



Surface chemistry of K-montmorillonite: Ionic strength, temperature dependence and dissolution kinetics

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ABSTRACT

The surface chemistry of K-montmorillonite was investigated by potentiometric titrations conducted at 25, 50 and 70 °C and at ionic strengths of 0.001, 0.01 and 0.1 M KNO₃. Proton adsorption decreases with electrolyte concentration at all pHs. The pH of zero net proton charge (PZNPC) decreases from 8.1 to 7.6 when the ionic strength increases from 0.001 to 0.1 M. Temperature has a very small effect on surface charge. A constant capacitance model that accounts for protonation/deprotonation of aluminol and silanol edge sites and basal plane H⁺/K⁺ exchange is used to fit the experimental data. H⁺ and OH⁻ adsorption to specific surface sites appear to account for the pH-dependence of the K-montmorillonite dissolution.

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1. Introduction

An important obstacle to understanding crystallochemical controls over smectite surface chemistry and montmorillonite dissolution kinetics is the heterogeneity of smectite surface charge, which can be influenced by composition, pH, ionic strength, particle–particle interactions, and formation of montmorillonite gels [1]. Historically attention has focused on pH-dependent edge and basal plane charging reactions (e.g., [2–5]). More recent models consider adsorption of metals such as Cu²⁺, Ni²⁺, Zn²⁺, Mn²⁺, Cs⁺, and Ln³⁺ and their effect on charge [6–10]. Important to all models of montmorillonite surface chemistry are assessments of site reactivity and estimation of edge and basal plane surface area and site densities [6,11–13]. Table 1 outlines the major features of montmorillonite surface complexation models and highlights the different ways that smectite surface charge has been modeled.

The numerous uncertainties involved in these models have motivated the development of theoretical models of clay edge surface structure, reactivity, and electrostatics that might ultimately predict experimentally measured surface behavior (e.g., [14]). For example, Bickmore et al. [15] and Churakov [16] used ab initio calculations to estimate surface constants. Surface protonation equilibrium constants have also been estimated theoretically for multisite models (MUSIC) [17,18] under the hypothesis that surface protonation constants would be a linear function of the Pauling bond

strength. Tournassat et al. [12] applied the MUSIC model to montmorillonite to consider the coordination environment for multiple cations on multiple surface sites. Bourg et al. [19] incorporated in their calculation the “spillover” of electrostatic potential from basal onto edge surfaces and for the stabilization of edge sites.

Experimental assessments of the influence of ionic strength on montmorillonite surface charge are particularly unclear. For example, Baeyens and Bradbury [7] suggested that their surface charge measurements were insensitive to ionic strength. However, Wanner et al. [20] found clear differences in the effects of ionic strength on surface charge at intermediate pH. More recently, some studies [1,11,21] showed titration curves at different ionic strengths that parallel each other. Few studies consider the effect of temperature on surface charge [21], making it difficult in particular to predict how the linkage between surface chemistry and surface-controlled smectite dissolution observed at 25 °C [22] operates at temperatures greater than 25 °C. Simplified models of the interface are used so that the broad influences of ionic strength and temperature on montmorillonite surface behavior might be identified. The present study experimentally examines the individual and combined effects of temperature and ionic strength on measured montmorillonite surface charge and then relates these to dissolution measurements.

2. Materials

The material used in this work is a bentonite from the Cortijo de Archidona deposit in Cabo de Gata region (Almería, SE, Spain), formed by hydrothermal alteration of volcanic tuff [23,24], and is

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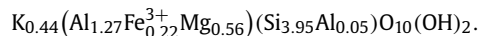
Table 1

Parameters of the surface complexation models proposed in the literature, for different montmorillonites at 25 °C.

