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Inorganic Particles as Colloidal Models. Effects of Size and Shape on the Electrokinetics of Hematite (α-Fe_2O_3)

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This paper deals with the electrokinetics of α-Fe_2O_3 (hematite) particles with the aim of checking their possible use as colloidal models. The key idea is that, since hematite can be prepared, in a controlled and reproducible way, as colloidal particles homogeneous in size and shape, these could be considered as model colloids to which theories developed for systems of given geometry might be applied. In this contribution, we first describe the electrophoretic mobility, μ_e, of pseudospherical hematite samples with very different diameters as a function of NaCl and $CaCl_2$ concentrations. Their electrokinetic behavior is compared with the predictions of a rigorous theory for the mobility of spheres, assuming that both types of particles have equal zeta potentials (ζ); apparently, smaller particles show a considerable effect of anomalous (Stern-layer) ionic conduction, less appreciable for particles larger in diameter. However, in the electrolyte concentration range (above 10^{-3} M) in which this surface contribution is masked by the bulk solution conductivity, a satisfactory agreement is found between measured and predicted mobility values. The study is repeated with spheroidal particles: we have used hematite spheroids of two different average sizes and axial ratios. The effect of pH and $Na(NO_3)$ concentration on the electrophoretic mobility of both spheroidal samples is compared to the predictions of models of the mobility of particles with spheroidal geometry; these models are valid for either thin double layers and arbitrary zeta potentials or low ζ and arbitrary ionic layer thickness. The coincidence in the predictions of ζ for both particles in most experimental conditions

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This article is dedicated to Professor Egon Matijević on the occasion of his 75th birthday.

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(and, furthermore, the fact that the zeta potential turns out to be the same for spherical and nonspherical particles) points not only to the usefulness of the theories in dealing with spheroids, but also, equally important, to the possibilities of hematite with nonspherical, but controlled, geometries as colloidal models.

INTRODUCTION

Until quite recently, the efforts applied to the preparation of monodisperse particles of controlled size and shape (in the colloidal range) were almost systematically due to the curiosity of colloid scientists; the generalized, perhaps not explicit, attitude was that such systems were interesting only from the academic point of view, with little, if any, practical significance. Presently, the situation has changed to a large extent: it is widely accepted that the availability of dispersed solids, with sizes in the range of the micron or below, and with controllable homogeneous size, shape, and composition, can be the starting point in the preparation of technologically useful materials, with unbeatable performance in many applications.[1–6]

The colloidal system chosen for this study consists of aqueous suspensions of monodisperse hematite (α-Fe_2O_3) particles with different sizes and geometries. Oxide suspensions have indeed been widely studied, as expected from the fact that iron oxides or hydroxides forming different minerals are frequent in natural environments, in addition to their practical applications in the preparation of pigments, catalysts, flocculating agents, and so on. Hence the significance of works published by Matijević and his coworkers in the seventies[7–9] describing the obtention of iron oxides and (oxi)hydroxides through forced hydrolysis of Fe(III) solutions with different anions. More recently, Sugimoto *et al.*[10–14] have devised a method to obtain hematite particles of different geometries (pseudocubic, platelet-like, peanut-like) by a gel-sol procedure that allows obtaining large quantities of particles, and they have carefully discussed their formation mechanisms.[12,13] The possibilities of obtaining hematite particles with such a variety of shapes and sizes open a wide field of interest in such materials from the point of view of colloid science. They enable the use of colloids with chemical composition – in particular, surface structure – independent, in principle, of either particle size and shape: they might be considered colloidal models to which different theories would be strictly applicable, although some of these theories have seldom been applied due to the lack of monodisperse particles of the required size and shape. Certainly, other materials can be prepared in the form of almost perfect spheres of different diameters, but it is more difficult to achieve the requirement of identical surface (electrical) structure (*i.e.*, identical surface charge) whatever the particle size.

An interesting example was recently described by Ho *et al.,*[15] concerning the preparation of polystyrene ellipsoids by stretching a polyvinyl alcohol film containing spherical polystyrene precursors. Depending on the stretching draw ratio, the same spherical starting particles may yield different axial ratios in the final ellipsoids, thus providing particles with essentially the same surface characteristics and different eccentricities. Their possible use as colloidal models was explored, by electrophoresis studies, in Ref. 16.

Hematite particles offer the possibility of analyzing how size and shape affect the different phenomena associated to the solid/solution interface, in particular, electrophoresis, the study of which is one of the aims of this paper. After describing the hematite particles and their synthesis route, their bulk crystal structure will be characterized. A subsequent electrokinetic study will be carried out, and the results interpreted in terms of theories valid for either spheres or spheroids, thus checking the possible applications of hematite as a model colloid.

EXPERIMENTAL

Materials

All chemicals used were supplied by Merck (Germany) with analytical quality. Water was doubly distilled, deionized and filtered through 0.2 μm pore membranes (Milli-Q Reagent Water System, Millipore, USA).

