

Electroacoustic Technique for Fast Monitoring of Colloidal Dispersion: Zeta Potential Titration of Alumina with Anionic Polyelectrolyte

Sarraf H. ^{*1}, Havrda J.², and Herbig. R³

^{1,2} Institute of Chemical Technology of Prague, Glass and Ceramics Dep., Technicka5, 166
28 Prague, Czech Republic;

³ Institut für Keramische Werkstoffe ,Gustav-Zeuner-Str. 3 D-09596 Freiberg, Germany

ABSTRACT

The zeta potential (ζ) of 2-vol% and 43-vol% suspensions of a commercial α -alumina powder has been measured using the electroacoustic technique called "ESA" and found to be in good agreement with values reported previously from micro-electrophoresis measurements. An increasingly negative ζ value was observed through semiautomatic addition of solutions of a polyelectrolyte (polyacrylic acid) dispersant Dolapix CE64 (Zschimmer & Schwarz, Germany) that is ethanolaminic salt of citric acid. The average particle size (d_{50}) obtained from laser light scattering Mastersizer (Malvern Instrument, UK) compared and showed the effect of dispersant, also coagulation near the isoelectric point. The results illustrate the efficacy of the electroacoustic technique for examining colloidal dispersions at different concentrations.

Keywords: Electroacoustic (ESA), Zeta potential, polyelectrolyte (Dolapix CE64)

INTRODUCTION

The dispersion of powders in liquids is an important process, particularly in the ceramics industry.[1] The monitoring of the state of aggregation is essential to determine if and when the suspension is dispersed to its primary particle size. Dispersion of aqueous colloidal systems often is achieved via control of the charge on the particles by various means, which include alteration of

pH, the addition of potential-determining ions, or the adsorption of charged polyelectrolytes.[2] Hence, measurement and control of the zeta potential (ζ) of the particles can be used to control the properties of the suspension.

The methods available for observing either the extent of dispersion or the charge on the particles often are indirect. Many are optical methods, which generally require dilution of the suspension, with consequent alteration of the equilibria that involve adsorption, unless particular care is taken to compensate for the dilution process. Other procedures are batch methods, which involve the irreversible alteration of suspension samples, as in centrifugation methods.

In this study, we describe the application of the recently developed electroacoustic technique to measure simultaneously ζ , the relative isoelectric point (iep) and average (d_{50}) particle size of different concentrated suspensions which determined using the laser light scattering method (Mastersizer 2000, Malvern, UK) as they are being dispersed. The method involves the application of an ac electric field across the suspension, at frequencies in the megahertz range. The charge on the particles causes them to "jiggle" in response to the alternating field; as a consequence of the difference between their density and that of the surrounding fluid, this motion generates

an ultrasonic wave at the same frequency.[3] The magnitude of the resulting ultrasonic wave can be used to calculate the charge on the particle, which determines its mobility and the electrophoretic ζ value. In the present study, this technique has been used to monitor the dispersion of a standard alumina powder through the addition of an anionic polyelectrolyte (Dolapix CE64) dispersant. Then, by the laser light scattering technique, the average (d_{50}) particle size of suspensions with different solid concentrations dispersed by optimum amount of Dolapix CE64 (after dilution) is measured.

MATERIALS AND PROCEDURES

The alumina particles used in this study were highly pure α - Al_2O_3 particles (AA04, Sumitomo Co., Japan), with an average particle diameter of $< 0.5 \mu\text{m}$ (as measured via equipment: Horiba CAPA-700 Particle Analyzer), and an average surface area of $13.57 \text{ m}^2/\text{g}$ (as measured via Brunauer-Emmett-Teller (BET) nitrogen adsorption).[4] A commercial anionic polyelectrolyte (Dolapix CE64 dispersant, Zschimmer & Schwarz, Germany) was used. This dispersant had an average molecular weight of 320 g/mol .

Analytical-reagent-grade sodium chloride (NaCl) was used to provide the background electrolyte. Also to determine the zeta potential as a function of pH for the samples, automatic titration is performed using the Merck brand 0.1 n HCl and 0.1 n NaOH solutions to adjust pH to the desired values from 3 up to 11, respectively. All solutions and suspensions were prepared with deionized water.

The electroacoustic (ESA) was calibrated as follows. A cell that contained a stirred water sample was equilibrated for at least 1 h at a temperature of 22.0°C . The pH was calibrated at pH values of 4, 7, and 11. If concentrated (>5 - $10 \text{ vol.}\%$) suspensions

were to be analyzed, then an air measurement was recorded; this measurement was stored in the computer and recalled for the sizing calculation. Finally, a freshly prepared colloidal alumina suspension was introduced into the cell and allowed to equilibrate at 22.0°C before electrokinetic sonic amplitude (ESA) measurements were made.

