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ORIGINAL CONTRIBUTION

R. C. Plaza
F. González-Caballero
A. V. Delgado

Electrical surface charge and potential of hematite/yttrium oxide core–shell colloidal particles

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R. C. Plaza · F. González-Caballero
A. V. Delgado (✉)
Departamento de Física Aplicada
Facultad de Ciencias,Universidad
de Granada, 18071 Granada, Spain
e-mail: adelgado@ugr.es
Fax: +34-958-243214

Abstract Interest in the synthesis of composite colloidal particles consisting of a core and shell with different compositions stems from the fact that such particles can be useful in processes where the properties of both core (e.g., size and shape homogeneity, ease of preparation in large amounts, magnetic characteristics, etc.) and shell (interfacial properties, porosity, chemical stability, etc.) might be of interest. However, the applicability must be based on a proper characterization of those properties. In this work, colloidal spheres of hematite (α-Fe_2O_3) were used as nuclei of mixed particles where the shell is yttrium oxide. The electrical properties of the aqueous interface are compared to those of the pure oxides by means of potentiometric titration of their surface charge and potential against pH, as a function of indifferent electrolyte concentration. It is found that the mixed particles efficiently mimic yttrium oxide, since the behavior of their surface electrical characteristics closely resembles that of the latter compound. Differences are found, however, that can be ascribed to an incomplete or porous coverage, but such divergences are of little significance when an overall comparison is carried out.

Key words Core–shell colloidal particles · Surface charge titration · Point of zero charge · Colloidal hematite · Colloidal yttrium oxide · Zeta potential · Surface potential

Introduction

Because of their many technological applications (in such fields as ceramics or audio-and video-tape manufacturing) and their frequent occurrence in natural and industrial environments, interest in the investigation of colloidal oxides is widespread. The synthesis and characterization of composite particles in which at least one of the components is an oxide is thus justified [1–5]. In this work, emphasis is on composite colloids consisting of an iron oxide (α-Fe_2O_3) core coated by an yttrium oxide shell: the properties of both the core (ease of synthesis with controlled size and geometry) and the shell (a ceramic material with a wide range of applications in such fields as high-temperature superconductivity) could, in principle, be taken advantage of. In previous work [6, 7], we have analyzed the electrokinetic, structural, and thermodynamic properties of spherical particles with such a composition.

The present investigation deals with the surface charge titration and surface potential calculation of the composite particles compared to that of the pure core or shell materials. Like in electrokinetics or hydrophobicity determinations, the efficiency of the coating in hiding the core properties should result in a significant similarity between the behavior of the surface charge of the core/shell particle and that of the yttrium oxide interface. The aim of this work is to check if this is in fact the case by comparing the dependence of the surface charge density and potential with both pH and ionic strength, for composite particles, iron oxide, and yttrium oxide.

Experimental

Materials

The core hematite particles were synthesized following the method of Matijević and Scheiner [8]: spherical and quite monodisperse (average diameter 60 ± 7 nm) particles were obtained. The mixed hematite/yttrium oxide colloids were prepared according to the techniques described in Refs. [4, 6]. Briefly, solutions containing 1.8 M urea (Panreac, Spain), 105 mg/l hematite spheres, and different yttrium nitrate (Merck, Germany) concentrations (Table 1) were heated at 90 °C for 9 h. After thoroughly cleaning by repeated cycles of centrifugation–redispersion in Milli-Q water (Millipore, France), the resulting particles, composed of a hematite core and an yttrium basic carbonate shell, were calcined at 800 °C for 3 h. Details of the samples used in this work are given in Table 1. Particle diameters were obtained from transmission electron microscopy micrographs, and the surface area was measured by Brunauer–Emmett–Teller analysis of N_2 adsorption in a Quantasorb Jr (Quantachrome, USA). Finally, Y_2O_3 was purchased from Merck (Germany) and, like the other chemicals, it was used as received.

