

Evaluation of theoretical viscosity models for concentrated emulsions at low capillary numbers

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Abstract

The theoretical models for the viscosity of concentrated emulsions are reviewed. All models predict that the relative viscosity of an emulsion, at low capillary numbers, is a function of dispersed-phase volume fraction and viscosity ratio (ratio of dispersed-phase viscosity to continuous-phase viscosity). The predicted values of relative viscosity from different theoretical models are compared with a large amount of experimental data. The cell model of Yaron and Gal-Or [Rheol. Acta 11 (1972) 241] predicts the relative viscosities of emulsions reasonably well over a wide range of dispersed-phase volume fraction and viscosity ratio. The cell model of Choi and Schowalter [Phys. Fluids 18 (1975) 420] overpredicts the relative viscosities, especially at high values of dispersed-phase volume fraction. The Phan-Thien and Pham model [J. Non-Newtonian Fluid Mech. 72 (1997) 305] underpredicts the relative viscosities of emulsions at high values of dispersed-phase volume fraction. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

An emulsion is a two-phase oil/water system where one of the phases is dispersed as droplets in the other. Emulsions also contain a third component, called the emulsifying agent or emulsifier, which has two principal functions: (1) to decrease the interfacial tension between oil and water, thereby enabling easier formation of the emulsion; (2) to stabilize the dispersed phase against coalescence once it is formed. Emulsions could be either oil-in-water (O/W) type or water-in-oil (W/O) type. In the former case, oil is the dispersed phase and in the latter case, water is the dispersed phase.

Emulsions play an important role in a number of industrial and household applications [1–4]. The use of such systems covers a broad field, ranging from lubrication and cooling of equipment in metal working processes to more delicate use as 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 [5]. Emulsions are of considerable importance in food applications as well [6].

In most of the applications just mentioned, the viscous properties of emulsions are of paramount importance. In particular, it is important to be able to predict the viscosity of the emulsion as a function of the dispersed-phase concentration. In the published literature, a large number of empirical viscosity equations containing one or more adjustable parameters have been proposed [7] for concentrated emulsions. Most of these empirical equations, however, are unreliable beyond the original data upon which they are based. Several authors [8–13] have also developed theoretical equations for the viscosity of dilute and concentrated emulsions. Unfortunately, these theoretical equations have received little attention in the literature despite their obvious advantages, such as: they contain no adjustable parameters and they provide better insight into the mechanisms governing the rheological behaviour of emulsions.

The objectives of this work are:

1. to briefly review various theoretical models for the viscosity of dilute and concentrated emulsions;
2. to compare the predictions of various theoretical models; and finally
3. to evaluate the models with a large amount of experimental data.

Note that the experimental evaluation of theoretical viscosity models for emulsions is lacking in the published literature.

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2. Theoretical background

A dispersion (emulsion or a suspension) can be treated as a homogeneous system and average quantities (velocity, velocity gradient, stress, rate of strain, etc.) can be defined if there exists a characteristic volume, ΔV , large enough to contain many particles (such that the statistical properties of the dispersion do not vary over ΔV) but much smaller than the flow scale [14] (see Fig. 1 for the schematic representation of a dispersion).

For a given set of macroscopic boundary conditions, there are many possible configurations of the dispersion [15]. A large number of such configurations make up an ensemble. An ensemble average of any quantity is defined as the average taken over the various values occurring in these configurations. If the dispersion is statistically homogeneous, an ensemble average at any point \hat{x} is identical with the volume average over a region about \hat{x} , of characteristic volume ΔV , for one realization [15].

Therefore, an average velocity gradient or similarly, an average rate of strain tensor in dispersions may be defined as

$$\langle \nabla \hat{u} \rangle = \frac{1}{\Delta V} \int_{\Delta V} (\nabla \hat{u}) dV \quad (1)$$

$$\langle \bar{d} \rangle = \frac{1}{2} [\langle \nabla \hat{u} \rangle + \langle (\nabla \hat{u})^T \rangle] = \frac{1}{\Delta V} \int_{\Delta V} \langle \bar{d} \rangle dV \quad (2)$$

The average stress tensor in the dispersion is similarly defined by

$$\langle \bar{\pi} \rangle = \frac{1}{\Delta V} \int_{\Delta V} \langle \bar{\pi} \rangle dV \quad (3)$$

provided that the effects of inertia in the dispersion are negligible [16,17].

