PII: S0955-2219(98)00147-2
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0955-2219/98/$—see front matter

Optimising the Dispersion on an Alumina Suspension Using Commercial Polyvalent Electrolyte Dispersants

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(Received 23 January 1998; accepted 16 May 1998)

Abstract

This paper describes the process optimisation of certain alumina ceramic aqueous suspensions by the use of three commercial and widely used dispersants. Three different commercially available dispersants — 'Darvan C' an ammonium poly(methacrylate), (R. T. Vanderbilt Company, Inc., USA), 'Aluminon' (aurintricarboxylic acid ammonium salt, Fluka Chemicals, UK) and 'Tiron' (4-5-dihydroxy-1, 3-benzenedisulfonic acid disodium salt, Fluka Chemicals, UK) have been employed as aqueous ceramic stabilising agents for a commercial alumina. It is shown that there is a critical concentration for each dispersant, which gives the lowest viscosity and other rheological parameters such as, the complex, storage and loss moduli. This critical concentration, which provides the lowest viscosity (called here the optimum concentration), was found as 1, 0·25 and 0·10 wt% for 'Darvan C', 'Aluminon' and 'Tiron', respectively, for the current alumina. The adsorption isotherm data show that, up to the optimum concentration, the dispersant molecules adsorb onto the alumina particles with a relatively high affinity. Beyond this concentration, the additive is virtually unadsorbed and then remains in the supernatant liquid and consequently interferes with the stabilising influence of the adsorbed species. Electrophoresis experiments have also been performed to measure the electrical potential of the alumina particles and to further establish a link to the origin of the concentration dependent stability of these suspensions.

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1 Introduction

A fundamental appreciation of the factors involved in colloidal ceramic processing, is a key element in the cause to attain and improve the desired properties of different types of ceramic materials. This is particularly the case for engineering ceramics where the mechanical strength can be improved by a factor of 3 to 4 by adopting the principals of colloidal chemistry in order to produce the most extensively dispersed particulate medium. An efficient use of organic or inorganic additives, which are generally surface active and control the inter-particle forces, which in turn affect the rheology of the system, is required. In many cases, the first goal is to obtain a green body in which the particles are homogeneously packed, inter-particle pores are small and narrowly distributed and free from localised excesses of organic or inorganic inclusions. By this route good quality sintered bodies may be produced.

Colloidal ceramic suspensions are widely used in wet ceramic processing[†] techniques such as slip casting, tape casting, pressure casting and centrifugal casting. Fine ceramic particles which are in the colloidal range ($\leq 1\,\mu m$) usually spontaneously aggregate in the dispersing medium due to the relatively high strength of the inter-particle van der Waals attractive forces. It is, therefore necessary to reduce the effect of these attractive van der Waals forces in order to impart a resistance against aggregation. In practice, this stability is achieved by introducing a repulsive force barrier between the particles. This repulsive barrier can be basically achieved by two generic mechanisms:

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A wet processing method in one in which a ceramic powder is mixed in a liquid in order to attempt to homogenise all the ingredients. The wet processing methods cover a major area of ceramic processing engineering.

1. Electrostatic stabilisation, and
2. Steric stabilisation.[1–5]

In the electrostatic stabilisation mechanism the charged particles develop an extended layer of oppositely charged ions in a polar (generally aqueous) medium, called an electrical double layer. When two such charged layers overlap, there is a repulsion between them and hence the particles remain separated.[1–6] The range of the double layer interaction decreases as the concentration of the oppositely charged ions in the aqueous medium increased.[2,6] Thus, it is reduced when 'screening' (oppositely charged) ions are introduced into the continuous medium; that is when the ambient ionic strength is increased. Steric stabilisation, on the other hand, is achieved by adsorbing or grafting a polymeric entity onto the particles. The adsorbed/grafted polymer more or less extends into the dispersion medium and the particles become stabilised due to the repulsion of the extended polymer layers in the continuous phase.[2–5] If the polymer is a polyelectrolyte, at certain pH values, it may provide a dual stability effect, which is called an electrosteric stabilisation.[2,3,5,6] All these factors operate in the present systems.

