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Effect of drop size distribution on the flow behavior of oil-in-water emulsions

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Abstract: The effect of drop size distribution on the viscosity was experimentally examined for oil-in-water emulsions at volume fractions of $\Phi = 0.5$, 0.63 and 0.8. At $\Phi = 0.5$, the hydrodynamic forces during drop collisions govern the viscosity behavior. The viscosity versus shear rate curve is scaled on the root-mean-cube diameter which is related to the number of drops per unit volume. At $\Phi = 0.8$, the resistance to flow arises from the deformation and rearrangement of thin liquid films between drops. The viscosity at a given shear rate is inversely proportional to the volume-surface mean diameter which is related to the total interfacial area per unit volume. However, since the drops come into contact and the liquid film separating adjacent drops is generated without drop deformation at $\Phi = 0.63$, the viscosity curve is not scaled on the mean diameter. The flow behavior near the critical volume fraction strongly depends not only on the mean drop size, but also on the width of the distribution.

Key words: Oil-in-water emulsions – steady shear viscosity – drop size distribution

1. Introduction

In dilute emulsions at equilibrium the drops are isolated and spherical. When the emulsion is subjected to shear flow, hydrodynamic forces cause two drops to make a doublet rotating around their mutual center of mass (Krieger and Dougherty, 1959; Lee, 1969). The rotating doublet dissipates more energy than hydrodynamically isolated drops. Therefore, the theories for dilute suspensions can be used to describe the emulsion rheology. In the previous papers (Otsubo and Prud'homme, 1992, 1994), we have reported that the viscosity versus shear rate curves for emulsions with different drop sizes are superimposed by a horizontal shift when the volume fraction does not exceed the critical value for touching spheres. The shift factor correlates with the root-mean-cube diameter, d_{rmc}, defined as

$$d_{rmc} = \left(\frac{\sum n_i D_i^3}{\sum n_i} \right)^{1/3} , \tag{1}$$

where n_i is the number of drops with diameter D_i. Since d_{rmc} provides the number of drops per unit volume, the scaling analysis shows that the hydrodynamic interactions during the shear-induced formation and breakup of doublet govern the viscosity behavior.

In highly concentrated emulsions, the drops cannot remain spherical and a thin liquid film (interface) is formed between two deformed drops (Princen, 1979). When the emulsion is subjected to shear forces, the liquid film must stretch or shrink until a critical strain is achieved that results in steady flow. The rheological properties are controlled by the network structures of liquid films. To quantitatively characterize the polyhedral structures, many authors (Princen and Kiss, 1986; Yoshimura and Prud'homme, 1988; Weaire and Fu, 1988) have used the volume-surface or Sauter mean diameter, d_{SV}, defined as

$$d_{SV} = \frac{\sum n_i D_i^3}{\sum n_i D_i^2} \, . \tag{2}$$

Because d_{SV} is simply related to the total interfacial area per unit volume, it is useful in correlating the drop size and the rheology for concentrated emulsions.

The appropriate average diameter dominating the flow behavior is d_{rmc} for dilute emulsions and d_{SV} for concentrated emulsions. The drop size distribution affects the rheology of emulsions in two different ways depending on whether the thin liquid films of continuous phase are formed or not. The purpose of present study is to understand the effect of drop size distribution on the rheology of emulsions in relation to the flow mechanism.

2. Experimental

The emulsions were of oil-in-water type. The oil was a mixture of 24 wt% tritolylphosphate and 76 wt% dioctylphthalate. The density was 1.017×10^3 kg m^{-3} and the viscosity was 6.54×10^{-2} Pa s. The continuous phase was a 20 wt% aqueous solution of an anionic surfactant (Alipal CD-128, GAF Corp.). The density was 1.009×10^3 kg m^{-3} and the viscosity was 2.65×10^{-3} Pa s. The interfacial tension was 3.3×10^{-3} Nm^{-1}.

Three stock emulsions labeled E1, E2, and E3 were prepared at a volume fraction of $\Phi = 0.97$. The details of preparation methods are described in the previous papers. The sample emulsions having narrow drop size distribution were prepared by diluting the stock emulsions with the continuous solution. The sample emulsions having wide distribution were prepared by mixing the dilute E1 and E3 emulsions. Two dilute emulsions of the same volume fraction were mixed at mixing ratios of E1/E3 = 80/20, 60/40, 40/60, and 20/80. Table 1 shows the drop size data for the original and mixed emulsions. The ratio d_{SV}/d_{rmc} may be used as a measure of the width of distribution.

The apparatus for rheological measurements was a System IV rheometer (Rheometrics Inc.) with a sensitive fluids transducer. The steady shear viscosity was measured in the range of $\dot{\gamma} = 1.0 \times 10^{-1}$ to 2.5×10^2 s^{-1} by the use of a parallel plate geometry. The plates are made of glass because the oil drops coalesce at metal and plastic surfaces. All emulsions show neither wall slip nor time dependence. The measurements were carried out at 25 °C.

