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Dependence of the rheological behaviour of electrostatically stabilized alumina slurries on pH and solid loading

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Alumina slurries with different solid loadings were prepared using aqueous solutions of hydrochloric acid the concentrations of which were predetermined as suitable for dispersing media; their rheological behaviour was investigated with respect to the pH of the slurry. In regions of low pH (below 3.5), the viscosity of the slurries gradually increased with decreasing pH of the slurry, irrespective of the amount of solid loading. Near the isoelectric point of alumina (about pH 8–8.5), the viscosities of the slurries were high and dependent on the solid loading. The pH range which exhibits the regions with low viscosity narrows on increasing the solid loading. These results were interpreted using an interparticle potential energy diagram for the slurry system. © *1998 Kluwer Academic Publishers*

1. Introduction

For the fabrication of a ceramic body through a wet-forming process, it is essential to prepare a homogeneous slurry. In particular, when the electrostatic stabilization process is involved during the dispersion of ceramic powder, the pH of the slurry should usually be adjusted to be far away from the isoelectric point (IEP) of a powder in order for it to possess high surface charges, because solid particles immersed in liquid media overcome the attractive van der Waals force based on the Deryaguin–Landau–Vervey–Overbreak theory [1].

The stability of particles is often evaluated from the rheological behaviour of the slurry since the rheology reflects the interaction between particles. In general, a slurry with homogeneous dispersion shows nearly Newtonian flow behaviour whereas a slurry with flocculation behaves in a pseudoplastic manner. Rheological behaviour validation by the pH adjustment of slurry is only found in a restricted pH range including the IEP [2, 3]. That is, pseudoplastic behaviour appears not only near the IEP but also in regions of low or high pH. These behaviours are not expected from the electrokinetic data since the magnitude of the measured zeta potential is still high in regions of validating pH.

On the other hand, mass and/or phase segregation during the consolidation of the slurry and excessive shrinkage during the drying of the consolidated body are detrimental to the precise design of advanced ceramics [4]. Although these problems can be overcome by the method of pressure filtration using a hydration short-range force [5], net shape forming by such methods as a gel casting [6] essentially requires the slurry to have maximum solid loading to prevent those problems. Omatete *et al.* [7] have studied the dependence of maximum solid loading on the pH of aqueous alumina and zirconia slurries. From the result that the maximum solid loading increases as a slurry pH departs from the IEP of alumina and zirconia powders, they concluded that the electrophoretic mobility of the powders determines the maximum solid loading. However, they did not explain why powder loading itself is impossible above or below the critical pH corresponding to the maximum solid loading.

The investigation of particle stability predicted from the shape of an interparticle potential energy curve will be beneficial to understanding the aforementioned rheological phenomena [8]. The interparticle potential energy curve is produced by plotting the net interparticle potential energy given as the summation of the electrical double-layer potential and van der Waals potential with respect to the separation distance between particles. The net interparticle potential energy appropriate for a ceramic system is expressed as follows [9] :

$$V(H) = 2\pi a\varepsilon_r\varepsilon_0\Psi_d^2 \ln[1 + \exp(-\kappa H)] - \frac{Aa}{12H} \qquad (1)$$

where H is the separation distance between two spherical particles of radius a, ε_r is the relative dielectric

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constant of the liquid medium, ε_0 is the dielectric permittivity of vacuum, Ψ_d is the surface potential at the diffuse part of electrical double layer, κ is the Debye–Hückel parameter and A is the effective Hamaker constant. Ψ_d and κ are two important factors dominating the shape of the curve since the choice of slurry system nearly fixes a, ε_r and A. Accordingly, the reliability of particle stability predicted from the potential energy curve depends on how the magnitudes of Ψ_d and κ are regulated with respect to the pH of slurry and solid loading.

For real calculations employing Equation 1, the experimentally inaccessible Ψ_d is replaced by the zeta potential measured using an extremely dilute suspension whose ionic atmosphere is similar to that of the slurry under investigation. Deliso *et al.* [10] have considered the dependence of the zeta potential on solid loading. They concluded that solid loading does not affect the zeta potential because results from both microelectrophoresis and the mass transport technique produce similar electrokinetic data. This conclusion is supported by the electrokinetic data obtained from the improved mass transport technique [11]. On the other hand, the Debye–Hückel approximation [1] indicates that κ should be determined by the ionic strength of the bulk solution where the electrical potential difference between solid particles and liquid media disappears. For a dilute colloidal suspension, the determination of κ is irrevelant because a liquid medium is assumed to be a reservoir of ionic species. Meanwhile, for concentrated suspensions such as a ceramic slurry, it is not simple because a significant amount of the potential-determining ions added initially and the background electrolyte are consumed by the adsorption on the surface of suspended particles [12].

