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Vera LUPTAKOVA *, *Anna NEMETHY* *, *Mieczysław ŻYŁA* **

SORPTIVE PROPERTIES OF SYNTHETIC MONTMORILLONITE

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A b s t r a c t. The paper deals with the results of examination of adsorption of methyl alcohol, argon and benzene vapours of five samples of montmorillonite obtained by hydrothermal synthesis from SiO_2, Al_2O_3 and MgO. The calculated data of specific surfaces and the distribution curves of pore volumes determined by means of desorption isotherms are discussed.

INTRODUCTION

The knowledge of physico-chemical properties of bentonites is of great importance to determine the possibility of their practical application. Their essential constituent — montmorillonite — often contains various amount of Fe, Ti and Mn. These admixtures are generally disturbing in determining the physico-chemical properties of montmorillonite. Consequently, the use of synthetical montmorillonite, free from these elements, is recommanded in such experiments.

Among several methods of synthesis, the hydrothermal one proposed by Noll (1936a, 1936b) is the most interesting. By applying increased pressures, this author obtained montmorillonites containing various interlayer cations as Na^+, K^+, Ca^{2+}, Be^{2+} and Cs^+. The $SiO_2 : Al_2O_3$ ratio in these experiments was constant (4 : 1) while the content of the third essential component — variable. The syntheses were carried out in alkaline medium. It was found that the third component considerably influences the course of montmorillonite synthesis.

Roy and Osborn (1954) obtained Al-montmorillonite from a mixture of SiO_2, Al_2O_3 and H_2O, with silica/alumina ratio = 3 : 1, by applying the pressure of 1200 atm. The attempts of these authors to synthetize a Mg-

* Dept. of Inorganic Chemistry, the Komensky University, Bratislava, Czechoslovakia.
** The Academy of Mining and Metallurgy, Cracow (Kraków), al. Mickiewicza 30, Poland.

-montmorillonite resulted in obtaining a product showing only very weak characteristic X-ray reflections.

Large-scale montmorillonite syntheses at approx. 1000 atm pressures were also carried out by D.M. Roy and R. Roy (1955). They started from mixtures composed of SiO_2, Al_2O_3, MgO and H_2O. The products were defined as montmorillonite but no physico-chemical properties of them were presented.

Recently, montmorillonite syntheses were performed by Kuchta and Masar (1973).

EXPERIMENTAL PART

The present authors have synthetized montmorillonite under hydrothermal conditions at 300°C and 87 atm, starting from the system composed of Al_2O_3, SiO_2, CaO, MgO and H_2O. The silica/alumina ratio was constant (4 : 1), whilst MgO content variable, differing by 0.5 mol in each experiment. The process was carried out in an autoclave of Hungarian production. Aluminium and magnesium oxides were obtained by thermal decomposition of $Al(NO_3)_3 \cdot 9H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$ at 700°C while SiO_2 used was chemical reagent produced by Lecham. The oxides were preliminarily well mixed, homogenized and then placed in autoclave. The syntheses lasted 7 days.

The obtained products were identified using X-ray, infrared spectrophotometric and thermal methods. All these date indicate them to be montmorillonites.

Since natural montmorillonites are good absorbents, five of the samples obtained by means of Kuchta and Masar method were examined to determine their absorptive properties.

All the montmorillonite samples under study were synthetized in the Department of Inorganic Chemistry of the Komensky University in Bratislava.

Molal proportions of oxides in the initial mixtures used to synthetize five montmorillonite samples in study are presented in Table 1.

Desorption studies enable not only to determine specific surface and polar character of surface of an adsorbent but also give some data on the

Table 1

Molal proportions of initial oxides in mixtures used for montmorillonite synthesis

Sample No	Molal proportion of the oxide		
	SiO_2	Al_2O_3	MgO
13	4,0	1,0	1,0
15	4,0	1,0	2,0
16	4,0	1,0	1,5
17	4,0	1,0	2,5
18	4,0	1,0	3,0

structure of pores in it. In order to define the polarity of surface, it is necessary to determine sorption capacity relative to the vapours of both polar and apolar substances. In our experiments, methyl alcohol was used as polar absorbate and argon and benzene as apolar ones.

Measurements of adsorption isotherms for methyl alcohol and benzene vapours were carried out by means of apparatus with capillary microburettes at temperature 298°K (Lasoń, Żyła 1963).

