Adsorption of perfluoropropane on the PAC microporous carbon adsorbent

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The adsorption of perfluoropropane (C_3F_8) on the PAC microporous carbon adsorbent, which is close in properties to monoporous adsorbents, was studied at temperatures of 216, 243, 295, 318, and 343 K in the pressure interval from 1 to $1 \cdot 10^5$ Pa. The adsorption isosters are well approximated by straight lines in the studied interval of temperatures and pressures. The dependence of the isosteric heats of adsorption on filling is described by a curve with a maximum in the region of high fillings. Such a curve is characteristic of adsorbents with a narrow pore size distribution.

Key words: adsorption, perfluoropropane, carbon adsorbent, isosters, heats of adsorption, porous structures.

Carbon adsorbents are characterized, as a rule, by a fairly broad pore size distribution. According to the known classification,[1,2] pores are grouped to micropores (r < 0.6—0.7 nm), supermicropores (0.6—0.7 nm < r < < 1.5—1.6 nm), mesopores (1.5—1.6 < r < 100—200 nm), and macropores (r > 100—200 nm). Here r is the equivalent pore radius, defined as the ratio of the double cross section area of the pore to its perimeter. The structural and energy heterogeneity of carbon adsorbents is manifested, in particular, in a diminution in the differential heats of adsorption with the filling of the micropore volume and adsorbent surface.

At high pore fillings the differential heats of adsorption of nonpolar gases and vapors on microporous adsorbents with a narrow pore size distribution first increase and then pass through a maximum. In particular, according to the data on methane and CO_2 adsorption on the PAC-10 carbon adsorbent, such dependences are characteristic of active carbons obtained from polyvinylidene chloride.[3,4] It seems of interest to understand whether these features depend on the adsorbate nature. In this work, perfluoropropane characterized by dispersion interactions with the surface of carbon sorbents was used as the adsorbate.

Experimental

The PAC active carbon obtained from polyvinylidene chloride by activation at 973 K was used in experiments. Before experiments, the adsorbent was outgassed on a gravimetric setup *in vacuo* to a constant weight at a pressure of $1 \cdot 10^{-2}$ Pa and 573 K for 2 h. The error of measurement of the amount of the adsorbed substance was ±1%, and that of the temperature measurement was ±0.2 K. Up to pressures near the saturated vapor pressure, the adsorption isotherm of benzene on this carbon at 298 K was reversible and showed no adsorption hysteresis loop and no upward turn characteristic of the region of capillary condensation. This indicates that the PAC active carbon is essentially microporous and does not contain mesopores. In the coordinates of the Dubinin—Radushkevich equation, the experimental points of the adsorption isotherm for benzene deviate from a linear dependence to the abscissa axis at high fillings of micropores. The linearization of the isotherm in the region of high fillings gives the characteristic energy E_0 = 31 kJ mol^{-1} and the micropore volume 0.43 cm^3 g^{-1}. Perfluoropropane (C_3F_8), named Freon-218 in refrigeration engineering,[5] is characterized by the molecular weight 188.03, temperature of normal boiling T_b = 236.4 K, critical temperature T_c = 345.0 K, critical pressure 2.679 MPa, and critical specific volume 1.59 m^3 kg^{-1}.

Perfluoropropane used in experiments had 99.98% purity and was subjected to vacuum degassing at 77 K to remove volatile admixtures. The saturated vapor pressure 0.0877 MPa at 233 K coincides with the reference data.

