MECHANISM OF ADSORPTION AND DESORPTION OF WATER VAPOR BY HOMOIONIC MONTMORILLONITES: 2. THE Li⁺, Na⁺, K⁺, Rb⁺ AND Cs⁺-EXCHANGED FORMS

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Abstract—Methods previously used to distinguish between water adsorbed on external surfaces and in the interlamellar space of Na-montmorillonite during adsorption and desorption of water vapor have been extended to a set of homoionic Li-, Na-, K-, Rb- and Cs-montmorillonite. The textural and structural features have been investigated at different stages of hydration and dehydration using controlled-rate thermal analysis, nitrogen adsorption volumetry, water adsorption gravimetry, immersion microcalorimetry and X-ray powder diffraction under controlled humidity conditions. During hydration, the size of the quasi-crystals decreases from 33 layers to 8 layers for Na-montmorillonite and from 25 layers to 10 layers for K-montmorillonite, but remains stable around 8-11 layers for Cs-montmorillonite. Each homoionic species leads to a one-layer hydrate, which starts forming at specific values of water vapor relative pressure. Li-, Na- and K-montmorillonite can form a two-layer hydrate. By comparing experimental X-ray diffraction patterns with theoretically simulated ones, the evolution of structural characteristics of montmorillonites during hydration or desorption can be described. Using structural and textural data, it is shown that during adsorption: (1) the rate of filling of interlamellar space of the one layer hydrate increases with the relative pressure but decreases with the size of the cations; and (2) the different hydrated states are never homogeneous.

Key Words—Adsorption, Desorption, Exchangeable cations, Immersion microcalorimetry, Montmorillonite, Relative humidity, Surface area, XRD.

INTRODUCTION

The sorption of water by phyllosilicates is governed by the size and charge of saturating cation, by the value and the localization of layer charge of the adjacent silicate sheets and by textural characteristics like the extension of layers in the ab plane (Tessier 1984). The former property has been applied to limit swelling of clayey soils by exchanging natural saturating cations by potassium ions (Veniale et al. 1986).

Monovalent and large cations stabilize the one-layer hydrate under a large range of relative humidity whereas small divalent cations stabilize the two-layer hydrate in the same domain (Tarasevitch and Ovcharenko 1975). Layer stacking type encountered in the case of well crystallized phyllosilicates such as vermiculite and saponite is determined by the nature of interlayer cations and the layer charge density (Suquet and Pezerat 1987). Montmorillonites exhibit a turbostratic stacking of quasi-crystals or tactoids (Aylmore and Quirk 1971). The basal spacings (d001) of montmorillonites dried at 200°C increase with the size of the exchangeable cation from 9.5 Å for Li- to 11.2 Å for Cs-montmorillonite (Martin-Vivaldi et al. 1963). Larger cations could present symmetrical or non-symmetrical stacking types corresponding respectively to 10.7 and 11.5 Å for Cs-montmorillonite (Besson 1980). Homogeneous hydrates of montmorillonites are characterized by a small range of d001. Numerous results assign 12.4 to 12.6 Å to the d001 of the one-layer hydrate of Na-montmorillonite and 15.4 to 15.6 Å to the d001 of the two-layer hydrate (Mooney et al. 1952, Glaeser and Méring 1968, Keren and Shainberg 1974, Iwasaki and Watanabe 1988). Less numerous results for other cations are scattered around the same values but do not always deal with homogeneous states (Mamy 1968, Kamel 1981).

Furthermore, textural features such as specific surface area in the dry state are affected by cation exchange (Ben Ohoud and Van Damme 1990). In clay pastes, narrow and numerous pores have been described in the case of Na-montmorillonite in dilute NaCl solutions whereas Ca-montmorillonite in CaCl2 aqueous solutions exhibit larger and less numerous pores (Tessier 1984). In montmorillonite suspensions, mean Stokes' diameters of tactoids are dependent on saturating cations (Na < K < Mg, Ca) (Whalley and Mulhins 1991). In the hypothesis that textural features are modified during the first stages of hydration, the nature
of the exchangeable cation would have a strong influence.

In the first papers of this series (Cases et al 1992a, 1992b), it was shown that a multiple analytical approach allowed us to reconsider earlier models for hydration-dehydration of Na-montmorillonite in the range of intracrystalline swelling (Mamy 1968, Sposito and Prost 1982, More and Hower 1986, Kraehenbuehl et al 1987). The main features were: (1) interstratified hydrates persist at all water vapor relative pressure values higher than 0.25. The one-layer hydrate is predominant for 0.25 < P/Po < 0.7 during adsorption, and 0.15 < P/Po < 0.6 during desorption, whereas the two-layer hydrate is predominant beyond these limits; (2) the specific surface area of quasi-crystals increases from 43 m²·g⁻¹ to 105 m²·g⁻¹ when water molecules adsorb mainly on external surfaces (P/Po < 0.25); (3) the driving force for intercrystalline swelling is a combination of the heat of immersion of exchangeable cations (Na) and the surface pressure on external surfaces; and (4) different hydration stages can be distinguished, corresponding to the solvation of exchangeable cations and to the filling of remaining interlamellar spaces. In the present paper the same approach was used to study the influence of the exchangeable cations Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺ on the textural and structural evolution of montmorillonite upon adsorption-desorption of water vapor.

