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The dependence of hematite site-occupancy standard state triple-layer model parameters on inner-layer capacitance

Yu Sik Hwang, John J. Lenhart *

Department of Civil and Environmental Engineering and Geodetic Science, The Ohio State University, Columbus, OH 43210, USA

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Abstract

Potentiometric acid–base titration data for three hematite samples that differed on the basis of specific surface area (17.4, 33, 83 m^2/g for hematite A, B, and C, respectively) was analyzed using the triple-layer model (TLM). The sensitivity of the TLM fits of the data to the choice of site density (N_s) was evaluated from 1.5 to 22 sites/nm^2. In general, little dependence in the quality of fit was determined, irrespective of the value of N_s. Values of the electrolyte adsorption equilibrium constants ($\log K^0_{\text{cation}}$ and $\log K^0_{\text{anion}}$) steadily increased with decreasing N_s. These constants are consistent with the commonly used 1.0 M standard state and when converted into comparable constants consistent with the site-occupancy standard state ($\log K^\theta_{\text{cation}}$ and $\log K^\theta_{\text{anion}}$) a single value for each respective constant was determined. Values of the inner-layer capacitance (C_1) were varied during these optimizations and increased with decreasing N_s, particularly below 5 sites/nm^2. The optimized C_1 values exhibited an apparent inverse relationship with specific surface area (i.e., C_1 for hematite A > C_1 for hematite B > C_1 for hematite C). The magnitude of change in C_1 with respect to N_s depended upon the magnitude of C_1 for each hematite as the higher the C_1 value, the greater was the change with respect to N_s. These results suggest when the site-occupancy standard state parameters are used to predict constants at different site density values without re-regression of titration data that variations in C_1 should be accounted for, particularly for low specific surface area samples that have a high C_1.

Keywords: Hematite; Surface complexation model; TLM parameters; Site density; Inner-layer capacitance; Specific surface area; FITEQL; Site-occupancy standard state

1. Introduction

Surface complexation models (SCMs) have been used for approximately 30 years as a useful tool to describe ion adsorption on mineral surfaces [1–5]. These models apply a thermodynamic approach to describe the formation of surface complexes between dissolved solutes and surface functional groups in a manner that is analogous to those for solution-phase complexation reactions. Models differ with respect to assumptions regarding surface site heterogeneity (single-site versus multi-site) and protolysis (1-pK versus 2-pK) [2,3,5]. To account for the influence of surface charge, SCMs incorporate a description of the electrical double layer (EDL) at solid/water interfaces. Assumptions regarding the structure of the EDL also differ, with constant-capacitance, diffuse-layer, and triple-layer EDL depictions utilized most often [3,4]. The utility of SCMs over empirical isotherm models (e.g., Langmuir isotherm) reflects in part their ability to account for shifts in the composition of the system at question.

Although surface complexation models have been successfully used to describe experimental data, their application in a predictive mode to describe solute behavior in response to natural or man-made perturbations has been limited [3,4]. One reason the predictive capability of SCMs is compromised is the need to determine numerous mineral- or media-specific model parameters [3]. For instance, seven parameters are required to describe the ionic strength dependence of mineral surface charge with the triple-layer model (TLM); the surface site density (N_s), the surface acidity equilibrium constants (K_{a1}, K_{a2}), the electrolyte adsorption equilibrium constants (K_{cation}, K_{anion}), and the inner- and outer-layer capacitances

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* Corresponding author. Fax: +1 (614) 292 3780.
E-mail address: lenhart.49@osu.edu (J.J. Lenhart).

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(C_1, C_2) [3]. In most studies, these parameters are obtained through an objective curve fitting approach applied to experimental surface acid–base titration data of a mineral. Unfortunately, the parameter sets obtained from this exercise are often non-unique and it is possible to fit titration data equally well using different sets of parameter values [6–9]. Hayes et al. [7] and Christl and Kretzschmar [9], for example, observed equally reasonable fits to titration data with N_s varied between 1 and 100 sites/nm^2, with each value of N_s producing a unique set of optimized model parameters.

Further complicating matters is that, depending upon the experimental or estimation method utilized, wide ranges of mineral surface site densities are reported and used in the literature (e.g., proton titration, tritium exchange, H_2O adsorption, and sorbate adsorption maxima) [4,10]. In general, tritium exchange produces high values of N_s, which are often consistent with crystallographic analyses of total site density. Low values are obtained from sorbate adsorption maxima, particularly anion sorbates, because site accessibility or reactivity often depends on the particular sorbate [4,10–12]. The site density-dependent parameter sets that result from these types of model optimizations are not readily compared or compiled and thus hinder efforts to predict adsorption processes [13].

