

## ADSORPTION OF ALCOHOLS BY SMECTITES: II. ROLE OF THE EXCHANGEABLE CATIONS

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**ABSTRACT:** Calculations previously used to distinguish between methanol adsorbed in micropores between clay microcrystals (external) and that present in the interlamellar space (internal) of variable charge Ca-montmorillonites have been extended to homoionic Li-, Na- and Ba-montmorillonites. It is shown that both the shape and the magnitude of the internal isotherms are in good agreement with X-ray diffraction data. Furthermore, the apparent molecular packing of methanol in the interlamellar space is related specifically to the nature of the charge balancing cation.

In the first paper of this series (Annabi-Bergaya *et al.*, 1979) it was shown that the microporous volume between clay particles plays an important role during the adsorption of polar molecules such as methanol and isopropanol. About half the adsorbed molecules are occluded within these micropores. They enter at low relative pressure and in order to distinguish between the micropore content and interlamellar content it was necessary to combine desorption isotherms with X-ray diffraction data from montmorillonites having a variable lattice charge, these being prepared from Camp Berteau montmorillonite using the so-called 'Hofman-Klemen effect'.

In this paper the desorption of methanol from the same montmorillonite with its full charge balanced by different cations has been studied in conjunction with X-ray diffraction measurements.

### EXPERIMENTAL

Homoionic samples of the  $<2\ \mu\text{m}$  fraction of Camp Berteau montmorillonite were prepared as described by Annabi-Bergaya *et al.* (1979). These were dried at  $50^\circ\text{C}$ .

Desorption isotherms were obtained with the all-glass instrument shown as Fig. 2 in Annabi-Bergaya *et al.* (1979). Measurements were made at  $23^\circ\text{C}$  using methanol relative pressures ranging from 0–0.9.

X-ray diffraction data were obtained using the oriented aggregates remaining after evaporating a dilute suspension at room temperature. Copper  $K_\alpha$  radiation was used and the relative methanol vapour-pressure was regulated in the specimen chamber of the X-ray diffractometer.

### RESULTS

Desorption isotherms are shown in Fig. 1. These decrease in the order  $\text{Li}^+ > \text{Ba}^{2+} > \text{Na}^+$

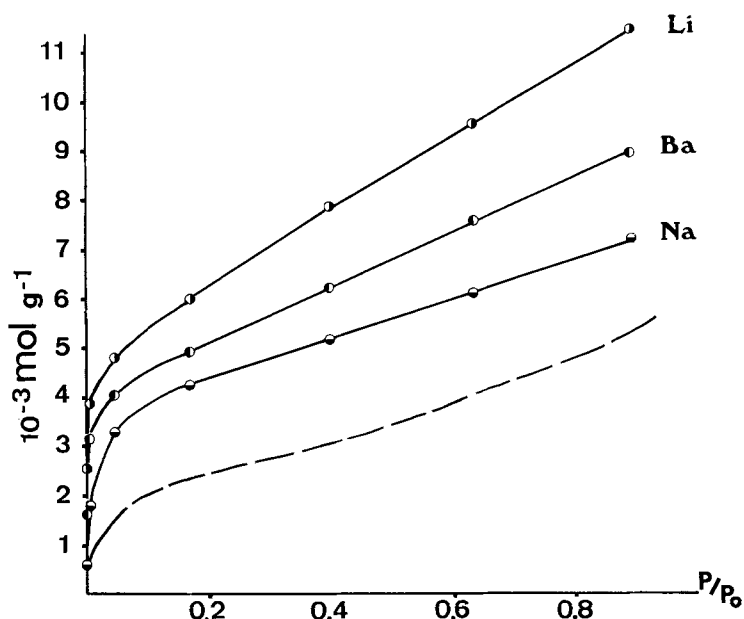


FIG. 1. Desorption isotherms of  $\text{CH}_3\text{OD}$  from homoionic montmorillonites at  $23^\circ\text{C}$ . The dashed curve represents the external isotherm.

in agreement with the relative polarizing power of the exchangeable cations. The dashed line in Fig. 1 represents what was previously termed the 'external isotherm', namely the contribution of the micropores to the adsorption isotherm (Annabi-Bergaya *et al.*, 1979).

