Study of the octadecylammonium—montmorillonite system

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The reaction of octadecylammonium (ODA) with montmorillonite gives successively rise to one-layer ($|1|\alpha_{\parallel}$) and two-layer ($|2|\alpha_{\parallel}$) complexes with ODA chains oriented parallelly with the surface of layer 2:1 and one-layer ($|1|\alpha_{\perp}$) and two-layer ($|2|\alpha_{\perp}$) complexes with ODA chains orientated under an angle exceeding 50° with respect to the surface of layer 2:1. These complexes come into existence in the Na-, Mg-, Ca-, Cu-, Co-, and (Ca, Mg)-forms of montmorillonite. The proceeding reaction exhibits, to a certain extent, both character of ion exchange and ODA sorption in the interlayer space. The $|2|\alpha_{\parallel} \rightarrow |1|\alpha_{\perp}$ transitions are at 0.8—1.0 mmol g⁻¹ ODA for all forms while the $|1|\alpha_{\perp} \rightarrow |2|\alpha_{\perp}$ transitions are to be observed at 1.7—2.0 mmol g⁻¹ ODA sorbed on the sample. The start of two-layer complex $|2|\alpha_{\perp}$ formation is accompanied by an increase in hydrophility of montmorillonite. As for the Cu- and Co-form of montmorillonite, it is supposed that the complexes of octadecylamine with Cu²⁺ and Co²⁺ are formed in the interlayer space. The presence of ODA in the interlayer space brings about changes in bonding within the structure of montmorillonite.

При реакции катиона октадециламмония (ОДА) с монтморильонитом в Na-, Mg-, Ca-, Cu-, Co- и (Ca, Mg)-формах монтморильонита постепенно образуются одно- ($|1|\alpha_{\parallel}$) и двухслойные ($|2|\alpha_{\parallel}$) комплексы с цепочками ОДА, ориентированными параллельно поверхности слоя 2:1, и одно- ($|1|\alpha_{\perp}$) и двухслойные ($|2|\alpha_{\perp}$) комплексы с цепочками ОДА, ориентированными под углом, превышающим 50°, к поверхности слоя 2:1. Происходящая реакция имеет частично характер ионного обмена, частично характер сорбции ОДА в межслойном прòстранстве. Переходы $|2|\alpha_{\parallel} \rightarrow |1|\alpha_{\perp}$ присутствуют во всех формах при 0,8—1,0 ммоль г⁻¹ ОДА, а $|1|\alpha_{\perp} \rightarrow |2|\alpha_{\perp}$ при 1,7—2,0 ммоль г⁻¹ ОДА, сорбированного образцом. Начало образования двухслойного комплекса $|2|\alpha_{\perp}$ связано с увеличением гидрофильности монтморильонита. Для Cu- и Co-форм монтморильонита предполагается образование комплексов октадециламина с Cu²⁺ и Co²⁺ в

межслойном пространстве. Наличие ОДА в межслойном пространстве вызывает изменения в структуре связей в монтмориљоните.

In most cases, the reactions of dissolved alkyl ammonium salts with montmorillonite are governed by the mechanism of ion exchange [1]. The arising organomontmorillonites are hydrophobic substances and their hydrophobic character is influenced by the kind of organic sorbate [2, 3], amount of water bound in the sample [4, 5], and degree of covering of the sorbent surface by organic cation [2]. The arrangement of interlayer sorbate predominantly depends on the size of organic cation entering into the interlayer space of montmorillonite [6]. Alkyl ammonium chains with the number of carbon atoms up to 10 form one layer of molecules ($d_{001} \approx 1.36$ nm) while chains with the number of carbon atoms 10—18 are able to form a two-layer complex in the interlayer space of montmorillonite ($d_{001} \approx 1.76$ nm) [7].

The aim of this study has been to compare the formation of the complexes of octadecylammonium (ODA) with monoionic forms of montmorillonite (Na-, Mg-, Ca-, (Ca, Mg)-, Cu-, Co-), to verify the assumption of equivalence of exchange $ODA^+ \rightleftarrows M^+$ in a reaction involving ion exchange in the interlayer space of montmorillonite and to ascertain whether the formation of an ordered complex of organic ions in the interlayer space reversely influences the structure of montmorillonite layer 2 : 1.

