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Stabilising Zirconia Aqueous Suspensions using Commercial Polyvalent Electrolyte Solutions

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Abstract

This paper describes a study of the stability of various aqueous zirconia HSY-8 (Tosoh, Holland) suspensions. The stability is achieved by utilising two commercially available dispersants, namely 'Aluminon' (aurintricarboxylic acid ammonium salt, Fluka Chemicals UK) and 'Tiron' (4-5-dihydroxy-1,3-benzenedisulfonic acid disodium salt, Fluka Chemicals, UK). Rheological, electrophoresis, sedimentation and adsorption measurement have been performed, and are reported, in order to investigate and characterise the stability of these suspensions. A good agreement is reported between the different techniques which identifies the optimum concentration of the corresponding dispersant; that is the condition which provides the most effective degree of sustained particle dispersion. The results for these zirconia suspensions are compared with those of an alumina AES-11 (Mandoval Ltd, Surrey, UK).

1 Introduction

The processing of submicron or colloidal ceramic particles in liquid media causes several problems during the different stages of the operation. Because of their very high surface area these particles form aggregates or agglomerates due to the action of van der Waals, or other attractive forces. These agglomerates must be broken down in the manufacture of the green (unfired) compacts in order to create an homogenous microstructure. Otherwise, these agglomerates will invariably produce large pores and non-uniform microstructures during the subsequent sintering, due to local differential shrinkages, in the final product. These agglomerates, in the wet processing of ceramics, can be largely eliminated and the discrete particle dispersion maintained by using methods which have their rationalisation in the principles of the colloidal chemistry. There is also a growing demand, from the environmental view point, to adopt to 'green', i.e. environment friendly, processes. Therefore, the use of an aqueous based ceramic process is preferred over processes which utilise organic solvents. The dispersion 'quality' of ceramic suspensions, prior to the forming process, must be controlled satisfactorily in order to maintain high standards of manufacturing and to obtain reproducible products. This is a significant challenge in aqueous based systems as the stabilising forces are relatively sensitive to the ambient conditions.

Various different types of methods can be used to characterise the dispersion quality of suspensions, and amongst these include, the rheological, sedimentation, adsorption and electrophoresis experiments. Rheology is perhaps the most frequently used probe to determine the agglomeration properties of concentrated ceramic powder suspensions, which are invariably a precursor to the final product. Rheology may also be used as an analytical tool for determining the optimum viscosity of a suspension; usually this means the minimum viscosity for the maximum solids loading. Also, in industry, rheological measurements are often used for routine quality control in order to minimise the inevitable batch-to-batch variations in the feeds before a ceramic suspension is processed further; e.g. slip cast or spray dried. In more sophisticated usages, the rheological behaviour can be used as a direct process parameter, which should be appropriately adjusted in order to obtain optimal green body properties after forming. The general and effective application of this approach requires a more fundamental understanding of the ceramic forming

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method in question in the context of the appropriate rheological behaviour associated with each forming process. In this paper we report the effects of two commercial dispersants, 'Aluminon' and 'Tiron', on the rheology of zirconia suspensions. Both of these dispersants are polyvalent organic salts. The zirconia suspensions were also characterised using adsorption isotherms and electrophoresis experiments, and the results are compared and contrasted with the rheological data. The results described in this paper for zirconia HSY-8 (Tosoh Europe, The Netherlands), are also compared with the results for an alumina AES-11 (Mandoval Ltd, Surrey, UK) which are described elsewhere.[1]

2 Experimental, Materials and Methods

2.1 Materials

A zirconia HSY-8 powder (from Tosoh Europe, The Netherlands) was used in this investigation; BET surface area of $8{\cdot}75\,\mathrm{m}^2\,\mathrm{g}^{-1}$ and a mean particle size of $0{\cdot}5\,\mu\mathrm{m}$. The two commercial dispersants used were 'Aluminon' and 'Tiron'. 'Aluminon' is an aurintricarboxylic acid ammonium salt and 'Tiron' is 4-5-dihydroxy-1, 3-benzenedisulfonic acid disodium salt. These chemicals are available from Fluka Chemicals, UK. The chemical structural formula are given elsewhere.[1]

2.2 Sample preparation, rheological and electrophoretic mobility measurements

The experimental details of these experiments are provided elsewhere.[2,3] All the suspensions used for the rheological studies were prepared as 40% v/v. The concentrations of the dispersants given here are wt% which is equivalent to the dry weight of the powder basis (dwb).