Results and Discussion

Perfluoropropane adsorption on the PAC microporous carbon adsorbent was studied at 216, 243, 295, 318, and 343 K in the pressure interval from 1 to $1 \cdot 10^5$ Pa. The obtained isotherms of absolute adsorption in the a—ln$p$ coordinates (Fig. 1) have an inflection point in the region of medium fillings of the micropore volume. A similar shape was found for the adsorption isotherms of gases on adsorbents with a narrow pore size distribution, in particular, methane on the PAC-10 carbon adsorbent[6] and inert gases on zeolite NaX.[7]

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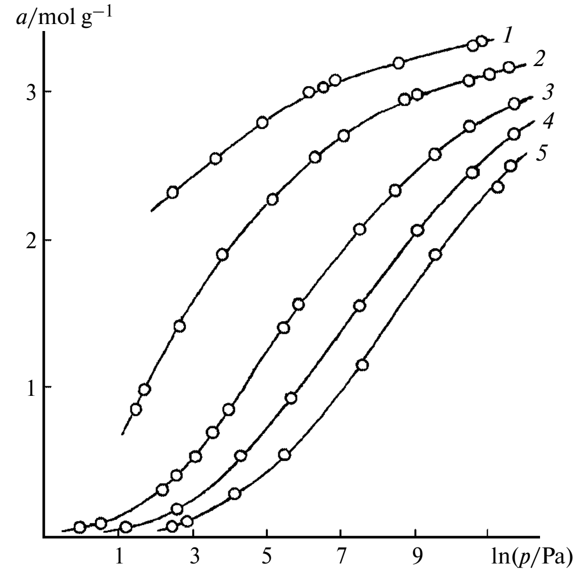

Fig. 1. Adsorption isotherms of perfluoropropane on the PAC microporous carbon adsorbent at 216 (*1*), 243 (*2*), 295 (*3*), 318 (*4*), and 343 K (*5*).

The adsorption isosters (Fig. 2) derived from the obtained isotherms are linear over the whole interval of pressures and temperatures, the behavior characteristic of the sorption of gases on microporous adsorbents.

The data obtained allow the calculation of the thermodynamic characteristic of the adsorption system. The general equation[8] can be used for the calculation of the differential isosteric heat of adsorption

$$q_{\mathrm{st}} = -RZ[1 - (\partial v_1/\partial a)_T/v_{\mathrm{g}}][\partial(\ln p)/\partial T^{-1}]_{\mathrm{a}} - \\ - (\partial p/\partial a)_T[v_1 - T(\partial v_1/\partial T)_{\mathrm{a}}], \quad (1)$$

where $q_{\mathrm{st}} = h_{\mathrm{g}} - (\partial H_1/\partial a)_T$ is the difference between the molar enthalpy of the equilibrium gas phase h_{g} and the differential molar enthalpy of the adsorbent—adsorbate system, R is the universal gas constant, $Z = pv_{\mathrm{g}}/(RT)$ is the compressibility coefficient of the gas phase, $v_1 = V_1(a,T)/m_0$ is the reduced volume of the adsorbent—adsorbate adsorption system, $V_1(a,T)$ is the adsorbent volume under experimental conditions including micropores, m_0 is the weight of the degassed adsorbent, $(\partial v_1/\partial a)_T$ is the differential molar volume of the adsorbent—adsorbate system taking into account the deformation of adsorbent during adsorption under isothermic conditions, v_{g} is the molar volume of the gas phase, a is the amount adsorbed determined as the full content of the substance in micropores, and $(\partial v_1/\partial T)_{\mathrm{a}}$ is the term characterizing the temperature dependence of the reduced volume of the adsorbent—adsorbate system under isosteric conditions (a = const). Equation (1) can be simplified because under the experimental conditions $Z = 1$; $(\partial v_1/\partial a)_T \ll v_{\mathrm{g}}$, and the first term in Eq. (1) is much greater than the second term due to negligible values of the $(\partial p/\partial a)_T$ and $(\partial v_1/\partial T)_{\mathrm{a}}$ derivatives. Therefore, we obtain

$$q_{\mathrm{st}} = -R[\partial(\ln p)/\partial T^{-1}]_{\mathrm{a}}. \quad (2)$$

