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The influence of pH and temperature on the rheology and stability of aqueous titanium dioxide dispersions

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Abstract

The effects of pH and temperature on the rheology and stability of aqueous dispersions of rutile (titanium dioxide) were investigated systematically. The dispersions exhibit shear-thinning behaviour, conforming to the Herschel–Bulkley or the Casson-type models in the shear rate range investigated. Extreme sensitivity with pH was observed, whereby the dispersion viscosity can be changed by as much as an order of magnitude with pH variation at constant volume fraction. The temperature effect study indicates that the relative contribution of Brownian motion and shear flow to the viscosity is dependent on the flocculation state of the dispersion. The rheological behaviour of the dispersions in this study has been explained in terms of hydrodynamic interactions between particles as well as non-hydrodynamic interactions. These observations have important implications in crossflow microfiltration of these dispersions. © 1997 Elsevier Science S.A.

Keywords: Rheology; Titanium dioxide; Concentrated dispersions; pH; Thermal effects

1. List of symbols

a	radius of particle/m
k	Boltzmann constant/J K^{-1}
K	consistency parameter/Pas^n
n	flow index
$Pé_r$	rotational Péclet number
T	absolute temperature/K

Greek letters

γ	shear rate/s^{-1}
η	apparent viscosity/Pas
η_r	relative viscosity
μ_o	dynamic viscosity of water/Pas
η_∞	constant viscosity at the infinite shear limit/Pas
τ	shear stress/Pa
τ_C	yield stress in the Casson model/Pa
τ_{HB}	yield stress in the Herschel–Bulkley model/Pa
τ_r	relative shear stress

2. Introduction

The motivation for this study was to understand some aspects of the crossflow microfiltration of dispersions. Crossflow microfiltration of dispersions is encountered in a wide variety of engineering applications, such a solid–liquid separation, water purification, and drilling operations. The primary focus of our study is the crossflow microfiltration of concentrated dispersions of titanium dioxide in water. These concentrated dispersions arise in various industrial applications such as paints, coatings, and joint treatment compounds. These systems typically exhibit complex rheological behaviour [1,2].

Models based on the theory of fouling phenomena and concentration polarization and hydrodynamic models have been developed to predict the steady state permeate flux of crossflow microfiltration (see, for example, Davis [3] and Belfort et al. [4]). These models can be loosely categorized as being based either on a film theory, following a development based on convection of matter towards the membrane and diffusion of the retained species back into the crossflow, possibly incorporating lift forces, or on a cake theory which applies Darcy's law to relate the filtration rate to the average pressure difference between inside the filter and the permeate line. However, the applicability of these models over a wide range of operating conditions, including temperature, crossflow velocity, pressure drop, particle size, particle concentration in the dispersion, pH, and electrolyte concentration, is in doubt because they do not consider the influence of all of the significant terms and their outcomes. For any model to be

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realistic it must be able to show the effects of the dispersion viscosity and particle–particle interactions, which may have hydrodynamic or non-hydrodynamic origins. The qualitative difference in the crossflow microfiltration behaviour of non-Newtonian dispersions under constant tangential feed and constant inlet pressure conditions, shown, for example, by Vassilieff et al. [5], are not consistent with the predictions of these models.

The rheological properties of dispersions are governed by the microstructure of the system. In these systems, the solid particles are relatively small and the interparticle forces are significantly pronounced so as to influence the microstructure, the state of aggregation of the dispersion and, consequently, the mechanical and rheological properties of the system. Thus, it is of interest to study the rheological behaviour of these systems in order to understand and control the flow behaviour and stability of these materials.