Table 1 Synthesized hematite/yttrium oxide core–shell particles

Sample	Initial $Y(NO_3)_3$ concentration (mM)	Particle diameter (± standard deviation) (nm)	Specific surface area (m^2/g)
A	1.1	130 ± 20	11.6
B	3.0	150 ± 20	18.8
C	4.9	110 ± 10	10.0

Methods

Surface charge determinations of all the oxides were carried out by potentiometric titration [9–12] using a Metrohm Dosimat E649 titrator (Switzerland), connected to a Crison 2002 pH meter (Spain). The titrating solutions were 26 mM NaOH and 33.5 mM HCl. Three different NaCl concentrations (10^{-3}, 10^{-2}, and 10^{-1} M) were used as the supporting electrolyte, and all the measurements were carried out at 25.0 ± 0.5 °C, under a N_2 atmosphere. The particle concentration of the oxide suspensions to be titrated was 1.2 g/l in all cases. In order to ensure equilibration of the suspensions upon addition of acid or base, the acidic and basic branches of the titration were run for 10 h each.

From the experimental values of the surface charge density, σ_0, in the different electrolyte conditions investigated, the surface potential, Ψ_0, was calculated from the following relation, deduced by Ohshima for the case of a 1–1 electrolyte [13]:

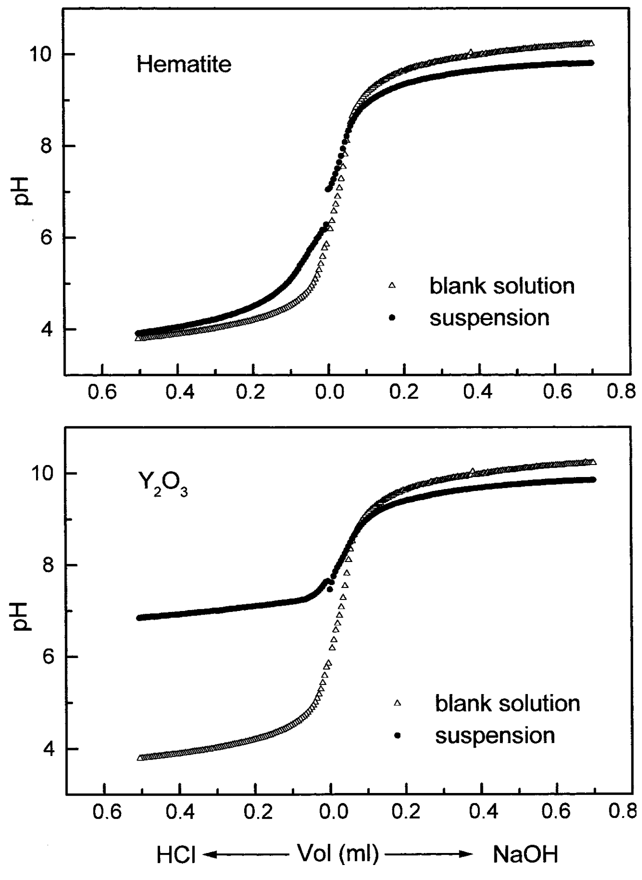

Fig. 1 Titration curves (pH versus volume of titrating solutions) for hematite and Y_2O_3 particles. Dispersion medium: 10^{-2} M NaCl

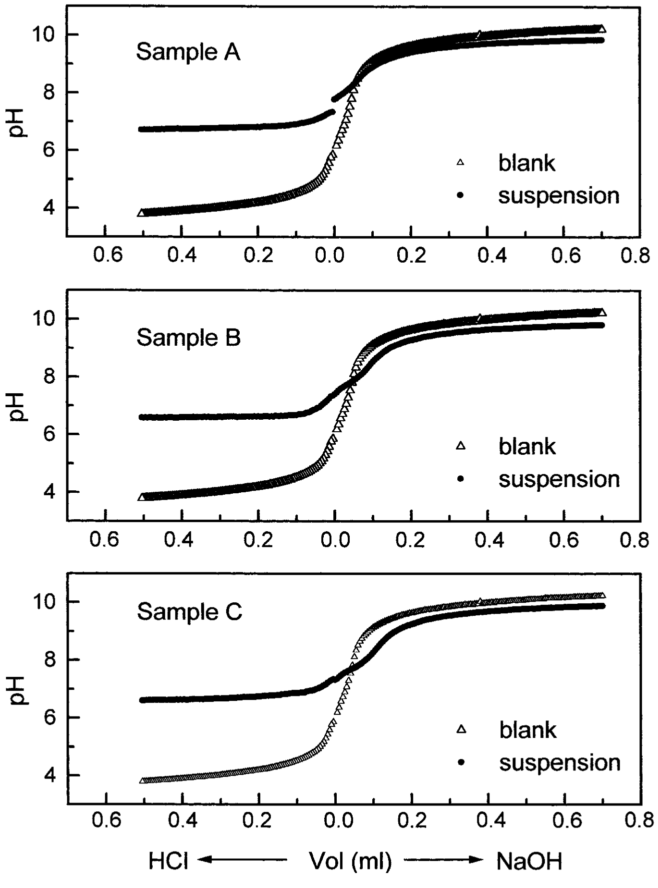

Fig. 2 Same as Fig. 1, but for composite particles A, B, and C (Table 1)

