

Zenon KŁAPYTA \*, Mieczysław ŻYŁA \*\*

## MODIFICATION OF SORPTION PROPERTIES OF Cu-MONTMORILLONITE WITH HEXADECYLPYRIDINIUM CATIONS

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**Abstract.** The paper presents the results of studies of sorption properties of Cu-montmorillonite modified with hexadecylpyridinium (HDP) cations. Samples of variable  $\text{Cu}^{2+}$  and HDP<sup>+</sup> content on the exchange positions were obtained. The amount of HDP cations was determined from IR spectra, whereas the mode of packing of organic substance in the interlayer spaces of montmorillonite was defined from X-ray diffraction patterns. The sorption properties of samples with respect to water, methyl alcohol, benzene and argon vapour were investigated.

### INTRODUCTION

Organic cations introduced into the exchange positions of montmorillonite generally reduce the specific surface area of that mineral. The size of the surface area, determined from argon or nitrogen sorption, depends on the amount of organic cations on the exchange positions. Montmorillonite that contain mixed cations, organic and inorganic, are usually systems in which the cations are subject to segregation, giving rise to disordered mixed-layer structures (Glaeser, Mering 1954; Barrer, Brumer 1962; McBride, Mortland 1973).

The segregation of cations may be incomplete. In that case, some interlayer spaces in montmorillonite contain both inorganic and organic cations. In such organo-mineral complexes the organic cations make the crystal lattice rigid in the  $c_0$  direction, and the resultant system shows the pro-

\* Institute of Energochemistry of Coal and Physicochemistry of Sorbents, Academy of Mining and Metallurgy, Cracow (Kraków, al. Mickiewicza 30).

\*\* Institute of Geology and Mineral Deposits, Academy of Mining and Metallurgy, Cracow (Kraków, al. Mickiewicza 30).

erties of a molecular sieve. Moreover, the specific surface area increases due to a higher degree of accessibility of the interlayer spaces to argon and nitrogen vapours (Barrer, McLeod 1955; Barrer, Reay 1957; McBride, Mortland 1973, 1975).

In an earlier publication the present authors investigated montmorillonite containing  $\text{Ni}^{2+}$  and hexadecylpyridinium cations (Żyła, Kłapyta 1976). It has been found that the organic and inorganic cations in those complexes show a tendency to segregation and that the interlayer spaces remain inaccessible to argon vapour. This paper presents the studies of montmorillonite containing  $\text{Cu}^{2+}$  and HDP cations in variable proportions.

## EXPERIMENTAL

Investigations were carried out on montmorillonite from Chmielnik. The mineral was transformed into Na-form by treating it with 1N NaCl solution. Cu-montmorillonite was obtained from the material thus prepared, using aqueous  $\text{CuCl}_2$  solution. Excess  $\text{CuCl}_2$  was washed out with distilled water in a centrifuge until the reaction to  $\text{Cl}^-$  ion was negative. Aqueous solutions of hexadecylpyridinium chloride with various contents of organic salt were added to the Cu-montmorillonite suspension and the mixture was stirred for two days. Then the samples were centrifuged and washed with distilled water until the reaction to  $\text{Cl}^-$  ion was negative. The specimens thus obtained were subjected to infrared spectroscopic and X-ray analyses and their sorption properties were determined.

Infrared spectroscopic analyses were carried out in the UR-10 spectrophotometer using KBr disks. X-ray powder patterns were recorded in the TUR M-61 diffractometer, using non-oriented powder preparations and samples sedimented on glass plates. Sorption investigations involved measurements of isotherms for water, methyl alcohol, benzene and argon vapour sorption. Isotherms for water, methyl alcohol and benzene vapour sorption were obtained at 298 K using microburettes for liquids (Lasoń, Żyła 1963) whereas those for argon sorption were determined at 77 K in sorption manostats (Ciembroniewicz, Lasoń 1972).