Metal oxides particles (and many other ceramic powders as well) may attain an electrical charge, depending upon the pH of the aqueous suspending medium, due to the dissociation/association of surface hydroxyl group with H^+/OH^- ions.[7–11] Dispersants which are primarily polyelectrolyte or polyvalent salts are often used to prepare well disperse ceramic suspensions. There are numerous and different kinds of dispersant used in the ceramic processing.[12,13] The dispersant molecules adsorb onto the surface of the ceramic particles and attain an electrical charge due to the dissociation of the chemical functional groups on the dispersant. The electrical charge on the dispersant, when adsorb onto the ceramic particles, becomes effectively the charge on the particles. Recently, a study that describes the effect of the molecular structure of low molecular weight organic dispersants, upon the adsorption and the dynamic electrophoretic mobility behaviour of alumina suspensions, has been reported.[14] In this study the number and the position of (–COOH) and (–OH) surface-active groups of the dispersants were systematically changed, and their behaviour compared with each other at different pH values. It was found that the adsorption and the dynamical electrophoretic mobility behaviour of the suspensions depend upon the number and the position of the surface-active groups. In this way the suspensions prepared using such dispersants become stable. In this paper we investigate and report the effects of three different dispersants namely, 'Darvan C' (R. T. Vanderbilt Company, Inc., USA), 'Aluminon' (Fluka Chemicals, UK) and 'iron' (Fluka Chemicals, UK), on the stability of a particular group alumina suspensions. 'Darvan C' is a polyelectrolyte whilst the other two are polyvalent organic salts. The stability of the suspensions is investigated using adsorption isotherms, electrophoresis and rheological measurements.

2 Experimental

2.1 Materials

Alumina AES-11 used in this study was 99·8% pure, which had a BET area of 8·14 m^2 g^{-1}, a mean particle size of 0·4 mm and was obtained from Mandoval Ltd, Surrey, UK. Three types of commercially available and practically used dispersants, with different types of molecular structure were used for the preparation of the aqueous suspensions. These commercial dispersants were:

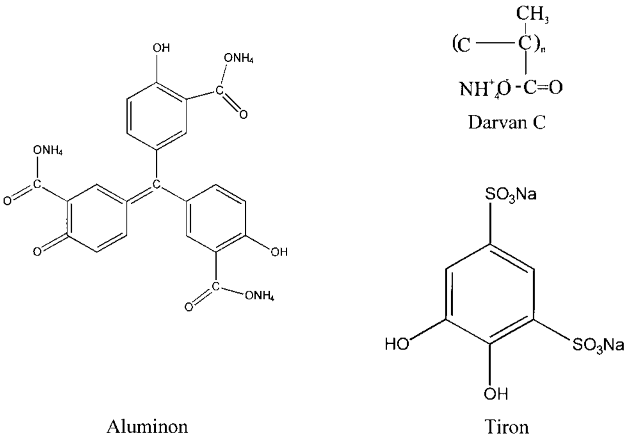
1. 'Darvan C' an ammonium salt of poly (methacrylate) (R. T. Vanderbilt Company, Inc, USA)
2. 'Tiron' (Fluka Chemicals, UK)
3. 'Aluminon' (Fluka Chemicals, UK)

'Tiron' ($C_6H_4Na_2O_8S_2$) is mainly composed of 4-5-dihydroxy-1,3-benzenedisulfonic acid disodium salt and is also called pyrocatechol-3,5-disulfonic acid disodium salt, with a molecular weight of 332·20 and an active component concentration of >99% (according to the supplier). 'Aluminon' ($C_{22}H_{23}N_3O_9$) is primarily aurintricarboxylic acid ammonium salt, with a molecular weight of 473·44 and active component concentration of >95% (according to the supplier). 'Darvan C' is the ammonium salt of poly(methacrylate), available in the form of an aqueous solution which contains 25% of the active component. All of these dispersants are soluble in water in all proportions. The commonly accepted chemical structure of the three dispersants is shown in Fig. 1.

