

A Novel Viscosity Correlation for Non-Newtonian Concentrated Emulsions

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The flow properties of concentrated oil-in-water and water-in-oil emulsions have been determined by using the Fann coaxial cylinder viscometer, the Weissenberg Rheogoniometer, and the Brookfield viscometer. Based on the extensive amount of experimental data collected, an empirical equation which correlates the relative viscosities of emulsions (both oil-in-water and water-in-oil) as a function of normalized dispersed phase concentration is proposed. According to the equation, if the viscosity of emulsion at any single dispersed phase concentration is known, the viscosity at other concentrations of dispersed phase can be predicted. A comparison of the correlation has been made with those proposed for solid-in-liquid suspensions. © 1985 Academic Press, Inc.

INTRODUCTION

The flow properties of concentrated emulsions are of interest in many applications. For example, the choice of mixing equipment and the power requirements for producing an emulsion are dependent upon the emulsion rheological properties. The prediction of the transport behavior of emulsions through pipelines (1–2) requires a knowledge of possible variations of viscosity with shearing rate as well as with concentration. Oil-well drilling (3), fracturing and acidizing processes (4), and all operations in which large volumes of concentrated emulsions are handled, require understanding and control of the viscous properties of concentrated emulsions. Despite the importance of the problem, there has been developed no commonly accepted theoretical or empirical expression (5) to correlate the viscosity of highly concentrated emulsions.

The development of an empirical correlation which correlates the relative viscosities of oil-in-water and water-in-oil emulsions as a function of dispersed phase concentration was the main objective of this study. Other objectives included:

(1) the prediction of the viscosities of different emulsion systems (over a range of dispersed phase concentration) using the correlation and comparison of the predicted values with the measured viscosities.

(2) a comparison of the proposed viscosity correlation for emulsions with those published for solid-liquid suspensions.

EXPERIMENTAL WORK

Oils

The oils used in this study were: Bayol-35, Bayol-35/CCl₄ mixture, Shell Vitrea 22, and Shell Vitrea 220. The water used throughout the experiments was deionized.

Bayol-35 is a refined white mineral oil. It has a density of 794 kg/m³ at 15°C and viscosity of 2.3 cst at 40°C.

Shell Vitrea 22 and Shell Vitrea 220 are highly-refined straight mineral paraffinic lubricating oils. Shell Vitrea 22 has a density of 858.2 kg/m³ at 15°C and a viscosity of about 22.5 cst at 40°C. Shell Vitrea 220 has a density of 881.7 kg/m³ at 15°C and a viscosity of about 210 cst at 40°C.

The Bayol-35/CCl₄ mixture was made up of 73.3% by volume Bayol-35 and 26.7% by volume analytical grade carbontetrachloride.

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The various emulsion systems studied were:

(a) Bayol-35-in-water emulsions at different temperatures over the dispersed phase concentration range of 40% to 69%.

(b) Shell Vitrea 220-in-water emulsions at different temperatures over a dispersed phase concentration range of 19% to 69%. The effect of aging was also studied for this system.

(c) Water-in-Bayol-35/ CCl_4 emulsions at room temperature ($26 \pm 1^\circ\text{C}$) over a dispersed phase concentration range of 0% to 75%.

(d) Water-in-Shell Vitrea 22 emulsions at room temperature over a dispersed phase concentration range of 50% to 60%.

Emulsifiers

The commercially available surfactants TRITON X-100 and SPAN 80 were used to stabilize the oil-in-water and water-in-oil emulsions, respectively. TRITON X-100 (isooctylphenoxy polyethoxy ethanol) is a nonionic water soluble emulsifier and SPAN 80 (sorbitan monooleate) is a nonionic oil soluble emulsifier.

Emulsification Procedure

The emulsions were prepared in approximately 900-ml batches. For systems other than Bayol-35/ CCl_4 , each concentration of emulsion was made freshly. However, for the Bayol-35/ CCl_4 system, higher concentrations were achieved by adding more dispersed phase to lower-concentration emulsion.

In all cases, oil-in-water emulsions were prepared by the agent-in-water method (emulsifier dissolved in the water phase) and water-in-oil emulsions were prepared by the agent-in-oil method (emulsifier dissolved in the oil phase). To prepare water-in-oil emulsions, 1.5% by volume of SPAN 80 based on the oil phase was used. To prepare oil-in-water emulsions (Shell Vitrea 220 and Bayol-35 emulsions), 0.5% by volume of Triton X-100 based on the water phase was used.