## RESULTS

### Infrared spectroscopic investigations

Infrared spectra of the samples studied (Fig. 1) reveal the presence of montmorillonite absorption bands as well as the maxima due to HDP cations occupying the exchange positions. Particularly pronounced are the bands produced by C—H valence vibrations within the  $\text{CH}_2$  and  $\text{CH}_3$  groups of the hydrocarbon chain ( $2850, 2920 \text{ cm}^{-1}$ ). Their intensity increases with an increase in the content of organic cations on the exchange positions of montmorillonite. As in the case of Ni-HDP-montmorillonite (Żyła, Kłapyta 1976), a gradual decrease in the intensity of the absorption bands produced by deformation ( $1630 \text{ cm}^{-1}$ ) and valence ( $3430 \text{ cm}^{-1}$ ) vibrations of interlayer water molecules has been noted. This fact indicates that  $\text{H}_2\text{O}$  is progressively replaced by HDP cations in the interlayer spaces.

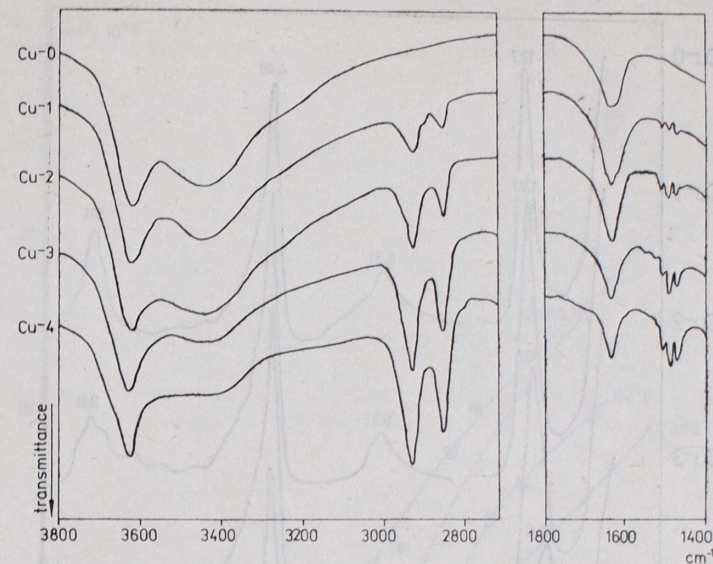


Fig. 1. Infrared spectra of Cu-montmorillonite (sample Cu-0) and Cu-HDP montmorillonite (samples Cu-1 to Cu-4)

Basing on infrared spectra, the approximate content of HDP cations occupying the exchange positions of montmorillonite was calculated. The spectra of Ni-montmorillonite with the known contents of HDP cations were utilized for that purpose (Żyła, Kłapyta 1976). To make quantitative determinations, the intensity of the absorption bands  $2850$  and  $2920 \text{ cm}^{-1}$  was measured with a planimeter. The contents of HDP cations determined by that method for samples Cu-1 to Cu-4 are, respectively, about 7, 15, 30 and 45% of the exchange positions.

### X-ray investigations

The results of X-ray investigations are presented in Figure 2. The X-ray diffraction pattern of Cu-montmorillonite (Cu-0) reveals the presence of  $00l$  reflections of the  $d_{hkl}$  values =  $12.7, 6.31, 3.11 \text{ \AA}^*$ . The reflection  $12.7 \text{ \AA}$  in the X-ray diffractogram of sample Cu-1 is slightly displaced to  $d_{hkl} = 13.0 \text{ \AA}$ , which is due to adsorption of a few HDP cations on the exchange positions of montmorillonite. In the case of sample Cu-2, this reflection is  $d = 13.7 \text{ \AA}$ . Further increase in the content of organic cations in the interlayer spaces in sample Cu-3 results in the formation of an organo-mineral complex with the mixed-layer structure. In this mineral layers with one and two sheets of flat-lying HDP cations are randomly interstratified ( $d_{hkl} = 15.5, 4.26, 3.50 \text{ \AA}$ ) (Fig. 2). An increase in the orga-

\*  $1 \text{ \AA} = 10^{-1} \text{ nm}$ .

