Rheology of double emulsions

Rajinder Pal

Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada

Abstract

New equations for the viscosity of concentrated double emulsions of core–shell droplets are developed using a differential scheme. The equations developed in the paper predict the relative viscosity (η_r) of double emulsions to be a function of five variables: a/b (ratio of core drop radius to shell outer radius), λ_{21} (ratio of shell liquid viscosity to external continuous phase viscosity), λ_{32} (ratio of core liquid viscosity to shell liquid viscosity), ϕ^{DE} (volume fraction of core–shell droplets in double emulsion), and ϕ_m^{DE} (the maximum packing volume fraction of un-deformed core–shell droplets in double emulsion). Two sets of experimental data are obtained on the rheology of O/W/O (oil-in-water-in-oil) double emulsions. The data are compared with the predictions of the proposed equations. The proposed equations describe the experimental viscosity data of double emulsions reasonably well.

© 2006 Published by Elsevier Inc.

Keywords: Emulsion; Multiple emulsion; Double emulsion; Rheology; Viscosity

1. Introduction

Double emulsions are "emulsions of emulsions." The dispersed phase of a double emulsion itself is an emulsion. For example, an oil-in-water-in-oil ($O_1/W/O_2$) double emulsion consists of small oil (O_1) droplets dispersed in aqueous phase (W) and this O_1/W emulsion itself is dispersed as large droplets in the continuous oil phase (O_2). In the case of a water-in-oil-in-water ($W_1/O/W_2$) double emulsion, an emulsion of small water (W_1) droplets in oil (O) is itself dispersed as large droplets in the continuous aqueous (W_2) phase.

Double emulsions are often prepared using a two-step procedure. In the *first* step, the primary emulsion is prepared. The primary emulsion in the case of a O/W/O double emulsion is a simple O/W (oil droplets-in matrix water) emulsion which is prepared using an oil and an aqueous solution of a high HLB (hydrophilic–lipophilic balance) surfactant. In the case of a W/O/W double emulsion, the primary emulsion is a simple W/O (water droplets-in matrix oil) emulsion which is prepared using water and a low HLB surfactant solution in oil. In the *second* step, the primary emulsion (O/W or W/O) is re-emulsified

in either an oil solution containing a low HLB surfactant to produce an O/W/O double emulsion or an aqueous solution of a high HLB surfactant to produce a W/O/W double emulsion. The second emulsification step is carried out in a low shear device so as to avoid expulsion of internal droplets to the external continuous phase.

Because of their special structure, double emulsions are highly suited for applications in the pharmaceutical, cosmetics and food industries [1–6]. They have also shown significant promise in waste water treatment and separation of hydrocarbons [7–12].

The understanding of the rheological behavior of double emulsions is important in many practical applications involving the usage of such systems. In particular, it is important to be able to predict the viscosity of double emulsions as a function of other appropriate variables.

While there is a substantial amount of literature published on rheology of simple emulsions [13–17], little attention has been given to double emulsions. Some papers have appeared recently on double emulsion rheology [18–22], but for the most part, they are qualitative in nature.

According to Matsumoto and co-workers [23–25], the viscosity of Newtonian double/multiple emulsions can be described by the following Mooney equation [26]:

E-mail address: rpal@cape.uwaterloo.ca.

$$\ln \eta_r = \frac{K_1 \phi^{DE}}{1 - K_2 \phi^{DE}}, \tag{1}$$

where η_r is the relative viscosity of the double emulsion, defined as the ratio of the double emulsion viscosity to the external continuous phase viscosity, ϕ^{DE} is the volume fraction of the total dispersed phase in the whole double emulsion, and K_1 and K_2 are empirical constants. For O/W/O type double emulsions, $\phi^{DE} = \phi_{oi} + \phi_w$ where ϕ_{oi} is the volume fraction of inner oil phase in the whole double emulsion and ϕ_w is the volume fraction of water in the whole double emulsion. In the case of W/O/W type double emulsion, $\phi^{DE} = \phi_{wi} + \phi_o$ where ϕ_{wi} is the volume fraction of inner aqueous phase in the whole double emulsion and ϕ_o is the volume fraction of oil in the whole double emulsion. For the double emulsions studied by Matsumoto and co-workers, the constant K_1 was found to vary from 2.3 to 3.2 and the constant K_2 varied from 0.5 to 1.9. Furthermore the constants K_1 and K_2 were found to depend on sample age, osmotic pressure, and stability of vesicular structure [24].

It is important to realize that the Mooney equation was originally developed for suspensions of rigid spherical particles. It cannot be applied to dispersed systems of liquid droplets such as simple or double emulsions.