A variable speed model 1-LV Gifford-Wood homogenizer was used to mix the oil and water. For each system, the speed and the time of mixing were kept constant throughout the dispersed phase concentration range.

Viscometers Used

For low viscosity emulsions (at lower concentrations), a Brookfield viscometer model LV with U.L. adapter was used.

For higher viscosity emulsions, most of the data were collected by use of the Fann coaxial cylinder viscometer model 35A. To check the reliability of this instrument, data for Bayol-35/ CCl_4 emulsions were also collected by use of the Weissenberg Rheogoniometer model R-18.

For dispersed phase concentrations less than 70%, the data obtained from the two instruments agreed very well. At higher concentrations, the Fann viscometer gave significantly higher viscosities.

RESULTS AND DISCUSSION

At lower concentrations of dispersed phase (<20%), the emulsions behaved like Newtonian fluids. At higher concentrations, the emulsions behaved like pseudoplastic fluids. The flow curves of shear stress versus shear rate were found to follow a linear relationship on a log-log plot. A power law model could be fitted to the data according to the equation

$$\tau = K(\dot{\gamma})^n \quad [1]$$

The power law parameters determined were then used to obtain the viscosities at different shear rates.

At very high shear rates, the flow curves showed a linear relationship between the shear stress and the shear rate on a linear plot. A Bingham model was fitted to this data according to the equation

$$\tau = \tau_y + \mu_p \dot{\gamma} \quad [2]$$

where μ_p , a plastic viscosity, is the slope of the linear portion of the flow curve and τ_y ,

a yield stress, is the intercept of the line drawn through the linear portion of the flow curve.

The factors (other than the shear rate) which affected the viscosity of the emulsions were: dispersed phase concentration, viscosity of the dispersed phase, temperature and the age of emulsion.

On increasing the dispersed phase concentration of emulsion, the viscosity was found to increase almost exponentially in all the emulsion systems studied.

To see the effect of viscosity of the dispersed phase on the viscosity of emulsion, a comparison of high shear rate (1020 s^{-1}) viscosity data of Bayol 35-in-water and Shell Vitrea 220-in-water emulsions was made. Shell Vitrea 220 was about 100 times more viscous than Bayol 35. Emulsion preparation variables such as the type and concentration of emulsifier, speed, and time of mixing (which could all affect the viscosity of emulsions) were the same in both the cases. The viscosity of Shell Vitrea 220 emulsions was found to be significantly higher than that of the Bayol emulsions.

On increasing the temperature, the viscosity of emulsions decreased significantly. The apparent viscosity versus the temperature data followed an Arrhenius-type relationship.

To see the effect of aging on the viscosity of emulsions, the high shear rate (1020 s^{-1}) viscosity data of fresh and aged (10 days) Shell Vitrea 220 oil-in-water emulsions was compared. The viscosity of aged emulsions was found to be lower than that of the fresh emulsions.

DEVELOPMENT OF VISCOSITY CORRELATION

In order to correlate the viscosity data of emulsions as a function of dispersed phase concentration, a parameter which will be a function of all the possible factors affecting the viscosity has to be incorporated into the correlation.

For solid-liquid suspensions, several workers (6-7) have used ϕ_{\max} to incorporate the effect of particle size and distribution in the correlation. ϕ_{\max} is the maximum volume concentration of solid phase that can be achieved in the suspension. At ϕ_{\max} or packed bed concentration of dispersed phase, the viscosity of the suspension becomes infinite. ϕ_{\max} can be determined experimentally by plotting $1/\mu_r$ versus ϕ and extrapolating the data to the point where $1/\mu_r$ is zero. This ϕ_{\max} will depend upon the particle size and size distribution of the dispersed phase. The suspension viscosity correlation proposed by Chong and co-workers (6) is

$$\mu_r \equiv \left[1 + 0.75 \frac{(\phi/\phi_{\max})}{1 - (\phi/\phi_{\max})} \right]^2 \quad [3]$$

A similar correlation was also proposed by Frankel and Acrivos (7):

$$\mu_r = \frac{9}{8} \left[\frac{(\phi/\phi_{\max})^{1/3}}{1 - (\phi/\phi_{\max})^{1/3}} \right] \quad [4]$$

In the case of emulsions, there is no well-defined ϕ_{\max} . The viscosity of emulsions is always finite although the rate of change of viscosity with concentration increases as the concentration increases. At very high concentrations of dispersed phase, there is a possibility of phase inversion (i.e., an o/w emulsion may invert to w/o emulsion and vice versa). The dispersed phase concentration at which this inversion occurs is usually uncertain. The mode of addition of dispersed phase is very critical. For example, at higher concentrations, if small amounts of dispersed phase are added, inversion will usually occur at very high concentrations. If larger amounts of dispersed phase are added, then inversion may occur at relatively lower concentrations. Furthermore, the phase inversion can involve an intermediate stage (8) where multiple phases (such as oil suspended in a continuous aqueous phase but with smaller water droplets suspended in the oil) are formed and this

will make the calculation of the inversion point more uncertain.

