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Comparative analysis of methods for determination of structural characteristics of carbon adsorbents

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Experimental data on the equilibrium adsorption of sulfur hexafluoride, methane, carbon dioxide, and benzene on carbon adsorbents of different porosity obtained in a wide pressure range at 298—408 K were analyzed. The adsorption volumes, surface areas, and sizes of slit-shaped pores of the carbons were determined using several independent methods. A method for determination of the adsorption volume from the experimental isotherm of excessive adsorption of gases and the total content equation was proposed. The resulting values are similar to the adsorption volumes calculated from the data for vapors. A new method for the calculation of the adsorbent surface area is described. The method is based on the dependence of the adsorption volume of adsorbent pores on the effective size of adsorbate molecules. A possibility to determine the average size of narrow slit-shaped carbon pores from the difference of the initial heats of adsorption of the gas under study on the carbon black and porous carbon adsorbent is considered.

Key words: adsorption, carbon sorbents, surface area, pore volume, slit-shaped pore width, pore radius.

One of the most important problems in adsorption is the determination of volumes and surface areas of micropores and mesopores and pore sizes of adsorbents.

The micropore volume (W_{mi}) of a carbon sorbent can be found by the Dubinin—Radushkevich (DR) equation on the basis of data on vapor sorption. We developed a method for the determination of the total adsorption volume (W) from gas sorption, which uses one experimentally measured adsorption isotherm of gas and the equation of adsorption isotherm of total content[1] (EIEA method).

Methods based on the Brunauer—Emmett—Teller (BET) equation, analysis of comparison plots (CP), and measurement of heats of wetting—immersion (HI) well recommended themselves for the calculation of the surface area of adsorbents (S). We have previously proposed[2] the method for the calculation of S from the difference of adsorption volumes determined using two adsorptives (method 2ad).

The average size of the slit-shaped pore width can be found from the Dubinin[3] and Stoeckli[4] equations. However, for the technology of separation of gas mixtures, it is most important to know the minimum width of slit-shaped pores of the carbon adsorbent rather than the average one. In the present work, we describe the method for the calculation of the minimum width of a slit-shaped pore (L_1) of a carbon adsorbent using the difference of isosteric initial heats of adsorption of the gas under study measured on the carbon black and a porous carbon adsorbent.

In addition, it was of interest to compare the results of determination of the W and S values and the width of slit-shaped pores (L) for a series of carbon adsorbents obtained by different methods, which were either developed by us or known earlier.

Experimental

Two adsorption setups were used: one setup was used for measurements at pressures below 0.1 MPa, and the second setup was used for measurements at high pressures. Isotherms of excessive adsorption of SF_6 ($P = 0.001$—2.4 MPa, $T = 298$—408 K), CH_4 ($P = 0.01$—25 MPa), and CO_2 ($P = 0.001$—7.0 MPa, $T = 298$—408 K) were obtained on a high-pressure volume-gravimetric adsorption setup.[5] Uptakes of benzene were measured on another setup ($P = 0.0001$—0.1 MPa) including a beam balance with a sensitivity of 10 μg and two pressure gauges that overlap the range of measured pressures from 0.133 to $1.33 \cdot 10^5$ Pa. Adsorptives were SF_6 (99.99%), CO_2 (99.8%), CH_4 (99.9%), benzene (reagent grade). Graphitized carbon black (GCB), nongraphitized carbon black Vulkan, microporous active carbon CMS (Switzerland), and domestic microporous carbons SKT-6, FAS, PAC, and AC-71 served as adsorbents. Active carbons of the SKT type were prepared from peat or a mixture of peat with other carbon-containing materials.[6] Active carbons of the FAS type were obtained from the polymeric raw materials,

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Table 1. Total adsorption volume (W) and the volumes of micropores (W_{mi}) and mesopores (W_{me}) for carbons of different porosity determined from benzene adsorption

Adsorbent	W	W_{mi}	W_{me}
		$cm^3 g^{-1}$	
SKT-6	0.8—0.6	0.4—0.6	0.18—0.25
FAS	0.8—1.0	0.2—0.5	0.3—0.45
PAC	0.4—0.5	0.4	0.04

viz., furfurol copolymer GFS-98, by step carbonization and vapor-gas activation. These carbons are classified as materials containing micropores and mesopores in equal ratios. They possess unique mechanical strength and are applied for the purification of human blood, plasma, and lymph.[6] The active carbon PAC was synthesized by the thermal decomposition of the polymeric raw materials. The active carbon AC-71, which is prepared from brown carbon, belongs to the class of supermicroporous carbons. A carbon tissue that manifested the properties of a microporous adsorbent was also studied. The characteristics of the pore system of the SKT-6, FAS, and PAC carbons are presented in Table 1.

