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A model of the two-stage condensation mechanism of water adsorption on nonporous carbon adsorbents

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The mechanism of adsorption of water molecules on nonporous carbon adsorbents has been suggested in terms of two different states of adsorbed water: stretched liquid water and water that occupies an intermediate state between the liquid and vapor. Two stages of adsorption were distinguished: condensation and pre-condensation that assumes the formation of molecular associates. The BET model was used to describe the pre-condensation stage. The equations of the adsorption isotherm for water vapor in the region of condensation process and the expression for the determination of the specific hydrophilic surface of adsorbents were found. Examination of the experimental data on adsorption of water vapor on nongraphitized samples of carbon adsorbents shows that in the region of polymolecular adsorption, all isotherms fall into a common curve determined by the equation of the stretched liquid film and can be calculated regardless of the properties of individual liquid water. The equation for adsorption of water vapor on the hydrophobic surface was obtained.

Key words: adsorption, nonporous carbon adsorbents, model of condensation mechanism.

Data on the properties of macroscopic water in different aggregate states and at different pressures are of great interest for studying the mechanism of water adsorption on carbon adsorbents (CA).[1]

The development of the phase diagram "chemical potential—entropy—temperature" for the H_2O—CA adsorption systems[2] suggested ambiguously that two states of water exist on the surface and in pores of CA: "stretched" liquid water and water that occupies an intermediate position between the liquid and gas. On the phase diagram, this unusual form of water occupies the region different from the state of bulk (nonadsorbed) water.

In this work, we attempted to describe the mechanism of water adsorption on CA taking into account these two states.

Liquid water and the boundary of its existence

To describe "stretched" liquid water, we can use the equation of state,[3] which is valid over a wide range of conditions limiting the existence of the liquid phase beginning from the spinodal to a pressure of 100 MPa over the 273—373 K temperature range:

$$p_{\mathrm{hst}} = p_{\mathrm{sp}}\left[1 - B\left(\frac{V_{\mathrm{sp}}}{V} - 1\right)^2\right], \tag{1}$$

where p_{hst}/mPa is the hydrostatic pressure on the liquid phase; p_{sp} is the pressure on the spinodal; V/cm^3 mol^{-1} is the molar volume of water; V_{sp}/cm^3 mol^{-1} is the molar volume of water on the spinodal; and B is a constant that depends on the temperature T only. For 20 °C, $p_{\mathrm{sp}} = -208$ MPa, $B = 17.829$, and $V_{\mathrm{sp}} = 22.3029$ cm^3 mol^{-1}.

The applied external pressure p_{hst} changes the volume V of liquid water and the related pressure of saturated vapor p_{s}. This dependence can be expressed by the equation[2]

$$\ln\frac{p_{\mathrm{s,0}}}{p_{\mathrm{s}}} = \frac{E}{RT}\left[\frac{V_{\mathrm{sp}}}{V} - \frac{V_{\mathrm{sp}}}{V_{\mathrm{s,0}}} + \ln\frac{V}{V_{\mathrm{s,0}}}\right], \tag{2}$$

where $p_{\mathrm{s,0}}$ and $V_{\mathrm{s,0}}$ are the vapor pressure and water volume on the binodal, respectively; p_{s} is the pressure of liquid vapor in the V volume, and the E value is determined by the formula:

$$E = 2V_{\mathrm{sp}}p_{\mathrm{sp}}B. \tag{3}$$

Equations (2) and (3) make it possible to determine the boundary of existence of stretched liquid water expressed in units of the relative pressure p/p_{s}. Substituting the values p_{sp}, V_{sp}, $V_{\mathrm{s,0}} = 18.00$ cm^3 mol^{-1}, and $p_{\mathrm{s,0}} = 2.33$ kPa, we obtain $(p/p_{\mathrm{s}})_{\mathrm{sp}} = 0.178$ for $T = 293$ K.

Models of adsorbent

Nonporous carbon adsorbents consist of amorphous carbon and crystallites, whose properties are close to

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those of graphite crystals. Amorphous carbon also contains carbon graphite nets, but they are chaotically arranged relative to each other. On edges of the graphite nets, in sites of their cleavage, carbon atoms are chemically linked with heteroatoms, predominantly with oxygen and hydrogen atoms.

