Adsorption phenomena at high pressures and temperatures.
2.* Methane adsorption on Rho zeolite

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Equilibrium isotherms of adsorption of methane on crystalline Rho zeolite were measured with the use of a precision volumetric-gravimetric setup that was developed for determining the equilibrium and kinetic parameters of adsorption in the pressure range of 0.1—160 MPa and temperature range of 300—600 K. The method of determining the accessible volume of an adsorption system (free volume + micropore volume) and the micropore volume of a sorbent was used. Two independent methods for calculation of micropore volume on the basis of the isotherms of excess adsorption were used. The discrepancy in the results of the calculation of the micropore volume by three independent methods is within the limits of the calculation accuracy. An evaluation of a change in the isosteric heats of the excess and absolute adsorption of methane on Rho zeolite was carried out in relation to filling and temperature. An evaluaton of the adsorption volume above the outer surface of the zeolite crystals was performed. The results of experimental investigations of methane adsorption on Rho zeolite can be used to solve the problem of encapsulation of gases by solid sorbents.

Key words: adsorption, micropore volume, surface, isostere, heat, zeolite.

Experimental studies of the adsorption of gases and vapors in the range of high pressures and temperatures are meaningful for further development of the excess method in the thermodynamics of adsorption.[2] The importance of the development of this approach in the theory of adsorption is obvious, because extensive thermodynamic values obtained experimentally have an excessive nature, and general concepts of the modern thermodynamics of adsorption do not allow one to describe new regularities that were obtained during experimental studies of the adsorption of gases and vapors at high pressures. Knowledge on the thermodynamic characteristics involving the values of absolute adsorption is not less important, because all molecules occurring in an adsorption field participate in this process. For recalculation of isotherms of excess adsorption into isotherms of absolute adsorption, exact values of the adsorption volume are necessary. Previously,[1,3] a procedure for study of nitrogen adsorption on NaA zeolite in the range of high pressures up to 160 MPa and temperatures of 300—600 K was described. This report is a continuation of those studies. The methane—synthetic Rho zeolite system was taken as the object of study. The structure of this zeolite includes cavities of only one size, which are identical to the α-cavities of NaA zeolite,[4] and a fraction of exchange cations is represented by cesium ions.[5]

Experimental

An overall diagram of the adsorption setup is described in the works.[1,3] The setup was modified by connection of a weight manometer in parallel to the Bourdon manometer in the measuring part of the setup; the principle of operation of the weight manometer is similar to that of an adsorption balance: An autoclave with a volume of 13.157 cm^3 is suspended to an ADV-200 M type, class 2, beam balance with a sensitivity of $5 \cdot 10^{-5}$ g per scale division. The beam balance was kept in a zero position during measurement with the aid of an inductive sensor, electric unit, and solenoid. The total sensitivity of the system (balance + steel spring) is $5 \cdot 10^{-4}$ g. The autoclave and capillary for gas supply were placed in an air thermostat in which a temperature of 300 K was maintained with an accuracy of ±0.1 degree. The beam balance and air thermostat with the autoclave were placed into the second air thermostat with a temperature of 297 K. The temperature of a sample was measured with a thermocouple clamped to the middle of the outside of the autoclave. The thermal electromotive force was measured with an Shch-300 instrument. Crystalline Rho zeolite was placed into the autoclave-adsorber of 5 cm^3 volume. The weight of the dehydrated and degassed

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* For Part 1 see Ref. 1.

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zeolite was equal to 2.5824 g; methane of 99.8 % purity was used as an adsorbate.

Measurement of the surface area was carried out on a conventional gravimetric adsorption setup with a torsion balance and sensitivity of 10 μg when the weight of the zeolite was equal to 0.8 g. Pressure was measured with two bellows manometers with the sensitivity of 0.133 Pa in the range of 10^{-3}—1 kPa and 1.33 Pa in the range of 1—100 kPa.

