

# Viscosity models for multiple emulsions

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## Abstract

The viscous behavior of multiple emulsions is investigated. Expressions are derived for the viscosity of dilute and concentrated multiple emulsions where the multiple emulsion droplet itself contains many internal droplets. Such systems are often referred to as Type-B and Type-C multiple emulsions in the literature (in Type-B systems, the multiple emulsion droplet contains several small internal droplets; in Type-C systems, the multiple emulsion droplet contains a large number of small internal droplets; in Type-A systems (not considered here), there is present only one internal droplet, that is, these systems consist of “core–shell” droplets). According to the proposed viscosity models, the relative viscosity of multiple emulsions of Types B and C depends on four variables: volume fraction of internal droplets within a multiple emulsion droplet ( $\phi^{PE}$ ), volume fraction of total dispersed phase in the whole multiple emulsion ( $\phi^{ME}$ ), ratio of primary-emulsion matrix viscosity to multiple-emulsion matrix viscosity ( $K_{21}$ ), and ratio of internal droplet viscosity to primary-emulsion matrix viscosity ( $K_{32}$ ). With the increase in any of these variables ( $\phi^{PE}$ ,  $\phi^{ME}$ ,  $K_{21}$ , or  $K_{32}$ ), the viscosity of the multiple emulsion generally increases. The predictions of the proposed models are compared with three sets of experimental data on the viscosity of multiple emulsions.

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## 1. Introduction

Multiple emulsions, also referred to as double emulsions, are “emulsions of emulsions”. The droplet of a multiple emulsion is itself composed of an emulsion of fine droplets. In other words, the multiple emulsion droplets themselves contain a number of internal droplets. Obviously, the size of a multiple emulsion droplet is significantly larger than the size of the internal droplets. Multiple emulsions are classified into three broad groups depending on the number of internal droplets present in the multiple emulsion droplets (Florence & Whitehill, 1981; Garti, 1997; Garti & Benichou, 2001): (1) Type-A multiple emulsion, where the multiple emulsion droplet consists of only one large internal droplet, that is, the multiple emulsion droplet is of “core–shell” type; (2) Type-B multiple emulsion, where the multiple emulsion droplet consists of several small internal droplets; and (3) Type-C multiple emulsion, where the multiple emulsion droplet consists of a large number of internal droplets.

Multiple emulsions (Types A, B or C) can be further classified as either oil-in-water-in-oil (O/W/O) multiple emulsion or water-in-oil-in-water (W/O/W) multiple emulsion. In the case of an O/W/O multiple emulsion, the internal droplets and the external continuous-phase (matrix) are composed of oil; the internal oil droplets are separated from the external oil phase by the aqueous phase. A W/O/W multiple emulsion consists of small aqueous droplets dispersed in oil and this water-in-oil (W/O) emulsion itself is dispersed as large droplets in the continuous aqueous phase.

As multiple emulsions are able to entrap important substances in the internal droplets, they are used in applications where controlled (slow and prolonged) release of important ingredients is desired. For example, many food products undergo an undesirable loss of quality due to rapid release of volatile flavour compounds during processing or storage

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(Dickinson, Evison, Gramshaw, & Schwöpe, 1994). One way to overcome this problem is to utilize a multiple emulsion with the flavour compound trapped in the internal droplets (Gaonkar, 1994). Other promising applications of multiple emulsions in the food industry include: (1) encapsulation and controlled release of nutrients; (2) manufacture of low calorie food products; and (3) manufacture of food products with improved sensoric characteristics (Dickinson, Evison, & Owusu, 1991; Owusu, Zhu, & Dickinson, 1992; van der Graff, Schroen, & Boom, 2005; Garti, 1997; Kim, Decker, & McClements, 2006).

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

The understanding of the viscous behavior of multiple emulsions is important in the formulation, handling, mixing, processing, storage, and pumping of such systems. Furthermore, viscometric studies can provide useful information on the stability of multiple emulsions (Kita, Matsumoto, & Yonezawa, 1977; Matsumoto & Kohda, 1980; Matsumoto, Inoue, Kohda, & Ohta, 1980; Jiao & Burgess, 2003). While there is a substantial amount of literature published on the rheology of simple emulsions (oil-in-water (O/W) and water-in-oil (W/O) emulsions), little attention has been given to multiple emulsions.

The main objective of this work is to develop and evaluate viscosity models for multiple emulsions.

## 2. Existing viscosity models for emulsions

### 2.1. Simple emulsions

For infinitely dilute simple emulsions where the interaction between the droplets is absent, Taylor (1932) derived the following viscosity equation:

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

where  $\eta_r$  is the relative viscosity of emulsion,  $\eta$  is emulsion viscosity,  $\eta_c$  is matrix (continuous phase) viscosity,  $\eta_d$  is dispersed-phase (droplets) viscosity, and  $\phi$  is volume fraction of dispersed phase.

Using the generalized self-consistent approach, Oldroyd (1953) extended the Taylor law (Eq. (1)) to non-dilute (moderately concentrated) emulsions. Oldroyd's equation is as follows:

$$\eta_r = \frac{\eta}{\eta_c} = \left[ \frac{10(K+1) + 3\phi(2+5K)}{10(K+1) - 2\phi(2+5K)} \right], \quad (2)$$

where  $K$  is the viscosity ratio (ratio of dispersed phase viscosity to matrix viscosity). In the limit  $\phi \rightarrow 0$ , Eq. (2) reduces to Eq. (1).