Studies of the rheological behaviour of dispersions of titanium dioxide have been conducted by previous researches [6–10]. The effect of pH, flocculation, polyacrylic acid adsorption, processing, and particle concentration on viscosity has been studied at the ambient temperature. They found that for titanium dioxide dispersions a change in the particle size leads to totally different rheological behaviour, that is, the effects of moving from an electrostatically stabilized to a sterically stabilized dispersion were observed. The addition of surfactant into the solution and increasing the pH level caused an increase in ionic strength of the system. However, the reason for the change in the rheological properties with temperature is poorly understood. To understand this behaviour, it is the objective of this paper to study the effects of temperature and pH on the rheology of titanium dioxide dispersions by analysing the relative contribution of the interaction forces and their relationship with the microstructure of the dispersion.

3. Experimental

3.1. Materials

The titanium dioxide used was rutile supplied by Tioxide Group Ltd., England. Rutile (density 4260 kg m^{-3}) has a higher refractive index, higher density and greater chemical stability than anatase. The crystal size for rutile TiO_2 pigments, which is distinct from particle size (0.25–0.40 μm), is 0.17–0.24 μm. Transmission electron microscopy was used to estimate the shape and aspect ratio of the rutile crystals, which were found to be approximately elliptic and 2 to 3, respectively. The particle size distributions were measured using a MasterSizer MS20 (Malvern Instruments Ltd., UK).

The dispersions were prepared by mixing the appropriate amounts of millipore-filtered water and titanium dioxide in a high-shear, Ultra-Turrax T25, mixer (Janke and Kunkel, IKA-Labortechnik, Germany), with the help of the dispersant CALGON (sodium hexametaphosphate). The samples were prepared containing 0.15% by weight of dispersant. Even as the volume percent of solids was varied, the mass of dispersant per unit mass of solids was kept unchanged. This was to ensure that there was always an adequate amount of dispersant available for steric stabilization.

Zeta potential measurements to obtain information on the state of charge at the solid–liquid interface were carried out by means of a microelectrophoresis device (Zetasizer 3, Malvern Instruments Ltd., UK).

The pH level of the system was adjusted by adding various amounts of HCl or NaOH to deionised water, which was used as the suspending medium employed. All soluble acid and alkali reagents used were analytical grade. The pH was measured with a pH meter Model 80 (Griffin and George Ltd., UK). The dispersion was stirred until a steady pH reading was obtained.

3.2. Rheological measurements

A Carri-Med Model CS 100 controlled stress rheometer, with either a double concentric or cone and plate system, was used for the steady shear measurements. However, the cone and plate system was used for the highest volumetric concentrations of solids in the samples (50 vol%) only. The temperature of the samples was controlled by a Peltier system. All measurements except those of the temperature effect study were conducted under ambient conditions ($T=20$ °C). Measurements of the effect of temperature were conducted for temperatures ranging from ambient to 50 °C. The temperature was maintained to within ±0.1 °C of the desired preset value. Water evaporation was potentially a serious problem when the experiment was performed above 30 °C. Therefore, the interface exposed to the atmosphere was coated with a thin layer of silicone oil to minimize evaporation. The rheological measurements suggested the use of a model of the Herschel–Bulkley type

$$\tau = \tau_{HB} + K\gamma^{n} \quad (1)$$

or of the Casson type

$$\tau^{1/2} = \tau_{C}^{1/2} + (\eta_{\propto}\gamma)^{1/2} \quad (2)$$

to characterize the rheological behaviour of these dispersions [11]. The existence of a yield stress has been observed, especially at the highest volumetric concentrations of solids. This value has been obtained by taking the first 5% of the shear stress/shear rate pairs and fitting a straight line which is then extrapolated to zero shear rate. It is hoped that this will correlate with the yield stress obtained from controlled shear rate instruments which are unable to measure the yield value directly and therefore normally some form of extrapolation is used. In addition, it should be noted that a positive value for the hysteresis loop area was obtained and this indicates that the samples with the highest concentrations of the solids had some thixotropy. In order to match results taken by controlled shear rate instruments, it is occasionally necessary to test material under controlled shear rate conditions and in the shortest time, consistent with the rheology of the sample. It is possible to do this in flow mode by using a firmware control loop in the instrument to simulate shear rate conditions. This has the effect of eliminating the history of the system (energy input, time, temperature, etc.) and the particle migration across or along the gap in the concentric system [12].

