

The onset of formation of the water liquid phase in pores of carbon adsorbents

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A two-stage mechanism of adsorption, including nucleation and condensation, was proposed to describe the formation of the water liquid phase in carbon adsorbents. Adsorption is assumed to occur in cylindrical pores. Nucleation is described by a modified BET model, and condensation is treated by the model of a stretched liquid film on a bent surface. The onset of formation of the liquid phase (OFLP) is determined from the intersection of the adsorption isotherms for these stages. The theoretical value of the relative pressure of OFLP varies over a wide range, decreasing with a decrease in the pore radius and reaching the relative vapor pressure of 0.178 for the spinodal state of water. The comparison method using isotherms of graphitized carbon black as the reference isotherms was applied for the determination of OFLP of water in real active carbons. This resulted in good agreement between theory and experiment.

Key words: water adsorption, condensation, adsorption—desorption hysteresis, spinodal state.

It has previously been shown¹ using the chemical potential—entropy—temperature state diagram that water adsorbed by carbon adsorbents exists in two states: at first the adsorbate has a state intermediate between the liquid and gas and then, as the adsorption increases, it is transformed into the state of a stretched liquid. We attempted to take into account these states in the model of two-stage adsorption² on the uniform planar adsorbent surface. In this work, this model was extended to porous carbon adsorbents. The main attention is given to the onset of formation of stretched liquid water in pores of the adsorbent.

Model of two-stage adsorption

The adsorption process can be divided into two stages: at stage I, nucleation occurs (pre-condensation), and stage II is inherent condensation. At stage I, the adsorption layer is described by the BET model,³ and at stage II, it is described by the model of a stretched liquid film.⁴ A supplement on the stability boundary of the adsorption layer structure was introduced into the BET model. It was assumed that the concept (on which the BET theory is based) on uniform vertical associates composing the adsorption layer determines nucleation only and does not describe the properties of the liquid layer. At a certain "average length," the associates become unstable, fuse, and transform into the state of a stretched liquid. On the adsorption isotherm, this transition point corresponds to the intersection of the iso-

therm of BET adsorption with the adsorption isotherm of a stretched liquid film³ (Fig. 1, *a*, point *l*). In Fig. 1, it is located in the region of higher relative pressures of the adsorbate vapor than another characteristic point (*sp*), which determines the boundary of the physical existence of the homogeneous liquid phase of water (spinodal). At

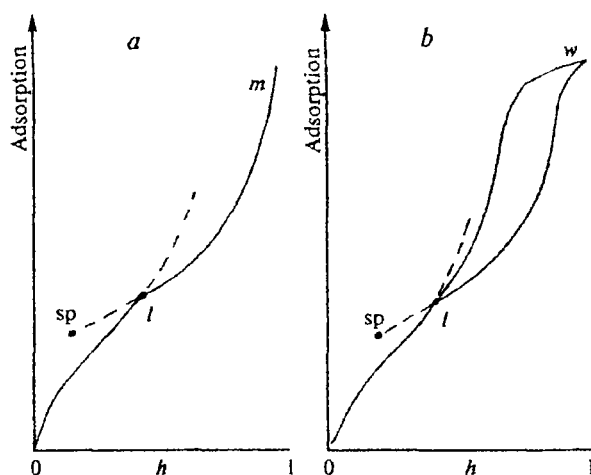


Fig. 1. Scheme of the two-stage process of water adsorption on nonporous (*a*) and porous (*b*) carbon adsorbents: stage of nucleation (*0h*) and stage of condensation (*lm* and *lw*): formation of the stretched liquid (*lm*) and capillary condensate (*lw*). Point *sp* indicates the spinodal state of water.

293 K, the relative pressure of water vapor on the spinodal¹ (h_{sp}) is equal to 0.178.

On nonporous carbon adsorbents, the position of point I is determined by the adsorbate—adsorbent interaction (the C constant in the BET equation) and begins at the relative pressure $h_I = 0.41$ ($1/C = 0$). A decrease in the C constant results in the shift of point I to the region of higher relative pressures of the adsorbate vapor.

