

Shear Viscosity Behavior of Emulsions of Two Immiscible Liquids

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The viscous behavior of oil-in-water (O/W) emulsions is studied over a broad range of dispersed-phase concentrations (ϕ) using a controlled-stress rheometer. At low-to-moderate values of ϕ ($\phi < 0.60$), emulsions exhibit Newtonian behavior. The droplet size does not exert any influence on the viscosity of Newtonian emulsions. However, at higher values of ϕ , emulsions exhibit shear-thinning behavior. The viscosity of shear-thinning emulsions is strongly influenced by the droplet size; a significant increase in the viscosity occurs when the droplet size is reduced. With the decrease in droplet size, the degree of shear thinning in concentrated emulsions is also enhanced. The viscosity data of Newtonian emulsions are described reasonably well by the cell model of Yaron and Gal-Or (*Rheol. Acta* 11, 241 (1972)), which takes into account the effects of the dispersed-phase concentration as well as the viscosity ratio of the dispersed phase to continuous phase. The relative viscosities of non-Newtonian emulsions having different droplet sizes but the same dispersed-phase concentration are scaled with the particle Reynolds number. The high shear viscosities of non-Newtonian emulsions can be predicted fairly well by the cell model of Yaron and Gal-Or (*Rheol. Acta* 11, 241 (1972)). © 2000 Academic Press

Key Words: emulsion; rheology; viscosity; non-Newtonian; oil-in-water emulsions.

1. INTRODUCTION

Emulsions consist of two immiscible liquids, one of which is dispersed in the other in the form of droplets. Stability to coalescence is achieved by the presence of an emulsifying agent or surfactant which is adsorbed around the droplet surfaces. Emulsions play an important role in a number of industrial and household applications. The use of such systems covers a broad field, ranging from lubrication and cooling of equipment in metal working processes to more delicate use like cosmetics. Emulsions are also encountered at nearly every step of the petroleum production and recovery operations, viz. within the underground porous media, at well heads, in phase separators, in flotation units, in crude oil transport facilities, and at various stages of the refining process (1). Emulsions are of considerable importance in food applications as well.

The understanding of the rheological behavior of emulsions is of importance in the many industrial applications just mentioned. The knowledge of the rheological properties of emulsions is required for the design, selection, and operation of the equipment

involved for mixing, storing, and pumping of emulsions. The measurement of the rheological properties of emulsions can also provide very useful information about the microstructure and stability of emulsions. Furthermore, the quality of emulsion-based products, such as texture and mouth-feel properties of emulsified food products, is directly linked to the rheological properties of the product.

In this work, the viscous behavior of oil-in-water (O/W) emulsions is studied over a broad range of dispersed-phase concentrations. The effects of the droplet size and dispersed-phase concentration on the steady shear viscosity of emulsions are determined. The viscosity data of Newtonian emulsions are described in terms of the cell models (2, 3) which take into account the effects of the viscosity ratio as well as the dispersed-phase concentration. The viscous behavior of non-Newtonian emulsions is interpreted in terms of relative viscosity versus particle Reynolds number.

2. THEORETICAL BACKGROUND

A vast amount of published literature exists on the rheology of solids-in-liquid suspensions (4–15). However, emulsions of two immiscible liquids have received less attention. The rheological behavior of emulsions is more complicated than that of solid-in-liquid suspensions as the dispersed particles of emulsions are deformable in nature. For example, at low concentrations of the dispersed phase, suspensions of spherical rigid particles exhibit Newtonian behavior whereas emulsions of deformable particles exhibit shear-thinning and viscoelastic properties, even at very low dispersed-phase concentrations (16, 17). Under a steady macroscopic shear flow, the droplets of emulsions are subjected to two opposing effects (1): (i) a viscous stress of magnitude, $\eta_c \dot{\gamma}$, that tends to elongate the droplet and (ii) a stress of magnitude, σ/R , that tends to minimize the surface energy and hence tends to maintain the droplet in a spherical shape. Therefore, the equilibrium shape of the droplet is governed by the ratio of viscous stress to σ/R ; this ratio is referred to as the capillary number (N_{Ca}),

$$N_{Ca} = \eta_c \dot{\gamma} / (\sigma / R), \quad [1]$$

where η_c is the continuous-phase viscosity, $\dot{\gamma}$ is the shear rate, R is the droplet radius, and σ is the interfacial tension. When

the capillary number is small ($N_{Ca} \rightarrow 0$), the deformation of the droplets is negligible and the droplets can be treated as spherical. However, at high capillary numbers, the deformation of droplets can be quite significant.

