Adsorption deformation in the microporous carbon adsorbent—benzene system and porous structure of adsorbents

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The relative adsorption deformation of several microporous carbon adsorbents was studied as a function of the benzene adsorption at relative pressure ranging from $1 \cdot 10^{-1}$ to 1.0 and at 293 K. A correlation between the maximum compression of the sample and the characteristic energy of benzene adsorption of the Dubinin—Radushkevich equation was obtained. Using data on the adsorption deformation, it is possible to identify the region with a specific pore size that cannot be evaluated with the help of the Dubinin—Radushkevich equation.

Key words: adsorption, adsorption deformation, microporous carbon adsorbent, porosity, characteristic energy, pore size.

The previous studies of adsorption of gases and vapor on active carbons have shown that granules of active carbon are isotropically expanded with extent of adsorption, pressure of the equilibrium phase, and temperature.[1,2] It has been assumed[3—6] that the Gibbs adsorption equation can be applied to describe deformation during adsorption on nonporous or macroporous adsorbents. For nonlocalized adsorption where an adsorbed substance behaves as a dimeric gas, a decrease in the differential free surface energy of the adsorbent—adsorbate system is equal to the surface pressure π which is the integral of the Gibbs adsorption equation:

$$\pi = RT\int_0^p \Gamma \, d(\ln p), \qquad (1)$$

where Γ is the excessive adsorption, p is the equilibrium gas pressure, T is temperature, and R is the universal gas constant. Assuming that the adsorption deformation of the adsorbent is a linear function of the surface pressure π, the expression for the linear deformation of the adsorbent has been obtained[5]:

$$\Delta l/l = \gamma RT\int_0^p \Gamma \, d(\ln p), \qquad (2)$$

where γ is the expansion constant related to the compression modulus of a solid. It follows from Eq. (1) that the surface pressure π is always positive and, hence, the adsorption deformation calculated by Eq. (2) also would always be positive. However, compression regions have been found for adsorption of vapor of organic substances and water on active carbons.[7,8] This behavior of carbon adsorbents is likely associated with the specific features of their porous structure. Adsorption activity of carbon adsorbents is a result of the developed system of micropores,[9,10] whose characteristic sizes are comparable to effective dimensions of the sorbed molecules.[11] According to the data of X-ray small-angle scattering,[12,13] micropores of carbon adsorbents are characterized by an effective size between 0.5 and 1.0 nm. Dimensions of the windows giving access to the interior of zeolites vary in the same interval.[14]

Considering the specific features of the microporous adsorbents, the authors of Refs. 15—18 attempted to develop the phenomenological theory of adsorption that takes into account both compression and expansion of the adsorbent during adsorption. Both the features of the porous structure of adsorbents and specific intermolecular interactions in micropores are significant for the development of the theory of adsorption deformation. Since the theory of volume filling of micropores[10] is widely used for the characterization of the microporous structure of carbon adsorbents, and benzene is used as the standard adsorptive, it seems of interest to use benzene adsorption to consider how the structural and energetic characteristics affect the deformation parameters of adsorbents.

Experimental

Adsorption of benzene vapor and adsorption deformation of microporous carbon adsorbents obtained from various raw materials were studied: ACS is active carbon of silicon carbide; SKT-2B and SKT-7B are active carbons derived from peat by sulfurous-potassium chemical activation; and FAS is active carbon of furfural-based polymer. Adsorption was measured with an accuracy of $\pm 2 \cdot 10^{-2}$ mg with a semiautomatic equipment using a vacuum gravimetric technique. Dilatometric measurements were carried out with an accuracy of $\pm 3 \cdot 10^{-4}$ mm

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on the previously described[19,20] setup. Six specially selected cylindrical granules of an adsorbent 1.6 mm in diameter separated by a distance of 0.5 mm from each other were loaded on the planar bottom of a quartz dilatometric tube (diameter ~12 mm) in one layer so that they filled the whole surface of the tube bottom. The upper surface of the adsorbent granules was covered by a polished plate of quartz glass with a diameter close to the inner diameter of the tube. Thus, at least three monolytic granules of the carbon adsorbent mechanically contacted with the upper plate and, correspondingly, the converter of dilatometer movement. A change in the sizes of active carbon granules during benzene vapor adsorption in experiments was transmitted to the core of an inductive converter of movements to change the electric signal detected in the experiment. All experiments were performed at 293 K. The accuracy of thermostatting was ±0.1 K. Prior to experiments, the adsorbent was outgassed for 8 h at 620 K to a residual pressure of 0.1 Pa.

