *Solv. Extr. Ion Exch.*, **5**, 739 (1987).
8) Li, N. N., R. P. Cahn, D.. Naden and R. W. M. Lai: *Hydrometallurgy*, **9**, 277 (1983).
9) Marr, R., M. Prötsch, J. Draxler and A. Kriechbaumer: *Ger. Chem. Eng.*, **6**, 365 (1983).
10) McSwain, C. V. and L. D. Durbin: *Separ. Sci.*, **1**, 677 (1966).
11) Nakashio, F., M. Goto, M. Matsumoto, J. Irie and K. Kondo: *J. Membr. Sci.*, **38**, 249 (1988).
12) Ohtake, T, T. Hano, K. Takagi and F. Nakashio: *J. Chem. Eng. Japan*, **20**, 443 (1987).
13) Vermeulen, T., J. S. Moon, A. Hennico and T. Miyauchi: *Chem. Eng. Progr.*, **62**, 95 (1966).

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