

DEVELOPMENT OF AMPHOTERIC SURFACTANT FOR LIQUID SURFACTANT MEMBRANE IN METAL EXTRACTION PROCESS

MASAHIRO GOTO, KAZUO KONDO AND FUMIYUKI NAKASHIO

Department of Organic Synthesis, Kyushu University, Fukuoka 812

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Introduction

It is well known that the surfactant plays an important role in the liquid surfactant membrane (LSM) process.⁵⁾ However, only a few commercial surfactants have been used so far and little attention has been paid to searching for other suitable surfactants. As reported in a previous paper,³⁾ the extraction rate of copper by LSM was found to be enhanced by the addition of a small amount of phosphoric and sulfonic acid surfactants. However, the anionic surfactants themselves did not form a stable W/O emulsion when using highly acid solution as an internal aqueous phase. In this study, a further advanced amphoteric surfactant which possesses an acceleration effect and produces a stable emulsion by itself was prepared as a new surfactant. Copper extraction by LSM using this amphoteric surfactant was carried out in a stirred tank and the W/O emulsion was demulsified by a continuous electrical coalescer.

1. Experimental

Figure 1 shows the structure of the new amphoteric surfactant synthesized in this work. Span 80 and polyamine (ECA4360J) were also used to compare the experimental results. Purified LIX65N was used as a carrier. The experimental procedure was the same as that described in previous papers.^{1,4)} Magnesium nitrate was added to the external aqueous phase to prevent the swelling of emulsion. The experimental conditions are listed in Table 1. Diameters of emulsion globules and internal water droplets were also measured. The experimental apparatus for demulsification was a continuous tubular electric coalescer, the same as that described in the previous paper.⁵⁾ The W/O emulsion in the clearance of 5.5 mm between the glass tube surrounding the electrode and the outer glass tube was demulsified by applying an AC potential of 0.5–5 kV. The experimental conditions are listed in Table 2.

2. Results and Discussion

2.1 Stability of W/O emulsion

To estimate the stability of W/O emulsion, a break-up rate constant, k_b , is defined by Eq. (1) according to the previous paper.¹⁾

$$\ln(1-\varepsilon) = -k_b \cdot t \quad (1)$$

where ε is breakup ratio obtained using Ni(II) as a tracer. The experimental results were arranged using Eq. (1) and the relation between k_b and the concentration of surfactant, C_s , for each surfactant is shown in Fig. 2. As is evident from Fig. 2, the

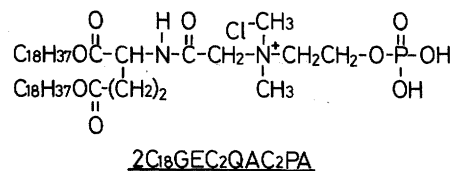


Fig. 1. Structure of newly synthesized amphoteric surfactant

Table 1. Experimental conditions for copper extraction by LSM

Volume of internal aqueous solution (1 N H ₂ SO ₄)	5 × 10 ⁻⁵ m ³
Volume of organic solution (<i>n</i> -heptane)	5 × 10 ⁻⁵ m ³
Volume of external aqueous solution	7 × 10 ⁻⁴ m ³
Concentration of copper in external aqueous solution (pH = 2.0)	5 mol/m ³
Concentration of carrier (purified LIX 65N)	50 mol/m ³
Stirring speed	5 s ⁻¹
Temperature	303 K
Breakup tracer and concentration in internal aqueous solution	Ni(NO ₃) ₂ , 5 mol/m ³

Table 2. Experimental conditions for demulsification

Volume ratio of internal aqueous solution to organic solution in W/O emulsion	$V_{\text{int}}/V_{\text{org}} = 1$
Internal aqueous solution	1 N H ₂ SO ₄ (100 mol/m ³ , CuSO ₄)
Organic solution <i>n</i> -heptane;	(LIX 65N: 50 mol/m ³)
Applied voltage	$E = 0.5\text{--}5 \text{ kV}$ (60 Hz)
Mean residence time	$\theta = 180 \text{ s}$

