ELECTROKINETIC CHARACTERISATION OF COLLOIDAL α-ALUMINA

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Abstract

Electrophoretic mobility (u_E) is an important measurable parameter in studying the electrokinetic properties of a colloid dispersion. This parameter is often converted into zeta potential (ζ) which plays a great role in the description of the stability towards aggregation of dispersed particles. In this paper, measurements of u_E of colloidal α-alumina dispersed in various concentrations of electrolyte are reported. It was observed that, the isoelectric points (the pH at which $u_E = 0$) occurred at 7.52 ± 0.32, 8.05 ± 0.11 and 7.95 ± 0.18 in NaCl, KCl and $NaNO_3$ respectively. The isoelectric point was observed to be a function of the type of electrolyte. The Na^+ and K^+ ions were observed to reduce the magnitude of u_E significantly compared with the Cl^- and NO_3^- ions. The estimates of ζ using various procedures showed variations of up to ± 25% at low electrolyte concentration. However, at high electrolyte concentration, no significant variations were observed.

Key words: colloid; electrophoretic mobility; zeta potential.

INTRODUCTION

Alumina (Al_2O_3) occurs naturally in various types of soils, sediments and rocks. It exists in various forms with different crystalline structures. The important forms of alumina are α-Al_2O_3, β-Al_2O_3 and γ-Al_2O_3, among these, α-Al_2O_3 is the most stable. Alumina is widely used in the manufacture of paints, abrasives, toothpaste, catalysts, glass, pigments, various ceramic products, refractories and inorganic fibres. In soil and geological studies, alumina plays an important role in regulating the composition of soil-water, sediment-water and other natural water systems (Huang and Stumm, 1973).

Due to these technological interests, the physico-chemical and structural properties of this material have been studied by various authors (Yopps and Fuerstenau, 1964; Smit and Holten, 1980; Cesarano III *et al*, 1988; Sprycha, 1989; Belmonte *et al*, 1994; Baumgarten *et al*, 1995). From these works, it is apparent that: a) The zeta potential is frequently reported without reporting the electrokinetic parameter used to estimate it, b) little information has been reported on α-Al_2O_3 compared with γ-Al_2O_3, and c) the isoelectric point (IP) of α-Al_2O_3 spans a wide range (3.3 to 9.2) (Yopps and Fuerstenau, 1964; Smit and Holten, 1980). These variations of IP may be due to various factors such as the electrokinetic method used in the study, particle size, chemical and mineralogical composition of the sample, method of sample preparation before analysis and type of electrolyte. It is therefore apparent that, this wide range of the IP of this material clearly needs further investigations. In addition, the measurable electrokinetic parameters such as electrophoretic mobility (u_E), used in estimation of zeta potential (ζ) also need to be reported.

In this paper, bulk and electrokinetic properties of α-alumina are reported. Bulk properties reported in this study are particle density (ρ_p), particle diameter (d_p), particle size distribution and specific surface area (A_{sp}). These parameters are necessary in interpretation of electrokinetic and surface properties of a colloid. Electrokinetic properties presented herein are u_E and ζ. Values of ζ were estimated from u_E using various analytical and numerical procedures. The knowledge of ζ is important in describing the stability of colloidal dispersions towards particle aggregation and it is of great assistance in processes involving

sedimentation, flotation and particle deposition (Hunter, 1981; Elimelech *et al*, 1995).

THEORETICAL BACKGROUND

When colloid particles are dispersed in a polar medium, their surfaces acquire electrostatic charge through various mechanisms (Hunter, 1981; Elimelech *et al*, 1995; Shaw, 1992). To maintain electrical neutrality, ions of opposite charge from the bulk liquid (called counter-ions) gather around the charged particle. These ions form the so-called Stern layer. Ions of the same charge as the particle and the rest of the counter-ions, remain diffusely distributed distant from this particle. These ions form the so-called diffuse layer (or Gouy layer). This assembly of ions around a charged particle is that referred to as electric double layer (EDL). The Stern layer is usually referred to as the immobile part of the EDL whereas the diffuse layer is the mobile part.

