Analysis of the Isoelectric Point in Moderately Concentrated Alumina Suspensions Using Electroacoustic and Streaming Potential Methods

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ABSTRACT

Alumina suspended in aqueous electrolytic solution was used as a model ceramic suspension to investigate the measurement precision and influencing factors for the determination of the isoelectric point (IEP) in moderately concentrated systems. Techniques used in this study include colloid vibration current (CVI), electrokinetic sonic amplitude (ESA), and particle charge detection (PCD). A number of important factors were examined, focusing on those related to sample preparation, measurement methodology and instrumentation. A total of 145 acid-base titrations were included in the analysis. Although sample preparation factors influence the magnitude of the measured signal, primarily due to agglomeration effects, these factors do not significantly impact the determination of the IEP for alumina. The primary factor affecting IEP precision and accuracy is the level of sample agitation during titration. Poor mixing gives rise to hysteresis phenomena that

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introduce large systematic errors. Colloid vibration current, ESA, and PCD produce comparable electrokinetic data over the solids volume fraction range between 1% and 10%, although some systematic differences are apparent. Further refinements in methodology and greater fundamental understanding are necessary to improve measurement agreement between different techniques and to reduce variability in IEP results.

INTRODUCTION

Electrokinetic measurements are widely utilized for characterizing the interfacial electrochemical properties and assessing colloidal stability in ceramic suspensions.[2–4] Of primary interest in this regards are the zeta potential (ζ) and the isoelectric pH (IEP). Zeta potential can be determined by a number of different techniques. The most familiar one involves the application of a d.c. electric field, which causes the charged particles to move with a steady state velocity. This is termed electrophoresis (or microelectrophoresis when employing a capillary cell), and by measuring the particle velocity at the hydrodynamic stationary layer (i.e., zero electro-osmotic velocity in the liquid), the electrophoretic mobility (velocity per unit field strength) is obtained. Zeta potential can then be calculated from mobility using, for instance, the Henry equation:[5]

$$\mu_E = \frac{2}{3}\frac{\varepsilon\varepsilon_0\zeta}{\eta}f(\kappa a) \tag{1}$$

where μ_E is the electrophoretic mobility, η is the viscosity of the medium, ε is the relative dielectric permittivity of the medium, ε_0 is the permittivity of a vacuum, and $f(\kappa a)$ is the Henry's constant, which varies from 1 at $\kappa a = 0$ (Hückel limit) to 1.5 at $\kappa a = \infty$ (Smoluchowski limit). Here $1/\kappa$ is the inverse Debye-Hückel parameter, which has dimensions of length, and a is the particle radius. The thickness of the electrical double layer is characterized by $1/\kappa$, and depends primarily on the electrolyte concentration ($\kappa = 3.288\sqrt{I}$ in nm^{-1} at 25°C in water, where I is the ionic strength).

As a general rule, electrophoretic techniques require very dilute suspensions ($\ll 0.01\%$ solids), as they depend on optical methods, such as laser Doppler scattering,[6] to determine particle velocity. This restriction carries some obvious drawbacks, as extreme dilution can induce chemical changes at the particle surface and in solution, which may in turn impact the electrokinetic behavior.[7] Contamination of the liquid phase is also a more pressing issue at extreme dilutions, as are sampling errors, which are more likely to occur when smaller quantities of powder are represented. Therefore, dilute samples must be prepared very carefully to avoid such problems.

Non-optical alternatives to electrophoresis have been developed to deal with non-dilute suspensions. These include colloid vibration potential (CVP, also called acoustophoresis), electrokinetic sonic amplitude (ESA) and streaming potential.

In CVP, a radio frequency (rf) acoustic field produced by a piezoelectric transducer induces a fluctuating motion in the particles as the waves propagate through the suspension.[8] The electrical double-layer at the particle–solution interface is periodically displaced relative to the particle by this induced motion. This gives rise to a system of oscillating dipoles, which generate an electrical field measurable in the form of a potential or the associated short circuit current (the latter being termed the colloid vibration current or CVI). Conversely, in ESA an rf electric field applied to the suspension causes the charged particles to vibrate, producing an acoustic signal detected by a transducer.[9] Electrokinetic sonic amplitude is reciprocally related to CVP.

Colloid vibration current, CVP, and ESA belong to a class of phenomena collectively known as the *electroacoustic effects*. All three quantities are proportional to the frequency-dependent dynamic electrophoretic mobility, $\mu(\omega)$:[9,10]

$$CVI \propto CVP K^* \propto ESA = \Phi\frac{\Delta\rho}{\rho}\mu(\omega)C_I R_Z \tag{2}$$

where K^* is the complex conductivity of the suspension, Φ is the solid phase volume fraction, $\Delta\rho$ is the density contrast between the solid and liquid, ρ is the density of the liquid, and C_I is an instrument constant. The term C_I contains device specific terms independent of the dispersed phase and requires calibration with a known material.[11] An additional term, R_Z, is added to account for the acoustic impedance match between the suspension

and the acoustic delay rod through which the acoustic signal passes during a measurement.[9,12] The complex function, R_Z, can be taken as equal to that of water and packaged with the instrument constant for moderate to low solids concentrations. At higher solids loadings, impedance will diverge increasingly from that of water, and must be determined directly by acoustic reflection measurements.

The dynamic mobility in Eq. (2) differs from the d.c. mobility in Eq. (1) as a consequence of particle inertia in the high-frequency field. The inertial effect becomes more significant as frequency or particle size increase. As a result, $\mu(\omega) \leq \mu_E$, with $\mu(\omega) \to \mu_E$ as $\omega \to 0$. As a point of reference, at a nominal frequency of 1 MHz, inertia becomes a significant factor for most ceramic particles larger than about 100 nm in diameter.[13] Consequently, for the majority of ceramic systems, an accurate calculation of ζ from electroacoustic data requires a correction for particle size.[14]

Electroacoustic devices have been incorporated into widely available commercial instrumentation beginning only in the late 1980s. On the other hand, streaming potential measurements, as originally conceived, have been used to measure the electrokinetic properties of powdered material compressed into porous plugs for many decades.[5] Streaming potential is proportional to the zeta potential of the powder surface and the applied pressure, ΔP, used to force the liquid through the porous plug:[5]

$$\psi_S = \frac{\varepsilon \varepsilon_0 \zeta}{\eta K_b} \Delta P \qquad (3)$$

where K_b is the bulk solution conductivity. Note the similarity in form between Eq. (3) and Eq. (1).