Results and Discussion

A change in the value of the weight g, recorded by the beam balance connected to the autoclave-adsorber, includes the weight of methane g_{free} in the free volume of the autoclave and capillary and the weight of adsorbed methane g_a, *i. e.*,

$$g = g_{free} + g_a = V_{free}\rho_g + W_a\rho_a, \qquad (1)$$

where ρ_g is the density of the equilibrium gas phase, V_{free} is the free volume of the autoclave and capillary, ρ_a is the average density of the adsorbed phase, and W_a is the adsorption volume of the zeolite. Equation (1) can be rewritten as follows:

$$g/\rho_g = V_{free} + W_a \cdot \rho_a/\rho_g. \qquad (2)$$

The data obtained at 299, 423, 473, and 503 K are represented in the coordinates of this equation (Fig. 1). As seen in a plot, in the high-pressure region (P > 80 MPa), the experimental data for three temperatures, 423, 473, and 503 K, are described by one straight line that is parallel to the abscissa. This gives evidence that in the region of rather high pressures, the density of an adsorbed phase approaches to that of a gas phase, *i.e.*, ρ_a/ρ_g tends to unity, hence the g/ρ_g parameter does not depend on P and equation (2) transforms into the equation

$$g/\rho_g = V_{free} + W_a = V_{acc}. \qquad (3)$$

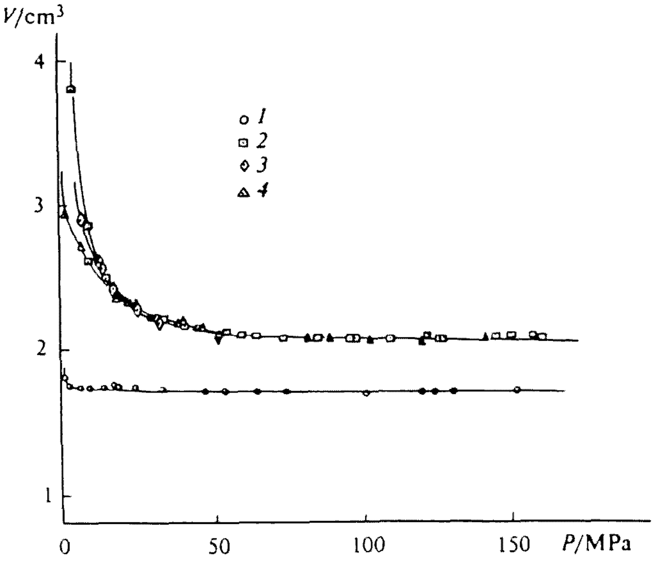

Fig. 1. Dependence of the volume $V = g/\rho_g$ on pressure at 299 (*1*), 423 (*2*), 473 (*3*), and 503 K (*4*).

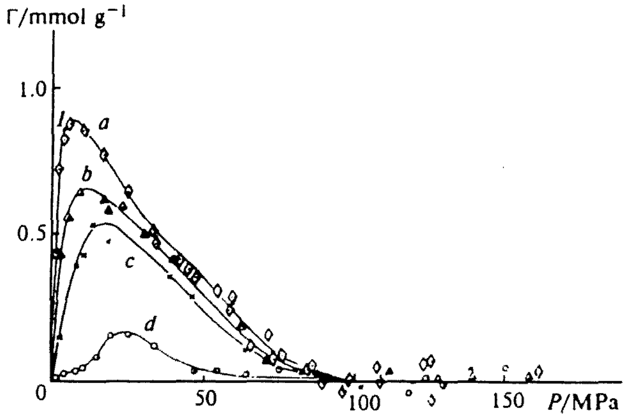

Fig. 2. Isotherms of excess adsorption of methane on Rho zeolite at 423 (*a*), 473 (*b*), 503 (*c*), and 299 K (*d*).

