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Photomicroscopic Observation of Dispersion State of Droplets in Flowing Emulsion[1]

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The viscosity of dilute emulsion with disperse phase of volume fraction $\phi=0.005$—0.06 was measured, and the dispersion state of emulsion droplets under shear was observed with a photomicroscope. Oil components used were aromatic hydrocarbons, *i.e.*, benzene, *o*-xylene, and toluene, and saturated hydrocarbons, *i.e.*, cyclohexane, decaline, *n*-hexane, *etc.* As emulsifier, Arlacel 60 or Arlacel 83 was used for W/O type emulsion and Tween 20 for O/W type one. For the W/O type emulsions of aromatic hydrocarbon of low emulsifier concentration (0.2%), Einstein's equation could be applied to the viscosity at a high rate of shear in the range of ϕ below 0.02, in spite of the presence of aggregates of droplets in the flowing emulsion. When ϕ becomes 0.04—0.06, the deviation from Einstein's equation was large. In the case of higher emulsifier concentration (1%), the deviation from Einstein's equation was noticeable even for $\phi=0.01$, when Arlacel 60 was used as stabilizer. The results may be brought about by the increase of effective volume fraction of disperse phase owing to the inclusion of continuous phase liquid in aggregates. In the case of W/O type emulsions of saturated hydrocarbon and O/W type ones, irrespective of the kind of oil phase liquid, the aggregates were completely redispersed into primary droplets at a high rate of shear, and Einstein's equation could be applied.

In our previous studies on non-Newtonian flow of W/O type emulsions,[2] we found that water-in-benzene emulsion (volume fraction of disperse phase, 0.1—0.6) showed the most noticeable dependence of viscosity on the rate of shear and that the dispersed droplets in the system formed large aggregates at a low rate of shear as compared with other emulsions prepared with hydrocarbons other than benzene *i.e.*, cyclohexane, liquid paraffin, *etc.* In order to study the characteristics of non-Newtonian flow of emulsions, photomicroscopic observation of the dispersion state of droplets under shear was made with dilute emulsions (volume fraction, 0.005—0.06),[3] and it was found that in water-in-benzene emulsion, the aggregates formed in the emulsion could not be redispersed into primary droplets even at higher rates of shear than 2000 sec^{-1}.

In this paper, photomicroscopic observations are described on the dispersion state of droplets in the flowing emulsions under shear, where the emulsions show Newtonian flow characteristics and their viscosities can be represented by Einstein's equation.

Experimental

Sample. W/O type emulsions were prepared by using either sorbitan monostearate (Arlacel 60) or sorbitan sesquioleate (Arlacel 83) as stabilizer, and O/W type emulsions by polyoxyethylene sorbitan monolaurate (Tween 20). The oil phase liquids such as benzene, toluene, *o*-xylene, cyclohexane, decaline, kerosene, liquid paraffin, *etc.* were mixed with carbon tetrachloride to adjust their density to that of water. The volume fraction of disperse phase ϕ was 0.005, 0.01, 0.02, 0.04, and 0.06. The emulsions were prepared from water and oil phase liquid containing the emulsifier by shaking by hand or by mixing together with a high-speed mixer.

Measurements. As shown in Fig. 1, a light source and a photomicroscope were placed perpendicular to the axis of the capillary of Maron-Belner type viscometer[4] (capillary: 0.064 cm in diameter and 25.4 cm in length) at an appropriate position where a part of thick glass of the capillary was flatened by polishing. In order to photograph the droplet image moving at a high rate of shear, a Xe-flash system having flash duration time less than 100 μ sec was used as the light source. The circuit of the flash system is shown in Fig. 2. The flashing tube is fed at 3 kV under generation of 15 kV trigger voltage in the starting electrode. Duration time is mainly determined by the capacity of the condenser connected in series with the flashing tube. The system used was provided with a 5 μF condenser.