Yaron and Gal-Or (1972) and Choi and Schowalter (1975) also developed viscosity equations for concentrated emulsions. To take into account the hydrodynamic interactions between the neighboring droplets, they used a cell model approach. Their equations are given as follows:

#### Yaron and Gal-Or (1972)

$$\eta_r = \frac{\eta}{\eta_c} = 1 + I_1(\lambda, K)\phi, \quad (3)$$

where

$$I_1(\lambda, K) = \frac{5.5[4\lambda^7 + 10 - (84/11)\lambda^2 + (4/K)(1 - \lambda^7)]}{10(1 - \lambda^{10}) - 25\lambda^3(1 - \lambda^4) + (10/K)(1 - \lambda^3)(1 - \lambda^7)}. \quad (4)$$

#### Choi and Schowalter (1975)

$$\eta_r = \frac{\eta}{\eta_c} = 1 + I_2(\lambda, K)\phi, \quad (5)$$

where

$$I_2(\lambda, K) = \frac{2[(5K+2) - 5(K-1)\lambda^7]}{[4(K+1) - 5(5K+2)\lambda^3 + 42K\lambda^5 - 5(5K-2)\lambda^7 + 4(K-1)\lambda^{10}]}. \quad (6)$$

In Eqs. (4) and (5),  $\lambda$  is defined as  $(\phi)^{1/3}$ .

For concentrated emulsions (simple O/W or W/O types), the cell model of Yaron and Gal-Or (1972) describes the viscosity data reasonably well (Pal, 2000, 2001a).

Using the differential effective medium approach, Pal (2001b) developed the following viscosity equations for concentrated emulsions:

$$\eta_r \left[ \frac{2\eta_r + 5K}{2 + 5K} \right]^{3/2} = \exp \left[ \frac{2.5\phi}{1 - \phi/\phi_m} \right], \quad (7)$$

$$\eta_r \left[ \frac{2\eta_r + 5K}{2 + 5K} \right]^{3/2} = \left[ 1 - \frac{\phi}{\phi_m} \right]^{-5\phi_m/2}. \quad (8)$$

Both equations describe the experimental viscosity data of simple emulsions very well. As the equations are non-linear, they are solved numerically for the relative viscosity.

## 2.2. Multiple emulsions

Matsumoto and co-workers (Kita et al., 1977; Matsumoto & Kohda, 1980; Matsumoto et al., 1980) were probably the first to study the viscous behavior of multiple emulsions. They used the Mooney equation (Mooney, 1951) to describe the viscous behavior of multiple emulsions:

$$\ell m \eta_r^{\text{ME}} = \frac{g\phi^{\text{ME}}}{1 - h\phi^{\text{ME}}}, \quad (9)$$

where “ $g$ ” and “ $h$ ” are empirical constants, and  $\phi^{\text{ME}}$  is the volume fraction of the total dispersed phase in the whole multiple emulsion. For the multiple emulsions studied by Matsumoto and co-workers, the constant “ $g$ ” was found to vary from 2.3 to 3.2 and the constant “ $h$ ” varied from 0.5 to 1.9.

The application of Mooney equation to describe the viscous behavior of multiple emulsions is questionable. The Mooney equation is appropriate only for simple emulsions under the condition that the viscosity of droplets is large as compared with the matrix viscosity. For simple emulsions, the correct form of the viscosity equation is Eq. (7), which reduces to the Mooney equation (Eq. (9)) in the limit  $K \rightarrow \infty$ .

Since the pioneering work of Matsumoto and co-workers, little progress has been made on modeling the viscous behavior of multiple emulsions. Pal (2006) has recently developed models for the relative viscosity of Type-A (core-shell droplet) multiple emulsions. One of the models proposed by Pal for Type-A multiple emulsions is as follows:

$$\eta_r^{\text{ME}} \left[ \frac{A\eta_r^{\text{ME}} + \left(\frac{5}{2}\right)BK_{21}}{A + \left(\frac{5}{2}\right)BK_{21}} \right]^{3/2} = \left( 1 - \frac{\phi^{\text{ME}}}{\phi_m^{\text{ME}}} \right)^{-5\phi_m^{\text{ME}}/2}, \quad (10)$$

where

$$A = \delta_1 + \frac{(a/b)^3\delta_2}{1 + K_{32}}, \quad (11)$$

$$B = \delta_3 + \frac{(a/b)^3\delta_4}{1 + K_{32}}. \quad (12)$$

The  $\delta_i$  depends on the ratio  $a/b$  only and are given as

$$\delta_1 = 4 - 25(a/b)^3 + 42(a/b)^5 - 25(a/b)^7 + 4(a/b)^{10}, \quad (13a)$$

$$\delta_2 = 15 - 42(a/b)^2 + 35(a/b)^4 - 8(a/b)^7, \quad (13b)$$

$$\delta_3 = 4 - 10(a/b)^3 + 10(a/b)^7 - 4(a/b)^{10}, \quad (13c)$$

$$\delta_4 = 6 - 14(a/b)^4 + 8(a/b)^7. \quad (13d)$$

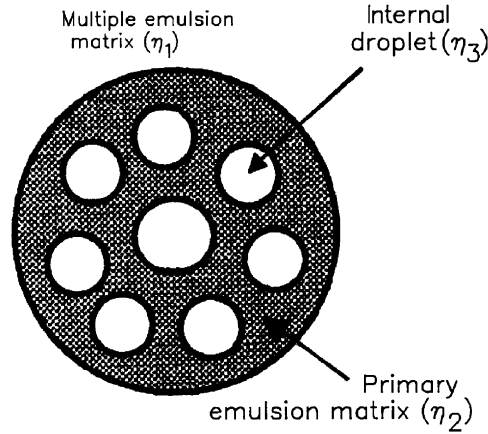


Fig. 1. Schematic diagram of a multiple emulsion droplet (Type-B or C). The viscosities of the multiple-emulsion matrix, primary-emulsion matrix, and internal droplet are  $\eta_1$ ,  $\eta_2$ , and  $\eta_3$ , respectively.

