Oscillatory, Creep and Steady Flow Behavior of Xanthan-Thickened Oil-in-Water Emulsions

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The rheological behavior of xanthan gum–thickened oil-in-water emulsions is studied with a cone-and-plate system using a constant-stress rheometer. Xanthan gum solutions and xanthan-thickened oil-in-water emulsions are strongly shear-thinning and viscoelastic in nature. The effects of polymer and oil concentrations on the rheological behavior of emulsions are investigated. The relative viscosity for the thickened emulsions, at any given oil concentration, increases with an increase in the shear rate, whereas the unthickened emulsions show the opposite trend. The theoretical models give reasonable predictions for the relative viscosity, storage modulus, and loss modulus of xanthan-thickened emulsions. The ratio of storage to loss moduli increases considerably with the increase in polymer and oil concentrations. The creep/recovery experiments confirm that the xanthan-thickened emulsions are highly viscoelastic in nature and that the degree of elasticity increases with the increase in polymer and oil concentrations.

Introduction

In the handling, mixing, storage, and pipeline transportation of emulsions, knowledge of rheological properties is required for the design, selection, and operation of the equipment involved. While there is a substantial amount of literature published on the rheology of emulsions prepared from Newtonian liquids (Sherman, 1968; Sherman, 1983; Pal and Rhodes, 1989; Pal, 1993), little attention has been given to emulsions in which the external phase (that is, continuous phase) is a non-Newtonian polymeric liquid even though such emulsions are quite important from a practical point of view. For example, high-molecular-weight polymeric thickeners, such as xanthan gum, rhamsan gum, guar gum, gum arabic, locust beam gum, hydroxyethyl cellulose, sodium carboxymethyl cellulose, and poly(acrylic acid), are frequently added to the external phase of many commercial emulsions of the oil-in-water type (Aqualon Co., 1988; Lochhead et al., 1989; Robins, 1991; Dickinson and Galazka, 1991; Gouldby et al., 1991). The main purpose of adding polymeric thickening agents is to modify the rheological behavior of the external aqueous phase, thereby retarding or even eliminating the processes leading to instability in emulsions (creaming, sedimentation, flocculation, and coalescence). In many food emulsions, there is an additional purpose for adding polysaccharide thickeners to the external phase, that is, to impart the required mouth-feel properties (and pleasing appearance) to the food products.

In this article, we report new results on the steady, oscillatory, and creep behavior of polymer-thickened oil-in-water emulsions. The effects of the dispersed-phase (oil) concentration and the polymer concentration on the rheology of emulsions are also determined.

The polymer studied is xanthan gum, which is a high-molecular-weight water-soluble heteropolysaccharide, secreted by the bacterium *Xanthomonas campestris*. The repeating unit of xanthan gum contains five sugar units consisting of two glucose units, two mannose units, and one glucuronic acid unit (Jansson et al., 1975; Kovacs and Kang, 1977; Baird, 1986). The molecular weight of the xanthan gum is approximately 2×10^6 as determined by light scattering (Carriere et al., 1993; Baird, 1986).

Xanthan gum is of great practical interest because of its widespread use in food, pharmaceutical, agricultural, oilfield, and other industrial applications (Kovacs and Kang, 1977; Baird, 1986). The unique physical and rheological properties of xanthan gum are responsible for its widespread use in various applications (Rochefort and Middleman, 1987; Carnali, 1992; Carriere et al., 1993).

Experimental Work

Materials

The emulsions were prepared using a Newtonian petroleum oil (trade name EDM) supplied by Monarch Oil Company, Canada. This oil is widely used as a lubricant and as a solvent. It has a mild odor and appears as an amber liquid. The viscosity of the oil batch used in this study was 5.8 mPa·s at 25°C. The water used throughout the experiments was deionized. The surfactant used was Triton X-100, a commercially available nonionic surfactant supplied by Rohm and Haas Co. This surfactant is currently manufactured by Union Carbide Co. The chemical name of Triton X-100 is isooctylphenoxypolyethoxy ethanol. The surfactant has a density of 1065 kg/m^3 and a viscosity of 240 mPa·s at 25°C. The polymer used was xanthan gum (trade name Kelzan) supplied by Kelco, a division of Merck & Co., Inc. The lot number of the xanthan sample used in the experiments was 80740A.

Procedure

A stock solution of 1 wt. % xanthan gum was prepared by slowly sifting a known amount of polymer powder into a known volume of gently agitated deionized water at room temperature (~ 21°C). A variable-speed homogenizer (Gifford-Wood Model 1-LV) was used to provide the necessary agitation and mixing of the fluid. The agitation was continued until the polymer was dissolved completely and the solution was lump-free. The required amount of the surfactant (0.4 wt. % Triton X-100) was then added to the polymer solution; the surfactant dissolved readily with gentle agitation. The stock solution was stored at room temperature for more than 12 hours prior to use. All subsequent solutions (0.5 and 0.167 wt. %) were prepared by mixing the stock solution with an appropriate amount of 0.4 wt. % Triton X-100 solution using the Gifford-Wood homogenizer.

The interfacial tension between oil and aqueous phase was measured using the drop-volume (drop weight) method. For the oil/deionized water system, the measured value was 35 mN/m. With the addition of surfactant to the aqueous phase, the interfacial tension decreased substantially. Its value for the oil/0.4 wt. % Triton X-100 solution system was approximately 2.5 mN/m. The addition of xanthan gum to the surfactant solution (0.4 wt. % Triton X-100 solution) did not alter the interfacial tension significantly. It is now well known that xanthan does not generally affect the interfacial tension of an oil-water interface because of its poor adsorption characteristics (Luyten et al., 1993; Dickinson and Euston, 1991; Reichman and Garti, 1991).

The emulsions of the oil-in-water type were prepared in batches of 300–350 g. The known amounts of aqueous polymer solution (containing 0.4 wt. % surfactant) and oil were sheared together in a homogenizer for about 2 min at a fixed speed. The emulsions produced were very stable with respect to coalescence.

The droplet sizes were measured by taking photomicrographs of the emulsion samples (diluted with the same continuous medium) using a Zeiss optical microscope equipped with a camera.

All the rheological experiments were done at 25°C. While most of the rheological measurements were carried out in a Bohlin controlled-stress rheometer (Bohlin CS-50) using a cone-and-plate measuring system, some steady shear data for concentrated emulsions were collected with a Fann coaxial cylinder viscometer as well, using different gap width systems. These latter measurements were done mainly to check the presence of wall effects (if any) and to confirm the measurements of the Bohlin rheometer. Table 1 gives further information about the various measuring systems utilized in the present study.

Table 1. Details of Rheological Measurements

Instrument	Meas. System	Types of Exp.	Dimensions of Meas. Systems
Bohlin CS-50	Cone-and-plate	Steady shear oscillatory creep	Plate Dia. = 60 mm Cone dia. = 40 mm Cone angle = 4° Gap at cone tip = 150 μm
Fan viscometer	Coaxial cylinder	Steady shear	R1–B1; gap width = 1.17 mm R1–B2; gap width = 6.14 mm

Results and Discussion

Rheology of polymer solutions

Figure 1 shows the plots of apparent viscosity (η) as a function of shear stress (τ) for three differently concentrated xanthan gum solutions. (Note that these solutions contain 0.4 wt. % Triton X-100.) The polymer solutions are non-Newtonian and they exhibit three different regions: the lower Newtonian region in the low shear stress range where the viscosity is constant, the shear-thinning region at intermediate stresses where the viscosity decreases substantially with the increase in shear stress, and the upper Newtonian region in the high shear stress range where the viscosity again becomes constant. Also, the flow curves shift upward with an increase in the polymer concentration, indicating an increase in the viscosity with the increase in polymer concentration. These characteristics are quite typical of many polymer solutions, but the unusual feature in the case of the xanthan solutions is that the magnitude of the viscosity changes involved, with

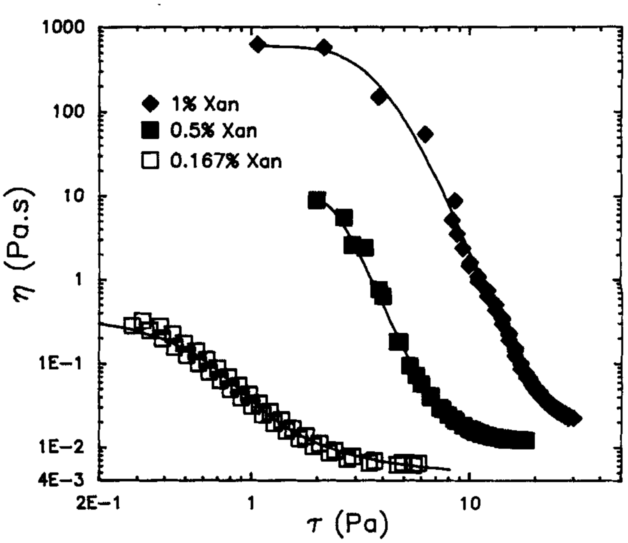


Figure 1. Apparent viscosity as a function of shear stress for xanthan gum solutions.

