Estimation of micropore size distribution in active carbons from adsorption isotherms of water vapor

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A possibility of estimation of the micropore size distribution in the carbon adsorbents with the developed micro- and mesoporous structure by analysis of the adsorption isotherms of water vapors was considered. At saturation water condenses in micropores in a form of a weakly compressed liquid. However, water molecules in micropores are packed not so closely as in the liquid because of steric hindrance. Therefore, the real density of water adsorbed in the micropores is lower than that of water adsorbed on an open surface and lower than the density of the normal liquid. An analysis of the adsorption isotherms of water vapors with account for the both opposite effects on the water density gives reliable data on the micropore sizes of the carbon adsorbents.

Key words: carbon adsorbents, water adsorption, linear micropore sizes.

Benzene is widely used as a standard adsorptive for characterization of the porous structure of adsorbents. It is of considerable practical interest to use other adsorptives, in particular, water, to estimate the parameters of the porous structure of adsorbents. In the present work, we considered the use of the adsorption isotherms of water vapor for characterization of micropores of the carbon adsorbents with the developed pore structure containing micro- and mesopores.

For adsorption of substances easily condensed at the experimental temperature, the adsorbate in the micropore volume is considered to be analogous to the compressed liquid. The average pressure of liquid compression $\bar{P}$ is proportional to the average adsorption potential developed as an average value of the differential molar work of adsorption $\bar{A}$ and is inversely proportional to the molar volume $v´$ of the adsorbate.[1,2] According to the theory of volume micropore filling, the $\bar{A}$ value is close to the characteristic energy of adsorption E.[3] Therefore,[4]

$$\bar{P} \approx v'^{-1} \int_{\theta=0}^{\theta=1} \bar{A} \mathrm{d}\theta \approx E\rho'/M, \qquad (1)$$

where $\rho´$ and M are the density and molar mass of the adsorbate, respectively; θ is the degree of filling of the micropore volume; and A is the differential molar work of adsorption.

Depending on E, the $\bar{P}$ values can achieve several thousands of atm, which should increase (taking into account different compressibilities of liquids) the adsorbate density by 10—20% over the density of the normal liquid ρ_0. However, the adsorbate density $\rho´$ does not exceed that of the non-compressed liquid, because molecules adsorbed in the pores of molecular sizes cannot form packings close to those in bulk liquids. Therefore, the adsorbate density should depend on the hydrostatic pressure and also on the ratio of the geometric characteristics of micropores to those of the adsorbate molecules.

The account of the both opposite effects on the adsorbate density can lead to the equation[4]

$$\rho´/\rho_0 = (v_0/v'')(F/0.74), \qquad (2)$$

where F is the fraction of the micropore volume occupied by molecules at their closest packing, v_0 is the molar volume of the liquid, and v'' is the molar volume of the liquid compressed at the pressure $\bar{P}$. The first cofactor in Eq. (2) $v_0/v'' > 1$ reflects the increase in the density under the effect of adsorption compression. The second cofactor $F/0.74 < 1$ corresponds to the effect of reduction in density. This effect appears because steric hindrance does not allow the molecules in the micropores to form packings similar to those in liquids. According to the rigid sphere model, the volume fraction occupied by the molecules at their closest packing, *i.e.*, for the case of molecular packing in the liquid, is equal to 0.74.

Evidently, the F value depends on both the K ratio of the molecule to pore sizes and on the pore shape. There-

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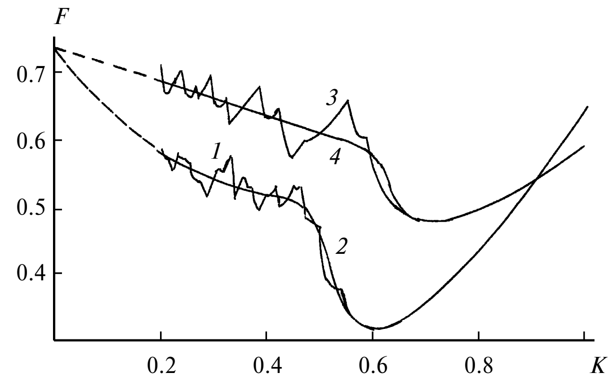

Fig. 1. Dependences of the ultimate filling (*F*) in the cylindrical (*1*, *2*) and slit-shaped (*3*, *4*) pores on the ratio of molecular to pore sizes (*K*): calculation (*1*, *3*) and averaged dependences (*2*, *4*).

fore, compact packings of the molecules (considered as rigid spheres) in infinite slit-shaped and cylindrical pores were geometrically modeled[5] in the interval of K changing from 1 to 0.2. The results of the modeling presented in Fig. 1 show that the cylindrical pores with only one degree of freedom (along the cylinder axis) are characterized by substantially lower F values than those for the slit-shaped pores where the molecular packing is not restricted in two directions. However, for the slit-shaped pores, according to the averaged dependence

$$F = 0.74 - 0.25K \qquad (3)$$

the F values in the interval of K changing from 0.6 to 0.2 are, on the average, by 13% lower than 0.74, which corresponds to the volume phase without steric hindrance.

