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The mechanism of the adsorption of water molecules on carbon adsorbents

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Abstract. **The results of studies on the mechanism of the adsorption of water molecules by nonporous and microporous carbon adsorbents carried out using various physicochemical methods are surveyed. The influence of the chemical state of the surface and of the porous structure of adsorbents on the heat of adsorption and the mechanism of filling of the carbon surfaces of micro- and mesopores of carbon adsorbents are analysed. The nature of the primary adsorption sites and the influence of the adsorption of water molecules on the X-ray diffraction parameters (microcrystalline structure) of carbon adsorbents are studied. The methods of investigation of the porous structure and chemical state of the surface of carbon adsorbents based on the analysis of water vapour adsorption isotherms are considered. The bibliography includes 80 references.**

I. Introduction

The adsorption of nonpolar molecules, in particular argon, krypton, nitrogen, oxygen, carbon dioxide, and various hydrocarbons on carbon adsorbents (CA) has been studied rather extensively. These adsorbable substances are widely used to determine the parameters of the porous structures and adsorption properties of CA.[1] For example, argon is used for determining the specific surfaces of solids having low specific surfaces; carbon dioxide is used to characterise ultramicroporous adsorbents, including coal. The 'subtraction' method developed in recent years, which is based on the simultaneous analysis of adsorption isotherms of carbon dioxide and nitrogen, is employed for the determination of the structural parameters of micropores of various types.[2] Benzene has been accepted as a standard vapour for characterising CA in the former USSR countries. In European countries, Japan, and USA, nitrogen and carbon tetrachloride are usually employed for this purpose.

The methods for the determination of the porous structure parameters from the adsorption isotherms of the above compounds are based on the use of physical adsorption equations. These are primarily the well-known Dubinin–Radushkevich, Dubinin–Astakhov, and Dubinin–Stoeckli equations of the theory of volume filling of micropores (TVFM), developed by the school of Academician Dubinin,[3–5] and also various equations of polymolecular adsorption theory, in particular, the Brunauer–Emmett–Teller (BET) equation,[1,5] and the Mikhail–Brunauer–Bodor (MP) equation, etc.[1]

The adsorption of water on carbon adsorbents has some peculiarities, compared with the adsorption of nonpolar substances. The characteristic features and peculiarities of the adsorption of water vapour on CA are primarily caused by the tendency of polar water molecules to form hydrogen bonds, the dispersion interactions with the carbon surface being relatively weak.

The attempts to develop methods for the analysis of the porous structures of CA using the water vapour adsorption isotherms published in the literature are based on various, sometimes mutually exclusive, views on the adsorption mechanism.

A distinctive feature of carbon adsorbents, which determines to a substantial degree the fields of their application, is their relative hydrophobicity. However, depending on the porosity and the chemical state of the surface, which can vary on prolonged storage or prolonged use of an adsorbent, the humidity of the medium may noticeably influence the adsorption capacity of CA toward substances of various types.[6,7] Therefore, the study of the general rules and peculiarities of the adsorption of water vapour on CA has acquired practical significance.

The study of the mechanism of the adsorption of water vapour on CA is supposed to answer the following questions: what is the role of the primary adsorption sites of CA in the adsorption of water molecules, what are these sites from a chemical viewpoint, where are they located, how do the molecules being sorbed interact with these sites, in what manner are the surface and the micropore volume of CA filled, and what changes in the adsorbent itself accompany the adsorption process?

Although a large number of studies dealing with the adsorption of water vapour on CA have appeared in the literature,[8–22] at present there are no unanimous views on the mechanism of the adsorption, the role of the chemical state of the surface, or the nature of the adsorption sites. The initial views on the mechanism of adsorption of water vapour can be divided into two main groups: (1) the concept of the capillary condensation mechanism of the filling of micropores (Juhola[11–13] is the most consistent adherent of this theory) and (2) the concept of primary adsorption sites and the specific interaction of water with the carbon surface (Pierce and Smith[14] and Dubinin[15] have

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developed this concept independently of one another). Dubinin and coworkers[15] have reported on the surface oxides of CA, which play an important role in the adsorption of water molecules. In addition, it has been suggested[16,17] that the specific features of the adsorption of water vapour on CA are due to changes in the properties of the adsorbate caused by an increase in the average number of hydrogen bonds. It has also been noted[18] that the peculiarity of the adsorption of water is due to the fact that the carbon networks move apart and water molecules penetrate into the interlattice space of the CA by the 'collective' adsorption mechanism.

Within the framework of the concept of primary adsorption sites (PAS), there are also several views on the mechanism of further filling of the adsorption space: (1) the 'island' mechanism, according to which the PAS serve as nuclei for the formation of micro-drops, whose coalescence results in the formation of the bulk phase[14,19,20] and (2) the monomolecular-layer mechanism, according to which hydrogen bonds play a prominent role in the formation of a monomolecular layer.[21,22]

The studies published in recent years also did not completely clarify the problem of the mechanism of the adsorption of water vapour on carbon adsorbents, in particular on activated carbon (AC). Some authors apply widely the Kelvin[13] and Sircar[23] equations, based on the capillary condensation mechanism of adsorption, while other workers draw attention to the fact that the presence of acidic oxygen-containing complexes in the CA increases the adsorption of water vapour and facilitates the filling of micropores.[24-27] At the same time, the presence of non-acidic oxygen complexes does not influence the polarity of the CA surface and does not increase the adsorption of water vapour.[28]

In the present review, attention is concentrated on the role of the chemical state of the surface and of the microporous structure of the CA in the adsorption of water vapour, the nature of the PAS, the character of the interaction of the adsorbed molecules with the PAS, and the mechanism of the filling of the pore volume. Therefore, we carried out a systematic analysis of experimental data on the adsorption of water vapour on CA differing in porosity and chemical state of the surface, as well as adsorption on identical CA studied by various physicochemical methods. A total of about 300 samples of CA obtained from various materials by a variety of procedures were studied.

All the CA studied were characterised in terms of the adsorption of nitrogen vapour at 77 K. The specific surfaces (S_{sp}) of nonporous CA were calculated by the BET equation or determined from comparative plots, which have been surveyed and described by Greg and Sing.[1] The so-called 'absolute' adsorption isotherm on the surface of graphitised thermal carbon black was adopted as the 'reference' isotherm in the analysis of graphitised CA samples,[29] while in the analysis of other CA, the averaged adsorption isotherm for nonporous technical carbon black samples[30] was used.

The parameters of the porous structures of microporous AC (the limiting volume of the adsorption space of micropores W_0 and the characteristic adsorption energy E_0) were calculated from the equations of the theory of the volume filling of micropores[5] using the comparative γ/F method of determining the surface area of mesopores.[30,31] The width of the micropores ($2x$) for the slit model was determined from the generalised Stoeckli equation,[32] which relates $2x$ (nm) to the characteristic adsorption energy E_0 (kJ mol^{-1}).

$$2x = \frac{10.8}{E_0 - 11.4}$$

From the W_0/x relationship, the geometric surface area of the slit-shaped micropores (S_g) was found.[4]

The parameters of mesoporous AC were determined by the MP method.[1,33]

Water vapour adsorption isotherms on technical carbon blacks and also on some AC (especially in the region of small relative pressures) were obtained in a vacuum adsorption unit using a beam microbalance having a sensitivity of 1.0 μg with weighed portions of about 2 g; adsorption on the other AC was measured using a McBain-type quartz spring balance having a sensitivity of about 3 μg with weighed portions of 100 mg. Low adsorbate pressures (less than 1.3 Pa) were measured by a capacitance membrane manometer with a sensitivity of 0.013 Pa.

Most of the experimental data on the adsorption of water vapour have been analysed by a comparative method,[34] which is widely used to determine the parameters of the porous structures of adsorbents from the adsorption isotherms of nonpolar substances.[1] In this case, the water vapour adsorption isotherm on nonporous graphitised carbon black was adopted as the 'reference' (standard) isotherm.[34]

II. Adsorption of water molecules on the surface of nonporous carbon adsorbents

1. Adsorbents with low concentrations of primary adsorption sites

In conformity with the concept of primary adsorption sites, when water molecules are sorbed on a nonporous carbon surface, they initially form hydrogen bonds with the PAS and, as the relative vapour pressure p/p_s (p_s is the saturated vapour pressure) increases, they form hydrogen bonds with one another too. Consequently, clusters of associated water molecules are formed around the PAS.[14] Kiselev and Kovaleva[35] have noted that the adsorption of water vapour on graphitised carbon black over the whole region of relative pressures remains insufficient for covering the entire surface with a continuous monomolecular layer. Apparently, the formation of 'islands' or clusters can account for the fact, observed by these authors, that the limiting adsorption at saturation of water molecules on surfaces of various carbon black samples, pretreated in a stream of hydrogen at 1973 K, is about 8 μmol m^{-2}, which is equivalent to approximately 50% of the surface being covered by a continuous water monolayer.[36] This value was obtained by plotting the absolute water vapour adsorption isotherms on various carbon black samples.[36]

Analysis of the data obtained by Golovko et al.[37], who studied the adsorption of water vapour on the surface of highly dispersed graphite, indicates that in this case too no continuous monomolecular layer is formed. One may suggest that, depending on the surface concentration of the PAS, the adsorption of water vapour may end in the formation of either separated clusters, existing in equilibrium with the saturated vapour, or of a continuous adsorption film on the surface. In the former case, the distance between the PAS (l_m) should be larger than a certain limiting size of the water clusters formed on the carbon surface, and the limiting adsorption at saturation (a_s) should be proportional to the number of PAS rather than to the surface

Table 1. The specific surfaces (S_{sp}), the numbers of primary adsorption sites (a_m), the distances between them (l_m), the total amounts adsorbed at saturation (a_s), and the numbers of statistical monomolecular layers (N_s) for the graphitised CA studied (samples *1–8*).

Sample	S_{sp}/m^2 g^{-1}	a_m/μmol g^{-1}	l_m/nm	a_s/μmol g^{-1}	N_s[a]
1	47	0.5	12.5	240	0.32
2	50	8.0	3.22	1200	1.50
3	51	12.0	2.66	1790	2.20
4	47	5.0	3.96	610	0.82
5	63	15.0	2.65	1790	1.80
6	50	2.5	5.76	390	0.49
7	33	1.6	5.85	250	0.48
8	100	4.0	6.44	590	0.37

[a] The N_s value was calculated for the area of the water molecule (0.105 nm^2) determined from the bulk density of water.

area of the CA. In the latter case, l_m should be smaller than the limiting size of the clusters and a_s should be proportional to the surface area of the CA.

A number of adsorbents prepared from ultradisperse technical carbon[38] with subsequent graphitisation at a temperature of 3073 K have been used as CA with low surface concentrations of PAS. As shown by mercury porosimetry, the initial sample *1* (Table 1) possessed a pore volume of 0.425 $cm^3\ g^{-1}$ with a narrow pore size distribution having a maximum near 25 nm. In order to deposit OH groups, sample *1* was chlorinated and then hydrolysed (samples *2* and *3*) by the procedure reported for a diamond surface.[39] Samples *4* and *5* were prepared by the oxidation of sample *1* in concentrated HNO_3 at 298 K and 373 K, respectively. In addition, sample *6*, prepared by treating the CA with phenol, was studied. Sample *7* differed from the initial sample *1* only by a lower specific surface and a higher PAS concentration. For comparison, Vulkan-7H carbon black graphitised at 3073 K (sample *8*), adopted as the 'reference' sample, was also studied.

Fig. 1 presents comparative plots for the adsorption of nitrogen vapour on samples *1–7* at 77 K. In these plots, the 'absolute' isotherm for adsorption on the surface of graphitised thermal carbon black was adopted as the reference isotherm.[29] For all the samples *1–7* studied, these plots are straight lines passing through the origin of coordinates. This indicates that the mechanisms of nitrogen adsorption on the samples studied and on the standard nonporous carbon surface are identical and that the surfaces of the adsorbents studied are energetically and structurally uniform. From the slopes of the comparative plots for the adsorption of nitrogen, the specific surfaces of the adsorbents (S_{sp}) may be determined.[29,30] Fig. 2 shows water vapour adsorption isotherms on some of these samples at 293 K, and Fig. 3 presents the comparative plots for the adsorption of water vapour. In this case, the water vapour adsorption isotherm on sample *8* was adopted as the standard. The slopes of the comparative plots for the adsorption of water are proportional to the concentration of the PAS (a_m).[34] The distance between the PAS (l_m) was calculated on the assumption that they are uniformly distributed over the surface.