EXPERIMENTAL

Materials

The investigation was carried out with a Wyoming montmorillonite (<2 μm fractions) supplied by CECA S.A. (Paris-France), previously dispersed, centrifuged and Na exchanged. Homionic samples of Li, Na, K, Rb and Cs were prepared by dialysing 12 g·liter⁻¹ montmorillonite suspensions with 0.5 N chloride solutions (analytical grade salts) of the suitable cation. The material was washed by dialysis until a chloride residual concentration of 10⁻³ N was obtained and then centrifuged. The suspended samples were then freeze-dried. After treatment, the purity of the samples was 99%, the major impurities being aluminum oxy-hydroxides. An approximate structural formula has been calculated from the chemical and electron microprobe analyses of the Na form according to a method proposed by J. Yvon et al (1990):

\[
\text{Si}_{3.883}\text{Al}_{0.117}\text{IV}(\text{Al}_{1.530}\text{Mg}_{0.25}\text{Fe}^\text{III}_{0.006}\text{Fe}^\text{II}_{0.207}\text{O}_{10})\text{VI}(\text{OH})_2\text{Na}_{0.380}
\]

The above formula corresponds to a theoretical exchange capacity of 101 meq/100 g whereas the cationic exchange capacity (CEC) determined by the ammonium displacement method (Caillerè et al 1982a) was found equal to 99.6 meq/100 g, with a percentage of homoionicity of 97.6 (in particular, K⁺ 0.4 meq/100 g and Ca²⁺ 2 meq/100 g).

Methods

To characterize the different states of the limited crystalline swelling during adsorption and desorption of water vapor, different methods have been used, particularly to define the initial textural properties of the samples in the dry state in relation with pretreatment.

**Controlled Transformation-Rate Thermal Analysis (CTRTA)** (Rouquerol 1989, Grillet et al 1988). This process allows one to overcome partial overlaps of successive dehydration steps when using conventional thermal analysis. The system operates in the reverse way of the conventional method, because the temperature is measured while a temperature dependent property of the substance, here the water-content, is modified at a constant rate. This rate is controlled at a value low enough to ensure the satisfactory elimination of the temperature and pressure gradients within the sample. The flow of gas evolved from the sample under a dynamic vacuum is used to control the heating of the furnace. For a constant composition of the water vapor evolved, the temperature-vs-time data may be immediately converted into temperature-vs-mass-loss data, and therefore to a conventional thermogravimetric curve. The experimental conditions selected in the present study were a sample mass of 300 mg, a residual pressure of 1~2 Pa over the sample and a dehydration rate of 2.4 mg/h.

**Nitrogen adsorption volumetry.** Complete nitrogen gas adsorption-desorption cycles were determined using a conventional volumetry adsorption equipment (Delon 1970). Prior to each experiment, about 500 mg of sample was outgassed to a residual pressure of 1.3 10⁻² Pa at 100°C for 16 hours.

**Water vapor adsorption measurements.** Water vapor adsorption measurements were carried out in a continuous gravimetric apparatus built around a Setaram MTB 10-8 symmetrical balance (Poirier et al 1987). Prior to each experiment, about 115 mg sample was outgassed under vacuum (1~2 Pa) to a temperature of 100°C. Water vapor was supplied from a source kept at 41°C, through a Grandville-Phillips leak valve, at a flow rate to ensure quasi-equilibrium conditions at all times. The adsorption isotherm, mass adsorbed at 30°C versus quasi-equilibrium pressure, was directly recorded on an X-Y recorder. Pressures were measured using a Texas fused silica Bourdon tube automatic gauge.

**Immersion microcalorimetry at 30°C.** Immersion microcalorimetry at 30°C was used to determine the enthalpy of immersion in water of the montmorillonite sample (about 100 mg of clay, outgassed under the
conditions given above for the gravimetric adsorption of water vapor, in a cell of about 6 cm$^3$ versus the pre-equilibrium relative pressure of water vapor following a method described by Grillet et al. (1988). The enthalpy curve was then used to derive the external specific surface area of quasi-crystals immersed in water (final state) by applying a modified Harkins and Jura procedure (Partyka et al., 1979, Cases and François, 1982, Fripiat et al., 1982).

X-ray powder diffraction. Patterns of oriented samples were recorded with an apparatus specially built for this study. The oriented samples were prepared by pipetting aliquots of a suspension (0.35 g of montmorillonite and 0.07 g of kaolinite (added to calibrate the curve detector) in 25 cm$^3$ of demineralised water) onto a mylar sheet covered with pharmaceutical gauze and evaporated to dryness in air. Dried clays films were separated from the mylar sheet, cut to appropriate size and set vertically on a sample holder enclosed in a chamber allowing the control of relative humidity and temperature.

Prior to any experiment, samples were outgassed at 1–2 Pa and 100°C for 4–24 hours by connecting the chamber to vacuum pumps. Vacuum is checked on a Pirani gauge. The sample is heated to the desired temperature by radiation from two cupels set around the sample holder. During experiments, the temperature (30°C) of the sample is controlled by water circulation in the double-wall of the chamber. The chamber is connected to a water vapor source. Acquisition of adsorption data at a given water vapor pressure is accomplished by recording the diffraction patterns at different times (1 hour, 2.30 hours and more than 4 hours (up to 72 hours depending of the time required to reach the plateau corresponding to an apparent equilibrium).