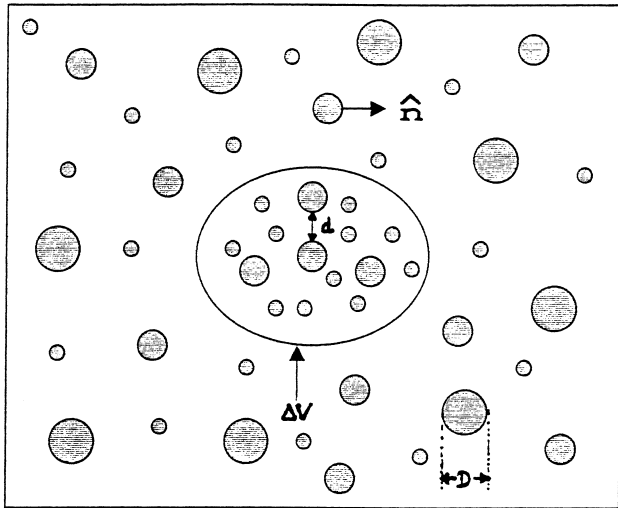


Fig. 1. A schematic representation of a dispersion. ΔV is the characteristic volume, large enough to contain many particles, but much smaller than the flow scale. d is the spacing between the particles, D the particle diameter, and \hat{n} a unit vector normal to the particle surface.

The integral in Eq. (3) can be broken up into integrals over the volume occupied by the continuous-phase fluid, ΔV_c , and by the dispersed phase, ΔV_d , to yield

$$\langle \bar{\pi} \rangle = \frac{1}{\Delta V} \int_{\Delta V_c} \langle \bar{\pi} \rangle dV + \frac{1}{\Delta V} \int_{\Delta V_d} \langle \bar{\pi} \rangle dV \quad (4)$$

Since

$$\bar{\pi} = -p\bar{\delta} + 2\eta_c\bar{d} \quad (5)$$

for the continuous phase, Eq. (4) becomes

$$\langle \bar{\pi} \rangle = \frac{1}{\Delta V} \int_{\Delta V_c} \{-p\bar{\delta} + 2\eta_c\bar{d}\} dV + \frac{1}{\Delta V} \int_{\Delta V_d} \langle \bar{\pi} \rangle dV \quad (6)$$

where p is the pressure and η_c the continuous-phase viscosity. From Eq. (6), the average stress tensor can be rewritten as [14,15]

$$\langle \bar{\pi} \rangle = -p\bar{\delta} + 2\eta_c\langle \bar{d} \rangle + \frac{1}{\Delta V} \sum_{i=1}^N \bar{S}_i \quad (7)$$

where N is the number of particles in the volume ΔV , and \bar{S}_i the “dipole strength” of particle i , given by

$$\bar{S}_i = \int_{A_i} [\hat{r}\bar{\pi} \cdot \hat{n} - \frac{1}{3}\bar{\delta}\hat{r} \cdot \bar{\pi} \cdot \hat{n} - \eta_c(\hat{u}\hat{n} + \hat{n}\hat{u})] dA \quad (8)$$

The above integration is carried out over the surface A_i of the particle i . Note that \hat{r} is a vector to the surface of the particle from the centre of the particle, \hat{n} is a unit vector normal to the particle surface, and $\bar{\delta}$ is a unit tensor. The term $(1/\Delta V)\sum_{i=1}^N \bar{S}_i$ in Eq. (7) can be interpreted as an extra stress tensor which represents the contribution to the average stress tensor due to the presence of the particles. The summation in this term over a large number (N) of identical particles in the volume ΔV is equivalent to N times an ensemble average of \bar{S} , i.e.,

$$\frac{1}{\Delta V} \sum_{i=1}^N \bar{S}_i = n\langle \bar{S} \rangle \quad (9)$$

where n is the number density of particles ($n=N/\Delta V$).

