The Acid/Base Chemistry of Montmorillonite

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Abstract

Alkalimetric and acidimetric titrations of montmorillonite suspensions were performed at ionic strengths varying from 0.005 to 0.5 M (NaNO₃). Deprotonation of surface hydroxyl groups exposed at the edge sites of montmorillonite platelets causes an overall negative charge in the alkaline pH range. The PZNPC of the edge sites was determined to be 6.1. In the acidic pH range, proton exchange at layer sites and protonation of edge sites occur simultaneously. The model parameters were evaluated from experimental data by using the diffuse double layer model. The observations made in these experiments are of key importance for modelling the near-field chemistry and the sorption behaviour of radionuclides.

1. Introduction

Bentonite clay is envisaged as buffer material in repositories for nuclear waste because of its favourable physical and chemical properties. Among these are the excellent swelling properties, especially of sodium bentonite, the extremely low permeability, and the capability of significantly retarding the migration of most radionuclides. The interaction of deep groundwaters with the clay surface is of importance as it affects the migration of radionuclides. Surface interactions at the clay/water interface, such an ion exchange and protonation/deprotonation reactions, exert control over both pore water and clay composition.

Modelling the interaction processes between bentonite and the constituents of aqueous solutions requires information on the surface properties of the clay fraction consisting of montmorillonite. Quantitatively, the most important interaction process is ion exchange, for which a comparatively large number of data on clays of various origins are available in the literature. However, as suggested in a recent report by Wanner *et al.* (1992), a minor type of surface sites, referred to as "edge sites", may have a significant effect on the chemical speciation of the bentonite pore water via interaction with protons, described as proton exchange reactions by Fletcher and Sposito (1989). In fact, such an interaction contributes to the pH control and can thus influence speciation and the transformation process of Na-montmorillonite to its Ca-form. The experi-

mental procedure to examine these interactions, the results and their evaluation are presented in this paper.

2. Materials and methods

2.1. Preparation of Na-montmorillonite

Na-montmorillonite has been prepared from the commercial bentonite MX-80 available from American Colloid. Bentonite has been pretreated using the procedure given by Sposito *et al.* (1981) in order to remove carbonate impurities. About 500 g of the < 2 μm fraction was flocculated by adding 8 dm³ of a solution containing 0.001 M HNO₃ in 1 M NaNO₃. The supernatant from each sample was decanted after centrifugation. The pH of the supernatant was measured. The clay was then redispersed in 1.5 times the original volume of the NaNO₃-HNO₃ solution and, after shaking for 20 min, again centrifuged. The procedure was repeated until the pH of the supernatant had dropped to pH = 3.0 which was achieved after 5 washings. The clay was then redispersed in 0.1 M NaNO₃ until the pH of the solution had stabilized between pH 5.1 and 5.3. The last two cycles were performed in 0.01 M NaNO₃ under argon. Finally, the clay was redispersed in 0.01 M NaNO₃ solution and stored in a refrigerator in glass flasks under argon. The BET surface area of the pretreated bentonite was determined to (31.53 ± 0.16) m²/g.

2.2. XRD

Bentonite material was sampled from the suspension after completing half of the pretreatment procedure and at the end of the pretreatment procedure. The recorded 12.45 Å *d*-spacing, typical for Na-montmorillonite, indicates that no structural transformation had taken place during the pretreatment of bentonite. After completion of the pretreatment procedure no calcite or feldspar related peaks were found, but minor peaks indicating quartz and cristobalite were observed.

2.3. The cation exchange capacity (CEC) of Na-montmorillonite

The CEC determinations after the pretreatment procedure resulted in 108 meq/100 g.

Table 1. Overview of the potentiometric titration experiments carried out in the present study

Titrations	I (M)	Number of titrations	pH range
Alkalimetric	0.005 (NaNO₃)	4	7–10.5
	0.05 (NaNO₃)	4	7–10.5
	0.5 (NaNO₃)	4	7–10.5
	0.5 (NaCl)	2	7–10.5
Acidimetric	0.005 (NaNO₃)	3	3.5–7
	0.05 (NaNO₃)	2	3.5–7
	0.5 (NaNO₃)	2	3.5–7

2.4. Potentiometric titrations

The interaction of protons and hydroxyl ions with the clay mineral surface was investigated by alkalimetric and acidimetric titrations under exclusion of CO_2 from the system. Calibration titrations were carried out and $E°$ and pK_w were determined for each ionic strength.

