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Surface structure of ferrihydrite: Insights from modeling surface charge

Nefeli Bompoti [a,*], Maria Chrysochoou [a], Michael Machesky [b]

[a] Department of Civil and Environmental Engineering, University of Connecticut, Storrs, CT, USA
[b] Illinois State Water Survey, Prairie Research Institute, Champaign, IL, USA

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ABSTRACT

Ferrihydrite (FH) plays an important role in controlling the fate and transport of many compounds in nature due to its large surface area and high reactivity. This study is the first attempt to build a surface complexation model using the recently proposed surface structure that incorporates tetrahedrally coordinated Fe atoms (Hiemstra, 2013). The ability of the model to describe the surface charge curves of FH with different preparation methods and Points of Zero Net Proton Charge (PZNPC) is tested. In general, FH particles that have been subject to aging are larger and have lower specific surface area (SSA) and higher PZNPCs. The structural model includes 2 types of singly coordinated (SC) oxygens that are present only on the (1-11) and (1-10) faces and 5 types of triply coordinated (TC) oxygens that are also present on the basal planes (001) and (00-1), for a total of 11 sites. The 11 -site model was able to simulate fresh FH datasets with PZNPC lower than 8.5, but could only simulate higher PZNPCs when the contribution of the more acidic basal planes was minimized. The available microscopic observations do not support this condition, which suggests TC groups on the basal planes likely have log K values higher than the macroscopic PZNPC. We attempted to test this hypothesis through three versions of simplified 3-site models, using SC and one TC on (1-10) and (1-11), with log K 8.0 (equal to fresh FH PZNPC) and one TC group on the basal planes with log K 9.5. This enables fitting of the PZNPC of aged FH datasets by adjusting the face contributions. An unresolved issue is whether this model accurately describes the relative contribution of SC and TC sites to the overall charge, which has implications for accurate description of specific ion adsorption.

1. Introduction

Ferrihydrite (FH) is one of the most common iron oxyhydroxides in soils and sediments, where it occurs both naturally and as result of human activities such as acid mine drainage. It has also been observed in Martian soils and several meteorites. In addition to its importance in geologic systems, its structure is also important in biological applications due to its resemblance to ferritin, an iron-storing protein. Finally, FH is a precursor phase in several materials that have technological and catalytic uses (Cornell and Schwertmann, 2003). FH possesses a high surface reactivity because it typically forms nanoparticles of very high surface area, for which theoretical values as high as ~1250 m^2/g have been reported (Villalobos and Antelo, 2012). Thus, understanding surface reactions of FH is critical in describing the geochemical cycling and behavior of iron in many natural and engineered systems, as well as predicting the fate and transport of the wide variety of chemical compounds that interact with iron oxides.

Such understanding has been complicated by the small diameter of FH nanoparticles (2–6 nm) and by its disordered structure, which prohibits the application of traditional structural analysis methods, such as X-ray Diffraction. The low degree of crystallinity of FH was thought to be linked to the high number of vacant Fe sites in the structure and the replacement of bulk oxygens with water or hydroxyl molecules (Cornell and Schwertmann, 2003). Until relatively recently, FH was considered to comprise three intermingled phases; the defect-free f-phase, the defect-rich d-phase and hematite-like crystallites (Drits et al., 1993). All three phases consisted of octahedrally-coordinated Fe with variable stacking sequences of the iron octahedra. In 2007, this model was overturned by Michel et al. (2007), who utilized synchrotron X-ray Pair Distribution Function analysis to propose a new structure based on a single phase, the isostructural mineral akdalaite ($Al_{10}O_{14}(OH)_2$); this structure contains ~20% of tetrahedrally coordinated Fe with a δ-Keggin-like local structure (Michel et al., 2007). This new structure stirred controversy in the geochemical community and several follow up studies to elucidate the structure (Cismasu et al., 2011; Maillot et al., 2011; Manceau, 2011; Michel et al., 2010; Peak and Regier, 2012; Pinney et al., 2009; Rancourt and Meunier, 2008; Xu et al., 2011). Currently there is experimental evidence supporting the new structure of FH.