Model of water adsorption in pores of adsorbent

Let us consider adsorbent with cylindrical pores with radius r and uniform inner surface. Let us accept that at stage I the nucleation of the liquid in the adsorption layer is described by the modified BET equation³

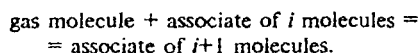
$$a = a_m Cgh / \{(1 - gh)[1 + (C - 1)gh]\}. \quad (1)$$

Here a_m is the monolayer capacity, C is the constant of the adsorbate—adsorbent interaction, $h = p/p_s$ is the relative vapor pressure, p is the equilibrium adsorbate pressure, p_s is the saturated water vapor pressure with the planar liquid—vapor interface, g is the factor taking into account the deviation of p_s from its value on the planar surface. As has been shown previously,² the hydrophobicity and hydrophilicity of the surface are determined in this model by the C constant. For the hydrophobic surface, the C constant is substantially lower than unity. Therefore, neglecting it in the denominator in Eq. (1), we obtain the equation of the BET adsorption isotherm for the hydrophobic surface²

$$a = a_m Cgh / (1 - gh)^2. \quad (2)$$

The BET theory has been developed for description of the adsorption of vapor of a liquid on a uniform planar adsorbent surface. Let us consider its main statement that allows the theory to be applied to the bent, in particular, cylindrical, surface of the adsorbent.

For example, let us consider the quasichemical deduction⁵ of the basic BET equation (in this case, in Eq. (1) $g = 1$). The main postulate of the theory is that molecular associates are formed on the uniform planar adsorbent surface according to the scheme⁵



The equilibrium constant K_s is determined by the equation

$$K_s = \theta_{i+1} / (\theta_i p) = 1/p_s. \quad (3)$$

Here θ is the concentration of the associate on the adsorbent surface; the adsorbate concentration in the gas is expressed through its pressure p . Summation of

the concentrations of all associates results finally in the main (at $g = 1$) equation (1).*

The use of the equality $K_s = 1/p_s$, which expresses, in the general case, the equilibrium of the saturated vapor with the bulk liquid, is valid for the planar liquid—vapor interface.⁶ It is reasonable to assume that in the considered model of a cylindrical pore, the reaction rate constant of formation of associates on the concave adsorbent surface K_r is equal to the reciprocal pressure of the saturated vapor of the liquid with the concave meniscus with the same curvature $K_r = 1/p_r$. The ratio of these constants determines the value $g = K_r/K_s = p_s/p_r$. It is assumed³ in the modified equation (1) that g takes values lower than unity ($g < 1$). In the theory under question, this corresponds to the adsorption on the convex adsorbent surface. For the concave surface $g > 1$, because the vapor pressure above the concave meniscus of the liquid is lower than that above the planar liquid surface.

The stage of condensation in pores with the formation of the layer of stretched liquid water is described by the equation²

$$\ln h = -4.34/\theta^3 - w/RT, \quad (4)$$

where θ is the adsorption value in monolayer units, w is the work consumed by the bending of the adsorption layer surface, R is the universal gas constant, and T is the temperature. Let us accept that changes in the g factor in Eqs. (1), (2) and in the w value in Eq. (4) for pores with a sufficiently long radius r are described by the Kelvin equation

$$\ln g = w/RT = \sigma v / (RT r). \quad (5)$$

Here σ and v are the surface tension and molar volume of the adsorbate in the adsorbent pores. For the BET model, they are arbitrary, which is defined by the fact that the properties of associates in the polymolecular layer and those of the liquid near saturation are close.