2.3 Sedimentation

Suspensions containing 15 ml of water and 5 g of the zirconia HSY-8 power with varying amounts of 'Aluminon' and 'Tiron' dispersant were ultrasonicated and stored in cylindrical tubes for ca. 4 months before the heights of the sediments measured.

3 Results and Discussion

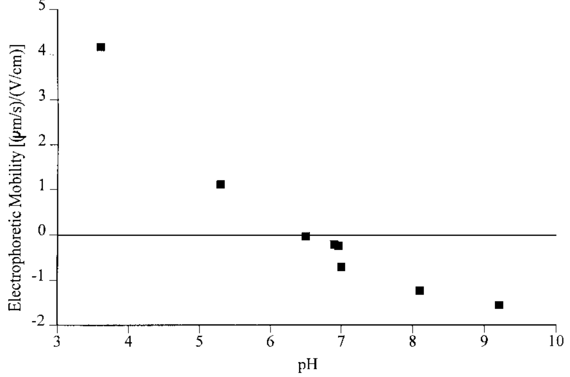

Fig. 1. Electrophoretic mobility as a function of pH value of zirconia HSY-8 suspensions.

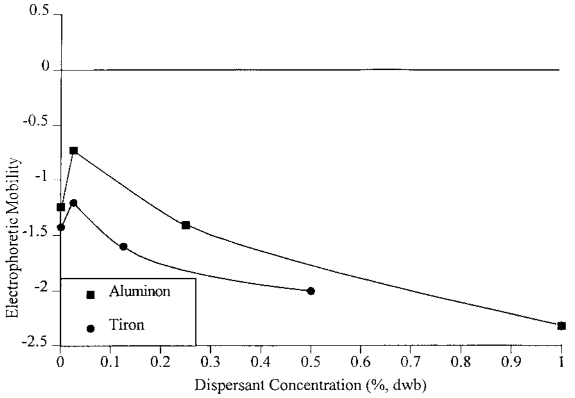

Fig. 2. Electrophoretic mobility of zirconia HSY-8 as a function of two dispersant ('Aluminon' and 'Tiron') concentration.

In Fig. 1, the electrophoretic mobility of the zirconia HSY-8 is shown as a function of the ambient pH. From the figure, the isoelectric point (iep) is identified at ca. pH 6·5. However, when the dispersants ('Aluminon' and 'Tiron') are adsorbed, the electrophoretic mobility of the particles is significantly changed. Figure 2 shows the electrophoretic mobility of the zirconia HSY-8 as a function of the dispersant concentration of 'Tiron' at a pH of 7·4 and 'Aluminon' at a pH of 7·2 (pH was adjusted using 1M KOH/HNO_3). The behaviour is similar to that of alumina AES-11[1] except that the electrophoretic mobility of the zirconia HSY-8 does not change sign (polarity) from positive to negative. This is due to the fact that zirconia HSY-8 has an iep at about pH 6·5, and at pH values of more than 6·5 the particles are thus always negatively charged. The addition of the dispersant simply makes the particles more negatively charged. Again, there is a maximum at the low dispersant concentrations. It is not established why this effect occurs but it may be that at low concentration the dispersants act effectively as a salt and hence changes in the electrophoretic mobility.