All of the aforementioned studies focused on the bulk FH structure and there was little discussion on the implication of the structure for surface properties. Surface complexation models that took surface structure into account continued to rely on the goethite structure to

* Corresponding author.
E-mail address: nefeli.bompoti@uconn.edu (N. Bompoti).

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derive FH surface properties such as site density and proton affinities (Antelo et al., 2010; Gustafsson et al., 2011; Hiemstra et al., 2009; Hiemstra and Van Riemsdijk, 2009; Tiberg et al., 2013; Villalobos and Antelo, 2012). Hiemstra (2013) recently published the first study that discussed the implications of the new structure for FH surface properties, and which also proposed a variation in the accepted structure. Surface depletion of two types of Fe polyhedra is postulated to be the controlling factor for various FH properties. The mineral core is considered to be hydrogen poor; however, the contribution of the surface is dominant for the macroscopic properties of FH. Based on this model, Hiemstra (2013) identified 12 different types of surface oxygens and calculated site densities and proton affinities for each. There is currently no experimental evidence that these calculated values are correct, or surface complexation models based on this new structure. Given the complexity of the proposed structure and the high number of reactive oxygen sites, experimentally verifying the surface structure is no easy task. Previous attempts to characterize goethite surface properties, which has four types of surface O atoms, relied on fitting titration curves (Hiemstra et al., 1996). However, the analysis indicated that titration curves may be fitted adequately using only two surface sites, although whether the log K's for those sites were equal or 4 log units apart resulted in similar fits to the titration curves. Thus, determining the proton affinities and site densities of surface O atoms is ambiguous when fitting individual titration curves.

An additional complication with modeling surface charge is the variable nature of FH; different methods of preparation, including initial iron concentration, rate of precipitation, and time of aging result to different particles sizes and degrees of crystallinity (Wang et al., 2013). The majority of studies report potentiometric titration results for freshly precipitated FH (Hsi and Langmuir, 1985; Davis, 1977; Fukushi et al., 2013; Girvin et al., 1991; Nagata et al., 2009) and some for aged FH (Antelo et al., 2010; Hofmann et al., 2005; Jain et al., 1999; Wang et al., 2013). As a result, substantial differences arise in the charging behavior, both in terms of magnitude and the point of zero net proton charge (PZNPC).

Modeling surface charge requires a significant number of parameters, including the available specific surface area (SSA), the number of proton reactive sites (Ns) and the equilibrium constants for proton ($\log K_{H+}$) and electrolyte binding ($\log K_{C+}$), ($\log K_{A-}$). In addition, the choice of the electrostatic (e.g., diffuse layer, Basic Stern, Triple Layer) and pK models (e.g., generic 2-pK, 1-pK, multisite complexation (MUSIC) (Hiemstra and Van Riemsdijk, 1996)) further increases the number of parameters to be entered or fitted by the model and different authors typically make different assumptions. Several attempts in unifying modeling approaches have been made. The seminal work of Dzombak and Morel (1990) utilized the generic 2-pK protonation model in combination with the Guoy-Chapman diffuse layer model to describe FH surface charge and ion sorption data. Sahai and Sverjensky (1997) and Sverjensky and Sahai (1996) developed a triple layer model for titration data on iron oxides by predicting the protonation constants with electrostatic and Born solvation theory. Ponthieu et al. (2006) employed the charge distribution (CD)-MUSIC approach to describe ion sorption and surface charge of goethite and amorphous iron oxyhydroxide based on the goethite surface structure using a single set of parameters. Although this approach provided good results for ion sorption, it could not capture the lower PZNPC of FH. Other attempts to model the FH surface behavior also relied on the goethite surface structure, but the log Ks (for singly- and triply-coordinated surface groups) used were much different in each study, including 8.06 (Hiemstra and Van Riemsdijk, 2009), 8.1 (Tiberg et al., 2013) 8.1–8.5 (Gustafsson, 2001; Gustafsson et al., 2009) and 8.7 (Antelo et al., 2010). In each case, the log Ks reflect the PZNPC of the particular dataset that was modeled.