100 ml of bentonite suspension (11.25 g/dm³, I = 0.0095 M or 11.80 g/dm³, I = 0.0185 M) were added to 125 ml of a $NaNO_3$ solution. Prior to use, the $NaNO_3$ solution was purged with argon for 1 h. The initial concentration of the electrolyte solution was adjusted to give a total concentration of 0.005 M, 0.05 M or 0.5 M $NaNO_3$ in 225 ml clay suspension. The pH of the freshly mixed suspension was constant within 30 min and ranged from 6 to 7.5 depending on the electrolyte concentration. Alkalimetric and acidimetric titrations were performed in separate experiments. E.m.f. readings were recorded after 1, 5 and 10 minutes after addition of the titrant. Drifts in the measured potential were between 0.5 and 1 mV in most cases, but in all cases less than 2 mV, between the readings after 5 and 10 minutes. In order to investigate a possible effect of chloride on the active montmorillonite surface sites, two alkalimetric titrations were performed using NaCl as a background electrolyte at I = 0.5 M. The surface titrations carried out in the present study are summarized in Table 1.

The results of the surface titrations are shown in Figure 1, where the surface proton concentration, $\Delta[H^+]$, is plotted against pH. Note that, in this context, pH refers to $-\log[H^+]$ measured at a given ionic strength. The surface proton concentrations were calculated with the expression

$$\Delta[H^+] = \frac{1}{a}\left([H^+]_t - [H^+] + \frac{K_w}{[H^+]} - C\right) \text{[mol/g]}$$

(1)

where [H⁺]ₜ total H⁺ concentration [mol/dm³]

[H⁺]   free H⁺ concentration in solution

K_w ion product of water from calibration titrations

C correction factor for proton consuming side reactions

a initial suspension concentration (solid/water ratio) [g/dm³]

Ionic strengths of the background electrolyte were I = 0.005 M, 0.05 M and 0.5 M. The concentration of surface protons, $\Delta[H^+]$, was calculated for each data point of an experimental run. Proton balance calculations are based on pH measurements recorded after an equilibration time of 10 min. Figure 1 shows that the titration of montmorillonite is reproducible for all concentrations of the electrolyte background. The scatter in the experimental data in the strongly alkaline pH range may be due to variations in the liquid-junction potential. Two distinct branches of the titration curves exist: $\Delta[H^+]$ is positive in the acidic pH range due to protonation, and negative in the alkaline range due to deprotonation of surface functional groups. Figure 1 further reveals that the degree of deprotonation increases with increasing ionic strength in the alkaline pH range. This characteristic behaviour of mineral surfaces is typically observed in the case of simple oxides such as γ-Al_2O_3, TiO_2 or FeOOH, cf. James and Parks (1982). It indicates that deprotonation of surface OH groups causes the negative charge (i.e. $\Delta[H^+] < 0$) on the surface of montmorillonite. Hence the results presented in Figure 1 provide convincing evidence for the fact that the acid/base properties of montmorillonite in the alkaline pH range are due to ionization of surface OH groups. From structural arguments we may infer that the reactive OH groups are likely exposed at the edge face of a montmorillonite platelet.

Figure 1 further reveals that the condition for zero net proton adsorption is achieved in the pH range 6.5 to 8 depending on the ionic strength of the electrolyte background. Below the PZNPC (point of zero net proton charge) of montmorillonite, the order in the ionic strength dependence of the titration curves in the acidic pH range is in conflict with experimental observations made for oxides. Figure 1 shows that the concentration of protons adsorbed on the surface, $\Delta[H^+]$, decreases with increasing ionic strength. If OH groups were the only surface functional groups accounting for the acid/base properties of montmorillonite in the acidic pH range, an increase in $\Delta[H^+]$ with increasing ionic strength would be expected. Such a dependence of surface proton concentration upon ionic strength has been reported for simple oxides such as γ-Al_2O_3, cf. James and Parks (1982). We hence may conclude that the OH groups of the edge face, which account for experimental observations in the alkaline pH range, are not the only surface functional groups reacting with protons in the acidic pH range. The reversal of the ionic strength dependence of $\Delta[H^+]$ in the acidic pH range can be explained if we assume that protons react with another type of surface sites in an ion-exchange type of reaction. This type of surface functional groups on montmorillonite reacting with protons are structural-charge surface sites (Anderson and Sposito, 1991).

