

Interaction of Long Chain Alkylammonium Cations with Reduced Charge Montmorillonite

J. BUJDÁK and H. SLOSIARIKOVÁ

Department of Inorganic Chemistry, Komensky University, 84215 Bratislava, Czechoslovakia.

B. ČÍČEL

Institute of Inorganic Chemistry, Slovak Academy of Sciences, 84236 Bratislava, Czechoslovakia.

(Received: 11 October 1991; in final form: 13 March 1992)

Abstract. Reduced charge montmorillonites (RCM) were prepared using lithium thermal treatment. The sorption of octylammonium (OA), dodecylammonium (DDA) and hexadecylammonium ions (HDA) on differently charged samples were studied. The amounts of DDA and HDA sorbed on each RCM exceed the cation exchange capacity (CEC) but that of OA exceeds only the CEC of samples with the lowest CEC. The sorption is affected not only by the layer charge but also by the formation of collapsed interlayer spaces in the lowest charged montmorillonites. X-ray measurements confirmed the decrease of the layer charge after lithium thermal treatment and the layer charge heterogeneity in RCMs.

Key words. Alkylammonium sorption, charge reduction, lithium thermal treatment, montmorillonite.

1. Introduction

The cation exchange capacity decreases after the thermal treatment of Li saturated montmorillonite [1–5]. Most authors suggest that small Li^+ cations migrate from the interlayer positions into the vacant octahedral sites and reduce the layer charge. Glaeser and Méhring [5], and Calvet and Prost [6] claimed that migration of small cations (Li^+ , Be^{2+} , Mg^{2+} , Al^{3+}) into the structure is a general phenomenon.

Many papers have been published concerning the alkylammonium exchange reaction with montmorillonite [7–10]. The arrangement of alkyl chains depends on the layer charge and the alkyl chain length [8, 11–17]. Short-chain alkylammonium cations are arranged into monolayers; long chain cations form bilayers. Pseudo-trilayers of kinked alkyl chains were observed using the highly charged smectites and long chain alkylamines or if the amount of sorbed alkylammonium cations exceeds the CEC. Besides trimolecular layers, paraffinic type of layers may be formed in these cases.

The aim of this study was to investigate the interaction of reduced charge montmorillonite with aqueous solutions of alkylammonium ions, and the effect of layer charge on the sorption and arrangement of alkyl chains in the interlayer space.

2. Experimental

2.1. PREPARATION OF RCMs

Montmorillonite was isolated as a fine fraction ($< 2 \mu\text{m}$) by sedimentation of a 4% aqueous suspension of Jelšovský Potok bentonite (Central Slovakia). The Li^+ ex-

changed form was prepared by multiple treatments with lithium chloride solution. Then it was washed with distilled water, until the excess of salt was removed. The Li saturated montmorillonite was left to dry slowly in air and then crushed to a powder. The Li^+ exchanged form was heated for 2–24 hours at temperatures of 135–210°C (Table I) to prepare the RCMs. These samples were saturated with

Table I. Temperature and time of lithium thermal treatments, and the CEC and UNC values of the montmorillonite samples.

| Sample | T/t (°C/h) | CEC (meq/g) | UNC* (%) |
|--------|--------------|-------------|----------|
| 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 |

* UNC (unsaturated negative charge) is expressed in percent of the value of CEC obtained for the original sample A.