Villalobos and Antelo (2012) also proposed a unified 2-pK model for FH using the goethite structure as a proxy. Based on their approach, they were able to simulate titration data by optimizing the SSA and shifting the PZNPC of all datasets to 8.7. Their justification of this approach was based on the following premises: a) that SSA is a highly uncertain parameter and thus should be adjusted; and, b) that poor CO_2 exclusion during acid/base titration experiments caused the lower PZNPC values (Villalobos and Leckie, 2000; Zeltner and Anderson, 1988).

To the knowledge of the authors there is no modeling study considering the recently postulated surfaced structure for FH. Accordingly, this study is the first attempt to model several sets of titration data with a unified surface complexation model, using the surface structure for ferrihydrite provided by Hiemstra (2013) and the CD-MUSIC formulation. Ultimately, the modeling exercise serves as indirect evidence to test the validity of the proposed structure and its applicability to the variable sizes and crystallinities of FH particles.

2. Experimental data and model description

2.1. FH surface charge datasets

Several FH titration data sets have been reported in the literature, for a wide range of ionic strengths and electrolytes. Table 1 lists the nine data sets used in this study and summarizes the reported preparation methods and titration parameters. Titration data for three electrolytes were included: $NaNO_3$, NaCl and KNO_3. The surface charge data sets are shown in Fig. 1a, plotted in C/g with respect to pH minus the PZNPC values shown in Table 1.

The first issue when evaluating surface charge data is the choice of SSA to normalize the data from C/g to C/m^2 that are then used as input to the model. Surface area is difficult to measure for reactive solids such as FH. Various techniques have been used to estimate surface area, with the BET method being the most popular (Brunauer et al., 1938). Although the BET method provides self-consistent results, it has significant limitations as both the pre-drying and the N_2 drying during the test cause particle agglomeration and reduction in the accessible SSA (Antelo et al., 2010; Dzombak and Morel, 1990). Most studies shown in Table 1 adopted the value of 600 m^2/g as originally reported by Davis et al. (1978), which relies on an empirical estimate. Although the theoretical estimation of surface area based on spherical particles of 20 Å and density of 3.57 g/cm^3 is 840 m^2/g, Davis et al. (1978) suggested 600 m^2/g in order to simulate their surface charge data. To overcome this uncertainty, SSA was treated as a fitting parameter in some modeling studies (Antelo et al., 2010; Villalobos and Antelo, 2012).

Plotting the surface charge curves in C/g clearly shows that studies with aged FH reported lower charging values compared to fresh FH. This is reasonable, given that aged suspensions are likely to have larger or agglomerated particles with lower SSA. Villalobos and Antelo (2012) showed that it is possible to come up with fitted SSA values for a variety of datasets, and using these fitted values, the different charging curves fall on top of each other when plotted in C/m^2 instead of C/g. This was also the case for the datasets shown in Fig. 1b when normalizing with SSA values reported in Table 1. These SSA values are considerably lower compared to the fitted values obtained by Villalobos and Antelo (2012); as will be discussed later, the high SSA values reported by these authors are necessitated by the low site density values used in their modeling approach, which were obtained from the goethite structural model. In addition, Villalobos and Antelo (2012) fixed the capacitance values, which is also not the preferred approach in this study. These issues will be further discussed in Section 3.2.

The differences among the datasets are attributed mainly to: a) preparation methods, b) aging times and experimental conditions after precipitation, c) titration method and, d) estimation of SSA. Specifically, the precipitation rate affects FH crystallinity (Cismasu et al., 2012), while freeze drying and time of aging could lead to particle aggregation and induce a more crystalline phase (Fuller et al., 1993; Greffié et al., 2001). In addition, different charging values are apparent in data sets obtained by titration with different electrolytes. Fukushi et al. (2013) and Nagata et al. (2009) performed potentiometric titrations

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