In the case of very *dilute* dispersions where there are very few particles present that they are far apart (and therefore, do not interact with each other), each particle behaves as if it were immersed in an infinite fluid subjected to bulk flow. In such situations

$$\frac{1}{\Delta V} \sum_{i=1}^N \bar{S}_i = n\bar{S} \quad (10)$$

where \bar{S} is the dipole strength of a single particle alone in an infinite fluid in which the rate of strain tensor far from the particle is $\langle \bar{d} \rangle$. Batchelor and Green [15] have shown that for very dilute dispersions

$$\bar{S} = \frac{20}{3}\pi R^3 \left[\frac{5\kappa + 2}{5(\kappa + 1)} \right] \eta_c \langle \bar{d} \rangle \quad (11)$$

where R is the particle radius, and κ the viscosity ratio of the dispersed phase to continuous phase. From Eqs. (10) and (11)

$$\frac{1}{\Delta V} \sum_{i=1}^N \bar{\bar{S}}_i = \frac{20}{3} n\pi R^3 \left[\frac{5\kappa + 2}{5(\kappa + 1)} \right] \eta_c \langle \bar{\bar{d}} \rangle \quad (12)$$

$$\frac{1}{\Delta V} \sum_{i=1}^N \bar{\bar{S}}_i = 5 \left[\frac{5\kappa + 2}{5(\kappa + 1)} \right] \eta_c \phi \langle \bar{\bar{d}} \rangle \quad (13)$$

where ϕ is the volume fraction of the dispersed phase. Therefore, the average stress tensor for very dilute dispersion of spherical particles is given by

$$\langle \bar{\bar{\pi}} \rangle = -p\bar{\bar{\delta}} + 2\eta_c \langle \bar{\bar{d}} \rangle + 5 \left[\frac{5\kappa + 2}{5(\kappa + 1)} \right] \eta_c \phi \langle \bar{\bar{d}} \rangle \quad (14)$$

The macroscopic or average stress tensor for the dispersion could also be written as

$$\langle \bar{\bar{\pi}} \rangle = -p\bar{\bar{\delta}} + 2\eta \langle \bar{\bar{d}} \rangle \quad (15)$$

where η is the effective viscosity of the dispersion. Upon comparing Eqs. (14) and (15), one obtains

$$\eta_r = \frac{\eta}{\eta_c} = 1 + \left[\frac{5\kappa + 2}{2(\kappa + 1)} \right] \phi \quad (16)$$

where η_r is the relative viscosity of the dispersion. Eq. (16) is the celebrated Taylor relation [8] for the relative viscosity of a very dilute emulsion.

The relative viscosity behaviour of dilute emulsions can be described by the Taylor relation (Eq. (16)) only if the emulsion droplets are spherical. Under a steady macroscopic flow, the droplets of emulsions are subjected to two opposing effects: (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 capillary number (N_{Ca}):

$$N_{Ca} = \frac{\eta_c \dot{\gamma}}{\sigma/R} \quad (17)$$

where $\dot{\gamma}$ is the shear rate, and σ 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 from spherical shape can be quite significant. Therefore, the Taylor equation (Eq. (16)) is valid only under the condition that the capillary number is small ($N_{Ca} \rightarrow 0$).

In the derivation of Taylor equation (Eq. (16)), the interaction between neighbouring drops (spherical) is neglected as the emulsion is very dilute. However, at finite concentrations of dispersed phase, the hydrodynamic interaction between droplets is significant. To take into account the hydrodynamic interaction between the neighbouring droplets,

Choi and Schowalter [11] and Yaron and Gal-Or [12] used a cell model approach. Their analysis leads to the following macroscopic stress tensor for emulsions when $N_{Ca} \rightarrow 0$:

$$\langle \bar{\bar{\pi}} \rangle = -p\bar{\bar{\delta}} + 2\eta_c [1 + I(\lambda)\phi] \langle \bar{\bar{d}} \rangle \quad (18)$$

where λ is $\phi^{1/3}$ and $I(\lambda)$ is given by Choi–Schowalter [11] (Eq. (19)) and Yaron and Gal-Or [12] (Eq. (20)):

$$I(\lambda) = \frac{2[(5\kappa + 2) - 5(\kappa - 1)\lambda^7]}{[4(\kappa + 1) - 5(5\kappa + 2)\lambda^3 + 42\kappa\lambda^5 - 5(5\kappa - 2)\lambda^7 + 4(\kappa - 1)\lambda^{10}]} \quad (19)$$

$$I(\lambda) = \frac{5.5[4\lambda^7 + 10 - (\frac{84}{11})\lambda^2 + (4/\kappa)(1 - \lambda^7)]}{10(1 - \lambda^{10}) - 25\lambda^3(1 - \lambda^4) + (10/\kappa)(1 - \lambda^3)(1 - \lambda^7)} \quad (20)$$

