Sorption of Hexadecylammonium Ions on Reduced Charge Montmorillonite

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Using lithium fixation, a series of montmorillonite samples were prepared which had reduced negative layer charges. The sorption of hexadecylammonium (HDA) ions was found to be controlled by the remaining layer charge. The relation between the amount of HDA sorbed by one gram of Li-treated montmorillonite and the cation-exchange capacity (CEC) of the sample was found to be

$$Q_{HDA}/(\text{mmol g}^{-1}) = 0.214 + 1.723\ CEC$$

for CEC values lower than 0.75 mmol g^{-1}. This relation was valid if the HDA present was sufficient to reach the saturation point. The amount of exchangeable Ca^{2+} ions desorbed after HDA sorption was only 83 to 93 % of the remaining CEC.

Following the interaction of alkylamine with a layer sorbent, intercalation compounds are formed. Intercalation of neutral molecules is common in materials with uncharged layers, e.g. ReCl$_3$, Ni(CN)$_2$, V$_2$O$_5$ · xH$_2$O [1]. If the layers are negatively charged and separated with interlayer space and exchangeable cations, the main intercalation mechanism is ion exchange. Such sorbents are smectites, vermiculites, vanadates(V) (CaV$_6$O$_{16}$ · xH$_2$O, KV$_3$O$_8$), niobates(IV, V) (K$_4$Nb$_3$O$_8$, K$_4$Nb$_6$O$_{17}$), and some other inorganic compounds [1].

The amount and the type of arrangement of intercalated alkylamines depends on the length of the alkyl chains, type of the sorbent surface, and the degree of sorption. However, other important factors affecting the sorption of alkylamines and the properties of the resulting intercalation compounds are the density and the magnitude size of the layer charge [2, 3].

After thermal treatment of Li-saturated montmorillonite exchangeable lithium ions migrate towards the vacant octahedral sites in layers and reduce layer charge [4—6]. The properties of reduced charge montmorillonites (RCM) have been studied strictly as a function of the layer charge [6—9]. In the present work, RCM were prepared as reported earlier by Bujdák et al. [10]. The influence of the remaining layer charge on the sorption of hexadecylammonium cations was then studied.

EXPERIMENTAL

A fraction with the particles smaller than 2 μm separated by sedimentation of bentonite from Jelšový Potok was used. It was Ca-saturated by repeated (3 times) washing with 1 M-CaCl$_2$ solution, washed till Cl$^-$ anions were present, dried at 60 °C and ground to pass a 0.2 mm sieve. The only mineral identified by X-ray diffraction in this sample was montmorillonite. Its structural formula calculated from chemical analysis is

$$(Si_{7.98}Al_{0.02})(Al_{3.01}Fe_{0.23}Mg_{0.76})O_{20}(OH)_4(Ca_{0.37}Na_{0.01}Mg_{0.01}K_{0.01})$$
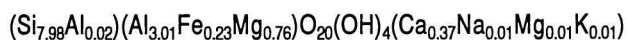
Li-exchange was carried out by repeated (3 times) saturation with lithium chloride solution of concentration 1 mol dm^{-3}, and subsequent washing, drying, etc. as in the case of Ca-exchanged fraction. The exchanged Li-forms were heated at the selected temperatures for various time (up to 24 h) to obtain samples with desirable values of the layer charge (Table 1). Lithium ions in heated samples were exchanged for Ca^{2+} ions and determined. Calcium saturated samples were treated as described above. Details of the method are given in paper [10].

Table 1. Temperatures and Times of Heating in the Preparation of the Samples and Reduction of CEC and Layer Charge

Sample	θ/°C (t/h)	CEC mmol g^{-1}	Layer charge %
A	–	1.042	100.0
B	135 (2)	0.794	76.2
C	135 (4)	0.771	73.9
D	150 (1)	0.715	68.6
E	150 (2)	0.673	64.6
F	135 (24)	0.579	55.5
G	150 (10)	0.533	51.2
H	180 (3)	0.379	36.4
I	210 (24)	0.158	15.2

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Hexadecylammonium acetate in an equivalent amount of acetic acid of concentrations 0.005, 0.01, 0.03, 0.05, 0.07, and 0.1 mol dm^{-3} was used as sorbate. For each run 25 cm^3 of the solution were mixed with 1 g of clay at 60 °C for 2 h. After 24 h the liquid and solid phases were separated by filtration at 60 °C and washed with distilled water.

The amount of sorbed hexadecylammonium was calculated from the determination of carbon in the solid phase, using a CHN analyzer, type 1104 (Erba). Desorbed calcium was determined in solution by complexometric titration with chelatone 3.