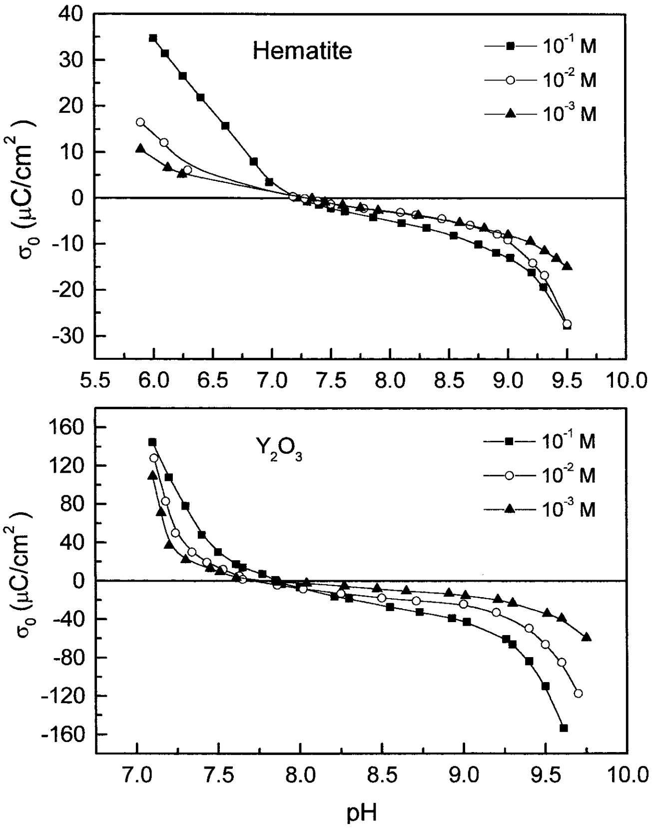

Fig. 3 Surface charge density of hematite and Y_2O_3 as a function of pH and NaCl concentration