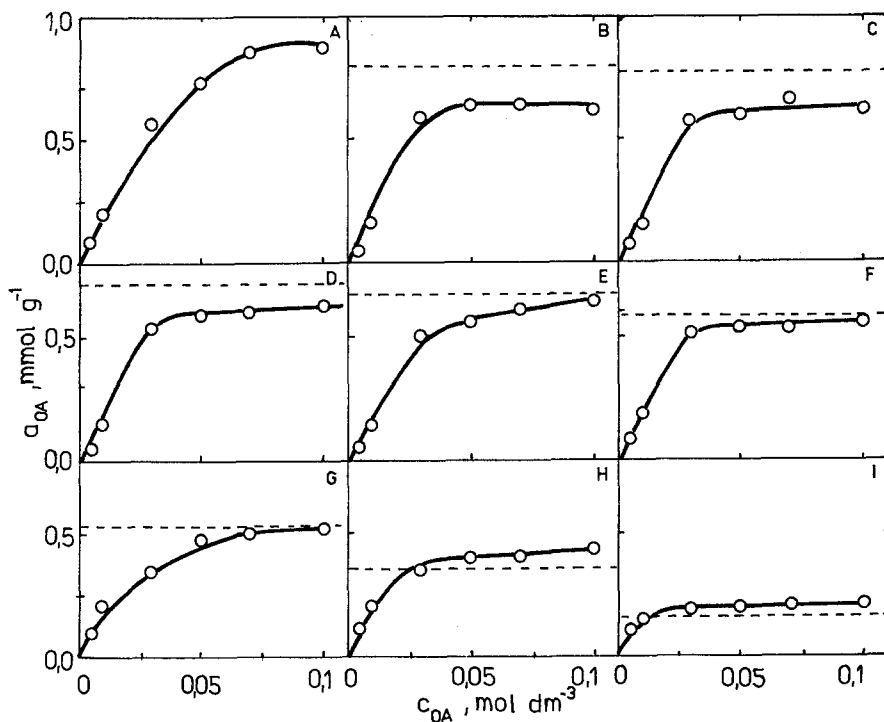


Fig. 1. Sorption of OA on montmorillonites with various layer charge (A–I). Dashed lines show the CEC of the samples.

calcium chloride to remove exchangeable Li^+ . The CEC values of the calcium exchanged forms of RCMs are listed in Table I.

2.2. SORPTION OF ALKYLAMMONIUM CATIONS ON MONTMORILLONITE

Solutions of alkylammonium salts were prepared by dissolution of the alkylamine in an aliquot amount of acetic acid and diluted to the defined volumes with distilled water. The following alkylamine concentrations were used: 0.005; 0.01; 0.03; 0.05; 0.07; 0.1 mol dm^{-3} . Montmorillonite (1 g) was treated with 25 mL of an alkylammonium solution at 60°C for 6 h. The suspension was kept at room temperature for a further 24 h. The suspension was filtered at 60°C and the excess of alkylammonium salt and free amine were washed out with hot distilled water. Displaced calcium cations were determined by complexometric titration. After air drying, the samples were ground to pass a 0.5 mm sieve.

The amount of sorbed amine/ammonium was calculated from carbon analysis (CHN analyzer, Hewlet-Packard, model 185).

A Philips diffractometer model PW 1050 and CuK_α radiation were used for X-ray diffraction.

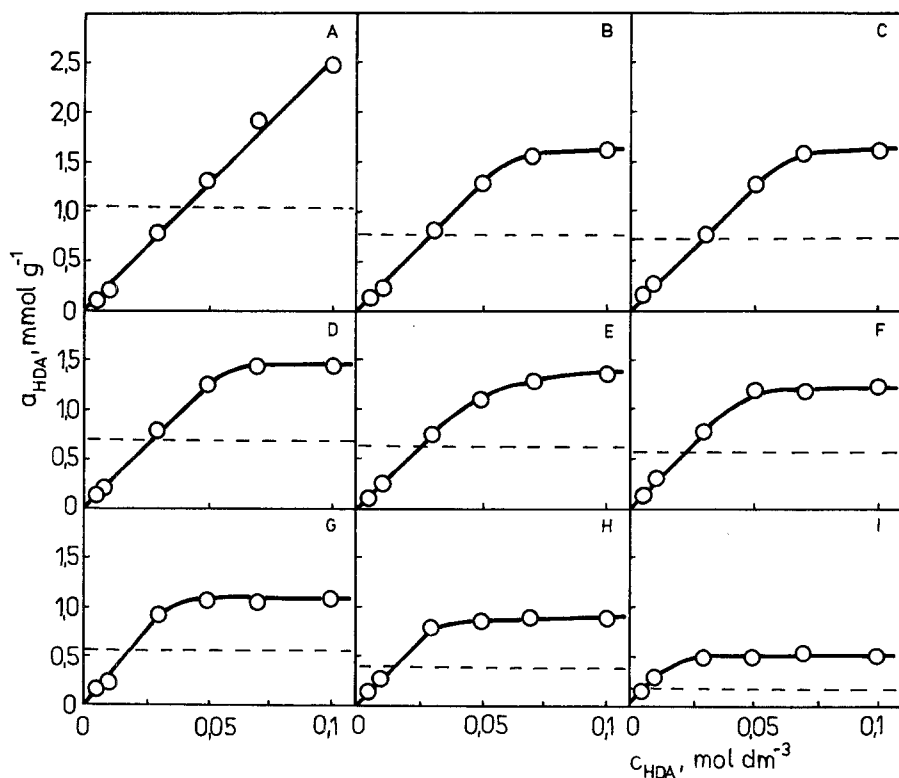


Fig. 2. Sorption of DDA on montmorillonites with various layer charge (A-I). Dashed lines show the CEC of the samples.

