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## SORPTION PROPERTIES OF MONTMORILLONITE MODIFIED WITH ALIPHATIC AMINE SALTS

UKD 549.623; 552.52].08montmorillonit: 541.183.5.03: 546.293

**Abstract.** The paper presents studies of the sorption properties of Na-montmorillonite and its derivatives obtained by modification with methyl- and ethylamine chlorides and n-octadecylamine. Argon, benzene and water were used as adsorbates. Experiments have shown that the sorption capacity of modified montmorillonite changes markedly compared with that of untreated sample.

### INTRODUCTION

Organic derivatives of montmorillonite, particularly those containing alkyloammonium cations, have been the subject of extensive studies due to their interesting physico-chemical properties. Generally speaking, organic montmorillonite complexes formed as a result of substitution of organic for inorganic ions are characterized by the rigidity of structure, and in the case of short-chained alkyloamines, by the accessibility of interlayer spaces to the molecules of certain adsorbates. Hence, in contrast to untreated montmorillonite, this group of organic montmorillonite complexes shows good sorption properties, especially with respect to inert gases (argon, nitrogen) (Barrer, Macleod 1954; Barrer, Macleod 1955; Barrer, Reay 1957; Barrer, Brummer 1963; Barrer, Millington 1967, and others).

It is generally held that the sorption of argon on Na-montmorillonite takes place only at the external surface. Some investigators, e.g. Thomas and Bohor (1968), noticing a marked increase in the sorption capacity of Na-montmorillonite during N<sub>2</sub> and CO<sub>2</sub> sorption, maintained that the molecules of apolar sorbates were also able to penetrate into the interlayer spaces of montmorillonite.

Aylmore (1977) found that the nitrogen sorption on Na-montmorillonite depends mainly on the method of outgassing of samples. Water remaining in the system promotes the penetration of adsorbate into the structure of the mineral, and this accounts for the increased sorption capacity observed by Thomas. From the paper published by Żyla (1973) it appears that the vacuum-heating of montmoril-

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lonite at 383–413 K enhances markedly the argon sorption. The cited author attributes this phenomenon to the fact that the interlayer spaces of montmorillonite are being rendered accessible to argon atoms during the thermal-vacuum modification. Knudson and McAtee (1974) studied the nitrogen sorption on montmorillonites containing sodium, barium and cesium cations, and found that no sorption occurred in the interlayer spaces.

The sorption of gases and vapours of apolar substances takes place undoubtedly on montmorillonite with organic cations in the interlayer spaces. The size of this effective free space, as well as the surface area of the complex being formed, depends on the specific volume of the penetrating organic cations, their orientation and packing density in the interlayer spaces of montmorillonite. The resulting internal porosity accounts for the pronounced increase in the sorption of gases and vapours of apolar substances.

## EXPERIMENTAL

Adsorption studies were carried out on organic montmorillonite complexes obtained by the substitution of alkyloamine for inorganic cations. Montmorillonite used for investigations was separated by sedimentation from bentonite of the Chmielnik deposit. Methyl- and ethylamine hydrochlorides and pure octadecylamine were used as modifiers. Further on, the derivatives of methyl-, ethyl- and octadecylamine montmorillonite will be designated respectively as MEA-, ETA- and OKT-Mt.

The modification was carried out by stirring and heating Na-montmorillonite water suspension with 1 n alkyloammonium salt solutions, and in the case of n-octadecylamine, with alcohol solution. After decantation the sediment was filtered, washed until the reaction to chloride ions was negative (in the case of salts), and dried at 323 K.

The isotherms for water and benzene vapour sorption were obtained at 298 K and for argon sorption at 77.5 K. Prior to measurements, the samples were outgassed to a pressure of  $1.33 \cdot 10^{-7}$  Pa at 378 K for Na-montmorillonite and at 323 K for modified samples.

