

$G$	= growth rate on susceptor	[cm/s]	$B$	= exit of reactant section
$Gr$	= Grashof number ( $= g\beta D_e^3(t_h - t_w)/\nu^2$ )	[-]	$h$	= reaction zone
$g$	= gravitational acceleration	[cm/s <sup>2</sup> ]	$w$	= wall
$k$	= mass transfer coefficient	[cm/s]	0	= inlet of reactor
$l$	= length of reaction zone	[cm]	<Superscript>	
$M$	= molecular weight of SiCl <sub>4</sub> ( $M=170$ )	[-]	-	= average
$m$	= atomic weight of Si ( $m=28$ )	[-]		
$Re$	= Reynolds number ( $= D_e \bar{v}/\nu$ )	[-]		
$r$	= radial distance	[cm]		
$r_s$	= outer radius of inner tube	[cm]		
$r_w$	= inner radius of outer tube	[cm]		
$S$	= cross-sectional area of annulus ( $= \pi(r_w^2 - r_s^2)$ )	[cm <sup>2</sup> ]		
$Sh$	= average Sherwood number ( $= \bar{k} D_e / \mathcal{D}$ )	[-]		
$Sh_{loc}$	= local Sherwood number ( $= k D_e / \mathcal{D}$ )	[-]		
$t$	= temperature	[K]		
$v$	= velocity in z-direction	[cm/s]		
$z$	= axial distance	[cm]		
$z_h$	= axial distance from leading edge of reaction surface	[cm]		
$\beta$	= volumetric coefficient of expansion	[K <sup>-1</sup> ]		
$\theta$	= angle in cylindrical coordinates	[rad]		
$\mu$	= viscosity	[Pa·s]		
$\nu$	= kinematic viscosity	[cm <sup>2</sup> /s]		
$\rho$	= density	[g/cm <sup>3</sup> ]		
<Subscripts>				
$A$	= entrance of reactant section			

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## DEMULSIFICATION KINETICS OF W/O EMULSION IN AN A.C. ELECTRIC FIELD

TADASHI HANO, TAKAAKI OHTAKE AND KAZUMI TAKAGI

*Department of Environmental Chemistry and Engineering, Oita University, Oita 870-11*

**Key Words:** Extraction, Demulsification, W/O Emulsion, Kinetics, Viscosity, Electric Field

The demulsification kinetics of W/O emulsion in a high A.C. electric field was investigated by using a batch cylindrical demulsifier in which a glass-sealed electrode was placed above a grounded copper disk electrode. The effects of emulsion preparation conditions (oil-phase viscosity, water drop size, water-phase holdup and surfactant concentration) and demulsifying conditions (agitation speed and temperature) on the demulsification rates were examined experimentally while keeping the applied voltage constant. The demulsification rates varied considerably with slight change of these conditions. The rate equation that expressed the above contributions in suitable functional forms gave satisfactory agreement with observed rates over a wide range of experimental conditions. Based on comparison with thermal demulsification without electric field, the accelerating effect of temperature rise was thought to be caused by the decrease of oil-phase viscosity and emulsion stability. Mixing of the demulsifier contents during the operation was found to be effective in promoting demulsification together with temperature rise.

### Introduction

The application of (W/O)/W emulsion to the extraction and concentration of very dilute components

has received a great deal of attention in, for example, the fields of hydrometallurgy, wastewater treatment, and purification of fermentation products.<sup>7,9,14</sup> In these processes, the breaking of W/O (water-in-oil) emulsion after extraction is necessary in order to

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recover the components concentrated in the inner water phase and to re-utilize the oil containing surfactants and carriers. In the various demulsification techniques proposed so far, the electrostatic method in which a high A.C. or D.C. voltage is applied to the emulsion is considered to be the simplest and most effective.<sup>2,4,5)</sup> By observations under a microscope, it became clear that electrostatic forces caused the coalescence of fine water drops and their growth to larger drops which then readily fell by electrostatic forces or gravity.<sup>2,5,12,13)</sup> The complex motion of water drops in the electric field makes it difficult to derive a generalized expression for demulsification rates. From the coalescence mechanism proposed so far, the following parameters are considered to affect the demulsification kinetics:<sup>5)</sup> (operating conditions) voltage, frequency, temperature, degree of mixing, shape and distance of separation of the two electrodes; (emulsion properties) density, viscosity, interfacial tension, water drop size, holdup, surfactant concentration in oil phase, electrolyte concentration in water phase; (electrical properties) conductivity, dielectric constant.

