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An empirical model predicting the viscosity of highly concentrated, bimodal dispersions with colloidal interactions

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Abstract The relationship between particle size distribution and viscosity of concentrated dispersions is of great industrial importance, since it is the key to get high solids dispersions or suspensions. The problem is treated here experimentally as well as theoretically for the special case of strongly interacting colloidal particles. An empirical model based on a generalized Quemada equation $\eta = \tilde{\eta}\left(1 - \frac{\phi}{\phi_{\max}}\right)^{-\varepsilon}$ is used to describe η as a function of volume fraction for mono- as well as multimodal dispersions. The pre-factor $\tilde{\eta}$ accounts for the shear rate dependence of η and does not affect the shape of the η vs ϕ curves. It is shown here for the first time that colloidal interactions do not show up in the maximum packing parameter and $\phi_{\max}$ can be calculated from the particle size distribution without further knowledge of the interactions among the suspended particles. On the other hand, the exponent ε is controlled by the interactions among the particles. Starting from a limiting value of 2 for non-interacting either colloidal or non-colloidal particles, ε generally increases strongly with decreasing particle size. For a given particle system it then can be expressed as a function of the number average particle diameter. As a consequence, the viscosity of bimodal dispersions varies not only with the size ratio of large to small particles, but also depends on the absolute particle size going through a minimum as the size ratio increases. Furthermore, the well-known viscosity minimum for bimodal dispersions with volumetric mixing ratios of around 30/70 of small to large particles is shown to vanish if colloidal interactions contribute significantly.

Key words Bimodal dispersions · Rheology · Generalized Quemada equation · Maximum packing fraction · Colloidal interactions

Introduction

Market competition, cost reduction, and environmental driving forces are pushing industrial researchers to formulate polymer dispersions with a particle loading as high as possible. The benefit will be an increased time-space yield during production, reduced transportation costs, and less energy consumption for the removal of solvent in the application process. At the same time the viscosity has to be kept low enough in order to ensure a sufficient heat transfer during polymerization as well as reasonable stir-, pump-, and sprayability during transport and application. Particle loadings beyond a volume fraction of 0.60 can only be achieved if the particle size distribution is either broad or bi- or multimodal. Consequently, the rheology and the packing possibilities of highly concentrated suspensions have been discussed intensively by academic as well as industrial researchers. The literature strongly focuses on suspensions of non-Brownian spheres (e.g., Farris 1968; Chong et al. 1971; Poslinski et al. 1988; Sengun and Probstein 1989, 1997; Gondret and Petit 1997) or on Brownian but so-called

hard spheres (Rodriguez and Kaler 1992; Chang and Powell 1994; Shikata et al. 1998). Only a few papers deal with the rheology of Brownian particle suspensions with either electrostatic (Zaman and Moudgil 1999; Richtering and Müller 1995) or steric interactions (Woutersen and de Kruif 1993; D'Haene and Mewis 1994; Greenwood et al. 1997) or a combination of both (Hoffman 1992; Chu et al. 1998).

Monodisperse suspensions can in principle pack in several ways with different maximum packing fractions, e.g., $\phi_m = 0.52$ for simple cubic, $\phi_m = 0.74$ for hexagonal or 0.63 for random close packing. For a random close packed bimodal system a maximum packing fraction $\phi_m = 0.87$ is achieved assuming $R_{large}/R_{small} > 10$ so that small particles together with the solvent molecules can be treated as a continuum. The small particle volume fraction then is $\xi_s = 0.27$ (Farris 1968). From simple geometrical considerations it follows that the small particles exactly fit into the pores between the large ones at a critical size ratio $R_{large}/R_{small} = 6.46$ (McGeary 1961). In this case the number ratio of small to large particles $N_{small}/N_{large} \approx 100$; that means there are much more small particles than interstices between large particles. Therefore, the simple picture of small particles filling the space between the large ones, thus providing a high maximum packing fraction and a low viscosity, is not valid for bimodal suspensions with size ratios like this. If the size ratio is below this critical value the lattice of the large particles may be expanded, and microphase separation or the formation of superstructures can also occur. These phenomena have been discussed intensively in the literature (e.g., Verhaegh and Lekkerkerker 1997; Bartlett and Pusey 1993). Despite the variety of packing possibilities, viscosity reduction in bimodal suspensions is a very general phenomenon and has been observed for large as well as intermediate and small size ratios. A minimum viscosity at a small particle volume fraction ξ_s of about 0.3 has been reported for suspensions of non-Brownian glass beads (Chong et al. 1971) as well as for Brownian hard sphere (Rodriguez and Kaler 1992) and colloidally interacting suspensions (Zaman and Moudgil 1999).

