EXTRACTION OF AMINE BY W/O/W EMULSION SYSTEM

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A mass transfer model for the extraction of amine in W/O/W emulsion systems having internal aqueous HCl solution phase is presented which takes into account the diffusion in W/O emulsion drops as well as the external mass transfer around W/O emulsion drops, and the effect of various parameters on the extraction rate is clarified. Experimental data on the extraction of aniline, *p*- and *m*-toluidine by W/O/W emulsion systems using a batch-type agitation vessel is discussed on the basis of the present model. It is found that the model can explain the tendency of the experimental data. The mass transfer mechanism in W/O emulsion drops is discussed on the basis of the experimentally evaluated value of effective diffusivity in W/O emulsion drops.

Introduction

Separation processes using liquid surfactant membranes, first developed by Li⁽⁸⁾, have been noted as a novel technique which can be used for the separation of hydrocarbons, the treatment of wastewater containing such contaminants as phenol and amine, and the recovery of heavy metals from acidic leach liquor. To establish the liquid surfactant membrane technique as a practical process, it is important to elucidate the permeation mechanism through the membrane. The mechanism of permeation without a carrier differs from that with a carrier, and the former is much simpler than the latter. However, very few papers have been presented on the permeation mechanism even for the case of physical permeation. Casamatta *et al.*⁽³⁾ analyzed the simplest case, i.e., the permeation of hydrocarbons in O/W/O emulsion system without chemical reaction.

A typical example of a more complicated case of practical importance where chemical reaction occurs in internal aqueous-phase drops and no carrier is contained in the membranes is the removal of phenol in a W/O/W emulsion which consists of an external aqueous phase containing phenol (phase I), internal aqueous phase droplets containing NaOH (phase III) and oil-phase membranes (phase II) separating the two aqueous phases as shown in Fig. 1. However, no paper on the permeation mechanism is available except a very simplified model by Cahn and Li⁽¹⁾. As will be shown later, the mechanism of the extraction

of amine by a W/O/W system with an internal aqueous phase containing HCl is the same as that of the extraction of phenol. In the present paper the experimental results for the extraction of amine, obtained using a batch-type agitation vessel, are discussed on the basis of a theoretical analysis which takes into account the mass transfer around the W/O emulsion drops as well as the diffusion in the W/O emulsion drops.

1. Theory

1.1 Chemical equilibrium

When amine dissolves in an aqueous solution of HCl, i.e., in phase III, the following equations hold.

- 1: External aqueous phase (phase I)
- 2: Oil membrane phase (phase II)
- 3: Internal aqueous phase (phase III)
- 4: Film of phase I around W/O emulsion drop
- 5: Peripheral oil layer in W/O emulsion

Fig. 1 Schematic diagram of W/O/W emulsion system

$$K_a = [\text{RNH}_2][\text{H}^+]/[\text{RNH}_3^+] = C[\text{H}^+]/P \quad (1)$$

$$K_w = [\text{H}^+][\text{OH}^-] \quad (2)$$

$$[\text{RNH}_3^+] + [\text{H}^+] = [\text{Cl}^-] + [\text{OH}^-],$$

$$(P + [\text{H}^+] = A + [\text{OH}^-]) \quad (3)$$

$$[\text{RNH}_2]_T = [\text{RNH}_2] + [\text{RNH}_3^+], \quad (T = C + P) \quad (4)$$

If $[\text{OH}^-] \ll [\text{Cl}^-]$, then the following equation is derived from Eqs. (1)–(4).

$$T = C(C + A + K_a)/(C + K_a) \quad (5)$$

The above equation is simplified as follows.

$$\text{region (a): } T = CA/K_a \quad (C \ll K_a \ll A) \quad (6a)$$

$$\text{region (b): } T = A \quad (K_a \ll C \ll A) \quad (6b)$$

$$\text{region (c): } T = C \quad (C \gg K_a, A) \quad (6c)$$

Figure 2 shows Eqs. (5) and (6) graphically. In the regions of (a) and (b) this curve is similar to Langmuir's adsorption isotherm. In the same figure is shown the relation of T/C vs. C which corresponds to the ratio of the total solubility of amine in the presence of HCl to that without HCl. The value of T/C is very large and almost constant ($=A/K_a$) in region (a), inversely proportional to C in region (b), and approaches unity in region (c).