Through various electrokinetic techniques (Hunter, 1981), the potential at the plane that separates the mobile and immobile parts of the EDL can be estimated. This potential is called zeta potential (ζ). Among these techniques, particle electrophoresis appears to be convenient as it provides information pertaining to individual or small groups of particles as opposed to an average effect of a packed bed (porous plug). Consequently, this method was used in this study. In this technique, u_E (defined as particle velocity per unit applied electric field is measured. This parameter (u_E) is subsequently converted to ζ using appropriate model of the EDL.

The theory describing the relationship between ζ and u_E has passed through a number of modifications and refinements. The main problem has been how to account for electrophoretic retardation, relaxation effects, surface conduction and properties of the fluid in the EDL. The details of these effects are discussed elsewhere (Hunter, 1981; Elimelech *et al*, 1995; Shaw, 1992). More recent developments of electrophoresis problem, which take into account of relaxation effects, include the works of Ohshima *et al* (1983), Zukoski and Saville (1986), O'Brien and White (1978), Mangelsdorf and White (1990); (1992); (1998); (1998). In most of these works, the particles are assumed to be spherical and monodispersed. Dukhin and Van de Ven (1994) have given an account for the case where the particles are polydispersed.

The problem of taking into account of the variation of liquid properties in the EDL has recently been studied by Mangelsdorf and White (1997). They presented a mathematical model for estimating dielectric properties of colloidal dispersions at various frequency domains of the applied electric field. Apparently, the difficulties in measuring these properties precisely (especially permittivity and viscosity) have made most of the workers in the field to resort to the use of either estimated ones or those in the bulk liquid.

Mangelsdorf and White (1990); (1992); (1998); (1998) have written a computer programme called WinMobil for computing ζ from u_E based on their model. This programme has two options, the first option does not include the effect of transport of ions in the Stern layer (Stern layer transport) and the second option takes into account of this effect.

MATERIALS AND METHODS

Materials

α-alumina (AKP 30 grade) obtained from Mandoval Zirconia sales Ltd, UK, was used as obtained. The chemical analysis shown in Table 1 is the specification of the manufacturer. It indicates that the material is of very high purity.

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

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

* Mandoval Zirconia Co. Ltd.

Chemicals

All chemicals used in the analysis were of analytical grade. Water used in all procedures, was high purity water produced by reverse osmosis, ion exchange, activated carbon adsorption and microfiltration (Elgastat spectrum R). The range of pH and conductance of this water were 5.5 -5.8 and 0.7 - 1.2 μS cm^{-1} respectively.

Methods

Particle density (ρ_p) was determined by pycnometry using water as the dispersion medium. Specific surface area (A_{sp}) of the material was determined using nitrogen gas adsorption and the BET method (ASAP 2000 System Micrometrics Instrument Corporation, USA). Particle diameter (d_p) and size distribution were determined using a laser diffraction analyser (MasterSizer, Malvern Instrument, UK). In determination of d_p and size distribution, the particles were dispersed in a solution of sodium carbonate and sodium hexa-metaphosphate in a weight ratio of 1:1 at a total 1% w/v at a pH of 10.5. The light scattering data were processed to give d_p size distribution using proprietary software.

Measurements of u_E

Measurements of u_E were made using a ZetaMaster (Malvern Instruments, UK). Particles were dispersed in electrolyte (0.2% w/v) with the aid of ultrasonication. Aliquots (50 mL) were withdrawn from this dispersion and their pH was adjusted by stepwise addition of acid or base of the corresponding salt. These samples were allowed to stand two days (48 hours) and the pH in each of these was measured before u_E measurement. All pH measurements were made using a Philips PW 9421 digital pH meter. For each u_E measurement, a set of 10 trials was made and each measurement was carried out in quadruplicate. The measurements were automatically processed using the proprietary software to give average values of u_E and their standard deviations. The overall standard deviation in u_E was ≤ ± 0.08 μm cm V^{-1} s^{-1} whereas the error in pH was ≤ 0.02 pH units. Measurements of u_E were made in various concentrations of NaCl, $NaNO_3$ and KCl.