More recently, a modification of the original concept has been developed that permits measurements of the streaming potential[15,16] or streaming current[17] on *dispersed* particles at non-dilute concentrations. In the particle charge detection (PCD) device, a suspension is contained within a cylindrical cavity constructed of a soft poly(tetrafluoroethylene) (PTFE) material and into which a vertically reciprocating piston is inserted. Particles temporarily adhere to the soft material of the cavity wall, so that as the moving piston forces the fluid to stream relative to the immobilized particles, an electrical potential is created within the annulus between the piston and cavity wall. Because streaming is induced by the piston motion rather than an applied pressure, Eq. (3) is not strictly applicable to PCD. However, the equation does indicate the principal dependencies of the PCD-derived potential, with the following exceptions. In the PCD method, the magnitude of the measured potential is also dependent on the number and size of the particles adhering to the PTFE wall. This may be an important issue in systems where agglomeration occurs, for instance during an acid-base titration. The potential is also inversely dependent on the square of the annulus width.[17]

The accuracy of ζ depends on many factors, some of which can not be controlled or known with a high degree of certainty. For CVI, CVP, and ESA, the calculated value of ζ is most reliable in the absence of significant surface conductivity, when κa is either very large or very small, and when the particle size distribution is narrow, well defined and in the sub-micrometer range.[11,14] For PCD, a quantitative measure of ζ is difficult to realize under conditions where the number and size of particles adhering to the containment wall is an unknown and variable factor. Frequently, however, it is the *relative changes* in electrokinetic potential that are of practical concern. In this case, the critical issues become (i) the precision of the measurement; (ii) reproducibility of the method; and (iii) the correspondence between different techniques. In a previous work,[18] it was shown that ESA and PCD produce well correlated potential-pH curves for moderately concentrated aqueous suspensions of α-Al_2O_3, SiC, and Si_3N_4. The curves followed the same characteristic and could be transformed into one another by a simple linear relationship. The precision was high for a solid phase volume fraction of 1%, and somewhat lower for 10% suspensions (note: particle concentrations are expressed throughout as the volume fraction of solids in %). At both concentrations the correlation between ESA and PCD remained linear, thus indicating a high degree of correspondence between the two techniques.

For a given material, the isoelectric point is of fundamental significance. The vast majority of advanced ceramics derive their surface charge in water from the adsorption and dissociation of protons at hydroxylated surface sites.[19] The IEP is the pH value at which particle polarity reverses and both ζ and μ_E are equal to zero. In the absence of specific chemical adsorption, the IEP should be coincident with the point of zero net charge (PZC) at the particle surface. In the presence of chemically adsorbing ionic species, the IEP will shift relative to the PZC in a direction depending on the charge ($+$ or $-$) of the adsorbed species. The IEP is therefore a key parameter in complex multicomponent suspensions, where

charge compatibility of different solid phases and chemical additives is critical.[20]

At issue is the often substantial variability of reported IEP values for a given ceramic material, as reflected in the literature.[21] For the most part, this variation can be attributed to the (i) chemical and phase purity of the material; (ii) chemical stability of the material in water; (iii) sample history; (iv) suspension preparation; or (v) technique and instrumentation used to measure the IEP.[7,22] The objective of the present investigation is to determine the sources of greatest variability for measurements on a model ceramic system at non-dilute particle concentrations and to establish a common basis for the comparison of data between different laboratories, techniques and instruments. Our work focuses on issues relating to suspension preparation, measurement methodology and measurement technique. Our purpose is not to evaluate or contrast commercial instrumentation, but rather to provide insight and guidance on the use of these techniques for analysis of non-dilute systems. We have chosen a submicrometer, high purity corundum (α-Al$_2$O$_3$) to serve as the model ceramic powder for these studies. Complementary experiments were performed using nanophase titania and alumina powders.

In determining the IEP by electrokinetic means, a quantitative determination of ζ is not required. Only the trend and sign of the measured signal is necessary to identify the IEP. In this case, it is possible to compare techniques that measure different aspects of the electrokinetic potential, without reference to a common unit of measurement. In the present work, we determine the IEP using three techniques (ESA, CVI, and PCD), over a range of solids concentrations spanning an order of magnitude. We also examine some key factors that influence the measurement of potential-pH curves at moderate concentrations and their impact on the apparent IEP derived from titration data. In future publications, we will report more detailed analyses of the various preparation and instrumental parameters affecting these measurements. The current work is part of a larger international effort focused on development of pre-standardization data and improved methodology for measurements in ceramic suspensions.

INSTRUMENTATION

Electrokinetic Sonic Amplitude

Two electroacoustic instruments were used for ESA measurements, the ESA8000 and the ESA9800 (Matec Applied Sciences, USA).[23] The 9800 is an upgraded version of the 8000, the primary difference being the internal electronics and control software. The measurement cell assembly of both systems contains the SP80 sensor, a 300 mL Teflon sample cell and Teflon cell head, probes for pH, temperature and conductivity, and an overhead impeller mixer. The SP80 immersion sensor is cylindrical in shape and contains an acoustic delay rod with a piezoelectric transducer mounted at one end and a planar gold electrode laminated to the opposite end (see Fig. 1). The reference electrode is positioned concentric to the planar sensing electrode and is separated by a nonconducting insert. A removable end cap with a cross bar positioned plane parallel to the electrode surface on the main probe body is attached to the reference. The primary purpose of the end cap is to improve measurement sensitivity by reducing the space between the otherwise concentrically positioned electrode pair to an odd multiple of $1/2$ the acoustic wavelength; in the configuration used here the multiple is one. The instrument works by applying a nominal 1 MHz voltage pulse at V_2 (in Fig. 1) and measuring the
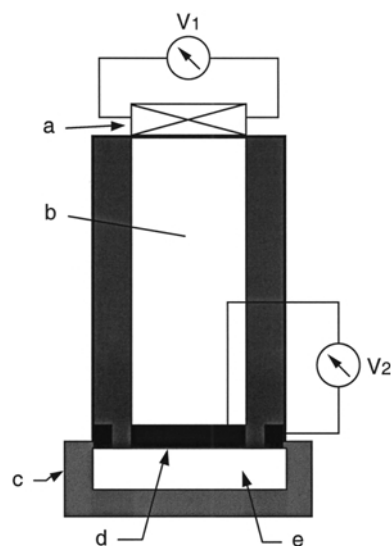

Figure 1. A simplified schematic showing the essential features of a cylindrical electroacoustic immersion sensor (side cut view): (a) piezoelectric transducer, (b) acoustic delay rod, (c) removable end cap in contact with outer electrode (ESA only), (d) planar sensing electrode, and (e) sensing zone. (Note: sensor and component dimensions are exaggerated for illustrative purposes).

resulting transducer voltage pulse at V_1. An automated dual microburette system is connected to the measurement cell and control system.

Colloid Vibration Current

Colloid vibration current measurements were made using a DT1200 acoustic-electroacoustic spectrometer (Dispersion Technology, USA). The CVI sensor is simillar in design and dimension to the SP80, but without the end cap and slightly smaller in diameter (see Fig. 1). In the present case, we use the CVI sensor in a magnetically stirred external cell that we designed and built to replicate the cell layout and dimensions used in the ESA system. The external cell consists of a support stand and Teflon cell head that accommodates a 300 mL Teflon sample cell, CVI sensor, temperature probe, and electrodes for pH and conductivity. Colloid vibration current measurements are performed by applying a nominal 3 MHz voltage pulse to the transducer at V_1 and measuring the short-circuit current at V_2.