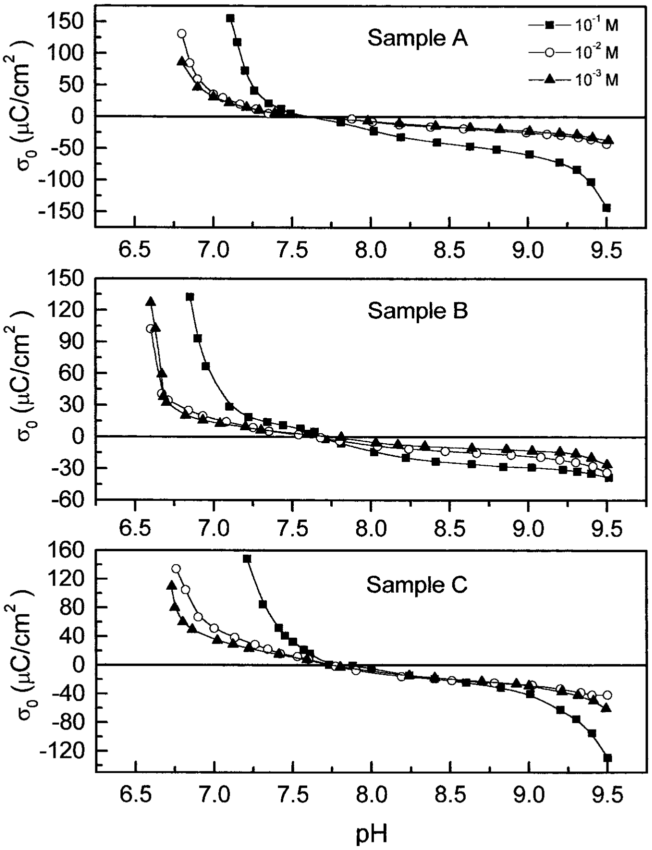

Fig. 4 Same as Fig. 3, for composite particles A, B, and C

$$\sigma_0 = \frac{2\varepsilon_r\varepsilon_0\kappa kT}{e}\sinh\left(\frac{e\Psi_0}{2kT}\right) \times\left[1+\frac{1}{\kappa a}\left(\frac{2}{\cosh^2(e\Psi_0/4kT)}\right) +\frac{1}{(\kappa a)^2}\left(\frac{8\ln[\cosh(e\Psi_0/4kT)]}{\sinh^2(e\Psi_0/2kT)}\right)\right]^{1/2}. \quad (1)$$

In this expression, $\varepsilon_r\varepsilon_0$ is the dielectric permittivity of the dispersion medium, κ is the reciprocal Debye length, e is the elementary charge, k is the Boltzmann constant, T is the absolute temperature, and a is the particle radius.

Zeta potentials were obtained from electrophoretic mobility data (Malvern Zetasizer 2c, UK) using the O'Brien and White theory [14].

Results and discussion

Surface charge

Examples of the experimental titration results, as pH versus titrating solution added, for the core (α-Fe_2O_3) and shell (Y_2O_3) materials, as well as for the composite particles, are given in Figs. 1 and 2. From the difference in the concentrations of acid or base necessary for reaching a given pH in both the suspension and the blank solution, σ_0 of the particles was obtained as a function of pH for the three NaCl concentrations studied. The results are plotted in Figs. 3 (hematite and yttrium oxide) and 4 (mixed particles A, B, and C). The general features of these curves are as expected for oxides:

1. The existence of a point of zero charge (PZC) that separates the regions of positive and negative surface charges.
2. A general trend of σ_0 to increase when the ionic strength is raised for a given pH.
3. σ_0 values of up to several tens of microcoulomb per centimeter squared, either positive or negative.

With the aim of gaining a clearer picture of the differences between the samples, and of the efficiency of the Y_2O_3 coating, we have summarized the results in Table 2, where values of the pH corresponding to the PZC (pH_{PZC}), as well as the surface charge density at pH 9, are detailed for the five types of particles.

Table 2 shows that α-Fe_2O_3 possesses the least charged interface and has the lowest pH_{PZC} (about 7.3); the latter appears comparable to that obtained by other authors [15], although it is remarkable that the pH_{PZC} of the oxides is most sensitive to the origin and treatment of the particles, and in the case of hematite,

Table 2 Values of pH_{PZC}, and σ_0 at pH 9 for the composite particles A, B, and C, the hematite core, and Y_2O_3 coating, as a function of NaCl concentration

Sample	[NaCl] (M)	pH_{PZC}	σ_0 (μC/cm^2) (pH 9)
Hematite	10^{-3}	7.3	−7.7
	10^{-2}	7.3	−9.0
	10^{-1}	7.3	−12.8
A	10^{-3}	7.6	−22.5
	10^{-2}	7.6	−24.5
	10^{-1}	7.6	−59.0
B	10^{-3}	7.7	−13.0
	10^{-2}	7.7	−18.0
	10^{-1}	7.7	−29.0
C	10^{-3}	7.8	−28.0
	10^{-2}	7.8	−29.0
	10^{-1}	7.8	−42.0
Y_2O_3	10^{-3}	7.9	−15.5
	10^{-2}	7.9	−24.0
	10^{-1}	7.9	−42.0

Table 3 Values of pH($\Psi_0 = 0$), pH($\zeta = 0$), and surface potential, Ψ_0, at pH 9, for hematite, yttrium oxide, and composite particles, as a function of NaCl concentration

Sample	[NaCl] (M)	pH($\Psi_0 = 0$)	pH($\zeta = 0$)	Ψ_0 (mV) (pH 9)
Hematite	10^{-3}	7.3	7.4	−191
	10^{-2}	7.3	7.3	−140
	10^{-1}	7.3	–	−99
A	10^{-3}	7.7	8.0	−244
	10^{-2}	7.7	8.0	−190
	10^{-1}	7.7	–	−174
B	10^{-3}	7.7	8.1	−215
	10^{-2}	7.7	8.0	−174
	10^{-1}	7.7	–	−138
C	10^{-3}	7.7	8.0	−258
	10^{-2}	7.7	8.0	−197
	10^{-1}	7.7	–	−158
Y_2O_3	10^{-3}	7.8	8.5	−224
	10^{-2}	7.8	8.5	−200
	10^{-1}	7.8	–	−160

values have been published ranging from 7 to 9 [10, 11, 16]. Concerning the pure Y_2O_3/solution interface, it is found to be more highly charged and shows the largest pH_{PZC} (about 7.9), a value comparable to that reported by Sprycha et al. [17].

