Effect of Droplet Size on the Rheology of Emulsions

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The effect of droplet size on the rheological behavior of water-in-oil and oil-in-water emulsions was investigated using a controlled-stress rheometer. Results indicate that the droplet size has a dramatic influence on emulsion rheology. Fine emulsions (water-in-oil or oil-in-water) have much higher viscosities and storage moduli than the corresponding coarse emulsions. The shear-thinning effect is much stronger in the case of fine emulsions. When coarse droplets are replaced by fine droplets (keeping total volume fraction of the dispersed phase constant), the resulting emulsion exhibits a minimum in rheological properties (viscosity, storage and loss moduli, time constant) at a certain proportion of fine droplets. However, the minimum in viscosity occurs only at low shear stresses. At high stresses, the viscosity of the mixed emulsion increases as the proportion of fine droplets increases. The study of the aging effect on the rheological behavior shows that water-in-oil emulsions age much more rapidly than the oil-in-water emulsions.

Introduction

The influence of droplet size on emulsion rheology is not well understood. Surprisingly, little work has been carried out on this problem despite its practical significance. Most previous publications on the effect of particle size deal with suspensions of solid particles. Following are the two practical situations where droplet-size effects on emulsion rheology could be extremely important: (a) pipeline transportation of highly viscous crude oils in the form of oil-in-water emulsions, and (b) off-shore crude-oil production.

The pipeline transportation of highly viscous crude oils in the form of oil-in-water emulsions has received special attention in recent years (Pal, 1993; Rimmer et al., 1992). The transportation of extremely viscous crude oils, such as bitumen and heavy oils, by pipelines is difficult, especially during cold weather. To facilitate the flow of very viscous crude in pipelines, it is necessary to reduce its viscosity either through the installation of heating equipment at frequent intervals along the pipeline, or through the addition of a low-viscosity hydrocarbon diluent. The former expedient is expensive and inconvenient, and the latter requires the availability of relatively large amounts of cheap diluent. These problems, however, can be avoided if the viscous crudes are transported as oil-in-water (O/W) emulsions. This concept has already been utilized commercially in a pipeline 21 km in length and 20 cm in diameter in California, and in a pipeline 238 km in length and 51 cm in diameter in Indonesia (Zakin et al., 1979). For emulsion pipelining to be economical, it is important to keep the oil concentration of the emulsion as high as possible and, at the same time, maintain the emulsion viscosity at a reasonable level. This can be achieved only by optimizing the droplet-size distribution. It is believed that the more polydispersed the droplet-size distribution, the lower the emulsion viscosity for a given dispersed-phase concentration.

The off-shore oil wells often produce the water-in-oil (W/O) type of emulsions. The emulsification of water and oil is believed to occur mostly in the choke valve. The droplet size of the emulsions depends on the pressure reduction across the choke valve. The larger the pressure reduction, the smaller the droplet size. As emulsions of different mean droplet sizes can be produced (depending upon the pressure reduction), it is important to understand the influence of the droplet size on the viscosity, and hence pipeline flow resistance, of emulsions.

This article reports *new* results on effects of droplet size on the rheology of emulsions. Both steady and oscillatory behavior of emulsions (O/W and W/O) are investigated, as well as various phenomena causing particle-size effects in dispersed-systems.

Literature Review

According to Einstein's theory for the viscosity of suspensions (Einstein, 1906, 1911), the relative viscosity is given as

$$\eta_r = 1 + \frac{5}{2}\phi, \tag{1}$$

where η_r is the relative viscosity (defined as the ratio of the suspension viscosity to the continuous medium viscosity) and ϕ is the volume fraction of the dispersed phase. This result is valid *regardless of the size of the particles*. However, there are two important assumptions involved in the derivation of this relation: (a) the suspension is very "*dilute*" so that the particles are far apart (isolated from one another), and (b) the particles are "*hard spheres*." The particles could be considered as hard spheres when the repulsive force (due to electrical double layer) and the attractive force (due to van der Waals attraction) between the particles are both negligible, and the adsorbed stabilizing layer thickness (δ), if any, is very small relative to the particle size (R), that is, δ/R is negligibly small. The particles, of course, are assumed to be rigid and nondeformable.

The effect of particle size becomes important if the assumptions just discussed are violated. Let us first consider *dilute* dispersions of "soft spheres" (as opposed to "hard spheres"). The particles are to be treated as soft spheres when either one or more of the following conditions are present: (a) a significant electrical double layer is present on the particle surface; (b) the thickness of the adsorbed stabilizing layer (surfactant layer) is significant with respect to particle size; (c) the solvation or hydration of particles is significant (solvation or hydration refers to a phenomenon whereby the continuous-phase liquid becomes immobilized at the particle surface); and (d) the particles are deformable like the emulsion droplets.

It is now well known that the presence of an electrical double layer on the surface of the particles results in an increase in the viscosity. This phenomenon is referred to as *electroviscous effect* (Goodwin, 1987; Krieger, 1972). For dilute dispersions, the electroviscous effect is associated with the distortion of electrical double layer from spherical symmetry by the shear field. The Maxwell stresses generated due to asymmetric electric fields tend to restore the symmetry of double layer, thereby opposing the flow. This results in extra dissipation of energy and hence an increase in viscosity. Smoluchowski (Sherman, 1970) was the first to consider electroviscous effect in dilute dispersions. He developed the following equation for the dispersion viscosity:

$$\eta_r = 1 + \frac{5}{2}\phi\left[1 + \frac{\left(\dfrac{\epsilon_c \zeta}{2\pi}\right)^2}{\eta_c k_c R^2}\right], \tag{2}$$

where k_c is the specific conductivity of the continuous phase; η_c is the viscosity of the continuous phase; ϵ_c is the dielectric constant of the continuous phase; and ζ is the zeta potential. Thus, the increase in relative viscosity (η_r) due to electroviscous effect is

$$\frac{5}{2}\phi\left[\frac{\left(\dfrac{\epsilon_c \zeta}{2\pi}\right)^2}{\eta_c k_c R^2}\right]. \tag{3}$$

This term includes the particle radius (R). The smaller the particle radius, the larger the increase in viscosity.

The presence of a thick adsorbed layer of surfactant or continuous-phase liquid (solvation effect) at the particle surface can also result in an increase in the viscosity of the dispersion. If δ is the thickness of the adsorbed layer, the effective dispersed-phase concentration (ϕ_e) of the dispersion is

$$\phi_e = \phi\left(1 + \frac{\delta}{R}\right)^3, \tag{4}$$

where ϕ is the true dispersed-phase (particle) concentration. Clearly, the effective volume fraction of dispersed phase (ϕ_e) and hence viscosity increases with the decrease in particle radius when ϕ and δ are kept constant.

