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Demulsification of Water-in-Oil Emulsions by Use of a High Voltage ac Field

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ABSTRACT

The demulsification kinetics of water-in-oil (W/O) emulsions in a high ac electric field was investigated by using a batch cylindrical demulsifier. The oil phase was liquid paraffin containing 1–10 wt% SPAN80 or ECA4360 as surfactant. The aqueous phase was deionized water containing 0–40 wt% H_2SO_4 solution. The rate of demulsification was studied experimentally. The effects of emulsion structure and properties (water drop size, aqueous-phase electrolyte concentration, surfactant concentration, surfactant type) and demulsifying conditions (applied voltage, distance between electrodes) on demulsification rates are discussed. An empirical correlation is presented for estimation of the demulsification rate of W/O emulsions in a high ac electrostatic batch demulsifier.

Key Words. W/O emulsion; Demulsification; Electric field; ac potential; Emulsion liquid membrane

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INTRODUCTION

An emulsion liquid membrane (ELM) system can be used efficiently in the extraction and concentration of solutes such as metal ions, weak bases, weak acids, and proteins from dilute aqueous solutions. The potential application of ELM technology has been employed successfully in the fields of hydrometallurgy (1, 2), water purification treatment (3, 4), hydrocarbon separation (5–7), and purification of biochemical (8–12) and biomedical (13, 14) products. The ELM system consists of an emulsion of two immiscible phases dispersed by agitation in a third phase. At the end of extraction operation, the emulsions are separated from the external continuous phase by settlement, and the internal concentrated phase may be recovered by breaking the emulsions into an enriched aqueous phase and an oil phase. This demulsification step is generally required for product recovery from stripped emulsions in a separation process using an ELM system. Therefore, an effective demulsification technique must be established in order for the ELM process to be truly developed into an industrial application. Among the many different methods of demulsification, the method of electrically enhanced demulsification in a high voltage field is one of the most effective demulsification methods (15, 16). The action of an electric field on an emulsion produces effects like drop disintegration, drop enlargement, and enhanced coalescence. High and low field intensities modify droplet displacements due to electrostatic forces. Various types of electric fields (ac or dc) facilitate droplet coalescence and drop enlargement in the dispersion (17).

The purpose of this study is to present experimental results on demulsification of W/O emulsions by application of a high voltage ac field in a batch system. The demulsification rates under various operational conditions are summarized in the form of a semimechanistic empirical correlation which may be useful for future design calculations.

EXPERIMENT

Two types of nonionic surfactants, SPAN80 (Wako Pure Chemical Industries) and ECA4360 (Exxon Chemical Co.), without further purification, were used for emulsion formulation. ECA4360 and SPAN80 are commercial products that have been commonly used in ELM formulations. Liquid paraffin (PO7174, Merck Co.) was chosen as the oil phase. The aqueous phases were solutions of sulfuric acid dissolved in deionized water of different concentrations. The water-in-oil (W/O) emulsions were prepared by dispersing the aqueous phase into the stirred surfactant–oil mixture. To obtain different drop sizes, the oil/water mixture was emulsified by a high shear stress mechanical homogenizer (Waring blender and IKA-Ultra-Turrax disperser) or/and ultrasonic equipment (SONIPREP type 150, MSE Scientific Instruments Co.) under different conditions. The drop size was determined by the microphotography method. The Sauter mean diameter was calculated by analyzing more than 200 drops for each sample.