The X-ray diffraction data are summarized in Table 1. The spacings corresponding to monolayer occupation of the interlamellar space were calculated from three rational basal reflections (001, 002 and 003). The range of relative pressures where the monolayer content is in equilibrium with the vapour phase depends upon the nature of the cation, decreasing in the order  $\text{Ba}^{2+} > \text{Na}^+ > \text{Li}^+$ . The  $d_{001}$  spacing corresponding to the monolayer state for  $\text{Ba}^{2+}$ ,  $\text{Na}^+$  and  $\text{Li}^+$  is  $12.7 \pm 0.2 \text{ \AA}$ . This value is noticeably smaller than that observed for the Ca-clay ( $13.2 \pm 0.2 \text{ \AA}$ ).

At higher relative pressures the basal spacing of the Na-montmorillonite remains near the value obtained for the monolayer state whereas for the Ba- and Li-clays 1–2 layer interstratification is indicated by the  $d_{001}$  spacing. At values of  $P/P_0 > 0.60$  a spacing approaching that of a two-layer solvate is obtained for Li-montmorillonite but neither the Ba- or Li-clay reaches the well-defined two-layer state observed for the Ca-clay at these relative pressures. At low relative pressures, the Na-clay is the only one in which a total desorption occurs, a spacing of  $9.7 \text{ \AA}$  being obtained at values of  $P/P_0 \leq 0.04$ . For the other two cations, 0–1 layer interstratified states are observed for  $P/P_0 < 0.04$ .

## DISCUSSION AND CONCLUSIONS

In order to determine the arrangement of the methanol molecules within the interlamellar space and their modes of binding with the internal surface and with the charge balancing cation it is important to calculate the internal isotherm. The easiest way to do this would

TABLE 1. CH<sub>3</sub>OD relative pressure ( $P/P_0$ ) vs corresponding  $d_{100}$  spacings. \*Indicates that three rational reflections (001, 002 and 003) were observed.

CH <sub>3</sub> OD relative pressure ( $P/P_0$ )	$d_{001}$ spacing		
	Ba <sup>2+</sup>	Na <sup>+</sup>	Li <sup>+</sup>
0.870	14.7	—	15.6
0.630	14.2	13.0	15.4
0.397	13.4	13.0	15.2
0.168	12.7*	12.7*	13.3
0.044	12.7*	12.7*	12.7*
0.004	12.7*	9.7	12.5
0	11.8	9.7	12.3

be to subtract the external isotherm from the experimental isotherms, an approach which has been shown to be valid for Ca-montmorillonites with variable charges. Objections can be made to this method, namely that the microporous volume could depend on the nature of the exchangeable cations. Indeed, it has been shown by various workers (Fripiat *et al.*, (1974); Poinسیون (1977)) that the texture of clay samples is sensitive to this factor.

However, since in montmorillonites with variable charges there is an almost constant contribution of the microporous volume to the total adsorption isotherm, it may be anticipated that this volume is not very sensitive to cationic substitutions in the interlamellar space. A better argument in favour of calculating the internal isotherm by subtracting the external isotherm represented in Fig. 1 from the experimental isotherm, would be the coherence between the X-ray diffraction data and the shape of these internal isotherms. It will now be shown that this coherence does exist.

The internal isotherms obtained in the manner described above are shown in Fig. 2. For the Na-clay, this isotherm is completely flat between  $P/P_0$  0.04 and 0.90. Obviously this plateau confirms the X-ray diffraction results which indicate that a monolayer is stable in the relative pressure region between 0.04 and 0.20. Also at higher pressure, the swelling is

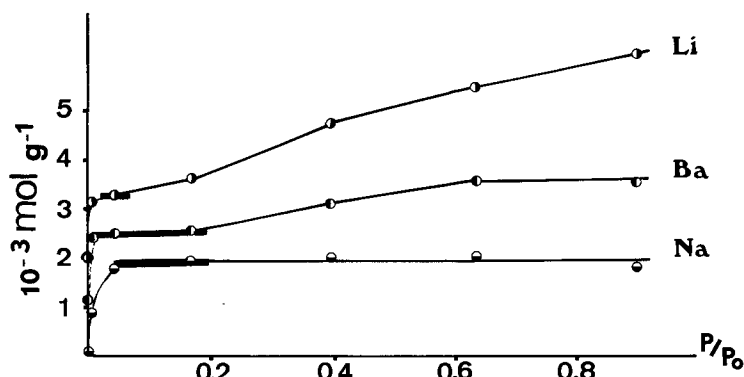


FIG. 2. CH<sub>3</sub>OD internal isotherms for homoionic montmorillonites. The extent of the monolayer domain is indicated by the heavy line.