Because of the many parameters to be examined, a complete rate equation which takes into account all these factors has not yet been presented. A few papers have reported the contribution of some of these factors while keeping other conditions constant.<sup>1,2,4,6,13)</sup> Their results, however, have not necessarily agreed with each other, probably because of the differences in demulsifier configuration employed. In the parameters listed above, the coalescence and falling processes of water drops are greatly affected by surroundings viscosity,<sup>3)</sup> but its effect has not been analyzed quantitatively in past works. The viscosity is also known to be one of the major factors that control emulsion stability.<sup>5,8,11)</sup> Therefore, in the present work the demulsification kinetics was investigated at constant voltage by examining primarily the effects of viscosity for each emulsion prepared under various

conditions. The contributions of drop size, holdup, surfactant concentration, agitation speed and operating temperature were studied to evaluate the demulsification rates.

## 1. Experimental Procedure

### 1.1 Demulsification apparatus and operation

The batch demulsification apparatus shown in Fig. 1 is similar to that used by Fujinawa *et al.*<sup>1)</sup> The demulsifier was made of acrylic-resin tube equipped with an annular jacket to keep the emulsion temperature constant during the run. The copper disk electrode, 41 mm in diameter, was set at the bottom and grounded. The glass-sealed electrode was made of 8 mm-diameter glass tube of 1 mm thickness and was placed 80 mm above the disk electrode. The tube was filled with saturated aqueous sodium chloride solution into which a 2 mm-diameter copper wire was immersed. A.C. 15 kV of 60 Hz was applied between the two electrodes in all experiments. Unless otherwise noted, the experiments were carried out using 120 cm<sup>3</sup> emulsion at 30°C without stirring the contents. After the start of demulsification, the variation of volume of both the water and oil layers was measured at an appropriate time interval.

### 1.2 Preparation of emulsion

The original W/O emulsion was prepared by mixing 40 cm<sup>3</sup> kerosene solution containing 2 wt% Span 80 (Kao-Atlas Co.) and 80 cm<sup>3</sup> aqueous solution of 20 mol/m<sup>3</sup> copper sulphate with homogenizer (Nihon Seiki Co.) at 83 s<sup>-1</sup>. The emulsion for the run was prepared by mixing 120 cm<sup>3</sup> original emulsion with 40 cm<sup>3</sup> solution of kerosene and liquid paraffin containing 2 wt% Span 80. The standard sample prepared by this method contained water drops of 5.33 μm average diameter and had 50% water-phase holdup. The viscosity of the oil phase was altered by changing the composition of oils used to dilute the original emulsion. Samples of different drop sizes were prepared by changing the agitation speed of the homoge-

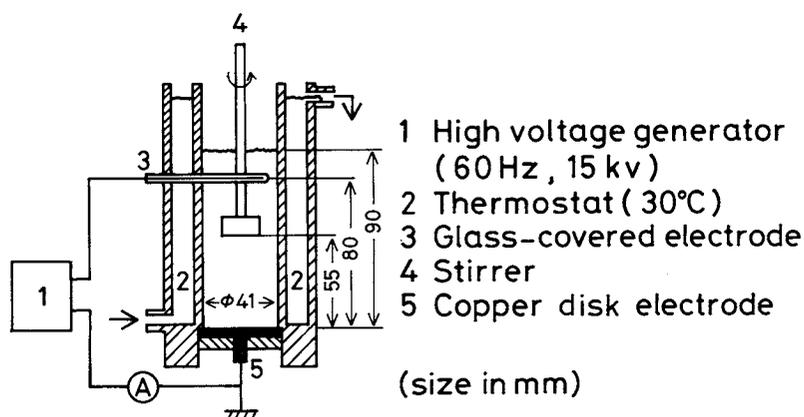


Fig. 1. Experimental apparatus

nizer in the range of  $50$  to  $183\text{ s}^{-1}$ . The water-drop diameter in these emulsions showed a log-normal distribution.<sup>8)</sup> The holdup of water phase was controlled by changing the volume ratio of dilution oil to original emulsion. The viscosity of oil phase and emulsion was measured with a Type B rotational viscometer (Tokyo Keiki Co.). The interfacial tension between aqueous solution and oil phase which constituted the emulsion was measured by a pendant drop method. Both measurements were conducted at the same temperature as in the demulsification run.