The demulsification apparatus used in this study is schematically shown in Fig. 1. The demulsifier was made of an acrylic resin tube with inside dimensions of 7 cm in diameter and 10 cm in height. A bare stainless plate was installed at the bottom of the cell and grounded. The high voltage glass-insulated electrode was made of a Pyrex glass cup of 6 cm outside diameter and 0.2 cm thickness, and it was placed 2–6 cm above the grounded electrode. The cup was filled with a 10-mL saturated sodium chloride aqueous solution into which a copper wire was immersed. For insulation purposes, 100 mL silicone oil was placed in the upper layer of the cup. A high ac electric potential of 2.5–20 kV (60 Hz) was applied between the two electrodes. The safe electric current was 5 mA. If the electric current jumped beyond 5 mA, the demulsification system automatically shut down. The amount of emulsion used in the cell was just enough to immerse the bottom of the cup. Each experiment was operated at room temperature. The heat generated due to electricity input was only minimal and hardly changed the temperature of the emulsion (less than 2°C) during the time of demulsification. The demulsification was thus assumed to be a constant temperature operation.

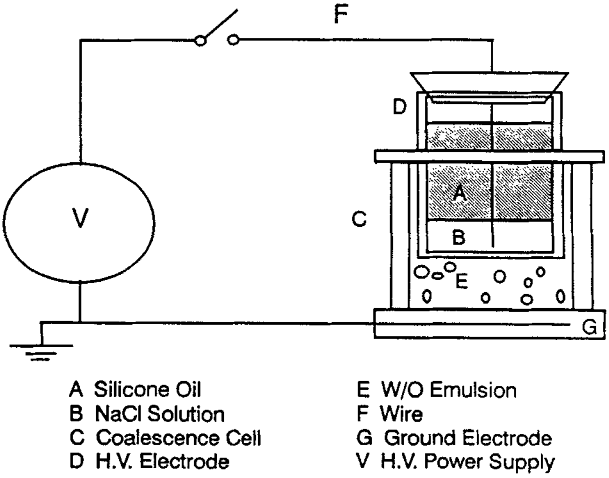

FIG. 1 The batch demulsifier.

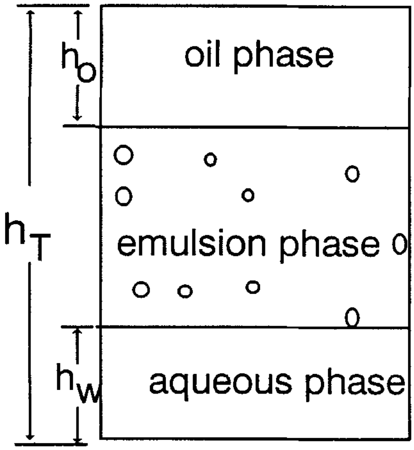

FIG. 2 A typical plot of phase separation of emulsions in the demulsification process.

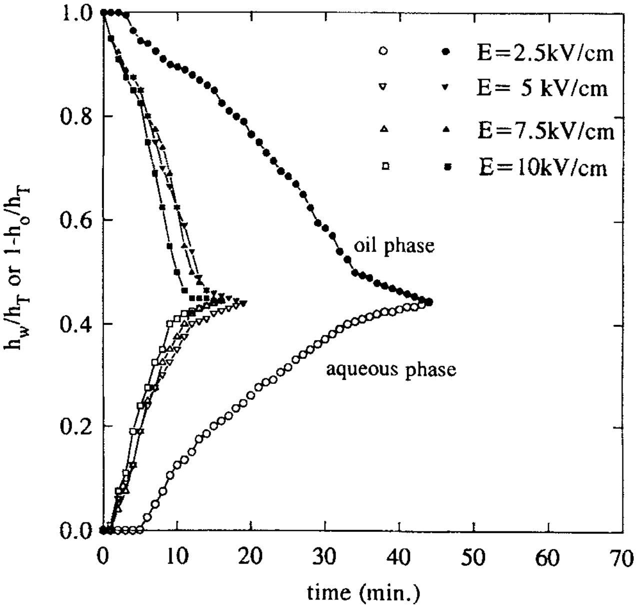

FIG. 3 A typical plot of variation of heights with time: C_s = 6 wt% ECA4360, C_e = 20 wt% H_2SO_4, ϕ = 0.5.

