Shear Yield Stress of Partially Flocculated Colloidal Suspensions

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A general expression was derived for the shear yield stress of a flocculated suspension of particles that is able to describe the effect of particle-size distribution, solid loading, pH, and hence, electrokinetics of the suspension. The model builds on an earlier model by incorporating the effect of the repulsive interaction between particles. Scaling of the data to the maximum yield stress at a given volume fraction provides a means of removing particle-size- and volume-fraction-related effects. The scaling process establishes that to a high level of precision, concentrated dispersions act, in interparticle interaction terms, as the sum of two-body interactions.

Introduction

The interactions between colloidal particles control, in a fundamental way, whether or not a suspension of particles is coagulated or dispersed. These interactions are typically the result of electrostatic, van der Waals, and/or steric and other more complex forces. An understanding of the role of these forces is important in particulate processing operations, since many are limited by suspension flow properties. For instance, in particulate fluid pumping, low-viscosity, highly dispersed suspensions are preferred, whereas for filtration and other solid–liquid separation processes, an aggregated particulate network is essential. It is the control of the flow of coagulated suspensions of colloidal particles that is of interest to this study.

Most particulate processing operators are familiar with the concept that the viscosity of a suspension increases with increasing solids fraction. Indeed, in most unit operations involving particulate fluids, it is the viscosity that is the limiting factor controlling higher solids processing. Increasing the solids concentration is characterized by non-Newtonian flow behavior and for flocculated suspensions, this can occur at quite low solids concentrations, certainly well removed from the theoretical hard-sphere limit of 64 vol. % solids. The latter limit can only be achieved for ideal, monosized, spherical particles.

For lower volume fraction, highly flocculated, non-Newtonian suspensions of particles, it is almost certainly the nature of the particle–particle interactions that dominates the suspension viscosity. Flocculated suspensions of particles at low volume fraction settle rapidly due to the coagulated nature of the particles and are non-Newtonian in their flow behavior. As the particle concentration is increased, the suspension reaches a point at which the particle network is "space filling" and the flocculated particle network spans the container. Particulate suspensions at concentrations above this so-called gel point (ϕ_g) show non-Newtonian flow behavior and in the limit of low shear, a finite yield strength (τ_y).

The yield strength is an important parameter in the processing of flocculated suspensions and is best viewed as the response of the suspension to an applied load. Suspensions behave in a linear elastic manner to applied stresses less than τ_y. For stresses above τ_y, the network fails under load and in the low shear-rate limit, the maximum stress prior to failure is designated as a yield value. Many workers measure this yield value by extrapolating curves of shear stress vs. shear rate to zero or very low shear along a low shear plateau. Great care must be taken in such measurements, especially for weakly flocculated suspensions showing weak gel-type behavior. Indeed, in many systems, true equilibrium data are hard to obtain. To overcome many of the artifacts associated with yield stresses measured by extrapolation, Nguyen and Boger

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(1985, 1992) adopted the static yield-stress measurement technique incorporating the vane-spindle. This technique has now been utilized in a variety of measurements and systems to highlight the interrelationship between interparticle forces and suspension rheology (Leong and Boger, 1991; Leong et al., 1992, 1996, 1993a,b,c; Liddell and Boger, 1996).

The literature on the interrelationship between measurable particle-surface chemical properties and suspension flow properties or yield stress is lengthy and in this context no novelty is claimed here. Examples of relevant work include the elastic floc model of Hunter and Nicol (1968), Firth (1976), and Firth and Hunter (1976), who showed scaling behavior between the Bingham yield stress of suspensions and surface properties and in particular, a dependence of the yield stress on the square of the zeta potential. An analog of their approach is utilized here. Another relevant model is the cell model of Tanaka and White (1980). Other approaches include attempts to describe the flocculated microstructure using a fractal style analysis (Potanin et al., 1995; Potanin and Russel, 1996), whereby the failure of the elastic response of the particle network is associated with the bond strength of the particle and hence to a characteristic microstructure for that bond strength.

These models, while useful in providing an investigative framework, exhibit only limited success in predicting the effects of particle size, polydispersity, and particle concentration on the yield stress of a particulate fluid. A downfall of many of the models is that they do not invoke explicitly the measurable particle-surface properties relevant to the force of interaction between particles. It is our opinion that this in itself limits their predictive role for strongly aggregated suspensions.

