Journal of Colloid and Interface Science 356 (2011) 442–453

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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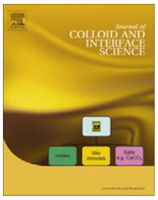

Influence of surface conductivity on the apparent zeta potential of TiO_2 nanoparticles

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A R T I C L E I N F O

Article history:
Received 15 October 2010
Accepted 5 January 2011
Available online 11 January 2011

Keywords:
Zeta potential
Electrophoretic mobility
TiO_2
Nanoparticle
Surface conductivity
Extended Stern model

A B S T R A C T

Zeta potential is a physico-chemical parameter of particular importance in describing ion adsorption and electrostatic interactions between charged particles. Nevertheless, this fundamental parameter is ill-constrained, because its experimental interpretation is complex, particularly for very small and charged TiO_2 nanoparticles. The excess of electrical charge at the interface is responsible for surface conductance, which can significantly lower the electrophoretic measurements, and hence the apparent zeta potential. Consequently, the intrinsic zeta potential can have a larger amplitude, even in the case of simple 1:1 electrolytes like NaCl and KCl. Surface conductance of TiO_2 nanoparticles immersed in a NaCl solution is estimated using a surface complexation model, and this parameter and particle size are incorporated into Henry's model in order to determine a constrained value of the zeta potential from electrophoresis. Interior conductivity of the agglomerates is calculated using a differential self-consistent model. The amplitude of estimated zeta potential is greater than that derived from the von Smoluchowski equation and corresponds to the electric potential at the outer Helmholtz plane calculated by our surface complexation model. Consequently, the shear plane may be located close to the OHP, contradicting the assumption of the presence of a stagnant diffuse layer at the TiO_2/water interface.

1. Introduction

Titanium dioxide is widely used as TiO_2 nanoparticles and has a large variety of potential applications in, for example, the biomedical, optical, and electronic fields [1,2]. Due to their small size, nanoparticles have a very high surface area to volume ratio and are thus of great scientific interest as they are a bridge between bulk materials and atomic or molecular structures. The properties of materials change as their size decreases to nanoscale and the proportion of surface atoms becomes significant. One of these properties, the surface ionization of titanium dioxide nanoparticles in contact with an electrolytic solution, has been studied extensively [1,3–10]. It is well known that the complexation reactions at the surface of an oxide mineral are strongly influenced by the development of the surface charge. The primary surface charge is determined by the reactions of protons with the surface. Surface complexation reactions between the surface sites and the ions from the bulk electrolyte at the Stern and in the diffuse layer neutralize the surface charge [11]. Surface charge properties are primarily determined using proton titration data. These data can be modeled using various electrostatic models such as the diffuse double layer, basic Stern, triple layer, or CD-MUSIC models [1,3–10]. Most sophisticated models are able to reproduce data for a wide range of experimental conditions but rely on the fitting of a large number of parameters whose physical significance is not always easy to justify. Moreover, the uniqueness of a set of parameters is not always obvious. On the other hand, less sophisticated models rely on the fitting of fewer parameters but often fail to reproduce the data under all of the experimental conditions studied. At present, there is no consensus on which is the "best model" to represent charged surfaces at oxide–water interfaces.

Of all the physico-chemical parameters characterizing the solid/water interface, the zeta potential is particularly important. It is the potential at the supposed slipping plane that separates the stationary and mobile phases in tangential flow of the liquid with respect to the surface. For example, in the case of a particle undergoing electrophoresis, because of the electrostatic interactions between the applied electric field and the hydrated counterions in the diffuse layer, the interface develops a surface of shear [12]. The electric potential at the slipping plane is of particular interest if we wish to estimate the critical coagulation concentration when studying nanoparticle agglomeration, for example [5,12,13]. The zeta potential is also a key parameter for the study of the transport properties of electrically charged materials like oxide and clay minerals [14–16]. It usually makes it possible to optimize the parameters of the electrostatic surface complexation models while assimilating the position of the shear plane to the position of the head end of the diffuse layer [10,17]. This

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doi:10.1016/j.jcis.2011.01.016

interpretation has, however, been challenged by recent studies on titanium dioxide nanoparticles that show that titration data cannot be reproduced together with zeta potential values without having a shear-plane position that changes as a function of the ionic strength. Bourikas et al. [9] and Panagiotou et al. [1] have shown that the shear-plane position (in log scale) is linearly dependent on the log value of the ionic strength. This physical model leads, however, to a surface representation in which the shear plane can be as far as 210 Å from the surface at an ionic strength of 10^{-4} M (Fig. 32 of [1]); the entire volume between the oxide surface and this shear plane is considered to be "stagnant." Moreover, this physical representation of the oxide surface rules out any use of the zeta potential as a constraint for surface charge models. The nature of the physical property that causes the separation between the stagnant diffuse layer and the "mobile" diffuse layer is, however, not given. Molecular dynamics studies and X-ray measurements on oxide and aluminosilicate surfaces tend to show that diffuse layer water properties (density, mobility, molecule orientation) are very similar to those of bulk water [18–20]. Electrophoretic mobility measurements are usually used to determine the zeta potential. However, zeta potential estimations can be erroneous due to the uncertainty concerning the value of the conversion factor used [12]. This could explain the "observed" shift of the shear-plane position as a function of the ionic strength in surface complexation models. Numerous authors [18–26] emphasize that the anomalous surface conductivity of particles might explain the low zeta potential values (in amplitude) determined from electrophoresis compared to values estimated by surface complexation models at the OHP and electrical conductivity measurements. They also state that the lateral motion of adsorbed counterions at the Stern layer must not be disregarded for some materials having a large excess of electrical charge at their surface (like clay minerals or latex suspensions). Little work has been done to characterize the surface conductance due to the Stern layer for titanium dioxide nanoparticles [27]. In addition, the surface conductivity of TiO_2 nanoparticles may be strong due to the small size of the elementary particles.

