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Su Jin Kim[a]; Sang Chai Kim[b]; Junjiro Kawasaki[c]
[a] DEPARTMENT OF INDUSTRIAL CHEMISTRY, CHUNGNAM SANUP UNIVERSITY, HONG SEONG, SOUTH KOREA [b] DEPARTMENT OF ENVIRONMENTAL ENGINEERING AND EDUCATION, MOKPO NATIONAL UNIVERSITY, MUAN, SOUTH KOREA [c] DEPARTMENT OF CHEMICAL ENGINEERING, TOKYO INSTITUTE OF TECHNOLOGY, TOKYO, JAPAN

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Separation of Hydrocarbons by Liquid Surfactant Membrane with a Batch Stirred Vessel

SU JIN KIM*
DEPARTMENT OF INDUSTRIAL CHEMISTRY
CHUNGNAM SANUP UNIVERSITY
HONG SEONG 350-800, SOUTH KOREA

SANG CHAI KIM
DEPARTMENT OF ENVIRONMENTAL ENGINEERING AND EDUCATION
MOKPO NATIONAL UNIVERSITY
MUAN 534-729, SOUTH KOREA

JUNJIRO KAWASAKI
DEPARTMENT OF CHEMICAL ENGINEERING
TOKYO INSTITUTE OF TECHNOLOGY
TOKYO 152, JAPAN

ABSTRACT

Extraction experiments on liquid membrane permeation were conducted in a batch stirred vessel to separate aromatics from an aromatics–nonaromatics binary mixture as an inner oil phase in the emulsion. The investigations were conducted under various material systems (hydrocarbon feeds, aqueous membrane phases) and the mass transfer coefficient in the emulsion (dispersed phase) was measured. Independently of the system of hydrocarbon feed and aqueous membrane solution, the mass transfer coefficient of the dispersed phase could be correlated with the dimensionless stirring time and the solubility of the aqueous membrane phase. The batchwise results agree fairly well with previous results reported for continuous operation.

INTRODUCTION

New separation technologies emerging in the petroleum refinery industry are meant to utilize the available aromatic components in light cycle oil

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* To whom correspondence should be addressed.

and to lower the concentration of toxic aromatic components (especially benzene) in automobile gasoline. The mutual separation of aromatic groups has been carried out by solvent extraction (e.g., the sulfolane method) but a new separation method which is more effective and less energetic would be desirable. A promising liquid membrane separation method was suggested by N. N. Li (1–3) in 1968. However, liquid membrane separation has not been applied to hydrocarbon separation, so it seemed meaningful to investigate the practical use of a liquid membrane separation for hydrocarbon separation. It has been reported that the original experimental apparatus involved a stirred vessel, a spray column (4), a packed column (5, 6), and an Oldshue–Rushton column (7). Most reports involved a batch stirred vessel. There were a few reports that the mass transfer coefficient for liquid membrane separation was systematically studied with a stirred vessel.

In this work, O/W/O emulsion liquid membrane separation has been carried out to separate aromatics from an aromatics–nonaromatics binary mixture with a batch stirred vessel, and the correlation for mass transfer coefficients in the emulsion (dispersed phase) was examined. A Sauter mean diameter O/W droplet, dispersed in an O/W/O-type emulsion, was measured, and then permeation experiments were carried out using a mixture of toluene and heptane, a mixture of benzene and hexane, and liquid membranes (saponin aqueous solution, saponin aqueous solution + sulfolane). Subsequently, mass transfer coefficients of the dispersed phase were measured. Also, the mass transfer coefficient of the dispersed phase for batch operation was compared with that for continuous operation.

EXPERIMENTAL

Apparatus and Method

Emulsification

A schematic diagram of the emulsion unit is shown in Fig. 1. A hydrocarbon feed (an inner oil phase) and an aqueous membrane solution were charged to a batch stirred vessel and emulsified at 10 s^{-1} of the stirred speed for 10 minutes. Thereafter they were emulsified while being recycled and circulated by a high speed homogenizer and stirrer for 10 minutes. Additional particles of O/W emulsion could be formed.

