

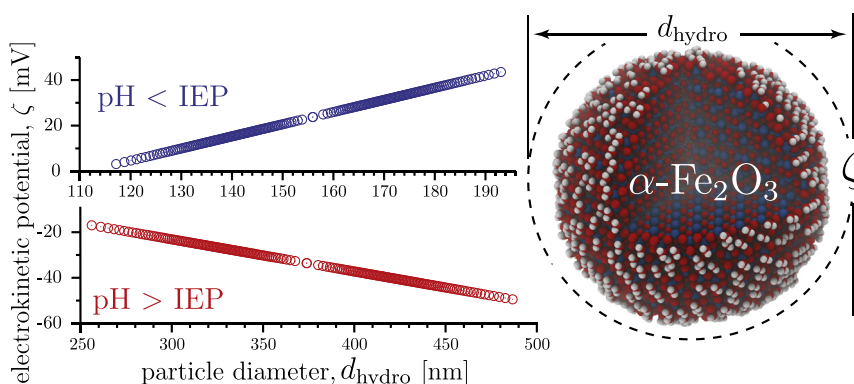


Regular Article

Probing size-dependent electrokinetics of hematite aggregates

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GRAPHICAL ABSTRACT



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ABSTRACT

Aqueous particle suspensions of many kinds are stabilized by the electrostatic potential developed at their surfaces from reaction with water and ions. An important and less well understood aspect of this stabilization is the dependence of the electrostatic surface potential on particle size. Surface electrostatics are typically probed by measuring particle electrophoretic mobilities and quantified in the electrokinetic potential (ζ), using commercially available Zeta Potential Analyzers (ZPA). Even though ZPAs provide frequency-spectra (histograms) of electrophoretic mobility and hydrodynamic diameter, typically only the maximal-intensity values are reported, despite the information in the remainder of the spectra. Here we propose a mapping procedure that inter-correlates these histograms to extract additional insight, in this case to probe particle size-dependent electrokinetics. Our method is illustrated for a suspension of prototypical iron (III) oxide (hematite, α -Fe₂O₃). We found that the electrophoretic mobility and ζ -potential are a linear function of the aggregate size. By analyzing the distribution of surface site types as a function of aggregate size we show that site coordination increases with increasing aggregate diameter. This observation explains why the acidity of the iron oxide particles decreases with increasing particle size.

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1. Introduction

Most particles immersed in an aqueous solution develop a surface charge that stabilizes their suspension [1]. The charged surface attracts electrolyte ions resulting in a spatial charge distribution known as the electrical double layer (EDL) [1,2].

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If charged particles are subjected to an external electric field, they move in the field together with a part of the surrounding ionic atmosphere (i.e., rigid part of EDL) [1]. The electrostatic potential developed at the boundary between this rigid part and the remaining EDL structure is referred to as the electrokinetic potential (ζ -potential) [1]. The ζ -potential is one of the most important EDL-descriptors, essential in assessing suspension stabilities, bacteria/viruses adhesion, and biomolecules surface electrostatics (e.g., proteins, liposomes, micelles) [3–8]. The ζ -potential is calculated from the electrophoretic mobility (u_e), which is a readily accessible property in a variety of experimental techniques based on the electrokinetic phenomena, however it is the most frequently obtained using Zeta Potential Analyzers (ZPA).

Commercially available ZPAs can record the electrophoretic mobility of suspended charged particles and their hydrodynamic diameter by exploiting the phenomenon of dynamic light scattering (DLS) [9–13]. In typical settings, ZPA provides frequency spectra (histograms) of the electrophoretic mobility or corresponding ζ -potential and particle hydrodynamic diameter (d_{hydro}). Unfortunately, only the average or maximal-intensity values are usually reported, thus a large amount of data associated with the shapes of these spectra are typically ignored despite their huge potential value.

In this report we propose a method to more fully utilize available data by mapping u_e (or ζ) and d_{hydro} distributions, which we will show can allow one to gain insight into the size-dependency of particle surface electrostatics. We illustrated our method for the prototypical iron (III) oxide hematite ($\alpha\text{-Fe}_2\text{O}_3$). Hematite is a naturally occurring semi-conductor, and one of the most stable iron (III) oxide minerals among a wide range of possible iron oxide phases. On the basis of the Kelvin equation it is generally accepted that the reactivity of hematite particles will increase with decreasing particle size, however at the nanoscale particle stability is not easily predictable and much is left to be understood [14]. Although our procedure is illustrated for metal oxide particles, we believe that it can be applied to other suspensions.

