## Adsorption-stimulated deformation of microporous carbon adsorbent

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Deformation of the ACC microporous carbon adsorbent during adsorption of carbon dioxide, nitrogen, and argon in the temperature interval from 243 to 393 K and at pressures of  $1-5 \cdot 10^6$  Pa was studied. The effect of adsorbent contraction was found in the initial temperature interval at relatively low pressures. However, the negative value of relative linear deformation  $\Delta L/L$  smoothly transforms into positive values with the pressure increase. Only the effect of adsorbent expansion is observed at high temperatures in the whole pressure interval. The dependence of the deformation effects for different systems on the adsorbent nature was revealed.

**Key words:** adsorption, active carbon, adsorption deformation, carbon dioxide, nitrogen, argon, high pressures.

Studying adsorption of gases and vapors, researchers usually imply that the solid is inert.<sup>1</sup> This assumption is valid for adsorbents with a relatively small specific surface and is inappropriate for microporous adsorbents with nearly all atoms involved in the adsorption interaction.<sup>2</sup>

Noninertness of an adsorbent is reflected primarily in the behavior of thermodynamic functions of the adsorption system, such as isosteric heat of adsorption, entropy, and heat capacity. The studies in wide temperature and pressure intervals show that for the correct calculation of the thermodynamic characteristics of the system the adsorption deformation of the adsorbent should be considered.<sup>3</sup>

For adsorption on microporous adsorbents, the isosteric heat of adsorption  $q_{st}$  is determined by the equation<sup>4</sup>

$$q_{\rm st} = -RZ \left(\frac{\partial \ln P}{\partial l/T}\right)_a \left[1 - \left(\frac{\partial v(a)}{\partial a}\right)_T / v_g\right] - \left(\frac{\partial P}{\partial a}\right)_T \left[v(a) - T \left(\frac{\partial v(a)}{\partial T}\right)_a\right],$$
(1)

where  $Z = Pv_g/(RT)$  is the compressibility coefficient of the gas phase at the pressure *P*, specific volume  $v_g$ , and temperature *T*;  $v(a) = V_1/m_0$  is the specific reduced volume of the adsorbent—adsorbate adsorption system;  $V_1$  is the volume of adsorbent—adsorbate system;  $m_0$  is the weight of the degassed adsorbent; *a* is the adsorption value defined as the full content; *R* is the universal gas constant.

It follows from Eq. (1) that noninertness of the adsorbent during adsorption can be mechanical, thermal, and energetic. The mechanical character of noninertness appears in a change in the adsorbent sizes during adsorption. To take into account the mechanical noninertness of the adsorbent, the terms  $(\partial v(a)/\partial a)_T$  and v(a) reflecting a change in the adsorbent volume during adsorption were introduced into the equation for the heat of adsorption. The thermal noninertness is determined by a change in the adsorbent volume with temperature under the isosteric conditions  $(\partial v(a)/\partial T)_a$ . The energetic noninertness of the adsorbent is a consequence of a possible change in the gradients and intensity of the sorption field in microporous, related to local changes in the adsorption field and induced, for example, by a high-energy specific interaction. This noninertness is accounted for by the terms  $(\partial \ln P/(\partial 1/T))_a$  and  $(\partial P/\partial a)_T$ .

When real microporous adsorbents containing micro-, meso-, and macropores are involved, adsorption in micropores is accompanied by capillary condensation in mesopores and layer-by-layer filling of the macropore surface. Adsorption and deformation on the ACC microporous carbon adsorbent are of special interest because this adsorbent contains no mesopores and its macropore surface is small. The correct calculation of the thermodynamic characteristics of the adsorption system needs experimental data on adsorption deformation in the whole region of temperatures and pressures, especially at high pressures where the deformation makes the greatest con-

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tribution to the thermodynamic characteristics of the system.

The phenomenon of adsorption deformation was described in several works.<sup>5,7–11</sup> However, the region of studied pressures and temperatures still remains insufficiently wide for determination of general regularities of this phenomenon. The purpose of this work is to obtain experimental data on the adsorption deformation on the ACC microporous carbon adsorbent in wide intervals of pressures and temperatures. Adsorption was studied for  $CO_2$ ,  $N_2$ , and Ar, which possess different physicochemical properties, in particular, different polarizabilities (Table 1), determining the energy of adsorption interaction.

