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SORPTION PROPERTIES OF HEULANDITE FROM RUDNO

UKD 549.670.3.08:541.183.59(438.31 Rudno)

Abstract. Investigations of sorption properties were carried out on a natural zeolite, heulandite, occurring in vacuoles of the melaphyres from Rudno near Cracow. Sorption isotherms for argon, water, methyl alcohol and benzene vapours were determined. It has been found that water and methyl alcohol sorption isotherms are above isotherms for benzene and argon. On the basis of isotherm shape analysis, the dominant pore radius has been defined.

INTRODUCTION

Heulandite, together with clinoptilolite, stilbite, epistilbite, ferrierite and brewsterite, belongs to the group of natural zeolites with a similar framework structure, the details of which have been the object of relatively recent studies. The minerals of that group have roused interest ever since clinoptilolite was found to possess some interesting sorption properties. Clinoptilolite sometimes forms substantial concentrations in nature, finding therefore practical application. These facts encourage studies of sorption properties of other zeolites, the more so as some of them, e.g. heulandite, can be obtained by synthesis (Koizumi, Roy 1960).

In an earlier publication the authors have defined the sorption properties of stilbite (Żyła, Żabiński 1976). This paper aims to discuss the sorption properties of heulandite occurring in vacuoles of the melaphyres from Rudno near Cracow. The chemical composition, morphological and optical

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features of that mineral, as well as the conditions of its occurrence were discussed by Piekarska and Gaweł (1953). X-ray and thermal analyses of this heulandite were made by Kubisz and Żabiński (1969). The approximate formula for heulandite from Rudno is:

$$(Ca_{2.5}Mg_{1.2}K_{1.2}Na_{0.2})\ Al_{7.6}Si_{27.8}O_{72} \cdot 23.9H_2O$$
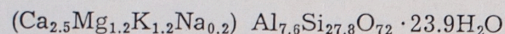
The above formula does not take into account an iron admixture as it has been found to be insignificant (about 0.5% Fe_2O_3) in the yellow variety of heulandite subjected to analysis.

Heulandite is monoclinic, Cm, with the unit cell parameters: $a = 17.73$, $b = 17.82$, $c = 7.43$ Å *, $\beta = 116°20'$ (Merkle, Slaughter 1968). In its crystal lattice well-defined layers formed by 6-, 5- and 4-member tetrahedral rings can be distinguished, lying in ac- at 0.25 and 0.75 along b. Open channels are formed by 10- and 8-member rings which also lie in ac- at 0.00 and 0.50 along b. According to Merkle and Slaughter, "heulandite has relatively open channels in three directions. Parallel to c-, channels of 10- and 8-member tetrahedral rings have dimensions of 7.05×4.25 Å and 4.60×3.95 Å, respectively. Parallel to a, channels of 8-member rings have dimensions of 5.40×3.90 Å. A third channel formed by 8-member rings is present at an angle of 50° to the a-axis; its dimensions are 5.20×3.90 Å. Two of the three Ca atoms in heulandite occupy positions near the intersections of the 10- and 8-member ring channels, and the third Ca occupies a position at the intersection of two 8-member ring channels."

ADSORPTION INVESTIGATIONS

In the studies of the structure of adsorbents, e.g. zeolites, adsorption methods involving the determination of adsorption and desorption isotherms for vapours and gases play a significant role. In this paper, vapours of polar (water, methanol) and nonpolar (benzene, argon) substances were used as adsorbates. The choice of adsorbates was determined not only by the differences in symmetry and nonpolarity but also by the accessibility of the pore structure to sorption in the mineral studied. Nearly every adsorbent has a double system of pores, comprising micro- and macropores, and it seems essential to know the content of dominant pores in the general porosity. This is possible if adsorbate molecules of different critical diameters are used. Adsorbate molecules having small critical diameters (water 2.20—2.80 Å, methanol 2.98—3.05 Å) can penetrate into the finest pores of the adsorbent whereas transitional pores and macropores are available for molecules with somewhat greater kinetic diameters (argon 3.83 Å, benzene 3.65—3.86 Å).

