

# ELECTRICAL DEMULSIFICATION OF W/O EMULSION BY CONTINUOUS TUBULAR COALESCER

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The continuous demulsification of W/O emulsion under applied A.C. voltage was investigated, using a tubular coalescer.

The effects of water-phase holdup, applied voltage and water-droplet size on demulsification rate were investigated, using emulsions prepared under various conditions. The rate was proportional to the  $-1$ ,  $0.5$  and  $3rd$  power of water-phase holdup, applied voltage and water-droplet size, respectively. The experimental equation taking these contributions into account showed satisfactory agreement with the observed values. Further, the effects of surfactant, extractant and solvent on the rate were examined and it was found that the combination of the three strongly affects the rate.

The energy consumption for continuous demulsification using the present apparatus is several  $kWh/m^3$ -emulsion, so this coalescer can be applied to industrial processing.

## Introduction

Novel separation processes using liquid surfactant membranes (henceforth LSM) have attracted practical interest in nuclear, hydrometallurgical and waste-water treatment processes.<sup>1,11)</sup>

However, in establishing the LSM process as an industrial separation means, it is very important to operate effectively the demulsification of W/O emulsion, which is the final step of the process. Methods such as centrifugation, heating and filtration, have been utilized to date to demulsify W/O emulsion. However, from the viewpoints of energy efficiency and repeated use of the demulsified organic phase, electrical demulsification is considered to be the best method at the present stage.<sup>6,9)</sup> An electrical demulsification apparatus has been operated in an LSM process of industrial scale for the recovery of zinc from waste-water, and it was reported that energy consumption by the apparatus was between  $0.5$  and  $5 kWh/m^3$ -emulsion.<sup>1)</sup>

Effects of several operation factors on the demulsification rate have already been studied, using various electrical coalescers.<sup>2,4,5,7,8,12,13)</sup> However, most studies have been limited to the system of Span 80 (Surfactant)-kerosene (solvent), using a batch apparatus. Furthermore, there are only a few studies involving continuous operation.<sup>1,10,12)</sup>

In this study, a tubular electrical coalescer for

continuous operation is devised to demulsify W/O emulsion effectively. The W/O emulsions are prepared by changing the preparation conditions (water-phase holdup, duration of exposure to ultrasonic waves, and agitation speed) and the composition of the liquid membrane (organic solvent, extractant and surfactant). The effects of water-phase holdup, applied voltage, water-droplet size and the materials of the liquid membrane on the demulsification rate are investigated by use of the electrical coalescer.

## 1. Experimental Apparatus and Procedure

Figure 1 shows the experimental apparatus used for continuous electrical demulsification, and the electrical coalescer is shown in detail in Fig. 2. The coalescer consists of a glass tube of 22 mm O.D. containing an electrode sealed within an 8 mm O.D. glass tube of 1 mm wall thickness. A.C. electric potential of  $0.5$ – $15$  kV (60 Hz) can be applied between ⑤ and ⑥ by a high-voltage transformer ⑧.

The aqueous phase was prepared by dissolving  $100 mol/m^3$  copper sulfate in  $500 mol/m^3$  sulfuric acid. The organic phase was prepared by dissolving a surfactant and an extractant in an organic solvent. The viscosity of the organic phase was measured with a Type E rotational viscometer (Tokyo Keiki Co.) at 298 K. The W/O emulsion was prepared by stirring aqueous and organic phases of equal volumes at 1000 rpm in a cylindrical vessel under ultrasonic irradiation for 5 minutes. The droplet size in all emulsions used was measured with a Microtrak

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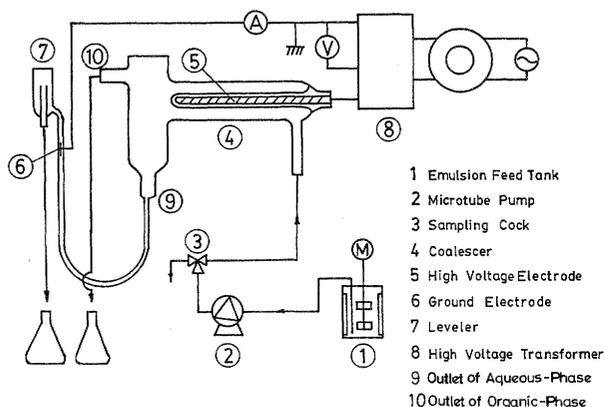


