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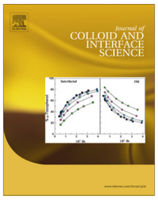

Influence of surface conductivity on the apparent zeta potential of TiO_2 nanoparticles: Application to the modeling of their aggregation kinetics

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ABSTRACT

Titanium dioxide nanoparticles (TiO_2 NPs) are extensively used in consumer products. The release of these NPs into aquatic environments raises the question of their possible risks to the environment and human health. The magnitude of the threat may depend on whether TiO_2 NPs are aggregated or dispersed. Currently, limited information is available on this subject. A new approach based on DLVO theory is proposed to describe aggregation kinetics of TiO_2 NPs in aqueous dispersions. It has the advantage of using zeta potentials directly calculated by an electrostatic surface complexation model whose parameters are calibrated by ab initio calculations, crystallographic studies, potentiometric titration and electrophoretic mobility experiments. Indeed, the conversion of electrophoretic mobility measurements into zeta potentials is very complex for metal oxide nanoparticles. This is due to their very high surface electrical conductivity associated with the electromigration of counter and co-ions in their electrical double layer. Our model has only three adjustable parameters (the minimum separation distance between NPs, the Hamaker constant, and the effective interaction radius of the particle), and predicts very well the stability ratios of TiO_2 NPs measured at different pH values and over a broad range of ionic strengths (KCl aqueous solution). We found an effective interaction radius that is significantly smaller than the radius of the aggregate and corresponds to the radius of surface crystallites or small clusters of surface crystallites formed during synthesis of primary particles. Our results confirm that DLVO theory is relevant to predict aggregation kinetics of TiO_2 NPs if the double layer interaction energy is estimated accurately.

1. Introduction

A number of studies have recently focused on the transport and fate of nanoparticles (NPs) in porous media and their potential risk for the environment and human health [1–5]. However, their transport is very difficult to predict due to their very high surface reactivity and, notably, to their versatility between their aggregated and dispersed states. Modeling their reactivity and mobility in an aqueous environment is, therefore, challenging [3,6,7].

Titanium dioxide (TiO_2) NPs are used in many consumer products (e.g. catalysts, paints, coatings, soaps, cosmetics, and sunscreens [7–9]) because they have a very high specific surface area and a sorption capacity for ionic and nonionic species [10,11]. Their application for soil remediation and water treatment shows great potential [12–14]. Their increasing use inevitably leads to their entering various environmental compartments and questions now arise concerning their mobility, fate and toxicity for humans and the environment.

Aggregation and deposition in porous media are the major processes controlling TiO_2 NPs transport [15]. Both processes are highly dependent on interaction energies between particles (aggregation), and between particles and the surrounding aquifer rock (deposition on the collector) [2,16,17]. The interaction forces between NPs and between the NPs and the collector are controlled by the intrinsic properties of NPs (chemical composition, size, and shape [2]) and by the intrinsic properties of the rock (chemical composition and surface roughness [16]). When immersed in an aqueous electrolyte, NPs and rock develop a surface charge (associated with the hydroxylation of their surface and specific ion adsorption) and an electrical double layer (EDL) to cancel it. EDLs around particles having similar chemical composition and crystal structure have the same polarity and strength. As a result, when two particles draw near each other, the overlapping double layers create a repulsive double layer force. This double layer force between NPs (of similar chemical composition and crystal structure) and rock can be repulsive if the EDLs of both materials have the same polarity (which fosters aggrega-

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tion), or attractive if the EDLs have opposite polarity (which fosters deposition) [6,7,17].

When NPs are repulsed from the rock surface, interaction energies between NPs greatly influence their aggregation [17]. TiO_2 NPs aggregate under specific chemical conditions (pH, ionic strength, the chemical nature of aqueous dissolved species) that reduce the repulsive double layer interaction energy between particles [10,11]. Aggregation of TiO_2 NPs decreases their mobility in porous media and may even clog the porosity if their concentration in water is high. It may therefore enhance their deposition [7,17]. However, their deposition can be reversible. Large quantities of TiO_2 NPs can be released into the environment if the pH of the pore water changes and moves away from the pH_{PZC} of TiO_2 NPs (PZC is the point of zero charge) or if the ionic strength of the pore water decreases to values below the critical coagulation concentration (CCC) [7,16,17]. It is, therefore, important to understand the aggregation of titanium dioxide NPs in water as a function of pH and ionic strength.

The double layer interaction energy is usually estimated using zeta potential data inferred from electrophoretic mobility measurements [10,18]. However, because of their excess of electrical charges at the solid/water interface and very high surface-to-volume ratio, metal oxide NPs can have a very high surface electrical conductivity. This is associated with the electromigration of electrical charges in the double layer around the particle and is inversely proportional to the size of the particle [18–21]. Surface conductivity significantly decreases the magnitude of the electrophoretic mobility of suspended particles when it is similar to or higher than the electrical conductivity of bulk water [18,19], i.e. at low ionic strengths (typically lower than 10^{-1} M), and for pH values distant from the pH_{PZC} of the particle [18]. Under these physicochemical conditions, the intrinsic or true zeta potential of the NPs can be significantly underestimated if the zeta potential is not corrected for the retardation effect due to surface conductivity. Both the resulting repulsive interaction energy between double layers of particles and their stability ratios can therefore be underestimated.

