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**PRELIMINARY STUDIES OF HYDROPHOBIZATION  
OF MONTMORILLONITE BY REACTION  
WITH ACETIC ACID ANHYDRIDE**

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**Abstract.** This paper presents the preliminary results of studies of hydrophobization of H- and Na-montmorillonite effected by reaction with acetic acid anhydride. Changes in hydrophilic properties of the resulting products were estimated from water vapour sorption isotherms.

INTRODUCTION

Owing to their peculiar properties organic complexes of montmorillonite find wide application in several branches of industry. This wide range of application of hydrophobized montmorillonites is due to both the hydrophobic and organophilic nature of their surface. Studies of the process of hydrophobization of montmorillonite with initial hydrophilic properties have not only theoretical but also practical significance.

Hydrophobization can be effected in two ways:

- by surface reactions (methylation, phenylation, acetylation) giving rise to covalent-type complexes,
- by formation of exchange ionic or polar complexes with a particular group of organic compounds.

Berger (1941) was the first to make synthesis of covalent montmorillonite complexes. He obtained methyl ester as a product of the reaction of montmorillonite with diazomethane. In the fifties, Deuel and his associates published several papers dealing with the formation of organo-montmorillonite complexes. Synthesis of these compounds was to prove the existence of surface silanol groups Si-OH, and their reactivity.

To obtain alcoxyl derivatives of montmorillonite, Deuel used a reaction

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intermediate — montmorillonite chlorite, which formed during the reaction of H- or Na-montmorillonite with thionyl chloride in an anhydrous medium (Deuel *et al.* 1950, 1951; Deuel 1957). Chloride thus obtained gave appropriate alcoxyl derivatives by reaction with anhydrous alcohols (methanol, ethanol, propanol, butanol). These derivatives exhibited hydrophobic properties, but the  $\equiv\text{Si-O-C}$  bond appeared to be unstable in the process of hydrolysis.

Phenylomontmorillonite, obtained by Friedel-Crafts synthesis from montmorillonite chloride and benzene in the presence of  $\text{AlCl}_3$  as a catalyst, showed good hydrophobic properties (Deuel *et al.* 1951, 1952, 1953; Deuel 1957; Gentili, Deuel 1957; Gentili 1957). X-ray, IR spectroscopic and DTA analyses yielded data confirming the substitution of silanol groups by phenyl radicals. Measurements carried out in Enslin apparatus showed that this phenyl derivative of montmorillonite possessed both hydrophobic and hydrophilic properties. To prove the presence of the covalent bond in phenylomontmorillonite, Deuel and Gentili decomposed it to low-molecular silicon organic compounds (Gentili, Deuel 1957). Infrared spectroscopic investigations revealed the presence of  $\equiv\text{Si-C}_6\text{H}_5$  bonds, which must have existed in the original compound as decomposition could not have been responsible for their formation.

Searching for new organic derivatives of montmorillonite, Spencer and Gieseking (1952) and Slabaugh (1952) carried out a reaction of montmorillonite with acetic acid anhydride, acetic acid and acetyl chloride. In contrast to hydrophilic (initial) H-montmorillonite, acetylated montmorillonite exhibited hydrophobic properties and adsorbed organic substances better than untreated mineral.

Synthesis of organic complexes of montmorillonite was subject to much difference of opinion. After analysing the experimental data, Barrer and Reay (1958) and Greenland and Russel (1955) arrived at the conclusion that silanol groups did not react with the above-mentioned reagents. It has been shown in several papers (Greenland, Russell 1955, Brown *et al.* 1952) that simple organic compounds are adsorbed on the surface of montmorillonite by physical adsorption forces and, in spite of that, they are difficult to remove. Even prolonged outgassing of these derivatives under high vacuum did not lead to desorption of the organic substance. It appears that the nature of the chemical bond between montmorillonite and organic substances is not quite clear.

Another type of organic derivatives of montmorillonite is represented by ionic complexes. In this group, worth noting are montmorillonite complexes with aliphatic amines and their primary, secondary, tertiary and quaternary salts (Barrer *et al.* 1955, 1957, 1963; Cowan, White 1958). It has been found that these complexes show many interesting properties, e.g. rigidity of the structure and selective sorption. Alkylammonium cations introduced into the interlayer spaces replace the inorganic cations in the process of ion exchange. Compared with the initial mineral, the complexes thus formed show a greater loss of interlayer water, which is reflected in less pronounced endothermic peak on DTA curves. Hydrophobization of the surface is complete when montmorillonite is saturated with alkylammonium cations introduced in the amounts equal to its exchange capacity (Ovtcharenko 1960, Kurilenko, Michaliuk 1959). It has also been found that there is a distinct relationship between the degree of hydrophobiza-

tion and the number of carbon atoms in the organic radical. The longer the alkyloamine chain, the more hydrophobic is the given complex.

