

IR Spectra of Octadecylammonium-Montmorillonite in the Range of the Si—O Vibrations

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Abstract. The bonding of octadecylammonium on the internal surface of montmorillonite influences the arrangement of the SiO_4 tetrahedra in the structure of montmorillonite. The effect can be observed in smectites with a relatively well-ordered structure as seen in the IR spectra of octadecylammonium-montmorillonite in the range of Si—O vibrations.

Key words. Clay, smectites, montmorillonite, octadecylammonium-montmorillonite, IR spectra, Si—O vibrations.

1. Introduction

A relatively large number of papers deal with the study of organoclay systems, many of them having been reviewed in monographs [1, 2]. Since 1949, when Jordan's study [3] appeared, the montmorillonite-*n*-alkylammonium systems and their technical utilization have been extensively investigated.

In our previous paper [4], we described the ion-exchange mechanism of the interaction between octadecylammonium and montmorillonite, with Na^+ , Ca^{2+} or Mg^{2+} as exchangeable cations. In the cases of Cu^{2+} and Co^{2+} as exchangeable cations, the organic substance is partly sorbed in the form of neutral molecules or complex cations. In any case the sorption extends the ion-exchange capacity.

The aim of the present study is to explain the changes caused by bound octadecylammonium in the region of the Si—O stretching vibrations in the tetrahedral network of a montmorillonite.

2. Experimental

The isolation of montmorillonite from bentonite (Jelšovský Potok, CSFR), the preparation of the Ca form and of the organomontmorillonites with octadecylammonium, their sedimentation volumes, interplanar distances and activity towards sorption of water vapour, have been described previously [4].

The IR spectra of the organomontmorillonites and of the starting Ca montmorillonite in Nujol mulls and KBr pellets were measured on a Perkin Elmer 598 spectrophotometer. A Philips PW 1050 goniometer (35 kV, 20 mA, CuK_α radiation) was used in the X-ray diffraction analysis.

3. Results and Discussion

The IR spectra of the organomontmorillonites and of the starting Ca montmorillonite are shown in Figures 1 and 2. It can be seen from Figure 1 that the band centred at 3620 cm^{-1} , corresponding to the stretching vibrations of the structural OH groups [5], is not influenced by increased amount of the organic cation sorbed. On the other hand, the spectra reveal a release of water molecules from the surface and interlayer space. In the spectrum of Ca montmorillonite this is manifested by

