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STUDIES OF THE KINETICS OF ADSORPTION OF ALIPHATIC ALCOHOLS AND WATER VAPOUR ON Mg-MONTMORILLONITE

A b s t r a c t. Kinetic curves were obtained for adsorption of water and lower aliphatic alcohols vapours, and from their shape diffusion coefficients were calculated. All the experiments were carried out on the magnesium form of montmorillonite separated from Milowice bentonite.

INTRODUCTION

The aim of this paper was to investigate the kinetics of adsorption of water and lower aliphatic alcohols vapours (methanol, ethanol, 1-propanol) on montmorillonite.

Owing to the specific adsorption properties, montmorillonites find wide application as adsorbents, fillers, carriers, catalysts, decolorizers, etc. The layer structure of montmorillonite and the resulting free interlayer spaces are largely responsible for sorption, specifically of polar substance vapours.

As appears from X-ray, thermal, adsorption and infrared absorption investigations, the adsorbed molecules of polar substances are bonded by three ways:

a) coordination of these molecules by exchangeable cations;

b) interaction of oxygen atoms of negative charge present on the surface of tetrahedral sheets with the molecules of polar adsorbates. It is feasible that hydrogen bonds form between them (Farmer, Mortland, 1966; van Olphen, 1965);

c) it is also possible that the adsorbate molecules are bound by OH groups of the octahedral layer. These groups are accessible only in places where the layers are discontinuous.

In the case of water adsorption, the adsorbed molecules can form either hexagonal planar sheets in the interlayer spaces or three-dimensional cation-water complexes. The binding of water molecules in these complexes has a character of ion-dipole interaction.

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Table 1

Characteristics of adsorbates

Adsorbate	p_o at 303 K $N/m^2 \cdot 10^{-4}$	$\mu[D]$	Particle size	
			width [nm]	length [nm]
H_2O	0.4241	1.84	0.276	—
CH_3OH	2.0795	1.69	0.298	0.305
C_2H_5OH	1.0437	1.70	0.386	0.365
$1-C_3H_7OH$	0.3632	1.66	0.386	0.463

The interlayer spaces of montmorillonite are equally accessible to water molecules and to somewhat larger methyl alcohol molecules. Their limited capacity is reflected in the amount of sorbed methanol and ethanol vapours. It has been found that the amount of moles of the adsorbed methanol molecules is 1.5 times greater than the amount of moles of the sorbed ethanol molecules. The amount of moles of sorbed 1-propanol molecules, on the other hand, is considerably less than that of moles of the ethanol molecules (Ziętkiewicz, Żyła, 1976). The above observations confirm the hypotheses not only of the limited capacity of the interlayer spaces and their sieve-molecular properties but also of the lack of any significant swelling of the structure of montmorillonite in response to the action of lower aliphatic alcohol molecules.

There is a great number of papers reporting the results of static adsorption studies while there are as yet hardly any dealing with the adsorption kinetics. Such studies can extend substantially our knowledge of the sorption mechanism, specifically of the sorption of polar substances. Therefore, the present authors made an attempt at determining the effect of the size of aliphatic alcohol molecules on the rate of their penetration into the structure of magnesium montmorillonite (Tab. 1).

EXPERIMENTAL

Apparatus

Kinetic studies were carried out using adsorption apparatus whose diagram is presented in Fig. 1.

The main element of the apparatus is a Sartorius vacuum electronic microbalance (3). A manometric pressure stabilizer (5) which operates a magnetic valve (7) metering the adsorbate vapours guarantees that the measurements are isobaric. A symmetric thermostat (6), regulating the temperature of both balance scales, ensures that the process is isothermic. Variations in mass and temperature are recorded by tape recordes (9, 10). The apparatus described is particularly useful for kinetic measurements. It gives additionally a possibility of controlling the outgassing and desorption processes, which is of prime importance when adsorption-desorption cycles are carried out on the same adsorbent sample. This is particularly important for systems of the montmorillonite-polar substance type exhibiting strong adsorbent-adsorbate interactions, for which the sorption process can be not fully reversible.
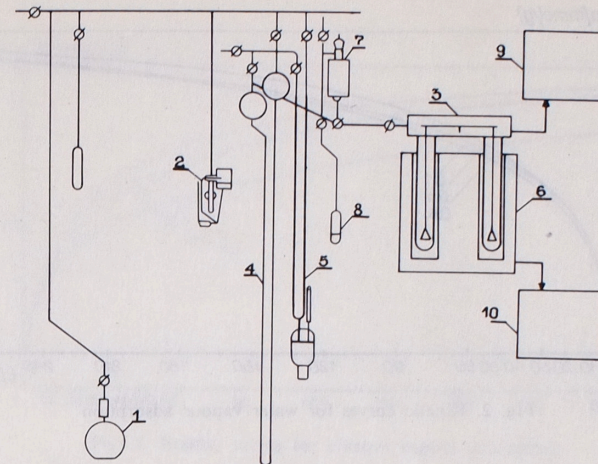