1.2 Development of model

The following assumptions are made to analyze the extraction rate of amine.

(1) The diffusion rate of amine in W/O emulsion drops is expressed by Eq. (7) using an effective diffusivity.

$$N = -D_e(\partial C_{II}/\partial r) \quad (7)$$

(2) The diameter of W/O emulsion drops is uniform.

(3) In phase III, chemical equilibrium is attained instantaneously. (4) The mass transfer rate of amine from phase II to III is expressed by the second term of the right-hand side of Eq. (9). These assumptions lead to the following basic equations (see Fig. 1).

$$-(1 - \phi')dC_I/dt = K_o a_o \{C_I - (C_{II}/K)_{r=R}\} \quad (8)$$

$$(1 - \phi)\partial C_{II}/\partial t = (D_e/r^2)\partial(r^2\partial C_{II}/\partial r)/\partial r - K_o a_i(C_{II} - KC_{III}) \quad (9)$$

$$\phi(dT_{III}/dC_{III})\partial C_{III}/\partial t = K_o a_i(C_{II} - KC_{III}) \quad (10)$$

$$\text{I.C.; } C_I = C_{I,0}, C_{II} = C_{III} = 0 \quad (0 \leq r \leq R) \text{ for } t = 0 \quad (11)$$

$$\text{B.C.1; } \partial C_{II}/\partial r = 0 \text{ for } r = 0, t > 0 \quad (12)$$

$$\text{B.C.2; } D_e(\partial C_{II}/\partial r) = K_o \{C_I - (C_{II}/K)_{r=R}\} \text{ for } r = R, t > 0 \quad (13)$$

The dimensionless forms of the above equations are

$$\partial y_I/\partial \theta = -\{3\phi'Bi/(1 - \phi')\}\{y_I - (y_{II})_{x=1}\} \quad (14)$$

$$\partial y_{II}/\partial \theta = [\partial^2 y_{II}/\partial x^2 + (2/x)(\partial y_{II}/\partial x) - \phi m(y_{II} - y_{III})]/(1 - \phi) \quad (15)$$

$$\partial y_{III}/\partial \theta = (Km/g(y_{III}))(y_{II} - y_{III}) \quad (16)$$

$$\text{I.C.; } y_I = 1, y_{II} = y_{III} = 0 \quad (0 \leq x \leq 1) \text{ for } \theta = 0 \quad (17)$$

$$\text{B.C.1; } \partial y_{II}/\partial x = 0 \text{ for } x = 0, \theta > 0 \quad (18)$$

Fig. 2 Chemical equilibrium of aniline-HCl system

$$\text{B.C.2; } \partial y_{II}/\partial x = (Bi/K)\{y_I - (y_{II})_{x=1}\} \text{ for } x = 1, \theta > 0 \quad (19)$$

where

$$g(y_{III}) = dT_{III}/dC_{III} = 1 + \alpha\beta/(y_{III} + \alpha)^2 \quad (20)$$

The basic equations can be numerically solved if seven parameters ϕ , ϕ' , K , $\alpha = K_a/C_{I,0}$, $\beta = A/C_{I,0}$, $Bi = K_o R/D_e$ and $m = 3K_i R^2/D_e R_i$ are given. The values of K_a are available⁵⁾, the partition coefficient K can be experimentally determined and ϕ , ϕ' , α and β are specified by the experimental condition. The last two parameters are difficult to evaluate because data on K_o , K_i and D_e are not available. However, if m is sufficiently large, phase III is considered to be in equilibrium with phase II. The term "equilibrium" means that C_{II} is related to C_{III} as follows.

$$C_{III} = KC_{II} \quad (21)$$

Thus, in the case of $m = \infty$, Eqs. (15) and (16) are combined to give Eq. (22).