Analyses of Al and Si show that proton consumption due to dissolution of the montmorillonite matrix was constant and very small. Al concentrations were around 2×10^{-6} M and Si concentrations around
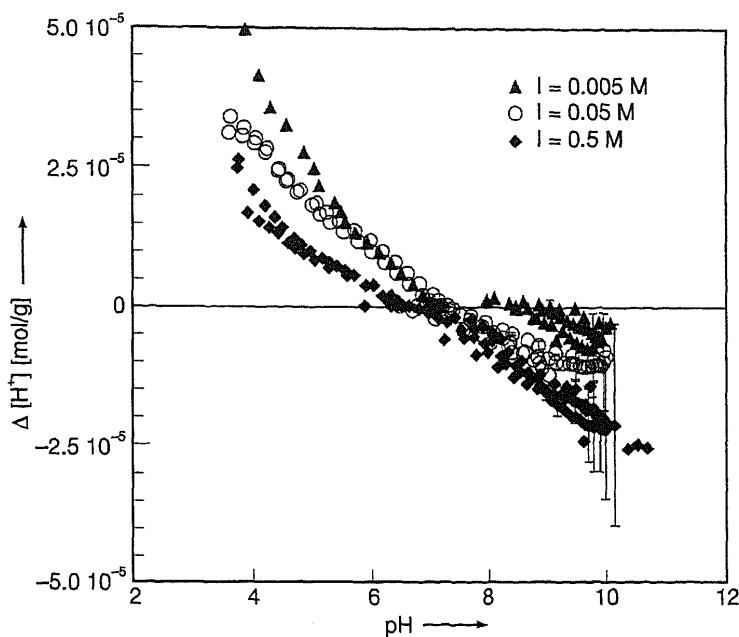
Fig. 1. Titration curves of Na-montmorillonite ($5\,g/dm^3$). Surface proton concentrations, $\Delta\,[H^+]$, are plotted as a function of pH for all titrations performed in the present study, cf. Table 1.

Table 2. Summary of measured surface protolysis reactions and data for montmorillonite as obtained by parameter optimisation in the present study

Surface protolysis reaction	Mass law equation	$\log K$
$\equiv SOH_2^+ \Leftrightarrow \equiv SOH + H^+$	$K_{a1}^{int} = \dfrac{(\equiv SOH^0)\{H^+\}}{(\equiv SOH_2^+)} \exp\left(-\dfrac{F\Psi}{RT}\right)$	-5.4
$\equiv SOH \Leftrightarrow \equiv SO^- + H^+$	$K_{a1}^{int} = \dfrac{(\equiv SO^-)\{H^+\}}{(\equiv SOH^0)} \exp\left(-\dfrac{F\Psi}{RT}\right)$	-6.7
$H^+ + NaX \Leftrightarrow HX + Na^+$	$K_x^0 = \dfrac{(x_{HX})(a_{Na})}{(x_{NaX})(a_H)}$	4.6
Site density TOT-SOH:	2.8×10^{-5} mol/g	
Site density TOT-X:	2.2×10^{-5} mol/g	

1×10^{-4} M. The proton balance was corrected, via the parameter C in Eq. (1), according to the hydrolysis constants of these species.

3. A surface chemical model for montmorillonite

3.1. Theoretical background

Clay minerals contain at least two types of surface functional groups: permanently charged surface functional groups created by ionic substitution within the crystal structure, and variably charged surface functional groups due to ionization of surface OH groups. The first type of surface sites is due to isomorphic substitution of, e.g., Al^{3+} for Si^{4+} within the tetrahedral surface layer causing a permanent charge on the mineral surface. The structural charge is compensated externally by cations interacting with structural-charge surface functional groups. Hereafter, this type of surface sites is denoted as structural-charge surface sites or "layer sites".