4. Results and discussions

4.1. Effect of pH

The effect of pH on the rheological properties of 30 vol% titanium dioxide/water dispersions is shown in Fig. 1. The results in Fig. 1 show that the dispersions are shear-thinning and are characterized by non-linear flow curves that converge at low shear rate to the yield stress of the dispersion. The position of the shear-thinning flow curves is pH-dependent. This is due to the different degrees of flocculation in the dispersion at different pH. The high shear stress behaviour at extremely high pH (pH 13), as observed in Fig. 1, may be explained by the fact that the high ionic strength of the system (due to NaOH addition) can lead to a reduction of the electrical double layer thickness, and flocculation reoccurs due to van der Waals forces.

Fig. 2 shows the effect of pH on the apparent viscosity of 1, 10, 30, and 50 vol% titanium dioxide dispersions. The viscosity was evaluated at the shear rate of 500 s^{-1}. On the basic side (pH 7–14), the viscosity first decreases with pH, reaching a minimum near pH 9, and then increases as the pH becomes higher. The low apparent viscosity behaviour is a strong indication that the dispersions are dispersed. On the acidic side (pH 7–0), the same trend is observed. As the pH decreases (i.e. through the addition of more HCl), the ionic strength is raised. This can lead to a decrease of the electrical double layer repulsion and flocculations occur due to van der Waals attractions. The high viscosity behaviour at pH 4, as observed in Fig. 2, may be explained by this ionic strength effect. The pH at maximum viscosity should correspond to the isoelectric point of the titanium dioxide. The isoelectric point is the pH at which the electrophoretic mobility is zero, which occurs when there is no net surface charge on the colloidal particle. At a pH below the isoelectric point, the surface charge for most metallic oxides such as alumina, titania, zirconia, is positive which is attributed to the protonation of the surface hydroxyl group [13].

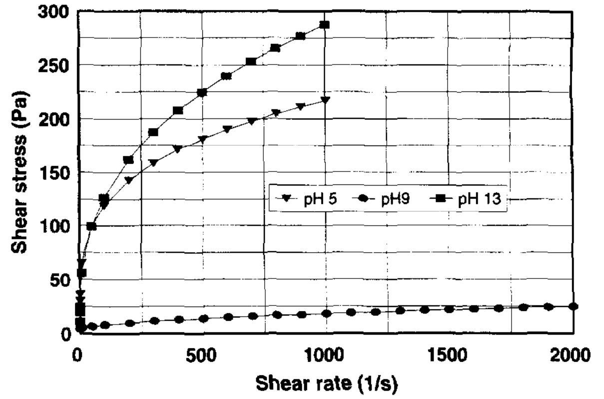

Fig. 1. Effect of pH on the flow properties of 30 vol% titanium dioxide dispersions at temperature 20 °C.

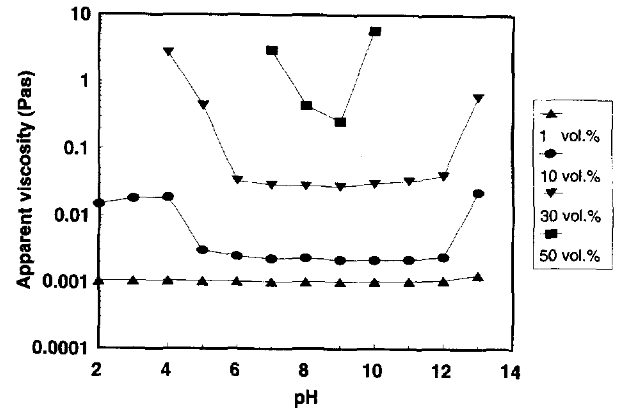

Fig. 2. Effect of pH on the apparent viscosity (evaluated at 500 s^{-1}) of 1, 10, 30, and 50 vol% titanium dioxide dispersions.