Desorption data are obtained by recording the diffraction patterns for different times after the step of decrease of pressure induced by pumping 15 seconds and by the decrease of the temperature of the water source. XRD data were obtained with CoKα radiation using a CGR goniometer and an Inel CPS 120 curved detector (Figure 1). Data were collected, during 20 to 40 minutes, simultaneously over 60 degrees (2θ) and were processed using a multichannel Varrox analyser (2048 channels for 60 degrees). The diffraction software implanted in a Compaq Deskpro 286 calculator allowed transfer of data from the analyser, automatic peak search and automatic calibration using the d$_{001}$ and d$_{002}$ peaks of kaolinite as an internal standard.

XRD powder patterns were compared with simulated ones. The software used has been developed in the Laboratory of Crystallography of Orléans, France, using the approach proposed by Drits and Sakharov (1976), Drits and Tchoubar (1990) and adapted by Besson and Kerm (Kerm, 1988) for the study of the intensity diffracted along the 00 rod in reciprocal space from disordered phyllosilicates. The input data file includes: (1) the abundances and positions of atoms in the different clay sheets (2:1 layer structure) and of water molecules in the interlamellar space (Data proposed by Pézerat and Méring (1954) and by Drits (1975) and adapted from Ben Brahim (1985), Ben Brahim et al. (1984, 1985, 1986) have been used); (2) the basal spacings corresponding to the different states of hydration (zero, one, two or three layers of water); (3) the proportions of the different hydrated states and the probabilities of succession of two kinds of layers; and (4) the distribution of the number of layers per quasi-crystals (tactoids). The detailed simulation procedure was described in previous works (Berend, 1991, Cases et al. 1992a).

**RESULTS**

**Characterization of the dry or initial state**

Figure 2 shows the CTRTA curves for the different homoionic montmorillonite samples. The successive dehydration steps usually shown by conventional thermogravimetric analysis are more clearly evident (Caillère et al., 1982b). Region I, between room temperature and 100°C, corresponds to the desorption of physically adsorbed water. The next region (100°C–around 500°C) corresponds mainly to the expulsion of water supposedly bound to exchangeable cations: the water loss decreases sharply with decreasing enthalpy of hydration of exchangeable cations (Table 1). The final loss (around 5%) in region III (>500°C) is due to the dehydroxylation of the structure.

Except for Li-montmorillonite, the water contents after dehydration at 100°C (Table 1) are slightly higher than results reported by Poinsignon and Cases (1978) and Cases et al. (1992a). This difference suggests a con-
The adsorption isotherms are of type II with a very important type H3 hysteresis loop (Sing 1982), corresponding to capillary condensation in mesopores. The shape of the loop is usually associated with aggregates of plate-like particles giving rise to slit-shaped pores, and corresponds to a narrow size distribution of lamellar mesopores (Cases et al. 1992a). A low pressure hysteresis also is observed extending to the lowest attainable pressures. It is weak for Li- (Figure 3), Na- and Rb-montmorillonites, and larger for K- (Figure 4) and Cs-montmorillonite. In addition, for the potassium exchanged form, the adsorption isotherms are not reproducible. Low pressure hysteresis except for Cs-montmorillonite, is assumed to be associated with the swelling and the change of the non-rigid porous structure formed by the organization of quasi-crystals upon N$_2$ adsorption rather than to an irreversible uptake of molecules in micropores, present in the initial sample, having the same width as that of the adsorbate molecule. This assumption is supported by previous studies because the low pressure hysteresis loop was not observed on the Na-montmorillonite sample obtained after air-drying (Cases et al. 1992a). Particularly for K-montmorillonite, physisorption is a destructive method and is not suitable for investigating mesoporosity. The total specific surface areas of samples calculated from the Brunauer-Emmet-Teller method (Table 2) increase with the radius size of the exchangeable cation. Assuming that powder contains discrete particles similar to square parallelepipeds of length ca. 3000 Å and thickness ca. a multiple of the $d_{001}$ given in Table 3, it is possible to calculate the mean size of the quasi-crystals (Cases 1985). The mean number of layers per quasi-crystals, decreases from 23 for Li-montmorillonite to 11 for Rb-montmorillonite. The model used to calculate the stacking of plates from adsorption data assumes the plates are perfectly stacked as in a deck of cards. This assumption is unlikely and leads to a coarse approximation because there is a good chance that the layers could be stacked in a stair-case-like fashion or in a fractal like fashion as suggested by Ben Ohoud and Van Dame (1990). However the use of the procedure of de Boer et al. (1966) reveals the presence of a small amount of micropores; nearly constant around 4 cm$^3$.g$^{-1}$ (0.006 cm$^3$.g$^{-1}$ converted to a liquid volume) except for Cs-montmorillonite, for which the basal spacing is large enough to allow some nitrogen molecules to be adsorbed in the interlamellar space. Surfaces available after the filling up of the micropores (real external surfaces areas of quasi-crystals) method (Table 2) increase with the radius size of the exchangeable cation. Assuming that powder contains discrete particles similar to square parallelepipeds of length ca. 3000 Å and thickness ca. a multiple of the $d_{001}$ given in Table 3, it is possible to calculate the mean size of the quasi-crystals (Cases 1985). The mean number of layers per quasi-crystals, decreases from 23 for Li-montmorillonite to 11 for Rb-montmorillonite. The model used to calculate the stacking of plates from adsorption data assumes the plates are perfectly stacked as in a deck of cards. This assumption is unlikely and leads to a coarse approximation because there is a good chance that the layers could be stacked in a stair-case-like fashion or in a fractal like fashion as suggested by Ben Ohoud and Van Dame (1990). However the use of the procedure of de Boer et al. (1966) reveals the presence of a small amount of micropores; nearly constant around 4 cm$^3$.g$^{-1}$ (0.006 cm$^3$.g$^{-1}$ converted to a liquid volume) except for Cs-montmorillonite, for which the basal spacing is large enough to allow some nitrogen molecules to be adsorbed in the interlamellar space. Surfaces available after the filling up of the micropores (real external surfaces areas of quasi-crystals)