Based on the data on liquid compressibility and adsorbate density and using Eq. (2), one can determine F and calculate the K ratio by the $F = \varphi(K)$ dependence and, hence, the size (H) of the slit-shaped pores or the diameter (D) of the cylindrical pores

$$H\,(D) = d'/K. \qquad (4)$$

Here d' is the equivalent diameter of the molecule in the compressed adsorbate, which can be determined from the condition that, according to the rigid sphere model, 74% of the liquid volume fall on the volume of the molecules when they are closely packed

$$d' = [(0.74v''/N_A)(6/\pi)]^{1/3}. \qquad (5)$$

According to Eqs (4) and (5), the calculations were carried out[6] for the carbon adsorbents for which $\rho' \approx \rho_0$. This relation can be applied, because the effect of adsorption compression in the case of high-affinity type adsorption is completely compensated by the effect of adsorbate loosening due to steric hindrance. The applicability of the slit-shaped pore model was concluded.[6] The results of estimation of the micropore size distribution using the slit-shaped pore model to the carbon adsorbents are independent of the geometric characteristics of the adsorbate molecules and agree with the X-ray small-angle scattering data.[7] According to the considered method, the dependence of the micropore size on the characteristic adsorption energy and affinity coefficient β is given by the equation

$$H\,(\text{nm}) = 10.8(\beta/E)^{2/3}. \qquad (6)$$

Using this equation, the mathematical model that describes development of the microporous structure of the active carbons during their progressive activation was developed.[8,9]

Water vapor adsorption on the microporous carbon adsorbents are characterized by very low values of the differential molar work of adsorption corresponding to volume filling of micropores. The characteristic energy of water vapor adsorption is low because of weak dispersion energies, and the region of micropore filling depends not only on their size range but is also determined to a greater extent by the chemical state of the surface: concentration of the primary hydrophilic adsorption sites. The formation, growth, and agglomeration of clusters from sorbed water molecules occur on the these sites, which results in micropore volume filling.[10] During the formation of a condensation phase, the adsorbate behaves as an extended liquid film.[11,12] When the micropores are saturated, they are filled with the fluidized adsorbate, and after the concave meniscus disappeared, the adsorption phase should experience the action of van der Waals forces and, therefore, a positive hydrostatic pressure. Due to the low adsorption energy, the values of the hydrostatic pressure compression are low. Taking into account the abnormally low water compressibility, they fail to compensate the effect of its loosened packing caused by steric hindrance induced by the commensurable size of the micropores and adsorbate molecules. Therefore, for water the values $\rho'/\rho_0 < 1$ and, as a result, the ultimate sorption micropore volumes are smaller than those for highly sorbed substances.[13,14] When the adsorption energy increases, for instance, due to the oxidation of the active carbons with nitric acid, the adsorbate density increases, resulting in a considerable decrease in differences in the sorption volumes measured with water and highly sorbed hexane.[14]

The ρ'/ρ_0 value for water can be estimated as the ratio of the micropore volume $v^{mi}{}_{H_2O}$ calculated from the data on the density of the normal liquid to the micropore volume found from an adsorptive (for example, benzene) for which ρ' and ρ_0 can be accepted equal:

$$(\rho'/\rho_0)_{H_2O} = v^{mi}{}_{H_2O}/v^{mi}{}_{C_6H_6}. \qquad (7)$$

However, the $v^{mi}{}_{H_2O}$ values could be estimated[13] from the adsorption isotherms of water vapor only for carbons containing virtually no mesopores. Presently, the systematic study of processes of water vapor adsorption on the carbon adsorbents makes it possible to differentiate adsorption in the micropores and adsorption on the mesopore surface[15] and to apply the method considered for determination of the micropore size distribution for the active carbons with the developed micro- and mesoporous structure.