The accessible volume (V_{acc}) calculated on the basis of the experimental data for three temperatures, 423—503 K (Fig. 1), is equal to 2.090±0.014 cm³. However, the figure shows that the values obtained at 299 K are significantly less than those measured at higher temperatures although those also fall onto the straight line that is parallel to the abscissa at the pressures P > 5 MPa. According to this data, V_{acc} is equal to 1.716±0.004 cm³ at 299 K. It is obvious that at the temperatures $T \geq 423$ K, the micropore volume of the zeolite enters the adsorption volume W_a,, and the difference between the pore volumes which are accessible for the adsorbate at 299 K and higher temperatures, V_{acc}, is equal to 0.144±0.014 cm³ g⁻¹. If the accessible volume is known, then, according to the definition of the excess adsorption,

$$\Gamma = [g - (V_c + W_a) \cdot \rho_g]/M_a, \qquad (4)$$

where M_a is the weight of the adsorbent.

Figure 2 shows the isotherms of the excess adsorption at four temperatures mentioned above. As is seen in the figure, each isotherm has a maximum that shifts to higher pressures with increase in the temperature of adsorption. On the basis of the isotherms of methane adsorption on the Rho zeolite obtained, the micropore volume was calculated with two independent methods.[6,7] The first approximation method for determining the adsorption volume W is concerned with a search for the point on the isotherm of excess adsorption in which $d\Gamma/d\rho_g = W$. On the isotherm of excess adsorption such a point is always located to the left of the maximum point (P_{max}). As the first approximation, $W_1 = 2\Gamma_{max}/\rho_B$ is accepted, where Γ_{max} is the adsorption in maximum point, ρ_B is the density of the equilibrium gas phase of methane at the point where $\Gamma = 0$. For example, the value of the maximum excess adsorption of methane (Γ_{max}) on the Rho zeolite for the isotherm of excess adsorption at 423 K was equal to 0.165 mmol/g and $\rho_B = 0.269$ g/cm^3. There is point *1* on the isotherm of the excess adsorption, in which the slope of the curve is equal to the W_1 value. When the value of excess adsorption Γ_1 in the point *1* was determined, one can make the second approximation, *i.e.*, to find $W_2 = 2\Gamma_1 \cdot \rho_B$ and point *2*, respectively, in which the value of the derivative $d\Gamma/dr = W_2$, *etc.* The iteration process converges fast (through 4—5 steps), and this allows one to find the value of the adsorption volume: $W = 0.108 \pm 0.038$ cm^3/g. More rigorous method for determining the adsorption volume on the basis of the isotherm of excess adsorption has been proposed in work.[6] The method is universal, because it is applicable for the adsorbents of any pore structure as well as for nonporous sorbents and is based on the use of the excess adsorption isotherm measured in a wide pressure range. The equation with indefinite parameters obtained by the methods of statistical thermodynamics[7] was used as the equation of the isotherm of absolute adsorption. It is supposed that the calculated value of excess adsorption, Γ^{calc}, can be represented as follows:

$$\Gamma_i^{calc}(P, T) = a_i(P, T) - \rho_i(P, T)\, W, \qquad (5)$$

where W is a constant, and some restrictions impose on the character of the $a_i(P, T)$ and $\rho_i(P, T)$ functions. By minimizing the functional

$$\varphi = N^{-1} \cdot \Sigma[(\Gamma_i^{exp} - \Gamma_i^{calc})/\Gamma_i^{exp}]^2 = \min \qquad (6)$$

