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CALCULATION OF THE ADSORPTION DEFORMATION OF A MICROPOROUS ADSORBENT

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A model of elastic adsorption deformation of microporous adsorbents is presented. The calculation results for the system argon–AUK microporous carbon adsorbent and their comparison to experimental data are given.

Keywords: *adsorption, adsorbents, deformation, adsorption deformation of adsorbents, elastic deformations, microporous adsorbents.*

Introduction. Methods [1] in which the role of the adsorbent surface is reduced only to creation of an adsorption field are of considerable current use in the description of adsorption equilibrium. The assumption that the adsorbent is absolutely inert makes it possible to substantially simplify the description of the equilibrium but is not adequate from the physical viewpoint. Even in the most simple case — that of adsorption on a flat homogeneous surface — we must allow, in the calculations, for the deformation of the solid body, which is related to the decrease in the surface tension of the adsorbent.

For microporous adsorbents, the value of the adsorption deformation, even at high pressures, is low [2], but the energy consumed by such deformation is considerable because of the high modulus of dilatation (compression) of the solid body. It can exert a substantial influence on the thermodynamic characteristics of adsorption systems, which are determined through adsorption and calorimetric experiments; therefore, it must be taken into account in calculations and modeling of adsorption processes.

Works devoted to the investigation and description of adsorption deformation involve, as a rule, studying the deformation of microporous carbon adsorbents [3–6]. The model proposed is intended for description of the elastic adsorption deformation of microporous adsorbents in interaction with gases.

Model. It is assumed in modeling that the microporous adsorbent has a homogeneous microporous structure. We consider it as a first approximation in the form of a parallelepiped with uniformly distributed nonintersecting slotted micropores of equal dimension. The modeled adsorbent is diagrammatically shown in Fig. 1. The initial volume of the modeled sample is equal to

$$V_0 = xyz\,.$$

Assuming that the deformation is isotropic, we can find the volume under free-dilatation (compression) conditions as

$$V = V_0 \left(1 + \frac{\Delta l}{l}\right)^3 ,$$

where $\Delta l/l = \Delta x/x = \Delta y/y = \Delta z/z$. In this case the expression

$$\Delta V = V_0 \left[\left(1 + \frac{\Delta l}{l}\right)^3 - 1\right] \tag{1}$$

is true for the change in the adsorbent volume.

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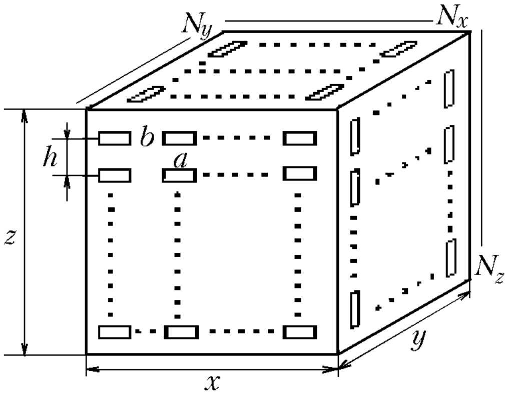

Fig. 1. Microporous adsorbent.

The initial volume of the adsorbent micropores is

$$V_{\mathrm{p},0} = bck_{\mathrm{cr}}\,(N_xN_yz + N_xN_zy + N_yN_zx)\,.$$

Taking into account that $N_x = x/h$, $N_y = y/h$, and $N_z = z/h$, we have

$$V_{\mathrm{p},0} = k_{\mathrm{p},0}V_0\,,\quad k_{\mathrm{p},0} = \frac{3bck_{\mathrm{cr}}}{h^2}\,.$$