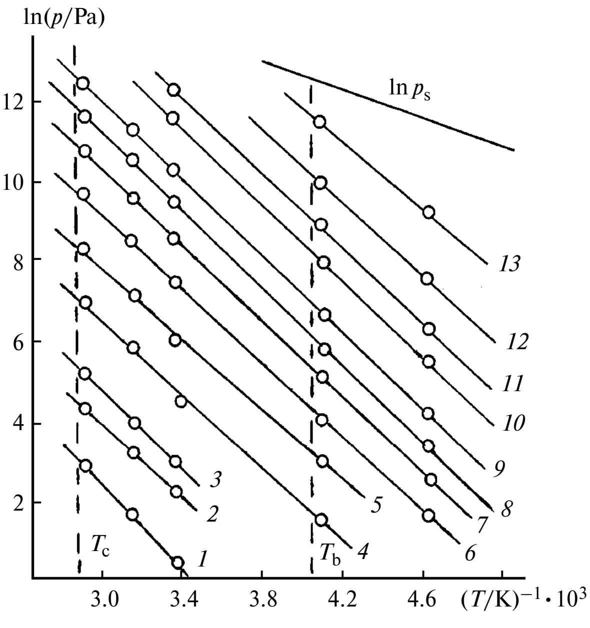

Fig. 2. Adsorption isosters of perfluoropropane on the PAC microporous carbon adsorbent for values of amount adsorbed equal to 0.1 (*1*), 0.3 (*2*), 0.5 (*3*), 1.0 (*4*), 1.5 (*5*), 2.0 (*6*), 2.3 (*7*), 2.5 (*8*), 2.7 (*9*), 2.9 (*10*), 3.0 (*11*), 3.1 (*12*), and 3.2 mmol g^{-1} (*13*).

As follows from the plot of the differential isosteric heat of perfluoropropane adsorption on the PAC carbon adsorbent against the amount adsorbed (Fig. 3), in the initial region of micropore filling (a < 0.2) the heat decreases sharply from 47 to 37 kJ mol^{-1} as adsorption proceeds, then it passes through a minimum at 37 kJ mol^{-1} in the interval 0.3 < a < 0.8 mmol g^{-1}, again increases to 43 kJ mol^{-1} at a = 3 mmol g^{-1}, and then decreases sharply.

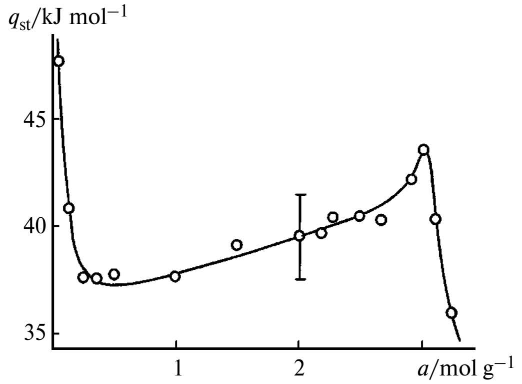

Fig. 3. Dependence of the differential isosteric heat of adsorption (q_{st}) of perfluoropropane on the PAC carbon adsorbent on the amount adsorbed (a).

The dependence of the isosteric heat of adsorption on the *a* value is characterized by two features: a sharp decrease in the initial region of fillings and a maximum at high micropore fillings. The maximum in these curves for carbon adsorbents is observed very rarely. Such plots were obtained for systems with the monoporous homogeneous adsorbent, such as zeolite. The conditions of synthesis and the properties of adsorbents of this class are described in the literature.[9—11] Based on the specific features of changing the isosteric heat with the amount of perfluoropropane adsorbed, we can conclude that the PAC microporous carbon adsorbent is mainly monoporous.

The initial sharp decrease in the heat of adsorption in a narrow interval of the initial fillings of micropores is likely caused by the gradual occupation of the strongest sites that appear in pores with the smallest equivalent radii comparable with the effective radius of the sorbed C_3F_8 molecules. After filling these micropores, the further adsorption process is volume filling of the micropores. As known,[12,13] in addition to the adsorbent—adsorbate interactions resulting in a decrease in q_{st} with filling, the interactions between adsorbed molecules increase. In the case of the monoporous homogeneous adsorbent, this results in an increase in the isosteric heat of adsorption with an increase in the filling of the micropore volume. However, at sufficiently high fillings, the mean distances between adsorbed molecules become short, and repulsion forces increase to drastically decrease the heat of adsorption.