$$\frac{\partial y_{II}}{\partial \theta} = \frac{1}{1 - \phi + (\phi/K)g(y_{III})} \left(\frac{\partial^2 y_{II}}{\partial x^2} + \frac{2}{x} \frac{\partial y_{II}}{\partial x} \right) \quad (22)$$

As will be explained later, when m is sufficiently large, the y_I vs. θ relation obtained from Eqs. (8)–(10) can be closely approximated by that from Eqs. (8) and (22). In this case, the value of Bi can be estimated as follows. (1) As shown in Fig. 7, experimental data with different initial concentrations of amine are plotted as y_I vs. $\log t$ (chart 1). (2) Numerical solutions of Eqs. (8) and (22) are plotted as y_I vs. $\log \theta$ for specified values of parameters ϕ , ϕ' , K , α and β corresponding to the experimental condition with Bi as a parameter (chart 2). A typical example is shown in Fig. 5. Here it should be noted that $C_{I,0}$ is related to parameters α and β . (3) Find the value of Bi which can give the best agreement between these two relations by fitting these two charts as shown in Fig. 7. By this procedure, $t_{\theta=1}$, the real time corresponding to $\theta = 1$, can be determined. Then D_e and K_o are calculated as follows.

Fig. 3 Effect of m on extraction rate ($\phi=0.5$, $\phi'=0.133$)

Fig. 5 Effect of Bi and $C_{I,0}$ on y_I vs. θ relation (aniline, $\phi=0.5$, $\phi'=0.133$)

Fig. 4 Effect of K on extraction rate ($\phi=0.5$, $\phi'=0.133$)

Fig. 6 Computed concentration profiles in W/O emulsion drop (aniline, $m=\infty$, $\phi=0.5$, $\phi'=0.133$)

$$D_e = R^2/t_{\theta=1} \quad (23)$$

$$K_o = BiD_e/R = BiR/t_{\theta=1} \quad (24)$$

When m is not so large, the determination of Bi may be difficult because it is also difficult to estimate the value of m which includes K_i , D_e and R_i .

As θ increases, equilibrium is attained among phases I, II and III. The equilibrium concentration is calculated from Eqs. (25) and (26) which are derived from material balance, chemical and phase equilibrium equations.

$$y_{I,\infty} = y_{II,\infty} = y_{III,\infty} = (-b + \sqrt{b^2 - 4ac})/2a \quad (25)$$

$$\left. \begin{aligned} a &= 1 - \phi' + \phi\phi' + K\phi'(1-\phi) \\ b &= \phi'[\phi\beta + \alpha\{\phi + K(1-\phi)\}] - (1-\phi')(1-\alpha) \\ c &= -(1-\phi') \end{aligned} \right\} \quad (26)$$

This is the lowest attainable concentration in phase I when the extraction is carried out ideally.

It should be noted that Eqs. (5), (6), (8)–(24) can be applicable to the extraction of weak acids such as phenol, cresol and xynol in W/O/W emulsion systems containing an internal aqueous phase of NaOH solution if K_a is substituted by K_w/K_a in these equations and A is defined as the initial concentration of NaOH.

1.3 Numerical solution

The basic equations were solved numerically by

means of a finite difference method. Figure 3 shows the effect of m on the y_I vs. θ relations, which indicates that the relation approaches that for $m=\infty$ as m becomes large, and that the solution for $m=10000$ can be approximated by that for $m=\infty$. However, it should be noted that this does not necessarily mean that phase III is completely in equilibrium with phase II. Equilibrium is attained when m is much larger. As shown in Fig. 4, when K is larger, the curve for $m=10000$ is approximated by that for $m=\infty$ more closely because the ratio of diffusional resistance in W/O emulsion drops to that between phase I and W/O emulsion drops becomes smaller. The same situation is encountered when Bi is small. It was also found that when $C_{I,0}$ is high, the equilibrium between phases II and III is attained at smaller value of m . This is explained as follows. As shown in Fig. 2, the higher the amine concentration, the lower is T/C , which means that the transfer of a small amount of amine from phase II to III is sufficient to equilibrate the two phases. Figure 5 shows how the effect of $C_{I,0}$ on y_I varies depending on Bi . When Bi is small, the y_I vs. θ curve is steep and the effect of $C_{I,0}$ on the y_I vs. θ relation is small. These characteristics are used to determine Bi from the experimental data.