RESULTS AND DISCUSSION

The sorption curves obtained for samples A to I with various layer charge are given in Fig. 1. The amount of hexadecylammonium sorbed on montmorillonite Q_{HDA} is expressed in mmol on 1 g of clay. For each layer charge the amount of sorbed HDA increases until the interlayer space and external surface is saturated. Obviously the layer charge controls the saturation point. Fig. 2 presents the dependences of HDA sorption on the layer charge. HDA concentrations of 0.005 and 0.01 mol dm^{-3} are too low to saturate any sample. For 0.03 M solution of HDA only sample I is completely saturated. For 0.05 M-HDA the samples E to I are saturated and B to D are very close to saturation. A similar situation pertains for 0.07 M-HDA. The adsorption curve for sample A (Fig. 1) does not show full saturation.

The relationship between the maximum value for Q_{HDA} and CEC is given in Fig. 3. The discrepancy
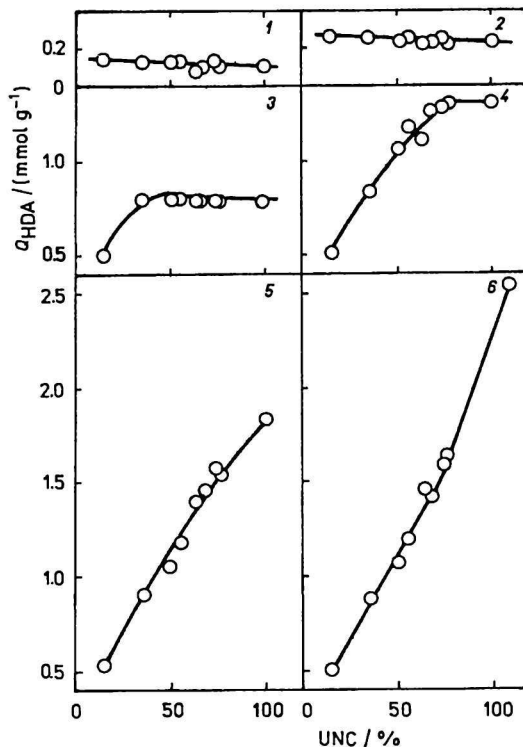

Fig. 2. Sorption of HDA as a function of increasing unsaturated negative layer charge (UNC) of montmorillonite. c_{HDA}/(mol dm^{-3}): 1. 0.005; 2. 0.01; 3. 0.03; 4. 0.05; 5. 0.07; 6. 0.1.

between the amount sorbed and the CEC suggests that some portion of the HDA is held on the surface in molecular state by van der Waals forces. A least-square evaluation of the first six points (CEC =
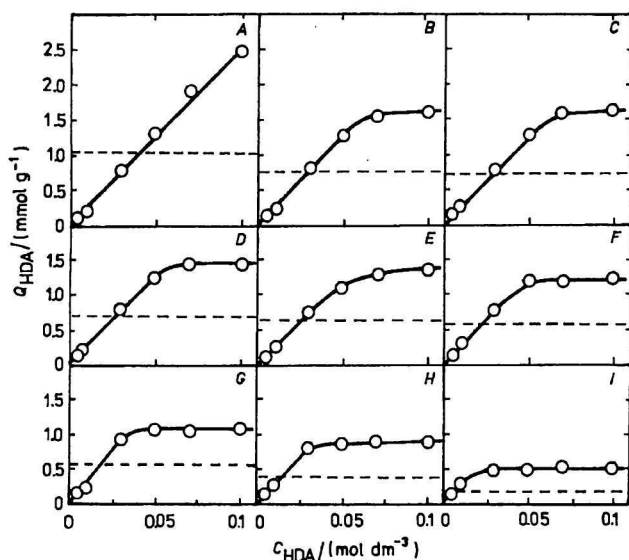

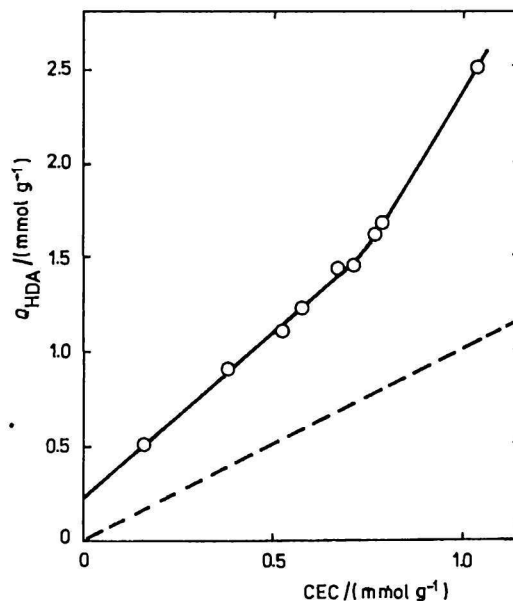**Fig. 1.** Sorption of HDA on montmorillonite with various layer charge (A to I). Dashed lines show the CEC of the samples.