After the start of demulsification, a clear upper oil phase and clear lower water phases were observed. As time proceeded, the emulsion phase in the middle layer decreased and finally disappeared. A schematic figure of these three zones is shown in Fig. 2. The variation of the heights of the oil layer (h_o) and the water layer (h_w) were measured at time intervals. A typical plot of the results is shown in Fig. 3. The heights of both water and oil layers increased as time elapsed. The slope of the linear part of each experimental curve was defined as the demulsification rate, k_w (aqueous phase) or k_o (oil phase).

RESULTS AND DISCUSSION

Effect of Applied Electric Field Strength

The variation of extent of demulsification with time was measured under different applied voltages (2.5–20 kV) with different distances (2–6 cm) between the two electrodes. The applied electric field strength was defined as the applied voltage divided by the distance. Figure 4 shows the effect of the applied electric field strength on the demulsification rate under otherwise constant emulsion conditions. It was found that the demulsification rate (k_w) increased with the applied electric field strength (E) and

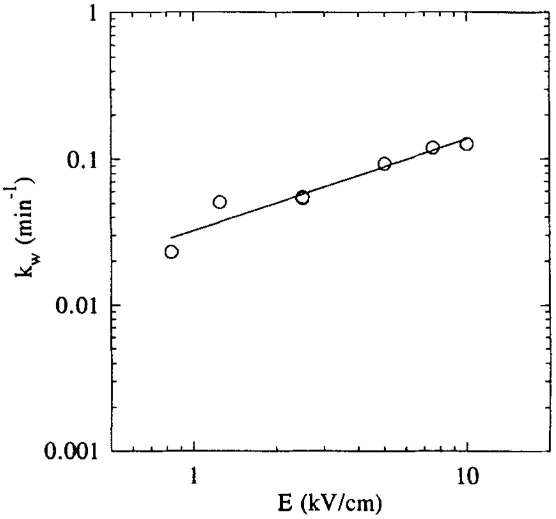

FIG. 4 Effect of electric field strength: C_s = 6 wt% ECA4360, C_e = 0, d = 15.2 μm, ϕ = 0.5.

was approximately proportional to a power of 0.626, that is,

$$k_w \propto E^{0.626} \tag{1}$$

The electric field facilitated the demulsification rate due to electrostatic forces. This finding coincides roughly with the result of Fujinawa et al. (18), who reported that the demulsification rate was proportional to $E^{0.5}$ for a W/O emulsion containing kerosene, SPAN80, and LIX64N as the oil phase and electrolyte solution as the aqueous phase.

Effect of Drop Size

It is known that demulsification proceeds by way of droplet coalescence and subsequent sedimentation of water droplets in the emulsion. Therefore, both coalescence rate and sedimentation rate will influence the overall demulsification rate. According to the theory of Stokes' law, the sedimentation rate is proportional to the droplet size to the power of 2. The larger the droplet size, the faster is the sedimentation rate.

The mechanisms promoting droplet coalescence by electric fields are not well understood. It is accepted that electric fields produce coalescing forces on the droplets in the emulsions. Many models (19) predict that the force is proportional to the field strength or to the square of it. Higher forces imply larger coalescence rates, which in turn produce higher sedimentation rates. Waterman (20) suggested that dipole coalescence operates throughout the bulk liquid in the field, and that the attractive coalescing force between the aligned droplets is proportional to the square of droplet size. Thus, the coalescing force increases enormously as coalescence proceeds. After the water droplets have been coalesced to sufficient sizes under the electric field, they start to settle rapidly.

Since emulsion droplet size changes continuously during demulsification, it is hard to sample and to determine the real droplet size during the demulsification process. Thus, the effect of droplet size on the demulsification rate in the experiment could only be studied by changing the initial droplet diameters from 14.4 to 27.0 μm at constant aqueous-phase holdup, electrolyte concentration, and surfactant concentration. The result is shown in Fig. 5. It was found that the demulsification rate increases significantly with droplet size and that k_w is proportional to $d^{2.21}$.

$$k_w \propto d^{2.21} \tag{2}$$

This result is similar to the results of previous authors. Fujinawa et al. (18) reported that k_w was proportional to d^3, and Hano et al. (21) concluded that k_w was proportional to $d^{3.5}$ in their systems.