Methods

Spherical (pseudocubic) hematite particles were prepared as explained in Ref. 9: sample SA was obtained by aging at 100 °C solutions containing 0.018 M $FeCl_3$ and 0.001 M HCl for 24 h. Sample SB was produced following the same procedure with 0.038 M $FeCl_3$ + 0.005 M HCl solutions aged at the same temperature for 13 days.

Elongated particles (samples EA and EB) were obtained by heating at 100 °C solutions containing 0.02 M $FeCl_3 + 2 \times 10^{-4}$ M NaH_2PO_4 (sample EA), and 0.02 M $FeCl_3 + 3 \times 10^{-4}$ M NaH_2PO_4 (EB). Solutions were aged for 4 days and 2 days, respectively.[17,18]

In all cases, the suspensions thus obtained were cleaned of unreacted chemicals by repeated (over 30 times in some instances) cycles of centrifugation and redispersion in Milli-Q water. The conductivity of the supernatant, together with the values of the isoelectric point (or pH of zero electrophoretic mobility) were used as tests of cleanliness of the systems.

Electrophoretic mobility measurements were performed at 25.0 ± 0.5 °C in a Malvern Zetasizer 2c electrophoresis apparatus (Malvern Instruments, England) on suspensions containing about 10^{-4} grams of solid per cm^3. Starting from stock hematite dispersions, the particle concentration, ionic strength and pH were adjusted, and the suspensions were left to equilibrate for 24 h under a nitrogen atmosphere in the refrigerator. If necessary, pH was readjusted immediately before taking measurements. The precision of electrophoretic mobility data can be estimated at ≈ 5%.

RESULTS AND DISCUSSION

Particle Structure and Morphology

Although an exhaustive study of the size and morphology of the particles obtained was carried out by Matijević and his collaborators in the original articles,[1,9,17] Figure 1 illustrates, as an example, two of the samples studied in the present work. It was found that samples SA and SB are almost spherical in shape (they actually appear as rounded cubes) and very monodisperse. The same quality as to homogeneity in shape and size was apparent in samples EA and EB: elongated hematite particles are also extremely homogeneous both in axial ratio and volume. Table I demonstrates the control that can be achieved in the dimensions of both spherical and non-spherical hematite: this table shows the size parameters of the four samples, obtained from TEM pictures after measuring at least 100 particles of each sample.

The structure of the particles was analyzed by XRD diffraction (Philips PW 1710 diffractometer, Cu-Kα radiation; the determinations were kindly performed by Dr. D. Martín of the University of Granada, Spain). Figure 2 shows the diffraction patterns obtained, together with data from the ASTM files for pure α-Fe_2O_3.[19] The correspondence of the main diffraction lines with the standard shows that all samples are in fact α-Fe_2O_3, although sample EB presents other low-intensity reflections corresponding mostly to goethite (β-FeOOH), precursor of hematite formation.[13] It is also worth mentioning that the particles are crystalline in all cases.

TABLE I

Size parameters of hematite particles (± S.D.)*

Sample	a/nm	b/nm	ε
SA	60 ± 7	–	–
SB	1100 ± 50	–	–
EA	75 ± 15	193 ± 24	2.6 ± 0.7
EB	43 ± 6	163 ± 22	3.8 ± 1.0

* a: short semi-axis (radius in SA, SB); b: long semi-axis; ε: axial ratio (b/a).