In this paper, new viscosity equations for double emulsions are derived. The equations developed in the paper are compared with experimental data on double emulsions.

2. Brief background

The globule of a double emulsion, consisting of several internal droplets, is often modeled as a core–shell droplet as shown in Fig. 1. If the inner core drop has a radius of a and the outer radius of the liquid shell is b, the volume fraction of the dispersed phase in the primary emulsion ϕ^{PE} can be expressed as:

$$\phi^{PE} = \frac{(4/3)\pi a^3}{(4/3)\pi b^3} = (a/b)^3. \tag{2a}$$

Thus, the ratio a/b is related to ϕ^{PE} as:

$$a/b = \left(\phi^{PE}\right)^{1/3}. \tag{2b}$$

For an infinitely dilute emulsion of core–shell droplets at low capillary numbers, Stone and Leal [27] have shown that the relative viscosity η_r is given by:

$$\eta_r = \frac{\eta}{\eta_1} = 1 + \frac{5}{2}\left(1 - \frac{3}{5}I\right)\phi^{DE}, \tag{3}$$

where ϕ^{DE} is the volume fraction of core–shell droplets in the double emulsion, I is a dimensionless factor function of radii ratio a/b and viscosity ratios λ_{21} ($= \eta_2/\eta_1$) and λ_{32} ($= \eta_3/\eta_2$),
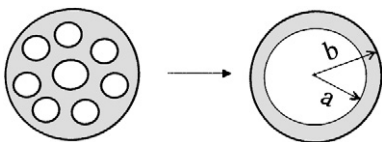

Fig. 1. Double emulsion globules consisting of several internal droplets is modeled as a core–shell droplet with core radius "a" and outside radius of shell "b."

η_1 is the viscosity of external continuous phase, η_2 is the viscosity of shell liquid, and η_3 is the viscosity of inner core liquid. The expression for I is as follows:

$$I = \frac{A}{A + B(\eta_2/\eta_1)}, \tag{4}$$

where

$$A = \delta_1 + \frac{(a/b)^3 \delta_2}{1 + \lambda_{32}}, \tag{5a}$$

$$B = \delta_3 + \frac{(a/b)^3 \delta_4}{1 + \lambda_{32}}. \tag{5b}$$

The δ_i's depend on ratio a/b only and are given as:

$$\delta_1 = 4 - 25(a/b)^3 + 42(a/b)^5 - 25(a/b)^7 + 4(a/b)^{10}, \tag{6}$$

$$\delta_2 = 15 - 42(a/b)^2 + 35(a/b)^4 - 8(a/b)^7, \tag{7}$$

$$\delta_3 = 4 - 10(a/b)^3 + 10(a/b)^7 - 4(a/b)^{10}, \tag{8}$$

$$\delta_4 = 6 - 14(a/b)^4 + 8(a/b)^7. \tag{9}$$

In the case of a very viscous outer shell liquid ($\lambda_{21} \to \infty$), $I \to 0$ and Eq. (3) reduces to the well-known Einstein equation for the viscosity of infinitely dilute suspension of rigid spheres [28,29]:

$$\eta_r = 1 + 2.5\phi^{DE}. \tag{10}$$

In the limit $a/b \to 0$, $I \to 1/(1 + \lambda_{21})$ and Eq. (3) reduces to the well-known Taylor equation for the viscosity of infinitely dilute emulsions [13]:

$$\eta_r = 1 + \left(\frac{1 + \frac{5}{2}\lambda_{21}}{1 + \lambda_{21}}\right)\phi, \tag{11}$$

where ϕ is the volume fraction of dispersed phase in a simple emulsion.

3. New viscosity equations for concentrated double emulsions

Equation (3) cannot be applied at finite concentrations of core–shell droplets as the hydrodynamic interaction between the droplets is ignored in the derivation. In this section, new equations for the viscosity of concentrated double emulsions (emulsions of core–shell droplets) are derived using the differential effective medium approach (DEMA). According to DEMA, a concentrated double emulsion is considered to be obtained from an initial continuous phase by successively adding small quantities of core–shell droplets to the system until the final volume fraction of the core–shell droplets is reached. At any arbitrary stage (i) of the process, the addition of a small amount of core–shell droplets leads to the next stage ($i + 1$). The double emulsion of stage (i) is then treated as an equivalent "effective medium," which is homogeneous with respect to new set of core–shell droplets added to reach stage ($i + 1$). The solution of a dilute double emulsion (Eq. (3)) is then applied to determine the increment increase in viscosity in going from stage (i) to stage ($i + 1$). The differential equation derived in this manner is integrated to obtain the final solution for a concentrated double emulsion. This differential effective medium approach was

originally employed by Bruggeman [30], who derived an equation for the dielectric constant of a concentrated suspension.