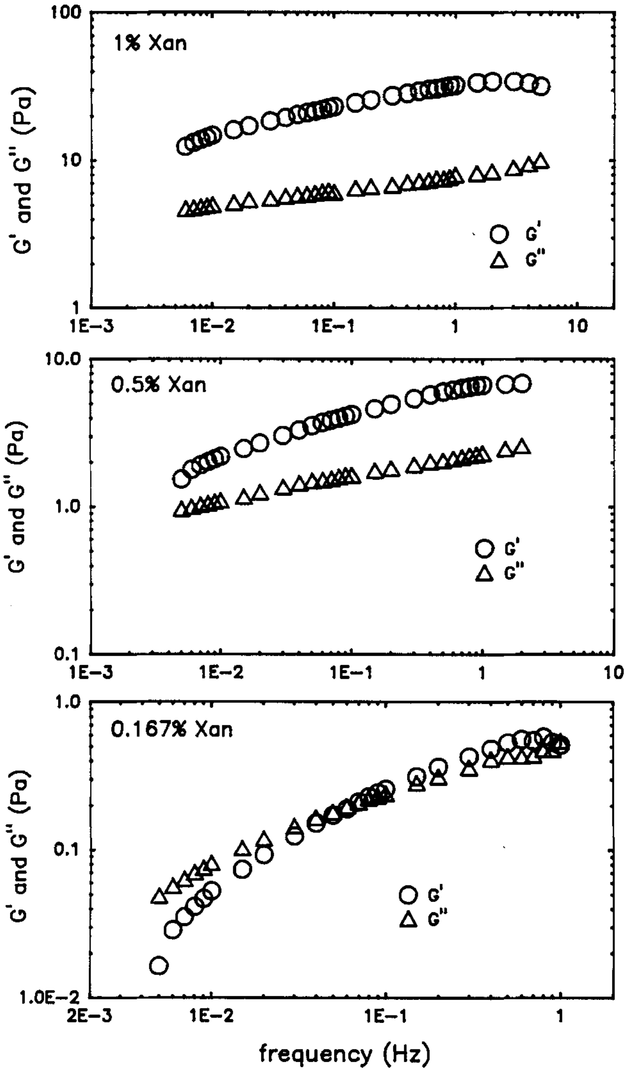


Figure 2. Storage and loss moduli for the xanthan gum solutions in the linear viscoelastic region.

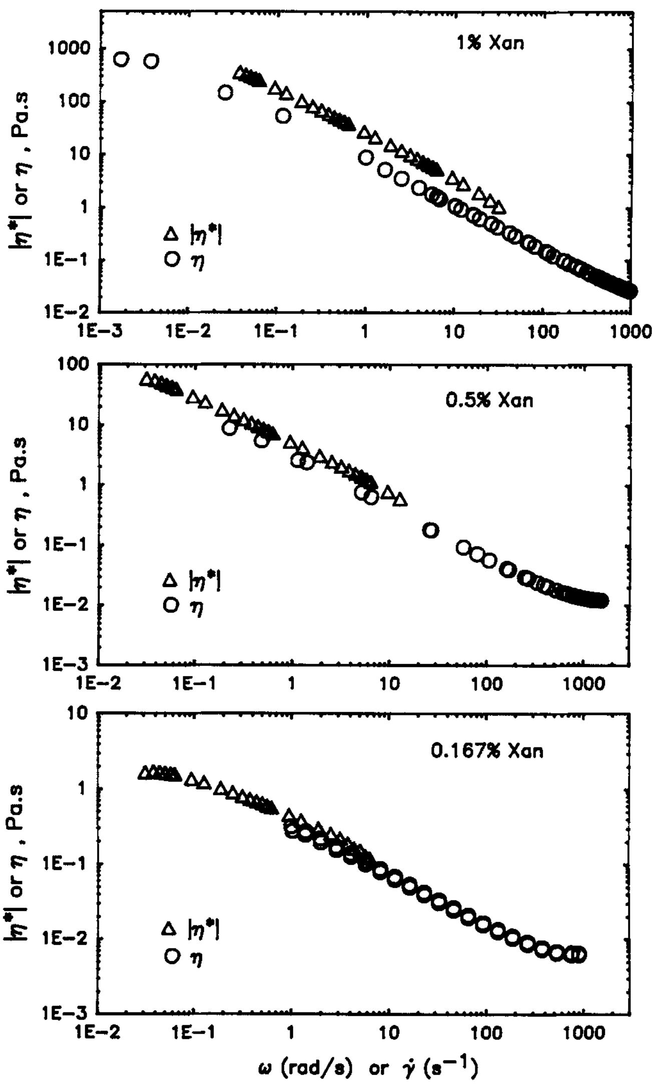


Figure 3. Complex viscosity data vs. steady shear viscosity data for xanthan gum solutions.

changes in shear stress (shear rate) and polymer concentrations, is very large.

Figure 2 gives the plots of storage modulus (G') and loss modulus (G'') for the polymer solutions in the linear viscoelastic region. An important point to note is that in the case of 1 and 0.5 wt. % xanthan solutions, the storage modulus is greater than the loss modulus over the entire frequency range, indicating that these polymer solutions are predominantly elastic. However, at a lower polymer concentration of 0.167 wt. %, the loss modulus is initially greater than the storage modulus at low frequencies, but at high frequencies, $G' > G''$. The crossover frequency, where $G' = G''$, is approximately 0.06 Hz.

From the observations noted thus far (strongly shear-thinning behavior, high storage modulus, etc.), it is clear that xanthan gum solutions are gel-like in nature and that the structure in the solutions is enhanced with the increase in the polymer concentration. Indeed, it has been suggested in the literature (Carnali, 1992; Baird, 1986) that xanthan molecules form a complex network in solutions due to hydrogen bonding and physical entanglements.

Figure 3 compares the complex viscosity (η^*) data with the steady shear viscosity data for xanthan solutions. The complex viscosities fall above the shear viscosities and the difference increases with the increase in polymer concentration, indicating that xanthan solutions do not obey the famous Cox-Merz rule (Cox and Merz, 1958). This is not surprising given the fact that xanthan solutions are highly elastic in nature. However, it should be noted that there is a good agreement between the dynamic viscosity η' (real part of the complex viscosity) and the steady shear viscosity in the low-frequency limit, as shown in Figure 4.

Rheology of xanthan-thickened oil-in-water emulsions

Figure 5 shows the apparent viscosity as a function of shear stress (τ) and shear rate ($\dot{\gamma}$) for emulsions prepared from 1 wt. % xanthan solution. The data are shown for various values of dispersed-phase (oil) concentration (ϕ). The flow