In the first approximation, nonporous CA can be presented as a set of similar microscopic crystallites with two types of surface *a* and *b*: *a*, planar basis facets of graphite and *b*, lateral edges of these facets containing oxygen and hydrogen atoms. The edges of the basis facets are shifted relative to one another and form a microrough surface with local holes and "combs." This geometric nonuniformity can be expressed through the curvature with a radius *r*, which distinguishes the model of surface *b* considered from the planar surface.

The total surface of facets *a* forms the hydrophobic surface A_{hphb}, and the total surface of facets *b* forms the hydrophilic surface A_{hphl}. The total surface is the following: $A_{\text{tot}} = A_{\text{hphb}} + A_{\text{hphl}}$.

Surface tensile strength

The molecular field, which falls off as the distance from the surface decreases, operates in the boundary volume between the adsorbent and the adsorption layer. This results in forces, some of which act in the plane parallel to the adsorbent surface. They are determined as tangential components of the pressure tensor p_t.

When the adsorbent and the adsorbed layer are considered, in the rough approximation, as a continuum generating the molecular field close to the field in the transition liquid layer adjacent to the gas, the dependence of p_t on the distance to the boundary surface *l* can be described by the Rusanov—Kuni equation,[4] which was obtained for the van der Waals fluid and is strictly fulfilled far from the interface:

$$p_t = p + \frac{\pi}{8V_0}\left[\frac{D'}{V'} - \frac{D_0}{V_0}\right]\frac{1}{l^3}\ , \qquad (4)$$

where *p* is the external pressure; D_0 and D' are constants of the interaction of liquid molecules and molecules of the neighboring gas phase, respectively; and V_0 and V' are the molar volumes of the liquid and gas phases, respectively.

The value and sign of pressure p_t are determined by the difference of the D/V ratio of the contiguous phases. At the interface of the adsorption layer with the gas phase, the molar volume of the gas phase V' is much higher than the molar volume of the condensed phase V_0, and since $p = p_s$ is much lower than p_t, they can be ignored. Therefore, p_t attains negative values:

$$p_t = -[(\pi D_0)/(8V_0{}^2l^3)]. \qquad (5)$$

At each point of the adsorption layer, the tangential component p_t operates to bring about extension of the layer. The action of p_t results in a change in the density of the substance in the layer. The thermodynamic equivalent of the p_t pressure was calculated from the change in the vapor pressure of the adsorbate (Eqs. (1) and (2)).

Model of the liquid stretched water film

At $p/p_s > 0.178$ water vapor can interact with the solid surface to form the liquid layer. The p_t pressure extends the liquid layer that formed, and a certain equilibrium pressure is established in the gas phase. It is the pressure of saturated vapor of the stretched liquid.

The equation describing the isotherm for adsorption with the formation of the stretched liquid film has been obtained previously:[5]

$$\ln(p_s/p) = b/\theta^3 - W/RT,\ \theta = \tau/d, \qquad (6)$$

where θ is the adsorption value expressed by the number of molecular layers; *d*/nm is the diameter of an adsorbate (water) molecule; τ/nm is the thickness of the layer; *W*/kJ mol^{-1} is the work of curvature of the film surface; and *b* is a constant that depends on the properties of the pure liquid:[6]

$$b = 2.5V_0\sigma_0/RTd, \qquad (7)$$

here V_0 and σ_0 are the molar volume and surface tension of the pure liquid. For water, $b = 4.34$ ($T = 293$ K).

Let us estimate the curvature of the liquid film on the surface, which is characterized by the *b* value. Let us accept that, according to the Thomson (Kelvin) equation,

$$W = 2(V_0\sigma_0/r), \qquad (8)$$

where *r*/nm is the curvature radius. Inserting expressions (7) and (8) into Eq. (6), we obtain the final equation of isotherm of water adsorption in the region of formation of the liquid film on the convex hydrophilic surface.

$$\ln(p_s/p) = 4.34/\theta^3 - 1.08/r \qquad (9)$$

BET model for description of the pre-condensation stage of adsorption. The Brunauer—Emmett—Teller (BET) model assumes that one-dimensional vertical associates (OVA) of different thicknesses are formed on the surface.[7]

The BET equation describing the adsorption isotherm in the modified variant[8] has the form

$$\theta = a/a_m = \frac{Cg(p/p_s)}{[1 - g(p/p_s)][1 + (C - 1)g(p/p_s)]}\ , \qquad (10)$$

where *a* is the adsorption value; a_m is the capacity of the monolayer; *C* is a constant of the adsorbate—adsorbent interactions that was introduced in the initial model to signify condensation of molecules from the gas phase to molecules on the free end of OVA; *p* is the equilibrium pressure of the adsorbate; p_s is the pressure of saturated vapor of the liquid adsorbate (water); and g is the factor that determines the deviation of this constant from the magnitude in the initial model where $g = 1$.

