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Short communication

Scaling of viscoelastic properties of emulsions

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Abstract

The scaling analysis of the viscoelastic properties of concentrated oil-in-water emulsions is presented. The scaling of the storage modulus (G') and loss modulus (G''), with respect to the droplet size, can be achieved successfully provided that G' or G'' are plotted as a function of ω/R^3, where ω is the frequency and R is the Sauter mean radius. Empirical correlations of G' vs. ω/R^3 and G'' vs. ω/R^3 are developed based on the experimental data for concentrated oil-in-water emulsions.

Keywords: Emulsion; Rheology; Viscoelasticity; Scaling; Modulus

1. Introduction

A vast amount of published literature exists on the rheology of emulsions and suspensions. A comprehensive review of the subject was recently published by Pal [1]. Surprisingly, the scaling of the rheological properties of emulsions has received little attention in the published literature. In particular, the scaling of the emulsion rheological properties with respect to the droplet size is not well understood [2]. This paper presents the scaling analysis of the viscoelastic properties of emulsions.

2. Scaling analysis

For emulsions having negligible Coulombic and van der Waals interactions, the storage modulus (G') and the loss modulus (G'') are expected to be functions of seven variables, namely, frequency (ω), continuous-phase viscosity (η_c), dispersed-phase viscosity (η_d), droplet radius (R), concentration of droplets, i.e., number density (n), interfacial tension (σ), and thermal energy (KT). Thus,

$$G' = f(\omega, \eta_c, \eta_d, R, n, \sigma, KT) \quad (1)$$

$$G'' = f(\omega, \eta_c, \eta_d, R, n, \sigma, KT) \quad (2)$$

The total number of basic dimensions involved in expressing all the variables in the above equations is 3, i.e., mass, length, and time. Since there are eight variables in the equation, the total number of independent dimensionless groups required to describe the viscoelastic properties are $8-3=5$. Therefore,

$$G'/\omega\eta_c = f(\kappa, \phi, N_{Ca}, N_{Pe}) \quad (3)$$

$$G''/\omega\eta_c = f(\kappa, \phi, N_{Ca}, N_{Pe}) \quad (4)$$

where κ is the viscosity ratio (η_d/η_c), ϕ is the volume fraction of the dispersed-phase ($=4\pi nR^3/3$), N_{Ca} is the capillary number ($=\omega\eta_c R/\sigma$), and N_{Pe} is the Peclet number ($=\omega\eta_c R^3/KT$). As emulsion droplets are generally quite large (> 1 μm), the effect of the Brownian motion (Peclet number) can be neglected. Thus,

$$G'/\omega\eta_c = f(\kappa, \phi, N_{Ca}) \quad (5)$$

$$G''/\omega\eta_c = f(\kappa, \phi, N_{Ca}) \quad (6)$$

The dimensional analysis just discussed is consistent with the recent theoretical work of Palierne [3]. According to Palierne's theoretical analysis of the linear viscoelastic behaviour of moderately-concentrated emulsions, the complex modulus of emulsions (G^*) is given by,

$$G^* = G_c^* \left[\frac{1+3\sum_i \phi_i H_i}{1-2\sum_i \phi_i H_i} \right] \quad (7)$$

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where G_c^* is the complex modulus for the matrix (continuous phase), ϕ_i is the volume fraction of droplets of radius R_i, and H_i is given as,

$$H_i=\frac{(4\sigma/R_i)(2G_c^*+5G_d^*)+(G_d^*-G_c^*)(16G_c^*+19G_d^*)}{(40\sigma/R_i)(G_c^*+G_d^*)+(2G_d^*+3G_c^*)(16G_c^*+19G_d^*)} \tag{8}$$