Fig. 1. Experimental apparatus for demulsification

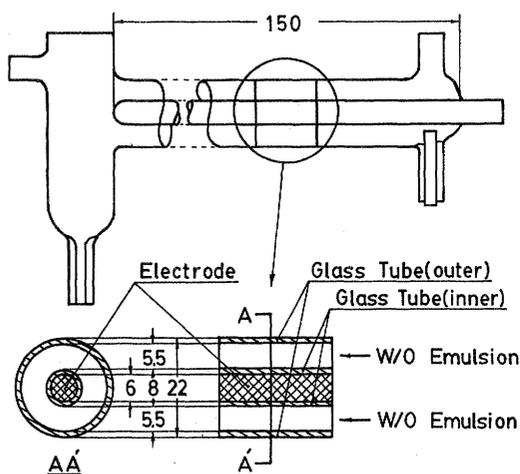


Fig. 2. Electrical coalescer

particle-size analyzer (NIKKISO Model 7995) and was represented by the Sauter mean diameter.

The emulsion was stored in a stirred tank (1), moderately stirred to prevent phase separation, and was supplied to the electrical coalescer (4) at a constant feed rate using a microtube pump (2). After the coalescer was filled with the emulsion, a high voltage was applied. The emulsion flowing through the clearance between the electrode and the outer glass tube of the coalescer was demulsified continuously under a constant A.C. potential. The experiments were carried out in the range of 0.5–15 kV. The applied voltage and the electric current were recorded simultaneously.

It was regarded as a steady state when the outflow rate of the demulsified aqueous phase became constant. Then, a small amount of the organic phase flowing out from the upper side of the coalescer (10) was collected and the residual water content was measured by the Karl-Fisher method. In the present study, steady state was reached when the emulsion was supplied to the coalescer for a period of about three times the mean residence time.

Nonionic surfactants such as Span 80, ECA4360J

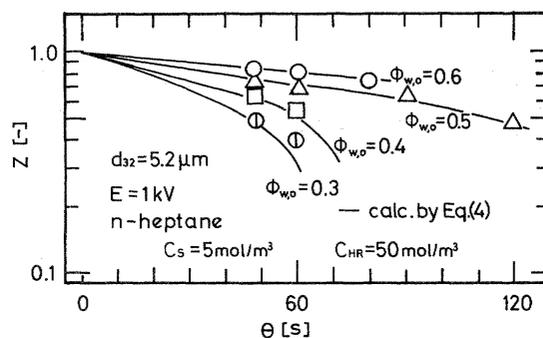


Fig. 3. Effect of initial water-phase holdup in emulsion on demulsification rate (surfactant;  $2C_{18}A^9GE$ , extractant; LIX65N)

and  $2C_{18}A^9GE^3$ ), and the cationic surfactant  $2C_{18}QA^3$ ) were used. Extractants used were a purified LIX65N and an unpurified D2EHPA. Four organic solvents—*n*-heptane, toluene and cyclohexane and kerosene—were used. Other inorganic reagents (copper sulfate, sulfuric acid) were reagent grade. The demulsification experiments were carried out at room temperature.

## 2. Experimental Results and Discussion

### 2.1 Evaluation of demulsification rate

Assuming that the demulsification rate is proportional to the  $n$ th power of the water content in the emulsion,  $\phi_w$ , and that the flow pattern of the emulsion in the coalescer is approximated by plug flow, the mass balance of water content in the coalescer can be expressed as follows:

$$-(v/V)d\phi_w/dx = k\phi_w^n \quad (1)$$

where  $v$  and  $V$  ( $=45$  ml) are the flow rate of the emulsion and the volume of the coalescer, respectively,  $x$  is a dimensionless distance from the inlet of the coalescer and  $k$  is a rate constant of demulsification. If the initial condition, that is,  $\phi_w = \phi_{w,0}$  at  $x=0$ , is given, Eq. (1) is integrated to give Eq. (2) at  $x=1$ .