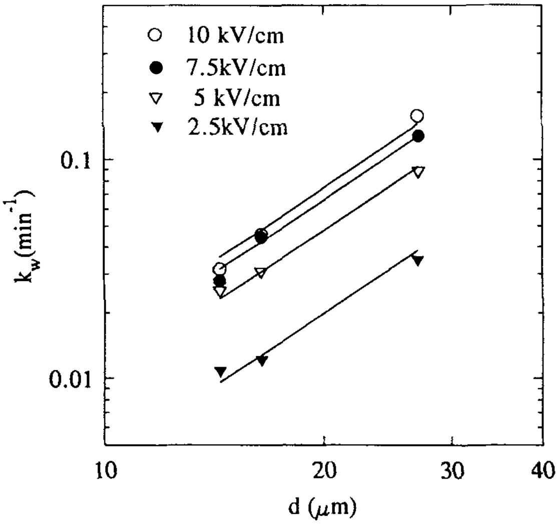

FIG. 5 Effect of drop size: C_s = 6 wt% ECA4360, C_e = 20 wt% H_2SO_4, $\phi = 0.5$.

Effect of Aqueous-Phase Electrolyte Concentration

H_2SO_4 was used as the aqueous-phase electrolyte, and the concentration (C_e) ranged from 0 to 40 wt% at constant aqueous-phase holdup, drop size, and surfactant concentration. Figure 6 shows that the demulsification rate decreased with an increasing concentration of H_2SO_4. By curve fitting of the data, the demulsification rate was found to be proportional to $1 - [0.898C_e/(1.2 + C_e)]$, i.e.,

$$k_w \propto 1 - \frac{0.898C_e}{1.2 + C_e} \tag{3}$$

The density of liquid paraffin is 0.88 g/cm^3. The density of 98 wt% H_2SO_4 is 1.8 g/cm^3 and that of water is 1 g/cm^3, so the higher the concentration of H_2SO_4, the larger the density difference between the dispersed water phase and the continuous oil phase. Generally, it may be stated that the greater the density difference between phases, the easier it is to demulsify. However, a higher electrolyte concentration in the aqueous phase enhances the electric shielding effect and results in reducing the electrostatic force. Such an effect overshadows the effect of density difference between a dispersed aqueous phase and a continuous oil phase. Thus, the overall demulsification rate decreases with an increasing aqueous-phase electrolyte concentration.

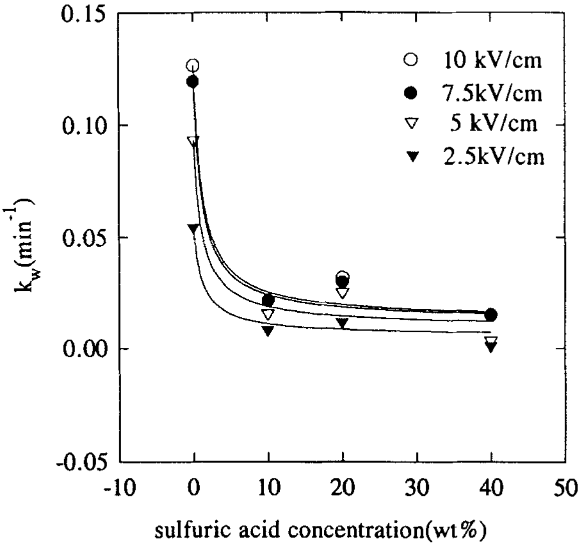

FIG. 6 Effect of electrolyte concentration: C_s = 6 wt% ECA4360, d = 15 μm, ϕ = 0.5.