Let us now consider a double emulsion with a volume fraction of core–shell droplets ϕ^{DE}. Into this double emulsion, a small differential quantity of new core–shell droplets is added. The increment increase in viscosity $d\eta$ resulting from the addition of the new core–shell droplets can be calculated from Eq. (3) by treating the double emulsion into which the new core–shell droplets are added as an equivalent effective medium of viscosity η. Therefore,

$$d\eta = \eta \left[\frac{5}{2} - \frac{\left(\frac{3}{2}\right)A}{A + B\eta_2/\eta} \right] d\phi^{DE}. \tag{12}$$

This equation can be rewritten as:

$$\frac{d\eta}{\left(\frac{5}{2}\eta\right)} + \frac{\left(\frac{3}{5}\right)A\,d\eta}{\left(A\eta + \frac{5}{2}B\eta_2\right)} = d\phi^{DE}. \tag{13}$$

Upon integration with the limit $\eta \to \eta_c$ at $\phi^{DE} \to 0$, Eq. (13) gives:

$$\eta_r \left[\frac{A\eta_r + \left(\frac{5}{2}\right)B\lambda_{21}}{A + \left(\frac{5}{2}\right)B\lambda_{21}} \right]^{3/2} = \exp\left(\frac{5}{2}\phi^{DE}\right). \tag{14}$$

This equation, referred to as Model 1 in the remainder of the paper, is expected to describe the relative viscosity of double emulsions only at low to moderate concentrations of core–shell droplets. At high values of ϕ^{DE}, Model 1 is expected to underpredict η_r because in the derivation of Eq. (12), it is assumed that the entire volume of the existing double emulsion before new core–shell droplets are added is available as free volume to the new core–shell droplets. In reality, the free volume to disperse the new droplets is significantly less, due to the volume preempted by the droplets already present. When new droplets are added to the double emulsion the increase in the actual volume fraction of the dispersed phase (core–shell droplets) is $d\phi^{DE}/(1 - \phi^{DE})$. Therefore,

$$\frac{d\eta}{\left(\frac{5}{2}\eta\right)} + \frac{\left(\frac{3}{5}\right)A\,d\eta}{\left(A\eta + \frac{5}{2}B\eta_2\right)} = \frac{d\phi^{DE}}{1 - \phi^{DE}}. \tag{15}$$

Upon integration with the limit $\eta \to \eta_c$ at $\phi^{DE} \to 0$, Eq. (15) gives:

$$\eta_r \left[\frac{A\eta_r + \left(\frac{5}{2}\right)B\lambda_{21}}{A + \left(\frac{5}{2}\right)B\lambda_{21}} \right]^{3/2} = \left(1 - \phi^{DE}\right)^{-5/2}. \tag{16}$$

This equation, referred to as Model 2 in the remainder of the paper, assumes that the volume fraction of dispersed phase (core–shell droplets) can reach unity as more and more core–shell droplets are added to the double emulsion. In reality, there exists an upper limit for ϕ^{DE}, referred to as ϕ_m^{DE} (maximum packing volume fraction of core–shell droplets in double emulsion), where the droplets just touch each other; any further increase in ϕ^{DE} causes significant deformation of core–shell droplets.

Mooney [26], in derivation of his well-known equation for the viscosity of concentrated suspension of spherical rigid particles, contended that the incremental increase in the volume

fraction of the dispersed phase when small differential quantity of new particles are added to an existing suspension of dispersed phase volume fraction ϕ^{DE}, is $d[\phi^{DE}/(1 - \phi^{DE}/\phi_m^{DE})]$ rather than $d\phi^{DE}/(1 - \phi^{DE})$ because of the packing difficulties of particles. Following Mooney, Eq. (15) should be revised as:

$$\frac{d\eta}{\left(\frac{5}{2}\eta\right)} + \frac{\left(\frac{3}{5}\right)A\,d\eta}{\left(A\eta + \frac{5}{2}B\eta_2\right)} = d\left(\frac{\phi^{DE}}{1 - \left(\frac{\phi^{DE}}{\phi_m^{DE}}\right)} \right). \tag{17}$$

Upon integration, Eq. (17) gives:

$$\eta_r \left[\frac{A\eta_r + \left(\frac{5}{2}\right)B\lambda_{21}}{A + \left(\frac{5}{2}\right)B\lambda_{21}} \right]^{3/2} = \exp\left[\frac{\frac{5}{2}\phi^{DE}}{1 - \frac{\phi^{DE}}{\phi_m^{DE}}} \right]. \tag{18}$$

This equation is referred to as Model 3 in the remainder of the paper.