In order to take into account the many factors which would affect the viscosity of emulsions, $(\phi)_{\mu_r=100}$ was arbitrarily chosen. $(\phi)_{\mu_r=100}$ is that concentration of dispersed phase at which the relative viscosity of the emulsion becomes 100. This concentration will be a function of all the possible factors which affect the viscosity of emulsions. For example, if the average particle size of an emulsion is lower, the relative viscosity will be higher and $(\phi)_{\mu_r=100}$ will be less. To determine $(\phi)_{\mu_r=100}$, the viscosity data were plotted as $(1/\mu_r) \times 10^3$ versus ϕ on a semilog plot (see Fig. 1 for a typical plot). The value of ϕ at which $(1/\mu_r) \times 10^3$ reached a value of 10 was taken as $(\phi)_{\mu_r=100}$. The plastic viscosity data for Shell Vitrea 220 oil-in-water emulsions was used to determine $(\phi)_{\mu_{pr}=100}$, where μ_{pr} is a relative plastic viscosity.

Figure 1 shows that different shear rates give different values of $(\phi)_{\mu_r=100}$. As the shear rate increases, the value of $(\phi)_{\mu_r=100}$ increases. This is because of the fact that at higher shear rates, the viscosities of the emulsions are lower and therefore a higher dispersed phase concentration is required to reach $\mu_r = 100$. Table I summarizes the values of $(\phi)_{\mu_r=100}$ obtained for different systems at different shear rates.

Having determined the values of $(\phi)_{\mu_r=100}$, the viscosity data of non-Newtonian emul-

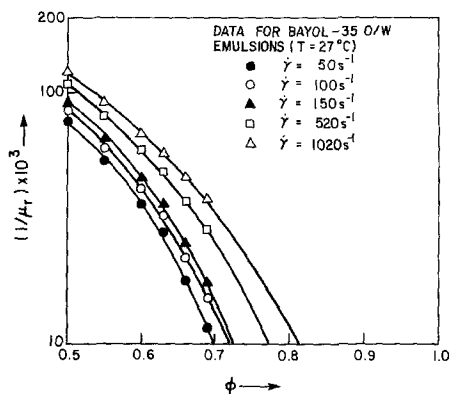


FIG. 1. Estimation of $(\phi)_{\mu_r=100}$.

TABLE I

Values of $(\phi)_{\mu_r=100}$ for Different Systems		
Type of system	Shear rate (s ⁻¹)	$(\phi)_{\mu_r=100}$
Bayol-35 oil-in-water emulsions (T = 27°C)	50	0.70
	100	0.72
	150	0.725
	520	0.7725
	1020	0.80
Bayol-35 oil-in-water emulsions (T = 35°C)	50	0.6925
	100	0.705
	150	0.722
	520	0.772
	1020	0.813
Bayol-35 oil-in-water emulsions (T = 64°C)	50	0.675
	100	0.702
	150	0.71
	520	0.755
	1020	0.788
Shell Vitrea 220 oil-in-water emulsions (T = 27°C)	10	0.675
	50	0.695
	150	0.705
	520	0.72
	1020	0.73
Bayol-35/CCL ₄ water-in-oil emulsions (T = 25°C)	10	0.66
	50	0.695
	520	0.77
	1020	0.802

sions were plotted as μ_r versus $\phi/(\phi)_{\mu_r=100}$ on a semilog plot. Figure 2 shows the plot of μ_r versus $\phi/(\phi)_{\mu_r=100}$. All the viscosity data for different systems at different shear rates fall on a single curve. The plastic viscosity data (μ_{pr} versus $\phi/(\phi)_{\mu_{pr}=100}$) also followed the same curve.

The data for Newtonian emulsions (i.e., lower dispersed phase concentration data) followed the same curve provided $(\phi)_{\mu_{pr}=100}$ was used as the normalizing dispersed phase concentration.