From Eqs. (15) and (18), it follows that

$$\eta_r = 1 + I(\lambda)\phi \quad (21)$$

Phan-Thien and Pham [13] have recently developed another viscosity equation for concentrated emulsions using the effective medium approach. Starting from the Taylor equation (Eq. (16)) and using the concept of effective medium, they developed the following differential equation for the viscosity of concentrated emulsions at low capillary numbers ($N_{Ca} \rightarrow 0$):

$$\frac{d\eta}{d\phi} = \frac{1}{1 - \phi} \left[\frac{\eta + (\frac{5}{2})\eta_d}{\eta + \eta_d} \right] \eta \quad (22)$$

where η_d is the dispersed-phase viscosity. The above differential equation can be solved by subjecting it to the following boundary condition:

$$\text{at } \phi = 0, \quad \eta = \eta_c \quad (23)$$

The solution of Eq. (22) subjected to the boundary condition of Eq. (23) is as follows:

$$\left(\frac{\eta}{\eta_c} \right)^{2/5} \left[\frac{2\eta + 5\eta_d}{2\eta_c + 5\eta_d} \right]^{3/5} = (1 - \phi)^{-1} \quad (24)$$

This solution can be rewritten in terms of the relative viscosity (η_r) and the viscosity ratio (κ) as follows:

$$\eta_r^{2/5} \left[\frac{2\eta_r + 5\kappa}{2 + 5\kappa} \right]^{3/5} = (1 - \phi)^{-1} \quad (25)$$

It should be noted that all the theoretical equations for emulsion viscosity (Eqs. (16), (21) and (25)) predict that the relative viscosity of an emulsion at low capillary numbers ($N_{Ca} \rightarrow 0$) is a function of the viscosity ratio κ ($=\eta_d/\eta_c$) and dispersed-phase volume fraction ϕ .

3. Predictions of theoretical models

Figs. 2–4 show the relative viscosities predicted from the models of Choi and Schowalter (Eqs. (19) and (21)), Yaron

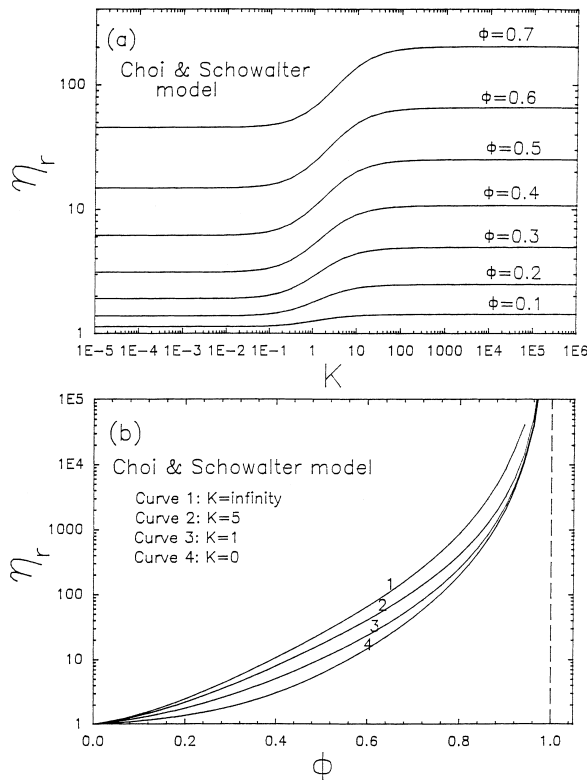


Fig. 2. Relative viscosities predicted by the Choi and Schowalter model.

