

# EFFECTS OF VISCOSITY ON DROP DIAMETER OF W/O EMULSION DISPERSED IN A STIRRED TANK

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The drop diameter of W/O emulsion dispersed in water was measured in a stirred tank. The Sauter mean drop diameter ( $d_{32}$ ) in an emulsion of low viscosity was inversely proportional to the square root of the Weber number which expressed the contribution of impeller diameter, agitation speed, and interfacial tension. In addition,  $d_{32}$  of highly viscous emulsion was proportional to the 0.8 power of the apparent viscosity. The drop diameter also varied with the method of pouring the emulsion into water.

## Introduction

Extraction processes with a liquid surfactant membrane prepared by dispersing W/O emulsion into water have become of interest in recent years. This method has the advantages that the membrane is thin and the interfacial area per unit volume is large. Therefore, it may be promising to apply the method to the separation and concentration of metals that are present at quite low level. In practical extraction processes with a liquid surfactant membrane, it is quite important to increase the stability of the liquid membrane. Viscous compounds such as liquid paraffin are usually added to the oil phase for that purpose. Consequently, the viscosity of W/O emulsion increases and the drop diameter, an important parameter in the discussion of extraction rates, changes more or less. The effects of operating conditions such as impeller diameter and agitation speed on emulsion drop size have been dealt with in a few papers.<sup>5-7,9)</sup>

In the study of liquid-liquid dispersions, in general, the mean drop diameter has been correlated by the Weber number and the contribution of viscosity has not been considered in empirical correlations, since most experiments were carried out with low-viscosity liquids.<sup>8,10)</sup> Some studies have determined the viscosity effects of either continuous or dispersed phases,<sup>1,2,11,12)</sup> but the oil phases studied were homogeneous liquids. Just recently, Kataoka and Nishiki<sup>6)</sup> reported the contribution of oil-phase vis-

cosity in an emulsion dispersion as the 0.25-0.75 power.

In the present study, mean drop diameter of the emulsion dispersed in water was measured at various impeller diameters and agitation speeds in a stirred tank. The effects of these parameters and emulsion viscosity on the drop diameter were discussed in order to propose new correlations.

## 1. Experimental

The original W/O emulsion was prepared by agitating 40 cm<sup>3</sup> kerosene solution containing 2 wt% Span 80 (Kao Atlas Co.) as a surfactant and 80 cm<sup>3</sup> aqueous solution of 0.05 mol/dm<sup>3</sup> nickel(II) sulfate using a homogenizer (Nippon Seiki Co.). The agitation time and speed were 10 min and 83 s<sup>-1</sup>, respectively. In some runs, the agitation speed was varied in the range of 50 to 183 s<sup>-1</sup> in order to change the diameter of inner water droplets. The emulsion for the run was prepared by diluting the original emulsion with a mixture of kerosene and liquid paraffin or machine oil containing 2 wt% Span 80. The volume fraction of water in the emulsion was altered by changing the mixing ratio. Then 100 cm<sup>3</sup> of this diluted emulsion was poured into 500 cm<sup>3</sup> of 0.05 mol/dm<sup>3</sup> aqueous copper(II) sulfate solution and the content was agitated at impeller speeds ranging from 3.33 to 5.83 s<sup>-1</sup>. The temperature was kept at 303 K during the run. Two pouring methods were employed in this study. In method A, the emulsion was gently settled above the aqueous solution and then stirred. In method B, the emulsion was poured by using a pipet into the center of the solution under agitation.