Typical concentration profiles in a W/O emulsion drop are shown in Fig. 6 where y_I is also shown on the right ordinate. It is clearly shown that there is a region near the peripheral part of the drop where T_{III} is high and almost constant, and this region gradually spreads toward the central part as θ increases. At the same time, T_{III} in this region decreases because amine accumulated near the periphery is transferred to the inner part and y_I is decreased during the extraction.

2. Experimental

W/O emulsions were prepared as follows. 50 cm³ of kerosine containing 5 vol % of Span 80 (Sorbitan monooleate) was added to an aqueous solution of HCl of the same volume. This solution was agitated for 15 min by a vibromixer (Kyoto Electronics, VM-02) equipped with a disc, 5 cm in diameter, which has 12 holes of 4.5 mm in diameter, and vibrates vertically at 120 cycles/s with an amplitude of 3 mm. Then the solution was sonicated by an ultrasonic homogenizer (Nihon Seiki Ltd., US-150, 150W) for 30 s. A batch-type agitated vessel made of Pyrex glass of 9 cm inner diameter and 14.5 cm height was used for the extraction experiment. A six-bladed turbine agitator 5 cm in diameter and 1 cm in width was used. To prevent the W/O emulsion phase, whose density is 0.9, from remaining at the surface as a layer, four intermediate baffles were equipped between the wall and the center of the vessel as recommended by Nagata⁸⁾. The experimental procedure was as follows. 100 ml of the W/O emulsion was added to the vessel containing 550 ml of deionized water under stirring. In about two minutes, the W/O emulsion was dispersed as drops in water. Then an aqueous amine solution was poured into the vessel so that the total volume became 750 ml. Samples were withdrawn, filtered to remove the W/O emulsion drops, and analyzed with an ultraviolet spectrophotometer (Shimadzu UV 200S). Hydrogen ion concentration was measured with a Horiba M-7E pH meter.

Partition coefficients of amines between water and kerosine were measured by shaking the two phases and analyzing the amine concentration in aqueous phase. The diameter of the droplets of the aqueous phase in W/O emulsions was measured by a microscopic method, and the size of W/O emulsion drops by a photographic method. The experimental conditions were as follows: the volume fractions ϕ , ϕ' were 0.5 and 0.1333, respectively, temperature was 298 K and the rotational speed was 188 rpm.

3. Results and Discussion

3.1 Partition coefficient and diameter of drops

The measured partition coefficients of amines are

Table 1 Summary of results

		Aniline	<i>m</i> -toluidine	<i>p</i> -toluidine
K	[—]	1.1	3.7	2.8
pK_a		4.596	4.73	5.08
$D_{II} \times 10^5$	[cm ² /s]	1.11	0.993	0.993
$D_{III} \times 10^5$	[cm ² /s]	1.01	0.905	0.905
$D_{e,exp} \times 10^5$	[cm ² /s]	1.7–2.0	1.4–1.9	1.3–1.5
E_{exp}	[—]	1.5–1.8	1.4–1.9	1.3–1.5
E by Eq. (31)	[—]	0.43	0.43	0.43
E by Eq. (32)	[—]	4.84	4.84	4.84
$K_o \times 10^3$	[cm/s]	4.3	4.4	4.7

Fig. 7 Effect of $C_{I,0}$ on extraction of aniline

shown in Table 1. Although it was anticipated that some fraction of amine might exist in the form of the dimer in kerosine, the monomer was found to be the predominant species because K was almost independent of amine concentration. Inspection of the W/O emulsion by a microscope showed that the aqueous-phase droplet was considerably uniform and the mean diameter was roughly 1 μ m. The size distribution of the W/O emulsion drops was relatively sharp and the average diameter was about 0.9 mm.