## **Experimental**

A model sample of the ACC microporous carbon sorbent was prepared from silicon carbide at 900 K by removing silicon with a chlorine flow followed by gaseous  $SiCl_4$  evolution.

A monolithic cylindrical sample with a length of 54.1 mm and a diameter of 11.4 mm was used. Before measurements, the adsorbent was evacuated for 6 h at 620 K to a residual pressure of 0.8 Pa.

To determine the characteristics of the microporous structure, data on benzene adsorption at 293 K were processed on the basis of the theory of volume micropore filling.<sup>12</sup> The following characteristics of the adsorbent sample were obtained: micropore volume  $W_0 = 0.47$  cm<sup>3</sup> g<sup>-1</sup>, characteristic energy of adsorption  $E_0 = 30$  kJ mol<sup>-1</sup>, and characteristic micropore half-width  $x_0 = 0.4$  nm. An inductive-type dilatometer designed for measuring small deformations of solids during adsorption in pressure and temperature intervals of  $1-2 \cdot 10^7$  Pa and 77-570 K, respectively, was used. The scheme of the dilatometer is shown in Fig. 1: the core (5) of the induction converter (6) of linear displacements is connected with the rod (4) supported on the quartz plate (2), which is placed on the sample (1). The latter is placed inside the ampule (3) between the quartz disks (2). The ampule is connected to the dilatometer body through the

**Table 1.** Relative deformation of the ACC adsorbent induced by the adsorption of gases with different physicochemical parameters

Gas	$ \eta _{\max}^{a}$ %	$\eta_{max}^{\ \ b}$	Size of molecule <sup>c</sup> /Å	$(\alpha \cdot 10^{30})^d$ /m <sup>3</sup>
CO <sub>2</sub>	0.117 <sup>e</sup>	0.6 <sup>e</sup>	5.1/3.7	2.594
N <sub>2</sub> Ar	$0.04 \ ^{e}$ $0.02 \ ^{e}$	$0.12^{J}$ $0.12^{e}$	4.1/3.0 3.84	1.734 1.626

<sup>a</sup> Maximum contraction.

<sup>b</sup> Maximum expansion.

<sup>c</sup> The nominator and denominator contain the length and width, respectively.

<sup>d</sup> Polarizability.

<sup>e</sup> At 243 K.

<sup>f</sup> At 393 K.



**Fig. 1.** Scheme of dilatometer for measuring the adsorption deformation of solids: *1*, adsorbent; *2*, quartz polished disks; *3*, ampule; *4*, rod; *5*, core; *6*, differential transformer; *7*, tube; *8*, vacuum valve; and *9*, screw.

screw (9). A change in the sample length results in the displacement of the core, which is detected by a V7-38 digital voltmeter using a transformer. The dilatometer is connected to a high-pressure adsorption installation through the tube (7) and vacuum valve (8).<sup>13</sup>

During experiments, the temperature in the dilatometer section containing the sample was maintained constant with an error of  $\pm 0.2$  K. The rest volume of the dilatometer along with the induction converter and the high-pressure installation were thermostatted in an air thermostat at 303 K.

The induction converter of displacements of the dilatometer was calibrated at 303 K using a set of standard plates with a thickness of 0.01-1.00 mm. The dilatometer was adjusted to changes in temperature and gas pressure on a "model" of fused quartz analogous to the adsorbent sample in shape and sizes.

Adsorption of CO<sub>2</sub> was studied using a gravimetric vacuum adsorption installation with the electronic compensation of the weight change in three intervals with limits of 1, 10, and 100 mg. The error of measurement did not exceed 1%. The gas pressure was determined by two M10 and M1000 pressure bellows gauges with measurement intervals of  $1-1\cdot10^3$  and  $10-1.5\cdot10^5$  Pa and errors of  $\pm 0.1$  and  $\pm 1.0$  Pa, respectively.

