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ORIGINAL CONTRIBUTION

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Electrophoresis of colloidal α-alumina

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Abstract Measurements of the electrophoretic mobility (u_E) of particles of colloidal α-alumina were made as a function of pH, electrolyte concentration and electrolyte type (NaCl, $NaNO_3$ and KCl) using two similar instrumental techniques. Significant differences (50% or less) in the values of u_E of particles in NaCl were obtained from the two instruments; however, the isoelectric points (IEPs) (the pH at which $u_E = 0$), estimated from the two sets of measurements, occurred at 7.5 ± 0.3 and 7.8 ± 0.05 and were not significantly different. The latter estimate corresponds with those for particles in KCl and $NaNO_3$ of 8.05 ± 0.11 and 7.95 ± 0.18, respectively, made using the same instrument and indicate that the IEP was a weak function of electrolyte type. When cations acted as counterions (pH > IEP), the absolute magnitudes and the ranges of u_E with electrolyte concentration were found to be significantly less than when anions acted as counterions (IEP > pH). Estimates of the zeta potential (ζ), made using various procedures, showed variations of up to 25% at low ratios of electrical-double-layer thickness (κ^{-1}) to particle radius (a) ($\kappa a \sim 10$) and were of a similar scale to differences in u_E, but no significant variations (95% confidence) in ζ were obtained at high values ($\kappa a \sim 200$).

Key words Colloid · Alumina · Electrophoretic mobility · Zeta potential

Introduction

Alumina (Al_2O_3) occurs naturally in various types of soils, sediments and rocks. It exists in a variety of crystalline habits. The common forms are α, β and γ, of which the former is the most stable under usual laboratory conditions. Alumina is used in the manufacture of paint, abrasives, toothpaste, catalysts, glass, pigments, various ceramic products, refractories and inorganic fibres. In natural water systems alumina regulates the composition of water via processes at the sediment–water interface [1].

The physicochemical, surface and structural properties of this material have previously received some attention. [2–7]; however, limited attention has been given to α-Al_2O_3 compared with the γ form. Estimates of the zeta potential (ζ) were frequently reported without the corresponding experimental values of the electrokinetic measurements on which they were based and the isoelectric point (IEP) of α-Al_2O_3 reportedly ranges from 3.3 to 9.2 [4, 5]. This range may arise from the electrokinetic method used, the particle size and shape, the surface chemical and mineralogical composition, the sample preparation and the composition of the electrolyte.

It is well established that knowledge of ζ is of value in estimating the stability of colloidal dispersions towards particle aggregation and this has application in processes involving sedimentation, flotation and particle deposition [8, 9].

The theory describing the relationship between ζ and the electrophoretic mobility (u_E) [10] has developed to include the effects of electrophoretic retardation, relaxation, surface conduction [8–19] and local modifications to the properties of the fluid in the electrical double layer [20]. Particles are usually assumed to be spherical and monodisperse; however, Dukhin and van de Ven [21] have included the particle number distribution function in calculations of ζ to consider the consequences of particle polydispersity.

In this communication, the appropriate bulk and electrophoretic properties of fine particles of α-alumina are reported as a function of pH and electrolyte concentration for various electrolytes. Estimates of the uncertainty in u_E (arising from the use of different instruments) and in ζ made using a variety of analytical and numerical procedures are presented.

Materials and methods

Materials

α-Alumina (AKP 30 grade, Mandoval Zirconia Sales, UK) was used as obtained. The chemical analysis reported by the manufacturer (Table 1) suggests that the bulk material is of high purity, 99.99 wt% Al_2O_3.

All the chemicals used were of analytical reagent grade. Water, of pH and specific conductance in the ranges 5.5–5.8 and 0.7–1.2 μScm^{-1}, respectively, was produced by reverse osmosis, ion exchange, activated carbon adsorption and microfiltration (Elgastat Spectrum R).