Krieger and Dougherty [31], in the derivation of their well-known equation for the viscosity of concentrated suspension of spherical rigid particles, argued that the incremental increase in the volume fraction of the dispersed phase when a small quantity of new particles are added to an existing suspension of concentration ϕ^{DE}, is $d\phi^{DE}/(1 - \phi^{DE}/\phi_m^{DE})$ rather than $d[\phi^{DE}/(1 - \phi^{DE}/\phi_m^{DE})]$ as thought by Mooney [26]. Following Krieger and Dougherty, Eq. (15) should be revised as:

$$\frac{d\eta}{\left(\frac{5}{2}\eta\right)} + \frac{\left(\frac{3}{5}\right)A\,d\eta}{\left(A\eta + \frac{5}{2}B\eta_2\right)} = \frac{d\phi^{DE}}{\left(1 - \frac{\phi^{DE}}{\phi_m^{DE}}\right)}. \tag{19}$$

Upon integration, Eq. (19) gives:

$$\eta_r \left[\frac{A\eta_r + \left(\frac{5}{2}\right)B\lambda_{21}}{A + \left(\frac{5}{2}\right)B\lambda_{21}} \right]^{3/2} = \left(1 - \frac{\phi^{DE}}{\phi_m^{DE}}\right)^{-5\phi_m^{DE}/2}. \tag{20}$$

This equation is referred to as Model 4 in the remainder of the paper.

4. Predictions of new viscosity equations

According to the new viscosity equations derived in Section 3, the relative viscosity of a double emulsion (emulsion of core–shell droplets) can be expressed as:

$$\eta_r = f\left(a/b, \lambda_{21}, \lambda_{32}, \phi^{DE}, \phi_m^{DE}\right). \tag{21}$$

Fig. 2 shows relative viscosity versus viscosity ratio λ_{21} (viscosity of shell liquid divided by viscosity of external continuous phase) plots for different values of a/b. The plots are generated from Model 4 (Eq. (20)) under the conditions: $\phi^{DE} = 0.50$, $\phi_m^{DE} = 0.637$, $\lambda_{32} = 0.10$. At a given value of a/b, the relative viscosity versus λ_{21} plot exhibits three distinct regions: constant η_r region at low values of λ_{21}, increasing η_r region at intermediate values of λ_{21}, and finally constant η_r region again at high values of λ_{21}. The radii ratio a/b affects the relative viscosity of double emulsions only in the intermediate range of λ_{21}. At very low and very high values of λ_{21}, η_r of double emulsion is independent of the radii ratio a/b. In the intermediate range of λ_{21}, the relative viscosity of a double emulsion increases with the increase in a/b. An increase in the ratio a/b implies a decrease in the shell thickness of the core–shell droplets of a double

R. Pal / Journal of Colloid and Interface Science 307 (2007) 509–515

emulsion. Thus, the relative viscosity of a double emulsion of core–shell droplets increases with a decrease in the shell thickness.

Fig. 3 shows relative viscosity versus viscosity ratio λ_{21} plots for two different values of viscosity ratio λ_{32} (viscosity of core liquid divided by viscosity of shell liquid). The plots are generated from Model 4 (Eq. (20)) under the conditions:
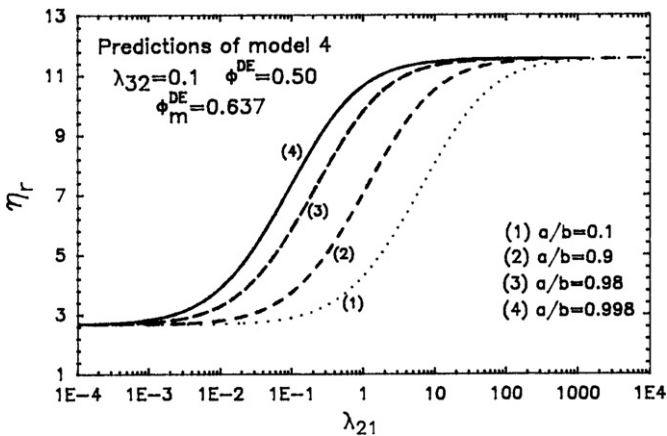