Experimental

Montmorillonite was isolated from bentonite (Jelšový Potok, Czechoslovakia) by sedimentation in 4 % aqueous suspension with e.s.d. under 2 μm. Individual forms were prepared by repeated treatment with the corresponding chlorides of 0.1 mol dm^{-3} concentration. The exchangeable cations in the prepared monoionic forms were determined according to [8].

The crystallochemical formula of the isolated montmorillonite was

$$[Si_{7.53}Al_{0.47}][Al_{2.99}Fe_{0.55}Mg_{0.45}]\, Ca_{0.47}O_{20}(OH)_4$$

Organomontmorillonites were prepared by treating the corresponding form of sorbent with a solution of octadecylammonium. The solutions of sorbate of 0.03 up to 0.3 mol dm^{-3} concentration were obtained by dissolving octadecylamine in a small amount of acetic acid and filling with water to the required volume. The ratio of solid phase to liquid phase in the course of sorption was 1 g of montmorillonite to 50 cm^3 of the sorbate solution of pertinent concentration. The suspension was kept for 2 h at 60 °C and intensively stirred. Then it was allowed to stand for 24 h at room temperature. After stabilization, the solid phase was separated by filtration and washed with 25 cm^3 of C_2H_5OH.

Carbon, nitrogen, and hydrogen were determined using CHN analyzer (Hewlett—Packard, model 185). X-Ray diffraction analysis was performed with an X-ray goniometer (Philips PW 1050) at 35 kV and 20 mA by using CuKα radiation. The DTA and TG curves were recorded by Derivatograph Q—1500 D (MOM, Budapest). The infrared spectra were taken in nujol suspension and KBr pellets at Perkin—Elmer 598.

The sedimentation volumes of organomontmorillonites were determined in the xylene—ethanol mixture (98 cm³ of xylene and 2 cm³ of ethanol). The weight of sample was 2 g. The sample was poured into a graduated cylinder containing the prepared mixture and thoroughly stirred. The sedimentation volume was read after 24 h.

The sorption and desorption of water vapour was investigated at $(25 \pm 0.5)\,°C$ over H_2SO_4 solutions exhibiting defined vapour pressures of H_2O. The obtained isotherms were evaluated by the BET method.
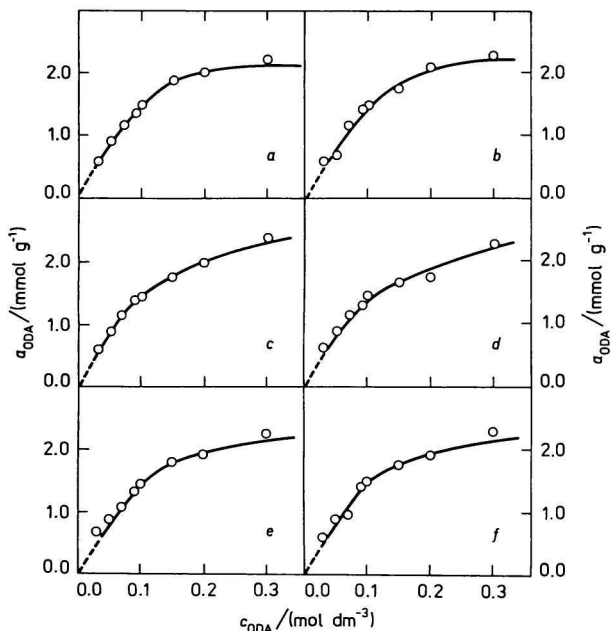

Fig. 1. Sorption isotherms of octadecylammonium.
a) (Ca, Mg)-Montmorillonite; b) Ca-montmorillonite; c) Mg-montmorillonite; d) Na-montmorillonite; e) Cu-montmorillonite; f) Co-montmorillonite.

Results and discussion

Fig. 1 represents the sorption isotherms of octadecylammonium on monoionic forms of montmorillonite. It is evident that neither the course of sorption isotherms nor the quantity of the sorbed octadecylammonium (0.21—0.25 mmol g⁻¹) is substantially influenced by the kind of exchangeable cation.