Particle Charge Detection

Streaming potential measurements were obtained using a PCD apparatus (Mütek GmbH, Germany). The measurement device (Fig. 2) consists of a cylindrical
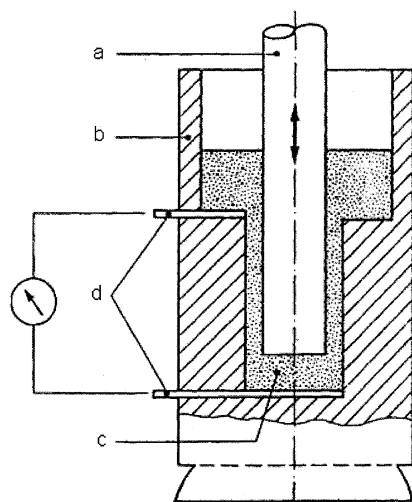
PTFE sample container containing a PTFE reciprocating piston. The suspension is held in the small gap between the container wall and piston surface, spanning a width of typically between 0.25 mm and 0.5 mm. Two gold electrodes are located in the container wall at the top and bottom of the gap, across which the streaming potential is measured, while sinusoidally varying the piston motion at a frequency of 4 Hz.

MATERIALS AND METHODS

Materials

The primary test powder used in this investigation was AKP-30 α-alumina (Sumitomo Chemical Co., Japan). The manufacturer's density value of 3.97 g cm^{-3} was used for calculating the volume fraction. The median particle diameter of AKP-30 is $0.31 \pm 0.01\ \mu m$ as determined by laser diffraction at pH 4.5. The alumina was mixed and distributed from a single batch to all participants in the study. Additional tests were made using a nanophase titania powder, P25 produced by Degussa (USA), with a size as reported by the manufacturer of 21 nm, and Grade A alumina (König Keramik, Germany), with an equivalent spherical diameter of about 60 nm calculated from the specific surface area provided by the manufacturer. All chemicals were reagent grade or better. Unless otherwise noted, test samples for acid-base titration were dispersed in an electrolyte solution containing 0.01 M $NaNO_3$ in deionized or distilled water and titrated using HNO_3 or NaOH.

Sample Preparation

A requisite weight of electrolyte solution is added to a known weight of powder in a Pyrex glass beaker to obtain the solids concentration and fluid volume required for a particular experiment. The suspension is stirred magnetically until completely wetted and well mixed, after which the pH is adjusted with HNO_3 to a value near 5.5. The powder is then dispersed using an immersion-type ultrasonic horn for a period of about 2–3 min at a high intensity setting. In select cases the pH is not adjusted, and this is referred to as the "native" pH of the powder (typically near pH 7). Samples are aged for about 2 h using a magnetic stirrer or mechanical shaker prior to measurement.

Figure 2. Schematic drawing of the PCD device: (a) PTFE reciprocating piston, (b) cylindrical PTFE sample container, (c) suspension in measuring well, and (d) gold electrodes.

Titration Protocols

Electroacoustic Techniques

For ESA and CVI, a sample containing 250 mL of test suspension is placed in the Teflon measurement cell. In the case of ESA, an autotitration protocol is used with a delay time of 60 s after each titrant addition. Each sample is titrated with 1 N NaOH to pH 10, and then back titrated with 1 N HNO$_3$ to pH 6. The time for a complete acid–base–acid cycle is approximately 90 min. In the case of CVI, titrations are performed manually, with fewer data points and longer equilibration times at each point, but with the total titration time similar to that used in ESA experiments. In both cases, combination glass pH electrodes are carefully calibrated against standardized buffers each day prior to beginning experimental work. Titrations are performed at ambient temperatures (22°C $\pm$ 1°C). Both electroacoustic devices were calibrated using a 10% suspension of Ludox TM silica according to the instrument manufacturer's directions. Calibration simplifies the comparison of titration curves within and between techniques, but is not effectual with regards to IEP determination.

Streaming Potential Technique

The PCD measurement container is filled with approximately 25 mL of suspension. Each sample is titrated with 0.1 M NaOH to about pH 10. Selected samples are then immediately titrated with 0.1 M HNO$_3$ to the beginning pH. An equilibration time of 2 min is allowed after reaching each pH point. At this rate, and with relatively fewer data points, the overall speed of titration is similar to that used in ESA and CVI measurements. The piston is continuously in motion throughout the course of a titration, and provides the mixing and agitation to maintain homogeneity and prevent sedimentation. The combination glass pH electrode is calibrated each week using standardized buffers.

Laser Doppler Electrophoresis Technique

The d.c. electrophoretic mobility of a dilute alumina suspension ($\sim$130 mg/L) was determined by laser Doppler (micro) electrophoresis (LDE) using a Zetasizer 3000HS (Malvern Instruments, Southborough, MA). This data was obtained at a temperature of 22 ± 0.1°C under conditions of "constant equilibrium dilution", in which the solid phase was first removed by centrifugation from a 5% suspension, then the original concentrate was diluted into the supernatant, thus preserving the chemical balance in the system. Titration was performed manually, using a protocol similar to that described above for CVI measurements. A dependence of the apparent IEP on solids concentration was observed over a range from 10 mg/L to 130 mg/L. Data indicates that the IEP values level off above 100 mg/L. Therefore only the titration curve obtained at the highest experimental solids loading was used for comparison.

RESULTS AND DISCUSSION

Figure 3 shows representative samplings of base titration curves for 5% solids concentration and for each of the three techniques involved in the study. Each corresponding y-axis has been scaled to provide a better indication of the degree of correlation that can be expected between the techniques over the tested pH test range. For purposes of comparison, the zeta potential-pH curve determined at dilute concentrations by LDE is included. The LDE curve has been plotted on the same scale used for CVI data.

The IEP test data for alumina powder represents a total of 145 acid and base titrations performed at three particle volume fractions (1%, 5%, and 10%) in three laboratories using five measuring devices (belonging to one of four previously identified commercial models, i.e., 2 PCD, 1 CVI, 2 ESA). The majority of titrations were performed using the HNO$_3$–NaOH–NaNO$_3$ system, but a small subpopulation of PCD titrations involved the less stable HNO$_3$–NH$_4$OH–NH$_4$NO$_3$ system because NH$_4$OH is frequently used in ceramic applications to adjust pH. Titrations in which NH$_4$OH was used as the base titrant are treated separately.