Fig. 2. Relative viscosity η_r versus viscosity ratio (λ_{21}) plots of double emulsions for different values of radii ratio a/b.
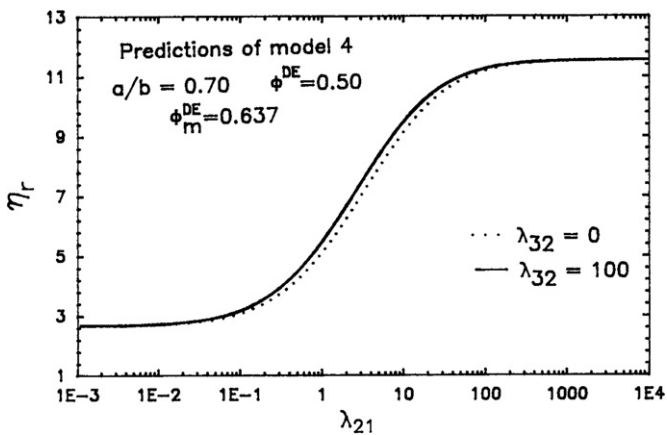

Fig. 3. Relative viscosity (η_r) versus viscosity ratio (λ_{21}) plots of double emulsions for two different values of the viscosity ratio λ_{32}.

$\phi^{DE} = 0.50$, $\phi_m^{DE} = 0.637$, $a/b = 0.70$. Clearly, the relative viscosity of a double emulsion is not strongly affected by the viscosity ratio λ_{32}. A slight increase in η_r occurs in the intermediate λ_{21} range when λ_{32} is increased from 0 to 100.

Fig. 4 shows the comparison between the prediction of different models under the conditions: $\phi^{DE} = 0.50$, $\phi_m^{DE} = 0.637$, $a/b = 0.90$, $\lambda_{32} = 0.10$. Model 1 (Eq. (14)) predictions are the lowest whereas Model 3 (Eq. (18)) predictions are the highest. The relative viscosities predicted by different models are in the following order: Model 3 > Model 4 > Model 2 > Model 1.

5. Experimental work

Two sets of oil-in-water-in-oil (O/W/O) double emulsions were prepared. A two-step procedure outlined in Section 1 was used to prepare the double emulsions. Table 1 gives the recipes for the preparation of these systems. Further information about the volume fractions of components and the range of radii ratio a/b (see Eq. (2b)) covered is given in Table 2.

The rheological measurements were carried out in the temperature range of 23–25 °C (23 °C for Set 1 and 25 °C for Set 2 double emulsions). The data were collected mostly with a Bohlin controlled-stress rheometer (Bohlin CS-50) using an appropriate sensor system. Some data were also collected using a Fann coaxial cylinder viscometer.
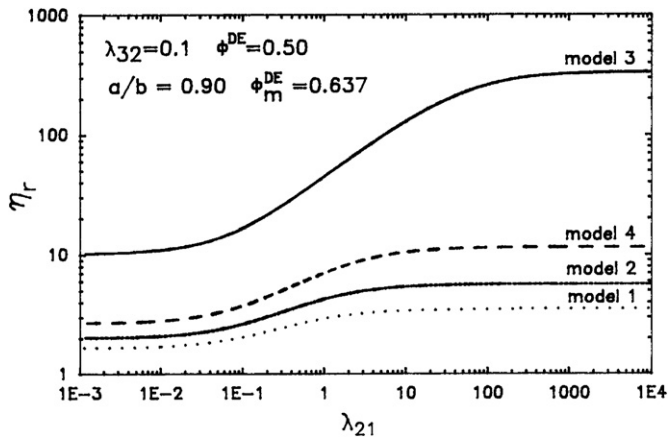

Fig. 4. Comparison between the predictions of different models.

Table 1
Recipes for the preparation of double emulsions

	O/W/O double emulsions (Set 1)	O/W/O double emulsions (Set 2)
Oil type	Shell CORENA-32 (highly refined mineral oil); viscosity 64 mPa s at 23 °C	Petroleum oil of viscosity 5.54 mPa s at 25 °C
Primary emulsion type	Oil-in-water (O/W)	Oil-in-water (O/W)
Volume fraction of oil in primary emulsion	0.28–0.64	0.742
Surfactant type and concentration used in the preparation of primary emulsion	Triton X-100, 2% by wt. based on aqueous phase	Triton X-100, 4% by wt. based on aqueous phase
External continuous phase of double emulsion	1% by wt. surfactant (Emsorb 2500) in oil	2.76% by wt. surfactant (Emsorb 2500) in oil
Volume fraction of primary emulsion in double emulsion	0.23–0.58	0.14–0.584

Table 2
Radii ratio a/b for the double emulsions investigated

Set No.	Volume fraction of oil in primary O/W emulsion	Volume fraction of primary emulsion in double emulsion	a/b
	0.28	0.23	0.654
	0.45	0.38	0.766
1	0.54	0.48	0.814
	0.60	0.54	0.843
	0.64	0.58	0.862
		0.14	
		0.22	
		0.356	
		0.427	
2	0.742	0.489	0.905
		0.509	
		0.551	
		0.563	
		0.584	

6. Comparison of experimental results with model predictions

Fig. 5 shows the relative viscosity versus shear stress plots of primary and double emulsions of Set 1. The primary O/W emulsions are Newtonian up to oil volume fraction (ϕ^{PE}) of 0.45. At higher values of oil concentration, the emulsions exhibit some shear-thinning. The O/W/O double emulsion exhibit non-Newtonian shear-thinning behavior over the whole range of ϕ^{DE} (volume fraction of primary emulsion in double emulsion).