In addition to the permanent charge at the layers, the morphological structure of clays also gives rise to a pH-dependent charge on the edge surface. The strongly pH-dependent charge of the edges is due to adsorption of the potential-determining ions H^+ and OH^- as a function of the solution pH. The surface properties of the edge surface of a clay mineral are similar to those found for oxide surfaces (Sposito, 1984; Wieland and Stumm, 1992). Hereafter, this type of surface sites is designated as variable-charge surface sites or "edge sites".

The interaction of protons with layer sites of Na-montmorillonite can be expressed as cation exchange reaction:

$$H^+ + NaX \Leftrightarrow HX + Na^+ \qquad K_x \qquad (2)$$
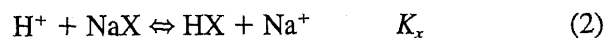
The equilibrium constants, K_{a1} and K_{a2}, for the protonation and deprotonation reactions of edge sites account for the amphoteric character of the OH groups, cf. Stumm and Morgan (1981) and Sposito (1984):

$$\equiv SOH_2^+ \Leftrightarrow \equiv SOH + H^+ \qquad K_{a1}^{app} \qquad (3)$$
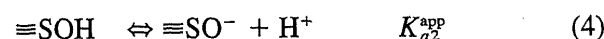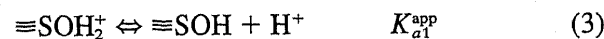
$$\equiv SOH \quad \Leftrightarrow \equiv SO^- + H^+ \qquad K_{a2}^{app} \qquad (4)$$

where $\equiv SOH$, $\equiv SOH_2^+$ and $\equiv SO^-$ respectively represent the different surface hydroxyl groups of the edge surface, and K_{a1}^{app} and K_{a2}^{app} are apparent acidity constants.

A number of different surface complexation models have been proposed in the last two decades for adequately modelling the binding of protons, cations and anions onto mineral surfaces. In the present study, we have chosen an improved version of the diffuse double layer model to describe the charge-potential relationship of the interfacial region. The diffuse double
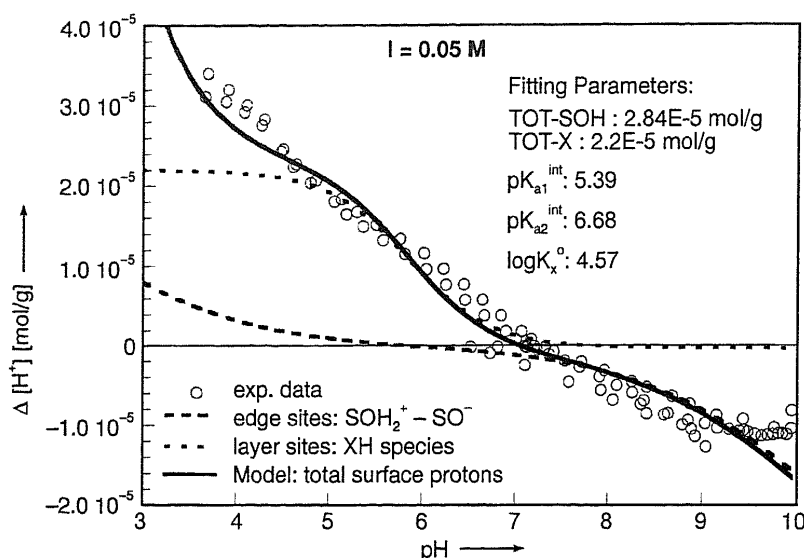
Fig. 2. Titration curve of Na-montmorillonite ($I = 0.05$ mol/dm³ NaNO₃, montmorillonite = 5g/dm³). $\Delta[H^+]$ corresponds to the protons bound by the mineral surface. This curve was used for optimizing the model parameters, and it shows also the contributions of edge and layer sites to the total titration curve. The results are presented in Table 2.

layer model (DDLM) originally proposed by Stumm *et al.* (1970) and Huang and Stumm (1973) has been reviewed and improved recently by Dzombak and Morel (1990). In the DDLM, all ions are adsorbed as co-ordination complexes within the surface plane, except the dissociated counter ions present in the diffuse layer. We refer to Dzombak and Morel (1990) for a detailed description.