Gases of special and high purity were used. The volume fraction of  $CO_2$ ,  $N_2$ , and Ar in these gases was at least 99.95, 99.9963, and 99.998%, respectively.

## **Results and Discussion**

The plots of the relative linear deformation of the ACC carbon adsorbent vs. relative pressure of CO<sub>2</sub> at temperatures from 243 to 393 K are presented in Fig. 2. As follows from the data in Fig. 2, in the region of low temperatures (T < 313 K) and initial region of equilibrium pressures (P < 0.25 MPa) the contraction of the sample achieves the value of 0.12% at 243 K. At higher



**Fig. 2.** Relative linear deformation of the ACC microporous carbon adsorbent as a function of the pressure during  $CO_2$  adsorption at temperatures: 243 (1), 293 (2), 313 (3), and 393 K (4).

pressures, the contraction is changed by expansion. At higher temperatures of the studied interval (T > 313 K), the expansion was the only result of the pressure increase. However, with the temperature increase the effect of relative expansion decreases from 0.6% at 293 K to 0.25% at 393 K. The plots of the relative linear deformation of ACC vs. pressure at different temperatures show an inversion, that is, different sequence of curves at initial and final pressures. As follows from the data in Fig. 2, for CO<sub>2</sub> the inversion region lies approximately in an interval of 0.3–0.5 MPa.

The character of the dependence of the relative linear deformation under the isothermic conditions is caused, to a great extent, by the behavior of the adsorption isotherms. The isotherms of adsorption of  $CO_2$  on the ACC microporous carbon adsorbent are presented in the a-P coordinates in a pressure interval of  $1-6 \cdot 10^6$  Pa and at temperatures from 243 to 393 K in Fig. 3. Adsorption at



**Fig. 3.** Isotherms of  $CO_2$  adsorption on the ACC microporous carbon adsorbent at temperatures: 243 (1), 293 (2), 313 (3), and 393 K (4).

pressures higher than 0.15 MPa was calculated using the linearity of adsorption isosteres. The adsorption isotherms are reversible and characterized by convexity toward the pressure axis. With the pressure increase the adsorption tends to the constant  $a_0$ , which is the limiting adsorption value. It follows from similarity of the deformation (see Fig. 2) and adsorption (see Fig. 3) curves that at high pressures the adsorption in micropores makes the main contribution to the deformation effect. Like the amount adsorbed, the relative linear deformation of the microporous carbon sorbent increases more slowly with the pressure increase.

The results of studying the adsorption deformation of the ACC adsorbent during nitrogen adsorption are presented in Fig. 4. They correspond in many aspects to the results for the ACC-CO<sub>2</sub> system. In the region of relatively low pressures at 243 and 293 K, the contraction to 0.046% is observed at 243 K, which then changes by the expansion to 0.08% at a pressure of 4.5 MPa. The maximum deformations upon contraction and expansion are much smaller than those observed for the adsorption of  $CO_2$ . When comparing the ACC-CO<sub>2</sub> and ACC-N<sub>2</sub> systems, one should mention differences in the shape of the curves along with the changes in the maximum values of deformation. For nitrogen adsorption at pressures higher than 1 MPa, the plots are almost linear, whereas for  $CO_2$ adsorption nonlinearity is observed in the entire pressure interval. It is of interest that the inversion of adsorption deformation for the ACC-N2 system (see Fig. 4) is shifted toward high pressures. Its properties (intersection of curves) can probably appear at pressures higher than 5 MPa.



Fig. 4. Relative linear deformation of the ACC microporous carbon adsorbent as a function of the pressure during  $N_2$  adsorption at temperatures: 243 (1), 293 (2), 313 (3), and 393 K (4).



**Fig. 5.** Relative linear deformation of the ACC microporous carbon adsorbent as a function of the pressure during Ar adsorption at temperatures: 243 (*1*), 293 (*2*), 313 (*3*), and 393 K (*4*).