Results and Discussion

The relative linear adsorption deformation of granules of the carbon adsorbent $\Delta l/l$ as a function of the relative benzene pressure p/p_s are presented in Fig. 1 for all samples of carbon adsorbents indicated above. The data on the ACS—C_6H_6 system were taken from the previously published work.[20] All curves exhibit the same trend. At low pressures, the sample is compressed, then with an increase in the adsorptive pressure the compression is retarded followed by expansion, which is again retarded as the pressure of the saturated benzene vapor is approached. However, some segments are different in shape especially in the vicinity of a maximum. The highest (0.49%) compression is observed for the FAS carbon, whereas SKT-7B is characterized by the lowest compression (0.16%). All curves cross the zero value of $\Delta l/l$ at $p/p_s < 0.25$ and go to the region of positive deformation whose maximum relative values reach 0.4%—0.6% at p/p_s close to 1.

The relative adsorption deformation as a function of the adsorption has a different character. The corresponding curves for the systems under study are presented in Fig. 2, *a*, *b*. As can be seen, filling of the major part of the micropore volume with benzene is accompanied by compression, and it is only in the relatively narrow region of high filling ($\theta > 0.9$) that the compression changes to a sharp expansion. For the SKT-2B carbon, the maximum expansion doubles and, for the SKT-7B carbon, triples the value observed for the maximum compression. For the FAS and ACS carbons, the expansion and compression values are virtually equal.

In the general case, adsorption deformation of microporous carbon adsorbents is a sequence of the combination of the dispersion interaction forces of

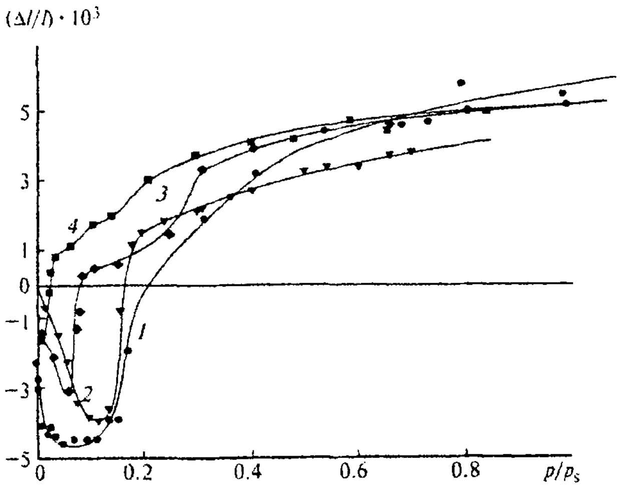

Fig. 1. Relative linear adsorption deformation of microporous carbon adsorbents as a function of the relative pressure of benzene vapor at 293 K: FAS (*1*), ACS (*2*), SKT-2B (*3*), and SKT-7B (*4*).