The use of the BET model for the water—carbon adsorbent system needs additional substantiation. It is accepted that the BET theory is usually fulfilled in the interval $p/p_s = 0.05$—0.35 and at $C > 10$. The pre-condensation region considered hereinafter is stretched to the saturation pressure $p/p_s = 1$ at very low C values ($C \rightarrow 0$). The region $p/p_s \rightarrow 1$ is considered as principally inappropriate for the BET theory, because it gives the value of spreading pressure without a physical sense. However, the BET theory is confined to the formation of only molecular associates (clusters) on the adsorbent surface and does not consider the mechanism of aggregation of the clusters to form the liquid layer. The transition to the liquid layer described in this work supplements the BET theory.

When the C constant is substantially lower than unity, we can neglect it in the denominator of Eq. (10) and obtain the expression

$$\theta = C_g(p/p_s)/[1 - g(p/p_s)]^2. \qquad (11)$$

This expression was used for the description of adsorption on the hydrophobic surface of CA.

Supplement to the BET model

In the BET model, the adsorption layer is a set of OVA of different thicknesses. Near saturation [$g(p/p_s) = 1$] in Eq. (10), the length of OVA becomes infinite, and it is reasonable to assume that at a certain "critical length," OVA lose their stability and pass to another state. Assume that this transition is accompanied by the formation of a film of the stretched liquid. The transition corresponds graphically to the intersection point l of the isotherm of polymolecular adsorption of the BET model with the adsorption isotherm for the liquid layer (Fig. 1). Let us designate the relative pressure corresponding to the inception of the liquification of the adsorbate as p^*/p_s. The region of the adsorption isotherm below the intersection with the isotherm of the liquid is considered as the pre-condensation region or the region of nucleation of the liquid.

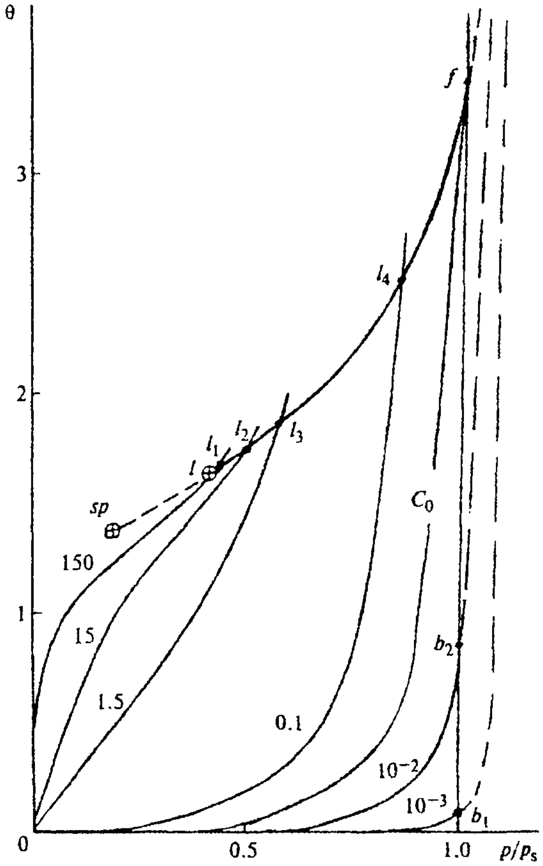

Fig. 1. Theoretical isotherms of water adsorption on nonporous CA related to different stages of the condensation process. Curve lf is the line of condensation with the formation of the stretched liquid film; curves $0l_1$, $0l_2$, $0l_3$, and $0l_4$ describe the formation of liquid nuclei according to the mechanism of polymolecular adsorption BET. Points l is the limit of existence of the liquid phase on the surface; sp is the spinodal state of the bulk liquid; l_1, l_2, l_3, and l_4 is the onset of formation of the liquid film (p^*/p_s); b_1,b_2, and f is the adsorption upon saturation ($p/p_s = 1$); dotted lines in the region $p/p_s > 1$ are the adsorption isotherms at the hypothetical positive external pressure. The values of the C constant in Eq. (10) are designated by the figures near the curves.