Adsorption isotherms for argon were obtained using sorption manostate apparatus (Ciembroniewicz, Lasoń 1972) at temperature 77°K. Adsorption and desorption isotherms obtained are presented in Figures 1, 2 and 3.

By applying the equation of B.E.T. theory:

$$V = V_m \cdot \frac{C_x}{(1 - x)\,[1 + (C - 1)\,x]}$$

and taking into account these parts of isotherms which correspond to relative pressures $P/P_0 = 0.05 - 0.35$, we may determine the values of spe-

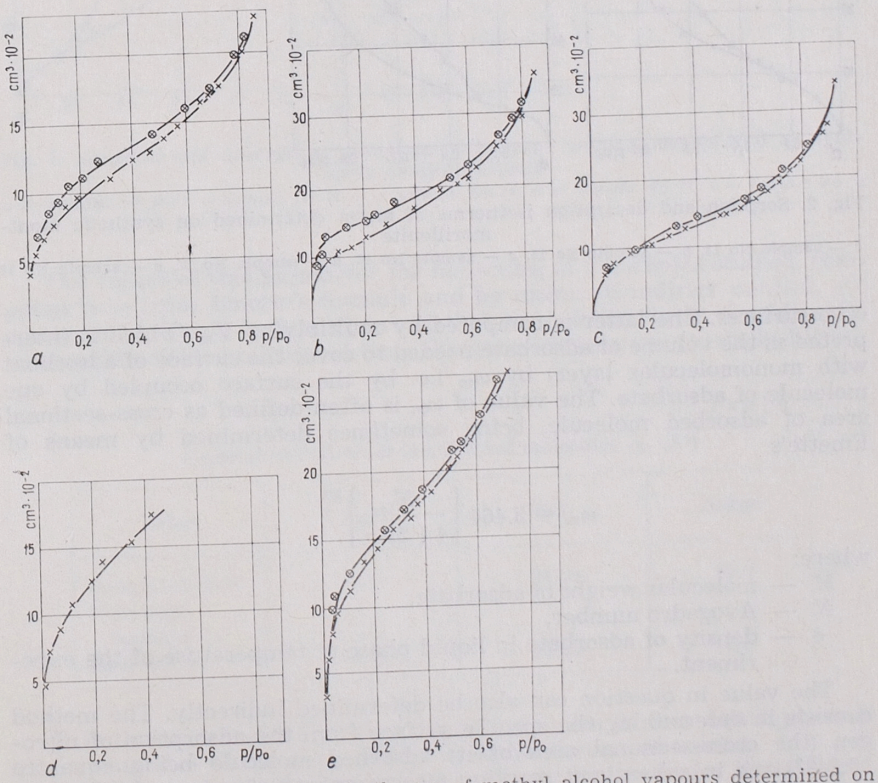

Fig. 1. Sorption and desorption isotherms of methyl alcohol vapours determined on synthetic montmorillonite

a — sample No 13, *b* — sample No 15, *c* — sample No 16, *d* — sample No 17, *e* — sample No 18