The excess uptake (Γ) values under equilibrium conditions were calculated by the equation

$$\Gamma = (m - \rho_g V_{acc})/m_{ads}, \quad (1)$$

where m is the weight of the adsorptive in the adsorber, ρ_g is the density of the equilibrium gas phase, V_{acc} is the accessible volume in the adsorber filled with the adsorbent, and m_{ads} is the weight of the solid adsorbent in the adsorber. The accessible volume V_{acc} for each of the above-listed adsorbents was determined from the difference of volumes of the empty adsorber and adsorbent. The volume of the solid adsorbent was calculated as the ratio of its weight to density (ρ_{ads} = 2.0 g cm^{-3}). The experimental isotherms of excessive adsorption of SF_6 on the adsorbents AC-71, CMS, PAC, FAS, and SKT-6 and carbon tissue TU at 298 K are presented in Fig. 1. The experimental isotherms of excessive adsorption of CO_2 on the adsorbents PAC and AC-71 are shown in Figs 2 and 3. The isotherms of excessive adsorption at other temperatures were published earlier.[7,8] The temperature plots of the logarithm of Henry's constant for SF_6 adsorption on the samples under study are shown in Fig. 4. Henry's

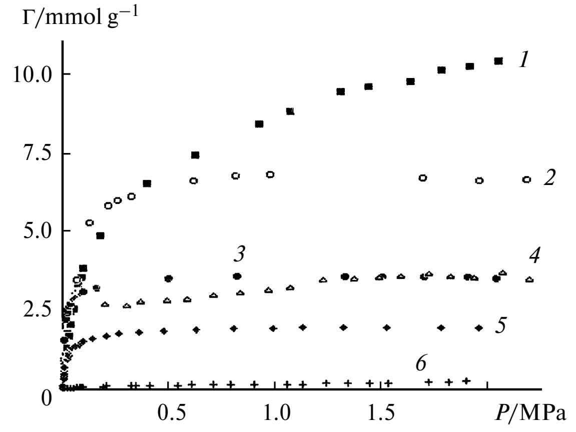

Fig. 1. Isotherms of excessive adsorption of SF_6 at 298 K on different adsorbents: carbons AC-71 (*1*), SKT (*2*), and PAC (*3*); carbon tissue (*4*); carbons CMS (*5*) and FAS (*6*).

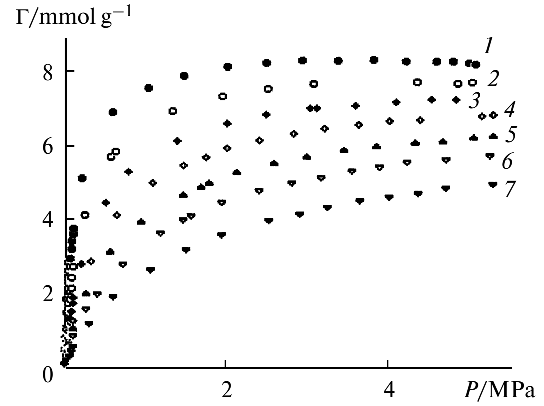

Fig. 2. Isotherms of excessive adsorption of CO_2 on the PAC carbon at 293 (*1*), 313 (*2*), 333 (*3*), 353 (*4*), 373 (*5*), 393 (*6*), and 423 K (*7*).

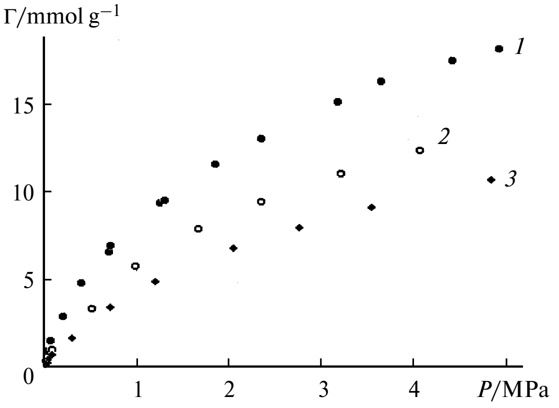

Fig. 3. Isotherms of excessive adsorption of CO_2 on the AC-71 carbon at 298 (*1*), 323 (*2*), and 347 K (*3*).

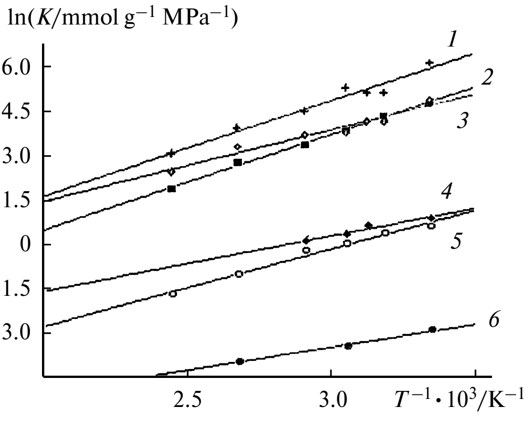

Fig. 4. Temperature plots of Henry's constants (K) for SF_6 adsorption on the adsorbents PAC (*1*), CMS (2), AC-71 (*3*), Vulkan carbon black (*4*), FAS (*5*), and GCB (*6*).

constants for each adsorption system were found by the approximation of the measured isotherms of equilibrium adsorption of SF_6, CH_4, or CO_2 using a multiconstant equation, which satisfactorily describes the experimental data and at $P \to 0$ it reduces to the Henry equation

$$\Gamma = (K_1P + K_2P^2 + K_3P^3)/(1 + K_1P + K_2P^2 + K_3P^3), \quad (2)$$

where Γ is the excessive uptake at a specified temperature and the corresponding pressure P, K_1 is Henry's constant, and K_2 and K_3 are the constants determined by the nonlinear regression method (the simplex and Newton methods).