The purpose of present study is to interpret the dependence of the rheological behaviour on the pH of the slurry and on the solid loading in an electrostatically stabilized aqueous alumina slurry, using the potential energy curves. To facilitate the determination of κ, only a HCl electrolyte was used for the adjustment of the pH and the slurries were prepared from loading alumina powder into aqueous solutions of HCl the concentrations of which were predetermined.

2. Experimental procedure

High-purity (greater than 99.99%)α-Al_2O_3 powder (AKP 20; Sumitomo Chemical, Osaka, Japan) was used in the experiment. Particle size analysis (Laser Micron Sizer 24; Seishin Kigyo, Tokyo, Japan) confirmed that the powder is composed of particles with a diameter of 0.2–1.8 μm and an average particle diameter of 0.56 μm. The specific surface area measured by the Brunauer–Emmett–Teller method (Quantasorb, Quantachrome, Syosset, NY, USA) is $4.5\ m^2\ g^{-1}$.

Aqueous solutions with concentrations between 10^{-4} and 10^{-1} M HCl were prepared from concentrated HCl solution (analytical grade) and the deionized water. After the powders equivalent to 20, 50 and 58 vol% had been poured into a fixed volume (typically $30\ cm^3$) of each HCl solution, ultrasonic agitation subsequent to hand mixing was carried out to break down the agglomerates and to obtain a slurry with homogeneous dispersion. The resultant slurries were equilibrated overnight after being sealed to prevent evaporation of water. Prior to the powder loading, the pH of the solutions was measured with a pH meter (model 340; Mettler Instrument, Hightstown, NJ, USA), using a combined electrode.

The viscosity of the slurry was measured at various shear rates with a concentric-cylinder-type viscometer (LVDTII +; Brookfield Engineering, Stoughton, MA, USA) equipped with a small sample chamber and a type 31 spindle. Prior to the viscosity measurement, ultrasonic agitation subsequent to hand mixing was employed to disperse the sediments formed during the equilibration process. The pH of the slurries was immediately measured as soon as the viscosity measurement had been completed.

The electrophoretic mobility of the powder was measured using microelectrophoresis apparatus (Zetameter 3.0; Zetameter, New York, NY, USA) as a function of pH. To identify the IEP of the powder, a mobility measurement was conducted in broad ranges of pH in the presence of a 0.01 M NaCl background electrolyte. In this case, HCl and NaOH were used for pH adjustment. Another mobility measurement was also performed in the absence of background electrolyte in order to retain an ionic atmosphere similar to that of our slurry. So, only HCl was used for the pH adjustment and the samples were also equilibrated overnight prior to the mobility measurement. The zeta potential was calculated from the measured mobility using the Smoluchowski equation [13].

3. Results and discussion

The values of the zeta potential as a function of pH in this work are presented in Fig. 1. The fact that the IEP appears at pH 8–8.5 coincides with other electrokinetic data for pure α-Al_2O_3[14, 15]. It should be noted that the effect of ionic strength on the zeta potential is negligible in the acidic region; this is different from the double-layer theory [16] which indicates a strong dependence of the zeta potential on the ionic strength. This phenomenon may arise from the dissolution reaction depicted by

$$\tfrac{1}{2}\,Al_2O_3 + 3H^+ \rightarrow Al^{3+} + \tfrac{3}{2}\,H_2O \qquad (2)$$

Once dissolved, alumina remains in solution in the form of Al species or precipitates at the surfaces of alumina particles; this depends upon the ageing time, the ionic atmosphere and the alumina concentration. The fact that the dissolution reaction affects the surface chemistry of solid particles immersed in aqueous media has been reported for SiO_2, B_4C and $La_{0.9}Sr_{0.1}MnO_3$ systems [17–19].

