Effects of micropore size and chemical nature of the surface of carbon adsorbents on the adsorption isotherms of water vapor

V. V. Gur´yanov,[a] G. A. Petukhova,[b]★ and N. S. Polyakov[b]†

[a]*Elektrostal´skoe Nauchno-proizvodstvennoe Ob´edinenie "Neorganika",
4 ul. K. Marx, 144001 Elektrostal´, Moscow Region, Russian Federation.
Fax: +7 (257) 5 0127*
[b]*A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences,
31 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (495) 952 5308. E-mail: petukhova@phyche.ac.ru*

Adsorption of benzene and water vapors on activated carbons of various microporous structure was studied. The values of the characteristic energy of adsorption of benzene and water vapors were compared and the affinity coefficients β_{H2O} for carbons with various degrees of activation were calculated. The values of the β_{H2O} coefficient for carbons with the same degrees of oxidation remain constant. This makes it possible to use the experimental data on benzene adsorption for prediction of the behavior of microporous activated carbons towards adsorption of water vapor.

Key words: activated carbons, theory of volume filling of micropores, characteristic energy of adsorption of benzene and water vapors, affinity coefficient.

Adsorption of the water vapor by carbon adsorbents (CA) depends on both the amount of primary oxygen-containing adsorption sites and on the micropore size.[1-5] It is known[2] that the micropores are filled at increasingly higher pressures when the concentration of the primary adsorption sites (PAS) decreases, for example, during surface hydrophobization. At the same time, the micropore volume is filled at lower pressures when the PAS concentration is increased, particularly during CA oxidation.[4] Meanwhile, it was found that the narrower micropores, the lower pressure is required for their filling with water.[3]

It was of interest to study water adsorption on adsorbents with a similar surface nature and a close number of PAS to elucidate the effect of porous structure and to weight the possibility to use parameters of the microporous structure determined by a reference substance, benzene, for estimating the degree of filling of the micropores of activated carbons (AC) with water. Benzene adsorption depends on the features of the porous structure only and is independent of PAS.

Experimental

A series of ashless spherical AC (FAS trademark) prepared by progressive gas-vapor activation was studied. These micro- and supermicroporous sorbents synthesized from furfural contain no micropores in fact. The adsorption isotherms of benzene

† Deceased.

and water vapors were studied at 293 K on a high-vacuum sorption setup with a spring quartz microbalance with a sensitivity of ~20 μg at loading up to 0.2 g in the range of relative pressures from 10^{-6} to 1.0. All samples were preliminarily evacuated at 673 K and a pressure of 10^{-3} Pa to a constant weight. The number of oxygen-containing functional groups on the CA surface was estimated by chemical titration with the use of the method of selective neutralization of these groups with bases of various strength.[4,6]

Results and Discussion

Parameters of the AC microporous structure were calculated from the adsorption isotherms of benzene vapor according to the equations of the theory of volume filling of micropores (TVFM).[7] As can be seen in Table 1, a wide range of the micropore volumes W_0 (0.36—1.28 cm^3 g^{-1}) is typical of AC of the FAS type and the values of the characteristic energies of the benzene adsorption vary from 26 to 10 kJ mol^{-1}, *i.e.*, they cover virtually the whole region for sorbing micro- and supermicropores. According to the model of infinite slit-shaped pores, the micropore size was determined from the equation[11,12]

$$H = 10.8\beta^{2/3}E^{-2/3}, \tag{1}$$

where H/nm is a micropore width; E/kJ mol^{-1} is the characteristic energy of adsorption; 10.8 (nm kJ$^{2/3}$ mol$^{2/3}$) is the numerical coefficient; β is the similarity coefficient, which relates the characteristic energy of adsorption of

Table 1. Parameters[a] of porous structure of AC

Sample FAS	$W_{0,1}$	$W_{0,2}$	$\bar{E}_0$[b]	H	V_{Me}	S_{Me}
	cm³ g⁻¹		/kJ mol⁻¹	/nm	/cm³ g⁻¹	/m² g⁻¹
FAS-1	0.36	—	26.2	1.22	0.39	50
FAS-2	0.45	—	23.0	1.33	0.45	55
FAS-3	0.53	—	20.5	1.44	0.47	62
FAS-4	0.71	—	18.0	1.57	0.51	79
FAS-5	0.59	0.42	13.3	1.92	1.26	188
FAS-6	0.60	0.53	12.4	2.02	0.75	150
FAS-6′[c]	0.56	0.50	12.3	2.02	0.78	150
FAS-7	0.40	0.48	11.5	2.12	—	147
FAS-8	0.51	0.77	10.2	2.30	2.76	364