Recently, Kapur et al. (1997) proposed a new approach to understanding the shear yield stress of concentrated particulate suspensions. The model defined the interdependence of the yield stress of a flocculated particulate dispersion on particle-surface properties, particle size, size polydispersity, and particle concentration. It takes specific cognizance of the three-dimensional, mechanically rigid particle network wherein the mean coordination number of the assemblage increases and the separation between the particles decreases with an increase in the volume fraction of the solid phase. In summary, the equation of Rumpf (1962) as elaborated by Molerus (1975), relating isotropic normal stress and isotropic normal interparticle force in a bed of single-sized spheres was modified to incorporate the size distribution of particles and extended to the subsequent network, the final structure of which depends on the interparticle force.

The previous model (Kapur et al., 1997) estimates the yield stress of flocculated suspensions as a function of solids loading and particle-size distribution, but only at the surface condition whereby the net electrostatic repulsion between particles is zero, the isoelectric point (IEP). The model was successful in yield-stress prediction for zirconia and titania suspensions, with the interparticle spacing between particles in the flocculated state as a fitting parameter.

The aim of the present work is to extend the earlier model of Kapur et al. (1997) to include the effect of particle–particle repulsion (at surface chemistry conditions away from the IEP, but still aggregated) and demonstrate the application of the model to another particle system, namely a well-characterized ceramic-grade alumina. Although outwardly a trivial addition, the non-IEP condition provides a dilemma as to the most appropriate way to incorporate the repulsion term. Surface-force apparatus and atomic-force microscopy experiments on interaction forces between hard surfaces show that for simple systems in the absence of molecular additives, the interaction is well described by DLVO theory at all but very short range (Larson et al., 1994; Pashley, 1981; Pashley, 1984). The assumption in simple systems that the repulsion between particles is well represented by the measured zeta potential or shear plane potential as incorporated in the classic DLVO model of particle–particle interaction (Hunter, 1987) appears reasonable.

Experimental Section

The solid chosen for study was a ceramic-grade alumina (AKP-30) ex Sumitomo Chemical Co. (Japan). To prepare suspensions for yield-stress measurement, a suspension of the desired volume fraction was mixed under dispersed conditions (pH 5–6) and sonicated for 1 min with a Branson B-30 sonifier at between 50 and 60% of maximum power. The sonifier had a vibrational output of 20 kHz, and the maximum power output was 350 W. The sample pH was then adjusted with concentrated base or acid to avoid dilution effects and sonicated for a further minute. The suspension was then allowed to stand for 2 h prior to measurement.

Water used in the study was from a Milli-Q system (Millipore) and all measurements were conducted at a constant background electrolyte concentration of 0.01 M KNO_3. The Hamaker constant for alumina in water was calculated from Liftshitz theory using spectroscopy data. The value was determined to be 5.3×10^{-20} J.

Shear yield-stress measurements were conducted using the vane-spindle technique. This technique has been described in detail by Nguyen and Boger (1985, 1992). Measurements were performed from 20 to 30 vol. % solids.

The dynamic electrophoretic mobility of the AKP-30 alumina sample was measured for particle concentrations from 2 to 30 vol.% using a Matec Acoustosizer (Colloidal Dynamics Pty., Ltd). The zeta potential was then calculated using the instrument software. Calculations implicit in this software, and indeed, all calculations, assumed a spherical particle shape.

Transmission electron microscopy analysis of the AKP-30 sample showed that while not ideal, the latter is not an unreasonable assumption. As discussed, all yield-stress data discussed herein pertain to coagulated suspensions at or near the isoelectric point.

Yield-Stress Model

The basic development of the yield-stress model follows explicitly from that presented in an earlier article (Kapur et al., 1997), and only an outline along with expansion of the model to incorporate interparticle repulsion will be presented here. The model assumes a polydisperse, flocculated particle suspension. Utilizing a plane cut through this bed of particles, the mean area of the disks cut by the plane, the number of spheres sliced, the mean force between particles, and the coordination number of the particles is incorporated into the model of Molerus (1975) to describe the interrelationship between stress and force in the particle bed. It was shown previously (Kapur et al., 1997) that a general expression for shear-yield stress of a polydisperse suspension of particles is

$$\tau_y = \frac{1}{6} \sum_j n_j \sum_i K_{ij} H_{ij}, \tag{1}$$

where τ_y is the yield stress; n is the number of particles lying in the jth size interval; $K(\phi)$ is the mean coordination number in a bed of monosize particles of solids volume fraction ϕ; and H is the bonding force between particles.