The aim of this paper is to work out a procedure which allows for a simple calculation of the viscosity of suspensions or dispersions at particle loadings and shear rates relevant for industrial applications. An empirical model based on a generalized Quemada equation is used to describe η as a function of volume fraction for mono- as well as multimodal dispersions. This model quantitatively describes the viscosity of a large number of bimodal suspensions with significantly different size and mixing ratios investigated here. Moreover, it qualitatively predicts well-known features of suspensions with colloidal interactions. In particular, it is shown, that the viscosity varies not only with the size ratio of large to small particles, but also depends on the absolute particle

size, and that the viscosity minimum for bimodal dispersions with volumetric mixing ratios of around 30/70 of small to large particles vanishes, if colloidal interactions contribute significantly.

Experimental

Samples

All dispersions were made by seeded emulsion polymerization. For our examinations, we used dispersions with a monomodal as well as dispersions with a bimodal particle size distribution. In order to produce bimodal dispersions with high solids content we started the polymerization with two different seeds differing in their average particle size. The initial amount of these seeds was governed by the desired particle size distribution. This is a convenient method to obtain bimodal dispersions with a very high viscosity because there is no need for mixing two monomodal dispersions and evaporation of water afterwards that could induce coagulation and agglomeration. All dispersions had the same chemical composition consisting of 99 parts butylacrylate, 1 part acrylic acid, 0.8 parts dodecylphenoxybenzene disulfonic acid sodium salt (Dowfax 2A1), and 0.2 parts sodium laurylsulfate.

The initiation was done either with sodiumperoxodisulfate, a so-called thermal initiation, or with the redox system ascorbic acid/tert-butylhydroperoxide. Thus we attained dispersions with the same particle size distribution but with different surface properties.

Measurements

Viscosity measurements were done with a controlled strain rotational rheometer Rheometrics RFS II equipped with a Couette ($R_i = 16$ mm, $R_a = 17$ mm) sample cell. All measurements were performed at 20 °C.

Particle size distributions were determined using the analytical ultracentrifuge technique (Mächtle 1992). Typical results are presented in Fig. 1, showing the differential mass distribution as a function of particle diameter. The mean size of each particle species was determined from the position of the maximum of the corresponding peak, and the relative fraction of each species was calculated from the area under each peak.

Results and discussion

Experiments

The viscosity of a large number of mono- and bimodal dispersions was determined as a function of shear rate and volume fraction. Data for a monomodal system with 250 nm particle diameter are shown in Fig. 2. These results are typical for all suspensions investigated here. Varying the particle concentration, two regimes differing with respect to the shape of the viscosity curves can be distinguished.

At volume fractions ϕ below a critical packing fraction ϕ_c the viscosity curves exhibit a Newtonian plateau at low shear rates followed by a shear thinning region, indicating that the dispersions behave like a liquid. The onset of shear thinning is shifted to higher shear rates and the degree of shear thinning decreases