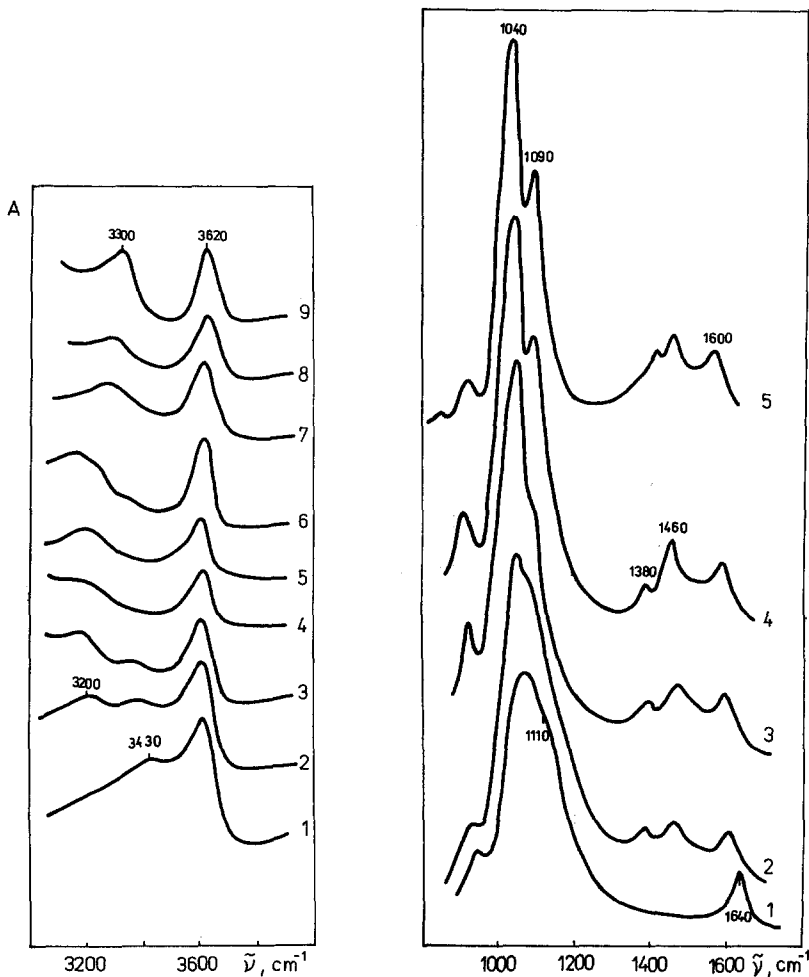


Fig. 1 (left). Infrared spectra ($3100\text{--}3900\text{ cm}^{-1}$) of Ca montmorillonite (1) and organomontmorillonites at different contents of bound octadecylammonium. (2) 0.60 mmol g^{-1} ; (3) 0.69 mmol g^{-1} ; (4) 1.18 mmol g^{-1} ; (5) 1.42 mmol g^{-1} ; (6) 1.47 mmol g^{-1} ; (7) 1.78 mmol g^{-1} ; (8) 2.12 mmol g^{-1} ; (9) 2.32 mmol g^{-1} .

Fig. 2 (right). Infrared spectra ($900\text{--}1700\text{ cm}^{-1}$) of Ca montmorillonite (1) and organomontmorillonites at different contents of bound octadecylammonium. (2) 0.32 mmol g^{-1} ; (3) 0.60 and 0.69 mmol g^{-1} ; (4) 1.18 , 1.42 , 1.47 , and 1.78 mmol g^{-1} ; (5) 2.12 and 2.32 mmol g^{-1} .

the disappearance of the band at 3430 cm^{-1} , assigned to O—H stretchings in water molecules bound by hydrogen bonds. This band disappears if the amount of the $\text{C}_{18}\text{H}_{37}\text{NH}_3^+$ cation bound to the montmorillonite is greater than 0.69 mmol g^{-1} . In this case, the ion-exchange reaction is complete and the product formed does not contain the exchangeable Ca^{2+} cations. However, for lower amounts of the bound organic cation (0.60 mmol g^{-1}), a slight shift of the OH stretching band to lower wavenumber was observed. This may be due to the strengthening of hydrogen bonds during the process of sorption and desorption.

The N—H stretching vibrations can be observed in a relatively wide range from $3350\text{--}3150\text{ cm}^{-1}$. Figure 1 shows that with increasing amount of bound octadecylammonium the N—H stretching bands are shifted to markedly higher wavenumbers. This is obviously due to the strengthening of the N—H bonds in $-\text{NH}_3^+$ and $-\text{NH}_2$ groups of the alkylammonium chain. The greatest shift was observed at an organic substrate content in the range $1.47\text{--}1.78\text{ mmol g}^{-1}$. At the highest amount of the organic sorbate, the N—H stretching vibration was observed at 3300 cm^{-1} . If the amount of organic compound sorbed is extending the value of the ion-exchange capacity, the N—H bond strengthening can be explained by sorption of neutral molecules of octadecylamine, with $\nu(\text{NH}_2)$ values higher than for $\nu(\text{NH}_3^+)$. However, it must be emphasized that this process occurs at higher sorption values, and it can probably also be related to a reorientation of the chains in the interlayer space of the montmorillonite to an arrangement which allows a higher sorption than that corresponding to its ion-exchange capacity.