3.2 Breakdown of W/O emulsion

The breakdown means that phase III droplets leave W/O emulsion drops and enter phase I. The fraction of HCl which leaks through the membrane is calculated by the following equations.

$$f = [\text{Cl}^-]_I (1 - \phi') / ([\text{Cl}^-]_{III,0} \phi \phi') \quad (27)$$

$$[\text{Cl}^-]_I = [\text{H}^+]_I + T_I / (1 + K_a / [\text{H}^+]_I) - K_w / [\text{H}^+]_I \quad (28)$$

Equation (28) is derived from Eqs. (1)–(4). The value of f was evaluated from the measured values of $[\text{H}^+]_I$ and T_I . It was found that f was less than 0.001 at $t = 10$ minutes under all experimental conditions, indicating that the membrane was sufficiently stable.

3.3 Extraction of amines

1) Effect of initial amine concentration The effect of $C_{I,0}$ on the time-course of the extraction of aniline is shown in Fig. 7. Although there is some scatter of the data, it can be seen that when $C_{I,0}$ is high, y_I is also high. To compare the experimental data with

(a) *m*-toluidine

(b) *p*-toluidine

Fig. 8 Extraction of toluidine

Fig. 9 Effect of [HCl] on extraction rate of aniline

the computed results based on the present model, it is necessary to estimate seven parameters. Parameters except Bi and m are easy to determine. K_i , which is included in m , was estimated as follows. Because the diameter of phase III droplets is about $1\ \mu\text{m}$ and the droplets may exist in a flocculated structure, the length of diffusion from phase II to III is roughly $1\ \mu\text{m}$. If the diffusivity of amine is assumed to be $1 \times 10^{-5}\ \text{cm}^2/\text{s}$, K_i is about $0.1\ \text{cm/s}$. When the interfacial resistance due to the surface active agent R_{int} is considered, K_i

Fig. 10 Comparison between $y_{I,\infty}$ and $y_{I,10}$ (aniline)

may be less than $0.1\ \text{cm/s}$ although to what extent K_i is reduced is not clear. Even if K_i is taken as low as $0.01\ \text{cm/s}$, m is as large as 10^5 . Thus the y_I vs. θ relation can be approximated by that for $m=\infty$ under the experimental conditions studied. In Fig. 7 are shown the computed results for $m=\infty$ and $Bi=10$, which satisfactorily simulate the data. The results of the extraction of *m*- and *p*-toluidine are shown in Fig. 8, where computed results are also shown.

2) Effect of HCl concentration As shown in Fig. 9, the effect of HCl concentration can be well expressed by the present model.

3) Comparison of y_I at $t=10\ \text{min.}$ with $y_{I,\infty}$ The comparison of $y_{I,10}$, y_I at $t=10\ \text{min.}$, with $y_{I,\infty}$ calculated from Eqs. (25) and (26) is shown in Fig. 10. When $y_{I,\infty}$ is low, $y_{I,10}$ is considerably higher than $y_{I,\infty}$. On the other hand, $y_{I,10}$ is very close to $y_{I,\infty}$ when $y_{I,\infty}$ is large. The curves both for $y_{I,\infty}$ vs. [HCl] and $y_{I,\infty}$ vs. $C_{I,0}$, which are very similar to the titration curve of the weak base-strong acid system, show that $y_{I,\infty}$ changes very rapidly with respective concentration at the concentration which is given by the condition of neutralization, i.e., $(1-\phi')C_{I,0} = \phi\phi'A$.