If the particles are nonrigid and deformable, additional complications arise in the rheological behavior of dispersions. Dispersions of deformable particles exhibit both shear thinning and elastic effects (normal stresses), even at low dispersed-phase concentrations (Oldroyd, 1953; Oldroyd, 1959; Choi and Schowalter, 1975; Frankel and Acrivos, 1970). These effects increase with the increase in droplet size as larger droplets undergo greater deformation. However, the viscosity shows an opposite trend; it increases with the decrease in droplet size because the smaller droplets tend to be more rigid.

From the discussion so far it is clear that in the case of soft-sphere dispersions, the particle-size effects come into play even when the dispersion is dilute. With the decrease in particle size, the viscosity tends to increase. However, the increase in viscosity is expected to be small for dilute systems.

Now consider concentrated dispersions of *hard spheres*. In concentrated dispersions, the particles can no longer be treated as isolated particles. At high concentrations, hydrodynamic interaction between the particles is important, that is, the distorted flow patterns around the particles overlap with each other. The hydrodynamic interaction increases as the separation distance between the particles decreases. For a given concentration of dispersed phase (ϕ), a decrease in particle size results in a decrease in the mean separation distance and hence an increase in hydrodynamic interaction and viscosity (Sherman, 1983). However, according to Hoffman (1992), the hydrodynamic interactions are related to the relative spacing between particles (rather than absolute value of spacing). The relative spacing is characterized by h/D, where h is the mean distance between the centers of neighboring particles and D is the particle diameter. Consequently, the viscosity of a dispersion of monosized hard spheres is expected to be a function of only particle concentration.

Another important phenomenon that needs to be considered in the case of concentrated dispersions is the Brownian motion (Krieger, 1972; Shikata and Pearson, 1994; van der Werff and de Kruif, 1989). If Brownian motion is significant (particles are small), dispersions of hard spheres can exhibit non-Newtonian shear-thinning behavior. The shear-thinning effect is due to competition between hydrodynamic and Brownian forces. Brownian forces tend to randomize the particles. As a consequence, particles collide with each other and form temporary doublets, triplets, and so on. Hydrodynamic force, on the other hand, results in ordering of the particles into layers and tends to destroy doublets and higher aggregates. At low shear rates, Brownian force dominates, and consequently there occurs a significant amount of rotation of doublets and triplets and so on. A rotating doublet (or higher aggregate) causes more dissipation of energy as compared with the same number of isolated particles, and therefore the viscosity of dispersion is high at low shear rates. With the increase in shear rate, the number of rotating doublets or higher aggregates decreases because the shear forces are strong enough to break such aggregates, and therefore the viscosity decreases with the increase in shear rate. According to Krieger (1972), the relative viscosity of hard-sphere dispersions is a function of dispersed-phase concentration (ϕ) and Peclet number (Pe):

$$\eta_r = f(\phi, Pe), \tag{5}$$

where the Peclet number is defined as

$$Pe = \dot{\gamma}\eta_c R^3/kT. \tag{6}$$

Here, $\dot{\gamma}$ is shear rate; η_c is continuous medium viscosity; k is Boltzmann's constant; and T is the absolute temperature. The relative viscosity vs. Peclet number plot for monosized dispersions of hard spheres exhibits three different regions (Pal, 1996): at low Peclet numbers, the relative viscosity is constant; at intermediate values of Peclet number, the relative viscosity decreases with an increase in Peclet number; and at high values of Peclet numbers, the relative viscosity becomes constant again. Therefore, the effect of particle size is important only at intermediate Peclet numbers. The viscosity tends to increase with the decrease in particle size at intermediate Peclet numbers. However, note that emulsions generally have droplet sizes larger than 1 μm, and therefore the effect of Brownian motion on the rheology of emulsions is expected to be small.

In the case of highly concentrated dispersions of hard spheres, the effect of polydispersity (size distribution) on the rheological behavior could also be significant. Several studies indicate that when two monodisperse systems, with different particle sizes but the same volume fraction of particles, are mixed together in varying proportions, the resulting dispersion exhibits a minimum viscosity at a certain composition (Chong et al., 1971; Rodriguez et al., 1992). The observed decrease in viscosity is due to the fact that the smaller particles serve to isolate or lubricate the large ones. It is interesting to note that a minimum in the viscosity is generally observed only when the mixed dispersion is bimodal. When three or more different sizes of particles are mixed together, but the total volume fraction of particles is kept constant, a minimum in viscosity is no longer observed. Instead, an increase in viscosity occurs as the proportion of the smallest size particles increases (Sherman, 1983).

The particle-size effects are equally important in the case of concentrated "soft-sphere" dispersions. This is particularly the case with dispersions having particle sizes considerably smaller than 1 μm. Various phenomena discussed earlier for dilute "soft-sphere" dispersions (electrical double layer, adsorbed stabilizing layer, hydration or solvation of particles, etc.) play a significant role in concentrated dispersions of fine particles. Also, the effect of Brownian motion is important for fine dispersions. Since the magnitude of all these phenomena depends on particle size, the particle-size effect plays a major role in determining the viscosity of concentrated "soft-sphere" dispersions of small particles. The viscosity generally increases significantly with the decrease in particle size. However, it should be noted that for most emulsions the effects of double-layer, adsorbed stabilizing layer, and Brownian motion, and so on, are relatively small, as emulsions generally have large droplet sizes (larger than 1 μm).

It is also important to note that while in the case of "hard-sphere" dispersions, the concentration of the dispersed phase cannot exceed the packed-bed concentration (maximum packing concentration where the viscosity becomes infinite), this is not true for "soft-sphere" dispersions of deformable particles (like emulsions). In the case of emulsions, the volume fraction of the dispersed phase (ϕ) could easily exceed that of the close-packed sphere configuration (ϕ_p). When $\phi > \phi_p$, the droplets, however, cannot remain spherical; they are deformed into polyhedral shape. The rheological properties of such highly concentrated emulsions are controlled by the network structure of thin liquid films of continuous phase formed between the droplets. Most rheological properties of these emulsions are directly related to σ/R, where σ is interfacial tension and R is the droplet radius in the undeformed spherical state. Thus, with the decrease in droplet size, the yield stress, viscosity, and elastic modulus, and so on, are expected to increase significantly (Princen, 1979, 1985; Princen and Kiss, 1986, 1989).

Based on the preceding review of the literature, the following general conclusions can be drawn regarding the effect of particle size:

1. For dilute dispersions of monodispersed *hard spheres*, the viscosity is independent of particle size. In concentrated systems, the viscosity is independent of particle size at low and high Peclet numbers. At intermediate Peclet numbers, the viscosity increases with the decrease in particle size due to Brownian motion. However, the Brownian motion effect is expected to be relatively small in the case of emulsions of large droplets (>1 μm).
2. For dilute and concentrated dispersions of monodispersed *soft spheres*, the viscosity increases with the decrease in particle size. The particle-size effect is particularly important for fine dispersions with particles considerably smaller than 1 μm.
3. For bimodal dispersions of *hard spheres* or *soft spheres* at high concentrations (near packed-bed concentrations), there occurs a minimum in viscosity at a certain composition of the two sizes. It is important to realize that when fine and coarse monodisperse systems, having the same volume fraction of particles, are mixed together, the viscosity of the resulting bimodal dispersion can be lower than that of the coarse monodisperse system even though there occurs a decrease in the average particle size.

