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PRELIMINARY INVESTIGATIONS OF SORPTION PROPERTIES OF STILBITE

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Abstract. Investigations of sorption properties were carried out on two stilbite specimens, from Strzegom (Poland) and Iceland. Sorption and desorption isotherms for argon and water, methyl alcohol and benzene vapours were determined. It has been found that water sorption isotherms are well above isotherms obtained for the other adsorbates.

Stilbite, together with heulandite, clinoptilolite, epistilbite, ferrierite and brewsterite, belongs to the group of natural zeolites with similar framework structure, the details of which have been the object of relatively recent studies. The structure of stilbite was determined by X-ray method by Galli and Gottardi (1966) and Slaughter (1970).

Stilbite is monoclinic, C2/m, with the unit cell parameters: $a = 13.69$, $b = 18.25$, $c = 11.31$ Å, $\beta = 128.2^\circ$ (Slaughter 1970). The "ideal" formula for stilbite is $\text{Na}_2\text{Ca}_4(\text{Al}_{10}\text{Si}_{26}\text{O}_{72}) \cdot 32\text{H}_2\text{O}$. Its crystal structure is characterized by intersecting channels of 10- and 8-member rings made up of silica-oxygen tetrahedra. The 10-member ring channels extend in the a-direction. Their smallest diameter is about 4.4 Å (Galli, Gottardi 1966). The 8-member ring channels are of two types: 1) bounded by almost equilateral rings (with the smallest diameter of 2.6 Å), and 2) bounded by narrow elongate rings. Both types of 8-member ring channels are parallel to c, making an angle of 128° with the axis of 10-member ring channels. Ca^{2+} cations are located in the centre of the largest part of the channels (cages), being surrounded by maximum eight water molecules. In contrast

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to other cations (Na^+ , Mg^{2+}), they are not bonded to Si-O framework oxygens. The mode of substitution of silicon by aluminium in the framework of zeolite shows a very low degree of ordering.

In view of the fact that channels of relatively large diameters are present in the structure of stilbite, Galli and Gottardi (1966) presumed that this zeolite may possess some interesting sieve properties. Following their suggestion, the present authors have made investigations of the sorption properties of stilbite.

Investigations were carried out on two samples of stilbite. One sample was derived from a granite quarry in Strzegom, where stilbite occurs in the form of honey-yellow crystalline aggregates on the walls of rock cavities (Zabiński 1975). Its chemical analysis has revealed a considerable prevalence of Ca^{2+} ions over the other cations (Na^+ , K^+ , Mg^{2+}). The other sample is a white stilbite from Iceland coming from the collections of the Department of Mineralogy and Geochemistry of the Academy of Mining and Metallurgy in Cracow. Its X-ray powder pattern is analogous to that of stilbite from Strzegom. The chemical analysis of a similar white stilbite from Iceland, given by Galli and Gottardi (1966), shows that Ca^{2+} is the dominant cation in this zeolite as well.

ADSORPTION INVESTIGATIONS

Polar substances, water and methyl alcohol, as well as nonpolar benzene and argon were used as adsorbates. Their choice was determined by the shape and size of molecules and the degree of their polarity.

Prior to adsorption measurements, stilbite samples were heated at about 573 K and simultaneously outgassed to obtain a vacuum of the order of 10^{-5} mm Hg. Argon adsorption isotherms at liquid nitrogen temperature were determined using sorption manostats (Ciembroniewicz, Lasoń 1972). Isotherms for the other adsorbates were obtained at 298 K using microburettes for liquids (Lasoń, Żyła 1963).

DISCUSSION

The isotherms obtained for sorption of polar and nonpolar substance vapours on stilbites are presented in Figures 1 and 2. To show clearly the differences in sorption properties, the isotherms of various adsorbates determined for the given adsorbent are plotted in the same Figure. The curves present the volume of adsorbed vapours (in cm^3 of liquid sorbate) against relative pressure, p/p_0 .