The theoretical isotherms of adsorption of water on the hydrophilic CA surface calculated by Eq. (9) for the liquid film (curve $splf$) at $r = 10$ nm and by Eq. (10) for the BET model (curves $0l_1$, $0l_2$, $0l_3$, and $0l_4$) are shown in Fig. 1. The points of transition l_1, l_2, l_3, l_4,..., l_i (p^*/p_s) are obtained when Eqs. (9) and (10) are solved jointly.

When the C value increases, the intersection point tends to some limiting value of p^*/p_s close to 0.410, which was obtained for the hypothetical adsorption CA—H_2O system with the planar liquid adsorbate layer formed from OVA with the strong adsorbate—adsorbent interaction ($C \rightarrow \infty$, $g = 1$ in Eq. (10)). Point l is the boundary of existence of the liquid phase of adsorbed water. Note that this boundary is considerably shifted from the spinodal for bulk water (point sp, $p/p_s = 0.178$). As the C constant decreases, the intersection point l_i is shifted toward higher p/p_s. At a certain value of the C constant (C_0), point l_i coincides with point f. The isotherm with the C_0 constant (for example, for $g = 0.9$, $C_0 = 0.039$) divides conventionally the family of BET isotherms into two types: isotherms of one type describe water adsorption on the hydrophilic ($C > C_0$) surface, and isotherms of another type describe water adsorption on the hydrophobic ($C < C_0$) surface.

Adsorption upon saturation

As can be seen in Fig. 1, the isotherm of liquid film (curve *lf*) and isotherms for the modified BET model intersect the axis $p/p_s = 1$ at certain final values of θ (points b_1, b_2, f) and then approach the region $p/p_s > 1$. This region is inaccessible for a standard adsorption experiment, since at $p/p_s > 1$ vapor is condensed outside the adsorbent. It is possible to retain the adsorption equilibrium at $p/p_s > 1$, if the external positive pressure acts upon the adsorption system.

Let us determine the relation between the adsorption value and external pressure in the general form. For this purpose, let us consider a system of two vessels I and II. Vessel I contains the adsorption system, and the adsorbate in the state of bulk liquid is present in vessel II. The vessels communicate through the gas phase, and the adsorption equilibrium is established in vessel I at the temperature T. Let us introduce a hypothetical gas into the system. It is not adsorbed and dissolved and has no effect on the removal of the adsorbate vapor between the vessels. The gas pressure p can change beginning from zero. For the adsorption system, the change in the isobaric potential G with the p pressure is determined by the equation:[4]

$$(\mathrm{d}G^{\mathrm{I}}/\mathrm{d}p)_t = V_s^{\mathrm{a}} - (A/a_s)(\mathrm{d}\sigma^{\mathrm{a}}/\mathrm{d}p)_t, \qquad (12)$$

and for the bulk liquid (if the contribution of the liquid—vapor interfacial surface A is neglected in Eq. (12)), it is determined by the equation

$$(\mathrm{d}G^{\mathrm{II}}/\mathrm{d}p)_t = V_s, \qquad (13)$$

here V_s^{a} is the molar volume of the adsorbate upon saturation; V_s is the molar volume of the liquid; σ^{a} is the surface tension at the adsorbate—vapor interface; A is the interfacial surface; and a_s is the adsorption value upon saturation. The following conditions are fulfilled in the equilibrium:

$$G^{\mathrm{I}} = G^{\mathrm{II}};\ (\mathrm{d}G^{\mathrm{I}}/\mathrm{d}p)_t = (\mathrm{d}G^{\mathrm{II}}/\mathrm{d}p)_t. \qquad (14)$$

After transformations of Eqs. (11)—(13), we obtain the final expression:

$$a_s = A/(V_s^{\mathrm{a}} - V_s)\cdot(\mathrm{d}\sigma/\mathrm{d}p)_t. \qquad (15)$$

The signs of the derivative $(\mathrm{d}\sigma/\mathrm{d}p)_t$ and difference $(V_s^{\mathrm{a}} - V_s)$ are unknown, but since a_s and A are positive values, the $(\sigma/\mathrm{d}p)/(V_s^{\mathrm{a}} - V_s)$ ratio is also positive.