Results and Discussion

Determination of adsorption volumes. The volume of micropores W_{mi} for microporous adsorbents can be calculated by the determination of the adsorption volume W using the experimental isotherm of excessive adsorption[1] by the adsorption equation of total content.[9] When deriving this equation, it was assumed that molecules sorbed in one pore have no energy effect on molecules in the neighboring pores, which is true, as a rule, for carbon sorbents. For carbon sorbents containing many mesopores along with micropores, W_{mi} can be calculated by the DR equation, and the adsorption volume in mesopores (W_{me}) can be determined by the Halsey equation[10] knowing the adsorption layer thickness and the surface area of the total surface of the adsorbent. The procedure of determination of W_{me} for sorbents with the developed mesoporosity in the presence of micropores has been described earlier.[8] The micropore volume of carbons can also be calculated by a comparison plot,[11] which is obtained from measuring the amount adsorbed of the same substance on the carbon black and the sample under study at the same temperature. The plot makes it possible to determine the maximum uptake (Γ_{max}), whereas the W value is calculated from the Γ_{max}/ρ_l ratio, where ρ_l is the adsorbate density equal to the density of the liquid at given P and T. The results of determination of W_{mi} and W_{me} for the carbon samples under study are presented in Table 2.

As can be seen from the data in Table 2, the micropore volumes calculated by the DR equation on the basis of the adsorption isotherms of CO_2 and C_6H_6 are similar to each other for all the carbons under study. The application of the same equation for the calculation of micropores for SF_6 adsorption resulted in lower values. This difference is related to the fact that SF_6 fills but a small fraction of slit-shaped pores, because the effective size of a spherically symmetric SF_6 molecule[12] is larger than the effective sizes of CO_2,[13] C_6H_6,[14] and CH_4 [15] molecules. The W values for the CMS and FAS carbons obtained by the EIEA method are similar to the W values found using other methods.

Table 2. Adsorption volumes of micropores (W_{mi}) of the carbon-based systems under study determined by different methods

Adsorptive	Method of determination	W_{mi}/cm^3 g^{-1}				
		CMS	PAC	SKT	FAS*	AC-71
N_2	DR	—	—	—	—	1.01
C_6H_6	DR	0.25	0.35	0.59	0.176	0.89
CO_2	DR	0.252	0.368	0.64	—	0.92
SF_6	DR	0.194	0.311	0.57	0.014	0.73
C_6H_6	CP	—	—	—	0.163	0.72
CH_4	EIEA	0.24	—	—	0.2	—

* The adsorption volume in mesopores (W_{me}) calculated by the Halsey method[8] using SF_6 as the adsorptive is equal to 0.04 cm^3 g^{-1}; according to the passport data, W_{me} = 0.3 cm^3 g^{-1}.

Unlike other microporous carbons, micropores of the FAS carbon are rather narrow and, therefore, the most part of them are inaccessible for such molecules as SF_6. This follows from both the data obtained for the adsorption of C_6H_6, CH_4 (Γ_{max} = 2 mmol g^{-1}),[8] and SF_6 (Γ_{max} = 0.2 mmol g^{-1})[8] and the calculated W values (see Table 2). The higher value W = 0.2 cm^3 g^{-1}, which was found by the EIEA method for FAS by methane, is related, most likely, to the fact that this method takes into account the whole adsorption volume, *i.e.*, $W_{mi} + W_{me}$. This agrees well with the data for W_{mi} (see Table 2) determined from the adsorption of benzene and SF_6. The supermicroporous AC-71 carbon has the highest W value, which is equal to 0.92—1.01 cm^3 g^{-1} and independent of the type of adsorptive.

Determination of the surface area of adsorbents. Several methods can be used for the calculation of the total surface area. Along with the traditional methods of calculation by the BET and comparative plot methods, we used the so-called γ-method and the method based on heats of immersion (HI). The surface area of sorbents can also be determined by the method[2] assuming the use of two molecules as adsorptives with adequate size differences. Knowing the difference between the effective radii of molecules of two adsorptives (r_a and r_b) and the adsorption volume values (W_a and W_b) determined from these two adsorptives (Table 3), the surface area can be determined by the equation

$$S = (W_a - W_b)/(r_b - r_a). \quad (3)$$

For example, for the determination of S, the adsorption volumes for the CMS ($W_a(SF_6)$ and $W_b(CH_4)$) and PAC ($W_a(SF_6)$ and $W_b(CO_2)$) carbons were taken from Table 2, and the values presented below were used as radii.

Molecule	SF_6	CH_4	CO_2	C_6H_6
r/nm	0.255	0.19	0.17	0.185

These radii were chosen from the conditions of orientation of a CO_2 molecule with two oxygen atoms pointing to the sorbent surface, and the benzene ring of an C_6H_6 molecule lying parallel to the surface of pore walls. It is

Table 3. Total surface area (S) and the surface area of mesopores (S_{me}) of the adsorbents under study

Adsorptive	Method of determination	Adsorbent						
		CMS	PAC	SKT	FAS	AC-71	GCB	Vulkan carbon black
					S/m^2 g^{-1}			
N_2	BET	—	—	—	—	2000	29	—
SF_6	BET	294	454	565	22	932	3.33	72
C_6H_6	BET	—	960	1310	616	1940	29	106
CO_2	BET	508	782	1180	—	1273	—	116
C_6H_6	HI	710	—	—	—	—	—	—
C_6H_6	CP	—	—	—	690	1870	—	—
CH_4, SF_6	2ad	708	—	—	—	—	—	—
N_2, SF_6	2ad	—	—	—	—	2060	—	—
CO_2, SF_6	2ad	682	670	824	—	2235	—	—
C_6H_6, SF_6	2ad	—	643	—	—	2142	—	—
					S_{me}/m^2 g^{-1}			
C_6H_6	CP	28	—	—	86	577	—	—
C_6H_6	HI	30	—	—	—	—	—	—
C_6H_6	γ-Method	—	—	—	78	—	—	—

necessary to choose the orientation relative to the adsorbent surface, because these molecules are spherically nonsymmetric. The studies of the N_2—zeolite adsorption system[2] confirmed that two nitrogen atoms of an N_2 molecule point to the adsorbent surface.

