		terminated	[s]
t_s	=	stirring time	[s]
V_s	=	sedimentation velocity of floc	[m·s^{-1}]
V_{sm}	=	sedimentation velocity of the largest floc	[m·s^{-1}]
W	=	moisture content of cake based on dry solid	[wt%]
W_i	=	initial moisture content of cake	[wt%]
ρ_e	=	effective density of floc	[g·m^{-3}]
μ	=	viscosity of medium	[Pa·s]

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DEVELOPMENT OF NEW SURFACTANT FOR LIQUID SURFACTANT MEMBRANE PROCESS

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Key Words: Membrane Separation, Liquid Membrane, Surfactant, Extraction, Emulsion, Interfacial Tension

To obtain more stable W/O emulsion for liquid surfactant membrane technique, a series of glutamic acid dialkyl esters and dialkyl type quaternary ammonium salts as new surfactants in place of Span 80 and polyamine were synthesized.

The adsorption equilibria between aqueous solution and organic solution containing the synthesized surfactants were elucidated and the stability of liquid surfactant membrane made of these surfactants was examined in a stirred tank.

A series of synthesized surfactants having two long alkyl chains in hydrophobic site gave more stable emulsion at a lower concentration compared with Span 80 and polyamine. Among them, glutamic acid dioleyl ester formed the most stable emulsion.

Introduction

The use of W/O/W multi-phase emulsion system has been a matter of great concern in various fields such as separation of metallic ions[9,15,20,22] and hydrocarbon,[7] immobilization of enzymes[21] and prolongation of drug release.[19]

In particular, the application of W/O/W emulsion system to the metal recovery process is an attractive approach to separation.[11,18,25] To develop and design the liquid surfactant membrane (henceforth LSM) process, it is very important to elucidate the effect of surfactant on the behavior of the emulsion, that is, the swelling and breakup of W/O emulsion droplets and the permeation rates of metallic ions through LSM.

In most work reported on metal extraction with LSM, commercial surfactants, e.g. Span 80 and polyamine, were used to stabilize LSM. No study on the effect of surfactant on LSM has been carried out so far.

The purpose of this work is to develop a new surfactant for LSM process because the commercial surfactant acts as carrier of water and/or solutes (e.g. acid and metal) in the internal and feed solu-

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tions.[3,4,6,17]

Recently, it was reported that the stability of W/O emulsion is remarkably enhanced as the surfactant molecules form the liquid crystal or lamella structure at W/O interface.[23,26]

From this viewpoint, and with the aim of improving the orientation of surfactant molecules at W/O interface, compounds having two long alkyl chains, that is, a series of derivatives of glutamic acid dialkyl esters (abbreviated as 2R-GE) and dialkyl-type quaternary ammonium salts (abbreviated as 2R-QA) were synthesized in this study and the stability of LSM made of the surfactant was examined in a stirred tank.

1. Experimental

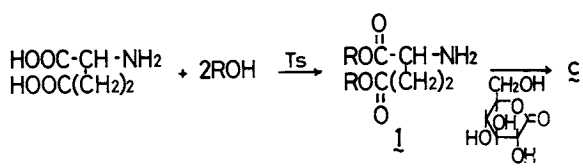
1.1 Reagents

Structures of the surfactants used are shown in **Fig. 1**.

a) Span 80 (Lot No. G56487M) purchased from Kishida Chemical Co. was used without further purification. Apparent molecular weight of Span 80 in toluene measured by vapor-phase osmometry was 604.6.

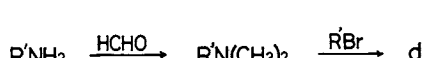
b) Polyamine (ECA 4360J) was purified by washing with acidic aqueous solution and successively alkaline aqueous solution. Apparent molecular weight was 758.2.

c) A series of derivatives of glutamic acid dialkyl esters were synthesized according to the following scheme.