$K_{21}$  is the ratio of shell liquid viscosity ( $\eta_2$ ) to external continuous phase viscosity ( $\eta_1$ );  $K_{32}$  is the ratio of inner core liquid viscosity ( $\eta_3$ ) to shell liquid viscosity ( $\eta_2$ ); “ $a$ ” is the core radius and “ $b$ ” is the outer radius of the liquid shell;  $\phi_m^{ME}$  is the maximum packing volume fraction of core-shell droplets in a multiple emulsion.

Thus the relative viscosity of a Type-A (core-shell droplet) multiple emulsion is a function of five variables:

$$\eta_r^{ME} = f(a/b, K_{21}, K_{32}, \phi_m^{ME}, \phi_m^{ME}). \quad (14)$$

To our knowledge, there are no models available in the literature for the viscosity of multiple emulsions of Types B and C where the multiple emulsion droplet contains several or many internal droplets (see Fig. 1).

### 3. New viscosity models for multiple emulsions

The viscosity of multiple emulsions of Types B and C (where the multiple emulsion droplet contains several or many internal droplets) can be modeled using a two-step approach: In the first step, the viscosity equation for a simple emulsion is used to determine the viscosity of a single droplet of a multiple emulsion. Note that the droplet of a multiple emulsion is itself a simple emulsion. In the second step, the droplets of a multiple emulsion are treated as “homogeneous” droplets of viscosity obtained from the first step. The viscosity equation of a simple emulsion is then applied once again to determine the viscosity of a multiple emulsion.

#### 3.1. Dilute multiple emulsion

Consider the case where the multiple emulsion is dilute (i.e., multiple emulsion droplets are far apart) and the primary emulsion is also dilute (i.e., internal droplets entrapped within a multiple emulsion droplet are far apart). The intrinsic viscosity of such a multiple emulsion, obtained from the two-step approach, is as follows (see Appendix A for derivation):

$$[\eta]^{ME} = \lim_{\phi^{ME} \rightarrow 0} [(\eta_r^{ME} - 1)/\phi^{ME}] = \left[ \frac{(1 + 2.5K_{21})(1 + K_{32}) + 2.5K_{21}(1 + 2.5K_{32})\phi^{PE}}{(1 + K_{21})(1 + K_{32}) + K_{21}(1 + 2.5K_{32})\phi^{PE}} \right], \quad (15)$$

where  $\phi^{PE}$  is the volume fraction of dispersed phase in the primary emulsion. In other words,  $\phi^{PE}$  is the volume fraction of internal droplets within a multiple emulsion droplet.  $K_{21}$  is the ratio of primary-emulsion matrix viscosity ( $\eta_2$ ) to multiple-emulsion matrix viscosity ( $\eta_1$ );  $K_{32}$  is the ratio of internal droplet viscosity ( $\eta_3$ ) to primary-emulsion matrix viscosity (see Fig. 1).

If the restriction of diluteness for the primary emulsion is relaxed, that is, the volume fraction of internal droplets within a multiple emulsion droplet can be large, the expressions for the intrinsic viscosity of a multiple emulsion, obtained from the two-step approach, are as follows:

$$[\eta]^{ME} = \left[ \frac{10(K_{32} + 1)(2 + 5K_{21}) + (2 + 5K_{32})(15K_{21} - 4)\phi^{PE}}{20(K_{32} + 1)(1 + K_{21}) + 2(2 + 5K_{32})(3K_{21} - 2)\phi^{PE}} \right], \quad (16)$$

$$[\eta]^{ME} = \left[ \frac{2 + 5K_{21} + 5I_1 K_{21} \phi^{PE}}{2(1 + K_{21} + I_1 K_{21} \phi^{PE})} \right], \quad (17)$$

$$[\eta]^{\text{ME}} = \left[ \frac{2 + 5K_{21} + 5I_2K_{21}\phi^{\text{PE}}}{2(1 + K_{21} + I_2K_{21}\phi^{\text{PE}})} \right], \quad (18)$$

where

$$I_1 = \frac{5.5[4\lambda^7 + 10 - (84/11)\lambda^2 + (4/K_{32})(1 - \lambda^7)]}{[10(1 - \lambda^{10}) - 25\lambda^3(1 - \lambda^4) + (10/K_{32})(1 - \lambda^3)(1 - \lambda^7)]}, \quad (19)$$

$$I_2 = \frac{2[(5K_{32} + 2) - 5(K_{32} - 1)\lambda^7]}{[4(K_{32} + 1) - 5(5K_{32} + 2)\lambda^3 + 42K_{32}\lambda^5 - 5(5K_{32} - 2)\lambda^7 + 4(K_{32} - 1)\lambda^{10}]} \quad (20)$$

and  $\lambda = (\phi^{\text{PE}})^{1/3}$ .

Eq. (16) is obtained using Oldroyd equation (Eq. (2)) for the primary emulsion and Taylor equation (Eq. (1)) for the multiple emulsion. Eq. (17) is obtained using Yaron and Gal-Or equation (Eq. (3)) for the primary emulsion and Taylor equation (Eq. (1)) for the multiple emulsion. Eq. (18) is obtained using Choi–Schowalter equation (Eq. (5)) for the primary emulsion and Taylor equation (Eq. (1)) for the multiple emulsion. As an example to illustrate the derivation procedure, the full derivation of Eq. (17) is given in Appendix B.