From Table 1, one can see that the number of PAS on the initial sample *1* is significantly smaller than that on the 'reference' graphitised carbon black and that this number increases sharply when the CA is oxidised. The S_{sp} values for samples *1–4* and *6* are virtually identical, while S_{sp} for sample *5*, obtained by boiling sample *1* in concentrated HNO_3, is somewhat higher. The values of a_s for samples *1*, *4*, *6*, *7*, and *8* correspond to the fractions of the close packed monolayer.

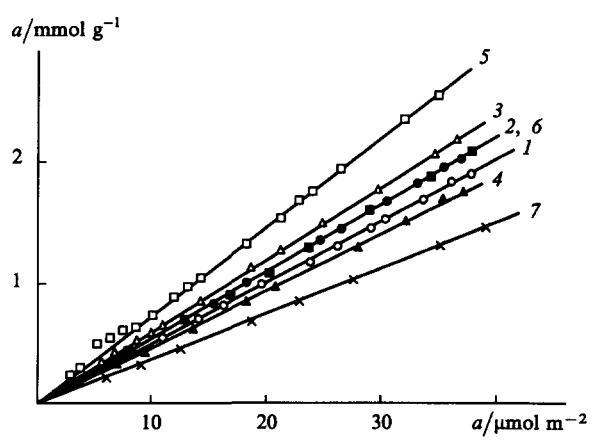


Figure 1. Comparative plots for the adsorption of nitrogen vapour on graphitised CA samples (*1–7*) at 77 K. The numbering of the samples in Figs 1–4 corresponds to that in Table 1.

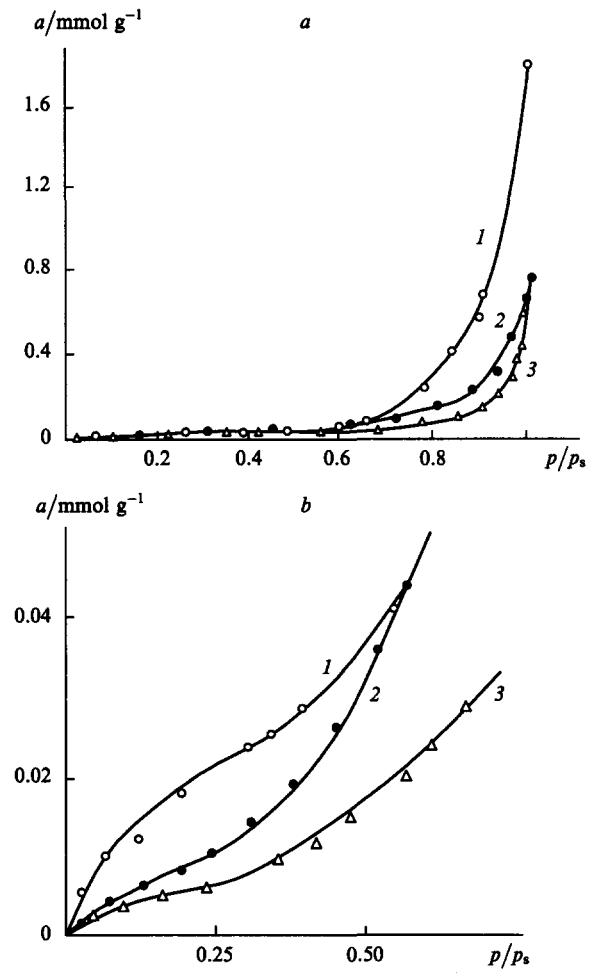


Figure 2. Water vapour adsorption isotherms at 293 K on the graphitised samples *3* (curve *1*), *4* (curve *2*), and *8* (curve *3*). The overall form of the isotherms (*a*) and the isotherms at low coverages (*b*).

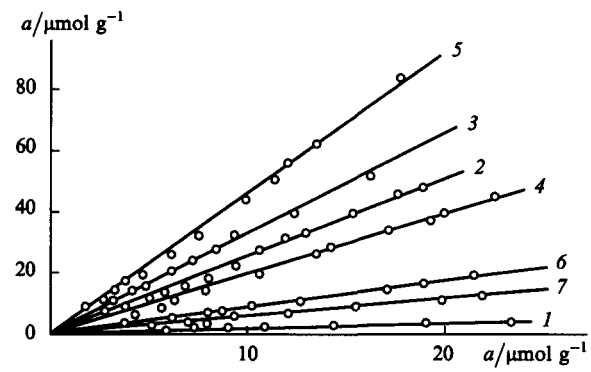


Figure 3. Comparative plots for the adsorption of water vapour on the graphitised samples *1–7* at 293 K.

The dependence of the total amount adsorbed at saturation a_s on the concentration of PAS a_m on graphitised CA is shown in Fig. 4. It is a straight line starting from the origin of coordinates. The slope of this straight line corresponds to the average number of water molecules in a cluster formed around a PAS at $p/p_s = 1$, which is approximately 150 molecules per site. The size of such a cluster can be evaluated from data on the numerical modelling of the adsorption of water molecules on a carbon surface.[40] If one assumes that the adsorbed water clusters are geometrically similar (a cluster consisting of 19 water molecules is a hemisphere 1.4–1.5 nm in diameter and 0.7 nm high[40]), a

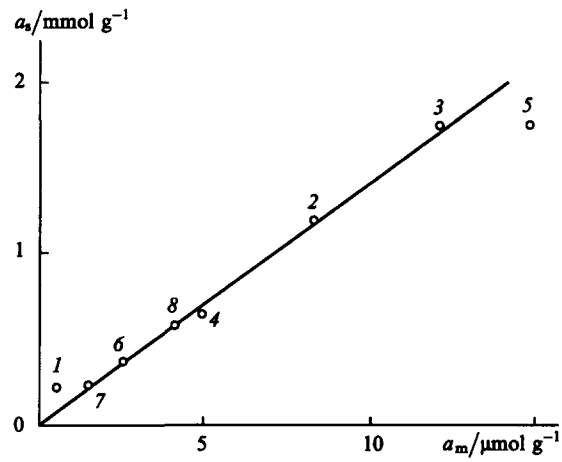


Figure 4. Dependence of the total amount of water vapour adsorbed at saturation on the number of primary adsorption sites (a_m) on graphitised CA samples.

cluster on a surface incorporating 150 water molecules should be about 3.0 nm in diameter and 1.5 nm high.

Thus, if the distance between the PAS l_m is larger than 3 nm, no continuous adsorption layer is formed on the surface of the graphitised CA. This result is supported by independent calorimetric measurements of the heats of immersion in water of sample *7* containing various quantities of preadsorbed water (Fig. 5).[41] From Fig. 5, one can see that the heats of immersion increase continuously as the quantity of preadsorbed water increases up to the total uptake at saturation, and reach 1.5 J g^{-1}. This means that the differential heats of adsorption calculated from the heats of immersion are lower than the heat of condensation over the whole range of coverages (curve *2* in Fig. 5). At low coverages, the differential heats agree with the isosteric heats calculated from the water vapour adsorption isotherms on this sample at 298, 293, and 273 K (curve *3*).

Taking into account the surface energy of normal water (118 mJ m^{-2}), one can infer that the heat of immersion equal to 1.5 J g^{-1} corresponds to the disappearance of 12.7 m^2 g^{-1} of the water surface, i.e. if the limiting quantity of water has been preadsorbed, the water molecules occupy about 40% of the whole surface of the graphitised sample, which amounts to 33 m^2 g^{-1} (see Table 1).

Thus, if the distance between the PAS is greater than the critical size of the clusters formed from water molecules adsorbed on the carbon surface, the clusters grow independently of one another until the amount adsorbed at saturation is achieved. By determining the amount of water vapour adsorbed at saturation, one can evaluate the number of PAS on the carbon surface.

It is noteworthy that the correct determination of the number of PAS for water molecules is very important in the approach outlined. The number of PAS on the CA can be calculated from the Langmuir equation for localised adsorption:

$$a = \frac{a_m bp}{1 + bp},$$

where p is the equilibrium pressure and b the energetic factor. This equation describes experimental adsorption isotherms in the region of low relative pressures where adsorption is mainly caused by the interaction of water molecules with PAS. The resulting number is identical with the number of acidic surface functional groups, which is determined by an independent method involving the neutralisation of these groups with a solution of Na_2CO_3. Determination of the number of PAS using the Dubinin–Serpinskii equations yields, as a rule, higher values of a_m,[42] which finally results in smaller distances between the PAS and, consequently, in lower values of the critical size of a cluster on the carbon surface.

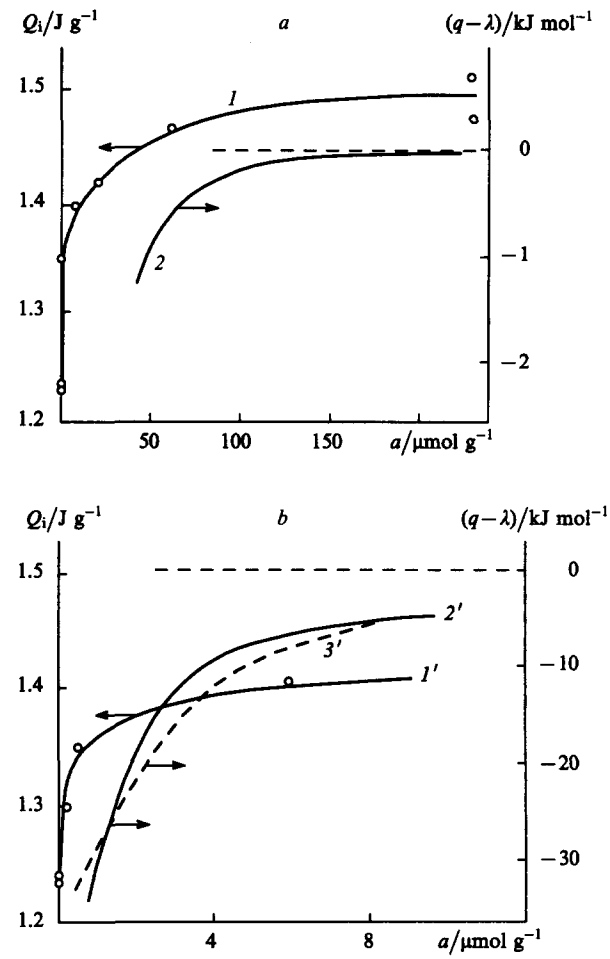


Figure 5. Dependence of the heat of immersion of sample *7* in water (Q_i) at 298 K on the quantity of preadsorbed water (curves *1* and *1′*) over the entire range of coverages (*a*) and in the initial section (*b*). The 'pure' differential heats of adsorption of water vapour ($q - \lambda$) were calculated from the Q_i values (curves *2* and *2′*). The isosteric heats of adsorption of water vapour on the same sample (curve *3′*) were calculated from the adsorption isotherms measured at 273, 293, and 298 K.

The first Dubinin–Serpinskii equation (DS-1) can be written as follows:

$$a = \frac{a_m ch}{1 - ch},$$

where c is a constant equal to the ratio between the adsorption and desorption rate constants and h the equilibrium relative pressure (p/p_s).

Allowance for the variation of the number of PAS present as new water molecules are adsorbed results in the second Dubinin–Serpinskii equation (DS-2):

$$h = \frac{a}{c(a_o + a)(1 - ka)},$$

where k is determined from the condition $a = a_s$ at $h = 1$, i.e.

$$k = \frac{1}{a_s} - \frac{1}{c(a_o + a_s)}.$$

Here a is the amount adsorbed at the relative pressure h, and a_s the amount adsorbed at $h = 1$.

2. Adsorbents with a relatively high concentration of primary adsorption sites

The adsorption of water vapour on CA with relatively high concentrations of PAS may result in the formation of a continuous adsorption layer. In this case, the total amount adsorbed at saturation should be proportional to the specific surface of the CA.