$$\phi_{w,0}^{1-n}(1-Z^{1-n}) = (1-n)k\theta \quad (n \neq 1) \quad (2)$$

$$Z = \phi_w/\phi_{w,0} \quad (3)$$

where  $Z$  is ratio of water content at  $x=1$  to that at  $x=0$  and  $\theta$  ( $=V/v$ ) is the mean residence time of the emulsion in the coalescer. The experiments were carried out at various values of  $\phi_{w,0}$ , and the relations between  $Z$  and  $\theta$  at several  $\phi_{w,0}$  values are shown in Fig. 3. The value of  $n$  to give the best correlation coefficient,  $r$ , between the left-hand side and the right-hand side of Eq. (2) was determined from the results. That value of  $n$  was found to be  $-1$  ( $r=0.995$ ) and the  $k$  value is  $8.2 \times 10^{-4} \text{ s}^{-1}$  for the system of LIX65N and  $2C_{18}A^9GE$  in *n*-heptane. Further, Eq. (2) is rewritten as the following expression with the  $n$ -value is  $-1$ .

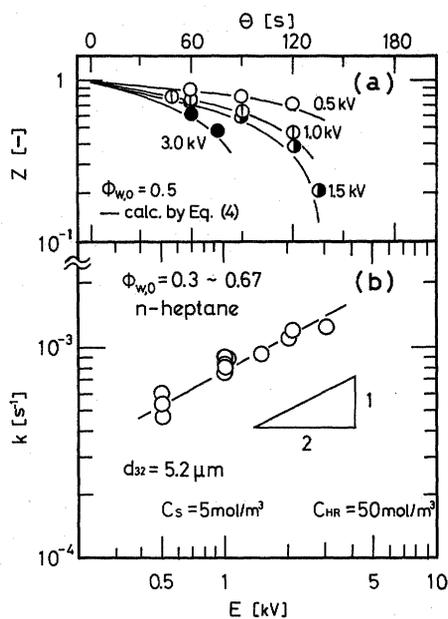


Fig. 4. Effect of applied voltage on demulsification rate (surfactant:  $2C_{18}A^9GE$ ; extractant: LIX 65N)

$$Z^2 = 1 - 2k\theta/\phi_{w,0}^2 \quad (4)$$

The solid lines in Fig. 3 are those calculated by Eq. (4) using the  $k$ -value. Good agreement between the experimental results and the calculated ones is obtained, so subsequent experimental results are discussed using the demulsification rate constant obtained by Eq. (4).

### 2.2 Effect of applied voltage

To investigate the effect of applied voltage on the rate, experiments were carried out under the condition of various applied voltages, keeping the other conditions constant. Figure 4(a) shows the relation between  $Z$  and  $\theta$  under the conditions mentioned in the figure. Apparently, the demulsification rate increases with increase in applied voltage. The rate constant,  $k$ , in Eq. (4) was obtained from the experimental results for each applied voltage,  $E$ , and the relation between  $k$  and  $E$  is shown in Fig. 4(b). As is evident, the rate constant is proportional to  $E^{0.5}$ . Fujinawa *et al.*<sup>4)</sup> reported the same dependency on the applied voltage in the system of Span 80-kerosene.

### 2.3 Effect of water-droplet size

The effect of water-droplet size on the rate was investigated by using emulsions of different mean diameter, which were prepared by changing the agitation rate and the duration of ultrasonic irradiation. The mean diameter of the water droplet was from 4.7 to 7.4  $\mu\text{m}$  and the distribution curve of the droplet diameters was a logarithmic normal distribution for each emulsion. Figure 5 shows the relation between  $k/E^{0.5}$  and the Sauter mean diameter of the water droplet for the system of LIX65N and  $2C_{18}A^9GE$  in  $n$ -heptane. Apparently, the demulsifica-

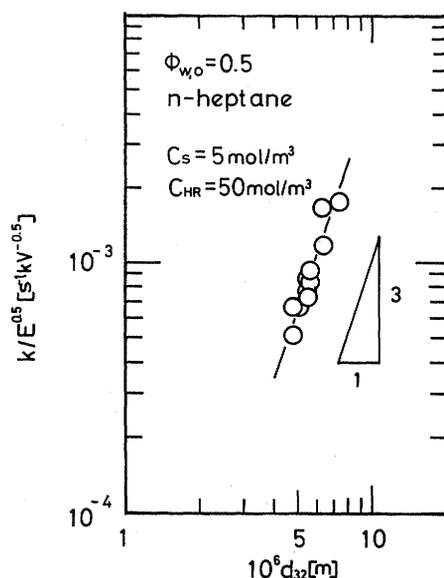


Fig. 5. Effect of water-droplet size on demulsification rate (surfactant:  $2C_{18}A^9GE$ ; extractant: LIX65N)

