The influence of low-temperature oxidation of active carbons by nitric acid on their physicochemical properties

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The influence of oxidation by nitric acid on the character of oxygen-containing functional surface groups and porous structure of active carbons is considered. Adsorption properties of the initial and oxidized carbons are studied using adsorption isotherms of vapor of *n*-hexane and polar substances (water and methanol).

Key words: active carbons, oxidation; surface chemistry; *n*-hexane, water, methanol, adsorption.

Oxidized carbons (OC) are known to possess a complex of valuable properties. They are used as cation-exchangers and are characterized by the high selectivity manifested in various systems.[1–3] They can be used as catalysts of protolytic and redox processes.[4–6] The oxidation of active carbons improves their sorption capacity with respect to various polar substances (in particular, to alcohols and water).[7,8] In the majority of the works on oxidation of carbon materials, the OC obtained were characterized only by their ability to absorb alkali. However, the main physicochemical properties of carbons are first of all related to their porous structure (the content of micro-, meso-, and macropores and their size distribution) and the nature of their surface.

The existence of various functional groups (carboxyl, phenol, alcohol, carbonyl, *etc.*) on the surface of oxidized carbon materials was established by various chemical and physicochemical methods.[9–11] For example, it has been shown previously[8] that four types of groups exist on the OC surface, and the ratio of strongly and weakly acidic carboxyl, phenol, and alcohol groups is 1 : 1 : 1 : 1. The analysis of the data of the other authors[1,9,12] indicates that substantial differences in the character of functional groups are observed even for carbons obtained on the same basis and oxidized by the same oxidants. Oxidized carbons can contain all groups indicated in different and not always equivalent amounts.[1,10,12–15]

In addition, there is no single opinion about the effect of oxidation and its conditions on the porous structure of the carbons obtained. For example, it has been suggested[16] that the oxidation of carbons by nitric acid exerts almost no effect on the limiting sorption volume. According to the published data,[17] the volume of pores can increase in oxidation, while the authors of Ref. 18 consider that the microporous volume decreases noticeably depending on the degree of oxidation. The data on the change in the size distribution of micro- and supermicropores for the carbons oxidized by HNO_3 at low temperatures and on their sorption properties are almost nonexisting.

Adsorption of polar substances, such as water and alcohols, occurs when hydrogen molecules are bound on the surface of oxygen-containing complexes, which are present at the boundary of carbon layers or in the sites of defects on walls of pores. The role of different surface functional groups in the adsorption of water is estimated.[19] It is shown that the number of primary adsorption centers (PAC) calculated by the Dubinin—Serpinskii equation (DS-2)[20] correlates (and often coincides in value) with the number of strongly acidic carboxyl and phenol groups. Their overall amount is not greater than 30 % of the total number of acidic groups on the carbon surface. The effect of the modification of the active carbon (AC) surface resulting in their hydrophobization has been previously studied in detail.[19,21,22] It is of interest to study the adsorption of polar substances (water and methanol) by AC samples modified toward the hydrophilization of the surface.

The purpose of this work is to study the character of the oxygen-containing functional groups on the surface of AC oxidized by nitric acid and the effects of oxidation and adsorbability of water vapor and methanol on the micro- and mesoporous structure of AC.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 1132—1137, May, 1996.

Experimental

Preparation of oxidized carbons. Three types of AC produced in Europe are considered as initial carbons: UO-3, PC-94, and CMS-H2. The low-temperature oxidation of AC was performed by a 50 % solution of HNO_3. Nitric acid was poured into a porcelain flask containing a sample of AC (10 g). The mixture was heated for 3 h in a water bath until boiling of the solution. When HNO_3 was added to the flask with the PC-94 sample, the suspension was warmed to ~100 °C for the first minutes, and nitrogen oxides evolved vigorously (which was not observed in the oxidation of UO-3 and CMS-H2). When the oxidation ceased, all samples were washed with distilled water to the neutral reaction (pH 6.5) in the wash water and dried at 105 °C until a constant mass was achieved.