Fig. 1 Differential particle size distribution from AUC measurements for different bimodal dispersions. The labels inserted in the diagrams give D_{large} and D_{small} in nm and the small particle volume fraction times 100 (i.e., B-915/310–10 means $D_{large} = 915$ nm, $D_{small} = 310$ nm, and $\zeta_s \approx 0.10$)
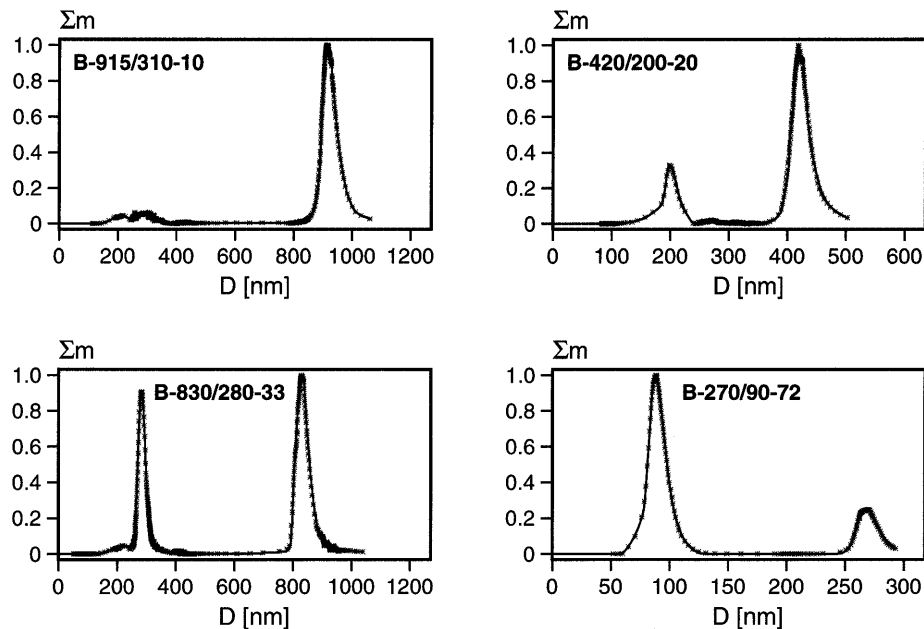
Fig. 2 Viscosity vs shear rate for a monomodal dispersion (diameter: 250 nm) at different particle loadings
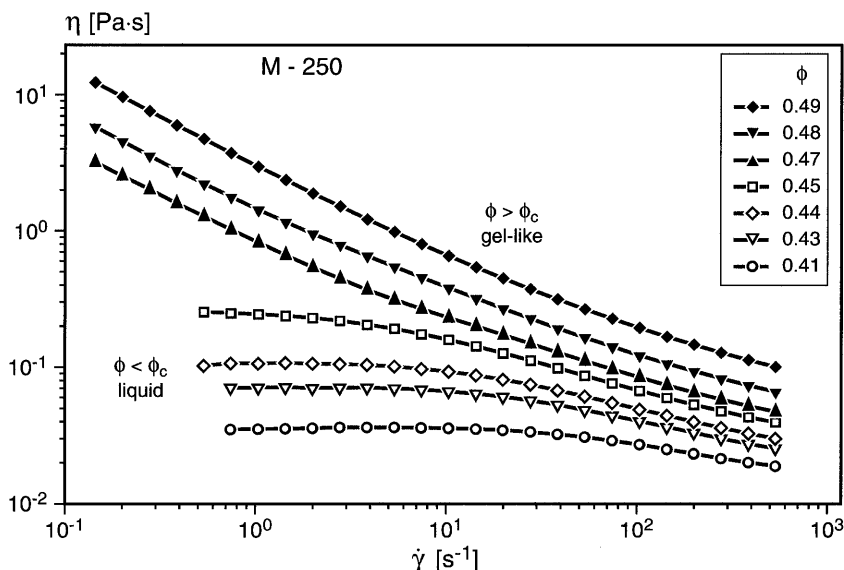
with decreasing volume fraction. The high shear limiting value of the viscosity is not reached within the shear rate range ($\dot{\gamma} < 500$ s^{-1}) investigated here.

For $\phi > \phi_c$ the dispersions are shear thinning in the whole shear rate range investigated and neither a high nor a low shear plateau is observed. The viscosity curves show a slight upward curvature at low shear rates indicating an apparent yield stress. At these volume fractions the dispersions show gel-like behavior. The shape of the flow curves hardly changes with the particle density in this regime and the variation of ϕ essentially results in a vertical shift of the viscosity vs shear rate

curves. Therefore, the relative change of viscosity with volume fraction is independent of shear rate and it is sufficient to discuss the effect of packing density on viscosity at a fixed shear rate.

Dispersions go through various flow fields during manufacturing and application; typical shear rates during stirring and pumping are in the range between 50 s^{-1} and 500 s^{-1}. From this point of view we have decided to analyze the effect of particle size distribution on viscosity at a shear rate of $\dot{\gamma} = 200$ s^{-1}. All viscosity data shown in the subsequent part of the paper are taken at this particular shear rate.

In Fig. 3 the viscosity of a bimodal dispersion with $R_{large} = 270$ nm, $R_{small} = 88$ nm, and a small particle volume fraction $\xi_s = 0.72$ is shown as a function of volume fraction.