Incorporation of the effects of particle interaction into the model requires an expression for the attractive and repulsive forces between particles. Using the postulate that particle interaction in the suspension is well described by DLVO theory, then the net force of interaction (H_{ij}) between two neighboring particles of size i and j due to van der Waals forces is

$$H_{ij} = \frac{A}{12h^2}\left[\frac{X_i X_j}{X_i + X_j}\right] \tag{2}$$

and for electrical forces is

$$H_{ij} = -\frac{2\pi\zeta^2\epsilon\kappa}{2(1+e^{\kappa h})}\left[\frac{X_i X_j}{X_i + X_j}\right]. \tag{3}$$

Equation 2 incorporates the expected van der Waals expression for the interaction of spherical particles (Israelachvili, 1991) where A is the Hamaker constant; h is the interparticle distance; and X_j is mean diameter of particles lying in the jth size interval. Equation 3 incorporates the Hogg–Healy–Fuerstenau (HHF) expression for electrical double-layer interaction (Hogg et al., 1966), where ζ is the interaction potential (assumed to be well represented by the zeta potential); κ is the inverse Debye length; and $\epsilon = \epsilon_0 D$ such that ϵ_0 is the permittivity of a vacuum and D is the dielectric constant. Since it was originally derived for an isolated pair of spheres, the HHF expression is not necessarily applicable to a network of particles, and as discussed later, the efficacy of using this expression to describe interactions in a concentrated particulate network is of considerable interest.

Successive substitutions of Eqs. 1–3 into Eq. 1 with reference to the original model (Kapur et al., 1997) then yields, after some manipulations, the following general expression for shear yield stress:

$$\tau_y = \frac{0.011}{\pi}\phi K(\phi)\left[\frac{A}{h^2(\phi)} - \frac{24\pi\epsilon\kappa\zeta^2}{(1+e^{h(\phi)\kappa})}\right]\sum_j \frac{S_j}{X_j}\sum_i S_i \times \left[\frac{X_i}{X_j + X_i - \sqrt{X_j^2 + 2X_i X_j}}\right], \tag{4}$$

where the forms of $K(\phi)$ and $h(\phi)$ are also as derived previously (Kapur et al., 1997) and S_j is the fraction of surface area associated with particles in the jth size interval. The relationship for $K(\phi)$ of Gotoh cited by Suzuki et al. (1981) was chosen as an expression relevant to the volume fraction range of interest to the present study (namely $\phi <$ approximately 0.5).

This had the form;

$$K(\phi) = \frac{36}{\pi}\phi; \quad \phi \leq 0.47, \tag{5}$$

and describes the mean coordination number of the suspension as a function of volume fraction. The parameter $h(\phi)$ is the separation distance between particles in the flocculated state, and in the absence of an independent methodology for decoupling the coordination of particles in the three-dimensional flocculated array from the force of interaction, the parameter was lumped with the concept of a particle crowding factor (χ), such that

$$h(\phi) = h_0\chi. \tag{6}$$

It will be shown that a mechanism now exists to decouple these two parameters such that $h(\phi)$ can be replaced by h_0, a characteristic separation distance whose physical significance is more easily visualized in a two-body interaction sense, and the form of χ determined by fitting volume fraction data at the isoelectric point for a zirconia suspension (Kapur, et al., 1997) is then

$$\chi = \chi_0 e^{(-4.5\phi)}. \tag{7}$$

These volume-fraction-dependent forms for the coordination number and the crowding factor are assumed to be general for a flocculated particulate suspension.

Results and Discussion

Yield-stress data for suspensions of AKP-30 alumina from 20 to 30 vol. % solids as a function of pH as measured using the vane technique are shown in Figure 1. The data show a characteristic parabolic profile with a maximum in the yield stress coincident with the iep of the solid surface. The zeta potential of the suspension as a function of pH under the same electrolyte conditions from 2 vol. % to 30 vol. % solids is shown in Figure 2.

Calculation of the zeta potential from electroacoustic measurements at volume fractions above ≈7 vol % uses an empirical relationship to correct for the effect of volume fraction such that the zeta potential remains constant (O'Brien, private communication, 1996). Not surprisingly therefore, the data show good coincidence as a function of volume fraction. Deviations from the single form for the data are assumed to be due to experimental rather than theoretical difficulties. Further details of the procedure involved in the correction between dynamic mobility and zeta potential at concentrations greater than ≈7 vol. % is presented elsewhere (Johnson et al., 1997).