[a] $W_{0,1}$ and $W_{0,2}$ are the micropore and supermicropore volumes; $\bar{E}_0$ is the characteristic energy of benzene vapor adsorption, H is the width of micropores, V_{Me} and S_{Me} are the volume and specific surface area of mesopores, respectively.
[b] Parameter was calculated for samples FAS-1—FAS-4 according to the one-member Dubinin—Radushkevich equation,[7,8] for samples FAS-5—FAS-8 as the weighted mean value[9] of the parameters evaluated according to the two-member equation of TVFM.[7,10]
[c] Modified sample.

the reference adsorptive (benzene), E_0, to that of the adsorptive under study, $E = \beta E_0$. For adsorption of benzene vapor $\beta = 1$. As can be seen in Table 1, the micropore width increases from 1.22 to 2.30 nm with decreasing E_0.

The AC samples presented in Table 1 can be subdivided into two groups, namely, microporous adsorbents, whose adsorption isotherms are described by the Dubinin—Radushkevich equation,[8] and supermicroporous adsorbents for which the two-member TVFM equation is applicable.[7,10] A moderate development of the mesopore volume and surface is usually typical of microporous AC. Supermicroporous AC have a highly developed mesoporous structure.

In spite of a wide range of the porous structure parameters, the concentration of the surface oxygen-containing groups remains virtually constant and is equal to 0.12±0.03 mmol g⁻¹, which fact is likely due to a similarity of the preparation conditions for all the FAS samples.

Typical adsorption isotherms of water vapor on micro- and supermicroporous AC are shown in Fig. 1. Isotherm *3* corresponds to the hydrophobized sample FAS-6′ prepared by modification of the surface[2] of sample FAS-6. The parameters of the carbon microporous structure do not change upon this hydrophobization in fact, whereas the number of the oxygen-containing functional groups at the surface of pores decreases by 5—6 times. Negligible adsorption values at $P/P_s < 0.5$ are typical of all the isotherms because of high hydrophobicity of the surface and a sharp raise in the region of micropore volume filling.

Earlier[13] it was shown that the Weibull distribution that leads to the Dubinin—Astakhov equation[14] is appli-
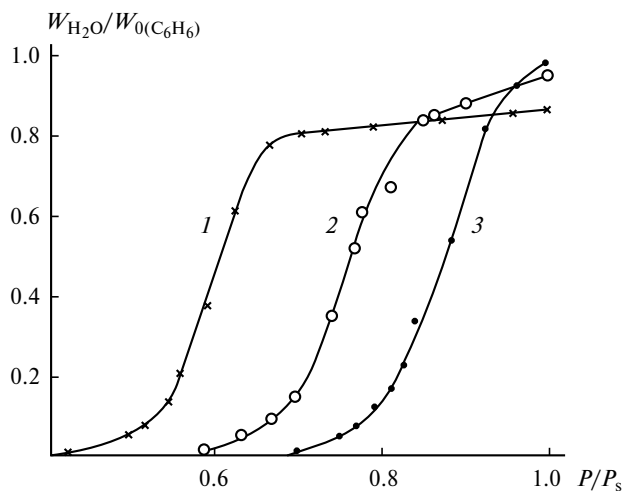

Fig. 1. Adsorption isotherms of water vapor on samples FAS-2 (*1*), FAS-6 (*2*), and hydrophobized sample FAS-6′ (*3*).

cable to the adsorption isotherms of water vapor on microporous adsorbents:

$$\theta = \exp[-A/(E_0\beta)]^n, \qquad (2)$$

where θ is the degree of micropore filling, A is the differential molar work of adsorption, n is the integral exponent in the Weibull distribution. The experimental adsorption isotherms presented in Fig. 1 can be described by equation (2). The exponent n decreases from eight to four with the increasing micropore size and this is likely due to both an increase in the nonuniformity of the microporous structure upon the deep activation of AC and to a lower concentration of water molecules in large pores. As the parameter n characterizes the degree of ordering of mol-