Fig. 2 gives the amount of exchangeable cations replaced by an octadecylammonium ion as a function of the quantity of the sorbed octadecylammonium in the

sample ($a_{ODA}/(\text{mmol g}^{-1}$)). In all cases, the concentration of inorganic cations is lower than the concentration of octadecylammonium present in the sample. The amount of exchanged cations increases with the content a_{ODA} in the sample for the
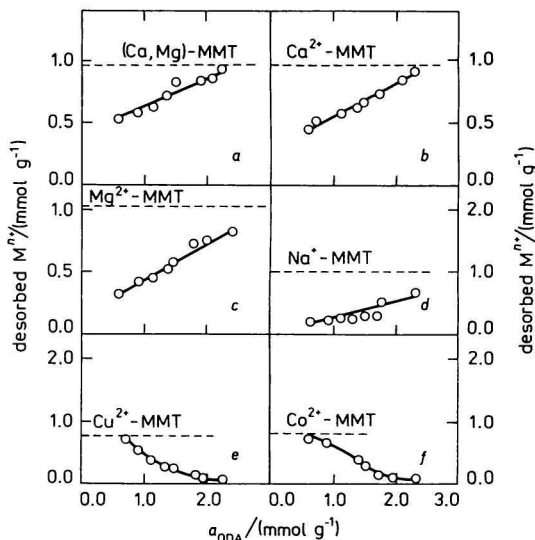

Fig. 2. Desorption of exchangeable cations of montmorillonite as a function of the amount of bound octadecylammonium.

a) (Ca, Mg)-Montmorillonite; b) Ca-montmorillonite; c) Mg-montmorillonite;
d) Na-montmorillonite; e) Cu-montmorillonite; f) Co-montmorillonite.

Mg-, Ca-, (Ca, Mg)-, and Na-form of montmorillonite. As for the Cu- and Co-form of montmorillonite, the amount of exchanged cations decreases with increasing quantity a_{ODA}. Some complexes of octadecylamine with inorganic cations may arise and these complexes remain bound in the interlayer space of montmorillonite.

For the sorption of octadecylammonium on montmorillonite, three stages of formation of the octadecylammonium—montmorillonite complex have been identified on the basis of the X-ray diffraction. Diffraction lines $d_{001} \approx 1.8$ nm, $d_{001} \approx 3.1$—3.4 nm, and $d_{001} \approx 5.0$—5.5 nm, successively appear with increasing amount of the sorbed octadecylammonium and the ratio of their mutual intensities changes. The progress of these changes is demonstrated in Fig. 3. As the ions and molecules of ODA fill only the interlayer space, we can subtract the width of the layer 2 : 1 (0.996 nm) from the above values. Then we obtain the height of interlayer from the following expression

$$d_{001}/\text{nm} - 0.996 \approx d_{001}/\text{nm} - 1 = \Delta d_{001}/\text{nm} \qquad (1)$$

The values of Δd_{001} are plotted against the amount of adsorbed octadecylammonium (a_{ODA}) in Fig. 4. The values of Δd_{001} corresponding to individual stages vary in the intervals 0.75—0.9 nm, 2.1—2.8 nm, and 4.2—4.7 nm. The value
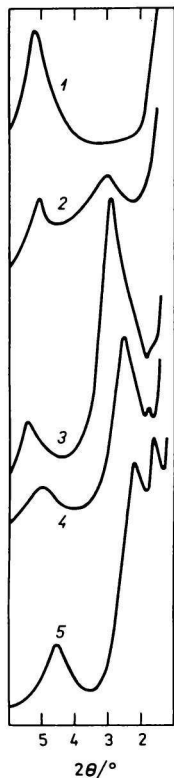
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Fig. 3. Diffraction pattern of Ca-montmorillonite for different contents of octadecylammonium.
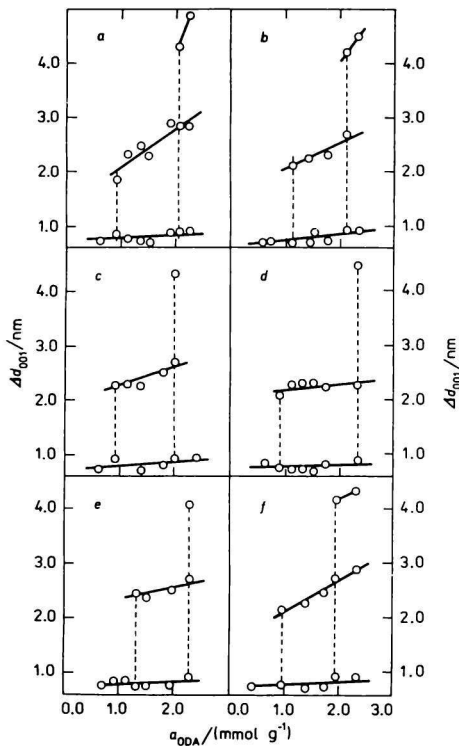1. 0.6 mmol g^{-1}; 2. 0.95 mmol g^{-1}; 3. 1.4 mmol g^{-1}; 4. 1.9 mmol g^{-1}; 5. 2.3 mmol g^{-1}.

