Acid-Base Properties of Ca-Montmorillonite from Benavila Region (Portugal)

Propriedades Ácido-Base da Montmorillonite Cálcica da Região de Benavila (Portugal)

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Abstract: Montmorillonite is a dioctahedral (2:1) phyllosilicate mineral that plays an important role in many industrial and environment applications. Due to their peculiar physicochemical properties, mainly controlled by electrostatic interactions, the study of the acid-base properties of this material has been of great importance in the last years. Thus, the understanding of the surface charge variation of montmorillonite, in order to obtain a better control of their physicochemical properties, become crucial.

The main goal of this research is to study the surface properties of montmorillonite, through the acid-base titrations of its suspension, under different conditions of ionic strength ([NaCl]=0.01M and [NaCl]=0.1M). The titration data was interpreted by surface complexation models (NEM and CCM) taking into account the absence and the presence of an electrical double layer (EDL) at the mineral-water interface where the electrostatic terms are involved (CCM).

The results show that 6 different species are involved on the protonation and deprotonation of surface sites: two acidic species (strong-SiOH₂⁺ and weak-AlOH₂⁺), two neutral species (SiOH and AIOH) and two basic species (weak-SiO⁻ and strong-AlO⁻).

Keywords: Montmorillonite, Surface properties, Surface charge density, Electrostatic influence, Surface complexation models.

Resumo: A montmorillonite pertence ao grupo das esmectites dioctádricas, sub-classe dos filossilicatos, e é frequentemente utilizada para fins industriais e ambientais. O estudo das suas propriedades ácido-base tem vindo a ser alvo de bastante interesse, uma vez que as suas excelentes propriedades físico-químicas dependem significativamente das interações eletrostáticas que ocorrem na interface mineral-água. Deste modo, torna-se fundamental compreender a variação da sua carga superficial com vista a uma melhor performance e um melhor controlo das suas propriedades.

O principal objetivo deste trabalho centra-se no estudo das propriedades superficiais da montmorillonite através de titulações potenciômtericas, em diferentes condições de força iônica ([NaCl]=0,01M e [NaCl]=0,1 M). Os resultados foram interpretados através da aplicação de modelos de complexação na superfície (MCS), tendo em conta a ausência e a presença de interações eletrostáticas.

Os resultados apresentados sugerem a formação de 6 espécies diferentes ao longo dos processos de protonação e desprotonação da superfície: duas espécies ácidas (forte-SiOH₂⁺ e fraco-AlOH₂⁺), duas espécies neutras (SiOH e AIOH) e duas espécies básicas (fraco-SiO⁻ e forte-AlO⁻).

Os valores dos parâmetros obtidos através dos modelos utilizados (NEM e CCM) são próximos. No entanto, verifica-se que a diferença entre ambos torna-se mais significativa com o aumento da influência eletrostática e com o aumento do pH.

Palavras-chave: Montmorillonite, propriedades da superfície, Densidade de carga da superfície, Influência eletrostática, Modelos de complexação na superfície.

1.Introduction

Clay minerals occur in sedimentary rocks and are frequently found in hydrothermal deposits (Meunier, 2005). Due to their adsorption, catalytic and ion-exchange properties, they play an important role in several industrial and environment applications (Churchman et al., 1995; de Pablo et al., 2011; Yao et al., 2014). Montmorillonite has a particular interest in the environment applications due to their peculiar physicochemical properties, such as low permeability and migration-retarding properties (Duc et al., 2005). The study of acid-base chemistry of clay surface is thus essential since their physicochemical properties are mainly controlled by electrostatic interactions (Delhorme et al., 2010; Kriaa et al., 2008; Laird, 1999).

Montmorillonite is a dioctahedral (2:1) phyllosilicate mineral with two tetrahedral sheets (SiO₄) linked to an octahedral sheet (Al₂O₃) (Murray, 2006). It carries a permanent negative charge on the basal planes caused by isomorphic substitutions of the central Si and Al ions in the crystal lattice for lower positive valence ions (eg: Al³⁺ for Si⁴⁺ in the tetrahedral layer and Mg²⁺, Fe²⁺ for Al³⁺ in the octahedral layer), which is independent of the physicochemical conditions of the surrounding medium and is the main contribution to the surface charge of montmorillonite (Delhorme et al., 2010; Nagy & Konya, 2010; TOMBÁČZ & Szekeres, 2004). This excess of negative lattice charge is
compensated by the exchangeable cations (Tombácz & Szekeres, 2006). On the other hand, the electroneutrality of the crystal edges gives rise to the transformation of the dangling oxygens into silanol (>SiOH) or aluminol (>AlOH) groups. These amphoteric sites are conditionally charged, acquiring positive or negative charge, depending on the pH of the solution. Silanol and aluminol sites may be protonated or deprotonated, depending on the pH, according to the following reactions (Tombácz & Szekeres, 2004; Zrinyi et al., 2004):

\[
\begin{align*}
&\equiv\text{SiOH} + H^+ \Leftrightarrow \equiv\text{SiOH}_2^+ \\
&\equiv\text{SiOH} \Leftrightarrow \equiv\text{SiO}^- + H^+ \\
&\equiv\text{AlOH} + H^+ \Leftrightarrow \equiv\text{AlOH}_2^+ \\
&\equiv\text{AlOH} \Leftrightarrow \equiv\text{AlO}^- + H^+
\end{align*}
\]