From Figures 1 and 2 it is evident that water vapour sorption isotherms are well above the isotherms obtained for the other adsorbates. This implies that the microporous structure is inaccessible to molecules of the adsorbates used, except water molecules which penetrate into the microporous regions of the zeolites studied. This fact may be accounted for by partial closing of the channel apertures by large cations (Ca^{2+} , Na^+); moreover, as appears from analysis of the kinetic molecule diameter of the ad-

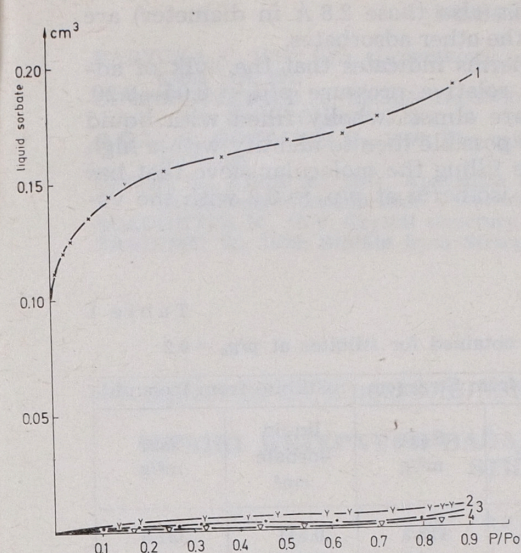


Fig. 1. Adsorption isotherms of water (1), methanol (2), benzene (3) and argon (4) obtained for stilbite from Strzegom

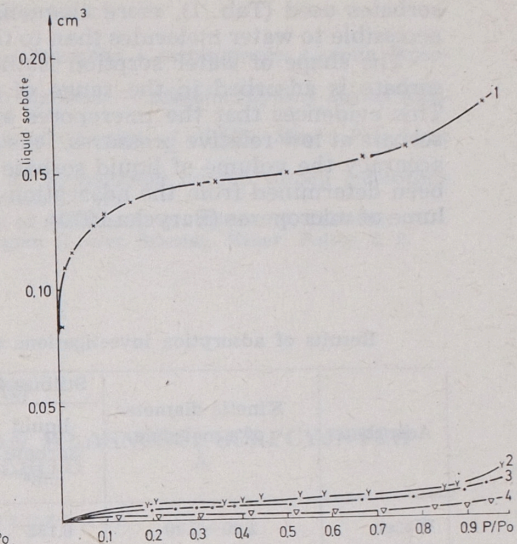


Fig. 2. Adsorption isotherms of water (1), methanol (2), benzene (3) and argon (4) obtained for stilbite from Iceland

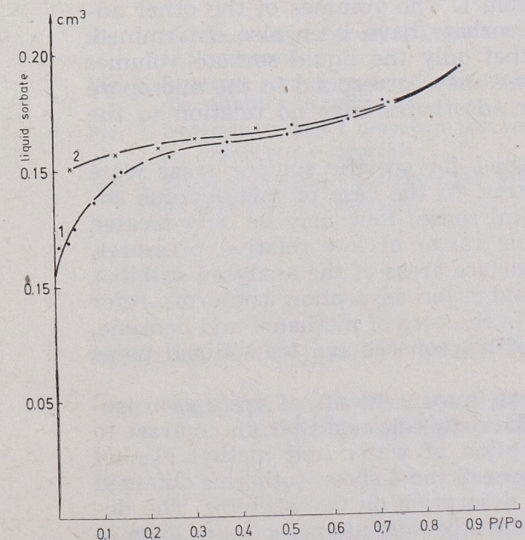


Fig. 3. Adsorption and desorption isotherms of water vapour obtained for stilbite from Strzegom

1 — adsorption, 2 — desorption

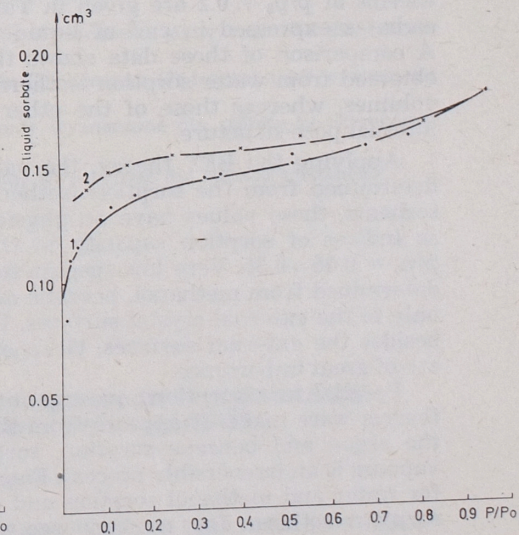


Fig. 4. Adsorption and desorption isotherms of water vapour obtained for stilbite from Iceland

1 — adsorption, 2 — desorption

sorbates used (Tab. 1), more channels (also those 2.6 Å in diameter) are accessible to water molecules than to the other adsorbates.

The shape of water sorption isotherms indicates that the bulk of adsorbate is adsorbed in the range of relative pressure $p/p_0 = 0.05-0.20$. This evidences that the micropores are almost wholly filled with liquid sorbate at low relative pressures. It is possible then to identify with a high accuracy the volume of liquid sorbate filling the molecular sieve that has been determined from the adsorption isotherm at $p/p_0 = 0.2$ with the volume of micropores (Barycka 1970).