Fig. 1. Adsorption apparatus

1 — vacuum system, 2 — Mc Leod rotary manometer, 3 — microbalance, 4 — oil manometer, 5 — pressure — controlling mercury manometer, 6 — thermostat, 7 — magnetic valve, 8 — capsule with adsorbate, 9, 10 — tape recorders

Properties of the adsorbent

Investigations were carried out on a montmorillonite sample separated by sedimentation (fraction < 1 μm) from the Milowice bentonite, with magnesium cations substituted in the interlayer spaces. X-ray analysis of an air-dry sample revealed that the basal 001 reflection has a value of 1.51 nm, characteristic of the magnesium form. This reflection testifies to the presence of a bimolecular interlayer H_2O sheet, typical of bivalent cationic forms.

Montmorillonite samples were prepared in the form of grains with diameters varying over a narrow range between 0.12 and 0.15 mm. Prior to measurements, the samples were predried at 378 K and then outgassed in the apparatus at 403 K. After measuring each kinetics, desorption was conducted by vacuum outgassing at the measurement temperature. It was found that desorption was not complete, with the amount remaining in the sample being constant for the given adsorbate irrespective of the pressure at which the measurement was made. This fact made it necessary to carry out desorption at elevated temperatures (403 K).

To trace any possible changes in the structure of montmorillonite in response to repeated adsorption-desorption cycles combined with heating, the kinetics measurements were repeated several times. The resulting kinetic curves showed very good agreement, which implies that there are no irreversible changes in the structure of montmorillonite.

Properties of the adsorbates

The basic properties of the adsorbates used are given in Table 1. It is evident that the adsorbate molecules show similar values of the dipole moments μ, differing primarily in size.
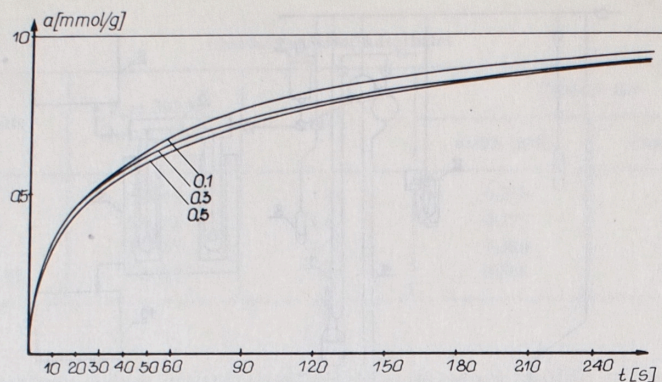
Fig. 2. Kinetic curves for water vapour adsorption

RESULTS

Kinetic curves for the adsorption of water and alcohols vapours were obtained at 303 K. Kinetics measurements were realized in two ways:

i) First, the kinetic curves was obtained directly at a given relative pressure (p/p_o = 0.1, 0.3, 0.5 and for methanol also at 0.02) on the sample not containing adsorbate vapours; these are called "single" kinetic curves. Before each experiment the sample had been outgassed with the simultaneous heating until the adsorbate was completely removed. The resulting curves are shown in Figs. 2—5, and

ii) Secondly, so called "step" kinetic curves were recorded. The first kinetic curve was recorded at the relative pressure p/p_o = 0.1 and after the adsorption equilibrium had been obtained, the sample was not outgassed but the subsequent kinetic curve was measured at the higher relative pressure 0.3 and then 0.5. This part of research enables us to investigate the adsorption process in given relative pressure ranges and therefore in given filling ranges. The resulting curves are shown in Figs. 6—9.
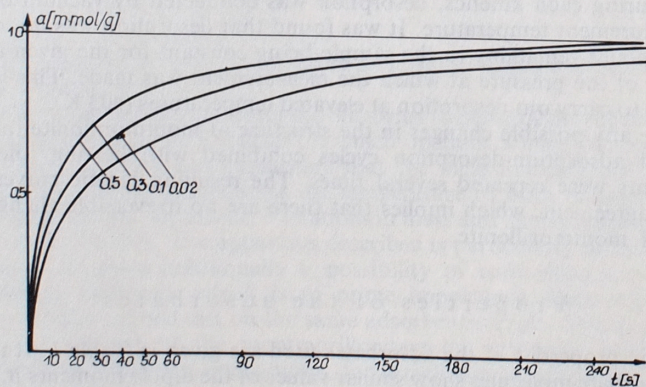

