Research paper

Clay particle charging in apolar media

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A B S T R A C T

Advancements in electrophoretic displays (e.g., the Amazon Kindle®) and new high-quality printing technologies (e.g., HP Indigo®) have been made possible by the ability to control and understand particle charging in apolar media. While previous work has investigated the acid-base charging mechanisms of oxides and similar particles which have only one charging mechanism in water, the purpose of this study was to determine if and how clay particles, which have two known aqueous charging mechanisms, charge in apolar media. Characterization of kaolinite and montmorillonite surface charging properties and mechanisms were conducted in apolar media utilizing different surfactants. It was found that clay particle charging behavior as a function of surfactant concentration mimicked the expected trend of previously studied oxides, which can charge only via an acid-base mechanism. Furthermore, by comparing the point of zero charge of the edge groups (edge PZC) or the point of zero net proton charge (PZNPC) of the clay particle to the empirical effective pH (pH_{Eff}) of the surfactant, the polarity of the particle charge can be predicted. In addition to particle charging, it was shown that the surfactants also improve the stability against aggregation and settling of the particles.

1. Introduction

Clay minerals are unique materials that find application in building materials, ceramics, paints, moisture barriers, and many other products (Jones, 1983; Liu et al., 2015; Murray, 2006; Van Olphen, 1977). Most are naturally-occurring layered phyllosilicates with particle diameters < 2 μm and thicknesses < 100 nm (Tombácz and Szekeres, 2006; Van Olphen, 1977; Yariv and Cross, 2001). While easily exfoliated and dispersible in water, they may also be modified with long chain alkylammonium cations to make "organoclays," which are swellable and dispersible in organic media where they find application as structure-forming and thickening agents in oil-based paints, greases, adhesives, cosmetics, etc. (Esfandiari et al., 2008; Jones, 1983; Moraru, 2001). Clay particles also appear to play an important role in the production of tar sand oil and bitumen recovery (Liu et al., 2015; Masliyah et al., 2011). Most applications involving clay minerals depend on the practitioner's ability to control their stability with respect to aggregation. In aqueous media they are generally stabilized against aggregation by electrostatic forces, whereas in nonaqueous "apolar media," i.e., media of ultra-low dielectric constant ($\varepsilon \approx 2$), it is presumed that they are stabilized or at least lubricated by their adsorbed layers of long-chain cations. It is possible, however, that electrostatic forces also play an important role in stabilizing organoclays in apolar media. While clay particle charging is well understood for aqueous systems, there is only limited knowledge of the process in non-aqueous environments. The

present research thus seeks to understand how clay particles charge in apolar media and strategies for controlling the sign and magnitude of such charging.

As a result of their layered structures consisting commonly of tetrahedral sheets of SiO_4 linkages and octahedral sheets forming $Mg_6O_{12}^{12-}$ or $Al_4O_{12}^{12-}$ linkages, clay minerals acquire charge in water by two distinct mechanisms. First, substitution of Si^{4+} atoms with lower-valence Al^{3+} atoms in the tetrahedral layers or occasionally lower-valence substitution of octahedral cations (Al^{3+} or Mg^{2+}), i.e., "isomorphic substitution," causes a permanent negative charge on the clay surfaces. In kaolinite, which is a 1:1 or tetrahedral-octahedral (TO) type clay mineral with a tetrahedral SiO_4 layer on only one side, for example, yields a cation exchange capacity (CEC) of 1–10 meq per 100 g (Berg, 2010; Van Olphen, 1977; Yariv and Cross, 2001). Montmorillonite is a 2:1 or TOT type clay mineral with tetrahedral layers on both the top and bottom surfaces resulting in a higher CEC than kaolinite, with values of 70–100 meq/100 g (Tombácz and Szekeres, 2004; Van Olphen, 1977; Yariv and Cross, 2001). The excess negative charges are balanced by a layer of adsorbed exchangeable cations such as Ca^{2+}, Mg^{2+}, Na^+, or K^+ which in water can dissociate and leave behind a permanent negative surface charge (Liu et al., 2015; Schoonheydt and Johnston, 2011). The second charging mechanism derives from the edges and, in the case of kaolinite, the bottom alumina octahedral sheets as well, which have –OH functional groups that are known to charge with pH dependence in water in the same way as mineral oxides.
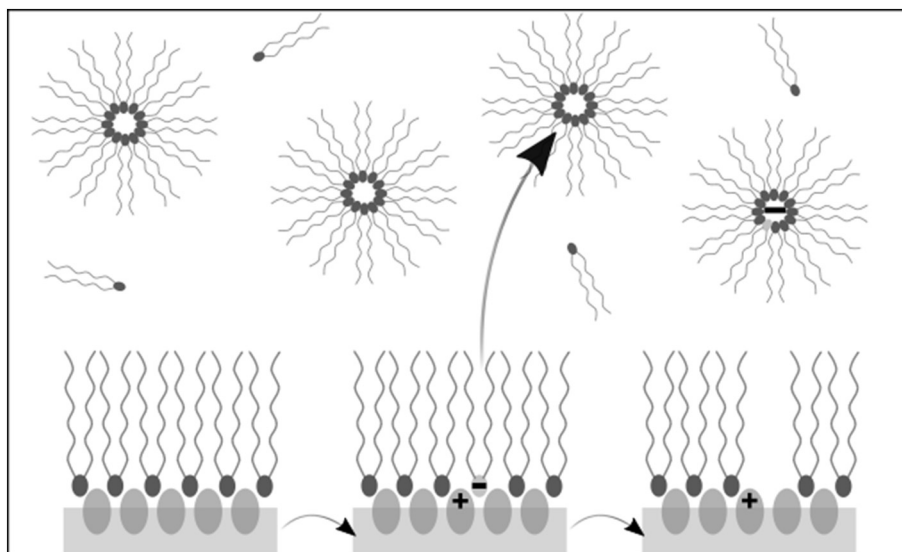
Fig. 1. Schematic showing acid-base adduct formation, dissociation of surfactant at particle surface, and charge stabilization inside an inverse micelle in the bulk.