4) Evaluation of D_e and K_o From Figs. 7–9, $t_{\theta=1}$ was calculated, and D_e and K_o were evaluated by Eqs. (23) and (24). The results are summarized in Table 1. Because the y_I vs. θ relation is considerably influenced by Bi as shown in Fig. 5, the accuracy of $t_{\theta=1}$ depends on how definitely Bi can be determined by comparing experimental and computed results. However, there

is actually some range in Bi which is thought to give good agreement between them. In addition, because D_e is calculated from Eq. (23), the error in measurement of R results in a considerable error in D_e . Thus, D_e 's in Table 1 are considered rough estimates. On the other hand, K_o is much less dependent on Bi and R . For example, when Bi is assumed to be 10, D_e and K_o are calculated to be 1.9×10^{-5} cm²/s and 0.0043 cm/s, and when Bi is 15, D_e and K_o are 1.4×10^{-5} and 0.0047, respectively, based on the experimental data shown in Fig. 7. In Table 1 are also shown the molecular diffusivities of amines estimated by the Wilke-Chang equation¹¹. The viscosity of oil phase was measured by an Ostwald viscometer and the average molecular weight was found to be 200 by means of vapor-pressure osmometry. Table 1 shows that D_{II} is nearly equal to D_{III} , and $D_{e,exp}$ is larger than D_{II} for each amine. To explain the relation between $D_{e,exp}$ and D_{II} or D_{III} , a mass transfer model was developed by modifying Russel's model¹⁰ presented for conductive heat transfer through porous media. This model is schematically shown in Fig. 11. A small cube represents a droplet of the internal aqueous phase, and a large cube an element which consists of a droplet of the internal aqueous phase and the membrane which surrounds the droplet. It is assumed that a W/O emulsion drop consists of a large number of such elements. Amine can diffuse in this element through two paths. One path is through 1 and 3 (path 1), and another is through 2 and 3 (path 2). If it is assumed that there is no concentration gradient in the direction perpendicular to the radial direction in 3, the effective diffusivity is given by

$$E = \frac{D_e}{D_{II}} = \frac{\gamma\phi^{2/3} + 1 - \phi^{2/3}}{\gamma(\phi^{2/3} - \phi) + 1 - \phi^{2/3} + \phi} \quad (29)$$

where $\gamma = D_{III}^*/D_{II}$, and D_{III}^* is the apparent diffusivity of amine through path 1 in phase III based on the concentration gradient of amine in phase II.

$$N_1 = -D_{III}^* \partial C_{III} / \partial r \quad (30)$$

Here N_1 is the flux of total amine in phase III. It should be noted that D_{III}^* is the apparent diffusivity which is evaluated by considering both the diffusion of amine in phase III in the form of RNH_2 as well as RNH_3^+ , and the interfacial resistance, R_{int} , between phases II and III. Because very few data are available on the interfacial resistance due to surface-active agent, it is very difficult to evaluate its contribution to the overall resistance. Here the discussion is made for the two extreme cases. Firstly, R_{int} due to a surface-active agent for liquid-liquid system was estimated to be about 80 s/cm⁹. If d is taken as 1 μ m, the diffusional resistance in phase III, a/D_{III} , is about 8 s/cm, which is much lower than R_{int} . In this case, D_{III}^* is remarkably decreased due to R_{int} , and γ can be

Fig. 11 Mass transfer model in W/O emulsion

approximately taken as zero. Then Eq. (29) reduces to

$$E = D_e/D_{II} = (1 - \phi^{2/3}) / (1 - \phi^{2/3} + \phi) \quad (31)$$

Table 1 indicates that E_{exp} ranges from 1.3 to 1.9, and E calculated from Eq. (31) is about one fifth-one third of E_{exp} . This discrepancy can be explained only when some bulk motion which enhances the diffusion in W/O emulsion drops is assumed.

Secondly, it was reported that addition of a surface-active agent does not influence gas absorption rate in a liquid-jet column even when liquid-phase mass transfer coefficient is as large as 0.16 cm/s⁴. This suggests that R_{int} is much lower than $1/0.16 = 6$ cm/s. Then, path 1 in Fig. 11 is not limited by R_{int} . In addition, if we consider that amine can diffuse in phase III in the form of RNH_2 as well as RNH_3^+ , and the concentration of RNH_3^+ is much higher than that of RNH_2 in region (a) of Fig. 2, the diffusional resistance in phase III may be greatly reduced. In this case, Eq. (32) is derived from Eq. (29) by putting γ infinitely large.

$$E = D_e/D_{II} = 1 / (1 - \phi^{1/3}) \quad (32)$$

As shown in Table 1, the value of E by Eq. (32) is about three times the experimentally observed values, which are between those by Eqs. (31) and (32). If γ is assumed to be 2.5, E by Eq. (29) is 1.6, which is in rough agreement with E_{exp} . However, further fundamental study on the mass transfer in emulsion systems is needed to discuss E_{exp} in detail.