The macroscopic stress tensor ($\bar{\pi}$) for emulsions in the absence of flocculation of droplets can be written as (18–20)

$$\begin{aligned} \bar{\pi} = & -P\bar{\delta} + 2\eta_c\bar{d} + \frac{(\eta_d - \eta_c)}{V} \int_{S_p} (\hat{u}\hat{n} + \hat{n}\hat{u}) dS \\ & + \frac{1}{V} \int_{S_p} \sigma \left(\frac{1}{3}\bar{\delta} - \hat{n}\hat{n} \right) dS, \end{aligned} \quad [2]$$

where P is the pressure, $\bar{\delta}$ is the unit tensor, \bar{d} is the macroscopic rate-of-deformation tensor, η_d is the dispersed-phase viscosity, V is the representative volume of the emulsion large enough to contain many droplets, S_p is the interfacial area of droplets within V , \hat{u} is the velocity vector, and \hat{n} is the unit vector normal to the droplet surface.

For *dilute* emulsions of nearly spherical droplets ($N_{Ca} \rightarrow 0$), it can be shown that (18)

$$\frac{(\eta_d - \eta_c)}{V} \int_{S_p} (\hat{u}\hat{n} + \hat{n}\hat{u}) dS = \frac{6}{5} \left(\frac{\eta_d - \eta_c}{\eta_d + \eta_c} \right) \eta_c \phi \bar{d} \quad [3]$$

and

$$\frac{1}{V} \int_{S_p} \sigma \left(\frac{1}{3}\bar{\delta} - \hat{n}\hat{n} \right) dS = \left[\frac{16\eta_c + 19\eta_d}{5(\eta_c + \eta_d)} \right] \eta_c \phi \bar{d}, \quad [4]$$

where ϕ is the volume fraction of the dispersed phase. Combining Eqs. [2]–[4] leads to the following result:

$$\bar{\pi} = -P\bar{\delta} + 2\eta_c\bar{d} + \left(\frac{5\kappa + 2}{\kappa + 1} \right) \eta_c \phi \bar{d}. \quad [5]$$

The macroscopic stress tensor for emulsions could also be written as

$$\bar{\pi} = -P\bar{\delta} + 2\eta\bar{d}, \quad [6]$$

where η is the emulsion viscosity. Upon comparing Eqs. [5] and [6], one obtains

$$\eta_r = \frac{\eta}{\eta_c} = 1 + \frac{(5\kappa + 2)}{2(\kappa + 1)} \phi, \quad [7]$$

where η_r is the relative viscosity. Equation [7] is the celebrated Taylor relation (21) for the relative viscosity of a very dilute emulsion.

In the derivation of Eqs. [3]–[5] and [7], the interaction between neighboring drops is not considered as the emulsion is

very dilute. However, at finite concentrations of the dispersed phase, the hydrodynamic interaction between droplets is significant. To take into account the hydrodynamic interaction between the neighboring droplets, Choi and Schowalter (2) and Yaron and Gal-Or (3) used a cell model approach and derived the following macroscopic stress tensor when $N_{Ca} \rightarrow 0$,

$$\bar{\pi} = -P\bar{\delta} + 2\eta_c[1 + I(\lambda)\phi]\bar{d}, \quad [8]$$

where λ is $\phi^{1/3}$ and $I(\lambda)$ is given by the following:

Choi–Schowalter (2),

$I(\lambda)$

$$= \frac{2[(5\kappa + 2) - 5(\kappa - 1)\lambda^7]}{[4(\kappa + 1) - 5(5\kappa + 2)\lambda^3 + 42\kappa\lambda^5 - 5(5\kappa - 2)\lambda^7 + 4(\kappa - 1)\lambda^{10}]}, \quad [9]$$

Yaron and Gal-Or (3),

$$I(\lambda) = \frac{5.5[4\lambda^7 + 10 - (84/11)\lambda^2 + (4/\kappa)(1 - \lambda^7)]}{10(1 - \lambda^{10}) - 25\lambda^3(1 - \lambda^4) + (10/\kappa)(1 - \lambda^3)(1 - \lambda^7)}. \quad [10]$$

From Eqs. [6] and [8], it follows that

$$\eta_r = 1 + I(\lambda)\phi. \quad [11]$$

The experimental data of this study are interpreted in terms of Eq. [11]. It is important to note that Eq. [11] is valid for Newtonian emulsions at low capillary numbers. Because of the low viscosity of the continuous phase and the small droplet size of oil-in-water emulsions investigated in the present work, the capillary numbers are negligibly small ($< 5 \times 10^{-3}$).

