Utilization of experimental sorption data in estimation of the heat of adsorption

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The work reported here deals with the possibilities and the problems of utilization of the experimental sorption data for the estimation of the heat of adsorption. The study is based on the own experimental equilibrium data obtained during the adsorption of n-alkane vapour on a synthetic zeolite surface in a flow stirred adsorber.

The relations in a form of adsorption isotherms based on the BET theory and the Jovanović conception of the adsorption mechanism have been chosen for the estimation of the heat of adsorption from the experimental adsorption equilibrium data.

Physical adsorption of gases and vapours on a solid surface is the consequence of an interaction between the surface of the solid phase (adsorbent) and adsorbed molecules. The unavoidable condition for the adsorption is a decrease of the Gibbs energy for the system composed of solid and gaseous phases during the process: $\Delta G = \Delta H - T\Delta S$. Since in the adsorption some degrees of freedom typical of the gaseous state inevitably disappear, the adsorption of gaseous molecules on a solid adsorbent is accompanied by a decrease of the entropy of the system: $\Delta S < 0$. Hence, the adsorbed phase (adsorbate) has fewer degrees of freedom in comparison with the surrounding gaseous phase (adsorptive).

Thus, the negative value of the change of the Gibbs energy, $\Delta G < 0$, is linked with the fulfillment of the following conditions: $\Delta H < 0$; $|T\Delta S| < |\Delta H|$. The physical adsorption will also be accompanied by a decrease of the enthalpy of the system, $\Delta H < 0$, *i.e.* the heat is always released during physical adsorption. This is the reason why it is important to know the value of the heat of adsorption in the given system. In the case of isothermal adsorption this heat must be removed from the system into the surroundings.

In order to estimate the heat of adsorption from experimental adsorption equilibrium data, we chose adsorption isotherms suitable for this purpose.

In the BET adsorption isotherm [1]

$$a = a_{\mathrm{m}} \frac{cX}{(1 - X)[1 + X(c - 1)]} \tag{1}$$

the formation of a multilayer adsorbate on the adsorbent surface is supposed. In a case of the adsorption at pressure of adsorptive p close to saturation pressure p_n at adsorption temperature (*i.e.* $p \rightarrow p_n$ and $X \rightarrow 1$), according to eqn (*1*) the value a will rise above all limits at arbitrary value of the dimensionless isotherm constant c. From the above mentioned it follows that the BET theory allows for an arbitrary system adsorbent—adsorbate at the condition $p \rightarrow p_n$ the formation of an unlimited number of layers of adsorbed molecules. Therefore, in practice the validity of eqn (*1*) is usually limited by the following condition

$$X < 0.3 \tag{2}$$

The dimensionless constant c of the isotherm is related to the heat of adsorption and is usually defined in the original form

$$c = \xi \exp\left[(E_1 - E_2)/RT\right] \tag{3}$$

The value of $\Delta E = E_1 - E_2$ can be calculated on the basis of the experimental adsorption equilibrium data after the estimation of the constant c of the BET isotherm using the foregoing eqn (*3*)

$$\Delta E = RT \ln (c/\xi) \tag{4}$$

The BET theory admits for the quantity ξ the following simplification

$$\xi \doteq 1 \tag{5}$$

and identifies the heat of adsorption for the second and higher adsorption layers with the heat of liquefaction of the adsorptive at adsorption temperature E_L

$$E_2 = E_3 = \quad = E_n \equiv E_L \tag{6}$$

At known value of the heat of liquefaction one can by means of eqn (*4*) determine also the heat of adsorption for the first adsorption layer E_1 straight on the adsorbent surface.

Jovanović adsorption isotherm [2, 3]

$$a = a_m[1 - \exp(-BX)]\exp(CX) \tag{7}$$

supposes the formation of a mobile multilayer adsorbate on the adsorbent surface. The author considers the adsorption process in higher adsorption layers to be equivalent with the adsorption process in the first layer, however, with a lower adsorption potential in comparison with the original uncovered adsorbent surface. In all other adsorption layers (beginning from the second), an equality of adsorption heats is assumed: $E_2 = E_3 = \quad = E_n$, but in contradiction with the BET theory, these heats of adsorption are not identified here with the heat of liquefaction E_L.

The dimensionless constants B, C in the isotherm (*7*) are defined uniquely

$$B = \frac{\vartheta_1 \delta p_n}{(2\pi m k_B T)^{0.5}} \qquad C = \frac{\vartheta_2 \delta p_n}{(2\pi m k_B T)^{0.5}} \tag{8}$$

These are related to the mean residence time of adsorbate molecules for the i-th adsorption layer

$$\vartheta_i = \vartheta_o \exp(\varepsilon_i/kT) \qquad i = 1, 2, \ldots, n \tag{9}$$

and also to the heat of adsorption.