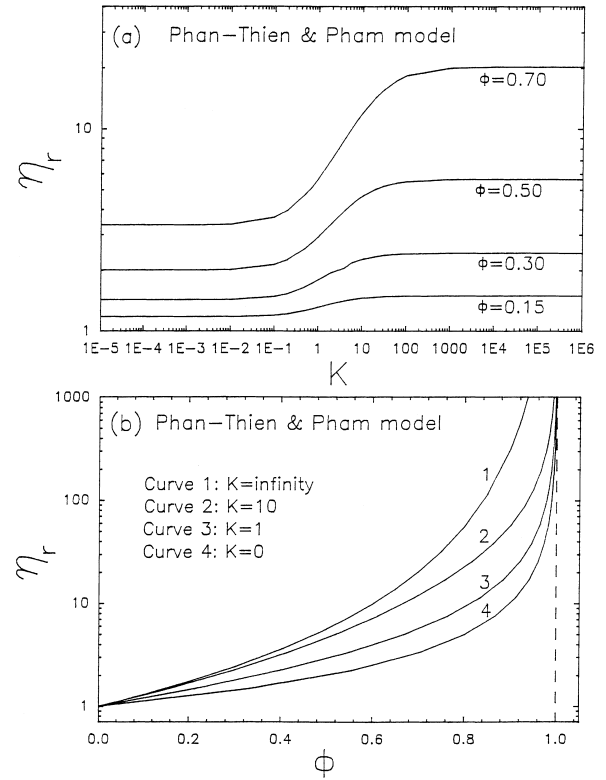


Fig. 4. Relative viscosities predicted by the Phan-Thien and Pham model.

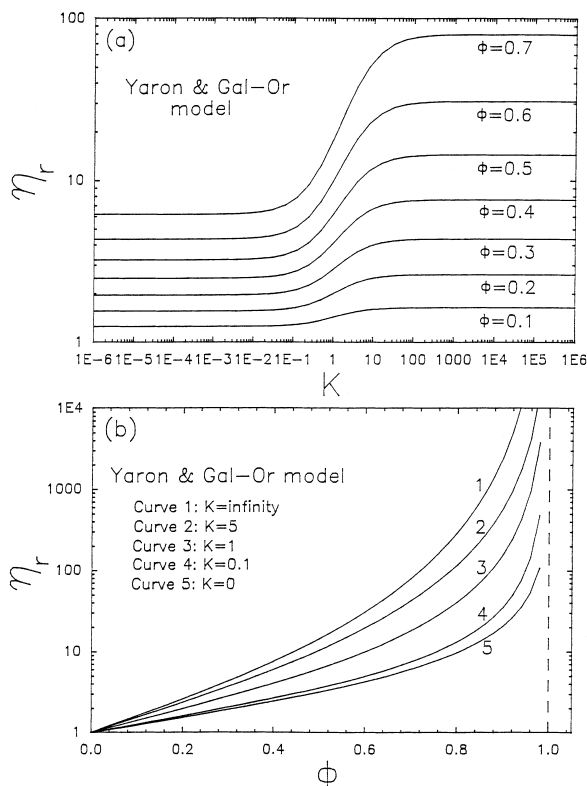


Fig. 3. Relative viscosities predicted by the Yaron and Gal-Or model.

and Gal-Or (Eqs. (20) and (21)), and Phan-Thien and Pham (Eq. (25)). All the three models predict that the relative viscosity at any given value of viscosity ratio κ increases with the increase in dispersed-phase volume fraction ϕ . Also, as $\phi \rightarrow 1.0$, the relative viscosity becomes infinite. At a fixed value of ϕ , the relative viscosity initially remains nearly constant with the increase in viscosity ratio κ . In the range $10^{-2} < \kappa < 100$, the relative viscosity increases with the increase in κ . At higher values of κ ($\kappa > 100$), the relative viscosity again becomes nearly constant, independent of κ .

Fig. 5 shows comparison between the predictions of various theoretical models at different values of ϕ . For $\phi < 0.30$, the Yaron and Gal-Or model predicts relative viscosities higher than those predicted by the Choi and Schowalter and Phan-Thien and Pham models over the full range of κ . The Phan-Thien and Pham model predicts the lowest values whereas the predictions of Choi and Schowalter model fall in between those of Yaron and Gal-Or and Phan-Thien and Pham models. At $\phi = 0.30$, the Yaron and Gal-Or and Choi and Schowalter models predict similar relative viscosities (Choi and Schowalter model predicts slightly higher values at high values of κ). The Phan-Thien and Pham model predicts much lower values of relative viscosity over the full κ range. When $\phi > 0.30$, the Choi and Schowalter model overtakes the Yaron and Gal-Or model and predicts the highest viscosities over the full κ range. The predictions from the Yaron and Gal-Or model fall in between those of Choi and Schowalter and Phan-Thien and Pham models at high values of ϕ .