3. Results and Discussion

Figures 1–3 show the relation between the amount of sorbed alkylammonium cations and the initial concentration of the alkylammonium solution. The sorption increases with the amount of alkylammonium cations in solution. The shape of the curves is close to linear in the range of lower concentrations. At higher concentrations, a limiting sorption was achieved. The value of this limit sorption depends on the CEC of montmorillonite and on the length of the alkylamine chains. Two main factors probably affect the sorption:

1. The type of binding forces between alkylamine or alkylammonium ion and the silicate matrix, (ionic interaction, van der Waals forces, H-bond).
2. Site of the bonding (internal surface, external surface).

The bonding between alkylammonium cations and the charged silicate surface is electrostatic, but additional physical, non-Coulombic forces cause adsorption of alkylamine. Van der Waals forces between the aliphatic residues and the surface, as well as between adjacent molecules or ions, contribute to the adsorption forces and become progressively significant when the molecular weight increases [18]. Therefore the sorption of HDA and DDA is higher than that of OA and exceeds the CEC of all samples.

However, the sorption of OA is in excess of the CEC of the samples with the lowest charge on the layers (H, I). It results from the formation of collapsed

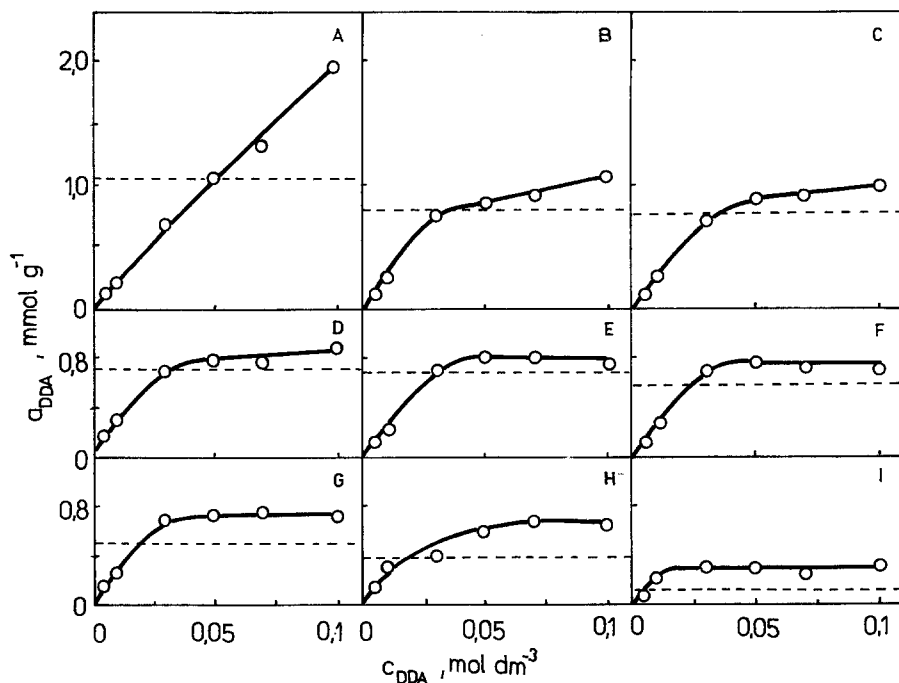


Fig. 3. Sorption of HDA on montmorillonites with various layer charge (A–I). Dashed lines show the CEC of the samples.