Methods

The particle diameter (d) and the mean particle diameter (d_v), on a volume basis, and size distribution were determined using laser diffraction (Mastersizer, Malvern Instrument, UK). The particles were dispersed in either water or a solution of sodium carbonate and sodium hexametaphosphate in a weight ratio of 1:1 at a total concentration of 1% w/v at a pH of 10.5. The solution was then diluted with water (about 1:1000) prior to analysis. Light scattering data were processed, on a model-independent basis, with proprietary software using default optical parameters. pH measurements were made using a Philips PW 9421 digital pH meter.

Measurements of u_E were made using automated instruments (Zetamaster and Zetasizer II, referred to as ZM and ZS, respectively, Malvern Instruments, UK). The particles (0.04–0.2% w/v) were dispersed in electrolyte with the aid of ultrasonication. Samples were withdrawn and their pH adjusted by stepwise addition of acid or base of the corresponding salt. They were allowed to stand (48 h) in sealed high-density polyethylene containers and their pH was then measured. Replicate aliquots were withdrawn from the samples and injected into the electrophoresis cells. These were cylindrical quartz tubes (4-mm diameter) housed in a water bath below which a Peltier device was positioned. The design is essentially the same in both instruments. Up to ten repeat measurements of light scattering from the intersection of the so-called stationary level and the horizontal mid-plane of the cell closest to the detection system were made. The data were processed using proprietary software to provide estimates of the average u_E and its standard deviation. Sample dispersions and support electrolyte solutions were prepared separately for use with each instrument using the same materials under near identical conditions.

Table 1 Chemical analysis of α-alumina specified by the manufacturer

Component	Al_2O_3	Fe	Si	Cu	Mg	Na
Wt%	99.99	0.002	0.005	0.001	0.001	0.001

Results

Particle size

The size distribution of the particles dispersed, in the presence of sodium hexametaphosphate, with the aid of ultrasonication indicates that 90% of the sample volume falls within the range $0.2 \le d \le 0.8$ μm (Fig. 1). The ratio of the volume-mean diameter (d_v) (0.4 μm) to the number-mean diameter (d_n) (0.34 μm) was found to be 1.18, indicating a reasonably monodisperse system. The value of d_v for dispersion in water was found to be 0.52 μm, just outside the range quoted by the manufac-

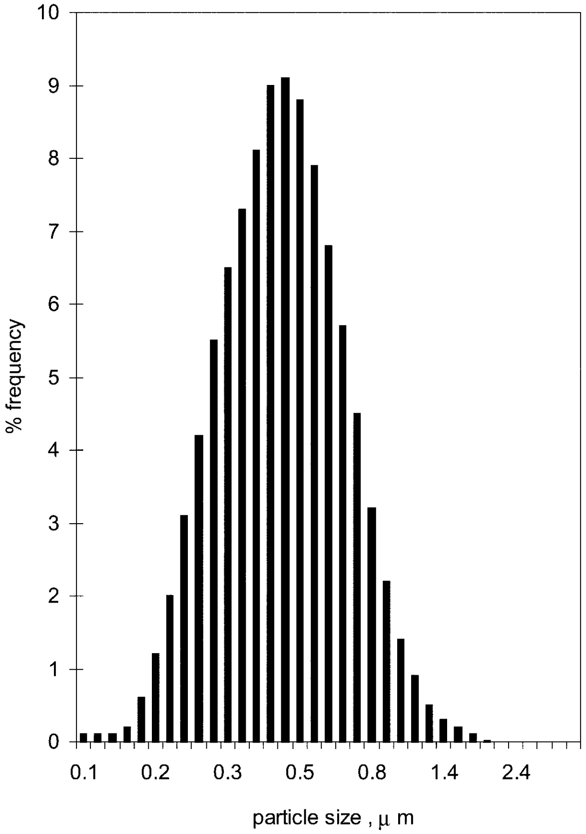

Fig. 1 Size distribution of α-alumina particles (volume frequency distribution)

turer (0.3–0.5 μm), and was sensitive to agitation of the dispersion.

u_{E} as a function of pH

The standard deviation in u_{E} at a given pH and electrolyte concentration was ± 0.08 μm cm V^{-1} s^{-1} or less and the error in the pH was estimated to be 0.02 pH units or lower.