Permeation Experiment

A batch stirred vessel of glass material (8 cm I.D. and 8 cm high) was used for the emulsion and solvent. An impeller of the six flat blade turbine type was placed on the middle axis. Four baffles were inserted.

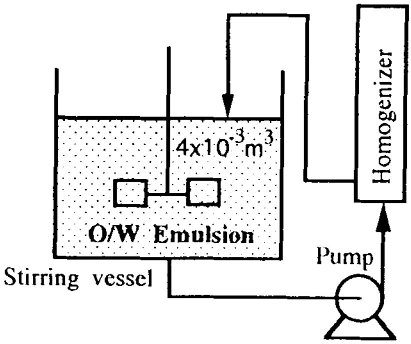

FIG. 1 Schematic diagram of emulsifier.

Solvent was added to the vessel and its temperature was increased to 30°C. Subsequently, the emulsion, also at 30°C, was added and stirring began. After a contact run, O/W/O emulsion was allowed to settle and the volumes of the raffinate phase (emulsion phase) and the extract phase (solvent phase) were measured. The extract phase was analyzed and its composition was determined. The raffinate phase was demulsified by adding acetone. At this time the composition of the oil phase was different from that of the raffinate phase because a part of the hydrocarbon in the raffinate phase had moved to the aqueous phase. Therefore, the oil phase aqueous phase ratio was sufficiently increased by adding hydrocarbons which were not in the material system (feed, solvent) so that content of the hydrocarbons in the aqueous phase might be ignored. This oil phase was separated, and then washed by water to remove acetone. The oil phase containing the resultant raffinate phase was analyzed, and the composition of raffinate phase was determined. The oil phase whose composition was known was emulsified, the above procedures were executed, and then the composition of the raffinate phase could be determined with confidence. Analysis of the oil phase and determination of the concentration of water content in the membrane solution were carried out with a gas chromatograph and calfischer moisturemeter (Kyoto Electronic Industrial Co., MKC-3P).

Measurement of an Emulsion Diameter (8)

Fluid paraffin dissolved with Span 85 was charged into a pipette, and the O/W/O emulsion which formed by contact between an O/W emulsion and a solvent for 80 seconds was introduced to the fluid paraffin mixture in the pipette. A part of it was collected and photographed with an optical microscope. About 300 O/W emulsions dispersed in the O/W/O emulsion in this photograph were measured, and a Sauter mean diameter (d_{32}) was determined.

Systems and Conditions

The material systems and conditions used are shown in Table 1. Two mixtures of aromatics and nonaromatics were used as the hydrocarbon feed: toluene (T) + heptane (Hp) (Feed I) and benzene (B) + hexane (Hx) (Feed II). Saponin aqueous solution (Membrane I) and saponin aqueous solution with sulfolane (Membrane II) were used as liquid membranes. A liquid membrane technology had a problem that the permeation of hydrocarbon was very slow. However, a polar material can be added to a liquid membrane to control its permeation rate or selectivity (9, 10). As a polar solvent was added to a liquid membrane, the solubility of the aromatics increased, and a faster permeation rate and a higher yield could be achieved. The Sauter mean diameter of an emulsion could be measured by maintaining a constant contact time and material system.

RESULTS AND DISCUSSION

Sauter Mean Diameter of O/W Emulsion (d_{32})

d_{32}, which was measured at t = 80 seconds, was assumed to be the value when about 50% of the aromatics in the hydrocarbon feed had been

TABLE 1
Systems and Experimental Conditions

Systems		
Feed	I	Toluene + heptane, $x_{T,0}$ = 0.5
	II	Benzene + hexane, $x_{B,0}$ = 0.5
Membrane	I	Water + saponin (for Feed I, II), C_S = 0.002
	II	Water + saponin + sulfolane (for Feed II), C_S = 0.002, C_{SUL} = 0.24
Solvent	I	Hexane for Feed I
	II	2,2,4-Trimethylpentane for Feed II