Fig. 4. Variation of the value of Δd_{001}/nm with the amount of bound octadecylammonium.
a) (Ca, Mg)-Montmorillonite; b) Ca-montmorillonite; c) Mg-montmorillonite; d) Na-montmorillonite; e) Cu-montmorillonite; f) Co-montmorillonite.

$\Delta d_{001} \approx 0.8$ nm is equivalent to two layers of octadecylammonium cations the chains of which are orientated parallelly with the plane of the surface atoms of oxygen in layer 2 : 1. This order is schematically represented in Fig. 5 (A). For montmorillonite from locality Jelšový Potok, the surface area corresponding to one univalent cation is equal to 2×0.492 nm^2 because the layer 2 : 1 has two surfaces. One octadecylammonium cation covers the area of 1.11 nm^2. If an interlayer of montmorillonite is fully filled with the ODA cations orientated parallelly with the plane of surface oxygen atoms of layer 2 : 1, it is valid for the interlayer $a_{ODA} = 0.316$ mmol g^{-1}. This complex is classified as a one-layer ODA—montmorillonite complex which is denoted $|1|\alpha_\parallel$ according to [9]. The sorption of two ODA layers parallel with the plane of surface oxygen atoms gives rise to the

complex $|2|\alpha_{\parallel}$ for which it is valid $a_{ODA} = 0.63$ mmol g^{-1}. The capacity of cation exchange for a sample of Jelšový Potok is according to the crystallochemical formula equal to 0.75 mmol g^{-1}. If the inorganic cations are fully replaced by the octadecylammonium cations, the system must also contain interlayers in which the octadecylammonium chains are orientated under an angle 50°—90° with respect to the plane of the surface oxygen atoms of layer 2 : 1 (complex $|1|\alpha_{\perp}$ according to [9]). In this way, the substance amount $a_{ODA} = 0.63$—1.7 mmol g^{-1} may be accommodated in an interlayer. A one-layer complex $|1|\alpha_{\perp}$ is schematically represented in Fig. 5 (B). Provided $a_{ODA} > 1.7$ mmol g^{-1}, a complex with two layers of octadecylammonium orientated almost perpendicularly to the reference plane originates in the system. This arrangement is schematically represented in Fig. 5 (C). It will be denoted by the symbol $|2|\alpha_{\perp}$.
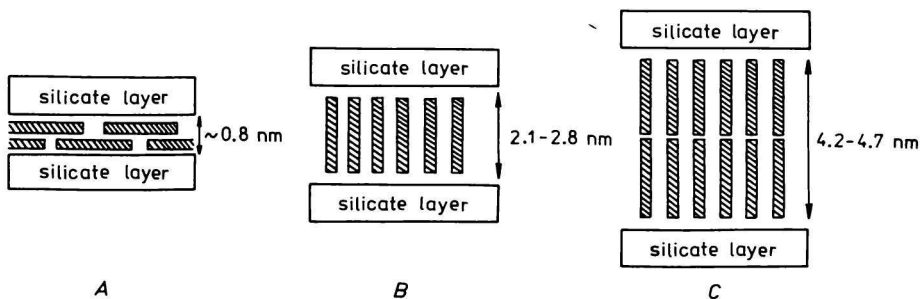

Fig. 5. Types of arrangement of octadecylammonium in the interlayer space of montmorillonite.

We consider the agreement of the calculated and measured contents of octadecylammonium sorbed at varied kinds of its deposition in the interlayer space to be acceptable. The contents for which the transition was observed are by 10—15 % greater than the calculated ones. We assume that this difference may be due to sensitivity threshold of the method used for identification.

Provided the orientation of the cations of octadecylammonium is not parallel with the layer 2 : 1, we first obtain lower values of d_{001} which gradually increase with the value of a_{ODA}. That is given by successive change in the mean angle of inclination of the chains of ODA cations with respect to the layer 2 : 1 till this angle approaches the value of 90°. For the ODA—montmorillonite complex $|1|\alpha_{\perp}$ these values vary in the range $\Delta d_{001} = 1.9$—2.5 nm ($d_{001} \approx 2.9$—3.5 nm) whereas they are in the range $\Delta d_{001} = 3.8$—4.9 nm ($d_{001} \approx 4.8$—5.9 nm) for complex $|2|\alpha_{\perp}$.