Figure 3 shows the adsorption isotherms of 'Aluminon' and 'Tiron' on zirconia HSY-8 at 25°C. The adsorption isotherms of these materials, on the zirconia, are similar to those of alumina AES-11. However, it appears from a comparison of the adsorption isotherms of alumina AES-11 and zirconia HSY-8 that the 'Aluminon' and 'Tiron' have a lesser affinity for adsorption onto zirconia HSY-8 as compared to the case of the alumina AES-11.[1] At low concentrations, both the dispersants adsorb onto the zirconia with a high affinity. However, at higher concentration levels a significant amount of the dispersants remains in the aqueous phase as the equilibrium ambient concentration which causes a significant increase in the amount of the dispersant that adsorbs on the zirconia HSY-8 particles. This partition is also observed by a visual examination of the suspensions for the case of the 'Aluminon' material, which produces a violet coloured aqueous solution.[3]

A slight difference in the calculated adsorbed amount of the dispersant was found in the results computed for the two methods used for the adsorption isotherms measurements. This is possibly due to the shift in the peaks of UV-Visible spectra before and after adsorption (see Ref. 3). The calibration curves for the 'Aluminon' and the 'Tiron' were constructed using the absorbance at the fixed wavelengths of 528 and 288 nm, respectively. The wavelength at 528 nm corresponds to a peak after adsorption, but without adsorption the peak is shifted to a higher value which gives a lower concentration value for the calibration curve. The consequence of this shift in the absorbance peak is that the amount adsorbed calculated by using absorbance at wavelength 528 nm will tend to provide a lower value. When the wavelength of 288 nm was used for the 'Tiron' absorbance measurement, the maximum absorbance peak was shifted to a lower wavelength value and this would now overestimate the adsorbed amount calculated using the absorbance method at wavelength of 288 nm.

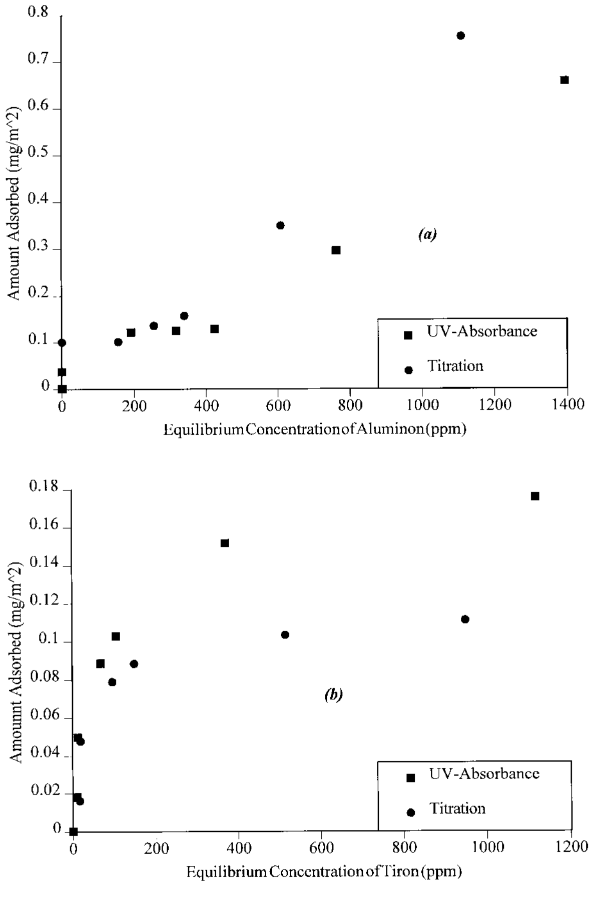

Fig. 3. Adsorption isotherms, amount of dispersant adsorbed on alumina HSY-8 as a function of equilibrium concentration using two methods (UV-absorbance and Titration), (a) for 'Aluminon' and (b) for 'Tiron', at 25°C.