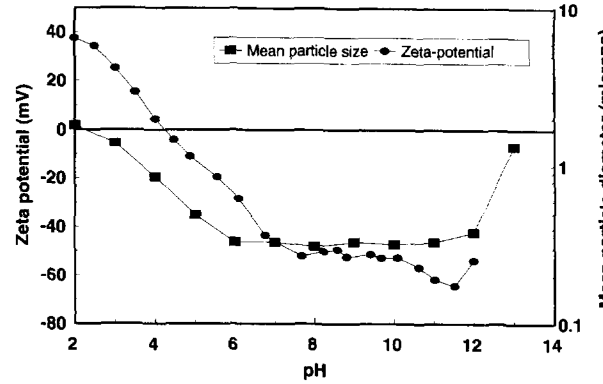

Fig. 3. The variation of zeta-potential and mean particle diameter with pH for rutile (titanium dioxide) used in the experiments.

In order to verify the effect of pH on the system behaviour, the zeta (ζ) potential vs. pH relationship was measured and is shown in Fig. 3. At pH 4.0, the ζ-potential was 4.4 mV, at pH 6.8 (the natural approximate pH of the dispersion) it was −43.6 mV, and at pH 9.4 it was −51.4 mV. The isoelectric point, or the point of zero electrophoretic mobility, is at pH 4.2. This value agrees well with a value of between 4 from the viscosity measurements and a value of about 5 obtained from particle size measurements (see Fig. 3). The electrophoretic mobility parameter, which is a measure of the velocity of a charged particle in an electric field, is dependent on the ionic strength, the presence of the dispersant, and the presence of an inorganic coating on the titanium dioxide particles. Since impurities are difficult to eliminate completely it is common to find a range in the isoelectric point quoted for the same material in the literature. A literature survey reveals that the isoelectric point reported for titanium dioxide varies from pH 4.0 to 6.1 [8,14,15].

A plot of the variation of the apparent viscosity (evaluated at 500 s^{-1}) as a function of the volumetric concentration of

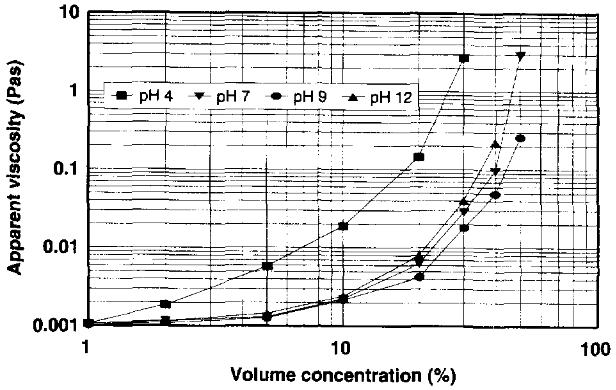

Fig. 4. Variation of apparent viscosity (evaluated at 500 s^{-1}) with the concentration of titanium dioxide dispersions used.

solids and pH (Fig. 4) shows that the viscosity increases strongly above the concentration of 10 vol% and depends on the pH of the dispersions. The results in Fig. 4 also show that the difference in viscosity between the different states of flocculation or dispersion can be very large. For example, one order of magnitude difference in viscosity is observed between the flocculated 10 vol% dispersion at pH 4 and the dispersed state dispersion at pH 9. The apparent viscosity is about 2.2 mPa s for the dispersed 10 vol% dispersion and 19 mPa s for the flocculated dispersion at pH 4.