RESULTS AND DISCUSSION

Bulk Properties

The bulk properties of this material determined in this work appear to be in good agreement with those specified by its manufacturer (Table 2). However, the manufacturer did not indicate the technique and dispersion medium used to arrive at the reported data.

Table 2. Bulk properties of the α-alumina sample

Source	This work	Manufacturer
ρ_p (g cm^{-3})	3.89 ± 0.04	3.80 - 3.90
d_p (μm)	0.40 ± 0.01	0.30 - 0.50
A_{sp} (m^2 g^{-1})	7.19 ± 0.19	5.0 - 10.0

The particle size distribution of this alumina shows that about 95% of the volume of the material have diameters within $0.2 \leq d_p \leq 1.4$ μm (Fig. 1). The estimated variance of the population was 0.2273 μm and the ratio of the number mean diameter to the volume mean diameter was 1.18. This suggests that the size distribution of this material is essentially monodisperse.

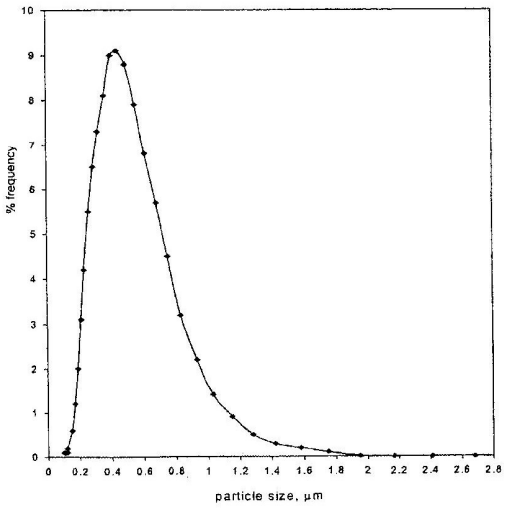

Figure 1. Size distribution of α-alumina particles (volume frequency distribution).

Electrophoretic mobility as a function of pH

Fig. 2 shows u_E as a function of pH in NaCl, from this it can be seen that the pH at which $u_E = 0$ (IP) spans the range $7.2 \leq$ pH ≤ 8.0 with an average of 7.52 ± 0.32. At the extreme acidic conditions (pH~ 3), u_E spans $1.0 \leq u_E$ 3.0 μm cm V^{-1} s^{-1}. Similarly at basic conditions (pH~ 9), u_E spans the range $-2.0 \leq u_E$ 1.0 μm cm V^{-1} s^{-1}.

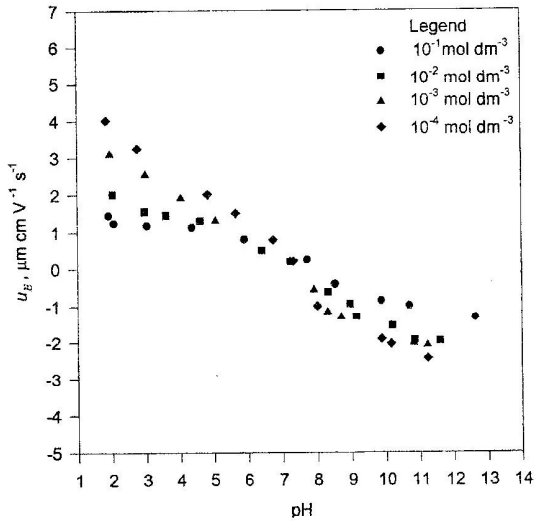

Figure 2. Electrophoretic mobility as a function of pH in various concentrations of aqueous NaCl.

The IP of this material in KCl occurs in the range of $7.9 \leq$ pH ≤ 8.2 with an average of 8.05 ± 0.11 (Fig. 3). At pH ~3, u_E has a wide range ($2.2 \leq u_E \leq 5.5$ μm cm V^{-1} s^{-1}) whereas at pH ~ 11, it has a narrow range ($-2.5 \leq u_E \leq -1.2$ μm cm V^{-1} s^{-1}) (Fig. 3).