For emulsions of two immiscible Newtonian liquids with uniform droplet size, Eq. (7) gives,

$$G'/\omega\eta_c=\frac{N_{Ca}\lambda_0(\lambda_1-\lambda_2)}{1+N_{Ca}^2\lambda_1^2} \tag{9}$$

$$G''/\omega\eta_c=\frac{\lambda_0(1+\lambda_1\lambda_2N_{Ca}^2)}{1+\lambda_1^2N_{Ca}^2} \tag{10}$$

where λ_0, λ_1 and λ_2 are,

$$\lambda_0=\left[\frac{10(\kappa+1)+3\phi(5\kappa+2)}{10(\kappa+1)-2\phi(5\kappa+2)}\right] \tag{11}$$

$$\lambda_1=\frac{1}{4}\left[\frac{(19\kappa+16)\{2\kappa+3-2\phi(\kappa-1)\}}{10(\kappa+1)-2\phi(5\kappa+2)}\right] \tag{12}$$

$$\lambda_2=\frac{1}{4}\left[\frac{(19\kappa+16)\{2\kappa+3+3\phi(\kappa-1)\}}{10(\kappa+1)+3\phi(5\kappa+2)}\right] \tag{13}$$

Thus, the dimensionless groups, $G'/\omega\eta_c$ and $G''/\omega\eta_c$ are functions of the viscosity ratio (η_d/η_c), dispersed-phase volume fraction (ϕ), and the capillary number (N_{Ca}). However, it is important to realize that the Palierne model is valid only for dilute to moderately-concentrated emulsions. At very high concentrations of dispersed-phase ($\phi > 0.70$), the rheological properties of the emulsions are controlled by the network structure of thin films of continuous-phase [4]. For such highly concentrated emulsions, Princen and Kiss [4] developed the following equation to predict the static-shear modulus (G),

$$G=1.769\frac{\sigma}{R}\phi^{1/3}(\phi-0.712) \tag{14}$$

Consequently, at high frequencies,

$$G'/\omega\eta_c=1.769N_{Ca}^{-1}\phi^{1/3}(\phi-0.712) \tag{15}$$

Note that for highly concentrated emulsions, the ratio ($G'/\omega\eta_c$) is independent of the viscosity ratio (η_d/η_c); it depends only on the dispersed-phase volume fraction (ϕ) and the capillary number (N_{Ca}).

3. Experimental work

The emulsions of oil-in-water (O/W) type were prepared from two different oils—odourless kerosene supplied by Fisher Scientific and light mineral oil supplied by Drug Trading. The viscosity and density of kerosene at 22°C were 2.2 mPa s and 0.79 g/ml, respectively. The mineral oil had a viscosity and density of 29.2 mPa s and 0.85 g/ml, respectively, at 22°C. A non-ionic surfactant (Triton X-100) was dissolved in deionized water so as to prepare a 2% by weight surfactant solution. The known amounts of the surfactant solution and oil were sheared together in a variable-speed homogenizer (Gifford–Wood Model 1-L) to prepare a known concentration emulsion. At any given oil concentration, two different droplet size emulsions were prepared, that is, fine and coarse emulsions. The coarse emulsion was prepared by keeping the shearing speed of the homogenizer and the duration of shearing small. The fine emulsions were prepared by using a higher shearing speed and increased duration of shearing.