Table 1

Results of adsorption investigations obtained for stilbites at $p/p_0 = 0.2$

Adsorbate	Kinetic diameter of a molecule Å	Stilbite from Strzegom		Stilbite from Iceland	
		liquid sorbate cm ³	S _{BET} m ² /g	liquid sorbate cm ³	S _{BET} m ² /g
Water	2.20—2.80	0.152	413.2	0.141	331.8
Methanol	2.98—3.05	0.0055	14.3	0.0063	32.8
Benzene	3.65—3.86	0.0037	10.7	0.0065	34.7
Argon	3.83	0.0019	5.1	0.0025	6.2

The volumes of micropores obtained from water vapour sorption isotherms at $p/p_0 = 0.2$ are given in Table 1. The volumes of the other adsorbates expressed in cm³ of liquid sorbate have been also determined. A comparison of those data shows that only the liquid sorbate volumes obtained from water sorption isotherms may correspond to the micropore volumes, whereas those of the other adsorbates bear no relation to the internal pore structure.

Applying the BET theory, the values for specific surface areas were determined from the sorption isotherms. In the case of microporous adsorbents, those values have no physical sense; they may be only treated as indices of sorption capacity in the range of low relative pressures, $p/p_0 = 0.05-0.35$. Very low specific surface areas of the analysed stilbites, determined from methanol, benzene and argon adsorption isotherms, refer only to the external crystal surfaces. In the case of methanol and benzene, besides the external surfaces, those of macropores and transitional pores are of great importance.

Parallel to adsorption investigations, measurements of desorption isotherms were made. It appears from the data obtained that, in contrast to the argon and benzene sorption, sorption of water and methyl alcohol vapours is an irreversible process. Figures 3 and 4 show isotherms obtained for water and methanol sorption and desorption on two stilbites. The desorption isotherm does not converge with the adsorption isotherm even at very low relative pressures.

From the adsorption isotherms, as well as from the data presented in Table 1 it may be inferred that the stilbite-type zeolites can be used, e.g. for dehydration of alcohols and exiccation of gases.

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WYNIKI WSTĘPNYCH BADAŃ WŁASNOŚCI SORPCYJNYCH STILBITU

Streszczenie

Wykonano badania własności sorpcyjnych dwóch okazów stilbitu: ze Strzegomia oraz z Islandii. Wyznaczono izotermy sorpcji i desorpcji argonu oraz par wody, alkoholu metylowego i benzenu. Stwierdzono, że izotermy sorpcji wody przebiegają znacznie powyżej izoterm pozostałych adsorbatów.

OBJAŚNIENIA FIGUR

- Fig. 1. Izotermy sorpcji wody (1), metanolu (2), benzenu (3) wyznaczone dla stilbitu ze Strzegomia
 Fig. 2. Izotermy sorpcji wody (1), metanolu (2), benzenu (3) i argonu (4) wyznaczone dla stilbitu z Islandii
 Fig. 3. Izotermy sorpcji i desorpcji par wody wyznaczone dla stilbitu ze Strzegomia
 1 — adsorpcja, 2 — desorpcja
 Fig. 4. Izotermy sorpcji i desorpcji par wody wyznaczone dla stilbitu z Islandii
 1 — adsorpcja, 2 — desorpcja

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РЕЗУЛЬТАТЫ ПРЕДВАРИТЕЛЬНЫХ ИССЛЕДОВАНИЙ СОРБЦИОННЫХ СВОЙСТВ СТИЛЬБИТА

Резюме

Проведено исследование сорбционных свойств двух образцов стильбита: из Стшегомя и с Исландии. Определено изотермы сорбции и десорбции аргона, а также паров воды, метилового алкоголя и бензена. Обнаружено, что изотермы сорбции воды проходят значительно выше изотерм остальных адсорбатов.

ОБЪЯСНЕНИЯ К ФИГУРАМ

- Фиг. 1. Изотермы сорбции воды (1), метанола (2), бензена (3) и аргона (4), полученные для стильбита из Стшегомя
- Фиг. 2. Изотермы сорбции воды (1), метанола (2), бензена (3) и аргона (4), полученные для стильбита с Исландии
- Фиг. 3. Изотермы сорбции и десорбции водяных паров полученные для стильбита из Стшегомя
1 — адсорбция, 2 — десорбция
- Фиг. 4. Изотермы сорбции и десорбции водяных паров полученные для стильбита с Исландии
1 — адсорбция, 2 — десорбция