### 1.3 Evaluation of demulsification rates

Figure 2 shows an example of demulsification behavior. The extent of demulsification, which was defined as the fraction of the separated water-phase volume against the initial one, showed a gradual increase at an early stage followed by constant increase and subsequent convergence to completion.

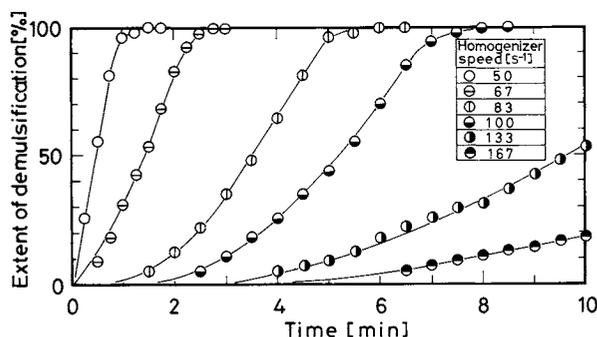


Fig. 2. Time course of demulsification ( $\mu_{\text{oil}} = 3.22\text{ mPa}\cdot\text{s}$ ,  $\phi_w = 0.62$ ,  $N = 3.33\text{ s}^{-1}$ )

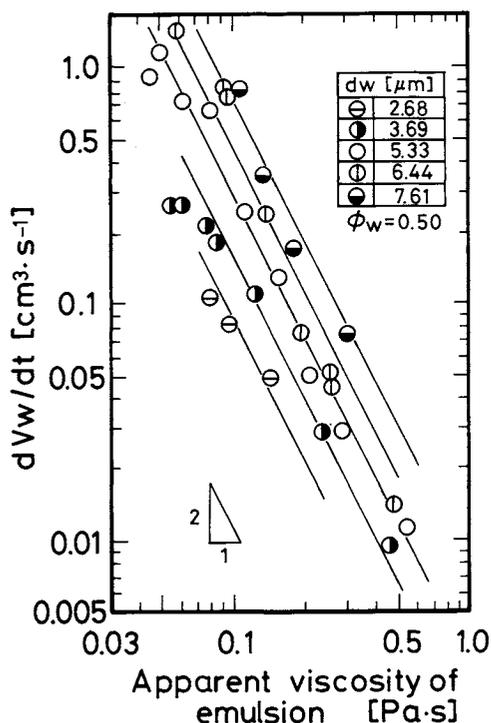


Fig. 3. Effect of emulsion viscosity on demulsification rate for emulsions of different drop size

Such a sigmoidal pattern may be obtained due to batch operation. The demulsification rate  $dV_w/dt$  was evaluated at the point of 50% demulsification where the water layer was formed at nearly constant velocity. The electric current was maintained at approximately  $0.22\text{ mA}$  until 80% demulsification was attained and then it dropped gradually

## 2. Experimental Results

The effects of operating and emulsification conditions were studied by examining the viscosity dependence of the demulsification rates for each emulsion.

### 2.1 Effect of water drop size

The effect of water drop size was studied by changing the diameter from  $2.68$  to  $7.61\text{ }\mu\text{m}$  at constant water-phase holdup and surfactant concentration. The results are plotted against the viscosity of emulsion and oil phase in Figs. 3 and 4, respectively. Each emulsion had the same dependence on emulsion viscosity ( $-2.0$  power) and oil-phase viscosity ( $-3.2$  power). In Fig. 3, the apparent viscosity at a shear rate of  $10\text{ s}^{-1}$  was adopted as the emulsion viscosity, since the emulsion was a non-Newtonian fluid. The exponent of the viscosity nevertheless remained constant at other shear rates because the parallel linear relation between logarithmic viscosity and logarithmic shear rates held for a series of the emulsion tested.<sup>8)</sup> Ino *et al.* correlated demulsification rates linearly with emulsion viscosity, which varied as a result of water-phase holdup change.<sup>2)</sup> In deriving