Table 2. Characteristics of the adsorption isotherms of warer vapor on AC

Sample FAS	$\bar{E}_0$ /kJ mol^{-1}	$P/P_{s(H_2O)}$ at $\theta = 0.368$	E_{H_2O} /kJ mol^{-1}	$\beta_{H_2O} = E_{H_2O}/\bar{E}_0$	$V_{s(H_2O)}/V_{s(C_6H_6)}$
FAS-1	26.2	0.57	1.44	0.055	0.85
FAS-2	23.0	0.59	1.27	0.055	0.87
FAS-3	20.5	0.61	1.18	0.058	0.90
FAS-4	18.0	0.63	1.13	0.065	0.82
FAS-5	13.3	0.73	0.80	0.057	1.49
FAS-6	12.4	0.74	0.73	0.059	0.94
FAS-7	11.5	0.77	0.63	0.055	0.90
FAS-8	10.2	0.81	0.52	0.051	1.27

ecules, then the mobility of molecules is limited during adsorption in small micropores because of location of most molecules on PAS. When the micropore sizes increase and hence the water clusters grow, the properties of the adsorbate molecules approach to those of a liquid and the parameter decreases.

It can be seen in Table 2 that the relative pressures corresponding to the characteristic point $\theta = 0.368$ regularly shift to higher pressures from 0.57 to 0.81. The characteristic energies of benzene vapor decrease in parallel to an increase in the micropore size. Taking into account that the Dubinin—Radushkevich (DR) equation[8] is a special case of the Dubinin—Astakhov equation (2) with $n = 2$, we can compare the characteristic energies of benzene vapor adsorption calculated according the DR equation with the characteristic energies of water adsorption determined according to equation (2). Let us designate the calculated ratio $E_{H_2O}/\bar{E}_0$ as β_{H_2O}. As can be seen in Table 2, the β_{H_2O} values remain constant and equal to 0.057 ± 0.007. Since β_{H_2O} is constant for all the AC, it is possibile to substitute the characteristic energies of the benzene adsorption to equation (2) and to find the P/P_s values for θ. Hence, we can construct the adsorption isotherms of water vapor. Table 2 also presents the ratios of the limiting adsorption volumes estimated from the adsorption of water and benzene.

Table 3 shows the results of calculation for the adsorption isotherms of water vapor based on the parameters W_0 and $\bar{E}_0$, which were estimated with respect to benzene, as well as the experimental data. The P/P_s values for various θ were calculated according to the equation

$$P/P_s = 1/\exp[E_0\beta_{H_2O}(-\ln\theta)^{1/n}/(RT)], \qquad (3)$$

which corresponds to Eq. (2) taking $\beta_{H_2O} = 0.057$ and $n = 6$ (as the mean value upon variation of n from eight to four).

As follows from Table 3, the P/P_s values for various θ increase regularly with the decreasing characteristic energy of benzene adsorption. The experimental and calculated values are in good agreement, confirming the applicability of the TVFM approach for estimation, based on the parameters of the microporous structure, of regions of steep rise on the adsorption isotherms of water vapor corresponding to the volume filling of micropores.

Figure 2 presents the calculated and experimental isotherms on the adsorbents one of which (FAS-1) contains only small micropores and another (FAS-8) contains large supermicropores along with small micropores. The calculated and experimental isotherms coincide in fact. However, the calculated isotherm for the small-pore sample flattens out at $\theta = W/W_0$ that is close to 0.8, since the