The understanding of the surface charge variation of montmorillonite allows a better control of their properties and has been awakening a great interest in the scientific community. Among the numerous works centered in this problem, several models were proposed in the literature (Dolder et al., 1996; Huertas et al., 1998; Kriaa et al., 2008).

In order to study the surface properties of montmorillonite, acid-base titrations of its suspension, under different conditions of ionic strength ([NaCl]=0.01M and [NaCl]=0.1M), were performed. Surface complexation models (SCM), in particular NEM and CCM models, were applied to describe and interpret the titration data taking into account an ideal behavior of the surface species, where the electrostatic interactions are ignored (NEM), and the presence of an electrical double layer (EDL) at the mineral-water interface where the electrostatic terms are involved (CCM).

2. Materials and methods

The montmorillonite selected for this study was gathered from Benavila Region, situated in central eastern Portugal. The <2 µm clay fractions were obtained by sedimentation from an aqueous suspension, according to Stokes’ Law, and were analyzed by X-ray diffraction (XRD) using a Philips X’Pert machine equipped with a CuKα radiation and a scanning speed of 1° 2θ/min.

The pH was measured with a pH meter (Corning 240) calibrated with buffer solutions (pH 4, 7, and 10 Merck, Germany). BET multipoint surface area (Gemini 2370 V5, Micrometerics, USA) of selected samples was carried out by measuring the volume of a mixture of He/N2 adsorbed at five different pressures. Prior to He/N2 adsorption, the samples were de-aired at 200°C for 10 h.

Crystal chemistry of montmorillonite was obtained from scanning electron microscopy equipped with energy dispersive spectrometer (SEM-EDS), completed with data from electron microprobe analysis using the <2 µm clay fractions. The structural formula calculated on a base of 11 atoms/O10(OH)2 corresponds to Ca-montmorillonite: Na_{0.14}Ca_{0.44}(Al_{1.28}Fe_{0.67}Mg_{0.56})(Si_{3.81}Al_{0.18})O_{10}(OH)_2, nH2O.

The potentiometric titrations were carried out according to the following procedure: to each 40 mL beaker, 2 g of montmorillonite and 40 mL of NaCl solution at concentrations of 0.01M and 0.1M were stirred until pH stabilization. Aliquots of 0.2 mL of 0.05M HCl were added progressively to the mixture, and the pH changes were recorded until pH=2. The same procedure was repeated to the basic titration with NaOH 0.05M until pH=10.

3. Results and discussion

The titration curves were obtained through the graphic representation of the proton surface charge density (σ_H) as a function of pH, for each ionic strength (Fig. 1). σ_i (mol/m²) was calculated according to eq.1 (Huertas et al., 1998; Kriaa et al., 2008):

\[
\sigma_H = \frac{V}{m} \left\{ \frac{\sum_i [H^+]_{i,b} K_{w,i} - [H^+]_{i,s} K_{w,i}}{[H^+]_{i,b} - [H^+]_{i,s}} \right\}
\]

where “b” and “s” represent the blank and sample solutions, respectively. m corresponds to the mass of montmorillonite (2g), V is the volume of the electrolyte solution (40 mL); [H+] is the solution proton concentration (mol/L); Kw is the dissociation of product of water (10⁻¹⁴) and S corresponds to the specific surface area (97 m²/g).

The experimental results show that two distinct branches exist: σ_H is positive in the acidic pH range due to protonation of surface sites, and negative in the alkaline range due to deprotonation. The point of zero net proton charge (PZNPC) is not the same at both ionic strengths and, therefore, there isn’t a common intersection of both curves as is common for the most inorganic phases. This means that there is a significant influence of ionic strength, occurring the shift to lower values of pH as ionic strength increases. The nonelectrostatic model (NEM) is the simplest SCM since it assumes the absence of the electrostatic interactions and that adsorption is a reversible process where the activity coefficients of the surface species remain constant during the experiments. According to this model, the equilibrium constants considering the protonation and deprotonation of the surface sites may be obtained by eq. 2 and eq. 3, respectively (Huertas et al., 1998; Kriaa et al., 2008):

\[
\begin{align*}
&K_{a1} = \frac{X_{MOH}a_{H^+}}{X_{MOH}^2} \quad (2) \\
&K_{a2} = \frac{X_{MOH}^2a_{H^+}}{X_{MOH}a_{H^+}} \quad (3)
\end{align*}
\]