Interestingly, the coated particles show σ_0–pH trends somewhat intermediate between those of the pure core and shell oxides. Thus, the pH_{PZC} of sample A is the average between those of iron and yttrium oxides, while samples B and C display zero surface charge for a pH closer to that of Y_2O_3. In contrast, the values of the surface charge at the representative pH of 9 (Table 2) are in all cases rather similar to those of yttria. Nevertheless, since the electrical surface properties of the yttria-covered particles are not identical to those of yttrium oxide, a patchwork or perhaps porous coating must be present, in agreement with our previous electrokinetic and thermodynamic data on the mixed particles [6, 7].

Surface and zeta potentials

An example of the type of pH dependences found for Ψ_0 is shown in Fig. 5. In this plot, the surface potential is represented as a function of pH for hematite, Y_2O_3, and sample C, and a constant NaCl concentration of 10^{-2} M. From this kind of data, Table 3 could be obtained: the surface potentials at pH 9 are reported for all the samples. This is a simple way to compare the potentials

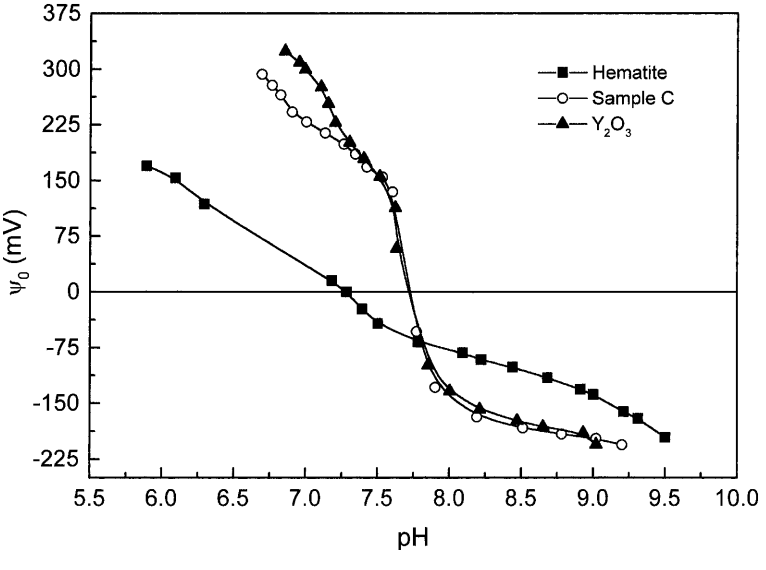

Fig. 5 Surface potential as a function of pH for hematite, yttrium oxide, and sample C particles as a function of pH in 10^{-2} M NaCl solutions