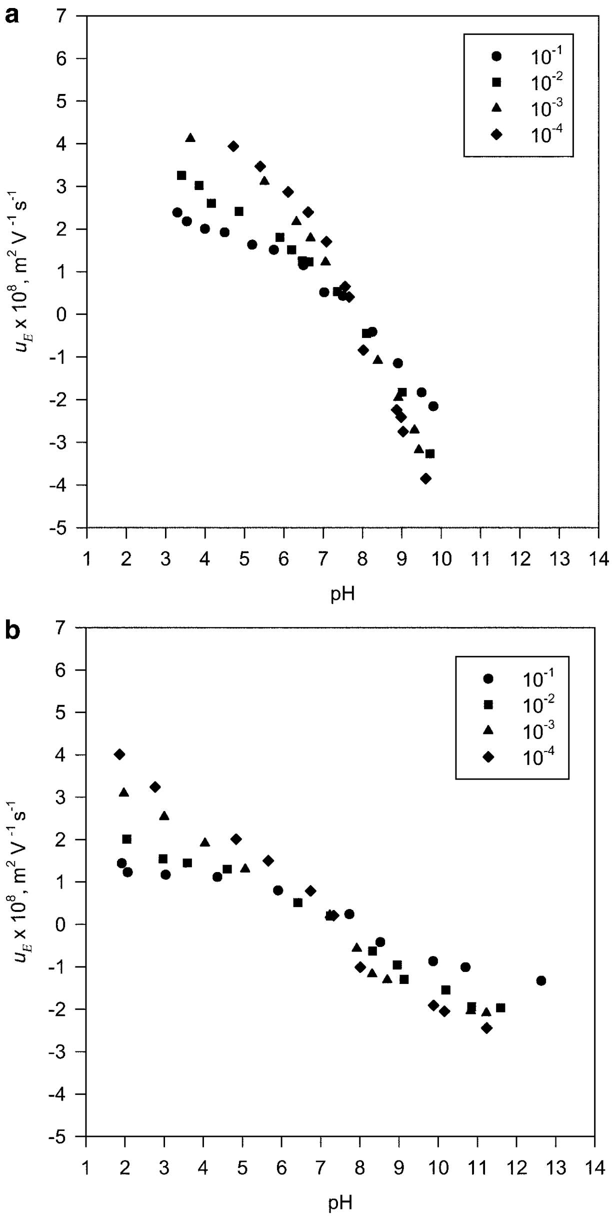

Fig. 2a Electrophoretic mobility (u_{E}) as a function of pH in aqueous NaCl (mol dm^{-3}) (Zetasizer II, *ZS*). **b** u_{E} as a function of pH in aqueous NaCl (mol dm^{-3}) (Zetamaster, *ZM*)

Significant differences (50% or lower) were observed in the measurements of u_{E} made with the ZS and ZM instruments for this alumina dispersed in aqueous NaCl (Fig. 2); $|u_{\mathrm{E}}|_{\mathrm{pH},c}$ (ZS) is generally greater than $|u_{\mathrm{E}}|_{\mathrm{pH},c}$ (ZM). At pH $\sim$ 3, as the electrolyte concentration decreases from 10^{-1} to 10^{-4} mol dm^{-3}, u_{E} increases from 2.5 to 4.0×10^{-8} m^2 V^{-1} s^{-1}, using the ZS (Fig. 2a), and increases from 1.0 to 3.0×10^{-8} m^2 V^{-1} s^{-1}, using the ZM (Fig. 2b). Similarly at pH $\sim$ 9, u_{E} lies in the ranges $-4.0 \leq u_{\mathrm{E}} \leq -2.0$ and $-2.0 \leq u_{\mathrm{E}} \leq -1.0 \times 10^{-8}$ m^2 V^{-1} s^{-1} with increasing electrolyte concentration for both instruments, respectively. Whilst the error between the two ranges of u_{E} might appear to be proportional at high pH (above the IEP), it is not the case at low pH below the IEP).

