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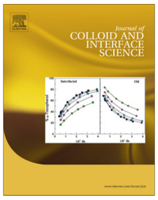

Influence of surface conductivity on the apparent zeta potential of amorphous silica nanoparticles

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ABSTRACT

Zeta potential is a physicochemical parameter of particular importance in describing ion adsorption and double layer interactions between charged particles. However, for metal-oxide nanoparticles, the conversion of electrophoretic mobility measurements into zeta potentials is difficult. This is due to their very high surface electrical conductivity, which is inversely proportional to the size of the particle. When surface conductivity is similar to or higher than the electrical conductivity of bulk water, it can significantly lower the electrophoretic mobility of the particles. It follows that the magnitude of the apparent zeta potential determined from the Smoluchowski equation (disregarding surface conductivity) can be grossly underestimated. We use a basic Stern model to describe the electrochemical properties and to calculate the true zeta potential of amorphous silica nanoparticles immersed in NaCl solution. The parameters of our surface complexation model are adjusted by potentiometric titration and electrophoretic mobility measurements at high salinity (10^{-1} M NaCl). Electrophoretic mobilities are calculated using Henry's electrokinetic transport model with specific surface conductivities and zeta potentials estimated by our surface complexation model. The very good agreement of calculated and measured electrophoretic mobilities confirms that the true zeta potential corresponds to the electrical potential at the outer Helmholtz plane (OHP). Consequently, the shear plane might be located close to the OHP. The assumption of the presence of a stagnant diffuse layer at the amorphous silica/water interface is therefore not required.

1. Introduction

For an electrically charged solid/liquid interface, the zeta potential (ζ) is defined as the local electrical potential at the slipping plane that separates the stationary and mobile phases in tangential flow of the liquid with respect to the surface [1,2]. This local electrical potential is determined experimentally using electrokinetic measurements involving cross-coupling electrokinetic phenomena. For instance, in electro-osmosis and electrophoresis, an electric force leads to a fluid flow, whereas in streaming current, an applied fluid flow produces an electric current. In these experiments, thermodynamic forces are responsible for fluxes and the material coupling property measured or modeled at the macroscopic level can be related to the microscopic zeta potential [3–5].

The zeta potential provides essential information about the electrochemical properties of the electrical double layer (EDL) at the interface between two phases (for instance, on sorption phenomena and the electrostatic interactions between particles controlling aggregation or flocculation) [1,2]. The electrochemical properties of the EDL are of fundamental interest for the modeling of the reactive transport of metal-oxide colloids and nanoparticles in porous media [6–8]. The aggregation kinetics of these particles in aqueous electrolytes are highly dependent on their electrostatic stabilization, which can be described by DLVO theory [9–11]. Their deposition is also controlled by electrostatic interactions between particles and the solid surface [12]. Furthermore, the dissolution kinetics of metal-oxide particles and the sorption of dissolved species on their surfaces depend on their electrochemical surface properties [13,14].

Being able to accurately predict the electrochemical properties of silica particles as a function of pH and salinity is of considerable importance in many fields including (i) industrial processes using silica particles for ceramics, chromatography, catalysis, and chemical mechanical polishing [15], (ii) high-tech industries using silica nanoparticles as carriers in biomolecular transport and drug delivery (pharmaceutical and biomedical technologies [11,16]), and (iii) studies of contaminant transport in the vadose zone involving, for instance, ions, nanoparticles, and colloids sorbed onto the surface of silica (e.g. [17–19]) or silica nanoparticles themselves [20,21].

Electrophoretic mobility measurements are commonly used to determine the zeta potential of metal-oxide nanoparticles

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[22,23]. However, the magnitude of the zeta potential can be significantly underestimated if electrophoretic mobility measurements are not corrected for the retardation force and relaxation effect associated with the surface electrical conductivity of the particles [24,25]. This is particularly true at low ionic strengths (typically $<10^{-2}$ M NaCl) because the electrical conductivity of the background pore water can be low with respect to the surface conductivity of metal-oxide nanoparticles [26]. Surface conductivity of metal-oxide nanoparticles is very high because it is inversely proportional to the size of the particle [26].

Since surface conductivity is due to the electromigration of counter and co-ions of the EDL along the surface of the particle, this excess of conduction can be estimated from an electrostatic surface complexation model describing the electrochemical properties of the interface. The parameters of the electrostatic surface complexation model can be adjusted by electrophoretic mobility and potentiometric titration measurements [14,26]. Recently, Leroy et al. [26] corrected successfully apparent zeta potentials of TiO_2 nanoparticles (P25) (calculated using the Smoluchowski equation) from their surface conductivity and showed that their intrinsic zeta potentials, in an NaCl solution can be underestimated by a factor 2–3. They found that the use of low apparent zeta potentials leads to the questionable assumption of the presence of a stagnant diffuse layer at the TiO_2/water interface [22], a point that is still a subject of controversy in the literature on interfacial electrochemistry. Surface conductivity can also be estimated using electrical conductivity measurements [25,27,28]. However, as for electrophoretic mobility experiments, the interpretations of these measurements are complex in the case of electrically charged and very small metal-oxide nanoparticles because the thickness of the diffuse layer can be similar to the particle size [29].