Figure 4 shows the IEP test data for 1% and 10% suspensions of alumina without regard to technique or titration direction (i.e., acid or base) and excluding the NH$_4$OH titrations. The data for 5% (not shown) is similar in average and spread to the 10% population. Mean and sample variance are reported separately for each solids concentration. Overall, the data indicates a somewhat lower average IEP and reduced spread at 10% (8.99 $\pm$ 0.32) relative to 1% (9.29 $\pm$ 0.51). In Fig. 5 the mean IEP and sample variance are shown as a function of technique. In this histogram, the numbers adjacent to each bar indicate the total number of titrations included in the statistical averaging. This figure also shows the
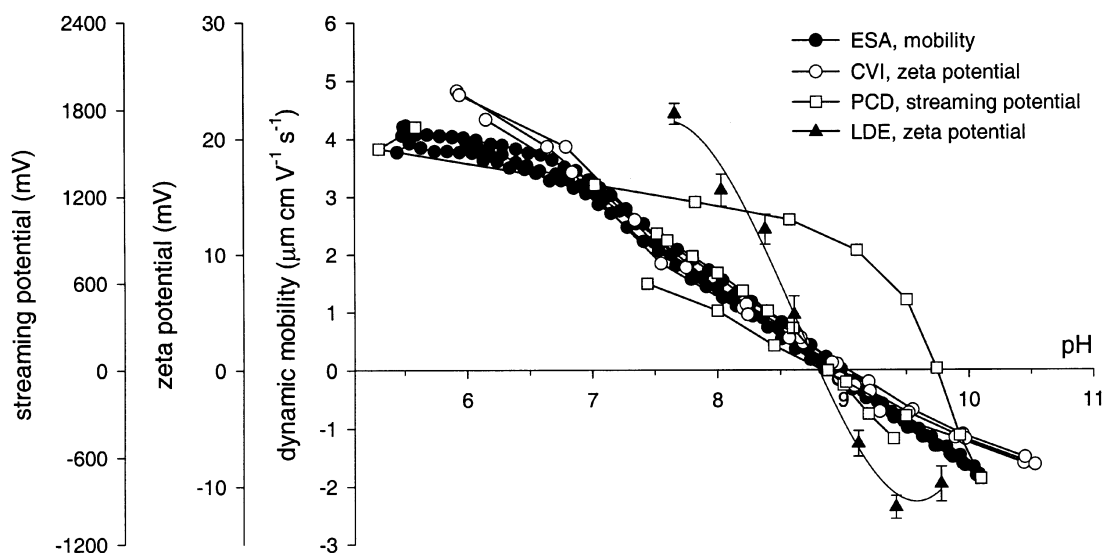
Figure 3. Electrokinetic curves for 5% AKP-30 alumina measured by CVI (zeta potential), ESA (dynamic mobility), and PCD (streaming potential). Zeta potential measured by LDE at a dilute concentration is shown for comparison. Three curves for each technique (except LDE) were more or less randomly selected to represent the typical spread in measured electrokinetic titrations.
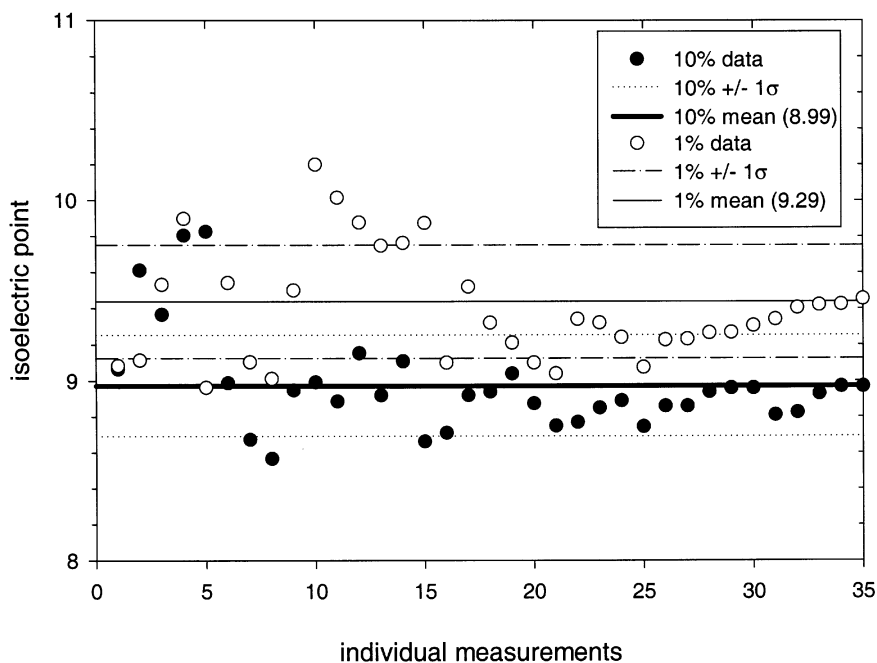

Figure 4. Isoelectric point test data for 1% and 10% suspensions of AKP-30 alumina, without differentiating between technique or titration direction (i.e., acid or base) and excluding the NH$_4$OH titrations. Horizontal solid and broken lines represent the mean and sample standard deviation, respectively.
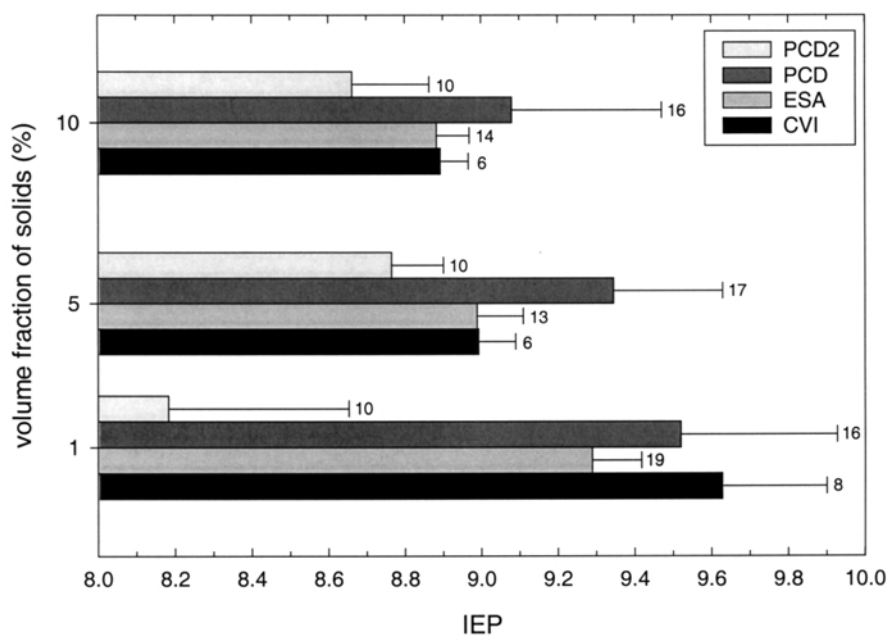
Figure 5. Histogram showing the mean IEP and standard deviation as a function of technique (CVI, ESA or PCD) for AKP-30 alumina. The numbers adjacent to each error bar indicate the total number of samples (individual titrations) included in the statistical averaging. Particle charge detection 2 represents samples in which NH_4OH was used as a base titrant.

PCD data obtained from titrations in which NH_4OH was used as the base titrant, indicated here as PCD2.

Solids Concentration Dependence

Overall, precision of measured IEP values (see Figs. 4 and 5) is poorest at the lowest solids loading used in the present study, corresponding to a volume fraction of 1%. For CVI and ESA, precision improves significantly and appears to level off at the higher solids loadings. The poor precision at 1% solids is not an unexpected result, if one considers that all three of these devices are optimized for concentrated systems and that the magnitude of the measured response, and the resulting signal-to-noise ratio, in each case depends in part on the number of particles being sensed, which depends on the solids loading.

It is particularly noteworthy that the mean IEP value (excluding NH_4OH titrations) in Fig. 5 varies with solids loading, increasing dramatically at 1%. The effect is most pronounced in the electroacoustic data, yet it is more continuous over the solids concentration range in the case of PCD. Furthermore, the agreement between ESA and

CVI data is very high at all but the 1% level, confirming that these two reciprocal techniques measure essentially the same information under similar conditions, and that instrument-specific differences play an insignificant role in IEP determination. The results for PCD titrations using NH_4OH as a base titrant (PCD2 in Fig. 5) indicate an opposing trend with respect to the dependence of IEP on solids loading, while at the same time exhibiting the largest standard deviation for any single set of data and the lowest mean IEP (8.18) at 1% solids, suggesting that the unstable nature of the acid–base equilibrium reaction, $NH_4^+ \leftrightarrow NH_3 + H^+$, and the proximity of the pK for this reaction ($\sim$9.3) to the IEP of alumina, may result in poor pH control during titration.