3. EXPERIMENTAL WORK

3.1. Materials

The emulsions were prepared using a petroleum oil (trade name EDM) supplied by Monarch Oil Co., Kitchener, Canada. The viscosity of the oil was 5.52 mPa s at 25°C. The water used throughout the experiments was deionized. The surfactant used for the preparation of emulsions was Triton X-100, a commercially available nonionic surfactant manufactured by Union Carbide Chemicals and Plastics Technology Corp., Danbury, CT. Triton X-100 is an octyl phenol ethoxylate with an average of 9–10 molecules of ethylene oxide. It is water soluble and has a high HLB (hydrophilic–lipophilic balance) value of 13.5.

3.2. Procedure

The oil-in-water emulsions were prepared by shearing together the known amounts of oil and aqueous surfactant solution (2.1% by weight Triton X-100) in a homogenizer (Gifford-Wood

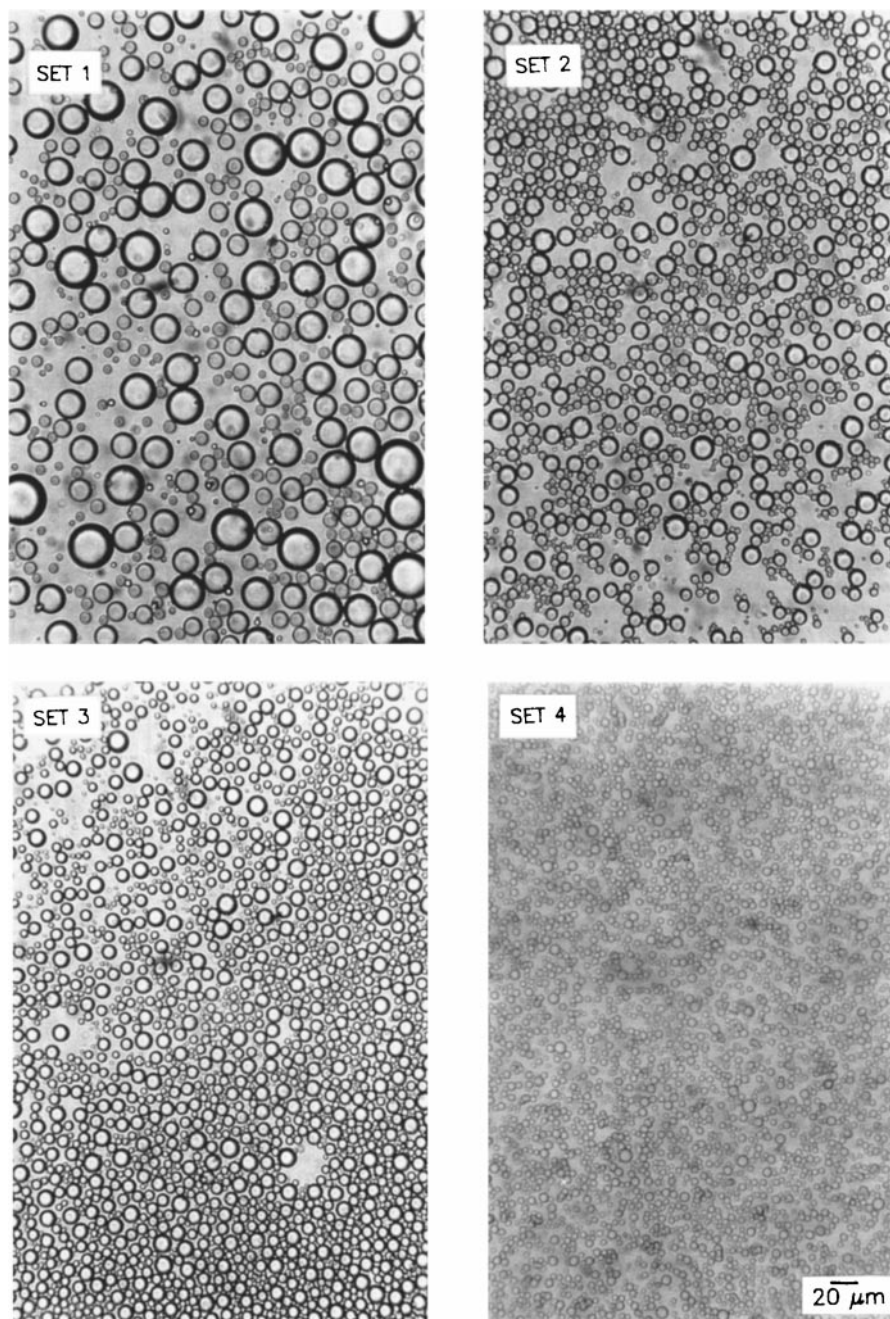


FIG. 1. Typical photomicrographs of sets 1–4 emulsions.

