The experimental study of the mechanism of physical adsorption of n-alkane vapours on a synthetic zeolite is presented. The applicability of two analytical models predicting the multilayer adsorption is evaluated by means of a rational fractional function used in the classical BET theory as well as the composite exponential function developed by Jovanović. The results indicate that a multilayer adsorption mechanism occurs in this system already at the beginning of the process, i.e. when only a part of the adsorbent surface area is occupied by a monomolecular adsorbate layer and when the partial pressure of adsorptive is even lower than 1 % in comparison with the saturation pressure of adsorptive at adsorption temperature.

The mechanism of adsorption of gases and vapours on the solid adsorbent surface can be evaluated on the basis of the analysis of adsorption equilibrium data as well as from the kinetics of the sorption process.

The present contribution is devoted to the study of physical adsorption mechanism of n-alkane vapours on a synthetic zeolite and is based upon the analysis of the experimental adsorption equilibrium data of n-hexane on synthetic zeolite 5A.

For an analytical expression of adsorption equilibrium the BET and Jovanović adsorption isotherms of multilayer adsorption have been chosen.

Derivation of the BET isotherm [1]

\[
\frac{p}{a(p_n - p)} = \frac{c - 1}{ca_m(p_n)} + \frac{1}{ca_m} (1)
\]

for multilayer adsorption was carried out on the assumption that the same forces that produce condensation are mainly responsible for the binding energy of multilayer adsorption. Constant c in eqn (1) is usually defined in the original form as

\[
c = \xi \exp \left[ (E_1 - E_2)/RT \right] (2)
\]

The BET theory identifies the heat of adsorption for the second and higher adsorption layers with the heat of liquefaction of the adsorptive \(E_L\) at adsorption temperature. On the basis of this assumption the authors [1] regard as evident that \(\xi\) will not differ much from unity: \(\xi = 1\).

BET isotherm has found a significant practical application in determining physical properties of solid surface (e.g. specific surface area, specific pore volume, internal porosity, differential and integral pore distribution) by standard sorption method.

Jovanović isotherm [2, 3]

\[
a = a_m [1 - \exp (-Bp)] \cdot \exp (Cp) (3)
\]

is based on recent approaches to the adsorption process. Jovanović presumes the adsorption process in higher adsorption layers to be the same as directly on the adsorbent surface. The “accessible surface” is represented by an adsorbate layer already formed, however, with a lower adsorption potential.

Relations, defining the isotherm constants \(B\) and \(C\), follow from the kinetic course of eqn (3)

\[
B = \vartheta_i K \quad C = \vartheta_i K (4)
\]

where

\[
K = \sigma/(2\pi mk_b T)^{0.5}
\]

The two constants \(B\), \(C\) describe adsorption in the first and in the second and/or higher adsorption layers, respectively.

In the case of monomolecular adsorbate layer formed directly on the adsorbent surface, eqn (3) can be simplified to

\[
a = a_m [1 - \exp (-Bp)] (5)
\]

For the estimation of the mean residence time of adsorbate molecules for the \(i\)-th adsorption layer, Jovanović proposes the following relation

\[
\vartheta_i = \vartheta_0 \exp \left[ c_i/(k_b T) \right] (6)
\]

where the oscillation period of nonadsorbed molecules in the adsorptive is taken as \(\vartheta_0 = 0.1\) ps.
This assumption follows from experimental data on adsorption of n-butane on glass spheres at various temperatures.

From comparison of eqns (3) and (5) it follows that due to the formation of higher adsorption layers above the first one the mass ratio of the adsorbate and the adsorbent increases \([\exp(Cp)]\)-fold, i.e. the plot of \(a\) as a function of \(p\) exhibits an exponential relationship.

From the viewpoint of validity of isotherms (1) and (3) for multilayer adsorption it is important that both equations consider formation of successive adsorption layers on certain places of the adsorbent surface prior to completion of adsorbate monolayer.

**EXPERIMENTAL**

Synthetic zeolite Calsit 5A in the form of spherical particles (composition \(w_1: 42\% \text{ SiO}_2, 37\% \text{ Al}_2\text{O}_3, 16\% \text{ CaO}, 5\% \text{ Na}_2\text{O}, \text{ Fe}_2\text{O}_3, \text{ MgO}\)) with the mineral density 2850 kg m\(^{-3}\), particles diameter 2.8—3.0 mm, specific surface area 590 m\(^2\) g\(^{-1}\), and specific pore volume 0.27 cm\(^3\) g\(^{-1}\) was used as an adsorbent. \(n\)-Hexane vapours carried by an inert gas (purified nitrogen) served as an adsorptive (\(X < 0.1\)).

Experimental adsorption equilibrium data were obtained in a laboratory flow gradientless reactor described in [4] with the free volume 101.2 cm\(^3\), at temperature 400 K, pressure 101.4 kPa, and volumetric adsorptive flow 0.75 cm\(^3\) s\(^{-1}\).

**RESULTS AND DISCUSSION**

The experimental adsorption equilibrium data obtained in this system show a relatively good agreement with the data in other work [5], even measured in other type of an equipment as well as under different conditions. They are presented in Fig. 1.

The following values of constants \(c\), \(B\), and \(C\) involved in eqns (1) and (3) were found from a set of experimental equilibrium data using the simplex method of nonlinear regression: \(c = 5600\), \(B = 7.96\) kPa\(^{-1}\), \(C = 0.0334\) kPa\(^{-1}\).