3.2. Sensitivity estimations

Uncertainties in $\Delta[H^+]$, as indicated in Figures 1 and 3, are estimated on the basis of Eq. (1) with the assumption that the uncertainty in $[H^+]$ dominates over the uncertainties in the other parameters of Eq. (1). Based on the calibration titrations and on the readings of the electrode potentials, the uncertainty in the measured pH is estimated to be ± 0.03. The propagation of errors leads to significant uncertainties at pH values above 10, cf. Figures 1 and 3.

3.3. Results and discussion

The surface chemical model for montmorillonite has been developed based on the following observation: Montmorillonite reveals oxide-like behaviour in the alkaline pH range as indicated by the sequence of the protonation curves given in Figure 1. In the acid pH range, however, the acid/base characteristics of montmorillonite show the features of an exchanger phase typically found in clay minerals. The following abbreviations will be used: SOH for surface OH groups (edge sites) and X for the ion exchange sites (layer sites).

The formal treatment of the pertinent protolysis and ion exchange reactions are described by Eqs. (2),

(3) and (4). The corresponding mass law equations are listed in Table 2. Fitting of the model parameters, K_{a1}^{int} and K_{a2}^{int}, K_x°, TOT-SOH and TOT-X, was performed with the least-square program GRFIT (Ludwig, 1992) which is an extended version of FITEQL (Westall, 1982). The model parameters were optimized for the experimental results determined in a NaNO₃ medium with ionic strength $I = 0.05$ M (Figure 2). The resulting model parameters are summarized in Table 2.

The total number of variable-charge sites, TOT-SOH, obtained from the fitting procedure is 2.8×10^{-5} mol/g (2.8 meq/100 g) corresponding to about 2.6% of the total CEC (108 meq/100 g). With an estimated specific surface area of the edge face of about 3 m²/g (i.e., 9.5% of the total BET surface area of (31.53 ± 0.16) m²/g), the surface site density of OH groups amounts to 5.7 sites/nm², which is within the range of the values typically obtained for oxide minerals (2 to 8 sites/nm²). The surface area of the basal planes hence amounts to 28.5 m²/g, i.e., 90.5% of the external BET-surface area. Although the validity of our estimate cannot be proved experimentally, the resulting site density is consistent with data reported in the literature.

The intrinsic acidity constants of the protolysis reactions, as defined in Table 2, evaluated from the experiments at $I = 0.05$ M are $pK_{a1}^{int} = 5.4$ and $pK_{a2}^{int} = 6.7$. The PZNPC is determined to be 6.1, indicating that the OH groups exposed at the surface of Na-montmorillonite are stronger acids than aluminol surface sites (PZNPC = 6.6 to 9.2) but less acidic than silanol groups (PZNPC = 2.9). From the composition of montmorillonite, one expects the presence of surface silanol- and aluminol groups whereas our results can be interpreted with one type of surface OH groups. This can be explained either as 1) presence of OH groups with intermediate acid/base characteristics at the montmorillonite surface or 2) that
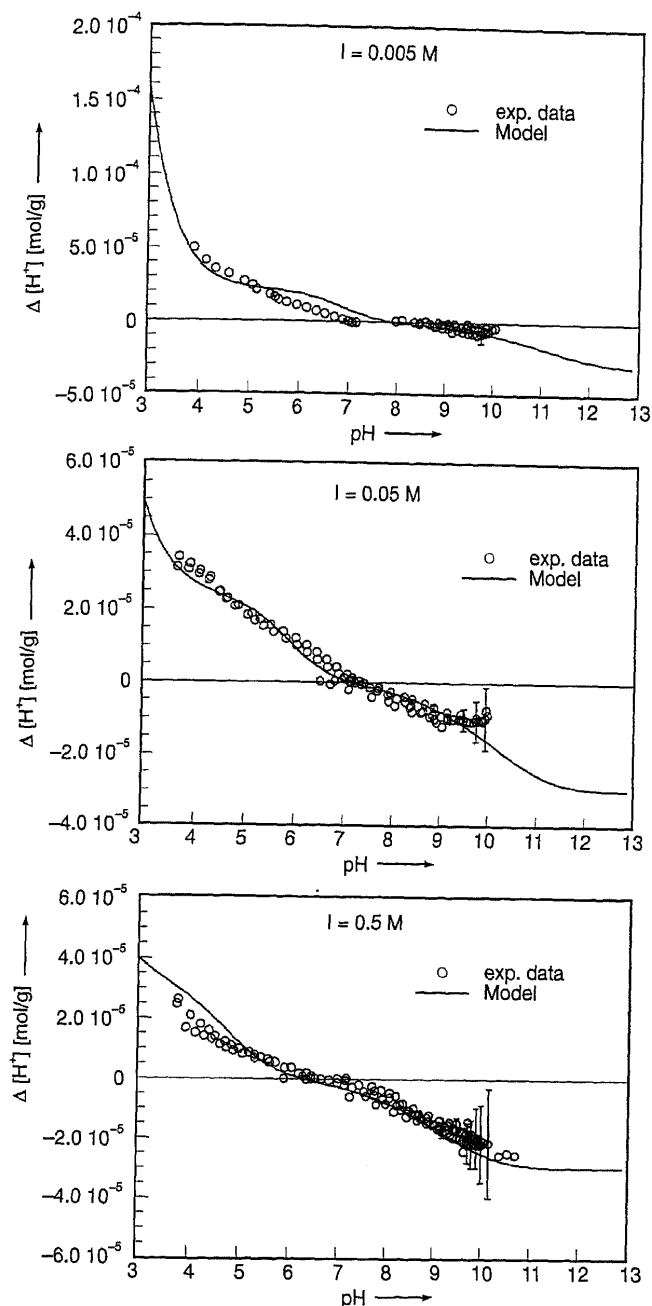
Fig. 3. Simulation of the titration curves of Na-montmorillonite (I = 0.005, 0.05 and 0.5 mol/dm³ NaNO₃, montmorillonite = 5g/dm³). Model computations (solid lines) were performed using the reactions and model parameters listed in Table 2.

