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# Physical Chemistry

## Adsorption of carbon dioxide on microporous carbon adsorbent PAU-10

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Carbon dioxide adsorption on the microporous carbon adsorbent PAU-10 within the 177.8—423 K temperature and $0.1—5.13 \cdot 10^6$ Pa pressure intervals was studied. The isosteres of absolute adsorption are well approximated by straight lines, which do not change their slope on going to temperatures higher than the critical temperature of $CO_2$. An increase in the differential molar isosteric heat of adsorption ($q_{st}$) at $0 < a < 1$ mmol g$^{-1}$ is explained by the influence of the endothermic effect of adsorption expansion of the adsorbent. In the region of high pressures and nonideal gas phase, $q_{st}$ is temperature-dependent.

**Key words:** adsorption, microporous carbon adsorbent, high pressures, carbon dioxide, adsorption heat, noninertness of adsorbent.

Adsorption on real microporous adsorbents containing micro-, meso-, and macropores is characterized by simultaneous capillary condensation and layer-by-layer coverage of the macropore surface along with adsorption in micropores.[1—4] For these adsorbents, it is difficult to distinguish the contribution of adsorption in micropores against the background of adsorption and capillary condensation in meso- and macropores.[5]

This work is aimed at studying of $CO_2$ adsorption on the microporous carbon adsorbent PAU-10 in a wide interval of parameters of adsorption equilibrium at temperatures higher and lower than the critical temperature. The study of adsorption on the PAU-10 adsorbent is of interest because it has no mesopores and the micropore surface is low.

### Experimental

$CO_2$ adsorption was studied on two setups. At pressures <150 kPa we used a gravimetric adsorption unit with electronic compensation of the mass change over three intervals with limits of 1, 10, and 100 mg, respectively. The error of adsorption measurement did not exceed 1%. The gas pressure was determined by two M10 and M1000 bellow pressure gauges with measurement intervals of $1—1 \cdot 10^3$ and $10—1.5 \cdot 10^5$ Pa and errors of 0.1 and 1 Pa, respectively. At pressures >150 kPa, adsorption was determined by the volumetric method.[6] The pressure of $CO_2$ was measured by an MP-60 (class 0.01) pressure gauge. The temperature of the adsorbent was set and maintained by liquid and electric thermostats with an error of 0.2 K and using temperature maintaning at the melting points of acetone (177.8 K), *n*-octane (216.4 K), and *n*-decane (243.5 K).[7]

Gaseous $CO_2$ was used in experiments. After purification by rectification and adsorption, the content of admixtures in the gas did not exceed 0.01%. The $p,v,T$ data were used in calculation of adsorption.[8] The structure of the microporous carbon adsorbent PAU-10 obtained from polyvinylidene chloride by activation at 970 K does not virtually contain mesopores and only few macropores. Before experiments the adsorbent was degassed *in vacuo* at 620 K and 0.01 Pa for 5 h to a constant weight. At 298 K the adsorption isotherms of benzene and *n*-pentane had no hysteresis loop and characteristic rise up to pressures close to the pressure of saturated vapor ($p_s$). This

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indicates the absence of meso- and macropores in the adsorbent. Processing of the data on benzene adsorption using the Dubinin—Radushkevich equation[9] gave the following parameters of the porous structure: micropore volume $W_0$ = 0.41 cm$^3$ g$^{-1}$, characteristic energy of benzene adsorption $E_0$ = 27.4 kJ mol$^{-1}$, and characteristic half-width of micropores for the "slit-like" model $x_0$ = 0.44 nm. The density of the adsorbent with micropores measured using the method of "helium-liquid picnometry" [10] was equal to 1.125 g cm$^{-3}$. This value was used for calculations of adsorption because it determines the absolute content of $CO_2$ in micropores.

## Results and Discussion

We have previously[11,12] studied the regularities of adsorption of nonpolar gases (methane and xenon) on the microporous carbon adsorbent PAU-10 in wide pressure ($p$) and temperature ($T$) intervals, which covered the sub- and supercritical regions of states of the equilibrium gas phase. These adsorption systems are characterized by linearity of adsorption isosteres within the whole studied pressure (0.1—20 · 10$^6$ Pa) and temperature (120—600 K) intervals. The isosteres of xenon and methane adsorption do not change their slope on going through the critical temperature of the gas phase both in the low-pressure region and at pressures lower and higher than the critical pressure.