Under dilute conditions, LDE yielded a value of 8.8 for the IEP of the alumina (see Fig. 3), which is within 0.2 pH units of the mean value for all techniques combined at 10% solids loading (8.99, see Fig. 4), within 0.1 pH units of the mean value for the electro-acoustic techniques combined at 10% solids (8.89, see Fig. 5), and within 0.3 pH units of the mean value for all data combined at 5% solids (9.07). Considering the dilution factor between the 10% suspension and the

optically dilute sample used in LDE measurements (better than three orders of magnitude), and the inherent error associated with pH measurements in concentrated suspensions (see discussion below), this level of correspondence between techniques is better than expected.

There are a number of possible contributing factors to explain the high IEP values associated with 1% solids. For both ESA and CVI, the supporting electrolyte can contribute an ionic background signal that is nearly independent of pH. The background contribution for $NaNO_3$ is extremely small relative to the particle signal, even at the low end of the particle concentration range. The ESA response for 0.01 M $NaNO_3$ is about $+0.008\,mPa\,m\,V^{-1}$ or $+0.02\,\mu m\,cm\,V^{-1}\,s^{-1}$ using the conversion factor for a 1% alumina suspension. This positive ESA signal will have the effect of shifting the apparent IEP by a small increment toward more basic pH values,[24] but the shift is not sufficient to noticeably influence measurements at 1% solids or higher.

Another contributing factor might be the reduced sensitivity and signal-to-noise ratio at 1%, which could contribute both systematic and random errors. It is worth noting that the ESA sensor, which is equipped with an end cap to provide greater sensitivity at lower solids concentrations, provides the lower, and presumably more accurate, IEP value at 1% compared to the CVI sensor, which lacks this accessory. It should be noted, however, that both techniques apparently overestimate the IEP at 1%. For PCD, the lower concentration results in fewer particles, on average, adhering to the PTFE walls. This leads to a reduction in sensitivity and precision similar to that experienced by the electroacoustic devices.

Another factor during PCD measurements is the dependence of suspension viscosity on solids concentration, particularly in the vicinity of the IEP. If the viscosity becomes too high, as in the case of nanophase particles at high solids loadings, the piston motion may become erratic, leading to increased error. On the other hand, if the viscosity is too low, for instance at low solids loadings and larger grain size, piston motion may be insufficient to prevent some vertical segregation from occurring, also leading to increased error. The latter effect may play an important at 1% solids in the case of alumina.

Other possible contributing factors may include some dependence of the chemical equilibria between the solid and liquid phase on solids concentration, and effective differences in the treatment of powders during sample preparation that result from the different solids concentrations used. Neither of these effects appears to be a significant factor in the present case, as was shown by the *constant equilibrium dilution* experiment using LDE measurements. Constant equilibrium dilution preserves both the chemical and physical conditions of the more concentrated source suspension. Therefore, it seems likely that the observed increase in the mean IEP measured at 1% cannot be attributed to any single phenomenon, but rather may be the end result of several different factors.

The results of this investigation lead us to conclude that 1% solids is probably below the optimum measurement range for CVI, ESA, and PCD, insofar as submicrometer ceramic suspensions are concerned. On the other hand, previously published results of electroacoustic measurements on Si_3N_4 have clearly demonstrated that the 2% solids level produces excellent precision,[25] comparable to the precision reported for 5% and 10% samples in the present study. Above 10%, we have encountered sporadic problems due to poor mixing and high viscosity near the IEP. An extended investigation of highly crowded systems would be necessary to make further progress, but this is beyond the scope of the present work whose focus is on moderate concentrations. We therefore maintain that the optimum solids volume fraction range for electrokinetic analysis of moderately concentrated ceramic suspensions using CVI, ESA, and PCD is from 2% to 10%.

Titration Method and Hysteresis

There are essentially three approaches for determining the IEP of a ceramic powder: (i) single point measurements on a series of suspensions equilibrated at different pH values; (ii) titration of two identical suspensions starting from the natural pH and proceeding in opposite directions; and (iii) titration of a single suspension after first adjusting the pH to a high or low value some distance from the probable IEP. The first method is rarely used because it is time and material consuming. The latter two methods were compared for the alumina system and found to produce identical results within the expected spread. This may not be true for less chemically stable aqueous systems, such as alkaline earth titanates or apatites. In this case, without further information, the best course of action is to apply method (ii). In the present case, since method (iii) requires the least amount

of time and material, it was accepted as the protocol for the majority of experiments reported here.

In a number experiments, an additional step was added to method (iii), such that following the initial base titration with NaOH, a back titration was performed with HNO_3. By doing this, we hoped to evaluate both the electrochemical stability of the alumina-solution system over the experimental time span and also the repeatability of the titration method on the same sample. The acid–base cycle produced, under certain conditions, the appearance of a pronounced hysteresis. That is, the forward and reverse curves did not always overlap, and in some cases the IEP values differed considerably. Hysteresis was observed for both electroacoustic and PCD techniques, although the conditions for occurrence appear to differ in these two cases and therefore they are treated separately.

F6   For electroacoustic measurements, a systematic investigation of various parameters determined that the primary cause of hysteresis is inadequate agitation of the suspension. A secondary factor is agglomeration. We observed that hysteresis tended to increase with solids concentration and to decrease with the degree of agitation used during titration. Figure 6 illustrates the effect of sample agitation on ESA titrations at moderate solids concentrations. In these experiments, the level of agitation was controlled by varying the impeller speed and by the presence or absence of supplemental magnetic stirring. The extent of hysteresis ranges from extreme, often lacking an observable IEP, to mild in which the IEPs are statistically coincident but the curves diverge at the outermost pH values. Poor agitation leads to both segregation and the formation of a paste-like coating on the electrode surface. Segregation results from the settling of agglomerated particles that form at pH values near the IEP. From Eq. (2) we see that any modification of the particle concentration near the sensor electrode surface will affect a change in the signal magnitude due to the dependence of both ESA and CVI on volume fraction. For ESA, the effect is exacerbated by the presence of the end cap on the sensor (see Fig. 1), which creates a hydrodynamically stagnated zone that promotes the deposition of a thick particulate coating. This coating has the effect of isolating the detector from the suspension and altering the apparent solids concentration at the electrode surface. As the coating is removed by the further addition of acid or base, the detector "sees" a radically different physicochemical environment, resulting in a sudden shift in the signal magnitude and phase. This situation gives rise to a hysteresis loop in which the IEP is *incorrectly identified* by both the acid and the base titration. Although agglomeration does not directly influence the position of the IEP (only the magnitude of the measured signal is modified by an increase in particle
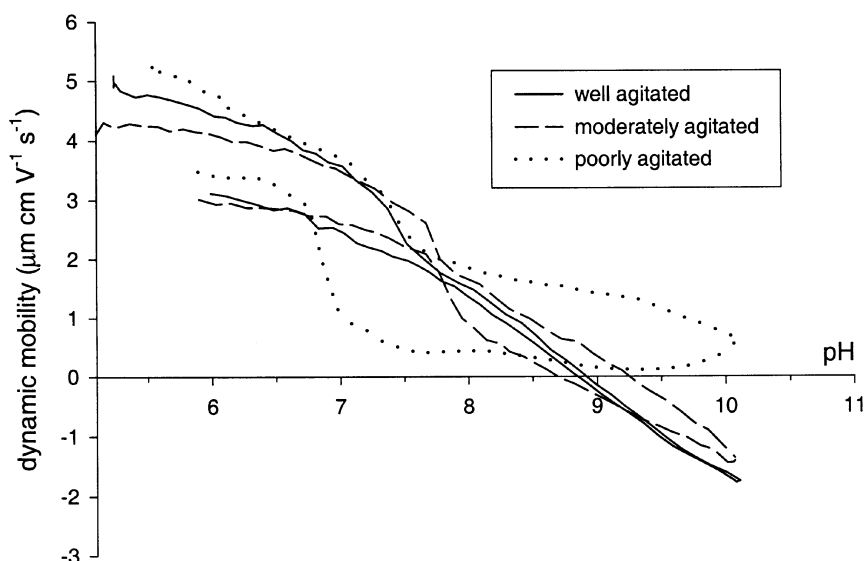