Model	Site	Site density (mmol kg ⁻¹)	log K X + Na ⁺ = XNa ⁺ (1) X' + Na ⁺ = XNa (2)	log K X + H ⁺ = XH ⁺ (1) X' + H ⁺ = XH (2)	log K SOH + H ⁺ = SOH ₂ ⁺	log K SO ⁻ + H ⁺ = SOH
Stadler and Schindler [6] CCM	>AlOH	59.8	–	–	8.16	8.71
	>SiOH	35.5	–	–	–	5.77
	>X	–	–	2.44 (1) ^a	–	–
Wanner et al. [20] CCM	>X	22	–	–	–	–
	>SOH	28	–	–	5.4	6.7
Zysset and Schindler [22] CCM	>X	44	–	0.02 (1)	–	–
	>AlOH	15	–	–	4.05–5.21	–
Bradbury and Baeyens [39] Baeyens and Bradbury [7] (NEM)	>S ^o OH	2	–	–	4.5	7.9
	>S ^{w1} OH	40	–	–	4.5	7.9
	>S ^{w2} OH	40	–	–	6	10.5
Kraepiel et al. [8] (DDLML)	>X	1020	–	–	–	–
	>SOH	28	–	–	5	8.5
Avena and De Pauli [11] (CCM)	>X	796	–0.77 (1)	1.07 (1)	–	–
	>SOH	41.4	–	–	2.97	6.1
Tombácz and Szekeres [1] (DDLML)	>X ⁻	700–1000	0.78 (2)	8.77 (2)	–	–
	≡AlOH	30	–	–	5.1	7.9
Ikhsan et al. [9] (ECCM)	>X	1048.75	2.2 (1) ^b	–	–	–
	>SOH	56.92	–	–	5	7.2
Tertre et al. [21] (DDLML)	>X	871.2	1.4 (2)	–2.2 (2)	–	–
	>SiOH	81.6	–	–	–	7.9
	>AlOH	40.8	–	–	5.1	8.5
Kriia et al. [61] (NEM)	>Al ₂ OH ₂ ⁺	250	–	–	3.02	–
	>AlOH	355	–	–	5.67	11.68
	>SiOH	105	–	–	–	9.85

^a CaX₂ + 2H⁺ = 2XH + Ca²⁺.^b (X'–K⁺) + H⁺ = (X'–H⁺) + K⁺.

the same used by Rozalén and co-workers [25,26] in montmorillonite dissolution experiments. The <4-μm fraction was separated by sedimentation and then converted to K-montmorillonite by dispersion of the clay fraction in a 0.5 M KCl solution. Chemical analysis of major elements was performed by X-ray fluorescence. The cation exchange capacity (CEC) is 99.8 cmol(+)kg⁻¹ and K⁺ was the only exchangeable cation. The calculated structural formula of the K-smectite corresponds to a montmorillonite end member:



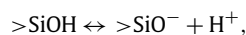
Only 0.38 K⁺ ions per formula unit are exchangeable, suggesting the presence of a small number of nonswelling layers. X-ray diffraction (XRD) patterns recorded on powder specimens and on oriented and glycolated mounts indicate that the sample is a dioctahedral smectite containing approximately 15% nonswelling layers, in agreement with the presence of nonexchangeable potassium determined by chemical analysis. No accessory phases were detected. Thermogravimetric and differential thermal analysis (TG-DTA) indicate >99% montmorillonite content. The specific surface area of the K-montmorillonite was measured by the Brunauer–Emmett–Teller (BET) method to be 111 m²g⁻¹ (±10%) using 5-point N₂ adsorption isotherms after degassing the sample for 2 days at 110 °C.

3. Surface complexation model

3.1. Montmorillonite surface chemistry

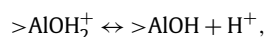
Phyllosilicate surface charge is the sum of permanent structural charge arising from heterovalent lattice substitutions, and hydrolyzable aluminol (>AlOH) and silanol (>SiOH) edge site charge. Bridging Al–O–Si or Al–O–Al sites will also exist and may contribute to surface reactivity [15,16]. Al and Si sites exposed on clay

edges can be modeled as behaving like their pure oxide equivalents [27,28], although later studies have noted that important differences exist in the behavior for hydrated minerals (e.g., [29]) and molecular modeling results suggest that their reactivity is likely more complex. Here we consider the simplest case where silanol sites on clays are assumed to behave similarly to Si sites on SiO₂; hence they can only act as proton donors through the surface complexation reaction:

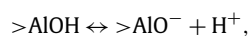


$$K_{Si} = \frac{\{>SiO^-\} \cdot [H^+]}{\{>SiOH\}} \cdot \exp\left(-\frac{F\psi}{RT}\right). \quad (1)$$

K_{Si} is the edge silanol surface equilibrium constant. F is the Faraday constant (96485 C mol⁻¹), ψ is the surface potential (V), R the molar gas constant, and T absolute temperature. The electrostatic term, $\exp(-F\psi/RT)$, accounts for the energy involved in moving protons to and away from the charged surface. Square brackets denote aqueous molar concentrations (mol L⁻¹); $\{ \}$ denotes surface concentrations (mol m⁻²). Edge Al sites are modeled as aluminol exhibiting amphoteric behavior similar to Al oxides, undergoing protonation at low pH and deprotonation at high pH:



$$K_{Al,1} = \frac{\{>AlOH\} \cdot [H^+]}{\{>AlOH_2^+\}} \cdot \exp\left(-\frac{F\psi}{RT}\right), \quad (2)$$



$$K_{Al,2} = \frac{\{>AlO^-\} \cdot [H^+]}{\{>AlOH\}} \cdot \exp\left(-\frac{F\psi}{RT}\right). \quad (3)$$

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