4. For soft-sphere dispersions of deformable particles, the rheological properties at concentrations above the close-packed sphere configuration are governed by the network structure of thin liquid films of continuous phase. The rheological parameters (yield stress, viscosity, elastic modulus, etc.) of such concentrated emulsions increase with the decrease in droplet size.

Experimental Work

Materials

The emulsions were prepared using a petroleum oil (trade name EDM) supplied by Monarch Oil Company, Kitchener, Canada. The viscosity of the oil was 5.8 mPa·s at 25°C. The water used throughout the experiments was deionized. Triton X-100 was used as a surfactant for the preparation of oil-in-water emulsions. This nonionic surfactant is manufactured by Union Carbide Co. Emsorb 2503 was used as a surfactant for the preparation of water-in-oil emulsions. Emsorb 2503 is manufactured by Henkel Corporation, Emery Group.

Procedure

For the preparation of water-in-oil emulsions, the surfactant (Emsorb 2503) was added to the oil phase. The surfactant dissolved readily in the oil upon gentle agitation. The concentration of the surfactant in the oil phase was kept 4 wt. %. For the preparation of oil-in-water emulsions, the surfactant (Triton X-100) was added to the aqueous phase. Triton X-100 dissolved in the aqueous phase upon gentle stirring. The concentration of the surfactant in the aqueous phase was kept 2 wt. %.

The emulsions were prepared in batches of about 500 g. A variable speed homogenizer (Gifford-Wood Model 1-L) was used to provide the necessary agitation and shearing of fluids. Three differently concentrated water-in-oil emulsions having water volume fractions of 0.55, 0.65, and 0.76 were prepared. For oil-in-water emulsions, only one concentration of oil was studied, that is, 74.5% by volume. At any given concentration of emulsion (W/O or O/W), two different droplet size emulsions were prepared—fine and coarse emulsions. The coarse emulsion was prepared by keeping the shearing speed of the homogenizer low. Also, the duration of shearing was kept small (1–3 min). The fine emulsion was prepared by using high shearing speed and increased duration of shearing (15–20 min).

The rheological behavior of fine and coarse emulsions was studied at 25°C. In the case of oil-in-water emulsions, the rheological behavior of various mixtures of fine and coarse emulsions was also investigated. For some emulsions (76 vol. % W/O and 74.5 vol. % O/W), the effect of aging on the rheological properties was determined as well.

Most of the rheological measurements were carried out in a Bohlin controlled-stress rheometer (Bohlin CS-50). A cone-and-plate measuring system was used. The cone diameter was 40 mm and the plate diameter was 60 mm. The cone angle was 4° and the gap at the cone tip was 150 μm. Some data also were collected with a Fann coaxial cylinder viscometer, having different gap widths. The measurements with the coaxial cylinder viscometer were done mainly to check the presence of wall effects (if any) and to confirm the measurements of the Bohlin rheometer.

The droplet sizes of emulsions were determined by taking photomicrographs. The samples were diluted with the same continuous phase before taking the photomicrographs. The photomicrographs were taken with a Zeiss optical microscope equipped with a camera.

Results and Discussion

Water-in-oil emulsions

Figures 1a–c show the photomicrographs of fine and coarse W/O emulsions at three different water concentrations. At any given water concentration, the droplet size of the fine emulsion is very small as compared with that of the corresponding coarse emulsion. The droplets of fine emulsions also exhibit a greater tendency to flocculate. Table 1 summarizes the droplet size data of W/O emulsions.

The viscosity vs. shear-stress plots for fine and coarse emulsions are compared in Figure 2. For all three water concentrations, the viscosity of fine emulsion is much higher than that of the corresponding coarse emulsion. Furthermore, the shear-thinning effect in fine emulsions is much stronger.

The observed increase in viscosity, upon reduction of droplet size, could be due to several possible reasons: (a) with the decrease in droplet size, the mean distance of separation between the droplets decreases, leading to an increase in hydrodynamic interaction and viscosity; (b) the thickness of the adsorbed surfactant layer (δ) with respect to the droplet size (R) becomes important as the droplet size is decreased (in other words, the increase in viscosity, upon reduction of droplet size, could be partly due to an increase in the effective dispersed-phase concentration); and (c) the width of the particle size distribution, or polydispersity, generally decreases with the reduction in droplet size (Barnes, 1994). Fine emulsions are more monodisperse. At high concentrations of dispersed phase, a decrease in polydispersity is expected to increase the viscosity. The observed increase in viscosity and shear-thinning effect with the decrease in droplet size could also be explained in terms of flocculation of fine droplets. As mentioned earlier, fine emulsions exhibited a greater tendency to flocculate. This increased tendency of flocculation could be due to at least two different mechanisms; first, the Brownian motion becomes important in the case of fine emulsions, as it tends to increase the collision, and hence flocculation, between droplets; and, second, the droplets are subject to van der Waals attraction force. With the decrease in droplet size, there occurs an increase in the surface area; therefore, the droplets may become poorly stabilized, and hence flocculate, if there is not enough surfactant available to cover the entire surface area (Barnes, 1994). Finally, at high concentrations of dispersed water phase ($\phi = 0.76$) a large difference in zero-shear viscosities of fine and coarse emulsions could be due to the formation of network structure of thin (continuous-phase) liquid films in the case of the fine emulsion. For monodisperse emulsion, the droplets come into close contact with each other when ϕ is approximately 0.74.

Figure 3 compares the storage modulus data for fine and coarse emulsions. The oscillatory measurements were carried out at a very low shear stress of 0.1 Pa. The stress-sweep experiments indicated that this stress was generally well