Inroads into mitigating deficiencies associated with SCMs have been made by devising approaches to estimate model parameters in an internally consistent manner [3,4,7,8,14,15]. Sahai and Sverjensky [14] developed an internally consistent set of TLM parameters utilizing site densities from tritium-exchange experiments and theoretical predictions of surface acidity equilibrium constants from electrostatic and Born solvation theory [16,17]. Independent estimation of TLM parameters like this facilitate parameter optimization, but site densities from tritium-exchange may exceed that for ions with relatively low maximum adsorption capacities (e.g., oxyanions) and overestimation of adsorption in high surface coverage systems often results [18]. Thus, careful attention must be paid to the selection of an appropriate site density when applying SCMs to describe anion adsorption.

Sverjensky [15,19] recently proposed a new standard state for surface site activity based upon a site-occupancy standard state that is independent of surface area and site density. Converting equilibrium constants for this new standard state (K^θ) from those determined on the basis of the conventional 1.0 M standard state for a reaction of the same stoichiometry (K^0) is accomplished using the following analytical relationship [15,19]:

$$K^\theta = K^0\left(\frac{N_s A_s}{N_\# A_\#}\right), \tag{1}$$

where N_s and A_s are the surface site density and specific surface area, respectively, for the sample in question. $N_\#$ and $A_\#$ correspond to values for the same properties at the hypothetical standard state. Using this relationship permits the determination of a set of equilibrium constants that are independent of site density or surface area. With these constants, parameters for crystallographically identical solids that differ in surface area or site density can be predicted without the need to collect additional surface titration data or to re-fit existing data. For example, Sverjensky and Fukushi [20] successfully applied this approach to predict K_{a1}, K_{a2}, K_{cation}, and K_{anion} for goethite consistent with a site density for anion adsorption of 2.5 sites/nm^2 using tabulated site-occupancy standard state constants from Sverjensky [15]. They did so in order to determine constants needed to model the adsorption of oxalate, which being an anionic adsorbate accesses a reduced set of surface sites.

In validating the relationships used to relate site-occupancy standard state constants to those based upon the conventional 1.0 M standard state Sverjensky [19] compiled a suite of surface titration data for goethite from the literature, including those of Hayes et al. [7] in which the site density was significantly varied. One observation from this analysis is that the equilibrium constants obtained at the lowest site density (i.e., 1 site/nm^2) deviate from those predicted by the relationships more than any other site density. Sverjensky [19] performed his analyses using a fixed value for the inner-layer capacitance (C_1) of 80 μF/cm^2. Others performing surface titration sensitivity analyses have reported, however, that optimal fits obtained at different site densities require an adjustment in C_1 [7,9]. Thus, when using relationships like those proposed by Sverjensky [15,19] to predict TLM parameters for a particular site density, caution may be needed regarding changes in C_1. The objective of this paper is to address this issue, which is directly related to the interdependences of the TLM model parameters. In this study, potentiometric surface titration data for three hematite preparations with different specific surface areas were used to optimize TLM parameters as a function of site density using FITEQL (version 4.0). The results of our analysis confirm that the new equilibrium constants are independent of site density over small ranges in N_s or as long as variations in C_1 are taken into account.

2. Materials and methods

Deionized (Milli-Q from Millipore or equivalent) and boiled water was used in all sample preparation and analyses. The salts ($FeCl_3$, NaCl and $NaClO_4$) used in this work were analytical grade or better and were used without further purification. Carbon dioxide free NaOH used as the base titrant was prepared using DILUT-IT solutions (J.T. Baker). The acid titrant was prepared using trace metal grade HCl or $HClO_4$ (Fisher Scientific).

2.1. Hematite preparation

Three different hematite preparations, reported previously [21–23], were used in the present study. All were prepared by forced hydrolysis of ferric chloride solutions. The main differences between preparations were iron concentration, initial solution pH, and aging time. The first sample, hematite A, has a low BET surface area (17.4 m^2/g) and was synthesized by adding 50 mL of 0.72 M $FeCl_3$ (in 0.001 M HCl) to 1.95 L boiling solution of 0.004 M HCl [21]. The suspension at 0.018 M total iron concentration was aged for 24 h at 100 °C. Hematite B