

Viscosity and storage/loss moduli for mixtures of fine and coarse emulsions

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Abstract

The rheological behaviour of fine (small droplets) and coarse (large droplets) emulsions, and their mixtures, was studied. Both oil-in-water and water-in-oil emulsions were investigated. The viscosity and storage modulus of fine emulsions are much higher than those of the corresponding coarse emulsions. The fine emulsions are also more shear-thinning. The low-shear viscosity of the mixed fine and coarse emulsions exhibits a minimum at a certain proportion of fine emulsion in the mixture. The depth of the viscosity-minimum is much larger in the case of oil-in-water emulsion. The storage and loss moduli of mixed oil-in-water emulsions exhibit minima at a certain proportion of fine emulsion only at high frequencies. No minima in moduli are seen in the case of water-in-oil emulsions. © 1997 Elsevier Science S.A.

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1. Introduction

The influence of droplet size and droplet size distribution upon 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 effects of particle size deal with suspensions of solid particles [1,2].

According to Einstein's theory for the viscosity of suspensions [3,4], the relative viscosity is given as:

$$\eta_r = 1 + 2.5\phi \quad (1)$$

where η_r is the relative viscosity (defined as the ratio of the suspension viscosity to the dispersion 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 three important assumptions involved in the derivation of Eq. (1), namely: (1) the suspension is very 'dilute' so that the particles are far apart, isolated from each other; (2) there are no non-hydrodynamic forces present, such as electrical double layer, van der Waals attraction and Brownian motion; and (3) the particles are rigid spheres. The effect of particle size becomes important if any of these assumptions are violated [5].

The dispersions of non-rigid and deformable particles exhibit a complex rheology. The deformation of the droplets

in shear flow leads to normal stresses and shear-thinning effect even when the dispersed-phase concentration is low [6–17]. The shear-thinning effect and the normal stresses generally increase with the increase in droplet size as larger droplets undergo greater deformation. The viscosity, however, shows an opposite trend, that is, it increases with the decrease in droplet size as smaller droplets tend to be more rigid.

At high concentrations of dispersed-phase, the interaction between the neighbouring particles becomes important and the particles can no longer be treated as isolated particles. For mono-disperse systems without any non-hydrodynamic interactions (electrical double layer, van der Waals attraction, Brownian motion), the particle size is not that important. However, in the case of concentrated poly-disperse systems, the polydispersity (size distribution) exerts a strong influence on the rheological properties. Several studies indicate that when two mono-disperse systems having different particle sizes, but the same volume fraction of particles, are mixed together in varying proportions, the resulting dispersion exhibits a minimum in the viscosity at a certain composition [1,2,18]. The observed decrease in viscosity, which is due to the fact that smaller particles serve to isolate or lubricate the large ones, is a function of the ratio between the particle radii. However, most of the published studies dealing with mixtures of fine and coarse dispersions are restricted to systems of solid particles. Little attention has been given to emulsions of oil and water.

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Table 1
Details of rheological measurements

Instrument	Measuring system	Type of experiments	Dimensions of measuring systems
Bohlin CS-50	Cone-and-plate	Steady shear and oscillatory	Plate diameter = 60 mm Cone diameter = 40 mm Cone angle = 4° Gap at cone tip = 150 μm
Fann viscometer	Coaxial cylinder	Steady shear	Rotor radius = 1.8415 cm Bob radius = 1.7245 cm Bob length = 3.8 cm Gap width = 0.117 cm

In this paper, new results on the effects of droplet size and droplet size distribution on the steady and oscillatory behaviour of emulsions are presented. Both oil-in-water (O/W) and water-in-oil (W/O) emulsions are investigated.

2. Experimental work

2.1. Materials

The emulsions were prepared using a light mineral oil. The mineral oil was a high quality liquid petrolatum used as a soothing massage oil, to cleanse and lubricate dry and inflamed skin, and for preparing external pharmaceutical products. The viscosity and density of the oil at 22 °C were 29.2 mPa s and 0.85 g cm⁻³, respectively. 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 non-ionic surfactant is manufactured by Union Carbide. Emsorb 2500 was used as a surfactant for the preparation of water-in-oil type emulsions. Emsorb 2500 is manufactured by Henkel Corporation, Emery Group.

2.2. Procedures

For the preparation of oil-in-water emulsions, the surfactant (Triton X-100) was dissolved in the aqueous phase. The concentration of the surfactant in the aqueous phase was kept 2 wt%. For the preparation of water-in-oil emulsions, the surfactant (Emsorb 2500) 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 4.13 wt%.

Two different droplet size oil-in-water emulsions (i.e. fine and coarse emulsions) having an oil volume fraction of 0.78 were prepared in batches of about 650 g each. A variable speed homogenizer (Gifford-Wood model 1-L) was used to provide the necessary agitation and shearing of fluids. The coarse emulsion was prepared by keeping the shearing speed of the homogenizer and the duration of shearing small. The fine emulsion was prepared by using a high shearing speed and an increased duration of shearing. Fine and coarse emulsions having lower volume fractions of oil were prepared by

diluting the concentrated ones (oil volume fraction of 0.78) with an appropriate amount of the same dispersion medium (2 wt% Triton X-100 aqueous solution).