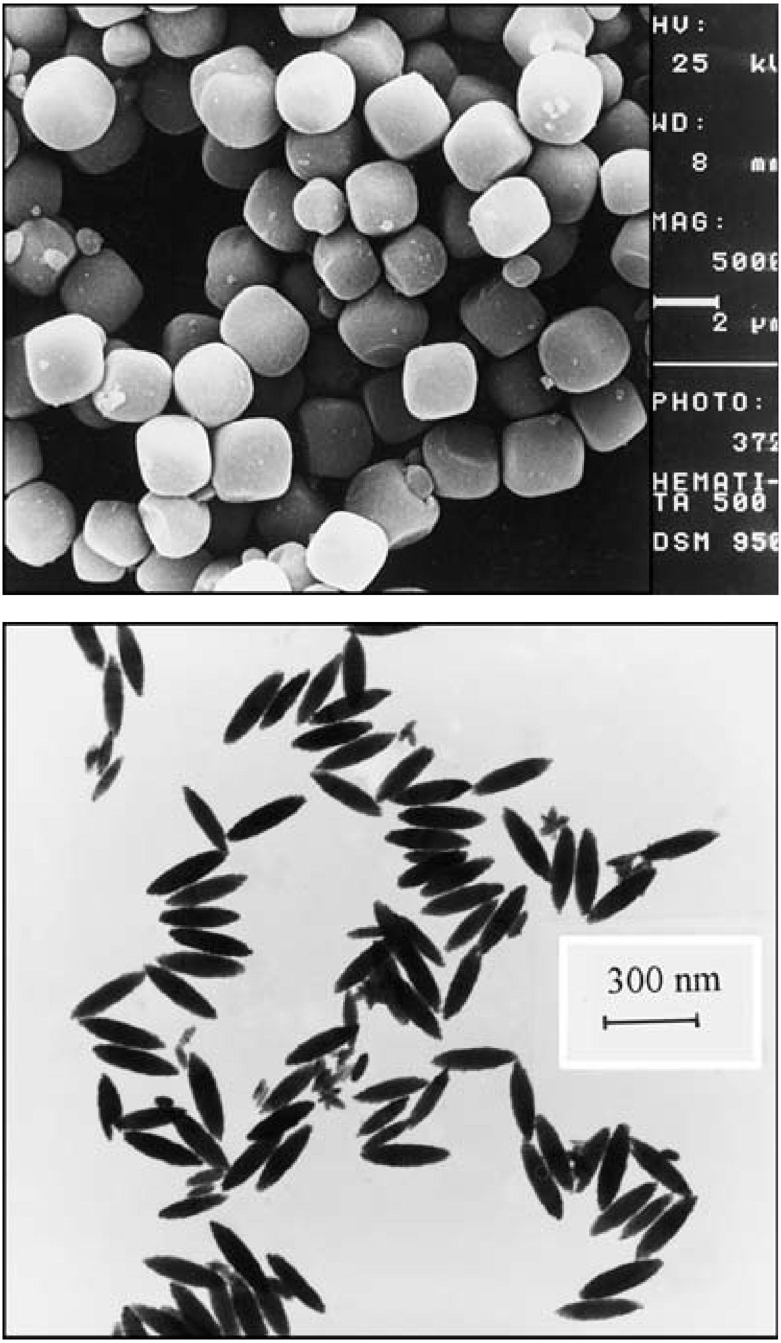

Figure 1. Electron microscope pictures of two of the samples studied. Top: sample SB, bottom: sample EB.

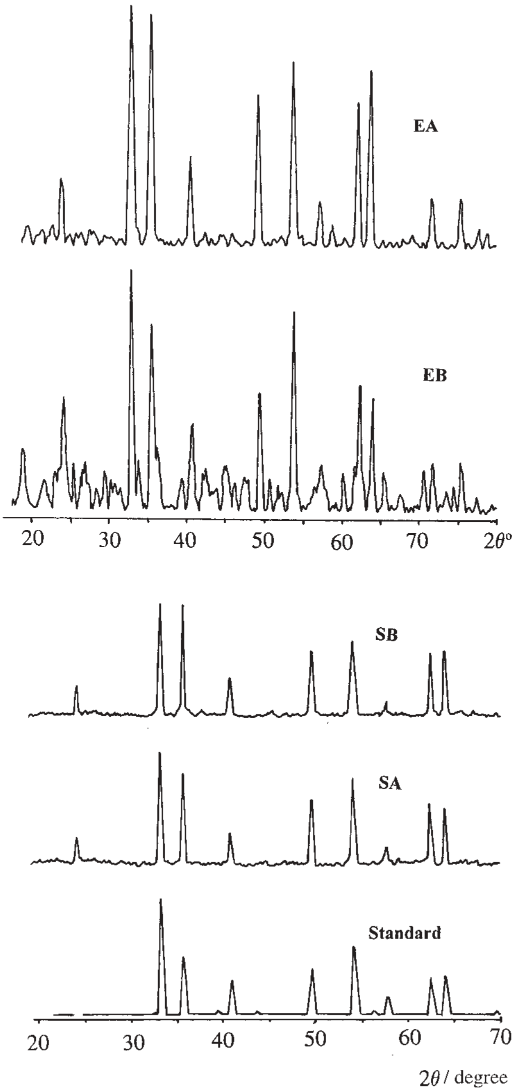

Figure 2. X-ray diffraction diagrams of hematite particles. The hematite standard is included for comparison.

Electrophoretic Mobility of Spherical Hematite: Effect of Particle Radius

To take advantage of the possibility of obtaining spherical particles of such different sizes as described above, but otherwise presumably identical, one might wonder what effect can be expected of the particle radius, a, on the mobility, assuming that the zeta potential of the interface, the ionic composition of the medium, temperature, *etc.*, are the same for the systems under comparison. We have used the electrophoresis theory of O'Brien and White[20] to obtain the data plotted in Figure 3. These theoretical data show that, in the conditions assumed (25 °C, 1 mM KCl, a ranging between 100 and 500 nm), the electrophoretic mobility μ_e increases with a, the effect being more significant the larger the value of zeta potential, ζ, ($\Delta\mu_e \cong 0.7$ μm s^{-1}/V cm^{-1} for $\zeta = 55$ mV; $\Delta\mu_e \cong 0.2$ μm s^{-1}/V cm^{-1} for $\zeta = 15$ mV).