Let us consider the data on $CO_2$ adsorption, which possesses a high linear quadrupole moment (4.1 · 10$^{-26}$ e.s.u.[13]). The isotherms of $CO_2$ adsorption on the microporous carbon adsorbent PAU-10 within the pressure interval of 1.0—5.13 · 10$^6$ Pa and at temperatures from 177.8 to 423 K are presented in Fig. 1 in the $a$ and ln$p$ coordinates. The adsorption isotherms are reversible and have an inflection point in the region of medium coverage. In the $a$—$p$ coordinates, the adsorption isotherms have no inflection point and are convex toward the pressure axis. At 177.8 K and 1 Pa, the adsorption equilibrium was established for ~5 h. The adsorption isosteres presented in Fig. 2 were plotted using the adsorption isotherms. It is seen that the adsorption isosteres are well approximated by linear plots in the whole region of measured pressures and temperatures. Linearity of the isosteres is not violated on going through the critical temperature of $CO_2$ ($T_{cr}$ = 304.19 K). The slope of the isosteres depends on the filling of the micropore volume of PAU-10.

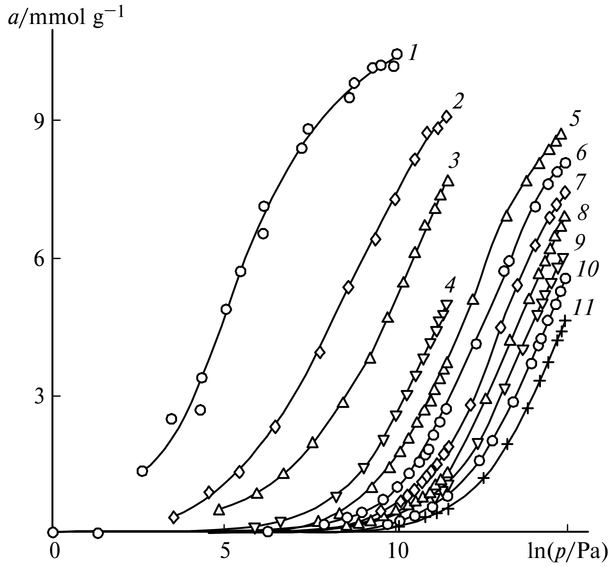

**Fig. 1.** Isotherms of $CO_2$ adsorption on the microporous carbon adsorbent PAU-10 at 177.8 (*1*), 216.4 (*2*), 243.5 (*3*), 273.1 (*4*), 293 (*5*), 313 (*6*), 333 (*7*), 353 (*8*), 373 (*9*), 393 (*10*), and 423 K (*11*).

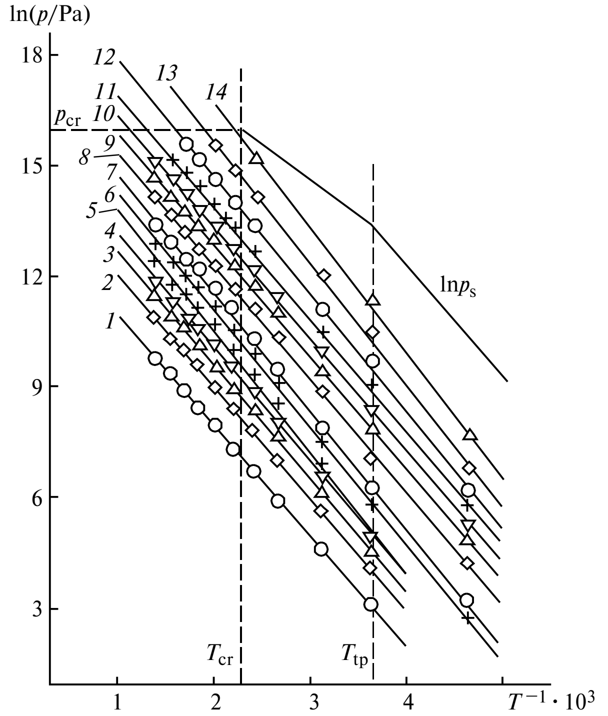

**Fig. 2.** Isosteres of $CO_2$ adsorption on the microporous carbon adsorbent PAU-10 at $a$ = 0.1 (*1*), 0.3 (*2*), 0.5 (*3*), 0.7 (*4*), 1.5 (*5*), 2.0 (*6*), 3.0 (*7*), 4.0 (*8*), 5.0 (*9*), 6.0 (*10*), 7.0 (*11*), 8.0 (*12*), 8.5 (*13*), and 9.2 mmol g$^{-1}$ (*14*). Designations: $T_{cr}$ is the critical temperature, $T_{tp}$ is the temperature of the triple point.