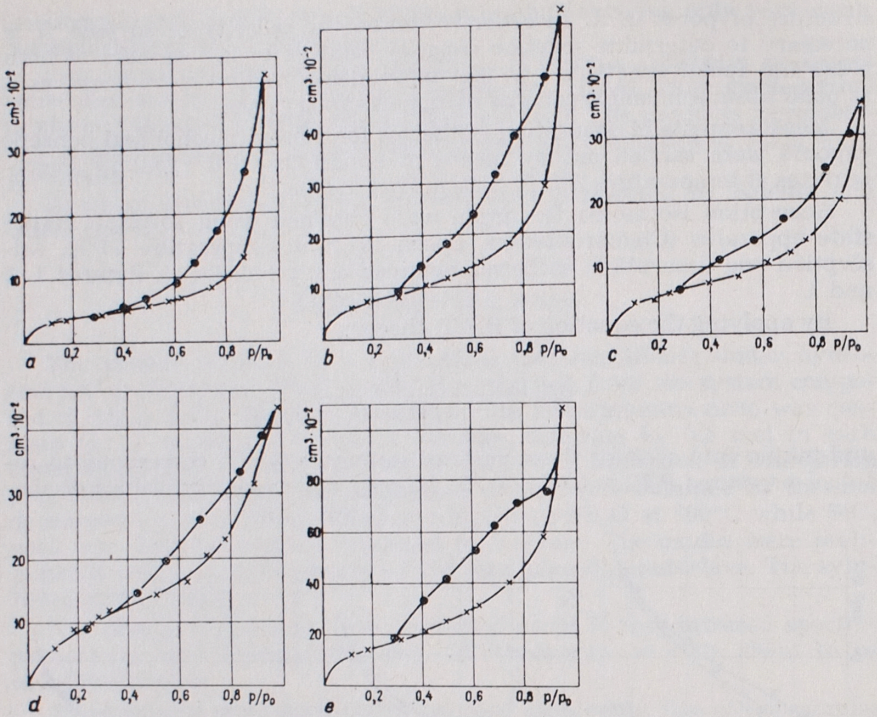

Fig. 2. Sorption and desorption isotherms of argon determined on synthetic montmorillonite

a — sample No 13, *b* — sample No 15, *c* — sample No 16, *d* — sample No 17, *e* — sample No 18

cific surfaces. The latter is computed by multiplying V_m (which is interpreted as the volume of adsorbate needed to cover the surface of adsorbent with monomolecular layer) by ω_m i.e. by the surface occupied by one molecule of adsorbate. The value of ω_m is often defined as cross-sectional area of adsorbed molecule, being sometimes determined by means of Emette's

$$\omega_m = 3.464 \left[\frac{M}{4\sqrt{2}N\sigma} \right]^{2/3}$$

where:

M — molecular weight of adsorbate,
N — Avogadro number,
σ — density of adsorbate in liquid phase at temperature of the experiment.

The value in question can also be determined indirectly. The method consists in determining the specific surface from the adsorption of nitrogen (the cross-sectional area of its adsorbed molecule being equal to 16.2 Å²) and in subsequent sorption measurements of vapours of the adsorbate under study. By dividing the surface of nitrogen by a_m obtained we find the cross-sectional area of adsorbed substance under examination.

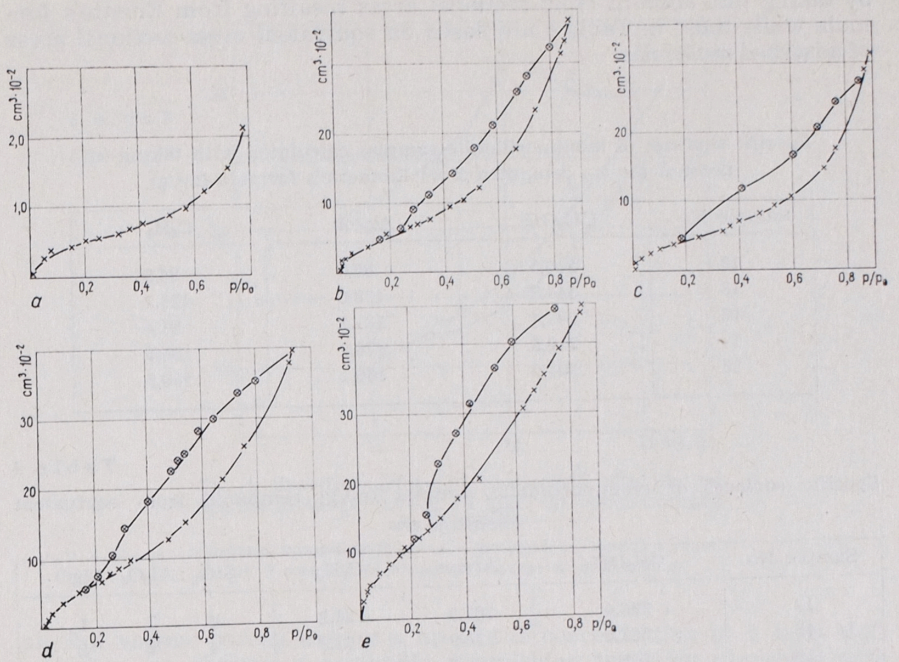

Fig. 3. Sorption and desorption isotherms of benzene vapours determined on synthetic montmorillonite

a — sample No 13, *b* — sample No 15, *c* — sample No 16, *d* — sample No 17, *e* — sample No 18

The values of this parameter for molecules of adsorbates studied, computed both from Emette's formula and by means of indirect method, are presented in Table 2. It is observed that they differ fairly considerably, whereas the values calculated from Emette's formula are generally higher.