For water-in-oil emulsions, only one concentration of water was studied i.e. 72 vol%. The fine and coarse water-in-oil emulsions, having a water volume fraction of 0.72, were prepared in batches of about 250 g each. As in the case of oil-in-water emulsions, the fine water-in-oil emulsion was prepared by using a high shearing speed and an increased duration of shearing.

At any given concentration of emulsion (O/W or W/O), several mixtures of fine and coarse emulsions were prepared with varying amount of the fine emulsion. The mixing of the fine and coarse emulsions was carried out with a hand stirrer. The rheological behaviour of the fine and coarse emulsions as well as the corresponding mixed emulsions was studied at 22 °C.

The rheological measurements for water-in-oil emulsions and concentrated oil-in-water emulsions (oil volume fraction of 0.78) were carried out in a Bohlin controlled-stress rheometer (Bohlin CS-50). A cone-and-plate measuring system was used. For oil-in-water emulsions having lower volume fractions of oil, and hence lower viscosities, the data were collected with a Fann coaxial cylinder viscometer. Table 1 gives further information about the measuring systems used in the present work.

The droplet sizes of emulsions were determined by taking photomicrographs. The photomicrographs were taken with a Zeiss optical microscope equipped with a camera.

3. Results and discussion

3.1. Oil-in-water emulsions

Fig. 1 shows the photomicrographs of fine and coarse oil-in-water emulsions. Clearly, the droplets of the fine emulsion are much smaller than those of the coarse emulsion. The Sauter mean diameters of the fine and coarse emulsions are 6.5 μm and 32 μm, respectively.

The viscosity versus shear stress plots for the fine and coarse oil-in-water emulsions at three different dispersed-phase (oil) concentrations (ϕ) are shown in Fig. 2. The

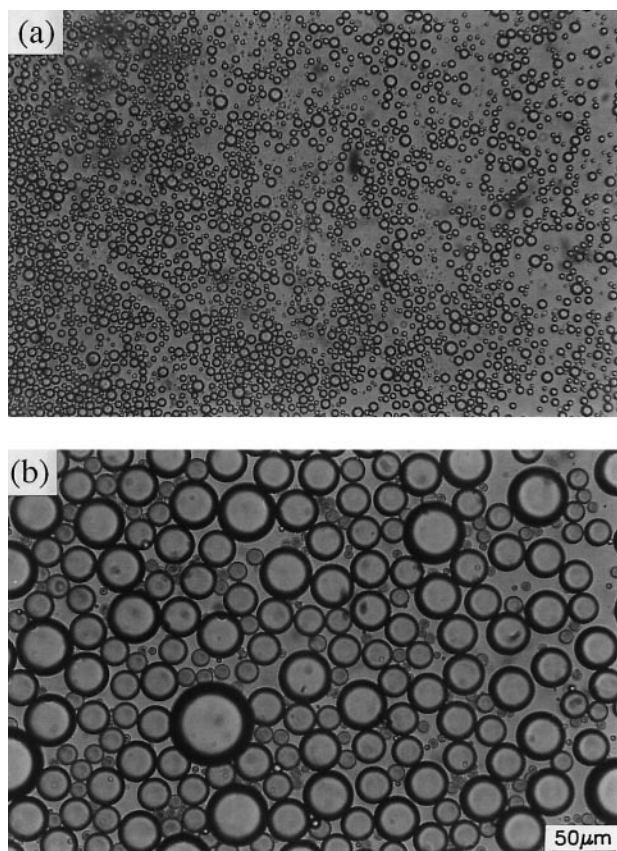


Fig. 1. Photomicrographs of fine and coarse oil-in-water emulsions. (A) Fine emulsion; (B) coarse emulsion.

viscosity of the fine emulsions is much higher than that of the corresponding coarse emulsions. For instance, the viscosity of the fine oil-in-water emulsion, having an oil volume fraction of 0.78, is almost 16 times that of the corresponding coarse emulsion at a shear stress of 1.2 Pa. However, the difference in viscosities of the fine and coarse emulsions decreases with the decrease in the dispersed-phase (oil) concentration. It should be noted further that fine emulsions tend to be more shear-thinning than the corresponding coarse emulsions, especially at high values of ϕ . For example, the viscosity of the fine oil-in-water emulsion ($\phi=0.78$) increases from 0.29 to 24.84 Pa s (almost 85 times) over a shear stress decrease from 62.4 to 0.9 Pa whereas the viscosity of the corresponding coarse emulsion increases from 0.042 to 1.5 Pa s (about 36 times) over the same stress range.