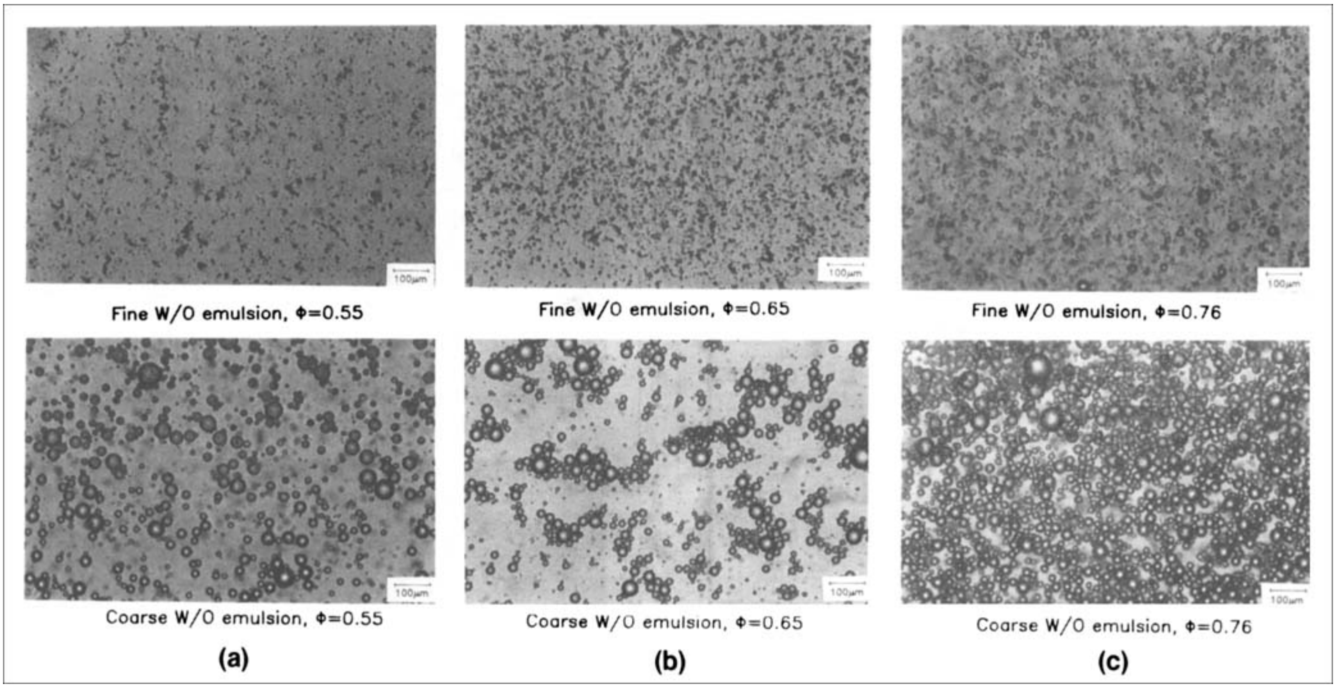


Figure 1. Fresh water-in-oil emulsions: (a) $\phi=0.55$; (b) $\phi=0.65$; (c) $\phi=0.76$.

within the linear viscoelastic region. Like viscosity, the storage modulus of fine emulsions falls well above the corresponding values of the coarse emulsions. Also, the difference in storage moduli of fine and coarse emulsions decreases with the increase in frequency.

Oil-in-water emulsions

Figure 4 shows the photomicrographs of fine and coarse O/W emulsions at an oil concentration of 74.5 vol. %. Clearly, the droplet size of the fine emulsion is much smaller than that of the coarse emulsion. Also, the fine emulsion appears to have a narrow distribution of droplet sizes. The approximate values of the volume average droplet sizes of the fine and coarse emulsions are 5 μm and 18 μm, respectively.

The flow curves for fine and coarse O/W emulsions are compared in Figure 5. Like W/O emulsions discussed earlier, the O/W emulsions exhibit a much higher viscosity when the droplet size is decreased. The storage modulus for the fine emulsion also is much higher than that of the coarse emulsion (Figure 6).

Figure 7 shows the viscosity vs. shear-stress plots for various mixed emulsions, prepared by mixing together the fine

Table 1. Droplet Size of Fresh Water-in-Oil Emulsions

Water Vol. Fraction (ϕ)	Emulsion	Approx. Vol.-Avg. Dia. (μm)
0.55	Fine	4
	Coarse	28
0.65	Fine	5
	Coarse	25
0.76	Fine	12
	Coarse	30

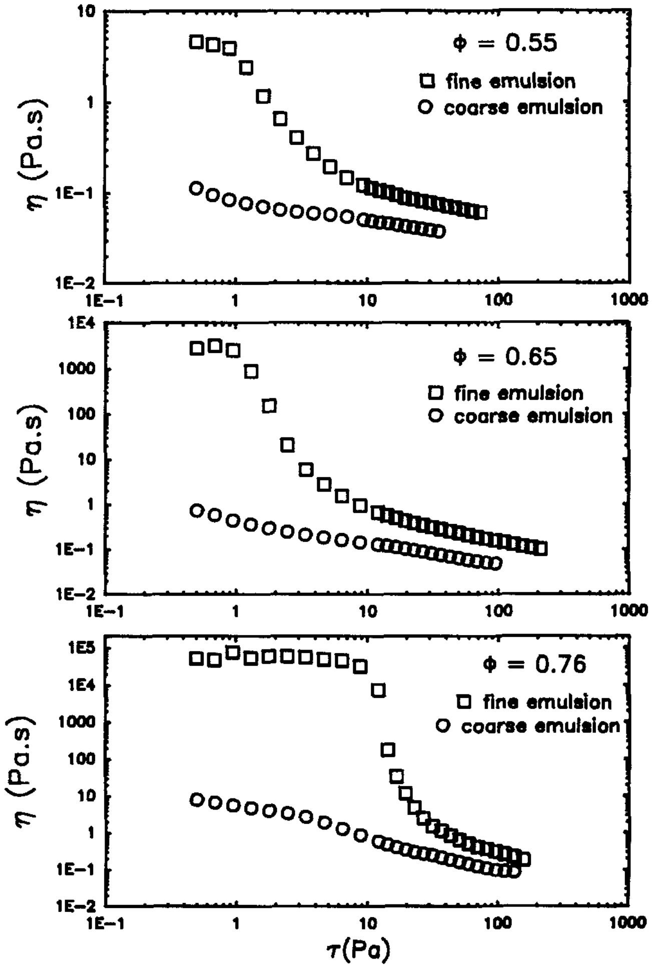


Figure 2. Viscosity vs. shear-stress for fresh water-in-oil emulsions at different water concentrations.