In $NaNO_3$, the IP occurs in the range of $7.7 \leq$ pH ≤ 8.2 with an average of 7.95 ± 0.18 (Fig. 4). The range of u_E at extreme acidic conditions ($1.5 \leq u_E \leq 5.8$ μm cm V^{-1} s^{-1} at pH ~ 3) is also wider compared with that at extreme basic conditions ($-3 \leq u_E \leq -1.8$ μm cm V^{-1} s^{-1} at pH ~ 11) (Fig. 4).

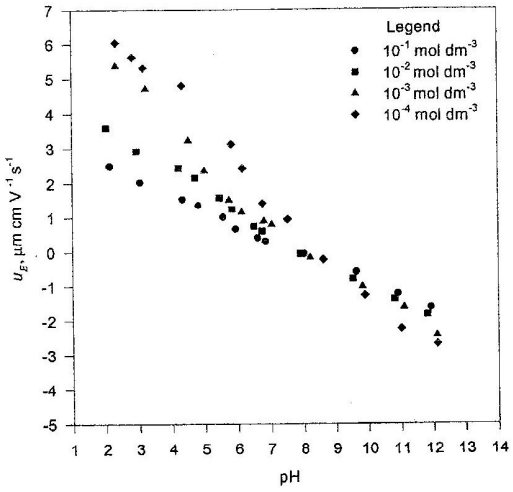

Figure 3. Electrophoretic mobility as a function of pH in various concentrations of aqueous KCl

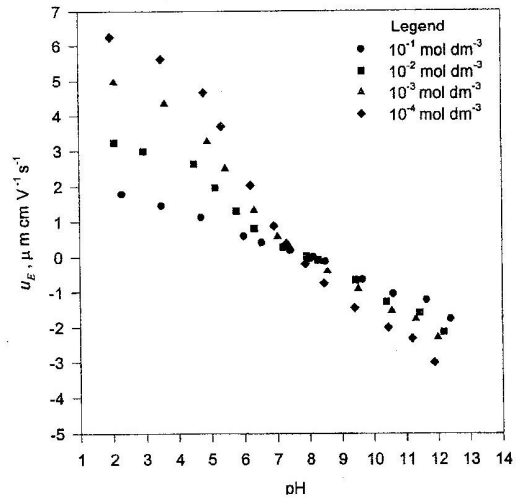

Figure 4. Electrophoretic mobility as a function of pH in various concentrations of aqueous $NaNO_3$

From these observations, the variations in the location of the IP ($7.5 \leq$ IP ≤ 8.2) appear to be significant. Although this range is narrower than that reported in literature ($3.3 \leq$ IP ≤ 9.2), it is apparent that the IP of this material is a function of the type of electrolyte. The variations of IP as a function of electrolyte concentration (c_0) for all electrolytes studied are small (typically ≤ 0.2 pH units) suggesting that it is a weak function of c_0. The wide and

narrow ranges of u_E at the extreme acidic and basic conditions may be described by considering the following factors:

a) Variation of the electrokinetic charge.
b) Variation of the thickness of the diffuse layer.
c) Adsorption of electrolyte ions (cations and anions) on the particle surface.

The increase in c_0 increases the electrokinetic charge, however, it appears that particles in high c_0 migrate slowly compared with those in low c_0. This may be explained as follows: as c_0 increases from 10^{-4} to 10^{-1} mol/dm^3, the thickness of the diffuse layer (κ^{-1}) estimated using standard procedures (Hunter, 1981), reduces significantly (Fig. 5). This compression of the diffuse layer reduces the movement of ions within it. In addition, the increase of c_0 increases the concentration of ions in the shear plane. All of these effects result in a decrease of the electrical force applied to the particle during u_E measurements and an increase in the viscous drag on the particle, which subsequently reduces the particle mobility.