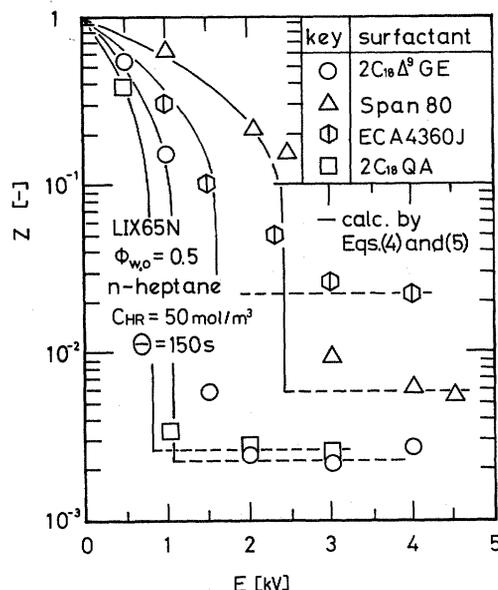


Fig. 6. Effect of surfactant on demulsification rate (broken line: limiting demulsification ratio, extractant: LIX65N;  $2C_{18}A^9GE$ :  $C_s = 5 \text{ mol/m}^3$ ; Span 80:  $C_s = 3 \text{ wt}\%$ ; ECA4360J:  $C_s = 5 \text{ wt}\%$ ;  $2C_{18}QA$ :  $C_s = 5 \text{ mol/m}^3$ )

tion rate is proportional to  $d_{32}^3$ . Fujinawa *et al.*<sup>2)</sup> and Hano *et al.*<sup>4)</sup> respectively reported the dependency on Sauter mean diameter to be 3 and 3.5 for the system of Span 80-kerosene.

### 2.4 Effect of surfactant and extractant

Figure 6 shows the effect of surfactants on the demulsification rate of the emulsion containing LIX65N in  $n$ -heptane. In a previous paper,<sup>3)</sup> we reported that a critical surfactant concentration exists for stabilizing the emulsion in a stirred tank. In a practical LSM operation it is necessary to use a surfactant concentration above the critical value. In

the present study, the concentrations of surfactants used are higher than the critical value and the stability of the emulsion at these concentrations was in the order  $2C_{18}A^9GE > 2C_{18}QA > \text{Span } 80 > \text{ECA4360J}^{10)}$  for the system of LIX65N in *n*-heptane. However, as is evident from Fig. 6, the ease of demulsification is in the order  $2C_{18}QA > 2C_{18}A^9GE > \text{ECA4360J} > \text{Span } 80$ . From these results, it is found that the difficulty of electrical demulsification of W/O emulsion is not necessarily proportional to the emulsion's stability. So it is possible to make up an emulsion that possesses both higher stability and ease of demulsification. Actually,  $2C_{18}A^9GE$  possesses these properties.

Hano *et al.*<sup>4)</sup> investigated in detail the effect of oil-phase viscosity on the rate, using a mixed solvent of kerosene and liquid paraffin. They reported that the demulsification rate is proportional to the  $-3.2$  power of the oil-phase viscosity. Using the result, the empirical rate constant in this study is derived from all the experimental results described above, as follows.

$$k = k' \cdot 0.5 d_{32}^3 \mu_{oil}^{-3.2} \quad (5)$$

However, as is evident from Fig. 6, a limiting demulsification ratio (broken lines in Fig. 6),  $Z_1$ , exists in all cases and the demulsification does not proceed farther than  $Z_1$  even under higher applied voltage or longer residence time. The value of  $Z_1$  depends greatly on the surfactant used. It is considered that very small water droplets which cannot be demulsified by the electric method exist in the emulsion. So the application of Eqs. (4) and (5) is limited to the region of  $Z > Z_1$ .