The observed increase in viscosity and shear-thinning effect upon reduction of droplet size, is likely due to an increase in particle–particle interactions and hence aggregation (flocculation) of droplets. With the decrease in droplet size, the number of droplets per unit volume of the emulsion (at a given ϕ) increases and the mean distance of separation between the droplets decreases. Consequently, droplet–droplet collisions and flocculation of droplets are expected to become important, especially for concentrated fine emulsions.

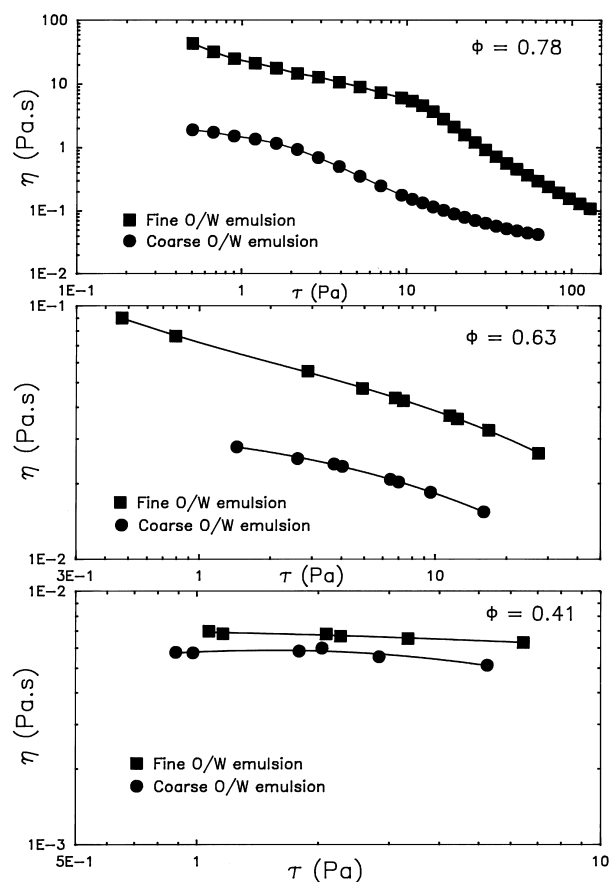


Fig. 2. Viscosity versus shear stress plots for fine and coarse oil-in-water emulsions.

The viscosity data for the mixed fine and coarse emulsions are shown in Fig. 3. An important point to note from Fig. 3 is that at low shear stresses, the viscosity of the emulsion decreases initially with the addition of fine emulsion to the coarse emulsion. However, at high concentrations of the fine emulsion, the viscosity of the mixed emulsion lies between the viscosities of the corresponding fine and coarse emulsions. It should also be noted that the shear-thinning effect in the emulsion decreases initially with the addition of fine emulsion to the coarse emulsion.

The variation of viscosity of the mixed emulsions with the increase in volume fraction of the fine emulsion is shown in Figs. 4–6 for three different oil concentrations. The viscosity goes through a minimum at low shear stresses. The minimum in viscosity occurs at a fine emulsion proportion of about 28vol%. This observation is consistent with the behaviour of suspensions of solid particles. Several studies on bimodal suspensions of solid particles [1,2,19] indicate that there occurs a minimum in zero shear viscosity when the fine particles account for about 25 to 35% of the total volume fraction of particles.

The decrease in viscosity with the addition of fine emulsion to a coarse emulsion (keeping ϕ constant) can be explained as follows: when a fine emulsion is added to a coarse emulsion at constant ϕ , the large droplets are replaced by fine ones. As

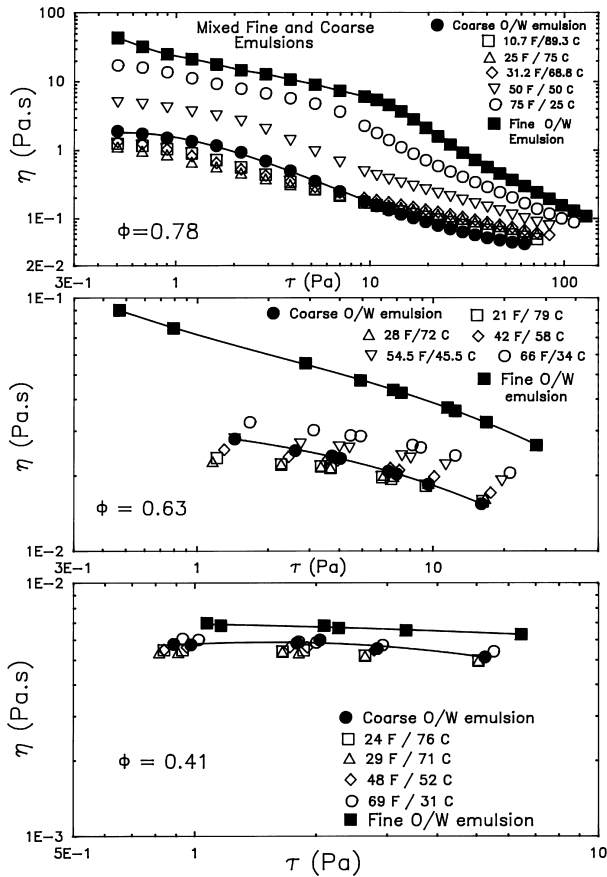


Fig. 3. Viscosity data for mixed fine and coarse oil-in-water emulsions.