Sediment heights as a function of concentration for the two dispersant ('Aluminon' and 'Tiron') are shown in Fig. 4. The height of the sediments is constant within the range 0·10 to 1·0% dwb for 'Aluminon' and 0·05 to 0·5% dwb for 'Tiron'. Below these concentration ranges there are small changes in the sediment heights but to a lesser extent as compared to alumina AES-11.[1]

Figures 5 and 6 represent the viscosity, as a function of the 'Aluminon' and 'Tiron' concentrations, respectively, at three different shear rates for the zirconia HSY-8 suspensions. For the 'Aluminon' dispersant, a concentration of about 0·2% dwb (0·23 mg m^{-2}) gives the lowest viscosity and for the 'Tiron' system the lowest viscosity is found when the concentration is about 0·125% (dwb) (0·14 mg m^{-2}). The change in the value of the viscosity from the lower concentrations to the optimum concentrations of the dispersant, is relatively small as compared to the alumina AES-11 suspensions for the same volume fraction and the same dispersants.[1,3] When the dispersant concentration is increased beyond the

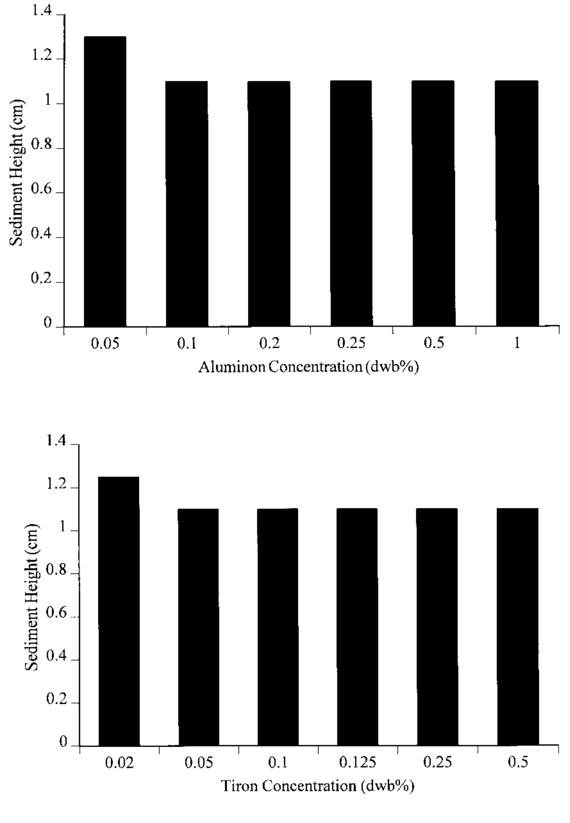

Fig. 4. Sediment height of zirconia HSY-8 as a function of dispersant concentration: (a) 'Aluminon' and (b) 'Tiron'.

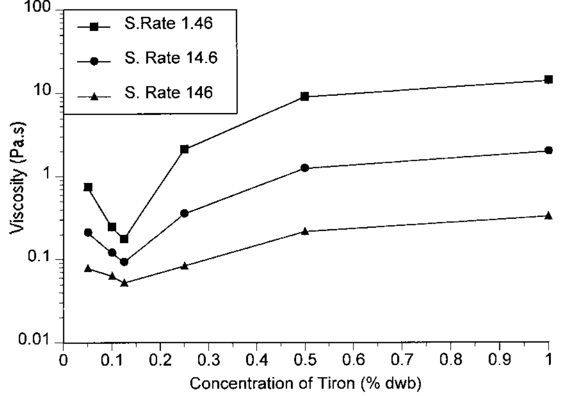

Fig. 5. Viscosity of zirconia HSY-8 40% v/v suspensions as a function of 'Aluminon' concentration (% dwb) at three different shear rates (1·46, 14·6 and 146 s^{-1}).