Fig. 2 shows the relation between the pH values of the HCl solutions used as the dispersing media and the pH values of the resultant alumina slurries. In the case of the 20 vol% α-Al_2O_3 slurry the pH of the

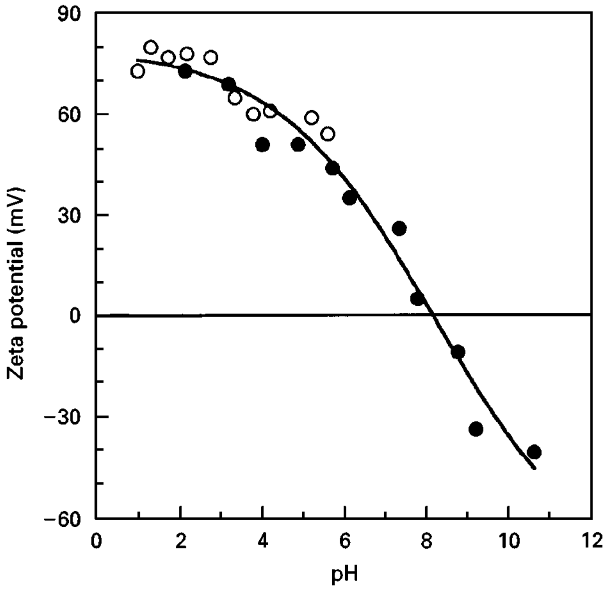

Figure 1 Zeta potential of alumina powder as a function of pH. (●), 0.01 M NaCl; (O), no electrolyte.

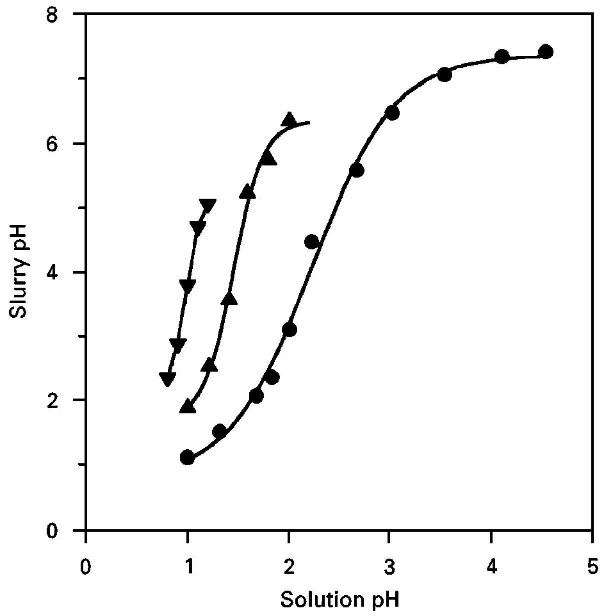

Figure 2 Variation in the pH of an alumina slurry with respect to the pH of HCl solutions used as the dispersing media. (●), 20 vol% α-Al_2O_3; (▲), 50 vol% α-Al_2O_3; (▼), 58 vol% α-Al_2O_3.

slurry increases with increasing pH of solution, finally converging to pH 7–8. This trend also appeared for the 50 and 58 vol% α-Al_2O_3 slurries. The fact that the slurry pH converges to the IEP is consistent with the results for mass titration in an aqueous α-Al_2O_3 system [20]. On the other hand, the use of HCl solutions with a low concentration as dispersing media meant that powder loading could not be achieved. As can be expected from Fig. 2, the critical pH values of the slurries for solid loading in 50 vol% α-Al_2O_3 and 58 vol% α-Al_2O_3 slurries are about 6.5 and 5.2, respectively. All the slurries obtained in this work showed pseudoplastic behaviours, but the degree of this behaviour was dependent upon both the pH of the slurry and solid loading.

Fig. 3 shows the effects of the pH of the slurry and solid loading on the slurry viscosity which is measured at a shear rate of $10.2\,s^{-1}$. At each solid loading, a gradual increase in the viscosity of the slurry appears in regions of low pH of the slurry, whereas the viscosity of the slurry rapidly increases near the IEP of alumina powder. As the solid loading increases, the pH range with low viscosity narrows, converging at pH 3–4.

If the suspension effect [21] is neglected, the pH of the slurry provides information on the H^+ concentration remaining in bulk solutions after protolytic surface reactions which formed the electrical double layer have been completed. Also, a more accurate determination of κ for the slurry system can be obtained from information on the dissolution of alumina particles in aqueous media. Takeda *et al.* [22] have examined the dissolution of α-Al_2O_3 powder in aqueous media by using the chelation and atomic absorption methods. According to their results, the amount of dissolved alumina increases from 1 to 20 ppm as the pH of the media departs from the IEP of alumina. This amount is equivalent to an Al^{3+} concentration of about 10^{-4} M assuming that the dissolved Al species exist in the form of Al^{3+}.