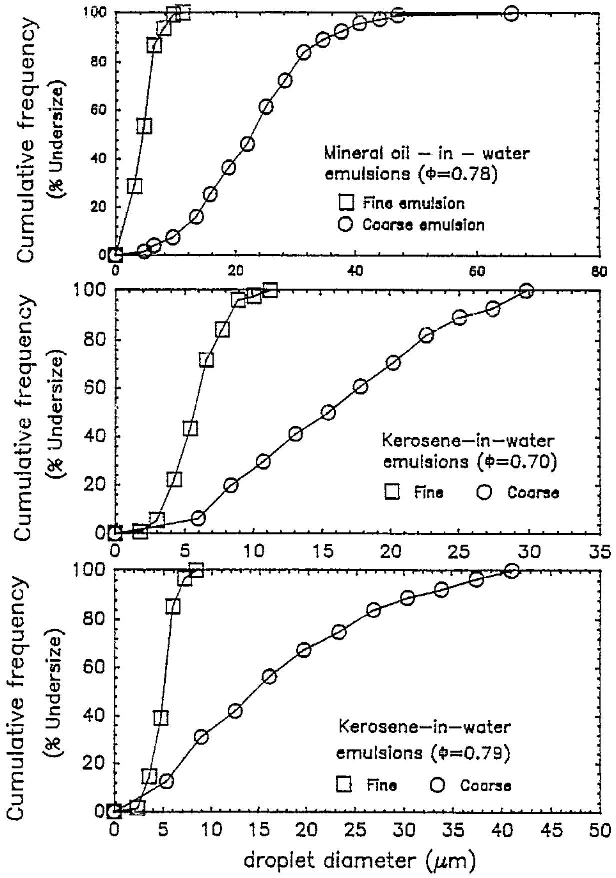

Fig. 1. Droplet size distributions of mineral oil-in-water ($\phi = 0.78$) and kerosene-in-water ($\phi = 0.70$ and $\phi = 0.79$) emulsions.

Table 1
Droplet size of emulsions

Type of emulsion	Oil concentration (ϕ)	Fine or coarse	Sauter mean diameter (μm)
Mineral oil-in-water	0.78	Fine	6.5
		Coarse	32
Kerosene-in-water	0.70	Fine	7.4
		Coarse	22
Kerosene-in-water	0.79	Fine	6
		Coarse	28

For kerosene-in-water emulsions, two different concentrations of oil were studied, i.e., 70% and 79% by volume. In the case of mineral oil-in-water emulsions, only one concentration of oil was studied, i.e., 78% by volume.

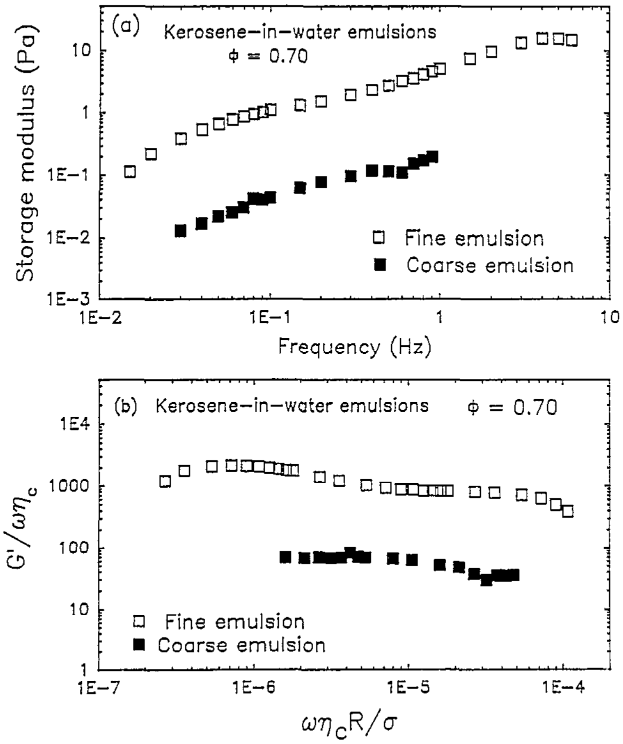

Fig. 2. (a) Storage modulus as a function of frequency for the fine and coarse kerosene-in-water emulsions ($\phi = 0.70$); (b) $G'/\omega\eta_c$ vs. $\omega\eta_c R/\sigma$ for the fine and coarse kerosene-in-water emulsions ($\phi = 0.70$).