### 3.2. Concentrated multiple emulsion

Now we consider the case where the primary and multiple emulsions are both non-dilute. Using the two-step approach, the following expressions are obtained for the relative viscosity of non-dilute multiple emulsions:

$$\eta_r^{\text{ME}} = \frac{10(K_{32} + 1)[10(K_{21} + 1) + 3\phi^{\text{ME}}(2 + 5K_{21})] + (2 + 5K_{32})\phi^{\text{PE}}[10(3K_{21} - 2) + 3\phi^{\text{ME}}(15K_{21} - 4)]}{20(K_{32} + 1)[5(K_{21} + 1) - \phi^{\text{ME}}(2 + 5K_{21})] + 2(2 + 5K_{32})\phi^{\text{PE}}[5(3K_{21} - 2) + \phi^{\text{ME}}(4 - 15K_{21})]}, \quad (21)$$

$$\eta_r^{\text{ME}} = 1 + Z_1\phi^{\text{ME}}, \quad (22)$$

$$\eta_r^{\text{ME}} = 1 + Z_2\phi^{\text{ME}}, \quad (23)$$

where

$$Z_1 = \frac{5.5[4\alpha^7 + 10 - (84/11)\alpha^2 + \{4(1 - \alpha^7)/(K_{21} + I_1K_{21}\phi^{\text{PE}})\}]}{[10(1 - \alpha^{10}) - 25\alpha^3(1 - \alpha^4) + \{10(1 - \alpha^3)(1 - \alpha^7)/(K_{21} + K_{21}I_1\phi^{\text{PE}})\}]}, \quad (24)$$

$$Z_2 = \frac{2[(5K_{21} + 2 + 5K_{21}I_2\phi^{\text{PE}}) - 5\alpha^7(K_{21} - 1 + I_2K_{21}\phi^{\text{PE}})]}{[4(K_{21} + 1 + K_{21}I_2\phi^{\text{PE}}) - 5(5K_{21} + 2 + 5K_{21}I_2\phi^{\text{PE}})\alpha^3 + 42K_{21}(1 + I_2\phi^{\text{PE}})\alpha^5 - 5(5K_{21} - 2 + 5I_2K_{21}\phi^{\text{PE}})\alpha^7 + 4(K_{21} - 1 + I_2K_{21}\phi^{\text{PE}})\alpha^{10}]}. \quad (25)$$

$I_1$  is given by Eq. (19) and  $I_2$  is given by Eq. (20), and  $\alpha$  is defined as  $(\phi^{\text{ME}})^{1/3}$ . Eq. (21) is obtained using the Oldroyd equation (Eq. (2)) twice. Eq. (22) is obtained using the Yaron and Gal-Or equation (Eq. (3)) twice. Eq. (23) is obtained using the Choi–Schowalter equation (Eq. (5)) twice. As an example to illustrate the derivation procedure, the full derivation of Eq. (22) is given in Appendix C.

## 4. Predictions of viscosity models for multiple emulsions

Fig. 2 shows the intrinsic viscosity of multiple emulsion  $[\eta]^{\text{ME}}$  as a function of viscosity ratio  $K_{21}$  for different values of  $\phi^{\text{PE}}$ . The viscosity ratio  $K_{32}$  is fixed at 100. The plots are generated from Eq. (17). At a fixed value of  $\phi^{\text{PE}}$  (the volume fraction of internal droplets in a multiple emulsion droplet), the intrinsic viscosity of a multiple emulsion initially remains nearly constant with the increase in the viscosity ratio  $K_{21}$ . In the range  $10^{-3} < K_{21} < 10$ , the intrinsic viscosity  $[\eta]^{\text{ME}}$  increases with the increase in  $K_{21}$ . At higher values of  $K_{21}$  ( $K_{21} > 100$ ), the intrinsic viscosity again becomes constant, independent of  $K_{21}$ . Also,  $[\eta]^{\text{ME}}$  at a given value of viscosity ratio  $K_{21}$  increases with the increase in  $\phi^{\text{PE}}$ .

The observed increases in  $[\eta]^{\text{ME}}$  with viscosity ratio  $K_{21}$  (at a fixed  $\phi^{\text{PE}}$ ) and with  $\phi^{\text{PE}}$  (at a fixed  $K_{21}$ ) can be explained in terms of fluid circulation within the multiple emulsion droplets. For homogeneous droplets, the transmission of stresses from the continuous-phase to dispersed-phase (droplet) causes fluid circulation within the droplets, and this reduces the distortion of flow pattern around the droplets in comparison with the distortion of flow pattern around the rigid particles. Reduced disturbance of fluid flow around the droplets leads to less dissipation of mechanical energy into friction. As a consequence, the viscosity of emulsion is lower than that of suspension of rigid particles. The reduction of fluid flow disturbance around the droplets depends on the viscosity ratio (ratio of droplet viscosity to continuous-phase viscosity);

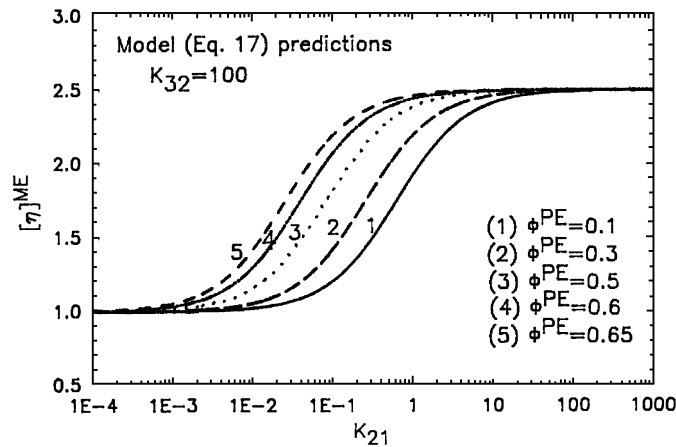


Fig. 2. Intrinsic viscosity of a multiple emulsion,  $[\eta]^{\text{ME}}$ , as a function of viscosity ratio  $K_{21}$  for different values of  $\phi^{\text{PE}}$ . The plots are generated from Eq. (17).