Table 1. Main C.T.R.T.A. results.

<table>
<thead>
<tr>
<th>Exchangeable cations (1)</th>
<th>Li$^+$</th>
<th>Na$^+$</th>
<th>K$^+$</th>
<th>Rb$^+$</th>
<th>Cs$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water molecules per exchangeable cation (2)</td>
<td>1.54</td>
<td>1.36</td>
<td>1.00</td>
<td>1.18</td>
<td>1.02</td>
</tr>
<tr>
<td>Water bound to exchangeable cations (3)</td>
<td>3.0</td>
<td>2.6</td>
<td>1.9</td>
<td>2.1</td>
<td>1.7</td>
</tr>
<tr>
<td>Structural water (4)</td>
<td>5.3</td>
<td>5.2</td>
<td>5.1</td>
<td>4.9</td>
<td>4.7</td>
</tr>
</tbody>
</table>

1 = Nature of exchangeable cations. 2 = Number of water molecules per exchangeable cation at 100°C. 3 = Amount of water bound to exchangeable cations in % of the final mass. 4 = Structural water expressed in % of the final mass.
can be determined following de Boer et al. (1966) procedure. The average size of quasi-crystals calculated from the values of external surface area corresponds to thicker stacks and decreases from 41 to Li-montmorillonite to 11 layers for Cs-montmorillonite.

**Water vapor adsorption-desorption isotherms**

Water vapor sorption isotherms are illustrated in Figure 5. Amounts of water adsorbed suggest that a one-layer hydrate forms for all montmorillonites corresponding to an amount of adsorbed water 6–7 mmol·g⁻¹. The two-layer hydrate state seems to be formed only for Li- and Na-montmorillonite (13–14 mmol·g⁻¹). The shape of the isotherms is influenced by the nature of exchangeable cation. The irregular shapes of both the adsorption and desorption branches of all isotherms suggest complex water adsorption mechanisms (Cases et al. 1992a). The adsorption phenomena occur on surfaces whose specific surface areas are not constant but depend on the relative pressure as is often the case for swelling clays. As expected from the high energy of hydration of Li⁺, the filling of the interlamellar space of Li-montmorillonite begins at very low relative pressure. In these conditions, it is impossible to determine the external specific surface area of the quasi-crystal using the BET procedure. For the other cations, the shape of the isotherms and the XRD patterns (Figure 6) reveal that adsorption occurs on external surfaces only at low relative pressure. Adsorption in the interlamellar space begins for particular values of the relative pressure decreasing with increasing the size of the exchangeable cation. Kawano and Tomita (1991) reported that after dehydration for one hour at 400°C, rehydration properties of smectites are strongly dependent on the size of the interlayer cations (K⁺ > Na⁺ > Ca²⁺ > Mg²⁺) because large ionic radii impair the fixation of cations in the hexagonal holes. The present results obtained after dehydration at 100°C can be explained by larger exchangeable cations creating larger basal spacings. This diminishes the interlayer forces of cohesion and therefore increases the accessibility of cations by water molecules.

**Adsorption isotherms on the external surfaces of montmorillonite can be compared to the reference ad-

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**Table 2.** Specific surface areas calculated from the B.E.T. method and volumes of micropores evaluated following the procedure of de Boer et al. (1966).

<table>
<thead>
<tr>
<th></th>
<th>Li⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Rb⁺</th>
<th>Cs⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vm (cm³·g⁻¹) (1)</td>
<td>8.6</td>
<td>9.65</td>
<td>10.65</td>
<td>15.4</td>
<td>29.8</td>
</tr>
<tr>
<td>Sₛₑ₉ (m²·g⁻¹) (2)</td>
<td>37.7</td>
<td>42.2</td>
<td>46.5</td>
<td>67.4</td>
<td>130.3</td>
</tr>
<tr>
<td>V (cm³·g⁻¹) (3)</td>
<td>4.0</td>
<td>3.4</td>
<td>3.2</td>
<td>5.6</td>
<td>19.1</td>
</tr>
<tr>
<td>Sₑₑ₉ (m²·g⁻¹) (4)</td>
<td>23.2</td>
<td>26.3</td>
<td>34.7</td>
<td>46.7</td>
<td>64.2</td>
</tr>
<tr>
<td>M (5)</td>
<td>41</td>
<td>33</td>
<td>25</td>
<td>17</td>
<td>11</td>
</tr>
</tbody>
</table>

1 = monolayer capacity calculated from the B. E. T. equation per unit mass of adsorbent. 2 = corresponding total specific surface area. 3 = total microporous volume per unit mass of adsorbent. 4 = external specific surface area calculated from de Boer et al. 1966 procedure, and 5 = average number of layers per particles or quasi-crystals derived from external surface area (average thickness of the elementary stacks).