Figure 6. Comparison of three ESA titration curves for 10% AKP-30 alumina suspensions obtained under different levels of agitation and illustrating the hysteresis phenomenon.

inertia or a decrease in the effective solids concentration near the electrode), agglomeration indirectly impacts the IEP measurement because it determines the level of agitation required to maintain homogeneity and prevent the formation of a surface coating.

Since hysteresis occurs mostly at the high end of the solids loading range, where measurement sensitivity is not an issue, one should be able to simply remove the end cap and recalibrate the sensor when working at volume fractions above 5%. We attempted this procedure, but found that removal of the end cap caused some unidentifiable electronic interference that scrambled the input signals from the various sensors. As a result, we were unable to test this measurement configuration, but in theory it should work. In addition to the end cap, the impeller speed should be optimized for maximum mixing, but not so high as to cause entrainment of air bubbles. A combination of impeller and magnetic stirring may be necessary in some highly viscous systems, and has worked well in some experimental tests on alumina at 10% solids.

Hysteresis also appears to be dependent on the primary particle size of the powder. Electroacoustic titrations on nanophase titania suspensions (Fig. 7) exhibited extreme hysteresis even at volume fractions as low as 2%. We are presently investigating size dependence and will report our findings in a subsequent publication. We believe, however, that the large interfacial area associated with nanosize particles is the primary cause for the observed hysteresis. Extremely small particles destabilize easily because of the their large surface-to-volume ratio. At sufficiently high concentrations they will undergo a sol–gel transformation,[26] which results in extensive agglomerated structures and very high viscosities that impede mixing. The result is a thick coating of the agglomerated material on the detector surface.

For PCD, the hysteresis effect is less well understood, but as demonstrated for two different alumina powders in Fig. 8, it seems to be most prominent at the lowest solids concentrations. In Fig. 8 three sets of individual IEP values measured for AKP-30 and Grade A alumina powders by the PCD technique using NH_4OH as base titrant are compared. The filled and open symbols represent the forward (base) and reverse (acid) titrations, respectively. It should also be noted that Grade A alumina, which displays a stronger trend, has a much smaller grain size relative to AKP-30. Further studies are required to reveal the exact origin of the hysteresis phenomenon in PCD titrations, but it is believed that particle size and agglomeration are important factors, as they appear to be for electroacoustic measurements. The effect seems to be particularly noticeable in systems where NH_4OH has been used as a titrant.
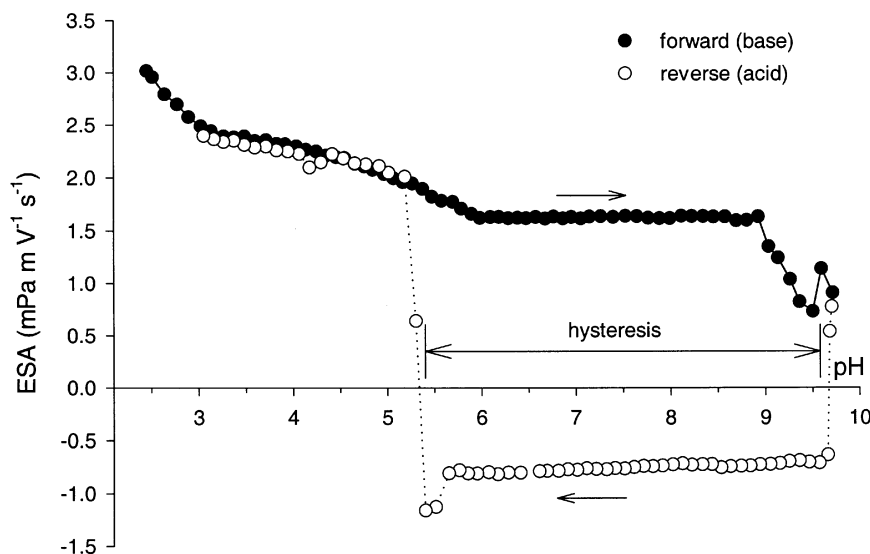

Figure 7. Electrokinetic curves measured by ESA for 2% nanophase P25 titania showing prominent hysteresis between forward (base) and reverse (acid) titrations.
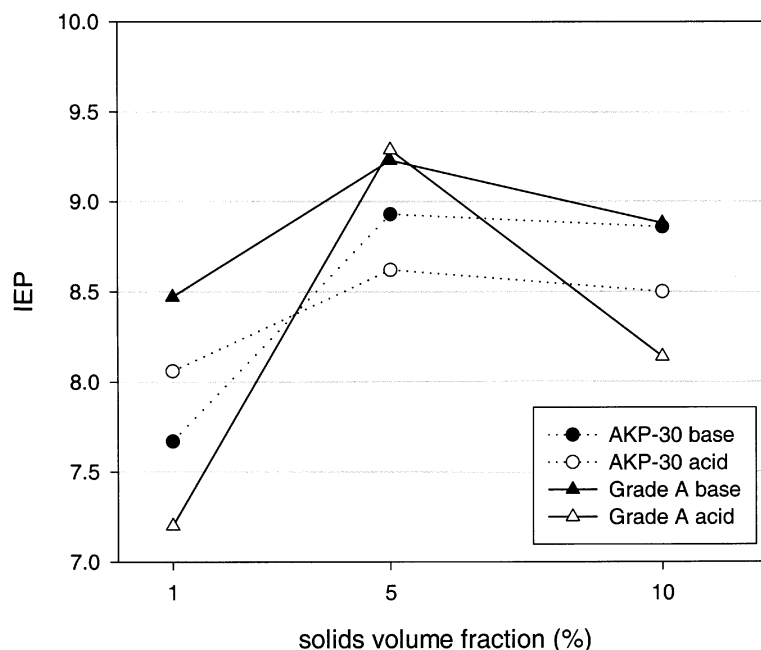
Figure 8. Three sets of IEP values each for AKP-30 and Grade A alumina measured by the PCD technique using NH_4OH as base titrant. The values are shown as a function of solids volume fraction for each acid–base titration pair, illustrating the degree and direction of hysteresis.