The micropore volume under isotropic deformation is

$$V_{\mathrm{p}} = bck_{\mathrm{cr}}\left(1+\frac{\Delta b}{b}\right)\left(1+\frac{\Delta c}{c}\right)\left(N_yN_zx\left(1+\frac{\Delta l}{l}\right)+N_xN_zy\left(1+\frac{\Delta l}{l}\right)+N_xN_yz\left(1+\frac{\Delta l}{l}\right)\right)$$

or

$$V_{\mathrm{p}} = V_0k_{\mathrm{p},0}\left(1+\frac{\Delta b}{b}\right)\left(1+\frac{\Delta c}{c}\right)\left(1+\frac{\Delta l}{l}\right).$$

The change in the micropore volume is

$$\Delta V_{\mathrm{p}} = V_0k_{\mathrm{p},0}\left[\left(1+\frac{\Delta b}{b}\right)\left(1+\frac{\Delta c}{c}\right)\left(1+\frac{\Delta l}{l}\right)-1\right]. \tag{2}$$

If the volume of the adsorbent solid phase is assumed to be constant, the change in the adsorbent volume will correspond to expression (2)

$$V_0\left[\left(1+\frac{\Delta l}{l}\right)^3-1\right] = V_0k_{\mathrm{p},0}\left[\left(1+\frac{\Delta b}{b}\right)\left(1+\frac{\Delta c}{c}\right)\left(1+\frac{\Delta l}{l}\right)-1\right].$$

Implying that the relative linear deformation is small [2, 3], we can write

$$\frac{3\Delta l}{l} \approx k_{\mathrm{p},0}\left[\left(1+\frac{\Delta b}{b}+\frac{\Delta c}{c}+\frac{\Delta b\Delta c}{bc}\right)\left(1+\frac{\Delta l}{l}\right)-1\right].$$

It should be noted that the quantity $\Delta b\Delta c/bc$ is much less than $\Delta b/b$ or $\Delta c/c$. Therefore, we set it nearly equal to zero. Finally, we obtain

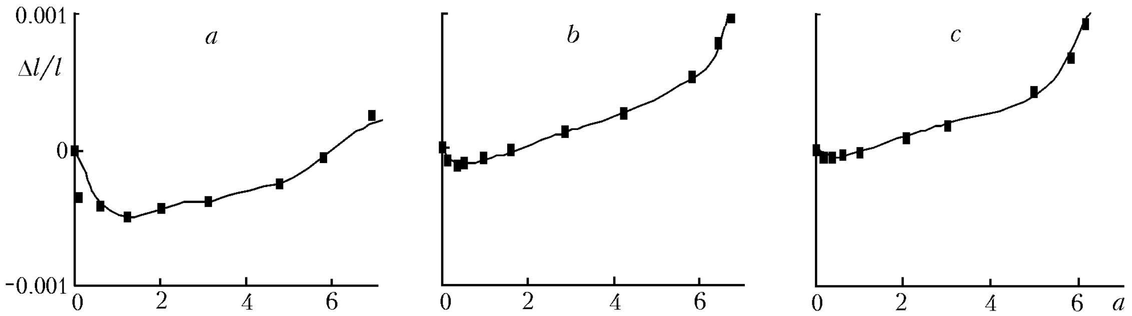

Fig. 2. Comparison of the deformation curves calculated from the model and values determined experimentally (points) for T = 243 (a), 273 (b), and 293 (c) K.

$$\frac{\Delta l}{l}=\frac{k_{\mathrm{p},0}\left(\frac{\Delta b}{b}+\frac{\Delta c}{c}\right)}{3-k_{\mathrm{p},0}\left(1+\frac{\Delta b}{b}+\frac{\Delta c}{c}\right)}. \tag{3}$$

To simplify the solution of the subsequent problem we disregard $\Delta c/c$. Thus, we obtain

$$\frac{\Delta l}{l}=\frac{k_{\mathrm{p},0}\frac{\Delta b}{b}}{3-k_{\mathrm{p},0}\left(1+\frac{\Delta b}{b}\right)}. \tag{4}$$

Expression (4) enables us to restrict our detailed consideration to only one micropore in modeling: calculating the micropore deformation, we can determine the deformation of the entire adsorbent.