Conditions	
ϕ_d (—)	0.1
ϕ_O (—)	0.5
t (s)	0–300
N (s^{-1})	8.33–18.5
T (°C)	30

transferred into the continuous phase. Figure 2 shows the relationship between d_{32} and the Weber number We [$= (N^2 d^3 \rho_d)/\sigma$)]. The calculated values and the experimental values of Egashira et al. (11) were used for the density of the dispersed phase ρ_d [$= \rho_O \phi_O + \rho_W (1 - \phi_O)$] and the interfacial tension between the dispersed phase and the continuous phase respectively. Results from Calderbank's empirical equation (12) are also plotted in Fig. 2. Our experimental data produced a good straight line, and a simplified empirical equation could be derived:

$$d_{32}/d = 0.153\mathrm{We}^{-0.6} \qquad 2 \times 10^2 < \mathrm{We} < 2 \times 10^3 \tag{1}$$

The results of our work are in close agreement with those of Calderbank.

The specific surface area (a) between an emulsion and the extraction phase in a batch stirred vessel was calculated by using Eq. (1) as follows:

$$a = 39.2\phi_d/(d\mathrm{We}^{-0.6}) \tag{2}$$

The thickness of a liquid membrane (δ) must be introduced to discuss mass transfer through a liquid membrane. However, it is very difficult to define the thickness of aqueous membrane phase because a large number of minute oil droplets are dispersed within the liquid membrane phase. Therefore, in this work a geometrically simplified dispersed-emulsion globule as shown in Fig. 3 is suggested. δ can be defined by using d_{32} and the volume fraction of the inner oil phase in the dispersed phase (ϕ_O). This defined δ can be expressed by using Eq. (1) as follows:

$$\delta = 0.0765d(1 - \phi_O^{1/3})\mathrm{We}^{-0.6} \tag{3}$$

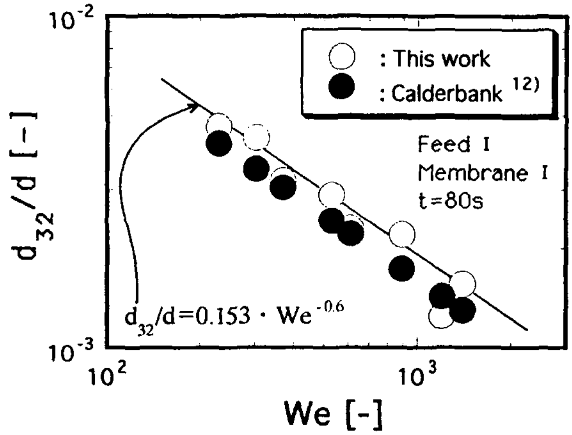

FIG. 2 Plot of d_{32} vs We.

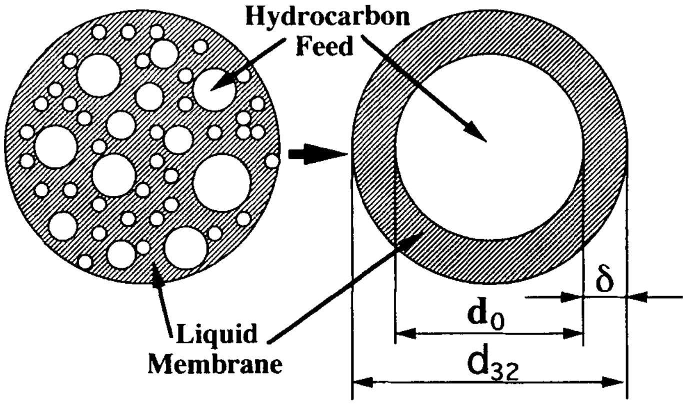

FIG. 3 Simplified model of O/W emulsion.