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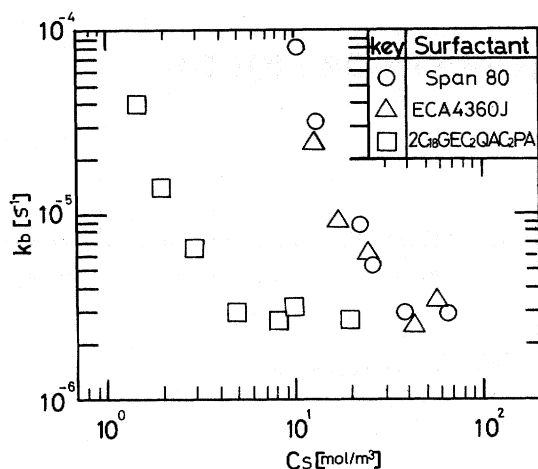


Fig. 2. Relation between k_b and surfactant concentration

amphoteric surfactant, $2C_{18}GEC_2QAC_2PA$, forms a stable emulsion at a low concentration which is about one-tenth the corresponding concentration of Span 80 or ECA4360J.

2.2 Extraction rate of copper by LSM

Changes of copper concentration in the external aqueous solution with elapsed time are shown in Fig. 3. The extraction rate of copper using the amphoteric surfactant is extremely high, and also slightly higher than that of using $2C_{18}A^9GE$ -anionic surfactant.³⁾ Under the experimental condition of pH less than 2, the extraction rate is controlled by the interfacial reaction between copper and the carrier at the surface of the W/O emulsion.²⁾ In such a case, the concentration change of copper ion with time can be expressed by the following equation:³⁾

$$-dC_{Cu}/dt = a \cdot k_f'(C_{Cu}/a_H) \quad (2)$$

where a is the interfacial area and k_f' is an apparent reaction rate constant. From Fig. 3 and measurements of the diameter of the W/O emulsion globule, the value of k_f' for each surfactant was obtained and the results are shown in Table 3. The solid lines in Fig. 3 are the calculated results using the k_f' values. The k_f' value of the amphoteric surfactant is about three and ten times the values of ECA4360J and Span 80, respectively. The main reason for this is considered to be an electrostatic interaction between copper ion and hydrophilic phosphoric-group of the amphoteric surfactant. As mentioned in the previous paper,³⁾ copper ion is attracted at the oil-water interface more strongly than proton, so that the extraction rate is considered to be enhanced. The increase in the rate leads to shortening the operation time in the LSM process, and the extraction efficiency becomes greater because the breakup and swelling of the W/O emulsion are suppressed.

2.3 Demulsification by electrical coalescer

Figure 4 shows the effect of surfactants on the

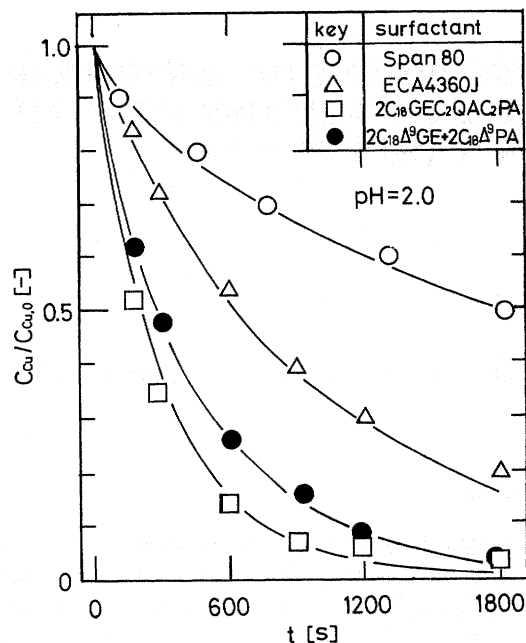


Fig. 3. Effect of surfactant on extraction rate of copper, surfactant concentration; Span80=3 wt%, ECA4360J=5 wt%, $2C_{18}GEC_2QAC_2PA$ =10 mol/m³, $2C_{18}A^9GE$ =10 mol/m³+ $2C_{18}A^9PA$ =2 mol/m³