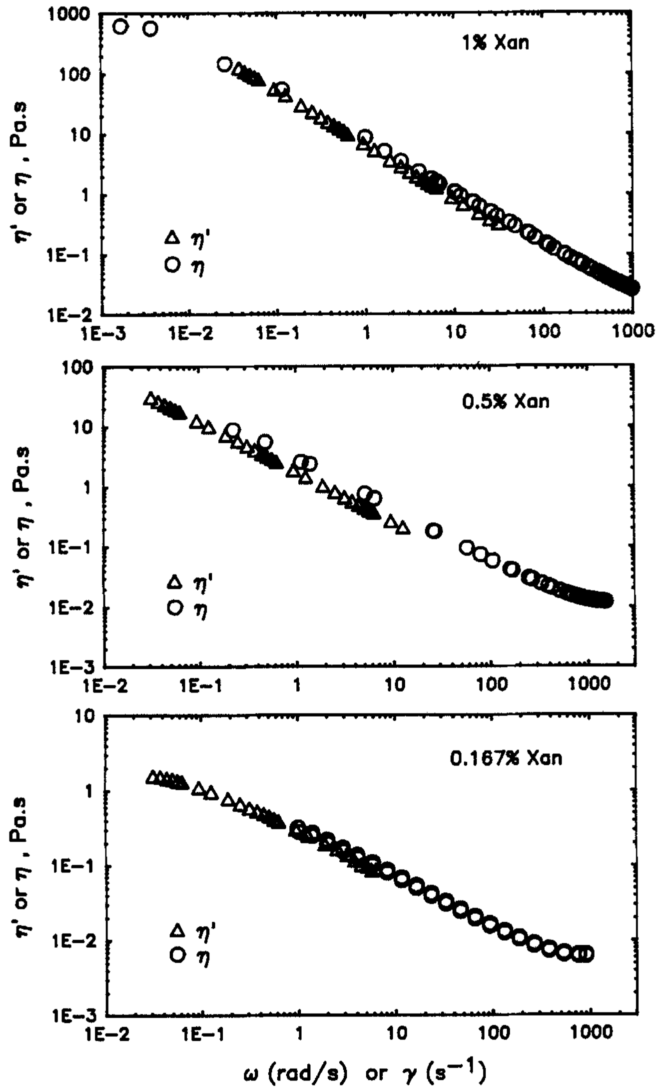


Figure 4. Dynamic viscosity data vs. steady shear viscosity data for xanthan gum solutions.

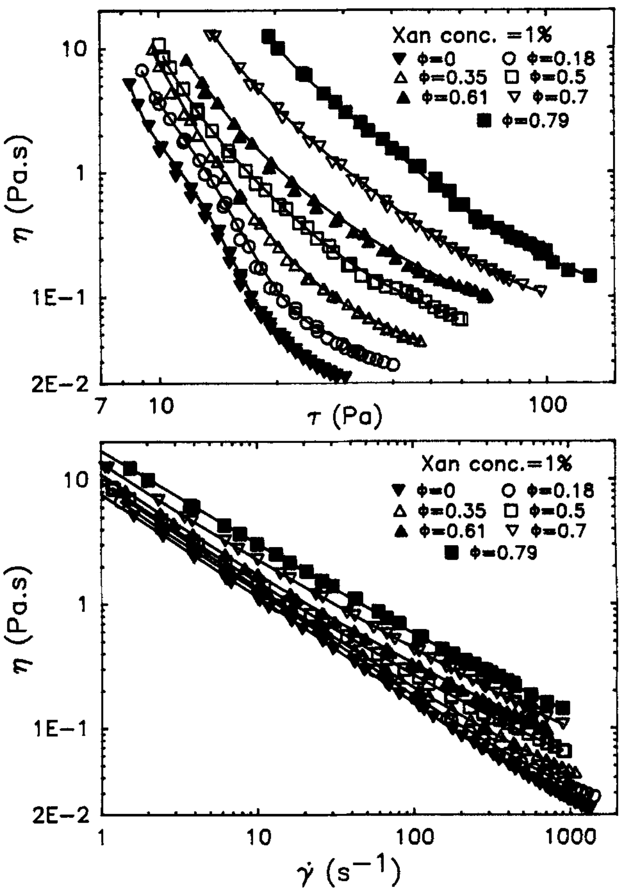


Figure 5. Apparent viscosity as a function of shear stress and shear rate for emulsions prepared from 1 wt. % xanthan solution.

curves for xanthan-thickened emulsions are similar to that of the xanthan solution. We observe a strong shear-thinning behavior and a Newtonian upper region (at high stresses/shear rates). Also, the flow curves shift upward toward higher viscosities with the increase in oil concentration.

The effect of polymer concentration on the viscosity of emulsions is shown in Figure 6. The oil concentration in these emulsions is kept the same (70 vol. %), but the polymer concentration is varied from 0 to 1 wt. %, based on the aqueous phase. As expected, the flow curves shift toward higher viscosities with the increase in the polymer concentration.

It should be noted that the emulsions were polydisperse with respect to droplet size. Figure 7a shows the droplet size distributions for emulsions at low and high values of dispersed-phase concentrations (ϕ). The droplet size increases with the increase in ϕ, although the increase is moderate; for example, the volume-average diameters of 18% oil-in-water (O/W) emulsion and 79% O/W emulsion are 7.4 and 10.7 μm, respectively. The effect of polymer concentration on the droplet size distribution is shown in Figure 7b. The oil concentration in these emulsions is 70 vol. %. With the increase in polymer concentration, the droplet size decreases. The volume-average diameters for 70% O/W emulsion with 0.5,

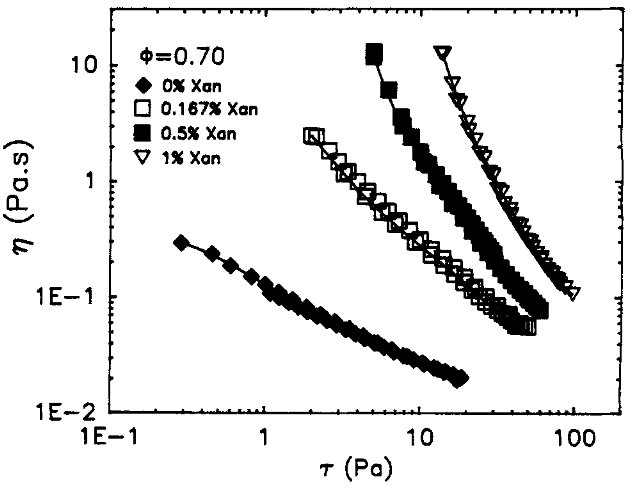
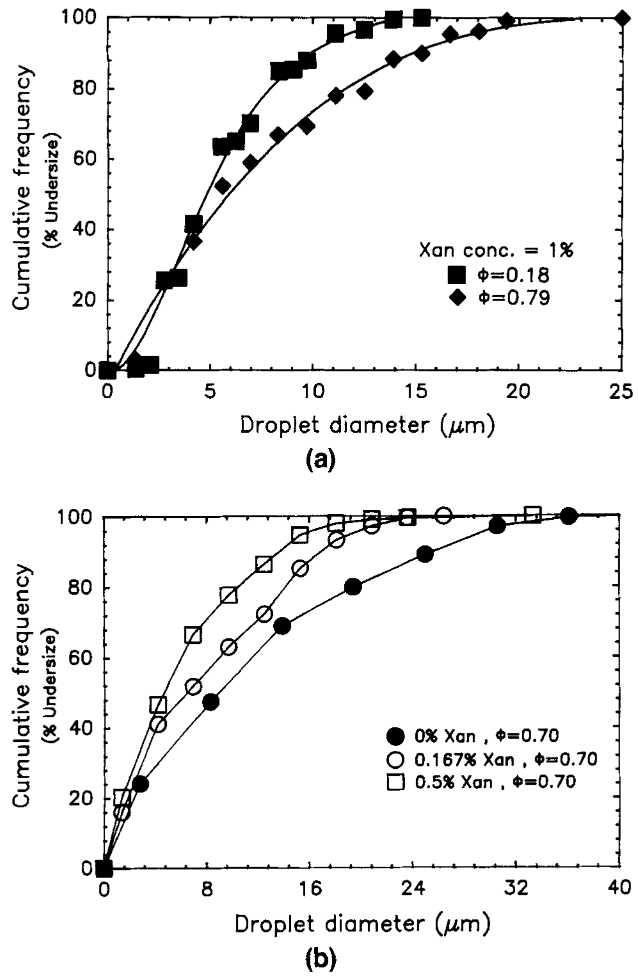


Figure 6. Effect of xanthan concentration on the viscosity of emulsions.



(a)

(b)

Figure 7. (a) Droplet size distributions for emulsions at low and high values of dispersed-phase (oil) concentration (ϕ). (b) Effect of polymer concentration on the droplet size distribution of 70% O/W emulsion.

0.167 and 0% polymer concentrations are 10.5, 12.6 and 18.9 μm, respectively.

Figure 8 compares the shear stress vs. shear rate data obtained from different instruments for the same emulsion. As mentioned earlier, most of the rheological data were collected using a cone-and-plate viscometer. The coaxial cylinder viscometer was used only to check the presence of "wall effects" (if any) in a highly concentrated (70% by volume oil) emulsion, at different polymer concentrations. The shear rates in the coaxial cylinder viscometer were calculated according to the method recommended by Yang and Krieger (1978) for non-Newtonian fluids. Figure 8 clearly shows a good agreement between the data obtained from different measuring systems, indicating that the wall effects were negligible. This is not surprising given the fact that the droplets of the emulsions were relatively small.

