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Surface potential of hematite particles in high concentration electrolytes: Electroacoustic measurements and suspension stability

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HIGHLIGHTS

- Zeta potential of hematite particles has been measured by electroacoustic method.
- Various 1:1 electrolytes from 1 mM to 10 M have been used.
- Neutralization of surface has been observed above 0.1 M.
- Stability of suspensions using DLVO theory has been experimentally checked.

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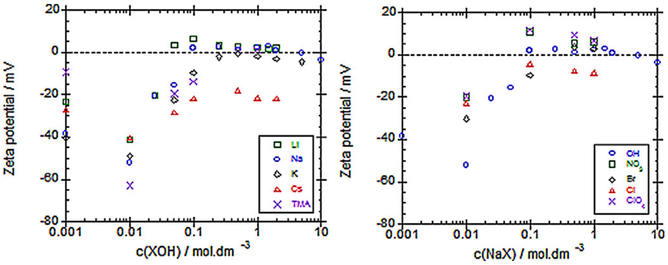
GRAPHICAL ABSTRACT



ABSTRACT

The behavior of hematite particles and their surface charge in the presence of various electrolytes ranging from 10^{-3} to 10 mol L^{-1} has been investigated. Zeta potential measurements were performed using an electroacoustic device, and results showed that the nature of the alkaline cation in solution (Li^+, Na^+, K^+, Cs^+ or tetramethylammonium) leads to the presence or absence of a charge neutralization for higher concentrations. This behavior follows the indirect Hofmeister series (lithium has the strongest effect) and may be attributed to the hard or soft nature of the cation. This effect was also shown by experiments with various anions (OH^-, Cl^-, Br^-, $NO_3{}^-$, $ClO_4{}^-$). Calculations using the classical DLVO theory predicted stability in agreement with the observed macroscopic behavior of the hematite suspensions, and most notably the rate and degree of sedimentation.

1. Introduction

Zeta potential of particles is an essential characteristic to evaluate the behavior of colloids, whether by predicting coagulation phenomena [1] or by studying the mechanisms of deposition [2]. Thus, the measurement of this value has become a classical protocol, just as size measurement, turbidimetry, or acid–base properties by titration, thanks to a new generation of instruments (Malvern Nano ZS, Brookhaven ZetaPALS, etc.) allowing fast and reliable measurements. However, these instruments are based on the optical measurements of the electrophoresis phenomenon, which leads to limitations in solid content due to light absorption, and in conductivity (or high ionic strength) due to the increase of electrical current. In numerous fields (environmental sciences, biology, etc.) the studied suspensions are within these limitations, and these instruments are very useful. However, for several industrial processes (ceramics, chemical baths, etc.) these limitations make the analysis of real samples impossible, leading to the more or less justified extrapolation of results obtained in "simplified" chemical conditions. Recently, instruments based on the electroacoustic principles have become commercially available, allowing

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the determination of the zeta potential of samples characterized by high conductivity and/or high solid content [3,4]. The first results obtained at high ionic strength have given an insight of a different surface chemistry for ions defined as "inert" according to zetametry results at low-ionic strength (i.e. Na^+, NO_3^-, etc.) [5–7].

In a previous communication, we reported zeta potential measurements of hematite particles in highly concentrated sodium hydroxide solutions and we investigated the specific effect of Na^+ concentration at various pH values [8]. This work was linked to the development of an electrolysis process using hematite suspensions to produce iron from ores with high environmental efficiency within the European project ULCOS (Ultra-Low CO_2 in Steelmaking) led by ArcelorMittal [9]. In order to understand the reactions occurring in the process, a good comprehension of the physicochemical characteristics of the hematite particles was needed, especially the surface potential which is a key parameter to understand the interactions with the cathode. Most methods used to determine the zeta potential are based on electrophoresis but they require the electrolyte to be of low concentration, usually less than 10^{-1} M. By contrast the industrial process requires a concentration in the electrolyte of 50% by weight, requiring the use of electroacoustic systems since they are not disturbed by high electrolyte conductivity.