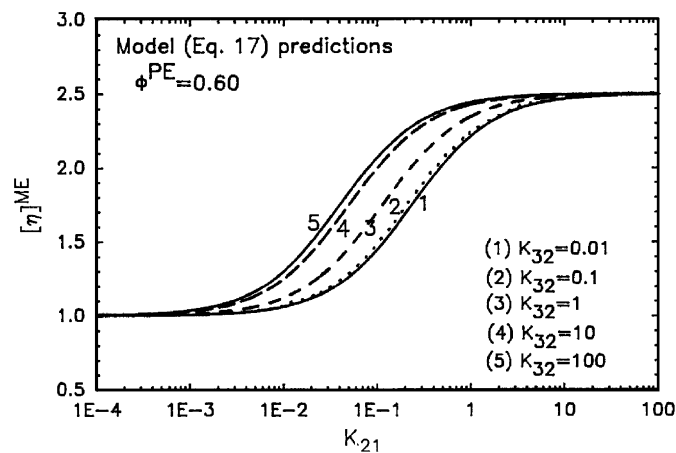


Fig. 3. Intrinsic viscosity of a multiple emulsion,  $[\eta]^{\text{ME}}$ , as a function viscosity ratio  $K_{21}$  for different values of viscosity ratio  $K_{32}$ . The plots are generated from Eq. (17).

with the increase in viscosity ratio, the distortion of flow pattern around the droplet increases. Assuming that multiple emulsion droplets can be treated as “homogeneous” droplets of effective viscosity  $\eta^{\text{PE}}$ , an increase in the viscosity ratio  $\eta^{\text{PE}}/\eta_1$  (ratio of multiple emulsion droplet viscosity to continuous phase viscosity) is expected to increase the distortion of flow pattern around the droplets, resulting in an increase in  $[\eta]^{\text{ME}}$ . Thus, the increases in  $[\eta]^{\text{ME}}$  with viscosity ratio  $K_{21}$  and with  $\phi^{\text{PE}}$  is due to increased distortion of flow pattern around the multiple emulsion droplets (note that  $\eta^{\text{PE}}$  increases with the increases in  $K_{21}$  and  $\phi^{\text{PE}}$ ).

Fig. 3 shows the plots of  $[\eta]^{\text{ME}}$  versus  $K_{21}$  for different values of viscosity ratio  $K_{32}$  at a fixed  $\phi^{\text{PE}}$  of 0.60. The plots are generated from Eq. (17). In the intermediate range of  $K_{21}$  ( $10^{-3} < K_{21} < 10$ ), the intrinsic viscosity of a multiple emulsion  $[\eta]^{\text{ME}}$  increases with the increase in  $K_{32}$  at any given value of  $K_{21}$ .

Fig. 4 shows comparison between the predictions of Eqs. (21)–(23) at different values of  $\phi^{\text{ME}}$  (volume fraction of the total dispersed phase). The values of  $\phi^{\text{PE}}$  and  $K_{32}$  are fixed at 0.5 and 1.0, respectively. Eq. (23) generally predicts the highest values of relative viscosity of a multiple emulsion, and Eq. (21) predicts the lowest values. The predictions of Eq. (22) generally fall in between the predictions of Eqs. (21) and (23). However, at a low  $\phi^{\text{ME}}$  value of 0.20, the predictions of Eqs. (22) and (23) almost overlap at  $K_{21}$  values larger than 0.1; at values of  $K_{21}$  lower than 0.1, Eq. (23) predicts lower values of relative viscosity of a multiple emulsion as compared with the Eq. (22).

## 5. Comparison with experimental data

Three sets of experimental viscosity data on multiple emulsions were considered to evaluate the models. Set 1 consisted of O/W/O type multiple emulsions. These emulsions were prepared using a petroleum oil (viscosity 5.54 mPa s at 25 °C). The surfactant used for the preparation of primary O/W emulsion was Triton X-100 (octylphenol ethoxylate). The