Let us consider the direct adsorption process when the thickness of the cylindrical adsorbate layer does not exceed some limiting value at which spontaneous capillary condensation occurs. In this case, according to the Laplace equation, the effective pore radius r depends on the radius of the cylinder only.⁷ It follows from Eqs. (4) and (5) that

$$\ln gh = -4.34/\theta^3. \quad (6)$$

In the model accepted,² the onset of formation of the liquid phase (OFLP) is determined from the inter-

* The interaction of molecules of the gas phase with the free adsorbent surface θ_0 is determined by the equation $C = \theta_1/(\theta_0 h)$, where $\theta_0 + \sum \theta_i = 1$. The overall adsorption value $\theta = \sum \theta_i$ ($i = 1, 2, 3, 4 \dots$). It follows from Eq. (3) that $\theta_{i+1} = \theta_i h = \theta_i^i h^i$ or taking into account θ_1 , $\theta_{i+1} = \theta_0 C h^{i+1}$. Then $\theta = \theta_0 (1 + 2h + 3h^2 + 4h^3 + \dots)$, $1 = \theta_0 [1 + Ch(1 + h + h^2 + h^3 + \dots)]$. From the last two equations, expressing the C constant through the sum of the series in parentheses, at $h < 1$, we obtain Eq. (1) ($g = 1$).

section point of the BET adsorption isotherm with the adsorption isotherm of the liquid film (see Fig. 1, *b*, point *l*). Taking into account $\theta = a/a_m$, we solve simultaneously Eqs. (1) and (6) to obtain

$$\ln g h_l = -4.34\{(1 - g h_l)[1/(C g h_l) + (C - 1)/C]\}^3. \quad (7)$$

The $g h_l$ value is calculated from Eq. (7) by numerical methods. In the limiting case, *i.e.*, for the limiting hydrophilic surface ($1/C = 0$), $g h_l = 0.41$. Thus, taking into account Eq. (5), the lowest value of the relative vapor pressure corresponding to OFLP of water in the hydrophilic pores of carbon adsorbents is determined by the expression

$$h_{l,\text{hph}} = 0.41/g = 0.41 \exp[-\sigma v/(RT r)]. \quad (8)$$

The equation suggests the position of the OFLP point in porous carbon adsorbents. As the pore radius decreases, the liquid phase is formed at a lower relative pressure than that on the planar surface. This pressure approaches the spinodal h_{sp} value.

At the same time, hydrophobization of the surface of nonporous carbon adsorbents results in an increase in the pre-condensation stage of adsorption,² and point *l* is shifted to the region of higher relative pressures of the adsorbate vapor. Numerical calculations using Eq. (7) show that the h_l value approaches unity as the *C* value decreases.

Thus, for estimate calculations by the model of the two-stage adsorption of water vapor in porous carbon adsorbents, a broader interval is assumed for the relative vapor pressure, which characterizes OFLP of water in adsorbent pores rather than that in the case of nonporous adsorbents. The interval begins from a pressure close to spinodal h_{sp} and is extended up to $h_{lq} = 1$.

Results and Discussion

It is rather difficult to determine experimentally OFLP of water in porous carbon adsorbents. The formation of the liquid phase is usually related to the onset of the hysteresis loop in the reducible adsorption-desorption cycle. The onset is found by graphical plotting of the adsorption isotherms with a reliability depending on the scale, the number of experimental points, and the accuracy of their determination. As a rule, overestimated values of h_l are obtained because the condensation in wedge-shaped pores, which is not accompanied by the formation of the hysteresis loop, is not taken into account.

OFLP can also be determined by comparative plots, and the choice of the reference system plays an important role in this case. We believe that the state of the adsorbate reference system should differ substantially from the state of the liquid. Water—graphitized carbon black systems are most appropriate for these purposes. On the chemical potential—entropy—temperature diagram, the state of water adsorbed on car-

bon blacks of this type is determined by the state of the substance in the "overspinodal region." Therefore, deviations from it on the state diagram are located in the region of either liquid or vapor. The vapor state is distinguished by an entropy value that is high as compared to the entropy of adsorbed water; hence, deviations from the "reference" isotherm in comparative plots can be referred to the formation of the liquid phase only.