The data obtained allow the calculation of the differential molar isosteric heat of adsorption ($q_{st}$), which is defined as a difference between the molar enthalpy of the equilibrium gas $h_g$ and differential molar enthalpy of the adsorbent—adsorbate system $(dH_l/da)_T$

$$q_{st} = h_g - (dH_l/da)_T. \qquad (1)$$

Taking into account the nonideality of the gas phase and adsorption and temperature noninertness of the adsorbent, we can write the equation for calculation of $q_{st}$ in the following form[14]:

$$q_{st} = -Rz[d(\ln p)/dT^{-1}]_a[1 - (dv_l/da)_T/v_g] - (dp/da)_T[v_l - T(dv_l/dT)_a], \qquad (2)$$

where $z = pv_g/RT$ is the compressibility factor of the gas phase, $v_g$ is the molar volume of the equilibrium gas, $R$ is the universal gas constant, $v_1(a,T) = V_1(a,T)/m_0$ is the specific volume of the adsorbent—adsorbate adsorption system, and $m_0$ is the weight of the degassed adsorbent. In our case and for all microporous adsorbents, $V_1(a,T)$ is the volume of the microporous solid along with micropores, which depends on the $a,p,T$ parameters of adsorption equilibrium.

It follows from Eq. (2) that the heat of adsorption depends on the $a,p,T$ parameters of the adsorption system, deformation of the system (adsorption $(dv_1/da)_T$, thermal $(dv_1/dT)_a$), and the properties of the equilibrium gas phase $(z,v_g)$. The estimations of the maximum values of the $(dv_1/da)_T$ and $(dv_1/dT)_a$ derivatives using the published data[12,15] showed that in the studied pressure and temperature interval $(dv_1/da)_T \ll v_g$, $T(dv_1/dT)_a (dp/da)_T \ll v_1(dp/da)_T$. Since, under these conditions, the correction itself is $v_1(dp/da)_T < 0.1$ kJ mol$^{-1}$, which does not exceed the error of determination of the heat of adsorption (~0.1 kJ mol$^{-1}$), $q_{st}$ was calculated using the following equation

$$q_{st} = -Rz[d(\ln p)/dT^{-1}{}_a. \qquad (3)$$

The plots of the differential molar isosteric heat of adsorption of $CO_2$ on PAU-10 *vs.* coverage calculated using Eq. (3) at different temperatures are presented in Fig. 3. It is seen that at low temperatures, in the region of the ideal gas state ($T$ = 177.9 K) and low coverage, the $q_{st}$ value increases from 26.3 to 29.4 kJ mol$^{-1}$, passes through a maximum at $a$ = 1.0 mmol g$^{-1}$, and then decreases smoothly. In the coverage interval $3.5 < a < 7.0$ mmol g$^{-1}$, the heat of adsorption remains virtually unchanged (~25 kJ mol$^{-1}$) and then increases smoothly to 27.0 kJ mol$^{-1}$ at $a$ = 9.5 mmol g$^{-1}$. In the region of high pressures where the gas phase becomes nonideal and $z < 1$, the temperature dependence of the heat of adsorption begins to appear. In particular, at $T$ = 290 K, $p = 3 \cdot 10^6$ Pa, the compressibility factor of the gas phase $z$ decreases to 0.82, and the correction for the heat of adsorption is ~20%. At higher pressures, this correction can reach[16] 70%. The fan of curves of the differential heat of adsorption shown in Fig. 3 for various temperatures at high pressures was obtained taking into account the properties of $CO_2$ in the region of the nonideal gas phase.