The relative viscosity of polymer-thickened emulsions $(\eta_r)_{\dot{\gamma}}$, defined as the ratio of emulsion viscosity to continuous-phase viscosity at the same macroscopic shear rate, is shown in Figure 9a. Interestingly, the relative viscosity increases with the increase in the shear rate for a given concentration emulsion. Figure 9b shows the relative viscosity vs. shear rate data for a 70% O/W emulsion at different polymer concentrations. While the relative viscosity increases with an increase in shear rate for the polymer-thickened emulsions, it shows a large decrease in the case of unthickened emulsion (0% xanthan). The increase in relative viscosity observed for the polymer-thickened emulsions can be explained in terms of an emulsion model of Taylor (1932):

$$\eta_r = 1 + \left(\frac{5k+2}{2k+2}\right)\phi. \qquad (1)$$

Here η_r is the relative viscosity, k is the ratio of the dispersed-phase viscosity (η_d) to the continuous-phase viscosity (η_c), and ϕ is the dispersed-phase concentration. For the polymer-thickened emulsions, the continuous-phase viscosity decreases quite substantially with the increase in shear rate, and therefore k increases by a large amount. According to the Taylor model, an increase in k implies a corresponding increase in the relative viscosity. However, in the case of unthickened (0% xanthan) emulsions where k is constant, the Taylor model predicts a constant relative viscosity at a given ϕ. For unthickened emulsions of low-viscosity Newtonian suspending media, droplet-droplet interactions and hence flocculation of droplets are important at high concentrations (such as 70 vol. % in the present case). Consequently, a major portion of the decrease in relative viscosity is expected to be due to deflocculation of dispersed droplets with an increase in the shear rate. However, some decrease in relative viscosity may be due to deformation of droplets with an increase in the shear rate.

Figure 10a compares the relative viscosity data for emulsions, prepared from 1 wt. % xanthan solution, with three well-known emulsion models: the Taylor model (Taylor, 1932); the Oldroyd model (Oldroyd, 1953, 1959); and the Choi-Schowalter model (Choi and Schowalter, 1975). The Oldroyd model and Choi-Schowalter model are given as follows:

$$\eta_r = \left[1 + \frac{(5k+2)}{2(k+1)}\phi + \frac{(5k+2)^2}{10(k+1)^2}\phi^2\right]\left[\frac{1+\lambda_1\lambda_2\dot{\gamma}^2}{1+\lambda_1^2\dot{\gamma}^2}\right]$$

Oldroyd (2)

$$\eta_r = \left[1 + \frac{(5k+2)}{2(k+1)}\phi + \frac{5(5k+2)^2}{8(k+1)^2}\phi^2\right]\left[\frac{1+h_1h_2\dot{\gamma}^2}{1+h_1^2\dot{\gamma}^2}\right]$$

Choi-Schowalter (3)

where λ_1, λ_2, h_1, and h_2 are given below:

$$\lambda_1 = \frac{(19k+16)(2k+3)}{40(k+1)}\left(\frac{\eta_c R}{\sigma}\right)\left[1 + \phi\frac{(19k+16)}{5(k+1)(2k+3)}\right] \qquad (4)$$

$$\lambda_2 = \frac{(19k+16)(2k+3)}{40(k+1)}\left(\frac{\eta_c R}{\sigma}\right)\left[1 - \phi\frac{3(19k+16)}{10(k+1)(2k+3)}\right] \qquad (5)$$

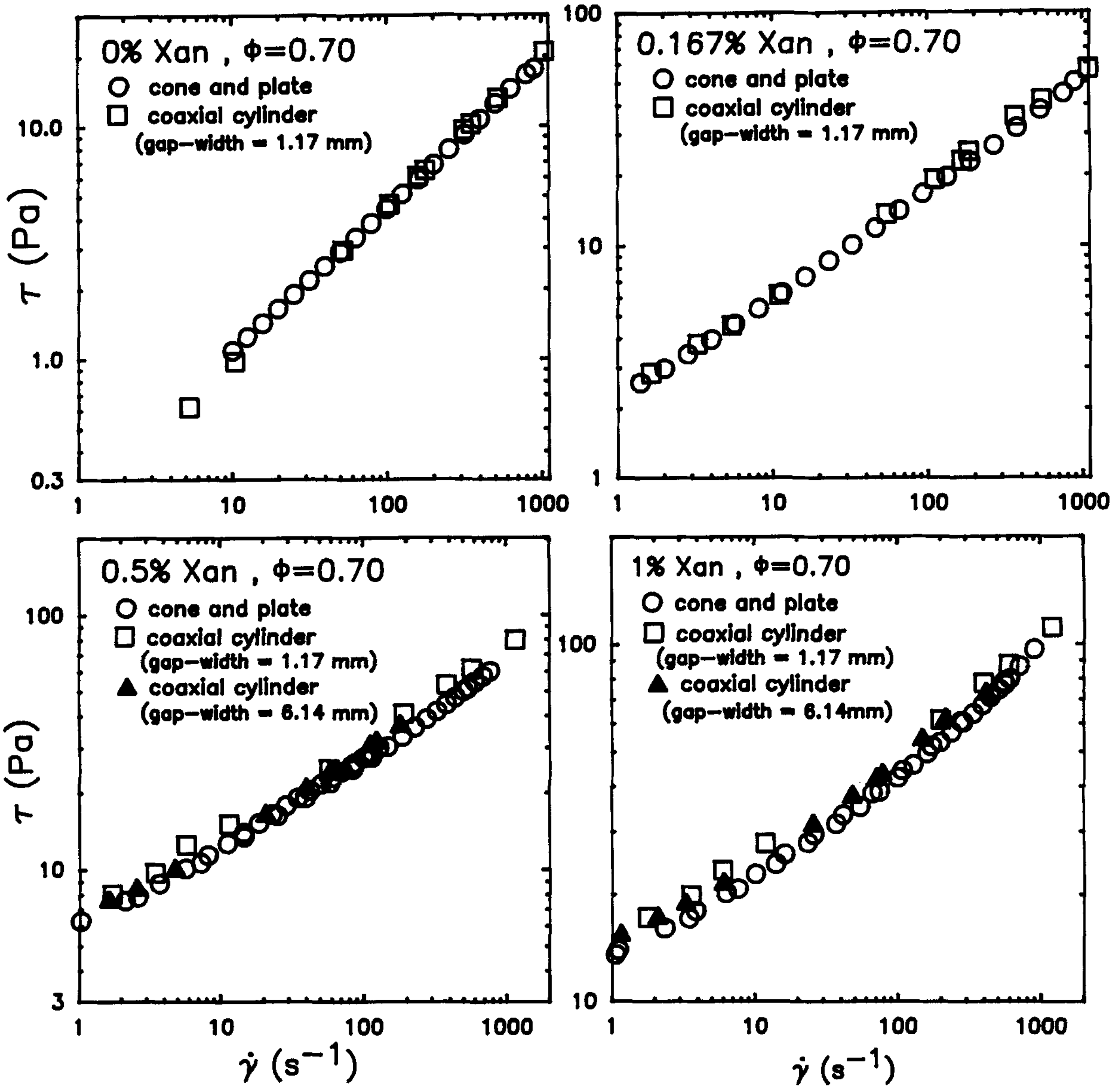


Figure 8. Shear-stress vs. shear-rate data obtained from different instruments for the same emulsion.

$$h_1 = \frac{(19k+16)(2k+3)}{40(k+1)}\left(\frac{\eta_c R}{\sigma}\right)\left[1+\frac{5(19k+16)}{4(k+1)(2k+3)}\phi\right] \quad (6)$$

$$h_2 = \frac{(19k+16)(2k+3)}{40(k+1)}\left(\frac{\eta_c R}{\sigma}\right)\left[1+\frac{3(19k+16)}{4(k+1)(2k+3)}\phi\right]. \quad (7)$$

In these equations, σ is the interfacial tension and R is the radius of the droplet. Since the present emulsions were polydisperse in nature, the volume-average radius was used in applying the preceding equations. Also, it should be noted that all three emulsion models just discussed were originally developed for emulsions of Newtonian liquids. To apply the models in the present situation, where the continuous phase of the emulsions is highly non-Newtonian, the value of the viscosity ratio k at any given macroscopic shear rate was calculated by using the continuous-phase viscosity at that shear rate. In other words, the effect of non-Newtonian continuous medium was incorporated in the models through the viscosity ratio k. The following points should be noted from Figure 10a: (1) the theoretical models predict the right trends in that the relative viscosity increases with an increase in the shear rate; (2) the Choi-Schowalter model predicts higher relative viscosities than the Oldroyd model, which, in turn, predicts slightly higher relative viscosities than the Taylor model; (3) at low values of dispersed-phase concentration ($\phi \leq 0.35$), the experimental data fall closer to Taylor and Oldroyd models; and (4) at high values of ϕ, the experimental data are in better agreement with the Taylor and Oldroyd models only at low values of shear rate, while at high values of shear rate, the data fall closer to the Choi-Schowalter model.