Study of the surface chemistry, porous structure, and adsorption properties of carbons. The method of selective neutralization by bases of different strengths was used to characterize different functional groups.[8,19] Solutions with carbons were titrated with $NaHCO_3$, Na_2CO_3, and NaOH. Sodium bicarbonate neutralizes the strongest acidic centers, soda neutralizes both strongly and weakly acidic carboxyl groups ($COOH^-$), and alkali neutralizes phenol groups (OH^-) along with the first and second groups mentioned. Since the treatment of AC with nitric acid results, as a rule, in the formation of a considerable amount of weakly acidic carboxyl and phenol groups, other groups were not considered.

The porous structure was studied by the adsorption of *n*-hexane vapor, which in this case turned out to be more suitable than the benzene that is often used for the characterization of the porous structure (because an additional interaction of π-bonds of C_6H_6 molecules with hydroxyl groups is possible on the OC surface). Isotherms of equilibrium adsorption of hexane, water, and methanol vapor were determined at 293 K on a high-vacuum sorption installation with a quartz spring microbalance (sensitivity from 2 to 6 μm with loading lower than 0.1 g).

Results and Discussion

Surface chemistry. Analysis of the data of selective neutralization of acidic oxygen-containing groups makes it possible to estimate the amounts of carboxyl and phenol groups on the surface of the initial and oxidized carbons. The results of the study of the chemical state of the surface of the carbons studied are presented in Table 1.

Table 1. Content of strongly and weakly acidic carboxyl and hydroxyl functional groups on the surface of AC

AC	Σ /mmol L^{-1}
UO-3	0.07
UO-3(ox)	1.61
PC-94	0
PC-94(ox)	1.96
CMS-H2	0.02
CMS-H2(ox)	1.81
SKT	0.40
SKT(ox)	1.90
BAU(ox)	2.00
FAU(ox)	2.10

The parameters of some initial and oxidized domestic AC (SKT, BAU, and FAU trade marks (Russia)) are presented in Table 1 for comparison.[1,19]

As seen from the data in Table 1, based on the surface state, all initial samples of the AC studied can be classified as sufficiently hydrophobic, because they virtually contain neither strongly nor weakly acidic carboxyl groups and contain a very insignificant amount of phenol groups (OH^-). Acidic functional groups in different ratios are present on the surface of the domestic active carbon SKT. Polyfunctional samples containing all groups mentioned are usually formed as a result of the oxidation of AC by nitric acid; for example, the oxidized samples SKT(ox), BAU(ox), and FAU(ox) are characterized by a wide set of surface functional groups. In principle, it is difficult to achieve the predomination of some functional groups on the OC surface. Samples with the predominant content of phenol groups can be obtained due to the decomposition of carboxyl groups upon thermal treatment. These are precisely the phenol groups that predominate on the OC surface after the oxidation of UO-3, PC-94, and CMS-H2 samples. It is unambiguous that the composition of the groups on the OC surface is associated with the initial raw material for AC and, perhaps, with the methods for their preparation. The highest degree of oxidation, as follows from the data in Table 1, is achieved in the case of the PC-94 sample.

Porous structure. It was of interest to follow the effect of the oxidation by nitric acid on the parameters of the porous structure of AC. The general forms of the adsorption isotherms of hexane differ insignificantly for the initial and oxidized AC: the oxidation of the UO-3 and CMS-H2 samples results in a small decrease in the limiting volume of the sorption space V_s (the value corresponding to $p/p_s = 1$), and the oxidation of PC-94 results in an increase in V_s.

To estimate the microporous structure of carbons, we used the classic equations of the volume micropore filling theory (VMFT), the Dubinin—Radushkevich equation (DR)[23]

$$a = (W_0/V)\cdot\exp\{-[A/(\beta E_0)]^2\} \tag{1}$$

and its binomial modification

$$a = (W_{01}/V)\cdot\exp\{-[A/(\beta E_{01})]^2\} + \\ + (W_{02}/V)\cdot\exp\{-[A/(\beta E_{02})]^2\}. \tag{2}$$

Here a/mmol g^{-1} is the amount of the absorbed substance at the temperature T and the relative pressure p/p_s; V is the molar volume of the adsorbate; $A = RT\ln(p_s/p)$ is the differential molar adsorption work function; E_0 is the characteristic adsorption energy of the standard substance (benzene) vapor; and β is the similarity coefficient of the substance studied (hexane) relative to the substance accepted as standard ($\beta = E/E_0$, where E is the characteristic adsorption energy of vapor of the substance studied); for hexane, $\beta = 1.29$ (calculated as the ratio of parachors of hexane and benzene).