The particle concentration dependence of the zero shear viscosity of liquid-like dispersions is often described by phenomenological equations like the Krieger-Dougherty equation (Krieger and Dougherty 1959):

$$\eta = \eta_{solvent} \left(1 - \frac{\phi}{\phi_{max}} \right)^{-2.5\phi_{max}} \tag{1}$$

or the equation derived by Quemada (1977):

$$\eta = \eta_{solvent} \left(1 - \frac{\phi}{\phi_{max}} \right)^{-2} \tag{2}$$

where $\eta_{solvent}$ is the viscosity of the dispersing agent or solvent, which is water in our case, and ϕ_{max} is the maximum packing fraction for a given particle size distribution. The advantage of the Krieger-Dougherty equation is, that it reduces to the correct Einstein equation in the limit of infinite dilution, whereas the Quemada equation gives the right divergence for η as ϕ approaches ϕ_{max}. For a monodisperse suspension with $\phi_{max} = 0.63$ the exponent in Eq. (1) is slightly lower than in Eq. (2). Trying to fit both equations to the experimental data in Fig. 3 with ϕ_{max} as an adjustable parameter shows that neither the Krieger-Dougherty nor the Quemada equation can match the shape of the experimentally determined $\eta - \phi$ curve. Therefore, we introduce an additional phenomenological parameter ε and propose a generalized Quemada equation (Gondrot and Petit 1997):

Fig. 3 Viscosity vs volume fraction for highly concentrated dispersions. Generalized Quemada Eq. (3) (— — —), Quemada Eq. (2) (– – –) and Krieger-Dougherty Eq. (1) (....) fitted to the experimental data (●) for a bimodal dispersion with $D_{large} = 270$ nm, $D_{small} = 88$ nm, and $\xi_s = 0.72$

$$\eta = \tilde{\eta} \left(1 - \frac{\phi}{\phi_{max}} \right)^{-\varepsilon} \tag{3}$$

The pre-factor $\tilde{\eta}$ determines the viscosity level and depends on shear rate, only. It does not affect the shape of the $\eta - \phi$ curve. Therefore, it will not be discussed further in the subsequent part of the paper. As demonstrated in Fig. 3, the generalized Quemada equation provides a very good fit to the experimental data.

A large number of mono- and bimodal dispersions with different absolute particle size, size ratio, and small particle volume fractions have been analyzed in an analogous way. The resulting values for the maximum packing fraction ϕ_{max} and the exponent ε are discussed in the next section.

As indicated by Eqs (1), (2), and (3) the viscosity of a concentrated suspension is strongly controlled by the ratio of its volume fraction to the maximum packing fraction. Consequently, technical improvements aim at an increase of ϕ_{max} through optimization of the particle size distribution in order to decrease the viscosity at a given particle loading. McGeary (1961) has performed intensive studies regarding the packing properties of multimodal suspensions of glass beads and Sudduth (1993) has presented the following mathematical parametrization of these data:

$$\phi_{max} = \varphi_n - (\varphi_n - \phi_{max}^{mono}) \exp\left(0.27 \left(1 - \frac{D_5}{D_1} \right) \right) \tag{4}$$
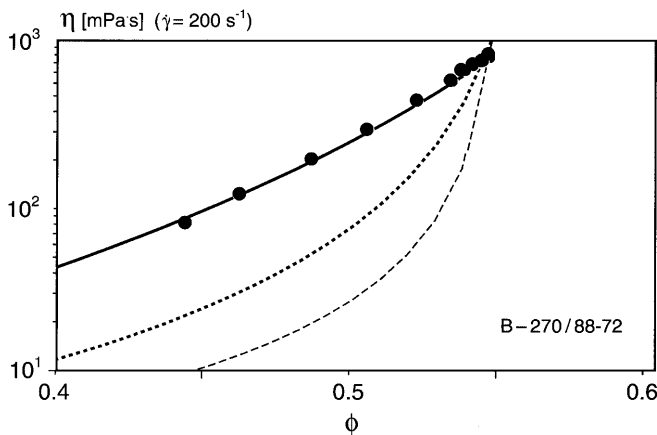
with

$$\varphi_n = 1 - \left(1 - \phi_{max}^{mono} \right)^n$$

and

$$D_x = \frac{\sum_{i=1}^{n} N_i d_i^x}{\sum_{i=1}^{n} N_i d_i^{x-1}}$$

where ϕ_{max} is the maximum packing fraction of an n-modal suspension of spherical particles, $\phi_{max}^{mono} = 0.63$ is the corresponding value for a monodisperse suspension, and D_x is the x-th moment of the particle size distribution, namely D_1 is the number average of the particle diameter.