These charge by an acid-base mechanism (Liu et al., 2015; Tombácz and Szekeres, 2006, 2004; Van Olphen, 1977; Yariv and Cross, 2001). At low pH values, –OH groups are protonated and thus acquire a positive charge, whereas at high pH values they are de-protonated and acquire a negative charge. At a particular pH, viz., the "point of zero charge" (PZC), dependent on the mineral's identity, the net charge is zero. For mineral oxides, the PZC is easily determined by a potentiometric titration, or an electrokinetic titration, leading to the "isoelectric point" (IEP), defined as the pH at which the particle electrophoretic mobility is zero. (In the absence of specific ion adsorption, the PZC and IEP are the same.)

Obtaining the acid-base properties of clay particles in water is challenging, however, due to the multiple charging mechanisms, lack of a common intersection point during raw titrations, ion exchange, and aggregation (Duc et al., 2005; Tombácz and Szekeres, 2004). The latter occurs at low-to-moderate pH values, when the edge charge is positive and the plate charge is negative, producing edge-to-plate aggregation. To determine only the acid-base properties of the –OH groups on the clay particles, the "edge PZC," or the point of zero net proton charge (PZNPC), must be determined (Tombácz and Szekeres, 2004). It is defined as the PZC of the amphoteric clay hydroxyl groups or the pH where the net proton surface charge density equals zero (Schroth and Sposito, 1996; Tombácz and Szekeres, 2004). In kaolinite, with one basal surface as well as the edge with hydroxyl groups, the PZNPC was found in one study to be 6–6.5 (Tombácz and Szekeres, 2006), and montmorillonite samples were found to have a value of 6.5 (Tombácz and Szekeres, 2004).

While the charging of mineral oxides and other materials in apolar media, which finds application in electrophoretic displays (e.g., the Amazon Kindle®) and digital printing (e.g., HP Indigo®), appears to be well-understood (Gacek and Berg, 2015a), the literature on the charging of clay particles in non-aqueous media is scant. One study investigated the surface charging of kaolinite particles in air using force microscopy techniques (Liu et al., 2015), and found that kaolinite nanoparticles had a heterogeneous surface potential distribution which was layer dependent. Another study investigated the charging of organoclays in media of intermediate dielectric constant and found the charging (as evidenced by measured electrophoretic mobility leading to zeta potentials) to be dependent on the identity of the dispersing medium. The charging was likely the result of acid-base interaction between the clay surfaces and the suspending medium, dependent on the relative donicity of the materials, as has been studied extensively for oxides and other minerals in moderate dielectrics (Labib and

Williams, 1984). The charging of clay particles in liquid media of ultra-low dielectric constant, i.e., "apolar media," appears not to have been investigated, and the present work is focused on this type of system. Such knowledge could lead to new or improved products consisting of clay dispersions in such media, and new methods for removing residual clay particles from oil (Liu et al., 2015).

1.1. Background

It is useful to review briefly the mechanism of charging mineral oxides and similar materials in apolar media. Stabilizing charge in such media is more difficult than in aqueous systems because the low dielectric allows coulombic attractive forces to be felt over much greater distances. The Bjerrum length λ_B, shown below, is the separation distance at which two opposite charges possess coulombic attractive energy equal to the thermal energy ($k_B T$).

$$\lambda_B = \frac{e^2}{4\pi\varepsilon\varepsilon_0 k_B T} \tag{1}$$

where ε is the dielectric constant of the medium, ε_0 is the permittivity of free space, and e is the elementary charge. In water, with a dielectric constant of 78, the Bjerrum length is ≈ 0.7 nm, a distance easily accommodated by the hydration shell of the ions, while in a medium of dielectric constant as low as 2, it is ≈ 28 nm. To maintain such large distances of separation required to stabilize the charges against recombination, it is believed that they must be housed within protective supramolecular structures such as inverse micelles. Once surfactants are added in sufficient concentration to form inverse micelles in such systems, they exhibit measurable electrical conductivity (Berg, 2010; Gacek and Berg, 2015a; Morrison, 1993; Smith and Eastoe, 2013).

There is abundant evidence in the literature suggesting that the charging of oxides or similar particles may ensue via the formation and subsequent dissociation of acid-base adducts between the adsorbing surfactant molecules and functional groups on the particle surfaces, as shown schematically in Fig. 1. The resulting charged surfactant ions are housed in the inverse micelles, and the charges on the particle surfaces are protected by adsorbed surfactant. Thus the acid-base mechanism has three steps: first, the polar head group of a surfactant molecule will adsorb to the particle surface and form an acid-base adduct; second, charge is transferred between the surface and the surfactant molecule depending on the acid-base properties; and third, the charged surfactant molecule is stabilized by an inverse micelle which allows it to desorb leaving an opposite charge behind (Gacek and Berg, 2015a;