(Γ^{exp} is the experimental value of excess adsorption), one can find the coefficients of the $a(P, T)$ function and the corresponding W value. The method has been probed for a series of adsorption systems, and it always gave a stable result toward the entering parameters.[8] The micropore volume in Rho zeolite calculated by this method is equal to 0.121 ± 0.039 cm^3/g. Comparing the values of the micropore volume obtained by three methods, one can conclude that they are within the limits of the calculation accuracy. The value of micropore volume $W = 0.144$ cm^3/g was further used for calculation of the isotherms of absolute adsorption and the heats of adsorption. Coincidence of the values of micropore volume obtained by three methods allows one to conclude that at 299 K, methane is adsorbed only at the outer surface of the zeolite. This fact can be explained by the structural peculiarities of this zeolite. The frame of the zeolite is formed by the cells which are connected with double six-membered rings of the aluminum—silicon—oxygen tetrahedra. Three eight-membered windows correspond to each α-cavity in Rho zeolite, and these windows are similar to the entering windows of NaA zeolite. Calculations show that the fraction of the volume occupied by α-cavities is higher in Rho zeolite than in A-type zeolite. The chemical formula of Rho zeolite studied is $Na_9Cs_3Al_{12}Si_{36}O_{96}$, and the molecular mass of a unit cell M = 3476.42. The positions near the plane of eight-membered rings are the most probable sites for the localization of Cs^+ cations in the Rho zeolite and the centers of six-membered rings are the most probable for Na^+ cations. The cesium cation ($\sigma_{Cs} = 0.165$ nm)[5] occurring in the eight-membered window decreases a cross-section in such a manner that the methane molecules cannot practically diffuse into the cavity of the zeolite at a room temperature.

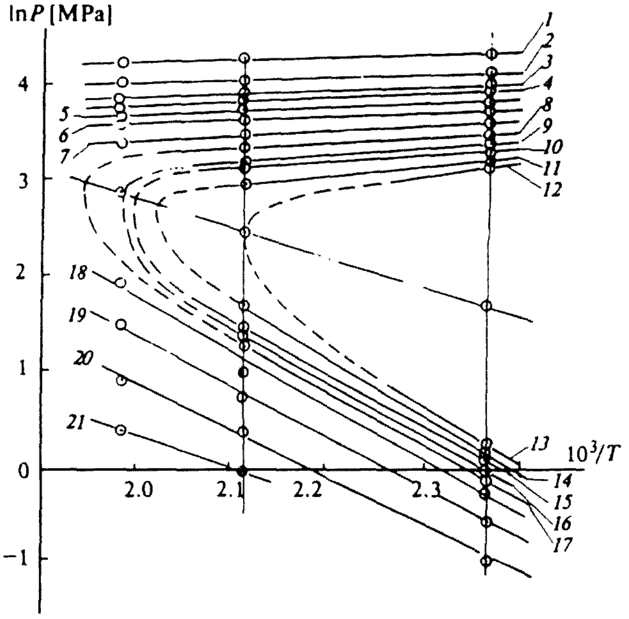

Fig. 3. Isosteres of excess adsorption of methane on Rho zeolite, mmol/g: 0.1 (*1, 20*); 0.2 (*2, 19*); 0.25 (*3*); 0.3 (*4, 18*); 0.35 (*5*); 0.4 (*6*); 0.45 (*7*); 0.5 (*8, 17*); 0.535 (*9, 16*); 0.55 (*10, 15*); 0.6 (*11, 14*); 0.645 (*12, 13*).

On the basis of the isotherms of excess adsorption, the isosteres of excess adsorption of methane on the Rho zeolite were calculated and are presented in Fig. 3. Previously,[3] the same isosteres were calculated for the adsorption of nitrogen on NaA zeolite. The isosteres of methane adsorption on Rho zeolite are similar in shape to those of N_2 on NaA: some of the isosteres are nonlinear and they pass through a point where the derivative transforms into infinity, the locus of these points forming a straight line.

The obtained family of isosteres of excess adsorption of methane makes it possible to calculate the dependence of the isosteric heats on filling (Fig. 4, *a*) and temperature (Fig. 4, *b*) with the use of an equation[8] deduced strictly for the excessive values on the basis of thermodynamics:

$$q_{st} = T\, V_g\, (dP/dT)_\Gamma = -\, R\, Z\, (d\ln P/dT^{-1})_\Gamma, \qquad (7)$$

where Z is the factor of compressibility, R is the gas constant, and V_g is the molar volume of methane in the equilibrium gas phase. For the ascending branches of