2. Materials and protocols

Hematite ($\alpha\text{-Fe}_2\text{O}_3$) nanoparticles (20–40 nm in diameter) were purchased from SkySpring Nanomaterials Inc. (99% $\alpha\text{-Fe}_2\text{O}_3$). The ζ -potential and hydrodynamic diameter were measured by a commercially available ZPA (NanoBrook 90Plus Zeta Potential Analyzer, Brookhaven Instruments Corporation, US). The titrations were carried out under argon atmosphere. All solutions were prepared using the distilled and deionized water and analytical grade electrolytes (KNO_3 , KOH , HNO_3). Particle suspensions were prepared 12 h before titrations in 0.001 mol/dm^3 KNO_3 electrolyte and kept at $\text{pH} = 3$.

2.1. Methodology

2.1.1. Experiment

Quasi-elastic dynamic light scattering (DLS) is the phenomenon behind the diameter and electrophoretic mobility measurements presented in this report. The DLS-apparatus measures the intensity autocorrelation function of light scattered by the suspended particles ($c(t)$). The particles are subjected to Brownian and electrophoretic (in case of the ζ -measurement) forces, resulting in a fluctuation of scattered light intensity (Doppler effect) [15,16].

2.1.2. Analysis

The normalized $c(t)$ function is related to a particle diffusion coefficient via the dynamic structure factor providing that the magnitude of the scattered electric field (or intensity) obeys

Gaussian statistics (Siegert relationship) [16]. By knowing the diffusion coefficient (D) one can calculate the hydrodynamic particle diameter, for instance by using the Stokes-Einstein relationship: $d_{\text{hydro}} = k_B T / (3\pi\eta D)$ (where k_B is the Boltzmann constant, η is a medium viscosity, and T is temperature). In order to convert electrophoretic mobility to ζ -potential, an appropriate electrokinetic theory has to be used for a given double-layer thickness and particle radius [17]. The thickness of the EDL is defined by the Debye length κ^{-1} as:

$$\kappa^{-1} = \sqrt{\frac{\epsilon\epsilon_0 k_B T}{N_A \sum_i z_i^2 c_i}} \quad (1)$$

where ϵ is the dielectric constant for solution, ϵ_0 is the vacuum permittivity, k_B is the Boltzmann constant, T is temperature, z_i and c_i are the charge number and molar concentration of ion i . In the case presented here (i.e., 0.001 mol/dm^3 KNO_3 , $T = 25^\circ\text{C}$, $\epsilon = 78.54$) the EDL thickness (κ^{-1}) is equal to 9.62 nm.

In the case of a thin double layer ($\kappa^{-1} \ll a$, where $a = d_{\text{hydro}}/2$ is a particle radius), the ζ -potential is given by the Smoluchowski relation (or Helmholtz-Smoluchowski) [17]:

$$\zeta = \frac{u_e \eta}{\epsilon\epsilon_0} \quad (2)$$

In the case of a thick double layer ($\kappa^{-1} \gg a$), the ζ -potential is related to the electrophoretic mobility via Hückel equation (or Hückel-Onsager) [17]:

$$\zeta = \frac{3}{2} \frac{u_e \eta}{\epsilon\epsilon_0} \quad (3)$$

To convert u_e to ζ for systems in the κa range between thick and thin EDL extremes one can use Henry's formula [17]:

$$\zeta = \frac{3}{2} \frac{u_e \eta}{\epsilon\epsilon_0 f_1(\kappa a)} \quad (4)$$

where $f_1(\kappa a)$ is the Henry's function that varies smoothly between 1 ($\kappa a \ll 1$, Hückel) to 1.5 ($\kappa a \gg 1$, Smoluchowski). The Henry's function can be approximated by the following Ohshima's relation [18,19]:

$$f_1(\kappa a) = 1 + \frac{1}{2} \left[1 + \left(\frac{2.5}{\kappa a (1 + 2 \exp(-\kappa a))} \right)^2 \right]^{1/2} \quad (5)$$

2.1.3. Mapping probability distributions

In this report we propose to fully utilize the data collected by a commercial ZPA to gain an insight into the particle-size-dependent electrostatics. We propose to map the particle size (d_{hydro}) onto electrophoretic mobility (u_e) by exploiting the reversibility [20] of their normalized probability distributions (P). Provided that proportionality relationship between u_e and d_{hydro} is known, then by setting $P^{-1}(u_e) = P^{-1}(d)$ one can get $u_e = f(d_{\text{hydro}})$ (where P^{-1} is an inverse of P).

On the one hand, this mapping procedure does not require any specific functional form of P , provided that a reversible (or piecewise reversible) representation can be established. Here however, we approximated the experimental histograms by a Gaussian function for the sake of computational simplicity.

On the other hand, one may notice that Gaussian statistics are inherent to many aspects of the DLS measurements. For instance, the Doppler broadening of scattered light frequencies (phenomena behind dynamic scattering) obeys the Gaussian distribution with a width of peak at half-height related to the particle diffusion coefficient [2]. The intensity autocorrelation function - the quantity directly measured in DLS - is also related to the structure factor only if the magnitude of scattered electric field/light intensity is

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