The mixture of L-glutamic acid, higher alcohol and *p*-toluenesulfonic acid in toluene solution was refluxed for four hours. After that, toluene was removed under reduced pressure and the reaction mixture was dissolved in chloroform to be washed with 5% sodium carbonate aqueous solution and successively deionized water. After chloroform was removed under reduced pressure, a small quantity of hydrochloric acid was added to the solution to form the hydrochloric acid salt. The solid salt was recrystallized from acetone. The mixture of this salt, glucone-δ-lactone and triethylamine in ethanol solution was refluxed for two hours. After the solvent was removed under reduced pressure, the product (c) was recrystallized twice from acetone.

d) A series of dialkyl-type quaternary ammonium salts were synthesized according to the following scheme.[14]



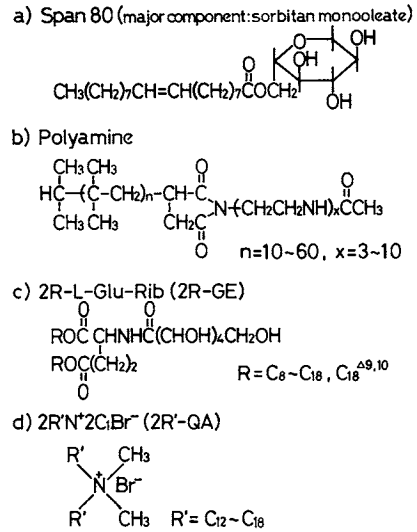


Fig. 1. Molecular structure of surfactants.

Tertiary amine was synthesized from alkylamine, formaldehyde and formic acid and was purified by distillation at reduced pressure. The final product (d) was prepared by reaction of tertiary amine with alkylbromide and recrystallized twice from ethyl acetate.

All surfactants synthesized here were identified by IR, NMR and elementary analysis.

The other inorganic and organic chemicals were commercial GR.

1.2 Measurement of interfacial tension

An organic solution was prepared by dissolving the surfactant in toluene. Interfacial tension between the organic solution and deionized water was measured at 303 K by the pendant drop method to examine the interfacial adsorption equilibrium of each surfactant. The specific gravity of both solutions was measured by pycnometer.

1.3 Stability of liquid surfactant membrane

The experimental apparatus used is a batch-type stirred glass cell with a 10 cm inner diameter and a 15 cm depth. The vessel is fitted with four stainless steel baffles, each of which is 1 cm in width and 15 cm in length. Stirring was carried out using a turbine impeller with a 5.3 cm diameter, having six flat blades connected with a speed controller.

The experimental conditions are listed in **Table 1**. Internal aqueous solution was prepared by dissolving nickel nitrate in deionized water. Organic solution was prepared by dissolving the surfactant in toluene. A W/O emulsion was made from equal volumes of the two immiscible solutions mentioned above by stirring at about 1000 rpm and under ultrasonic irradiation with frequency of 22 kHz and output of 600 W for 300 s in a large test tube. A measured volume of this emulsion was then added to the third phase in the vessel, which was the feed aqueous solution contain-

Table 1. Experimental conditions

Volume of feed aqueous solution (external aqueous phase)	$V_{w,e}=7\times10^{-4}$ m^3
Volume of internal aqueous solution	$V_{w,i}=5\times10^{-5}$ m^3
Volume of organic solution in W/O emulsion phase	$V_{org}=5\times10^{-5}$ m^3
Breakup tracer and its concentration in internal aqueous solution	$Ni(NO_3)_2$ $C_{Ni}=5$ mol/m^3
Occlusion tracer and its concentration in feed aqueous solution	$Mn(NO_3)_2$ $C_{Mn}=5$ mol/m^3
Stirring speed	$n_s=3.3$ s^{-1}
Experimental temperature	$T=303$ K

ing manganese, and was stirred at 200 rpm. The vessel was situated in a bath through which water maintained at 303 K was circulated. Samples of about 3–4 cm^3 were taken at intervals. After the emulsion phase was separated from the feed solution, dioxane was added to the emulsion phase until the emulsion phase became homogeneous. The volume ratio of water to toluene in the emulsion phase was determined by gas chromatography. Concentrations of nickel in the feed solution caused by breakup of LSM and of manganese in the emulsion phase caused by occlusion of W/O emulsion were determined by atomic absorption spectrochemical analysis.

The mean size of internal aqueous droplet was measured by a centrifugal automatic particle analyzer (HORIBA, CAPA-500). The experimental procedure was the same as that described in the previous papers.[13,17]

When Cu(II) alone was used as breakup tracer, the real degree of breakup was not revealed due to interaction between Cu(II) and the surfactants, Span 80 or polyamine. So Ni(II) and Cu(II) were dissolved in internal aqueous solution and the concentration of Ni(II) was measured to estimate the breakup exactly. The validity of this method was investigated in detail by preliminary experiments.

2. Result and Discussion

2.1 Measurement of interfacial tension

The relation between interfacial tension and concentrations of five typical surfactants is shown in **Fig. 2**. As is evident from Fig. 2, it was proved that the synthesized surfactant having two long alkyl chains made the interfacial tension low at a lower concentration compared with commercial surfactants, e.g. Span 80 and polyamine.