The IEPs of α-alumina (estimated by interpolation) were found to span the range $7.7 \leq \mathrm{pH} \leq 7.9$ using the ZM (Fig. 2a) and increased with decreasing electrolyte concentration, with an average of 7.80 ± 0.05 and spanned the range $7.2 \leq \mathrm{pH} \leq 8.0$ using the ZS (Fig. 2b), with an average of 7.52 ± 0.32. A *t* test involving six degrees of freedom and which assumes that IEP $\neq f$ (electrolyte concentration) indicates no significant difference between these two average values (at the 95% confidence level). With the latter instrument, the spread of the u_{E} data with electrolyte concentration as pH moves away from the IEP is broadly similar in both directions, whereas the u_{E} data below the IEP, obtained with the ZM, showed no tendency to disperse with electrolyte concentration in the range 5 < pH < 8.

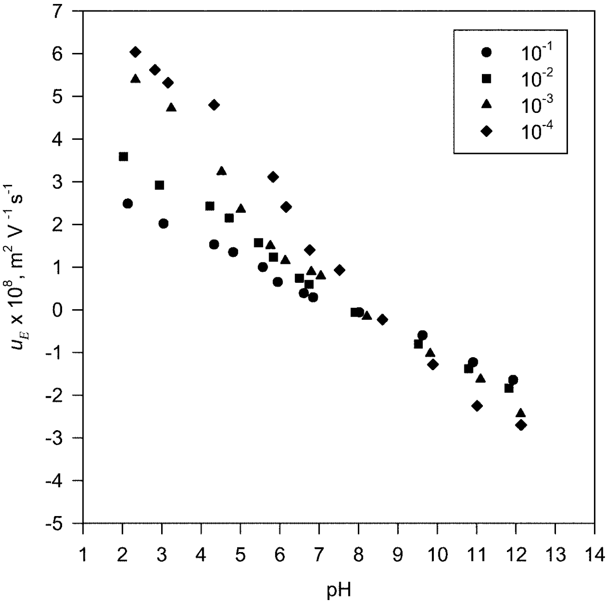

Fig. 3 u_{E} as a function of pH in aqueous KCl (mol dm^{-3}) (ZM)

The IEPs of this material in KCl, estimated from data obtained with the ZM, occur in the range $7.9 \leq \mathrm{pH} \leq 8.2$, with an average of 8.05 ± 0.11 (Fig. 3). At pH ~ 3, u_E has a wide range ($2.2 \leq u_E \leq 5.5 \times 10^{-8}\ \mathrm{m^2\ V^{-1}\ s^{-1}}$) with electrolyte concentration whereas at pH ~ 11, it has a significantly narrower range ($-2.5 \leq u_E \leq -1.2 \times 10^{-8}\ \mathrm{m^2\ V^{-1}\ s^{-1}}$).

In $NaNO_3$, the IEPs, estimated from data obtained with the ZM, occur in the range $7.7 \leq \mathrm{pH} \leq 8.2$, with an average of 7.95 ± 0.18 (Fig. 4). The range of u_E with electrolyte concentration at pH ~ 3 ($1.5 \leq u_E \leq 5.8 \times 10^{-8}\ \mathrm{m^2\ V^{-1}\ s^{-1}}$) is the widest of the three electrolytes examined. At pH ~ 11 the range is $-3 \leq u_E \leq -1.8 \times 10^{-8}\ \mathrm{m^2\ V^{-1}\ s^{-1}}$, which is intermediate between the ranges for NaCl and KCl.

Discussion

This small difference in d_v detected between particles analysed in the presence and absence of sodium hexametaphosphate probably arises from a slight instability of the particles in water. In the absence of electrolytes the pH was close to that of the water, but sufficiently far from the IEP of the particles to inhibit rapid aggregation.