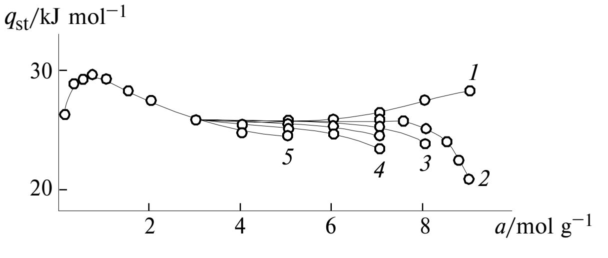

**Fig. 3.** Differential molar isosteric heat of adsorption of $CO_2$ on the microporous carbon adsorption PAU-10 as a function of adsorption at 177.8 (*1*), 293 (*2*), 313 (*3*), 353 (*4*), and 423 K (*5*).

The constancy of differential molar isosteric heat of adsorption of $CO_2$ on PAU-10 at $3.0 < a < 7.0$ mmol g$^{-1}$, *i.e.*, in the region of the ideal gas state, confirms the conclusion[11,17] about the uniform distribution of micropores in the PAU-10 adsorbent. Uniformity of the adsorbent, in the given case, appears as that minor distinctions in the energy of adsorption sites arranged in micropores do not affect the intensity of adsorbate—adsorbate interactions, which result in an increase in the heat of adsorption of the system.[14] The increase in the differential molar isosteric heat of adsorption of $CO_2$ on PAU-10 at $T$ = 177.8 K and $a > 7.0$ mmol g$^{-1}$ is likely related to a predominant increase in the energy of intermolecular interaction between the adsorbed $CO_2$ molecules. The further increase in coverage decreases sharply the average distance between the molecules in the adsorbate and enhances the repulsion forces between both the adsorbed molecules and micropore walls. The energy of $CO_2$ adsorption decreases sharply because new molecules have to sorb on still weaker adsorption sites. The adsorbent expands, and the differential molar heat of adsorption decreases.[18]

Let us consider reasons for an increase in $q_{st}$ in the initial region of micropore coverage at $a < 1.0$ mmol g$^{-1}$. In this region of micropore coverage, the heat of adsorption usually decreases after the sites with the maximum adsorption energy are filled. The adsorbent is considered to remain inert during adsorption. The observed increase in the differential molar isosteric heat of adsorption of $CO_2$ on the microporous carbon adsorbent PAU-10 suggests that, in this case, the adsorbent is not inert. The increase in the heat of $CO_2$ adsorption observed previously[19] for the initial region of micropore volume coverage in zeolite NaX was explained by the endothermic contribution of the energy of zeolite crystalline lattice expansion during the interaction of the $CO_2$ molecules with the $Na^+$ cations in zeolite cavities.

A minor amount of Cl and H atoms linked to the carbon framework remains in the PAU-10 carbon adsorbent upon its synthesis from polyvinylidene chloride at 970 K.[20] These atoms, probably, bear partially uncompensated charges, which at high temperatures favor the formation of HCl molecules evolved during polyvinylidene chloride pyrolysis.

The specific interaction of the $CO_2$ molecules with these atoms in micropores and with the $Na^+$ cations in zeolite NaX results in the expansion of the carbon adsorbent[15] and, correspondingly, the appearance of an additional endothermic contribution to the heat of adsorption. It is known that micropores in active carbons are formed due to burning out of hexagonal layers in carbon crystallites.[21] Probably, after the synthesis of the active carbon, the Cl and H atoms from the starting polymer remain and are localized on the micropore surface. We may attempt to estimate the average number of specific adsorption sites per micropore. The maximum in the curve of the heat of adsorption at $a$ = 1.0 mmol g$^{-1}$ corresponds probably to the limiting number of such adsorption sites in 1 g of adsorbent. Accepting that 1 g of the PAU-10 active carbon contains ~$10^{20}$ micropores,**[21]** for the maximum adsorption of $CO_2$ of ~10 mmol $g^{-1}$ the number of these sites per micropore does not exceed, on the average, 10% of the maximum $CO_2$ adsorption, which is close to previous estimations.**[20]**

Thus, the isosteres of $CO_2$ adsorption on the PAU-10 microporous carbon adsorbent are linear within the intervals of pressures from 0.1 to $5.13 \cdot 10^6$ Pa and temperatures from 177.8 to 423 K, and the increase in the differential molar isosteric heat of adsorption in the initial region of micropore coverage indicates that the adsorbent is noninert during adsorption.

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