The adsorption equilibrium of surfactant is expressed as follows:

$$Sf_{org} \underset{}{\overset{K_s}{\rightleftharpoons}} Sf_{ad} \qquad (1)$$

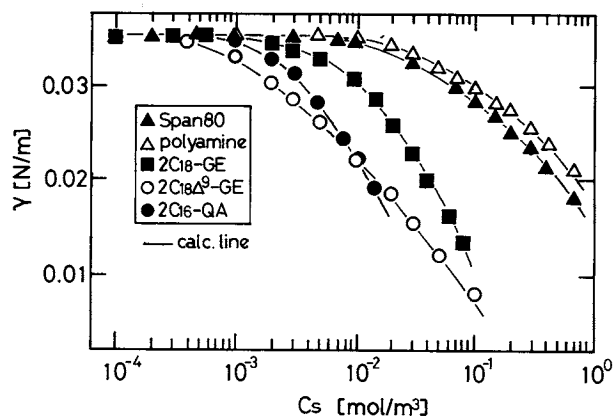


Fig. 2. Interfacial tension between aqueous and toluene-containing surfactants.

where K_s is the adsorption equilibrium constant and the subscript ad denotes adsorption state at interface. The relation between interfacial tension and the amount of surfactants adsorbed at the interface is expressed by Gibbs' adsorption equation (Eq. (2)). Assuming a Langmuir adsorption isotherm (Eq. (3)) to express the relation between the amount of surfactants adsorbed and C_s, the relation between interfacial tension and C_s is derived as Eq. (4).[10,12]

$$-d\gamma=\frac{RT}{S_{sf}}\frac{K_s}{(1+K_sC_s)}dC_s \qquad (2)$$

$$K_s=\frac{\Theta_s}{C_s(1-\Theta_s)} \qquad (3)$$

$$\gamma=\gamma_0-\frac{RT}{S_{sf}}\ln(1+K_sC_s) \qquad (4)$$

where γ_0 is the interfacial tension between toluene and water (in this study, $\gamma_0=0.035$ N/m) and S_{sf} is the interfacial area occupied by unit mole of the surfactant.

The values of K_s and S_{sf} are obtained from the experimental results of interfacial tension and Eq. (4) by nonlinear regression using a modified Marquardt method.[27]

The results are listed in **Table 2**. As shown in Table 2, the K_s value of glutamic acid dioleyl ester is very large compared with those of Span 80, polyamine and other synthesized surfactants.

The solid curves in Fig. 2 were calculated by Eq. (4) using the constants in Table 2.

2.2 The stability of liquid surfactant membrane

The behavior of emulsion droplets is very complicated and the properties of the emulsion are considered to be much affected by surfactants' characteristics. Therefore, in this study, the effect of surfactant on the stability of a liquid membrane was investigated in a system without extraction.

To estimate the stability of the liquid surfactant membrane, the degree of breakup, ε, is defined by Eq.

Table 2. Adsorption equilibrium constant and interfacial area occupied by unit mole of each surfactant

Surfactant	K_s [m³/mol]	S_{sf} [m²/mol] (Å²/molecule)
Span 80	18.2	3.84×10^5 (64.0)
Polyamine	1.5	1.35×10^6 (225)
$2C_8$-GE	32.4	1.12×10^5 (18.6)
$2C_{10}$-GE	31.7	1.19×10^5 (19.9)
$2C_{12}$-GE	18.9	1.67×10^5 (27.8)
$2C_{14}$-GE	19.9	1.70×10^5 (28.4)
$2C_{16}$-GE	19.7	1.84×10^5 (30.7)
$2C_{18}$-GE	58.7	1.93×10^5 (32.2)
$2C_{18}\Delta^9$-GE	583	3.87×10^5 (64.5)
$2C_{12}$-QA	3.0	8.50×10^4 (14.2)
$2C_{14}$-QA	19.7	9.40×10^4 (15.6)
$2C_{16}$-QA	48.1	1.01×10^5 (16.8)
$2C_{18}$-QA	60.4	1.21×10^5 (20.2)

(5).

$$\varepsilon=(V_{w,e}C_{Ni,e})/(V^0_{w,i}C^0_{Ni,i}) \qquad (5)^*$$

Assuming that the rate of breakup of LSM is proportional to $(1-\varepsilon)$, the rate is expressed as follows:[2)]

$$\frac{d\varepsilon}{dt}=k_b(1-\varepsilon) \qquad (6)$$

When Eq. (6) is integrated under the initial condition ($t=0$, $\varepsilon=0$), Eq (7) is derived.

$$\ln(1-\varepsilon)=-k_bt \qquad (7)$$

k_b in Eq. (7) is defined as the breakup rate constant. Experimental results were arranged by Eq. (7) and typical examples are shown in **Fig. 3**.