The state of the adsorbate in micropores is characterized by its differential molar entropy ΔS, which can be determined by the Gibbs—Helmholtz equation[14]

$$\Delta H = \Delta G + T\Delta S, \quad (3)$$

where all values were calculated relatively to the standard state, *viz.*, the liquid phase of the adsorptive at a given temperature. The change in the Gibbs energy of adsorption ΔG is equal to the differential maximum molar work of adsorption taken with the negative sign

$$\Delta G = -A = RT\ln(f/f_s), \quad (4)$$

where f and f_s are the volatilities of the equilibrium and saturated vapors of the adsorptives, respectively. The change in enthalpy ΔH in Eq. (3) is equal to the pure differential heat of adsorption

$$\Delta H = -q = q_l - q_{st}, \quad (5)$$

where q_l is the heat of condensation of adsorptive vapors at a given temperature. Taking into account Eqs. (4) and (5), we obtain from Eq. (3)

$$\Delta S = [q_l - q_{st} + RT\ln(f_s/f)]/T. \quad (6)$$

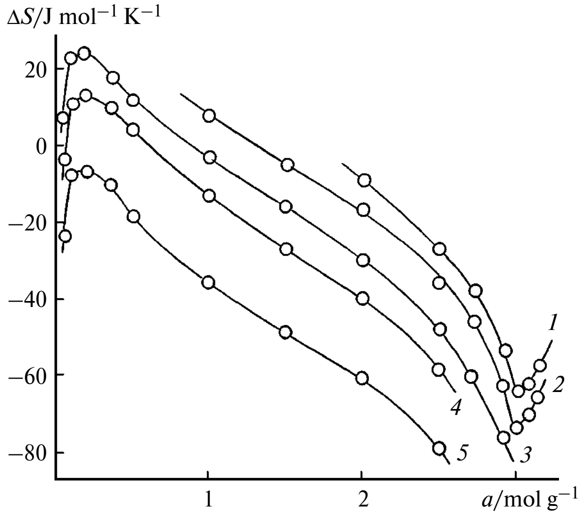

Fig. 4. Plots of the differential molar entropy of adsorption (ΔS) of perfluoropropane on the PAC carbon adsorbent *vs.* amount adsorbed (a) at 216 (*1*), 243 (*2*), 295 (*3*), 318 (*4*), and 343 K (*5*).

As follows from the plots of the differential molar entropy *vs.* amount adsorbed (Fig. 4) calculated relatively to the entropy of the liquid, the differential entropy of adsorbed perfluoropropane in the PAC microporous carbon adsorbent at small amounts adsorbed (a < 0.2 mmol g^{-1}) increases, passes through a maximum at $a \approx 0.2$ mmol g^{-1}, and then decreases in a wide region of fillings of the micropore volume. The maximum of the differential entropy of adsorption at small fillings of the pore volume can likely be accounted for the same reasons as the decrease in the differential heat of adsorption: the primary filling of the narrowest micropores with a high energy is replaced by the filling of the rest micropore volume of the active carbon. The decrease in the entropy is favored by an increase in the intermolecular interaction in the adsorbate. In the region of high fillings ($a \approx 3$ mmol g^{-1}), the entropy of the adsorbate passes through a minimum and increases sharply with the further filling of the micropore volume (T = 243, 216 K). A similar behavior of the differential entropy of the adsorbate at high fillings of micropores of the monoporous adsorbents was observed[15] for the Xe—zeolite NaX and CF_3Cl—NaX adsorption systems.

It is likely that the appearance of the minimum of entropy at high fillings of micropores is a characteristic feature of physical adsorption of gases and vapors on monomicroporous adsorbents. Its appearance is probably related to the formation of associates of adsorbed molecules in micropores due to development of lateral attraction forces. However, at high micropore fillings, the attraction forces are replaced by sharply increasing repulsion forces. Therefore, the further increase in the micropore filling results in the rearrangement of the associates and a sharp increase in the differential entropy of the adsorbate.

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