In accordance with (*9*), the heat of adsorption for the first adsorption layer E_1 is defined as follows

$$E_1 = N_A k_B T \ln(\vartheta_1/\vartheta_o) = RT \ln(\vartheta_1/\vartheta_o) \tag{10}$$

Similarly for the second and higher adsorption layers

$$E_2 = RT \ln(\vartheta_2/\vartheta_o) \tag{11}$$

The value of $\Delta E = E_1 - E_2$ can be calculated on the basis of the experimental adsorption equilibrium data after determining the constants B, C in the isotherm (*7*) by means of the following expression

$$\Delta E = RT \ln(\vartheta_1/\vartheta_2) \tag{12}$$

or using relations (*8*) directly from

$$\Delta E = RT \ln(B/C) \tag{13}$$

Experimental

Laboratory flow stirred adsorber was used for the adsorption equilibrium measurement. n-Heptane vapour served as an adsorptive. Its partial pressure ranged up to 1.5 kPa. Molecular sieve synthetic zeolite 5A was used as an adsorbent, specific surface area 580 $m^2 g^{-1}$; specific pore volume 0.265 $cm^3 g^{-1}$ Purified nitrogen was used as a carrier gas. Adsorption temperature was 130 °C.

Results and discussion

Results on the basis of the BET theory

The constant c in the isotherm (*1*) determined from the experimental adsorption equilibrium data using the method of nonlinear regression attained the value $c = 3730$. The reproducibility of adsorption equilibrium measurement has been proved by two independent experiments. The condition (*2*) of the validity of eqn (*1*) is fulfilled, since the relative pressure of adsorptive is within the interval of the experimental values $0 < X < 0.007$.

According to eqn (*4*) and with regard to relation (*5*), the value of ΔE is $27.6\ \mathrm{kJ\ mol^{-1}}$

The value of E_2 according to [4] is

$$E_2 \equiv E_\mathrm{L} = 29.5\ \mathrm{kJ\ mol^{-1}}$$

Hence the heat of adsorption for the first adsorption layer

$$E_1 = \Delta E + E_2 \doteq 57.1\ \mathrm{kJ\ mol^{-1}}$$

Results on the basis of the Jovanović isotherm

The constants B, C in the isotherm (*7*) determined from the experimental adsorption equilibrium data using the method of nonlinear regression attained the following values: $B = 2560$, $C = 22.8$.

The value of ΔE calculated from eqn (*13*) is $15.8\ \mathrm{kJ\ mol^{-1}}$

The value of E_2 found by use of eqn (*11*) and with regard to eqns (*8*) is $40.8\ \mathrm{kJ\ mol^{-1}}$

The value of E_1 calculated from eqn (*10*) and with regard to eqns (*8*) is $56.6\ \mathrm{kJ\ mol^{-1}}$

From the data obtained a good agreement between the values E_1 calculated by both methods is evident. Also, as it can be seen from Fig. 1, both isotherms

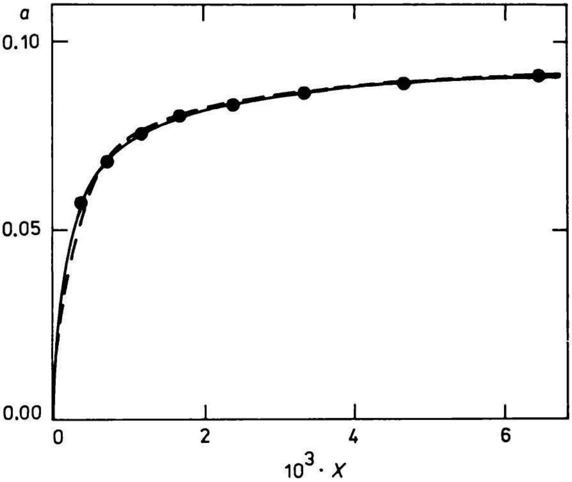

Fig. 1. n-Heptane adsorption equilibrium curves.
● Experimental; —— calculated according to eqn (*1*); — — — calculated according to eqn (*7*).

fit the experimental adsorption equilibrium very satisfactorily. However, a great deviation between the values of E_2 is observed, which is connected also with great differences between the values of ΔE.

With regard to the uniqueness of definitions (*8*) for the constants in the Jovanović isotherm (*7*), the simplification (*5*) introduced by the BET theory seems to be nonacceptable in this system. Further, it should be remarked that also the assumption of identity between the heat of adsorption for the second and higher adsorption layers E_2 and the heat of liquefaction of the adsorptive at adsorption temperature E_L presented by the BET theory can hardly be acceptable in a system n-alkane—synthetic zeolite.

For the foregoing reasons, the heat of adsorption predicted by Jovanović conception of the adsorption mechanism should be preferred to results given by taking into account the BET theory.

Symbols

a	relative mass fraction of adsorbate on the adsorbent
a_m	relative mass fraction of adsorbate on the adsorbent the surface of which is covered with a complete unimolecular layer
B, C, c	dimensionless constants in isotherms
E_i	heat of adsorption for the *i*-th adsorption layer
E_L	heat of liquefaction of the adsorptive
k_B	Boltzmann constant
m	mass of the adsorbate molecule
N_A	Avogadro's number
p	equilibrium pressure of adsorptive
p_n	saturation pressure of adsorptive at adsorption temperature
R	gas constant
T	absolute temperature
X	relative pressure of adsorptive: $X = p/p_\mathrm{n}$
δ	effective surface for the interaction of the molecule
ε_i	adsorption energy of a molecule for the *i*-th adsorption layer
ξ	preexponential factor in eqn (*3*)
ϑ_o	mean oscillation period of nonadsorbed molecules in the adsorptive
ϑ_i	mean residence time of adsorbate molecules for the *i*-th adsorption layer
π	Ludolf number

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