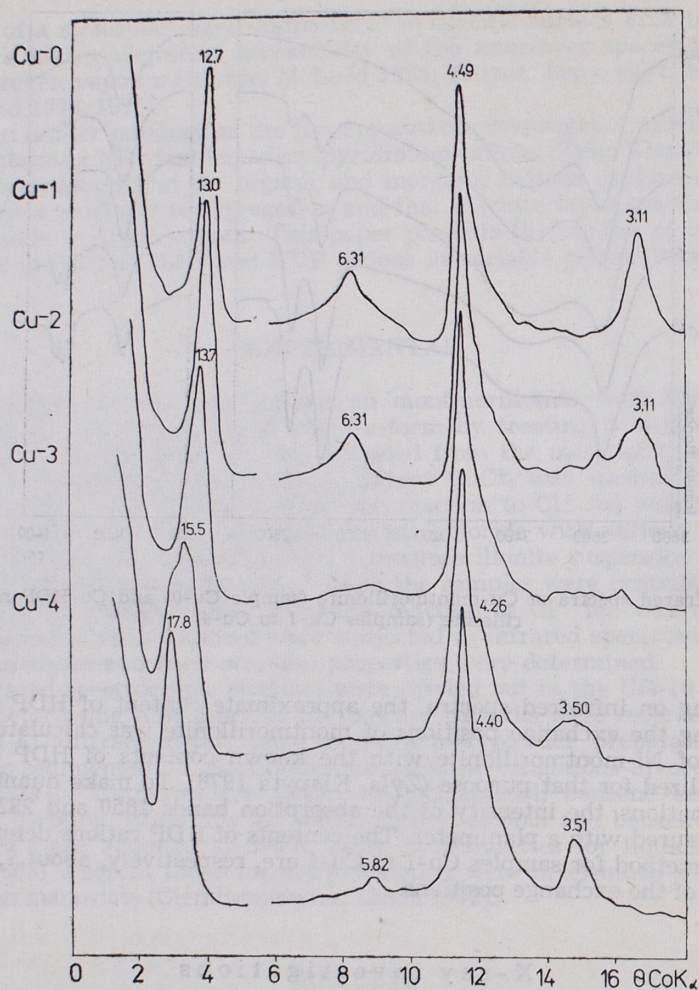


Fig. 2. X-ray diffraction patterns of Cu-montmorillonite and Cu-HDP montmorillonite

nic cation content up to about 45% of the exchange positions in sample Cu-4 gives rise to two sheets of organic cations lying flat in the interlayer spaces ( $d_{hkl} = 17.8, 4.40, 3.51 \text{ \AA}$ ) (Fig. 2).

### Sorption investigations

The isotherms obtained for water vapour sorption are shown in Figure 3. From their shape the BET values for specific surface areas were calculated and listed in Table 1; they were treated, however, only as indices of sorption capacity in the range of low relative pressures, neglecting their