Analysis of the shear yield-stress data of Figure 2 shows that the maximum value in the yield stress occurs at a point where the suspension is fully flocculated, that is, where the

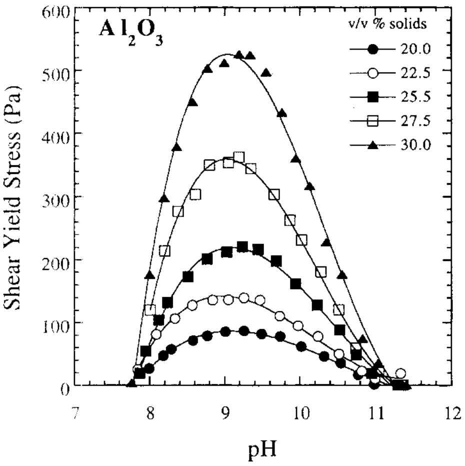

Figure 1. Yield stress vs. volume fraction of a suspension of AKP-30 alumina particles in 0.01-M background electrolyte as measured by the vane technique.

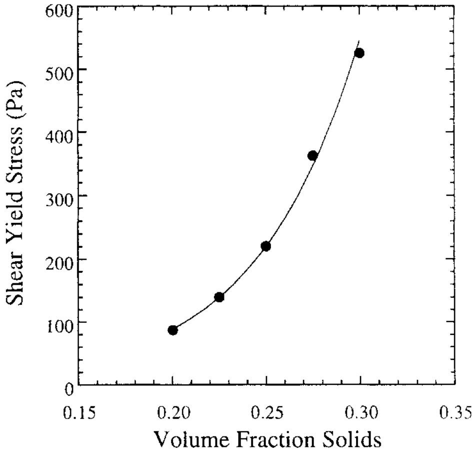

Figure 3. Model fit to the maximum value of the yield stress as a function of volume fraction solids.

zeta potential, $\zeta = 0$. Under these conditions, the model equation now reduces to the form derived previously (Kapur et al., 1997), namely:

$$\tau_{y\max} = \frac{0.011}{\pi}\frac{A\phi K(\phi)}{h^2(\phi)}\sum_j \frac{S_j}{X_j}\sum_i S_i \times \left[\frac{X_i}{(X_j+X_i)-\sqrt{X_j^2+2X_iX_j}}\right]. \qquad (8)$$

The peak yield stress for each solid loading and the corresponding pH were determined by a spline fit to the data followed by an optimization routine. Figure 3 shows excellent agreement between the shear yield stress of flocculated suspensions as a function of solid content and Eq. 8. The closest distance of approach between two particles was calculated as 9.8 Å based on optimization of fits to the data. The value obtained, while different from the 5.5 Å selected for zirconia suspensions, is not outside of our expected range based on the distance of closest approach of clay plates and other oxide-like surfaces as determined by X-ray diffraction (Norrish and Raussell-Colom, 1963).

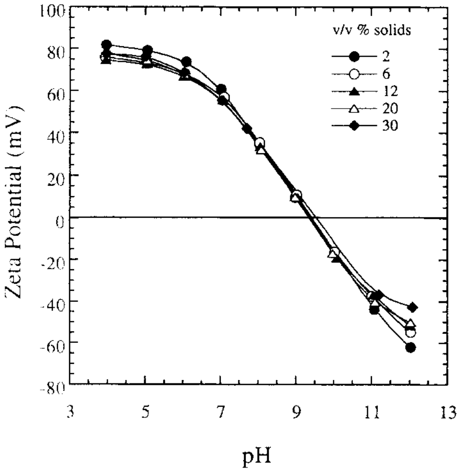

Figure 2. Zeta potential as a function of pH and volume fraction for AKP-30 alumina particles as measured using electroacoustics.

From the zeta potential vs. pH curve, shown in Figure 2, the isoelectric point of alumina calculated with the help of spline fit and optimization routine was found to be 9.42. The value calculated assuming coincidence of measured surface properties and yield stress as the pH corresponding to maximum yield stress gives an iep range from 9.2 to 9.3, with a mean value of 9.24. No satisfactory explanation is available for this pH shift or mismatch, although it is assumed to be a suspension effect created by the use of different pH electrodes for the electroacoustic and yield-stress measurements. Clearly, it is not possible to fit the model to the data accurately unless the pH term in the former is shifted by a small amount (0.18 of a pH unit). Accordingly, all model calculations were carried out, without any loss of rigor, with the replacement:

$$\mathrm{pH} \rightarrow \mathrm{pH} + 0.18. \qquad (9)$$

A check on the trends in the data as a function of volume fraction can be obtained by scaling the experimental data. To do this, a normalized shear yield stress may be computed by rescaling the actual yield stress by the maximum yield stress of the flocculated suspension in the following manner:

$$\bar{\tau} = \frac{\tau_y}{\tau_{y\max}}. \qquad (10)$$

Figure 4 shows that the measured data collapse remarkably well onto a single normalized yield-stress curve that is invariant of the solid content, the solid line representative of a model that will be elucidated shortly.