$\phi_O = 0.375$, which was obtained at $t = 80$ seconds, was used for calculating δ. The value of δ calculated from Eq. (3) was 2.74×10^{-5} m. To investigate the reasonableness of Eq. (3) our value of δ was compared with the value of δ of Goswami et al. (13). Our value, $\delta = 2.74 \times 10^{-5}$ m, is 10 times larger than Goswami's, $\delta = (1.57\text{–}5.0) \times 10^{-6}$ m. As δ defined by Goswami is inversely proportional to d_{32}, the difference between the value of δ in this work and the value of δ of Goswami resulted from difference between d_{32} ($= 1.97 \times 10^{-4}$ m) measured by this work and d_{32} ($= 2.0 \times 10^{-3}$ m) assumed by Goswami. If the $d_{32} = 1.97 \times 10^{-4}$ m of this work is used instead of the $d_{32} = 2.0 \times 10^{-3}$ m of Goswami, the value of δ of Goswami becomes $(1.57\text{–}5.0) \times 10^{-5}$ m. Subsequently, the value of δ of this work nearly agrees with the value of δ of Goswami. $\delta = 2.74 \times 10^{-5}$ m and $a = 3.05 \times 10^3$ m^{-1} calculated from Feed I and Membrane I at $t = 80$ seconds were used for calculating the mass transfer coefficients irrespective of the material systems studied.

Permeation

Yield

Yield of component i, Y_i, defined by Eq. (4), was calculated for each component in order to investigate the permeation rate.

$$Y_i = (Ey_i)/(R_0 x_{i,0}) \tag{4}$$

Figure 4(a) shows the time course curves of yield for aromatic and paraffin hydrocarbons with each material system. The permeation rate of

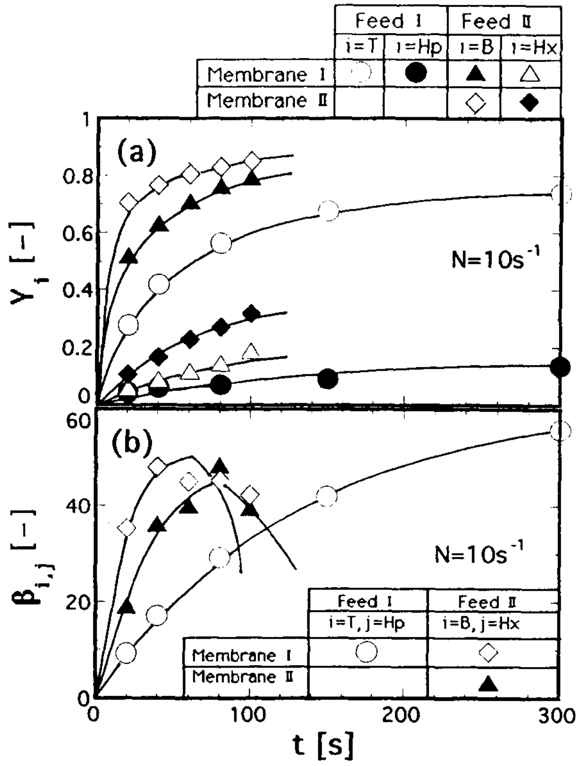

FIG. 4 Time courses (a) of yield and (b) of selectivity.

hydrocarbon through liquid membranes depends on the diffusivity and, in particular, on the solubility of a hydrocarbon in liquid membranes (14). Thus, in each aromatic or paraffinic hydrocarbon, the hydrocarbon with a smaller carbon number due to its higher solubility in membrane solution showed a larger permeation rate than that with a larger carbon number. In addition, when the yields were compared between hydrocarbons with the same carbon number, the permeation rates of aromatics were higher than those of paraffins. The addition of a slight amount of sulfolane to the membrane solution enhanced the permeation rates of the permeates. In particular, benzene permeated so rapidly in the case with sulfolane that yields of 70% could be attained within as short a contact time period as 20 seconds. The permeation rates of benzene with and without sulfolane were compared from the slopes of yield curves at $t = 0$. The slope of benzene with sulfolane was about twice as great as that without sulfolane.