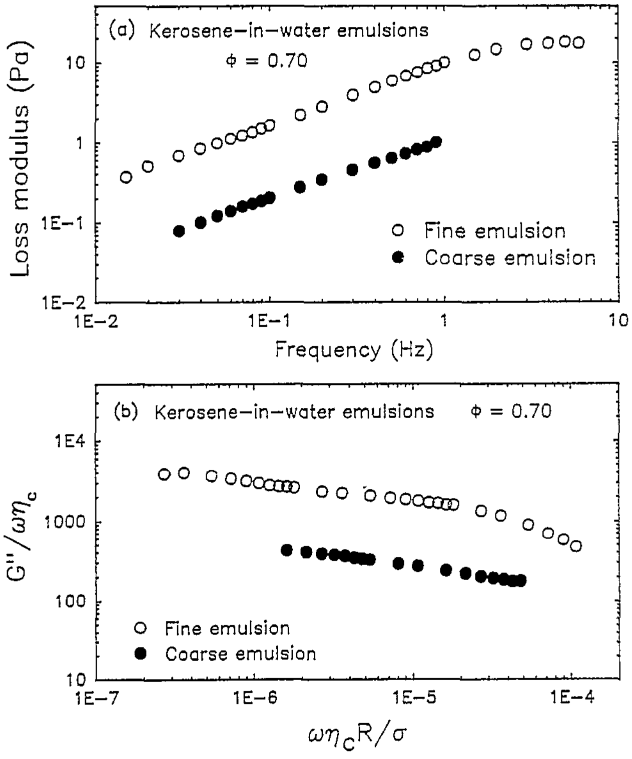

Fig. 3. (a) Loss modulus as a function of frequency for the fine and coarse kerosene-in-water emulsions ($\phi = 0.70$); (b) $G''/\omega\eta_c$ vs. $\omega\eta_c R/\sigma$ for the fine and coarse kerosene-in-water emulsions ($\phi = 0.70$).

The interfacial tension was measured using the drop volume (drop weight) method. For kerosene/surfactant-solution system, the interfacial tension was 1.3 mN/m. In the case of the mineral oil/surfactant–solution system, the interfacial tension was 2.3 mN/m.

The droplet sizes of the emulsions were determined by taking photomicrographs. The samples were diluted with the same continuous-phase (i.e., 2% by weight Triton X-100 solution) before taking the photomicrographs. The photomicrographs were taken with a Zeiss optical microscope equipped with a camera.

The storage and loss moduli of the fine and coarse emulsions were determined at 22°C using a controlled-stress rheometer (Böhlin CS-50). The oscillatory measurements were carried out at a low shear stress of 0.1 Pa. 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.

4. Results and discussion

The droplet size distributions of the emulsions are shown in Fig. 1. Clearly, the droplets of the fine emulsions are much smaller than the droplets of the corresponding coarse emulsions. The Sauter mean diameters of the emulsions are summarized in Table 1.

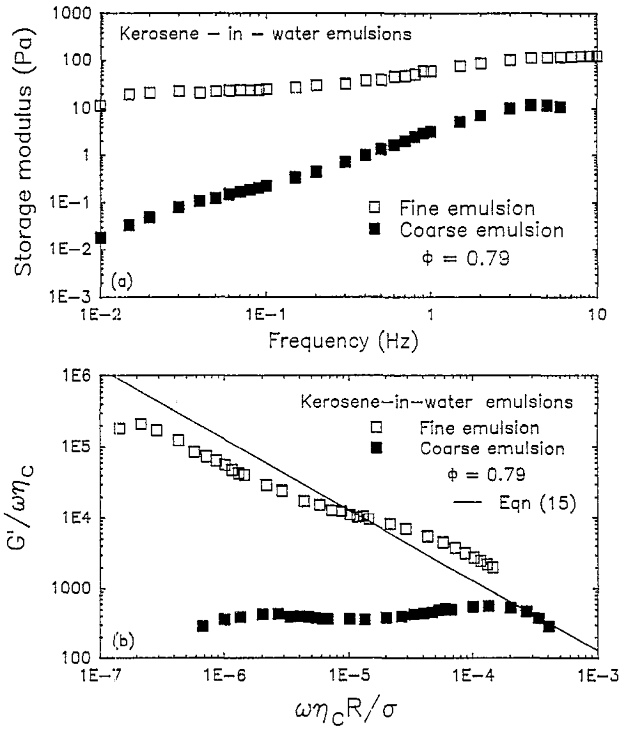

Fig. 4. (a) Storage modulus as a function of frequency for the fine and coarse kerosene-in-water emulsions ($\phi = 0.79$); (b) $G'/\omega\eta_c$ vs. $\omega\eta_c R/\sigma$ for the fine and coarse kerosene-in-water emulsions ($\phi = 0.79$).