It follows from Eq. (15) that at $V_s^{\mathrm{a}} = V_s$ the adsorption value upon saturation increases indefinitely. This implies that the adsorbent is completely "flooded" with water as the p pressure increases. The process continues until the interfacial surface of the liquid with the immersed adsorbent becomes minimum.

Capacity of the monolayer

The equation of liquid layer (9) and BET Eqs. (10) and (11) contain the θ value related to the value of the experimental adsorption a by the expression

$$a = \theta a_m A, \qquad (16)$$

here $a_m/\mu\mathrm{mol\ m^{-2}}$ is the value of monolayer capacity per surface unit, and A/m^2 is the surface area. Adsorption on the hydrophilic surface under standard conditions and on the hydrophobic surface at positive external pressure proceeds until a liquid water layer with an indefinite thickness is formed. In all cases, the a_m value is determined from the molar volume of liquid water $a_m = V^{-2/3}N^{-1/3} = 17.26\ \mu\mathrm{mol\ m^{-2}}$ ($V = 18\ \mathrm{cm^3\ mol^{-1}}$, $N = 6.02\cdot10^{23}$). The model of a continuous film on the hydrophilic CA surface makes it possible to determine the value of its surface area A_{hphl} using one or several points on the adsorption isotherm in the region of condensation, *i.e.*, in the interval of relative pressure from 0.41 to 1. Inserting the value $a_m = 17.26$ into Eq. (16) and then θ into Eq. (9), we obtain, after the transformation

$$A_{\mathrm{hphl}} = 35.33a(\ln p_s/p + 1.08/r)^{1/3}. \qquad (17)$$

Here a is expressed in mmol $\mathrm{g^{-1}}$. The A_{hphl} value enters Eq. (10) at $C > C_0$.

Comparison with experiment

According to the classification of Brunauer, adsorption of water vapor on carbon adsorbents gives isotherms of the II, III, and V types. Isotherms concave to the p/p_s axis in the whole adsorption region are related to the III type. In the condensation mechanism considered, isotherms of the III type correspond to the pre-condensation stage of adsorption.

Isotherms of the II type describe both the pre-condensation stage and the condensation process. Strictly speaking, isotherms including both these processes do not belong to a certain type, because they consist of segments of isotherms of two types (perhaps, II and III), which intersect in a certain point. They can be distinguished as an independent type of adsorption isotherms including a break of the isotherm. However, in real isotherms, this break is smoothened, and they are close in shape to isotherms of the II and V types.

Oxidized carbon blacks. The parameters of nonporous CA, on which water adsorption is described by isotherms of the V type, are presented in Table 1.

The theoretical and experimental isotherms of water adsorption on hydrophilic adsorbent surfaces, for which A values were pre-calculated by Eq. (17), are shown in Fig. 2, *a*, *b*. As can be seen in Fig. 2, all points in the region of polymolecular adsorption within the values close to f are adjacent to the theoretical isotherm deter-

