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SORPTION COMPLEXES OF MONTMORILLONITE WITH AMMONIUM ORGANIC CATIONS

UKD 549.623.9:548.734.534.422.4

Abstract. The article presents the results of X-ray and infra-red spectroscopic examinations performed on montmorillonite sorption complexes with ammonium organic cations containing one or two aliphatic chains of different length. In the former case, a bimolecular, in the latter — a monomolecular layer of organic ions is formed in the interlayer space, the planes of carbon zigzags being perpendicular to 001 planes of montmorillonite. Montmorillonite complexes with cations containing one aliphatic chain are characterized by the values of $d_{001} \approx 18.1 \text{ \AA}$; for the cations with two chains, on the other hand, $d_{001} \approx 13.7 \text{ \AA}$. The organic substance does not form hydrogen bonds with montmorillonite network; it causes, however, the interlayer water to be removed.

INTRODUCTION

Exchange reactions of montmorillonite with organic ions permit the regulation of physico-chemical properties of this mineral. This, among other things, affords the possibility of obtaining hydrophobic and organophilic compounds which find their application in industry as fillers and thickeners.

The present authors obtained ion-exchange complexes of montmorillonite with ammonium organic cations, characterized by different numbers of atoms in the aliphatic chain. The resulting organo-montmorillonite compounds were subjected to X-ray (diffractometric) and infra-red spectroscopic examinations in order to determine the manner of packing of long-chain organic cations in interlayer spaces and to establish the character of their bonds with montmorillonite.

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PREPARATION OF ION-EXCHANGE COMPLEXES

To obtain ion-exchange complexes, montmorillonite from Milowice (Bolewski *et al.*, 1970) with cation-exchange capacity of 44 mval/100 g was used. The mineral was converted into Na-form. To achieve this, water suspension of montmorillonite was mixed for two hours with ionite Amberlite IR-120 in sodium form. The ionite/montmorillonite volumetric ratio was 1:10. It is necessary to convert montmorillonite into sodium form considering the easier exchange of Na⁺ by organic cations than is the case with exchangeable Ca²⁺ (Kurylenko, Michaljuk 1959). For Na-montmorillonite the quantity of the sorbed organic substance is greater as well; this is connected with greater dispersion by which the sodium form of this mineral is characterized.

Sorption complexes were obtained with five ammonium salts (Tab. 1) of different molecule size. They were prepared in the following way: 20 g of montmorillonite in sodium form was dispersed in 380 ml of distilled water containing 2 weight per cent of Na₂CO₃ in relation to the solid phase. 1% aqueous solution of an appropriate ammonium salt was then added, its relation to montmorillonite being 20—25 weight per cent, and the suspension was mixed for one hour. This amount of organic substance ensures its maximum sorption on montmorillonite (Kurylenko, Michaljuk 1959). The obtained sorption complexes were filtered on the Büchner funnel and washed three times with distilled water. The samples were dried at 100—110°C.

X-RAY EXAMINATIONS

On the basis of X-ray diffractograms, the examined organomontmorillonite complexes may be divided into two groups. The first group comprises montmorillonite compounds with cations of the salts I and II (MI and MII, Tab. 1). The diffraction patterns of these samples in low-angle θ range demonstrate the presence of basal reflections corresponding to the values of $d_{001} \approx 18.1$ Å. The second group consists of the compounds III, IV and V. They form complexes with montmorillonite (MIII, MIV, MV) with the values of $d_{001} \approx 13.7$ Å (Fig. 1).

Expansion of the montmorillonite unit cell in *c* direction depends on the size of the organic molecule, the amounts of sorbed substance and the manner of its packing. For the tested Na-montmorillonite, which does not contain any interlayer water, $d_{001} \approx 9.6$ Å.