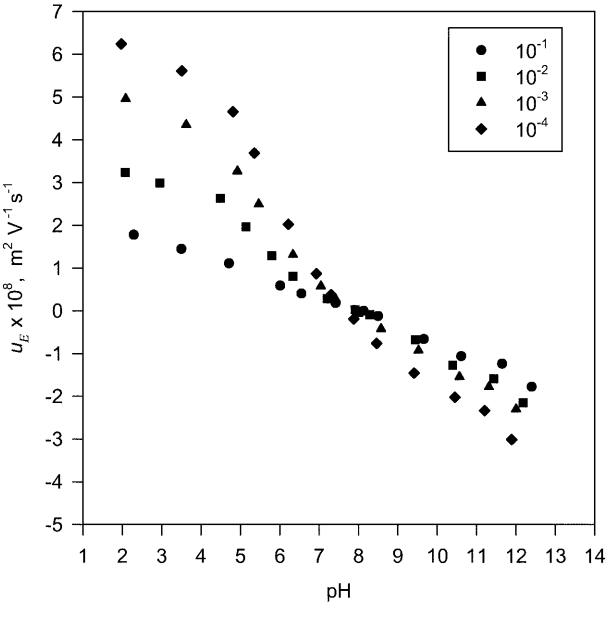

Fig. 4 u_E as a function of pH in aqueous $NaNO_3$ ($\mathrm{mol\ dm^{-3}}$) (ZM)

The large differences between the values of u_E of particles in aqueous NaCl obtained from two electrophoresis instruments may have several causes. Both instruments employ closed cells where application of a homogeneous electric field results in a balance between electroosmotic and laminar return flows with a so-called stationary level where measurements are usually made. Location of this level is made manually with the ZS, but automatically by the ZM. The similarity of the IEPs estimated from sets of measurements from each instruments suggests that consistent mislocation of the stationary level did not contribute significantly to the observed differences in u_E. Differences may also arise from a combination of factors associated with the manner in which the instruments manage application of the electric field, the thermal control and the data for estimating u_E, and processes such as aggregation, sedimentation and particle immobilisation at cell walls, which are functions of the residence time of the sample in the cell. The processes may affect the symmetry and location of the stationary level in a highly unpredictable manner. The time required for data collection and the consequent residence time of the sample in the cells is considerably longer for the ZS than for the ZM and suggests it to be the less sophisticated of these instruments in many respects relating to precision and accuracy of measurements.

Assuming some internal consistency of the data obtained with the ZM, the variations in the location of the IEPs with electrolyte concentration (about 0.2 pH units) and of the average values for each electrolyte type suggest that it is a rather weak function of both electrolyte type and concentration.

Various numerical and analytical procedures described in the literature were used to estimate ζ from u_E (Table 2). The κa value, which is a parameter input to numerical procedures, was estimated in the usual way [8, 12], where $a = d_v/2$. Estimates of ζ_{Smol}, ζ_{Henry}, ζ_{Huntr} and $\zeta_{\mathrm{Win\text{-}1}}$, for a given u_E, made at $\kappa a \sim 200$ ($10^{-1}\ \mathrm{mol\ dm^{-3}}$ NaCl) using these procedures (Fig. 5) show no significant difference at 96% confidence by a paired *t* test, but a significant difference (25%) was

Table 2 Various analytical and numerical procedures used in estimation of the zeta potential from the electrophoretic mobility

Procedure	Equation number or type of procedure	References	Abbreviation
Smoluchowki's equation	Eq. (3.3.1) [8]	[8], p 69; [10]	ζ_{Smol}
Henry's equation	Eq. (3.3.5) [8]	[8], p 71; [11]	ζ_{Henry}
Hunter	Eq. (3.7.14) [8]	[8], p 109	ζ_{Huntr}
WinMobil-1 (without Stern layer transport)	Numerical	[15]	$\zeta_{\mathrm{Win\text{-}1}}$
WinMobil-2 (with Stern layer transport)	Numerical	[15]	$\zeta_{\mathrm{Win\text{-}2}}$