The smallest deformation effects of the ACC microporous carbon adsorbent were found for Ar adsorption. The plots of the adsorption deformation of ACC during Ar adsorption at temperatures from 243 to 393 K and in the pressure interval from  $1 \cdot 10^2$  to  $5 \cdot 10^6$  Pa are presented in Fig. 5. As follows from the data in Fig. 5, in the low-temperature region (243-293 K) at pressures of 0.4-0.8 MPa, as for CO<sub>2</sub> and N<sub>2</sub> adsorption, the adsorbent contraction is observed reaching 0.02% at 243 K and going to the expansion region with the pressure increase. The maximum expansion achieves the value of 0.12% at 243 K. Only adsorbent expansion is observed at high temperatures (313-393 K) in the whole interval of measured pressures. The region of inversion temperatures of the deformation curves for this system is well pronounced and lies at 1.5-2.0 MPa.

The limiting deformation effects of expansion and contraction for the adsorption systems under study and some physical characteristics of the gases are presented in Table 1.

It follows from the data presented in Table 1 that an increase in the polarizability of gases increases the maximum contraction of the sample at the lowest temperature (243 K). The maximum expansion depends to a less extent on the polarizability of gases. The maximum expansion values for the CO<sub>2</sub>—ACC and Ar—ACC systems were obtained at 243 K. The maximum  $\eta_{max}$  value for the N<sub>2</sub>—ACC system was obtained at 393 K (at 243 K the maximum expansion  $\eta_{max}$  is 0.082%). For the first two systems, the inversion of curves occurs, while for the N<sub>2</sub>—ACC system the inversion will presumably occur at higher pressures, which are beyond the experiment de-

scribed. The dimensions of molecules<sup>14</sup> presented in Table 1 are comparable with the adsorbent pore sizes. Therefore, the initial contraction of the adsorbent is a sequence of the interaction of adsorbed molecules with the opposite micropore walls. This effect is observed for relatively low temperatures. However, as the pressure increases the amount adsorbed molecules decreases, the mean distance between the adsorbed molecules decreases, and repulsion forces increase. This results in an increase in the internal pressure tending to stretch the adsorbent as observed in the experiment.

The curves of adsorption deformation at high temperatures behave in a different manner. In this region for all systems under study, the adsorption deformation is positive in the whole pressure interval. These differences in the behavior of the adsorption deformation curves of the ACC microporous adsorbent can be related to a change in the adsorption mechanism: as the temperature increases, the transition from the partially localized adsorption to the delocalized one occurs.

The adsorption deformation of the adsorbent exerts a substantial effect on the calculation of the isosteric heat of adsorption. According to our results, at pressures higher than 4–5 MPa, corrections to the isosteric heat of adsorption can reach 10–15% and more of the initial value. This influence of the adsorption deformation is due to its sharp increase at high pressures and, correspondingly, to the approach of the  $(\partial v(a)/\partial a)_T$  derivative to the specific volume for the gas phase  $v_g$ . Taking into account the adsorption deformation of the adsorbent, corrections to the work of the adsorbent contraction (expansion) should be introduced in measurements of the differential calorimetric heat of adsorption.

Thus, the deformation of the ACC microporous carbon adsorbent was studied in temperature and pressure intervals of 243-393 K and 1-5.10<sup>6</sup> Pa, respectively, during adsorption of CO<sub>2</sub>, N<sub>2</sub>, and Ar. The differences were revealed for the extent of deformation effects for different systems depending on the adsorbate nature. In the general case, the adsorption deformation is a sequence of the summation of the forces of adsorbate-adsorbate and adsorbate-adsorbent interactions. At small fillings in the region of low temperatures, attraction forces of the gas by the opposite walls of the adsorbent micropore are predominantly manifested. They result in the contraction of the sample in the initial region. The distance between the molecules decreases with an increase in the micropore filling, and attraction is replaced by repulsion to expand the micropores and the sample on the whole.

The greatest deformation effects are characteristic of adsorption of gases with the highest polarizability. At high temperatures (T > 313 K) for all systems, the adsorption deformation is positive in the whole interval of pressures studied.

The temperature inversion of the deformation curves, which is specifically manifested for each of the systems studied, was found.

Allowance for adsorption deformation needs introduction of corrections in the isosteric heat of adsorption, which are 10-15% in the region of high pressures.

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