Basing on the obtained X-ray data, Δd was calculated. For the MI and MII complexes these values approximate 8.5 Å; for MIII, MIV and MV — 4.1 Å (Table 1). The above results suggest that for the cations I and II a bimolecular layer of organic cations with the aliphatic chain parallel to the sheet surfaces is sorbed in the interlayer space of montmorillonite; for the compounds III—V, on the other hand, a monomolecular layer is built in. The effective thickness of the organic molecules, calculated on the basis of their models, is the smallest in the direction parallel to the plane of the carbon zigzag of the chain. This effective

Table 1

 Δd^* values and minimum thicknesses of ammonium cations in complexes with montmorillonite

Symbol of the complex	Name of the organic salt	Chemical formula	R	Minimum thickness of the appropriate ammonium cation, Å	Δd , Å
MI	Trimethylammonium bromide	$[(CH_3)_3NCH_3R] Br$	C ₁₆ H ₃₃	4.8	8.5
MII	Alkylidimethylbenzylammonium chloride	$[(CH_3)_2NCH_2C_6H_5R] Cl$	C ₁₆ H ₃₃ —C ₁₈ H ₃₇	5.3	8.5
MIII	Dialkylidimethylammonium chloride	$[(CH_3)_2NR_2] Cl$	C ₁₂ H ₂₅ —C ₁₄ H ₂₉	4.8	4.0
MIV	Dialkylidimethylammonium chloride	$[(CH_3)_2NR_2] Cl$	C ₁₆ H ₃₃ —C ₁₈ H ₃₇	4.8	4.1
MV	Dimethyldistearylammonium chloride	$[(CH_3)_2NR_2] Cl$	C ₁₇ H ₃₅	4.8	4.2

 $\Delta d = d_{001} - 9.6$ Å.

thickness ranges from 4.8 to 5.3 Å (Tab. 1), whereas the thickness of the hydrocarbon chain itself, measured in this direction, is equal to 4 Å. It is characteristic that complexes with the values of $d_{001} = 18.1$ Å are formed with cations containing one aliphatic chain, while for the cations with two chains the distances d_{001} equal 13.7 Å.

The formation of complexes with mono- or bimolecular layer of organic cations has been also corroborated by the results of nitrogen determinations, which were performed with Kjeldahl method for the samples MII and MIII. For the former, the content of organic cations amounts to 41.1, whereas for the latter it is 28.5 mval/100 g. Thus in the MII complex, the exchange positions of montmorillonite are occupied in 93% by ammonium organic ions, whereas in MIII — in 64% only.

INFRA-RED SPECTROSCOPIC EXAMINATIONS

Infra-red spectroscopic examinations* revealed the lack of hydrogen bonds between organic cations and montmorillonite crystalline lattice. This results from the fact that ammonium cations used for the examinations have no polar groups which are capable of forming such bonds. On the obtained spectrograms there occur separate absorption bands of montmorillonite and sorbed organic molecules. The spectra of the sorption complexes MI and MII reveal a conspicuous decrease in the intensity of the absorption band connected with the stretching vibrations of interlayer water molecules in montmorillonite (3430 cm^{-1}) when compared to the intensity of this band on the spectrum of Na-montmorillonite (Fig. 2). This fact testifies to the decrease in the quantity of interlayer water, the substantial part of which has been probably removed by large hydrophobic organic cations. The loss of interlayer water in the MIII—MV complexes is considerably smaller.

CONCLUSIONS

1. X-ray examinations have demonstrated the penetration of ammonium cations into montmorillonite interlayer spaces. In the case of cations containing one aliphatic chain, complexes with two layers of organic substance are formed; cations with two aliphatic chains in a molecule, on the other hand, form complexes with a monomolecular layer of organic substance. They do not form hydrogen bonds with the oxygens of montmorillonite network. The fact of forming bimolecular layers in the interlayer space by the cations with one aliphatic chain could be interpreted as follows: only this manner of packing affords a maximum neutralization of montmorillonite layer negative charge by ammonium cations. The surface area of the cross-section of montmorillonite unit cell, parallel to 001, approximates 47.7 Å^2 . Connected with this area is $-0.7 e$ (of the elementary negative charge). On the other hand,

*) The examinations were performed with C. Zeiss UR-10 spectrophotometer, using samples in the form of Nujol mulls and KBr disks.