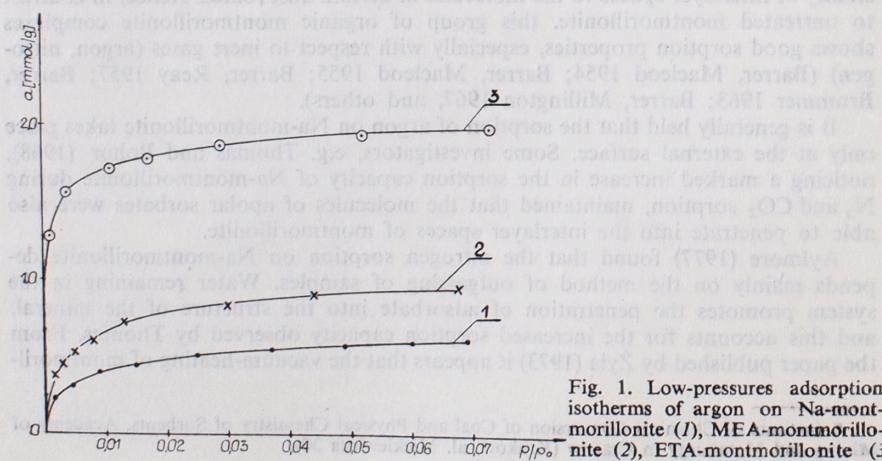


Fig. 1. Low-pressure adsorption isotherms of argon on Na-montmorillonite (1), MEA-montmorillonite (2), ETA-montmorillonite (3)

## RESULTS

The primary parameter characterizing a porous adsorbent is the limiting volume of its adsorption space, i.e. micropore volume. Using the linear form of Dubinin-Raduszkiewicz's equation for argon adsorption isotherms at very low pressures (Fig. 1), the volume  $W_0$  and the equation constant  $B$  were determined for each sample. The results are given in Table 1.

The poor argon sorption on OKT-Mt appeared to be non-measurable at low pressures of this adsorbate. From Table 1 it is evident that the micropore volume of ETA- and MEA-Mt samples increases markedly compared with the volume of the untreated sample.

The constant  $B$  is connected with the porous structure of adsorbent. Its least

Table 1  
Parameters of the Dubinin-Raduszkiewicz-equation for the investigated samples

Sample	Na-Mt	MEA-Mt	ETA-Mt
$W \text{ cm}^3/\text{g}$	0,0218	0,0354	0,0615
$B \times 10^{-6}$	1,87	1,87	0,64

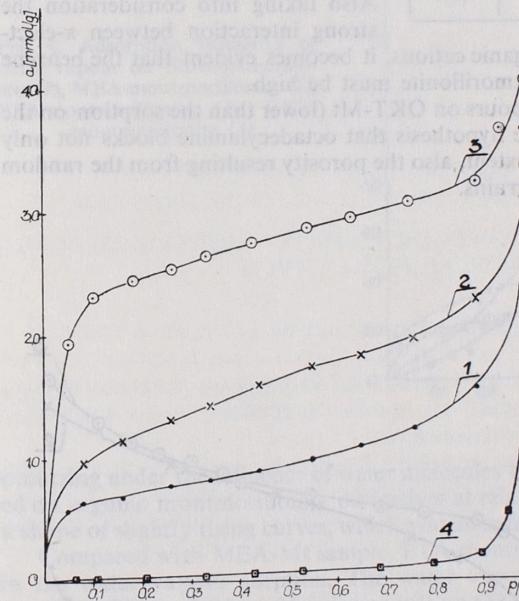


Fig. 2. Adsorption isotherms of argon on Na-montmorillonite (1), MEA-montmorillonite (2), ETA-montmorillonite (3), OKT-montmorillonite (4)

value for ETA-Mt points to the strongest interaction between argon atoms and the surface of this sample.

The argon adsorption isotherms obtained over the full range of relative pressures are shown in Figure 2. From their shape the volume of adsorbed gas (in  $\text{cm}^3$  of liquid sorbate/1 g of adsorbent) at relative pressures  $P/P_0 = 0.2, 0.4, 0.7$  was determined (Table 2). The greatest sorption capacity with respect to argon has been noted for the sample modified with ethylamine hydrochloride. The decreased argon adsorption on OKT-Mt can be accounted for by the blocking of intergranular porosity by the organic substance.