Model 1-L). To determine the effects of droplet size on the viscous behavior of emulsions, four sets (set 1, set 2, set 3, and set 4) of oil-in-water emulsions with different average droplet sizes were prepared. The droplet size was varied from one set to another by varying the speed and duration of shearing in the homogenizer. For any given set, a highly concentrated oil-in-water emulsion (oil volume fraction nearly 0.72) was first prepared. This emulsion was then diluted with different amounts of the same continuous phase (2.1% by weight Triton X-100 aqueous solution) to prepare emulsions having lower oil volume frac-

tions. Thus, in any given set of emulsions, the droplet size was kept constant but the oil volume fraction was varied.

The rheological measurements were carried out in a Bohlin controlled-stress rheometer (Bohlin CS-50) using the double-gap cylindrical geometry. The data were collected at a temperature of 25–26°C. The droplet sizes of emulsions were determined by taking photomicrographs. The samples were diluted with the same continuous phase before the photomicrographs were taken. The photomicrographs were taken with a Zeiss optical microscope equipped with a camera. The interfacial tension between

the oil and aqueous phase was measured using the drop-volume method. For the oil/deionized water system, the measured value was 33.5 mN/m. With the addition of surfactant (Triton X-100) to the aqueous phase, the interfacial tension decreased substantially. Its value for the oil/surfactant solution system was ≈ 1.5 mN/m.

4. RESULTS AND DISCUSSION

Figure 1 shows the typical photomicrographs of sets 1–4 emulsions. Clearly, set 1 emulsions are much coarser than set 4 emulsions. The droplet sizes of sets 2 and 3 emulsions fall between those of sets 1 and 4 emulsions. It should be noted further that the emulsions in any given set are not monodisperse; that is, all droplets are not of the same size. This can be seen clearly in Fig. 2 which shows the droplet size distribution of the four sets of emulsions. As the emulsions were not monodisperse, an average droplet size was determined. About 700–800 droplets were counted to determine the Sauter mean diameter. The Sauter mean diameters were as follows: set 1, 21.4 μm ; set 2, 9.12 μm ; set 3, 8.1 μm ; set 4, 4.6 μm .

The viscosity versus shear stress plots for the four sets of emulsions are shown in Fig. 3. At low values of ϕ (volume fraction of dispersed phase), the emulsions exhibit Newtonian behavior in that the viscosity is constant and independent of shear stress. At high values of ϕ , emulsions exhibit shear-thinning behavior; that is, the viscosity decreases with the increase in shear stress. The degree of shear thinning in non-Newtonian emulsions increases with the increase in ϕ .

Figure 4 shows a comparison of flow curves for different sets (that is, different average droplet sizes) at the same value of ϕ . Clearly, the droplet size has a major effect on the viscosity of concentrated emulsions. Emulsions with smaller average droplet diameters are much more viscous than the ones with larger average droplet diameters. Also, a decrease in average droplet diameter enhances the shear-thinning behavior of emulsions. It is interesting to note that the effect of droplet size decreases with the decrease in the volume fraction of the dispersed phase. This can be seen more clearly in Fig. 5 where viscosity at a fixed shear stress of 0.1137 Pa is plotted as a function of ϕ for all four sets of emulsions. As can be seen, the data for all four sets (different average droplet diameters) fall on the same curve when