A nuclear magnetic resonance study [23] on the aqueous solutions of $AlCl_3$ shows that the dominant forms of Al species in solution are $[Al(H_2O)_6]^{3+}$ below pH 3.5, $[Al_{13}(OH)_{28}O_4(H_2O)_8]^{3+}$ at pH between 3.5 and 4.5, and $[Al(OH)_3]^0$ above pH 4.5. Considering the above results, H^+ and Cl^- can be regarded as the major ionic species in solution because the concentration of Al ionic species below pH 4 is lower than that of H^+ and the presence of non-ionic $[Al(OH)_3]^0$ species above pH 4 reduces the concentration of Al ionic species. The electroneutrality

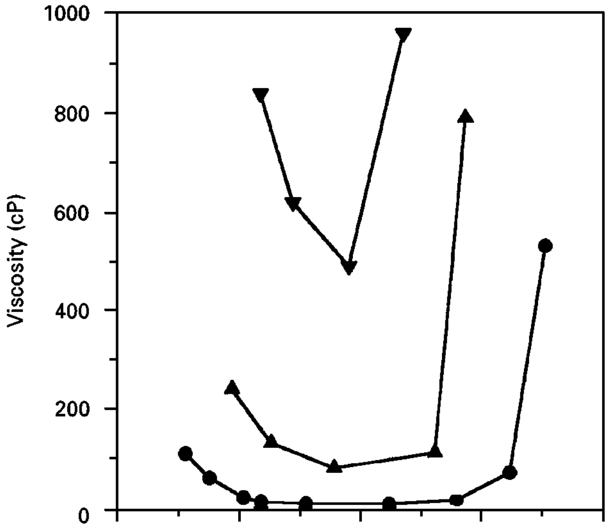

Figure 3 Apparent viscosity of the alumina slurry with different solid loadings as a function of slurry pH. (●), 20 vol% α-Al_2O_3; (▲), 50 vol% α-Al_2O_3; (▼), 58 vol% α-Al_2O_3.

constraint for the bulk solution is in proportion to the concentrations of H^+ and Cl^-. Under this condition, it is possible to estimate the parameter κ for our system from the pH of slurry, which represents the concentration of H^+ in the bulk solutions [1] :

$$\kappa\ (\mathrm{m}^{-1}) = 3.29\times10^{9}\times(10^{-\mathrm{pH}})^{1/2} \quad \text{at } 25\,^{\circ}\mathrm{C} \qquad (3)$$

However, in this case, it is difficult to explain the dependence of the rheological behaviour (as shown in Fig. 3) on solid loading at a certain pH of slurry using the interparticle potential energy curve obtained from Equation 1 because both κ and the zeta potential are independent of the solid loading. Also, because of this, the ionic strength of HCl solutions was chosen as a reference for the determination of κ.

The interaction between the particles was investigated for particles of different sizes because the alumina powder is composed of particles with various diameters from 0.2 to 1.8 μm in our slurry system. To simplify this, the effective radius, a_{eff}, of two particles with different radii a_1 and a_2 replaced a in Equation 1 according to Hogg *et al.* [24]:

$$a_{\mathrm{eff}} = 2a_1a_2/(a_1 + a_2) \qquad (4)$$

In order to obtain interparticle potential energy curves corresponding to a certain pH of the slurry at each solid loading, an A value of 6.7×10^{-20} J, was deduced for particle sizes $a_1 = 0.1\,\mu\mathrm{m}$ and $a_2 = 0.5\,\mu\mathrm{m}$ by Horn *et al.* [25]. Also, the zeta-potential value adopted from fitting the curve in Fig. 1 and the κ value calculated from Equation 3 was inserted into Equation 1. The two particle sizes were chosen by considering that the density of small particles is higher than that of large particles.

Fig. 4a, b and c shows the interparticle potential energy diagrams obtained at various pH values of the slurry for alumina with solid loadings of 20 vol%, 50 vol% and 58 vol% α-Al_2O_3, respectively. As can be seen in Fig. 4, in pH regions with low viscosity (as shown in Fig. 3 at each solid loading), a high potential energy barrier and a shallow secondary minimum were observed. The former prevents the alumina particles from falling into a deep primary minimum and the latter prevents the particles from staying at the position of the secondary minimum. In contrast with the above case, a low potential energy barrier and a deep secondary minimum were observed in regions of the pH where a steep or gradual rise in the viscosity, respectively, occurred. Although the potential energy barrier is a little higher than about $10\,kT$ (where k is the Boltzmann constant and T is the absolute temperature) which is generally accepted as the criterion of Brownian coagulation [26], these results are qualitatively in agreement with viscosity data, as shown in Fig. 3. Also, it observed that the potential energy barrier disappeared above a pH corresponding to a steep rise in the slurry viscosity. At this point, strong flocs form in the slurry, and further addition of alumina powder to the slurry leads to growth of the flocs. It is suggested that the eventual percolation of the flocs reduces the capability for powder loading.