Aggregates of droplets at various rates of shear were photo-

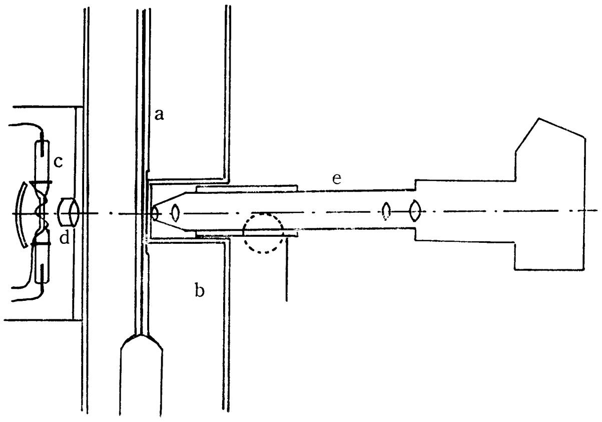

Fig. 1. Vertical section of apparatus.
a. Capillary portion of viscometer
b. Water bath
c. Xe flash tube
d. Condenser
e. Photomicroscope

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[1] Presented at the 21st Symposium of Colloid Chemistry, Kyoto, Nov. 3, 1968.

[2] K. Suzuki, S. Matsumoto, T. Watanabe, and S. Ono, This Bulletin **42**, 2773 (1969).

[3] K. Suzuki, T. Watanabe, and S. Ono, Proc. 5th Intern. Congr. Rheology, Vol. 2, 339 (1970).

[4] S. H. Maron and R. J. Belner, *J. Appl. Phys.*, **26**, 1457 (1955).

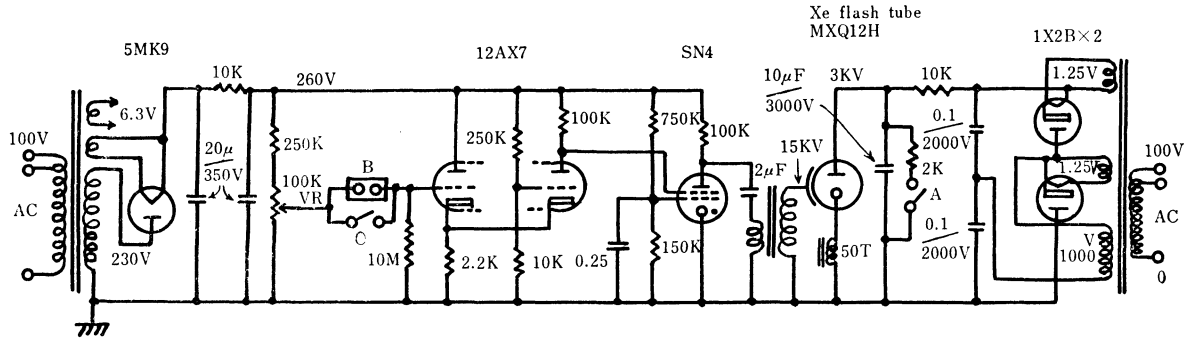

Fig. 2. The circuit of the flash system.
A : Discharge Button B : to Camera Synchro-plug C : Flash Button

graphed and at the same time the viscosity of the emulsion was measured. Measurements were carried out at 32°C in a constant-temperature bath. Viscosity was expressed in terms of relative viscosity η_{rel} defined by

$$\eta_{\mathrm{rel}} = \frac{\text{Viscosity of emulsion}}{\text{Viscosity of continuous phase containing emulsifier}}$$

Results and Discussion

With the exception of W/O type emulsions of aromatic hydrocarbon having volume fraction $\phi=0.04$—0.06, all emulsions showed Newtonian flow characteristics at high rates of shear over 100 sec^{-1}. Relative viscosity (η_{rel}) of the emulsions under a shear stress at the capillary wall, 17 dyne/cm^2, at which the rates of shear exceed 2000 sec^{-1}, are plotted against ϕ (Figs. 3, 4, and 5). The solid lines are drawn according to Einstein's equation.