In this manner, Rowlands et al. [3] measured the zeta potential of gibbsite particles in NaCl solutions up to 3 M. Their results showed a shift of the isoelectric point by about 2 pH units toward alkaline pH in presence of 0.5 M NaCl, and a zeta potential remaining positive over the whole range of pH when concentration is increased to 3 M. Similarly, Kosmulski et al. [4] observed a shift in the IEP of anatase particles in the presence of sodium ions by increasing the NaI concentration from 10^{-1} to 0.5 M, and at a concentration of 1 M, the zeta potential was positive over the entire pH range. This phenomenon has also been observed on other metal oxides, such as alumina or hematite. These observations would imply that in general, at high ionic strength, specific adsorption occurs on metal oxides for ions with weak interactions at low concentrations (Na^+, K^+, Cl^-, etc.). This idea was supported by Kosmulski and Rosenholm [5,6], who interpret their electroacoustic data with alkali metal cations, notably lithium and sodium, as a specific adsorption from concentrated solutions. Complementary studies on alumina in a wide selection of electrolyte solutions [6,7] allowed for a better understanding of the mechanisms at play. It was demonstrated that an affinity series, or so-called Hofmeister-type series, Li > Na > K > Cs is highlighted. This series can be interpreted in the framework of the hard and soft acids and bases theory (HSAB) [10]. Hard cations will therefore have a better affinity toward the surfaces of metal oxides, since the negative hydroxyl group is considered as hard, which explains the affinity series found for alumina. The nature of the anion will define the degree of competitiveness of the cation between the anion and the surface. A hard anion will have a stronger interaction with a cation and therefore limit the adsorption of cations on the metal oxide. This explains why the charge reversal is observed with $NaNO_3$, but not with NaCl.

A particular interest is given to the comparison between the results obtained by means of electroacoustic measurements, and their actual macroscopic validity. It is well known that the zeta potential can be used as a good index of the stability of a suspension [11], or the adhesion probability of colloidal particles onto massive substrates [12]. Usually, it is accepted that particles with an absolute value of zeta potential higher than 20 mV are stable. Other studies apprehended the relationship between the zeta potential and the rheological properties of dispersions [13–15], and confirmed that the maximal aggregation rate was obtained around the isoelectric point. This behavior follows the DLVO (Derjaguin, Landau, Verwey and Overbeek) theory, where the interaction force between two particles is the sum of the electrostatic forces and the Van der Waals forces, the last term being always attractive. The intensity of the Van der Waals forces depends on the Hamaker constant of the solid/solvent/solid system, and remains of the same order of magnitude for all metal oxides, yielding the common rule-of-thumb of 20 mV.

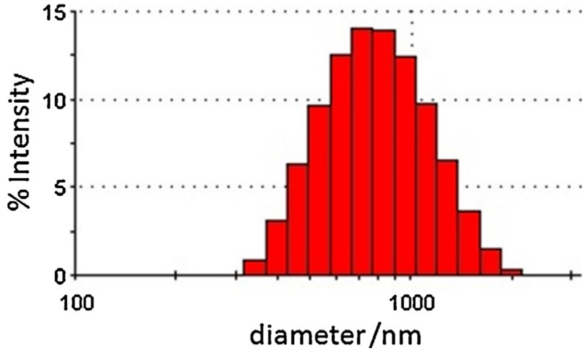

Fig. 1. Size distribution of Fe_2O_3 particles in NaOH 1 M after the application of ultrasound for 3 min.

In the present work, we present calculated zeta potential values of hematite obtained from electroacoustic measurements in the presence of different alkaline hydroxides (Li^+, Na^+, K^+, Cs^+ or tetramethylammonium). A correlation between the size and nature of the cation and the zeta potential values is presented. A closer look is also given to the nature of the counter-anion as we present zeta potential measurements for different sodium salts (OH^-, Cl^-, Br^-, NO_3^-, ClO_4^-). Finally, we present some sedimentation experiments that allow for a macroscopic correlation to the microscopic behavior of the hematite particles. Calculations of the electrostatic barrier using the DLVO theory are compared to the results and confirm the performed measurements.

2. Materials and methods

2.1. Materials

The iron oxide (hematite) was of 99.9% purity (NOAH Technologies) and was used as received. X-ray powder diffraction is presented in Fig. S1, confirming the purity of hematite. Suspensions of hematite into various electrolyte solutions were prepared a day before the experiments. As observed by scanning electron microscopy (Fig. S2), the size of individual particles ranged from 50 nm to 500 nm. Granulometry measurement using Malvern Nano ZS has shown that hematite particles formed agglomerates of ca. 800 nm (Fig. 1).

Sodium hydroxide (VWR) was of AnalaR Normapur quality. The various hydroxides and salts (Alfa Aesar) were at least of 97% + purity. Purified water (Millipore system, resistivity 18.2 MΩ cm) was used.

2.2. Zeta potential measurements

The DT-300 system from Quantachrome/Dispersion Technology was used for the electroacoustic experiments [16]. Before each new measurement, a calibration of the probe is done in a particle-free solution, and the background current is automatically subtracted from the suspension measurements. Moreover, ultrasounds are applied for 3 min in the suspensions before any experiment using a sonotrode (UP100H model from Hielscher). Each sample used had a volume of 100 mL and the solid content in hematite in the samples was 20 g L^{-1}. No corrections for viscosity and density of the solution were applied, because the difference in values obtained with the corrected media or water constants was within the error