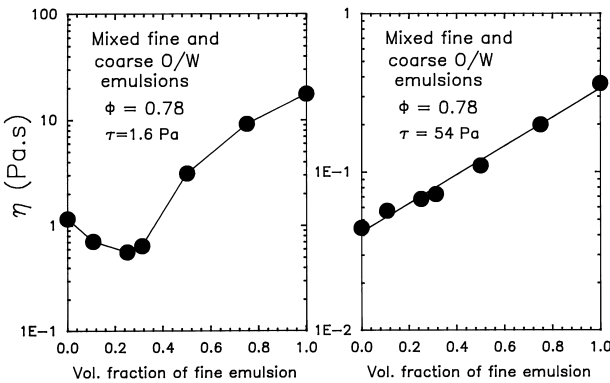


Fig. 4. Viscosity of mixed fine and coarse oil-in-water emulsions ($\phi = 0.78$) as a function of volume fraction of fine emulsion.

the fine droplets can easily fit into the voids present in the flocs or aggregates of large droplets, the net effect of adding the fine droplets is to separate the flocs, and this leads to an increase in the mobility of the flocs. Due to increased mobility of the flow units, the viscosity of the emulsion decreases. As aggregation (flocculation) of droplets is stronger at high values of ϕ , the droplet size effect is also expected to be strong at high ϕ . This can be seen clearly in Fig. 7 where the low-stress viscosity data for the mixed emulsions are compared at three different values of the dispersed-phase (oil) concentration, ϕ . The depth of the viscosity-minimum at a high ϕ

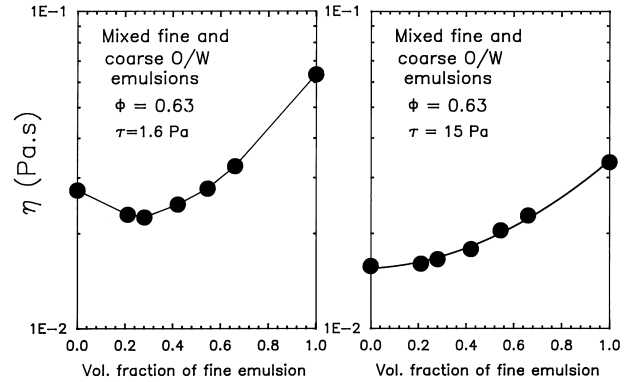


Fig. 5. Viscosity of mixed fine and coarse oil-in-water emulsions ($\phi = 0.63$) as a function of volume fraction of fine emulsion.

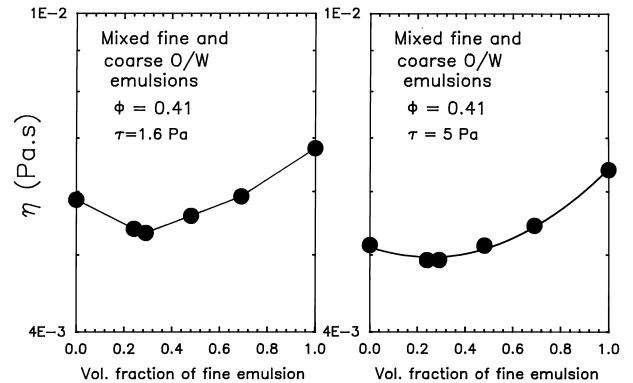


Fig. 6. Viscosity of mixed fine and coarse oil-in-water emulsions ($\phi = 0.41$) as a function of volume fraction of fine emulsion.

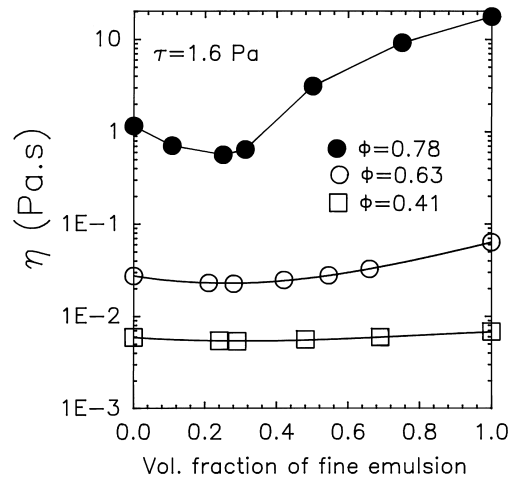


Fig. 7. Comparison of viscosity data for mixed emulsions at three different values of dispersed-phase (oil) concentration, ϕ .

value of 0.78 is much larger as compared with that at lower ϕ values.