Table 2. Parameters of the micro- and mesoporous structures determined from the adsorption isotherms of hexane vapor

Parameter	UO-3	UO-3(ox)	PC-94	PC-94(ox)	CMS-H2	CMS-H2(ox)
W_{01}/cm^3 g^{-1}	0.452	0.401	0.485	0.490	0.282	0.251
W_{02}/cm^3 g^{-1}	0.088	0.163	—	—	—	—
E_{01}/kJ mol^{-1}	20.38	19.65	24.30	20.21	27.71	27.73
E_{02}/kJ mol^{-1}	7.51	7.64	—	—	—	—
x_{01}/nm	0.49	0.51	0.41	0.49	0.36	0.36
x_{02}/nm	1.33	1.31	—	—	—	—
$W_0°$/cm^3 g^{-1}	0.547	0.574	0.486	0.480	0.281	0.251
E_0/kJ mol^{-1}	17.74	17.33	24.64	20.56	28.70	27.08
x_0/nm	0.56	0.58	0.42	0.48	0.35	0.37
δ/nm	0.26	0.43	0.18	0.19	$7.85 \cdot 10^{-2}$	$2.01 \cdot 10^{-2}$
V_{meso}/cm^3 g^{-1}	0.071	0.042	0.030	0.057	0.011	0.023

The following parameters of the porous structure of carbons can be determined from these equations: W_{01} and W_{02}, the volumes of micro- and supermicropores, respectively; E_{01} and E_{02}, the characteristic adsorption energies of the standard substance in micro- and supermicropores related to the mean half-width of micropores (x_0) by the correlation

$$x_0 = k/E_0,$$

where k is the coefficient that can be calculated by several known expressions. The value k = 10 kJ mol^{-1} (see Ref. 24) is appropriate with high accuracy.

The Dubinin—Stoeckli equation (DS)[24] is development of the VFMT.

$$W = \frac{W_0^\circ}{2\sqrt{1+2m\delta^2A^2}}\exp\left(\frac{mx_0^2A^2}{1+2m\delta^2A^2}\right)\times$$
$$\times\left[1+\mathrm{erf}\left(\frac{x_0}{\delta\sqrt{2\pi}\cdot\sqrt{1+2m\delta^2A^2}}\right)\right] \tag{3}$$

In addition to the volume ($W_0°$) and size (half-width) of micropores (x_0), this equation contains a third parameter (δ) that characterizes the volume distribution of micro- and supermicropores; $m = [1/(\beta k)]^2$. Equations (1)—(3) were used for the analysis of the experimental isotherms in the range of p/p_s from $1 \cdot 10^{-5}$ to 0.25, because this is precisely the range in which micro- and supermicropores are filled.

The volume of mesopores V_{meso} was calculated from the correlation

$$V_{meso} = V_s - W_0°. \tag{4}$$

The parameters of the porous structure of the carbons studied are presented in Table 2. It should be mentioned that the initial sample of CMS-H2 is a microporous sorbent with a very narrow size distribution of micropores (δ = 0.0785 nm at x_0 = 0.36 nm) and it contains almost no mesopores, which is caused by the method of the preparation of molecular-sieve carbon adsorbents. The degree of nonuniformity of the microporous structure and the average size of micropores increase in the following series: CMS-H2, PC-94, and UO-3. For example, the adsorption isotherm for the PC-94 sample is well described by both the monomial DR equation (see Eq. (1)) and the DS equation (see Eq. (3)) (δ = 0.18 nm). The UO-3 sample contains a small amount of supermicropores along with micropores (the isotherm is described by the binomial DR equation, see Eq. (2)), and the degree of the size distribution of micropores δ is 0.26 nm according to the DS equation (see Eq. (3)).