Table 2

Cross-sectional areas of adsorbed molecules ω_m (Å²)

Value	CH_3OH	C_6H_6	Argon
Computed from Emmette's formula	18,11	30,60	13,8
Equivalent	29,11	45,22	16,6

It is thus concluded that packing of molecules in free liquid phase is more dense that of the same molecules at the surface of a solid.

The values of specific surfaces of montmorillonites under study calculated from sorption isotherms for methyl alcohol, benzene and argon are presented in Tables 3 and 4, whereby the data of Table 3 were computed

by taking into account cross-sectional areas resulting from Emette's formula while those in Table 4 are based on equivalent cross-sectional areas of adsorbed molecules.

Table 3

Specific surfaces of montmorillonite samples calculated with taking into account the ω_m computed from Emmette's formula (m^2/g)

Sample No	CH_3OH	Argon	C_6H_6
13	210,5	85,0	84,9
15	344,3	178,6	121,1
16	247,4	131,3	91,4
17	310,5	176,9	186,5
18	304,0	366,1	250,5

Table 4

Specific surfaces of montmorillonite samples (m^2/g) computed from equivalent values of ω_m

Sample No	CH_3OH	Argon	C_6H_6	$SiO_2 : Al_2O_3 : MgO$		
13	338,4	102,3	128,2	4	1	1
15	553,5	214,9	182,9	4	1	2
16	397,7	158,0	138,1	4	1	1,5
17	499,1	333,2	281,6	4	1	2,5
18	488,6	440,4	378,3	4	1	3,0

DISCUSSION OF RESULTS

When analyzing the obtained data we may note a systematic increase of specific surfaces with growing amounts of MgO introduced into the crystal lattice. This phenomenon is observed both in sorption of polar and apolar substances.

The increase of sorption of vapours of methyl alcohol can be explained by assuming the possibility of formation of additional polar centres in montmorillonite crystal lattice, the number of which depends on the amount of Mg present. This phenomenon results from the structure and properties of natural montmorillonites.

As reported by other authors, the concentration of negative charges on the surface of montmorillonite layer depends considerably on the grade of substitution of aluminium ions in octahedral sites by magnesium. Consequently, synthetic montmorillonites containing more magnesium are susceptible to the process of formation of negatively charged sorption centres.

The shape of the curve *A* (Fig. 4), showing the relation between specific surface and MgO content in montmorillonite, indicates that the increase of polar centres of sorption is limited. So e.g. the amount of methyl

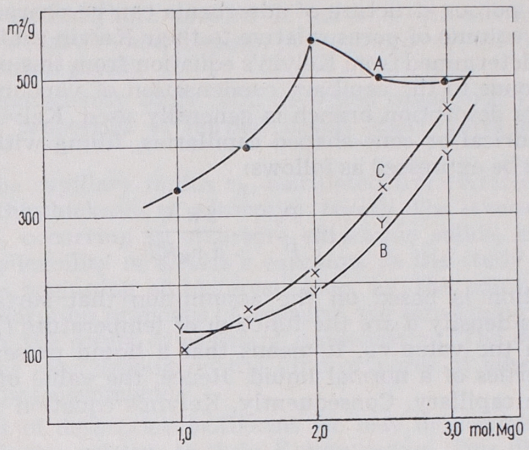

Fig. 4. Specific surface of montmorillonite plotted against molal proportion of MgO introduced during its synthesis
(surfaces computed from: *A* — sorption of methyl alcohol, *B* — sorption of argon, *C* — sorption of benzene)

alcohol vapour sorbed increases up to the concentration of 2 mols MgO and then we observe a negligible diminishing tendency connected with establishing of equilibrium. It is supposed that no matter of higher concentration of MgO in the initial mixture of oxides no further substitution of Al ions by Mg is possible during synthesis of montmorillonite under conditions applied by the authors. Very characteristic is also the shape of the curves *B* and *C* showing the variation of specific surface determined from the sorption of benzene vapours and argon respectively. These both curves are nearly parallel but the *B* one (sorption of benzene) is situated below the *C* curve of argon. This is probably due to different accessibility of pores in montmorillonite lattice resulting from various sizes of molecules of the adsorbates used. We have to note the variation of specific surfaces determined from the sorption of methyl alcohol vapours relative to the values of argon surfaces which vary from 3 to 1.