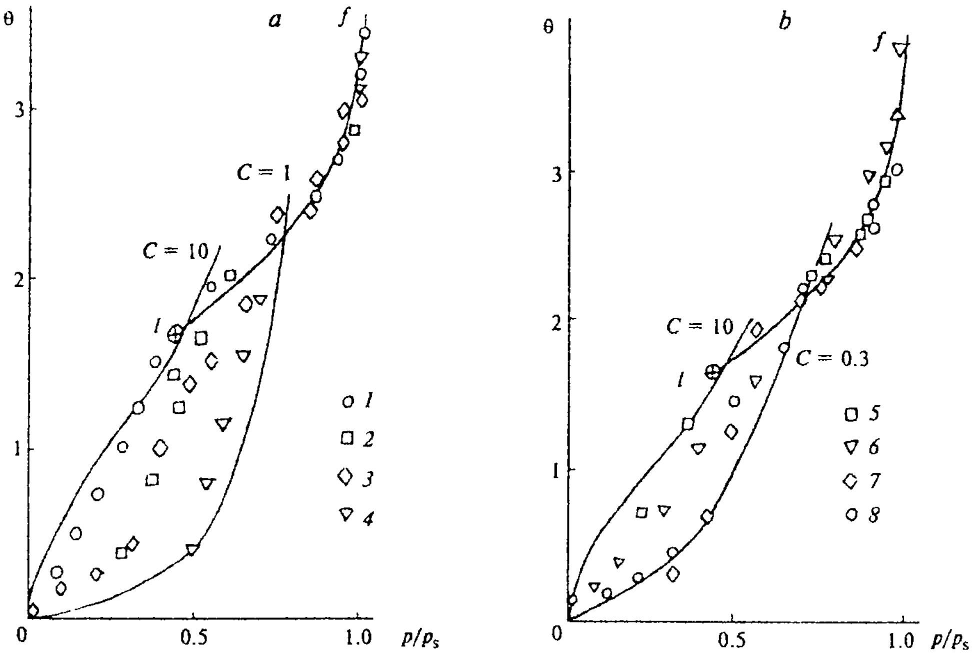

Fig. 2. Comparison of theoretical isotherms of water adsorption on nonporous CA (solid lines) with experimental data (points): *a*, industrial carbon blacks; *b*, "Sferon-6" carbon black subjected to thermal treatment (the data in Ref. 10). Numbers of points correspond to numbers of carbon blacks in Table 1. Curve *lf* is the formation of the stretched film of liquid water.

mined by the equation of stretched liquid film (9), which has the curvature $r = 10$ nm (curve *lf*) and was calculated regardless of the properties of the bulk liquid water (see Eq. (2)). In the region of relative pressures (>0.8), all points lie on one curve *lf*. In the intermediate region of p/p_s, various CA form the isotherms of water adsorption arranged between the theoretical BET isotherms with the *C* constants equal to 10 and 0.3. It is difficult to determine the p^*/p_s values for each sample from experiments. Most likely, the nonuniformity of the surface also affects the transition of the isotherm from the pre-condensation region to the condensation region: the theoretical break on the real isotherm is replaced by the smooth transition. However, the initial formation of the liquid phase during the strong interaction of water molecules occurs in the region close to the theoretical value $p/p_s = 0.41$ (point *l*).

Table 1. Adsorption parameters of oxidized carbon blacks

Carbon black	Temperature of treatment/°C (medium)	A_{tot}	A_{hphl}	A_{hphb}	A_{hphb}/A_{tot} (%)	C_{BET}[b]	p/p_s[c]
		$m^2\ g^{-1}$					
TC-A[a]	Starting sample	160	47	113	70	1.0	0.70
TC-B[a]	Starting sample	85	43	42	49	1.5	0.66
TC-C[a]	Starting sample	90	55	35	38	5.0	0.55
TC-D[a]	Starting sample	240	88	162	63	2.0	0.63
Sferon-6	200 (vacuum)	115	48	67	58	7.0	0.52
Sferon-6	900 (vacuum)	109	27	82	75	2.0	0.65
Sferon-6	1000 (vacuum)	109	22	87	80	2.0	0.65
Sferon-6	1100 (H)	108	12	96	88	0.7	0.70

[a] TC is technical carbon.
[b] Calculation by Eq. (18).
[c] Onset of condensation.

The *C* values for each CA sample are presented in Table 1 (penultimate column). These values were obtained from Fig. 2, *a*, *b* by the p/p_s values corresponding to $\theta = 1$. In this case, it follows from Eq. (11) that

$$C = 1 + \frac{1 - 2g(p/p_s)}{[g(p/p_s)]^2}. \qquad (18)$$

The *C* parameters calculated by this equation have the character of averaged or effective values. They can be used to estimate the degree of hydrophilicity of the surface and to evaluate the onset of condensation (see Table 1, penultimate column). Note that the *C* value for autoadsorption of water, *i.e.*, for hypothetical adsorption of water molecules on the liquid water surface with the formation of polymolecular adsorption according to the BET model and calculated from its condensability, is equal to 15.3.[9]

Table 2. Adsorption parameters of graphitized carbon blacks

Sample	Carbon black	Conditions of treatment	A_{tot} /m^2 g^{-1}	$C_{BET} \cdot 10^3$	a_s	PAC[b]
					μmol m^{-2}	
1	UTC[a]	Starting sample	47	1.4	5.1	0.01
2	UTC[a]	Chlorination+hydrolysis	50	21	24.0	0.16
3	UTC[a]	Chlorination+hydrolysis	51	28	35.0	0.23
4	UTC[a]	HNO_3, 20 °C	47	18	13.0	0.11
5	UTC[a]	HNO_3, 100 °C	63	32	28.0	0.23
6	UTC[a]	Phenol	50	16	7.8	0.05
7	UTC[a]	Starting sample	39	6	5.6	0.18
8	Vulkan-7N	2800 °C	100	4	5.9	0.04
9	GTC	3000 °C	7.6	5	7.7	–

[a] UTC is ultradispersed technical carbon.