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All experiments were performed with a stirred tank made of glass and equipped with four stainless steel baffle plates. The inside diameter of the tank was 0.105 m. The impellers employed were six-bladed fan turbines made of stainless steel or acrylic resin, of diameters 0.04, 0.05 and 0.06 m. To prevent incomplete dispersion of W/O emulsion, the impeller was located at such a position that the upper end of the blade was in contact with the interface between the emulsion and aqueous solution. The dispersed drop diameters of the W/O emulsion were measured by taking photographs through the tank wall using an electronic flash at a prescribed time after starting the agitation. The Sauter mean diameter ( $d_{32}$ ) observed after 30 min agitation was regarded as the steady-state drop diameter. In some runs, drop diameter increased after reaching the minimum, in which case the minimum diameter was adopted as the steady-state drop diameter. The emulsion viscosity was measured by a type B rotational viscometer (Tokyo Keiki Co.). Since the emulsion showed non-Newtonian behavior, the viscosity observed at a shear rate of  $10\text{ s}^{-1}$  was considered as the apparent viscosity in the treatment of data. The apparent interfacial tension between the oil phase in the emulsion drop and the external water phase (aqueous copper(II) sulfate solution) was measured by a pendant drop method.

In the correlation of drop diameter stated below, the interfacial tension and viscosity measured before mixing the emulsion with aqueous solution were used to simplify the treatment. Although these values changed to some extent during dispersion, no appreciable influence on the correlation was observed.

## 2. Results

### 2.1 Effects of oil-phase composition

Figure 1 shows the variation of the apparent emulsion viscosity  $\mu$ , the apparent interfacial tension  $\sigma$  between the oil phase in the emulsion drop and the external water phase, and the steady-state mean diameter  $d_{32}$  of emulsion drops when the volume fraction  $\phi_p$  of liquid paraffin in oil phase is raised. The viscosity progressively rose as  $\phi_p$  increased, whereas the interfacial tension decreased at  $\phi_p > 0.25$ . The drop diameter, however, was nearly constant at  $\phi_p < 0.25$  and then increased. This behavior was close to the viscosity change pattern. The increase of drop diameter with decreasing interfacial tension shown in Fig. 1 is not in accord with the results reported so far. This may be because of the larger contribution of the viscosity compared to that of the interfacial tension.

### 2.2 Effects of volume fraction $\phi_w$ of water in W/O emulsion

Figure 2 shows the variation of  $\mu$ ,  $\sigma$ , and  $d_{32}$  with the volume fraction  $\phi_w$  of water in W/O emulsion. Both the interfacial tension and the viscosity in-

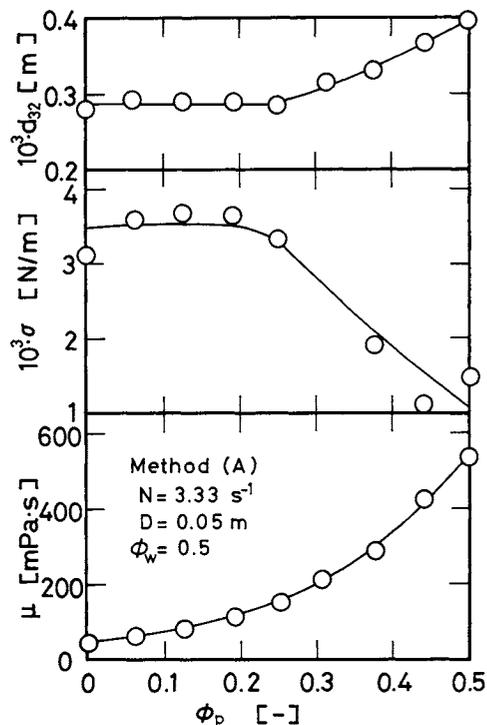


Fig. 1. Effects of oil phase composition on  $d_{32}$ ,  $\mu$ , and  $\sigma$ .