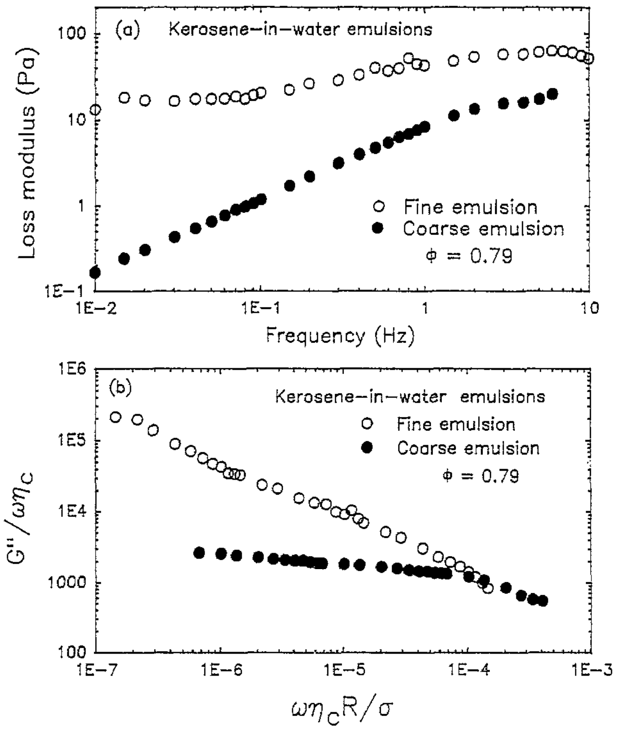

Fig. 5. (a) Loss modulus as a function of frequency for the fine and coarse kerosene-in-water emulsions ($\phi=0.79$); (b) $G''/\omega\eta_c$ vs. $\omega\eta_c R/\sigma$ for the fine and coarse kerosene-in-water emulsions ($\phi=0.79$).

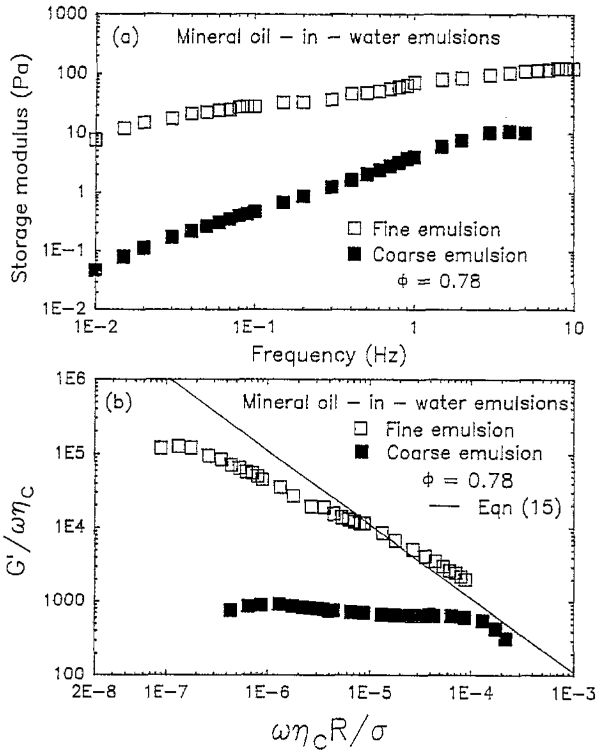

Fig. 6. (a) Storage modulus as a function of frequency for the fine and coarse mineral oil-in-water emulsions ($\phi=0.78$); (b) $G'/\omega\eta_c$ vs. $\omega\eta_c R/\sigma$ for the fine and coarse mineral oil-in-water emulsions ($\phi=0.78$).