By rearrangement of eqn (2) arising from the BET theory and using recommended simplifications \(E_L \equiv E_L\) and \(\xi \approx 1\), one gets

\[
\Delta E = E_1 - E_L = RT \ln c
\]  
(7)

After substituting the experimentally determined constant \(c\), it follows that the value of \(\Delta E = 28.7\) kJ mol\(^{-1}\). Taking into account the fact that the heat of liquefaction \(E_L\) of \(n\)-hexane at adsorption temperature equals 25.6 kJ mol\(^{-1}\) [6] and this value is in accordance with the BET theory considered as identical with the heat of adsorption for the second and higher adsorption layers, one can easily determine from eqn (7) the heat of adsorption for the first adsorption layer \(E_1 = \Delta E + E_L = 54.3\) kJ mol\(^{-1}\).

Using eqn (6) and Jovanović assumptions, the heat of adsorption \(E_1\) is given by the relation

\[
E_1 = N_A k_B T \ln \left(\frac{\theta_1}{\theta_0}\right) = RT \ln \left(\frac{\theta_1}{\theta_0}\right)
\]  
(8)

Combining eqns (4) and (8) yields

\[
E_1 = RT \ln \left[\frac{B(2\pi m k_B T)^{0.5}}{(\sigma \theta_0)}\right]
\]  
(9)

After substituting the experimentally determined value of constant \(B\), there results (assuming the values of other quantities are known) \(E_1 = 54.9\) kJ mol\(^{-1}\).

Using the experimentally determined constant \(C\) one can similarly obtain the heat of adsorption for the second and higher adsorption layers \(E_2 = 36.7\) kJ mol\(^{-1}\). Then, the value of \(\Delta E = E_1 - E_2 = 18.2\) kJ mol\(^{-1}\) which can also be calculated directly from the following equation

\[
\Delta E = RT \ln \left(\frac{B}{C}\right)
\]  
(10)

obtained from combining eqns (4) and (6).

It follows from experimental results that the heats of adsorption for the first adsorption layer obtained by BET and Jovanović isotherms are in a very good agreement (54.3 and 54.9 kJ mol\(^{-1}\), respectively). Hence both models which consider
multilayer adsorption and are expressed analytically by adsorption isotherms (1) and (3) are suitable for this purpose, despite the fact that they represent different functions from the mathematical point of view. The fit of experimental equilibrium data to isotherm equations (1) and (3) results in very similar correlation coefficients.

However, the values of the heat of adsorption for the second and higher adsorption layers following from BET and Jovanović models (25.6 and 36.7 kJ mol\(^{-1}\), respectively), disagree very significantly. This arises from different views on the mechanism of adsorption and formation of higher adsorption layers in both theories.

If the formation of higher adsorption layers was accompanied by a release of the heat of adsorption equal to the heat of liquefaction of the adsorptive at adsorption temperature supposed by the BET theory, the equilibrium pressure of adsorptive would have to be close to the saturation pressure of adsorptive (i.e. 497.4 kPa [6] for n-hexane at adsorption temperature). In reality, however, the highest experimental pressure of adsorptive used did not exceed 7 kPa, which was about 70-times lower value than the saturation pressure of adsorptive. Moreover, if the higher adsorption layers were formed only with the release of the heat of liquefaction, these could hardly be formed prior to the monomolecular adsorbate layer even at the pressure of adsorptive lower than 1 kPa which was about 500-times lower value than the saturation pressure of adsorptive at adsorption temperature.

From this point of view one can conclude that the simplification in eqn (7) recommended by the BET theory is not justified in this system. This is in agreement with the results of Kemball and Schreiner [7] who revealed that the value of the factor \(\xi\) involved in eqn (2) fulfils condition \(\xi \approx 1\) only exceptionally since the real value depends also upon the properties of the system. \(\xi\) may be equal to 1 only when the entropy of adsorption is equal to the entropy of liquefaction of the adsorptive since the factor \(\xi\) is related to the ratio of the so-called condensation coefficients and frequencies of oscillations of adsorbate molecules perpendicular to the solid surface in the first, second and/or higher adsorption layers. Similarly, the heat of adsorption for the second and higher adsorption layers cannot be equal to the heat of liquefaction of the adsorptive at adsorption temperature.

Jovanović isotherms (3) and (5) may serve as a convincing evidence of multilayer adsorption of n-alkane vapours on a synthetic zeolite surface even at a very low relative pressure of adsorptive \(X\). While the multilayer adsorption isotherm (3) fits the experimental data very satisfactorily the monolayer adsorption isotherm (5) is not in a good agreement with them.

**SYMBOLS**

- \(a\), relative mass fraction of the adsorbate on the adsorbent
- \(a_m\), relative mass fraction of the adsorbate on the adsorbent surface supposing complete monomolecular adsorbate layer
- \(B, C, c\), isotherms constants
- \(E_i\), heat of adsorption for the \(i\)-th adsorption layer
- \(E_L\), heat of liquefaction of the adsorptive at adsorption temperature
- \(k_B\), Boltzmann constant
- \(m\), mass of an adsorbate molecule
- \(p\), equilibrium pressure of adsorptive
- \(\rho_n\), saturation pressure of adsorptive at adsorption temperature
- \(R\), gas constant
- \(T\), absolute temperature
- \(X\), relative pressure of adsorptive: \(X = p/p_n\)
- \(e_i\), adsorption energy of a molecule for the \(i\)-th adsorption layer
- \(\xi\), preexponential factor in eqn (2)
- \(\tilde{v}_i\), mean residence time of adsorbate molecules for the \(i\)-th adsorption layer
- \(\sigma\), effective surface for the interaction of the adsorbate molecule

**REFERENCES**