4.2. *Effect of temperature*

The rheological behaviour of 10 and 30 vol% titanium dioxide dispersions at different temperatures and also at different pH values are shown in Figs. 5 and 6. The results in Figs. 5 and 6 show that the dispersions are shear-thinning and are characterized again by a non-linear flow curve for all temperatures studied. The mechanism of shear-thinning of a dispersion of fine particles is a result of a reduction in the effective volume of the disperse phase caused by deflocculation of the particles upon shearing [16]. In the case of sterically stabilized systems, partial compression of the steric barrier due to shear, and therefore a reduction in the hydrodynamic volume fraction, could be the cause of shear-thinning [17]. Figs. 5 and 6 also show low and intermediate shear regions in certain conditions. In the low shear limit, Brownian motion of the particles is expected to be in control, whereas in the high shear limit the shear-induced motion (hydrodynamic effects) dominates over the Brownian contribution to the particle interactions. The location of the intermediate shear-thinning region will depend upon the relative strength of Brownian and shear-induced contributions. This balance will be affected by several parameters such as particle size, temperature, and concentration. Temperature has a strong effect on the apparent viscosity of the dispersions. In all cases, the apparent viscosity η of the dispersions decreased with temperature.

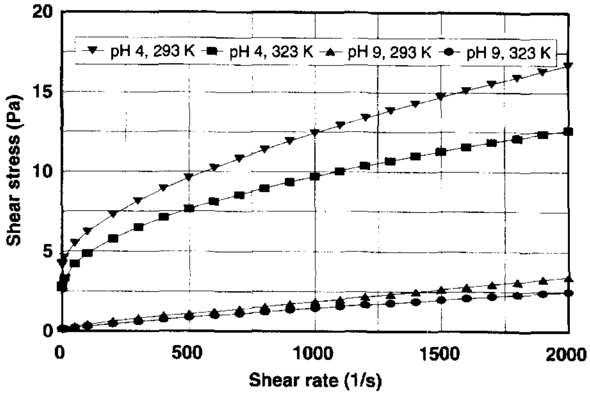

Fig. 5. Effect of temperature on the flow properties of 10 vol% titanium dioxide dispersions at pH 4 and pH 9.

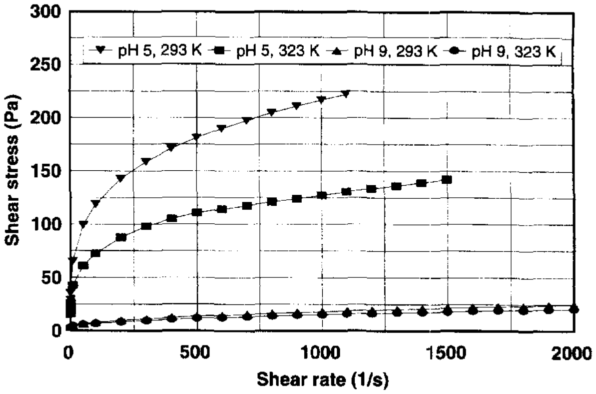

Fig. 6. Effect of temperature on the flow properties of 30 vol% titanium dioxide dispersions at pH 5 and pH 9.

A discussion of the theoretical aspects of Brownian motion has been given by several authors including Brenner [18]. Brownian motion can be conveniently decomposed as a rotational Brownian motion and a translational Brownian motion. For systems subjected to simple shear flow, the effects of Brownian motion and shear are superimposed and their relative importance is governed by the magnitude of the rotational and translational Péclet number. For spherical particles, the rotational Péclet number is defined as

$$\text{Pé}_r = 8\pi\mu_0\gamma a^3/kT \qquad (3)$$

where μ_0 is the viscosity of the medium (water), γ is the shear rate, a is the radius of a particle, k is the Boltzmann constant, and T is the absolute temperature. According to Eq. (3), increasing Pé_r corresponds to increasing shear rate γ. Thus, the dispersion displays shear-thinning behaviour. This shear-thinning behaviour for dispersions of non-spherical particles can be explained as follows. The shear flow tends to promote alignment of the particles in such a manner as to alleviate the viscous stress and, hence, to reduce the viscosity. The rotational Brownian motion, on the other hand, tends to randomize the particle orientations, thereby destroying the alignment and increasing the viscosity. This corresponds to high viscosity at low Pé_r. Therefore, shear and Brownian motion have opposite effects on the dispersion viscosity, and both effects can be correlated to a single dimensionless variable, Pé_r (Brenner [18]).