The aim of this work is to study the possible influence of TiO_2 nanoparticle surface conductivity on its electrophoretic mobility in the hope that this will lead to zeta potential values in agreement with those predicted by electrostatic surface complexation models (without considering large variations of the distance between the outer boundary of the compact layer and the inner boundary of the diffuse layer). Surface speciation models are needed to calculate the surface conductance of TiO_2. For this reason, the model developed recently by Panagiotou et al. [1] and alternative models are critically evaluated in the second chapter of this study. In the third chapter, we discuss the theories used to convert electrophoretic mobility to zeta potential and calculate surface conductance due to the double layer. In the fourth chapter, we describe our modeling strategy and use the proposed methodology to estimate the "intrinsic" zeta potential of titanium dioxide P25 in a NaCl electrolyte from electrophoresis.

2. Electrostatic models for titanium oxides

2.1. Panagiotou et al. model (2008)

Panagiotou et al. [1] proposed a triple plane model (TPM, [6]) for the titanium oxide (P25) solid–solution interface in $NaNO_3$ and KNO_3 electrolyte solutions. This model is based on a state-of-the-art description of the TiO_2 surface properties with regard to protonation–deprotonation processes using the recent ab initio calculations and DFT developments for this material. Two main surface functional groups were found to be responsible for the surface reactivity:

$$Ti_2O^{-0.57} + H^+ \rightleftharpoons Ti_2OH^{+0.43} \quad \log K_1, \tag{1}$$

$$TiO^{-0.35} + H^+ \rightleftharpoons TiOH^{+0.65} \quad \log K_2. \tag{2}$$

Total surface site density was fixed at a value of 5.6 sites nm^{-2} obtained from crystallographic considerations. Total surface area was 50 $m^2\,g^{-1}$ according to BET measurements.

The surface ionization model was then combined with a triple plane model, and the predictions were used together with potentiometric titration, microelectrophoresis, and streaming potential experiments to describe the electro-chemical properties of the TiO_2 surface. Both surface sites were considered to behave similarly with a given cation (Na^+ and K^+) or anion (NO_3^-). This simplification enabled the authors to reduce the number of adjustable parameters for their model:

$$Ti_2O^{-0.57} + Na^+ \rightleftharpoons Ti_2O^{-0.57} - Na^+ \quad \log K_{Na}, \tag{3}$$

$$TiO^{-0.35} + Na^+ \rightleftharpoons TiO^{-0.35} - Na^+ \quad \log K_{Na}, \tag{4}$$

$$Ti_2OH^{+0.43} + NO_3^- \rightleftharpoons Ti_2OH^{+0.43} - NO_3^- \quad \log K_{NO3}, \tag{5}$$

$$TiOH^{+0.65} + NO_3^- \rightleftharpoons TiOH^{+0.65} - NO_3^- \quad \log K_{NO3}. \tag{6}$$

In the triple plane model, the charge of sorbing cations and anions is not attributed to only one electrostatic plane but is distributed over the three planes (0, 1, 2), thus adding two additional fitting parameters (Δz_0 and Δz_1 or Δz_1 and Δz_2) for each sorbed species at each surface site (Fig. 1). Again, both surface sites were considered to behave similarly with a given cation or anion.

The parameters of this model are given for a $NaNO_3$ electrolyte background in Table 1. We reproduced their model using PHREEQC v2.17 [28]. We were not able to reproduce their titration curves using the parameters in the reference publication. The tabulated protonation/deprotonation constants (log K_1 and log K_2) had to be changed slightly in order to obtain results in full agreement with the data. Hereafter, we refer to this modified model as "reference model" (Table 1). Surface charge predictions are given in Fig. 2 together with surface potential at the 2-plane, which is considered to be the head end of the diffuse layer. This parameter can be compared to the zeta potential.

Panagiotou et al. [1] reported zeta potential values far below the potential values of the 2-plane (in absolute value). They interpreted this to be a consequence of a shift of the shear plane (where the zeta potential is located) from this 2-plane. While calculating the distance d from the 2-plane to the shear plane, they found a log–log linear relationship between the ionic strength I (in M) and d (in nm):

$$\log d = -0.5115 \log I - 0.7229. \tag{7}$$

2.2. Alternative models

While the data of Panagiotou et al. [1] could be very well reproduced by their TPM model, it could also be reproduced with the simpler basic Stern model (BSM). The BSM parameters (Table 1) give surface charge results nearly identical to those of the TPM reference model in $NaNO_3$ electrolyte (Fig. 2), although the BSM requires only five fitting parameters instead of 10 for TPM. This raises the question of the uniqueness of the TPM parameter set. In principle, this problem can be overcome by fitting a large range of data obtained under the same experimental conditions but testing different electrolyte types. Panagiotou et al. [1] provided titration data in a KNO_3 electrolyte background and were able to fit them adequately only by attributing an association constant (log $K_K = -1.1$) and a charge distribution ($\Delta z_{1K} = 0$, $\Delta z_{2K} = 1$) for K^+ at the surface, while keeping the other parameters constant. A good agreement can also be obtained with the BSM model (Fig. 3) adding only an association constant (log $K_K = -1.7$) for K^+. There is a