Table 3. Diameters of emulsion globule and internal water droplet, and apparent rate constant for each surfactant

Surfactant	$10^6 d_{p32}$ [m]	$10^3 d_{E32}$ [m]	k_f' [mol/m ² s]
Span 80	4.63	0.272	2.8×10^{-6}
ECA4360J	7.38	0.349	9.9×10^{-6}
$2C_{18}GEC_2QAC_2PA$	5.41	0.302	2.9×10^{-5}

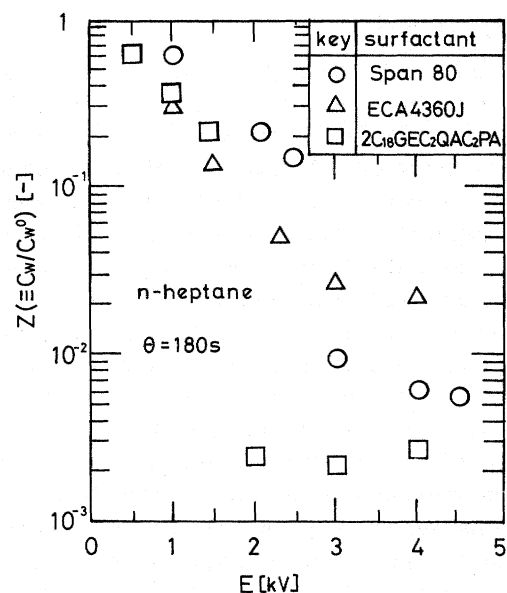


Fig. 4. Effect of surfactant on demulsification rate, surfactant concentration; Span80=3 wt%, ECA4360J=5 wt%, $2C_{18}GEC_2QAC_2PA$ =10 mol/m³

residual water content, Z , in the W/O emulsion demulsified by the continuous electrical coalescer. Z is defined by Eq. (3).

$$Z = C_w / C_w^0 \quad (3)$$

where C_w is the water content in the W/O emulsion. In this figure, E represents the applied voltage. From Fig. 4, it is found that the residual water content in the W/O emulsion demulsified at $E > 3$ kV becomes smaller in the order, ECA4360J > Span 80 > 2C₁₈GEC₂QAC₂PA. When using ECA4360J, the organic solution regenerated by demulsification was turbid even when applying high voltage (10 kV). The energy required for realizing a demulsification efficiency greater than 98% so as to use the organic solution repeatedly were 0.14 (2C₁₈GEC₂QAC₂PA), 0.22 (Span 80) and 0.44 (ECA4360J) kWh/m³-emulsion. The emulsion made of the amphoteric surfactant was found to be most efficiently demulsified by the electrical coalescer.

Nomenclature

a	= interfacial area defined by ($V_E/V_{w,e}$)($6/d_{E32}$)	[1/m]
a_H	= activity of hydrogen ion	[mol/m ³]
C_{Cu}	= concentration of copper in external aqueous solution	[mol/m ³]

C_w	= water content in emulsion	[kg/m ³]
d_{E32}	= Sauter mean diameter of emulsion globule	[m]
d_{p32}	= Sauter mean diameter of internal water droplet	[m]
k_b	= breakup rate constant	[1/s]
k_f'	= apparent reaction rate constant	[mol/m ² s]
t	= extraction time	[s]
Z	= residual water content in demulsified emulsion	[—]
ε	= breakup ratio	[—]

<Subscripts>

E	= emulsion phase
e	= external aqueous phase
0	= initial value

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