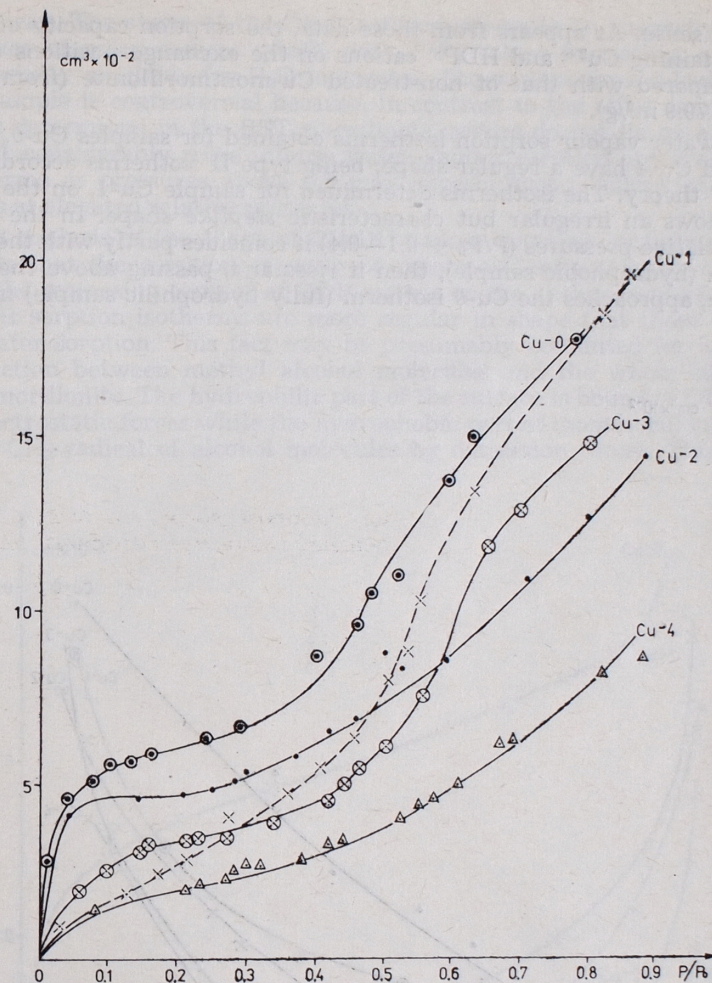


Fig. 3. Isotherms for water vapour adsorption on Cu-montmorillonite and Cu-HDP montmorillonite

Specific surface area

Table 1

Sample	Adsorbate		
	water	methyl alcohol	argon
m <sup>2</sup> /g			
Cu-0	186.4	353.6	40.0
Cu-1	95.4	318.1	14.6
Cu-2	121.5	206.9	10.6
Cu-3	95.4	149.8	7.0
Cu-4	70.9	141.8	6.0

physical sense. As appears from those data, the sorption capacity of samples containing  $\text{Cu}^{2+}$  and HDP<sup>+</sup> cations on the exchange positions decreases compared with that of non-treated Cu-montmorillonite (from 186.4 down to 70.9  $\text{m}^2/\text{g}$ ).

The water vapour sorption isotherms obtained for samples Cu-0, Cu-2, Cu-3 and Cu-4 have a regular shape, being type II isotherms according to the BET theory. The isotherms determined for sample Cu-1, on the other hand, shows an irregular but characteristic *steplike* shape. In the range of low relative pressures ( $P/P_0 = 0.1-0.4$ ) it coincides partly with the Cu-4 isotherm (hydrophobic sample), then it rises and, passing above the Cu-3 isotherm, approaches the Cu-0 isotherm (fully hydrophilic sample) in a si-

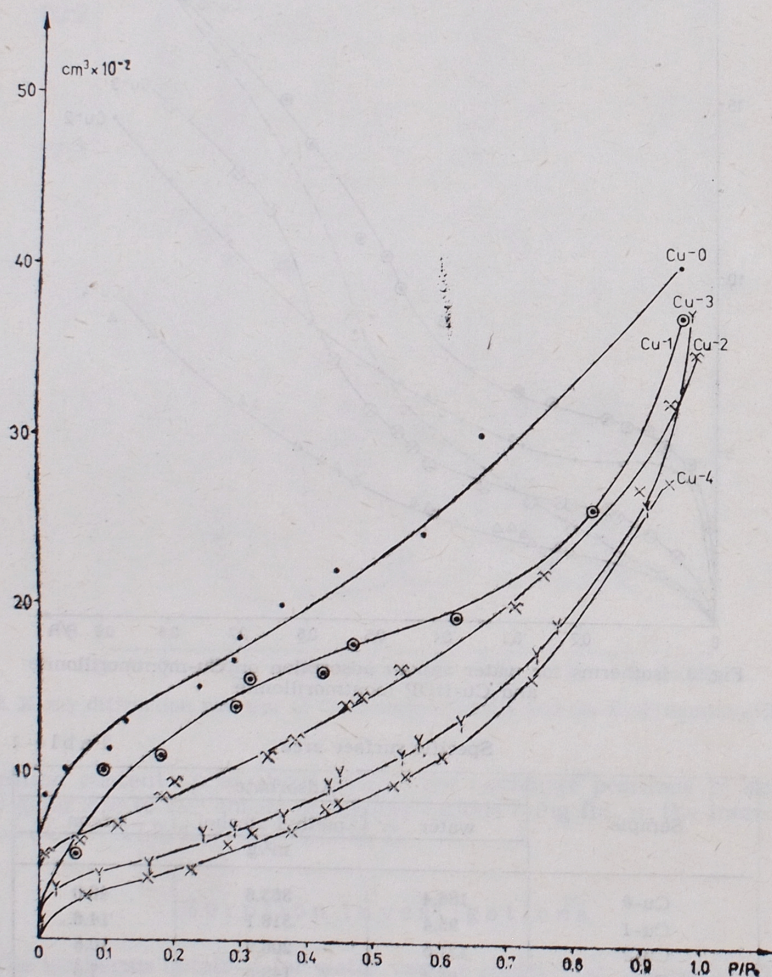


Fig. 4. Isotherms for methyl alcohol vapour adsorption on Cu-montmorillonite and Cu-HDP montmorillonite