exchange reactions. The fraction of surface sites reactive in our experiments is presumably attributable to structural-charge surface sites exposed at the external planes. The thermodynamic constant for the Na/H exchange is determined to be $\log K_X^\circ = 4.6$ and indicates a strong affinity of the external layer sites for protons. The total number of surface sites, i.e., the number of variable-charge sites plus structural-charge sites, amounts to 5×10^{-5} mol/g. This value is comparable with surface site densities of montmorillonite obtained from potentiometric titrations as reported by Zysset (1992), Stadler and Schindler (1993) and Charlet et al. (1993). Note also that the surface chemical model for montmorillonite presented in this study is consistent with the qualitative model proposed for illitic clay minerals by Beene et al. (1991).

The validity of the proposed model can be evaluated by predicting the total proton density at the montmorillonite surface, i.e., $\Delta[H^+]$, as function of pH for I = 0.005 M and I = 0.5 M using the modelling parameters listed in Table 2. Model predictions (solid lines) and experimental data are compared for ionic strengths I = 0.005 M, I = 0.5 M and again for I = 0.05 M (see also Figure 2). For all ionic strengths, model prediction and experimental results agree well in the alkaline pH range where surface OH groups are the only charge-determining surface sites. The total proton density, $\Delta[H^+]$, measured in this pH range is controlled by the deprotonation of OH groups. Agreement between experimental results and model computation is less accurate but still satisfactory in the acid pH range. At pH < 7, both surface OH groups and layer sites contribute to the surface proton density, $\Delta[H^+]$. Figure 3 shows that the proposed surface chemical model adequately describes the pH-dependent protonation of the montmorillonite surface in the range I = 0.005 M to 0.5 M.

Acknowledgments

Al(III) are adsorbed onto silanol groups and, hence, the functional surface sites are $\equiv$Al(OH)OH₂ groups.

The total number of structural-charge sites which are accessible for Na/H exchange reactions under the given experimental conditions amounts to 2.2×10^{-5} mol/g (2.2 meq/100 g). This value corresponds to about 2% of the total CEC (CEC = 108 meq/100 g). We interpret this results as follows: Only a small fraction of layer sites are in equilibrium with the aqueous solution during the potentiometric titration of montmorillonite as conducted in this study. This is most likely a kinetic constraint imposed by limiting the equilibration time of our experiments to 10 min. A longer equilibration time would probably increase the fraction of structural-charge sites accessible for Na/H

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