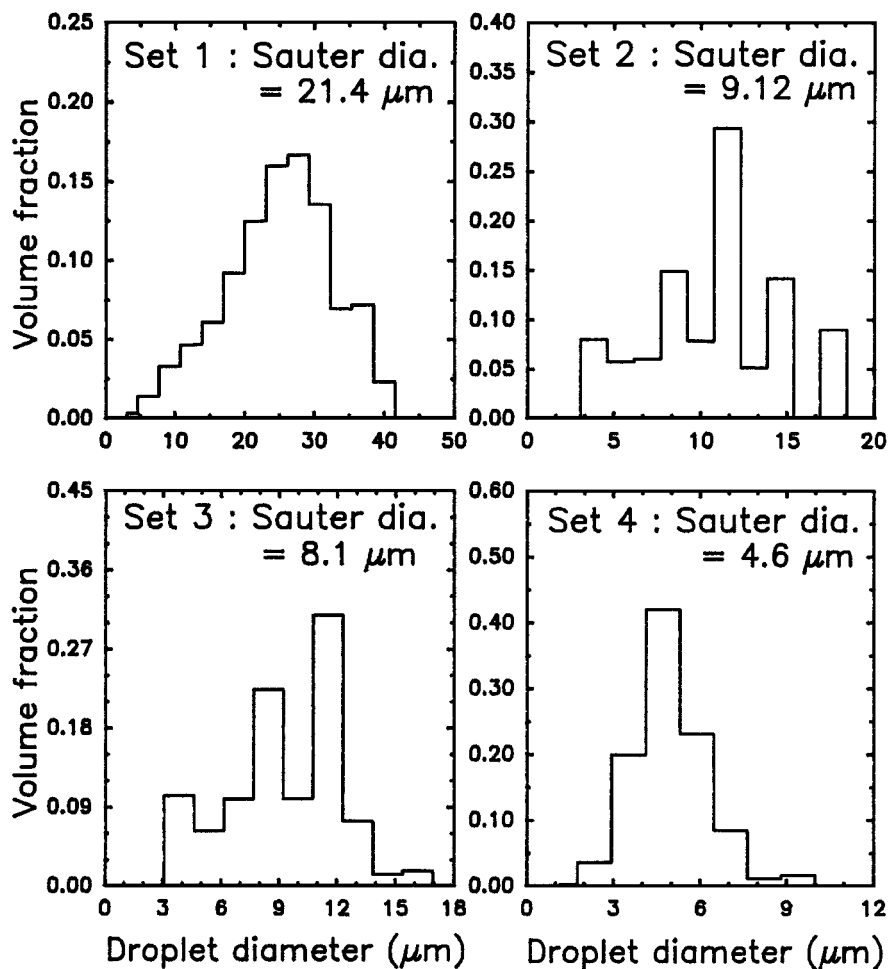


FIG. 2. Droplet size distributions of sets 1–4 emulsions.

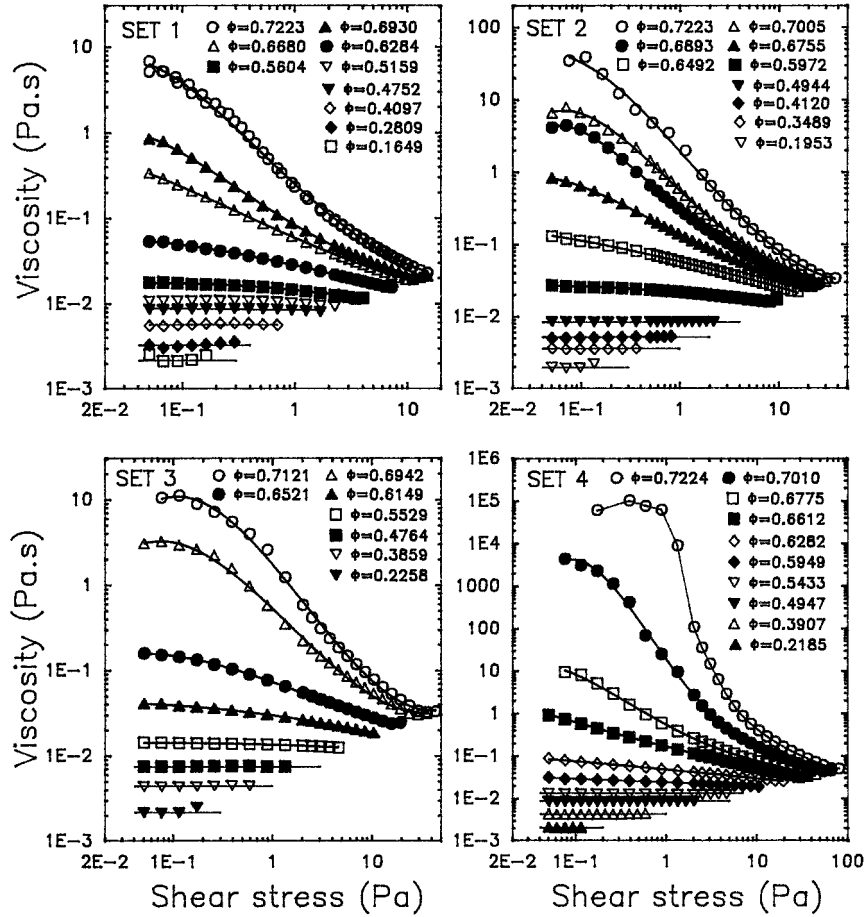


FIG. 3. Viscosity versus shear stress plots of emulsions.

$\phi \leq 0.60$. However, at high values of ϕ , the droplet size effect becomes important. The viscosities of finer emulsions (set 4, Sauter mean diameter of $4.6 \mu\text{m}$) are much higher than those of the coarser emulsions (set 1, Sauter mean diameter of $21.4 \mu\text{m}$).