We have used Eq. (4) to calculate ϕ_{max} from the particle size distributions of our bimodal suspensions as determined from the analytical ultracentrifuge measurements. In Fig. 4 these values are compared to those obtained from fitting Eq. (3) to the viscosity vs ϕ data. Each data point in that plot represents a particular, separately polymerized suspension. Obviously, there is a strong linear correlation (correlation coefficient $R = 0.95$) between these differently determined maximum packing values. This is surprising since the viscosity measurements were performed on dispersions of colloidally interacting Brownian spheres, whereas

Eq. (4) describes the packing properties of non-Brownian hard spheres. Obviously, the packing parameter ϕ_{max} is independent of the interactions among the particles and can be predicted from the particle size distribution alone.

The values for the exponent ε extracted from fitting Eq. (3) to the η vs ϕ data are shown in Fig. 5 vs the number average mean particle diameter D_1 of the corresponding bimodal suspension. Two series of bimodal mixtures have been investigated. These series differ with respect to the initiation of the polymerization which is expected to result in a different particle surface structure and hence a different repulsive interaction
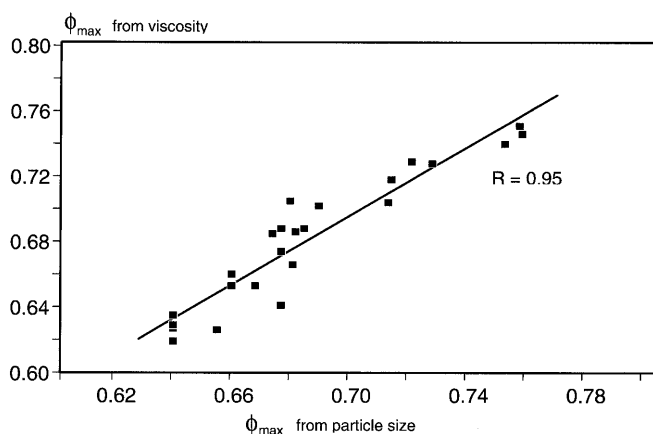
Fig. 4 Maximum packing fraction ϕ_{max} as determined from a fit of Eq. (3) to the $\eta - \phi$ data for various mono- and bimodal dispersions vs ϕ_{max} as calculated from the particle size distribution according to Eq. (4)
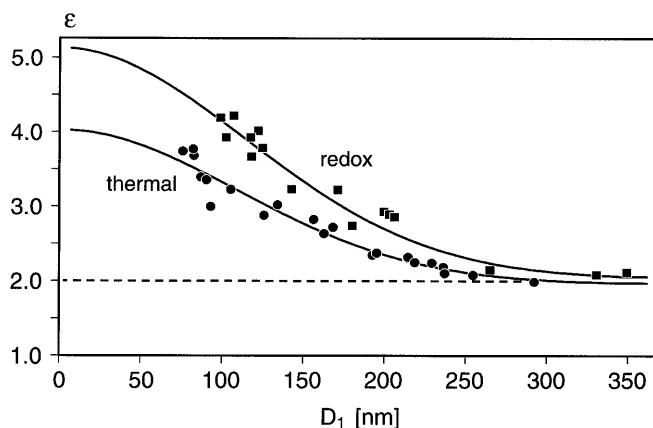
Fig. 5 Exponent ε as determined from a fit of Eq. (3) to the $\eta - \phi$ data for various mono- and bimodal dispersions vs the corresponding number average of the particle diameter D_1. Two sets of mixtures polymerized with redox (■) and thermal (●) initiation have been investigated. The lines correspond to fits of Eq. (5) to the experimental data

among the particles. In both cases ε starts from a limiting value of 2 for large mean particle diameters but strongly increases as D_1 decreases and values larger than 4 are obtained at mean particle diameters below 100 nm. This increase is less pronounced for the systems which were thermally initiated than for those were the polymerization was started using a redox agent.