The water used in all the experiments, to make different suspensions/samples, was taken from a Purite (Purite Ltd., Oxon, UK) water purifying unit, which uses a combination of deionisation and reverse osmosis processes.

2.2 Sample preparation, rheological and electrophoretic mobility measurements

A Bohlin VOR rheometer (Bohlin Rhelogi, Lund, Sweden) was used for the rheological characterisation of the suspensions which were dispersed using a ultrasonic probe; Vibra-Cell VCX 600 (Sonic and



Darvan C

Aluminon

Tiron

Fig. 1. Molecular structure of the three dispersant used. For 'Darvan C' *n* is between 100 and 160 (Mw 10 000–16 000).

Materials, CT, USA). The electrophoretic mobility of the suspensions was carried out using a Zeta Master (version PCS, Malvern Instruments, UK) microelectrophoresis instrument. The average mobility was taken from the mean of at least 15 different experimental runs.

Before performing rheological characterisation, the samples were presheared at a very high shear rate of 960 s^{-1} for ca 3–4 min followed by at least a 2 min rest period in order to provide a common and consistent shear history for the systems. The viscosity at low shear rates was measured first, stepping up to higher shear rates, covering the shear rate range of 10^{-1} to 10^{3} s^{-1}. All the experiments were performed at 25°C. Initially, for the dynamic measurements a 'strain sweep' measurement was performed in which the imposed strain amplitude was varied while the frequency was maintained constant at 1 Hz. The values of the G^*, G' and G'' moduli were measured as a function of the strain in order to identify the so-called 'linear viscoelastic region' in which the viscoelastic properties of the system are relatively independent of the applied strain. After identifying the linear viscoelastic region, the imposed strain was fixed within this region and the frequency was varied (usually from 0·05 to 10 Hz). This is called here the 'oscillatory measurement'. The results reported in this paper are for a frequency of 1 Hz.

All the suspensions used for rheological characterisation contained 40% by volume alumina powder. The methods used to prepare suspensions, as well as the details of the electrophoretic mobility and rheological measurements are essentially the same as those described elsewhere.[15]

2.3 Adsorption isotherms

Stock solutions containing 1% w/v of the dispersants ('Aluminon' and 'Tiron') were prepared and then diluted to 40 ml aliquots of known concentration using deionised water. For the 'Darvan C' case, the concentration of the stock solution prepared was 4% w/v. Using approximately 15 ml of these aliquots, eight or so suspensions containing about 5 g of the ceramic powder were prepared. For the 'Aluminon' dispersant the concentration ranged from 0 to 1% dwb of the dry oxide powder; for 'Darvan C' 0 to 4% dwb and for 'Tiron' the concentration range was 0 to 0·5% dwb. All the suspensions were first ultrasonicated and then equilibrated for 48 hours in a tumbler agitator in sealed glass tubes. The particles were separated by using an MSE 25 centrifuge at 13 000 rpm for 6 h and the clear supernatant was carefully removed for subsequent spectroscopic characterisation in order to ascertain the composition of the solution.

A UV-Vis Spectrophotometer (Perkin–Elmer 554) was used to measure the concentration of the supernatant dispersant resulting from the separation of the particles. In order to quantitatively asses the adsorbed amount of the dispersant, calibration curves were constructed for all the three dispersants. The wavelengths 528, 288 and 232 nms were used for the 'Aluminon', 'Tiron' and 'Darvan C' dispersants, respectively, in order to monitor the dispersant concentration From the calibration curves the difference in concentration before and after the adsorption were calculated in order to compute the adsorption isotherms.