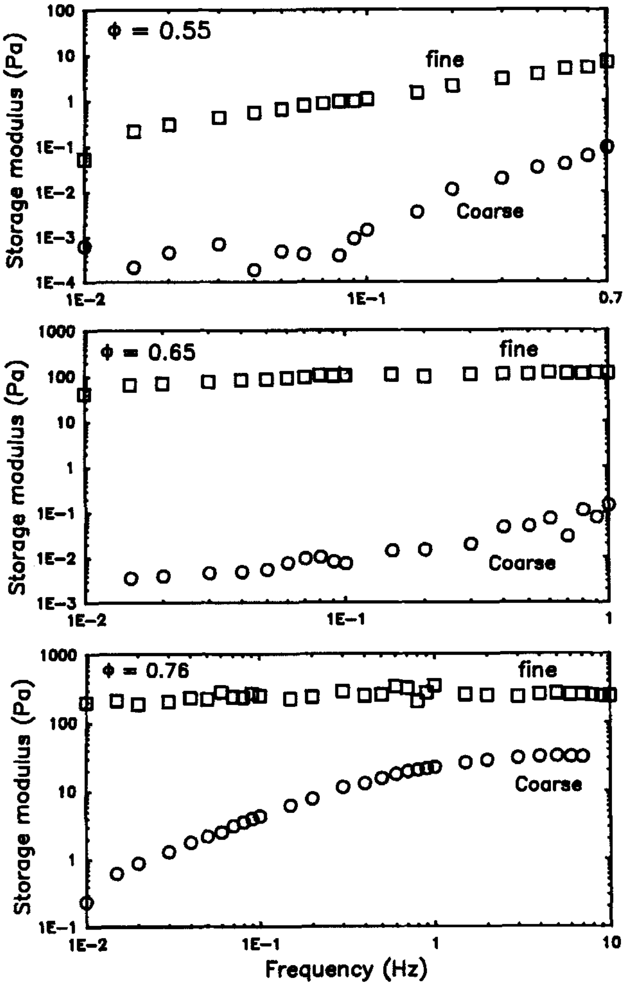
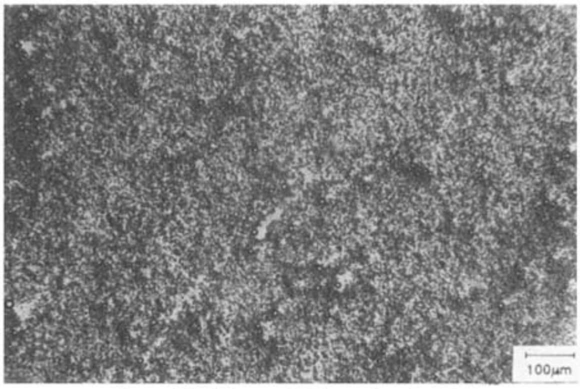


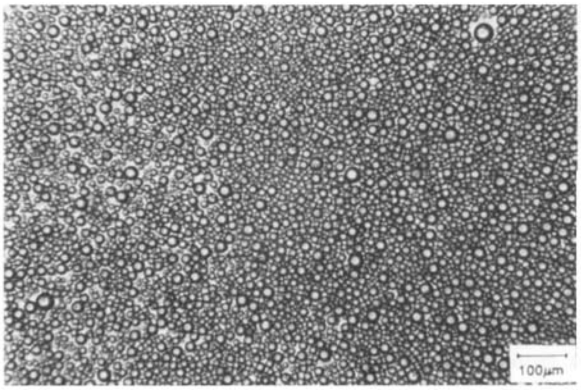
Figure 3. Storage modulus vs. frequency for fresh water-in-oil emulsions at different water concentrations.

and coarse O/W emulsions (ϕ = constant = 0.745) in varying proportions. When coarse droplets are replaced by fine droplets (keeping ϕ constant), the flow curves of the resulting emulsions initially fall below the flow curve of the coarse emulsion, provided that the shear stress is not very high. At high stresses, the flow curves of the mixed emulsions fall above the coarse emulsion curve for all proportions of fine emulsion. For mixed emulsions having the proportion of fine emulsion greater than 65% by volume, the entire flow curve (full range of stress) falls above that of the coarse emulsion.

The plots of viscosity vs. volume fraction of fine emulsion in the mixed emulsions are shown in Figure 8 at two different values of shear stress. At a low value of shear stress (τ = 0.9 Pa), the viscosity goes through a minimum. The minimum in viscosity occurs at a fine emulsion proportion of about 36 vol. %. This observation is quite consistent with suspensions of solid particles. Several studies on bimodal suspensions of solid particles (Chong et al., 1971; Parkinson et al., 1970; Rodriguez et al., 1992) indicate that a minimum in the zero-shear viscosity occurs when the fine particles account for about 25% to 35% of the total particle volume fraction. However, no minimum viscosity is observed at a high shear stress of 30 Pa.



Fine O/W emulsion, Φ=0.745



Coarse O/W emulsion, Φ=0.745

Figure 4. Fresh oil-in-water emulsions: ϕ = 0.745.

Instead, the viscosity increases as the proportion of the fine emulsion increases.

The storage and loss moduli data for the mixed emulsions are shown in Figure 9. When the proportion of the fine emulsion in the mixed emulsion is increased, the modulus (storage or loss) vs. frequency curves initially fall below that of the coarse emulsion. However, at high proportions of fine emulsion (>65 vol. %) the modulus data fall above those of the

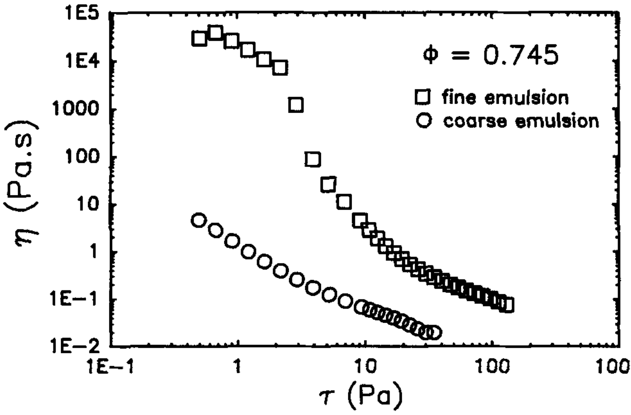


Figure 5. Viscosity vs. shear stress for fresh oil-in-water emulsions: ϕ = 0.745.

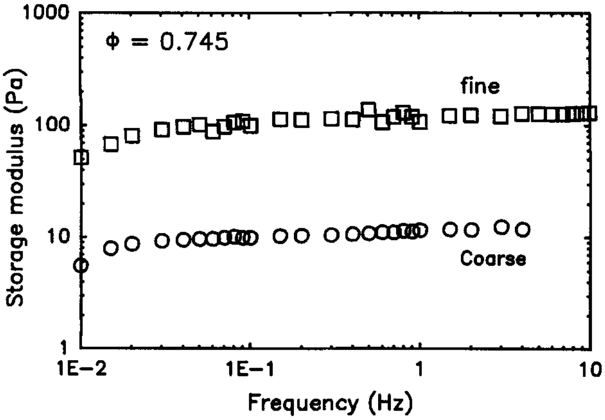


Figure 6. Storage modulus vs. frequency for fresh oil-in-water emulsions: $\phi = 0.745$.

coarse emulsion. The plots of storage and loss moduli as functions of volume fraction of fine emulsion in the mixed emulsion are shown in Figure 10 at two different frequencies. Both the storage and loss moduli plots exhibit a minimum. The minimum in storage and loss moduli plots occurs at a fine emulsion proportion of about 36% by volume when the frequency is low (0.02 Hz). At a high frequency of 0.5 Hz, the minimum appears to shift to a lower volume fraction of fine emulsion, approximately 0.2.