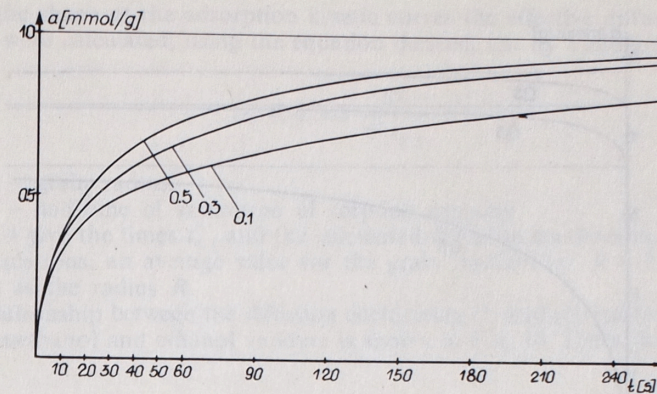Fig. 3. Kinetic curves for methanol vapour adsorption

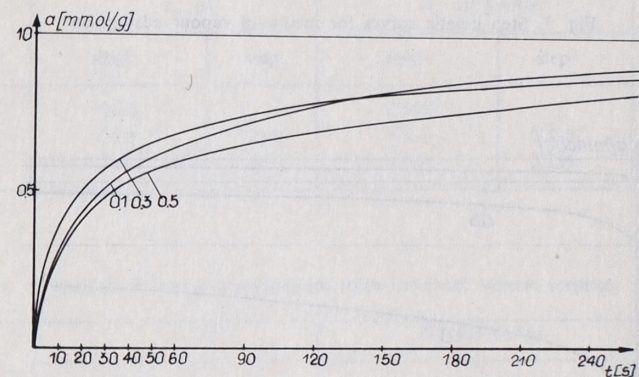Fig. 4. Kinetic curves for ethanol vapour adsorption

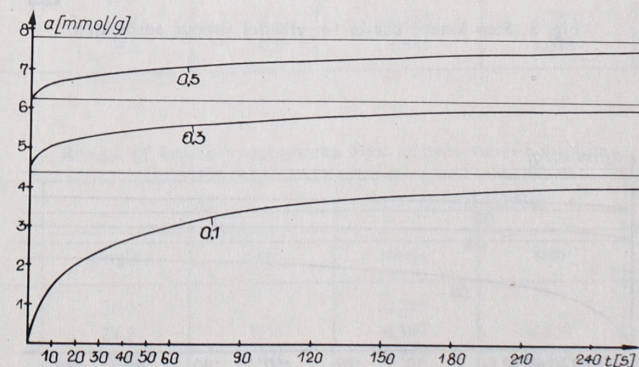Fig. 5. Kinetic curves for 1 — propanol vapour adsorption

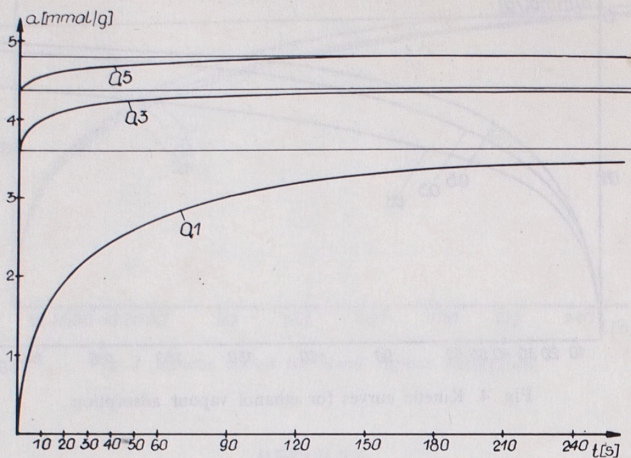Fig. 6. Step kinetic curves for water vapour adsorption

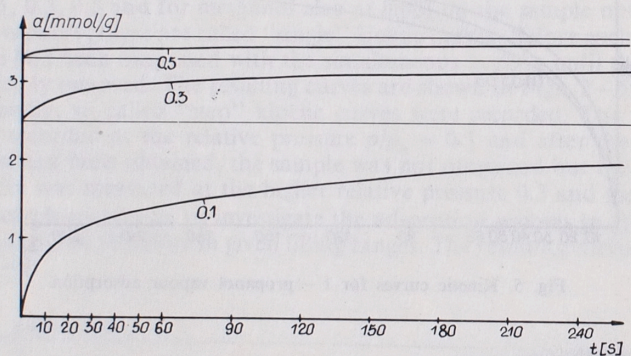Fig. 7. Step kinetic curves for methanol vapour adsorption