Table 2 presents the values of S_{sp}, a_s, l_s, and a_s as well as the number of statistical monomolecular layers N_s for such carbon black samples. The designations of the samples and the specific surfaces of the majority of carbon blacks studied were taken from two papers[29,30] (the values of S_γ are given as the S_{sp}). In addition, samples of technical carbon PM-75, Ukhta channel carbon black (UKhT-K), and C-7 type acetylenic carbon black[29] with 5.5% of deposited pyrocarbon (AC-5.5) were studied. All the samples were subjected to preliminary heat treatment at 1273 K. As can be seen from Table 2, the l_m values for these samples are smaller than the critical cluster size, which indicates that the formation of a continuous adsorption film is possible. The a_s values for these carbon blacks correspond to the formation of 1.7 ± 0.3 statistical close-packed monolayers.

The plot of a_s against S_{sp} for the CA listed in Table 2 is shown in Fig. 6. This plot is linear and starts from the origin of coordinates. In this case, the slope of the straight line makes it possible to determine the amount of water vapour adsorbed at saturation per unit carbon surface: it is equal to approximately 26 μmol m^{-2}.

Table 2. The specific surfaces, the numbers of PAS, the distances between them, the total amounts adsorbed at saturation, and the numbers of statistical monomolecular layers for carbon blacks with high concentrations of PAS.

Sample	Carbon black	S_{sp}/ $m^2\ g^{-1}$	a_m/ μmol g^{-1}	l_m/ nm	a_s/ μmol g^{-1}	N_s
1	S-3	31	0.013	1.99	0.85	1.75
2	PM-75	68	0.061	1.36	1.85	1.74
3	S-4	73	0.027	2.11	1.90	1.66
4	ST-4	84	0.283	0.70	2.85	2.16
5	ST-6	87	0.023	2.50	2.25	1.65
6	ST-7	91	0.060	1.59	2.50	1.75
7	S-8	95	0.220	0.85	2.20	1.48
8	AS-5.5	97	0.022	2.71	2.75	1.81
9	ST-8	112	0.337	0.74	3.25	1.85
10	UKhT-K	120	0.311	0.80	2.90	1.54
11	ST-10	126	0.068	1.75	2.95	1.49
12	S-9	126	0.132	1.26	2.50	1.27

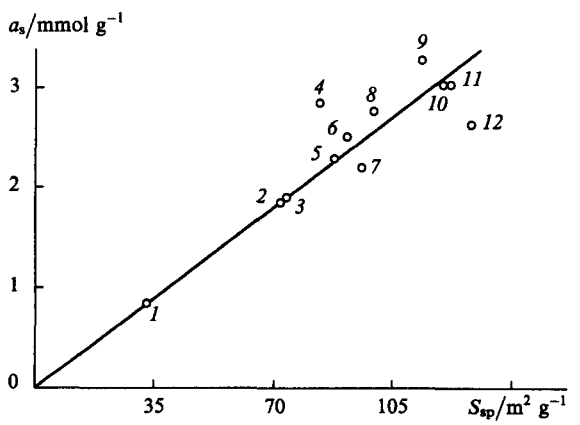


Figure 6. Dependence of the total amount of water vapour adsorbed at saturation on the specific surfaces of nonporous CA. The numbering of the samples corresponds to that in Table 2.

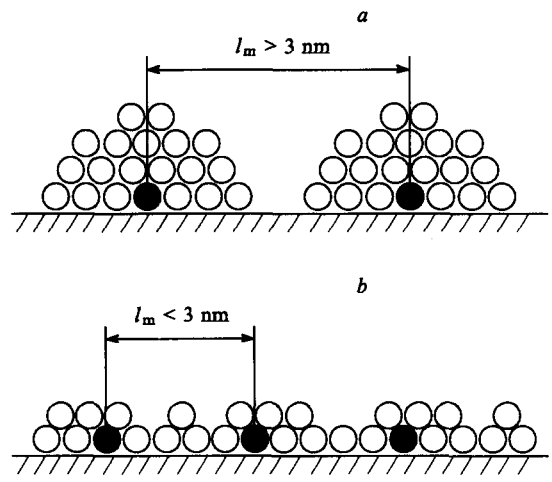


Figure 7. Schematic illustration of the coverage of the surfaces of nonporous CA with different surface concentrations of PAS: (*a*) l_m > 3 nm; (*b*) l_m < 3 nm.

The linear relationship between the amount of water vapour adsorbed at saturation and the S_{sp} of nonporous carbon adsorbents makes it possible to determine the surface areas of nonporous and mesoporous carbon adsorbents. This method has also been used[43] to evaluate the surface area of the mesopores of AC containing micro- and mesopores.

Thus, depending on the surface concentration of PAS on nonporous CA, two schemes for the filling of the surface can be suggested (Fig. 7). The first scheme (Fig. 7*a*) corresponds to a concentration of PAS below the critical concentration, when clusters of adsorbed molecules are formed and grow independently of one another until a limiting value of approximately 150 molecules per site is reached. The second scheme (Fig. 7*b*) corresponds to a rather high surface concentration of PAS, when a continuous adsorption layer is formed.

III. Adsorption of water molecules on activated carbons

The parameters of the porous structures of some typical representatives of the AC studied are listed in Table 3. The AC-1 and AC-5 samples were prepared from coal by steam activation, and their properties are close to those of industrial AC samples of AG-3 and AG-5 types. The peat-based AC-2 and AC-3 samples are similar in their properties to industrial recovered AC of the ART type. The AC-6, AC-7, and AC-8 samples were prepared under laboratory conditions from furfural. AC-4 is an industrial AC of the MSC-5 type (Japan), and AC-10 and AC-11 are industrial AC of the SKT-6A and SKT types, respectively. AC-9, AC-Ts, and AC-U-3 were obtained under laboratory conditions; the former two samples were prepared by the carbonisation of silicon and zirconium carbides respectively, while the latter (AC-U-3) was prepared from polyacrylonitrile.

Apart from the microporous AC listed in Table 3, ultramicroporous AC-U-1 (based on polyacrylonitrile) and AC-U-2 (an AC with MSC-4A molecular-sieve properties) samples, a supermicroporous coal-based AC-U sample, and a mesoporous AC-M (from molybdenum carbide) sample have also been studied. The specific surfaces of AC-M and AC-U are 470 and 1870 $m^2\ g^{-1}$ respectively. The total amounts of nitrogen adsorbed at saturation W_s on these samples are 0.85 and 1.44 $cm^3\ g^{-1}$, and the average pore sizes (the half-widths x) calculated from these values for the slit model are 1.8 and 0.77 nm, respectively. AC-U-1 and AC-U-2 virtually do not adsorb benzene.

Table 3. Porous structure parameters of typical representatives of the activated carbons studied.

Sample	S_m /m^2 g^{-1}	W_o /cm^3 g^{-1}	E_o /kJ mol^{-1}	x/nm
AC-1	100	0.28	19.0	0.71
AC-2	35	0.40	24.4	0.42
AC-3	140	0.26	19.5	0.67
AC-4	18	0.20	32.4	0.28
AC-5[a]	–	0.18	23.6	0.85
		0.38	10.4	
AC-6	30	0.32	34.0	0.24
AC-7	120	0.60	19.8	0.64
AC-8	300	0.67	17.6	0.87
AC-9	30	0.47	21.8	0.52
AC-10	–	0.55	21.4	0.54
AC-11	20	0.49	21.5	0.53
AC-Ts	25	0.82	17.8	0.84
AC-U-3	~0	0.10	29.2	0.30

[a] The calculation was carried out using the two-term equation of the theory of volume filling for a bidisperse porous structure; the x values have been averaged.[4] The calculation by the Dubinin–Stoeckli equation yields S_m = 300 m^2 g^{-1}, W_o = 0.38 cm^3 g^{-1}, x = 0.73 nm.

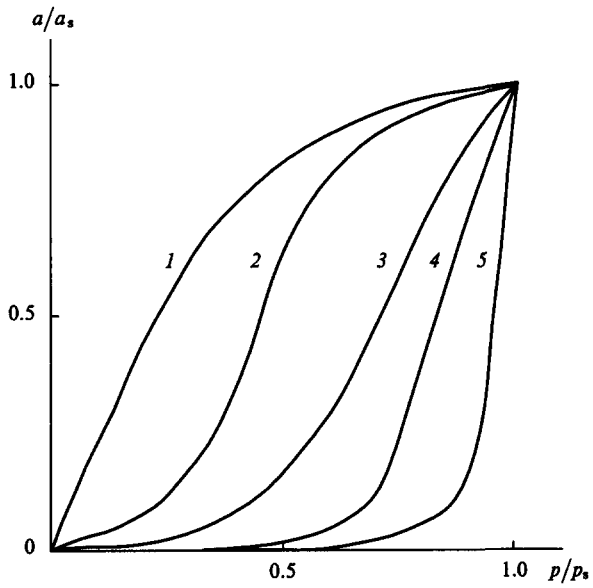


Figure 8. Water vapour adsorption isotherms in relative coordinates for typical AC: AC-U-1 (*1*), AC-2 (*2*), AC-1 (*3*), AC-7 (*4*), AC-M (*5*).

The parameters of the porous structures of other AC will be presented as required.

The adsorption isotherms for water vapour on the AC studied cover almost the whole range of known adsorption isotherms. Fig. 8 shows adsorption isotherms on typical AC in relative coordinates, a/a_s against p/p_s. The shapes of these adsorption isotherms vary from the atypical curve for the ultramicroporous AC-U-1, which is convex over the whole pressure range, to the concave curve for the mesoporous AC-M.

1. Adsorption isotherms at low coverages

While studying the adsorption of water vapour on AC, particular attention was concentrated on the initial sections of the adsorption isotherms, since this region had scarcely been investigated before, though it may provide valuable information concerning the number and nature of PAS and the mechanism of the interaction of water molecules with PAS.

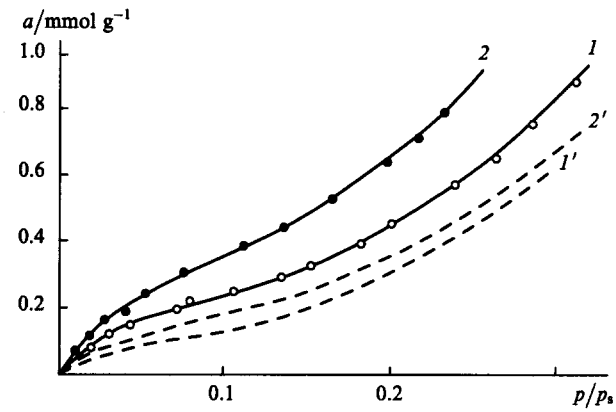


Figure 9. Initial sections of water vapour adsorption isotherms at 293 K on AC-1 and AC-2 evacuated at 293 K (curves *1* and *2*) and 673 K (curves *1'* and *2'*). The circles represent the adsorption isotherms for samples containing 0.6 and 1.8 mmol g^{-1} of firmly bound water respectively.

In Fig. 9, the initial sections of the isotherms for the adsorption of water vapour on two AC evacuated at 293 and 673 K are shown as examples. It can be seen that they have noticeable convex sections at relative pressures below 0.05–0.10. The presence of the convex sections indicates that, in the region of low relative pressures, the adsorption occurs predominantly on PAS. The number of PAS can be determined from the known Langmuir equation for localised adsorption. It is equal to the parameter a_m of the Langmuir equation. As a rule, the numbers of PAS for various AC are close to the amounts adsorbed at $p/p_s = 0.1$.

The numbers of PAS found from the Langmuir equation have been compared with those determined using the Dubinin–Serpinskii equation.[42] It was shown that a_m calculated from the Langmuir equation differs appreciably from and is virtually always lower than the number of PAS (a_o) found from the Dubinin–Serpinskii equation. In our opinion, a_m has a more clear physical meaning than a_o, since it is determined from the initial section of the adsorption isotherm, whose character is governed by the interaction of adsorbed molecules with PAS. This is also supported by the data reported[44–46] for oxidised AC for which the degree of adsorption of water vapour at $p/p_s = 0.1$ is practically identical with the number of acidic functional groups determined using the Boehm method, by neutralising these groups with bases of various strengths.[47]

Fig. 9 indicates that, when the temperature of preliminary evacuation is increased from 293 to 673 K, the water vapour adsorption isotherm is located in a lower position, which is associated with the decrease in the number of PAS on heating an AC.