As is evident from Fig. 3, a good linear relationship between t and $\ln(1-\varepsilon)$ was obtained in all experiments. Thereafter, the breakup rate constant, k_b, defined by Eq. (7), was used concerning the stability of LSM.

The relations between the breakup rate constants, k_b, and concentrations, C_s, of Span 80 and polyamine are shown in **Fig. 4**, where experimentally determined critical surfactant concentrations, C_{sr}, are also shown. For all surfactants the emulsions attained a stable region where the breakup rate was kept constant above a critical surfactant concentration. The breakup rate constant rapidly increases below that concentration and the emulsion becomes very unstable.

The effect of Span 80 concentration on the stability of LSM has been studied by several investigators. Takahashi *et al.*[24)] reported that the degree of breakup rapidly rises below 1.0 wt% of Span 80 concentration using kerosene as organic solvent. Akiba *et al.*[1)] reported that breakup was depressed when using a Span 80 concentration above 2 wt% in uranium

* It was confirmed that the effect of occlusion on $V_{w,e}$ was negligibly small under all experimental conditions.

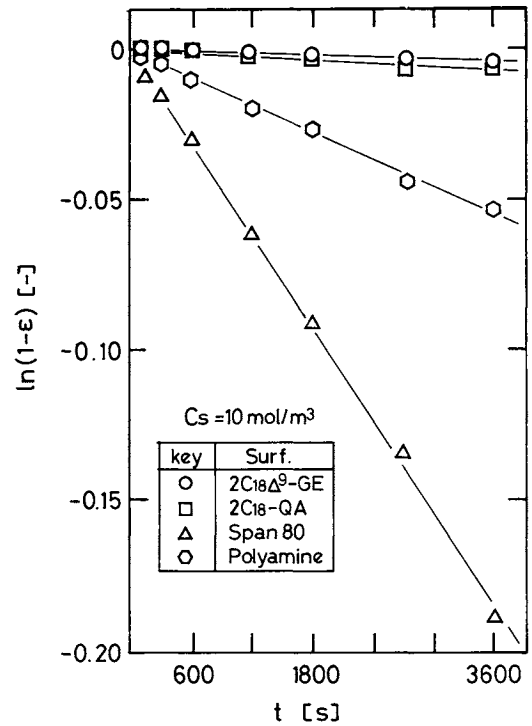


Fig. 3. Rate of breakup of liquid surfactant membrane.

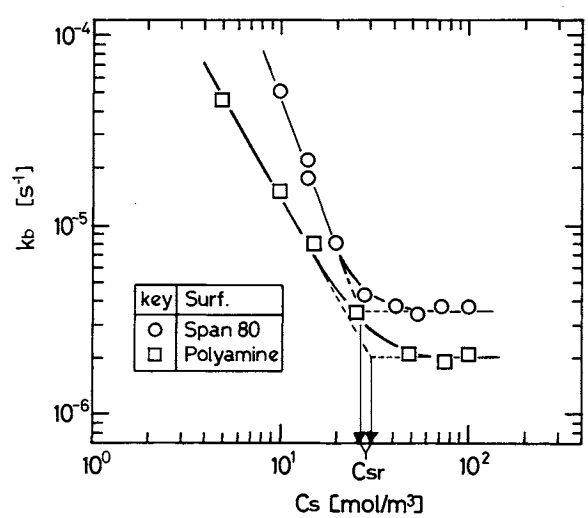


Fig. 4. Effect of concentration of commercial surfactant on breakup.

extraction by LSM. In the previous paper,[13)] we showed that breakup could be negligible when using a Span 80 concentration above 2 wt% in copper extraction by LSM. In the present experiments without extraction, the liquid membrane was stabilized above 27 mol/m³ ($\equiv$1.9 wt%) of Span 80 concentration, and this result agreed with the above results.

On the other hand, the effect of polyamine on the stability of LSM has not been reported so far. As is evident from Fig. 4, polyamine forms a more stable emulsion compared with Span 80.