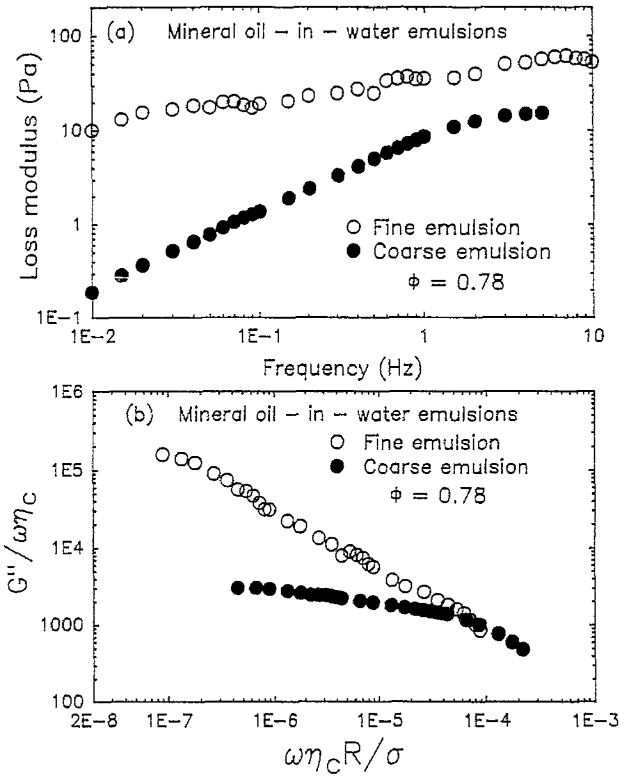

Fig. 7. (a) Loss modulus as a function of frequency for the fine and coarse mineral oil-in-water emulsions ($\phi=0.78$); (b) $G''/\omega\eta_c$ vs. $\omega\eta_c R/\sigma$ for the fine and coarse mineral oil-in-water emulsions ($\phi=0.78$).

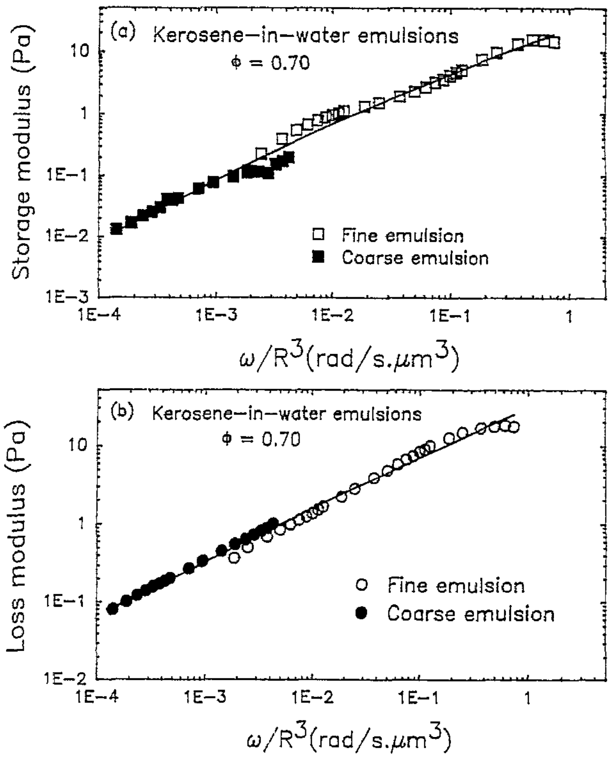

Fig. 8. (a) Storage modulus as a function of ω/R^3 for the fine and coarse kerosene-in-water emulsions ($\phi=0.70$); (b) Loss modulus as a function of ω/R^3 for the fine and coarse kerosene-in-water emulsions ($\phi=0.70$).