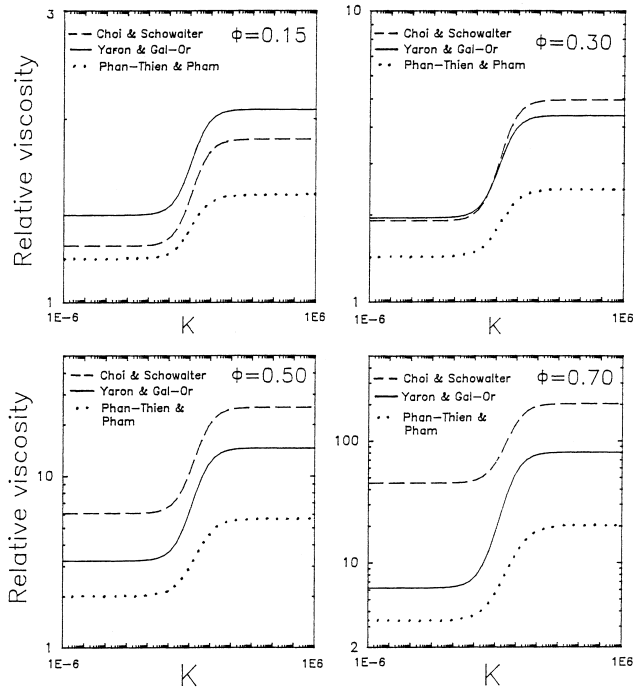


Fig. 5. Comparison between the predictions of various theoretical models at different values of dispersed-phase volume fraction (ϕ).

4. Comparison of theoretical models with experimental data

Two sets of literature data and 17 sets of data from our work on emulsions are considered to evaluate the theoretical viscosity models. These data were selected on the basis

of the following criteria: (a) the capillary number is small ($N_{Ca} \rightarrow 0$), and (b) the emulsions are de-flocculated. It should be noted that the theoretical models discussed in the preceding section are valid for de-flocculated emulsions at low capillary numbers. Table 1 gives further details on the various emulsion systems considered in the present work.

Figs. 6 and 7 show comparisons between the experimental data and theoretical predictions for different values of the viscosity ratio κ . At low values of ϕ ($\phi \leq 0.20$), the experimental data generally follow the Phan-Thien and Pham model (Eq. (25)) more closely. At higher values of ϕ , the experimental data follow the Yaron and Gal-Or model (Eqs. (20) and (21)) more closely. The Choi and Schowalter model (Eqs. (19) and (21)) overpredicts the relative viscosities especially at ϕ values greater than about 0.20. Overall, the best model is the Yaron and Gal-Or model; it gives reasonable predictions of relative viscosities at different values of κ and ϕ . It is interesting to note that the relative viscosity of de-flocculated emulsions at low capillary numbers ($N_{Ca} \rightarrow 0$) is independent of the droplet size; none of the theoretical models discussed here involve the droplet size. Experimental evidence for the droplet size independence of relative viscosity is shown in Fig. 7a. Emulsions having different Sauter mean diameters (set 1–21.4 μm , set 2–9.12 μm , set 3–8.1 μm , and set 4–4.6 μm) exhibit nearly the same relative viscosities.

In Fig. 8, the experimental relative viscosity data are compared with the predictions of the theoretical models at a fixed value of ϕ , i.e., $\phi=0.50$. A wide range of viscosity ratio κ is covered ($10^{-4} < \kappa < 10^6$). For $\kappa \leq 10$, the experimental data follow the Yaron and Gal-Or model quite well. When $\kappa > 10$, the experimental relative viscosities fall somewhat below