milar way. The shape of the Cu-1 isotherm seems to be suggestive of the presence of polar centres which, with  $P/P_0$  values increasing, are made successively available for  $\text{H}_2\text{O}$  molecules. The surface area calculated for that sample is controversial because, in contrast to the other samples, the points determined in the BET co-ordinate system do not lie on a straight line. A considerably more intense water vapour sorption observed on the isotherms at pressures above 0.5 may suggest that swelling of samples occurs at elevated relative pressures.

An analysis of the shape of  $\text{CH}_3\text{OH}$  vapour sorption isotherms (Fig. 4) reveals that the sorption capacity of montmorillonite samples decreases with the increasing content of HDP cations on the exchange positions. The  $\text{CH}_3\text{OH}$  sorption isotherms are more regular in shape than those obtained for water sorption. This fact may be presumably accounted for by strong interaction between methyl alcohol molecules and the whole surface of montmorillonite. The hydrophilic part of the surface is bound to OH groups by electrostatic forces while the hydrophobic part of montmorillonite binds the  $-\text{CH}_3$  radical of alcohol molecules by dispersion forces. This way of

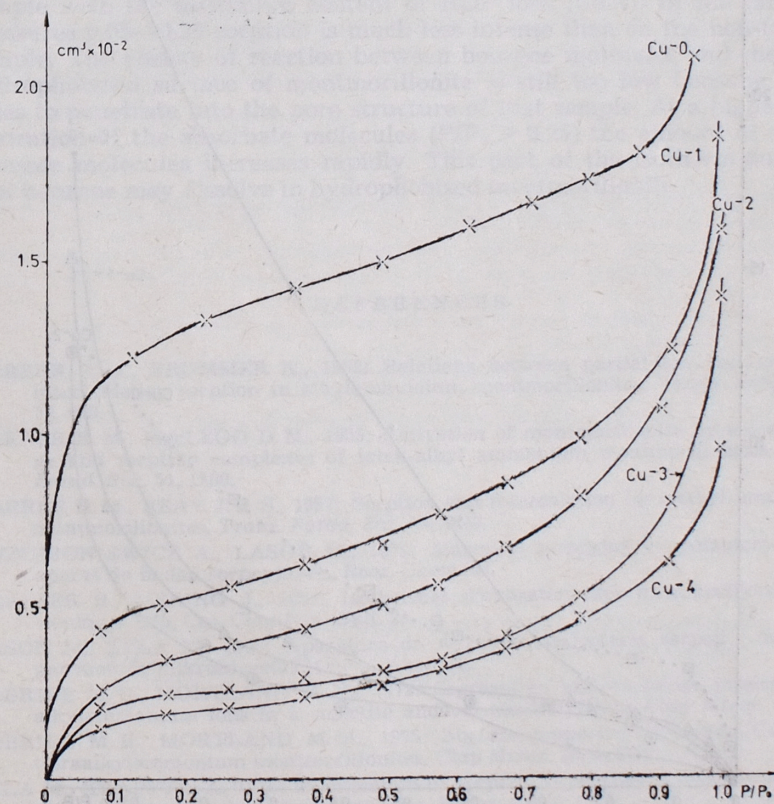


Fig. 5. Isotherms for argon vapour adsorption on Cu-montmorillonite and Cu-HDP montmorillonite

binding of  $\text{CH}_3\text{OH}$  molecules is also reflected in higher surface area values compared with those determined from water vapour sorption. This is probably because alcohol molecules penetrate more readily into the interlayer spaces of montmorillonite. The pronounced decrease in the specific surface area noted as copper cations are exchanged for HDP cations can be accounted for by the fact that the interlayer spaces of montmorillonite become inaccessible to methyl alcohol.

Argon sorption yields some interesting data. Table 1 gives the values for specific surface area calculated from the shape of isotherms (Fig. 5).