The relations between the concentration of surfactants, C_s, and breakup rate constants, k_b, are

shown in **Figs. 5** and **6** in the cases of glutamic acid dialkyl ester and quarternary ammonium salts type surfactants, respectively.

These synthesized surfactants having two long alkyl chains formed a more stable emulsion at a lower concentration compared with Span 80 and polyamine. For example, using as surfactant glutamic acid dioleyl ester, a concentration of 1.5 mol/m^3 is enough to obtain a liquid surfactant membrane with $k_b = 3.5 \times 10^{-6}$ ($\varepsilon = 1.3\%$ at 3600 s). The 27 times and 17 times the concentration mentioned above are necessary to form the same LSM in the cases of Span 80 and polyamine respectively.

The number of total surfactant molecules, N_s, in LSM is estimated by Eq. (8).

$$N_s = C_s V_E (1 - \Phi_{wi}) \mathrm{N} \tag{8}$$

where V_E is the volume of emulsion, Φ_{Wi} is holdup of an inner aqueous solution in emulsion, ($\Phi_{wi} = V^0_{w,i}/V^0_E$), and N is the Avogadro number.

The total interfacial area, A, between organic and aqueous solutions is expressed as follows:

$$A = n_p \pi d_p^2 + n_E \pi d_E^2 \simeq n_p \pi d_p^2 \tag{9}$$

where n_p and n_E are the number of inner dispersed droplets and emulsion droplets, and d_p and d_E are the diameter of the droplets, respectively. Generally $d_p =$ 1–10 μm, $d_E = 0.1$–1 mm and $n_E/n_p > 10^5$ under the experimental condition, so the second term in Eq. (9) can be negligible.

$$V_E = n_E \frac{\pi}{6} d_E^3 \tag{10}$$

$$\Phi_{wi} = \frac{n_p d_p^3}{n_E d_E^3} \tag{11}$$

Equation (9) is rewritten by above Eqs. (10) and (11) as

$$A = \frac{6\Phi_{wi}}{d_p} V_E \tag{12}$$

The number of surfactant molecules necessary to cover the whole interfacial area, N_s, is expressed by Eq. (13).

$$N_s = (A/S_{sf}) \cdot \mathrm{N} \tag{13}$$

So the concentration of surfactants necessary to form the monolayer at the interface was estimated by Eq. (14), the combination of Eqs. (8), (12) and (13).

$$C_s = \frac{6\Phi_{wi}}{(1 - \Phi_{wi})} \cdot \frac{1}{d_p S_{sf}} \tag{14}$$

For example, in the case of $\Phi_{wi} = 1/2$ and $2C_{18}\Delta^9$–GE, the critical concentration, C_{sc}, is calculated to be 1.8 mol/m^3 from the data of diameter of inner dispersed droplets obtained and the interfacial area occupied by unit mole, $S_{sf} = 3.87 \times 10^5$ m^2/mol in Table 2. As is evident from Fig. 5, the breakup rate constant increased rapidly below the critical concentration.

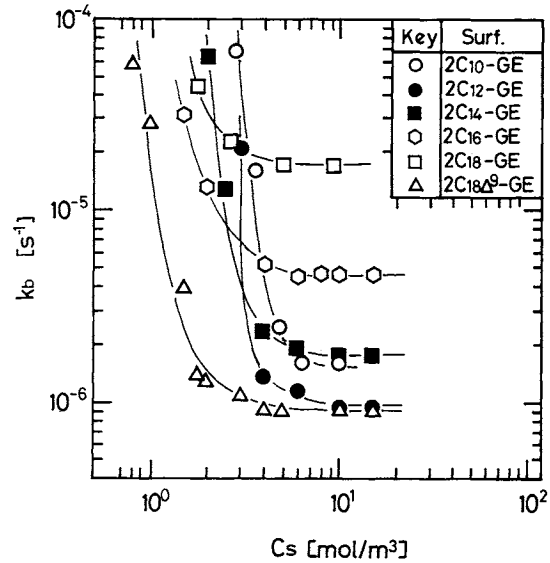


Fig. 5. Effect of concentration of 2R-GE on breakup.