The storage and loss moduli data for the fine and coarse oil-in-water emulsions at $\phi = 0.78$ are shown in Fig. 8. The oscillatory measurements were carried out at a very low shear stress of 0.1 Pa. Fig. 8 reveals the following important points: (1) the storage and loss moduli of the coarse emulsion are much lower than those of the fine emulsion; (2) the coarse emulsion is predominantly viscous in that the storage mod-

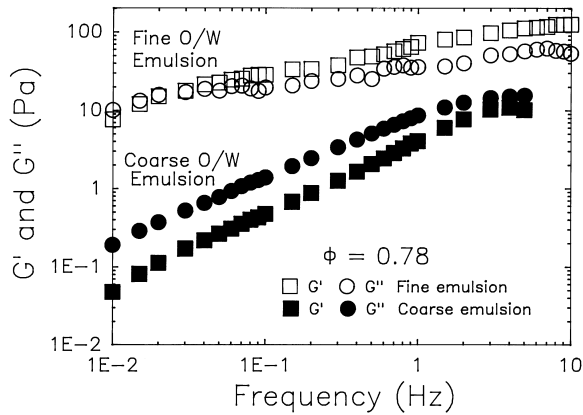


Fig. 8. Storage and loss moduli data for fine and coarse oil-in-water emulsions ($\phi=0.78$).

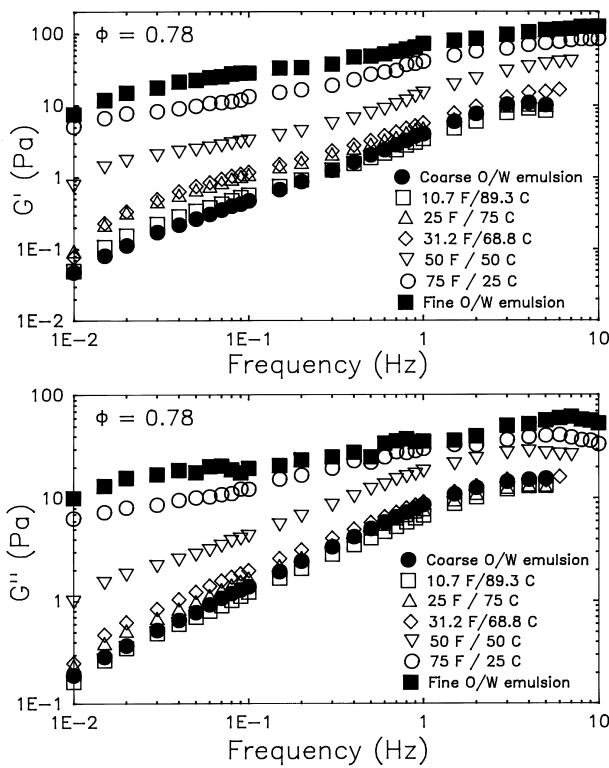


Fig. 9. Storage and loss moduli for mixed fine and coarse oil-in-water emulsions ($\phi=0.78$).

ulus (G') falls below the loss modulus (G'') over the entire frequency range; and (3) the fine emulsion is predominantly elastic, G' falls above G'' over most of the frequency range investigated. An increase in the moduli values, upon reduction of droplet size, clearly indicates that droplet-droplet interactions increase with the decrease in droplet size.

The moduli data for the mixed fine and coarse emulsions are shown in Fig. 9. The moduli values initially decrease with the addition of fine emulsion to the coarse emulsion, especially at high values of frequency. With further increase in fine emulsion content, the moduli data for the mixed emulsion fall between the corresponding values for the coarse and fine emulsions. The variation in the storage and loss moduli of

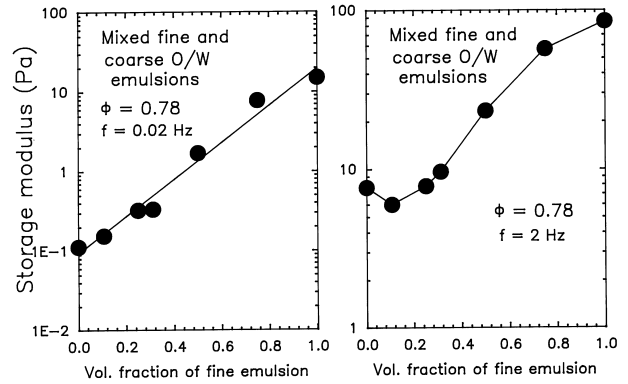


Fig. 10. Storage modulus of mixed fine and coarse oil-in-water emulsions ($\phi=0.78$) as a function of volume fraction of fine emulsion.