Leroy et al. [18] recently developed a surface conductivity model for TiO_2 NPs immersed in a 1:1 aqueous electrolyte (KNO_3, $NaNO_3$, NaCl). In their work, surface conductivity of the Stern and diffuse layers are calculated by an electrostatic surface complexation model. Their electrokinetic transport model takes into account the retardation effect due to surface conductivity of elementary NPs on the electrophoretic mobility of the aggregate. Leroy et al. [18] adjusted the parameters of their extended Stern layer model (ESM) using both potentiometric titration and electrophoretic mobility experiments. Their corrected zeta potentials appear to be at least double the apparent zeta potentials estimated using the Smoluchowski equation. These authors also showed that potentiometric titration and electrophoretic mobility measurements of TiO_2 NPs can be predicted without the use of the unrealistic assumption of the presence of a stagnant diffuse layer at the TiO_2/water interface [8,9].

Snoswell et al. [22] and Liu et al. [10] used the DLVO theory (constant charge approximation and linear superposition approximation, respectively) to correctly predict measured stability ratios of TiO_2 NPs immersed in a 1:1 aqueous electrolyte solution (KCl and NaCl, respectively). However, they used low apparent zeta potentials (not corrected for surface conductivity) and therefore predict low repulsive double layer interaction energy between particles. Snoswell et al. [22] found an unrealistically low value of 2×10^{-20} J for the Hamaker constant of the TiO_2–H_2O–TiO_2 interface compared to values reported in the literature, which are between 4×10^{-20} J [23] and 9.4×10^{-20} J [24]. The predictions of Liu et al. [10] were only in quantitative agreement with the measured stability ratios of anatase NPs, which have two different sizes (mean radius of either 5 or 50 nm). The aggregation kinetics model of Liu et al. [10] underestimated stability ratios at low ionic strengths (2×10^{-3} M and 7×10^{-3} M NaCl for particles with a mean radius of 5 and 50 nm, respectively). Moreover, their measured stability ratios of anatase particles with a mean radius of 50 nm were not representative of stability ratios of pure TiO_2 NPs because their particles contained large quantities of impurities (silicon and phosphorous).

We provide here an aggregation kinetics model based on the DLVO theory and combined with a precise description of the electrochemical properties of the TiO_2 NPs/water interface (using an extended Stern model) that is valid regardless of the size of the NPs [18,25]. The aggregation kinetics model uses true zeta potentials calculated directly by our electrostatic surface complexation model. The combined model is presented and tested against the stability ratios of pure TiO_2 NPs reported by Snoswell et al. [22] at different pH values and in a KCl solution.

2. Theoretical background

2.1. Aggregation kinetics models

In aggregating systems, the coagulation rate is usually expressed by the stability ratio, W, which is the ratio of the fast kinetic constant, k_f, to the slow kinetic constant, k_s [26]. The aggregation rate is rapid when all collisions result in aggregation in the absence of energy barriers, and slow in the presence of any repulsive energy barrier (unfavorable conditions) that restricts aggregation to the primary minimum. The stability ratio of suspended particles in aqueous environments can be predicted using various DLVO and non-DVLO theories. The classic DLVO theory applies to smooth and spherical colloidal particles immersed in water [27,28] through two types of interaction energies. The first is generally repulsive, due to the overlapping of the particles' EDLs and the second is attractive, due to London–van der Waals (VDW) interactions. However, NP aggregates have a more complex stability ratio than that of perfectly spherical and smooth colloidal particles, notably because of the discreteness of the surface charge [29,30], the arising of relaxation processes [31–33], the presence of additional non-DLVO forces [34,35], and the surface roughness of the particles [22,36]. The classic DLVO theory frequently overestimates the experimental NP aggregation and deposition rates, probably by overlooking this complexity related to these well-known characteristics [22,29,37,38].

Kallay et al. [39] combined an electrostatic surface complexation model (basic Stern model, BSM) and an aggregation model based on the DLVO theory to predict the stability ratios of anisotropic rutile particles (length of 170 ± 70 nm and width of 45 ± 10 nm) immersed in a 1:1 aqueous electrolyte (LiCl, KCl, CsCl). The parameters of their BSM were calibrated by crystallographic studies, potentiometric titration and electrophoretic mobility measurements. Their approach [39] allows direct estimation of the electrical potential at the outer Helmholtz plane (OHP). However, these authors used the constant potential assumption [40] to estimate interaction energies between particles and a too-simple equation to predict stability ratios. Indeed, this equation assumes that the stability ratio is approximately proportional to the exponential of the scaled maximum interaction energy. Additionally, Kallay et al. [39] did not compare their predictions to measured stability ratios.

Non-DLVO theories have recently been proposed to explain the weaker-than-expected stability of NP aggregates [41,42]. Kallay and Zalac [41] consider that small NPs (radius <5 nm) surrounded by a diffuse layer are similar to ions surrounded by their ion clouds because their size is small compared to the thickness of the electric