Table 1
Summary of various emulsion systems considered in the present work

Set No.	Type of emulsions	Range of ϕ	Viscosity ratio (κ)	Reference number	Comments
1	O/W	0.165–0.516	5.52	[18]	Emulsions for sets 1–4 were prepared from the same oil and aqueous phase. However, the Sauter mean diameter was different for different sets: set 1–21.4 μm , set 2–9.12 μm , set 3–8.1 μm , set 4–4.6 μm
2	O/W	0.195–0.349	5.52	[18]	
3	O/W	0.226–0.553	5.52	[18]	
4	O/W	0.219–0.543	5.52	[18]	
5	O/W	0.296–0.635	1170	Unpublished data	Heavy oil-in-water emulsions
6	O/W	0.10–0.60	4.15×10^{-3}	[19]	Polymer-thickened emulsions
7	O/W	0.10–0.60	1.12×10^{-2}	[19]	Polymer-thickened emulsions
8	O/W	0.155–0.60	5.82×10^{-2}	[20]	Polymer-thickened emulsions
9	O/W	0.165–0.55	2.57	[21]	Mineral oil emulsions
10	O/W	0.50	3.87×10^{-4}	[22]	Polymer-thickened emulsions
11	O/W	0.50	5.82×10^{-2} –1.95	[20]	Polymer-thickened emulsions
12	O/W	0.50	60.85	[23]	Mineral oil emulsion
13	O/W	0.50	1106.4	Unpublished data	Mineral oil emulsion
14	O/W	0.50	3.25×10^5	Unpublished data	Bitumen-in-water emulsion
15	W/O	0.50	0.153	[24]	Petroleum oil emulsion
16	W/O	0.50	0.447	[21]	Oil phase consisted of a mixture of CCl_4 and refined mineral oil
17	O/W	0.50	256.8	[21]	Lubricating oil emulsion
18	O/W	0.50	1.7–64.2	[25]	Limpid and viscous paraffin emulsions
19	O/W	0.50	0.834–123.1	[26]	Emulsions were prepared from three different oils: nujol, benzene and olive oil. The aqueous phase consisted of either sodium oleate or saponin

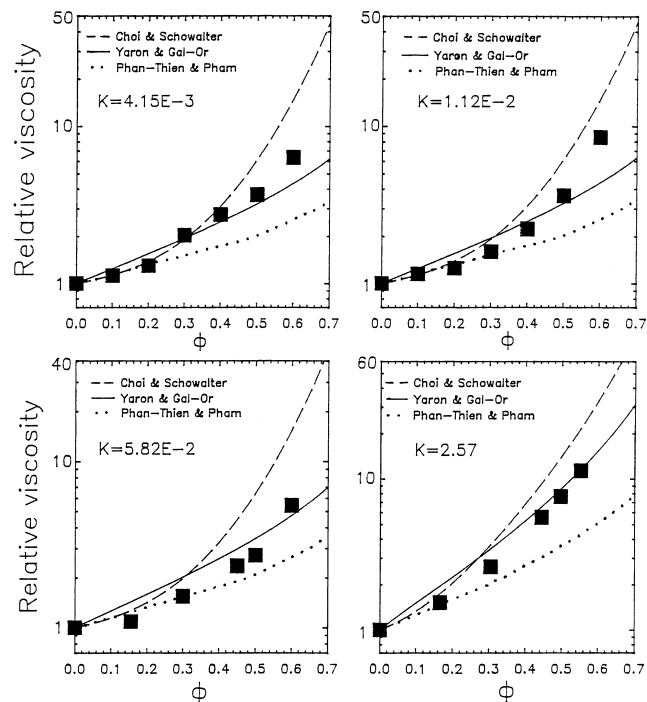


Fig. 6. Comparisons between the experimental data and theoretical predictions for different values of the viscosity ratio (κ).

the predictions of the Yaron and Gal-Or model although the deviation is not large. The Choi and Schowalter model overpredicts the relative viscosities whereas the Phan-Thien and Pham model underpredicts the relative viscosities over the full range of κ values. Thus, it can be concluded that the Yaron and Gal-Or model represents the experimental data more accurately as compared with the other two theoretical models.

Fig. 9 shows a parity plot of the relative viscosities predicted by Yaron and Gal-Or model and those obtained experimentally. The data include all 19 sets (see Table 1).