From isotherms obtained for benzene sorption (Fig. 3) it appears that the sorption

of benzene vapours on samples modified with methyl- and ethylamine hydrochlorides increases markedly. This is due to the higher degree of accessibility of the interlayer spaces of modified samples to flat benzene molecules, and to the change in the chemical character of the sample surface from hydrophilic to hydrophobic. It follows therefore that benzene molecules react better with organic cations than with

polar centres in the structure of montmorillonite. Owing to their flat structure, the molecules of this adsorbate can adjust to the shape of free spaces being formed between the organic cations (Barrer 1955). From the further studies of Barrer (1957, 1967) it appears that benzene molecules sorbed by organic montmorillonite complexes are arranged in a single layer, assuming a position normal to the interlayer surfaces. Also taking into consideration the strong interaction between  $\pi$ -elect-

Table 2  
Sorption capacity of the investigated samples with respect to argon

$P/P_o$	Na-Mt	MEA-Mt	ETA-Mt	OKT-Mt
0,2	0,022	0,035	0,072	0,001
0,4	0,025	0,045	0,080	0,002
0,7	0,034	0,055	0,088	0,003

rons of benzene molecules with organic cations, it becomes evident that the benzene vapour sorption on modified montmorillonite must be high.

The low sorption of benzene vapours on OKT-Mt (lower than the sorption on the untreated sample) substantiates the hypothesis that octadecylamine blocks not only the interlayer pores but, to a large extent, also the porosity resulting from the random arrangement of montmorillonite grains.

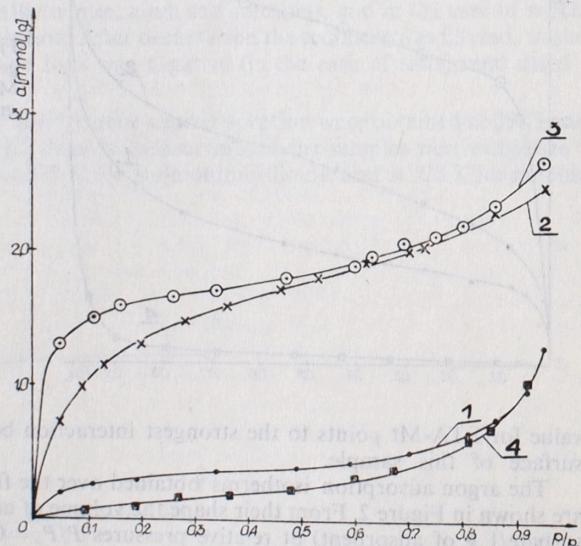


Fig. 3. Adsorption isotherms of benzene vapour on Na-montmorillonite (1), MEA-montmorillonite (2), ETA-montmorillonite (3), OKT-montmorillonite (4)

The hydrophobization of montmorillonite by the organic substances used is also reflected in the shape of water vapour sorption isotherms (Fig. 4). A characteristic phenomenon is the slight increase in the amount of sorbed water vapour shown by MEA- and ETA-Mt samples (up to the relative pressure  $P/P_o = 0.15$ ), compared with the sorption determined on untreated montmorillonite. This increase can be

accounted for in the following way: the alkylammonium cations push apart the layers of montmorillonite and thus render other polar centres accessible to water molecules.

At relative pressures higher than 0.15 the water vapour sorption on MEA- and ETA-Mt samples is considerably lower than the sorption on untreated montmorillonite. This is due to the blocking of polar centres of modified montmorillonite by the cations of organic substances. The isotherms determined for water vapour sorption on untreated montmorillonite is a steeply rising curve, which is due to systematic swelling