Alumina suspensions were prepared 2, 10 vol% and 43 vol% (8, 31 and 77 wt%, respectively) in two sets of by adding unwashed alumina to deionized water with constant stirring and after ball milling of suspensions with 30 min and 500 rpm. Then, the resulting suspension was sonicated for 3 min and stirred for an additional 30 min. After the suspension was added to the ESA sample cell, solid NaCl was added until the conductivity was $\sim 0.06 \text{ S/m}$, which corresponds to a background salt concentration of 0.006 M NaCl .

ESA measurements were recorded as the pH was titrated from pH 4 to pH 11. Then, polymer Dolapix CE64 at pH 9 was added at a particular concentration using a microsyringe, the pH was readjusted to pH 11, and ESA measurements were made over the same pH range (from pH 11 to pH 4). Approximately 3 min were allowed for the pH to equilibrate after each addition of the polymer solution. After attaining a value of pH 4, more polymer solution was added and, again, after ~ 3 min, the pH of the suspension was readjusted to pH 4 and then titrated to pH 10. This procedure then was repeated.

When the conductivity attained a value of $\sim 0.2 \text{ S/m}$, because of the increase in salt concentration from the multiple pH titrations, the experiment was stopped and a new sample was used. An appropriate amount of polymer solution was added to match the amount obtained in the previous pH titrations, and then the titration procedure was continued.

While these ESA experiments were being performed, suspension stabilities were measured crudely by observing the flocculation behavior of a portion of the sample in a Pasteur pipette. This method was used to describe the colloid qualitatively through its sedimentation behavior.

Measurements also were made to study the effect of adding Dolapix CE64 to suspensions at fixed values of pH 6 and pH 9, to determine the concentrations at which surface coverage is complete. To minimize the pH variation at pH 6, a polymer sample was adjusted to that pH, using 0.1 n HCl, and then added to the colloidal suspension at pH 6. Therefore, the effect of polymer addition could be monitored using increases in the conductivity. The same procedure was repeated at pH 9, using the polymer in its standard form.

Rheological studies were performed on concentrated (43 vol%) suspensions, using a concentric cylinder rheometer (Sensor Z41, RV1, Thermo Haake, Ltd., Germany), which is able to measure the corresponding viscosity and shear stress under controlling shear rate. The total volume of the suspension was ~14 mL. Separate samples were prepared at the required Dolapix CE64 concentrations and pH.

RESULTS

Electroacoustic measurements allow the ζ values to be determined directly on relatively concentrated alumina suspensions without dilution. Figure 1(a) shows the ζ values that have been obtained from an electroacoustic titration of a 2-vol% suspension of the alumina. Similar results were obtained for the ESA value which is proportional to zeta potential, as shown in Figure.1(b).

The top curves in Fig. 1 (a),(b) show the pH dependence of ζ and ESA in the pH range of 4-11.

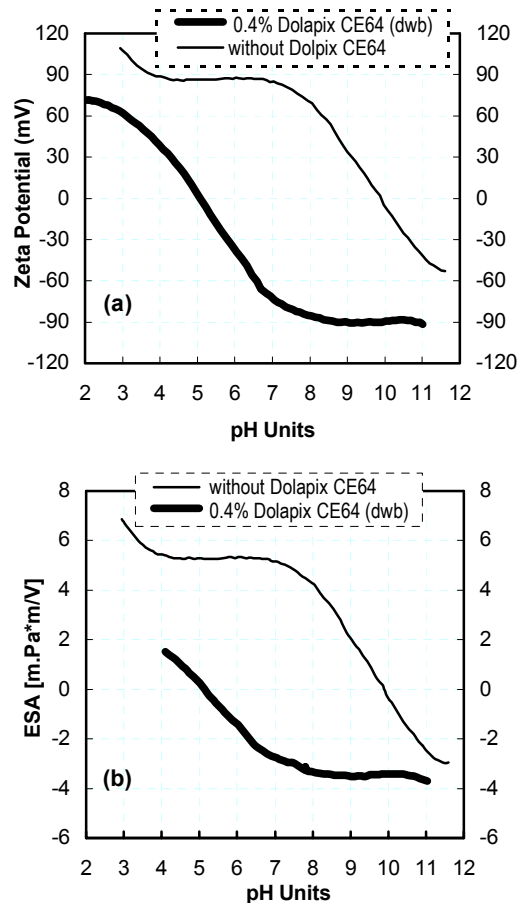


Figure 1. Electroacoustic zeta potential (a) and ESA value (b) -dependence on pH and the added Dolapix CE64 concentration expressed as a dry weight percentage of alumina.