Sorption isotherms for water, methyl alcohol and benzene vapours were determined at 298 K using microburettes for liquids (Lasoń, Żyła 1963). Argon sorption isotherms were obtained at 77 K in sorption manostats (Ciembroniewicz, Lasoń 1972). All the isotherms obtained are presented in Figures 1 and 2; those in Figure 1 show the relationship between the amount of adsorbed vapours of liquid sorbate (in cm³) and the relative

* 1 Å = 0.1 nm.
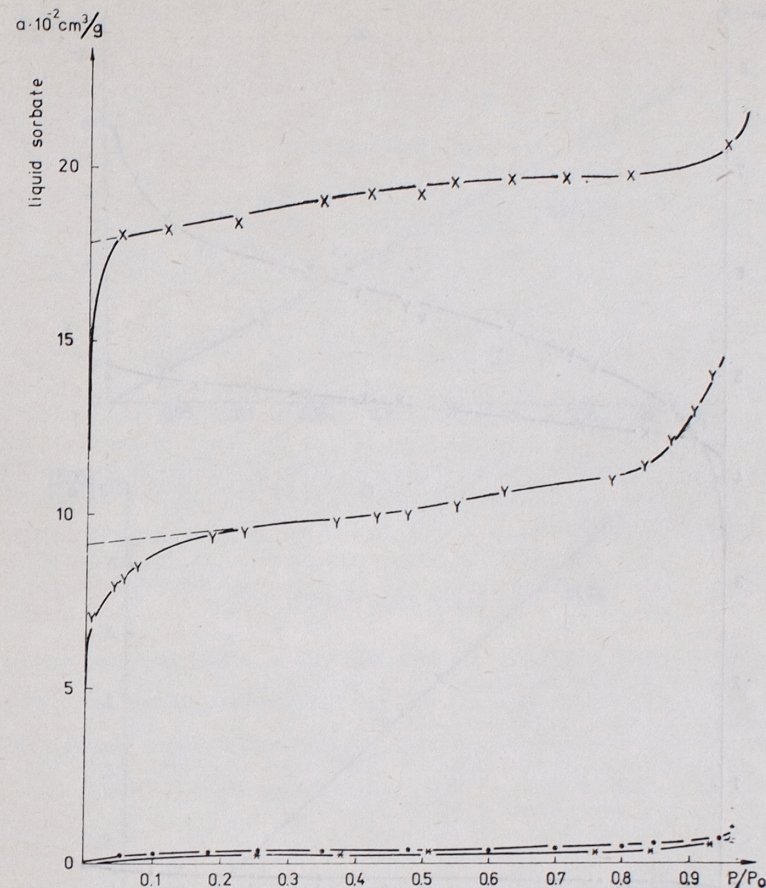
Fig. 1. Adsorption isotherms of water (Y), methanol (X), argon (●) and benzene (✳)
(cm³ of liquid sorbate)

pressure p/p_o. The plots in Figure 2 illustrate the same dependence, with the amount of sorbed vapours expressed in mmol/g.

As appears from the figures, heulandite exhibits sieve properties. This is evidenced by the amount of sorbed vapours of respective adsorbates. The amount of sorbed benzene or argon vapours is so insignificant as to imply that adsorption takes place only on the external surfaces of heulandite crystals. It can also be inferred that the diameter of heulandite micropores is smaller than the kinetic diameter of argon molecules (3.83 Å). Taking into account the fact that sorption capacity of heulandite with respect to water and methyl alcohol vapours is several dozen times greater, the diameter of its micropores can be defined as larger than 3.05 Å.