In addition to the UV-visible absorbance measurements, a potentiometric titration method was also used to evaluate the amount of the dispersant adsorbed. First, a stock solution (100 ml) containing 1% w/v of the ceramic powder was prepared. Twenty ml of this solution was taken and the pH was adjusted to 3·5 with 0·1 M HNO_3. At this pH the surface active groups of the dispersants are completely associated. The volume of the base (0·1 M KOH) required to attain a pH value of 9·5 was then noted. At this pH the surface active groups of the dispersant are completely dissociated. The stock solution was diluted with water to produce a series of 20 ml aliquots of known concentration. The same procedure was repeated for eight or so samples and a calibration curve (a straight line), as the volume of the base as a function of equilibrium concentration of the dispersant, was constructed. The same procedure was repeated for the supernatants, and the difference in the volume of the base used was noted. The amount of the dispersant adsorbed was then calculated. A slight difference in the calculated adsorbed amount of the dispersant was found in the results computed for the two methods (see below).

The concentrations of the dispersants given here in this paper are on a wt% basis which is equivalent to the dry weight of the powder basis (dwb) and are based upon the ‘as supplied sample’ mass and not upon the active compound basis.

2.4 Sedimentation

Suspensions containing 15 ml of water and 5 g of alumina AES-11 power with varying amounts of ‘Aluminon’ and ‘Tiron’ dispersant were ultrasonicated and left in cylindrical tubes for ca. 4 months before the heights of the sediments were measured.

3 Results and discussion

Figure 2 shows the adsorption isotherms of ‘Aluminon’, ‘Tiron’ and ‘Darvan C’ on alumina AES-11 at 25°C. It can be seen that all of these three dispersants have a rather high affinity for adsorption onto the alumina AES-11. Concentrations corresponding to 0·25%, 0·125% and 1% dwb of ‘Aluminon’, ‘Tiron’ and ‘Darvan C’, respectively, adsorb onto the alumina particles with negligible equilibrium ambient concentrations remaining in the aqueous phase. The difference observed in adsorption isotherms using two different techniques for ‘Aluminon’ and ‘Tiron’ is probably due to the shift in the adsorption peaks, which were used to construct the calibration curves, before and after adsorption.

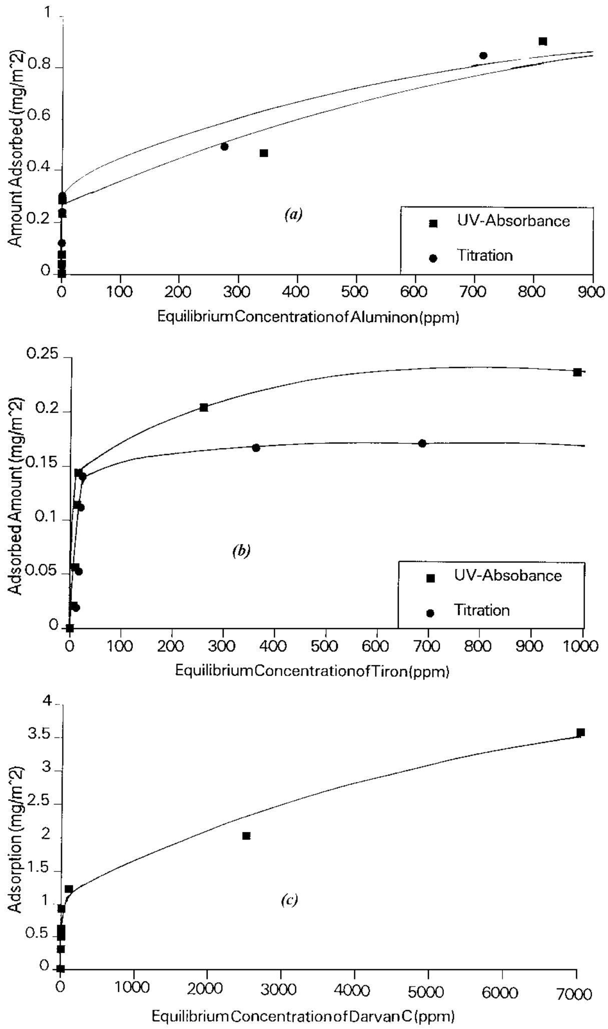


Fig. 2. Adsorption isotherms, the amount of dispersant adsorbed on Alumina AES-11 as a function of equilibrium using two methods (UV-absorbance and titration) at 25°C: (a) ‘Aluminon’ and (b) ‘Tiron’; (c) ‘Darvan C’ (UV-obsorbance only).