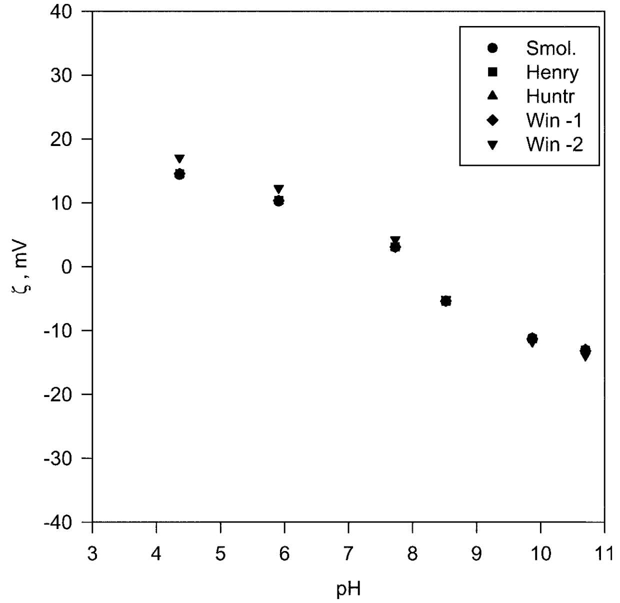

Fig. 5 Zeta potential (ζ) (estimated using various procedures) as a function of pH (NaCl 10^{-1} mol dm^{-3})

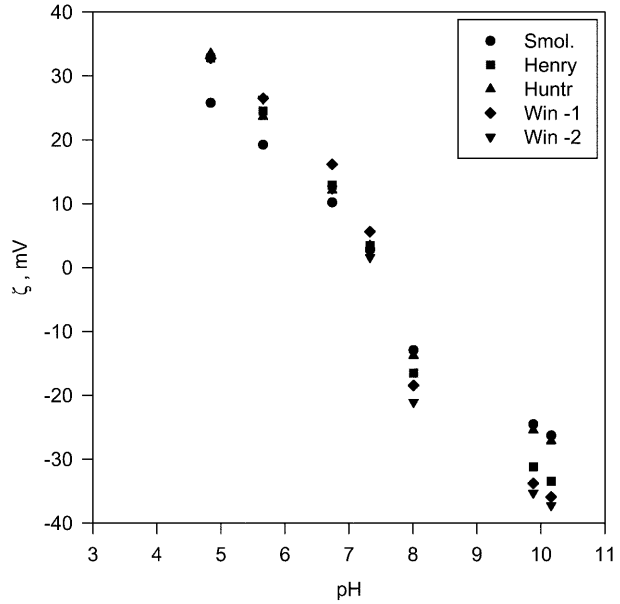

Fig. 6 ζ (estimated using various procedures) as a function of pH (NaCl 10^{-4} mol dm^{-3})

detected, on the same basis, between $\zeta_{\text{Win-1}}$ and $\zeta_{\text{Win-2}}$, suggesting that Stern layer charge transport was significant. Estimates of ζ for various u_{E} made at $\kappa a \sim 7$ (10^{-4} mol dm^{-3} NaCl) show significant variation (Fig. 6) especially at pH ≤ 5 and pH ≥ 9. Their absolute values generally decrease in the order $\zeta_{\text{Win-2}} > \zeta_{\text{Huntr}} > \zeta_{\text{Win-1}} > \zeta_{\text{Henry}} > \zeta_{\text{Smol}}$.