Isotherms obtained for water and methyl alcohol vapour sorption require separate discussion. As seen in figures 1 and 2, the isotherms change
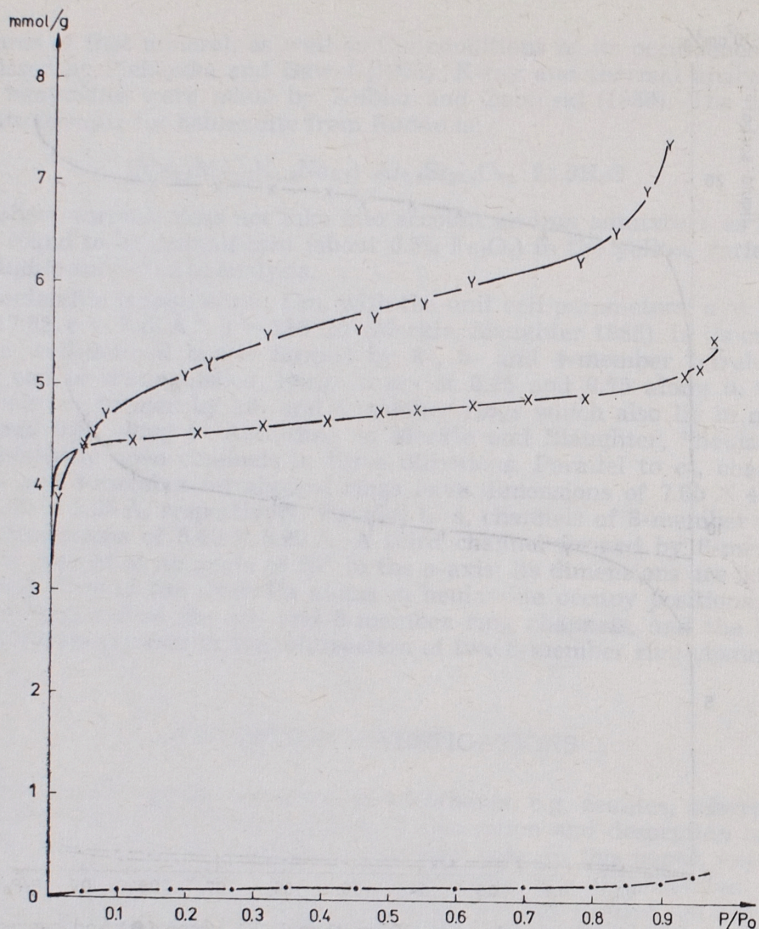
Fig. 2. Adsorption isotherms of water (Y), methanol (X) and argon (●) (mmol/g)

their sequence depending on how the amount of adsorbed vapours was expressed (cm³ of liquid sorbate per gram of adsorbent or mmol/g). The volume of adsorbed methyl alcohol is nearly twice greater than that of water adsorbed in liquid state. Prolonging the water and methanol isotherms in figure 1 until they intersect the ordinate, volumes of water and methanol adsorbed at low relative pressures were determined (V_{H_2O} = = 0.091, V_{CH_3OH} = 0.178 cm³). The ratio of those volumes is 1.94, being close to the ratio of the maximum cross-sectional area ω of a methyl alcohol molecule to the corresponding value for a water molecule.

$$\frac{V_{CH_3OH}}{V_{H_2O}} = \frac{0.178 \text{ cm}^3}{0.091 \text{ cm}^3} = 1.94; \quad \frac{\omega \text{ CH}_3\text{OH}}{\omega \text{ H}_2\text{O}} = \frac{18.2 \text{ Å}^2}{10.5 \text{ Å}^2} = 1.73$$
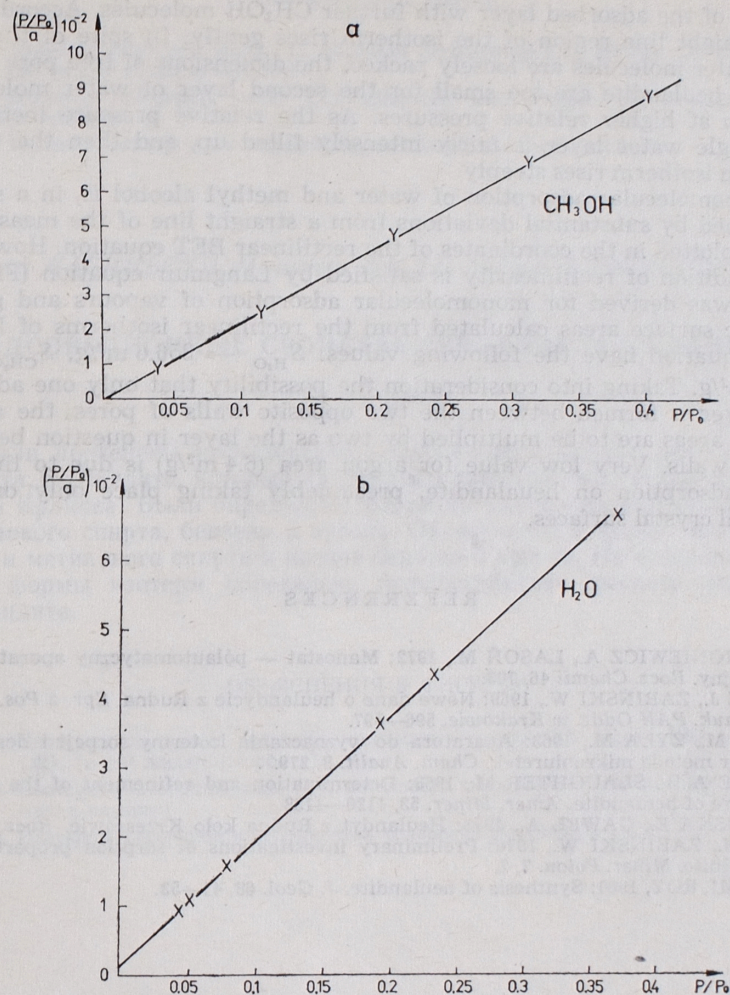