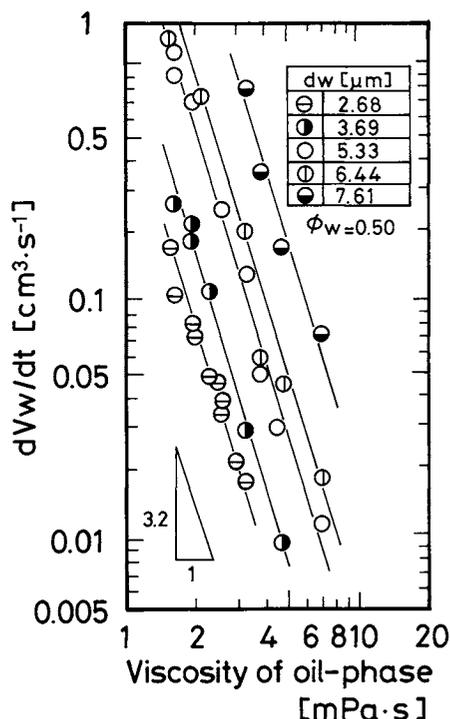


Fig. 4. Effect of oil-phase viscosity on demulsification rate for emulsions of different drop size

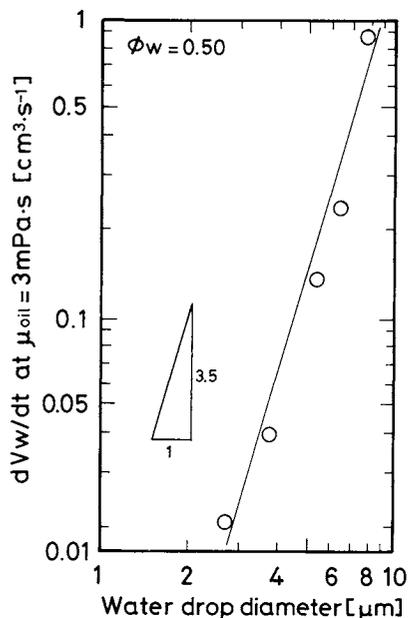


Fig. 5. Effect of water drop size on demulsification rate

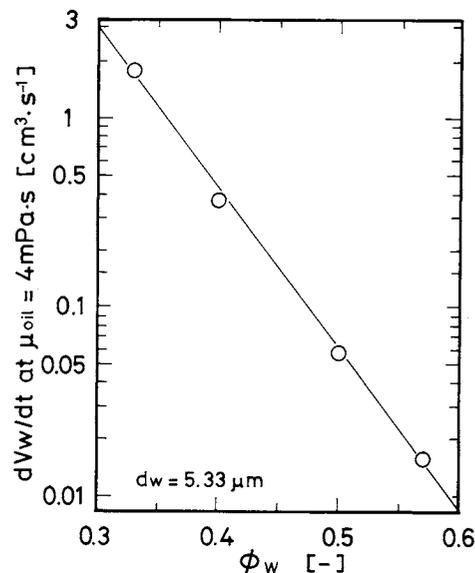


Fig. 7. Effect of water-phase holdup on demulsification rate

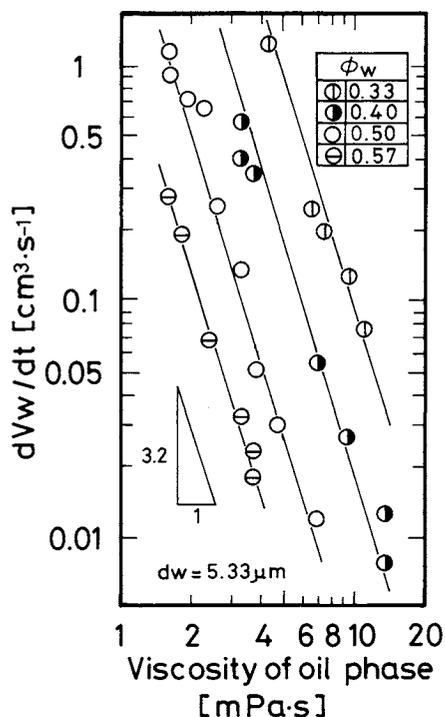


Fig. 6. Effect of oil-phase viscosity on demulsification rate for emulsions of different water-phase holdup

the equation which correlates the demulsification kinetics, it is considered preferable to employ oil-phase viscosity rather than emulsion viscosity because the latter varies with drop size and water-phase holdup in addition to oil-phase viscosity. Therefore, the oil-phase viscosity was used to analyze the experimental data in the following discussion. **Figure 5** shows the dependence on drop size at a certain oil-phase viscosity. The drop size in this figure is the Sauter mean diameter. The exponent 3.5 obtained is