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**Table 3.** Determination of the evolution of the external surface area on homoionic montmorillonite for lower values of water vapor relative pressure taking into account the reference isotherms of Hagymassy et al. 1969 (Berend 1991).

<table>
<thead>
<tr>
<th></th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Rb⁺</th>
<th>Cs⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>P/P₀ (1)</td>
<td>0.025 to 0.2</td>
<td>0.025 to 0.2</td>
<td>0.025 to 0.07</td>
<td>0.025</td>
</tr>
<tr>
<td>C (2)</td>
<td>23</td>
<td>12</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Sₑₑ₉ (3)</td>
<td>42.5 to 83.4</td>
<td>44.6 to 77.5</td>
<td>50.5 to 74.3</td>
<td>79.0</td>
</tr>
</tbody>
</table>

1 = range of relative pressure considered. 2 = energetic constant of the B. E. T. theory. 3 = evolution of the external specific area of quasi-crystals with increasing relative pressure in the range considered.

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**Figure 4.** Adsorption-desorption isotherms of nitrogen at 77 K onto Wyoming K-montmorillonite and reproducibility.

**Figure 5.** Water adsorption and desorption isotherms onto Li-, Na-, K-, Rb-, and Cs-montmorillonites.

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Adsorption and desorption of water vapor by homoionic montmorillonites

Figure 6. Evolution of the values of d(001) for montmorillonites saturated by the indicated cation during hydration and dehydration.

...adsorption isotherms of water vapor of non-porous samples with the same BET energetic constant, C (Hagymassy et al. 1969, Berend 1991). For a given value of P/Po, if Qa is the amount of water adsorbed per gram of montmorillonite, the surface coverage of the reference isotherm taken into account, N_A the Avogadro number and σ the cross-sectional area of the water molecule strongly adsorbed on the external surface, the specific surface area of montmorillonite S is given by the relationship:

\[ S = (Qa/\theta)N_A\sigma \]  

(1)

The specific surface areas of Na-, K- and Rb-montmorillonite are found to increase with P/Po for every value of the constant C (Cases et al. 1992a) (Table 3). Subsequently, the value of the constant C is chosen in order to obtain the same surface area by applying the BET procedure to the beginning of water adsorption isotherms and to nitrogen adsorption isotherms. The classical value of 14.8 Å² proposed by Harkins and Jura (1944) was used for σ.

XRD patterns

Typical XRD patterns of oriented samples are given in Figures 7–9 for samples in the initial state (zero-layer hydrate state), and for samples in quasi-equilibrium with relative pressures between 0.4–0.6 and 0.92–0.98 respectively. The evolutions of basal spacings, d(001), during hydration and dehydration are presented in Figure 6. Usually for low relative pressures, the kinetics of swelling of most montmorillonites are rapid. The equilibrium time can reach 24 hours and sometimes 72 hours for highest relative pressures. During adsorption, interstratified structures are present for the whole range of relative pressures because the curves present no steps (Figure 6). Only the most hydrated states seem to be homogeneous. Another evidence for the presence of interstratified structures is given by the absence of plateaus and steps on the water vapor ad-

Figure 7. Observed X Ray diffraction tracings of samples in the initial state (dry state). K represents kaolin peaks added in the XRD experiments for internal calibration of the curved detector and M, the montmorillonite peaks.

adsorption isotherms (Figure 5). During desorption quasi-homogeneous states expected at about 10 Å for the dry state (OS), ~12.4 Å for the one-layer hydrate state (1S) and ~15.5 Å for the two-layer hydrate state (2S) alternate with interstratified structures. To understand the mechanism of water uptake, it is now important to consider the possible change of the external surface of quasi-crystals during hydration.

Characterization of the final size of quasi-crystals

The final size of the quasi-crystals can be determined by measuring the heat of immersion of homoionic montmorillonites after preadsorption of increasing numbers of water layers (Cases and François 1982, Fripiat et al. 1982, Cases et al. 1992a). The immersion enthalpies of montmorillonites obtained from the dry state equal 70 J·g⁻¹ for Li- and Na-montmorillonite and around 30–40 J·g⁻¹ for the other montmorillonites. Enthalpies of immersion decrease with precov-}

INITIAL STATE (dry state)
ergic sites on the external surfaces and in the interlamellar space. Constant values are measured during the hydration of the quasi-constant interstratified 0S/1S structure of Li-montmorillonite and during adsorption of water molecules on the external surface of Na- and K-montmorillonite. In this latter case, this phenomenon is mainly due to the large difference between the surface area of the sample before immersion (Table 3) and the corresponding value after immersion in water (about 800 m²·g⁻¹).