Modeling Results. In modeling, we subdivide the adsorbent micropore into identical fragments of certain dimensions, in which, e.g., no more than 300 molecules can be found. In these fragments, we calculate the pressures and the relative deformations which are the same for the remaining fragments, too, by virtue of the assumption of a uniformly filled micropore.

Implying that all micropores are identical and have a dimension of the order of 1 nm (i.e., no more than three adsorbate molecules can be arranged over the height in the micropore cross section), we can determine the relative deformation of one micropore in the case of localized adsorption as follows:

$$\frac{\Delta b}{b}=\frac{1}{E}\left[-\sigma_1 N_1+\sigma_2 N_2\right]. \tag{5}$$

Using experimental data for the relative linear deformation of the adsorbent, we can calculate σ_1 and σ_2 at the initial and final steps of adsorption respectively. Indeed, at the beginning of the process of adsorption, we have $N_2 \cong 0$ in formula (5), whereas at the end, we have $N_1 \cong 200$ and $N_2 \cong 100$ in the fragment under study. Next, in modeling in different adsorption regions, we prescribe N_1 and N_2 in expression (5) so that the correlation between the theoretical and experimental data is maximum. In this case it is clear that $N = aN_{\max}/a_{\max}$.

The adequacy of the obtained results of modeling to the results of experimental investigations enables us to speak of the possibility of using the model proposed. The deformation curves calculated from the model and the values determined experimentally (points) for T = 243 K (a), T = 273 (b), and T = 293 (c) are compared in Fig. 2. The data of experimental investigations [3] of the relative linear deformation $\Delta l/l$ of the microporous carbon adsorbent AUK (active carbon from silicon carbide) in interaction with carbon are presented as points, whereas the modeling results are shown as solid curves.

Conclusions. The proposed model describing the adsorption deformation of microporous carbon adsorbents in interaction with gases makes it possible to relate the value of deformation of one micropore to the value of deformation of the entire adsorbent. The possibility of using this model is confirmed by a satisfactory agreement between the results of the calculations carried out for the argon–AUK microporous carbon adsorbent system and the experimental data. The work can be of practical interest when different technological processes of separation and degassing in the region of high pressures are performed.

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NOTATION

a, running value of the equilibrium adsorption, mole/kg; $a_{\max}$, maximum value of the equilibrium adsorption, mole/kg; b and c, lengths of the micropore sides on the plane (length and width), m; E, Young modulus, Pa; h, initial distance between the centers of micropores, m; k_{cr}, coefficient allowing for the crookedness of micropores; $k_{\mathrm{p},0}$, initial porosity of the adsorbent; N_1 and N_2, number of adsorbed molecules interacting and noninteracting with the micropore walls; $N_{\max}$, maximum number of adsorbate molecules in a micropore fragment ($N_{\max} = N_1 + N_2$); N_x, N_y, and N_z, number of micropores along each direction; V and V_0, running and initial volumes of the adsorbent, m^3; $\mathrm{V_p}$ and $V_{\mathrm{p},0}$, running and initial volumes of the adsorbent micropores, m^3; x, y, and z, dimensions of the undeformed adsorbent, m; $\Delta b/b$ and $\Delta c/c$, relative linear deformations of a micropore in the plane; $\Delta l/l$, relative linear deformation of the adsorbent; $\Delta x/x$, $\Delta y/y$, and $\Delta z/z$, relative linear deformations of the adsorbent along the axes; ΔV, change in the adsorbent volume under deformation, m^3; ΔV_{p}, change in the volume of the adsorbent micropores under deformation, m^3; σ_1, pressure produced by the adsorbed molecules N_1 in a given fragment in interaction with the micropore walls (this pressure is responsible for contraction in localized adsorption; in nonlocalized adsorption, in the region of elevated temperatures, the minus sign of σ_1 should be replaced by the plus sign), Pa; σ_2, pressure produced by the adsorbed molecules N_2 that are not in direct contact with the micropore walls in a given fragment. Subscripts: 0, initial value; cr, crookedness, sinuosity; p, pore.

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