Fig. 3. Sorption of HDA related to the CEC of montmorillonite with the layer charge reduced by Li fixation. c_{HDA} = 0.1 mol dm^{-3}. — — — The CEC of the sample.
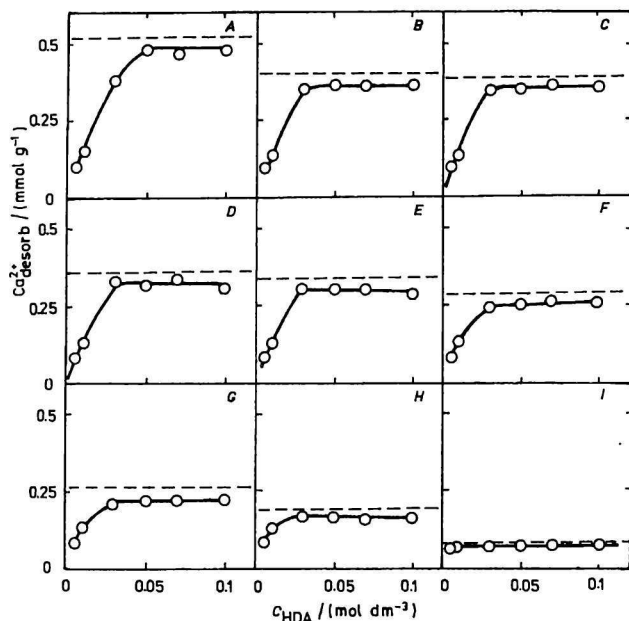
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Fig. 4. The Ca^{2+} released by exchange for HDA ions from montmorillonite with layer charge reduced by Li fixation. Dashed lines represent the amount of exchangeable Ca^{2+} ions in the samples A—I.

0.16—0.71 mmol g^{-1}) gave an empirical relation between Q_{HDA} and CEC

$$Q_{HDA}/(\text{mmol g}^{-1}) \doteq 0.21 + 1.72 \text{ CEC} \quad (r = 0.99) \quad (1)$$

The value of 0.21 mmol g^{-1} derived from eqn (1) is assumed to be the amount of HDA sorbed on the external or internal surface of crystallites. The slope of the line calculated for the last three points is 3.63 compared to 1.72 from eqn (1). The sorption of HDA at CEC values between 0.77 mmol g^{-1} and 1.04 mmol g^{-1} is more than double the CEC of the sample, while for CEC values below 0.75 mmol g^{-1} it is lower (eqn (1)). Lithium fixation causes interstratification of nonswelling (0.96 nm) and swelling layers [10]. Such interstratification can bring about a limitation in the swelling ability of the system. Swelling ability and density of layer charge is reflected in the above-mentioned change of the slope.

Sorption of HDA from solution is accompanied by the release of exchangeable Ca^{2+} cations from the montmorillonite, which is presented in Fig. 4. For samples A to C the first three points represent equivalent ion exchange of Ca^{2+} for HDA$^+$. This is valid for the first two points in samples D to H. These results confirm that the oversaturation process does not proceed until the ion-exchange reaction is complete. The amounts of desorbed Ca^{2+} ions represent 83 to 93 % of exchangeable Ca^{2+} ions present in the samples. Some calcium cations are trapped in the structure of montmorillonite and are not released even at the highest concentration of hexadecylammonium ions.

CONCLUSION

The sorption of hexadecylammonium on Li-treated montmorillonite is controlled by the unsaturated negative layer charge. The lower the layer charge, the lower the HDA amount sorbed on the solid phase. Cation exchange is the first step of the process, and oversaturation the second one.

REFERENCES

1. Whittingham, M. S. and Jacobson, A. J., *Intercalation Chemistry*, p. 595. Elsevier, Amsterdam, 1982.
2. Lagaly, G. and Weiss, A., *Proc. Int. Clay Conf., Tokio, 1969*, Vol. I, p. 61. Israel University Press, Jerusalem, 1969.
3. Lagaly, G., *Solid State Ionics 22*, 43 (1986).
4. Hofmann, U. and Klemen, R., *Z. Anorg. Allg. Chem. 262*, 95 (1950).
5. Tettenhorst, R., *Am. Mineral. 47*, 769 (1962).
6. Calvet, R. and Prost, R., *Clays Clay Miner. 19*, 175 (1971).
7. Clementz, D. M. and Mortland, M. M., *Clays Clay Miner. 22*, 223 (1974).
8. Clementz, D. M., Mortland, M. M., and Pinnavaia, T. J., *Clays Clay Miner. 22*, 49 (1974).
9. Brindley, G. W. and Ertem, G., *Clays Clay Miner. 19*, 399 (1971).
10. Bujdák, J., Slosiariková, H., Nováková, L., and Číčel, B., *Chem. Papers 45*, 499 (1991).

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