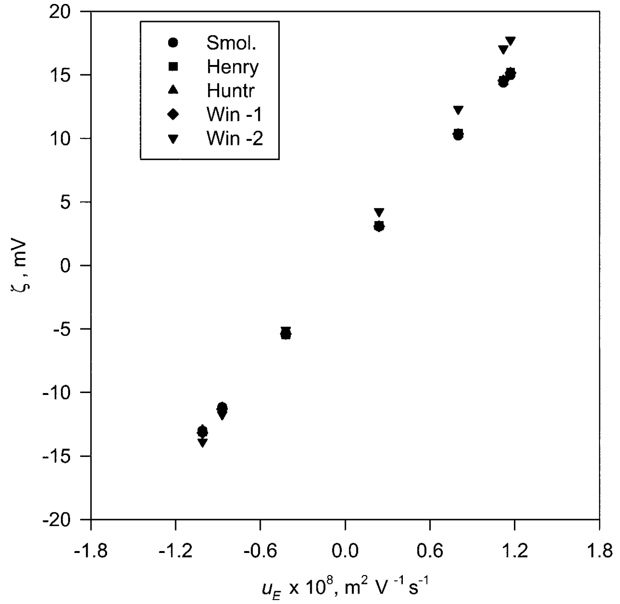

Fig. 7 ζ (estimated using various procedures) as a function of u_{E} (NaCl 10^{-1} mol dm^{-3})

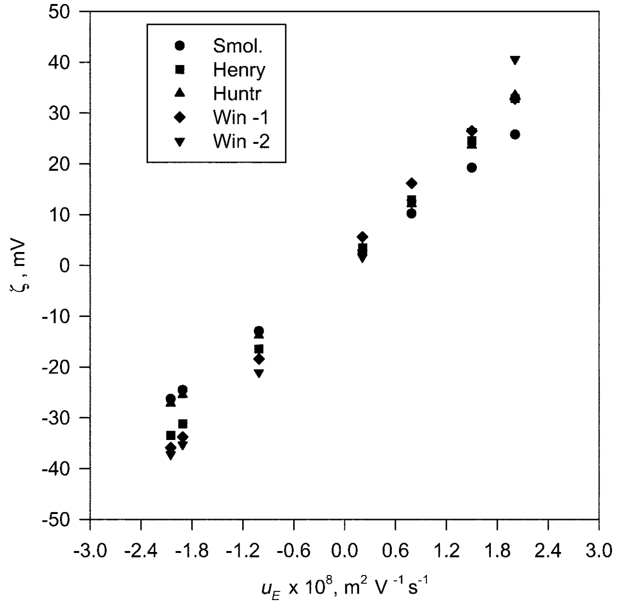

Fig. 8 ζ (estimated using various procedures) as a function of u_{E} (NaCl 10^{-4} mol dm^{-3})

The relationships between the various estimates of ζ and u_{E} for high κa (about 200) are approximately linear and are very similar (Fig. 7), whereas at low κa (about 7), they show significant spread and deviation from linearity (Fig. 8). Estimates of $\zeta_{\text{Win-1}}$ as a function of pH and electrolyte concentration for alumina particles in NaCl, KCl and $NaNO_3$ suggest that

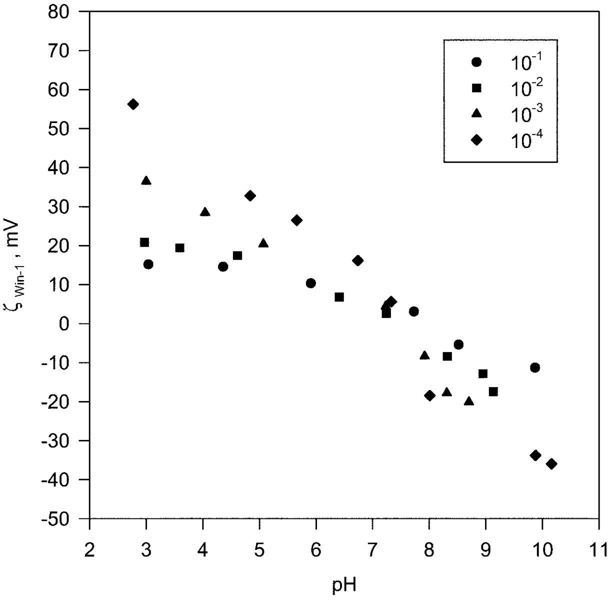

Fig. 9 $\zeta_{\text{Win-1}}$ as a function of pH (aqueous NaCl, mol dm^{-3})