Effect of Surfactant Concentration

ECA4360 was used as the surfactant at concentrations ranging from 1 to 10 wt% at constant aqueous-phase holdup and electrolyte concentration. Figure 7 shows the effect of surfactant concentration (C_s) on the demulsification rate. Due to the fact that different surfactant concentrations cause different emulsion drop sizes, the effect of C_s on demulsification rate was corrected to $k_w/d^{2.21}$ vs C_s in Fig. 7 in order to normalize the effect of drop size, i.e.,

$$\frac{k_w}{d^{2.21}} \propto 1 + 0.27C_s - 0.02985C_s^2 \qquad (4)$$

There appears to be a maximum point in the curves of Fig. 7. Colinart et al. (22) pointed out that the addition of surfactant to the oil phase brought about two effects, i.e., 1) an increase of the viscosity of the oil phase and 2) the emulsion drops became easier to swell. 1) and 2) have completely opposite effects on the stability of emulsion drops, and, in a sense, these effects compete. Thus, for purposes of application and easy demulsification, the surfactant concentration in the oil phase should be formulated at approximately 5%.

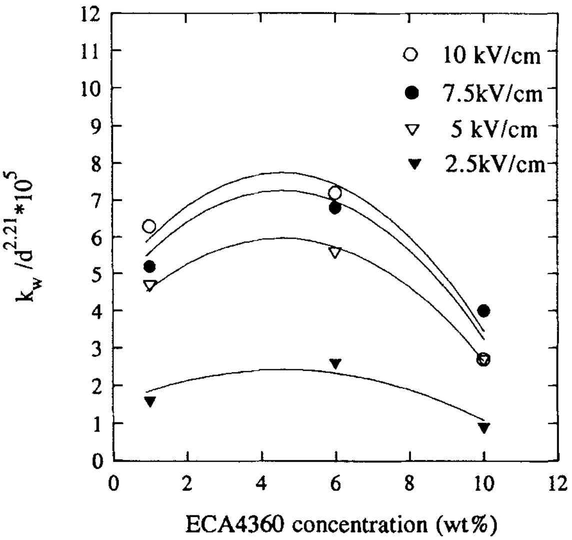

FIG. 7 Effect of surfactant concentration on $k_w/d^{2.21}$: C_e = 20 wt% H_2SO_4, ϕ = 0.5.

Effect of Surfactant Type

ECA4360 and SPAN80 are the two most common surfactants used in ELM. Figure 8 shows that the rates of demulsification in an ac electric field also depend on the type of surfactants used in the make-up of emulsions. ECA4360 is easier to demulsify than SPAN80, and the effect of H_2SO_4 concentration on the demulsification rate of ECA4360 is greater than that of SPAN80. This effect may be related to the different molecular structures and viscosities of these two surfactants.

Derivation of the Correlation Equation

A correlation equation of the demulsification rate may be derived by summarizing the experimental results and Eqs. (1)–(4):

$$k_w = 5.86\times 10^{-5} E^{0.626} d^{2.21} \left(1 - \frac{0.898C_e}{1.2 + C_e}\right)(1 + 0.27C_s - 0.02985C_s^2) \quad (5)$$

Figure 9 compares the experimental and calculated demulsification rates. It is concluded that Eq. (5) can be used to predict the experimental results to within a ±50% error. The correlation equation gave a simple estimation for the design of a demulsification process for the operating ranges used in

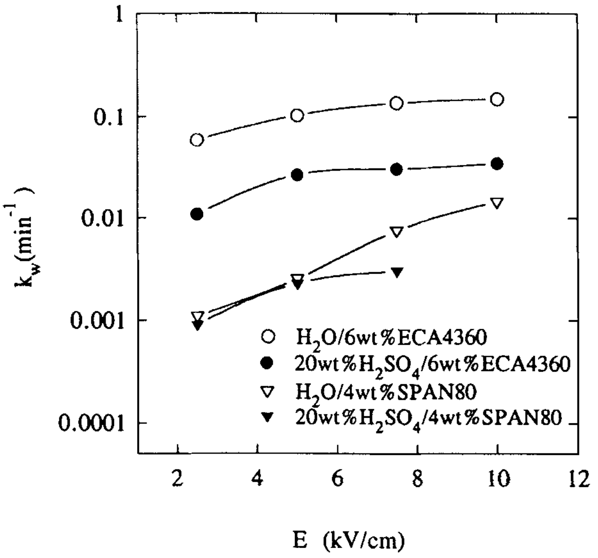

FIG. 8 Effect of surfactant type.