Barrer, Kelsey (1961), Barrer, Brummer (1963) carried out investigations of sorption of inert gases, straight- and branched-chain hydrocarbons and polar substances on montmorillonites showing partial or complete substitution by methyl- and ethylammonium cations.  $\text{N}^+(\text{CH}_3)_4$  and  $\text{N}^+(\text{C}_2\text{N}_5)_4$  ions are large but have a compact structure. They cause the layer of the mineral to part, thus promoting the formation of ample free space accessible to adsorbate molecules. Montmorillonite modified in this way assumes a zeolitic structure and exhibits good sieve properties. It has also been noted that there is a correlation between sorption of nonpolar substances and the degree of exchange of inorganic for organic ions.

## EXPERIMENTAL AND RESULTS

Montmorillonite to be hydrophobized was separated by sedimentation from bentonite from Jawor. After converting it into the hydrogen and sodium forms, hydrophobization was effected by reaction with acetic acid anhydride. In the first stage, our attention was focussed on selection and optimum reagent concentration, temperature and reaction time. Then hydrophobization was carried out and the samples were used to obtain isotherms for water vapour sorption. Prior to measurements, samples of untreated mineral were outgassed at 378 K in a vacuum up to  $1.33 \cdot 10^{-3}$  N/m<sup>2</sup>. Hydrophobized montmorillonite was outgassed without being heated simultaneously. Water vapour sorption isotherms were determined at 298 K using microburettes for liquids.

Figure 1 shows isotherms obtained for water vapour sorption on initial

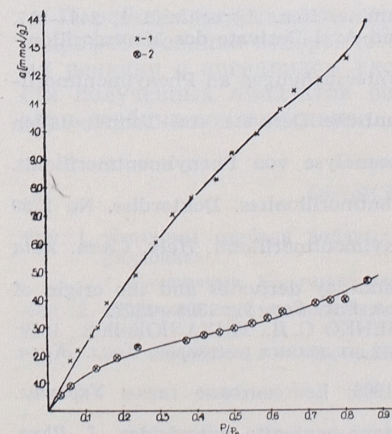


Fig. 1. Adsorption isotherms of water vapour on H-montmorillonite  
1 — initial, 2 — hydrophobic form

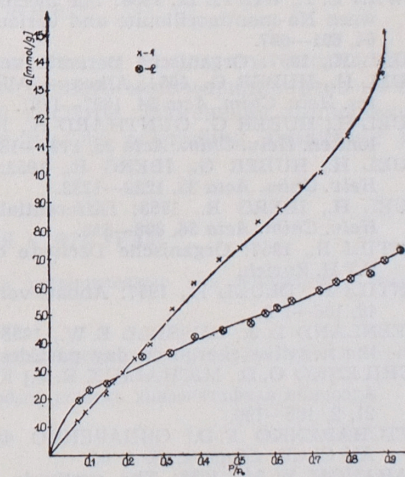


Fig. 2. Adsorption isotherms of water vapour on Na-montmorillonite  
1 — initial, 2 — hydrophobic form

H-montmorillonite and montmorillonite subjected to hydrophobization. The isotherms reveal that sorption capacity of hydrophobized sample is markedly lower than that of initial H-montmorillonite.

Figure 2 illustrates the change in sorption capacity of Na-montmorillonite. In this case, the sorption capacity decreases when the relative pressure  $p/p_0$  exceeds 0.15.

The experimental data do not allow the authors to define the amount of reaction that has taken place between montmorillonite and acetic acid anhydride. They encourage them, however, to carry on the studies of hydrophobization of montmorillonite involving sorption of vapours of non-polar substances, as well as analysis of the hydrophobization products by other physico-chemical methods.

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#### WSTĘPNE BADANIA NAD HYDROFOBIZACJĄ MONTMORILLONITU METODĄ REAKCJI Z BEZWODNIKIEM KWASU OCTOWEGO

#### Streszczenie

W pracy przedstawiono wstępne wyniki badań nad hydrofobizacją montmorillonitu wodorowego i sodowego w reakcji z bezwodnikiem kwasu octowego. Zmiany w hydrofilności uzyskanych produktów oceniono na podstawie przebiegu izoterm sorpcji par wody.

#### OBJAŚNIENIA FIGUR

- Fig. 1. Izotermy sorpcji par wody wyznaczone na montmorillonicie wodorowym  
1 — pierwotnym, 2 — hydrofobizowanym
- Fig. 2. Izotermy sorpcji par wody wyznaczone na montmorillonicie sodowym  
1 — pierwotnym, 2 — hydrofobizowanym

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#### ПРЕДВАРИТЕЛЬНЫЕ ИССЛЕДОВАНИЯ ГИДРОФОБИРОВАНИЯ МОНТМОРИЛЛОНИТА ПУТЁМ РЕАКЦИИ С АНГИДРИДОМ УКСУСНОЙ КИСЛОТЫ

#### Резюме

В работе представлены предварительные результаты исследований гидрофобирования водородного и натриевого монтмориллонитов во время реакции с ангидридом уксусной кислоты. Изменения гидрофильности полученных продуктов оценивались на основании характера изотерм сорбции водяных паров.

#### ОБЪЯСНЕНИЯ К ФИГУРАМ

- Фиг. 1. Изотермы сорбции водяных паров установленные для водородного монтмориллонита  
1 — первичного, 2 — гидрофобированного
- Фиг. 2. Изотермы сорбции водяных паров установленные для натриевого монтмориллонита  
1 — первичного, 2 — гидрофобированного