Figure 7 shows the effect of surfactants on the demulsification rate of the emulsion containing D2EHPA. Table 1 shows the mean diameter of the water droplet and the oil-phase viscosity in the emulsion for the system of LIX65N and D2EHPA in *n*-heptane with four kinds of surfactant. The solid lines in Figs. 6 and 7 were calculated by using Eqs. (4) and (5). Approximate agreement between the experimental results and the calculated ones was obtained. However, when the cationic surfactant  $2C_{18}QA$  and D2EHPA were used, it was impossible to explain the experimental result by the same  $k'$  value as above. Figure 8 shows the relation between  $k$  and  $E^{0.5} d_{32}^3 / \mu_{oil}^{3.2}$  except for the result when using D2EHPA and the cationic surfactant. The value of  $k'$  was obtained from this figure by the least squares method to be 132 and 65 for LIX65N and D2EHPA, respectively. The rate constant for LIX65N was about twice that for D2EHPA. It is considered that the demulsification rate is much influenced by an extractant possessing a strong interfacial activity. In particular, when a combination of such an extractant and an ionic

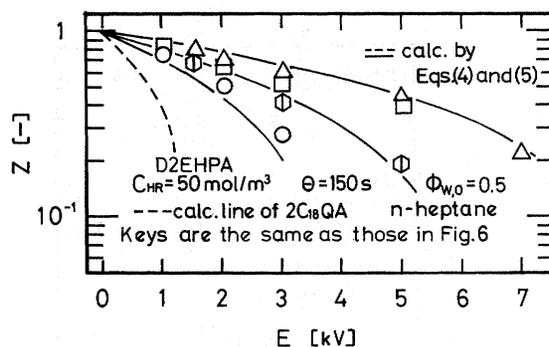


Fig. 7. Effect of surfactant on demulsification rate (extractant: D2EHPA; experimental conditions are the same as for Fig. 6 except for extractant.)

Table 1 Mean diameter and oil-phase viscosity of emulsion, and demulsification rate constant at  $E=1$  kV for surfactant for *n*-heptane

Extractant	Surfactant	$10^6 d_{32}$ [m]	$10^3 \mu_{oil}$ [Pa·s]	$10^4 k_{cal}$ [s <sup>-1</sup> ]	$10^4 k_{obs}$ [s <sup>-1</sup> ]
LIX65N	$2C_{18}QA$	5.21	0.447	9.8	9.9
	$2C_{18}A^9GE$	5.16	0.468	8.2	8.2
	ECA4360J	5.53	0.508	7.8	7.6
	Span 80	4.55	0.485	5.0	5.4
D2EHPA	$2C_{18}QA$	5.97	0.445	7.3	3.4
	$2C_{18}A^9GE$	5.51	0.467	4.9	4.3
	ECA4360J	5.89	0.513	4.5	4.1
	Span 80	4.62	0.482	2.6	2.5

The values of  $k'$  in Eq. (5) are 132 and 65 for LIX65N and D2EHPA.

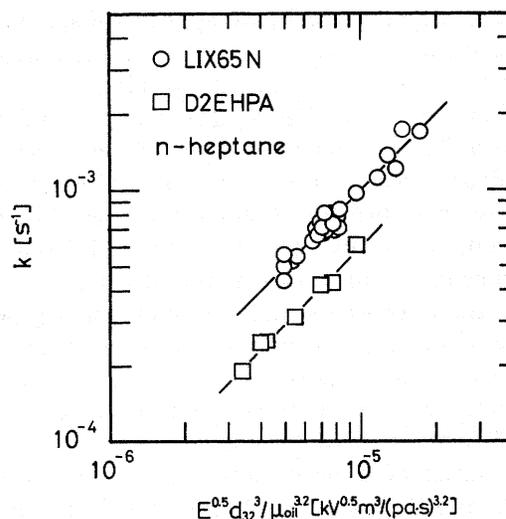


Fig. 8. Relation between  $k$  and  $E^{0.5} d_{32}^3 / \mu_{oil}^{3.2}$  in Eq. (5)

surfactant was used the demulsification of the emulsion became considerably difficult. Further, the W/O emulsion made of  $2C_{18}QA$  was not demulsified even by an applied voltage as high as 15 kV when using 500 mol/m<sup>3</sup> NaCl solution as the aqueous phase in the emulsion.<sup>10)</sup> At present, information about the

nature of the oil-water interface is insufficient to explain quantitatively the experimental results obtained. More detailed studies by surface chemistry along with electrochemistry are necessary.