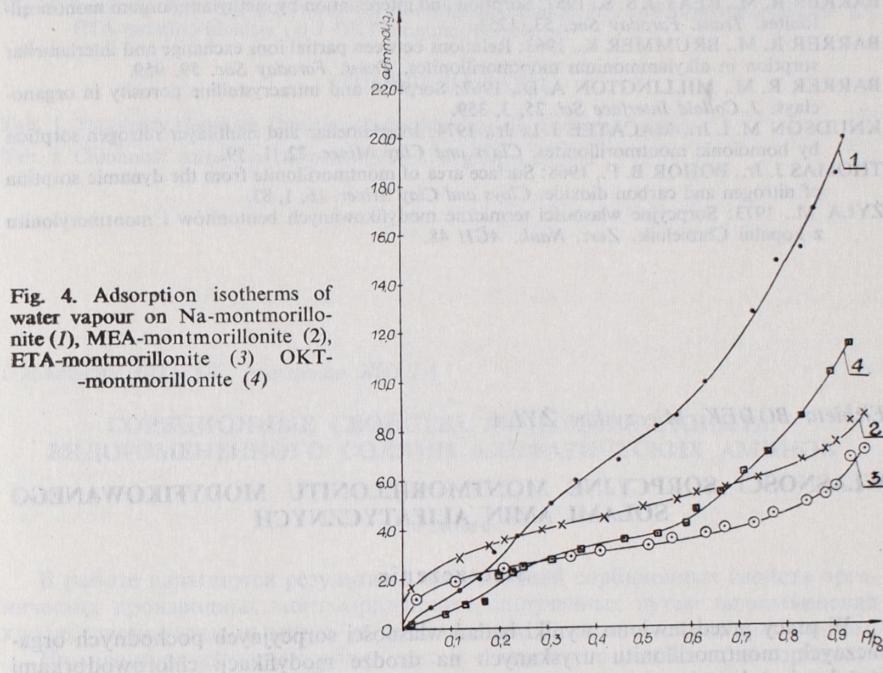


Fig. 4. Adsorption isotherms of water vapour on Na-montmorillonite (1), MEA-montmorillonite (2), ETA-montmorillonite (3), OKT-montmorillonite (4)

occurring under the influence of water molecules being sorbed. The isotherms obtained on organic montmorillonite derivatives at relative pressures  $P/P_o = 0.2 - 0.9$  have a shape of slightly rising curves, which evidences that their structure has become rigid.

Compared with MEA-Mt sample, ETA-montmorillonite shows a greater decrease in the water vapour sorption. The water vapour sorption determined at relative pressures  $P/P_o = 0.05 - 0.25$  is lower still on OKT-Mt sample. The increase in water vapour sorption on this sample, observed above a relative pressure of 0.25, is due to the penetration of water molecules into the interlayer spaces through the external layer of octadecylamine. It follows therefore that this form of montmorillonite does not have a rigid structure, which is presumably due to the small amount of octadecylamine molecules in the interlayer spaces of montmorillonite.

From the above studies it is evident that the best results in the modification of montmorillonite with alkyloamines are obtained using ethylamine hydrochloride. The ETA-montmorillonite modification shows high argon and benzene vapour sorption and very low water vapour sorption.

Translated by Hanna Kisielewska

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## WŁASNOŚCI SORPCYJNE MONTMORILLONITU MODYFIKOWANEGO SOLAMI AMIN ALIFATYCZNYCH

### Streszczenie

W pracy przedstawiono wyniki badań właściwości sorpcyjnych pochodnych organicznych montmorylonitu uzyskanych na drodze modyfikacji chlorowodorkami metyl- i etyloaminy oraz n-oktadecyloaminy.

Z przebiegu izoterm sorpcji argonu wynika, że największą chłonność sorpcyjną wykazuje montmorylonit modyfikowany chlorowodorkiem etyloaminy. Widoczne zmniejszenie adsorpcji argonu w przypadku pochodnej oktadecyloamoniowej montmorylonitu tłumaczyć można blokowaniem porowatości międzyziarnowej przez substancję organiczną.

Analogiczne zmiany chłonności sorpcyjnej badanych próbek zaobserwowano przy sorpcji par benzenu. Przyczyną zwiększonej sorpcji na próbkach metyl- i etyloamoniowego montmorylonitu jest wzrost dostępności przestrzeni międzypakietowej modyfikowanych próbek dla płaskich cząsteczek benzenu, oraz zmiana chemicznego charakteru powierzchni próbek z hydrofilnej na hydrofobową. Niska sorpcja par benzenu na pochodnej oktadecyloamoniowego montmorylonitu (mniejsza od sorpcji na próbce wyjściowej) potwierdza możliwość blokowania przez oktadecyloaminę nie tylko porowatości międzypakietowej, lecz w dużym stopniu porowatości wywołanej swobodnym ułożeniem ziaren montmorylonitu.