The isoelectric point (iep) and ζ values (iep = pH 9.86 and ζ = 87 mV at pH 4, respectively) are about 1 unit and 40 mV higher than the reported values (iep = pH 8.7 and ζ = 47 mV at pH 4, respectively) shown in the figures from a paper by Cesarano *et al.*[4] for a very dilute suspension of this alumina. These differences can be related to the higher surface area and different preparation process of alumina.

The lower curves in Fig. 1(a), (b) show the pH dependence of the effect on the ζ and ESA values of the addition of polymer to the 2-vol%-alumina suspension.[5] The adsorption of Dolapix CE64 reduced the values of both ζ and ESA from their initial

positive values at pH <9.8; above this pH, the alumina particles were negatively charged but adsorption still occurred, to increase the negative ζ and ESA values. This increase in the negative ζ values is expected, because the polymer is anionic at all pH values in the range of 4-11.[5]

Figure 2 demonstrates the agreement between the results of the 2-vol% and 10-vol% suspensions of the shift of the iep to smaller pH values with an increase in the amount of Dolapix CE64. The two curves are indistinguishable when the Dolapix CE64 concentration is expressed in terms of a weight percentage of alumina.

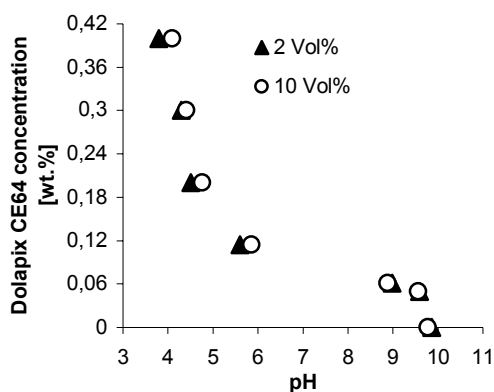


Figure 2. pH- dependence of the isoelectric point (iep), relative to concentration of added Dolapix CE64, for (▲) 2-vol% and (○) 10-vol% suspensions.

In addition to ζ , the conductivity of the suspension, which is recorded automatically by the ESA equipment (MATEC, Applied Science, USA) software, was noted. At pH 6, the value of ζ decreased from +85 mV to approximately -73 mV after 0.4% Dolapix CE64 was added. At this point, the conductivity, which had been approximately constant (1288 $\mu\text{s}/\text{cm}$), began to increase linearly as to (1750 $\mu\text{s}/\text{cm}$ by 0.4 wt.% Dolapix). We interpret this point as the amount of Dolapix CE64 required for saturation of the surface; the excess then contributes to the increased conductivity up to 1936 $\mu\text{s}/\text{cm}$ (by adding 0.5 wt.%

DolapixCE64). At pH 9, the polymer is completely saturated by electrosteric stabilization effect; the optimum amount (0.4 wt.%) of polymer that is required reflects the increased negative charge of the Dolapix CE64 polyelectrolyte at the higher pH value.

In addition to ζ , a measure of the mass-average particle size can be obtained from the laser light scattering (Mastersizer-2000, Malvern, UK) technique. Figure 4 shows the Dolapix concentration - dependence of the mean (d_{50}) diameter of the particles in: a 2-vol% suspension (A) in the absence of Dolapix CE64, 2-vol% (B) and 43 vol% (C, after dilution to 2 vol%) suspensions both with the optimum amount 0.4 wt.% Dolapix CE64. The value of (d_{50}) 0.486 μm at pH 9, is in good agreement with our estimates of 0.4-0.5 μm from TEM measurements. As the dispersant Dolapix is increased, the particle size (d_{50}) decreases until an optimum is reached at pH 9.1.

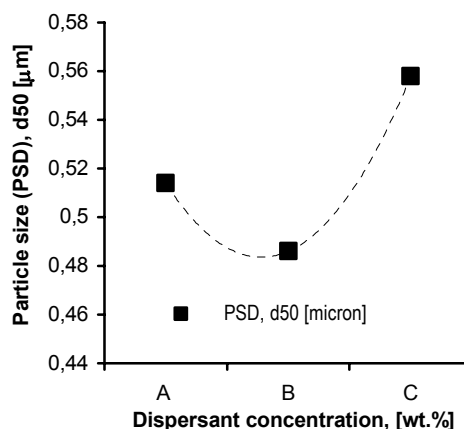


Figure 4. Mean (PSD, d_{50}) particle size, as a function of pH, for a 2-vol%(A) alumina suspension in the absence of Dolapix, 2-vol% (B) and 42 vol% (C) both with the optimum amount of DolapixCE64.