Using the Harkins and Jura formula, the plateau observed at high relative pressure can be used to derive the external specific surface of quasi-crystals immersed in water, \( S_{\text{eff}} \) (Table 5). The value obtained for Na-montmorillonite is lower than that presented recently (105 m²·g⁻¹, Cases et al 1992a). The definition of the position of the plateau in the high precoverage domain lacks precision because preadsorption and immersion phenomena are not totally reproducible as they are affected by small changes in the experimental conditions. Indeed, in this range of precoverage a compromise must be chosen as high clay weights are needed for an acceptable thermic response of the apparatus whereas low clay quantities ensure a perfect swelling of the clay in the cell. A longer precoverage time was considered for Li-montmorillonite. The mean value of the enthalpy of immersion was used for Rb- and Cs-montmorillonite. The values of the external surface areas derived in this manner are close to those obtained by treating the water adsorption isotherms just before water molecules start entering the interlamellar space (Table 3). These values which are related to the mean size of quasi-crystals during adsorption will therefore be used in subsequent modellings. They are calculated without any assumption concerning the value of the cross-sectional area of the water molecule adsorbed on the solid. For Na-, K-, Rb- and Cs-montmorillonites, the external surface areas of quasi-crystals are constant during the filling of the interlamellar space.
Table 4. Parameters used for the simulation of XRD patterns.

<table>
<thead>
<tr>
<th>Ion</th>
<th>M in initial state (1)</th>
<th>(d_{app}) (A) (2)</th>
<th>(d_{001}) (A) (2)</th>
<th>(d_{002}) (A) (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>apparent (d_{app})</td>
<td>Scherrer formula</td>
<td>zero-layer hydrate</td>
<td>one-layer hydrate</td>
</tr>
<tr>
<td>Li⁺</td>
<td>10</td>
<td>8</td>
<td>9.6–10.0</td>
<td>12.0–12.2</td>
</tr>
<tr>
<td>Na⁺</td>
<td>12</td>
<td>9</td>
<td>9.55</td>
<td>12.5</td>
</tr>
<tr>
<td>K⁺</td>
<td>9</td>
<td>7</td>
<td>9.95</td>
<td>12.5</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>18</td>
<td>10</td>
<td>10.25–10.6</td>
<td>12.5</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>20</td>
<td>11</td>
<td>10.7–11.5</td>
<td>12.4</td>
</tr>
</tbody>
</table>

1 = the range of thicknesses of unit layers making the diffracting domain in the interference function. 2 = basal spacings corresponding to the 001 reflections.

DISCUSSION

Simulation of the X-ray powder patterns in the small-angle X-ray scattering domain (the 001 reflection) at various hydration states

The comparison of simulated XRD patterns with the experimental ones is not an easy task because of the disordered structure of the samples and of the experimental procedure used i.e., oriented preparations analyzed in reflection. This results in four main problems: 1) measured and calculated intensities do not agree for small angles which make the determination of the mean number of layers in a stack (quasi-crystal), \(M\), inaccurate; 2) relative intensities of first order reflection and harmonics are often not consistent with the models predicting less intense harmonics; 3) background noise is sometimes important for higher relative pressures; and 4) large differences in the clay structure in the range of the two-layer hydrate often correspond to small changes in the XRD pattern due to the poor accuracy obtained in the small angle region. Consequently the positions of the reflections were taken into account rather than the widths or relative intensities of the reflections. The precision obtained was better than 10% except in the range of the two-layer hydrate, where it is difficult to choose between a quasi-homogeneous state and an interstratified one (for example 100% 2S or 10% 3S; 70% 2S; 20% 1S).

The parameters used for the simulation are given in Table 4. For Li-montmorillonite two states in the zero-layer state have been taken into account (Li-H₂O, 10 Å and Li, 9.4 Å (Suquet et al. 1982). Small changes in the positions of interlayer cations or water molecules do not affect the XRD pattern except for the Cs⁺ cation.

Basal spacings of the models have been set taking into account the harmonics of the more homogeneous states and results from the literature. The mean numbers \((M)\) of layers per stacks were determined in order to obtain a good superimposition of the positions of the experimental and calculated reflections. These values are higher than values obtained using the width of the \(d_{001}\) reflection particularly for Rb- and Cs-montmorillonites which present symmetrical (hexagonal cavities face to face) and non-symmetrical (hexagonal cavities shifted) stacking types, noted 0S Sym and 0S Non Sym respectively in Figures 11 and 12. During adsorption, the amounts of symmetrical and non-symmetrical dry state were taken equal for Cs-montmorillonite. But in order to explain the broadening of peaks \(d(002)\) and \(d(004)\) and the high value of the position of the peak \(d(002)\), the different states (0S Sym, 0S Non Sym, 1S) were assumed to be separated (unmixed) for values of relative pressure from 0.15 to 0.50 (Figure 11).

Proportions of the different hydrates versus \(P/P_0\) during adsorption and desorption are illustrated on Figures 11 and 12, respectively. A distinction has been made between symmetrical and non-symmetrical stacking types for Rb- and Cs-montmorillonite in the dry state. This determination, only a rough estimate for the hydrated state, will not be taken into account.