As shown in Fig. 3, with the emulsion stabilized with 0.2% Arlacel 60, Einstein's equation could be applied to represent η_{rel} of the benzene emulsions with ϕ below 0.02. Figure 6 shows microscopic photographs obtained with the benzene emulsion with $\phi=0.01$. We see that the size of aggregates decreases with the increase of rates of shear. However, the droplets in the flowing emulsion are not dispersed as primary droplets even at high rates of shear of 500—3000 sec^{-1}. When ϕ of benzene emulsions increased to 0.04—0.06, the discrepancy between the observed value of η_{rel} and that calculated by Einstein's equation became large, and the viscosity could be represented by an equation consisting of series of power of ϕ as follows.

$$\eta_{\mathrm{rel}} = 1 + 2.5\phi + 14\phi^2 + 50\phi^3$$

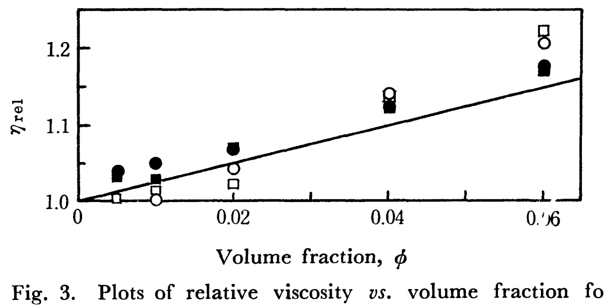

Fig. 3. Plots of relative viscosity *vs.* volume fraction for W/O emulsions stabilized by 0.2% Arlacel 60 at 32°C.
Solid line, calculated by Einstein's equation.
Medium: ○ Benzene (+CCl_4), □ Benzene (+CCl_4) prepared by Mixer, ● Cyclohexane (+CCl_4), ■ Cyclohexane (+CCl_4) prepared by Mixer

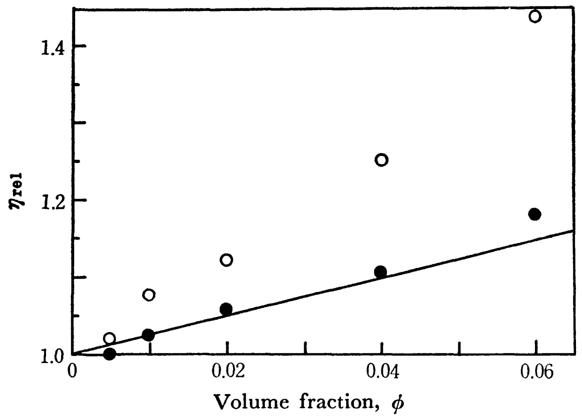

Fig. 4. Plots of relative viscosity *vs.* volume fraction for W/O emulsions stabilized by 1.0% Arlacel 60 at 32°C.
Solid line, calculated by Einstein's equation.
Medium: ○ Benzene (+CCl_4), ● Cyclohexane (+CCl_4)

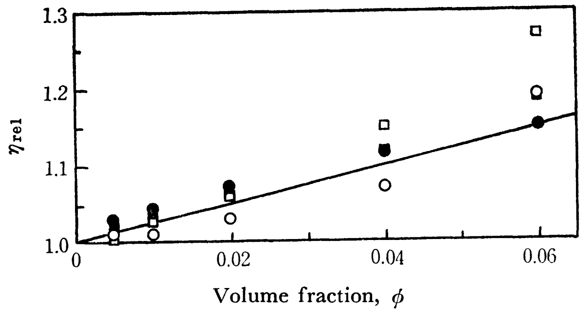

Fig. 5. Plots of relative viscosity *vs.* volume fraction for W/O emulsions stabilized by Arlacel 83 at 32°C.
Solid line, calculated by Einstein's equation.
Medium:
○ 0.2% Arlacel 83-Benzene (+CCl_4)
● 0.2% Arlacel 83-Cyclohexane (+CCl_4)
□ 1.0% Arlacel 83-Benzene (+CCl_4)
■ 1.0% Arlacel 83-Cyclohexane (+CCl_4)

In cyclohexane emulsions shown in Fig. 3, the droplets were completely dispersed as primary ones at high rates of shear of 500—3000 sec^{-1} irrespective of the values of ϕ. The results obtained with toluene and *o*-xylene emulsions were similar to those obtained with benzene system, and the results with the systems using such saturated hydrocarbones as decaline, *n*-