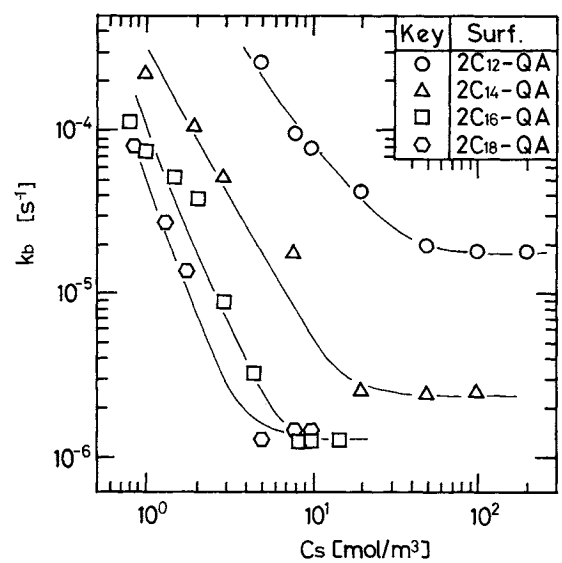


Fig. 6. Effect of concentration of 2R-QA on breakup.

The relation between the breakup rate constant and surfactant concentration is shown in **Fig. 7**, varying the Φ_{wi} value. As the Φ_{wi} value increases, that is, as the interfacial area increases, a higher surfactant concentration was needed to stabilize the emulsion. The concentration corresponds approximately to that forming the monolayer of the surfactant, C_{sc}, that is, the critical surfactant concentration. ($C_{sc} =$ 3.6 mol/m^3 when $\Phi_{wi} = 2/3$; $C_{sc} = 1.4$ mol/m^3 when $\Phi_{wi} = 1/3$).

Hochhauser[8] and Akiba *et al.*[1] reported that the emulsion was more stable with decreasing Φ_{wi} value in the case of Span 80. But in this study using $2C_{18}\Delta^9$–GE, the membrane stability was independent of the

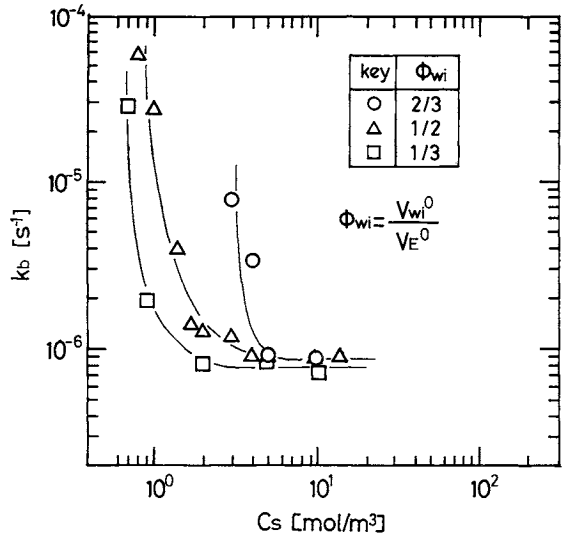


Fig. 7. Effect of concentration of $2C_{18}\Delta^9$-GE and Φ_{wi} on breakup.

Φ_{wi} value ($\Phi_{wi}=1/3$–$2/3$), and the emulsion formed was very stable in all cases. The critical surfactant concentration was determined by Eq. (14) and S_{sf} value in Table 2 and the values of C_{sc} are listed in **Table 3**. In the cases of the synthesized surfactants, these experimental results agree with the calculated one. However, about two times and ten times the calculated critical concentration were needed for Span 80 and polyamine, respectively.

Fujinawa *et al.*[5] also pointed out that a critical number of layers of adsorbed molecule existed at the interface to stabilize the emulsion when they studied the effect of dispersed droplets diameter on the breakup of emulsion in copper extraction using Span 80. Since the commercial surfactants contain various components, it is difficult to study in detail the effect of surfactants. But using a series of synthesized surfactants in a practical LSM operation, the concentration of surfactants above the critical one calculated by Eq. (14) was enough to stabilize the membrane.

In **Figs. 8** and **9**, the relations between the alkyl chain length of surfactants and the breakup rate constant are shown in the cases of using glutamic acid dialkyl ester and quaternary ammonium salts type surfactants, respectively.