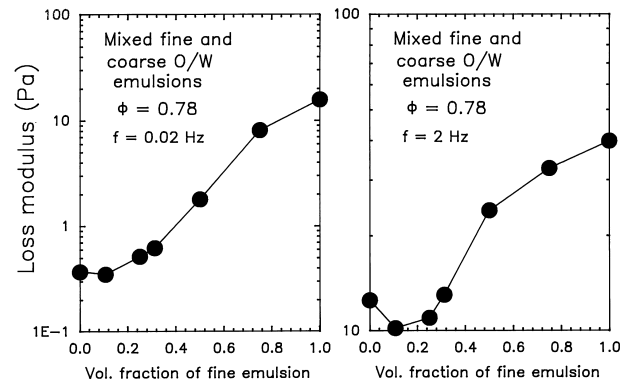


Fig. 11. Loss modulus of mixed fine and coarse oil-in-water emulsions ($\phi=0.78$) as a function of volume fraction of fine emulsion.

the mixed emulsion with the increase in fine emulsion content is shown in Figs. 10 and 11. At high frequencies, both storage and loss moduli go through a minimum. The minimum in the moduli occurs at a fine emulsion proportion of about 20 vol%.

3.2. Water-in-oil emulsions

Fig. 12 shows the photomicrographs of the fine and coarse water-in-oil emulsions at a dispersed-phase (water) concentration (ϕ) of 0.72. The droplets of the fine emulsion are much smaller than those of the coarse emulsion. Furthermore, the fine emulsion is nearly mono-disperse i.e. all the droplets are of similar size. The Sauter mean diameters of the fine and coarse water-in-oil emulsions are 2.5 μm and 16.5 μm , respectively.

The viscosity versus shear stress data for the fine and coarse water-in-oil emulsions at $\phi=0.72$ are shown in Fig. 13. The following points should be noted from Fig. 13: (1) the viscosity of the fine emulsion is much higher than that of the coarse emulsion; (2) the difference in the viscosities of the fine and coarse emulsions decreases with the increase in shear stress; and (3) the fine emulsion is much more shear-thinning as compared with the coarse emulsion. From these observations, it is clear that droplet-droplet interactions are much stronger in the case of the fine emulsion. The high degree of shear-thinning effect in the fine emulsion is likely due to flocculation of droplets. Due to the presence of London-van

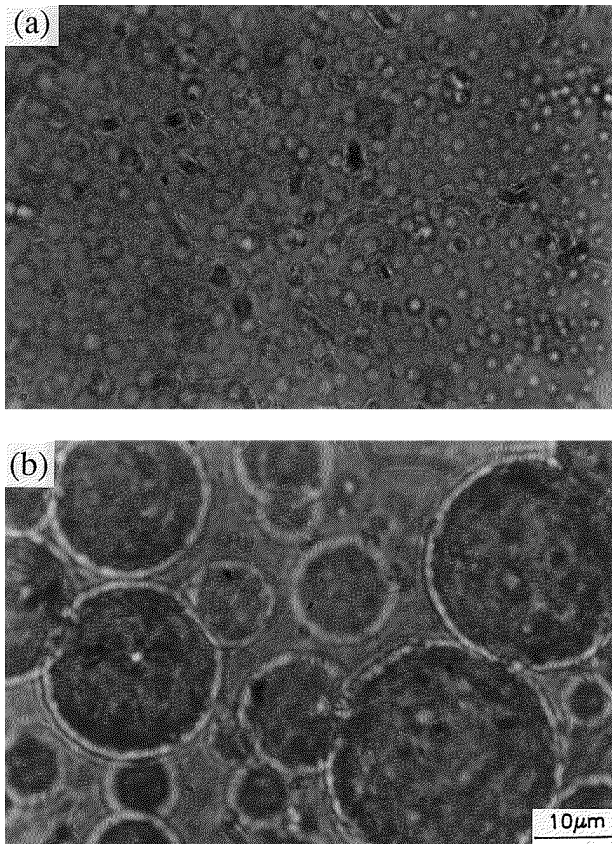


Fig. 12. Photomicrographs of fine and coarse water-in-oil emulsions. (A) Fine emulsion; (B) coarse emulsion.

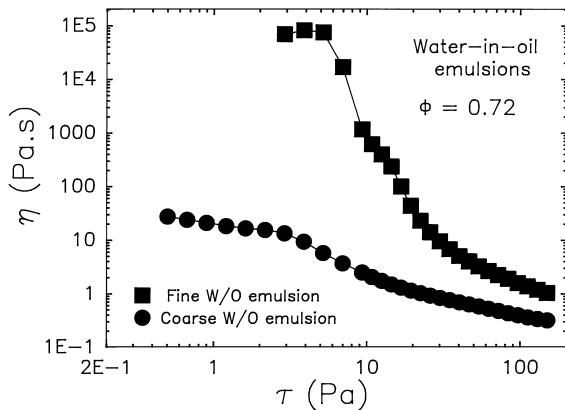


Fig. 13. Viscosity versus shear stress plots for fine and coarse water-in-oil emulsions ($\phi=0.72$).

der Waals attractive forces between the droplets, the droplets are expected to flocculate especially when the separation distance between the droplets is small (as in the case of concentrated fine emulsion). When flocs of droplets are formed, they immobilize a significant amount of the continuous phase within themselves. Upon increasing the shear stress (or shear rate), the size of the flocs decreases and this process releases some of the continuous phase originally immobilized within the flocs. As a result, the effective dispersed-phase concentration decreases. This leads to a decrease in the viscosity and hence, a shear-thinning effect is observed.