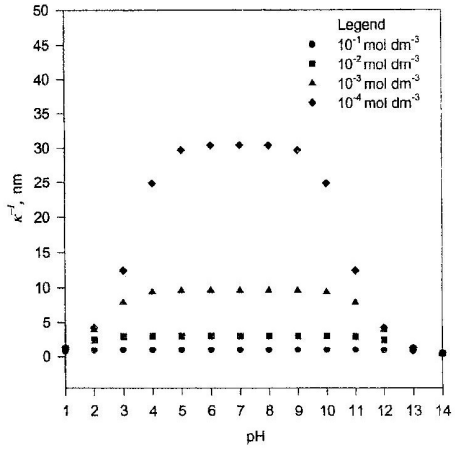

Figure 5. Estimates of thickness of the diffuse layer of ions formed around a charged particle suspended in various concentrations of a 1:1 electrolyte plotted against pH.

The presence of adsorbed ions (cations and anions) in the region where the shear plane is located has an effect on u_E similar to those arising from compression of the diffuse layer. However, various ion characteristics such as its extent of ion hydration (effective volume), packing characteristics, location of the charge, polarizability and mobility may significantly influence their amount in this region. It can be seen (Table 3) that, due to small hydrated ionic radii of Cl^- and NO_3^- ions and relatively more mobile compared with Na^+ and K^+ ions, they are likely to be more in this region. Since above IP, the positive charge is screened by anions whereas below IP the negative charge is screened by cations, it appears that despite of their large quantities in this region, the anions (Cl^- and NO_3^- ions) has little effect on u_E compared with the cations (Na^+ and K^+ ions) (Figs. 2-4). This effect is more pronounced in Fig. 4, suggesting that the NO_3^- ion has either significantly little effect on u_E or it experiences difficulties in getting into this region.

Table 3 Hydrated ionic radii and ionic mobility of various species (Israelachvili, 1992; Adamson, 1979).

Ion	Hydrated ionic radii (nm)	Ionic mobility ($cm^2\ V^{-1}\ s^{-1}$) x 10^4
H^+	0.28	36.30
OH^-	0.30	20.50
Na^+	0.36	5.19
K^+	0.33	7.62
Cl^-	0.33	7.91
NO_3^-	0.34	7.40

Zeta potential as a function of pH

In this work, various numerical and analytical procedures described in the literature were used to estimate ζ from u_E (Table 4). The κa values (Fig. 6) which are basic inputs for the numerical procedures were estimated using standard procedures described in the literature (Hunter, 1981; Shaw, 1992). The estimates of ζ made at constant κa values using the various procedures as a function of pH in 10^{-1} mol/dm^3 ($\kappa a \sim 209$) and 10^{-4} mol/dm^3 ($\kappa a \sim 7$) NaCl are shown in Figs. 7 and 8 respectively. From Fig. 7, it can be seen that, $\zeta_{Smol.}$, ζ_{Henry}, ζ_{Huntr} and ζ_{Win-1} show no significant difference. A paired t-test at 96% confidence level on these ζ values showed no significant statistical difference. However, a similar t-test between ζ_{Win-1} and ζ_{Win-2} showed a significant difference. These differences clearly reflect the effect of correction for the Stern layer transport.

Table 4 Various analytical and numerical procedures used in estimation of ζ from u_E.

Procedure	Equation number/ type of procedure	Abbreviation
Smoluchowki's Equation*	Eq. 3.3.1	$\zeta_{Smol.}$
Henry's Equation*	Eq. 3.3.5	ζ_{Henry}
Hunter and O'Brien*	Eq. 3.7.14	ζ_{Huntr}
WinMobil-1 (without Stern layer transport)+	Numerical	$\zeta_{Win\text{-}1}$
WinMobil-2 (with Stern layer transport)+	Numerical	$\zeta_{Win\text{-}2}$

* ref.(Hunter, 1981); + ref. (Mangelsdorf and White, 1990)