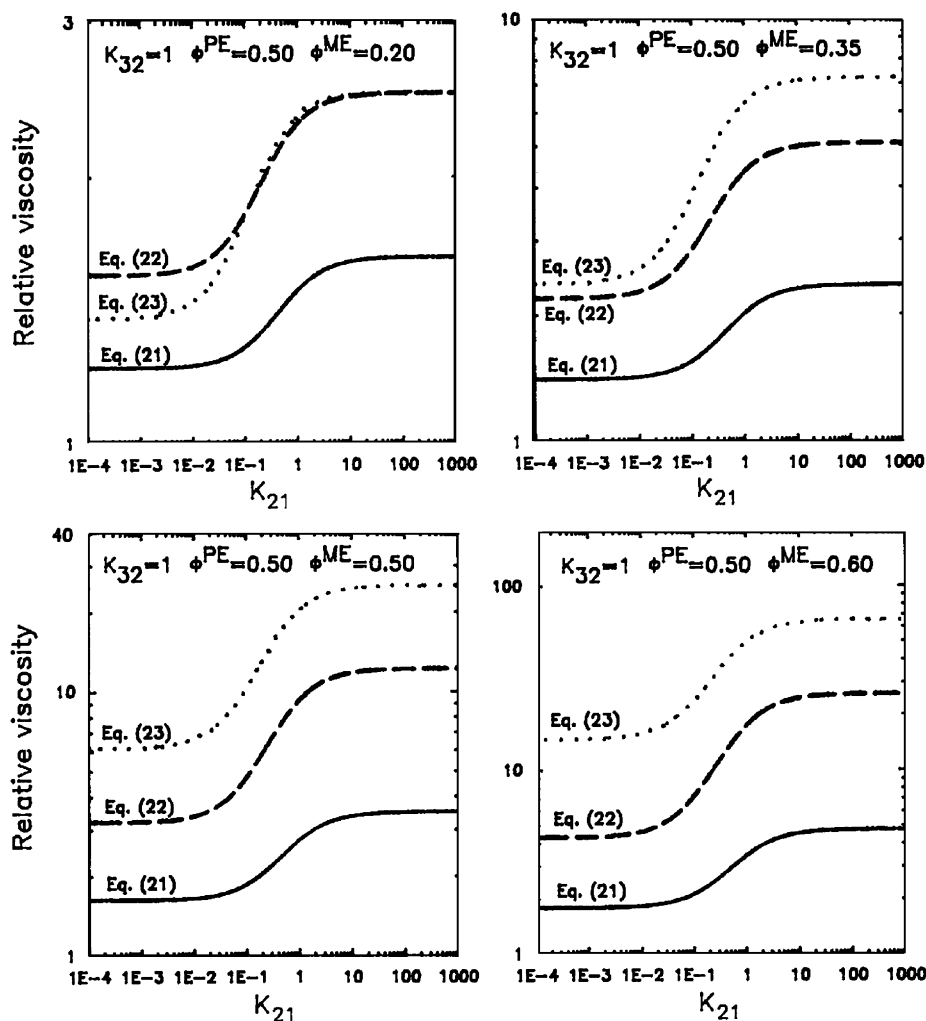


Fig. 4. Comparison between the predictions of the proposed models.

surfactant used in the external oil phase of O/W/O multiple emulsion was Emsorb 2500 (sorbitan monooleate). The multiple emulsions were prepared using a two-step procedure outlined in Section 1. In the first step, the primary O/W emulsion was prepared by shearing together the known amounts of aqueous (4% by weight Triton X-100 in de-ionized water) and non-aqueous (petroleum oil) phases in a variable speed homogenizer. The mixture was sheared at a high speed so as to produce fine oil droplets. The volume fraction of oil in the primary emulsion ( $\phi^{PE}$ ) was 0.742. In the second step, the primary emulsion was re-emulsified in the external oil phase (2.76% by weight, Emsorb 2500 in petroleum oil). The second emulsification step was carried out at a slow homogenizer speed so as to avoid the release of internal phase droplets of the primary emulsion to the external phase. The viscosity of multiple emulsions was measured at 25 °C in a Bohlin controlled-stress rheometer (Bohlin CS-50) using a cylindrical double-gap geometry. The photomicrographs of primary and multiple emulsions were taken with a Zeiss optical microscope equipped with a camera. The emulsion samples were diluted with the same external phase before taking the photomicrographs. The diameter of oil droplets of the primary O/W emulsion was less than 6  $\mu\text{m}$ . The multiple emulsion droplets were as large as 110  $\mu\text{m}$  in diameter. A large number of small oil droplets were entrapped within the multiple emulsion droplets indicating that the multiple emulsion droplets were of “Type-C”. Set 2 multiple emulsions were of O/W/O type and Set 3 multiple emulsions were of W/O/W type. The multiple emulsion droplets in both cases were of “Type-C”. The detailed information about preparation, materials, and characterization of Sets 2 and 3 multiple emulsions can be found in the original references (Pal, 1996 for Set 2 multiple emulsions and De Cindio, Grasso, and Cacace, 1991 for Set 3 multiple emulsions).

Table 1 summarizes some of the relevant information about the three experimental systems. The systems cover a broad range of viscosity ratios  $K_{21}$  and  $K_{32}$ .

As the proposed models are valid for undeformed spherical droplets, only the low shear data were considered for comparison.

Table 1

Experimental multiple emulsion systems considered in the present work

Set no.	Multiple emulsion type	Viscosity ratio, $K_{21}$	Viscosity ratio, $K_{32}$	$\phi^{PE}$	$\phi^{ME}$	Reference
1	O/W/O (type C)	0.20	4.864	0.742	0–0.584	New data
2	O/W/O (type C)	$1.56 \times 10^{-2}$	64	0.28–0.60	0–0.54	Pal (1996)
3	W/O/W (type C)	62	$6 \times 10^{-2}$	0.15	0–0.50	De Cindio, Grasso, and Cacace (1991)

Note: The viscosity of oil (liquid paraffin, density 0.88 g/mL) was not specified in the paper by De Cindio et al. (1991). The typical value of the viscosity of heavy liquid paraffin (180 mPa s) is used here.

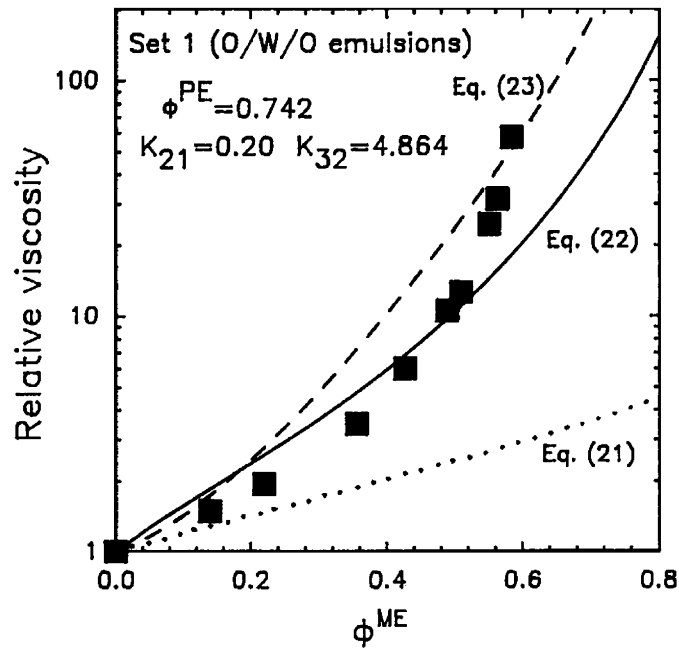


Fig. 5. Comparison between experimental data of Set 1 multiple emulsions (O/W/O type) and predictions of various models.