As follows from these data, montmorillonite samples containing the highest amount of Mg is equally accessible both to methyl alcohol molecules and to argon atoms.

Comparatively high sorption capacity of montmorillonite samples No 17 and 18 is most probably due to the formation of strongly developed micropore system. In order to explain the change of pore system, the curves of interdependence between pore volumes and Kelvin radii were constructed.

DISTRIBUTION OF PORE VOLUMES

The porosity of solids can be evaluated by means of two methods:
1) mercury porosimetry, and
2) densimetry.

Very often porous structure of adsorbents can be characterized by determining the volume of pores relative to their Kelvin radius. This distribution can be determined from Kelvin's equation from this part of isotherm which corresponds to the capillary condensation of vapours, whereby for computation its desorption branch is generally used. Kelvin's equation is valid for cylindrical or cone-shaped capillaries, filling with well wetting liquids and can be expressed as follows:

$$\ln \frac{P_0}{P} = \frac{2\,\sigma\,M}{d\,r_K RT}$$

Kelvin's equation is based on the assumption that surface tension of a liquid and its density d are the function of temperature (T) only and do not depend on the value r_K. It means that a liquid present in capillary displays properties of a normal liquid. Hence, the value of p depends on the radius of a capillary. Consequently, Kelvin's equation can be applied only to:

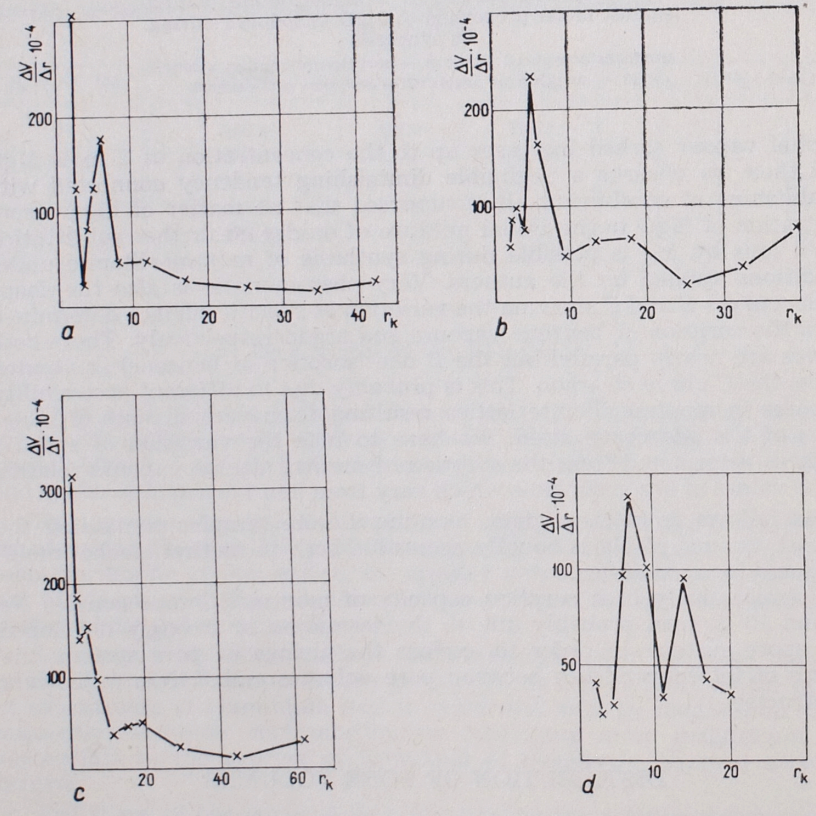

Fig. 5. Distribution of pore volumes plotted against Kelvin radius determined from desorption isotherm of methyl alcohol
a — sample No 13, *b* — sample No 15, *c* — sample No 16, *d* — sample No 17

1) this part of adsorbate present in pores of an adsorbent which is subjected to condensation and displays properties of normal liquid (macro-pores and transition pores),

2) pores of sufficiently large radii in which condensed vapours of adsorbate display properties of normal liquid (macropores and transition pores).