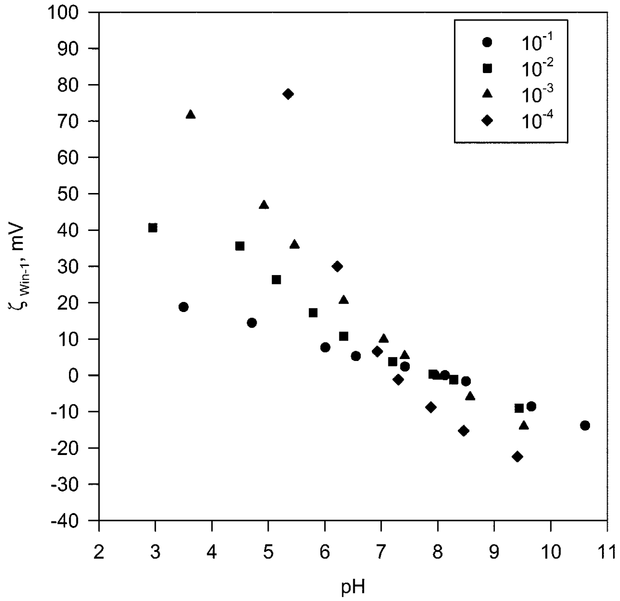

Fig. 11 $\zeta_{\text{Win-1}}$ as a function of pH (aqueous $NaNO_3$, mol dm^{-3})

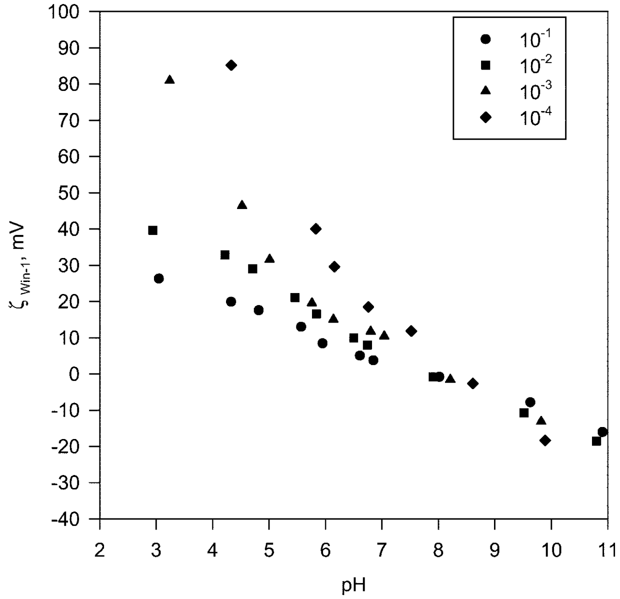

Fig. 10 $\zeta_{\text{Win-1}}$ as a function of pH (aqueous KCl, mol dm^{-3})

$|\zeta_{\text{Win-1}}|$ is generally greater for a positively charged surface at a given distance (in terms of pH) from the IEP (Figs. 9, 10, 11).

Estimates of $\zeta_{\text{Win-2}}$ are generally greater in magnitude than those of $\zeta_{\text{Win-1}}$ and involve the use of various parameters (site density, surface dissociation constants, inner and outer Stern layer capacitances) whose precise and appropriate values are often not well known. It is apparent that the variation in estimates of ζ are of a similar order to experimental variation in u_{E} arising from an attempt to independently reproduce the dataset. As errors in u_{E} are propagated as errors in ζ, acquisition of precise and/or appropriate values of the former is desirable. Errors may arise from a variety of subtle and time-dependent factors, not all of which will be subject to independent control with any particular equipment or instrument. As sets of u_{E} data often serve to validate or assist the solution of models of electrical double layers through ζ, their reproducibility, rather than repeatability, is valuable information to modellers; however, it does not often appear to be reported and this work suggests that it warrants some attention.

Conclusions

1. This source of α-alumina exhibits IEPs in the range $7.5 < \text{pH} < 8.2$ in 1:1 aqueous NaCl, $NaNO_3$ and KCl electrolytes which appear to be weak functions of electrolyte type and concentration.
2. Poor reproducibility between sets of u_{E} data leads to uncertainty in ζ, similar in scale to the differences in ζ obtained by various methods from a precise value of u_{E}.

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