In order to study the influence of the conditions in the preparation of the samples in more detail, AC-1 was evacuated at 673 K at a pressure of 10^{-2} Pa to constant weight, and, after cooling the sample to 293 K, three adsorption (to $p/p_s = 0.2$) and desorption cycles were carried out successively. The results of these experiments are shown in Fig. 10. In the fourth cycle, measurements were continued until the saturated vapour pressure was achieved, and, starting from the fifth cycle, a reproducible curve was obtained. As a result, the full adsorption isotherm (Fig. 11) was obtained, characterised by the so called 'open' hysteresis in which the desorption branch lies above the adsorption branch over the whole range of relative pressures (curve *1* in Fig. 11). The next adsorption-desorption cycle (curve *2* in Fig. 10) virtually did not lead to an increase in the quantity of firmly bound water, and the adsorption isotherm became reversible at low p/p_s with 'closed' hysteresis in the region $p/p_s = 0.3–1.0$.

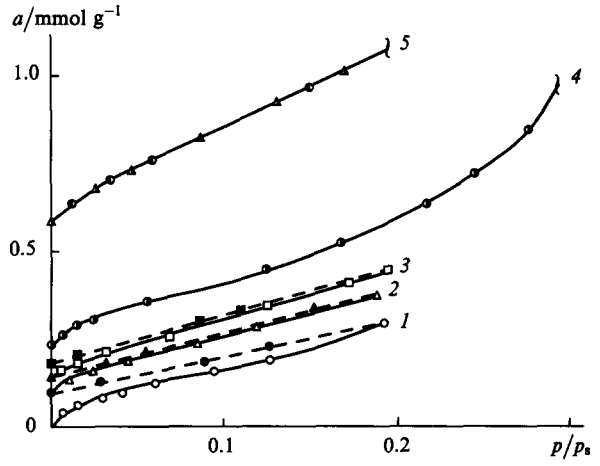


Figure 10. Water vapour adsorption (open symbols) and desorption (filled symbols) isotherms at 293 K on a AC-1 sample evacuated at 673 K. The numbers denote the numbers of adsorption-desorption cycles.

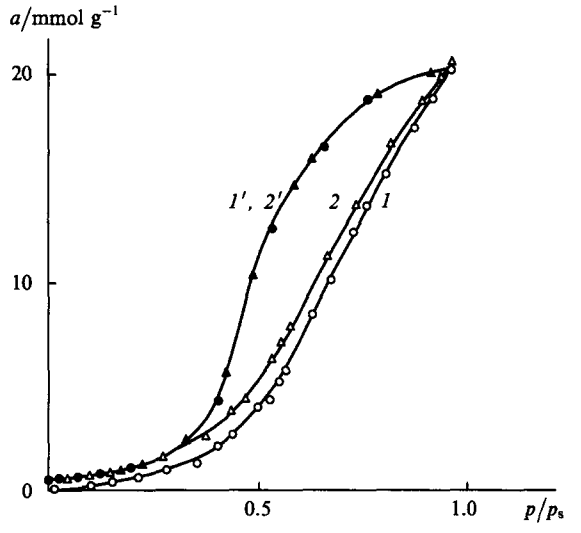


Figure 11. Full isotherms for the first (curves *1* and *1'*) and second (curves *2* and *2'*) adsorption (*1* and *2*) and desorption (*1'* and *2'*) cycles on AC-1 at 293 K.

The results presented in Figs 9 and 10 indicate that, after the thermal desorption of a sample at an elevated temperature (600–700 K), irreversible sorption (chemisorption) of water occurs synchronously with physical adsorption. Chemisorption also takes place at pressures of $10^{-1}-10^{-2}$ Pa during intervals between adsorption measurements. Therefore, each subsequent adsorption-desorption cycle occurs with a larger initial mass of the sample than the previous one. This chemisorption process causes the 'open' hysteresis on the water vapour adsorption isotherm on an AC subjected to preliminary evacuation at an elevated temperature.

The increase in the number of PAS with increase in the quantity of firmly bound water indicates that the firmly bound water acts as PAS. Irreversible adsorption of water vapour on AC was observed previously;[9,48,49] it has also been observed in a study of the interaction of an atomically pure graphite surface with water.[50]

Apart from the initial sections of the water vapour adsorption isotherms on AC-1 and AC-2 evacuated at 293 and 673 K, Fig. 9 also shows the adsorption isotherms on samples that have been evacuated at 673 K and then rehydrated. As one can see, preliminary heating of the samples results in a decrease in the amount of water adsorbed in the region of low p/p_s. After the rehydration of AC, the adsorption isotherms obtained for unheated and rehydrated samples coincide. Thus, a substantial proportion of the PAS are destroyed when the sample is heated to 673 K, and are almost entirely restored when the sample is rehydrated.

The numbers of PAS for some AC evacuated at 293 and 673 K and also for a number of AC, modified through oxidation in moist air at 623 K, deashing in HCl, successive deashing in HF and HCl, and heat treatment in an argon atmosphere at temperatures between 1273 and 2073 K, are presented in Table 4. It can be seen from this table that preliminary heating results in a decrease in the number of PAS for all the initial AC, except AC-9. In the case of AC-9, the number of PAS does not change on preliminary heating.

Table 4. The numbers of PAS (a_m/mmol g^{-1}) on the initial and modified AC at various evacuation temperatures (T_{evac}).

Sample	Method of pretreatment	The number of PAS after evacuation at	
		293 K	637 K
AC-1	None	0.30	0.16
	Oxidation	0.32	0.43
	Deashing with HCl+HF	0.40	–
	Heat treatment at		
	1273 K	0.10	0.10
	1473 K	0.08	0.08
	1673 K	0.07	0.07
	1773 K	0.06	0.06
	1873 K	0.05	0.05
	2073 K	0.03	0.03
AC-2	None	0.41	0.21
	Oxidation	0.44	0.44
AC-6	None	0.60	0.20
AC-7	"	0.41	0.08
AC-8	"	0.21	0.05
AC-9	"	0.20	0.20
AC-10	"	0.53	0.20
AC-U-1	"	1.24	0.34
AC-S	"	0.19	0.16
AC-M	"	0.70	0.20

The role of oxidation in air at 623 K does not reduce merely to an increase in the number of PAS. In fact, when the preliminary evacuation of AC-1 and AC-2 is carried out at 293 K, the numbers of PAS on the initial and oxidised samples are close, while in the case of evacuation at 673 K, the a_m values for oxidised samples are much larger than those for the initial ones. The major distinction in the adsorption behaviour of the initial and oxidised AC is that for samples oxidised in moist air, the change in the number of PAS on heating the AC from 293 to 673 K is substantially less pronounced. The oxidation not only leads to a change in the total concentration of PAS, but results in an increase in the ratio between the relatively unstable oxygen-containing surface compounds that are removed by moderate heating (in particular, chemisorbed water) and more thermally stable surface groups.

As can be seen from Table 4, heat treatment of AC in an argon atmosphere at 1273–2273 K leads to a continuous decrease in a_m.[42] When the treatment temperature is higher than 1273 K, the adsorption isotherms do not depend on the

conditions in which the sample is prepared for the experiment, i.e. the numbers of PAS on the heated and unheated samples are identical.

Extensive deashing by successive treatment with HCl and HF of the compounds evacuated at 293 K results in an increase in the number of PAS; i.e. the adsorption properties of the AC during their deashing are mostly influenced by the chemical modification of the surface, leading to an increase in the number of surface functional groups acting as PAS, rather than by the removal of oxygen-containing ash elements.

2. Heats of adsorption of water vapour at low coverages

The results obtained in studies of the adsorption of water vapour on CA in the region of low relative pressures attest to a substantial role of PAS in the adsorption. Useful information about the character of the interaction of adsorbed water molecules with PAS can be gained from the heats of adsorption of water vapour. Fig. 12 presents the dependences of isosteric heats (q_{st}) on the amount of adsorbed water vapour for some AC.[51] They all have a characteristic shape: in the range of low coverages, the q_{st} values are lower than the heats of condensation, but they increase with increase in coverage, and for high degrees of adsorption the q_{st} are constant and somewhat higher than the heats of condensation. For some AC, the $q_{st}(a)$ dependence goes through a maximum. A similar form of the dependence of the heat of adsorption on the amount adsorbed has been previously postulated in a study of the characteristic features of water vapour adsorption on CA.[17] We may note that our data are supported qualitatively by a calorimetric measurement of the heat of adsorption of water vapour on an AC previously evacuated at 298 K.[52]

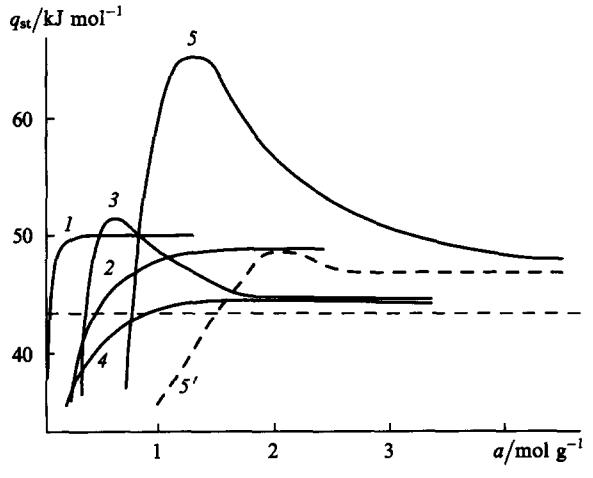


Figure 12. Dependence of isosteric heats of adsorption on the amount of adsorbed water for AC-1 (*1*), AC-2 (*2*), AC-N (*3*), AC-U-2 (*4*), and AC-U-3 (*5* and *5′*). Here and in Fig. 13, the dashed line represents the heat of condensation of water vapour.

It should be noted that the relationships for differential and isosteric heats of adsorption are applicable only to reversible adsorption cycles. As was shown above, the adsorption of water may be complicated by chemisorption, which distorts the results obtained in calculations of heats of adsorption. Strictly speaking, samples of a particular AC evacuated at different temperatures differ from one another in the chemical state of the surface and the concentration of PAS. For example, for AC-U-3, the variation of the temperature of experiments from 283 to 303 K leads to a substantial loss of the firmly bound water, and, as this takes place, the number of PAS considerably decreases. Therefore, two dependences of q_{st} against the amount adsorbed are shown in Fig. 12 for the AC-U-3 sample. One of them corresponds to the temperature range 283–293 K (curve *5*) and the other is for 293–303 K (curve *5′*). It has been shown[51] that the nonlinearity of adsorption isosteres, typical for most AC, hampers a precise quantitative determination of the isosteric heat of adsorption (q_{st}); however, the situation remains qualitatively the same.

In the region of low coverages, water molecules are mainly adsorbed on PAS, and the number of PAS is not invariable for a particular AC but depends on the temperature.

In this respect, it is expedient to refer the quantity of adsorbed water (a) to the number of PAS (a_m), which should be found separately for each temperature. This approach to the determination of heats of adsorption is equivalent to allowance for the temperature dependence of the adsorption-active surface of an adsorbent. The quantity a/a_m characterises the average number of water molecules adsorbed on one PAS.

To determine q_{st}, adsorption isotherms are plotted in terms of the a/a_m–p coordinates. The differential heats of adsorption q_Θ determined from these relationships for small a/a_m are given in Fig. 13. From this figure, one can see that in the region of small a/a_m the heats of adsorption virtually do not depend on the amount adsorbed within the limits of experimental error and are lower than the heat of condensation of water vapour. The method of determining heats of adsorption described can be used only in the region of low coverages, when there is less than one adsorbed water molecule per single PAS and the assumption that adsorption mostly occurs on PAS is obeyed sufficiently rigorously. When more than two or three water molecules are adsorbed on each PAS, the q_Θ values are also invariable and are somewhat higher than the heat of condensation of water vapour.

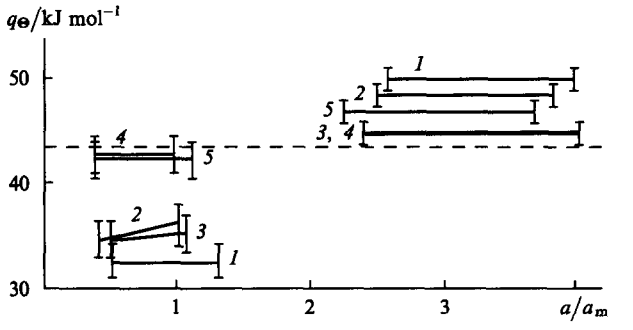


Figure 13. Dependence of the heats of adsorption of water vapour q_Θ on a/a_m for AC-1 (*1*), AC-2 (*2*), AC-N (*3*), AC-U-2 (*4*), and AC-U-3 (*5*).