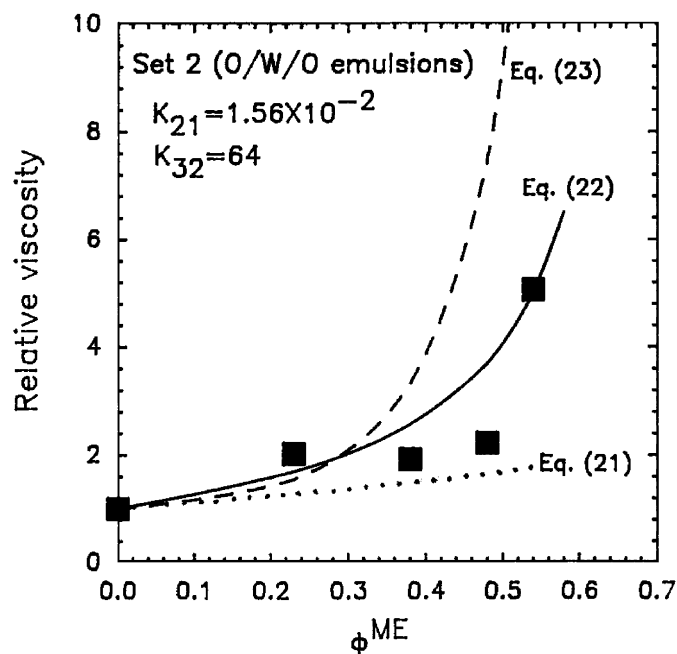


Fig. 6. Comparison between experimental data of Set 2 multiple emulsions (O/W/O type) and predictions of various models.



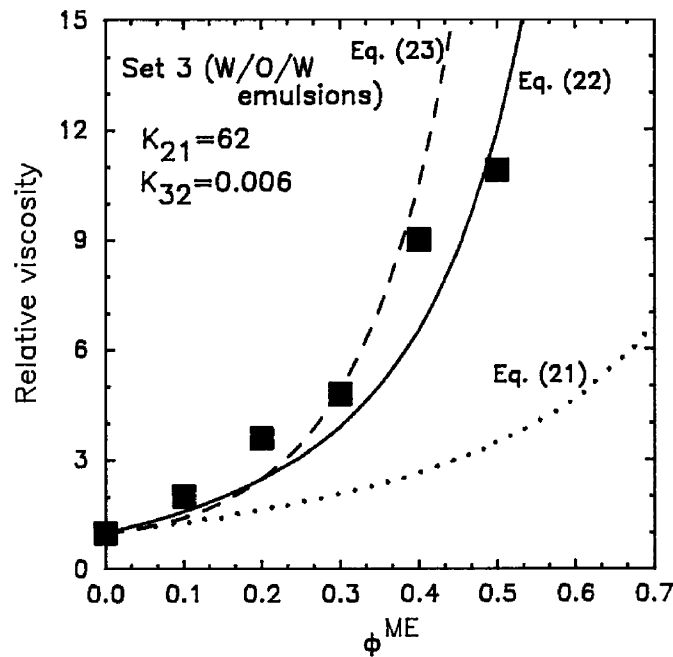


Fig. 7. Comparison between experimental data of Set 3 multiple emulsions (W/O/W type) and predictions of various models.

Figs. 5–7 show comparisons between experimental data and model predictions (Eqs. (21)–(23)). Eq. (21) generally under predicts the viscosity of all three multiple emulsion systems. Eq. (22) describes the experimental viscosity data of all three systems reasonably well. Eq. (23) generally over predicts the viscosity for O/W/O multiple emulsions of Sets 1 and 2. However, the predictions of Eq. (23) are reasonable in the case of W/O/W multiple emulsions of Set 3, especially when  $\phi^{ME} < 0.4$ ; at higher values of  $\phi^{ME}$ , Eq. (23) over predicts the viscosity. Finally, it should be noted that there were no adjustable parameters present in the models.

## 6. Concluding remarks

Viscosity equations are developed for dilute and concentrated multiple emulsions of Types B and C; the droplets of these multiple emulsions themselves consist of several or many internal droplets. The relative viscosity of multiple emulsions depends on four variables:  $\phi^{PE}$  (volume fraction of internal droplets within a multiple emulsion droplet),  $\phi^{ME}$  (volume fraction of total dispersed phase in the whole multiple emulsion),  $K_{21}$  (ratio of primary-emulsion matrix viscosity to multiple-emulsion matrix viscosity), and  $K_{32}$  (ratio of internal droplet viscosity to primary-emulsion matrix viscosity). The viscosity of a multiple emulsion generally increases with the increases in  $\phi^{PE}$ ,  $\phi^{ME}$ ,  $K_{21}$ , or  $K_{32}$ . The proposed models are evaluated using three sets of experimental viscosity data on O/W/O and W/O/W types of multiple emulsions.