At low values of ϕ, the hydrodynamic interaction between the droplets is expected to be less important, and therefore

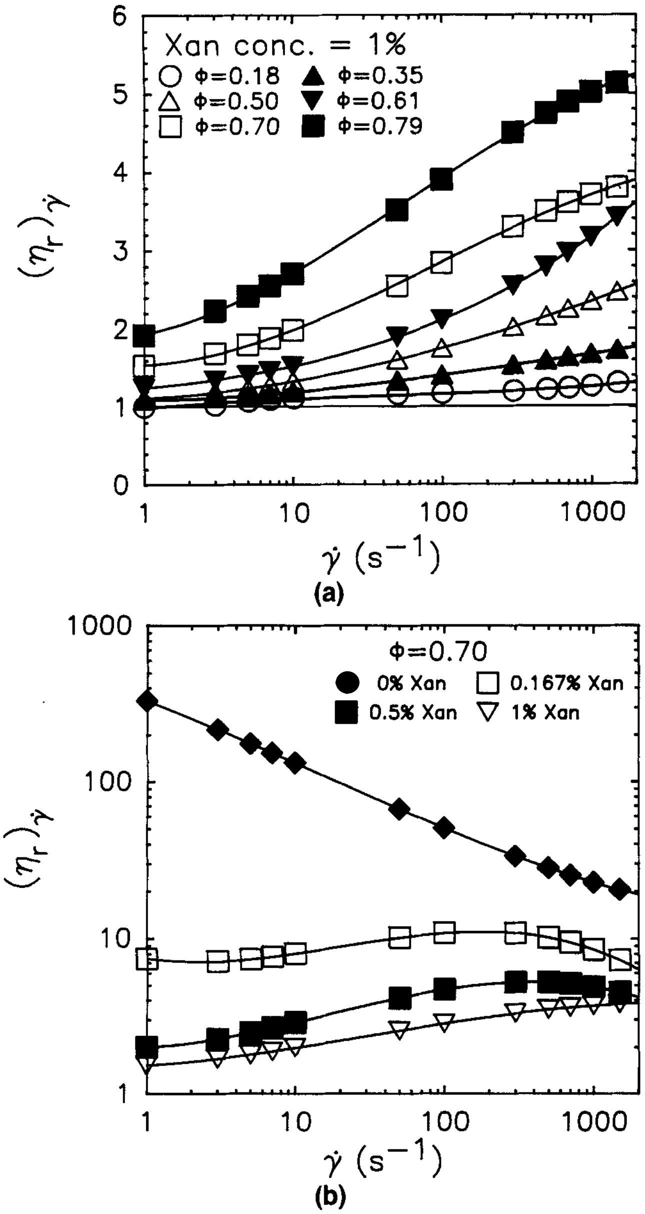


Figure 9. (a) Relative viscosity of emulsions as a function of shear rate; (b) effect of polymer concentration on the relative viscosity of 70% O/W emulsion.

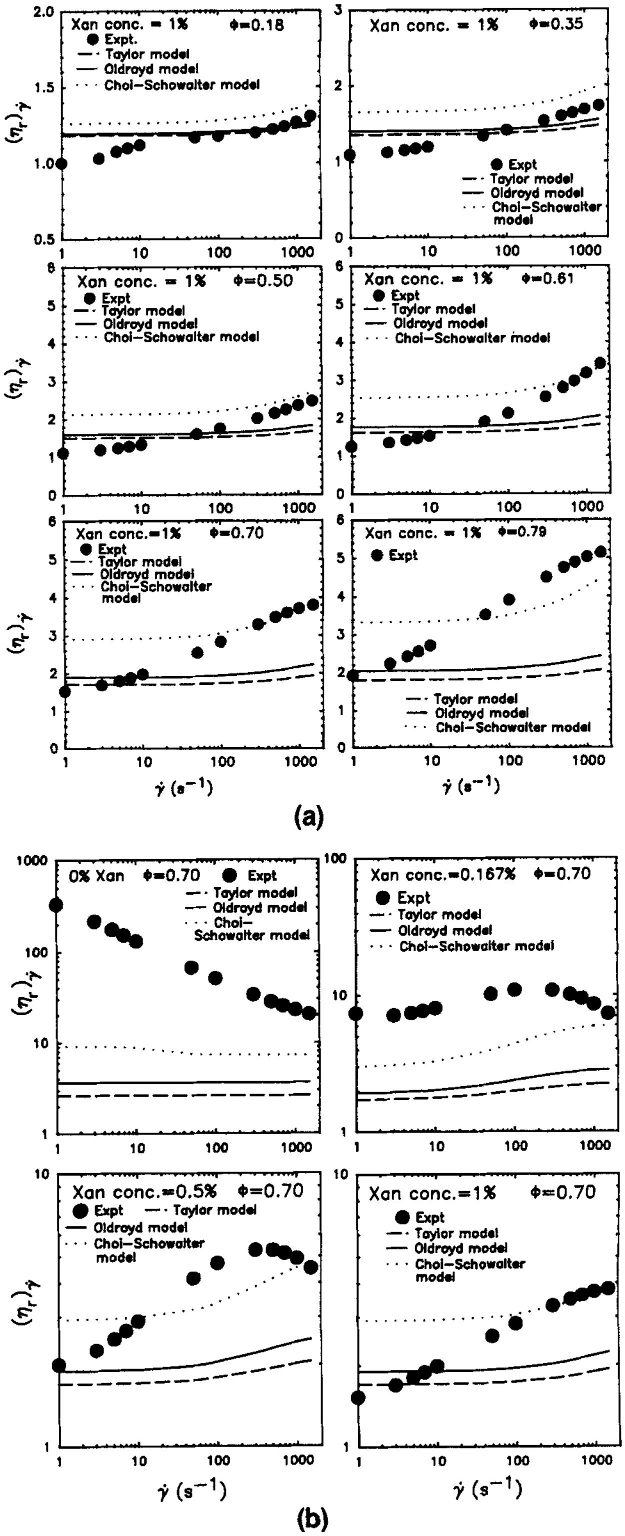


Figure 10. (a) Relative viscosity data for emulsions (prepared from 1 wt. % xanthan solution) vs. emulsion models of Taylor, Oldroyd, and Choi-Schowalter; (b) relative viscosity data for emulsions (prepared from differently concentrated xanthan gum solutions) vs. emulsion models of Taylor, Oldroyd, and Choi-Schowalter.

we observe better agreement between the experimental data and the Taylor or Oldroyd models. At high values of ϕ, the agreement between the experimental data and the Taylor and Oldroyd models is good at low values of shear rate because at low shear rates, the continuous-medium viscosity is very high. At high values of shear rate where the continuous-phase viscosity is relatively small, the hydrodynamic interaction between the droplets is expected to be important, and consequently we see better agreement between the experimental data and the Choi-Schowalter model. (Note that the Choi-Schowalter model does consider hydrodynamic interaction between the droplets.)