Table 2
The values of coefficients in Eqs. (16) and (17)

System	A_0	A_1	A_2
Kerosene-in-water emulsion ($\phi = 0.70$), G'	1.3642	6.7416×10^{-1}	-4.657×10^{-2}
Kerosene-in-water emulsion ($\phi = 0.70$), G''	1.4726	6.0679×10^{-1}	-1.5223×10^{-2}
Kerosene-in-water emulsion ($\phi = 0.79$), G'	2.017	1.5381×10^{-1}	-1.4767×10^{-1}
Kerosene-in-water emulsion ($\phi = 0.79$), G''	1.7392	2.2624×10^{-2}	-1.15×10^{-1}
Mineral oil-in-water emulsion ($\phi = 0.78$), G'	2.0487	1.7555×10^{-1}	-1.1249×10^{-1}
Mineral oil-in-water emulsion ($\phi = 0.78$), G''	1.6897	1.397×10^{-1}	-1.0038×10^{-1}

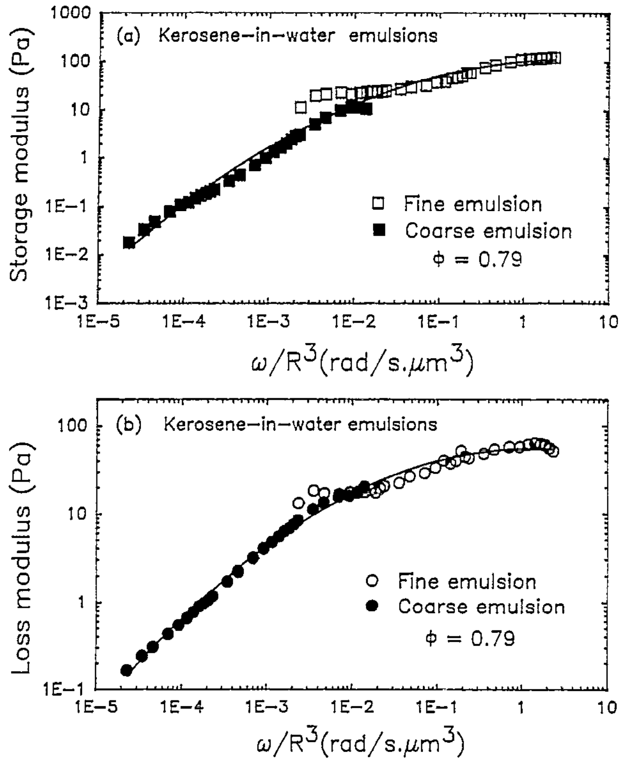

Fig. 9. (a) Storage modulus as a function of ω/R^3 for the fine and coarse kerosene-in-water emulsions ($\phi = 0.79$); (b) Loss modulus as a function of ω/R^3 for the fine and coarse kerosene-in-water emulsions ($\phi = 0.79$).

The storage and loss moduli data for the kerosene-in-water emulsions at two different oil concentrations ($\phi = 0.70$ and $\phi = 0.79$) are shown in Figs. 2–5. The same figures also show the plots of the dimensionless group, $G'/\omega\eta_c$ or $G''/\omega\eta_c$, as a function of the capillary number, $\omega\eta_c R/\sigma$. In the case of the highly concentrated kerosene-in-water emulsion with $\phi = 0.79$, Eq. (15) is shown as a solid-line (see Fig. 4). Note that Eq. (15) is applicable only when $\phi > 0.712$. Figs. (2)–(5) reveal the following points—(a) the storage and loss moduli of the fine emulsions are much higher than those of the corresponding coarse emulsions; (b) the scaling of the viscoelastic properties in terms of $G'/\omega\eta_c$ or $G''/\omega\eta_c$ vs. the capillary number, $\omega\eta_c R/\sigma$ is poor; and (c) for the highly concentrated emulsion ($\phi = 0.79$), Eq. (15) predicts reasonable values of $G'/\omega\eta_c$ at high capillary numbers, as expected.

The storage and loss moduli data for the mineral oil-in-water emulsions ($\phi = 0.78$) are shown in Figs. 6 and 7. The mineral oil-in-water emulsions behave like the kerosene-in-water emulsions in that the storage/loss moduli increase significantly upon the reduction of droplet size and that the correlation of the dimensionless group $G'/\omega\eta_c$ or $G''/\omega\eta_c$ with respect to the capillary number is poor. Also, Eq. (15) gives reasonable predictions of $G'/\omega\eta_c$ only at high capillary numbers.