Moreover, the capillary radius r_K, calculated from Kelvin's equation is diminished by the thickness of adsorption layers. The lowest capillary radius (15—20 Å), occurring in structure of porous solids, corresponds to the limit of applicability of Kelvin's equation. In the study of adsorption phenomena, the beginning of histeresis loop, i.e. the point in which adsorption and desorption branches of isotherm are converging, is considered to correspond to the origin of capillary condensation. The occurrence and size of histeresis loop depend on the kind of pores of adsorbent and on adsorbate used in experiments.

On the basis of desorption isotherms we may determine the distribution of pore volumes relative to their Kelvin radius. This distribution can be presented diagramatically by plotting $\Delta V/\Delta r$ values (ordinate axis) versus Kelvin radii in Å (abscissae). The value of Kelvin radius corresponding

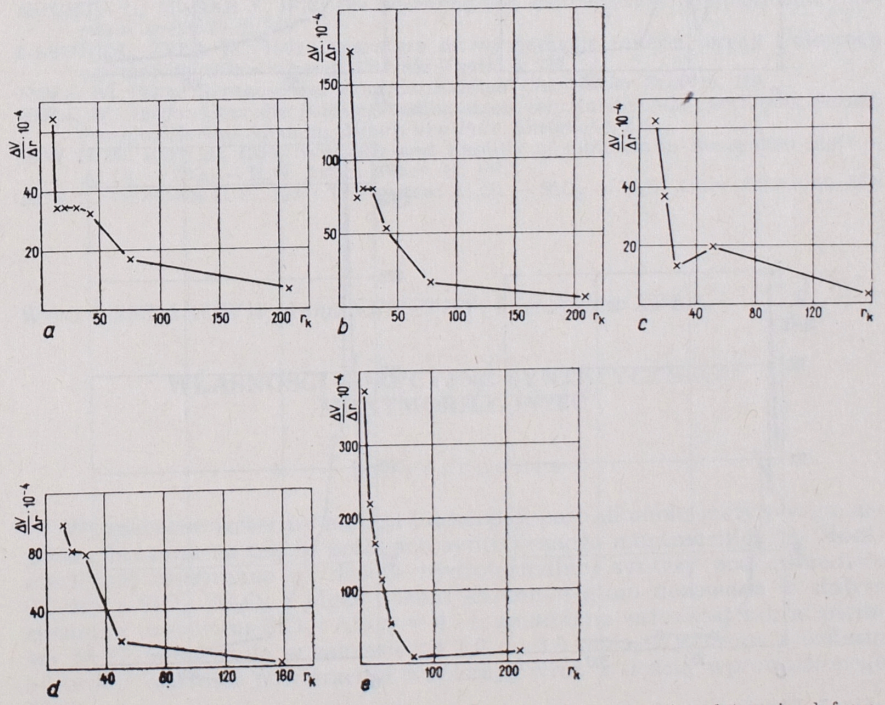

Fig. 6. Distribution of pore volumes plotted against Kelvin radius determined from isotherm of argon desorption
a — sample No 13, *b* — sample No 15, *c* — sample No 16, *d* — sample No 17, *e* — sample No 18

in this diagram to the maximal pore volume is accepted to represent the radius of dominant pores in a given adsorbent.

When analyzing the curves of distribution of pore volumes determined from desorption isotherms of methyl alcohol vapours (Fig. 5), the occurrence of a peak, corresponding to Kelvin radius approx. 5 Å, is observed. The most characteristic distribution is connected with sample No 18 where a double peak is observed. The first corresponds to the radius of approx. 7 Å while the second to that of 14 Å. It should be noted that this samples displays the highest sorption capacity. This is probably due not only to