Error Due to pH Measurement

The measurement of pH plays a central role in IEP determination and is often responsible for much of the associated measurement error. It is well established that the commonly used glass membrane electrode will generate different pH values depending on the hydrodynamic environment to which it is exposed. In other words, a well-stirred suspension will produce a lower pH value than a quiescent suspension. Therefore it is important to calibrate the pH electrodes under measurement conditions.

The so called *suspension effect* is thought to result from the influence of the electrically charged colloidal phase on the ion diffusion potential in the neighborhood of the H^+-permeable membrane of the pH electrode.[27] If this were true in the present case, then we should expect to find the effect absent near the IEP where the particles are uncharged. The exact origin of the suspension effect is debatable, and may vary depending on the system conditions and the pH electrode used. Regardless, the effect if present should be most pronounced at higher solids concentrations. Therefore, we looked for the presence of a suspension effect in 10% alumina suspensions. Figure 9 shows the magnitude of this effect for pH measurements in 10% alumina as a function of the nominal suspension pH value. In these experiments, suspensions were prepared according to standard protocol described previously for electroacoustic titrations. Following aging, the pH in the suspension was recorded in a stirred cell, after which the solid phase was removed by high speed centrifugation and the pH of the supernatant was measured under near identical hydrodynamic conditions. The pH electrode was calibrated just prior to the experiment and a temperature thermocouple sensor was utilized to compensate for any temperature-dependent variations in pH. Replicate samples were prepared and tested for each nominal pH value. The difference between the pH in the suspension and it's corresponding supernatant ($pH_{susp} - pH_{super}$) gives the systematic error attributed to the so-called suspension effect. As shown in Fig. 9, the average pH error due to the presence of the colloidal phase, although fairly constant at about 0.2 pH units, can be negative or positive depending on the pH range. Also,
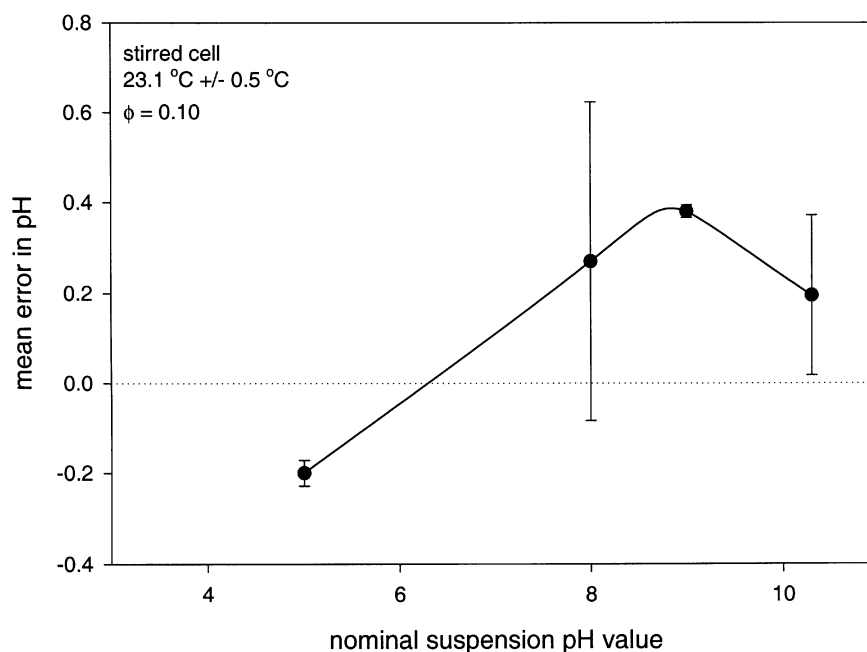
Figure 9. The magnitude of the suspension effect for pH measurements in 10% alumina as a function of the nominal pH value. The difference between the pH in the suspension and the corresponding supernatant ($pH_{susp} - pH_{super}$) yields the systematic error attributed to the suspension effect.

it is apparent that a significant suspension effect is present in the pH region near the IEP of alumina. This would appear to exclude ion diffusion phenomena as a source in this case, since the particles carry little or no charge in this pH range, and the observed effect exhibits a maximum error near the IEP.

The standard deviation shown in Fig. 9 also provides some indication of the dependence of measurement precision on the hydrogen ion activity in the alumina-water system at the high end of the moderate concentration range. The repeatability of pH measurements should be poor near neutral pH where both the hydrogen ion concentration and the buffering capacity are low; this is reflected in the relatively large standard deviation associated with a nominal value of pH 8 in Fig. 9. At high pH, the standard deviation is also large, probably as a result of the low proton concentration and nearness to the outside limit of the calibration range. A clear relationship between particle charge and the pH error associated with the suspension effect in the present case is not well apparent. We infer from this data that the contribution of the suspension effect to the error in IEP determination for alumina is from 0.3 to 0.4 pH units at 10% solids; the contribution is probably insignificant at solids concentrations much below 5%. It is not established whether these values depend on material properties. It is conceivable that a calibration curve could be determined for a particular material and concentration, and then used to correct titration pH values to arrive at a more accurate IEP determination. We furthermore conclude that the uncertainty in pH measurement alone (excluding the systematic suspension effect), for a properly calibrated glass electrode in moderately concentrated suspensions under typical measurement conditions, can be expected to range from about ±0.05 to ±0.1 pH units, depending on the solids concentration and pH range. This level of uncertainty is sufficient to account for most of the variation observed for CVI and ESA measurements at 5% and 10% solids. For PCD, this error accounts for less than half of the observed spread at any of the solids concentrations tested. The uncertainty in pH measurement (excluding the suspensions effect) is expected to increase when the system is not at or near steady state. Thus, during fast titration of a suspension the error in pH measurement will be greater compared to slow titration. This dependence can be eliminated by testing the depen-

dence of IEP on the delay time between titrant addition and pH measurement.

Sample Preparation

The manner in which the powder is dispersed in the liquid phase, and the treatment history of the resulting suspension prior to measurement, may impact the characterization of electrokinetic properties. In particular, any treatment that influences the degree of agglomeration or shifts the chemical equilibrium in the suspension, should be examined. We have analyzed a number of controllable sample preparation factors including aging time, initial pH, and level of deagglomeration achieved via high intensity ultrasonic disruption.

For the AKP-30 alumina test powder, aging of the suspension from 2 hr to 24 hr caused no significant variation in the measured IEP above that of normal scatter. A systematic investigation of a number of other sample preparation factors has been completed using the ESA technique. Due the extensive nature of this work, the results will be detailed separately in a future publication. Briefly, these experiments have shown that, for electroacoustic measurements, the initial degree of agglomeration within the test suspension has no significant influence on the determination of the IEP, but it will influence to varying degrees the magnitude of the electroacoustic signal at any given pH value not corresponding to the IEP. In this study, samples were deagglomerated to varying degrees by ultrasonic treatment and pH adjustment prior to aging, whereas in some cases the suspensions were left untreated except for gentle mechanical mixing. The measured IEP values for alumina showed no significant dependence on treatment history. However, the initial agglomerate size in the suspension prior to titration will affect the signal magnitude via inertial damping of the induced oscillation, as described previously. But this effect does not impact the IEP in moderately concentrated suspensions, since the particles do not oscillate when the net surface potential is zero.