In the range $1200\text{--}1700\text{ cm}^{-1}$ bands can be observed from the δCH_3 vibrations (1380 cm^{-1} and 1460 cm^{-1}), which are not influenced by an increasing amount of the sorbed organic cations. The release of water molecules is connected with the shift of the $\delta\text{ OH}$ band of water molecules to 1600 cm^{-1} which corresponds to $\delta\text{ NH}_3^+$ vibrations.

We have reported [4] that the structure of the interlayer space of a montmorillonite depends, at a constant sorbent, on the amount of bound $\text{C}_{18}\text{H}_{37}\text{NH}_3^+$ cations. We have identified a double-layer arrangement with alkylammonium chains parallel to the silicate surface (d_{001} value 1.8 nm , organic cation amount 0.69 mmol g^{-1}), a perpendicular one-layer arrangement (d_{001} value from 2.1 to 2.8 nm , organic cation amount $1.18\text{--}1.78\text{ mmol g}^{-1}$) and a perpendicular double-layer arrangement (d_{001} value from 4.2 to 4.7 nm , organic cation amount $2.12\text{--}2.32\text{ mmol g}^{-1}$).

The sorbate chain arrangement in the interlayer space is accompanied by changes in the Si—O stretching band position in the tetrahedral network. As seen from Figure 2, the shoulder in the IR spectrum of the starting montmorillonite at about 1110 cm^{-1} is markedly reduced at the perpendicular sorbate chain orientation (spectrum 4).

Generally, the most intense IR bands of dioctahedral smectites occur in the range $1000\text{--}1200\text{ cm}^{-1}$, which correspond to silicon—basal oxygen vibrations, Si—O—(Si), and to perpendicular silicon—apical oxygen vibrations, Si—O—(Al), i.e. those involving oxygens from the common plane in the tetrahedral and octahedral network [5]. The shoulder at about 1110 cm^{-1} is assigned just to that perpendicular vibration.

Lerot and Low [6] have studied the changes in Si—O stretching positions during the process of swelling of montmorillonite. They found that the increasing water amount did not influence the individual Si—O band intensities and positions. At higher water content a marked increase was observed of the intensity of the absorption band, corresponding to the perpendicular vibration. This effect may be explained by changes in layer orientation as a consequence of an increase in the interlayer distance. Thus, the greater part of the layers absorbs the IR radiation under an angle other than zero. With increasing water content, a decrease of the main band width (maximum at about 1000 cm^{-1}) and increase of its intensity were observed.

These changes in the IR spectrum of Ca montmorillonite were also confirmed by our measurements in the range of Si—O vibrations, in a sample prepared in a slurry form containing about 50% of montmorillonite (Figure 3).

The effect mentioned above allows us to interpret the changes in the IR spectrum of a smectite caused by bonding of a sorbate with a long aliphatic chain. The bonding of octadecylamine (as cation, or a neutral molecule) into the interlayer space is accompanied by a marked intercrystalline swelling, during which a perpen-

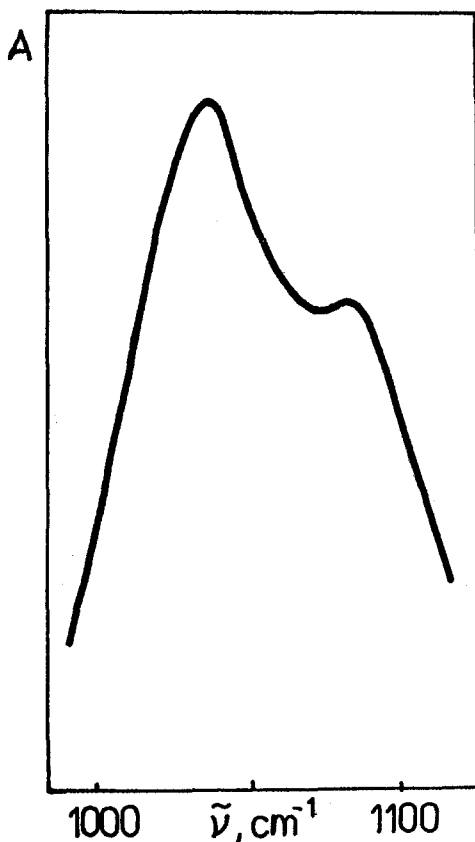


Fig. 3. Infrared spectrum of Ca montmorillonite in a slurry form.