This behavior is easy to understand in terms of the physical basis of electrophoretic motion: as a increases, the total surface charge on the particle should increase as a^2, and the same trend will show the force exerted on the particle by the external field. Simultaneously, the Stokes viscous friction increases linearly with a, hence the net force must increase with size. However,[20] these are not the only forces acting on the particles; others are the electrophoretic relaxation force (associated with the deformation of the dou-

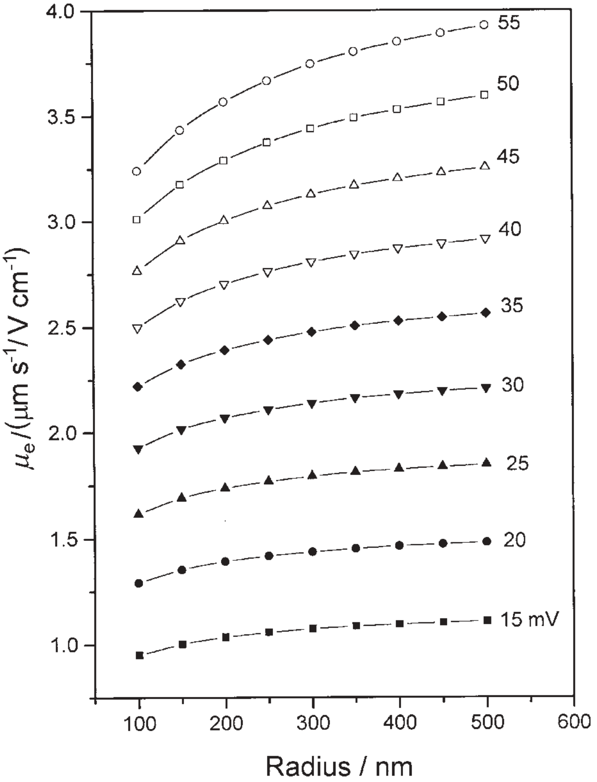

Figure 3. Electrophoretic mobility of spheres as a function of particle radius for the zeta potentials indicated. Temperature: 25 °C; ionic strength: 10^{-3} M KCl.

ble layer under the applied field) and the electrophoretic retardation, due to the electroosmotic slip of the liquid on the particle surface. The former is roughly proportional to ζ^2, and to the particle surface area, but it is important only if $1 \leq \kappa a \leq 10$ (κ is the reciprocal Debye length, and it is proportional to the square root of the ionic strength; the minimum value of κa in the suspensions of Figure 3 is $\cong 10$). The second retardation force mentioned is proportional to a^2, but the mobility decrease associated with it is always smaller than the increase due to the electric force.[20]

Let us now consider the experimental results obtained on the variation of μ_e with the concentration of 1–1 and 2–1 electrolytes, in the case of samples SA and SB (Figure 1, and Table I). Figure 4 shows the results as μ_e – concentration plots for all systems. The mobility is negative because all experiments were carried out at pH = 10, in order to ensure sufficient surface charge on the particles (in neutral pH conditions, such charge is almost zero, since the point of zero charge of hematite is around pH = 7–8). As ob-

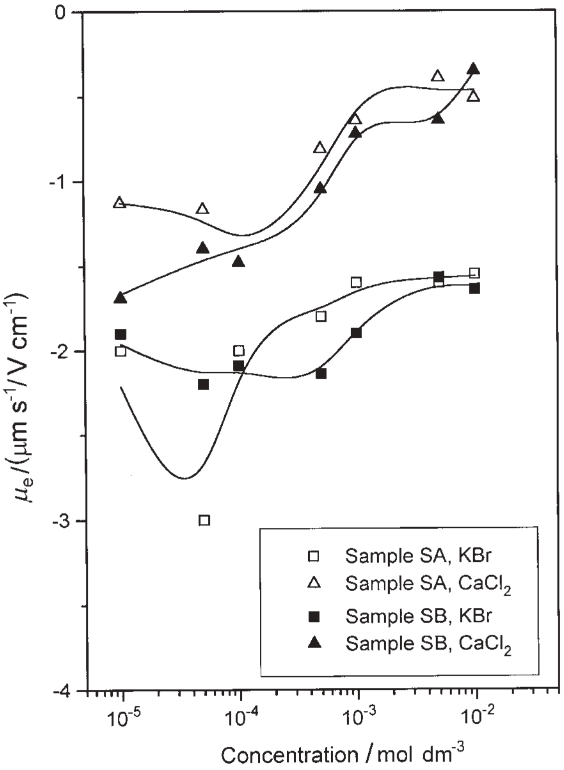

Figure 4. Electrophoretic mobility of samples SA and SB as a function of the concentration of KBr and $CaCl_2$ at pH = 10.

served, although above $\approx 10^{-4}$ M the trends of variation are similar for both hematite samples and both electrolytes (μ_e decreases with concentration because of the compression of the diffuse part of the double layer), for lower concentrations of any of the electrolytes sample SA shows a mobility maximum most pronounced in KBr solutions, and less deep in $CaCl_2$, and SB particles have a shallow $|\mu_e|$ maximum in KBr, and a definitely monotonous decrease in $CaCl_2$ solutions.