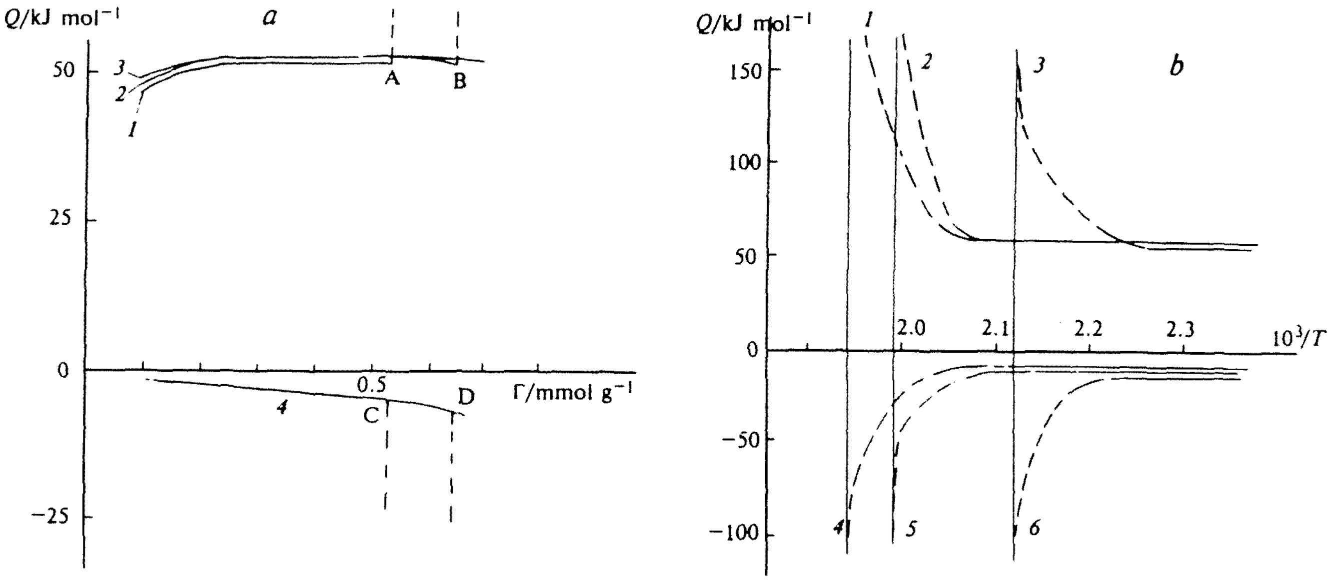

Fig. 4. *a.* Dependence of the heat of excess adsorption (Q) on filling: 503 (*1*), 473 (*2*), 423 (*3*), 503 K (*4*). *b.* Dependence of the heat of excess adsorption (Q) on temperature, Γ/mmol · g^{-1}: 0.5 (*1, 4*); 0.535 (*2, 5*); 0.645 (*3, 6*).

the isotherms of excess adsorption (see Fig. 2), where $P < P_{\max}$, the heat of adsorption has a positive value and is equal to 52 kJ mol^{-1}, and in the region where $P > P_{\max}$, the heats of adsorption have negative and significantly lower values: −7 to −2 kJ mol^{-1}. As is seen, in both pressure regions ($P < P_{\max}$ and $P > P_{\max}$), the heat of excess adsorption depends slightly on filling only for the linear segments of the isosteres. As soon as the isostere begins to deviate from linearity, the heat of adsorption begins to increase up to infinity. The values of adsorption after which the heats of adsorption begin to increase with filling, are designated by dash lines in Fig. 4, *a*. The factor of compressibility $Z = PV/RT$ for methane changes within the limits of 10 % in the 423—503 K temperature range and 1—160 MPa pressure range. Therefore, the isosteric heats of excess adsorption practically coincide in the range of linear isosteres (see curves *1—4* in Fig. 4, *a*). With a deviation of the isosteres from linearity, the isosteric heat of excess adsorption begins to increase (or decrease) up to $\pm\infty$. These changes are seen well in a plot (Fig. 4, *b*) presenting the dependences of the isosteric heats of excess adsorption on the temperature for a series of isosteres. Previously,[9] it has been shown that at high temperatures the isosteric heat is independent of the filling ($q_{st} = 2RT$) and should tend to infinity. But in our case, the behavior of the excess isosteric heats of adsorption observed, in particular an interruption, is due to the presence of a maximum on the isotherm of the excess adsorption (see Fig. 2), at which the slope is equal to zero. The values of the heats tending to infinity should correspond to this slope. On the other hand, analysis of Fig. 2 shows that in the $P < P_{\max}$ region an exothermic process is observed and in the $P > P_{\max}$ region an endothermic process takes place. The transition from positive values of the heats of excess adsorption to negative ones should occur through zero value. However, this conclusion contradicts the dependence described by equation (7).