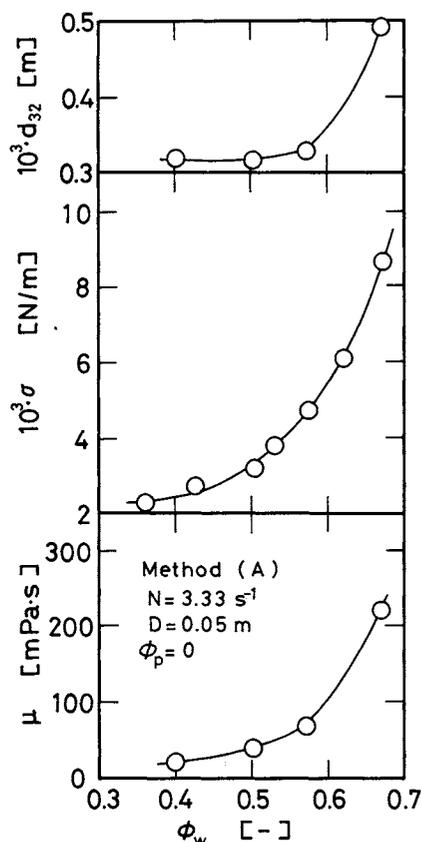


Fig. 2. Effects of water volume fraction in emulsion on  $d_{32}$ ,  $\mu$ , and  $\sigma$ .

creased considerably as  $\phi_w$  increased, resulting in a sharp increase of drop diameter at  $\phi_w > 0.6$ .

### 2.3 Effects of agitation speed

Figure 3 shows the effects of agitation speed  $N$  on

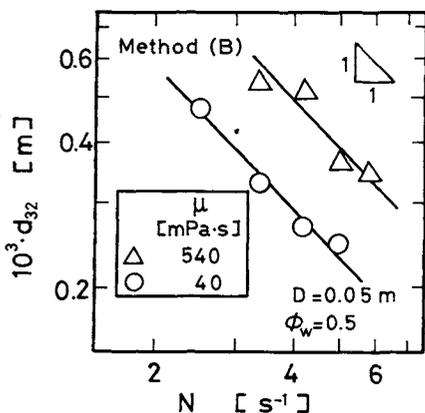


Fig. 3. Effects of agitation speed on drop diameter.

the drop diameter for two kinds of emulsion having apparent viscosity of 540 and 40 mPa · s. In these runs, the viscosity was altered by changing the oil-phase composition. Both emulsions showed an inverse proportionality of  $d_{32}$  to  $N$  which was in agreement with past studies.<sup>5,7)</sup>

#### 2.4 Effects of impeller diameter

Figure 4 shows the effects of impeller diameter  $D$  on the drop diameter for two kinds of emulsion having apparent viscosity of 290 and 60 mPa · s. The viscosity was altered in the same way as in Fig. 3. The values of  $d_{32}$  were found to be inversely proportional to the square root of  $D$ , which was also in agreement with past studies.<sup>5,7)</sup>

#### 2.5 Effects of W/O emulsion viscosity

The effects of viscosity on the drop diameter were examined since a different correlation was obtained depending upon the viscosity, as shown in Figs. 3 and 4. Figure 5 shows the relation between the emulsion viscosity and drop diameter at  $N = 3.33 \text{ s}^{-1}$  and  $D = 0.05 \text{ m}$ . The viscosity in these runs was altered by adding liquid paraffin or machine oil to the original emulsion. The drop diameter was found to increase when the viscosity exceeded 150–200 mPa · s, whereas there was no effect in the low-viscosity region.

### 3. Discussion

#### 3.1 Correlation of drop diameter with the Weber number

In most works concerning liquid–liquid dispersion, drop diameter has been correlated by using the Weber number ( $We = N^2 D^3 \rho / \sigma$ ).<sup>8,10)</sup> The same correlation was applied to the present case. Figure 6 plots the drop diameter observed at three impeller diameters (0.04, 0.05 and 0.06 m) and two agitation speeds (3.33 and 5.00  $\text{s}^{-1}$ ). Each emulsion having low, medium and high viscosity gave parallel straight lines with slopes of  $-0.5$ . This dependence on the Weber number is the same as that reported by Imai and Furusaki<sup>5)</sup> and Kishimoto *et al.*<sup>7)</sup> On the other hand, different dependence was reported, such as  $-0.89$

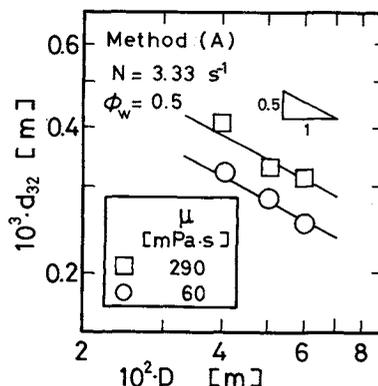


Fig. 4. Effects of impeller size on drop diameter.