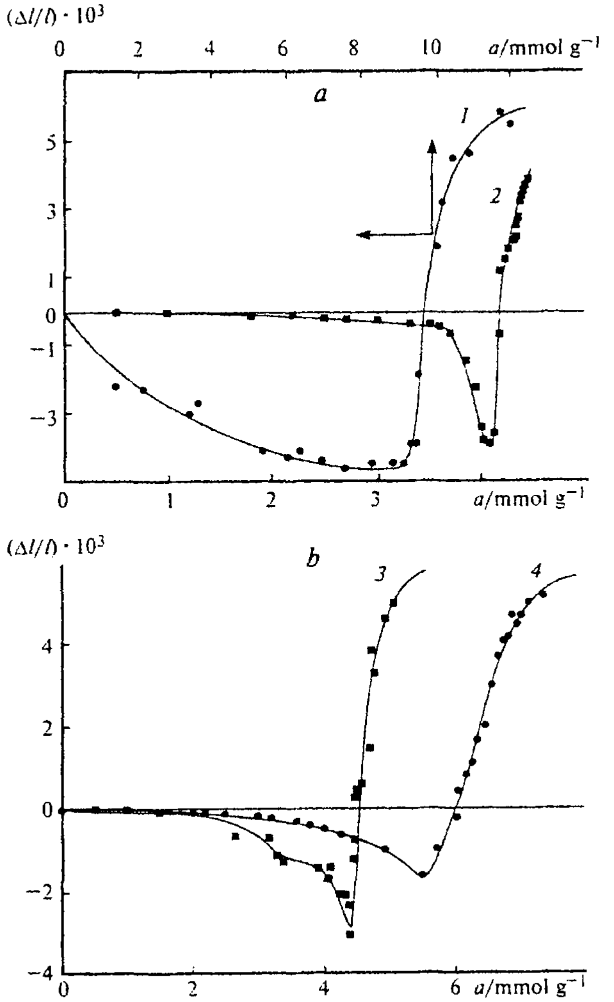

Fig. 2. Relative linear adsorption deformation of microporous carbon adsorbents as a function of the benzene vapor adsorption at 293 K: *a*, FAS (*1*) and ACS (*2*); *b*, SKT-2B (*3*) and SKT-7B (*4*).

Table 1. Parameters of the relative adsorption deformation and porosity of samples

Parameter	FAS	AC of SiC	SKT-2B	SKT-7B
η_{min} (%)	0.49	0.38	0.25	0.16
η_{max} (%)	0.53	0.40	0.52	0.58
θ at $\Delta l/l = 0$	0.91	0.94	0.88	0.90
E_{01}/kJ mol^{-1}	34.5	33.0	30.2	27.1
E_{02}/kJ mol^{-1}	11.5	5.6	4.2	2.6
x_1/nm	0.35	0.36	0.40	0.45
x_2/nm	1.00	2.10	2.90	4.60
W_{01}/cm^3 g^{-1}	0.11	0.36	0.41	0.59
W_{02}/cm^3 g^{-1}	0.83	0.04	0.03	0.03

Note: η_{min} is the minimum compression, η_{max} is the maximum expansion, and θ is the micropore filling.

adsorbed molecules with atoms of the solid and between each other. The contribution of these interactions depends on filling of micropores with adsorbed molecules.[21] At low fillings, interactions of benzene with the opposite walls of micropores of the carbon adsorbent predominate, resulting in the compression of crystallites and granules of the adsorbents. As the micropores are progressively filled, the interactions of the adsorbed molecules between each other and with micropore walls increase, the average distances between the molecules decrease, and the attraction changes to repulsion, resulting in a sharp expansion of the micropores and of the bulk sample. In the point of zero deformation, the attraction and repulsion forces of the molecules with the microporous solid are equal. The characteristic points of the deformation curves and parameters of the porous structure of the carbon adsorbents (SKT-2B, SKT-7B, and ACS) derived from the theory of volume filling of micropores are presented in Table 1.

The isotherms of benzene adsorption in the coordinates of the Dubinin—Radushkevich equation are presented in Fig. 3.

$$a = a_0\exp[-(A/E_0)^2] \tag{3}$$

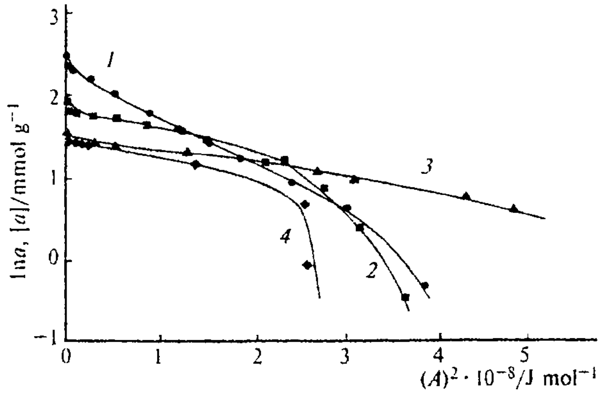

Fig. 3. Adsorption isotherms of benzene vapor on microporous carbon adsorbents at 293 K in the coordinates of the Dubinin—Radushkevich equation (3): FAS (*1*), SKT-7B (*2*), SKT-2B (*3*), and ACS (*4*).