As can be seen from the data in Table 2, the oxidation exerts an effect on the size distribution of micro- and supermicropores and on the volume of mesopores. The low-temperature oxidation of the microporous CMS-H2 sample by nitric acid results in a decrease in the limiting sorption volume and decomposition of some micropores, transforming them into mesopores. In the case of PC-94, the average size of micropores increases, evidently due to the decomposition of some fine micropores. The substantial increase in the volume of supermicropores (W_{02}) due to the decomposition of some micropores themselves (W_{01}) is more pronounced in the case of UO-3. This results in a sharp increase (almost twofold) in the nonuniformity of the microporous structure of this carbon.

Thus, it follows from the analysis of the parameters of the DR and DS equations that the oxidation of AC results in the transformation of some micropores into supermicropores and mesopores, and the nonuniformity of the microporous structure also increases in the case of carbon UO-3.

Adsorption of water vapor and methanol. For comparison, let us consider how the oxidation of the samples studied by nitric acid affects the values of the limiting sorption volume V_s upon the adsorption of vapor of nonpolar hexane and polar substances (methanol and water). The analysis of the data presented in Table 3 shows that for all sorbents the oxidation by nitric acid results in an increase in the V_s values upon the adsorption of vapor of polar substances, while V_s increases only for PC-94 upon the adsorption of hexane, and a small decrease in the limiting sorption volume is observed for the UO-3 and CMS-H2 samples. The almost complete coin-

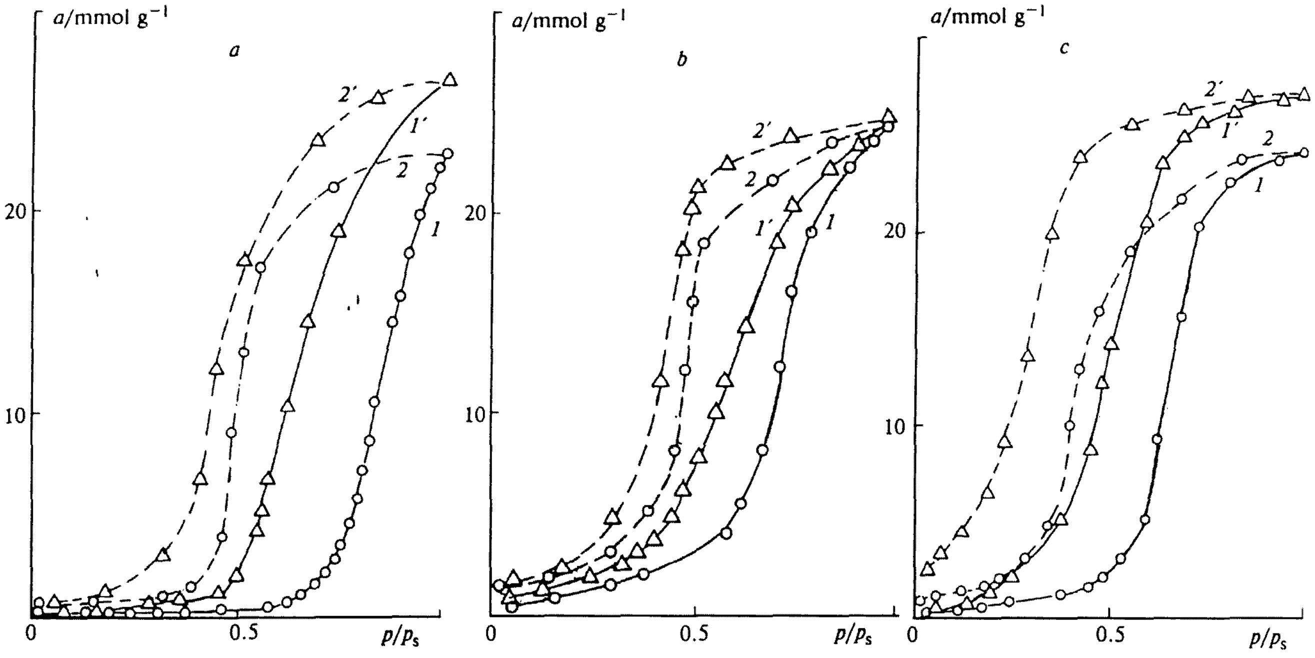

Fig. 1. Isotherms of adsorption (*1*, *1'*) and desorption (*2*, *2'*) of water vapor by the initial (*1*, *2*) and oxidized (*1'*, *2'*) active carbons UO-3 (*a*), PC-94 (*b*), and CMS-H2 (*c*).

cidence of the V_s values upon the sorption of hexane and methanol is observed for the carbon molecular sieves CMS-H2 with the uniform microporous structure and small sizes of micropores, and the ratio of the degree of filling of the sorption space with water to that with hexane increases from 0.74 to 0.90.