In order to verify whether or not Brownian interactions are the dominant mechanism in these dispersions, temperature

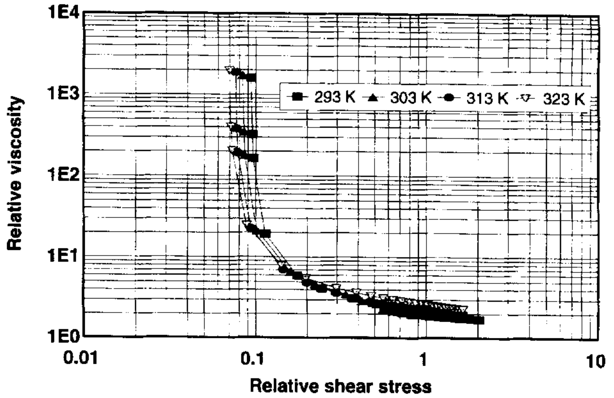

Fig. 7. Temperature scaling for 10 vol% titanium dioxide dispersions at pH 9.

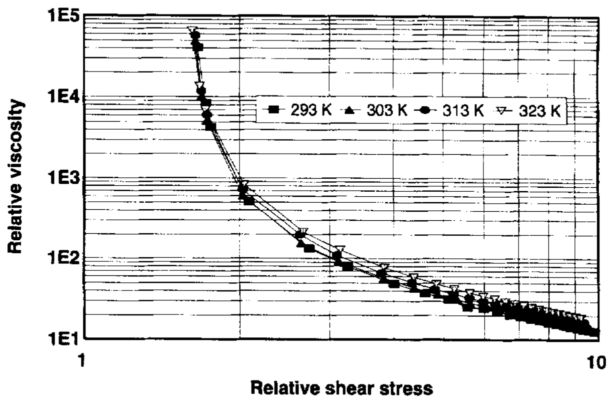

Fig. 8. Temperature scaling for 30 vol% titanium dioxide dispersions at pH 9.

scaling is applied. The rheology of suspensions of Brownian hard spheres has been studied using the dimensional analysis of Krieger [19,20]. This dimensional analysis reveals a unique relationship between the relative viscosity η_r and the dimensionless shear stress τ_r

$$\eta_r = \eta/\mu_o = f(\eta\gamma a/kT) \qquad (4)$$

If the curves at different temperatures superimpose upon one another, the dispersion is said to be governed by Brownian interactions. The plot of the experimental data using the above relations is shown in Figs. 7–9. It can be seen that the curves for different temperatures superimpose very well. However, for the 10 vol% dispersion, the curves at low values of τ_r deviate from one another. The interactive forces other than the Brownian motion were probably responsible for the lack of scaling achieved for this dispersion. The superposition at high shear for all dispersion concentrations used indicates that hydrodynamic forces dominate the flow behaviour in this regime, whereas in the low shear regime the rheology of the 30 and 50 vol% dispersions is controlled by Brownian forces.

In order to clarify the effect of temperature on the interactive forces between particles, the rheogram of the shear stress of the dispersions (τ) against the shear stress of the medium ($\mu_0\gamma$) at various temperatures is shown in Fig. 10. This method is based on the mechanism of a degree of agglomeration which is a result of the dynamic equilibrium