Table 3. Comparison of the calculated (I) and experimental (II) relative pressures (P/P_s) of water vapor for various fillings θ of the AC micropore volume

| Sample	P/P_s values at θ											
	0.05		0.10		0.25		0.50		0.70		0.75	
	I	II	I	II	I	II	I	II	I	II	I	II
FAS-1	0.48	0.48	0.51	0.50	0.52	0.55	0.56	0.57	0.60	0.62	0.61	0.65
FAS-2	0.52	0.51	0.54	0.54	0.57	0.56	0.60	0.61	0.64	0.64	0.65	0.66
FAS-3	0.56	0.55	0.58	0.57	0.60	0.60	0.64	0.62	0.67	0.62	0.68	0.63
FAS-4	0.60	0.54	0.61	0.56	0.64	0.61	0.67	0.65	0.70	0.72	0.71	0.76
FAS-5	0.69	0.60	0.70	0.65	0.72	0.71	0.75	0.75	0.77	0.77	0.78	0.77
FAS-6	0.71	0.64	0.72	0.68	0.74	0.72	0.76	0.77	0.78	0.80	0.82	0.84
FAS-7	0.72	0.69	0.73	0.72	0.75	0.77	0.78	0.81	0.80	0.83	0.80	0.85
FAS-8	0.75	0.72	0.76	0.77	0.78	0.77	0.80	0.83	0.82	0.84	0.82	0.85
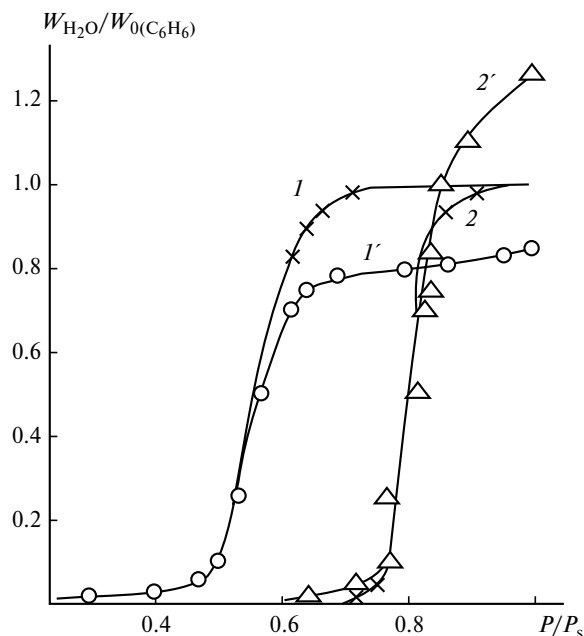
Fig. 2. Calculated (*1, 2*) and experimental (*1´, 2´*) adsorption isotherms of water vapor on AC with micropore volume of 0.36 (*1, 1´*) and 1.28 (*2, 2´*) cm^3 g^{-1}.

adsorption volume measured with respect to water is substantially lower than the W_0 value estimated with respect to benzene. This is due to steric hindrances in micropores, which prevent the formation of molecular packings similar to those in common liquids.[15]

As seen in Table 2, the lower $V_{s(H_2O)}$ values compared to $V_{s(C_6H_6)}$ are typical of most samples. For supermicroporous adsorbents with the most developed surface area and essential mesopore volume (samples FAS-5 and FAS-8), $V_{s(H_2O)} > V_{s(C_6H_6)}$. Respectively, the experimental isotherm of sample FAS-8, which describes adsorption not only in micropores but also in mesopores, is positioned above the calculated values in the $P/P_s > 0.85$ region.

Water adsorption on AC is generally determined by the energy of specific interactions of the polar molecules with the surface oxygen-containing groups and the formation of hydrogen bonds. Therefore, the β_{H_2O} values are functions of the PAS concentration. For instance, the β_{H_2O} value decreases nearly by half from 0.057 to 0.031 after the additional hydrophobization of the FAS carbon, resulting in the decrease of the content of the surface oxygen-containing groups from 0.12 to 0.02—0.04 mmol g^{-1}. As a result, the micropore volume in the hydrophobized sample FAS-6´ with the parameters of the microporous structure, which are similar to those of sample FAS-6, is filled at substantially higher relative pressures (see Fig. 1).

Hence, when the micropore volume of AC is filled by water molecules, the affinity coefficient depends to a significant extent on the chemical state of the surface, namely, the number of the functional oxygen-containing groups. The β_{H_2O} value remains constant for carbons with similar technological preparation parameters and, hence, with the same degree of the surface oxidation. This makes it possible to use the TVFM for the evaluation and prediction of the AC adsorption properties during adsorption of water vapor.

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