The isoelectric point (iep), the pH value where the net electric potential on the particles is zero, for the alumina AES-11 was found to be at pH ~7·5 when no dispersant was adsorbed. The iep shifted to pH ~4·0 when 1% dwb ‘Darvan C’ was incorporated.[12,16]

In Fig. 3 the electrophoretic mobility of alumina AES-11 at a pH 7·2, as a function of the dispersant concentration, is shown. The figure shows that, as the adsorbed concentration of the dispersant is increased from 0 to 0·02% dwb, the electrophoretic mobility at pH 7·2 increases to a more positive value and when more dispersant is added the electrophoretic mobility changes sign (polarity) indicating that the particles are now negatively charged. Any further addition of the dispersant increases the absolute value of the electrophoretic mobility of the particles. This change in the electrophoretic mobility of the particles is consistent with the behaviour observed in the adsorption isotherm experiments (Fig. 2). The more dispersant that is adsorbed gives rise to a more negative electrophoretic mobility of the particles. The maximum observed in Fig. 3, when the concentration of the dispersant was 0·02% dwb, maybe due to the fact that at low concentrations, the dispersants effectively act as a ‘screening’ salt and thereby causes a change in the electrophoretic mobility. However, it is not certain that the latter effect causes the peak observed.

To establish the critical optimum dispersant concentration, that is the amount which gives the lowest viscosity, the concentrations of the dis-

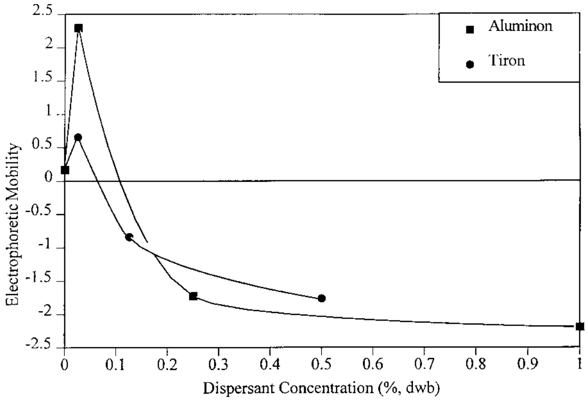


Fig. 3. Electrophoretic mobility of alumina AES-11 as a function of two dispersants (‘Aluminon’ and ‘Tiron’) concentration at a pH 7·2 ± 0·1.

persants were varied for a fixed volume fraction of the particulate material.

In Figs 4–6 the viscosities of 40% (v/v) suspensions, as a function of the concentration of 'Darvan C', 'Aluminon' and 'Tiron', are shown at three different shear rates. The optimum amount of the dispersants, which gave the lowest viscosity at all the shear rates, is ca 1% dwb for 'Darvan C', ca 0·25% dwb for 'Aluminon' and about 0·125% dwb for 'Tiron'. This concentration corresponds to a surface coverage of 1·23, 0·31 and 0·125 mg m^{-2} for 'Darvan C', 'Aluminon' and 'Tiron', respectively.

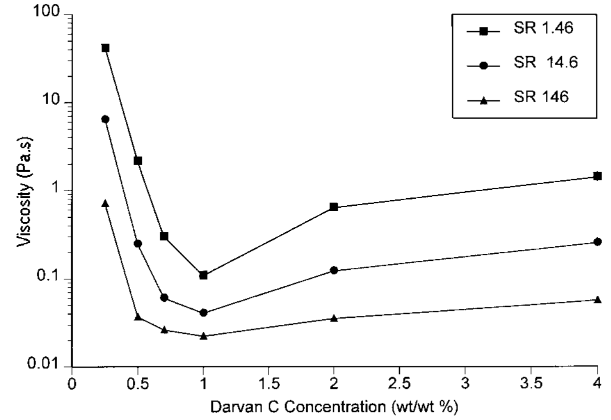


Fig. 4. Viscosity of alumina AES-11 40% v/v suspensions as a function of 'Darvan C' concentration (% dwb) at three different shear rates (SR) (1·46, 14·6 and 146 s^{-1}).