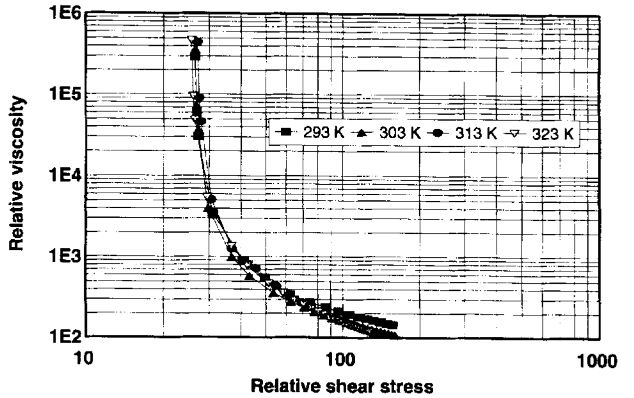

Fig. 9. Temperature scaling for 50 vol% titanium dioxide dispersions at pH 9.

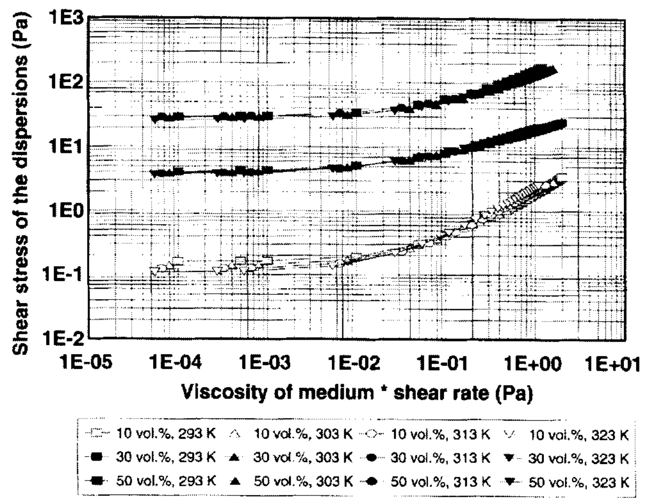

Fig. 10. Rheogram of the shear stress of the dispersions against the shear stress of the medium at various temperatures for 10, 30, and 50 vol% titanium dioxide dispersions at pH 9.

(determined by hydrodynamic forces) and interactive forces between particles. If the particle–particle interaction force is not affected by temperature, one master curve can be obtained in this manner for various temperatures. Using this master curve, the viscosity of the dispersion can be estimated at any temperature, because the viscosity of the medium is already known.

The results shown in Fig. 10 did not produce a single master curve for the 10 vol% dispersion, indicating that a change in the interactive forces took place with temperature. It can be seen from this figure that an increase in temperature produces a reduction in the dispersion shear stress. This observation can be explained as a result of a decrease in the interactive forces between particles with temperature. Fig. 10 also shows for the 10 vol% dispersion that at low shear rates the relative viscosity (which is represented by the ratio of ordinate to abscissa) is dominated by the interparticle interaction (no single master curve achieved), whereas at high shear rates the hydrodynamic force is more important (master curve obtained).

In summary, we note that in the absence of shear the equilibrium structure of the dispersion and the viscosity both depend on the balance between Brownian motion forces on the one hand and electrostatic, steric and van der Waals forces on the other. The effect of shear flow is always to align particles and consequently to lower the viscosity.

5. Conclusions

The rheological measurements for titanium dioxide dispersions of different concentrations have indicated that their rheological behaviour is of the shear-thinning type. This behaviour can be modelled by the Herschel–Bulkley or Casson rheological relationships. The results also show that the apparent viscosity increases sharply with increasing volumetric concentration of solids when the latter exceeds 10 vol%.

The results of the pH effect study indicate that it is possible to control the flocculation state and, consequently, the rheological behaviour of titanium dioxide dispersions by adjusting the pH level of the system. The mechanism by which pH affects the system behaviour is by influencing the surface charge of the titanium dioxide particles and, consequently, the electrostatic attraction between these particles.