Figure 11 shows the plot of the mean time constant for the mixed emulsions as a function of the volume fraction of the fine emulsion. The mean time constant (λ) was calculated from the storage and loss moduli data as follows (Bird et al., 1987):

$$\lambda = \lim_{\omega \to 0} \left(\frac{G'}{\omega G''} \right). \tag{7}$$

In our measurements, the lowest frequency employed was 0.01 Hz, and therefore the time constant (λ) was evaluated at 0.01 Hz. Clearly, the time constant plot also exhibits a minimum value at a fine emulsion proportion of about 36 vol. %.

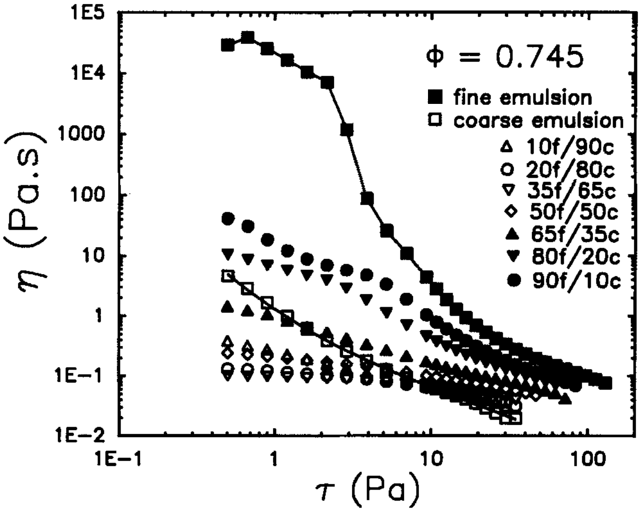


Figure 7. Viscosity vs. shear-stress for various mixtures of fine and coarse oil-in-water emulsions: $\phi = 0.745$.

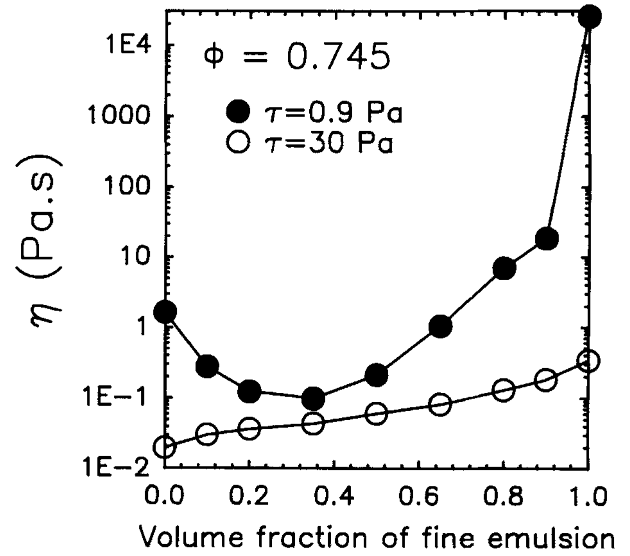


Figure 8. Viscosity vs. volume fraction of fine emulsion in the mixed oil-in-water emulsions: $\phi = 0.745$.

The observed decrease in various rheological parameters (viscosity, moduli, time constant) with the addition of fine

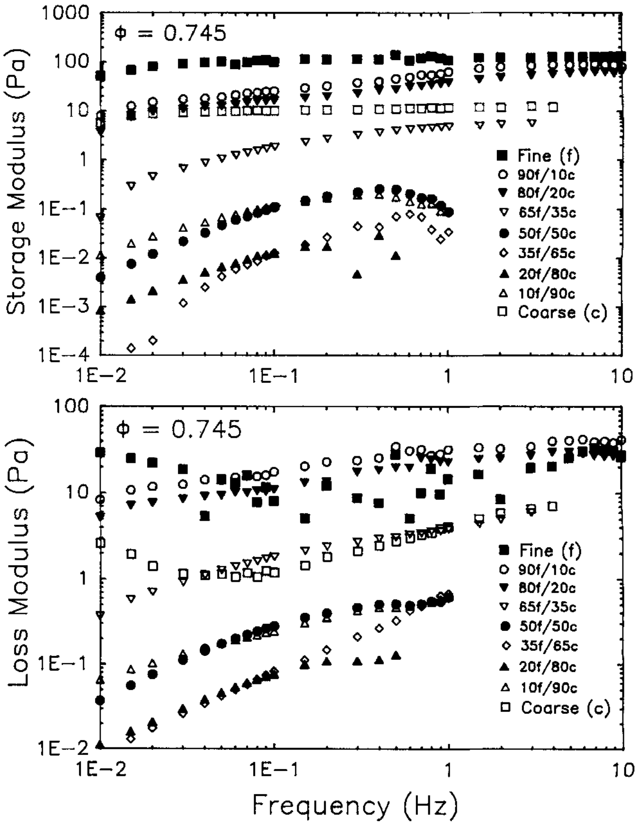


Figure 9. Storage and loss moduli as functions of frequency, for various mixtures of fine and coarse oil-in-water emulsions: ϕ = constant = 0.745.

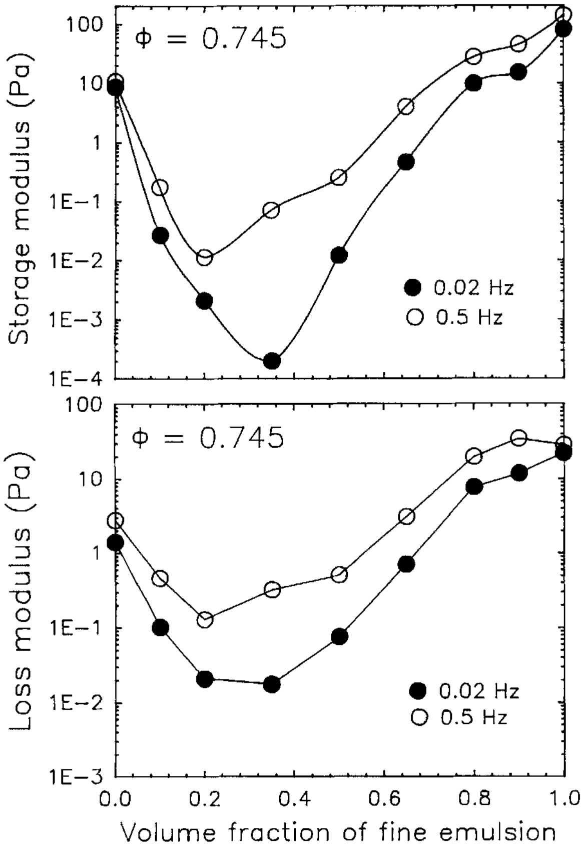


Figure 10. Storage and loss moduli as functions of volume fraction of fine emulsion in the mixed oil-in-water emulsions: $\phi = 0.745$.