Table 5. Specific surface areas of the quasi-crystals after immersion in water.

<table>
<thead>
<tr>
<th>Ion</th>
<th>(S_{HU}) (m²·g⁻¹) (1)</th>
<th>(M) (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td>75.3</td>
<td>9</td>
</tr>
<tr>
<td>Na⁺</td>
<td>84.0</td>
<td>8</td>
</tr>
<tr>
<td>K⁺</td>
<td>41.8</td>
<td>18</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>55.4</td>
<td>13</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>85.6</td>
<td>8</td>
</tr>
</tbody>
</table>

1 = surface calculated using the Harkins and Jura formula. 2 = corresponding mean number of layers in the quasi-crystals assuming a model of parallelepiped.

Figure 10. Enthalpy of immersion (dots and line) and water adsorption isotherms (line) vs. precoverage relative pressure for Li-, Na-, K-, Rb-, and Cs-montmorillonites.
later on. In the initial state, 100% of OS is assumed. During adsorption, 10% IS is observed for P/Po equals to 0.02 for Li-, 0.33 for Na-, 0.30 for K-, 0.20 for Rb-, and less than 0.08 for Cs-montmorillonite. About 50% IS is observed for all homoionic montmorillonites at P/Po = 0.5. For higher values of P/Po: 1) a two-layer state hydrate is formed for Li-, Na- and to a lesser extent for K-montmorillonite; (2) the one-layer state develops for Cs-montmorillonite; and (3) seems to be unchanged for Rb-montmorillonite. Quasi-homogeneous 2S of Li- and Na-montmorillonite are observed for P/Po higher than 0.9 taking into account the previous reservations. Desorption of two-layer states for Li-, Na-, and K-montmorillonite leads to a large proportion of one-layer state and a small proportion of zero-layer state (Figure 12). Complete closure of the layers takes place at P/Po values which decrease with decreasing cation size. For Rb- and Cs-montmorillonite a small decrease of IS is observed for P/Po higher than 0.2 and a complete interlamellar space closure for lower values of P/Po.

Textural evolution during water adsorption

From the previous results and according to Cases et al (1992a), it can be assumed that during the first stage of water adsorption the elementary tactoids of Li- and Na-montmorillonite, of about 40–30 layers thick in the dry state, are split into smaller ones corresponding to about 8–9 layers thick. The specific surface area of these tactoids remains constant even at the highest relative pressures investigated.

The specific surface area of Cs-montmorillonite remains constant in the dry state and during hydration at about 65–80 m²·g⁻¹, corresponding again to about 8 layers per tactoid. This value agrees with the result obtained by applying the Scherrer formula to the d₃₀₁ line broadening of Cs-montmorillonite in the dry state. It is the thickest stack found for all the cations investigated.

K- and Rb-montmorillonite show an intermediate evolution. A trend to splitting is observed (Table 3) in the first stage of water hydration but the opposite trend appears for higher relative pressure resulting in a more compact texture of the hydrated material.

Literature results (Cebula et al. 1980, Stul and Van Leemput 1982, Schramm and Kwak 1982) show that the surface area of dry montmorillonite increases with the size of the cation and that in dilute suspensions, the mean number of layers per tactoid increases with the cation atomic weight from 1 for Li⁺ to 4 (or 5 depending of the equation used) in the case of Cs⁺. Such results involve a splitting of the tactoids saturated with the smaller cations, in agreement with the present work.

A large discrepancy is noticeable between the number of layers per tactoid obtained with the Harkins and Jura formula (Table 5) and results reported by Schramm and Kwak (1982). The difference can be assigned to the fact that the bulk concentration of the final state obtained with immersion microcalorimetry is 8 times higher than the dilute bentonite suspensions (2 g per liter) investigated by these authors.

Connection between water adsorbed on external surface and water present in interlamellar space

For a given relative pressure, the total amount of water present in montmorillonite is the sum of the initial water content (Qinit, Table 1, line 2) and of the experimental adsorbed amount (Qa). The surface coverage θext of the external surface area of quasi-crystals is given by the reference isotherm of a non-porous adsorbent having the same BET energetic constant (Table 3, Hagymassy et al. 1969). The surface areas (S) are known from nitrogen adsorption, water vapor adsorption and microcalorimetry measurements. The external water amount (Qext) can be derived using the reference isotherm and equation (1).
The remaining water is internal. It is mainly adsorbed in the interlamellar space (about 7–8 mmol·g⁻¹ for a monolayer) and to a limited extent in the microporosity. The limit between micropores and interlamellar space is somewhat imprecise for Cs-montmorillonite which has a high d₀₀₁ value in the dry state. In this case, the interlamellar space could become part of intra-aggregate porosity.

Plotting of the internal and external adsorption-desorption isotherms (Figure 13) shows that the internal water content is higher than the external one in the whole range of relative pressures investigated. External water cannot be neglected. It increases sharply at low and at high relative pressures.