Fig. 3. Adsorption isotherms in the coordinates of Langmuir equation (a, b)

A comparison of the values for those ratios reveals that heulandite adsorbs similar amounts of water and methyl alcohol molecules. This statement is borne out by the shape of isotherms for which the amount of sorbed vapours is expressed in mmol/g. Up to a relative pressure of 0.05, the amounts of adsorbed methyl alcohol and water molecules are almost identical. At higher pressures, the adsorbed water molecules begin to outnumber the methyl alcohol molecules. Such behaviour can be accounted for if it is assumed that the single layer of adsorbed molecules which forms in this process is complemented with further molecules. Due to a larger size of the CH_3OH molecule, the alcohol layer fits better in the free volumes of heulandite, which is most likely the reason for not very intensive up-

-filling of the adsorbed layer with further CH_3OH molecules. Accordingly, the straight line region of the isotherm rises gently. In spite of the fact that water molecules are loosely packed, the dimensions of free pore volumes in heulandite are too small for the second layer of water molecules to form at higher relative pressures. As the relative pressure increases, the single water layer is fairly intensely filled up, and then the water sorption isotherm rises steeply.

Monomolecular adsorption of water and methyl alcohol is, in a sense, confirmed by substantial deviations from a straight line of the measuring points plotted in the coordinates of the rectilinear BET equation. However, the condition of rectilinearity is satisfied by Langmuir equation (Fig. 3), which was derived for monomolecular adsorption of vapours and gases. Specific surface areas calculated from the rectilinear isotherms of Langmuir equation have the following values: S_{H_2O} — 356.6 m²/g, S_{CH_3OH} — 495.7 m²/g. Taking into consideration the possibility that only one adsorption layer is formed between the two opposite walls of pores, the above surface areas are to be multiplied by two as the layer in question belongs to two walls. Very low value for argon area (6.4 m²/g) is due to limited argon adsorption on heualandite, presumably taking place only on the external crystal surfaces.

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WŁASNOŚCI SORPCYJNE HEULANDYTU Z RUDNA

Streszczenie

Wykonano badania własności sorpcyjnych naturalnego zeolitu, heulandytu, występującego w wakuolach melafirów z Rudna. Wyznaczono izotermy adsorpcji dla par wody, alkoholu metylowego i benzenu oraz dla argonu. Stwierdzono wysoką sorpcję wody i alkoholu metylowego a niską benzenu i argonu. Na podstawie analizy kształtu izoterm określono dominującą średnicę mikroporów heulandytu.

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АДСОРБЦИОННЫЕ СВОЙСТВА ГЕЙЛАНДИТА ИЗ РУДНА

Резюме

Были проведены исследования поглощающих свойств натурального зеолита, гейландита, который находится в вакуолях мелафиров из Рудна около Кракова. Были определены изотермы адсорпции паров: водяных, метилового спирта, бензена и аргона. Обнаружено большое поглощение воды и метилового спирта и низкое бензена и аргона. На основании анализа формы изотерм определено преобладающий диаметр микропор гейландита.