To calculate the surface of mesopores S_{me}, we used the CP method with two adsorptives, *viz.*, benzene and sulfur hexafluoride, when they are adsorbed on the FAS and AC-71 carbons at 298 K, and the Vulkan carbon black was considered as the adsorbent with the planar surface.

The results of determination of the surface areas of all the adsorbents under study are presented in Table 3. The highest S values for nearly all adsorbents are provided by the BET method, if C_6H_6 is used as the adsorptive. The S values calculated by the same method for CO_2 are somewhat lower for all adsorbents than those calculated for benzene. Especially low S values for all adsorbents are observed when SF_6 is used as the adsorptive. For the CMS carbon, the S values obtained by the 2ad method (see Tables 2 and 3) coincide well with S obtained from HI and somewhat higher than S calculated by the BET equation using the data on CO_2 and SF_6 adsorption. The S values for the PAC and SKT carbons obtained by the 2ad method are lower than the values obtained by the BET method for benzene and CO_2 adsorption but higher than those for SF_6. For the FAS carbon, the S values calculated by the BET and CP methods using benzene as the adsorptive differ sharply from S obtained from the data on SF_6 sorption, which is related to specific features of the microporous system of this carbon. For the AC-71 carbon, the method for S determination based on the use of two adsorptives gives the results similar to the data obtained by the BET method for N_2 and C_6H_6 and by the CP method for C_6H_6.

The lowest surface area values were obtained by the BET method when SF_6 was used as the adsorptive.

To explain this phenomenon, we can consider the conditions of using the BET method. Its application to adsorption systems is related to several restrictions.[11] In the classical interpretation of the BET equation

$$(P/P_s)/[a(1 - P/P_s)] = (1/a_mB) + [(B - 1)/(a_mB)](P/P_s) \quad (4)$$

the B coefficient associated with the molar heat of adsorption should be higher than two.

For sulfur hexafluoride adsorption on the carbon adsorbents under study, $B > 10$. Our measurements were carried out in the same temperature interval (197—531 K) for which the surface area of an SF_6 molecule, which is equal to 0.264—0.267 nm^2, is recommended for use in the calculations of the adsorbent surface area.[16] The same concerns the use of CO_2. However, as can be seen from the data in Table 3, the surface area of GCB determined by the BET method for SF_6 is by ~8.8 times smaller than S calculated from the adsorption of C_6H_6 and N_2 (77 K).

To explain this discrepancy, let us attempt to consider specific features of adsorption on a heterogeneous surface. Adsorption on this surface is equivalent to that on a discrete system of sites different in energies of interaction with an adsorbable molecule. In this case of a considerable energy heterogeneity, especially that of active sites can be discriminated. A comparison of the S values determined by the BET method for the same substances as for the Vulkan carbon black, which differs from GCB by a substantially greater number of active sites, shows that the ratio of S obtained from C_6H_6 adsorption to S obtained from SF_6 adsorption is only 1.4, being much lower than that for GCB. The energy of interaction of SF_6 molecules on these sites can be determined by the slope of the linear temperature plots of $\ln K$ for the GCB and Vulkan carbon black (see Fig. 4). These values are similar to each other, *i.e.*, the initial heats of adsorption of sulfur hexafluoride on samples of these carbon blacks are approximately equal. Thus, for SF_6 adsorption on the above materials, the BET method determines, in fact, the number of especially active sites rather than the number of adsorption sites corresponding to a compact monolayer. For instance, if the content of active sites is determined by the limiting amount adsorbed, which was found from the BET equation, the following results are obtained. One gram of the Vulkan carbon black contains $27.2 \cdot 10^{19}$ active sites, and only $1.26 \cdot 10^{19}$ active sites are available in one gram of GCB, *i.e.*, their number on the Vulkan carbon black is ~20 greater than that on GCB.

Determination of the width of slit-shaped carbon pores. The pore width (L) can be determined from the Dubinin equation using the characteristic energy (E_0) for a standard vapor (benzene) or the affinity coefficient. When studying the carbons, it was found[3] that the product of the inertia radius by the characteristic adsorption energy E_0 is constant and close to 14.8 kJ nm mol^{-1}. Inertia radii of micropores are directly related to the half-width size of slit-shaped carbon pores ($L/2$ to 0.7 nm). The region of supermicropores (0.7—1.6 nm) is also believed to be satisfactorily determined from the Dubinin—Radushkevich equation[17]

$$L/2 = 12.0/E_0, \tag{5}$$

where $E_0 = E/\beta$ (E is the characteristic energy of the adsorbate, and β is the affinity coefficient calculated by different methods). We determined the β coefficient through the ratio of parachores of the substance under study and benzene ($\beta = 0.66$, 0.391, and 0.4 for SF_6, CH_4, and CO_2, respectively). The following formula for the calculation of the average width of planar slit-shaped carbon micropores is known[4]:

$$L = 10.8/(E_0 - 11.4). \tag{6}$$

Several experimental facts indicate that in samples of the carbons under study slit-shaped pores exist predominantly. For instance, for benzene adsorption ($\sigma_1 = 0.66$ nm)[15] the time of equilibration in micropores of the FAS carbon does not exceed 20 min, whereas for methane adsorption ($\sigma = 0.38$ nm)[13] it increases by several times and virtually no adsorption of SF_6 (the molecules are close to spheres with $\sigma = 0.51$ nm)[18] is observed under the same conditions. This indicates that a planar benzene molecule, whose large cross section (σ_1) is parallel to one of the surfaces of an adsorbent pore, can diffuse into these pores, whereas spherical molecules with $\sigma > 0.5$ nm cannot penetrate into the pores. This experiment also indicates that the cross section σ_2 of a benzene molecule is <0.37 nm.

Table 4. Characteristic energy of adsorption (E_0), initial heat of adsorption (q_{st}), width (L), and minimum width (L_1) of slit-shaped pores of the carbons under study

Adsorptive	Method*	Adsorbent				
		CMS	PAC	SKT	FAS**	AC-71**
				E_0/kJ mol^{-1}		
SF_6	D	23.0	30.0	20.5	20.9, 2.31	17.8, 3.81
CO_2	D	25.4	26.3	19.5	—	14.7
C_6H_6	D	26.1	32.8	20.6	24.8, 1.96	12.7
				L/nm		
SF_6	St	0.93	0.58	1.19	1.14, <0	1.71, <0
SF_6	D	1.04	0.80	1.17	1.15, 10.4	1.35, 6.3
CO_2	St	0.77	0.72	1.34	—	3.27
CO_2	D	0.94	0.91	1.23	—	1.63
C_6H_6	St	0.73	0.50	1.17	0.81, <0	8.30
C_6H_6	D	0.92	0.73	1.17	0.97, 12.24	1.89
				q_{st}/kJ mol^{-1}		
SF_6	—	24.9	25.0	—	21	18.6
CO_2	—	—	21.0	—	—	18.3
CH_4	—	15.5	—	—	16	—
				L_1/nm		
SF_6	EM	0.75	0.75	—	0.81	0.84
CO_2	EM	—	0.61	—	—	0.68
CH_4	EM	0.73	—	—	0.71	—
C_6H_6	EM	—	—	0.55	—	—

* D is the calculation by the Dubinin equation, St is the calculation by the Stoeckli equation, and EM is the calculation by the energy method proposed in the present work.

** If two values are given, they concern the cases of revealing the primary and secondary porosity of carbons, respectively.

The results of calculations of the characteristic energy and sizes of slit-shaped pores by Eqs (5) and (6) are given in Table 4.

If a system of micropores is presented by slit-shaped pores, then it is important to determine both the average and minimum slit widths. We propose an energy method (EM) to determine the size of the carbon pore width that makes it possible to calculate the lowest limit of the slit width. The method is based on the knowledge of the initial heats of adsorption (q_{st}), which depend only on the adsorbate—adsorbent interaction and the mean potential energy (E) of an adsorbed molecule[19]

$$q_{st} = R[\mathrm{d}(\ln K)/\mathrm{d}(1/T)] = -N_A E - 0.5RT, \tag{7}$$

where K is Henry's constant, R is the gas constant, and N_A is Avogadro's number. It is assumed that the potential of interaction of a molecule to the adsorbent surface $\Phi(z)$ referred to one mole depends only on the distance from the molecule to the surface (z). Henry's constant is defined as

$$K = (1/RT)\int\{\exp[-\Phi(z)/(RT)] - 1\}dz. \quad (8)$$

It is known that molecules are adsorbed on the strongest adsorption sites in the initial filling region and, from the viewpoint of the carbon structure, in the narrowest pores with the average width L_1. The initial heat of adsorption of the same substance on the active carbon is higher than that on the surface of carbon blacks. This can be explained by the fact that the mean potential energy of a molecule in a slit-shaped carbon pore is summated of two components. The first of them equals the energy of interaction with one surface of a slit-shaped pore, and another component is equal to the energy of interaction with another surface of this pore. Let us assume that the adsorbed molecule is localized tightly close to the carbon atoms that form the pore surface, *i.e.*, occupies the position, whose potential energy is minimum. In this case, the first component is equal to the potential energy of interaction with the carbon black surface. If we know how the potential of interaction of a molecule with the adsorbent surface changes with the distance z, then the difference in the initial heat of adsorption in the pore and on the carbon black surface gives the size of the narrowest pores of the carbon material. Thus, to determine the width of a slit-shaped carbon pore, one has to calculate the mean energy (potential of interaction of an adsorbate molecule) for different z values.

To calculate the energy of interaction of an adsorbate molecule at the distance z from the plane, which passes through the centers of the carbon atoms forming the surface of the adsorbent slit, one can use the expression for the interaction potential $\Phi(z)$[19]

$$\Phi(z) = -(1/6)(C\rho\pi/z^3)[1 - (R_0{}^6/15z^6)], \quad (9)$$

where C is the constant of dispersion interaction, ρ is the density of the adsorbent lattice accepted to be 2.0 g cm^{-3} for the carbon adsorbents, and R_0 is the sum of van der Waals radii of the adsorbate and adsorbent molecules.