Selectivity

The selectivity of an aromatic hydrocarbon i (i = B, T) in reference to a paraffin hydrocarbon j (j = Hx, Hp) is defined as

$$\beta_{i,j} = (y_i/x_i)/(y_j/x_j) \tag{5}$$

Figure 4(b) shows the time course curves of the selectivities with each material system. The selectivity of toluene (i = T) in reference to heptane (j = Hp), $\beta_{T,Hp}$, increased with increasing stirring time. However, the selectivity of benzene (i = B) in reference to hexane (j = Hx), $\beta_{B,Hx}$, had a maximum (14–16), and the maximum $\beta_{B,Hx}$ with sulfolane was higher than that without sulfolane. This tendency indicated that compositions could change with stirring time. That is, $\beta_{B,Hx}$ as defined by Eq. (5), which could be expressed as $(y_B/y_{Hx})\cdot(x_{Hx}/x_B)$, must increase when the permeation rate of benzene is higher than that of hexane because in such a case both (y_B/y_{Hx}) and (x_{Hx}/x_B) increase with stirring time. $\beta_{B,Hx}$ must decrease toward a final value of 1 after a long stirring time. Subsequently, a time course curve of $\beta_{B,Hx}$ must have a maximum.

Mass Transfer Coefficient for Dispersed Phase

The total rate of mass transfer for the permeable component consists of the rate of permeation, the rate of membrane breakage, and the rate of mechanical entrainment. Kawasaki et al. (8) reported that the mass transfer rate found after considering membrane permeation, membrane breakage, and mechanical entrainment was nearly equal to that found after considering membrane permeation alone within the stirring time used in this work. Therefore, the effects of membrane breakage and mechanical entrainment for mass transfer for the permeable component are neglected in this work. Assuming that mass transfer of each component occurred only by membrane permeation, the transfer rate of component i could be expressed as

$$d(Ey_i)/dt = P_i a V(x_i - y_i) \tag{6}$$

The emulsion and solvent were in the dispersed and continuous phases, respectively, over the entire experimental conditions of this work. The overall mass transfer resistance of an ideal one-dimensional plate liquid membrane, $1/(P_i a)$, can be derived as Eq. (7) from the mass transfer resistances of the inner oil phase, the liquid membrane, and the continuous phase [$1/(k_{I,i}a)$, $1/(p_{W,i}H_i a)$, and $1/(k_{c,i}a)$, respectively] (14).

$$1/(P_i a) = 1/(k_{I,i}a) + 1/(p_{W,i}H_i a) + 1/(k_{c,i}a) \tag{7}$$

In the case of an emulsion liquid membrane, it seems that the first term and the second term on the right-hand side of Eq. (7) (which represent an emulsion structure and mass transfer characteristics) (17) are dependent on each other. Therefore, if the mass transfer resistance of the dispersed phase, $1/(k_{d,i}a)$, was the sum of the first term and the second term on the right-hand side of Eq. (7), it could be expressed as (6)

$$1/(P_i a) = 1/(k_{d,i}a) + 1/(k_{c,i}a) \tag{8}$$

The mass transfer resistance might depend greatly on the dispersed phase because the distribution coefficient (solubility, H_i) of component i within a liquid membrane in the second term on the right-hand side of Eq. (8) was very small within the whole material system used for this experiment. Subsequently, Eq. (8) could be rewritten as

$$P_i = k_{d,i} \tag{9}$$

$k_{d,i}$ can be calculated by substituting Eq. (9) into Eq. (6). It can also be

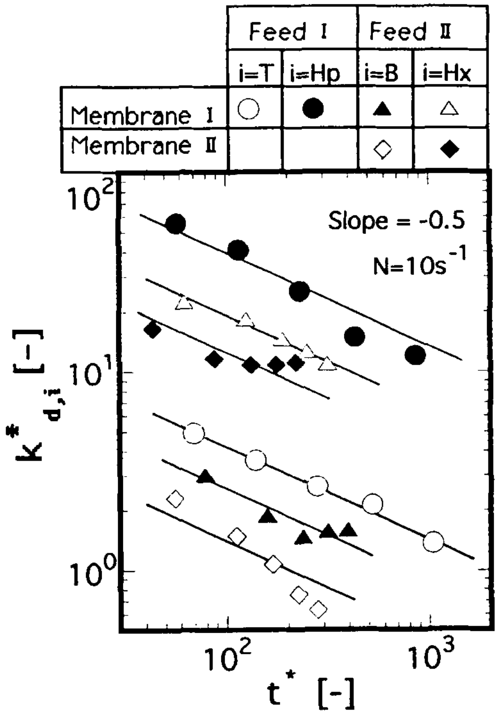

FIG. 5 Plot of $k^*_{d,i}$ vs t^*.