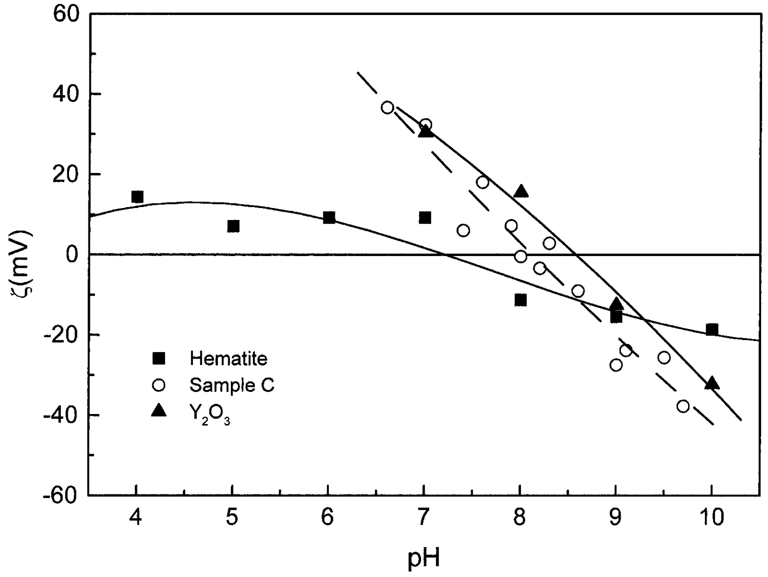

Fig. 6 Same as Fig. 5, but for zeta potentials

of the composite particles to those of the pure oxides. Note how, as observed with σ_0, Ψ_0 is very similar for the three coated samples and Y_2O_3, while they are all clearly different from hematite. Furthermore, all composite particles reach a zero surface potential at a pH coincident, within experimental uncertainty, with that of Y_2O_3.

Let us now consider how this behavior compares to that of a much more accessible quantity, namely, the zeta potential, ζ. The ζ–pH relationship for the same samples and NaCl concentration as in Fig. 5 is displayed in Fig. 6. Table 3 allows the comparison between the pH values for which both the electrokinetic and surface potentials of the particles are zero. While pH($\zeta = 0$) and pH($\Psi_0 = 0$) are close to each other (the isoelectric point is slightly higher in all cases), the actual values of the potentials for the whole pH interval are quite different, as Fig. 7 demonstrates: for any pH (other than that corresponding to the neutral state of the surface) $|\Psi_0|$ is significantly larger than $|\zeta|$, a clear indication that there is a large potential gradient in the Stern layer. This is very often the case with most colloidal systems, particularly with oxides [18], and it clearly indicates that an important number of ions compensating the surface charge are located in the inner part of the double layer of all our samples. The role of this considerable Stern layer charge on tangential charge transport (inner-layer surface conductance) is beyond the scope of the present investigation. The small differences between pH($\zeta = 0$) and pH($\Psi_0 = 0$) and the existence of a common intersection point of the σ_0–pH curves for different ionic strenghs (Figs. 3, 4) are an indication of the absence of specific adsorption of either Na^+ or Cl^- ions from the supporting electrolyte solution. These results confirm that sodium chloride is an indifferent electrolyte for both hematite– and yttrium oxide–solution interfaces.

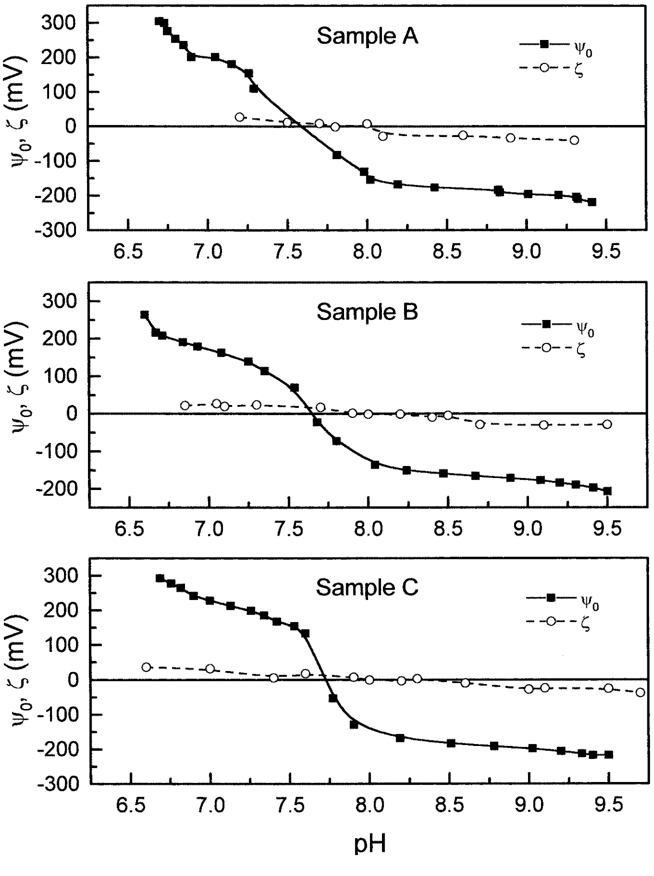

Fig. 7 Comparison between the pH dependences of surface and electrokinetic potentials for samples A, B, and C. Ionic strength: 10^{-2} M NaCl

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