This increase in mean (d_{50}) particle size reflects coagulation, which occurs as the ζ value decreases because of high solid concentration (43-vol%) and no longer

provides sufficient electrostatic repulsion between the particles. The optimum amount of Dolapix can cause electrosteric effect and decreases mean particle size near to the original size. However, the increase in size can be reflected in the sedimentation volume because of changing of the pH value, which for suspension with 2 vol% as illustrated in Fig.5. Sedimentation volume displays maxima at the iep (pH 9.8). However, the increase in the apparent particle size correlates well with other properties that reflect the coagulation behavior based on pH-dependency.

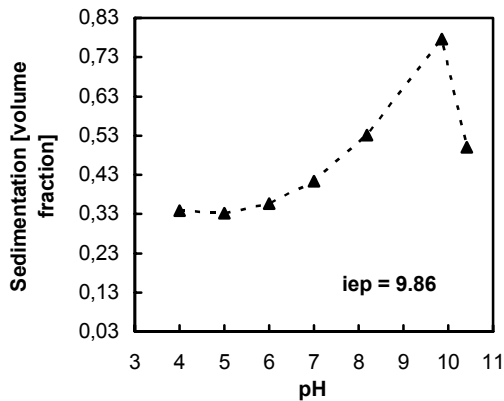


Figure.5. pH dependence of (▲) sedimentation volume for a 2-vol% alumina suspension.

The addition of Dolapix CE64 to a concentrated, 43-vol% suspension at pH 9.1 provided electrosteric dispersion (see Fig. 6). An increase in the absolute magnitude of the negative ESA (that is proportional to ζ) value paralleled a decrease in the η value of the suspension as the particles dispersed. At the same time, the mean PSD (d_{50}) of both suspensions: 2-vol% and 43-vol% (after dilution to 2 vol%) that were calculated from the laser light scattering Mastersizer 2000 (Malvern Instrument, UK) decreased from 0.514 μm at pH 9 in the absence of Dolapix CE64, to 0.486 μm and slightly increased to 0.586 μm , after the addition of the optimum amount 0.4 wt% of Dolapix CE64.

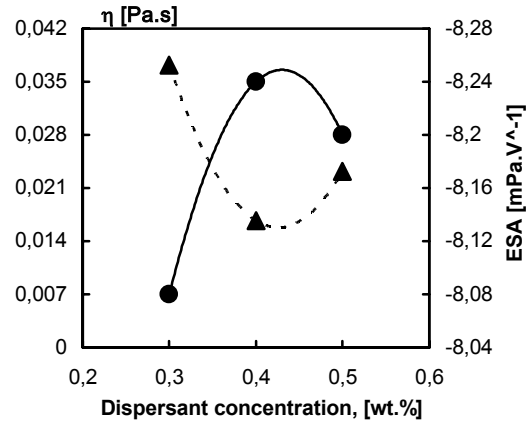


Figure 6. Effect of addition of PMA-NH₄ on the (▲) viscosity and (●) ESA for a 43-vol% alumina suspension at pH 9.

The so-measured Bingham yield value showed an approximately inverse correlation with ζ^2 (see Fig. 7), as expected from the "elastic floc" model of Firth and Hunter[6] for a coagulated sol. In this model, ζ -potential is a measure of the attractive force between the particles in a floc, which determines the floc volume ratio. Then, van de Ven and Hunter[7] showed that the Bingham yield value is a measure of the viscous energy required to move liquid into and out of the floc as it becomes distorted, and that this relation is similarly dependent on ζ^2 .

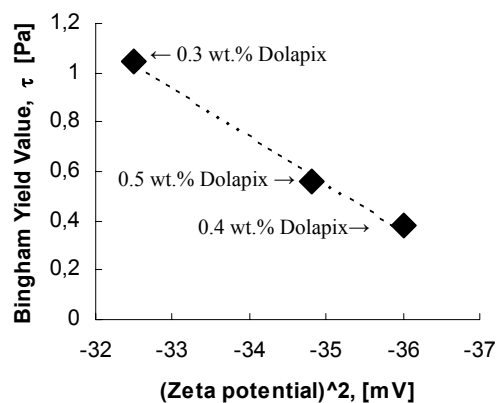


Figure 7. Correlation of the Bingham yield value with zeta potential ζ for a 43-vol% alumina suspension with different concentrations (wt%) of Dolapix CE64 at pH 9.