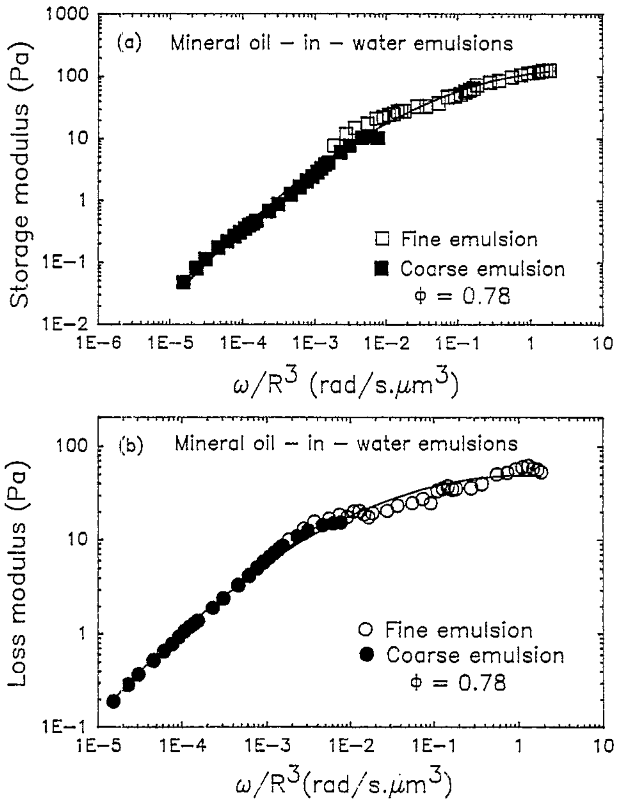

Fig. 10. (a) Storage modulus as a function of ω/R^3 for the fine and coarse mineral oil-in-water emulsions ($\phi = 0.78$); (b) Loss modulus as a function of ω/R^3 for the fine and coarse mineral oil-in-water emulsions ($\phi = 0.78$).

5. Correlation of viscoelastic properties

As seen in Section 4, the scaling of the viscoelastic properties, with respect to the droplet size, is unsuccessful when the data are plotted as $G'/\omega\eta_c$ or $G''/\omega\eta_c$ vs. $\omega\eta_c R/\sigma$. However, an excellent correlation is obtained when the storage and loss moduli data are plotted as a function of ω/R^3. Figs. 8–10 show the plots of the storage and loss moduli data for the fine and coarse emulsions, as a function of ω/R^3. As can be seen, the viscoelastic properties of emulsions with different average droplet sizes can be correlated quite well in terms of G' vs. ω/R^3 or G'' vs. ω/R^3. The solid curves shown in Figs. (8)–(10) are representative of the following empirical equations,

$$\log_{10} G' = \sum_{n=0}^{2} A_n [\log_{10}(\omega/R^3)]^n \qquad (16)$$

$$\log_{10} G'' = \sum_{n=0}^{2} A_n [\log_{10}(\omega/R^3)]^n \qquad (17)$$

where G', G'' are in Pa, ω in rad/s, and R in µm. The coefficients A_n are summarized in Table 2. It is interesting to note that Sherman [5,6] also found that the static-shear modulus of flocculated emulsions is proportional to $1/D_m{}^3$, where D_m is the volume–mean diameter of emulsions.

6. Concluding remarks

The storage and loss moduli data for the concentrated oil-in-water emulsions having different droplet sizes can be correlated reasonably well with respect to ω/R^3. Empirical correlations of G' vs. ω/R^3 and G'' vs. ω/R^3 are developed for the concentrated kerosene-in-water and mineral oil-in-water emulsions. The experimental work in the present study was restricted to two oils. More work needs to be done with different viscosity oils and at different oil concentrations to determine the general validity of the empirical scaling correlations proposed in this paper.

Acknowledgements

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