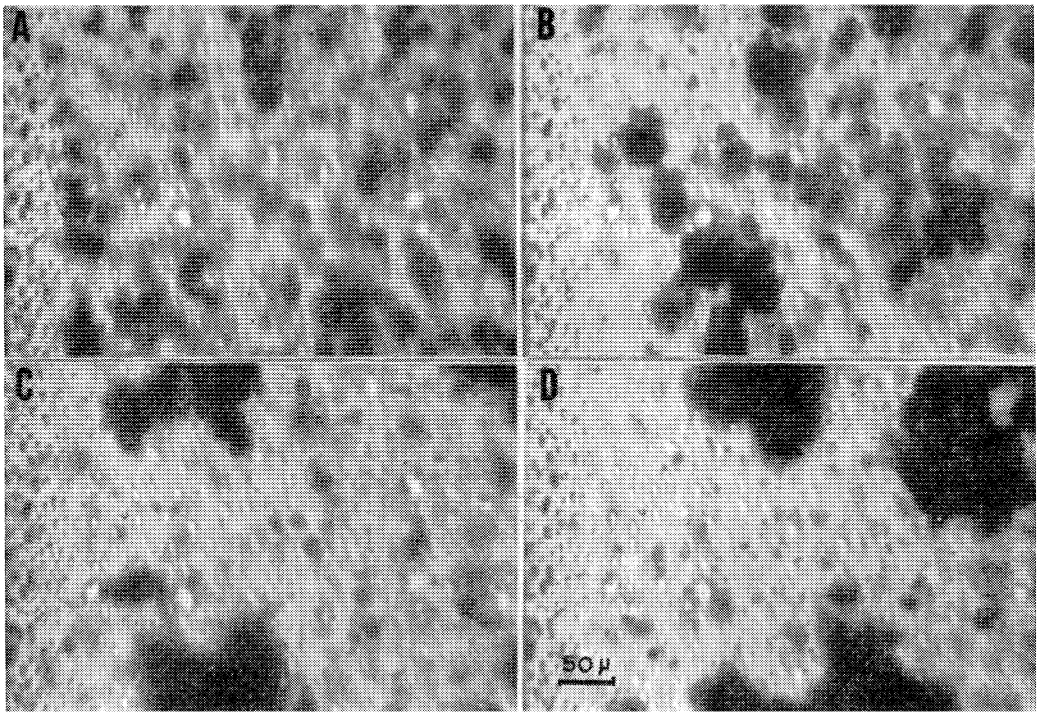

Fig. 6. Water in benzene (+CCl_4) emulsions (ϕ=0.01) stabilized by 0.2% Arlacel 60 prepared by mixer.
shear stress, rate of shear — shear stress, rate of shear
A; 17.2 dyn/cm², 2740 sec⁻¹ — B; 7.65 dyn/cm², 1218 sec⁻¹
C; 3.48 dyn/cm², 555 sec⁻¹ — D; 1.43 dyn/cm², 228 sec⁻¹

hexane, *etc.* as the suspending fluids were similar to those obtained with cyclohexane systems.

As shown in Fig. 4, in the benzene emulsions stabilized with 1% Arlacel 60, there were marked discrepancies between the value of η_{rel} and that calculated by Einstein's equation even with the emulsion of $\phi=0.01$. Even with the emulsion of $\phi=0.005$ showing Newtonian flow characteristics at a high rate of shear, the droplets in flowing emulsions were not dispersed as primary droplets. The size of aggregate was smaller in the case of emulsion stabilized with 1% Arlacel 60 (Fig. 7) than that with 0.2% Arlacel 60 (Fig. 6B). Thus, the higher values of η_{rel} of the former emulsion than the latter seems to be due to the increase of effective volume fraction of the disperse phase resulting from the formation of aggregate occluding the continuous phase liquid in the cluster of droplets.

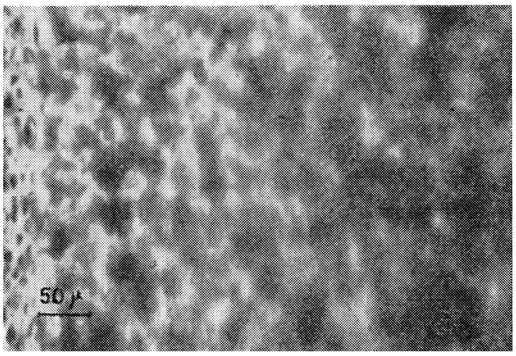

Fig. 7. Water in benzene (+CCl_4) emulsion (ϕ=0.01) stabilized by 1.0% Arlacel 60 prepared by shaking by hand observed at shear stress, 8.34 dyn/cm², and rate of shear, 1230 sec⁻¹.