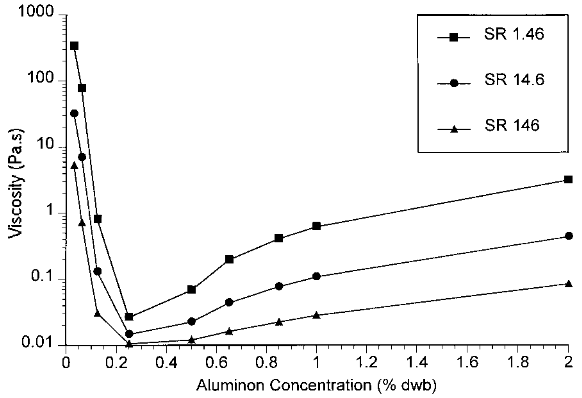


Fig. 5. Viscosity of alumina AES-11 40% v/v suspensions as a function of 'Aluminon' concentration (% dwb) at three different shear rates (SR) (1·46, 14·6 and 146 s^{-1}).

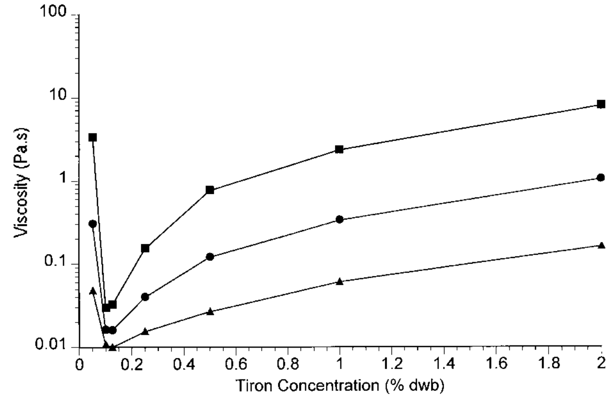


Fig. 6. Viscosity of alumina AES-11 40% v/v suspensions as a function of 'Tiron' concentration (% dwb) at three different shear rates (■ 1·46, ● 14·6 and ▲ 146 s^{-1}).

Dynamic rheological results for the alumina AES-11 40% (v/v) suspensions, as a function of the 'Darvan C' concentration, at frequency of 1 Hz, are shown in Fig. 7. The dynamic viscosity shows the same trends that were observed in the shear viscosity data at a shear rate 1·46 s^{-1}. However, the dynamic viscosity is several orders of magnitude higher than that of shear viscosity at 0·25 and 0·5% dwb. Moreover, for concentrations close to the optimum value and higher, i.e. 0·7% dwb of 'Darvan C', and for the higher the shear viscosity at a shear rate of 1·46 s^{-1} the dynamic viscosity at 1 Hz is similar. Both the values of storage modulus, G′, and the complex modulus, G*, are significantly higher than those of the loss modulus, G″, at all the concentrations of 'Darvan C' more than 1% and less than 0·5% dwb. However, at 'Darvan C' concentrations between 0·5 and 1% dwb the difference in the G′ and G″ values is small. When the concentration of the 'Darvan C' is increased to more than 1% dwb the values of loss, storage and complex moduli increase gradually.