Figure 10b compares the relative viscosity data with the

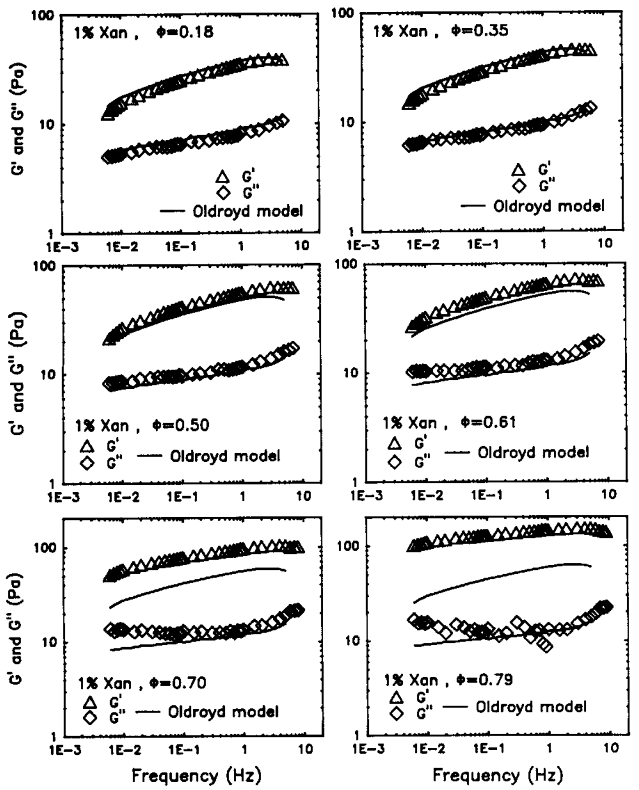


Figure 11. Storage and loss moduli for the emulsions (prepared from 1 wt. % xanthan solutions) in the linear viscoelastic region.

emulsion models for 70% O/W emulsions, prepared from differently concentrated xanthan gum solutions. For unthickened (0% xanthan) emulsion, the experimental data fall well above the theoretical models; at low shear rates, the discrepancy between the experimental data and the models is large, while at high shear rates, the deviation decreases. As mentioned earlier, emulsions of low viscosity Newtonian suspending media are likely to form flocs of droplets at high dispersed-phase concentrations. Consequently, the non-Newtonian behavior in such emulsions is caused by two different mechanisms: deflocculation of droplets with an increase in shear rate, and deformation of droplets with shear rate. In the present situation, the former mechanism dominates, and therefore we observe a strong shear-thinning behavior and much higher viscosities than those predicted by the models. At high shear rates, the deviation between the experimental data and theoretical models is relatively small because of the deflocculation of droplets.

With an increase in the polymer concentration, the viscosity of the continuous phase increases. Consequently, droplet-droplet nonhydrodynamic interactions and flocculation of droplets become less important and we observe relatively better agreement between the models and the experimental data.

Figure 11 gives the plots of storage and loss moduli, in the linear viscoelastic region, for emulsions prepared from 1 wt. % xanthan solution. For comparison purposes, the values of the moduli predicted from the following Oldroyd model (Oldroyd, 1953) are also shown:

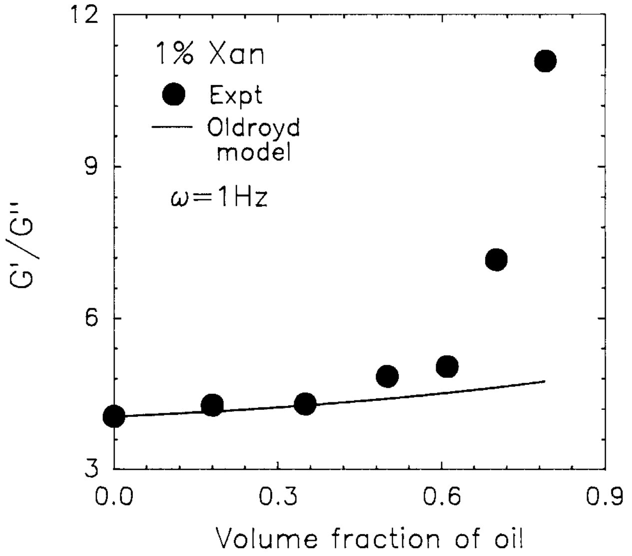


Figure 12. The ratio of storage modulus to loss modulus (G'/G'') as a function of dispersed-phase (oil) concentration.

$$G^* = G_c^*\left[\frac{1+3\phi H}{1-2\phi H}\right] \tag{8}$$

where

$$H = \frac{(4\sigma/R)(2G_c^* + 5G_d^*) + (G_d^* - G_c^*)(16G_c^* + 19G_d^*)}{(40\sigma/R)(G_c^* + G_d^*) + (2G_d^* + 3G_c^*)(16G_c^* + 19G_d^*)} \tag{9}$$

and G_c^* and G_d^* are complex moduli of continuous and dispersed phases, respectively. Figure 11 reveals the following important points: (1) the storage modulus (G') for various differently concentrated emulsions falls above the loss modulus (G'') over the entire frequency range, indicating that the emulsions prepared from 1 wt. % xanthan solution are predominantly elastic; and (b) the Oldroyd model gives good prediction of G' and G'' over the entire frequency range for emulsions with dispersed-phase concentration $(\phi) \leq 0.61$. At higher values of ϕ, the Oldroyd model predicts the values of the loss modulus reasonably well, but the storage modulus predicted is lower than the experimental values. The deviation tends to increase with an increase in ϕ.

The high values of the storage modulus exhibited by xanthan-thickened emulsions is due to two reasons: first, the continuous phase of the emulsions (1% xanthan solution) itself is predominantly elastic, and, second, an additional mechanism for elasticity in emulsions is present, that is, the elasticity of shape. This latter effect can be clearly seen in Figure 12 where we have plotted the ratio of storage modulus to loss modulus for emulsions as a function of dispersed phase concentration. With an increase in the dispersed-phase concentration, the ratio G'/G'' increases significantly. For dispersed-phase concentrations lower than 61% ($\phi \leq 0.61$), the increase is moderate, while for higher values of ϕ ($\phi > 0.61$), the increase is quite dramatic due to interaction between the droplets. The Oldroyd model underpredicts the values of

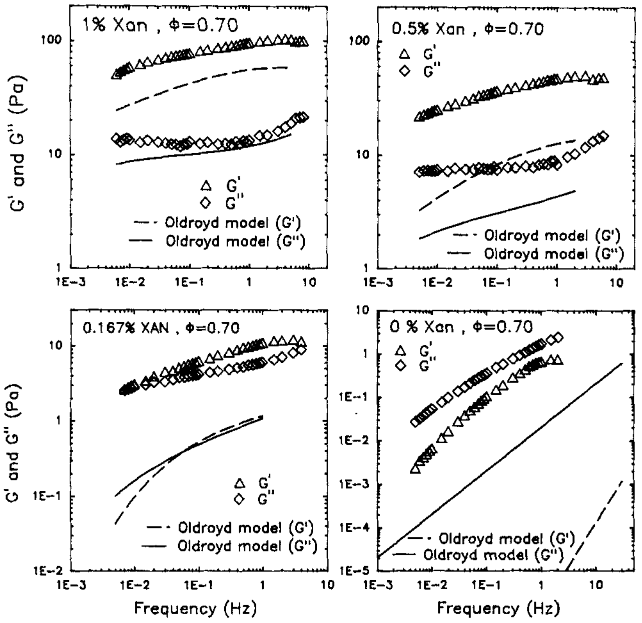


Figure 13. Effect of polymer concentration on G' and G'' for 70% O/W emulsion.

G'/G'' at high ϕ ($\phi > 0.61$) because the model was originally developed for dilute emulsions and therefore, it does not take into account the interaction between the droplets.

Figure 13 shows the effect of polymer concentration on G' and G'' for emulsions with a fixed value of dispersed-phase concentration, $\phi = 0.70$. While the emulsions prepared from 1% and 0.5% by weight xanthan solutions are predominantly elastic over the entire frequency range, the emulsions prepared from solutions of lower concentrations of polymer exhibit a different behavior. At a polymer concentration of 0.167% by weight, G'' tends to be larger than G' below the crossover frequency of about 7×10^{-3} Hz, but at higher frequencies, $G' > G''$. It should be noted that the crossover frequency in the present case of 70% O/W emulsion is much lower than the crossover frequency for 0.167 wt. % xanthan solution without any added oil droplets (where crossover frequency ~0.06 Hz). For 70% O/W emulsion without any added polymer, the loss modulus (G'') is greater than the storage modulus (G') over the entire frequency range, indicating that this emulsion is predominantly viscous. It should further be noted that the deviation between the experimental data (for G' and G'') and the Oldroyd model increases with a decrease in polymer concentration. In fact, for polymer concentrations of 0.167 wt. % and lower, the deviation is quite large. The discrepancies between the experimental data and the Oldroyd model at low polymer concentrations are quite expected. The Oldroyd model considers deformation of droplets as the only mechanism for elasticity and non-Newtonian behavior in emulsions, whereas in the low viscosity suspending media, it is the droplet-droplet nonhydrodynamic interactions that play a major role. The viscoelastic behavior in concentrated emulsions of low viscosity suspending media is therefore mainly due to flocculation of droplets.