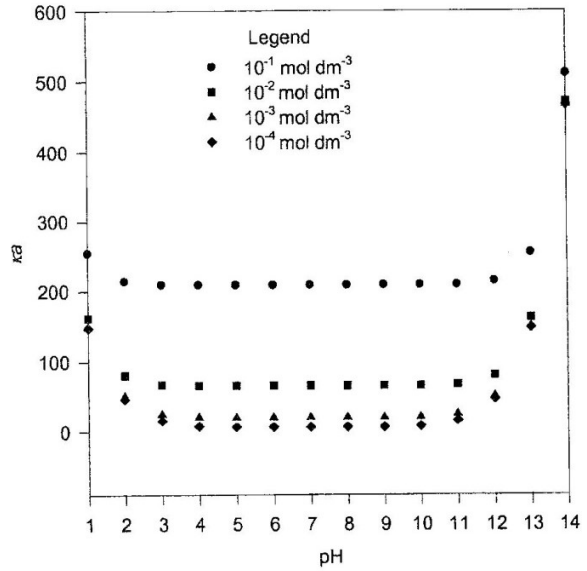

Figure 6. Estimates of the dimensionless quantity, κa, in various concentrations of a 1:1 electrolyte plotted against pH.

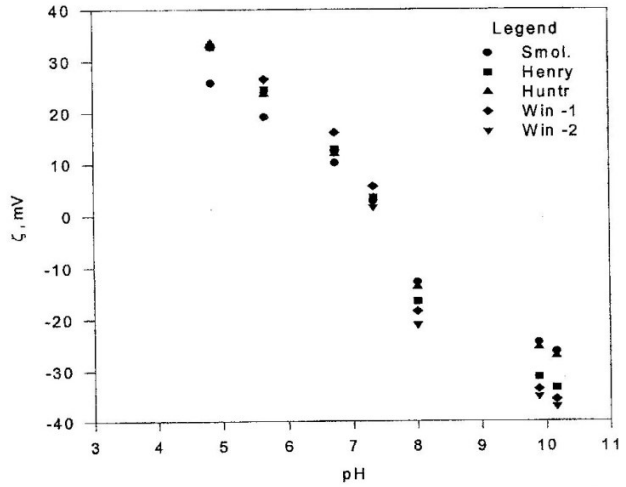

Figure 7. Various estimates of zeta potential plotted against pH (10^{-1} mol/dm^3 NaCl).

In Fig. 8, the estimates of ζ show significant variations especially at pH $\leq$ 5 and pH $\geq$ 9 and their absolute values generally decrease in the order of $\zeta_{\text{Win-2}} > \zeta_{\text{Huntr}} > \zeta_{\text{Win-1}} > \zeta_{\text{Henry}} > \zeta_{\text{Smol.}}$. A paired t-test at 96% confidence level on $\zeta_{\text{Win-1}}$ and $\zeta_{\text{Win-2}}$ showed a significant difference of up to $\pm$ 25%. Similar variations have been observed in the intermediate concentrations of NaCl and in the systems involving KCl and $NaNO_3$ (Ntalikwa, 2000). It is apparent that, these variations in ζ reflect the contribution of various effects such as electrophoretic retardation, relaxation and surface conductance.

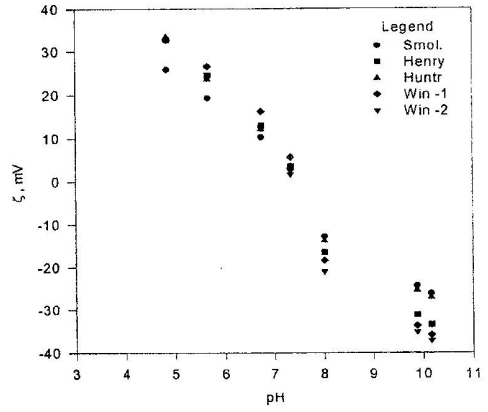

Figure 8. Various estimates of zeta potential plotted against pH (10^{-4} mol/dm^3 NaCl).