Sonnefeld et al. [23] performed three different types of measurements (potentiometric titration, electro-acoustic, and electrical conductivity experiments) to accurately estimate the electrochemical properties of spherical amorphous silica nanoparticles (Degussa Aerosil OX50) immersed in the NaCl solution. The dynamic electrophoretic mobility of silica nanoparticles was determined by electro-acoustic measurements that are less sensitive than electrophoresis to the concentration of particles in solution [30]. Sonnefeld et al. [23] used the theory of O'Brien et al. [30] to correct electrophoretic mobilities from surface conductivity. However, this theory considers only surface conductivity of large (colloidal) particles with no Stern layer and a thin diffuse layer (compared to the size of the particle) at their interface. Moreover, like Panagiotou et al. [22], Sonnefeld et al. [23] also considered the presence of a stagnant diffuse layer at the silica/water interface, whereas we believe this assumption is questionable.

Laven and Stein [31] measured both the electrophoretic mobility and the dynamic viscosity of very dilute aqueous dispersions of amorphous silica nanoparticles (Ludox). They found very high experimental viscosities compared to their viscosity predictions, particularly for basic pH (pH = 8.7) and low salinity (salinity < 10^{-2} mol L^{-1} KCl). Laven and Stein [31] assume that the very high viscosity of amorphous silica nanoparticles (Ludox) is associated with the presence of a thick, gel-like surface layer on the particle. They assume that the surface of these nanoparticles may form swollen gels with extended chains of polysilicic acid branching out into the medium. Allison [32] developed a spherical gel layer model to predict successfully the electrophoretic mobility and viscosity measurements of Laven and Stein [31]. This author assumes that the inner core of the spherical particle is surrounded by a diffuse gel layer. In his model, the gel layer has a specific fraction of the particle mass and charge. However, his spherical gel layer model is not able to reproduce correctly measured surface charge densities of Ludox silica. In addition, for acid and neutral pH, the assumption of the presence of a diffuse gel layer at the surface of amorphous silica is still a subject of debate.

To the best of our knowledge, there has been no attempt, to date, to estimate the intrinsic zeta potential and surface conductivity of the amorphous silica nanoparticles using a basic Stern model coupled with an electrokinetic transport model. We propose here a unified and consistent model of the electrochemical properties of the silica/water interface for 1:1 aqueous electrolytes (e.g., NaCl or KCl). After a state of the art of the different surface complexation models, our electrostatic surface complexation and electrokinetic transport models are presented and the two models are validated by comparison with potentiometric titration, electrophoretic mobility and electrical conductivity measurements.

2. Theoretical background

2.1. Surface complexation models for silica

Because of its relatively simple surface chemistry compared to other oxides like titanium dioxide, silica is often used as a reference material for testing electrical surface complexation models. Several models were therefore proposed for the silica/water interface immersed in various electrolyte solutions. These models differ with regard to protonation–deprotonation reactions and the structure of the silica/water interface [14,23,33–35]. They include the 2-p*K* ([14,34,35]) and 1-p*K* models ([33]) for the surface protonation–deprotonation reactions, the triple layer model (TLM, [35]), and the basic Stern model (BSM, [33]) for the structure of the mineral/water interface.

2.1.1. Protonation–deprotonation reactions

At the silica surface, there are two types of groups – singly Si-coordinated, >SiOH (silanol), and doubly Si-coordinated, $>Si_2O$ (siloxane) [33]. In the normal pH range of acid–base titration (pH between 2 and 12), the estimated $\log K$ values (K being the equilibrium constant) of the protonation–deprotonation reactions of the doubly Si-coordinated group are very low and this group can therefore be considered to be non-reactive [33]. Only the singly Si-coordinated group is considered to be reactive.

Two principal p*K* models simulate the protonation reactions of the singly Si-coordinated group [34,36,37]. The most common is the 2-p*K* model, which assumes two protonation reactions of singly Si-coordinated sites [14,23,34]:

$$> \mathrm{SiOH} + \mathrm{H}^+ \Longleftrightarrow\ > \mathrm{SiOH}_2^+, K_1, \tag{1}$$

$$> \mathrm{SiO}^- + \mathrm{H}^+ \Longleftrightarrow\ > \mathrm{SiOH}, K_2, \tag{2}$$

where ">" refers to the mineral framework and $K_{1,2}$ are the two equilibrium constants (at the standard state) associated with the surface adsorption of protons.

The 2-p*K* model considers that two surface species, $>SiO^-$ and $> SiOH_2^+$, are responsible for the surface charge density of silica. This model was successfully used by Sverjensky and co-workers [14,35,38] to predict various acid–base titrations of amorphous silica (Degussa, Ludox and Cabosil commercial silicas) and led to the validation of the 2-p*K* model over a broad pH range (pH 2–12) and considering several 1:1 electrolyte solutions. Sverjensky and co-workers [14,35,38] calculated the $\log K_1$ and $\log K_2$ values considering the Born solvation theory, electrostatic interaction of the adsorbing proton with a surface oxygen and an underlying metal ion, and an intrinsic binding of the proton to the surface.

Due to the very low $\log K_1$ value (from $\log K_1 = -1.8$ to $\log K_1 = -1.0$, [14]), the protonation of the neutral silanol group in the normal pH range considered for titration is not very likely [33]. Some