### 2.5 Effect of organic solvent

Figure 9 shows the relation between  $Z$  and  $\theta$  when using four kinds of organic solvents. The demulsification rate is found to be influenced by the organic solvent. The viscosities of the oil phase containing both  $2C_{18}A^9GE$  ( $5 \text{ mol/m}^3$ ) and LIX65N ( $50 \text{ mol/m}^3$ ) were  $0.468$  (*n*-heptane),  $0.636$  (toluene),  $0.879$  (cyclohexane) and  $1.073$  (kerosene)  $\text{mPa}\cdot\text{s}$ . The effects of the organic solvent on the rate could not necessarily be explained by using Eqs. (4) and (5). When toluene was used, the demulsification rate was considerably lower than the expected values shown by the broken line in Fig. 9.

In addition to the factors taken into consideration in Eq. (5), the difference in specific gravity between aqueous and oil phases and the dielectric constant of the oil-phases, etc. must be considered to elucidate the solvent effect. Especially, an aromatic solvent gives worse results than other solvents regarding stability, swelling<sup>10)</sup> and demulsification of the emulsion. Consequently, it is considered that the use of an aromatic solvent is unsuitable for an LSM process.

In the LSM process, it is most important to make up the best constitution (surfactant, extractant, solvent and internal aqueous phase, etc.) taking account of the stability and swelling of the emulsion, the permeation rate of the solute and the demulsification rate.

### 2.6 Energy consumption for demulsification

In establishing the LSM process as an industrial operation, it is necessary to demulsify continuously a large quantity of W/O emulsion effectivity. Figure 10 shows the relation between electric current density and applied voltage during demulsification. The solid line in the figure shows the relation where the coalescer is filled with an aqueous solution of  $500 \text{ mol/m}^3$  sulfuric acid- $100 \text{ mol/m}^3$  copper sulfate. It is found that the relation between electric current density and applied voltage during demulsification is the same as that of the aqueous solution independently of the organic solvent of the emulsion. The electric power during the demulsification is very low, and is only a few watts in the present study. It is considered that electrical demulsification is advantageous from the viewpoint of energy consumption compared with other demulsification methods, such as heating or centrifugation.

In a continuous operation, a demulsification ratio of about 99% is necessary for repeated use of the demulsified organic phase. In this study, the energy consumption,  $P$  [ $\text{kWh/m}^3$ ], for the demulsification of  $1 \text{ m}^3$ -emulsion is between 0.05 and 2 from the

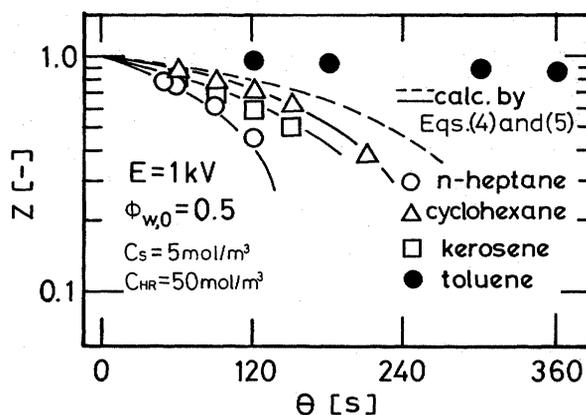


Fig. 9. Effect of organic solvent on demulsification rate (surfactant:  $2C_{18}A^9GE$ ; extractant: LIX65N)

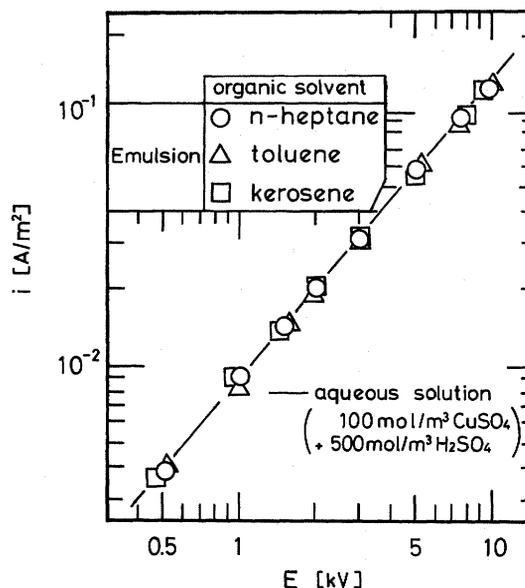


Fig. 10. Relation between applied voltage and electric current density (surface area of electrode =  $3.8 \times 10^{-3} \text{ m}^2$ )

experimental results in Figs. 6 and 10. The effect of the scale-up of the electrical coalescer must be investigated for the treatment of a larger quantity of emulsion.