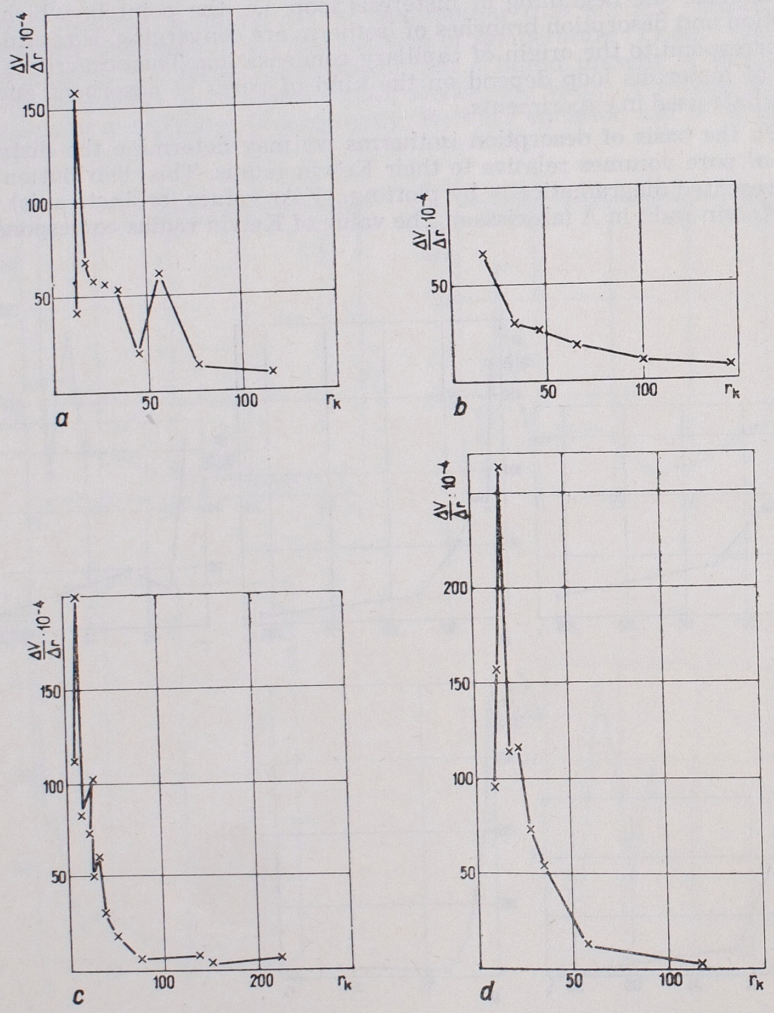

Fig. 7. Distribution of pore volumes plotted against Kelvin radius determined from desorption isotherm of benzene

a — sample No 15, *b* — sample No 16, *c* — sample No 17, *d* — sample No 18

the change of concentration of surface charges of montmorillonite in question but also to different structure of pores.

The distribution curves determined from isotherms of argon desorption are presented in Figure 6. We observe here a transition from a double system of pores corresponding to 12 and approx. 40 Å to a homogeneous one consisting of pores approx. 12 Å in size (sample No 18). Analogical distribution of pore volumes was found to occur in the case of argon sorption on natural montmorillonites.

This process of homogenization of pores is also observed on the distribution curves of pore volumes constructed from benzene desorption studies. Sample No 18, containing the highest amounts of magnesium, displays dominant pore size corresponding to 17 Å (Fig. 7).

The problem of porosity of synthetic montmorillonites is very interesting and will be discussed in another publication after accomplishing detailed porosimetric and densimetric investigations.

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Wera LUPTAKOWA, Anna NEMETHY, Mieczysław ŻYŁA

WŁASNOŚCI SORPCYJNE SYNTETYCZNEGO MONTMORILLONITU

Streszczenie

Wyznaczono izotermy sorpcji i desorpcji par: alkoholu metylowego, argonu i benzenu na pięciu próbkach syntetycznego montmorillonitu. Montmorillonit otrzymano na drodze hydrotermalnej syntezy pod ciśnieniem 87 atm z SiO_2, Al_2O_3 i MgO. Tlenki krzemu i glinu dozowano w stałym stosunku molowym $SiO_2 : Al_2O_3 = 4 : 1$, zmieniano natomiast udział molowy MgO co 0,5 mola w zakresie od 1,0 do 3,0 mola. Wyliczone z izoterm adsorpcji wartości powierzchni wzrastają wraz z ilością wprowadzonego MgO.

Krzywe rozkładu objętości porów w funkcji promienia kelwinowskiego zmieniają swój przebieg w zależności od składu chemicznego montmorillo-

nitu. Krzywe uzyskane na próbkach o maksymalnej ilości wprowadzonego tlenku glinu są analogiczne do krzywych uzyskanych na montmorillonitach naturalnych.