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## Appendix A. Derivation of Eq. (15)

Eq. (15) is derived using the two-step approach described at the start of Section 3. In the first step, the Taylor equation (Eq. (1)) is used to determine the viscosity of a dilute primary emulsion. As the droplets of a multiple emulsion are composed of a primary emulsion, the viscosity obtained in this first step is also the viscosity of a single droplet of a multiple emulsion. Thus

$$\frac{\eta^{PE}}{\eta_2} = 1 + \left[ \frac{1 + 2.5K_{32}}{1 + K_{32}} \right] \phi^{PE}, \quad (A1)$$

where  $\eta^{PE}$  is the primary emulsion viscosity (same as the viscosity of a single multiple-emulsion droplet),  $\eta_2$  is the primary-emulsion matrix viscosity,  $K_{32}$  is the ratio of internal droplet viscosity ( $\eta_3$ ) to primary-emulsion matrix viscosity, and  $\phi^{PE}$  is

the volume fraction of dispersed phase in the primary emulsion (same as the volume fraction of internal droplets within a multiple emulsion droplet).

In the second step, the droplets of a multiple emulsion are treated as “homogeneous” droplets of viscosity  $\eta^{\text{PE}}$  obtained from Eq. (A1). The Taylor equation (Eq. (1)) is used once again to determine the viscosity of a dilute multiple emulsion. Thus

$$\frac{\eta^{\text{ME}}}{\eta_1} = 1 + \left[ \frac{1 + 2.5(\eta^{\text{PE}}/\eta_1)}{1 + (\eta^{\text{PE}}/\eta_1)} \right] \phi^{\text{ME}}, \quad (\text{A2})$$

where  $\eta^{\text{ME}}$  is the multiple emulsion viscosity,  $\eta_1$  is the multiple-emulsion matrix viscosity, and  $\phi^{\text{ME}}$  is the volume fraction of the multiple emulsion droplets in the whole multiple emulsion.

Substitution of  $\eta^{\text{PE}}$  from Eq. (A1) into Eq. (A2) gives

$$\eta_r^{\text{ME}} = \frac{\eta^{\text{ME}}}{\eta_1} = 1 + \phi^{\text{ME}} \left[ \frac{(1 + 2.5K_{21})(1 + K_{32}) + 2.5K_{21}(1 + 2.5K_{32})\phi^{\text{PE}}}{(1 + K_{21})(1 + K_{32}) + K_{21}(1 + 2.5K_{32})\phi^{\text{PE}}} \right], \quad (\text{A3})$$

Eq. (15) follows from Eq. (A3) upon using the definition of the intrinsic viscosity.

## Appendix B. Derivation of Eq. (17)

Eq. (17) is valid for dilute multiple emulsions without the restriction of diluteness on the primary emulsion. It is derived using the Yaron and Gal-Or equation (Eq. (3)) for the viscosity of primary emulsion and the Taylor equation (Eq. (1)) for the viscosity of dilute multiple emulsion. Thus, the viscosity of a primary emulsion (which is the same as the viscosity of a single droplet of a multiple emulsion) is given as

$$\frac{\eta^{\text{PE}}}{\eta_2} = 1 + I_1(\lambda, K_{32})\phi^{\text{PE}}, \quad (\text{B1})$$

where  $I_1(\lambda, K_{32})$  is a function of  $\lambda$ , defined as  $(\phi^{\text{PE}})^{1/3}$ , and viscosity ratio  $K_{32}$ . The function  $I_1$  is given by Eq. (19).

The viscosity of a dilute multiple emulsion is obtained from the Taylor equation (Eq. (1)) by treating multiple emulsion droplets as homogeneous droplets of viscosity  $\eta^{\text{PE}}$ , given by Eq. (B1). Thus

$$\eta_r^{\text{ME}} = \frac{\eta^{\text{ME}}}{\eta_1} = 1 + \phi^{\text{ME}} \left[ \frac{2 + 5K_{21} + 5I_1K_{21}\phi^{\text{PE}}}{2(1 + K_{21} + I_1K_{21}\phi^{\text{PE}})} \right]. \quad (\text{B2})$$

Eq. (17) follows from Eq. (B2) upon using the definition of intrinsic viscosity.

## Appendix C. Derivation of Eq. (22)

Eq. (22) is valid for multiple emulsions without the restrictions of diluteness on primary and multiple emulsions. It is derived using the Yaron and Gal-Or equation (Eq. (3)) twice. Thus, the viscosity of a primary emulsion (which is the same as the viscosity of a single droplet of a multiple emulsion) is given as

$$\frac{\eta^{\text{PE}}}{\eta_2} = 1 + I_1(\lambda, K_{32})\phi^{\text{PE}}, \quad (\text{C1})$$

where  $I_1$  is given by Eq. (19) and  $\lambda = (\phi^{\text{PE}})^{1/3}$ .

Upon using the Yaron and Gal-Or equation (Eq. (3)) once again, the viscosity of a multiple emulsion can be expressed as

$$\frac{\eta^{\text{ME}}}{\eta_1} = 1 + Z_1\phi^{\text{ME}}, \quad (\text{C2})$$

where  $Z_1$  is given by Eq. (24). The expression for  $Z_1$  (Eq. (24)) is obtained from the expression for  $I_1$  (Eq. (19)) by replacing  $\lambda$  with  $\alpha$ , where  $\alpha = (\phi^{\text{ME}})^{1/3}$ , and  $K_{32}$  with the viscosity ratio  $\eta^{\text{PE}}/\eta_1$ . Note that the viscosity ratio  $\eta^{\text{PE}}/\eta_1$  is given as

$$\frac{\eta^{\text{PE}}}{\eta_1} = \left( \frac{\eta^{\text{PE}}}{\eta_2} \right) \left( \frac{\eta_2}{\eta_1} \right) = K_{21} [1 + I_1(\lambda, K_{32})\phi^{\text{PE}}], \quad (\text{C3})$$

where  $K_{21}$  is the viscosity ratio  $(\eta_2/\eta_1)$  and  $\eta^{\text{PE}}/\eta_2$  is given by Eq. (C1).

Eq. (C2) is the same as Eq. (22) written in the form of a relative viscosity of a multiple emulsion.

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