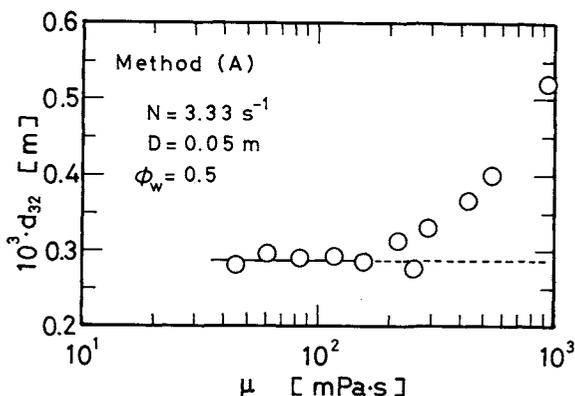


Fig. 5. Effects of emulsion viscosity on drop diameter.

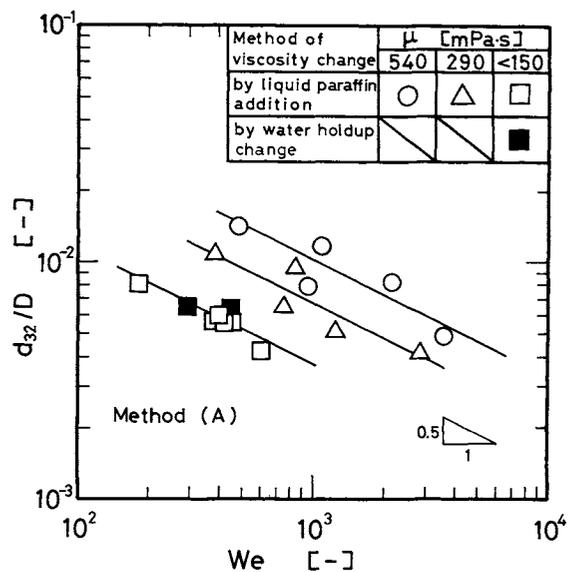


Fig. 6. Correlation of drop diameter with the Weber number (emulsion poured by method A).

power (Takahashi *et al.*<sup>9)</sup>) or  $-0.375$  power (Kataoka and Nishiki<sup>6)</sup>), using the same surfactants. These inconsistencies are considered to arise from differences in experimental apparatus (impeller type and position) and data treatment methods (sampling time and diameter measuring method.)

#### 3.2 Effects of dispersed-phase viscosity

As can be seen from Fig. 6, the drop diameter

increased with increasing dispersed-phase viscosity. To obtain equations which predicted the effects of viscosity, the values of  $(d_{32}/D)We^{0.5}$  were plotted against the emulsion viscosity for all the experimental data. The results are shown in Fig. 7, where  $\mu$  is the apparent viscosity at a shear rate of  $10\text{ s}^{-1}$ . It is proved that  $(d_{32}/D)We^{0.5}$  is proportional to  $\mu^{0.8}$  when  $\mu$  exceeds  $160\text{ mPa}\cdot\text{s}$ . Consequently, the correlations for drop diameter could be written as follows.

$$d_{32}/D = 0.12We^{-0.5} \quad \text{for } \mu < 160\text{ mPa}\cdot\text{s} \quad (1)$$

$$d_{32}/D = 0.0020\mu^{0.8}We^{-0.5} \quad \text{for } \mu > 160\text{ mPa}\cdot\text{s} \quad (2)$$