It is instructive to compare the normalized results with the predictions of the model. Substitution of Eqs. 4 and 8 into

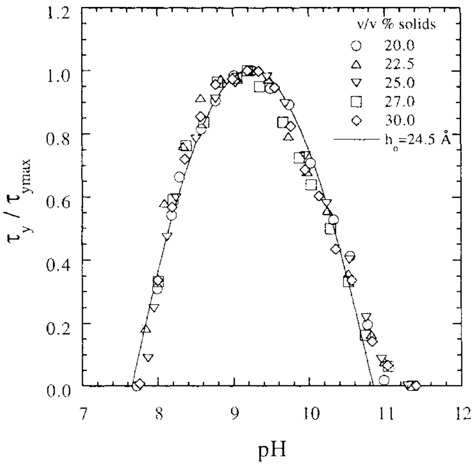

Figure 4. Normalization of the experimental data of Figure 1 to the maximum yield stress at each volume fraction.

The fit is as presented in Eq. 12.

Eq. 10 gives the following expression for the normalized yield stress:

$$\bar{\tau} = 1 - \frac{24\pi\epsilon\kappa\zeta^2 h^2(\phi)}{A[1 + e^{\kappa h(\phi)}]}, \tag{11}$$

which is, interestingly enough, independent of particle size and shows the same ζ^2 dependence predicted by Firth (1976) and Firth and Hunter (1976).

Calculations incorporating the zeta potential taken from Figure 2 are displayed in Figure 5. The model predicts the form of $\bar{\tau}$ to be a relatively weak function of solids loading. Given the excellent correlation with the model at the iep, it is reasonable to conclude that the increasing divergence of the theoretical curves with deviation from the iep condition is primarily due to the term in the model accounting for particle–particle repulsion.

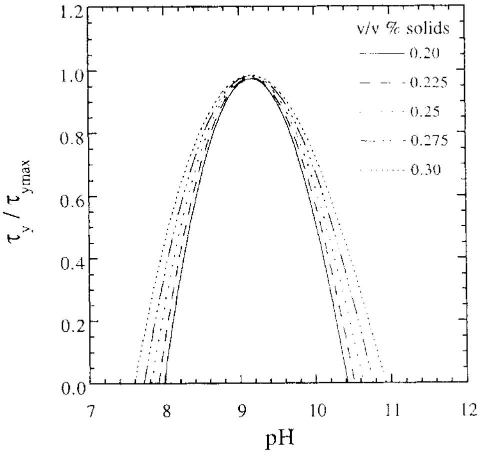

Figure 5. Model fit to the normalized yield stress data of Figure 1.

The fit is as presented in Eq. 11.

There are numerous, mostly speculative reasons why the model and experimental data away from the iep do not coincide. The overlap of the data upon normalization as shown in Figure 4 suggests a constant value of the interaction potential with volume fraction, although as the volume fraction is increased, double-layer overlap or exclusion must occur. The average size of the particles and salt concentration utilized in these experiments precludes double-layer overlap, even for the 30 vol. % data, and other explanations seem more likely.

The most likely and logical explanation is that h_0 is independent of volume fraction and is a single quantity. This is closer then to a classic electrostatic description and invokes some physical but very few mathematical changes to the model. It also allows one to lump χ with the $K(\phi)$ term as a network description that is independent of the interparticle spacing. Overall, this simplifies the model and removes the volume fraction dependence from the repulsive term. The incorporation of the crowding term along with the coordination number such that the interparticle structure is incorporated into a single term is probably more physically sound and results in a form of $\bar{\tau}$ with only one unknown, namely h_0, and no other dependencies other than the experimentally measured zeta potential. The simplified form of $\bar{\tau}$ is thus

$$\bar{\tau} = 1 - \frac{24\pi\epsilon\kappa\zeta^2 h_0^2}{A[1 + e^{\kappa h_0}]}. \tag{12}$$

A fit to the data in Figure 4 using Eq. 12 is shown as the solid line in the same figure. A value of h_0 of 24.5 Å was found to give the best fit to data, with a high sensitivity of the model to the value of h_0. The value is substantially above the value of 9.8 Å found by fitting iep data to Eq. 8, but this value is dependent on the form of $K(\phi)$ and χ and based on an initial value for $h_0 = 5.5$ Å chosen to fit to zirconia yield-stress data, assuming an interparticle spacing dominated by a single layer of water at the particle surface. The latter value for h_0 was also based on scaling of energy rather than force of interaction data. Not unexpectedly, this procedure produced a lower value of h_0 and perhaps more importantly, there was little rigor in its determination.