The best fit curve through the data is represented by

$$\mu_r = \left[1 + \frac{1.342\phi/(\phi)_{\mu_r=100}}{1.194 - \phi/(\phi)_{\mu_r=100}} \right]^{2.226} \quad [5]$$

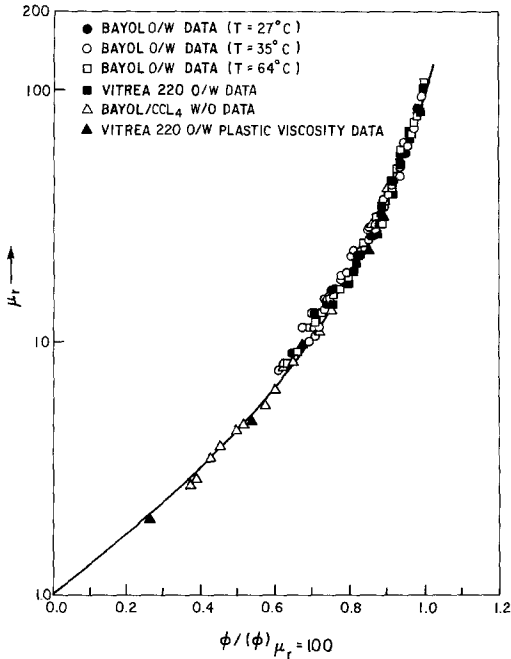


FIG. 2. Relative viscosity versus the normalized concentration.

In order to compare this result with the viscosity correlations proposed for suspensions (Eqs. [3] and [4]), ϕ_{max} was determined in terms of $(\phi)_{\mu_r=100}$ by substituting a value of $\mu_r = 100$ into these correlations and the following new relationships (for suspensions) between μ_r and $\phi/(\phi)_{\mu_r=100}$ were obtained:

For the Chong and co-workers correlation

$$\phi_{max} = \frac{13}{12}(\phi)_{\mu_r=100} \quad [6]$$

∴ Chong's model reduces to

$$\mu_r = \left[1 + \frac{0.75\phi/(\phi)_{\mu_r=100}}{13/12 - \phi/(\phi)_{\mu_r=100}} \right]^2 \quad [7]$$

For the Frankel and Acrivos correlation

$$\phi_{max} = 1.034(\phi)_{\mu_r=100} \quad [8]$$

∴ the Frankel and Acrivos model reduces to

$$\mu_r = \frac{9}{8} \left[\frac{\{\phi/(\phi)_{\mu_r=100}\}^{1/3}}{1.011 - \{\phi/(\phi)_{\mu_r=100}\}^{1/3}} \right] \quad [9]$$

A comparison of all three correlations is made in Fig. 3. All the correlations pass through the point where $\mu_r = 100$ and $\phi/(\phi)_{\mu_r=100} = 1$. The present correlation exceeds the predictions of the solid-liquid suspension ones. The displacement of the emulsion data above the solid suspension data is possibly related to aggregation and deformation of the emulsion particles. These effects are not considered in suspension correlations. However, an exact explanation is not known at this time. An interesting point to note is that at concentrations where $\phi/(\phi)_{\mu_r=100}$ approaches values slightly greater than 1.0, the solid-liquid suspension correlations give infinite viscosities whereas the present correlation gives finite viscosities. This is because of the fact that emulsion viscosity will always remain finite due to the deformable nature of the dispersed phase whereas suspensions will have infinite viscosities as packed bed concentrations (ϕ_{max}) are approached.

PREDICTION OF VISCOSITY OF EMULSIONS FROM THE PROPOSED CORRELATION

In order to predict the viscosity of emulsion at different dispersed phase concentrations,

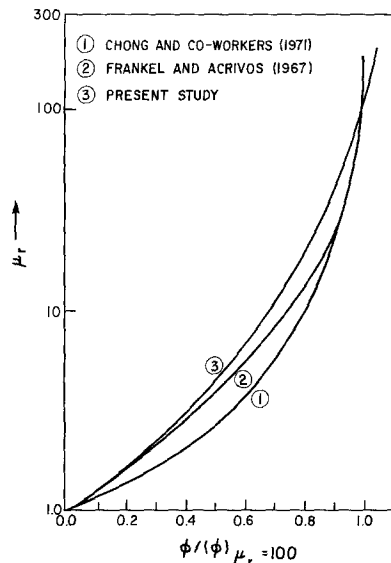


FIG. 3. Comparison of suspension viscosity models with the present emulsion viscosity model.

viscosity versus the shear rate data at any single concentration is required. Using the values of known relative viscosity, at a given shear rate, and known dispersed phase concentration we can determine $(\phi)_{\mu_r=100}$ from the correlation. For any other dispersed phase concentration (in the non-Newtonian range), $\phi/(\phi)_{\mu_r=100}$ can be calculated and this value when substituted in the correlation will give relative viscosity at the shear rate under consideration. This procedure can then be repeated to calculate relative viscosities at other shear rates.