Experimental

Adsorption isotherms of water and benzene vapors were obtained at 293 K on a high-vacuum sorption setup equipped with a quartz spring microbalance with a sensitivity of ~20 μg at the load up to 0.2 g in the interval of relative pressures from 10^{-6} to 1.0. Measurements were carried out with an unchanged weighed sample to exclude the influence of heterogeneity of the product on the results. At first the adsorption isotherm of water vapors and then that of benzene were determined. Evacuation was carried out at 673 K and under a pressure of 10^{-3} Pa until a constant weight was achieved. Measurements were carried out on the ash-free spherical active carbon FAS with the developed micro- and mesoporous structure.

Results and Discussion

Adsorption of benzene vapors. The adsorption isotherms of benzene and water vapor on the FAS active carbon under study are presented in Fig. 2. It can be seen from the adsorption isotherms of benzene that the adsorbent has a well developed mesopore volume filled at $\rho/\rho_s > 0.85$ along with the micropores. To determine their specific surface, the δ-method[16] was used, which is based on analysis of the regions of the isotherms above the *B* point, which reflects such a state when the micropores and the first adsorption layer on the mesopore surface are filled. The difference $a - a_B = \delta$ between the amount adsorbed a above the B point and the amount adsorbed a_B in the B point characterizes adsorption in the second or third adsorption layer. The ultimate capacity of the second and third adsorption layer $a_{m(2;3)}$ is determined from the ratio $a_{m(2;3)} = \delta_0/2.42$, where δ_0 is the amount adsorbed corresponding to the interception point of the linear regions of the δ-plots $\log\delta = \varphi(\log P_s/P)$ with the axis logδ. The specific mesopore surface is determined from the $a_{m(2;3)}$ value and molecular surface $w_0 = 0.304$ nm calculated from the density of liquid benzene under assumption of a spherical symmetry of molecules, because the effects of localization and surface orientation of the molecules characteristic of the first layer are absent in the second and subsequent layers.

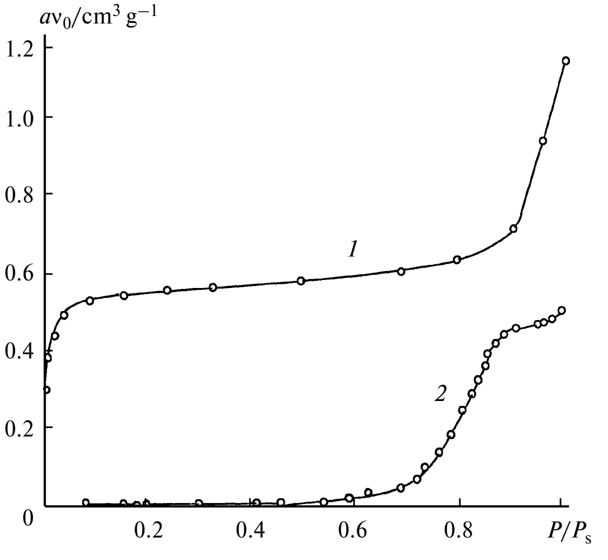

Fig. 2. Adsorption isotherms of benzene (*1*) and water (*2*) vapors at 293 K on the FAS active carbon.

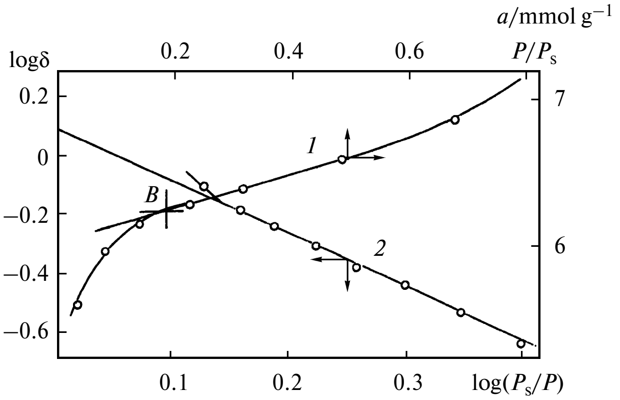

Fig. 3. Region of the adsorption isotherm of benzene vapors (*1*) and the corresponding δ-plot (*2*) in the coordinates $\log\delta - \log P_s/P$.

The amplified region of the isotherm (for determination of the position of the *B* point) and the corresponding δ-plot are shown in Fig. 3.