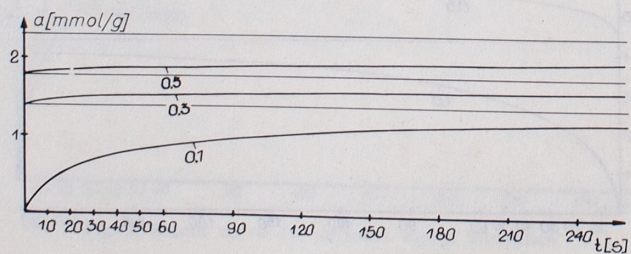Fig. 8. Step kinetic curves for ethanol vapour adsorption

Fig. 9. Step kinetic curves for 1-propanol vapour adsorption

From the shape of the adsorption kinetic curves the effective diffusion coefficients D_e were calculated, using the equation derived, i.a. by Timofieyev:

$$D_e = 0.308 \frac{R^2}{\pi^2 t_{0.5}}$$

where: R — grain radius,

$t_{0.5}$ — half-time of saturation of sorption capacity

Tables 2−4 give the times $t_{0.5}$ and the calculated diffusion coefficients D_e.

In calculations, an average value for the grain fraction i.e. $R = 0.0675$ mm, was taken as the radius R.

The relationship between the diffusion coefficients D_e and the relative pressure of water, methanol and ethanol vapours is shown in Fig. 10. From the shape of

Table 2

Results of kinetic investigations from water vapour sorption

p/p_o	$t_{0.5}$ [s]		$D_e \cdot 10^7$ [cm²/s]		$D_e \cdot 10^7$ [cm²/s]
	single	step	single	step	
0.1	26.0		0.547		0.423
0.3	25.8	29.0	0.551	0.490	0.491
0.5	28.2	56.4	0.504	0.252	0.439

Table 3

Results of kinetic investigations from methanol vapour sorption

p/p_o	$t_{0.5}$ [s]		$D_e \cdot 10^7$ [cm²/s]		$D_e \cdot 10^7$ [cm²/s]
	single	step	single	step	
0.02	23.4		0.607		0.739
0.1	15.6		0.911		0.991
0.3	10.8	8.1	1.316	1.755	1.238
0.5	9.6	10.8	1.481	1.316	1.355

Table 4

Results of kinetic investigations from ethanol vapour sorption

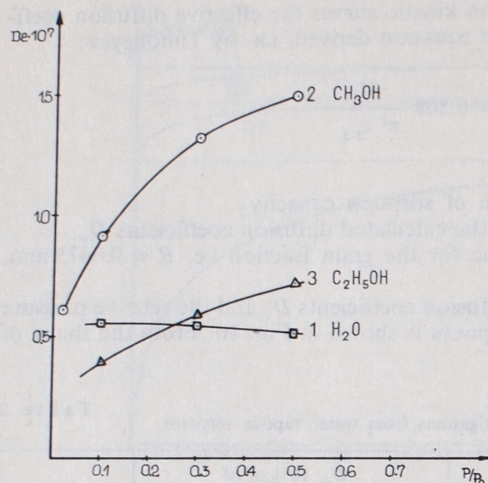| p/p_o	$t_{0.5}$ [s]		$D_e \cdot 10^7$ [cm²/s]		$D_e \cdot 10^7$ [cm²/s]
	single	step	single	step	
0.1	36.5		0.389		0.572
0.3	24.2	31.0	0.587	0.458	0.706
0.5	20.0	110.0	0.711	0.129	0.768

Fig. 10. Relationship between diffusion coefficients and relative pressure
1 — wáter, 2 — methanol, 3 — ethanol

curves it is evident that pressure affects significantly the diffusion coefficients in the case of methyl and ethyl alcohols. At the same time, the values of these coefficients decrease with the increasing size of the alcohol molecule.

A curve for the diffusion coefficient versus relative pressure for n-propyl alcohol has not been presented because its shape is irregular, presumably due to changes in the adsorption mechanism of this alcohol. Owing to the size, the penetration of 1-propanol molecules into the interlayer spaces is limited.

The effective diffusion coefficients were also calculated from the formula:

$$\gamma = \frac{a_t}{a_{max}} = \frac{2S}{V}\sqrt{\frac{D_e t}{\pi}}$$

which on a simplifying assumption that the shape of grains is spherical, can be restated in the form:

$$\gamma = \frac{6}{R}\sqrt{\frac{D_e t}{\pi}}$$

From the γ vs. $\sqrt{t}$ kinetic curves D_e can be determined because initially, up to a value of 0.4, they are straight lines. The results are presented in Tables 2–4.