DISCUSSION

The electroacoustic technique provides a convenient and reliable method of rapidly measuring the ζ value of relatively concentrated colloidal suspensions. Very good agreement is observed between ζ and its pH dependence for the same alumina measured on very dilute solutions via microelectrophoresis[4] and those measured here on 2-vol%, 10-vol% and 42-vol% suspensions. The agreement between the different methods of measuring particle size is less precise, which, however, is understandable in so far as the material is known not to be monodisperse.

A pH-concentration profile could be quickly and semiautomatically obtained for the adsorption of the Dolapix CE64 polyelectrolyte onto concentrated suspensions of alumina, in contrast with the multiple potentiometric titrations that are required by conventional techniques. There have been many studies of the adsorption of polyelectrolytes onto alumina. In a typical study that was published recently, the adsorption of PAA was measured on a 2-wt% suspension via equilibration and centrifugation, followed by chemical analysis, whereas the ζ value was measured on a 0.01% suspension via microelectrophoresis.[5] In the present study, ζ is measured directly by electroacoustic ESA technique as the polyelectrolyte is added to the concentrated suspension.

The observed ζ value showed a good correlation with the sedimentation volume and η , which allows it to be used as a surrogate for these properties under conditions for which the polymeric polyelectrolyte confers electrostatic stabilization of the suspension. (Under acidic conditions, the correlation between η and ζ breaks down when the polymer is almost neutralized and bridging flocculation can occur.)

The particle size obtained from the laser light scattering method also reflects the dispersion and coagulation, which occurs near the iep of the suspension. Together, the size and ζ value provide a convenient and rapidly obtained description of the adsorption and dispersion of the alumina suspension with a polyelectrolyte. An "acoustophoresis" method has been reported previously that describes the "relative acoustophoretic mobility" as Darvan C was added to alumina suspensions.[8] That method measures the colloidal vibration potential generated when an ultrasonic field is applied to the suspension. The colloidal vibration potential is the reciprocal of the ESA that has been measured in the present work.[9]

Johnson *et al.*[10] reported electroacoustic and rheology measurements on this same alumina at up to a concentration of 30 vol%. The electroacoustic measurements can be made for more concentrated suspensions close to the processing conditions and results can be correlated empirically. Although we have reported results of the maximum 43vol% (77 wt%) concentrated suspension, which was not reported before. Furthermore, the rapidity of the technique allows the prospect of real-time process control, using measurements on process streams.

It can be concluded that the value of ζ measured via the electroacoustic (ESA) method allows measurement of the minimum amount of dispersant required to give a value that is consistent with observations made of the slip viscosity of an 77 wt% suspension.

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REFERENCES

1. G. D. Parfitt, *Dispersion of Powders in Liquids*. Applied Science Publishers, London, U.K., 1981.
2. R. J. Hunter, *Zeta Potential in Colloid Science*. Academic Press, London, U.K., 1981.
3. R. W. O'Brien, D. W. Cannon, and W. N. Rowlands, "Electroacoustic Determination of Particle Size and Zeta Potential," *J. Colloid Interface Sci.*, 173, 406-18 (1995).
4. J. Cesarano III, I. A. Aksay, and A. Bleier, "Stability of Aqueous α -Al₂O₃ Suspensions with Poly(methacrylic acid) Polyelectrolyte," *J. Am. Ceram. Soc.*, 71 [4] 250-55 (1988).
5. D. Santhiya, G. Nandini, S. Subramanian, K. A. Natarajan, and S. G. Malghan, "Effect of Polymer Molecular Weight on the Adsorption of Polyacrylic Acid at the Alumina-Water Interface," *Colloids Surf. A*, 133, 157-63 (1998).
6. R. J. Hunter, *Foundations of Colloid Science*. pp. 1042-46. Clarendon Press, Oxford, U.K., 1989.
7. T. G. M. van de Ven and R. J. Hunter, "The Energy Dissipation in Sheared Coagulated Sols," *Rheol. Acta*, 16, 534-43 (1977).
8. J. F. Kelso and T. A. Ferrazzoli, "Effect of Powder Surface Chemistry on the Stability of Concentrated Aqueous Dispersions of Alumina," *J. Am. Ceram. Soc.*, 72 [4] 625-27 (1989).
9. R. W. O'Brien, P. Garside, and R. J. Hunter, "The Electroacoustic Reciprocal Relation," *Langmuir*, 10, 931-35 (1994).
10. S. B. Johnson, A. S. Russell, and P. J. Scales, "Volume Fraction Effects in Shear Rheology and Electroacoustic Studies of Concentrated Alumina and Kaolin Suspensions," *Colloids Surf. A*, 141, 119-30 (1998).