[b] PAC are primary adsorption centers.

Graphitized carbon blacks. Taking into account the expression obtained for a_m (16), we can write the final equation of isotherm of water vapor adsorption on the hydrophobic CA surface in the following form:

$$a = \frac{17.3CAg(p/p_s)}{[1 - g(p/p_s)]^2}, \tag{19}$$

where *A* is the total surface of graphitized carbon black determined, *e.g.*, from adsorption of nitrogen.

The parameters of some graphitized carbon blacks treated by oxidants under different conditions and the corresponding values of *C* constants are presented in Table 2.

The *C* values were determined from slopes of isotherms plotted in the coordinates a and $g(p/p_s)/[1 - g(p/p_s)]^2$ (Fig. 3). The g factor was determined in such a way that the isotherm in these coordinates was close to a straight line. In the first approximation, for water on nonporous adsorbents, $g = 0.9$.

Graphitized carbon blacks (see Table 2, samples *1*—*4*) were obtained from ultradispersed technical carbon followed by graphitization at 3000 °C. Oxidized carbon blacks (samples *2*—*3*) were prepared by the application of OH^- groups on the surface of the starting sample *1* by chlorination followed by hydrolysis by the known procedure.[1] Samples *4* and *5* were obtained by the oxidation of sample *1* in concentrated HNO_3 at 20 and 100 °C, respectively. Sample *6* is CA treated by phenol. Sample *7* differs from the starting sample *1* by a smaller surface. Sample *8* is the Vulkan-7N carbon black graphitized at 2800 °C, and sample *9* is thermally graphitized carbon black.[11]

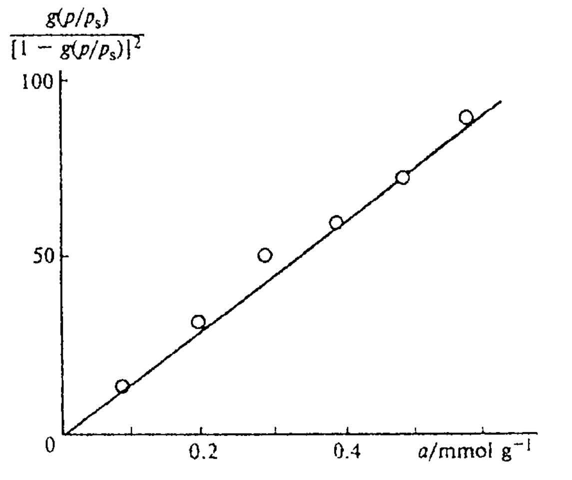

Fig. 3. Isotherm of water adsorption on the "Vulkan-7N" carbon black in coordinates of Eq. (13). Solid line is calculation, points are experiment.

It is seen in Table 2 that sample *1* has the minimum value of the *C* constant ($C = 0.0014$), and the maximum value is demonstrated by the same sample treated by nitric acid at 100 °C (sample *5*, $C = 0.032$). The comparison of the *C* constants with the values of primary adsorption centers shows some correlation between them.

* * *

The models of the condensation process (the model of liquid water film and BET model) chosen for the description of the pre-condensation state of the adsorbate agree, as a whole, with the experiment. Note that a rigorous checking of the models includes, as a minimum, a comparison of them with the experiment by three thermodynamic parameters of adsorption: adsorption isotherm, heat (entropy), and heat capacity of the adsorbate. All these characteristics are related to the free energy of adsorption and its derivatives with respect to temperature: the first derivative is the entropy of the adsorbate and the second derivative is its heat capacity. For each model, all these thermodynamic parameters have certain analytical expressions, and the calculations by these expressions can be compared to experimental data obtained in independent adsorption-calorimetric experiments. Our further studies assume the comparison of the models considered by the heat and entropy of adsorption.

At the same time, the limiting point of the beginning of condensation found by the calculation ($p^*/p_s = 0.410$) confirms satisfactorily the condensation mechanism of adsorption. All known points on the isotherms of water adsorption on CA, which were obtained at an adsorption value higher than the monolayer, approach this limit but do not exceed it.

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