The surface of all initial samples contains almost no oxygen-containing acidic surface complexes, *i.e.*, PAC. As can be seen from Fig. 1, this is manifested by low *a* values for the initial regions of the adsorption isotherms of water vapor and results in an incomplete filling (by 68—85 %) of the sorption space with water. The degree of filling was estimated from the adsorption of hexane (see Table 3).

At the same time, the adsorbability of water and parameters of the porous structure, in particular, those of micro- and supermicropores, are related.[25] The effect of the size of micro- and supermicropores on the shift of the adsorption isotherms of water vapor along the p/p_s axis and the *c* parameter of the DS-2 equation (see Ref. 19), which describes the adsorption of water by AC in a wide range of relative pressures, is established. The shift of the isotherms toward the increase in the p/p_s values is proportional to the size of micropores, and the kinetic constant *c* is inversely proportional to their size and tends to unity on going from micropores to supermicropores to mesopores.

A similar situation is observed in the given case as well. The existence of supermicropores ($x_{02} \approx 1.3$ nm) in the UO-3 sample and the nonuniformity of the microporous structure ($\delta = 0.26$ nm) explains the fact that the adsorption isotherm of water "rises" at high relative pressure (~0.85). As the size of micropores decreases and the degree of their uniformity increases, the form of the isotherms of the initial samples changes from the stretched form, as in the case of UO-3 (see Fig. 1, *a*), to the more convex S-like one, as for CMS-H2 (see Fig. 1, *c*).

The oxidation of the AC results in a noticeable "rise" of the initial regions and the shift of the adsorption isotherms of water toward the lower relative pressures.

The adsorption isotherms of methanol vapor by AC differ sharply from those for water and are identical to the adsorption isotherms of hexane vapor, *i.e.*, they have convex forms (Fig. 2, *a*—*c*). It is evident that the existence of the methyl group is sufficient for the predominant dispersion interaction in the case of methanol molecules. This results in the I type (according to the BDDT classification)[26] of the adsorption isotherms of methanol. At the

Table 3. Values of limiting sorption volumes (p/p_s = 1)

AC	V_s/cm^3 g^{-1}			V_s(MeOH)/V_s(C_6H_{14})	V_s(H_2O)/V_s(C_6H_{14})
	C_6H_{14}	MeOH	H_2O		
UO-3	0.611	0.513	0.415	0.84	0.68
UO-3(ox)	0.606	0.584	0.485	0.96	0.80
PC-94	0.515	0.477	0.442	0.93	0.85
PC-94(ox)	0.547	0.503	0.446	0.92	0.82
CMS-H2	0.293	0.273	0.218	0.93	0.74
CMS-H2(ox)	0.274	0.277	0.247	1.00	0.90