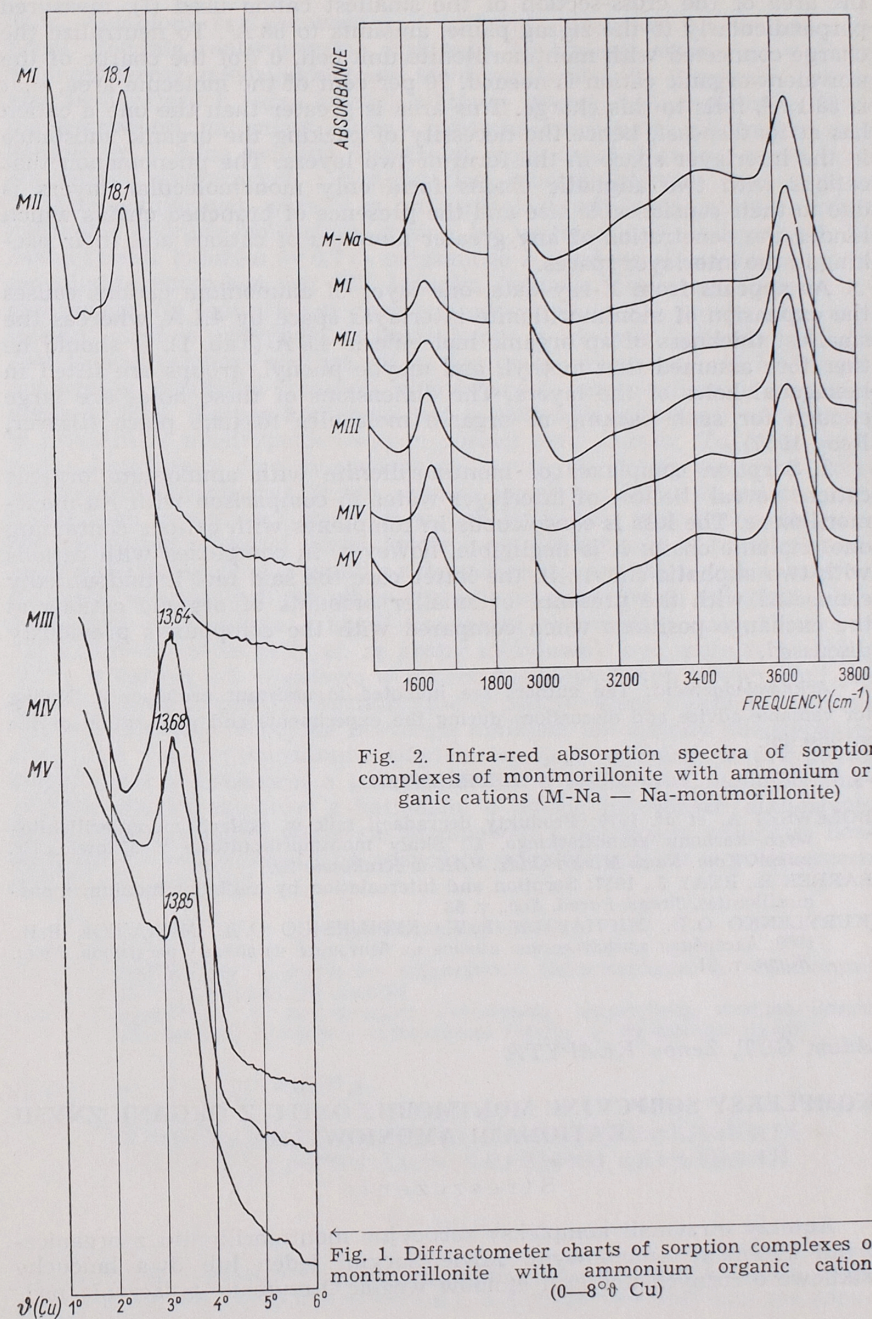


Fig. 2. Infra-red absorption spectra of sorption complexes of montmorillonite with ammonium organic cations (M-Na — Na-montmorillonite)