Fig. 14 shows the viscosity data for the mixed fine and coarse water-in-oil emulsions ($\phi=0.72$). The viscosity of the emulsion decreases only slightly at low shear stresses with the initial addition of fine emulsion to the coarse emulsion. At higher concentrations of fine emulsion, the viscosity data for the mixed emulsions fall between the data for the fine and coarse emulsions. It is interesting to note that the viscosity data for the mixed emulsions fall closer to those of the coarse emulsion even at high proportions of the fine emulsion.

The variation of viscosity of the mixed emulsions with the increase in volume fraction of the fine emulsion is shown in Fig. 15. At a low shear stress of 0.67 Pa, the viscosity of the mixed emulsion goes through a minimum at a fine emulsion content of about 24 vol%. At a high shear stress, the viscosity of the mixed emulsion only increases with the increase in fine emulsion content.

The storage and loss moduli data for the fine and coarse water-in-oil emulsions ($\phi=0.72$) are given in Fig. 16. Fig. 16 reveals the following points: (1) the fine emulsion behaves more like an elastic solid in that the storage modulus (G') is high and nearly flat, independent of the frequency; (2) the coarse emulsion behaves more like a viscous liquid and the storage modulus falls off sharply at lower frequencies; and (3) the loss modulus (G'') of the fine emulsion exhibits a significant scatter, and only at low frequencies, G'' of the

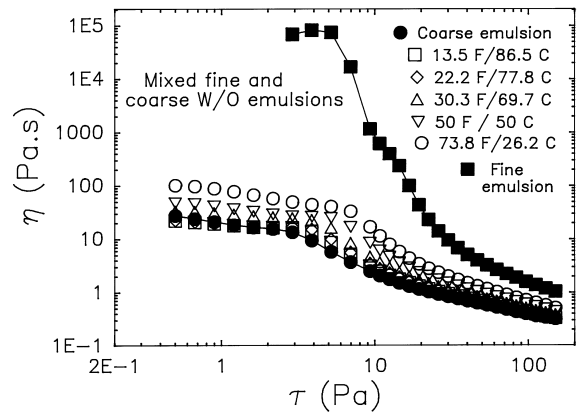


Fig. 14. Viscosity versus shear-stress plots for mixed fine and coarse water-in-oil emulsions ($\phi=0.72$).

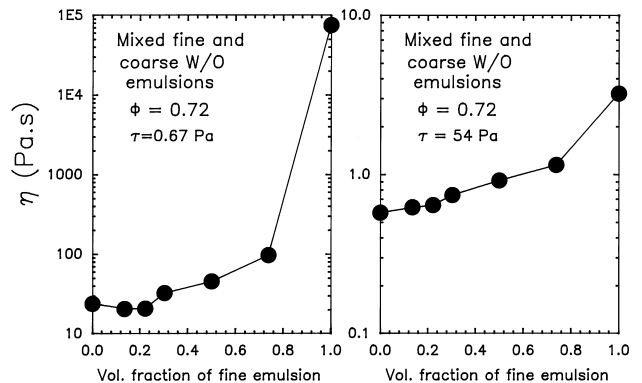


Fig. 15. Viscosity of mixed fine and coarse water-in-oil emulsions ($\phi=0.72$) as a function of volume fraction of fine emulsion.

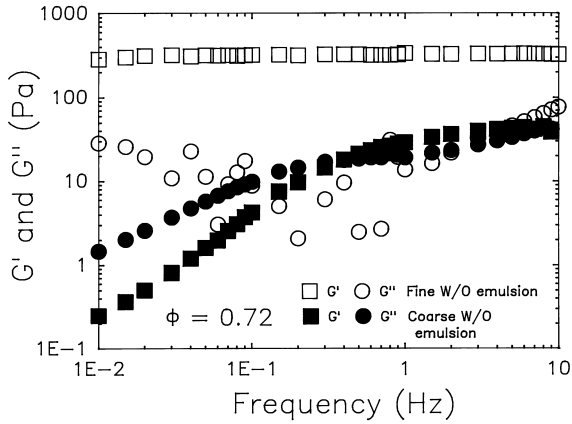


Fig. 16. Storage and loss moduli data for fine and coarse water-in-oil emulsions ($\phi=0.72$).

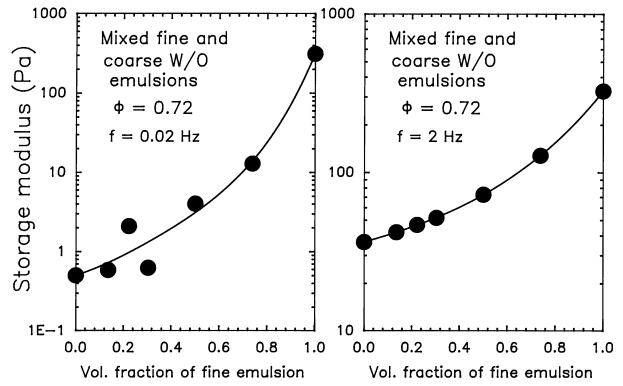


Fig. 18. Storage modulus of mixed fine and coarse water-in-oil emulsions ($\phi=0.72$) as a function of volume fraction of fine emulsion.