There are few examples of investigating the effect of surfactants on the stability of LSM. Martin *et al.*[16] investigated the stability of LSM, in the cases of using Span 20 ($n=12$) and Span 80 ($n=18\Delta^9$), and reported that more stable emulsion was obtained when Span 80 was used as emulsifier. Watanabe, Tanaka *et al.*[26] also investigated the matter, using sixteen commercial surfactants, and reported that sorbitan sesquioleate could form the most stable emulsion. They mention that molecules of sorbitan sesquioleate were closely

Table 3. Critical concentration of each surfactant defined by Eq. (14)

Surfactant	d_i [μm]	C_{sr} [mol/m^3]	C_{sc} [mol/m^3]
Span 80	1.2	27	13
Polyamine	1.6	31	2.8
$2C_{10}$-GE	5.4	5.0	9.2
$2C_{12}$-GE	6.8	4.2	5.3
$2C_{16}$-GE	8.8	3.2	3.7
$2C_{18}$-GE	8.2	3.1	3.8
$2C_{18}\Delta^9$-GE	8.7	2.0	1.8
$2C_{18}\Delta^9$-GE(*)	8.7	4.2	3.6
$2C_{18}\Delta^9$-GE(**)	8.5	1.2	1.4
$2C_{12}$-QA	3.8	35	14
$2C_{14}$-QA	3.3	17	20
$2C_{16}$-QA	5.5	7.0	11

(*) $\Phi_{wi}=2/3$, (**) $\Phi_{wi}=1/3$. The other is $\Phi_{wi}=1/2$.

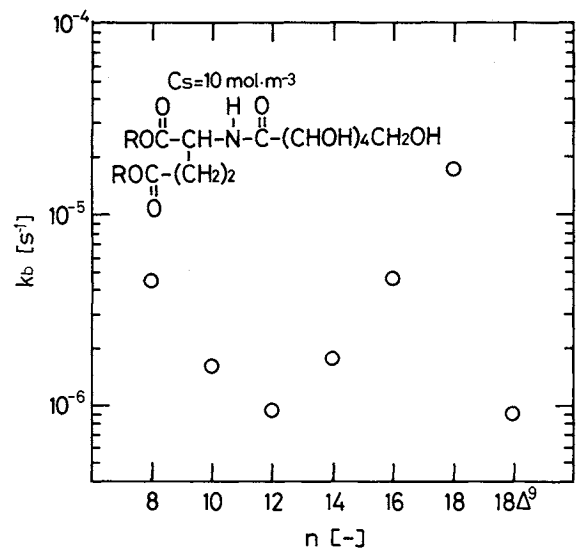


Fig. 8. Effect of alkyl chain length of 2R-GE on breakup.

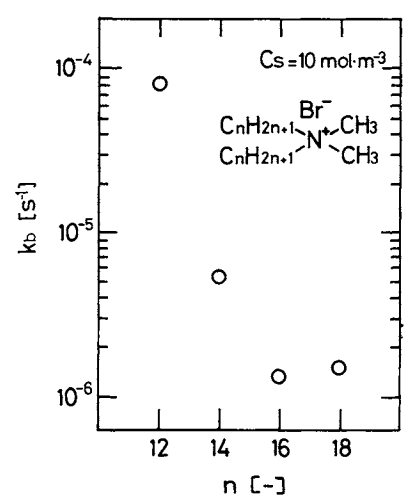


Fig. 9. Effect of alkyl chain length of 2R-QA on breakup.

oriented at the interface by the measurement of ESR spectra.

In the case of glutamic acid dialkyl ester sur-

factants, $2C_{12}$–GE ($n=12$) formed a stable emulsion, but as the alkyl chain length was further increased the stability of emulsion was not improved. But $2C_{18}\Delta^9$–GE having two oleyl chains in the hydrophobic site formed the most stable emulsion. On the other hand, in the case of quaternary ammonium salts type surfactants, as the alkyl chain length was increased the stability of emulsion was increased to attain the constant, k_b, obtained at the number of alkyl chain length over 16.

The structures of quaternary ammonium salts type surfactants are different from those of other surfactants having ester or amide bond. Therefore, from this viewpoint, these surfactants are anticipated to form a stable emulsion even when a strong acid or alkaline solution is used as inner dispersed phase.

Conclusion

Development of new surfactants for LSM is necessary to practice the LSM process. In this study, instead of the commercial surfactants, Span 80 and polyamine, new surfactants having two long alkyl chains were synthesized in order to improve the orientation of surfactant molecules at a water-oil interface. The stability of LSM formed by using these surfactants was examined, and the following results were obtained.

(1) A series of synthesized surfactants having two long alkyl chains made the interfacial tension low at lower concentration compared with Span 80 and polyamine. And the adsorption equilibrium constant of $2C_{18}\Delta^9$–GE was largest, $K_{sf}=583\,m^3/mol$, among all these detergents.

(2) When a series of synthesized surfactants were used in a practical LSM operation, the concentration of surfactant calculated by Eq. (14) was enough to stabilize the emulsion.