For $a_B = 6.22$ mmol g^{-1}, $a_{m(2;3)} = 0.52$ mmol g^{-1} and, hence, the specific mesopore surface is the following:

$$S^{me} = a_{m(2;3)} w_0 N_A = 94\ (\mathrm{m^2\ g^{-1}}).$$

For ultimate adsorption in micropores, the amount adsorbed $a_{m(1)}$ in the first layer, where benzene is characterized[17] by planar arrangement of molecules relative to the surface at the molecular surface value $w = 0.40$ nm^2 due to the high adsorption energy, should be subtracted from the amount adsorbed at the *B* point. Then the amount adsorbed in the micropores is the following:

$$a^{mi}{}_{C_6H_6} = a_B - S^{me}(wN_A)^{-1} = 5.83\ (\mathrm{mmol\ g^{-1}}).$$

The parameters of the porous structure of the active carbon determined from the adsorption isotherm of benzene vapors are given below.

w_0 /cm^3 g^{-1}	E_0 /kJ mol^{-1}	H /nm	v^{mi} /cm^3 g^{-1}	S^{me} /m^2 g^{-1}	v^{me} /cm^3 g^{-1}
0.543	18.85	1.52	0.518	94	0.645

Adsorption of water vapor. As can be seen from the data in Fig. 2, the micropore volume is filled with water in the region of high relative pressures. At $P/P_s \approx 0.9$ the isotherm reaches a plateau and then shows an upward turn due to adsorption on the mesopore surface. The amount adsorbed at $P/P_s = 0.95$ ($a^{mi}{}_{H_2O}$ = 26.83 mmol g^{-1}, $a^{mi}{}_{H_2O}$ = 0.483 cm^3 g^{-1}) corresponds[15] to the micropore volume, and the amount adsorbed in the mesopores equals the difference between the amounts adsorbed at $P/P_s = 1$ and $P/P_s = 0.95$ (a^{me} = 2.16 mmol g^{-1}). Taking into account that the ultimate amount of water adsorbed α_s per surface unit of the active carbon mesopores is[15] 23 μmol m^{-2} and corresponds to the formation of 1.5 dense monomolecular layers, one can determine the mesopore surface

$$S^{me}{}_{H_2O} = a^{me}\alpha_s{}^{-1} = 94\ (\text{m}^2\ \text{g}^{-1}).$$

The obtained value coincides with the specific mesopore surface determined by the δ-method from the adsorption isotherm of benzene vapor, indicating that the both methods are adequate and micropore volume values found by these methods are reliable.

The results of estimation of the carbon micropore size from the adsorption isotherm of water vapors are given below.

ρ'/ρ_0	$\bar{A}$	E	$\bar{P}$ /MPa	v''/v_0	F	K	d'	H
	J mol^{-1}						nm	
0.9324	533	557	28.5	0.988	0.681	0.235	0.347	1.48

The difference between the water density in the micropores and the liquid density was determined by Eq. (7) from the found micropore volumes corresponding to the adsorption isotherms of water and benzene vapor. The average differential molar work of adsorption A was determined by graphical integration of the plot $\theta = a/a^{mi}{}_{H_2O} = Q(A)$ in the interval of θ changing from 0.05 to 0.95. For comparison we also present the characteristic adsorption energy from the Dubinin—Astakhov equation[3]

$$\theta = \exp[-(A/E)^n], \tag{8}$$

which well approximates the considered isotherm in the interval θ = 0.58—1.0 at the E value close to $\bar{A}$. The decrease in the molar volume of water due to its adsorption compression compared to the molar volume of the normal liquid (v''/v_0) was determined from the experimental data on water compressibility at 20 °C approximated[18] by the Tait equation

$$1 - v''/v_0 = C\ln(1 + \bar{P}/D), \tag{9}$$

in which the C and D constants are equal to 0.12677 and 2720 and the $\bar{P}$ value calculated by formula (1) was 281 atm (28.5 MPa). This value is by almost an order of magnitude lower than $\bar{P}$ = 222 MPa calculated from the adsorption isotherm of benzene vapor and it corresponds to an insignificant (<1.5%) decrease in the molar volume. The F value determined by Eq. (2) according to the averaged dependence $F = \varphi(K)$ (see Eq.(3)) is conformed with the K ratio of the equivalent diameter of molecules d' to the H pore width corresponding to the packing in the micropores of 4.3 layers of water molecules. For d' = 0.347 nm (see Eq. (5)) it follows from Eq. (4) that the size of the slit-shaped micropores of the active carbon under study equals 1.48 nm. The difference between this value and H = 1.52 nm calculated from the adsorption isotherm of benzene vapor is less than 3%.

Thus, the water density upon saturation can be estimated due to a possibility of determination of the ultimate amount adsorbed in the micropores. A comparison of the opposite effects of adsorption compression and loosening on the adsorbate density gives reliable data on the micropore sizes of the active carbons with the developed micro- and mesoporous structure.

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