From our viewpoint, the general character of the dependence of the heats of adsorption on the amount adsorbed agrees well with the mechanism of the adsorption of water vapour on CA considered above. Since the heat of adsorption on a PAS is related to the energy of formation of a hydrogen bond, the heat of adsorption should be equal to the energy of one hydrogen bond plus the energy of dispersion interaction. The energy of interaction of water molecules with a model PAS (a carbonyl group), found by numerical modelling,[40] is ~ 32 kJ mol^{-1} for the optimum arrangement of water molecules. Thus, it is reasonable to expect that in the region of low coverages the heat of adsorption should be smaller than the heat of condensation (~ 44 kJ mol^{-1}), which is itself somewhat greater that the energy of formation of two hydrogen bonds.

The fact that the heats of adsorption of water vapour at low coverages are lower than the heat of condensation implies that adsorbed molecules do not interact with one another and, in this sense, water molecules are adsorbed like the molecules of a gas. A similar suggestion was made previously[48] judging from kinetic data. However, some authors including those just cited[48] have obtained heats of adsorption at low coverages, larger than the heat of condensation. Among other reasons, this may be due to

the fact that, in most of these studies, measurements were carried out with CA evacuated at elevated temperatures. As has already been noted, in this case, apart from physical adsorption, chemisorption of water molecules takes place. It is this effect that has most probably been observed in the above studies.[48,53,54] The substantial energy evolved during chemisorption (the possibility of a chemical reaction also cannot be ruled out)[49,55] results in high calorimetric heats of adsorption in the region of low coverages. For high coverages, all the authors have obtained nearly constant heats of adsorption, which are somewhat higher than the heat of condensation of water vapour. This is explained by the fact that, as the clusters around the PAS grow, the average number of hydrogen bonds per molecule increases, and, consequently, the heat of adsorption also increases and can exceed the heat of condensation, owing to the contribution of the dispersion interactions of water molecules with the adsorbent.

The results obtained in another study[53] agree qualitatively with the scheme considered. It was found that, for relatively low temperatures (243–293 K), the heat of adsorption is nearly equal to the heat of condensation over the whole range of coverages studied; when the temperature is increased to 333–491 K, the quantity of firmly bound water acting as PAS decreases noticeably. In addition, when the temperature of the experiments is increased, one can study the region of low coverages at normal water vapour pressures. Under these conditions, the q_{st} values for small amounts adsorbed are much smaller than the heat of condensation, and grow rapidly as the degree of adsorption increases.[53]

3. Adsorption in the region of moderate and high coverages

The influence of the concentration of PAS on the full adsorption isotherm can be demonstrated by studying the adsorption of water vapour on various AC with similar microporous structures but different concentrations of PAS. The different types of interaction of the nonpolar nitrogen molecules and the polar water molecules with CA should lead to dissimilar mechanisms of adsorption on the surface and also to dissimilar mechanisms of the filling of the pore volume of a CA. Adsorbents that adsorb nitrogen in like manner can be essentially dissimilar towards the adsorption of water vapour. Fig. 14 shows relative isotherms for the adsorption of water vapour and nitrogen on two AC samples (AC-3 and AC-1). It can be seen that the degrees of adsorption of nitrogen on these two samples are close to one another over the whole p/p_s range (i.e. the samples possess similar porous structures). However, the amounts of water vapour adsorbed are significantly different, and only at $p/p_s \approx 1$ do they converge. These distinctions are due to the fact that the number of PAS on AC-3 is smaller than that on AC-1 by a factor of approximately six.

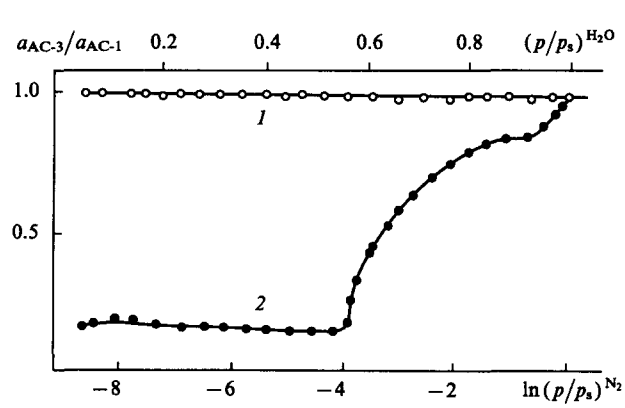


Figure 14. The ratios of the amount of nitrogen vapour adsorbed at 77 K (curve *1*) and the amount of water vapour adsorbed at 293 K (curve *2*) on AC-3 to the corresponding amounts adsorbed on AC-1.

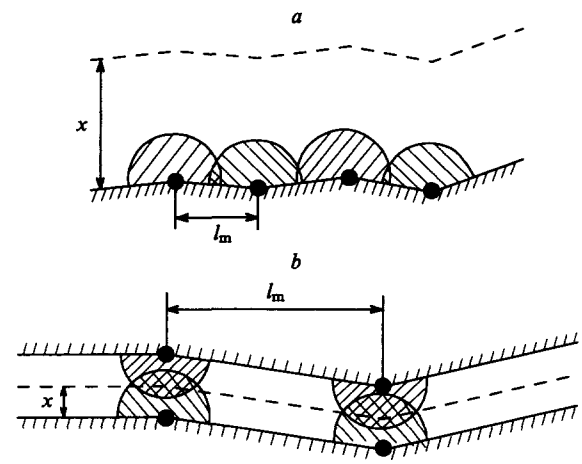


Figure 15. Schematic illustration of the filling of the pore volume of AC with various ratios of the average distance between the PAS (l_m) to the half-width of slit-like pores (x).

Thus, in the initial range of p/p_s, the adsorption of water on AC, similarly to that on nonporous CA, occurs on PAS, around which clusters of adsorbed water molecules can in principle form and grow. Generally, two schemes can be suggested to describe how the pore volume is filled as the clusters around PAS grow (Fig. 15). If the distance between the PAS is smaller than the width of a pore and smaller than the critical size of a cluster on a carbon surface, the clusters can coalesce as they grow to give a continuous adsorption layer on the surface of pores (Fig. 15*a*). For relatively narrow pores and a low concentration of PAS, one should expect that water molecules adsorbed on opposite walls of a pore would interact, forming bridge bonds (Fig. 15*b*).

The schemes presented indicate that the manner in which pores are filled depends both on the structure and on the chemical nature of the surface. At the same time, for low coverages, the mechanisms of the adsorption of water molecules on nonporous, mesoporous, and microporous CA are identical and are governed by the interaction with PAS. Fig. 16 shows isotherms for the adsorption of water vapour (referred to the numbers of PAS) on Vulkan-7H carbon black graphitised at 3073 K, mesoporous AC-M, ultramicroporous AC-U-3, and microporous AC-1, AC-2, AC-5, and AC-N. The data reported for some nonporous carbon blacks of the Graphon type[19,56] are also shown in this figure.

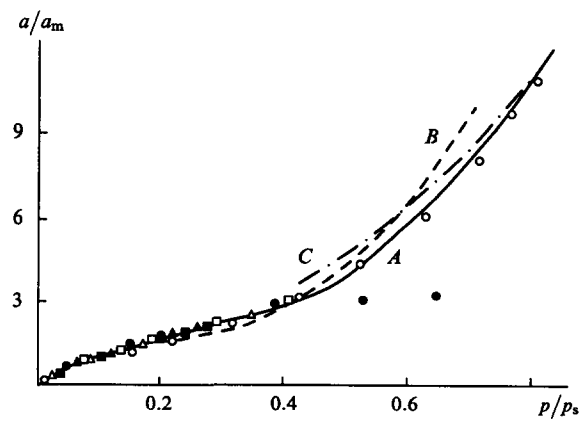


Figure 16. Water vapour adsorption isotherms in terms of the $(a/a_m) - (p/p_s)$ plots on Vulkan-7H carbon black (curve *A*), the mesoporous AC-M (*1*), the ultramicroporous AC-U-3 (*2*), the microporous AC-1 (*3*), AC-2 (*4*), AC-5 (*5*), AC-N (*6*), and also on Graphon carbon blacks (curves *B* and *C*).

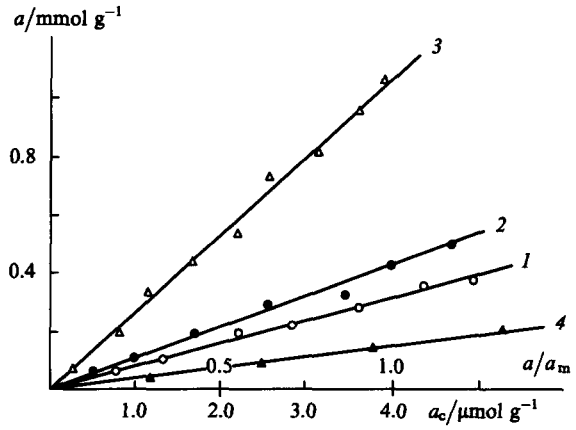


Figure 17. Comparative plots for the adsorption of water vapour in the region of low coverages for AC-1 (*1*), AC-2 (*2*), AC-U-1 (*3*), and AC-5 (*4*).

The similarity of the mechanisms by which water molecules are adsorbed on all CA in the range of small p/p_s is manifested, in particular, as follows. If the adsorption isotherm on separate PAS (or, to a first approximation, on a graphitised carbon black) is adopted as the reference isotherm, the comparative plots obtained for low coverages are straight lines starting from the origin of coordinates. The slopes of these straight lines are proportional to the concentrations of PAS. The initial sections of the comparative plots for some AC are shown in Fig. 17. Deviations of these plots from linearity should be expected in those cases where the mechanism of adsorption on a particular sample departs from independent cluster formation.

The coalescence of clusters yielding a continuous film should be shown on the comparative plots by a sharp downward deviation from the linear dependence. Among all the AC studied, these deviations from linearity were observed only for two adsorbents with relatively wide pores. Comparative plots for mesoporous AC-M and for AC, prepared by heat treatment of AC-1 at 2073 K [AC-1(2073)], with a specific surface of 110 $m^2\ g^{-1}$ are shown in Fig. 18. Adsorption on a continuous adsorption film apparently occurs less effectively than on free clusters. The abscissae of the break points allow one, in principle, to calculate the specific surfaces of adsorbents from the relationship $S = L^2 a_m N$, where L is the diameter of clusters at the instant they coalesce, a_m concentration of the clusters, and N the Avogadro number.

The validity of the adsorption scheme considered can be more clearly demonstrated by determining the amount adsorbed at the instant the clusters coalesce from the concentration of the PAS, from the specific surface of the sample (found by using nitrogen adsorption), and from the cluster sizes calculated by numerical modelling,[40] and by comparing the result with the ordinate of the break on the comparative plot. The adsorbed amounts calculated by this procedure for the AC-M and AC-1(2073) samples are 3.6 and 1.9 mmol g^{-1}. These values are close to the ordinates of the break points in Fig. 18, which confirms the validity of the adsorption mechanism suggested.

For adsorption on microporous AC, deviations from linearity (breaks) are seen on comparative plots even for low coverage, and they are directed upwards (Fig. 19*a*). This shape of comparative plots shows that interaction between water molecules adsorbed on the opposite walls of pores (i.e. the formation of bridging bonds) results in an increase in adsorption compared with that on separate sites. In addition, the narrower the micropores, the smaller is the abscissa of the break point. This is more clearly seen in Fig. 19*b*, where the comparative plots are given in reduced coordinates: the amounts adsorbed, expressed as numbers of molecules per adsorption site for the AC studied, are plotted as the ordinate, and the corresponding values for the reference carbon black Vulkan-7H(3073) are plotted as the abscissa.

Fig. 20 presents the correlation between the abscissa of the break point and the cube of the average size, x, of the micropores, calculated from the nitrogen vapour adsorption isotherms.

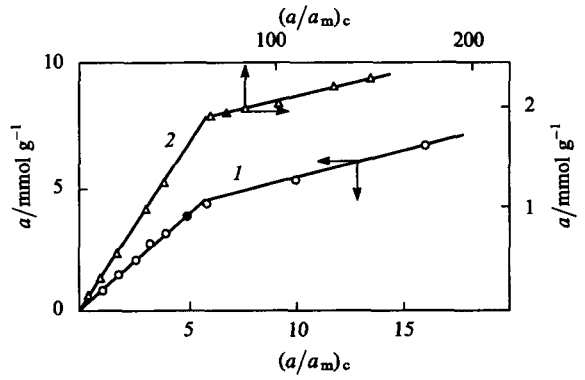


Figure 18. Comparative plots for the adsorption of water vapour on the mesoporous AC-M (*1*) and AC-1 (at 2073 K) (*2*).