These correlations predict that the dispersed-phase viscosity influences the drop diameter in the dispersion of W/O emulsion. Since most of the studies published so far have dealt with liquid-liquid dispersion systems of low viscosity and without surfactants, they have neglected the contribution of dispersed-phase viscosity except for a few papers. Yamaguchi *et al.*<sup>12)</sup> reported that the interfacial area per unit drop volume was proportional to the  $-0.13$  power of the dispersed-phase viscosity. This means  $d_{32}$  is proportional to  $\mu^{0.13}$ , which is different from the present results. The lower dependence may be due to low viscosity of liquid-liquid dispersion systems studied without surfactant. Calabrese *et al.*<sup>1,11)</sup> reported the dependence on the dispersed-phase viscosity as the  $3/8$  power in high-viscosity samples ( $5000\text{--}10000\text{ mPa}\cdot\text{s}$ ) and the  $3/4$  power in moderate-viscosity samples ( $100\text{--}1000\text{ mPa}\cdot\text{s}$ ), whereas the influence was negligible in low-viscosity samples ( $1\text{--}100\text{ mPa}\cdot\text{s}$ ). Although strict comparison is not possible since the viscosity in the present study is the apparent value at a certain shear rate, the dependence observed in low- and moderate-viscosity liquids is close to the present results. Kataoka and Nishiki proposed new correlations which included the viscosity ratio of oil and outer aqueous phase.<sup>6)</sup> The dependence on oil-phase viscosity reported is about half the present result. Since the emulsion viscosity is a complex function of oil-phase viscosity, water holdup, and surfactant concentration,<sup>4)</sup> it is difficult to explain the difference in dependence. This point will be discussed in the next paper.

### 3.3 Effects of emulsion pouring method

The experimental data presented in Figs. 6 and 7 were obtained by employing method A, in which the emulsion was settled on the water layer before stirring. In this case, the entrainment of external water phase into the emulsion drop was as high as 5 to 30% of the initial emulsion volume. On the other hand, Fujinawa *et al.*<sup>3)</sup> attained less entrainment by adding

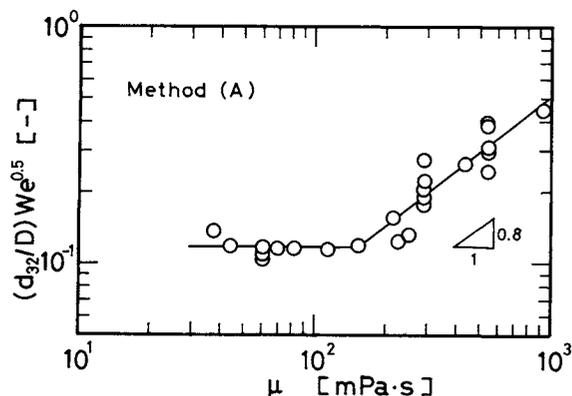


Fig. 7. Relation between  $(d_{32}/D)We^{0.5}$  and  $\mu$ .

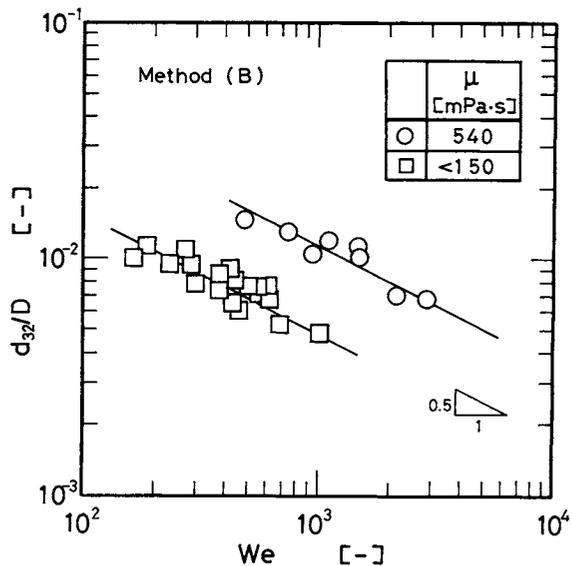


Fig. 8. Correlation of drop diameter with the Weber number (emulsion poured by method B).