The problem of the position of the external boundary of the carbon black with respect to an adsorbed molecule is related to the choice of the numerical value of the equilibrium distance z_0 that affects the energy of repulsion. The variation of the z_0 parameter can bring the London method to correspondence with the method of direct summation over the lattice. It was shown[19] by the description of the calculation of the potential energy of interaction between a molecule and a planar adsorbent (carbon black) that $z_0 = 0.765R_0$ is associated with the position of the molecule corresponding to the potential energy minimum on the carbon black surface. Then we can write for the carbon black

$$q_{st} = -N_A\Phi(z_0) - 0.5RT. \quad (10)$$

At low fillings both on the surface of the carbon black and in narrow carbon pores, the energy of adsorbate—adsorbate interaction can be neglected. Let us consider that the total mean potential energy of one molecule for adsorption on carbon is equal to the sum of the energy of its interaction with both walls of the adsorbent pore. In this case, the molecule itself occupies such a position on the surface that corresponds to the minumum of its potential energy. To check Eqs (9) and (10), we compared the heats of adsorption of CH_4, CO_2, and SF_6 on the carbon black calculated by Eqs (9) and (10) with the experimentally obtained q_{st} values. An average measurement temperature of 342 K was used for the calculation of the isosteric heats of adsorption by Eq. (10).

The C constant in Eq. (9) can be found by two methods. The first of them (Eq. (11)) is based on the assumption that the Lennard-Jones potential (Φ) can be applied to calculation of the interaction between molecules of different nature. To calculate the Lennard-Jones potential, the parameters ε/k (maximum energy of attraction of two atoms or molecules) and σ (their efficient diameter) should be known. The ε/k value is calculated as the geometric mean of these parameters for an adsorbate molecule and an adsorbent atom, and σ is their arithmetic mean

$$R_0 = \sigma_{av} = (\sigma_a + \sigma_b)/2.$$

In this case,

$$C = 4\varepsilon\sigma_{av}{}^6/k. \quad (11)$$

According to the second method, C is calculated by the Kirkwood—Müller equation

$$C = -6m_ec^2\{(\alpha_a\alpha_b)/[(\alpha_a/\chi_a) + (\alpha_b/\chi_b)]\}, \quad (12)$$

where m_e is the rest mass of an electron, C the velocity of light, α_i is the statistical polarizability of a molecule, and χ_i is the diamagnetic susceptibility of the substance.

What of the methods for calculation of C does better correspond to adsorption on the carbon adsorbents? The first method of calculation (by Eq. (11)) assumes that adsorptive molecules should be spherically symmetric, and then the C parameters can be taken from experiments on the viscosity of gases or from the second virial coefficient.[13] Let us consider the case where a nonspherical CO_2 molecule is adsorbed on the carbon black. If in the calculation of C by Eq. (11) a CO_2 molecule is still considered spherically symmetric and the values $\sigma(CO_2)$ = 0.40 nm and ε/k = 190 K, which were determined from experiments on gas viscosity, are used,[13] then the same σ value should be used in Eqs (9) and (10). Substituting thus found C value into these equations, we obtain the heat of adsorption $q_{st,1}$ = 8.12 kJ mol^{-1} (Table 5). This value is substantially lower than the experimental one (14.3 kJ mol^{-1}). Unlike $q_{st,1}$, for the adsorption of a tetra-

Table 5. Parameters α, χ, σ, and ε/k for molecules of the adsorptives and sorbent and the initial heats of adsorption (q_{st}) calculated using these parameters

Sorbent, adsorptive	$\alpha \cdot 10^{30}$	$\chi \cdot 10^{36}$	σ^a /nm	ε/k /K	$q_{st,1}{}^b$	$q_{st,2}{}^c$	$q_{st}{}^{exp}$
	m^3				kJ mol^{-1}		
C	0.937	10.54	0.335	28			
CH_4	2.60	20.37	0.382	148	6.41	11.6	11.7[20]
CO_2	2.65	34.34	0.400	190	8.12	14.6	14.3
SF_6	6.54	73.05	0.551	201	13.5	9.3	13.4
C_6H_6	12.31	90.98	0.527	440	22.0	24.0	36.2[20]

[a] For gases, from the data on viscosity.

[b] Calculated using Eq. (11).

[c] Calculated using Eq. (12).

hedral CH_4 molecule a similar calculation of the *C* parameter by Eq. (12) gives $q_{st,2}$ = 11.6 kJ mol^{-1}, which agrees well with the experimental value (11.7 kJ mol^{-1}).[20] The calculation of q_{st} using the first method results in a lower value: 6.41 kJ mol^{-1} (see Table 5). When *C* is calculated by the second method, *i.e.*, Eq. (12), the value of this constant is affected only by α and χ for a CO_2 molecule and C atoms (see Table 5). To determine the heat of adsorption from Eqs (9) and (10), one can use another σ value of a nonspherical molecule that reflects both its structural features and a possible orientation relative to the adsorbent surface. Since a CO_2 molecule is linear, it is described by two σ parameters: σ_1 = 0.51 nm and σ_2 = 0.292 nm.[18] Assume that a CO_2 molecule is adsorbed on the carbon sorbent surface through two oxygen atoms. In this case, the calculated $q_{st,2}$ value (see Table 5) well coincides with our experimental data. For SF_6 adsorption (the symmetry of an SF_6 molecule is similar to spherical) on the carbon black, the first method for calculation of *C* gives the q_{st} value coinciding with the experimental one (13.4 kJ mol^{-1}), whereas the second method gives a value of 9.3 kJ mol^{-1}. For a benzene—carbon black system, the q_{st} values calculated by Eqs (9) and (10) are much lower than the experimental values ($q_{st}{}^{exp}$ = 36.2 kJ mol^{-1}) (see Table 5). Reliable published data on the second structural parameter for a benzene molecule (σ_2) are lacking. If the experimental q_{st} value is accepted for the benzene—carbon system, then σ_2 = 0.283 nm is obtained for benzene using the *C* constant calculated by Eq. (12) and expressions (9) and (10).