In Eq. (3), a_0 is the limiting adsorption at $p/p_s = 1$, E_0 is the characteristic adsorption energy, and A is the differential molar work of adsorption:

$$A = RT\ln(p_s/p), \tag{4}$$

where p_s is the pressure of saturated benzene vapor.

As follows from Fig. 3, the adsorption isotherms of benzene deviate from linearity in the region of small fillings of micropores. The adsorption isotherms can be described by the binomial Dubinin—Radushkevich equation derived for adsorbents with biporous structure:

$$a = a_{01}\exp[-(A/E_{01})^2] + a_{02}\exp[-(A/E_{02})^2], \tag{5}$$

where a_{01} and a_{02} are the limiting values of benzene adsorption in porous structures 1 and 2, and E_{01} and E_{02} are the corresponding characteristic adsorption energies.

The parameters in Eq. (5) were selected by the gradient descent method. These parameters for the SKT-2B, SKT-7B, and ACS adsorbents are also presented in Table 1. For the FAS adsorbent, we failed to obtain a stable complex of the parameters in Eq. (5). The values for these angles presented in Table 1 were obtained from the correlation between the maximum compression of the adsorbent and the characteristic adsorption energy of benzene. It follows from Table 1 that only for structure 1 do the structural and energetic parameters correspond to standard parameters of adsorption in micropores,[11] for which $E_0 > 13$ kJ mol^{-1} and $x <$ (08—0.9) nm. Therefore, only these parameters of adsorption systems will be further considered.

In the theory of volume filling of micropores, the effective half-width (radius) of micropores (x) is related to the characteristic adsorption energy (E_0) by the equation[22]

$$x = 12/E_0. \tag{6}$$

If the substance is adsorbed on the carbon adsorbent only due to dispersion interactions, the potential energy of interaction can be presented as the sum of the energies of interaction of the molecule with each atom of the solid[23]

$$U(r) = -C\Sigma 1/r_i^6 + B\Sigma 1/r_i^{12}, \tag{7}$$

where C is the dispersion attraction constant, B is the repulsion constant, and r is the distance between the adsorbate molecule and adsorbent atom. In contrast to the interactions on the open surface, *i.e.*, on nonporous solids, the adsorption interactions extend over the whole volume of the microporous solid and include interactions with atoms of the opposite walls of micropores. The interactions of adsorbed molecules with atoms of the opposite walls of micropores would result in the compression of the adsorbent, which is observed in our experiments when the micropore volume is gradually filled. At the point of maximum compression, most likely, the energy of attraction of the adsorbate molecules by the opposite walls of micropores considerably exceeds the repulsion energy. The repulsion energy can be neglected in the expression for the potential energy of interaction $U(r)$ and, therefore, for the point of maximum compression we have

$$U(r) = -C\Sigma 1/r_i^6. \qquad (8)$$

Therefore, the total force leading to the deformation is the following:

$$F = -\mathrm{d}U(r)/\mathrm{d}r, \qquad (9)$$

and it follows from Eq. (8) that

$$F = D'\cdot\Sigma 1/r^7, \qquad (10)$$

where D' is constant. Let us consider that in the initial region of filling of the micropore volume, the effective half-width of micropores x can be adapted in the first approximation as the average distance from the center of gravity of the adsorbed molecule to the pore walls r. Then taking into account Eq. (6), for the average force of maximum adsorption compression, we obtain

$$\bar{F} = DE_0^7, \qquad (11)$$

where D is constant. Since the adsorption deformation of the adsorbents under study is low and reversible, the maximum deformation of the solid is proportional to the maximum average active force in the limits of fulfillment of Hooke's law

$$|\Delta l/l|_{\max} = kE_0^7, \qquad (12)$$

where k is a constant related to the compression modulus of the microporous adsorbent—benzene system.