The existence of such mobility maxima is now a classical topic for discussing on electrokinetic phenomena. Assuming that no specific interactions occur between K^+ or Br^- and the hematite surface (and there is evidence that this is indeed the case, see, *e.g.*, Refs. 21–23), the explanation must lie in the actual structure and dynamics of the electric double layer. The mentioned behavior has been reported by other authors, mainly in connection with the electrokinetics of polymer colloids.[24–27] Various explanations have been proposed to account for the existence of such mobility maxima in the case of polymer latexes, ranging from preferential adsorption of coions in the inner part of the double layer[28,29] to the existence of protruding polyelectrolyte chains from the particle surface (hairy layers, see Refs. 30, 31). None of these arguments seem to be applicable to the oxide/solution interface, hence another mechanism, most likely of universal presence in certain ranges of ionic strength, can be claimed to be adequate, namely, the existence of diffusion and electromigration (not electroosmotic) ion fluxes in the Stern layer, called the dynamic Stern layer (DSL) in such conditions.[30–33] Although different treatments have been proposed to account for this mechanism in the study of very different electrokinetic phenomena,[30–34] a simple model, analytically solvable, elaborated by Dukhin and Semenikhin[35] will be used in this work. According to these authors, the dimensionless electrophoretic mobility,

$$\tilde{\mu}_e = \frac{2\eta e}{3\varepsilon_o \varepsilon_r k_B T} \mu_e \tag{1}$$

(where $\varepsilon_o \varepsilon_r$ is the dielectric permittivity of the solution, η its viscosity, and the other symbols have their usual meaning) is related to the dimensionless zeta potential ($\tilde{\zeta} = e\zeta / k_B T$) through:

$$\tilde{\mu}_e = \frac{3}{2}\tilde{\zeta} - F(\kappa a, \tilde{\zeta}, \tilde{\psi}_s, p) \tag{2}$$

p being the ratio between the diffusion coefficients of ions (counterions and coions are assumed to have equal diffusivities) in the Stern layer and in the bulk (we shall assume $p = 1$ hereafter), and $\tilde{\psi}_s$ is the dimensionless Stern layer potential. F is a complicated analytical function of the double layer

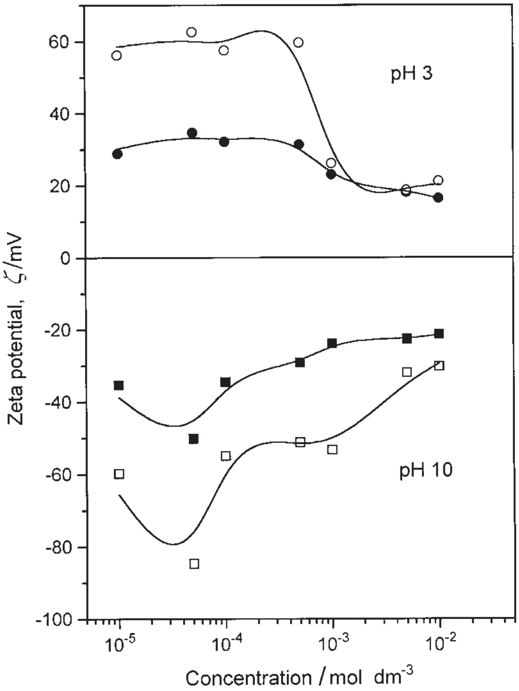

Figure 5. Zeta potential of SA particles as a function of KBr concentration at pH = 3 and 10. Full symbols: standard electrokinetic model; open symbols: DSL (Dynamic Stern Layer) model.

parameters indicated. The main problem in using Eq. (2) is that the Stern potential is not an experimentally accesible quantity. We propose to estimate it from the titratable surface charge, σ_o, using:[36]

$$\sigma_o = \frac{\varepsilon_r \varepsilon_o}{a}(1+\kappa a)\psi_s C \qquad (3)$$

where C is a correction factor calculated as proposed by Stigter.[36] All these calculations yield the zeta potential values of sample SA as a function of KBr concentration, plotted in Figure 5, where ζ obtained using the standard electrokinetic model is also shown for comparison. As observed, the DSL theory predicts larger absolute zeta potential values, but the maxima in the $|\zeta|$ – concentration plots do not disappear using the DSL model. Other experimental techniques, particularly dielectric spectroscopy[37] might help in clarifying this problem, but they are beyond the scope of this paper.

Comparison between theoretical and experimental effects of particle radius on μ_e can be made by calculating the ratio $\mu_r = \mu_e(\mathrm{SB}) / \mu_e(\mathrm{SA})$ as a

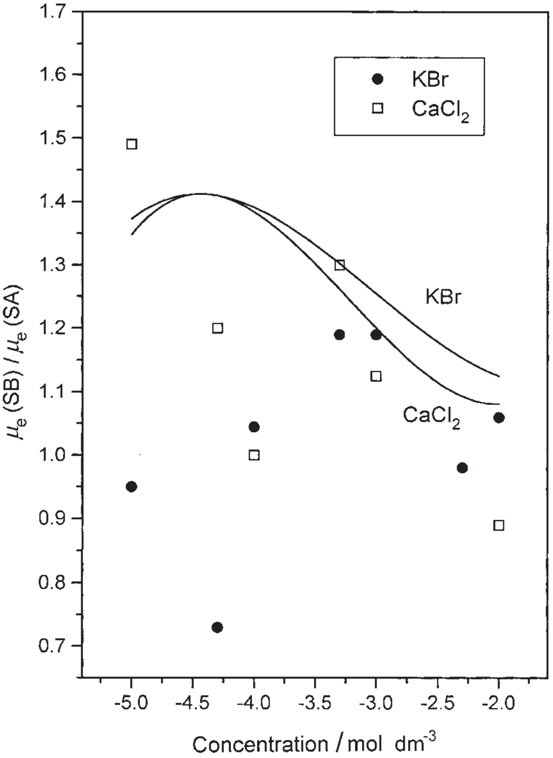

Figure 6. Experimental and calculated ratios between the electrophoretic mobility of sample SA and that of sample SB as a function of KBr and $CaCl_2$ concentrations (symbols: experimental data; lines: theory of O'Brien and White).