Równolegle przeprowadzone badania sorpcji par wody wykazały zmniejszenie chłonności sorpcyjnej próbek modyfikowanych substancjami organicznymi w odniesieniu do chłonności sorpcyjnej wyjściowego montmorylonitu.

## OBJAŚNIENIA FIGUR

- Fig. 1. Izotermy adsorpcji argonu w zakresie niskich ciśnień na Na-montmorylonicie (1), MEA-montmorylonicie (2), ETA-montmorylonicie (3)
- Fig. 2. Izotermy adsorpcji argonu na Na-montmorylonicie (1), MEA-montmorylonicie (2), ETA-montmorylonicie (3) i OKT-montmorylonicie (4)
- Fig. 3. Izotermy adsorpcji par benzenu na Na-montmorylonicie (1), MEA-montmorylonicie (2), ETA-montmorylonicie (3) i OKT-montmorylonicie (4)
- Fig. 4. Izotermy adsorpcji par wody na Na-montmorylonicie (1), MEA-montmorylonicie (2), ETA-montmorylonicie (3) i OKT-montmorylonicie (4)

## OBJAŚNIENIA TABEL

Tab. 1. Parametry równania Dubinina-Raduszkiewicza dla badanych próbek

Tab. 2. Chłonność sorpcyjna badanych próbek względem argonu

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## СОРБЦИОННЫЕ СВОЙСТВА МОНТМОРИЛЛОНИТА, ВИДОИЗМЕНЕННОГО СОЛЯМИ АЛИФАТИЧЕСКИХ АМИНОВ

### Резюме

В работе излагаются результаты исследований сорбционных свойств органических производных монтмориллонита, полученных путем видоизменения хлористоводородными метил- и этиламиналами, а также н-октадецилоамином.

Из характера изотерм сорбции аргона следует, что наибольшую сорбционную поглощаемость обнаруживает монтмориллонит, модифицированный хлористоводородным этиламином. Заметное уменьшение адсорбции аргона в случае производной октадециламониевого монтмориллонита можно объяснить блокировкой межзерновой пористости органическим веществом.

Аналогичные изменения сорбционной поглощаемости изучаемых образцов наблюдались при сорбции паров бензола. Причиной повышенной сорбции на образцах метил- и этиламмониевого монтмориллонита является увеличение доступности межпакетного пространства видоизмененных образцов для плоских молекул бензола, а также изменение химического характера поверхности образцов из гидрофильной на гидрофобную. Невеликая сорбция паров бензола на производной октадециламониевого монтмориллонита (меньше сорбции на исходном образце) подтверждает возможность блокировки октадециламином не только межпакетной пористости, но и в большей степени пористости, вызванной свободной упаковкой зерен монтмориллонита.

Одновременно проведенные исследования сорбции паров воды обнаружили уменьшение сорбционной поглощаемости видоизмененных органическим веществом образцов по отношению к сорбционной поглощаемости исходного монтмориллонита.

## ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Изотермы адсорбции аргона в диапазоне низких давлений на Na-монтмориллоните (1), MeA-монтмориллоните (2), ЭТА-монтмориллоните (3)

Фиг. 2. Изотермы адсорбции аргона на Na-монтмориллоните (1), MeA-монтмориллоните (2), Эта-монтмориллоните (3) и Окт-монтмориллоните (4)

Фиг. 3. Изотермы адсорбции паров бензола на  $\text{Na}$ -монтмориллоните (1),  $\text{MeA}$ -монтмориллоните (2),  $\text{EtA}$ -монтмориллоните (3) и Окт-монтмориллоните (4)

Фиг. 4. Изотермы адсорбции паров воды на **Na-монтмориллоните** (1), **МсА-монтмориллоните** (2), **Эта-монтмориллоните** (3) и **Окт-монтмориллоните** (4)

## СПИСОК ТАБЛИЦ

Табл. 1. Параметры уравнения Дубинина-Радушкевича для изучаемых образцов

Табл. 2 Сорбционная поглощаемость изучаемых образцов в отношении аргона