OBJAŚNIENIA FIGUR

Fig. 1. Izotermy sorpcji i desorpcji par alkoholu metylowego wyznaczone na montmorillonicie syntetycznym
a — próbka nr 13, *b* — próbka nr 15, *c* — próbka nr 16, *d* — próbka nr 17, *e* — próbka nr 18

Fig. 2. Izotermy sorpcji i desorpcji argonu wyznaczone na montmorillonicie syntetycznym
a — próbka nr 13, *b* — próbka nr 15, *c* — próbka nr 16, *d* — próbka nr 17, *e* — próbka nr 18

Fig. 3. Izotermy sorpcji i desorpcji par benzenu wyznaczone na montmorillonicie syntetycznym
a — próbka nr 13, *b* — próbka nr 15, *c* — próbka nr 16, *d* — próbka nr 17, *e* — próbka nr 18

Fig. 4. Zależność wartości powierzchni właściwej w funkcji udziału molowego MgO wprowadzonego w procesie syntezy montmorillonitu
(powierzchnie liczono: *A* — z sorpcji alkoholu metylowego, *B* — z sorpcji argonu, *C* — z sorpcji benzenu)

Fig. 5. Rozkład objętości porów w funkcji promienia kelwinowskiego wyznaczony z izotermy desorpcji alkoholu metylowego
a — próbka nr 13, *b* — próbka nr 15, *c* — próbka nr 16, *d* — próbka nr 17

Fig. 6. Rozkład objętości porów w funkcji promienia kelwinowskiego wyznaczony z izotermy desorpcji argonu
a — próbka nr 13, *b* — próbka nr 15, *c* — próbka nr 16, *d* — próbka nr 17, *e* — próbka nr 18

Fig. 7. Rozkład objętości porów w funkcji promienia kelwinowskiego wyznaczony z izotermy desorpcji benzenu
a — próbka nr 15, *b* — próbka nr 16, *c* — próbka nr 17, *d* — próbka nr 18

Вера ЛУПТАКОВА, Анна НЕМЕТИ, Анджей ЖИЛА

СОРБЦИОННЫЕ СВОЙСТВА СИНТЕТИЧЕСКОГО МОНТМОРИЛЛОНИТА

Резюме

Определялись изотермы сорбции и десорбции паров метилового спирта, аргона и бензола на пяти образцах синтетического монтмориллонита. Монтмориллонит был получен путем гидротермального синтеза под давлением 87 атм. с SiO_2, Al_2O_3 и MgO. Окислы кремния и алюминия дозировались в постоянном мольном соотношении $SiO_2 : Al_2O_3 = 4 : 1$, менялось же мольное содержание MgO через 0,5 моля в интервале от 1,0 до 3,0 молей. Величины поверхностей, вычисленные по изотермам абсорбции возрастают соответственно увеличению количества MgO.

Кривые распределения объема пор в зависимости от радиуса Кельвина изменяют свою форму в соответствии с химическим составом монтмориллонита. Кривые, соответствующие образцам с максимальным количеством добавленного глинозема тождественны с кривыми, полученными по естественным монтмориллонитам.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Изотермы сорбции и десорбции паров метилового спирта на синтетическом монтмориллоните
a — образец № 13, *b* — образец № 15, *c* — образец № 16, *d* — образец № 17, *e* — образец № 18

Фиг. 2. Изотермы сорбции и десорбции аргона на синтетическом монтмориллоните
a — образец № 13, *b* — образец № 15, *c* — образец № 16, *d* — образец № 17, *e* — образец № 18

Фиг. 3. Изотермы сорбции и десорбции паров бензола на синтетическом монтмориллоните
a — образец № 13, *b* — образец № 15, *c* — образец № 16, *d* — образец № 17, *e* — образец № 18

Фиг. 4. Зависимость величины поверхности от молярного количества MgO, добавляемого в процессе синтеза монтмориллонита
вычисленные поверхности: *A* — по сорбции метилового спирта, *B* — по сорбции аргона, *C* — по сорбции бензола

Фиг. 5. Распределение объема пор в зависимости от радиуса Кельвина, определенное по изотерме десорбции метилового спирта
a — образец № 13, *b* — образец № 15, *c* — образец № 16, *d* — образец № 17

Фиг. 6. Распределение объема пор в зависимости от радиуса Кельвина, определенное по изотерме десорбции аргона
a — образец № 13, *b* — образец № 15, *c* — образец № 16, *d* — образец № 17, *e* — образец № 18

Фиг. 7. Распределение объема пор в зависимости от радиуса Кельвина, определенное по изотерме десорбции бензола
a — образец № 15, *b* — образец № 16, *c* — образец № 17, *d* — образец № 18