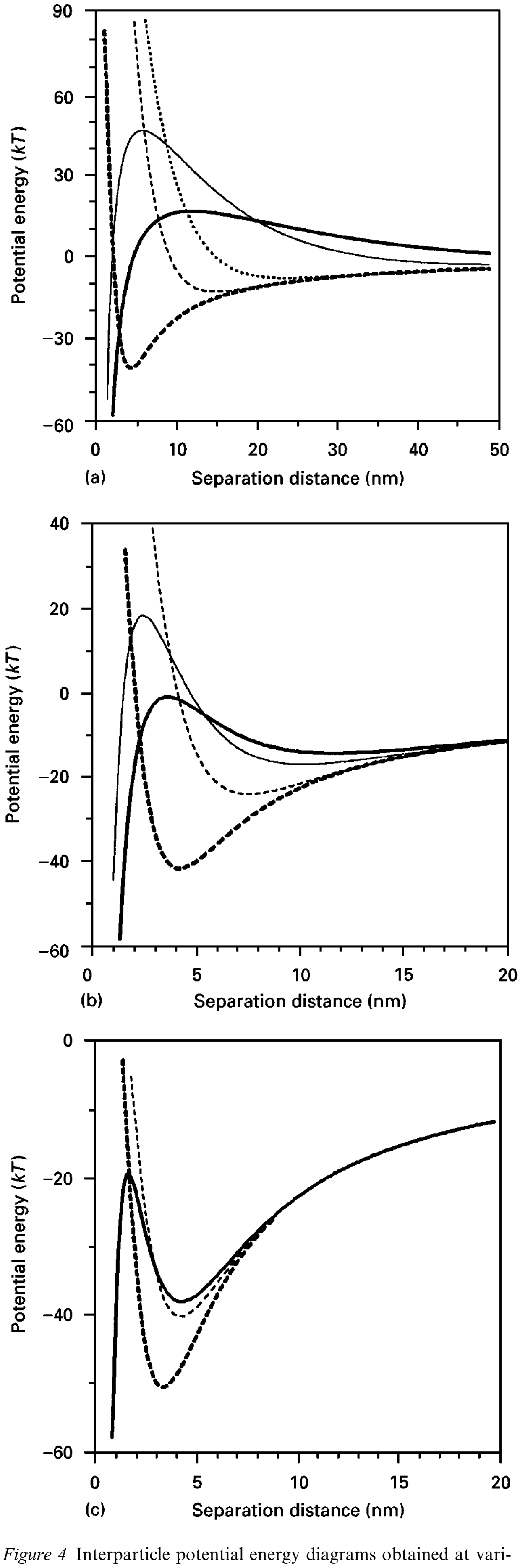

Figure 4 Interparticle potential energy diagrams obtained at various pH values for alumina slurries with solid loadings of (a) 20 vol% α-Al_2O_3 (▪▪▪▪), pH 1.1; (-----), pH 2.4; (········), pH 4.5; (▬▬), pH 6.5; (——), pH 7.1) (b) 50 vol% α-Al_2O_3 (▪▪▪▪), pH 1.9; (-----), pH 3.6; (▬▬), pH 5.8; (——), pH 6.4) and (c) 58 vol% α-Al_2O_3 (▪▪▪▪), pH 2.9; (-----), pH 4.2; (——), pH 5.1).

4. Conclusion

An interparticle potential energy diagram obtained from the Debye–Hückel parameter which is estimated from the ionic strength of the initial HCl solution used as a dispersing medium is effective for understanding the dependence of the rheological behaviour of electrostatically stabilized aqueous α-Al_2O_3 slurries upon the pH of the slurry and solid loading. It is suggested that powder loading is not possible in regions above a critical pH (corresponding to maximum solid loading) and below pH 3 (in regions showing a gradual rise in viscosity). This is attributed to the disappearance of the potential energy barrier in the former, and the presence of a deep secondary minimum in the latter.

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