Fig. 1. Diffractometer charts of sorption complexes of montmorillonite with ammonium organic cations ($0-8^\circ \theta$ Cu)

the area of the cross-section of the smallest cation used (I), measured perpendicularly to the zigzag plane, amounts to 83 \AA^2 . To neutralize the charge connected with montmorillonite unit cell, 0.7 of the charge of the univalent organic cation is needed. 70 per cent of the molecule area, that is 58.1 \AA^2 , falls to this charge. This area is greater than the one a cation has at its disposal, hence the necessity of packing the organic substance in the interlayer space in the form of two layers. The phenomenon that cations with two aliphatic chains form only monomolecular layers is due to their considerable size and the presence of branched chains which hinder the penetration of any greater numbers of cations and their packing in the interlayer spaces.

As appears from X-ray data, one layer of ammonium cations causes the expansion of montmorillonite interlayer space by 4.1 \AA , whereas the smallest thickness of an organic molecule is 4.8 \AA (Tab. 1). It should be therefore assumed that methyl, and maybe phenyl, groups are fitted in hexagonal holes of the layers. The dimensions of these holes are large enough for such packing of organic molecules to take place (Barrer, Reay 1957).

2. Sorption complexes of montmorillonite with ammonium organic cations reveal the loss of interlayer water in comparison with Na-montmorillonite. The loss is conspicuous in complexes with cations containing one aliphatic chain; it is negligible, however, in complexes with cations with two aliphatic chains. In the latter case the said fact is undoubtedly connected with the presence of smaller amounts of organic cations at the exchange positions when compared with the compounds previously discussed.

Acknowledgement: The authors are indebted to assistant professor J. Kubisz for valuable advice and discussions during the experiments and preparation of the manuscript.

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KOMPLEKSY SORPCYJNE MONTMORILLONITU Z ORGANICZNYMI KATIONAMI AMONIOWYMI

Streszczenie

Autorzy otrzymali kompleksy sorpcyjne montmorillonitu z organicznymi kationami amoniowymi zawierającymi jeden lub dwa łańcuchy alkilowe o różnych ilościach atomów węgla. Otrzymane połączenia pod-

dano badaniom rentgenowskim i spektrofotometrycznym w podczerwieni. Badania rentgenowskie wykazały, że kationy amoniowe wnikają w przestrzenie międzypakietowe montmorillonitu. W przypadku kationów zawierających jeden łańcuch alkilowy tworzą się kompleksy z dwiema warstwami, natomiast kationy z dwoma łańcuchami alkilowymi dają kompleksy z jedną warstwą substancji organicznej. Kationy te nie tworzą wiązań wodorowych z tlenami sieci montmorillonitu. Fakt tworzenia bimolekularnych warstw w przestrzeniach międzypakietowych przez kationy z jednym łańcuchem można by wytłumaczyć następująco: Na zubożenie ładunku ($=0,7e$) związanego z komórką elementarną montmorillonitu potrzebne jest 70% ładunku jednowartościowego kationu organicznego. Na ładunek ten przypada odpowiednio 70% powierzchni cząsteczki, czyli w przypadku najmniejszego z użytych kationów $58,1 \text{ \AA}^2$. Jest to powierzchnia większa niż kation ma do dyspozycji ($47,7 \text{ \AA}^2 =$ powierzchnia przekroju komórki elementarnej montmorillonitu równoległego do 001), dlatego konieczne jest upakowanie substancji organicznej w przestrzeni międzypakietowej w postaci dwu warstw. To, iż w przypadku kationów o dwu łańcuchach alifatycznych tworzy się tylko jedna warstwa substancji organicznej, wynika zapewne z faktu, że znaczne rozmiary tych cząsteczek i obecność w nich łańcuchów rozgałęzionych utrudnia wnikanie większej liczby jonów i ich upakowanie w przestrzeniach międzypakietowych. Jak wynika z danych rentgenowskich, jedna warstwa kationów amoniowych powoduje rozsuniecie pakietów na odległość $4,1 \text{ \AA}$. Natomiast najmniejsza grubość cząsteczki organicznej (tab. 1) wynosi $4,8 \text{ \AA}$. Należy zatem przyjąć, że grupy metylowe i być może fenyl (MII) tkwią w całości lub częściowo w lukach heksagonalnych powierzchni pakietów. Badania spektrofotometryczne w podczerwieni wykazały, że omawiane kompleksy sorpcyjne zawierają mniejsze ilości wody międzypakietowej niż Na-montmorillonit. Ubytek ten jest wyraźny w przypadku kompleksów z kationami o jednym łańcuchu alkilowym, natomiast nieznaczny dla kompleksów z kationami o dwóch łańcuchach alkilowych. W przypadku drugim wiąże się to zapewne z obecnością mniejszej liczby kationów organicznych na pozycjach wymiennych niż w połączeniach opisanych poprzednio.