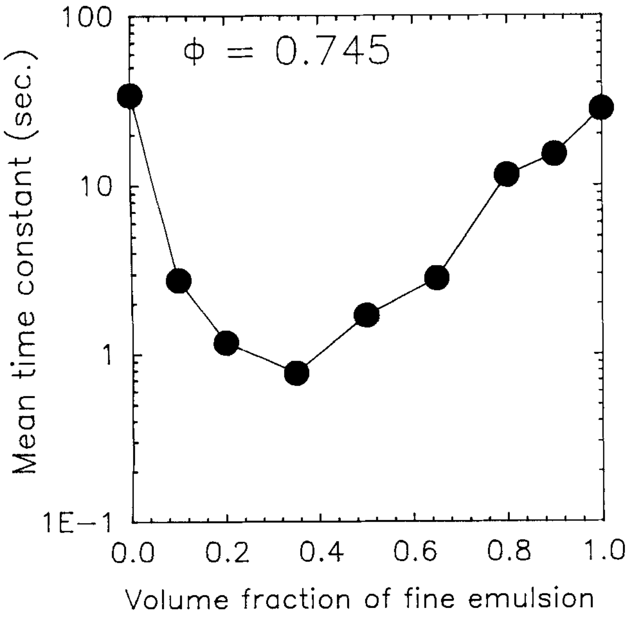


Figure 11. Mean time constant vs. volume fraction of fine emulsion in the mixed oil-in-water emulsions: $\phi = 0.745$.

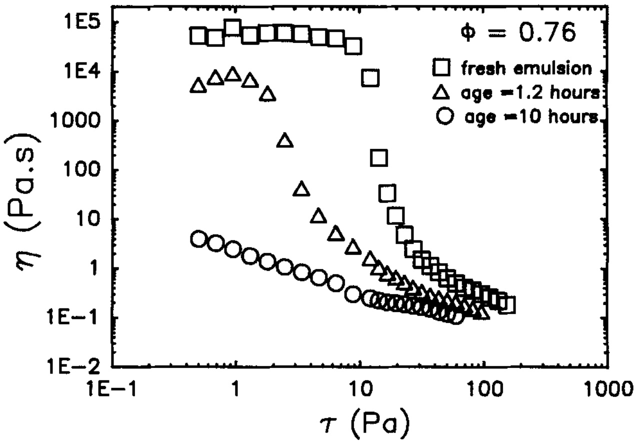
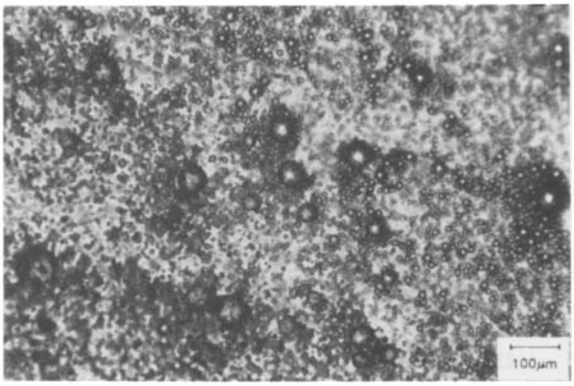
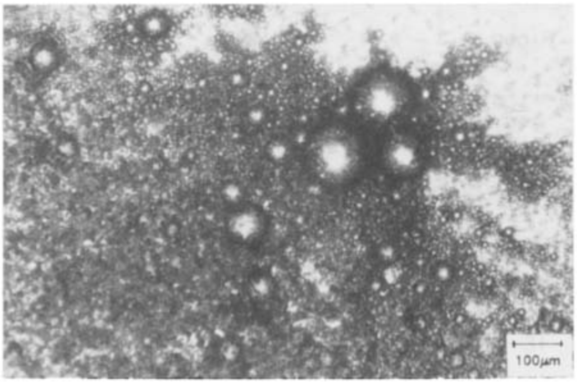


Figure 12. Flow curves of fresh (originally fine) and aged water-in-oil emulsions.

emulsion to a coarse emulsion could be explained in terms of ϕ_p, the maximum packing concentration of droplets. At $\phi > \phi_p$, the droplets are deformed into polyhedral shape and a network structure of thin liquid films of continuous phase is generated. The volume fraction of the emulsions under consideration is 0.745. At this high concentration, the droplets are expected to come into close contact with each other to form a network structure of thin liquid films. When a fine emulsion is added to a coarse emulsion (keeping ϕ constant), the large droplets are replaced by the fine droplets. As these fine droplets can easily fit into the voids between the large



Aged W/O emulsion (originally fine), Φ=0.76



Aged W/O emulsion (originally fine), Φ=0.76

Figure 13. Aged water-in-oil emulsion (originally fine): $\phi = 0.76$ (age, 10 h).

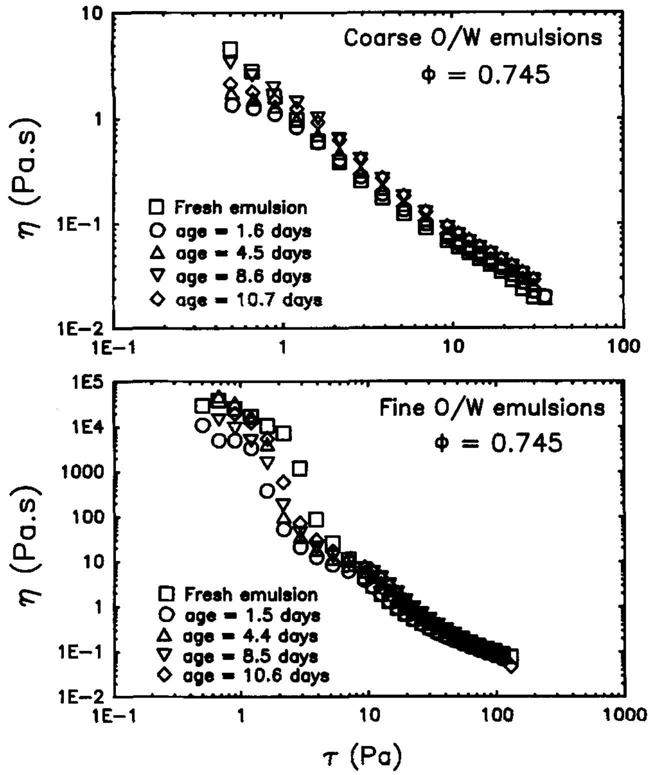


Figure 14. Effect of aging on the viscosity of oil-in-water emulsions: $\phi = 0.745$.

droplets, the net effect of adding the fine droplets is to separate the large ones, and consequently the droplets are no longer closely packed. Due to the increased mobility of the droplets, the rheological parameters of the emulsion decrease significantly. From the data shown in Figures 8, 10 and 11, it is clear that the lubrication effect of fine particles is maximum when the fine emulsion proportion of the mixed emulsion is about 36 vol. %. With further increase in the proportion of the fine emulsion, the rheological parameters start increasing due to crowding/jamming of particles.