With the use of the value of the micropore volume W = 0.144 cm^3/g found with equation (3), the isotherms of excess adsorption were recalculated to the isotherms of absolute adsorption for three temperatures: 423, 473, and 503 K (Fig. 5).

On the basis of the isotherms of absolute adsorption, the adsorption isosteres were obtained (Fig. 6).

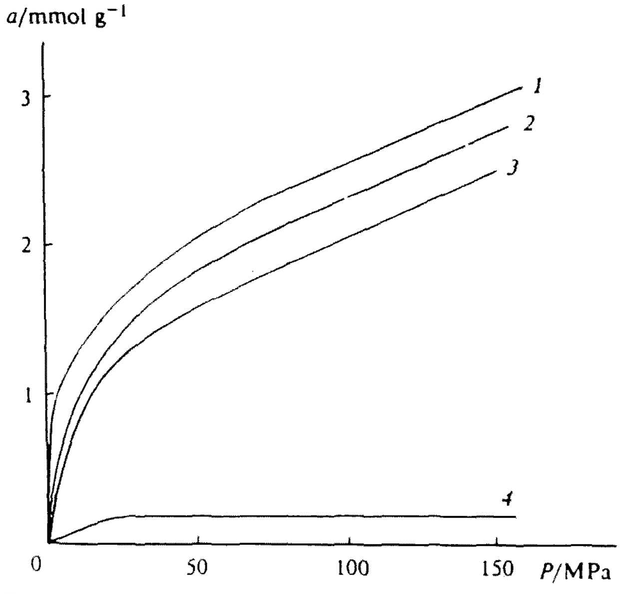

Fig. 5. Isotherms of absolute adsorption of methane at 423 (*1*), 473 (*2*), 503 (*3*), and 299 K (*4*).

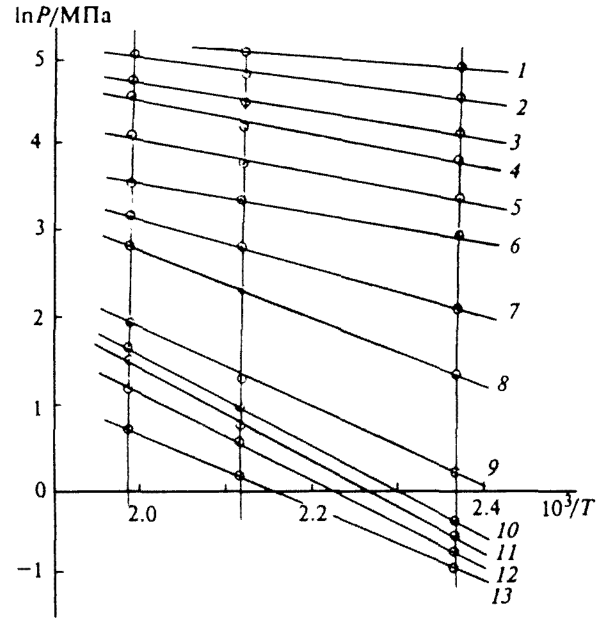

Fig. 6. Isosteres of absolute adsorption of methane, mmol/g: 2.8 (*1*), 2.5 (2), 2.2 (*3*), 2.0 (*4*), 1.7 (*5*), 1.5 (*6*), 1.2 (*7*), 1.0 (*8*), 0.6 (*9*), 0.5 (*10*), 0.4 (*11*), 0.3 (*12*), 0.2 (*13*).