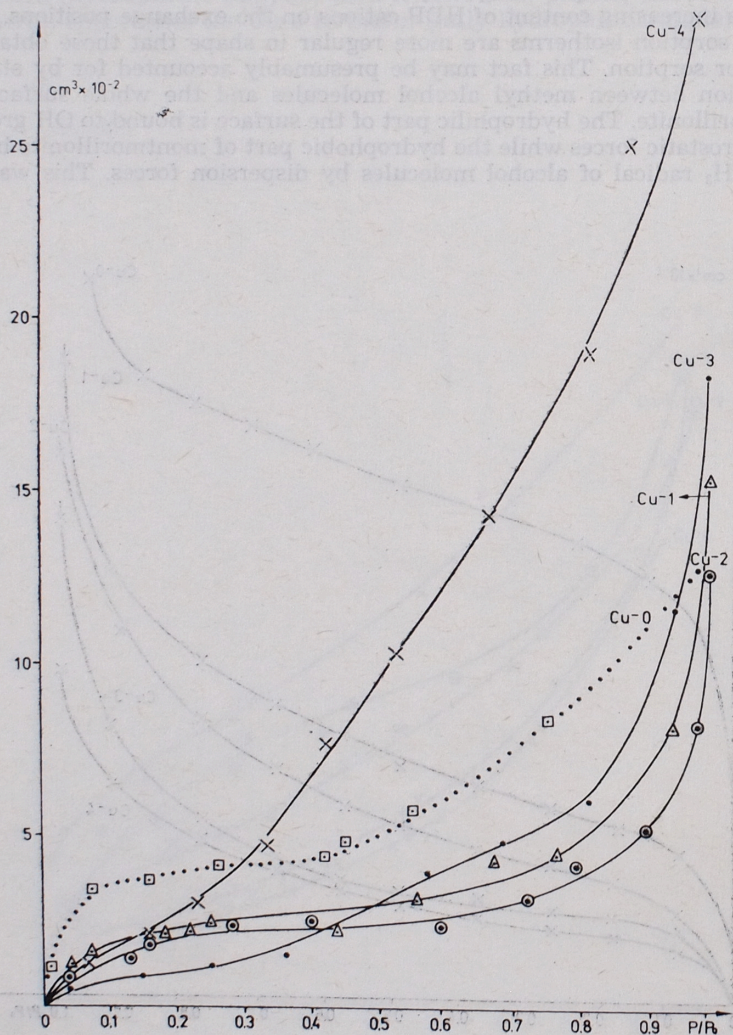


Fig. 6. Isotherms for benzene vapour adsorption on Cu-montmorillonite and Cu-HDP montmorillonite

It is generally held that argon sorption occurs predominantly on the external surfaces of montmorillonite grains and only sporadically in the interlayer spaces. A marked decrease in the surface area from 40 down to  $6 \text{ m}^2/\text{g}$  which follows the introduction of HDP cations may be accounted for both by the larger size of grain aggregates of montmorillonite and diminished porosity due to blocking of the interlayer spaces by the HDP cations.

Compared with argon isotherms, those obtained for benzene vapour sorption (Fig. 6) are very irregular in shape. Due to this, the surface areas were not calculated and changes in the sorption capacity are discussed on the basis of available sorption isotherms. The non-treated montmorillonite sample (Cu-0) shows substantial sorption capacity in the range of low relative pressures (0.05—0.10), which may suggest a high degree of microporosity. In the range of relative pressures 0.1—0.5, the amount of sorbed benzene molecules increases insignificantly due to the lack of transitional porosity. At pressures above 0.7 the isotherms rise considerably, and sorption has most likely an intergranular character.

Worth noting is the isotherm obtained for benzene sorption on the sample with the maximum content of HDP ions (Cu-4). In the range of pressures 0.05—0.20 sorption is much less intense than on the non-treated sample. The energy of reaction between benzene molecules and the little hydrophobized surface of montmorillonite is still too low benzene molecules to penetrate into the pore structure of that sample. At a higher concentration of the adsorbate molecules ( $P/P_0 > 0.25$ ) the amount of sorbed benzene molecules increases rapidly. This part of the isotherm suggests that benzene may dissolve in hydrophobized montmorillonite.