**Filling of the interlamellar space**

As the amount of the external water and the concentrations of the different hydrate states are known over the whole range of relative pressure, the uptake of water in the interlamellar space can be calculated assuming that:

1. The internal lamellar specific area $S_{int}$ varies according to the relation
   
   $$ S_{int} = (801.3 - (S_{ext} - S_{ext\,lat})) $$

   where $S_{ext}$ represents the total external specific surface area and $S_{ext\,lat}$ the lateral external specific surface area. If the tactoids are assumed parallelepipeds, $S_{ext\,lat}$ is equal to 5.1 m²·g⁻¹, 6.7 m²·g⁻¹ and 8.3 m²·g⁻¹ in the dry state, monolayer hydrate, two-layer hydrate respectively (Cases 1985).

2. Models of the one-layer hydrate and two-layer hydrate proposed by Ben Brahim et al. (1985) for Na-béidellite are valid for homoionic montmorillonites. Cross sectional areas of 7.8 Å² ($\sigma_1$) for the water molecule in the one-layer hydrate and 8.7 Å² ($\sigma_2$ and $\sigma_3$) in the two- and three-layer state are assumed.

   The amount of water, $Q_{int}$, in mmol g⁻¹, adsorbed in the interlamellar space as a monolayer ($i = 1$), bilayer ($i = 2$) and third layer ($i = 3$) is given by the relation

   $$ Q_{int} = i \cdot S_{int}/2 \cdot \sigma_i \cdot N_A $$

   (3)

   For given abundances of relative proportions $W_i$ of each type of layer, the theoretical adsorbed amount in the interlamellar space $Q_{int\,th}$ is given by the relation

   $$ Q_{int\,th} = W_0 * Q_{int\,0} + W_1 * Q_{m1} + W_2 * Q_{m2} + W_3 * Q_{m3} $$

   (4)

   Figure 14. Evolution of the filling up of interlayer water versus mean interlamellar swelling during water adsorption of Li-, Na-, K-, Rb-, and Cs-montmorillonites.

   Figure 15. Evolution of the filling up of interlayer water versus mean interlamellar swelling during water desorption of Li-, Na-, K-, Rb-, and Cs-montmorillonites.
The filling up of the interlamellar space is obtained from the ratio \( Q_{\text{int}}/Q_{\text{int,th}} \), where \( Q_{\text{int}} \) is the experimental amount of water in the internal space previously calculated. The mean interlamellar swelling is defined as the sum of \( W_i \) balanced by \( i \) (Figures 14 and 15). The lack of accuracy at small diffraction angles makes the filling-up estimate less precise at high relative pressures. Filling-up of the interlamellar space of montmorillonites lies mainly in the range between 50\% and 100\%. Higher values can be obtained. In the case of Li-montmorillonite, the evolution with time of XRD patterns suggests slower swelling kinetics than for iso-therms. In the case of K-montmorillonite, the external amount of adsorbed water seems to be underestimated taking into account the Harkins and Jura surface at low relative pressures. An increase of the external surface area occurs probably as it has been observed during adsorption for the same relative pressure.

Upon adsorption a large filling-up of the interlamellar space (\( >40\% \)), decreasing with increasing cation size, is observed at the very beginning of innercrystalline swelling. The filling-up increases with increasing swelling particularly for the larger cations. In the case of Li- and Na-montmorillonite, a decrease is observed during the formation of the two-layer hydrate state. For Na- and K-montmorillonite, the completion of the water monolayer on the external surfaces (Figure 13) occurs at the same relative pressure as the beginning of the formation of the one-layer hydrate. The same correspondence can be noted for the completion of the bilayer on the external surface of Li- and Na-montmorillonite and the beginning of the formation of the two-layer hydrate state. The surface pressure seems to be a driving force for swelling in addition to the heat of hydration. This was previously demonstrated in the case of Na-montmorillonite by Cases et al. (1992a).

Upon desorption a sharper decrease of the filling-up is observed for the closure of the layers except in the case of K-montmorillonite, which seems to keep water enclosed in the inter-aggregate porosity or interlamellar space. The final remaining filling-up decreases with increasing cation size, except for K\(^+\). In the case of Li- and Na-montmorillonite a decrease of the filling-up is also observed during the transition from the two-layer hydrate to the one-layer hydrate.

CONCLUSIONS

The study of five homoionic montmorillonites saturated by alkaline cations allows us to support the mechanism of adsorption and desorption of water vapor obtained on a single Na-montmorillonite by Cases et al. (1992a):

1) All the montmorillonites form interstratified hydrated states during adsorption. The opening of the layers occurs as defined relative pressure values which depend on the hydration energy of the cation and on \( d_{001} \) in the dry state. More homogeneous states are encountered during desorption.

2) Surface areas of Li- and Na-montmorillonite increase during water adsorption, as expected from the splitting of quasi-crystals. However a tendency to aggregation can be noted during the formation of the one-layer hydrate of K- and Rb-montmorillonite. Cs-montmorillonite remains unchanged during water vapor adsorption.

3) The bidimensional surface pressure acts as a driving force for the innercrystalline swelling only for small basal distances (\( d_{001} < 10 \text{ Å} \)) and for average energies of hydration, as is typically the case for Na-montmorillonite.

4) For all montmorillonites, the filling-up of the interlamellar space varies during the completion of a hydrated state. This corresponds to the solvation of exchangeable cations and to the filling-up of the remaining interlamellar space. Solvation of the larger cations involves a lower number of water molecules per cation.

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REFERENCES


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