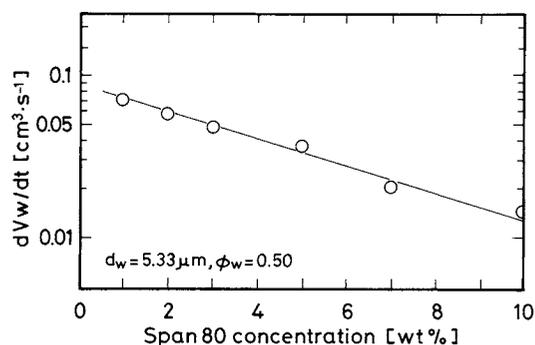


Fig. 8. Effect of surfactant concentration on demulsification rate

close to that of Fujinawa *et al.* who reported 3.0.<sup>11)</sup>

## 2.2 Effect of water-phase holdup

**Figure 6** shows the dependence on the oil-phase viscosity of emulsions having 33 to 57% water-phase holdup. The slopes of all straight lines were the same as in **Fig. 4**. The contribution of holdup derived from **Fig. 6** could be expressed well by an exponential function as shown in **Fig. 7**. The demulsification rate was found to increase considerably with a slight decrease of water-phase volume. The rapid rate decrease with holdup may be attributed to the variation of electrical properties by the increase of water content in the emulsion.

## 2.3 Effect of surfactant concentration

The increase of surfactant Span 80 concentration retarded the demulsification exponentially as shown in **Fig. 8**. Fujinawa *et al.* obtained a  $-0.5$  power dependence concerning the same point.<sup>11)</sup> The demulsification depression by surfactant has been explained as an effect of an increase in stability of the interface surrounding each water drop.<sup>4,13)</sup> The range of surfactant concentration studied, however, is over

1 wt%, which is rather in excess of the critical micelle concentration. Therefore, it is difficult to expect further stability increase by surfactant addition in the present case. To elucidate the cause of rates decrease, the experimental points shown in Fig. 8 were replotted in the same manner as in Fig. 4 while taking into account the increase of oil-phase viscosity by surfactant addition. As a result, all the points agreed with the correlating line for  $d_w = 5.33 \mu\text{m}$  in Fig. 4. This finding indicated that the rate decrease caused by the increase of surfactant concentration was mainly because of viscosity rise.

#### 2.4 Effect of agitation speed in demulsifier

There existed a linear relationship between the demulsification rates and the agitation speeds of the demulsifier, as shown in Fig. 9. Although the exact mechanism of the acceleration observed is not clear, stirring is supposed to increase the probability that water drops are brought into the electric field formed by the two electrodes. The dependence on the oil-

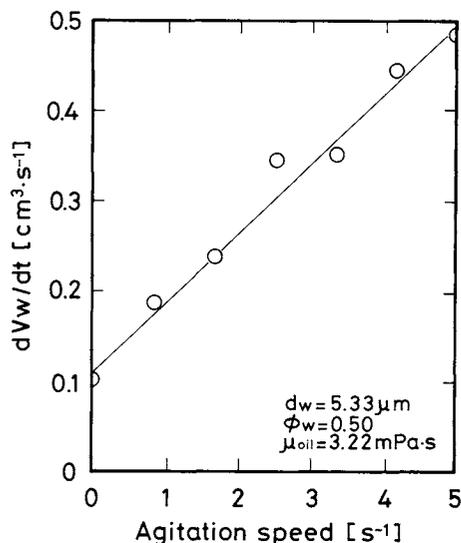


Fig. 9. Effect of agitation speed on demulsification rate

phase viscosity under stirring was the same as in Fig. 4 regardless of agitation speed.