Determination of the type of the curve deviating from the reference curve is of principal significance. Two variants of deviation are possible: a gradual deviation and intersection of two curves in a point. We believe that intersection in a point should be preferred, since the deviation indicates the transition from one state to another. In terms of the two-stage model of adsorption considered,² this deviation begins at point *l*. The use of comparative plots for the analysis of the properties of water—carbon adsorbent adsorption systems has previously been studied in detail.⁸ Vulkan-7N carbon black was used as the reference system, system on which the adsorption isotherm of water is sufficiently well described by Eq. (2) with the parameters² $C = 0.0042$, $g = 0.9$, $a_m = 17.3 \mu\text{mol m}^{-2}$, and $A = 100 \text{ m}^2 \text{ g}^{-1}$. In this work, it was used as the reference isotherm for the determination of OFLP of water in pores of active carbons.

The comparative plots for two active carbons, mesoporous AG-2 (*a*) and fine-porous PAU-1 (*b*), are presented in Fig. 2. As previously,⁸ the initial region of the comparative plot is described by straight line 0*l*; a distinct break related to the formation of the liquid phase of water is observed at point *l*. Point *l* is the

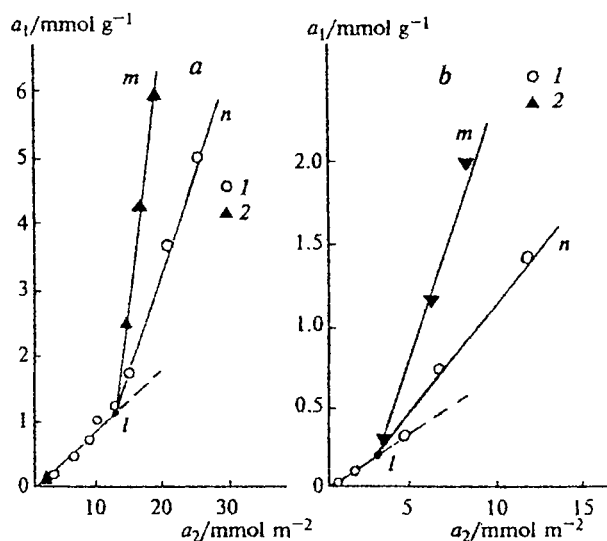


Fig. 2. Comparative plots for determination of the onset of formation of the liquid phase of water (point *l*) on active carbons: mesoporous AG-2 (*a*) and fine-porous PAU-1 (*b*). 1, adsorption; 2, desorption. a_1 is adsorption on active carbon, and a_2 is adsorption on Vulkan-7N carbon black.

Table 1. Values of the relative vapor pressure h_l corresponding to the onset of formation of the liquid phase of water in pores of active carbons

Carbon	h_l	x^a/nm	$W^b/\text{cm}^3 \text{ g}^{-1}$
PAU-1	0.23	0.41	0.44
AU-1M	0.37	0.45	0.55
BKS-1	0.40	0.72	0.57
AG-8	0.42	0.56	0.30
AG-2	0.46	0.67	0.44
FAS-E	0.61	0.68	0.70

^a x is the half-width of pores of adsorbents.

^b W is the volume of pores of adsorbents.

intersection of two lines reflecting the adsorption (ln) and desorption (lm) branches of the adsorption isotherms of water on these adsorbents. The relative pressures corresponding to OFLP of water in pores of different active carbons are presented in Table 1.

As seen in Table 1, the relative pressure h_l corresponding to OFLP of water in pores of active carbons varies from 0.23 to 0.61. According to conclusions of the theory, the minimum h_l value approaches the spinodal value $h_{sp} = 0.178$ as the pore diameter decreases. However, no direct correlation between the position of point $l(h_l)$ and the half-width of pores x is observed. This is most likely related to the fact that in real adsorbents pores have a specific distribution over sizes and the

liquid phase is formed in the narrowest pores, whereas the x value determines the half-width of the main number of pores.

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