OBJASNIENIA FIGUR

- Fig. 1. Dyfraktogramy kompleksów sorpcyjnych montmorillonitu z organicznymi kationami amoniowymi ($0-6^\circ\theta$)
- Fig. 2. Spektrogramy w podczerwieni kompleksów sorpcyjnych montmorillonitu z organicznymi kationami amoniowymi (M-Na — Na-montmorillonit)

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СОРБИОННЫЕ КОМПЛЕКСЫ МОНТМОРИЛЛОНИТА С ОРГАНИЧЕСКИМИ АММОНИЕВЫМИ КАТИОНАМИ

Резюме

Авторами получены сорбиционные комплексы монтмориллонита с органическими аммониевыми катионами, содержащими одну или две алки-

ловых цепи с разными количествами атомов углерода. Подученные соединения анализировались рентгеновскими и спектрофотометрическим (в инфракрасном) методами. Рентгеновские анализы показали, что аммониевые катионы проникают в межпакетные пространства монтмориллонита. В случае катионов, содержащих одну алкиловую цепь, образуются комплексы с двумя слоями, а катионы, включающие две алкиловых цепи, дают комплексы с одним слоем органического вещества. Эти катионы не образуют водородных связей с атомами кислорода в решётке монтмориллонита. Образование бимолекулярных слоев в межпакетных пространствах катионами с одной алкиловой цепью можно объяснить следующим образом. Для нейтрализации заряда ($= 0,7e$), связанного с элементарной ячейкой монтмориллонита, требуется 70% заряда одновалентного органического катиона. На этот заряд приходится соответственно 70% поверхности молекулы, что составляет, при наименьшем из использованных катионов, $58,1 \text{ \AA}^2$. Эта поверхность больше той площади, какой располагает катион ($47,7 \text{ \AA}^2$ = площадь сечения элементарной ячейки монтмориллонита параллельно 001). Отсюда следует необходимость упаковки органического вещества в межпакетном пространстве в виде двух рядов. Тот факт, что в случае катионов с двумя алифатическими цепями образуется лишь один слой органического вещества можно объяснить тем, что значительные размеры этих молекул и присутствие в них разветвленных цепей затрудняют проникновение большого количества ионов и их упаковку в межпакетных пространствах. Из рентгеновских данных следует, что скин слой аммониевых катионов раздвигает пакеты на расстояние $4,1 \text{ \AA}$. Толщина же самой маленькой органической молекулы составляет $4,8 \text{ \AA}$ (табл. 1). Таким образом следует предполагать, что метиловые группы и, возможно, фенил (MII) полностью или частично внедряются в гексагональные промежутки поверхности пакетов. Спектрофотометрические анализы в инфракрасном показали, что рассматриваемые сорбционные комплексы содержат меньшее количество межпакетной воды по сравнению с Na-монтмориллонитом. Этот убыток проявляется отчетливо у комплексов с катионами, включающими одну алкиловую цепь, а у комплексов с катионами, содержащими две алкиловых цепи, он незначителен. Во втором случае это обусловлено, вероятно, меньшим количеством органических катионов на обменных позициях, по сравнению с ранее описанными соединениями.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Дифрактограммы сорбционных комплексов монтмориллонита с органическими аммониевыми катионами ($0 - 6^\circ \theta$)

Фиг. 2. Инфракрасные спектры поглощения сорбционных комплексов монтмориллонита с органическими аммониевыми катионами (M-Na — Na-монтмориллонит)