To use the correlation for Newtonian emulsions (i.e., at lower dispersed phase concentrations), the relative plastic viscosity of any single concentration non-Newtonian emulsion is required. Using the relative plastic viscosity and the dispersed phase concentration we can determine $(\phi)_{\mu_{pr}=100}$ from the correlation. For any other dispersed concentration (in the Newtonian range), $\phi/(\phi)_{\mu_{pr}=100}$ can be calculated and this value when substituted in the correlation will give the predicted relative viscosity.

The correlation has been tested for the following systems:

(a) Water-in-oil emulsions where oil phase was Shell Vitrea 22.

(b) Aged oil-in-water emulsions where oil phase was Shell Vitrea 220.

(c) Heavy oil-in-water emulsions where oil phase was cold lake heavy crude oil. The data for this system was taken from the published literature (9).

For Shell Vitrea 22 w/o emulsions, $(\phi)_{\mu_r=100}$ at different shear rates was determined by using the correlation and the viscosity data of 60% emulsion. Knowing $(\phi)_{\mu_r=100}$, $\phi/(\phi)_{\mu_r=100}$ was calculated for other concentrations (50% and 55%) at different shear rates and these values were then substituted in the correlation to calculate the predicted μ_r values.

For aged Shell Vitrea 220 o/w emulsions, $(\phi)_{\mu_r=100}$ at different shear rates was determined by using the viscosity data of 68.6%

emulsion. The relative viscosity μ_r , was then predicted for other concentrations (65.13%, 62%, 59%, and 53.85%) at different shear rates by using the correlation.

For heavy oil-in-water emulsions, $(\phi)_{\mu_r=100}$ at a shear rate of 1000 s^{-1} was determined by using the viscosity data of 71.2% emulsion. Knowing $(\phi)_{\mu_r=100}$, μ_r at 1000 s^{-1} was predicted for other concentrations in the range of 40%–71.2% by using the correlation.

Figure 4 shows the comparison between the predicted viscosity values and the true (measured) viscosities. There is a good agreement between the predicted and the measured values and in most cases the deviation of the predicted from the measured values is less than 6%.

CONCLUSIONS

Based on the experimental data, an equation which correlates the relative viscosities of both o/w and w/o emulsions as a function of normalized dispersed phase concentration is proposed. Comparison of the proposed correlation with those published for solid-liquid suspensions show that for $0.30 < \phi/(\phi)_{\mu_r=100} < 1.0$, the proposed correlation gives higher viscosities.

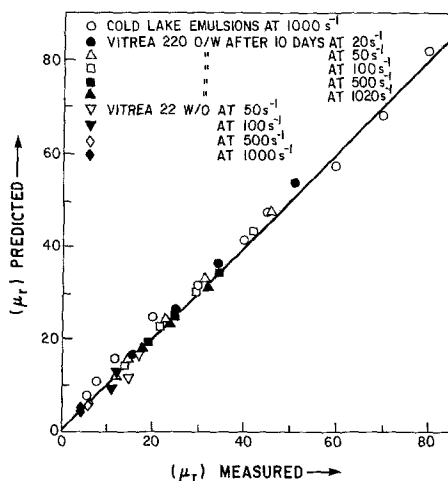


FIG. 4. Predicted relative viscosity versus the measured relative viscosity.

The proposed correlation could be used to predict the viscosity of emulsion at different dispersed phase concentrations provided the viscosity of emulsion at any single concentration is known. The predicted and the measured values of viscosities for three emulsion test systems were found to be in close agreement.

Finally, it is recommended that the correlation should be used only in the concentration range for which it is tested (i.e. $\phi(\phi)_{\mu_r=100} < 1$).

APPENDIX NOMENCLATURE

K = Consistency index, $\text{Nm}^{-2} \text{s}^n$

n = Flow behavior index, dimensionless

o/w = Oil-in-water emulsion

w/o = Water-in-oil emulsion

Greek Letters

ϕ = ratio of dispersed phase volume to the total volume, dimensionless

$\dot{\gamma}$ = shear rate, s^{-1}

μ_r = relative viscosity, dimensionless

τ = shear stress, Nm^{-2}

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