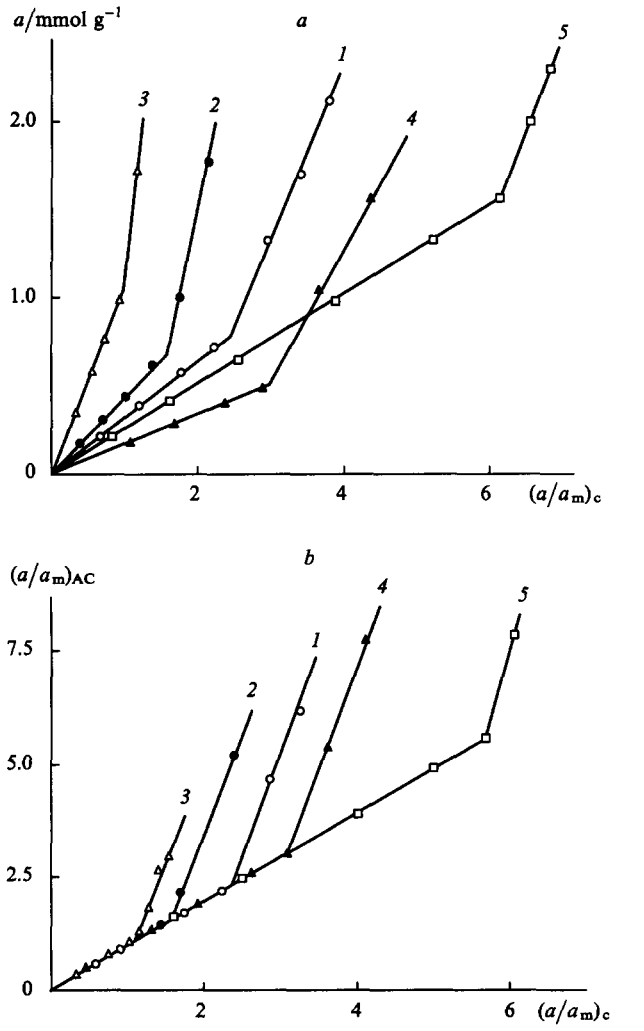


Figure 19. Comparative plots for the adsorption of water vapour on the microporous AC-1 (*1*), AC-2 (*2*), AC-U-1 (*3*), AC-5 (*4*), and AC-8 (*5*) in terms of the normal (*a*) and reduced (*b*) coordinates.

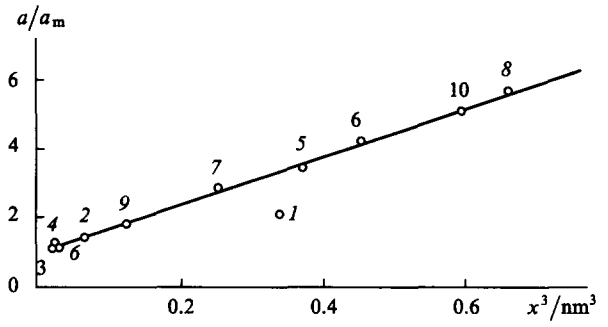


Figure 20. Correlation between the abscissa of the break point on comparative plots and the cube of the average size of micropores in AC-1 (*1*), AC-2 (*2*), AC-U-1 (*3*), AC-4 (*4*), AC-5 (*5*), AC-S (*6*), AC-7 (*7*), AC-8 (*8*), AC-9 (*9*), and AC-N (*10*).

The value of x can be found from the initial and middle sections of the water vapour adsorption isotherms on microporous AC.

The results obtained show that, when the micropores of the AC are filled with water, bridge bonds are formed. As this takes place, a relatively loose openwork structure, a 'lace', is produced in which the density of water is lower than that in the bulk phase. This can account for the fact that calculations of the limiting sorption volumes of AC from water vapour adsorption isotherms using the density of bulk-phase water usually afford smaller micropore volumes than calculations from the adsorption isotherms for other substances.[57] In principle, if the density of the adsorbed water is known, one can evaluate the size of the micropores by the foregoing procedure.[57]

Another method of evaluating the sizes of micropores of AC from adsorption and desorption isotherms for water vapour has also been reported.[58] The method is based on determining the width of the hysteresis loop between particular points on the adsorption and desorption isotherm branches. All the adsorption isotherms considered in this study have saturation sections, and the sharp rise of these isotherms ends at relative pressures of 0.8–0.9, and this limits the field of application of this method. In addition, it is known[59] that water vapour adsorption isotherms on ultramicroporous AC exhibit no hysteresis at all. One should also take into account the fact that repetition of the adsorption-desorption cycle for the same AC increases the amount of water adsorbed at saturation and diminishes the hysteresis loop,[60] which also hampers the use of this method.

The method of determining a porous structure from water vapour adsorption isotherms based on the formation of a monomolecular layer[4,22] at relative pressures of about 0.6 has been advantageously used for some AC. A common drawback of all the methods of calculation of specific surfaces based on the adsorption of water molecules is that for these calculations one must know the cross-sectional area of a water molecule; this value in its turn depends substantially on the oxidation state of the surface. It is likely that, for AC having typical micropores with diameters of the order of 4–5 water molecules, the overall adsorbed amounts are identical, whether a dense monomolecular layer or a loose 'openwork' packing is formed. In other words, the density of adsorbed water forming bridge bonds is approximately half that of liquid water. Hence, about two loose layers of the openwork packing are equivalent to a continuous monomolecular layer.[22] This is indirectly supported by the fact that the cross-sectional areas of water molecules differ by a factor of almost two: calculations give 0.06–0.08 to 0.13 nm^2 depending on the method, while the experimental results are 0.128 ± 0.54 nm^2.[61] A value of 0.148 nm^2 has been adopted as the cross-sectional area for a water molecule on carbon black.[20] Data on the linear dimensions of various molecules including water, obtained by various authors who have used different computational methods, have been analysed and systematised.[62] For a water molecule, values ranging from 0.276 to 0.348 nm were reported.

Dubinin and coworkers[63,64] later restricted the field of application of the previously suggested method[4,22] to activated carbons with a 'normally' oxidised surface and a narrow size distribution of micropores, while for a broader region of micropore sizes they suggested a calculation for a monomolecular layer from the point of inflection, determined with the aid of the Weibull equation,[63] which is used to describe experimental water vapour adsorption isotherms. The authors[63] showed that the inflection points, indicating, in their opinion, the formation of monomolecular layers on various AC, lie at p/p_s from 0.5 to 0.75, which expands significantly the applicability of this method of determining the porous structure of an AC. However, it should be noted that, since the experimental water vapour adsorption isotherms on ultramicroporous and mesoporous AC (see Fig. 7) have no normal inflection points, the approach suggested can scarcely be applied to these materials. For the same reason, this method cannot in principle be applied to nonporous CA.

Methods of determining the porous structure parameters based on the formation of a monomolecular water layer in the micropores of an AC are also not general, as the amounts of water adsorbed on various AC at the same relative pressure can differ appreciably, depending on the chemical state of the surface. For example, it has been shown[65] that the proportion of the surface of carbon blacks occupied by water at a relative pressure of 0.6 can vary from 10% to 450%, that is, 0.1 to 4.5 monomolecular layers are formed. Some authors dispute altogether the possibility of formation of a monomolecular layer on the surface of nonporous CA during adsorption of water vapour.[26,43]

As regards the above result,[65] it should be noted that the amount of water vapour adsorbed at saturation, which corresponds to the formation of more than two monomolecular layers, is associated, in our opinion, with the filling of the surface ultramicropores formed on oxidation of carbon blacks. Oxidation can not only be carried out by special treatment, but can also occur during storage in air, and may be accompanied by the formation of surface ultramicropores.[65] The presence of these surface ultramicropores can be demonstrated by a joint analysis of water vapour adsorption isotherms on ultramicroporous AC and Spheron-6 carbon black.[59]

It should be noted that the determination of the parameters of the microporous structure from water vapour adsorption isotherms by any method, including that suggested by us, is somewhat conventional, because the results obtained are compared with data on the adsorption of other substances (nitrogen or benzene), and for this purpose a particular model of the porous structure is introduced. Unfortunately, up to now, there are no other direct and reliable methods of studying the microporous structures of CA. The use of tunnelling electron microscopy may prove to be promising in this field; however, no systematic studies of CA by this method have yet been carried out.

IV. The nature of the primary adsorption sites

The nature of the PAS has been studied by temperature-programmed desorption with mass spectrometric analysis of substances being evolved, by neutralising surface oxides with bases of various strengths, and by X-ray photoelectron spectroscopy.

1. Temperature-programmed desorption

The substances evolved during the heating of AC have been analysed using mass spectrometry with a linear variation of the temperature of samples (a MAT-311A spectrometer, Varian, USA). Prior to heating, the samples were evacuated at 293 K and a pressure of 10^{-5} Pa for 12 h. Figs 21 and 22 show the temperature dependences of the rate of H_2O, CO_2, and CO evolution at heating rates of 5 K min^{-1} for initial and rehydrated

AC-U-1. As can be seen, the H_2O/CO_2 ratio depends on the type of AC. Some overlapping peaks on the curves correspond to various functional groups and their fragments. Joint desorption of H_2O and CO_2 is typical of AC-1. Analogous spectra were obtained for AC-2. It may be assumed that water is chemisorbed on these AC via lactone type groups, which accounts for the joint desorption of H_2O and CO_2.[67] Actually the groups being desorbed can be regarded as a complex carbonic acid $H_2O:CO_2$. In our opinion, the presence of an H_2O peak and a low-temperature CO_2 peak in the spectrum of the rehydrated substance is evidence in support of the chemisorption of water. The evolution of CO at high temperatures may occur either via the decomposition of the corresponding groups or via the chemical reaction with the lattice carbon of CO_2, formed on decomposition of carboxylic or lactone groups.

The spectrum recorded for the polymer-based AC-U-1 differs essentially from those for AC-1 or AC-2. The CO_2 band contains two peaks, one of which (in the high-temperature region) is close to the CO peak. Therefore, the following scheme can be proposed. Water is evolved due to decomposition of two carboxy-groups, yielding an anhydride structure. The low-temperature CO_2 peak results from decomposition of separate carboxy-groups, and the joint desorption of CO and CO_2 is associated with the decomposition of the anhydride structures at high temperatures. This scheme is in full agreement with the results of a study of IR spectra of Saran-type AC,[68] which are similar to the AC-U-1 studied by us.

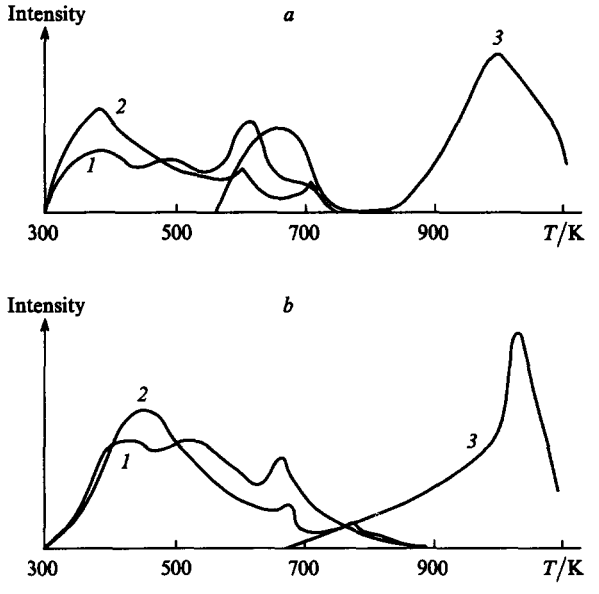


Figure 21. Temperature dependence of the rate of H_2O (*1*), CO_2 (*2*), and CO (*3*) evolution during the heating of the initial AC-1 (*a*) and the AC-1 rehydrated in water vapour after preliminary evacuation at 673 K (*b*) at a rate of 5 K min^{-1}.