Where X_i corresponds to the molar fraction of the surface species and a_{H^+} is the aqueous proton activity. The equilibrium constants are related to σ_H through the eq. 4 (Huertas et al., 1998; Kriaa et al., 2008):

\[
\sigma_H = \sum_i \theta_i \frac{a_{H^+}}{K_{a1,i}a_{H^+}} - \sum_j \theta_j \frac{a_{H^+}}{K_{a2,j}a_{H^+}} \quad (4)
\]
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where $\Theta_M$ is the total surface site density. To achieve the equilibrium constants, our experimental titrations curves were fitted by least-square nonlinear regression analyses and it was assumed that, from acidic to alkaline conditions, 2 protonations and 2 deprotonations occurred. Each process was independently analyzed and the regression fit provided the values of the surface densities, from which equilibrium constants were determined. In both cases, the most acidic sites ($\text{SiOH}_2^+$ - $\Theta_1$) released the protons at about pH 4 and the respectively neutral species are formed. The same occurred with weak acid sites ($\text{AlOH}_2^+$ - $\Theta_2$) from pH=4 to pH=5. The PZNPC for each curve corresponds to pH=5.17 ([NaCl]=0.01M) and to pH=4.68 ([NaCl]=0.1M). The deprotonation of neutral species ($\text{SiOH}$ and $\text{AlOH}$) occurred first at pH=5.5, where weak basic sites ($\text{SiO}^-$ - $\Theta_3$) were formed, and then at approximately pH=7.5 where the most basic sites ($\text{AlO}^-$ - $\Theta_4$) were formed (Fig. 1). The surface density values and the equilibrium constants determined, according to NEM, are presented in Table 1.

The constant capacitance model (CCM) was used in order to interpret the titration data taking into account the influence of electrostatic interactions at the mineral-water interface. In this case, the EDL behaves as a flat capacitor whose capacitance ($C$) may be obtained by the representation of $\sigma_H$ as a function of the surface potential ($\Psi$) (volt), according to eq. 5 (Huertas et al., 1998; Kriaa et al., 2008):

$$\sigma_H = C\Psi$$

Table 1. Surface site densities $\Theta$ (mol/m$^2$) and equilibrium constants for protonation and deprotonation reactions calculated from NEM.

<table>
<thead>
<tr>
<th>$I$ (M)</th>
<th>$\Theta_1$</th>
<th>$pK_a_1$</th>
<th>$\Theta_2$</th>
<th>$pK_a_2$</th>
<th>$\Theta_3$</th>
<th>$pK_a_3$</th>
<th>$\Theta_4$</th>
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</tr>
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<td>0.76</td>
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<td>1.12</td>
<td>9.07</td>
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The equilibrium constants were corrected for the coulombic energy of the charged mineral surface through the determination of the intrinsic equilibrium constants using the equations 6 and 7, and the $\Theta$ values were estimated by extrapolating the sections of the titration curves to low or high pH (Huertas et al., 1998; Kriaa et al., 2008).

$$K_{a_1} = K_{a_1}^{(int)}e^{(f\Psi/RT)} \quad (6) \quad K_{a_2} = K_{a_2}^{(int)}e^{(f\Psi/RT)} \quad (7)$$

Table 2 shows the surface parameters calculated according to the CCM. The corrected equilibrium constants are very close to the same determined according to the NEM. However, there is a slightly decrease of the equilibrium constants at both ionic strengths, related to weak and strong basic sites, as the negative surface potential increases and the capacitance decreases, showing that the electrostatic influence is more significant as pH increases.

Table 2. Surface site densities $\Theta$ (mol/m$^2$), Capacitances (F/m$^2$) and equilibrium constants for protonation and deprotonation reactions calculated from CCM.

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Given the parameters obtained by CCM, the speciation of the involved species was estimated over the pH range, as shown in figure 2.

4. Conclusions

The acid-base properties of montmorillonite were studied using the titration data. Six different species involved on the protonation and deprotonation of surface sites were identified: two acidic species (strong-$\text{SiOH}_2^+$ and weak-$\text{AlOH}_2^+$), two neutral species ($\text{SiOH}$ and $\text{AlOH}$) and two basic species (weak-$\text{SiO}^-$ and strong-$\text{AlO}^-$). The speciation of these species was estimated over the pH range, according to the calculated parameters. The SCM were implemented for our titration data in order to determine the equilibrium constants associated to protonation and deprotonation processes. The values
obtained by the two models (NEM and CCM) are close in both cases. However, the electrostatic influence become more significant as pH increases, since there is a slightly decrease of the second equilibrium constants at both ionic strengths as the negative surface potential increases and the capacitance decreases.

The results obtained will serve to a better understanding of surface properties of Portuguese Ca-montmorillonite in order to provide a better control of their physicochemical properties and to predict and study, more efficiently, their behavior in different mechanism that involves the interaction with the surface.

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References