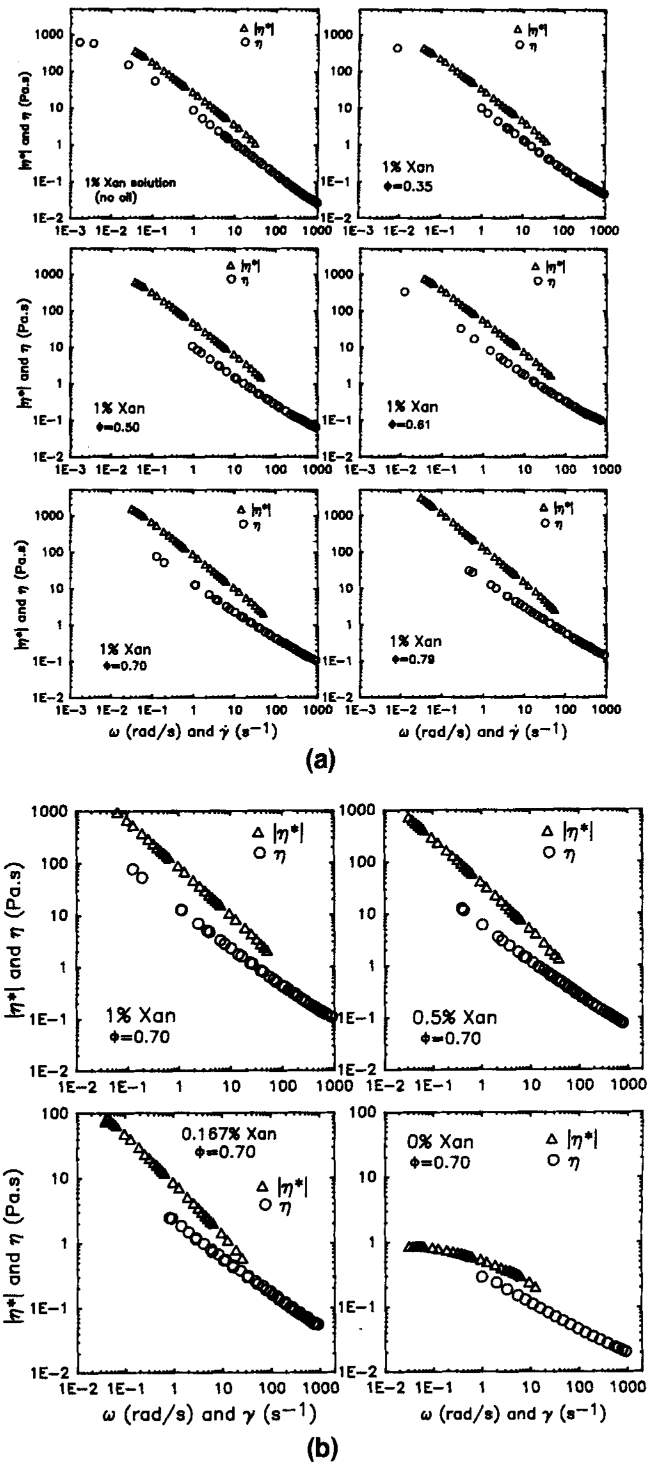


Figure 14. (a) Complex viscosity data vs. steady shear viscosity data for emulsions prepared from 1% xanthan solution; (b) complex viscosity data vs. steady shear viscosity data for 70% O/W emulsion at different polymer concentrations.

The complex viscosities of emulsions, prepared from 1% by weight xanthan solution, are compared with the corresponding steady shear viscosities in Figure 14a. The complex viscosities fall well above the steady shear viscosities for various differently concentrated emulsions. Thus, the Cox-Merz rule is not obeyed by the emulsions. There are at least two reasons for this deviation: first, the continuous phase of the emulsion itself does not obey the Cox-Merz rule, and second, the Oldroyd model predicts that the dynamic viscosity, rather than the complex viscosity, of emulsions should match the steady shear viscosity. Figure 14b compares complex viscosities with steady shear viscosities for emulsions of fixed oil concentration ($\phi = 0.70$), but having different polymer concentration. Again, the complex viscosities fall well above the steady shear viscosities, and the deviation appears to increase with the polymer concentration.

The dynamic viscosities of emulsions are compared with the steady shear viscosities in Figures 15a and 15b. Figure 15a shows the data for emulsions, prepared from 1 wt. % xanthan solution, at various different oil concentrations. Figure 15b shows the data for emulsions, prepared from various different polymer concentrations, at a fixed oil concentration of 70 vol. %. The dynamic viscosities appear to agree quite well with the steady shear viscosities, particularly at low frequencies. At high frequencies, the dynamic viscosities generally tend to be lower than the steady shear viscosities, except for the unthickened (0% xanthan) 70% O/W emulsion where the dynamic viscosities tend to fall above the steady shear viscosities.

Figure 16a shows the creep/recovery behavior for emulsions, prepared from 1% by weight xanthan solution, at different oil concentrations. The compliance (J), defined as the ratio of strain to stress, is plotted as a function of time. The creep/recovery experiments were conducted as follows: a constant shear stress of 1 Pa was applied to the emulsion sample using cone-and-plate geometry, and the resulting strain was monitored as a function of time. The imposed stress was suddenly removed after 500 s and recovery, on release of the stress, was monitored for another 500 s. Figure 16a indicates that the polymer solution (1% xanthan) and the emulsions prepared from it are viscoelastic in nature. They all exhibit an instantaneous elastic compliance and a recoverable compliance. The emulsions become more elastic with an increase in the dispersed-phase (oil) concentration. In fact, the highly concentrated emulsion containing 79 vol. % oil exhibits elastic solidlike behavior; the creep compliance in this case reaches an equilibrium value and when the stress is removed, the recovery is nearly complete.

Figure 16b shows creep and recovery behavior of 50% O/W emulsion, prepared from 1 wt. % xanthan solution, at various different stress levels. At low stresses (1, 2 Pa), viscoelastic behavior is observed, but at high stresses (4, 8 and 12 Pa), the emulsion behaves like a viscous liquid in that the creep compliance increases proportionally with time and that the recovery is negligible after removal of stress. The slope of the creep compliance vs. time plot increases with an increase in the shear stress, implying that the viscosity decreases with the shear stress (note that the slope is inversely proportional to the viscosity).

The creep and recovery plots for a fixed oil concentration emulsion (70% O/W) at different polymer concentrations indicated that the emulsion becomes more elastic with the increase in the polymer concentration; at high polymer concentrations (0.5%, 1 wt. %), the creep compliance at any given time was quite small and the percent recovery was high, whereas at a low polymer concentration of 0.167 wt. %, the viscous flow dominated and the percent recovery in compliance was small.