Generally, k depends, for various adsorbents, on the specific micropore volume, the number of micropores in the bulk of adsorbent granules, and the compression modulus of the framework-forming carbon material. According to some estimations,[24] the number of micropores in 1 g of various microporous carbon adsorbents is approximately constant and amounts to $\sim 10^{20}$. The resistance of the granules towards attrition of the adsorbents under study is 85—99%. These parameters of carbon adsorbents allow k to be considered as a constant value for the adsorbents under study.

Thus, it follows from Eq. (12) that the maximum value of compression of the microporous carbon adsorbent is proportional, in the first approximation, to E_0^7. This function for the adsorption systems under study is presented in Fig. 4, suggesting that the SKT-7B, SKT-2B, and ACS—benzene adsorption systems exhibit, in a good approximation, a linear relationship between the maximum relative adsorption compression of the adsorbent and characteristic adsorption energy (to the 7th power). The function obtained was used as the first approximation for the selection of the parameters in Eq. (5) for the FAS—benzene system.

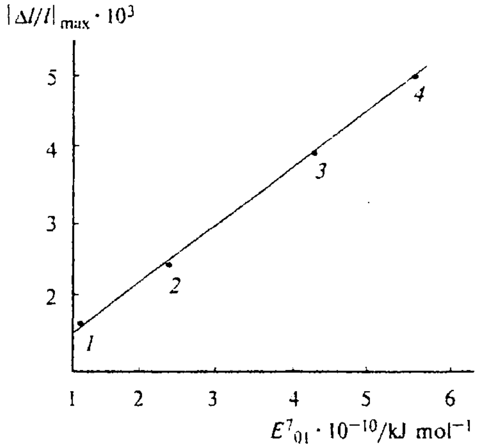

Fig. 4. Maximum relative compression of microporous carbon adsorbents as a function of the characteristic energy of benzene vapor adsorption (E_{01}/kJ mol^{-1}): SKT-7B (*1*), SKT-2B (*2*), ACS (*3*), and FAS (*4*).

The refined parameters of the biporous structure of FAS are presented in Table 1. Comparison of two porous structures presented for the FAS adsorbent in Table 1 shows that the large pore volume of porous subsystem 2 (W_{02} = 0.83 cm^3 g^{-1}) disguises porous subsystem 1 (W_{01} = 0.11 cm^3 g^{-1}) and substantially changes the characteristic adsorption energy. However, Eq. (12) shows that the maximum deformation effects occur due to adsorption in porous subsystem 1, whose effective half-width of micropores is 0.35 nm. It follows from Table 1 that porous subsystem 2 of FAS has parameters close to the upper limit of values characteristic of supermicropores.[22] Since the dispersion attraction forces (10) sharply decrease with an increase in the effective half-width of micropores x, the contribution of porous subsystem 2 to the adsorption deformation can be neglected. Point *4* in Fig. 4 was obtained for subsystem 1 by calculations performed using Eq. (5) taking into account function (12). The parameters found for the microporous structure of the FAS carbon adsorbent confirm the linear relationship between the maximum adsorption compression of carbon adsorbents and characteristic energy of benzene adsorption to the 7th power (Eq. (12)).

Thus, based on the data on adsorption and adsorption deformation of the systems "microporous carbon adsorbents—benzene" at T = 293 K, we were able to obtain the correlation between the maximum adsorption compression of the adsorbent $|\Delta l/l|_{\max}$ and characteristic energy E_0 of benzene adsorption. It was shown for the adsorption system FAS—benzene that using dilatometric data one can examine in great detail the carbon adsorbent structure and find in it subsystems with pore sizes that lie outside the applicability of the Dubinin—Radushkevich isotherm.

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