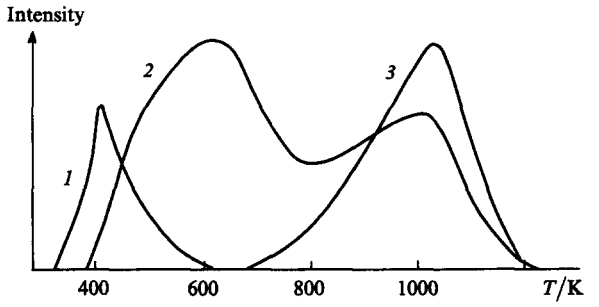


Figure 22. Temperature dependence of the rate of H_2O (*1*), CO_2 (*2*), and CO (*3*) evolution during the heating of AC-U-1 at a rate of 5 K min^{-1}.

Oxidation of these AC yields initially anhydride groups, which undergo hydrolysis by atmospheric moisture to give acid groups. These COOH groups are linked in pairs by hydrogen bonds.

A study on the nature of oxygen-containing functional groups in oxidised AC carried out recently by temperature-programmed desorption[69] has confirmed the existence of acidic carboxy-groups yielding a CO_2 peak at 600 K, and of anhydride groups with a CO_2 peak at 900 K. A significant role in the formation of 'CO_2 complexes' is played by the temperature of the oxidation of the AC in air or in nitric acid.[69] It has been found[44,70] that the quantity of CO_2 evolved is usually equivalent to the amount of alkali required to neutralise the acidic groups of AC.

From the adsorption results and data derived from temperature-programmed desorption, one may conclude that a part of the PAS (as a rule, the smaller one) are acidic carboxy-groups, thermally stable below 673 K. Adsorption on heated AC at low p/p_s occurs predominantly on these sites. The majority of the PAS on the AC prepared from natural raw materials (peat, coal, or wood) are chemisorbed water molecules, which are removed during heating simultaneously with CO_2. In this case, water molecules are apparently chemisorbed on lactone type groups, which can be regarded as complex carbonic acid adsorbed on the AC surface.

Water molecules chemisorbed on anhydride groups (carboxy-groups linked in pairs via hydrogen bonds) and individual carboxy-groups act as the PAS on Saran and other polymer-based AC.

2. Neutralisation of surface groups with bases of various strengths

The nature of the PAS has also been studied by the familiar Boehm[47] procedure, consisting in the neutralisation of the acidic groups with bases of various strengths. This procedure is being advantageously used to analyse the composition of acidic surface groups on oxidised AC, carbon blacks, and graphites. When the acidic groups being neutralised are weak, the interpretation of the titration data is more complicated, since neutralisation may be accompanied by the simultaneous ion exchange and direct hydrolysis of nonprotonated surface groups. We have carried out potentiometric titrations with a 0.05 N HCl solution of 0.05 N solutions of $NaHCO_3$, Na_2CO_3, NaOH, and C_2H_5ONa after they had been shaken with samples of AC.

Fig. 23 shows the potentiometric titration curves for the titration of solutions of NaOH (*a*) and Na_2CO_3 (*b*) with 0.05 M HCl after 20 ml of this NaOH or Na_2CO_3 solution had been shaken with 1 g of AC-1, AC-2, or AC-9 for two days. From Fig. 23*a*, one can see that in the case of AC-1 and AC-2, the titration curves for NaOH are similar to those for Na_2CO_3. One may assume that the surfaces of AC-1 and AC-2 contain the chemisorbed complex carbonic acid, $H_2O:CO_2$, which passes into the alkaline solution as Na_2CO_3 during interaction with water. This agrees with the data obtained by temperature-programmed desorption.

This characteristic of the titration of an NaOH solution, after shaking it with some of the AC, hampers a quantitative determination of the concentration of acidic groups of different strengths on the AC surface. In addition, it is known that inert electrolytes, for example KCl, added to a KOH solution substantially influence the results of the titration carried out after shaking the AC with this alkaline solution.[71] Since the mechanism of the action of inert electrolytes remains unclear, the authors[71] mostly used the data obtained on neutralisation of relatively strong acidic groups with a solution of Na_2CO_3.

Table 5 presents the concentrations of acidic surface groups neutralised by a solution of Na_2CO_3 (a_N), together with the number of PAS determined from water vapour adsorption isotherms on AC preliminarily heated at 673 K. One can see that these values are rather close, and it is quite probable that the convex section of the water vapour adsorption isotherm on the AC evacuated at 673 K is caused by the adsorption of water

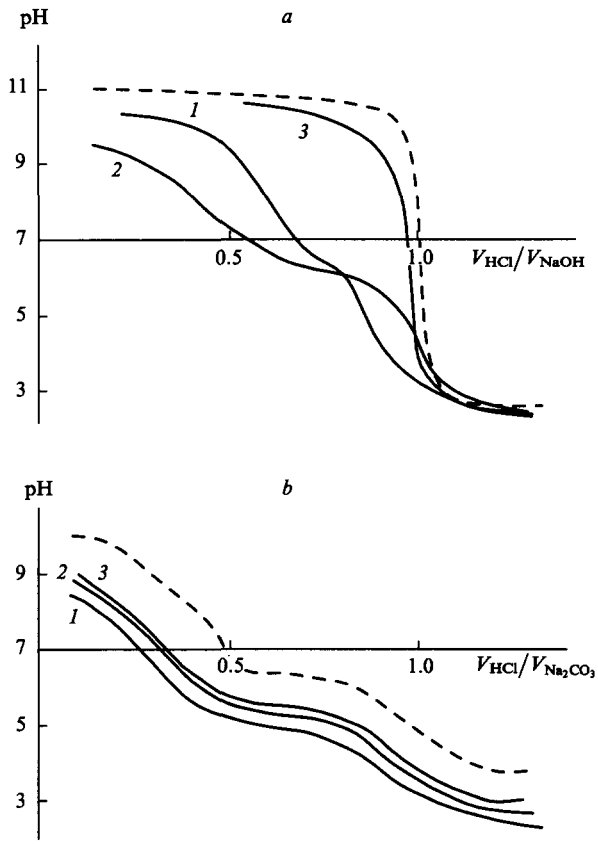


Figure 23. Curves for potentiometric titration with 0.05 N HCl of the NaOH (*a*) and Na_2CO_3 (*b*) solutions resulting from shaking 20 ml of 0.05 N NaOH and Na_2CO_3 respectively with 1 g of AC-1 (*1*), AC-2 (*2*), and AC-9 (*3*). The titration curves for the initial solutions of NaOH and Na_2CO_3 are shown by dashed lines.

molecules on relatively strong acidic carboxy-groups, which are not destroyed on heating to 673 K, as the PAS.[47] For nonporous graphitised Vulkan-7H carbon black, the number of surface groups neutralised with a Na_2CO_3 solution is 0.005 ± 0.002 mequiv. g^{-1}, which agrees with the data on the adsorption of water vapour ($a_m = 0.004$ mmol g^{-1}).

A correlation between the number of acidic groups determined by conductimetric titration and the amount adsorbed at point *b* (according to the BET equation) on the convex section of the water vapour adsorption isotherm has also been noted in a study[45] of the heats of immersion of a polymeric AC in water.

Despite the fact that quantitative analysis of the results of the titration of weakly acidic groups is difficult, one can make some qualitative conclusions. The titration curves for AC-9 have the normal shapes typical for the titration of a strong base with a strong acid. The numbers of acidic groups, neutralised with NaOH and Na_2CO_3, are close, i.e. the surface of AC-9 mostly contains strongly acidic groups, which are not removed on heating to 673 K. The adsorption properties of AC-9 with respect to water vapour almost do not depend on the evacuation temperature, i.e. adsorption occurs on thermally stable strongly acidic groups.

Table 5. The number of acidic surface groups neutralised by a solution of Na_2CO_3 (a_N) and the number of PAS (a_m) on the AC samples evacuated at 673 K.

Sample	a_N/mequiv. g^{-1}	a_m/mmol g^{-1}
AC-1	0.12	0.16
AC-2	0.16	0.21
AC-2 (oxidised)	0.50	0.44
AC-6	0.18	0.20
AC-7	0.09	0.08
AC-8	0.04	0.05
AC-9	0.18	0.20

It was shown previously that evacuation of AC-1 at 673 K leads to an appreciable decrease in the number of PAS, and the chemisorption of water molecules virtually restores the number of the PAS. In our opinion, the results obtained by the neutralisation of acidic groups are consistent with this assumption. When AC-1 is shaken with NaOH, some of the surface groups pass to the solution as Na_2CO_3. This results from the interaction of NaOH with weakly acidic groups on the surface of AC-1 (the complex carbonic acid, $H_2O:CO_2$). A relationship between the quantity of water, irreversibly adsorbed by the AC, and the number of oxygen-containing surface groups that decompose on heating to evolve CO_2 has also been observed in a study of the adsorption of water on AC modified with potassium permanganate and nitric acid.[44]

3. X-Ray photoelectron spectroscopy

The adsorption properties of AC with respect to water vapour are determined by an active part of the oxygen present, rather than by its total amount. The proportion of active oxygen can be evaluated by X-ray photoelectron spectroscopy. For this purpose, an AC sample was ground in an agate mortar and deposited as a suspension in water or ethanol on a support. After the evaporation of the liquid, the supported sample was introduced into the sluice compartment of an ESCA-3 MARK-2 spectrometer (VG, UK). The analysis was carried out after evacuation of the AC to a pressure of 10^{-9} Pa. X-Rays (magnesium K_α line) with $h\nu = 1253$ eV served as the ionisation source. The spectra were calibrated against an external standard [C 1*s* peak (285.0 eV) from a hydrocarbon layer on a gold support]. The O 1*s* spectra were recorded prior to and after heating the supported sample in the spectrometer compartment to 650 K. The O/C relative concentration was determined from the ratio between peak surface areas with allowance for the corresponding ionisation cross-sections. Simultaneously with the O 1*s* spectrum, the mass spectra of the desorbed substances were recorded using a built-in mass spectrometer. The oxygen spectrum is complex. Its detailed interpretation is complicated by difficulties associated with the calibration of the peak components; however, it may be noted that when the sample is heated, the spectrum component with a higher bond energy diminishes sharply[72] and evolution of H_2O and CO_2 occurs. The quantity of oxygen removed is estimated from the O : C ratios in the initial and heated AC.

Table 6 presents the O : C ratios for some AC as examples and also these ratios for AC-1 heat treated in argon at 1273 to 2273 K, oxidised in moist air at 623 K, and deashed with HCl or with HCl and HF in succession. As can be seen from the table, when the initial AC-1 is heated to 673 K, most of the oxygen remains in the AC, whereas the number of PAS is almost halved, as was shown above from the adsorption data (see Table 4). This indicates that most of the PAS on this AC are unstable oxygen-containing groups removed during heating to 673 K, in particular chemisorbed water. The overall amount of oxygen in AC-1 ensures a number of PAS a_m of 0.30 mmol g^{-1}. When 14% of the oxygen is removed, the number of PAS diminishes to 0.16 mmol g^{-1}, i.e. the adsorption-active oxygen comprises about a quarter of its overall content, which agrees with the data obtained by Boehm.[47]

Treatment of the AC in a moist air flow at 623 K does not result in an increase in the overall oxygen content (see Table 6); it actually decreases somewhat, due to the removal of some of the surface oxygen-containing groups on heating the sample. However, the relative change in the O/C concentration caused by heating decreases from 0.14 to 0.11 under these conditions.

Table 6. The O:C ratios calculated for some AC from X-ray photoelectron spectra prior to and after heating of the AC.

Sample	Method of treatment	O:C ratio (%)	
		before heating	after heating
AC-1	None	13.7	11.8
	Heat treatment at		
	1773 K	8.0	8.0
	2073 K	3.0	3.0
	Oxidation	12.3	10.9
	Deashing with		
	HCl	12.5	10.5
	HCl + HF	7.4	5.1
AC-2	None	20.0	–
AC-U-1	"	15.0	–
AC-10	"	39.0	–

Thus, oxidation in a moist air flow at 623 K results in an increase in the proportion of thermally stable oxygen-containing groups, rather than in the overall amount of oxygen on the AC. It is this effect that stabilises the number of PAS on the oxidised AC when it is heated from 293 to 673 K (see Table 4).

V. The influence of the adsorption of water vapour on the parameters of the microcrystalline structure of activated carbons

Valuable information about the mechanism of the adsorption of water molecules, the location of the PAS, and also the relationship between microporous and microcrystalline structures of adsorbents can be obtained from X-ray diffraction studies of AC adsorbing water vapour.