function of the concentration of both KBr and $CaCl_2$; the experimental variation of that ratio is compared for suspensions at pH = 10 to theoretical predictions in Figure 6 (the model of O'Brien and White is used, and it is assumed that the zeta potential calculated for SA is also valid for SB).

The minimum shown by μ_r (mainly in the case of KBr solutions) is clearly related to the maximum in (μ_e) characteristic of sample SA (Figure 4). Note also that μ_r is close to unity in many instances, although, particularly in $CaCl_2$ solutions, μ_e tends to be >1. Theoretical curves show that μ_r must be above 1 in all cases, and larger if the electrolyte is 1–1. Figure 6 also demonstrates that μ_r decreases at high electrolyte concentrations (low zeta potentials), since the effect of size is more noticeable the larger the value of $|\zeta|$. Briefly, a moderate agreement is found between theory and experiment outside the critical region of low electrolyte concentration, and hematite seems to make an excellent colloidal model in such conditions, allowing us to check the validity of electrokinetic theories. Further studies, similar to the one proposed here, could be useful in this direction.

Electrophoresis of Spheroidal Hematite Particles. Effects of Average Size and Axial Ratio

Although considerable advances have been made in the theory of electrophoresis of colloidal particles with cylindrical or spherical geometries, the analysis corresponding to other shapes was virtually linked to the classical Smoluchowski formula ($\mu_e = \varepsilon_r\varepsilon_0\zeta/\eta$). However, since the end of the 1980's several models have been produced dealing with the electrophoresis of revolution ellipsoids; although they are not as general and precise as the theories developed for spheres, they can, in principle, be applied to many practical situations.[38–41] We will focus here on the model of O'Brien and Ward,[38] valid for spheroids with thin double layers (ka >> 1, kb >> 1, with a, b semiaxes of the spheroid; the case $b > a$, prolate spheroids, is of interest to us) and arbitrary values of ζ; also, the theory of Yoon and Kim[40] could be useful: in this case, the zeta potentials must be low, but the double layer may have any thickness.

Whatever the model chosen, few studies have been devoted to the electrokinetics of spheroids of uniform size and shape, this meaning that the models have seldom been checked against experimental data (one exception is the recent work by Ho *et al.*[16]). The usefulness of elongated hematite – which could be reasonably modeled as spheroidal in shape – could be manifested also in this issue.

Comparison between the theories developed in Refs. 38 and 40 is somewhat complicated by the following fact: the correction to Smoluchowski electrophoretic mobility, μ_e(Smol.), implied by Yoon and Kim does not essentially depend on the ζ-value of the particles, whereas the O'Brien and Ward theory (which includes double layer polarization or relaxation effects) differs from Smoluchowski's not only because of particle dimensions, but also because of the different relaxation processes associated with different zeta potentials.

In order not to excessively enlarge this discussion, we have chosen a single, moderate zeta potential (ζ = 50 mV) to establish the comparison; the calculations based on both theories are shown in Figure 7 for different axial ratios and κa values. Note that:

i) In both cases, μ_e differs more from μ_e(Smol.) the smaller the values of both κa and b/a; the ratio μ_e/μ_e(Smol.) is always less than 1, and tends to unity where the surface curvature is small at any point (κa >> 1, κb >> 1).

ii) The two models approach each other for κa above ≈ 30, about the critical value of most electrokinetic theories of thin double layer particles.

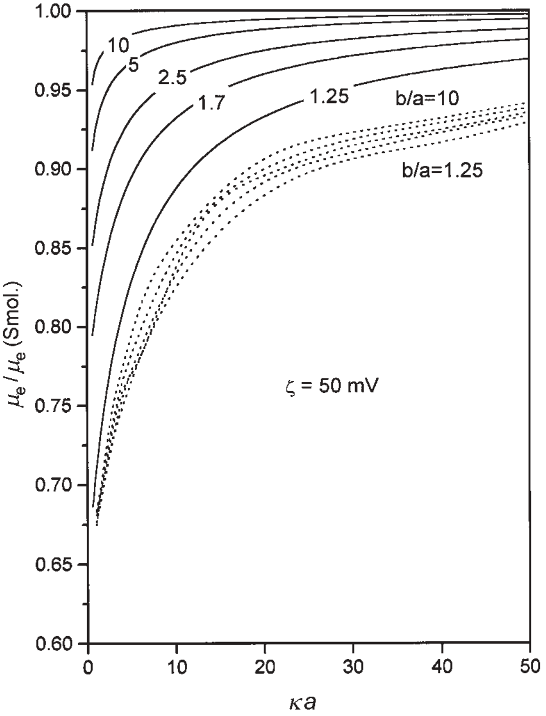

Figure 7. Electrophoretic mobility (relative to Smoluchowski formula: Smol.) of spheroids as a function of κa (a: short semi-axis) for different values of b/a (b: long semi-axis). Full lines: O'Brien and Ward;[38] dotted lines: Yoon and Kim.[40]