The temperature effect study indicates that the relative contribution of Brownian motion and shear flow to the viscosity is dependent on the concentration of the dispersion. For concentrated dispersions, Brownian motion promotes particle–particle interactions. However, the effect of Brownian motion on the 10 vol% dispersion was found to be much less significant than for concentrated dispersions. Our work shows that for such concentrated aqueous dispersions of the titanium dioxide, temperature-independent curves can be obtained if one plots the relative viscosity against the relative shear stress in dimensionless form.

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References

[1] Th.F. Tadros, Physical stability of suspension concentrates, Adv. Colloid Interface Sci. 12 (1980) 141–261.
[2] D.A.R. Jones, B. Leary, D.V. Boger, The rheology of concentrated colloidal suspension of hard spheres, J. Colloid Interface Sci. 147 (1991) 479–495.
[3] R.H. Davis, Modeling of fouling of crossflow microfiltration membranes, Sep. Purif. Methods 21 (1992) 75–126.
[4] G. Belfort, R.H. Davis, A.L. Zydney, The behaviour of suspensions and macromolecular solutions in crossflow microfiltration, J. Membr. Sci. 96 (1994) 1–58.
[5] C.S. Vassilieff, I.G. Momtchilova, R.A. Krustev, Cross-flow microfiltration of kaolinite-in-water dispersions, Colloids Surf. A 92 (1994) 231–247.
[6] K. Umeya, T. Kanno, Effect of flocculation on the dilatant flow for aqueous suspensions of titanium dioxides, J. Rheol. 23 (1979) 123–140.
[7] A.S. Rao, Rheology of aqueous dispersions of alumina, titania and a mixture of alumina and titania powders, J. Dispersion Sci. Technol. 8 (1987) 457–465.
[8] H. Strauss, H. Heegn, I. Strienitz, Effect of PAA adsorption on stability and rheology of TiO_2 dispersions, Chem. Eng. Sci. 48 (1993) 323–332.
[9] P.V. Liddell, D.V. Boger, Influence of processing on the rheology of titanium dioxide pigment suspensions, Ind. Eng. Chem. Res. 33 (1994) 2437–2442.
[10] T. Sato, Effect of particle concentration on physical properties of titanium dioxide suspensions, J. Dispersion Sci. Technol. 17 (1996) 83–96.
[11] Q.D. Nguyen, D.V. Boger, Measuring the flow properties of yield stress fluid, Annual Rev. Fluid Mech. 24 (1992) 47–88.
[12] D. Leighton, A. Acrivos, The shear-induced migration of particles in concentrated suspensions, J. Fluid Mech. 181 (1987) 415–439.
[13] Y.K. Leong, D.V. Boger, D. Parris, Surface and rheological properties of zirconia suspensions, Trans IChemE, Part A 69 (1991) 381–384.
[14] W.R. Bowen, X. Goenaga, Properties of microfiltration membranes. Part 3. Effect of physicochemical conditions on crossflow microfiltration at aluminium oxide membranes, I. Chem. E. Symp. Ser. 118 (1990) 107.
[15] R. Hunter, Foundations of Colloid Science, Vol. I, Oxford Science Publications, Oxford, 1987, p.386.
[16] J. Mewis, A.J.B. Spaull, Rheology of concentrated dispersions, Adv. Colloid Interface Sci. 6 (1976) 173–200.
[17] C.E. Chaffey, I. Wagstaff, Shear thinning and thickening rheology. II. Volume fraction and size of dispersed particles, J. Colloid Interface Sci. 59 (1977) 63–75.
[18] H. Brenner, Suspension rheology, in: W. Schowalter (Ed.), Progress in heat and mass transfer. Vol. 5, Pergamon, Oxford, 1972, pp.89–129.
[19] I.M. Krieger, T.J. Dougherty, A mechanism for non-Newtonian flow in suspension of rigid spheres, Trans. Soc. Rheol. 3 (1959) 137–152.
[20] I.M. Krieger, A dimensional approach to colloid rheology, Trans. Soc. Rheol. 7 (1963) 101–109.