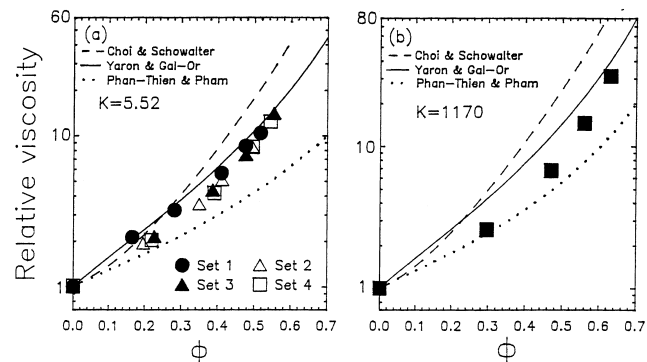


Fig. 7. Comparisons between the experimental data and theoretical predictions. Note that Fig. 7a shows the relative viscosity data of emulsions having different average droplet sizes. The Sauter mean diameter of the four sets of data shown in Fig. 7a are as follows: set 1–21.4 μm , set 2–9.12 μm , set 3–8.1 μm , and set 4–4.6 μm .

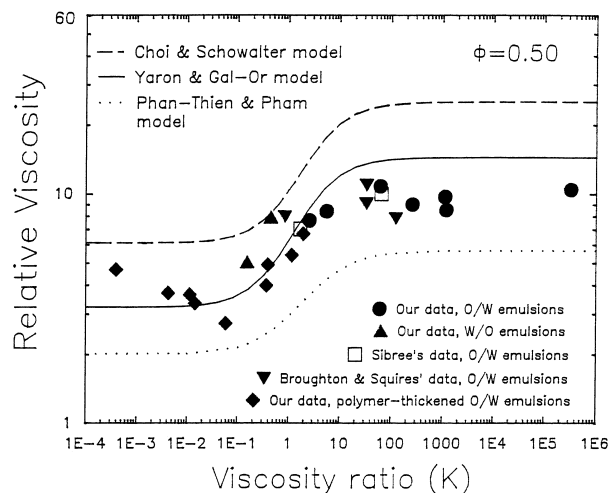


Fig. 8. Comparison between the experimental data and theoretical predictions at a fixed dispersed-phase volume fraction (ϕ) of 0.50.

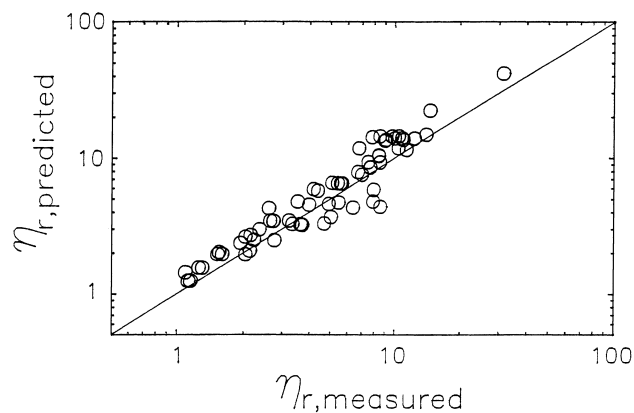


Fig. 9. Parity plot: Yaron and Gal-Or model prediction versus experimental values of relative viscosities.

A fairly good agreement is obtained between the predicted and the experimental values.

5. Conclusions

Based on the review and analysis of theoretical models presented in the paper, the following conclusions can be made:

- At low capillary numbers ($N_{Ca} \rightarrow 0$), the relative viscosity of de-flocculated emulsions depends only on the dispersed-phase volume fraction (ϕ) and viscosity ratio (κ).
- At a fixed value of ϕ , the relative viscosity initially remains nearly constant when the viscosity ratio κ is increased. In the range $10^{-2} < \kappa < 100$, the relative viscosity increases with the increase in κ . When $\kappa > 100$, the relative viscosity again becomes constant, independent of κ .

- Overall, the best model for the viscosity of concentrated emulsions is the cell model of Yaron and Gal-Or [12]; it gives reasonable predictions of relative viscosity over a wide range of ϕ and κ . The Phan-Thien and Pham model [13] gives good predictions of relative viscosity only at low values of ϕ . At high values of ϕ , the Phan-Thien and Pham model underpredicts the relative viscosities whereas the Choi and Schowalter model [11] overpredicts the relative viscosity.

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