Let us now consider how the theories described apply to experimental mobility data for EA and EB samples (Table I); we will describe the variation of μ_e with pH (at constant ionic strength, 10^{-2} M $NaNO_3$), and with the concentration of $NaNO_3$ at pH = 3 and 10. The experimental results are plotted in Figures 8 (μ_e – pH) and 9 (μ_e – $[NaNO_3]$): comparison of these data with others already published on the electrokinetics of spherical hematite[42] does not bring any particularly new issue, and hence they will not be discussed any more. Let us rather consider how to apply the theoretical models; it seemed to us that the best method to establish a comparison between the models and, furthermore, to check their validity against measured data, was to calculate ζ using the two theories and for all the experimental conditions.

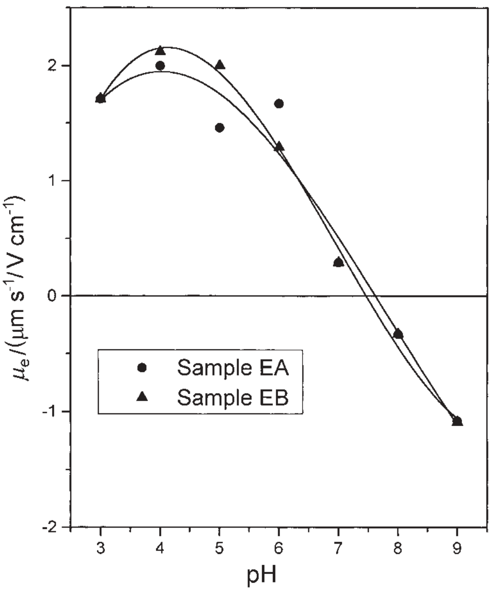

Figure 8. Electrophoretic mobility of samples EA and EB as a function of pH (ionic strength: 10^{-2} M $NaNO_3$).

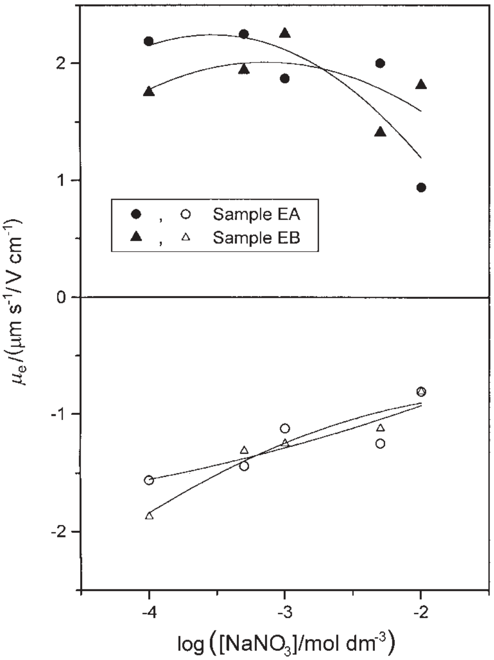

Figure 9. Electrophoretic mobility of samples EA and EB as a function of $NaNO_3$ concentration at pH = 3 (top) and 10 (bottom).

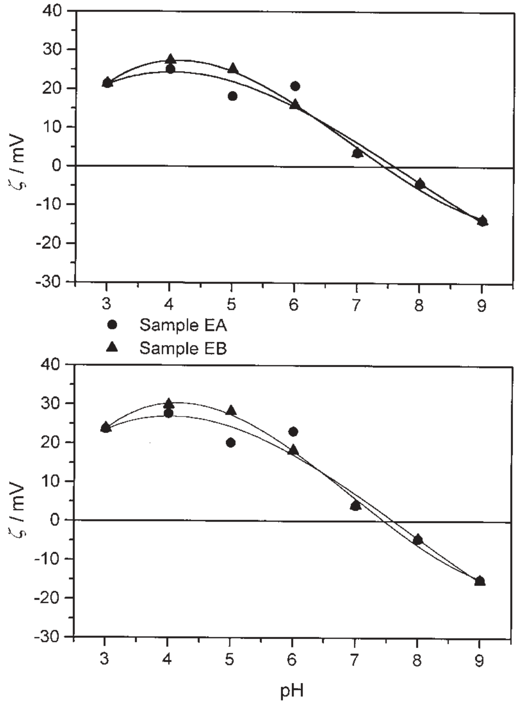

Figure 10. Zeta potential of samples EA and EB as a function of pH, using the models of O'Brien and Ward (top) and Yoon and Kim (bottom).

Figure 10 shows our estimations of ζ using the two theories. Both of them clearly predict the same ζ – pH trends, and almost identical zeta potentials for each sample and pH value for both EA and EB, in spite of their geometrical differences. It seems that the solid/solution interfaces appear identical for the two kinds of particles, as expected; they are different in average size for different axial ratios, but show almost identical zeta potential. Let us point out that κa is about 25 for all pH values, *i.e.,* the system is well within the range of validity of the models used.