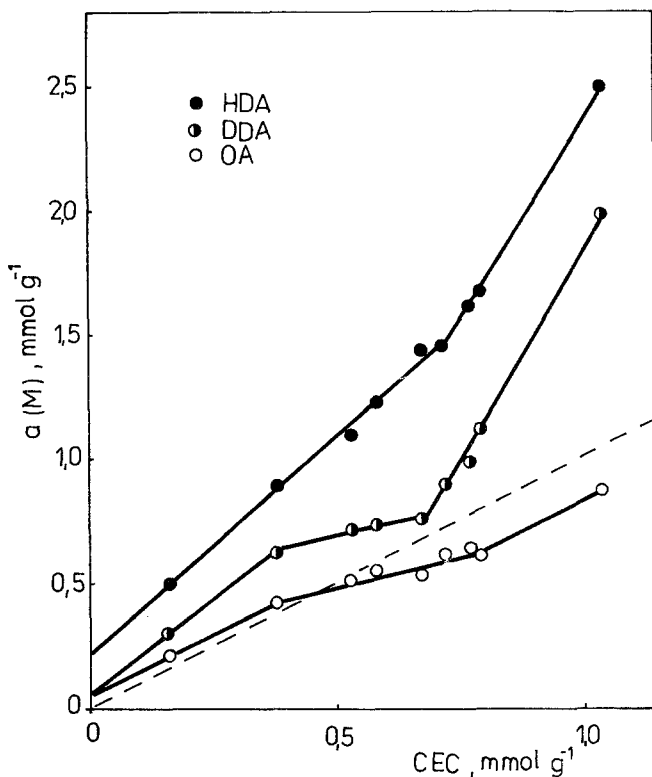


Fig. 4. Sorption of alkylammonium salts as a function of the layer charge of the montmorillonite. The concentration of the alkylammonium solution was 0.1 mol dm^{-3} .

non-swelling interlayers in these lowest charge samples. It can be assumed that the external surface, including the edges of the collapsed layers, is the main site for amine bonding. It follows that the ratio of alkylamine bonded by van der Waals forces to alkylamine bonded by Coulombic interaction is greater on the external than on the internal surface.

Probably, the amount of van der Waals bonded amine on the basal surface is also affected by the arrangement of the amine chains. Reorientation to the paraffinic structure enhances the empty space for the intercalation of further molecules of alkylamine.

The dependence of HDA sorption on unsaturated negative charge (UNC) was described separately [19]. The sorption of alkylamines from the 0.1 mmol dm^{-3} solution of calcium saturated montmorillonites as a function of the layer charge are given in Figure 4. It is affected by the changes of the layer charge density, the size of the available surface area and by the length of the alkyl chains. The different slopes are probably caused by reorientation of the organic chains. This reorientation enables the oversaturation by van der Waals bonded molecules or ion pairs [20].

The amounts of calcium cations replaced by alkylammonium ions were measured. The increase of alkylamine concentration leads to larger replacement of

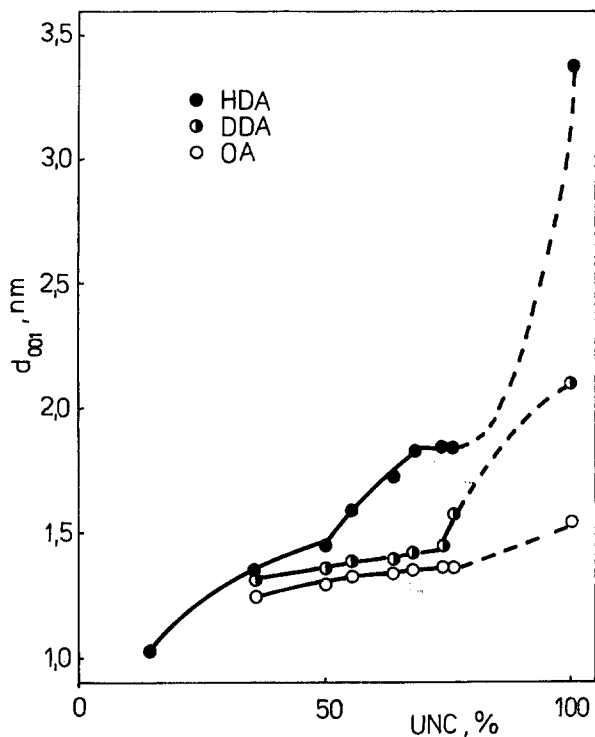


Fig. 5. d_{001} Values of alkylammonium derivatives as a function of the layer charge of the montmorillonite. The compounds were prepared by sorption from solutions of concentration 0.1 mol dm^{-3} .

calcium up to a maximum value of about 90% CEC. Adjacent organic cations may block the access of the interlayer liquid still containing calcium ions [21]. The effect of the alkylamine chain length and the UNC of RCM on calcium replacement was not observed.