(3) Glutamic acid dioleyl ester formed the most stable LSM as compared with the other synthesized surfactants, Span 80 and polyamine.

Acknowledgment

The authors wish to express their thanks to Prof. Toyoki Kunitake of Kyushu University for his valuable suggestions.

Nomenclature

A	=	total interfacial area	[m^2]
C_s	=	concentration of surfactant in organic phase	[mol/m^3]
C_{sc}	=	critical surfactant concentration calculated by Eq. (14)	[mol/m^3]
C_{sr}	=	observed critical surfactant concentration	[mol/m^3]
d_E	=	diameter of emulsion droplet	[m]
d_p	=	diameter of inner dispersed droplet	[m]
K_s	=	adsorption equilibrium constant of surfactant	[m^3/mol]
k_b	=	breakup rate constant defined by Eq. (7)	[1/s]
N	=	Avogadro number	[—]
N_s	=	number of total surfactant molecules	[—]
n	=	alkyl chain length of surfactant	[—]
n_E	=	number of emulsion droplets	[—]
n_p	=	number of inner dispersed droplets	[—]
n_s	=	stirring speed	[1/s]
R	=	gas constant	[Nm/mol·K]
S_{sf}	=	interfacial area occupied by one mole of surfactant	[m^2/mol]
T	=	temperature	[K]
t	=	time	[s]
V_E	=	volume of emulsion	[m^3]
V_w	=	volume of aqueous solution	[m^3]
γ	=	interfacial tension	[N/m]
ε	=	degree of breakup defined by Eq. (5)	[—]
θ_s	=	occupied ratio by surfactant	[—]

〈Subscripts〉

ad	=	adsorption state
e	=	feed aqueous solution
i	=	internal aqueous solution
0	=	initial state
org	=	organic phase

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DEVELOPMENT OF A COMPILER-TYPE SIMULATOR FOR PRESSURE SWING ADSORPTION AND ITS APPLICATION TO OXYGEN ENRICHMENT IN AIR

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Key Words: Pressure Swing Adsorption, Simulation, Compiler, Microcomputer, Bulk Separation, Gas Separation, Langmuir Isotherm, Nonisothermal, Process Synthesis

A PSA compiler is proposed. To cover various types of combination of columns, it has new commands relevant to PSA operation such as single-column modules and coupled-column modules. It also has commands for specifying conditions, managing column allocation and displaying outputs. The user describes the system structure and operating conditions by these commands, and the compiler interprets his program and returns the data that he wants. Hence he can investigate the effect of various manipulating variables as well as various system structures promptly. Up to six components, eight columns and four kinds of adsorbents in each column can be treated. In spite of such high flexibility, this compiler is implemented in a personal computer for handiness.

Oxygen enrichment in air by a triple-column PSA is simulated for two different types of column combinations.

Introduction

Pressure swing adsorption (PSA) is a cyclic process for separation of gas mixtures and is widely applied industrially in hydrogen purification, air separation, air drying and so on. However, its theoretical analysis is difficult, because it is a nonisothermal cyclic process with various specific boundary conditions.

For separation of dilute species such as air drying or separation of CO_2, the change in flow rate due to adsorption or desorption in the column is negligibly small. The equilibrium theory model was used by Turnock and Kadlec,[22] Shendalman and Mitchell,[21] Weaver and Hamrin,[23] Chan *et al.*,[3] Cheng and Hill[4,5] and Knaebel and Hill.[15] Further, models including the effect of finite mass transfer resistance were developed by Mitchell and Shendalman,[16] Kawazoe and Kawai,[13] Carter and Wyszynski,[1] Raghavan *et al.*[17] and Hassan *et al.*[10] Also, a similar model was presented by Chihara and Suzuki[7] who considered the nonisothermal effect due to heat of adsorption.

For bulk separation such as air separation, the change in flow rate along the column becomes significantly great. Fernandez and Kenney[9] used an equilibrium model to analyze the separation of oxygen and nitrogen in air by a single-column PSA process. Raghavan and Ruthven[18] considered the mass transfer resistance. Yang *et al.*[2,8,25,26] simulated the bulk separation of a binary and ternary gas mixture by taking the heat transfer in the column into consideration.

Although there are many reports in the literature about the simulation of PSA, we may say that the PSA systems operated commercially are more complicated than those described in the literature. Usually, multiple kinds of adsorbents are used and inlet packings such as gel are installed to eliminate moisture or carbon dioxide and to recover the heat at low temperature. Furthermore, for synthesis of a PSA system,

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