### Conclusions

Demulsification of W/O emulsion by an electrical coalescer was carried out under various experimental conditions, and the following results were obtained.

1) The demulsification rate increased with decrease in initial dispersed phase holdup in W/O emulsion and with increase in both water-droplet diameter and applied voltage. These effects are explained by Eqs. (4) and (5).

2) The constitution of the LSM system (surfactant, extractant and solvent, etc.) strongly affected the demulsification rate. In particular, when an ionic surfactant was used the demulsification behavior was complicated.

3) The energy consumption of continuous demulsification by the electrical coalescer was very low compared with that of the other demulsification methods. This tubular coalescer for electrical demulsification can therefore be applied to practical use in continuous LSM operation.

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#### Nomenclature

$C_{HR}$	= concentration of extractant	[mol/m <sup>3</sup> ]
$C_s$	= concentration of surfactant	[mol/m <sup>3</sup> ]
$d_{32}$	= Sauter mean diameter of water droplet	[m]
$E$	= applied voltage	[kV]
$i$	= electric current density	[A/m <sup>2</sup> ]
$k$	= demulsification rate constant defined by Eq. (1)	[s <sup>-1</sup> ]
$k'$	= proportional constant in Eq. (5)	[s <sup>-1</sup> · kV <sup>-0.5</sup> · m <sup>-3</sup> · (Pa · s) <sup>3.2</sup> ]
$r$	= correlation coefficient	[—]
$V$	= coalescer volume	[m <sup>3</sup> ]
$v$	= flow rate of emulsion	[m <sup>3</sup> /s]
$x$	= dimensionless distance measured from inlet of coalescer	[—]
$Z$	= residual water content in demulsified emulsion defined by Eq. (3)	[—]
$\theta$	= mean residence time	[s]
$\mu$	= viscosity	[Pa · s]

$\phi_w$  = water-phase holdup [—]

#### <Subscripts>

$0$	= initial value
$cal$	= calculated value
$obs$	= observed value
$oil$	= oil-phase
$w$	= water-phase

#### Literature Cited

- 1) Draxler, J. and R. Marr: *Chem. Eng. Process*, **20**, 319 (1986).
- 2) Fujinawa, K., M. Morishita, M. Hozawa, N. Imaishi and H. Ino: *J. Chem. Eng. Japan*, **17**, 632 (1984).
- 3) Goto, M., M. Matsumoto, K. Kondo and F. Nakashio: *J. Chem. Eng. Japan*, **20**, 157 (1987).
- 4) Hano, T., T. Ohtake and K. Takagi: *J. Chem. Eng. Japan*, **21**, 345 (1988).
- 5) Hsu, E. C. and N. N. Li: *Separ. Sci. Technol.* **20**, 115 (1985).
- 6) Ino, H., N. Imaishi, M. Hozawa and K. Fujinawa: *Kagaku Kogaku Ronbunshu*, **9**, 263 (1983).
- 7) Kataoka, T. and T. Nishiki: *J. Chem. Eng. Japan*, **12**, 16 (1986).
- 8) Kriechbaumer, A. and R. Marr: *ACS Symp. Ser.* **272**, 381 (1985).
- 9) Martin, T. P. and G. A. Davies: *Hydrometallurgy*, **2**, 315 (1976/1977).
- 10) Nakashio, F., M. Goto, M. Matsumoto, J. Irie and K. Kondo: *J. Membr. Sci.*, **38**, 249 (1988).
- 11) Nakashio, F., K. Kondo and M. Matsumoto: *Kagaku Kogyo*, **39**, 511 (1988).
- 12) Yamaguchi, M., A. Kobayashi, K. Ohbori and T. Katayama: *Kagaku Kogaku Ronbunshu*, **11**, 729.
- 13) Yamaguchi, M., K. Ohbori, O. Kondo and T. Katayama: *Kagaku Kogaku Ronbunshu*, **14**, 483 (1988).