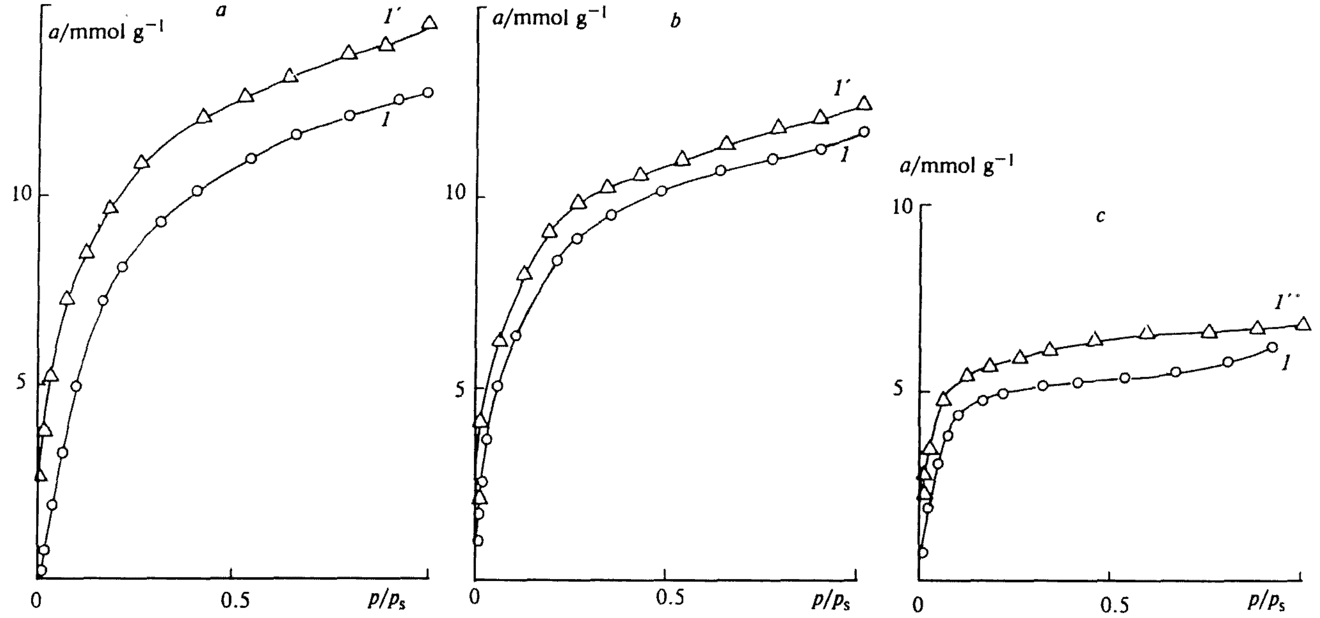

Fig. 2. Isotherms of adsorption of methanol vapor by the initial (*1*) and oxidized (*1'*) active carbons UO-3 (*a*), PC-94 (*b*), and CMS-H2 (*c*).

same time, some peculiarities related to the specific interaction upon the adsorption of methanol are manifested.

First, the oxidation of the AC, *i.e.*, an increase in the number of acidic surface groups, results in an enhancement of the degree of filling of the adsorption space of micropores for methanol compared to the initial carbons, as shown above.

Second, the contribution of specific interactions depends on the peculiarities of the porous structure of AC. The adsorption isotherms of methanol vapor are presented in Figs. 3 and 4 in the coordinates of the linear DR equation for the range of relative pressures from $1 \cdot 10^{-4}$ to 0.2, and the parameters of the DR and DS equations are presented in Table 4. The similarity coefficient β for

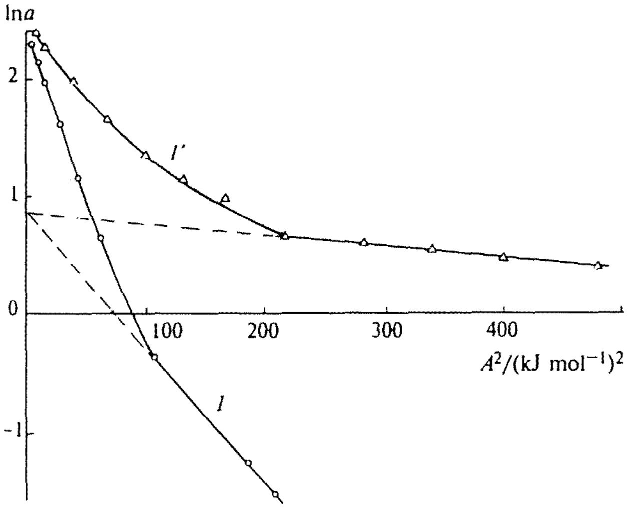

Fig. 3. Isotherms of adsorption of methanol vapor in the coordinates of the binomial DR equation for the initial (*1*) and oxidized (*1'*) carbons UO-3.