The shear-thinning behavior observed for double O/W/O emulsions is due to deformation and orientation of droplets in shear flow. When an emulsion is subjected to shear flow, the equilibrium shape of the droplet and the orientation of the droplet with respect to the flow direction are governed by two dimensionless quantities: viscosity ratio (ratio of droplet-to-matrix viscosities) and capillary number. The capillary number is the ratio of hydrodynamic stress to interfacial stress. The hydrodynamic stress tends to stretch the droplet out into a filamentary shape, whereas the interfacial stress tends to contract the droplet into a sphere. As the shear rate is increased, the capillary number also increases and the droplet becomes more elongated. The angle between the major axis of the droplet and the flow direction also decreases with the increase in shear rate or capillary number. The elongation and orientation of droplets result in a decrease in emulsion viscosity.

Fig. 6 shows the relative viscosity versus shear stress plots of primary and double emulsions of Set 2. The same primary O/W emulsion was used in the preparation of all these double emulsions. The primary O/W emulsion having an oil volume fraction of 0.742 exhibits highly shear-thinning behavior. The O/W/O double emulsions are Newtonian (viscosity does not vary with shear stress) at a low to moderate values of the primary emulsion volume fraction. At high values of the primary emulsion volume fraction ($\phi^{DE} \geqslant 0.489$) the viscosity of the double emulsion decreases with the increase in shear stress, indicating shear-thinning increases with the increase in ϕ^{DE}.

Fig. 7 shows the comparison between the experimental data and the predictions of various models developed in the paper.
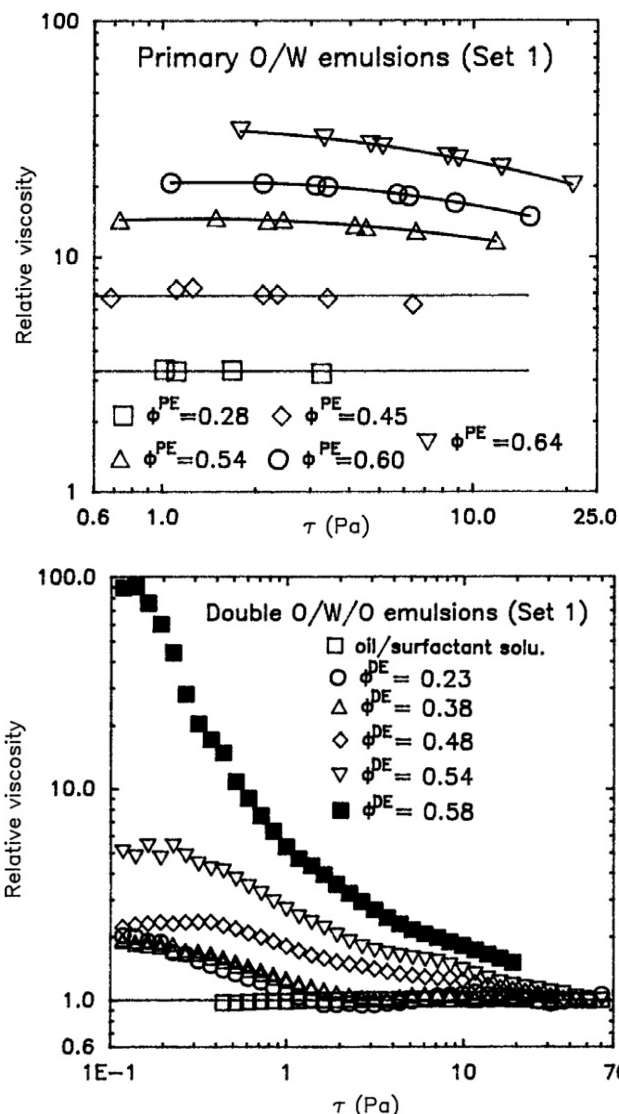

Fig. 5. Relative viscosity versus shear stress plots of primary O/W and double O/W/O emulsions of Set 1.