In all estimations of ζ, the absolute values of $\zeta_{\text{Win-2}}$ are generally greater than those of $\zeta_{\text{Win-1}}$. This is mainly due to the selection of various parameters (site density, surface dissociation constants, inner and outer Stern layer capacitances) associated with this procedure. These parameters are known with uncertainty, however, they are necessary in order to define the Stern layer adsorption isotherm. This suggests that the choice of a theory to be used in estimation of ζ is significant in order to arrive at its representative values. The inclusion of the Stern layer transport in estimation of ζ is a very satisfactory addition, however, a degree of caution must be exercised in its application because of the uncertainties involved in the input parameters.

The relationships between ζ and u_E for the five procedures used to estimate ζ in 10^{-1} and 10^{-4} mol/dm^3 NaCl are shown if Figs. 9 and 10 respectively. This relationship converges to a linear relationship at high κa (~ 209) (Fig. 9). However, at low κa (~ 7), the relationship shows significant deviations from linearity (Fig. 10). These observations are consistent with the literature (O'Brien and White, 1978; Mangelsdorf and White, 1990).

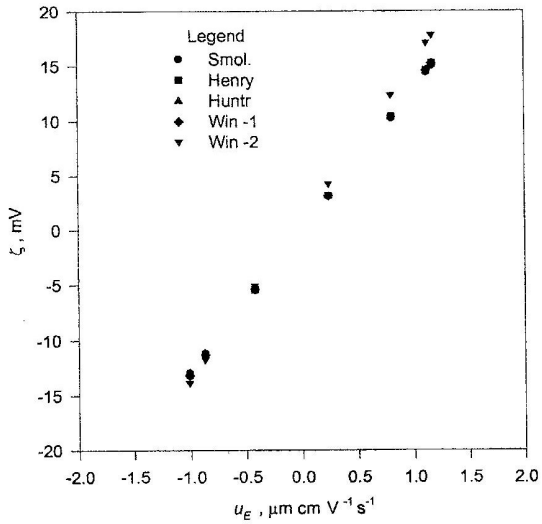

Figure 9. Estimates of Zeta potential versus electrophoric mobility (10^{-1} mol/dm^3 NaCl)

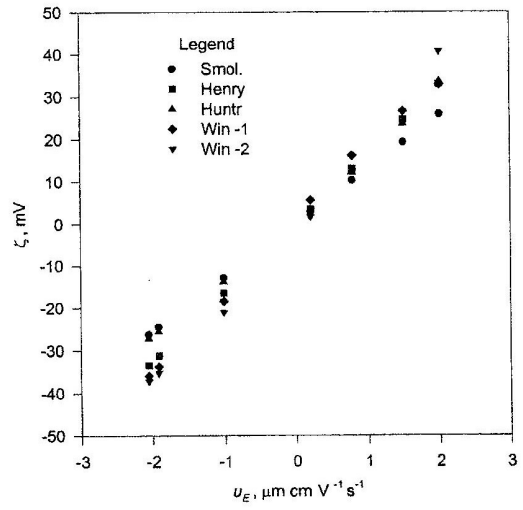

Figure 10. Estimates of zeta potential versus electrophoretic mobility (10^{-4} mol/dm^3 NaCl).

Since the treatment of the electrophoresis problem is advanced in the case of the

WinMobil programme, compared with the analytical equations, this paper recommends the use of this procedure in estimation of ζ from u_E for the α-alumina particles. Because of the uncertainties involved in the use of WinMobil-2, WinMobil-1 was chosen and used in the subsequent estimations of ζ. The results are presented in Figs. 11, 12 and 13 in various concentrations of NaCl, KCl and $NaNO_3$ respectively. It can be seen that for the pH range $3 \leq pH \leq 11$, ζ spans the range $-30 \leq \zeta \leq 80$ mV (Figs. 11-13). Since a colloid suspension is unstable towards coagulation at $\zeta = 0$, this observation suggests that the dispersion of this material in any of the electrolytes studied is more stable (towards coagulation) at low pH (~3) than at high pH (~11).