Carbon adsorbents normally consist of amorphous carbon and crystalline areas (crystallites), whose faces can form the walls of micropores. In X-ray diffraction patterns, the amorphous part is manifested as background scattering, while the structure of crystallites is characterised by two reflections: a more intense (002) reflection, the angle of which allows one to determine the distance between the graphite-like layers (d), and a weak (10) reflection corresponding to the ordering of atoms in the graphite-like layers.[73] The (10) reflection is actually a band that usually incorporates several unresolved lines — (100), (004), and (110). From the width of the (002) reflection, the X-ray diffraction parameter L_c characterising the 'height' of crystallites, i.e. the dimensions of the prismatic faces of the crystallites, can be estimated, while the width of the (10) band makes it possible to find the L_a parameter characterising the dimensions of the basal faces of crystallites. The relative intensity of the reflection provides information about the degree of crystallinity of the carbon material.[73,74]

Since the X-ray diffraction patterns of the AC do not change when the surface is covered with oxides, it has been assumed[75] that oxygen is located at the corners of hexagons made up of carbon atoms. If we accept this assumption and take into account the fact that a proportion of the oxygen must be incorporated in the PAS, we find that the distances (l_m) between them should be of the same order of magnitude as the sizes of the crystallites L_a. To a first approximation, l_m can be estimated on the assumption that the PAS are uniformly distributed over the total surface of the AC ($S_g + S_m$).

The total surfaces ($S_g + S_m$) of AC found from nitrogen adsorption isotherms at 77 K, the numbers of the PAS (a_m) determined from water vapour adsorption isotherms at 293 K, and the distances between them (l_m) are listed as examples in Table 7. The L_a parameters and half-widths (x) for the slit model of pores are presented for comparison. One can see that the average distances between PAS for the majority of AC vary over a rather narrow range and are close, on average, to the sizes L_a of the crystallites forming the structure of the AC. The L_a parameters of the AC studied are consistent with the values reported[76] for various AC.

Table 7. The total specific surfaces ($S_g + S_m$), the numbers of PAS (a_m), the distances between them (l_m), the X-ray diffraction parameters L_a, and average half-widths x for some of the CA studied.

CA	(S_g+S_m)/ $m^2\ g^{-1}$	a_m/ mmol g^{-1}	l_m/nm	x/nm	L_a/nm
1	494	0.30	1.65	0.71	2.10
2	987	0.41	2.00	0.42	2.20
4	435	0.48	1.23	10.28	1.86
5[a]	820	0.16	2.92	0.73	–
6	1363	0.60	1.94	0.24	2.20
7	1058	0.41	2.07	0.64	3.30
8	1070	0.21	2.90	0.87	3.70
9	934	0.20	2.79	0.52	–
10	1019	0.53	1.79	0.54	2.36

[a] The calculations were carried out using the Dubinin – Stoeckli equation. Calculation by the two-term equation of the theory of volume filling yields a total specific surface of 713 $m^2\ g^{-1}$ and $x = 0.85$ nm.

A comparative X-ray diffraction study of various CA adsorbing water vapour makes it possible to identify the changes in adsorbents caused by the adsorption of water molecules. The adsorption of water vapour on some of the AC leads to a decrease in the interplanar spacing;[77] however, it is not clear whether this is a common characteristic feature of all AC and what is the physical meaning of these changes.

The results of a comparative X-ray diffraction analysis of CA are presented in Figs 24 and 25. The X-ray diffraction patterns were obtained on a DRON-3M diffractometer using CuK_α radiation (a Ni filter) by reflection from a flat sample, ground up beforehand and rubbed into a round cell. The measurements were carried out at room temperature; prior to the measurements, the samples were dried at 373 K and saturated with water vapour for 48 h. The interplanar spacings d and the intensities I of the (10) band, relative to the background, were determined for samples dried at 373 K and for samples saturated with water vapour.

Figs 24 and 25 present, among other data, the results of X-ray diffraction studies for those CA which are not listed in Tables 2 or 3. The d parameters for the dried samples studied varied from 0.355 nm for the P267-E carbon black to 0.462 nm for supermicroporous AC-S.

These figures indicate that the changes in the interplanar spacings (Δd) and intensities (ΔI) of the (10) band occurring after saturation of various AC with water vapour have some features in common. The average interplanar spacing d always decreases on adsorption of water molecules, and moist samples have closer d values than the dry ones. It is likely that water molecules, whose size is only slightly smaller than the distance between the graphite-like layers, influence the arrangement of the edge carbon atoms, located on the defective surfaces of crystallites, which makes a contribution to the change in the average interplanar spacing.

The Δd values increase as d increases up to a certain limiting value, after which they diminish (Fig. 24). At the same time, the intensity of the (10) band referred to the background increases for some of the samples (ΔI is positive) and decreases for others (ΔI is negative) (Fig. 25). The dependence of ΔI on d for moist samples of most of the AC studied is nearly linear (the samples with the maximum d value deviate from the general relation). This type of variation of Δd and ΔI with d can be explained in terms of the following scheme (Fig. 26). In the case of samples with small d values, the adsorption of water molecules on the edge dislocations of the graphite-like layers leads to a decrease in

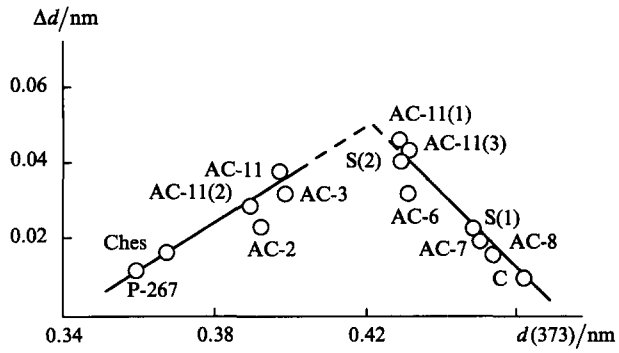


Figure 24. Dependence of $\Delta d = d(373) - d(H_2O)$ for samples dried at 373 K [$d(373)$] and samples saturated with water vapour [$d(H_2O)$] on $d(373)$. The points are labelled in conformity with the designations of the CA used in Tables 2 and 3. Additional designations are as follows: P is an industrial carbon black of the type P267-E, 'Ches' is a 'Chesacarb' type carbon black produced in the Czech Republic, S(1) is a modification of the supermicroporous AC-S, S(2) is AC-S treated with concentrated HNO_3, AC-11(1) and AC-11(2) are samples of AC-11 treated at 1173 K in an Ar or NH_3 atmosphere respectively, and AC-11(3) is AC-11 treated with concentrated HNO_3.

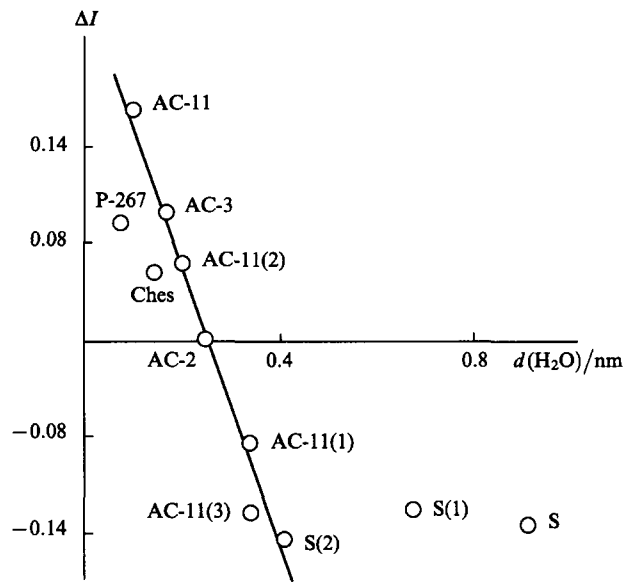


Figure 25. Dependence of the intensity difference $\Delta I = I(H_2O) - I(373)$ for samples saturated with water vapour [$I(H_2O)$] and those dried at 373 K [$I(373)$] on $d(H_2O)$ for moist samples. The designations are the same as in Fig. 24.

the interplanar spacing and simultaneously makes the mutual arrangement of the layers more ordered (Fig. 26*a*). For samples with medium d values, a decrease in d, virtually unaccompanied by an ordering of the networks, is possible (Fig. 26*b*). For samples with large d values, the adsorption of water molecules may result in a decrease in the interplanar spacing with a simultaneous distortion of the mutual arrangement of the layers (Fig. 26*c*). When d is further increased, the adsorption of water molecules does not influence it.

Thus, the character of the variation of the interplanar spacing d and of the relative intensity I of the (10) band after the adsorption of water vapour confirms the hypothesis that the adsorption occurs from the sides of the prismatic faces of the crystallites, where edge defects are located. This conclusion is also supported by the data on the influence of the adsorption of water

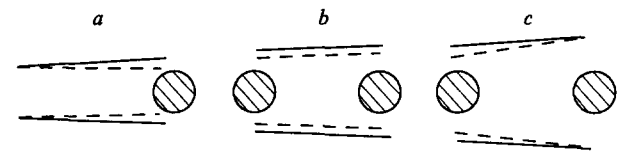


Figure 26. Schematic arrangement of water molecules near graphite-like layers at the edges of crystallites. The solid and dashed lines show the corresponding arrangement of the graphite-like layers prior to and after the adsorption of water molecules.

molecules on the L_a parameter characterising the size of the basal faces of the crystallites. Table 8 presents the L_a and L_c parameters for some AC dried at 373 K and saturated with water. One can see that L_a increases due to the adsorption of water vapour in all cases, and the larger the value of L_a, the larger the relative increase in $\Delta L/L_a$. At the same time, L_c varies slightly and irregularly. These results indicate that the adsorption of water molecules leads to the elongation of the carbon layers, and improvement of the latter.

Table 8. X-Ray diffraction parameters L_a and L_c for samples dried at 373 K and saturated with water.

Sample	L_a/nm		L_c/nm	
	373 K	H_2O	373 K	H_2O
AC-1	2.10	2.55	1.82	1.79
AC-6	2.20	3.10	0.98	1.02
AC-7	3.30	4.39	0.89	0.94
AC-8	3.70	5.00	0.75	0.94
AC-10	2.36	2.64	1.02	1.02
AC-S	2.14	3.67	0.89	0.86
AC-U-2	1.78	2.34	1.64	1.58

The combination of X-ray diffraction analysis in the study of the adsorption of water vapour with the determination of adsorption isotherms in the study of the formation of the porous structure of the AC in the carbonisation and activation stages makes it possible to demonstrate in some cases a bimodal size distribution of the micropores of some AC, associated with the presence of two independent structures.[78] Apart from the normal micropores, revealed by nitrogen vapour adsorption isotherms, some AC can contain ultramicropores revealed by water vapour adsorption isotherms.[78] This is due to the sensitivity of the adsorption of water vapour at low relative pressures to the size of very small micropores. The water vapour adsorption isotherm on these AC has a typical 'wave-like' shape, whereas the nitrogen vapour adsorption isotherm at 77 K has the normal shape.[78,79]

Thus, it may be stated that the water vapour adsorption isotherms are more sensitive in a certain sense to the features of the porous structure than adsorption isotherms for other adsorbable substances; this allows one to identify fine details of CA structures. Later, Naono and Hakuman[80] arrived at the same conclusion while studying the porous structures of silica gels and also iron and titanium oxides.

In general, one may conclude that the differences between the mechanisms of the adsorption of nitrogen and water vapours on CA are manifested by different effects of the chemical state of the surface and the porous structure of the CA on the form of the nitrogen and water vapour adsorption isotherms. Therefore, experimental data concerning adsorption of nitrogen and water vapour complement each other and provide more comprehensive and detailed characteristics of the porous structure of the CA.

The data obtained by X-ray diffraction agree with the previously suggested schemes for the filling of the micropore volume with water. The similarity of the L_a and l_m values, on the one hand, and their comparison with the x values, on the other hand, imply (see Tables 7 and 8) that for the majority of AC the distances between the PAS are larger than the half-widths of the micropores, so that the filling of the micropore volume with water molecules involves the formation of bridge bonds between the PAS located on the opposite walls of micropores. Thus, the character of the filling of the pore volume with water depends on the ratio between the widths of slit-like pores and the surface concentration of the PAS, which is determined, in its turn, by the average size of the crystallites forming the porous structure of the activated carbons.

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