As the proposed models are valid for underformed spherical droplets, only the low shear data are considered for comparison. The data are plotted as: $\eta_r[(A\eta_r + 2.5B\lambda_{21})/(A + 2.5B\lambda_{21})]^{3/2}$ versus ϕ^{DE}. As can be seen, the experimental data of primary and double emulsion can be described reasonably well with Model 4 (Eq. (20)) using a single ϕ_m^{DE} value of 0.58. Model 3 (Eq. (18)) overpredicts the data when the same value of ϕ_m^{DE} (0.58) is used. Model 1 (Eq. (14)) and Model 2 (Eq. (16)) underpredict the data.

7. Concluding remarks

Four new equations are developed for the viscosity of concentrated double emulsions of core–shell droplets. Out of the four models developed in the paper, two models (Models 1 and 2) predict the relative viscosity of double emulsions to be a function of four variables: a/b, the ratio of core drop radius (a) to shell outer radius (b); λ_{21}, the ratio of shell liquid
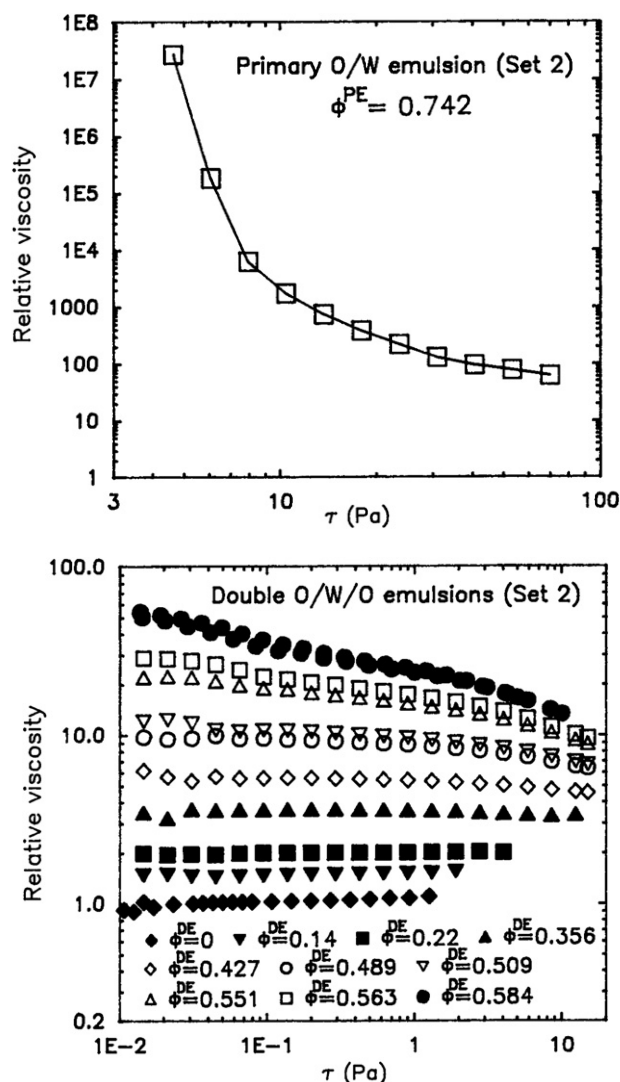
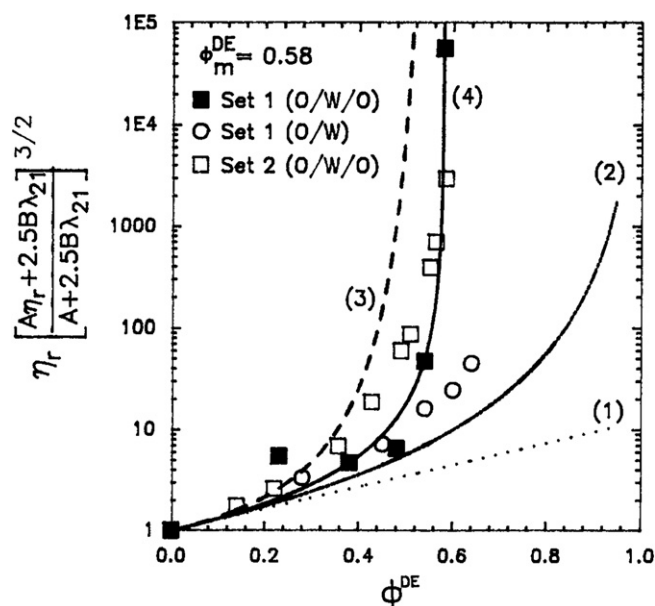Fig. 6. Relative viscosity versus shear stress plots of primary O/W and double O/W/O emulsions of Set 2.