dicular sorbate orientation is reached. In this way, the interlayer distance is markedly increased (similarly as in montmorillonite slurried with water), the orientation of the SiO_4 tetrahedra is changed, most probably towards a better ordered arrangement and more marked manifestation of the perpendicular Si—O vibrations. In the case of bonding of small molecules, or cations, such an effect was not observed.

The nature of the sorbent–sorbate interaction is determined not only by the size of the bound sorbate, but mainly by the arrangement of the sorbate in the interlayer space resulting from smectite crystallochemistry. This can be shown on two other sorbates: Wyoming (U.S.A.) and Blišany (CSFR) montmorillonites.

The Wyoming montmorillonite, according to X-ray diffraction analysis, has a well-ordered structure, as has the Jelšovský Potok montmorillonite. The sorption of octadecylamine on both clay minerals is accompanied by changes in the Si—O vibration bands (Figure 4). The value for the Wyoming organomontmorillonite at an organic compound content of 1.2 mmol g^{-1} is equal to 2.8 nm. On the other hand, the Blišany montmorillonite cannot be characterized as a well-ordered structure. In this sample, no change in the octadecylamine chain orientation from parallel to perpendicular occurred (at $\text{C}_{18}\text{H}_{37}\text{NH}_3^+$ content of 1.0 mmol g^{-1} the d_{001} value is 1.86 nm). In this case, after sorption of the organic cation, the spectrum in the region of the Si—O vibrations remained almost unchanged (Figure 4).

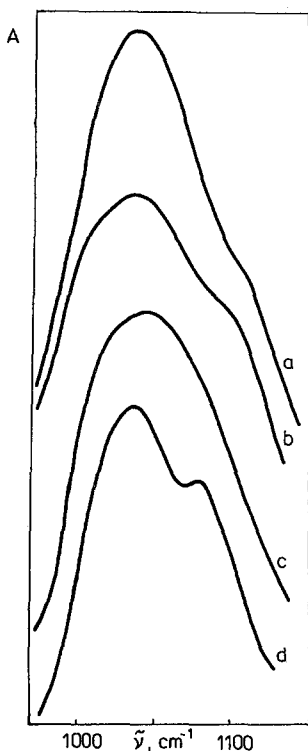


Fig. 4. Infrared spectra ($980\text{--}1150 \text{ cm}^{-1}$) of Blišany montmorillonite (a), Blišany octadecylammonium-montmorillonite (b), Wyoming montmorillonite (c), Wyoming octadecylammonium-montmorillonite (d).

Our results show that, at a suitable sorbate orientation, the bonding of an alkylamine with a long alkyl chain has, to a certain extent, an influence on the arrangement of the SiO_4 tetrahedra. Nevertheless, that effect can be observed in smectites with a relatively well-ordered structure which allows an intercrystalline swelling.

References

1. B. K. G. Theng: *The Chemistry of Clay Organic Reactions*, Adam Hilger, London (1974).
2. A. C. D. Newman (Ed.): *The Chemistry of Clays and Clay Minerals*, Longman, London (1987).
3. J. W. Jordan: *Mineralog. Mag.* **28**, 598 (1949).
4. H. Slosiariková, B. Čičel and J. Hronský: *Chem. Papers* **40**, (5) 585 (1986).
5. V. C. Farmer and J. D. Russell: *Spectrochim. Acta.* **20**, 1149 (1964).
6. L. Lerot and P. F. Low: *Clays Clay Min.* **24**, 191 (1976).