The isosteric heat of adsorption was estimated with the equation

$$q_{st} = -ZR(1 - V_a/V_g)(\mathrm{d}\ln P/\mathrm{d}T^{-1})_a, \tag{8}$$

where q_{st} is the isosteric heat of adsorption, V_a is the partial molar volume of methane in the adsorbed phase, and V_g is the molar volume of methane in the equilibrium gas phase. Although exact V_a values in the high-pressure region are unknown, the deformation of the crystals of the zeolite upon adsorption is small, *i.e.*, a change in $\mathrm{d}V_a/\mathrm{d}a$ is less than an experimental error, and the V_a/V_g ratio is much less than unity, so one can neglect it.

Figure 7 presents the dependence of the isosteric heat of adsorption on filling. The adsorption values in mmol/g are plotted along one abscissa, and the corresponding values of the average number of molecules per cavity of Rho zeolite are plotted along another abscissa; the point on the ordinate with Q = 24 кJ/mol corresponds to the value of the differential heat of the methane adsorption at 0.1 MPa and 293 K;[10] the region which was not studied experimentally is designated by a dash line. Discrepancies between the isosteric heats of absolute adsorption for different temperatures are within the limits of experimental accuracy.

In the initial range of filling, the heat of adsorption increases due to arising intermolecular interaction methane—methane. With a rise in a number of the methane molecules in the cavity of the zeolite, the repulsive forces appear after $n > 2$, and the isosteric heat of adsorption decreases respectively. The differential heat of methane adsorption on the same sample of the Rho zeolite measured calorimetrically at 0.1 MPa and 293 K,[10] which is equal to 24 kJ/mol, is in line with our results (Fig. 7). As was shown above, at 299 K, methane diffuses very slowly into the zeolite pores and is adsorbed generally at the outer surface of the crystals. Therefore, the value of the differential heat of adsorption of 24 kJ/mol corresponds to the interaction of the methane molecules with outer surface of the zeolite crystals. At higher temperatures, the methane molecules penetrate into the zeolite pores faster and the adsorbate—adsorbate interaction does not manifest itself in this case. The heat of adsorption increases up to 37 kJ mol^{-1}, respectively. The difference between the heats of adsorption upon filling a cavity by one and two molecules is equal to ~6 kJ/mol (see Fig. 7). Calculation of the energy of the pair interaction CH_4—CH_4 performed according to the Lennard—Jones model[11] without considering polarizability showed that the energy of dispersive interaction at the distance of σ = 0.3822 nm is equal to ~5 kJ/mol. Thus, one can conclude that the intermolecular interactions of the methane molecules contribute mainly to a change in the heat of adsorption.

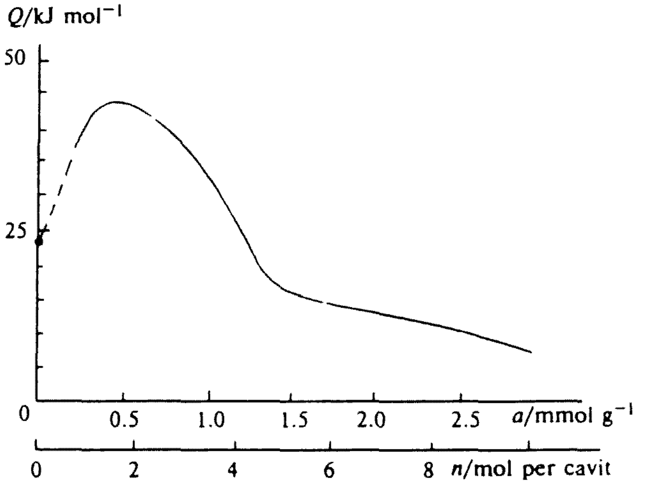

Fig. 7. Dependence of the heat of absolute adsorption on filling.