When the 'Aluminon' and 'Tiron' materials are used as the dispersants for the alumina AES-11 40% (v/v) suspension, the dynamic rheological results are similar to those of the 'Darvan C' suspensions; i.e. the complex, storage and loss moduli first decrease as the concentration of the dispersants is increased. At the concentrations of 0·25% dwb for 'Aluminon and 0·10% (0·125%) dwb for 'Tiron', i.e. the optimum concentrations, all of the moduli and the dynamic viscosities have their lowest values (Figs 8 and 9). When the concentration of the dispersant is increased beyond the optimum value, the storage,

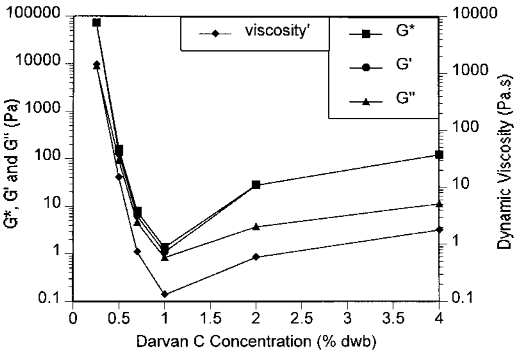


Fig. 7. G*, G′, G″ and dynamic viscosity of alumina AES-11 40% v/v suspensions against 'Darvan C' concentration (% dwb) at a frequency of 1 Hz.

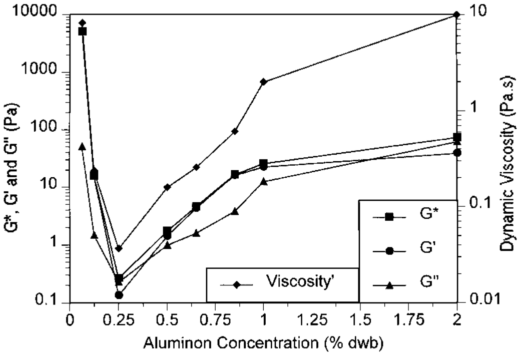


Fig. 8. G*, G′, G″ and dynamic viscosity of alumina AES-11 40% v/v suspensions against 'Aluminon' concentration (% dwb) at a frequency of 1 Hz.

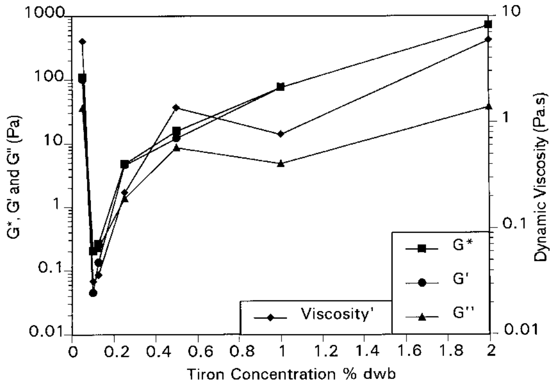


Fig. 9. G*, G′, G″ and dynamic viscosity of alumina AES-11 40% v/v suspensions against 'Tiron' concentration (% dwb) at a frequency of 1 Hz.

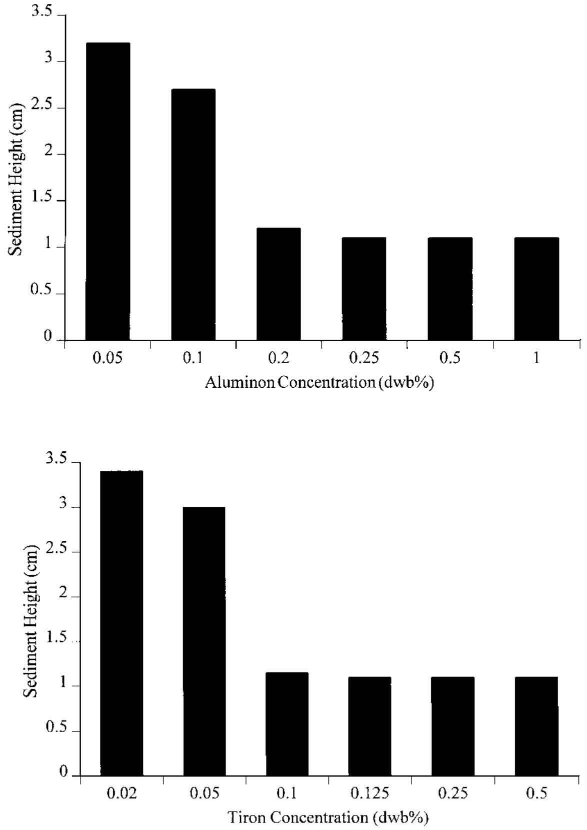


Fig. 10. Sediment height of Alumina AES-11 against dispersant concentration: (top) 'Aluminon' and (bottom) 'Tiron'.