The fitting method utilizing Eq. 12 is less empirical and the value of h_0 is still reasonable for nonideal particles with respect to particle roughness and shape. Indeed, the value is not substantially different from the value of approximately 20 Å measured by X-ray diffraction techniques as the interplate spacing for vermiculite flocculated to the primary minimum (Norrish and Raussell-Colom, 1963). Despite these similarities, the value of h_0 almost certainly contains contributions from the roughness of the particles and the extent of the electrical double layer around the particle relative to this roughness.

The implication for χ of an independent determination of h_0 is that χ_0 is now a fitting parameter for the volume-fraction dependence of the yield stress. This allows decoupling of particle–particle interaction from network structure that is a logical extension of the model. It is not clear at this point whether or not χ shows a weak particle-size dependence. Only detailed data on a range of well-described particle-size distributions across a range of volume fractions will elucidate this information. Incorporation of the suggested changes gives the general form

$$\tau_y = \frac{0.011}{\pi}\phi\frac{K(\phi)}{\chi^2}\left[\frac{A}{h_0^2} - \frac{24\pi\epsilon\kappa\zeta^2}{(1+e^{h_0\kappa})}\right] \times \sum_j \frac{S_j}{X_j} S_i \left[\frac{X_i}{X_j + X_i - \sqrt{X_j^2 + 2X_iX_j}}\right]. \quad (13)$$

where $\chi_0 = 3.8$.

The second scenario is that the interaction potential is not constant but increases slightly with volume fraction. Although not the preferred option for reasons stated earlier, multiplication of the HHF equation with a simple power function of solid content is observed to be sufficient to cause the theoretical yield stress curves to collapse onto a single normalized curve and show good correlation to the data of Figure 4. No scientific basis for such an approach is forthcoming at this stage.

The ultimate test of the model will only come from comparison to further experimental work on disparate systems under different background salt conditions. Such data sets are not available at present. Recent work (Liddell and Boger, 1996) on titania suspensions in which the yield stress was normalized as a function of pH in the same manner as in Figure 4, also showed excellent data overlap and no hint of a volume-fraction dependence of the data. The lower salt concentration used in this work and the wider volume fraction range makes the concept that the interaction potential is changing with volume fraction to be the more difficult of the preceding arguments to rationalize. Recent work on alumina at constant volume fraction (Zhou, 1997) for different particle sizes indicates that the data are also well described by Eq. 12. The volume-fraction dependence of these data is still to be elucidated. It is a reasonable indication nonetheless that the form of the model shown in Eq. 13 is indeed the best representation of the true scenario. If correct, the process of normalization of the yield-stress behavior as a function of pH is a powerful indicator of the form of the interparticle potential as a function of volume fraction. Only further work will show if it is a good indicator of volume-fraction-dependent changes in ζ. This will require work at higher volume fractions and different particle-size and salt concentrations. Such analysis will also be a powerful test of the h_0 and χ parameters.

It almost goes without saying that a more sophisticated, but a much more computationally complex, model of double-layer interaction incorporating a nonempirical form for the three-dimensional particulate structure would lead to better results, although the agreement with experiment of the current model is more than reasonable, especially once the structure and size-dependent terms are factored out through normalization.

Summary and Conclusions

In summary, we have derived a general expression for the shear yield stress that is able to describe the effect of particle-size distribution, solid loading, pH, and hence, electrokinetics of the suspension. The model incorporates two corrections relative to that presented earlier: (1) a minor shift in pH of the order of 0.18 unit due to mismatch between the iep-determined electrokinetically and the pH of maximum yield stress, and a (2) a further rearrangement of the terms describing the three-dimensional structure of the flocculated network such that the attractive and repulsive terms in the model describing the force of interaction has a classic form. As an aside, the expression in Eq. 11 has the potential for development of a new technique for measuring the zeta potential in concentrated slurries from purely mechanical–rheological measurements, without a knowledge of the particle-size distribution. This in itself is an exciting possibility, validating the importance of incorporating the interaction potential in the model.

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