When the process is repeated with the effect of [$NaNO_3$] on μ_e, the plots in Figure 11 are obtained. Similar trends of variation of the mobility with ionic strength, and the similarities between the zeta potentials of EA and EB (whatever the theory used) for each composition of the dispersion medium are again obtained. However, the values of ζ are somewhat higher for Yoon and Kim's model (although the difference amounts to, at the most, 20% of O'Brien and Ward's predictions); up to a concentration of $\approx 5 \times 10^{-3}$ M, $\kappa a \leq 20$, the differences must originate from the large κa limitation of

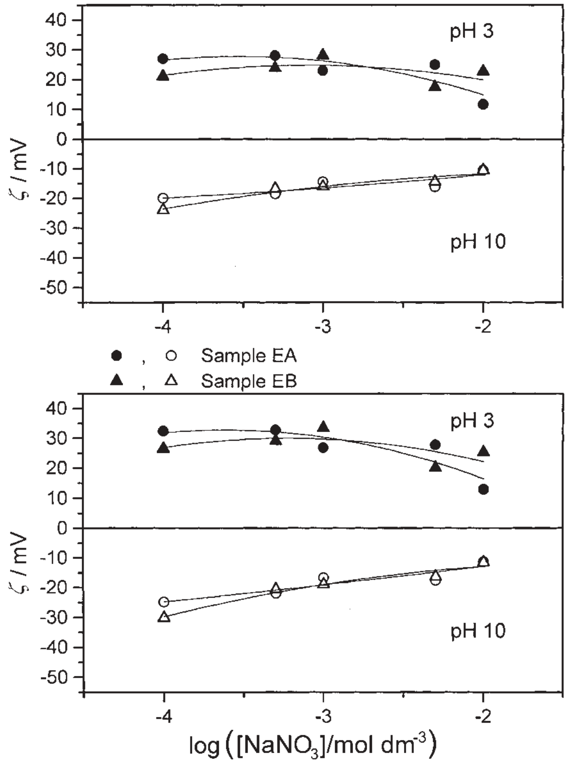

Figure 11. Zeta potential of EA and EB particles plotted *vs.* the concentration of sodium nitrate, at pH = 3 and 10. Top: O'Brien and Ward's model; bottom: Yoon and Kim's.

O'Brien and Ward's model. Let us finally mention that the zeta values of EA and EB in Figure 11 compare well with those of Figure 5 for spherical SA and SB particles.

In conclusion, we hope to have shown that hematite samples of spherical and spheroidal shapes can be used with advantage as colloidal models of both geometries, if prepared under the controlled and reproducible conditions first enunciated by E. Matijević and coworkers. Furthermore, two theories on the electrophoresis of spheroids have been checked using hematite models; they both appear to successfully explain the mobility of spheroidal particles, within the ranges of values of ζ and κa for which they were envisaged.

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SAŽETAK

Anorganske čestice kao modelni koloidi. Utjecaj veličine i oblika na elektrokinetička svojstva čestica hematita (α-Fe_2O_3)

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Elektrokinetička svojstva α-Fe_2O_3 (hematita) istraživana su zbog njegove moguće primjene kao modelnog koloida, jer se hematit može pripremiti kontrolirano i reproducibilno kao koloid česticâ jednakog oblika i veličine. Stoga se na hematit može primijeniti teorijski model vezan uz neku geometriju. U prvom se dijelu rada prikazuje elektroforetska pokretljivost dva uzorka hematita približno sferičnih čestica znatno različitih promjera. Istražen je utjecaj koncentracije NaCl i $CaCl_2$. Pri interpretaciji rezultata primijenjena je stroga teorija, a pretpostavljeno je da su zeta-potencijali (ζ) za obje vrste čestica jednaki. Za razliku od većih čestica, izgleda da manje čestice pokazuju znatnu pojavu anomalne vodljivosti (Sternov sloj). U području koncentracija elektrolita iznad 10^{-3} mol/dm^3, gdje je doprinos površine maskiran vodljivošću otopine, nađeno je zadovoljavajuće slaganje između mjerenih i računskih vrijednosti za elektroforetsku pokretljivost. Na isti su način proučavane i dvije vrste sferoidnih čestica, različitih po veličini i odnosu osi. Mjeren je utjecaj pH i koncentracije $NaNO_3$ na elektroforetsku pokretljivost. Eksperimentalni su rezultati uspoređeni s teorijskim predviđanjima za čestice sferoidne geometrije. Ti modeli vrijede za tanke dvosloje i proizvoljne ζ-potencijale, a također i za niske ζ-potencijale i proizvoljne debljine ionskog sloja. U većini je slučajeva nađeno slaganje između rezultata i predviđanja. Također je nađeno slaganje između ζ-potencijala za sferne i sferoidne čestice. To je slaganje ukazalo na primjenjivost teorija razvijenih za sferoidne čestice, a također i na mogućnost primjene nesferičnih hematitnih čestica kao modelnih koloida.