If montmorillonite is saturated with octadecylammonium, we may observe that three separate phases successively come into existence. These phases are able to coexist at the highest values of a_{ODA}. According to X-ray analysis, a part of the interlayer space remains saturated with octadecylammonium in two parallel layers

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($\Delta d_{001} \approx 0.8$ nm) only. The integral intensity of this diffraction line does not change during further saturation ($a_{ODA} > 1$ mmol g^{-1}) (Fig. 3). We assume that the cause of a low degree of sorption is a small local density of negative charge in a given region. According to investigations by *Weiss* and *Lagaly* [10, 11], we may expect that only a part of the interlayer space shall so sorb octadecylammonium that a two-layer ODA—montmorillonite complex with the aliphatic chains orientated under an angle of 50°—90° with respect to the plane of layer 2 : 1 is to be formed.

According to the measured X-ray diffraction patterns, the ODA——montmorillonite complexes form separate phases. We did not observe any formation of mixed layered structures containing two or three components.
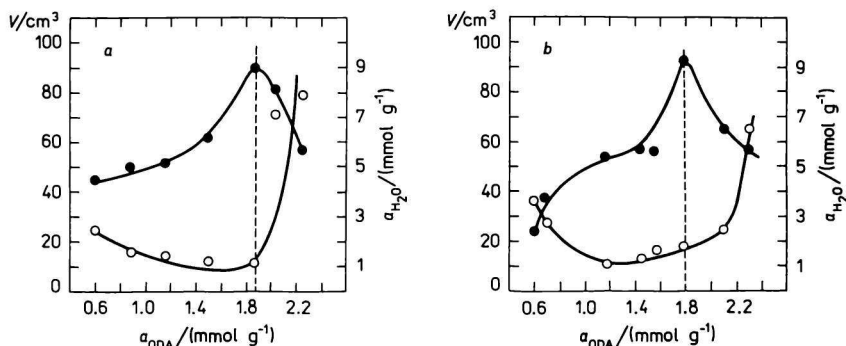

Fig. 6. Variation of sedimentation volume V (●) and water content (○) with the amount of bound octadecylammonium.
a) (Ca, Mg)-Montmorillonite; *b*) Ca-montmorillonite.

A comparison of the amount of sorbed octadecylammonium with the calculated value of negative charge on montmorillonite ($a = 0.75$ mmol g^{-1}) shows that both processes, *i.e.* exchange of cations and sorption of octadecylammonium in the interlayer space, take place in montmorillonite.

The evaluation of the dependence of H_2O concentration on increasing amount of sorbate leads to the conclusion that the concentration of water in individual three types of complexes is different (Fig. 6). According to the content of H_2O, we may order the ODA—montmorillonite complexes in the following series

$$|1|\alpha_\perp < |2|\alpha_\parallel < |2|\alpha_\perp$$

We assume that a portion of originally present water remains included in the interlayer space provided this space is not fully occupied by sorbate.

The sorption of organic substances in montmorillonite is accompanied by a change in the content of sorbed water. The content of water determined from mass loss on TG curves was confronted with the sedimentation volume of

organomontmorillonites measured in the xylene—ethanol mixture (Fig. 6). As this relationship shows analogous character for all forms, we are presenting only two examples. It is obvious from Fig. 6 that the intracrystalline swelling in a less polar organic medium is achieved at a lower content of water in sample. It is in the region where the sorption isotherm begins to manifest only small variations in the quantity of sorbed organic cation ($a_{ODA} > 1.8$ mmol g^{-1}) and complex $|1|\alpha_\perp$ prevails in the system.

The measurement of sorption and desorption of water vapour in samples with different a_{ODA} enabled us to calculate the surface area of montmorillonite suitable for sorption of polar molecules. In agreement with measurement of water content and measurement of sedimentation volume of samples in the xylene—ethanol mixture, the results given in Table 1 show the minimum of hydrophility at equal content of sorbent in the ODA—montmorillonite complex. It is again the sample with predominating complex $|1|\alpha_\perp$ immediately before the point of saturation of sample with octadecylammonium necessary for formation of complex $|1|\alpha_\perp$ in the whole volume. The start of formation of two-layer complex $|2|\alpha_\perp$ is connected with an increase in hydrophility of organomontmorillonite.