The increase in viscosity with the decrease in droplet size could be due to an increase in the hydrodynamic interaction between the droplets. When the droplet size is decreased, the mean separation distance between the droplets decreases. For example, the mean surface-to-surface distance (a_m) between mono-sized spherical particles is given by (22)

$$a_m = 6R(1 - \phi)/2\phi. \quad [12]$$

Therefore, for a fixed volume fraction of the dispersed phase, the mean surface-to-surface distance decreases with the decrease in droplet radius. A decrease in the separation distance between the droplets is expected to enhance the hydrodynamic interaction.

The increase in viscosity and shear-thinning behavior of emulsions with the decrease in droplet size could also be due to aggregation/flocculation of droplets. As the mean separation distance between the droplets decreases with the decrease in droplet size,

the chances of aggregation/flocculation due to van der Waal's attraction between the droplets increases.

In Fig. 6, the relative viscosity versus ϕ data of Newtonian emulsions are compared with the theoretical models discussed earlier. As expected, the relative viscosities are much higher than those predicted by the Taylor model (Eq. [7]). The Taylor model (21) is expected to be valid for only very dilute emulsions. The cell model of Choi and Schowalter (2) overpredicts the relative viscosities when $\phi > 0.3$. The cell model of Yaron and Gal-Or (3) gives reasonably good prediction of the relative viscosities of emulsions. Note that there is no adjustable constant involved in the Yaron and Gal-Or model unlike several other empirical models proposed in the literature (23).

The relative viscosity of non-Newtonian emulsions, at a given ϕ , varies with shear rate (shear stress) as well as the droplet size (see Fig. 4). To take into account the effect of droplet size, the relative viscosity data of non-Newtonian emulsions are scaled with respect to the particle Reynolds number ($N_{Re,p}$), defined as

$$N_{Re,p} = \rho_c \dot{\gamma} R^2 / \eta_c, \quad [13]$$

where ρ_c and η_c are the continuous-phase density and viscosity, respectively, R is the Sauter mean radius, and $\dot{\gamma}$ is the shear rate.

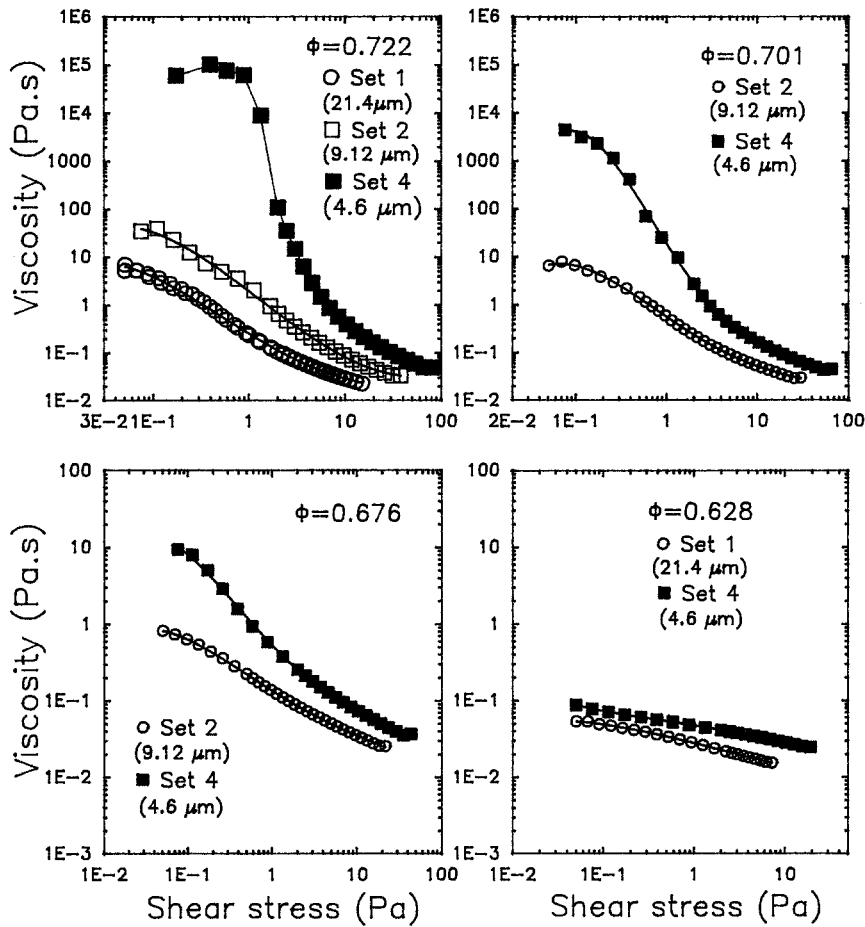


FIG. 4. Comparison between flow curves of emulsions of different sets (different droplet sizes).