calculated from the slopes at each stirring time of time course curves for the permeated amount of hydrocarbon component i.

Figure 5 showed the relationship between $k^*_{d,i}$ [$= (k_{d,i}\delta)/\rho_W D_i H_i)$] and t^* [$= (tD_i)/\delta^2$], where $k^*_{d,i}$ is the ratio of $k_{d,i}$ of a batch stirred vessel to $k_{d,i}$ of an ideal one-dimensional plate liquid membrane, and t^* is a dimensionless stirring time. The diffusivity of component i, D_i, within a liquid membrane was calculated from the Wilke–Chang equation (18). McAuliffe's experimental values (19) were used for distribution coefficients of Membrane I, and the experimental values of this work were used for those of Membrane II. $k^*_{d,i}$ was proportional to $t^{*-0.5}$ irrespective of the material systems used. The reasons for this result are not yet clear, although our results agree with film penetration theory. Clarification of the reasons for the results will require further study.

Figure 6 showed the relationship between $k^*_{d,i}/t^{*-0.5}$ and H_i. The results of any material system used fall within ±30% and are on the same straight line whose slope is -0.5. This tendency might be attributed to the composite factors; the characteristic concentration distribution of bulk separation which was formed within the emulsion [16], additions in a membrane

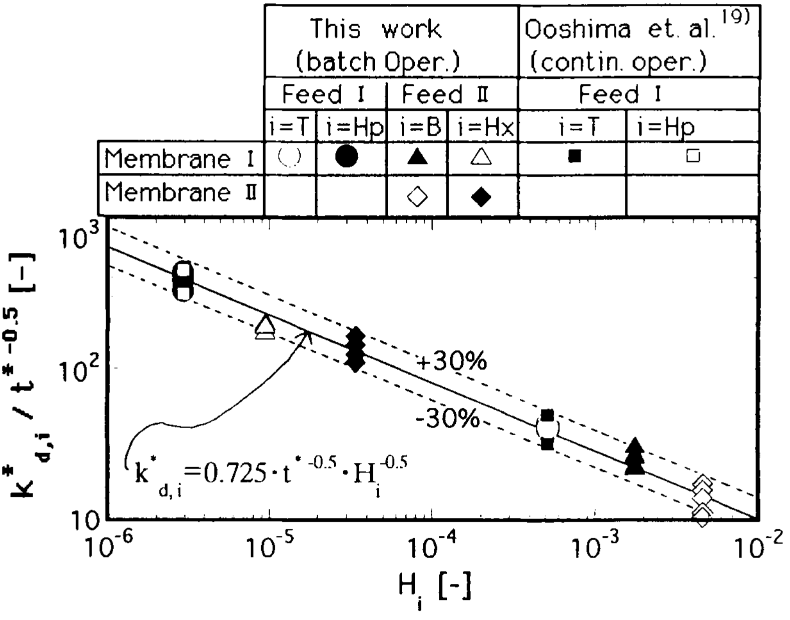

FIG. 6 Plot of $k^*_{d,i}/t^{*-0.5}$ vs H_i.

solution of surfactant and permeation promoter, the solubility due to the coexistence of various hydrocarbon components, membrane breakage and mechanical entrainment, etc. Figure 6 also shows the results Ooshima et al. (20) obtained in continuous operation using the same size of stirred vessel and material system (Feed I, Membrane I) as the batch operation in this work. Ooshima et al.'s $k^*_{d,i}$ could be calculated by using the corresponding mean residence time of continuous operation to a stirring time of batch operation. The result of this work is in good agreement with that of continuous operation. From the above results, the simplified correlation equation for the dispersed phase could be obtained.