#### 2.5 Effect of operating temperature

Figure 10 shows Arrhenius-type plots of the demulsification rates, which demonstrate a sharp rate increase with temperature rise. Such an acceleration effect of temperature has not been studied in detail so far, although temperature is one of the most fundamental operating parameters. An apparent activation energy of 80 kJ/mol was calculated from this plot. As mentioned previously, the demulsification rate is proportional to the  $-3.2$  power of the oil-phase viscosity. The viscosity varied with temperature and its dependence was expressed satisfactorily by the well-known Andrade equation as shown in Fig. 10. To evaluate the intrinsic temperature dependence of the demulsification rates where the viscosity effect was separated, the product of the rates and the 3.2 power of the oil-phase viscosity at each temperature were replotted in the same figure. The resulting temperature dependence also satisfied the Arrhenius-type equation having an apparent activation energy of 22.5 kJ/mol. This may express the change of emulsion stability with temperature rise.

### 3. Discussion

#### 3.1 Derivation of the correlating equation

The correlating equation of the demulsification kinetics was derived as follows by summarizing the experimental results obtained in the preceding section.

$$dV_w/dt = 4.18 \times 10^5 \exp(-22500/RT) \mu_{oil}^{-3.2} d_w^{3.5} \\ \times (6.5 + 3.93N) \exp(-19.6\phi_w) \\ \times \exp(-0.111C_s)$$

Figure 11 compares the observed and calculated demulsification rates. There was relatively good agreement over a wide range of operating condi-

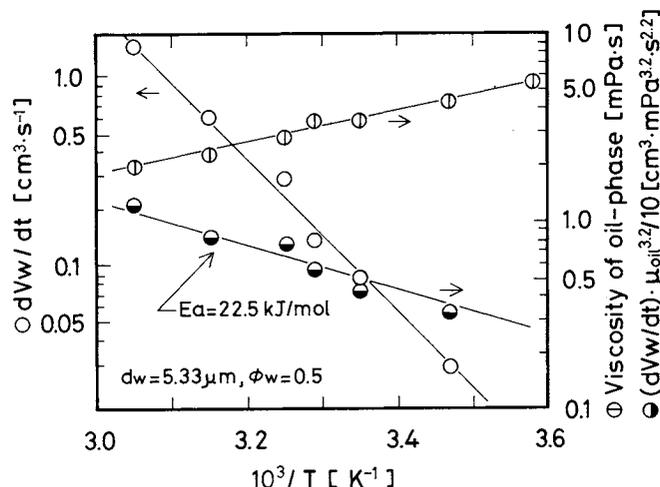


Fig. 10. Temperature dependence of demulsification rate and oil-phase viscosity

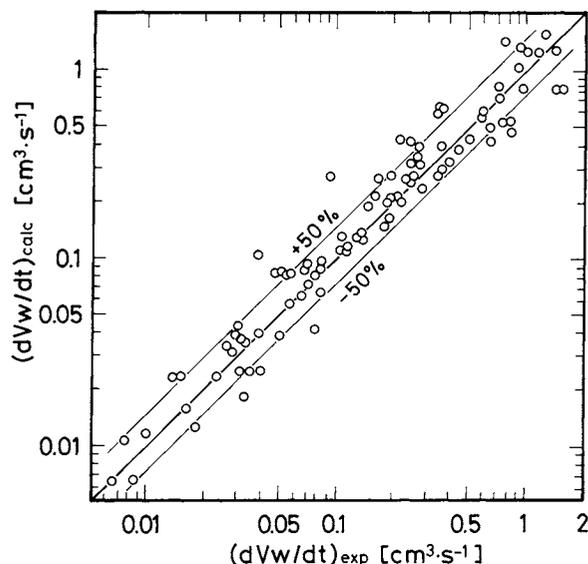


Fig. 11. Comparison of calculated and observed demulsification rates

tions, although some data showed over 50% deviation. Fujinawa *et al.* presented a correlation that considered the effects of water-drop size, surfactant concentration, holdup, electrode distance, and applied voltage.<sup>1)</sup> Their results concerning the dependence on water drop size and surfactant concentration do not differ much from those in this study. As for the holdup effect, however, the exponential decrease shown in Fig. 7 was quite different from their results where the rates decreased moderately. According to observations under a microscope, demulsification proceeds by way of coalescence and subsequent sedimentation of water drops.<sup>2,5,12,13)</sup> It is not clear which is the rate-controlling process of the demulsification. Therefore, the above-mentioned rate equation should be regarded as expressing the overall effect of various parameters.