the complex, as well as the loss moduli, increase appreciably and the loss modulus is less than the storage and the complex moduli except at the optimum concentration. The dynamic viscosity is of a comparable magnitude to that of the shear viscosity at a shear rate of 1·46 s^{-1} except at low concentrations where the two viscosities differ significantly. These trends are essentially the same as those that were observed for the shear viscosity against the dispersant concentration trends, and are due to the same reasons which were explained earlier.

Figure 10 depicts the sedimentation height plotted against the concentration of 'Aluminon' and 'Tiron'. It is shown that, as the concentrations is increased, the sediment height decreases indicating that a more consolidated structure of the particulate is formed. After reaching a minimum the further increase in the dispersant concentration makes no difference to the sediment height. The minimum concentration which gives the least sediment height is, ca 0·20–0·25% dwb for 'Aluminon' and ca 0·10–0·125% for 'Tiron'. The amounts of the 'Aluminon' and 'Tiron' dispersants which give the lowest viscosities (and other parameters) agree well with those found in the sedimentation experiments for which the optimum amount (least concentration of the dispersant to give the minimum sediment height) was found to be between 0·10 and 0·125% dwb for 'Tiron' and between 0·20 and 0·25% dwb for 'Aluminon'. Although there are different particulate volume fractions involved in the sedimentation and rheological experiments, the correspondence in the optimum amount values of the dispersants is very good. Comparing the rheological and the adsorption isotherms results when 'Darvan C', 'Aluminon' and 'Tiron' are used as dispersants, it can be seen, from Fig. 2, that the concentration of the dispersants which gives the lowest viscosity (and also the other rheological parameters) for the alumina AES-11 suspensions corresponds to the situation where virtually all of the dispersants are adsorbed and there is also a negligible amount of the free dispersant remaining in the continuous phase.

As the concentration of the free dispersant is increased above the optimum amount, the equilibrium solution concentration of the dispersants increases. This excess equilibrium bulk concentration of the dispersants now acts as a free electrolyte in the suspension disturbing the electrostatic forces within the system and hence increasing the viscosity. The various rheological, sedimentation and adsorption isotherm measurements are in good common agreement with each other suggesting that the a monolayer of the dispersants adsorbed onto the alumina AES-11 particulate provides the optimum stability under the experimental conditions adopted in this study.

4 Conclusions

The three commercial dispersants 'Darvan C', 'Aluminon' and 'Tiron', which have been investigated with regard to their effect upon the stabilisation of the alumina AES-11 suspension, are all found to be capable of producing well stabilised suspensions. This is noted in both the rheological and sedimentation studies. However, the viscosities of the 'Darvan C' stabilised suspensions are slightly higher than those of the 'Aluminon' and 'Tiron' systems. The electrophoretic mobility measurements and adsorption isotherms are consistent with the experimental results obtained for the rheological and sedimentation characteristics in this study. The three dispersant molecules adsorb onto the alumina particles and produce a negative charge upon the surface of the particles and this is thought to be the basis of the mechanism of the stabilisation of the suspensions. Any amount of the dispersant, above the optimum concentration, which remains in the aqueous phase functions effectively as a 'screening' electrolyte and thus reduces the range and strength of the double layer repulsion, and hence increases the viscosity. Elsewhere, we have shown that there is a good correlation between the dispersion quality and both the green and sintered density.[12,16,17] The data serve to illustrate that the response of these systems is consistent with the predictions provided by the general framework available within the prior knowledge of colloid science and emphasise the importance of providing and maintaining particles dispersed during the colloidal processing of ceramic powders.

Acknowledgements

The authors thank the support provided by the EEC's Human and Capital Mobility Programme. Partial funding to AUK by Government of Pakistan is also gratefully acknowledged.

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