The χ, α, σ, and ε/k [13] parameters for the molecules used by us as adsorptives and adsorbent and the initial heats of adsorption q_{st} calculated by two methods for these systems are presented in Table 5 along with the experimental values of the heat of adsorption. The calculated q_{st} values for three adsorptives, *viz*., CH_4, CO_2, and SF_6, coincide rather well with the experimental data for their adsorption on the carbon black. This allows us to calculate the isosteric heat of molecules adsorbed in slit-shaped carbon pores by Eqs (9) and (10). In a slit-shaped pore with the L_1 width, the potential energy of an adsorbed molecule *E*, which is present in Eq. (7), is

$$E = E_1 + E_2 = \Phi(0.765\sigma_{av}) + \Phi(L_1 - 0.765\sigma_{av}), \quad (13)$$

$$q_{st}(\text{carbon}) - q_{st}(\text{carbon black}) = -N_A\Phi(L_1 - 0.765\sigma_{av}). \quad (14)$$

Solving Eq. (14) with respect to L_1, we obtain the slit width of the carbon for which the heat of adsorption is q_{st}(carbon).

Let us consider in detail the adsorption of SF_6 on the AC-71 carbon. The experimental value of the initial heat of adsorption for this system is 18.6 kJ mol^{-1}, and that for SF_6 adsorption on the carbon black is 13.4 kJ mol^{-1}. According to Eq. (14), the energy of interaction of N_A molecules on the same surface of a slit-shaped pore of width L_1 at a distance of $0.765\sigma_{av}$ (σ_{av} = (0.51 + 0.335)/2 = 0.423 nm) from the pore with the opposite surface is equal to −18.6 (AC-71) + 13.4 (carbon black) = −5.2 kJ mol^{-1}. Let us determine the distance z_1 from the center of the molecule to the opposite surface of the slit. The value of the distance is the solution of the equation $\Phi(z)$ = −5.2 kJ mol^{-1}, where $\Phi(z)$ is calculated by formula (9). The calculation gives $1.23\sigma_{av}$. Then

$$L_1 = R_0 + z_1 = (0.765 + 1.23)\sigma_{av} = 0.84 \text{ nm}. \quad (15)$$

The dependence of the energy of an SF_6 molecule adsorbed on the carbon in a slit with a width of $2\sigma_{av}$ at the distance z_1 is shown in Fig. 5. The results of calculations of the pore width L_1 for carbons by the proposed method (EM) for several systems are given in Table 4.

The characteristic energy E_0 values for the PAC carbon (see Table 4), which were determined from three adsorptives and are related to the initial porosity, exceed E_0 of all other carbons. For the CMS, FAS, and SKT adsorbents, the E_0 values found from all adsorptives decrease. The lowest values were obtained for the super-

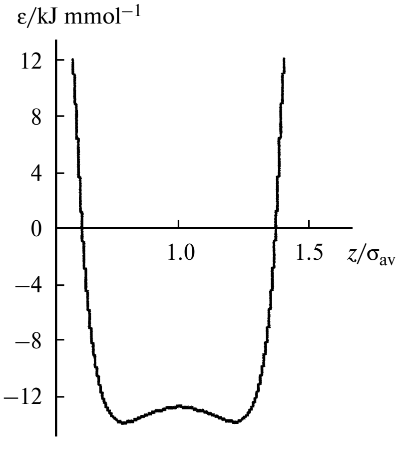

Fig. 5. Interpolation curve for determination of the distance *z* (distance to the opposite wall of the slit) for the SF_6—carbon AC-71 system.

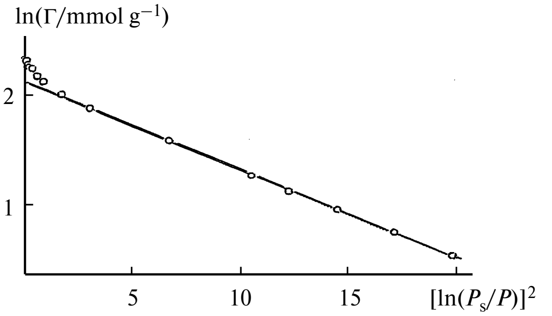

Fig. 6. Isotherm of excessive adsorption of SF_6 on the AC-71 carbon at 298 K in the coordinates of the DR equation.