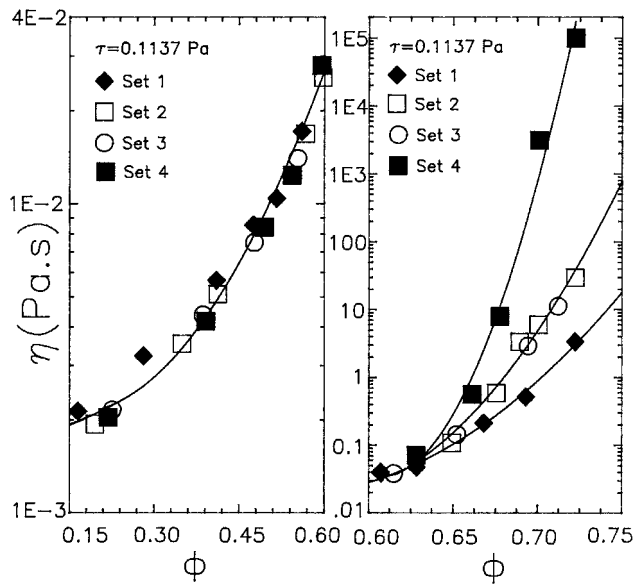


FIG. 5. Viscosity versus dispersed-phase concentration (ϕ) plots of emulsions at a fixed shear stress of 0.1137 Pa.

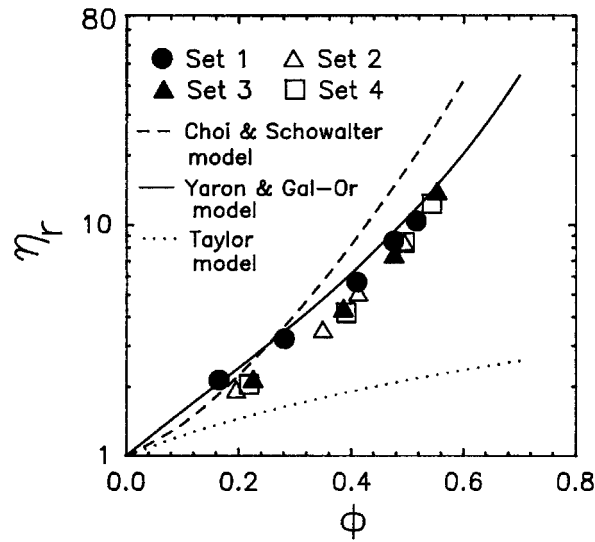


FIG. 6. Comparison of relative viscosity data of Newtonian emulsions with the theoretical emulsion models.