the emulsion dropwise into the center of the aqueous solution during stirring. This pouring method, named method B, was applied to examine the effects on drop diameter. Figure 8 shows the relationship between the Weber number and the drop diameter in method B for two kinds of emulsion having different viscosity. Parallel straight lines having a slope of  $-0.5$  were obtained for each emulsion, like the results for method A. The scattering of the data is relatively small, probably because of low water entrainment, whereas the diameter is about 10–20% larger than that in method A. This may arise from the difference in drop formation pattern at the initial non-stationary stage, although no satisfactory explanation can be offered at present.

### Conclusion

Steady-state mean drop diameter of W/O emulsion dispersed in water was measured in a stirred tank under various conditions, and the following results were obtained.

1) Drop diameter was influenced by impeller diameter, agitation speed, and interfacial tension. These contributions could be correlated by the Weber number.

2) The effects of dispersed-phase viscosity on the drop diameter were observed for viscous emulsion. The drop diameter increased in proportion to the 0.8 power of the viscosity when the emulsion viscosity measured at a shear rate of  $10 \text{ s}^{-1}$  exceeded  $160 \text{ mPa}\cdot\text{s}$ .

3) Although drop diameter changed with the methods of pouring emulsion into water, the effects of operating conditions could be described by a similar expression.

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#### Nomenclature

$D$	= impeller diameter	[m]
$d_{32}$	= Sauter mean diameter of W/O emulsion drops	[m]
$N$	= agitation speed in dispersion of emulsion	$[\text{s}^{-1}]$
$We$	= Weber number ( $= N^2 D^3 \rho / \sigma$ )	[—]
$\rho$	= density of continuous phase	$[\text{kg}/\text{m}^3]$
$\mu$	= viscosity of W/O emulsion	$[\text{mPa}\cdot\text{s}]$

$\sigma$	= interfacial tension between oil phase in emulsion drop and external water phase	$[\text{N}/\text{m}]$
$\phi_p$	= volume fraction of liquid paraffin in oil phase	[—]
$\phi_w$	= volume fraction of water in W/O emulsion	[—]

#### Literature Cited

- 1) Calabrese, R. V., T. P. K. Chang and P. T. Dang: *AIChE J.*, **32**, 657 (1986).
- 2) Eckert, R. E., C. M. McLaughlin and J. H. Rushton: *AIChE J.*, **31**, 1811 (1985).
- 3) Fujinawa, K., T. Morishita, M. Hozawa and H. Ino: *Kagaku Kogaku Ronbunshu*, **11**, 293 (1985).
- 4) Hozawa, M., M. Morishita, N. Imaishi, K. Fujinawa and H. Ino: *Kagaku Kogaku Ronbunshu*, **9**, 686 (1983).
- 5) Imai, M. and S. Furusaki: *Kagaku Kogaku Ronbunshu*, **10**, 707 (1984).
- 6) Kataoka, T. and T. Nishiki: *J. Chem. Eng. Japan*, **19**, 408 (1986).
- 7) Kishimoto, S., T. Ikeda, T. Kokugan and M. Shimizu: *Kagaku Kogaku Ronbunshu*, **11**, 616 (1985).
- 8) Komazawa, I.: "Kiho Ekiteki Bunsan Kogaku," p. 108, Maki Shoten, Tokyo (1982).
- 9) Takahashi, K., F. Ohkubo and H. Takeuchi: *Kagaku Kogaku Ronbunshu*, **6**, 651 (1980).
- 10) Taniyama, I.: "Kiho Ekiteki Kogaku," p. 113, Nikkan Kogyo Sinbunsha, Tokyo (1969).
- 11) Wang, C. Y. and R. V. Calabrese: *AIChE J.*, **32**, 667 (1986).
- 12) Yamaguchi, I., S. Yabuta and S. Nagata: *Kagaku Kogaku*, **27**, 576 (1963).