Table 1

Surface areas S of organomontmorillonites determined by the BET method

(Ca, Mg)-Montmorillonite		Ca-Montmorillonite	
$a_{ODA}/(\text{mmol g}^{-1})$	$S/(\text{m}^2\text{ g}^{-1})$	$a_{ODA}/(\text{mmol g}^{-1})$	$S/(\text{m}^2\text{ g}^{-1})$
0	425.0	0	513.5
0.60	48.8	0.60	62.1
0.89	38.8	0.69	40.8
1.17	22.3	1.18	64.5
1.37	16.2	1.42	47.1
1.48	11.9	1.47	16.4
1.88	9.2	1.78	9.6
2.03	18.9	2.12	20.1
2.23	27.8	2.32	31.2

Some changes in infrared spectra in the region of stretching Si—O vibrations ($\bar{v} = 800$—1200 cm^{-1}) were observed with all samples. The changes observed in the course of saturation of Na-montmorillonite (locality Jelšový Potok) with octadecylammonium are documented in Fig. 7. The sorption of ODA is accompanied by intense change in the shape of absorption bands and the wavenumbers shift from 1040 cm^{-1} to 1027 cm^{-1}, from 930 cm^{-1} to 914 cm^{-1}, and from

851 cm^{-1} to 834 cm^{-1}. The successive changes with increasing concentration a_{ODA} are to be seen in Fig. 7.

We assume that some changes in bonding within the layer $2 : 1$ are caused by homogeneous electrostatic field produced by the chains of ODA sorbed in the interlayer space. The splitting of the main band of Si—O vibrations at $\bar{v} = 1027$ cm^{-1} (see band at the content $a_{ODA} = 0.62$ mmol g^{-1}) into two bands ($\bar{v} = 1027$ cm^{-1} and $\bar{v} = 1080$ cm^{-1}) shows that there are two kinds of bonding of ODA to the surface of layer $2 : 1$ of montmorillonite in the ODA—montmorillonite complexes.
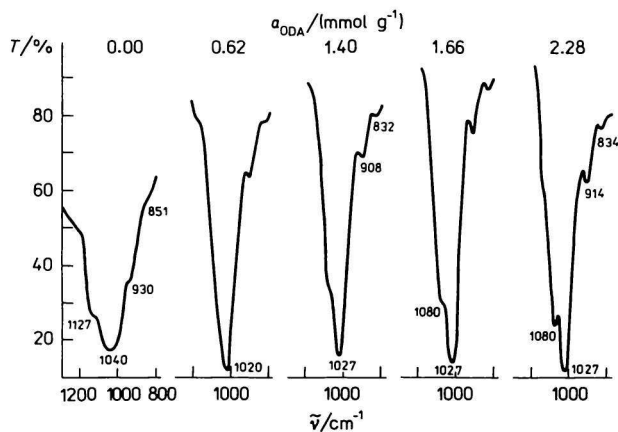

Fig. 7. Infrared spectra of Ca-montmorillonite at different contents of bound octadecylammonium.

Conclusion

According to the presented results, the mechanism of octadecylammonium sorption into the interlayer space is equal for all investigated forms. First of all, complex $|2|\alpha_{\|}$ arises, then complex $|1|\alpha_{\perp}$ follows and lastly, complex $|2|\alpha_{\perp}$ appears. The transitions $|2|\alpha_{\|} \rightarrow |1|\alpha_{\perp}$ occur for all forms at $a_{ODA} = 0.8$—1.0 mmol g^{-1} of octadecylammonium bound in the interlayer space of montmorillonite. The transitions $|1|\alpha_{\perp} \rightarrow |2|\alpha_{\perp}$ appear at $a_{ODA} = 1.7$—2.0 mmol g^{-1}.

According to crystallochemical formula, the capacity of montmorillonite (Jelšový Potok) for cation exchange is 0.75 mmol g^{-1}. The highest contents of sorbed octadecylammonium are in the range 2.0—2.26 mmol g^{-1}. The start of formation of two-layer complex $|2|\alpha_{\perp}$ is accompanied by an increase in hydrophily of organomontmorillonite. The reaction involves both the exchange of ions and the

sorption of octadecylammonium cations into the interlayer space of montmoril-
lonite. The measured relationships indicate that both these processes proceed
simultaneously.

The presence of organic sorbents in the interlayer space brings about consider-
able changes in bonding relations within the layer 2 : 1 of montmorillonite.

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