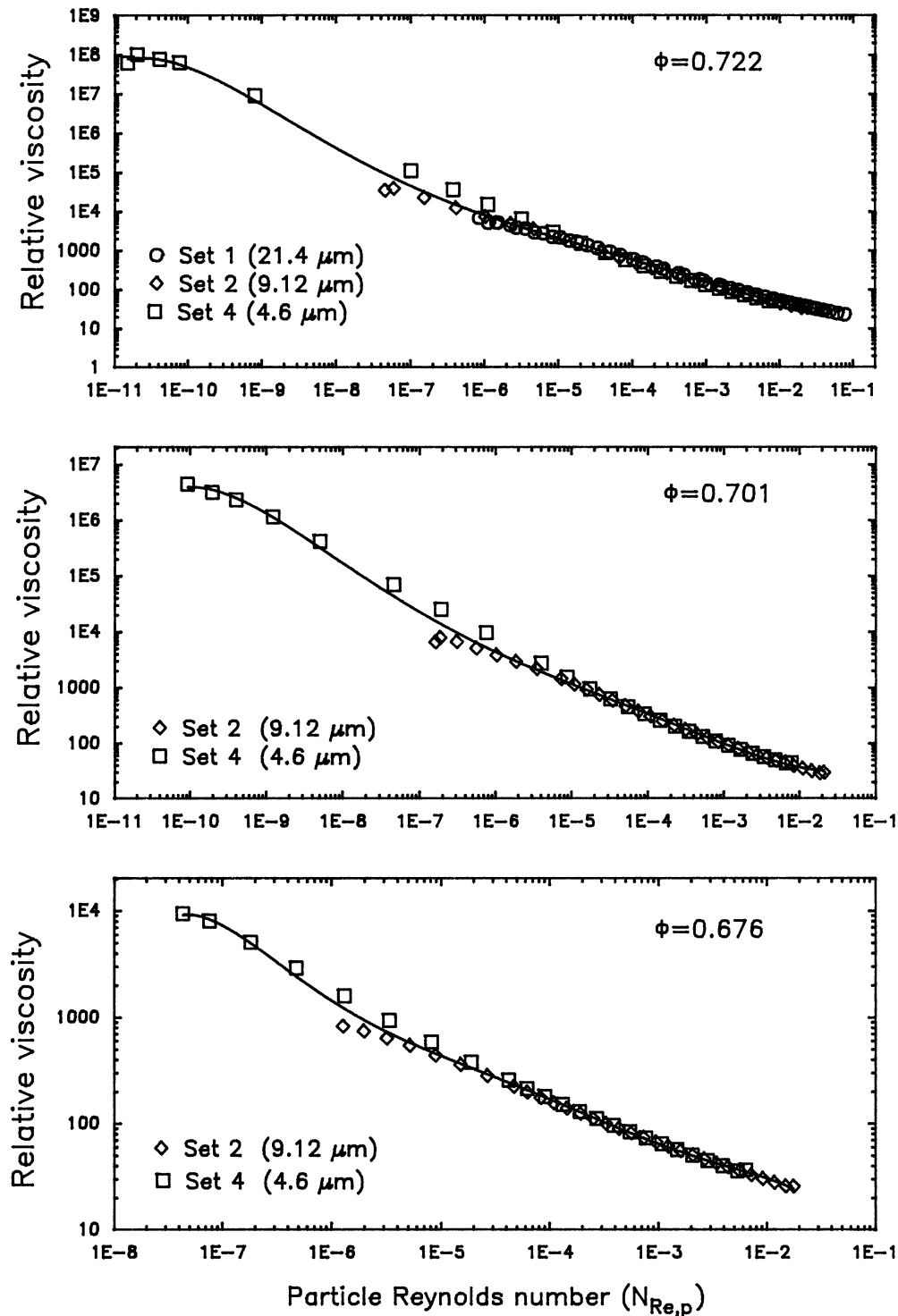


FIG. 7. Scaling of relative viscosity of non-Newtonian emulsions (of different droplet sizes) with the particle Reynolds number.

Figure 7 shows the relative viscosity versus $N_{Re,p}$ plots at various values of dispersed-phase concentrations. At any given ϕ , η_r versus $N_{Re,p}$ data for emulsions of different average droplet sizes fall on the same curve. Thus, the relative viscosity data for the oil-in-water emulsions having different

droplet sizes can be scaled very well with the particle Reynolds number.

In Fig. 8, the relative viscosity of non-Newtonian emulsions at a high shear rate ($N_{Re,p} = 10^{-2}$) is compared with the theoretical models. Interestingly, the cell model of Yaron and Gal-Or (3)

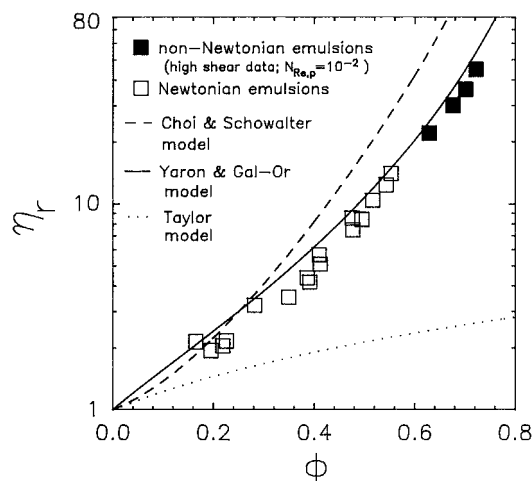


FIG. 8. Comparison of high-shear relative viscosity of non-Newtonian emulsions with the theoretical emulsion models.

gives a good prediction of high shear viscosity of non-Newtonian emulsions.

5. CONCLUSIONS

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

- The effect of droplet size on the viscosity of oil-in-water emulsions becomes important only at high values of dispersed-phase concentrations ($\phi > 0.60$).
- For concentrated oil-in-water emulsions ($\phi > 0.60$), the reduction in droplet size results in a significant increase in the viscosity. Also, the shear-thinning effect becomes stronger when the droplet size is reduced.
- The viscosity data of Newtonian emulsions can be described reasonably well by the theoretical model of Yaron and Gal-Or (1972). This model takes into account the effects of the dispersed-phase concentration as well as the viscosity ratio and it has no adjustable parameters.

- The relative viscosities of non-Newtonian emulsions having different droplet sizes but the same dispersed-phase concentration can be scaled reasonably well with the particle Reynolds number.

- The high shear viscosities of non-Newtonian emulsions can be predicted fairly well by the Yaron and Gal-Or (1972) model.

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