$$\begin{gathered} k^*_{d,i} = 0.725 t^{*-0.5} H_i^{-0.5} \\ 2.0 \times 10 < t^* < 1.0 \times 10^3 \\ 2.5 \times 10^{-6} < H_i < 5.0 \times 10^{-3} \end{gathered} \tag{10}$$

When a stirred vessel was employed as a contacting unit, $k_{d,i}$ could be estimated from Eq. (10). Therefore, the purity of material separated by countercurrent multistage on a practical scale and the energy required for separation could be forecast.

CONCLUSION

(1) The Sauter mean diameter of an O/W emulsion dispersed in an O/W/O emulsion could be expressed as a Weber number. The results of this work agree with other reported results.

(2) Independent of material systems (hydrocarbon feeds, aqueous membrane solutions), the mass transfer coefficient in the emulsion could be correlated with dimensionless stirring time and solubility of the membrane phase. The results of batch operation in this work could be applied to continuous operation.

NOMENCLATURE

a	specific interfacial area between dispersed phase and continuous phase (m^{-1})
C_S	mass fraction of saponin in aqueous membrane phase (—)
C_{SUL}	mass fraction of sulfolane in aqueous membrane phase (—)
D_i	diffusivity of component i in aqueous membrane phase ($m^2 \cdot s^{-1}$)
d	impeller diameter (m)
d_O	diameter of inner oil droplet in dispersed phase (m)
d_{32}	Sauter mean diameter of dispersed phase (m)
E	mass of continuous phase (kg)

H_i	distribution coefficient of component i in aqueous membrane phase (—)
$k_{c,i}$	continuous phase mass transfer coefficient of component i ($kg \cdot s^{-1} \cdot m^{-2}$)
$k_{d,i}$	dispersed phase mass transfer coefficient of component i ($kg \cdot s^{-1} \cdot m^{-2}$)
$k^*_{d,i}$	dimensionless dispersed phase mass transfer coefficient of component i $[(= (k_{d,i} \cdot \delta)/(\rho_W \cdot D_i \cdot H_i)]$ (—)
$k_{I,i}$	mass transfer coefficient of component i in inner oil ($kg \cdot s^{-1} \cdot m^{-2}$)
N	stirring speed (s^{-1})
P_i	overall permeability of component i ($kg \cdot s^{-1} \cdot m^{-2}$)
$p_{W,i}$	permeability of component i in aqueous membrane phase ($kg \cdot s^{-1} \cdot m^{-2}$)
R	mass of dispersed phase (kg)
T	operating temperature (°C)
t	stirring time (s)
t^*	dimensionless stirring time $[= (tD_i)/\delta^2)]$ (—)
V	volume of total liquid (m^3)
We	Weber number $[= (N^2 d^3 \rho_d)/\sigma]$ (—)
x_i	mass fraction of component i in dispersed phase (—)
Y_i	yield defined by Eq. (4) (—)
y_i	mass fraction of component i in continuous phase (—)

Greek

δ	thickness of aqueous membrane phase (m)
ϕ_d	volume fraction of dispersed phase (—)
ϕ_O	volume fraction of inner oil phase in dispersed phase (—)
ρ_d	density of dispersed phase $[= \rho_O \phi_O + \rho_W(1 - \phi_O)]$ ($kg \cdot m^{-3}$)
ρ_W	density of aqueous membrane phase ($kg \cdot m^{-3}$)
σ	interfacial tension between dispersed phase and continuous phase ($kg \cdot s^{-2}$)

Subscript

B	benzene
c	continuous phase
d	dispersed phase
Hp	Heptane
Hx	Hexane
i	component i
j	component j
O	inner oil phase

S	saponin
SUL	sulfolane
T	toluene
W	aqueous membrane phase
0	at initial ($t = 0$)

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