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### **MODYFIKACJA WŁASNOŚCI POWIERZCHNIOWYCH Cu-MONTMORILLONITU PRZY ZASTOSOWANIU KATIONÓW HEKSADECYLOPIRYDINIOWYCH**

#### Streszczenie

W pracy przedstawiono wyniki badań nad modyfikacją własności sorpcyjnych Cu-montmorillonitu przy zastosowaniu kationów heksadecylopirydyniowych (HDP). Otrzymano próbki zawierające kationy organiczne w ilościach 7, 15, 30 i 45% pozycji wymiennych montmorillonitu. Zawartości te określono przy zastosowaniu spektroskopii w podczerwieni. Badania rentgenowskie wykazały, że kationy HDP tworzą w przestrzeniach międzypakietowych montmorillonitu jedną lub dwie warstwy monomolekularne. W niektórych próbkach stwierdzono struktury mieszanopakietowe. Jak wynika z badań sorpcyjnych, chłonność sorpcyjna Cu-montmorillonitu względem par wody i alkoholu metylowego zmniejsza się ze wzrostem ilości kationów HDP na pozycjach wymiennych. Podobnie zmienia się chłonność sorpcyjna względem par argonu. Przebieg izoterm sorpcji benzenu wskazuje natomiast na wzrost ilości adsorbowanych cząsteczek tego związku w miarę obsadzania pozycji wymiennych przez kationy HDP.

#### OBJAŚNIENIA FIGUR

- Fig. 1. Spektrogramy w podczerwieni Cu-montmorillonitu (próbka Cu-0) i Cu-HDP montmorillonitu (próbki Cu-1 do Cu-4)
- Fig. 2. Dyfraktogramy rentgenowskie Cu-montmorillonitu i Cu-HDP montmorillonitu
- Fig. 3. Izotermy adsorpcji par wody na Cu-montmorillonicie i Cu-HDP montmorillonicie
- Fig. 4. Izotermy adsorpcji par alkoholu metylowego na Cu-montmorillonicie i Cu-HDP montmorillonicie
- Fig. 5. Izotermy adsorpcji par argonu na Cu-montmorillonicie i Cu-HDP montmorillonicie
- Fig. 6. Izotermy adsorpcji par benzenu na Cu-montmorillonicie i Cu-HDP montmorillonicie

Zenon KŁAPYTA, Мечислав ЖИЛА

### **МОДИФИКАЦИЯ ПОВЕРХНОСТНЫХ СВОЙСТВ Cu-MONTMORILLONITA ПОСЛЕ ИСПОЛЬЗОВАНИЯ ГЕКСАДЕЦИЛОПИРИДИНОВЫХ КАТИОНОВ**

#### Резюме

В работе изложены результаты исследований над модификацией поглощающих свойств Cu-монтмориллонита после использования для этого гексадецилопиридиновых катионов (HDP). Были получены образцы

содержащие органические катионы в количестве 7, 15, 30 и 45% обменных позиций монтмориллонита. Это содержание было отождествлено при помощи инфракрасной спектроскопии. Рентгеновские исследования показали, что катионы HDP дают в междупакетных пространствах монтмориллонита один или два мономолекулярных слоя. В некоторых образцах обнаружены смешаннопакетные структуры. Из сорбционных исследований следует, что поглощающая ёмкость Cu-монтмориллонита к водяному пару и парам метилового спирта снижается по мере возрастания количества катионов HDP на обменных позициях. Подобным образом изменяется поглощающая ёмкость к парам аргона. В то же время изотермы поглощения бензена показывают, что количество поглощённых частиц этого соединения возрастает по мере заполнения обменных позиций катионами HDP.

#### ОБЪЯСНЕНИЯ К ФИГУРАМ

- Фиг. 1. Инфракрасные спектры Cu-монтмориллонита (образец Cu-0) и Cu-HDP монтмориллонита (образцы с Cu-1 по Cu-4)
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- Фиг. 3. Изотермы адсорбции водяного пара в Cu-монтмориллоните и Cu-HDP монтмориллоните
- Фиг. 4. Изотермы адсорбции паров метилового спирта в Cu-монтмориллоните и Cu-HDP монтмориллоните
- Фиг. 5. Изотермы адсорбции паров аргона в Cu-монтмориллоните и Cu-HDP монтмориллоните
- Фиг. 6. Изотермы адсорбции паров бензена в Cu-монтмориллоните и Cu-HDP монтмориллоните