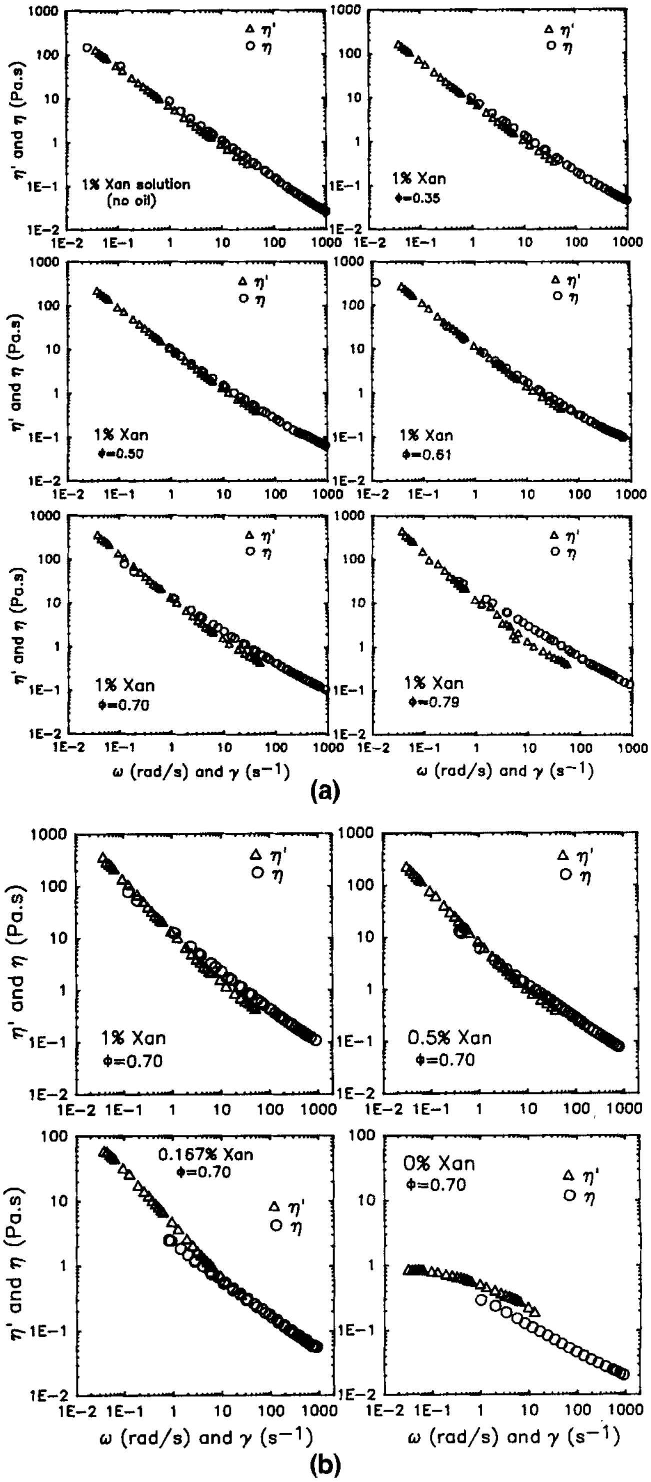


Figure 15. (a) Dynamic viscosity data vs. steady shear viscosity data for emulsions prepared from 1% xanthan solution; (b) dynamic viscosity data vs. steady shear viscosity data for 70% O/W emulsion at different polymer concentrations.

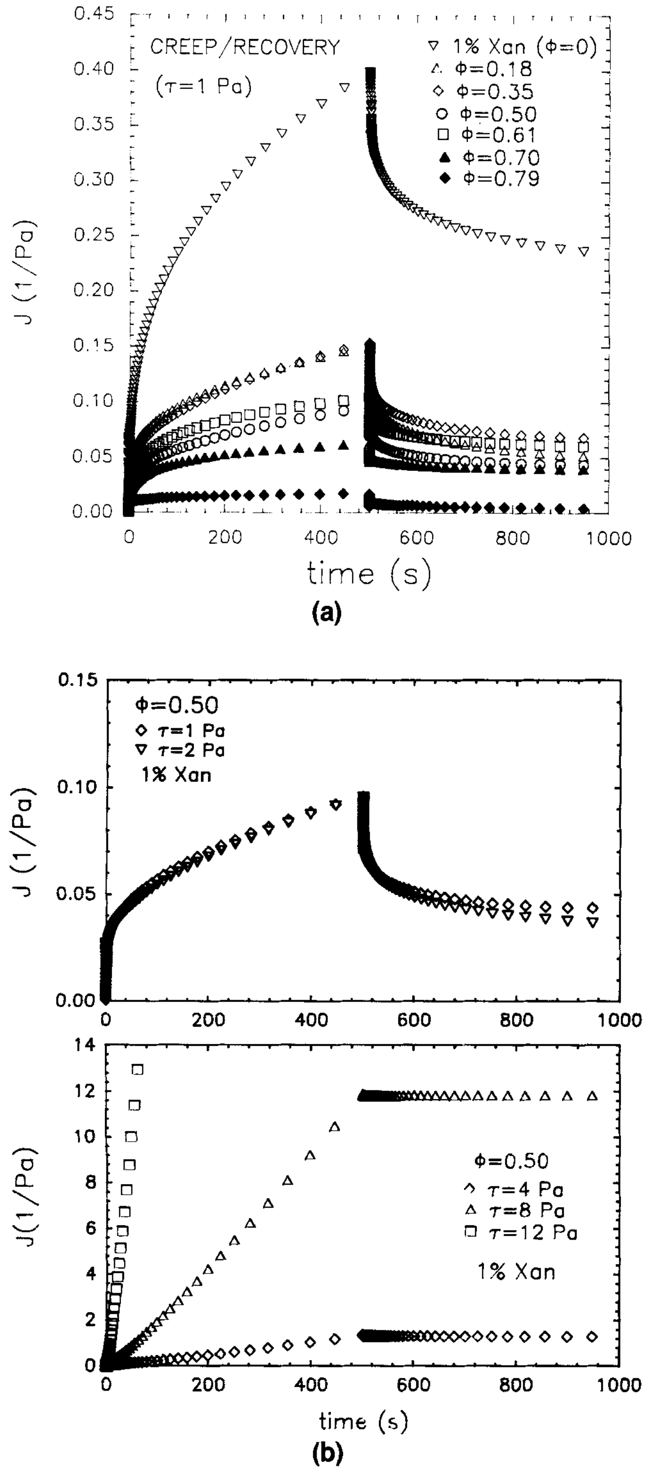


Figure 16. (a) Creep and recovery behavior for emulsions prepared from 1% xanthan solution; (b) creep and recovery behavior of 50% O/W emulsion at various different stress levels.

Conclusions

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

- Xanthan gum solutions are strongly shear thinning and viscoelastic in nature. With the increase in polymer concentration, the solutions become predominantly elastic; the ratio of storage to loss modulus increases substantially with the polymer concentration and the polymer solutions do not follow the Cox-Merz rule.
- Xanthan-thickened oil-in-water emulsions exhibit strongly shear-thinning behavior. The viscosity of emulsions increases with the increase in dispersed-phase (oil) concentration and polymer concentration.
- The relative viscosity for unthickened emulsion, at any given shear rate, is much higher than that of the xanthan-thickened emulsion at the same dispersed-phase concentration.
- The relative viscosity for xanthan-thickened emulsions increases with an increase in the shear rate, whereas the unthickened emulsions show the opposite trend, that is, the relative viscosity decreases with the shear rate. The increase in relative viscosity observed for xanthan-thickened emulsions is due to an increase in ratio of dispersed-phase to continuous-phase viscosity with the shear rate. A decrease in the relative viscosity for unthickened emulsion is due to deflocculation of droplets.
- The relative viscosities predicted for xanthan-thickened emulsions using the Taylor, Oldroyd, and Choi-Schowalter models are quite realistic. At low values of dispersed-phase concentration, the experimental data fall closer to Taylor and Oldroyd models. At high values of dispersed-phase concentration, the experimental data are in good agreement with the Taylor and Oldroyd models only at low values of shear rate, but at high values of shear rate the data agree better with the Choi-Schowalter model. For the unthickened emulsions where the continuous-phase viscosity is quite low, the experimental data fall way above the values predicted by the theoretical models. The main reason for this deviation is believed to be the droplet-droplet nonhydrodynamic interactions (flocculation) in low-viscosity suspending media.
- Xanthan-thickened emulsions are highly viscoelastic in nature. With the increase in polymer concentration the emulsions become predominantly elastic in the frequency range investigated. The ratio of storage to loss modulus increases considerably with the increase in polymer concentration and dispersed-phase (oil) concentration. Furthermore, the xanthan-thickened emulsions do not follow the Cox-Merz rule.
- The Oldroyd model for the complex modulus of emulsions gives reasonably good predictions of storage and loss moduli for the xanthan-thickened emulsions up to a dispersed-phase concentration as high as 61 vol. %. At concentrations greater than 61 vol. %, the experimental data tend to deviate from the model. In the case of the unthickened emulsions, the Oldroyd model severely underpredicts the values of the storage and loss moduli. This is expected because the Oldroyd model considers deformation of droplets as the only mechanism for viscoelasticity in emulsions, whereas in unthickened emulsions of low viscosity suspending media, the main mechanism for viscoelasticity is flocculation of droplets.
- The creep/recovery experiments confirm that the xanthan-thickened emulsions are highly viscoelastic in nature and that the degree of elasticity increases with the increase in polymer concentration and dispersed-phase (oil) concentration.

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