



Surface charge and interfacial potential of titanium dioxide nanoparticles: Experimental and theoretical investigations

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ABSTRACT

Size dependent surface charging and interfacial potential of titanium dioxide (TiO₂) nanoparticles are investigated by experimental and theoretical methods. Commercially available TiO₂ (P25) nanoparticles were used for surface charge determinations by potentiometric titrations. Anatase particles, 10 and 22 nm in diameter, were synthesized by controlled hydrolysis of TiCl₄, and electrophoretic mobilities were determined at a fixed pH but at increasing salt concentrations. Corrected Debye–Hückel theory of surface complexation (CDH–SC) was modified to model the size dependent surface charging behavior of TiO₂ nanoparticles. Experimentally determined surface charge densities of rutile and P25 nanoparticles in different electrolytes were accurately modeled by the CDH–SC theory. Stern layer capacitances calculated by the CDH–SC theory were in good agreement with the values found by the classical surface complexation approach, and the interaction of protons with OH groups is found to be less exothermic than for iron oxide surfaces. Moreover, the CDH–SC theory predicts that the surface charge density of TiO₂ nanoparticles of diameter <10 nm is considerably higher than for larger particles, and pH at the point of zero charge (pH_{pzc}) shifts to higher pH values as the particle size decreases. The importance of including the particle size in calculating the zeta potentials from mobilities is demonstrated. Smoluchowski theory showed that 10 nm particles had lower zeta potential than 22 nm particles, whereas a reverse trend was seen when zeta potentials were calculated by Ohshima's theory in which particle size is included. Electrokinetic charge densities calculated from zeta potentials were found to be only one third of the true surface charge densities.

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1. Introduction

Surface and interfacial properties of nanoparticles such as surface charge density and zeta potential are extremely important in determining their reactivity, the stability in complex media, self-assembly properties, capacity for assembling nanoarchitectures by bottom-up approaches, interaction with cells, and adsorption of proteins [1]. Most of the surface chemical properties of colloidal particles are treated as dependent only on the material and independent of size. Despite the obvious importance of particle size dependent surface charge density and zeta potential, relatively little information is available in the literature. There are some experimental studies in which size dependent surface charging has been investigated for hematite (α -Fe₂O₃) [2], magnetite (Fe₃O₄) [3], anatase (TiO₂) [4], and silica (SiO₂) [5–9] nanoparticles of diameter less than 50 nm. However, contradictory results have been reported. In some studies, enhanced surface charge densities were reported for 30 and 8 nm silica particles [6,7], whereas in another study, similar charge densities were found for 30, 50, and 80 nm silica [14].

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Recently, Brown et al. [8,9] have shown by using the X-ray absorption near edge spectroscopy (XANES) and X-ray photoelectron spectroscopy (XPS) that the surface charge density of 7–9 nm silica particles is higher than that for 22–25 nm particles. Size dependent zeta potentials of nanoparticles have also been reported in a number of studies [2,3,10–15]. As in the case of size dependent surface charging, there is no clear trend observed from these experimental studies. For example, results of Blute et al. [5] indicate that 6 nm silica particles have lower zeta potential in 0.01 M NaCl than 15 nm particles. On the other hand, Madden et al. [2] found higher zeta potential for 7 nm α -Fe₂O₃ compared with 25 nm particles. Monte Carlo simulations and theories based on integral equations predict that at constant surface charge and salt concentration, the zeta potential of nanoparticles decreases as the particle size decreases [16–18].

There are a number of practical difficulties that might be the cause of the contradictory experimental results reported for particle size dependent surface charging and zeta potential. Nanoparticles aggregate strongly and once particles are aggregated, their surfaces will behave very differently compared to mono-dispersed particles. Consequently, their surface charge and zeta potential will be more like large micrometer sized particles [19]. Another

difficulty in determining the particle size dependent zeta potential is that the surface protonation state may be altered as the particle size changes. Small particles can acquire higher protonation/deprotonation compared with the larger particles at the same pH and salt concentration. It is therefore likely that the effect of decreasing zeta potential due to a decrease in the particle size (as predicted by theory) is masked by the increase in the surface charge. Consequently, such counter acting effects will result in higher zeta potential for small particles compared to larger particles. Thus, careful experimental considerations are needed to discriminate these effects. Care should also be taken in interpreting the experimental results. For example, zeta potentials generally reported in the literature are calculated from the mobility measurements by simple Smoluchowski theory [20] often used as the default analysis in many instruments. This theory assumes a linear relationship between the mobility and the zeta potential, and particle size is ignored. However, for small highly charged particles in low electrolyte concentrations, nonlinearity and particle size have to be taken into account [21].