The limiting value of $\varepsilon = 2$ reached for $D_1 > 250$ nm is in good agreement with the exponent of divergence for the viscosity of hard sphere dispersions observed experimentally (De Kruif et al. 1985) as well as predicted theoretically (Brady 1993). This is reasonable since, due to the high ionic strength (estimated ion concentration > 0.05 mol/l) the range of the electrostatic interactions is much shorter than the mean particle separation at the investigated particle volume fractions. Thus, if D_1 is large enough these dispersions behave like hard sphere suspensions with respect to the viscosity. On the other hand, the increase of ε with decreasing mean particle size is attributed to the effect of colloidal interactions. As the mean particle separation decreases, colloidal interactions among the particles are getting more and more important and this leads to a much stronger divergence of the viscosity than expected for hard spheres. The differences in ε observed for the two differently polymerized systems further support the interpretation that the increase of ε is governed by colloidal interactions. A dependence of these particle-particle interactions on the structure and chemical composition of the particle surface seems to be reasonable, but a detailed interpretation of the relationship between particle interactions and polymerization conditions is beyond the scope of this work.

Model calculations

Equation (3) can be used to calculate the viscosity of highly concentrated, multimodal suspensions as a function of volume fraction. The maximum packing fraction ϕ_{max} can be calculated from the particle size distribution according to Eq. (4). The exponent ε depends on the colloidal interactions and its dependence on particle size has to be determined from viscosity measurements for a particular type of suspension. We have investigated the effect of particle size and mixing ratio on the viscosity of bimodal suspensions. These model calculations are based on the ε (D_1) data for the thermally initiated dispersions. In order to describe these data numerically, we have fitted the following phenomenological equation to the data presented in Fig. 5:

$$\varepsilon = \varepsilon_\infty - (\varepsilon_0 - \varepsilon_\infty) \exp\left(-\left(\frac{D_5}{\overline{D}}\right)^2\right) \tag{5}$$

Also the pre-factor $\tilde{\eta}(\dot{\gamma} = 200\ s^{-1})$ which has been determined for this system has been used.

The effect of particle size ratio on viscosity is shown in Fig. 6. For these calculations $D_{large} = 800$ nm, a total volume fraction $\phi = 0.6$, and a small particle volume fraction $\xi_s = 0.25$ have been chosen. Obviously the viscosity strongly decreases as the size of the small particles decreases, goes through a minimum at $D_{large}/D_{small} \approx 4$, and then increases again as the size ratio further increases. This minimum is a consequence of the increase of ε with decreasing mean particle diameter. If ε is kept constant the viscosity decreases monotonically with increasing size ratio, as expected for hard sphere suspensions (Chong et al. 1971). In Fig. 6 this is shown for $\varepsilon = 2$.

The variation of viscosity as a function of small particle volume fraction has been considered for two sets of mixtures with a similar size ratio $D_{large}/D_{small} = 3.1$ but different absolute particle sizes. The results are shown in Fig. 7. In both cases the total volume fraction ϕ was set to 0.6 and the ε (D_1) data for the thermally initiated dispersions were used to perform the calculations. For the mixture of large particles (680 nm and 210 nm, $\varepsilon = 2$ for any value of ξ_s) the viscosity goes through a minimum for a small particle volume fraction $\xi_s \approx 0.25$. This is in accordance with the well-known behavior of Brownian (Rodriguez and Kaler 1992) as well as non-Brownian hard sphere suspensions (Chong et al. 1971; Gondrot and Petit 1997). In contrast, the viscosity increases monotonically with ξ_s for a mixture of small particles (250 nm and 80 nm) with a similar size ratio. This is again due to the fact that ε increases with increasing number of small particles (corresponding to a decrease in D_1) as a consequence of the contribution of colloidal interactions. These results correspond very well with experimental data on electrostatically stabilized polystyrene dispersions (Horn 1999). For their system the well-know viscosity minimum at a volumetric mixing ratio of around 30/70 of small to large particles is found at high ionic strength, where the electrostatic particle interactions are strongly suppressed, but vanishes at low ionic strength, where colloidal interactions contribute significantly.

Conclusion

The relationship between particle size distribution and viscosity of highly concentrated, gel-like dispersions has been treated here experimentally as well as theoretically for the special case of strongly interacting colloidal particles. An empirical model based on a generalized Quemada equation $\eta = \tilde{\eta}(1 - \frac{\phi}{\phi_{max}})^{-\varepsilon}$ is used to describe η as a function of volume fraction for mono- as well as multimodal dispersions. The pre-factor $\tilde{\eta}$ accounts for the shear rate dependence of η and does not affect the shape of the η vs ϕ curves.