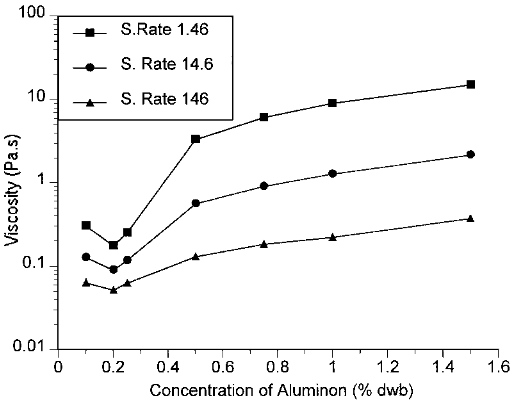

Fig. 6. Viscosity of zirconia HSY-8 40% v/v suspensions as a function of 'Tiron' concentration (% dwb) at three different shear rates (1·46, 14·6 and 146 s^{-1}).

optimum concentration the viscosity increases significantly.

This result is consistent with the data provided by the adsorption isotherms, and also possibly by the electrophoresis experiments. For example, when the 'Tiron' concentration was increased from 0·05 to 0·125% (or 0·10%) (dwb) the viscosity of the alumina AES-11 suspensions, at a shear rate of 1·46 s^{-1}, decreased by two orders of magnitude and for the zirconia suspension the decrease in the viscosity under the same conditions is relatively small (a factor of ca. 2 for 'Aluminon' and a factor of ca. 4 for 'Tiron'). With the 'Aluminon' dispersant, the differences in rheological behaviour for the alumina AES-11 and the zirconia HSY-8 are similar to that of the 'Tiron' system. When the concentration of the dispersant is increased beyond the optimum amount, the effects on the alumina AES-11 and zirconia HSY-8 are rather similar; i.e. the increase in the viscosity is of the same order of magnitude. In the adsorption isotherm experiments, it was observed that, for the alumina AES-11, when the concentration of 'Aluminon' was increased from 0·10 to 0·25% (dwb), virtually all the dispersant was adsorbed onto the powder. In contrast, in the case of the zirconia HSY-8 there was only a small increase in adsorption when the concentration of 'Aluminon' was increased from 0·10 to 0·20% (and 0·25%) (dwb). However, beyond the optimum concentration the extents of the adsorption of the 'Aluminon' and 'Tiron' were quite similar for both the alumina and zirconia suspensions. A similar difference was found for the case of the 'Tiron' dispersant for both the alumina and zirconia suspensions. Both the adsorption isotherms and the rheological experiments were carried out under the same conditions of the ambient pH. Similarly, in the sedimentation experiment it was found that when the concentration of the 'Aluminon' for the alumina AES-11 suspension is increased from 0·10 to 0·25% (and 0·20%) dwb, the difference in the sediment heights was more than double. In contrast, for the zirconia HSY-8 suspension there was only a very small difference in sediment heights.[2] The same kind of difference was observed when the 'Tiron; was used as the dispersant. From the trends of the electrophoresis experiments (Fig. 2) it appears that the difference in the electrophoretic mobility of the zirconia HSY-8 particles was small as compared to that of the alumina AES-11 particles and was always negative when the concentration of 'Aluminon' and 'Tiron' dispersant is changed from low concentrations to the optimum concentration. However, the pH values of the suspensions used for the electrophoresis experiment were not same as those used in the rheological experiments.

In the dynamic measurements, when the 'Aluminon' was used as a dispersant with the zirconia HSY-8, the dynamic viscosity as a function of 'Aluminon' concentration is comparable in magnitude to that of shear viscosity at a shear rate of 1·46 s^{-1}; (Figs 7 and 8). Close to the optimum value of the concentration of these dispersants, the storage modulus is less than that of the loss and complex moduli, but at concentration more than the optimum, the storage and complex moduli are significantly higher than that of the loss modulus.