Table 1. Drop diameter

Emulsion	d_{SV} (μm)	d_{rmc} (μm)	d_{SV}/d_{rmc}
E1	8.8	8.3	1.07
E2	15.4	13.1	1.18
E3	26.3	24.8	1.06
EM(80/20)	10.2	8.9	1.15
EM(60/40)	12.1	9.7	1.25
EM(40/60)	14.8	11.1	1.33
EM(20/80)	18.9	13.5	1.40

3. Results and discussion

Figure 1 shows the shear rate dependence of the viscosity for emulsions at $\Phi = 0.5$. The viscosity decreases with increasing shear rate and becomes constant. At high shear rates the Newtonian viscosities are equal for all emulsions. In this intermediate concentration regime, the Newtonian viscosity is determined by the volume fraction alone and not by the drop size distribution. E1, EM(80/20), and EM(60/40) emulsions show identical viscosity behavior, and therefore only the data from E1 are plotted. For these three emulsions larger drops have no significant effect on the shear-thinning flow. The transition from shear-thinning to Newtonian flow depends on the volume fraction of the smaller drops. Increasing the volume fraction of smaller drops moves the transition to higher shear rates. The viscosity curves for E2 and EM(20/80) emulsions are very similar. These two emulsions have almost the same drop sizes as measured by d_{rmc}, while they have different values of d_{SV}. Since the hydrodynamic interactions between drops are induced during the collisions, the viscosity curve can be scaled on d_{rmc} which is related to the number of drops per unit volume.

Figure 1 gives two important suggestions in a practical sense. First, the viscosity of emulsions is easily controlled by adding a small portion of emulsion consisting of smaller drops. The viscosity at low shear rates can be markedly increased without significant increase in the high-shear-rate Newtonian viscosity. Second, the viscosity is not strongly affected by the existence of large drops. In unstable emulsions, the drops tend to coalesce and the drop size is gradually increased. However, the flow behavior does not change even though the coalescence proceeds to some

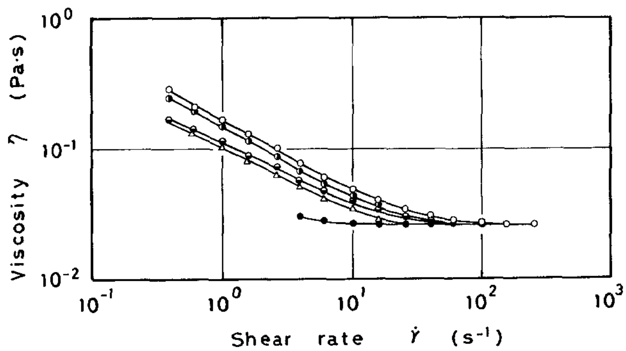

Fig. 1. Shear rate dependence of viscosity for emulsions at $\Phi = 0.5$: E1 (○), EM(40/60) (◑), EM(20/80) (◒), E3 (●), E2 (△)

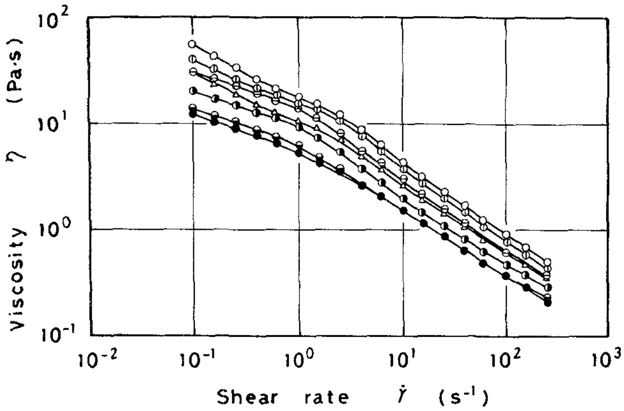

Fig. 2. Shear rate dependence of viscosity for emulsions at $\Phi = 0.8$: E1 (○), EM(80/20) (◑), EM(60/40) (⊖), EM(40/60) (◑), EM(20/80) (◒), E3 (●), E2 (△)

extent. The rheological properties of emulsions are insensitive to the initial stage of coalescence.