The equilibrium adsorption isotherms of benzene on the same sample of Rho zeolite was measured on another experimental setup at room temperature (291 K). Benzene cannot penetrate to the pores of the Rho zeolite at room temperature because of steric hindrance, therefore, the adsorption isotherm of benzene measured is due to the adsorption on the outer surface of the zeolite crystals. The surface area, *S*, of the zeolite crystals calculated with the BET method was equal to 4.8 m^2/g. On the basis of the kinetic diameter σ of the methane molecule and the value of the maximum excess adsorption $\Gamma_{max} \approx a_{max}$ at 299 K and the surface area S, the maximum adsorption volume at the outer surface of the zeolite single crystals, W, was found to be 0.008±0.003 cm^3/g, and a maximum number of statistical monolayers is equal to three. The isotherm of absolute adsorption at 299 K (Fig. 5, curve *4*) was calculated from the difference between the accessible volume V_{acc} and maximum adsorption volume W at the surface (see equation (3)). However, the above-presented calculation of the adsorption volume created by the outer surface of the crystals is based on an idealized model, whereas in fact, a dense packing of three layers of the methane molecules and a sharp boundary of the transition to the density of the equilibrium gas phase are highly improbable. According to another method,[6] the adsorption volume calculated on the basis of the isotherm of excess adsorption at 299 K measured experimentally proved to be equal to 0.05±0.02 cm^3/g. When the outer surface area of the crystals is equal to 4.8 m^2/g, the corresponding height of the adsorption layer on the surface of the crystals is equal to ~10 nm. Apparently, such a great height of the adsorption layer of methane at the surface of the crystals at 299 K is unlikely. Therefore, to determine the height of the adsorption layer, it is necessary to carry out similar measurements on a nonporous solid adsorbent.

References

1. A. A. Pribylov, S. M. Kalashnikov, and V. V. Serpinskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1233 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 1105 (Engl. Transl.)].
2. J. W. Gibbs, *Termodinamicheskie raboty*, Moscow—Leningrad, 1950 [J. W. Gibbs, *The Collected Works*, Vol. 1, *Thermodynamics*, 1928, New York, London, Toronto].
3. A. A. Pribylov, V. V. Serpinsky, and S. M. Kalashnikov, *Zeolites*, 1991, **11**, 846.
4. H. E. Robson and D. P. Shoemaher, *Mol. Sieves*, Zurich. 1974, 106.
5. *Spravochnik khimika [Handbook on Chemistry], 2-nd ed.*, Khimiya, Moscow, 1962. 381 p.
6. T. S. Yakubov, L. G. Shekhovtsova, and A. A. Pribylov, *Izv. Akad. Nauk, Ser. Khim.*, 1996 (in press) [*Russ. Chem. Bull.*, 1996, **45** (Engl. Transl.)].
7. V. A. Bakaev, *Dokl. Akad. Nauk SSSR*, 1966, **167**, 369 [*Dokl. Chem.*, 1966, **67** (Engl. Transl.)].
8. V. A. Bakaev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1971, 2648 [*Bull. Acad. Sci. USSR, Div. Chem.* Sci., 1971, **20**, 2516 (Engl. Transl.)].
9. A. A. Lopatkin, *Teoreticheskie osnovy fizicheskoi adsorbtsii [Theoretical Bases of Physical Adsorption]*, Izd. Mosk. Gos. Univ., Moscow, 1983, 344 p. [in Russian].
10. A. A. Isirikyan, L. Currie, G. F. Stoeckli, and T. S. Yakubov, *Zh. Fiz. Khim.*, 1995, 311 [*Russ. J. Phys. Chem.*, 1995, **69** (Engl. Transl.)].
11. J. Hirschfelder, Ch. Curtiss, and R. Bird, *Molekulyarnaya teoriya gazov i zhidkostei*, Izd. Inostr. Lit., Moscow, 1961, 915 p. [J. O. Hirschfelder, Ch. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, John Wiley and Sons, Inc., New York; Chapman and Hall, London, 1954].

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