Traditionally surface charging of metal oxide particles dispersed in an electrolyte solution is modeled by the so-called surface complexation (SC) approach. In the SC approach, surface charging due to protonation and deprotonation reactions of hydroxyl groups is described by equilibrium constants along with a suitable model of the double layer. The double layer theories used in the traditional SC approach are exclusively based on the Gouy–Chapman (GC) model of an electric double layer. The GC model is based on an analytical solution of the nonlinear Poisson–Boltzmann (PB) equation by considering the particle surface as a planar charged wall and ions as point charges. The SC model has been used extensively to interpret experimental surface charge as well as ion adsorption data on various metal oxides [22]. However, an important limitation of the SC approach is that it cannot be applied to particles of diameter <10 nm because the planar wall assumption can be significantly violated due to the curvature of the double layer as noted by Ridley et al. [4] in the case of 10 nm TiO₂. Moreover, a consequence of considering ions as point charges is that at sufficiently high charge densities, the predicted concentration of counter ions near a charged surface can become unrealistically high [23]. Thus, for an accurate calculation of the charging behavior of nanoparticles, theories in which the counter ion size is taken into account are highly desirable. Simulation methods such as molecular dynamics (MD) and Monte Carlo (MC) [24] are comparatively less approximate than analytical theories, and ion size effects can easily be accounted for. Theoretical approaches such as Molecular Statistics (MS) [25] and Molecular Dynamics (MD) simulations have also been applied to calculate the surface charging of metal oxides [26]. However, these approaches have not been used for examining the size dependence of the surface charging of nanoparticles at different pH values. Simulating pH at molecular level requires enormous computational power which has been an obstacle in the use of MD for pH dependent surface charging.

Recently, a new form of surface complexation theory, the Corrected Debye–Hückel theory of surface charging (CDH-SC), was developed and used to predict the surface charge densities of goethite nanoparticles [19,27,28]. Experimentally determined surface charging behavior of goethite particles was successfully predicted, and the particle size dependent surface charge densities calculated by the CDH theory were in excellent agreement with MC simulations.

The aim of present study is to modify the CDH-SC theory for predicting the surface charging behavior of TiO₂ surfaces and to explore the particle size dependent surface charge densities and interfacial potential, i.e., zeta potential by combining theory and experiments. For this purpose, the specific interaction energy of protons with the OH groups present on TiO₂ surfaces was

determined and used in the CDH theory to model the experimentally determined surface charge densities of rutile and P25. Furthermore, the CDH-SC theory was used to predict the particle size dependent surface charge densities of TiO₂ nanoparticles in a size range of 1–100 nm. Electrophoretic mobilities of stable suspensions of 10 and 22 nm anatase particles at pH 2–2.5 were determined at increasing salt concentrations. The effect of nanoparticle size on the zeta potential was evaluated by calculating the zeta potential from mobility data using the Smoluchowski theory [20] and Ohshima's model [29,30]. Electrokinetic charge densities at increasing salt concentrations were calculated from the zeta potentials by using the Gouy–Chapman model.

2. Methods: theory and experiment

2.1. CDH-SC theory

In the CDH-SC theory, a metal oxide nanoparticle is considered as a sphere having only one type of surface sites randomly distributed on the particle surface. Charging of an oxide surface is described by a simple three-dimensional harmonic oscillator model in which the interacting proton has a specific frequency and interaction energy. The hydration of an oxide surface is described by a layer of water molecules adjacent to the particle surface which is called the capacitor layer and has width (w_c). A relationship between capacitance (C) and thickness of this layer in the CDH-SC theory is given below:

$$C = \frac{\epsilon_0 \epsilon}{w_c + \frac{d}{2}} \quad (1)$$

where ϵ_0 is the permittivity of vacuum, ϵ is the relative permittivity of the medium, and d is the counter ion diameter. The screening of a charged surface in an electrolyte solution is described by the formation of a diffuse double layer, and at sufficiently high surface charge densities, a condensed counter ion (I_c) layer is also formed between the capacitor and the diffuse layers. In the I_c layer, counter ion size effects are included in the form of excluded volume and hole correction in the electrostatic energy. A consequence of the formation of the I_c layer is that the apparent bare surface charge is reduced due to the screening by counter ions. The interaction of this effective charged surface with the bulk electrolyte is then obtained by linear response approximation. The CDH-SC theory is formulated in terms of free energy density functionals. The properties of charged particles immersed in an electrolyte solution such as the surface charge density, effective charge, and thickness of the I_c layer are obtained by minimizing the free energy density functionals. A detailed description of the CDH-SC theory is given in Refs. [19,27].

2.2. Experimental methods

2.2.1. Synthesis

The colloidal sols of TiO₂ were synthesized by means of low-temperature controlled hydrolysis of TiCl₄. In a typical synthesis, TiCl₄ (99%) was cooled at -16°C and 5.2 mL \pm 0.05 of this solution was added drop wise to 200 mL of de-ionized (MilliQ) water under vigorous stirring. The synthesis was mostly done by using a 1:40 TiCl₄:H₂O volume ratio with a resulting TiO₂ concentration of 18 g L⁻¹. TiO₂ particles of different sizes were obtained by optimizing the reaction temperature, dialysis time/temperature, and storage time/temperature. The temperature of water and the reaction solution was precisely controlled by using a temperature control unit. Hydrolysis of TiCl₄ in water generates a solution with very low pH and high Cl⁻ ion concentration. There is risk that the synthesized TiO₂ nanoparticles may start to aggregate in the Cl⁻ rich solution. In order to increase the stability, the ionic strength of

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