Figure 2 shows the shear rate dependence of the viscosity for emulsions at $\Phi = 0.8$. With increasing drop size, the viscosity decreases over the entire range. Figure 3 shows the relation between the viscosity at $\dot{\gamma} = 1\ s^{-1}$ and $1/d_{SV}$. The plots lie on a straight line, showing that the viscosity is proportional to the total interfacial area per unit volume. The linear dependence is also established at different shear rates and the curves can be satisfactorily superimposed by a vertical shift. In highly concentrated emulsions, the network structures of thin liquid films between deformed drops are fully developed. Since the deformation and rearrangement of thin liquid films are fundamental mechanisms in rheology of foam and concentrated emulsions (Princen, 1985; Kraynik and Hansen, 1986; Khan and Armstrong, 1987), d_{SV} is the appropriate measure for characterizing the drop size distribution. The linear relation between the viscosity and interfacial area supports the structural models in which the interfacial forces are the origin of fluid stresses. However, the viscosity curve in Fig. 2 seems to have a break point at about $\dot{\gamma} = 2\ s^{-1}$, although the concentrated emulsion is expected to show plastic yield with a slope of -1. According to our previous studies, the break point disappears when the viscosity ratio of the internal to external phases decreases. The shear-thinning behavior at low shear rates may arise from the flow in thin liquid films. Due to a combined effect of elasticity of interface and viscous dissipation inside drops and thin films, the concentrated emulsion would show viscoelastic relaxation. By the dynamic measurements, the relaxation time has been found to increase with continuous phase viscosity.

Figure 4 shows the shear rate dependence of the viscosity for emulsions at $\Phi = 0.63$. All emulsions are shear thinning over the entire range. In contrast to the viscosity behavior at volume fractions of $\Phi = 0.5$ and 0.8, the curve shape varies strongly with the drop size distribution. The most interesting feature is that the viscosity at $\dot{\gamma} = 10\ s^{-1}$ decreases at first, passes through a minimum, and then increases with increasing fraction of small drops. The decrease in mean drop size does not necessarily cause a viscosity increase. When the volume fraction of dispersed phase is increased to a certain value in an emulsion, the drops come to contact and liquid film separating adjacent drops is generated. The fraction of 0.63 cor-

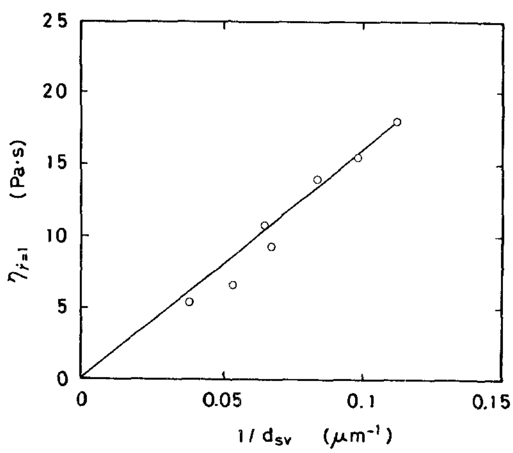

Fig. 3. Relation between viscosity at $\dot{\gamma} = 1\ s^{-1}$ and the reciprocal of the volume-surface mean diameter

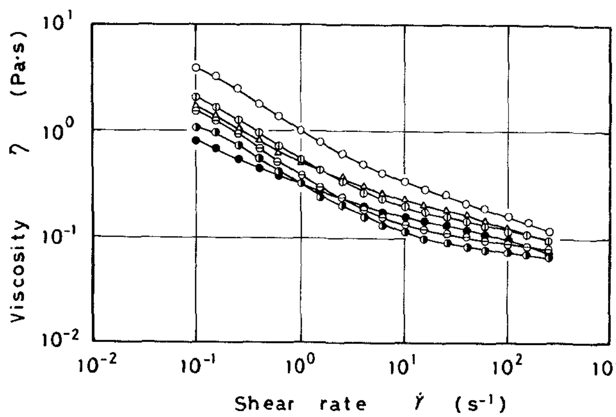

Fig. 4. Shear rate dependence of viscosity for emulsions at $\Phi = 0.63$: E1 (○), EM(80/20) (◑), EM(60/40) (⊖), EM(40/60) (◑), E3 (●), E2 (△)

responds to a critical value for touching drops in E1 and E3 emulsions. In emulsions having bimodal drop size distribution, the volume fraction can exceed the maximum close packing of large drops without drop deformation, if the small drops occupy the interstitial pockets between large ones. The pockets provide free space for small drops. Therefore, when some portion of large drops is replaced by small ones under a condition of constant volume fraction, the fluidity of emulsions is increased. Since the viscosity behavior varies in complex manner, it is difficult to directly relate the rheology and mean drop size. The rheological properties of emulsions near the critical volume fraction strongly depend not only on the mean drop size but also on the width of the distribution.

4. Conclusions

For dilute emulsions, the viscosity versus shear rate curve is scaled on the root-mean-cube diameter which is related to the number of drops per unit volume. The hydrodynamic forces during drop collisions govern the viscosity behavior. For highly concentrated emulsions, the viscosity at a given shear rate is inversely proportional to the volume-surface mean diameter which is related to the total interfacial area per unit volume. The resistance to flow is induced by deformation and rearrangement of thin liquid films. However, since the drops come to contact and the liquid film separating adjacent drops is generated without drop deformation at $\Phi = 0.63$, the viscosity curve is not scaled on the mean diameter. The flow behavior near the critical volume fraction strongly depends not only on the mean drop size but also on the width of the distribution.

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