microporous carbon AC-71. The increased E_0 values for the CMS, PAC, SKT, and FAS carbons for benzene adsorption can be explained by the fact that the benzene molecule with the hexagonal ring oriented parallel to the surface of pore walls can penetrate into narrower slit-shaped pores. A great scatter of the E_0 values for the C_6H_6—FAS and SF_6—FAS systems is related to the sorption of benzene molecules in micropores, which are inaccessible for SF_6 molecules. The isotherm of excessive adsorption of SF_6 on the FAS carbon at 298 K in the coordinates of the DR equation is shown in Fig. 6. It is seen that the experimental data in a region of P/P_s = 0.005—0.4 (below Γ = 0.164 mmol g^{-1}) are well described by a linear dependence. For this filling region, the characteristic energy E_1 was determined and the carbon pore width was calculated using Eqs (5) and (6) (see Table 4). For the region of higher fillings (Γ > 0.164 mmol g^{-1}), the procedure of determination of the secondary porosity parameters of the carbon[21] shows that for SF_6 adsorption on the FAS carbon the experimental data in the coordinates of the DR equation (see Fig. 6) also obey a linear dependence. This makes it possible to determine the characteristic energy E_2 = 1.525 kJ mol^{-1} (E_0 = 2.31 kJ mol^{-1})[4] related to the secondary porosity, and the pore width, which corresponds to this energy, can be calculated by Eq. (5): L = 10.4 nm. The calculation by Eq. (6) gives a negative value of L, which cannot be accepted as a slit width. It can be assumed that SF_6 molecules are adsorbed on the FAS carbon mainly in supermicropores, in an insignificant part of micropores, and on the mesopore surface. A similar procedure was carried out for the FAS—C_6H_6 and AC-71—SF_6 systems (see Table 4).

A comparison of the pore widths of the microporous carbons calculated by Eqs (5) and (6) for all adsorptives shows that for the PAC carbon the difference is the highest, whereas it is lower for the CMS carbon. All the values coincide rather well for the SKT carbon. The width of the narrowest pores L_1, which were calculated by the EM method, for the PAC and CMS carbons are similar to the L values determined by Eqs (5) and (6). Therefore, the CMS carbon and especially monoporous PAC carbon have a rather narrow pore distribution. The microporous SKT carbon has a broader pore distribution as compared to PAC and CMS, because L_1 is substantially smaller than L calculated by Eqs (5) and (6).

For the FAS and AC-71 carbons, the L values calculated by these methods depend strongly on the adsorptive used. For instance, for the AC-71—CO_2 system, the calculation by Eq. (6) gives a negative value, which indicates that the method is inappropriate in this case.

The isotherm of excessive adsorption of SF_6 on the AC-71 carbon at 298 K in the coordinates of the DR equation is linear in a wide pressure interval (Fig. 7). The characteristic energy of adsorption E_0 and the slit-shaped pore width were calculated from this isotherm (see Table 4). Unlike the FAS carbon where micropores are not virtually involved in SF_6 adsorption, the results for the AC-71 carbon confirm the role of supermicropores in adsorption. As can be seen from the data in Table 4, the average pore width of the FAS carbon determined by the Stoeckli equation is higher than that found by Eq. (5). This means that Eq. (6) can be applied only to the micropore region.

The results showed that, according to the proposed approach, the W values obtained by the EIEA method

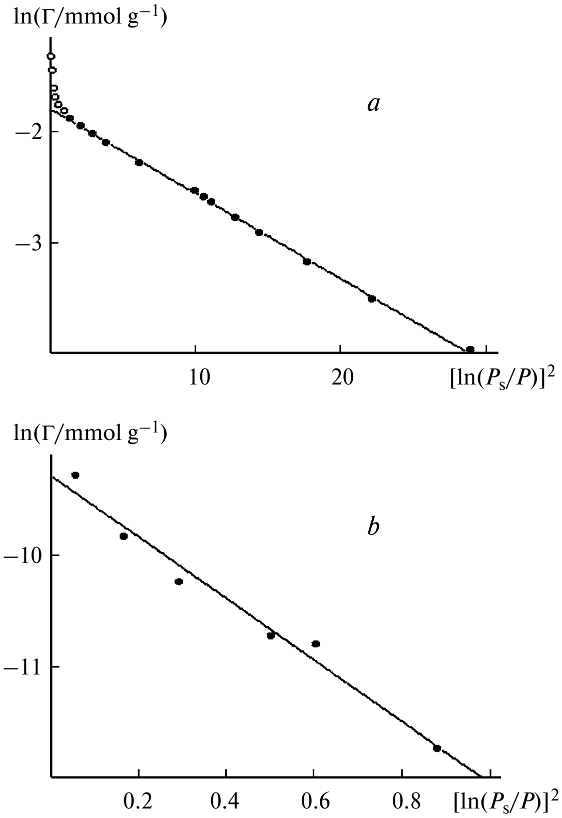

Fig. 7. Isotherm of excessive adsorption of SF_6 on the FAS carbon at 298 K in the coordinates of the DR equation for the primary (*a*) and secondary (*b*) porosity of the carbon.

agree with *W* for the CMS and FAS carbons determined by other methods. The method for calculation of the surface area for two adsorbates for the CMS and AC-71 carbons gave the values that coincide satisfactorily with the values obtained by different methods for several adsorbates (except for SF_6). The BET method gave underestimated values of the surface area at the same temperatures at which SF_6 adsorption was studied on the indicated carbon samples. Using the SF_6—AC-71 system as an example, we considered a possibility to determine the size of the slit-shaped carbon pore width from the difference of the initial heats of adsorption on the carbon black and carbon adsorbent using the dependence of the mean potential energy of adsorbed molecules on the distance from the surface of the carbon adsorbent. Since the method for calculation of the slit-shaped carbon pore width from the initial heats of adsorption gives the average size of a group of the narrowest pores, Eq. (5) gives apparently the average size of micropores and supermicropores while only the micropore size can be determined using Eq. (6).

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