TABLE 2. Cross-sectional area ( $\sigma$ ) computed from the molecular packing observed for CH<sub>3</sub>OD adsorbed by homoionic montmorillonites.  $n_m$  is the monolayer content obtained from Fig.2.

Cation	$n_m$ (mmol)	$\sigma$ (Å <sup>2</sup> )
Li <sup>+</sup>	3.3	19
Ba <sup>2+</sup>	2.5	24
Ca <sup>2+</sup>	2.5	25
Na <sup>+</sup>	2.0	31

near that observed for the monolayer solvate ( $d_{100}=13$  Å). For the Ba-clay, the plateau extends from about  $P/P_0=0.004$  to  $P/P_0\sim 0.20$ . Above this pressure, namely in the range where the X-ray diffraction data are indicative of a 2-1 layer interstratified state, the internal isotherm rises but at high relative pressure ( $P/P_0\approx 0.80$ ) the internal content is still much less than twice the monolayer content.

For the Li-clay the monolayer content obtained at  $P/P_0=0.04$  is about  $3.3 \times 10^{-3}$  mol/g as shown by the heavy line in Fig. 2. At  $P/P_0=0.87$  the internal content is about  $6.1 \times 10^{-3}$  mol/g, i.e. slightly below the experimental value expected for the two-layer solvate. This is again in agreement with the information contained in Table 1 since the  $d_{001}$  spacing is  $15.5 \pm 0.1$  Å. An interesting consequence is the fact that the monolayer content changes markedly with the nature of the charge balancing cations. Within the interlamellar space the molecular packing ( $\sigma$ ) can be calculated as follows

$$n_m \times N \times \sigma = \frac{a \times b \times N}{M}$$

where  $n_m$  is the monolayer content determined from the results in Fig. 2;  $a \times b$  is the basal area of the unit cell,  $M$  is the molecular weight of the unit cell and  $N$  is the Avogadro number. The values of  $\sigma$  are shown in Table 2. As anticipated,  $\sigma$  shows a variation of about 50% in going from Li<sup>+</sup> to Na<sup>+</sup> but there is a clear indication that different molecular arrangements exist in the interlamellar space depending on the nature of the exchangeable cation.

These arrangements will be studied using the IR data in the next paper.

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RÉSUMÉ: Les calculs précédemment utilisés pour faire la distinction entre le méthanol adsorbé par les micropores situés entre les microcristaux d'argile (externe) et celui qui est présent dans l'espace interlamellaire (interne) des montmorillonites de Ca à charge variable ont été appliqués aux montmorillonites homoïoniques de Li, Na et Ba. On montre que tant la forme que la

grandeur des isothermes internes présentent une bonne corrélation avec les données de diffraction des rayons X. En outre, le remplissage apparent de l'espace interlamellaire par les molécules de méthanol a une relation spécifique avec la nature du cation compensateur.

**KURZREFERAT:** Bei der Adsorption von Methanol an verschieden geladenen Ca-Montmorilloniten kann mit Hilfe von Berechnungen eine Unterscheidung getroffen werden zwischen dem Methanolanteil, der in Mikroporen zwischen den Tonmikrokristalliten (extern) adsorbiert wird und dem Anteil, der sich in Zwischenschichten (intern) befindet. Diese Berechnungen wurden auf Li-, Na- und Ba-Montmorillonite ausgedehnt. Dabei kann gezeigt werden, daß sich sowohl die Form als auch die Größe der internen Isotherme in guter Übereinstimmung mit röntgenographisch erhaltenen Daten befindet. Weiterhin ist die scheinbar molekulare Packung des Methanols in den Zwischenschichten besonders auf die Natur der ladungsausgleichenden Kationen zurückzuführen.

**RESUMEN:** Los cálculos utilizados anteriormente para distinguir entre el metanol adsorbido en los microporos entre los microcristales (externo) de arcilla y el presente en el espacio interlaminar (interno) de Ca-montmorillonitas de carga variable se han empleado también para les montmorillonitas homioiónicas -Li, -Na y -Ba. Se demuestra que tanto la forma como la magnitud des las isothermas internas concuerdan bien con los datos de difracción de rayos X. Además, la aglomeración molecular aparente del metanol en el espacio interlaminar está relacionada específicamente con la naturaleza del catión equilibrador de la carga.