In the present study, the oil-phase composition was altered to increase the viscosity. Therefore, it is necessary to confirm that the variation of oil-phase properties other than viscosity is negligible during the composition change. The density change was slight since it differed by only about 10% for kerosene and liquid paraffin. The interfacial tension between oil phase and water phase was also found to remain almost constant. The change of electrical parameters was studied for the dielectric constant since the electrical force on a water drop is proportional to the dielectric constant of the continuous phase.<sup>3)</sup> The dielectric constant of kerosene containing Span 80 is reported as 2.1–2.2 F/m,<sup>1)</sup> and this is close to that of alkyl naphthenes, which are a major component of liquid paraffin. Therefore, the dielectric constant of oil phase is thought to remain constant. Consequently, the contribution of the oil-phase prop-

erties other than viscosity could be considered negligibly small in the present case.

As pointed out in the introduction, a number of factors affect the demulsification kinetics. It should be noted that the present equation was obtained for emulsions whose water and oil phases were respectively a copper sulfate solution and a mixture of kerosene, liquid paraffin and Span 80. The applicability of the proposed rate equation to emulsions prepared with other organic solvents, surfactants and carrier molecules will be discussed in a subsequent paper. The contribution of demulsifier configuration, which becomes important in scale-up, will also be treated.

### 3.2 Comparison with thermal demulsification

Examination of the temperature effect suggested a decrease of emulsion stability at high temperature. In general, the emulsifying ability of surfactants decreases with temperature rise.<sup>11)</sup> To compare electrostatic demulsification behavior with its thermal counterpart where demulsification occurs due only to stability decrease, demulsification without electric field was carried out at high temperature. Emulsions having large water drops were utilized to accelerate the demulsification, and the contents were agitated to prevent the creaming of emulsion during long operation time. The thermal demulsification in the range of 50 to 75°C yielded an apparent activation energy of about 90 kJ/mol, which was close to the 80 kJ/mol observed under an electric field. This result means that the temperature effect observed under an electric field indicates a decrease of emulsion stability.

### 3.3 Favorable conditions to accelerate demulsification

The increase of oil-phase viscosity, which is desirable to suppress emulsion breakup in extraction processes,<sup>8,9)</sup> is unfavorable for demulsification. Two ways to accelerate demulsification without adding any organics to decrease the oil-phase viscosity may be suggested by the present study. 1) Operation at high temperature is effective as described in the preceding section, although it requires warming. 2) Stirring of the emulsion during operation is another way which is simple compared to raising the temperature. Even mild stirring results in a marked increase in the rate. These suggestions may be useful for continuous extraction processes with W/O emulsion.

### Conclusion

The kinetics of electrostatic demulsification was investigated by examining primarily the effects of viscosity for each emulsion prepared under various conditions, and the following results were obtained.

1) Demulsification behavior was affected by both emulsifying and demulsifying conditions. The demulsification rate increased considerably with increasing water-drop size and with decreasing oil-phase

viscosity, water-phase holdup and surfactant concentration. These effects were expressed by power or exponential functions. Temperature had a pronounced acceleration effect which could be described by an Arrhenius-type equation. Stirring of the emulsion during the operation was found to promote demulsification and its contribution was expressed by a linear function.

2) A rate equation composed of suitable functions for each factor showed satisfactory agreement with observed rates over a wide range of experimental conditions.

3) The temperature dependence of thermal demulsification was close to that of electrostatic demulsification. Therefore, the acceleration by temperature rise under an electric field was thought to be caused by a decrease of emulsion stability and oil-phase viscosity.

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#### Nomenclature

$C_s$	= surfactant concentration	[wt%]
$d_w$	= water drop diameter in W/O emulsion	[ $\mu\text{m}$ ]
$N$	= agitation speed of demulsifier	[ $\text{s}^{-1}$ ]
$R$	= gas constant	[J/mol·K]
$T$	= temperature	[K]
$t$	= time	[s]
$V_w$	= volume of water phase separated	[ $\text{cm}^3$ ]

$\mu_{\text{oil}}$	= oil-phase viscosity	[mPa·s]
$\phi_w$	= water-phase holdup	[-]

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