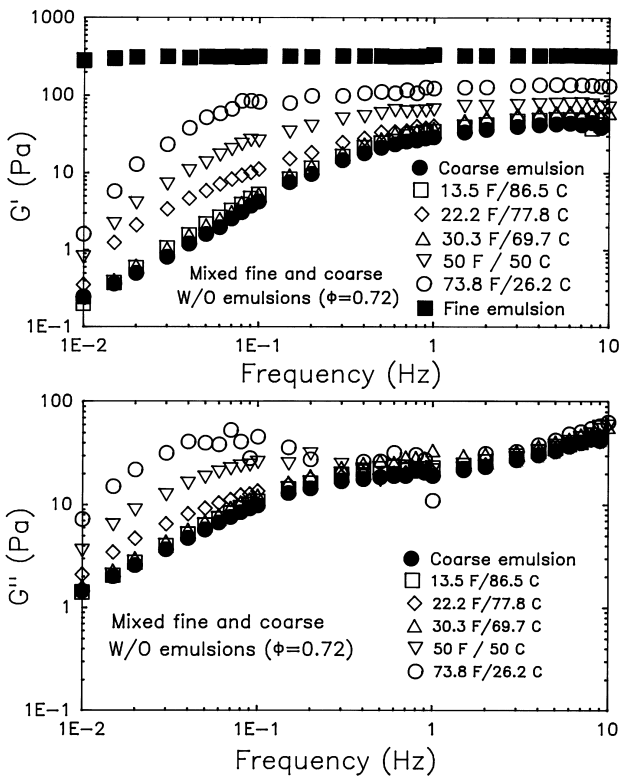


Fig. 17. Storage and loss moduli for mixed fine and coarse water-in-oil emulsions ($\phi=0.72$).

fine emulsion is higher than that of the coarse emulsion. The solid-like behaviour of the fine emulsion (high and flat G') is clearly indicative of the formation of network structure (flocculation) of droplets.

The storage and loss moduli for the mixed fine and coarse water-in-oil emulsions are shown in Fig. 17. The data for the mixed emulsions fall between the corresponding data for the fine and coarse emulsions. The storage modulus increases non-linearly with the increase in volume fraction of the fine emulsion, as shown in Fig. 18. The loss modulus increases with the increase in volume fraction of the fine emulsion (see Fig. 19) only at low frequencies. At high frequencies, the

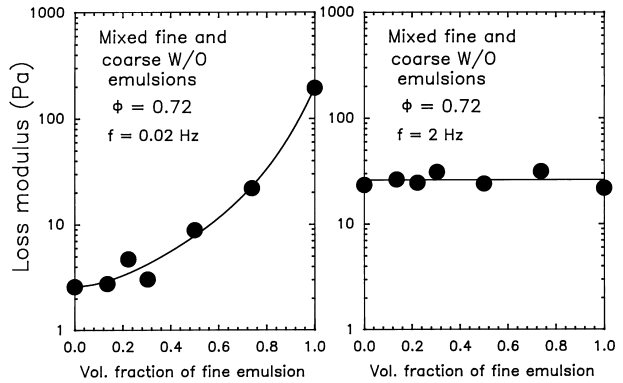


Fig. 19. Loss modulus of mixed fine and coarse water-in-oil emulsions ($\phi=0.72$) as a function of volume fraction of fine emulsion.

loss modulus of the mixed emulsions is almost constant, independent of the volume fraction of the fine emulsion.

4. Conclusions

On the basis of the results of this study, the following conclusions can be made:

1. The viscosity of the emulsions (O/W or W/O) increases substantially upon reduction of the droplet size.
2. The shear-thinning effect in emulsions (O/W or W/O) is enhanced upon reduction of the droplet size.
3. The low-shear viscosity of the mixed fine and coarse emulsions (O/W or W/O) goes through a minimum. In the case of O/W emulsions, the minimum in viscosity occurs at a fine emulsion proportion of about 28 vol%. The mixed W/O emulsions exhibit a minimum in viscosity at a fine emulsion content of about 24 vol%.
4. Upon reduction of droplet size, the emulsions (O/W or W/O) become much more elastic. The storage modulus undergoes a substantial increase when the droplet size is reduced.
5. In the case of mixed O/W emulsions, the storage and loss moduli at high frequencies exhibit minima at a fine emulsion proportion of about 20 vol%. No minima are seen in the case of W/O emulsions.

6. The increase in the rheological parameters (viscosity, shear-thinning effect, moduli) with the decrease in the droplet size can be explained in terms of flocculation of droplets. Upon reduction of droplet size, aggregation of droplets is expected to increase.

Acknowledgements

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