As shown in Fig. 5, in the benzene emulsions stabilized with Arlacel 83, discrepancies between the value of η_{rel} and that calculated by Einstein's equation was more marked with emulsions of high emulsifier concentration than those of lower concentration in the range of higher values of ϕ. However, the size of aggregate observed at a high rate of shear was smaller with emulsions of high emulsifier concentration. The increase in η_{rel} with the increase of emulsifier concentration is brought about by the increase of effective volume fraction of disperse phase owing to the formation of aggregate occluding the continuous phase liquid and/or owing to the increased solvation of droplets surface with the perfection of the emulsifier layer

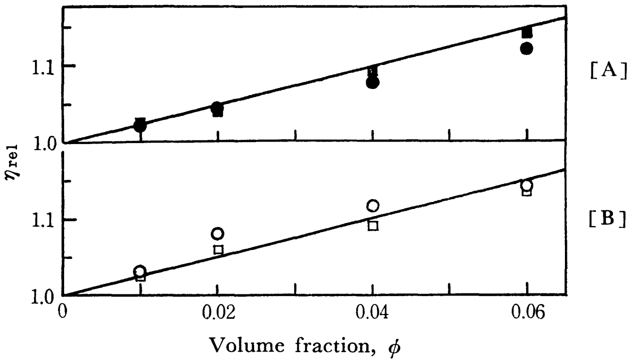

Fig. 8. [A] and [B], plots of relative viscosity *vs.* volume fraction for O/W emulsions stabilized by 0.01% Tween 20 at 32°C.
Solid line, calculated by Einstein's equation.
Disperse phase: ○ Benzene (+CCl_4), □ Benezene (+CCl_4) prepared by Mixer, ● Cyclohexane (+CCl_4), ■ Cyclohexane (+CCl_4) prepared by mixer

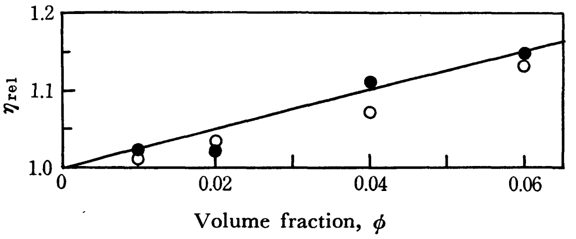

Fig. 8. [C], plots of relative viscosity *vs.* volume fraction for O/W emulsions stabilized by 0.1% Tween 20 at 32°C. Solid line, calculated by Einstein's equation.
Disperse phase: ○ Benzene (+CCl_4), ● Cyclohexane (+CCl_4)

around the droplets.

The above results show that in the case of water in benzene emulsion, droplets in the flowing emulsion at rates of shear below 3000 sec^{-1}, could not be dispersed as primary droplets. Albers and Overbeek⁵⁾ estimated the effective van der Waal's constant A between the water droplets in water in benzene emulsion from the minimum rate of shear to reach Newtonian region *i.e.*, to cause complete redispersion, and found a rather low value of $A=0.4\times10^{-14}$ erg based on the experimental value of the minimum rate of shear of <100 sec^{-1} for the emulsion stabilized by 1% Span 85 (sorbitan trioleate) of $\phi=0.14$ and 200 sec^{-1} for the one stabilized by 1% Span 60 (sorbitan monostearate) of $\phi=0.175$. It should be mentioned that such a low value of A obtained by Albers and Overbeek was due to incomplete confirmation of the complete dispersion of droplets in the system.

In the case of O/W type emulsions irrespective of the kind of oil phase liquid, the aggregates formed in the emulsion were completely redispersed into primary droplets at a high rate of shear and Einstein's equation could be applied to represent the observed values of η_{rel} with the emulsions of values of ϕ as high as 0.06 as shown in Fig. 8.

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5) W. Albers and J. Th. G. Overbeek, *J. Colloid Sci.*, **15**, 489 (1960).