DISCUSSION

An analysis of the kinetic curves has revealed that the mechanism of water and aliphatic alcohols adsorption is different, depending on the relative pressure and filling. In the case of water adsorption, slight differences in the diffusion coefficients have been noted for different degrees of filling. This fact indicates that the adsorbate is transferred in the same way over the investigated range of pressures (Fig. 10). For methanol and ethanol the rate of adsorption increases markedly with increasing pressure (higher values of diffusion coefficients — Fig. 10). For

the homologous series of alcohols, the diffusion coefficients decrease with the increasing size of adsorbate molecules, which behaviour is well reflected in the shape of progressive kinetic curves.

The size of adsorbate molecules has also a pronounced effect on the time of attaining of adsorption equilibria, i.e. on the shape of the final section of kinetic curves. Worth noting is the high rate of methyl alcohol adsorption compared with the adsorption of water and other alcohols.

A comparison of the amount of adsorbed vapours at equilibrium states indicates that there is a marked dependence of the adsorption magnitude on the molecule size (e.g., adsorption of 1-propanol at $p/p_o = 0.5$ is about four times less than water adsorption).

Due to the fact that the adsorption-desorption process was repeated several times, it was possible to show that the montmorillonite studied had invariable sorption properties and, therefore, the stability of its structure under the experimental conditions was demonstrated.

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BADANIA KINETYKI ADSORPCJI PAR ALKOHOLI ALIFATYCZNYCH I WODY NA Mg-MONTMORILLONICIE

Streszczenie

Przeprowadzono badania kinetyki adsorpcji par wody i niższych alkoholi alifatycznych na magnezowej formie montmorillonitu. Pomiary wykonano przy użyciu mikrowagi z automatyczną, ciągłą rejestracją zmiany masy adsorbentu. Z krzywych kinetycznych obliczono współczynniki dyfuzji. Przedyskutowano zależność wartości współczynników dyfuzji w funkcji zapełnienia adsorbatem struktury porowatej montmorillonitu. Uwzględniono wpływ wielkości cząsteczek stosowanych adsorbatów na szybkość procesu adsorpcji.

OBJAŚNIENIA FIGUR

Fig. 1. Aparat adsorpcyjny
1 — układ próżniowy, 2 — manometr obrotowy Mc Leoda, 3 — mikrowaga, 4 — manometr olejowy, 5 — manometr rtęciowy sterujący ciśnieniem, 6 — termostat, 7 — zawór magnetyczny, 8 — ampułka z adsorbatem, 9, 10 — rejestratory taśmowe

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ИССЛЕДОВАНИЕ КИНЕТИКИ АДСОРБЦИИ ПАРОВ АЛИФАТИЧЕСКИХ СПИРТОВ И ВОДЫ НА Mg—МОНТМОРИЛЛОНИТЕ

Резюме

Проведены исследования кинетики адсорбции паров воды и лёгких алифатических спиртов на магниевой форме монтмориллонита. Измерения выполнены с помощью микровесов с автоматической, непрерывной регистрацией изменения массы адсорбента. По кинетическим кривым рассчитаны коэффициенты диффузии. Обсуждена зависимость значений коэффициентов диффузии как функций заполнения адсорбатом пористой структуры монтмориллонита. Рассмотрено влияние величины молекул, применяемых адсорбатов, на скорость процесса адсорбции.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Адсорбционный аппарат

1 — вакуумная система, 2 — поворотный манометр МакЛеода, 3 — микровесы, 4 — масляный манометр, 5 — ртутный манометр, управляющий давлением, 6 — термостат, 7 — магнитный клапан, 8 — ампула с адсорбатом, 9, 10 — ленточные регистраторы

Фиг. 2. Кинетические кривые адсорбции паров воды

Фиг. 3. Кинетические кривые адсорбции паров метилового спирта

Фиг. 4. Кинетические кривые адсорбции паров этилового спирта

Фиг. 5. Кинетические кривые адсорбции паров н-пропилового спирта

Фиг. 6. Кривые ступенчатых кинетик адсорбции паров воды

Фиг. 7. Кривые ступенчатых кинетик адсорбции паров метилового спирта

Фиг. 8. Кривые ступенчатых кинетик адсорбции паров этилового спирта

Фиг. 9. Кривые ступенчатых кинетик адсорбции паров н-пропилового спирта

Фиг. 10. Зависимость коэффициентов диффузии от относительного давления

1 — вода, 2 — метиловый спирт, 3 — этиловый спирт