Colloidal interactions do not show up in the maximum packing parameter. The experimentally determined ϕ_{max} values agree very well with predictions from an empirical expression derived for non-colloidal suspensions with arbitrary particle size distribution. So this parameter can be extracted from the particle size distribution without further knowledge of the nature and strength of the interactions among the suspended particles.
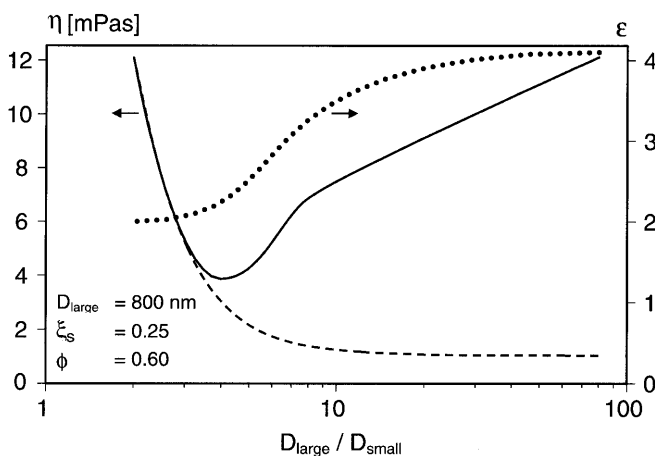
Fig. 6 Viscosity vs particle size ratio calculated according to Eq. (3). Model parameters: $D_{large} = 800$ nm, $\phi = 0.6$, $\xi_s = 0.72$, ϕ_{max} calculated from Eq. (4); (———) ε (D_1) taken from a fit of Eq. (5) to the experimental data in Fig. 5 for thermal initiation; (– – –) analogous calculation assuming $\varepsilon = 2$; (......) dependence of ε on the particle size ratio (right y-axis)
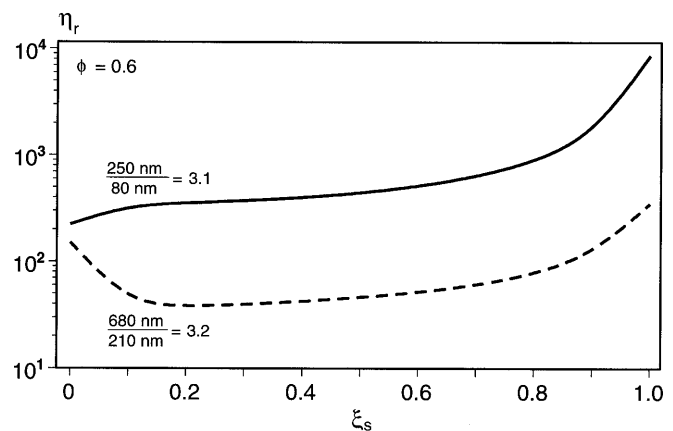
Fig. 7 Viscosity vs small particle volume fraction ξ_s calculated according to Eq. (3). Model parameters: $\phi = 0.6$, ϕ_{max} calculated from Eq. (4), $\varepsilon(D_1)$ taken from a fit of Eq. (5) to the experimental data in Fig. 5 for thermal initiation; (———) $D_{large} = 250$ nm, $D_{small} = 80$ nm, $D_{large}/D_{small} = 3.1$; (– – –) $D_{large} = 680$ nm, $D_{small} = 210$ nm, $D_{large}/D_{small} = 3$

The exponent ε is controlled by colloidal interactions. Starting from a limiting value of 2 for non-interacting either colloidal or non-colloidal particles, ε generally increases strongly with decreasing particle size depending on the range and strength of the colloidal interactions. For a given particle system ε then is a function of the number average mean diameter D_1 only. The presented model describes the viscosity of a large number of suspensions investigated here quantitatively. Moreover, it qualitatively predicts well-known features of bimodal suspensions with colloidal interactions. In particular, it is demonstrated that the viscosity of bimodal dispersions varies not only with the size ratio of large to small particles, but also depends on the absolute particle size going through a minimum as the size ratio increases. Furthermore, the model predicts that the well-known viscosity minimum for bimodal dispersions with volumetric mixing ratios of around 30/70 of small to large particles vanishes if colloidal interactions contribute significantly.

Effects like this severely limit the development of colloidal suspensions with high particle loadings.

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