As shown in Table 1, K_o is almost constant irrespective of amines studied. K_o is expressed by

$$1/K_o = 1/k_w + 1/Kk_o \quad (33)$$

k_w was estimated to be 0.0032 cm/s using the equation of Calderbank *et al.*² presented for mass transfer in liquid-liquid dispersions in which the dispersed phases are free to move under the action of gravity. k_o is roughly equal to 0.03 cm/s if the thickness of a peripheral membrane in a W/O emulsion drop is a few μ m⁷. Thus the relation $1/k_w \gg 1/Kk_o$ holds, indicating that K_o is independent of K in agreement with the experimental data.

Conclusion

The extraction of amines was carried out in WO/W/emulsion systems using a batch-type agitated vessel, and the results were discussed based on a mass transfer model which takes into account the diffusion both in and around a W/O emulsion drop. Based on the model of mass transfer in W/O emulsion systems, some explanations were made to interpret the experimentally evaluated values of D_e .

Nomenclature

A	= concentration of Cl^- in phase III	[mol/m ³]
a	= length shown in Fig. 11	[m]
a_i	= interfacial area between phase II and III per unit volume of W/O emulsion	[m ⁻¹]
a_o	= interfacial area between phase I and II per unit volume of W/O/W emulsion	[m ⁻¹]
Bi	= $K_o R/D_e$ (Biot number)	[—]
C	= concentration of amine (RNH_2)	[mol/m ³] or [ppm]
D	= molecular diffusivity	[m ² /s]
D_e	= effective diffusivity defined by Eq. (7)	[m ² /s]
D_{III}^*	= apparent diffusivity in phase III defined by Eq. (30)	[m ² /s]
d	= length shown in Fig. 11	[m]
E	= D_e/D_{II}	[—]
f	= fraction of breakdown	[—]
K	= partition coefficient	[—]
K_a	= dissociation constant	[mol/m ³]
K_i	= overall mass transfer coefficient between phase II and III	[m/s]
K_o	= overall mass transfer coefficient between phase I and W/O emulsion drop	[m/s]
K_w	= product of concentrations of H^+ and OH^-	[mol ² /m ⁶]
k_o	= mass transfer coefficient of peripheral membrane of W/O emulsion	[m/s]
k_w	= mass transfer coefficient of phase I around W/O emulsion drop	[m/s]
m	= $3K_i R^2/R_i D_e$	[—]
N	= molar flux	[mol/m ² ·s]
P	= concentration of RNH_3^+	[mol/m ³]
R	= radius of W/O emulsion drop	[m]

R_i	= radius of phase III droplet	[m]
R_{int}	= interfacial mass transfer resistance	[s/m]
r	= radial distance	[m]
T	= total concentration of amine ($= C + P$)	[mol/m ³]
t	= time	[s]
x	= r/R	[—]
y_I	= $C_I/C_{I,0}$	[—]
y_{II}	= $C_{II}/KC_{I,0}$	[—]
y_{III}	= $C_{III}/C_{I,0}$	[—]
α	= $K_a/C_{I,0}$	[—]
β	= $A/C_{I,0}$	[—]
γ	= D_{III}^*/D_{II}	[—]
ϕ	= volume fraction of phase III in W/O emulsion	[—]
ϕ'	= volume fraction of W/O emulsion in W/O/W emulsion	[—]
θ	= $D_e t/R^2$	[—]
<Subscripts>		
0	= initial value	
I	= phase I (external aqueous phase)	
II	= phase II (organic membrane phase)	
III	= phase III (internal aqueous phase)	

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