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

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 (\(\alpha\)-Fe\(_2\)O\(_3\)) 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 and 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 (\(\alpha\)-Fe\(_2\)O\(_3\)) 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 N₂ adsorption in a Quantasorb Jr (Quantachrome, USA). Finally, Y₂O₃ was purchased from Merck (Germany) and, like the other chemicals, it was used as received.

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 N₂ 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, σ₀, in the different electrolyte conditions investigated, the surface potential, Ψ₀, was calculated from the following relation, deduced by Ohshima for the case of a 1–1 electrolyte [13]:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial Y(NO₃)₃ concentration (mM)</th>
<th>Particle diameter (± standard deviation) (nm)</th>
<th>Specific surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.1</td>
<td>130 ± 20</td>
<td>11.6</td>
</tr>
<tr>
<td>B</td>
<td>3.0</td>
<td>150 ± 20</td>
<td>18.8</td>
</tr>
<tr>
<td>C</td>
<td>4.9</td>
<td>110 ± 10</td>
<td>10.0</td>
</tr>
</tbody>
</table>

Fig. 1 Titration curves (pH versus volume of titrating solutions) for hematite and Y₂O₃ particles. Dispersion medium: 10⁻² M NaCl

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