Fig. 7. Comparison between experimental data and predictions of various models developed in this work. The numbers shown on the plots refer to model number. In the case of simple O/W emulsion (Set 1), ϕ^{DE} is the volume fraction of oil in simple O/W emulsion.

viscosity to external continuous phase viscosity; λ_{32}, the ratio of core liquid viscosity to shell liquid viscosity; and ϕ^{DE}, the volume fraction of core–shell droplets in the double emulsion. The remaining two models (Models 3 and 4) contain an additional parameter, that is, the maximum packing volume fraction (ϕ_m^{DE}) of un-deformed core–shell droplets.

With the increase in viscosity ratio λ_{21}, the relative viscosity (η_r) of a double emulsion increases significantly. The relative viscosity also increases significantly with the increase in the radii ratio a/b when λ_{21} is in the intermediate range of $10^{-2} < \lambda_{21} < 100$. The viscosity ratio λ_{32} has a marginal effect on the relative viscosity of double emulsions. Based on two sets of experimental data on the viscosity of concentrated double emulsions of O/W/O (oil-in-water-in-oil) type, Model 4 (Eq. (20)) appears to be superior to other models developed in the paper.

Acknowledgment

References

[1] N. Garti, A. Benichou, in: J. Sjoblom (Ed.), Encyclopedic Handbook of Emulsion Technology, Dekker, New York, 2001, pp. 377–407.
[2] E. Dickinson, J. Evison, J.W. Gramshaw, D. Schwope, Food Hydrocolloids 8 (1994) 63.
[3] E. Dickinson, J. Evison, R.K. Owusu, Food Hydrocolloids 5 (1991) 481.
[4] R.K. Owusu, Q. Zhu, E. Dickinson, Food Hydrocolloids 6 (1992) 443.
[5] N. Garti, A. Aserin, Adv. Colloid Interface Sci. 65 (1996) 37.
[6] J.W. Frankenfeld, G.C. Fuller, C.T. Rhodes, Drug Dev. Commun. 2 (1976) 405.
[7] S.S. Davis, Chem. Ind. October (1981) 683–687.
[8] R.P. Cahn, N.N. Li, J. Membr. Sci. 1 (1976) 129.
[9] H. Itoh, M.P. Thien, T.A. Hatton, D.I.C. Wang, J. Membr. Sci. 51 (1990) 309.
[10] W.S. Ho, T.A. Hatton, E.N. Lightfoot, N.N. Li, AIChE J. 28 (1982) 662.
[11] P. Colinart, S. Delepine, G. Trouve, H. Renon, J. Membr. Sci. 20 (1984) 167.
[12] P.J. Pickering, C.R. Southern, J. Chem. Technol. Biotechnol. 68 (1997) 417.
[13] G.I. Taylor, Proc. R. Soc. London A 138 (1932) 41.
[14] N.A. Frankel, A. Acrivos, J. Fluid Mech. 44 (1970) 65.
[15] R. Pal, AIChE J. 42 (1996) 3181.
[16] R. Pal, Food Hydrocolloids 20 (2006) 997.
[17] R. Pal, J. Rheol. 45 (2001) 509.
[18] R. Pal, Langmuir 12 (1996) 2220.
[19] B.R. Midmore, T.M. Herrington, Prog. Colloid Polym. Sci. 112 (1999) 115.
[20] B.M. van der Horst, H.C. Langelaan, A.D. Gotsis, Prog. Colloid Polym. Sci. 115 (2000) 315.
[21] R. Pal, Ind. Eng. Chem. Res. 37 (1998) 2052.
[22] L. Olivieri, M. Seiller, L. Bromberg, E. Ron, P. Couvreur, J.L. Grossiord, Pharm. Res. 18 (2001) 689.
[23] Y. Kita, S. Matsumoto, D. Yonezawa, J. Colloid Interface Sci. 62 (1977) 87.
[24] S. Matsumoto, M. Kohda, J. Colloid Interface Sci. 73 (1980) 13.
[25] S. Matsumoto, T. Inoue, M. Kohda, T. Ohta, J. Colloid Interface Sci. 77 (1980) 564.

[26] M. Mooney, J. Colloid Sci. 6 (1951) 162.
[27] H.A. Stone, L.G. Leal, J. Fluid Mech. 211 (1990) 123.
[28] A. Einstein, Ann. Phys. 19 (1906) 289.
[29] A. Einstein, Ann. Phys. 34 (1911) 591.
[30] D.A.G. Bruggeman, Ann. Phys. 24 (1935) 636.
[31] I.M. Krieger, T.J. Dougherty, Trans. Soc. Rheol. 3 (1959) 137.