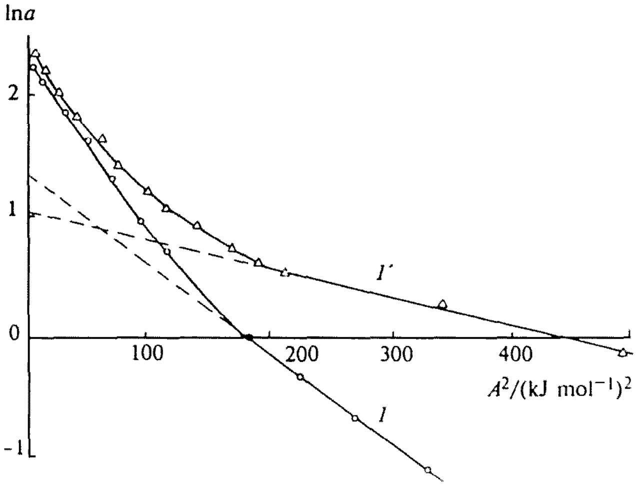

Fig. 4. Isotherms of adsorption of methanol vapor in the coordinates of the binomial DR equation for the initial (*1*) and oxidized (*1'*) carbons PC-94.

Table 4. Parameters of the microporous structure determined from the adsorption isotherms of methanol vapor

Parameter	UO-3	UO-3(ox)	PC-94	PC-94(ox)	CMS-H2	CMS-H2(ox)
W_{01}/cm^3 g^{-1}	0.098	0.096	0.153	0.110	0.242	0.257
W_{02}/cm^3 g^{-1}	0.403	0.403	0.320	0.333	—	—
E_{01}/kJ mol^{-1}	20.20	63.64	27.76	45.21	21.28	28.23
E_{02}/kJ mol^{-1}	11.63	16.37	13.78	17.75	—	—
W_0°/cm^3 g^{-1}	0.502	0.573	0.442	0.495	0.240	0.258
E_0/kJ mol^{-1}	12.20	17.10	16.74	16.82	21.26	28.05
δ/nm	0.184	0.347	0.164	0.270	$3.05 \cdot 10^{-2}$	$3.97 \cdot 10^{-2}$

methanol is calculated as the ratio of the parachors for methanol and benzene and is equal to 0.45.

As seen from Figs. 3 and 4, the adsorption isotherms of methanol vapor for the carbons (both initial and oxidized) are well approximated by two linear regions, *i.e.*, by the binomial DR equation. For the oxidized samples, the extremely high values of the characteristic adsorption energy E_{01} (~45 and 64 kJ mol^{-1}) correspond to the small values of the volume of micropores themselves W_{01}. This is caused by an increase in the fraction of the adsorption energy due to hydrogen bonds at low pressures. The following regularity is evident: when the size of micropores decreases and the degree of uniformity increases, the characteristic adsorption energy E_{01} and, hence, the contribution of specific interactions decrease. If the size of micropores is comparable with that of methanol molecules, as in the case of the initial and oxidized samples of CMS-H2, the contribution of dispersion interactions is unambiguously predominant. Therefore, the satisfactory convergence of the DR and DS parameters estimated from the adsorption isotherms of methanol and hexane (*cf.* Tables 2 and 4) is observed.

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Thus, the oxidation of three different AC results in the chemical modification of their surface to form a considerable amount of oxygen-containing functional surface groups, phenol groups being predominant.

The low-temperature oxidation of the carbons by nitric acid slightly changes the porous structure. The oxidation by HNO_3 exerts the greatest effect on the active carbon containing all varieties of pores (micro-, supermicro-, meso-, and, naturally, macropores). The parameters of the porous structure estimated by the DR equation testify to the change in the ratio between the volumes of micro-, supermicro-, and mesopores in the oxidation process, and the results obtained from the DS equation testify to the enhancement of the nonuniformity of the microporous structure.

Dispersion interactions are the major ones in adsorption of methanol on AC, and the mathematical apparatus of VFMT makes it possible to describe the adsorption of methanol vapor by carbons with different degrees of oxidation of the surface. It is evident that an increase in the size of molecules on going from H_2O to MeOH is sufficient for the predomination of the energy of the adsorption caused by the dispersion interaction rather than the adsorption due to hydrogen bonds, even despite the presence of the OH^- group in both adsorbates. In addition to the chemical state of the surface, such parameters of the porous structure of active carbons as the size of micropores and their volume distribution (dispersion) are important factors that affect the ratio of the dispersion and specific interactions.

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Received October 19, 1995;
in revised form November 27, 1995