One of the benefits of working with moderately concentrated suspensions, as opposed to dilute systems, is the greatly reduced sensitivity of the system toward contamination and solubility issues. Minor and trace contaminants, such as residual phosphate from pH buffer for example, that may significantly alter the surface properties of ceramic oxides and hydroxides in dilute suspension, are much less significant in moderately concentrated systems due to the large adsorptive interface present (i.e., the potential effect is attenuated by dilution of the contaminant species over a much larger surface area). The same rule applies to sparingly soluble ceramics like barium titanate, in which barium ion is leached into solution leaving behind an oxide-enriched phase. At sufficiently high solids concentrations, the barium loss on a per unit surface area basis is relatively small, and the average electrochemical properties of the system remain largely unaffected.[7] The solution concentration of the dissolved species is controlled entirely by the thermodynamic equilibrium solubility parameter for the solid-solution system, irregardless of solids concentration.

Other Factors

Additional factors that may impact electroacoustic measurements include changes in sound speed and acoustic impedance as the volume fraction reaches the upper end of the moderate range. These changes primarily affect the magnitude of the electroacoustic signal, and are not likely to impact the determination of IEP significantly, at least not in the moderate concentration range. Another factor to consider is calibration. None of the three techniques investigated can produce a quantitative value for zeta potential without calibration to a material of known potential. This is fairly easily accomplished for CVI and ESA using a commercial Ludox TM sol diluted to a solid volume fraction of 10% in 0.01 M KCl or KNO_3. According to the instrument manufacturers, this suspension should produce a value of $\zeta = -38$ mV at 25°C. The PCD technique presents a more difficult challenge for calibration, since the number and size of the particles adhering to the PTFE walls is variable and unknown, and the calibration would be sensitive to small variations in the dimensions of the annulus.[17] Fortunately, for IEP determination it is not absolutely necessary to calibrate the response signal in any of these techniques; calibration is useful, though, for more convenient comparisons of electrokinetic curves between different instruments and laboratories.

CONCLUSIONS

We have investigated electrokinetic measurements of alumina using CVI, ESA, and PCD as a model for developing guidelines and improving methodology for

the characterization of moderately concentrated aqueous suspensions of submicrometer ceramic particles. As a result of this study we offer the following recommendations for practical application of these techniques.

i.   A solids concentration of at least 2% and no greater than 10% should be used. The optimum concentration for most purposes is 5%.

ii.   If a supporting electrolyte is employed, and this practice is recommended in order to obtain better reproducibility, then $NaNO_3$ provides the best combination of low reactivity towards most ceramic materials and minimal electroacoustic response. Ammonium nitrate also generates a small (negative) electroacoustic signal and can be substituted for sodium nitrate, but ammonium ion is not chemically stable at alkaline pH values and may interfere with measurements in this pH range. The choice of electrolyte for PCD measurements is not so critical, and any stable, indifferent ion pair will suffice. For most purposes, an electrolyte concentration of 0.01 M is adequate to maintain constant ionic strength between pH 3 and pH 10. At extreme pH values, the addition of acid or base will significantly contribute to both conductivity and ionic strength, and can also result in a significant contribution to the electroacoustic background signal. The electrolyte concentration should not exceed 0.05 M under most circumstances, but particularly for solids concentrations below 5% where the electroacoustic signal from the ions may be significant relative to the particle signal. Higher electrolyte concentrations will also destabilize the suspension and lead to agglomeration.

iii.   Titrants should be nonreactive hard acids or hard bases of high purity and with concentrations appropriate for the sample volume and solids loading. This means that NH_4OH is a poor choice for a base titrant, and should certainly be avoided for titrations in which pH values exceed nine. The recommended system for obtaining the most reliable and reproducible titration results using any of the measuring techniques tested here, and for most ceramic applications, is HNO_3–$NaOH$–$NaNO_3$.

iv.   The solid phase itself can also contribute ions to the solution. For improved accuracy at the low end of the solids concentration range (below 5%), the background electroacoustic signal should be separately measured and subtracted from the sample signal when using CVI or ESA measurements. To account for any contributions from the solid phase, the background signal is best determined by preparing a suspension then removing the solid phase by centrifugation and measuring the supernatant. The ionic signal is largely independent of pH, so a single measurement is generally adequate. For a chemically stable material, it is probably necessary only to measure the pure electrolyte solution instead of the supernatant. The presence of a significant ionic background signal is often indicated by a characteristically abrupt jump in the electroacoustic signal of a suspension over an extremely narrow pH range in the neighborhood of the apparent IEP.

v.   For CVI and ESA measurements, stirring should be maximized during titration to the extent that air bubbles are not entrained and the electrode surface remains continually bathed in suspension. It may be necessary, especially at the higher solids loadings, to continually adjust the mixing rate or use supplemental stirring in order to compensate for increased viscosity and sedimentation near the IEP. This is a general drawback of working in the moderate concentration range.

vi.   For PCD, the optimum concentration range is dependent on grain size. This is attributed primarily to the dependence of suspension viscosity on grain size, an effect which becomes particularly important when the pH approaches the IEP. Finer particles tend to form thicker suspensions when they agglomerate. Therefore at the IEP, when the solid loading is too high, movement of the piston becomes erratic and the measurement error increases. The error increases also when the solids loading becomes too low, as a result of the lower signal-to-noise ratio produced by fewer particles adhering to the container wall. The following solid volume fraction ranges are empirically determined for optimum PCD measurement conditions: 1% to 10% for submicrometer sized powders down to a grain size of about 100 nm, and 0.1% to 1% for nanophase powders with grain sizes below about 100 nm.

vii.   Although the rate of titration does not appear to be a critical factor for the alumina system studied here, it is well known that other less stable or more slowly responding ceramic systems may express a significant rate dependence. To test for this dependence, an unknown powder should initially be titrated at two or more widely varying titration speeds. This can be accomplished by changing the equilibration or delay time in an automated titration. If a time dependence is indicated, then further analysis may be necessary to obtain the appropriate set of conditions for a titration.

viii.   A high quality combination glass pH electrode with a rapid response time and sufficient robustness to withstand the abrasive environment of a concentrated ceramic suspension, should be used. The electrode

should be calibrated against NIST-traceable (or equivalently standardized) buffers under similar stirring conditions as those used during the actual titration experiment, in order to reduce the error in pH measurement. It is recommended that pH electrodes be calibrated on a daily basis, and buffers should be refreshed at least weekly, depending on the level of use. Alkaline buffers, especially, are subject to change over time due to the absorption of atmospheric CO_2.

Because the design characteristics of each apparatus used in this investigation vary somewhat according to, among other factors, their sensor limitations and sample needs, a certain degree of variation in measured results between techniques is inevitable. In order to minimize this variation, it is necessary to develop a standard sample preparation procedure and compatible measurement protocols, and to use chemicals and materials that meet certain quality criteria. Further refinements in methodology and greater fundamental understanding are necessary to improve measurement agreement between different techniques and to reduce variability in IEP results. We are presently working to address this need

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