this study. Fujinawa et al. (18) presented a similar correlation for kerosene containing SPAN80 in 1984:

$$\frac{dV_w}{dt} = 1.4 \times 10^8 E^{0.5} H^{1.3} d^3 C_s^{-0.5}(1 - \phi) \tag{6}$$

Hano et al. (21) proposed a correlation for kerosene and liquid paraffin containing SPAN80 in 1988:

$$\frac{dV_w}{dt} = 4.18 \times 10^5 e^{(-22.500/RT)} \mu_{\text{oil}}^{-3.2} d^{3.5}(6.5 + 3.93N) e^{(-19.6\phi)} e^{(-0.111C_s)} \tag{7}$$

Goto et al. (23) proposed a correlation for the rate constant of demulsification in 1989:

$$k \propto E^{0.5} d^3 \tag{8}$$

A theoretical approach to the demulsification mechanism of W/O emulsions under an electric field has not been available in the literature. Although semiempirical correlations such as Eq. (5) and those of others (18, 21) do not elucidate the true mechanism that leads to a more general demulsification rate equation, the correlation presented in this report may be recommended for estimation calculations and the design of a demulsifi-

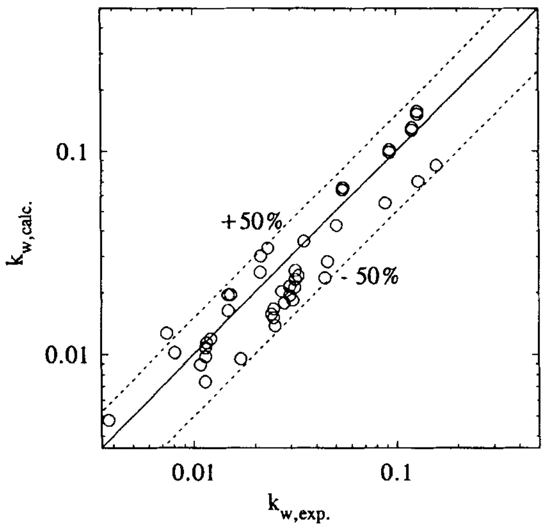

FIG. 9 Comparison of experimental data with correlation equation.

cation process similar to our experimental system. Further semitheoretical analysis of the demulsification process using an ac field must be encouraged.

CONCLUSION

An experimental study has been conducted on the demulsification of W/O emulsions by using a high voltage ac field. A semimechanistic empirical correlation, Eq. (5), is presented for design calculations of a demulsification process similar to our experimental system. Further theoretical approaches to this problem should be anticipated.

NOTATION

C_e	concentration of aqueous-phase electrolyte (wt%)
C_s	concentration of surfactant in oil phase (wt%)
d	aqueous-phase droplet diameter (μm)
E	electric field strength (kV/cm)
h_o, h_w, h_T	heights of oil phase, water phase, and total volume (cm)
H	distance between two electrodes (cm)
k	rate constant of demulsification (s^{-1})
k_o, k_w	demulsification rate of oil phase and water phase (min^{-1})

N	agitation speed of demulsifier (s^{-1})
R	gas constant (J/mol·K)
T	temperature (K)
t	time (s)
V	applied electric voltage (kV)
V_w	volume of aqueous phase separated (cm^3)
μ_{oil}	oil-phase viscosity (mPa·s)
ϕ	aqueous phase holdup (—)

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