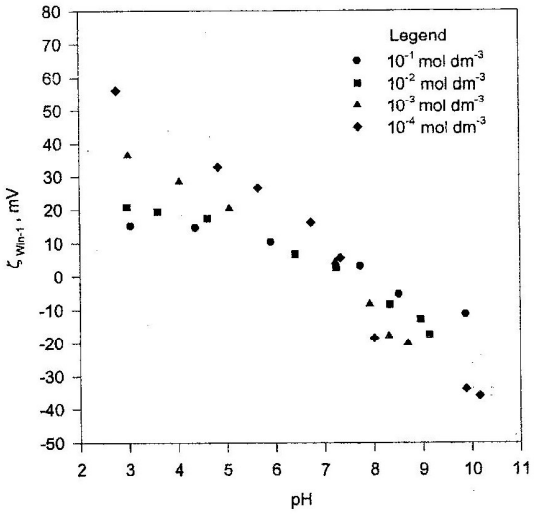

Figure 11. Effect of pH and concentration of NaCl on zeta potential (WinMobil-1).

CONCLUSIONS

From this study following conclusions can be made:

1. This material exhibits IPs in the range $7.5 \leq IP \leq 8.2$ in NaCl, $NaNO_3$ and KCl electrolytes, which is a weak function of the type of electrolyte and the electrolyte concentration (c_0).
2. The presence of cations as counter ions in the EDL significantly reduces the absolute magnitude of u_E at constant c_0 compared with when anions act as counter ions in the EDL.

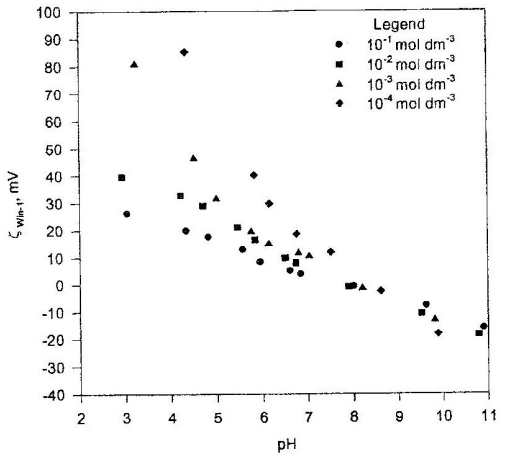

Figure 12. Effect of pH and concentration of KCl on zeta potential (WinMobil-1)

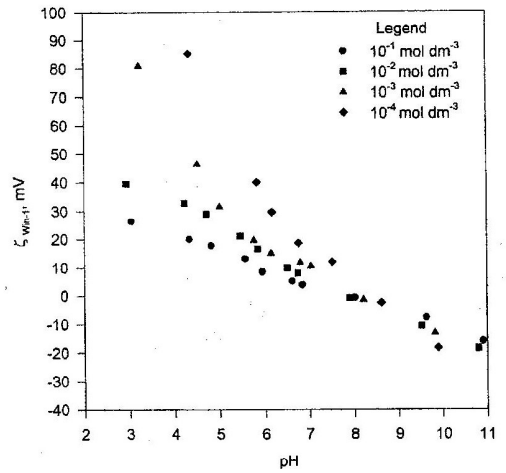

Figure 13. Effect of pH and concentration of $NaNO_3$ on zeta potential (WinMobil-1).

3. At high electrolyte concentration (high κa values), all procedures for estimation of ζ from u_E converge to a linear relationship, however, at low electrolyte concentrations (low κa values), these procedures deviate significantly from linearity.

NOMENCLATURE

a	Particle radius (m)
A_{sp}	Specific surface area of the particle ($m^2\ g^{-1}$)
c_0	Electrolyte concentration (mol/L)
d_p	Particle diameter (m)
u_E	Electrophoretic mobility (μm cm $V^{-1}\ s^{-1}$)
κ	Debye - Hückel parameter (m^{-1})
ρ_p	Particle density (g cm^{-3})
ζ	Zeta potential (mV)

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