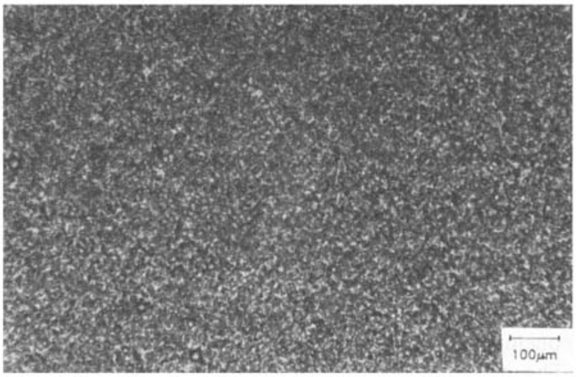
Effect of aging

The effect of aging on the rheological properties of both W/O and O/W emulsions was investigated. In the case of W/O emulsions, the aging behavior of the originally fine emulsion, having $\phi = 0.76$, was studied. For O/W emulsions, both fine and coarse emulsions, having $\phi = 0.745$, were investigated.

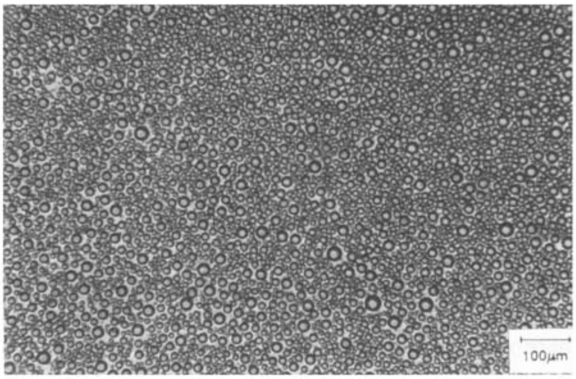
Figure 12 compares the flow curves of the fresh (originally fine) and aged W/O emulsions. As can be seen, these emulsions age rather rapidly. Upon aging, the viscosity decreases dramatically; also, the shear-thinning effect decreases. The reduction in viscosity with aging is more severe at low to moderate values of shear stress. The storage modulus of the W/O emulsions also decreased significantly upon aging. Figure 13 shows the photomicrographs of the aged W/O emulsion, after 10 hours of aging. Upon comparing the photomicrographs of Figure 13 and Figure 1c (fine emulsion), it is obvious that a significant number of large droplets appear with aging. Both the mean droplet size and the width of the droplet size distribution increase with aging. The coarsening of droplets could be due to either coalescence or "Ostwald ripening." The observed decrease in viscosity and storage modulus is likely due to an increase in both the mean droplet size and the polydispersity.

The effect of aging on the viscosity of O/W emulsions is shown in Figure 14. Clearly, the aging effect exhibited by the O/W emulsions is nowhere near as severe as that observed in the case of W/O emulsions (Figure 12). At low shear stresses, the viscosity of the O/W emulsions (both coarse and fine emulsions, originally) appears to decrease initially with aging, although the decrease is only marginal. With further increase in the age, the viscosity tends to increase to the original level. A similar trend was observed in the storage modulus data at low frequencies. However, at high shear stresses and frequencies, the changes in the viscosity and storage modulus, upon aging, are negligible. The photomicrographs of the aged O/W emulsions are shown in Figure 15. Upon comparing these photomicrographs with those of the corresponding fresh emulsions (Figure 4), the changes in droplet sizes do not appear to be substantial.

Finally, Figure 16 compares the shear-stress vs. shear-rate data obtained from different instruments for the same emulsions (aged O/W emulsions). As mentioned earlier, the coaxial cylinder viscometer was used only to check the presence of "wall effects" (if any) in highly concentrated emulsions. The shear rates in the coaxial cylinder viscometer were calculated according to the method recommended by Yang and



Aged O/W emulsion (originally fine), Φ=0.745



Aged O/W emulsion (originally coarse), Φ=0.745

Figure 15. Aged oil-in-water emulsions: $\phi = 0.745$ (age, 10.7 days).

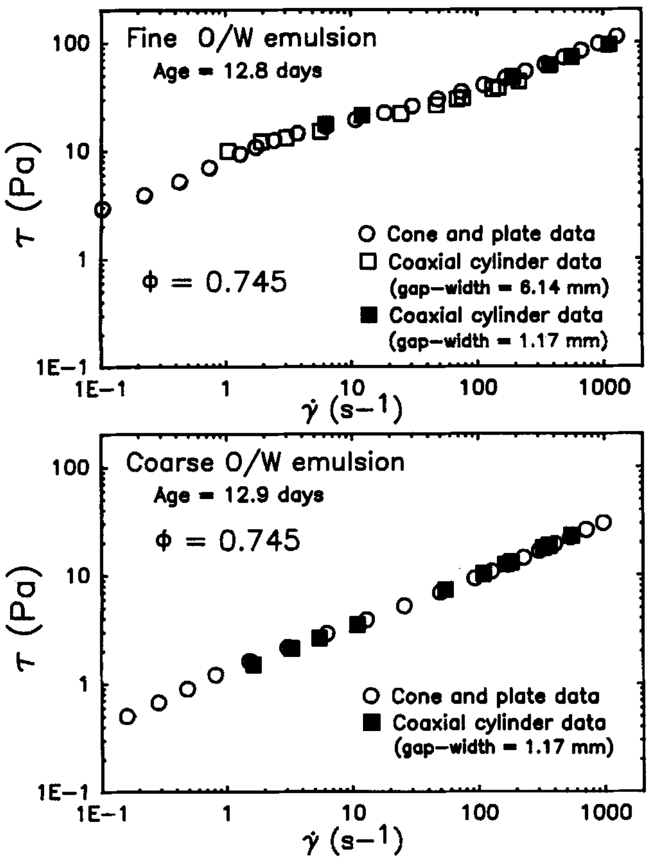


Figure 16. Rheological data from different instruments for the same emulsions.

Krieger (1978) for non-Newtonian fluids. Figure 16 clearly shows a very good agreement between the data obtained from different measuring systems, indicating that the wall effects were negligible in our measurements.

Conclusions

Based on the experimental results and analysis, the following conclusions can be made:

- The reduction in droplet size results in a dramatic increase in the viscosity and storage modulus of the concentrated W/O and O/W emulsions. Also, the shear-thinning effect becomes even stronger in the case of fine emulsions.
- When concentrated fine and coarse O/W emulsions, with different droplet sizes but the same volume fraction of droplets, are mixed together in varying proportions, the resulting mixed emulsion exhibits a minimum in viscosity, storage and loss moduli, and time constant at a certain proportion of the fine droplets.
- The rheological parameters of W/O emulsions decrease substantially upon aging of the emulsion. The decrease in the rheological properties is caused by the coarsening of the droplets. The aging effect exhibited by the O/W emulsions is nowhere near as severe as that observed in the case of the W/O emulsions.

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