The effect of layer charge on the basal spacing of alkylammonium–montmorillonites formed by sorption from solution of the highest concentration of alkylamine is shown in Figure 5. Five types of interlayers can be formed with increasing charge density and chain length: no replacement, monolayers, bilayers, pseudotrimolecular layers and paraffinic type arrangements. Sample I, with the lowest charge, forms no intercalated compounds. The monolayer plateau (d_{001} is about 1.36 nm) is obtained in samples with relatively low layer charge. The values of d_{001} for sample H confirm that a part of the interlayers remain collapsed. This sample has a mixed-layer structure. By increasing the layer charge, monolayers rearrange into bilayers (d_{001} is 1.77 nm). This rearrangement was observed at the highest layer charge in the OA–montmorillonite (samples B, A); Sample A–OA also contains monolayers and rearrangement is not complete. Increasing the length of the alkylamine leads to lower values (samples (G–B)–DDA; samples (H–E)–HDA). The last types of alkylamine arrangement in the interlayer are pseudotrimolecular layers and paraffinic layers. Sample A forms intercalation compounds exhibiting one of these arrangements with DDA and the paraffinic type of layers with HDA. However, the

d_{001} values of samples (B–D)–HDA exceed 1.77 nm. It may be assumed that there are also pseudotrimolecular layers in the interlayers. The results are consistent with those of Lagaly and Weiss [11] and confirm the charge heterogeneity in the original montmorillonite and prepared RCM samples. Charge heterogeneity is the cause of the mixed layer structure of the alkyl-ammonium derivatives.

References

1. U. Hofmann and R. Klemen: *Z. Anorg. Chem.* **262**, 95 (1950).
2. R. Green-Kelly: *Clay Min. Bull.* **2**, 52 (1953).
3. J. P. Quirk and B. K. G. Theng: *Nature* **187**, 967 (1960).
4. R. T. Tettenhorst: *Am. Mineral.* **47**, 769 (1962).
5. R. Glaeser and J. Méring: *C. R. hebd. Séanc. Acad. Sci. Paris* **265D**, 833 (1967).
6. R. Calvet and R. Prost: *Clays Clay Min.* **19**, 175 (1971).
7. C. T. Cowan and D. White: *Trans. Faraday Soc.* **54**, 691 (1958).
8. A. Weiss: *Clays Clay Min.* **10**, 191 (1963).
9. B. K. G. Theng, D. J. Greenland, and J. P. Quirk: *Clay Min.* **7**, 1 (1967).
10. E. F. Vansant and J. B. Uytterhoeven: *Clays Clay Min.* **20**, 47 (1972).
11. G. Lagaly and A. Weiss: *Proc. Int. Clay Conf. Tokyo* (1969), Vol. 1, ed. L. Heller, Israel University Press, Jerusalem, p. 61.
12. G. Lagaly and A. Weiss: *Proc. Inter. Clay Conf. Mexico City* (1975), ed. S. W. Bailey, Applied Publishing, Wilmette, Illinois, p. 157.
13. M. S. Stul and W. J. Mortier: *Clays Clay Min.* **22**, 392 (1974).
14. G. Lagaly, M. Fernandez Gonzalez and A. Weiss: *Clays Clay Min.* **11**, 173 (1976).
15. G. Lagaly: *Clays Clay Min.* **16**, 1 (1981).
16. P. B. Malla and L. A. Douglas: *Agr. Abst.* (1984) Annual Meetings of ASA, CSSA, SSSA, Las Vegas, Nevada, p. 274.
17. A. C. Olis, P. B. Malla and L. A. Douglas: *Clays Clay Min.* **25**, 39 (1990).
18. W. H. Slabaugh and F. Kupka: *J. Phys. Chem.* **62**, 599 (1958).
19. J. Bujdák, H. Slosiariková and B. Číćel: *Clay Min.* submitted.
20. A. Patzkó: *Proc. 7th Euroclay Conf. Dresden* 91, Greifswald (1991), p. 827.
21. James L. McAtee, Jr.: *Am. Mineral.* **44**, 1230 (1959).