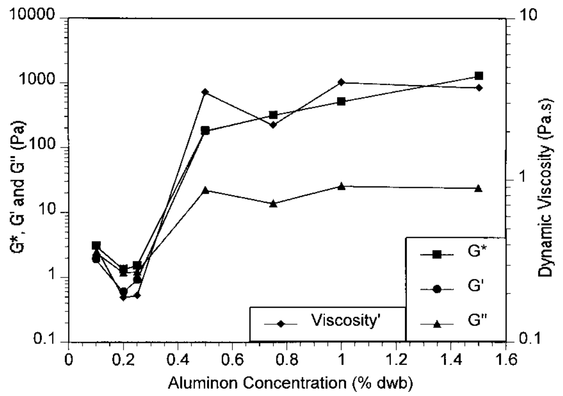

Fig. 7. G*, G′, G″ and dynamic viscosity of zirconia HSY-8 40% v/v suspensions against 'Aluminon' concentration (% dwb) at a frequency of 1 Hz.

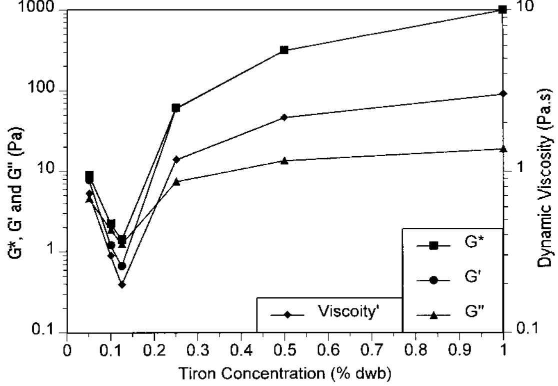

Fig. 8. G*, G′, G″ and dynamic viscosity of zirconia HSY-8 40% v/v suspensions against 'Tiron' concentration (% dwb) at a frequency of 1 Hz.

At the concentration of 0·5% dwb the dynamic viscosity and the loss modulus are higher than that observed from the trend in the shear viscosity and the complex and the storage moduli. When the 'Tiron' dispersant is used with the zirconia HSY-8, the behaviour is similar to that of zirconia HSY-8 with 'Aluminon'. The lowest dynamic viscosity was found when the concentration of the 'Tiron' was 0·125% dwb, where the loss modulus is less than the storage and complex moduli when the concentration is 0·10 and 0·125% dwb. When the concentration of an electrolyte dispersant exceeds the optimum amount, the excess amount resides in the continuous medium and acts a free electrolyte, which screens the effective charge on the particles and enhances the van der Waals attractive forces and as a results the particles start aggregating. This aggregation effect increases the viscosity as well as the complex, storage and loss moduli.

4 Conclusions

The zirconia HSY-8 suspensions stabilised using 'Aluminon' and 'Tiron' exhibit virtually the same character.[1] Both these dispersants decrease the viscosity and the other rheological parameters, such as the complex, storage and loss moduli, at their optimum concentration as compared to the suspensions with less than optimum dispersant concentration. However, in this concentration range, i.e. lower than the optimum, the effect of these dispersants is comparatively less than for the case of the corresponding alumina AES-11 suspensions. Above the optimum dispersant concentration, the rheological characteristics of the alumina AES-11 and zirconia HSY-8 suspensions are quite similar. This similarity in the rheological behaviour in this region indicates that the stability of the suspensions is primarily electrostatic in origin and that any unadsorbed dispersant in the aqueous phase functions as a 'free' electrolyte thereby decreasing the range of electrostatic repulsion and hence increasing the viscosity and other rheological parameters by facilitating agglomeration. The data from the adsorption isotherms, the sedimentation data and the electrophoretic mobility measurements are all quite consistent with the observed rheological behaviour.

The rheological response has frequently been used to maintain the quality of suspensions as a mean to optimise the production of optimal ceramic components.[3–5] The current study confirms, for the system, that the rheological tool provides a sensitive and casual probe for assessing the degree of dispersion and the influence of the ambient variables. In summary, the various effects observed are quite consistent with the established precedents in colloid science particularly in the context of electrostatic stabilisation. Whilst the electrostatic effect is very effective in facilitating good dispersions, by its nature the magnitude of the stabilising forces are relatively sensitive to the system variables such as dispersant concentration (and ambient pH). Hence, the predicament of providing the consistent stability of their actions in routine production where the control of such factors are difficult to achieve and maintain.

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