The heat of adsorption of water on nonporous hydrophilic carbon adsorbents in the model of two-stage adsorption

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The behavior of integral and differential heats of adsorption of water in the region of transition from the first stage of adsorption (formation of clusters) to the second stage (formation of a stretched liquid film) was considered. The curve of integral heat of adsorption has an inflection at the transition point, and the differential heat of adsorption changes jumpwise. The values of these effects were estimated by the simplest model of formation of one and two hydrogen bonds between a water molecule and an adsorption center on the surface of the carbon adsorbent. Curves of differential heat of adsorption with transition points for real systems are presented.

Key words: heat of adsorption, carbon adsorbents, stretched liquid water.

The model of two-stage adsorption of water on carbon adsorbents is based on two states of adsorbed water that have previously been determined from the experimental data using the "chemical potential—entropy—temperature" diagram.[1] The formation of associates whose state occupies an intermediate position between the states of the liquid and vapor is assumed at the first stage. A stretched liquid film or a capillary condensate, which in the diagram occupies the region between the binodal and spinodal, forms at the second stage.

In this work, we consider the differential and integral heats of water adsorption on hydrophilic nonporous carbon adsorbents in terms of the model mentioned. This is associated with the task of studying these heats on going from the first stage of adsorption to the second stage and the possibility of determining experimentally the transition point in calorimetric experiments. The main attention is given to the differential heat of adsorption.

Theoretical equations for heats of adsorption

At the first stage of adsorption, the adsorption layer is described by the BET model, and the model of a stretched liquid film is used for the second stage.[2] The BET model is supplemented by the stability boundary of the adsorption layer structure. It is assumed that at a certain "average length" the associates become unstable, aggregate, and transform into the state of stretched liquid. On the adsorption isotherm, this point is determined by the intersection of the isotherm of BET adsorption with the adsorption isotherm corresponding to the formation of the stretched liquid film[2,3] (Fig. 1, point *l*). It is localized in Fig. 1 to the right of another characteristic point "sp" that defines the boundary of existence of the homogeneous liquid phase of water (spinodal). For 293 K, the relative pressure of water vapor on the spinodal is h_{sp} = 0.178. On carbon

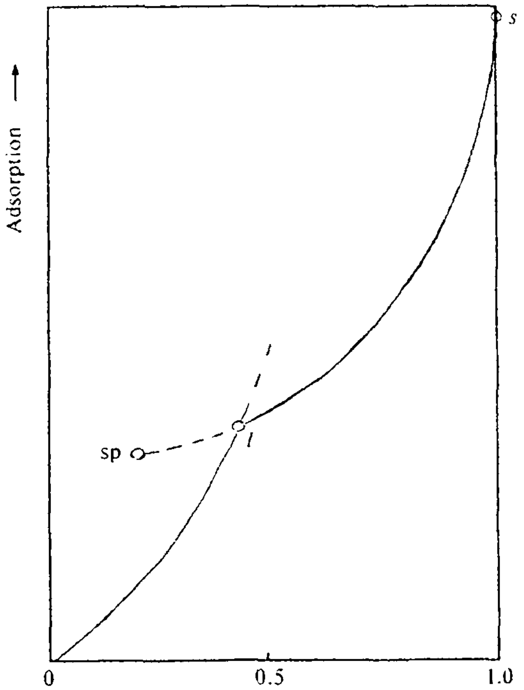

Fig. 1. Scheme of the isotherm of water adsorption on the hydrophilic surface of the carbon adsorbent in the model of two-stage adsorption: 0*l*, formation of associates according to the BET model; *ls*, formation of the stretched liquid film; *l*, transition of the first stage to the second stage; and sp, limit of physical existence of the liquid phase of water (spinodal).

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adsorbents, the position of point *l* is defined by the adsorbate—adsorbent interaction (constant *C* in the BET equation) and starts at the relative pressure $h = 0.41$ (high *C*). A decrease in the *C* constant results in the shift of point *l* toward higher relative pressures of the adsorbate vapor.

Let us introduce designations of heats of adsorption: Q^* and Q are the differential and integral molar heats of adsorption (kJ mol^{-1}), and q is the integral specific heat of adsorption per mass unit of the adsorbent (kJ g^{-1}).

Designation of the heat to the first or second stages of adsorption is by subscripts (1 and 2). The differential and integral heats are related by the equations

$$Q = a^{-1}\int_0^a Q^* \mathrm{d}a, \qquad (1)$$

$$q = Qa, \qquad (2)$$

where a is the adsorption (mol g^{-1}).

First stage. The equations for the differential and integral heats of adsorption in terms of the BET model have previously been obtained.[4,5] They have the form

$$Q_1^* = Q_0 - (Q_0 - L)[2h + (C - 2)h^2]/[1 + (C - 1)h^2], \qquad (3)$$

$$Q_1 = Q_0 - (Q_0 - L)h, \qquad (4)$$

where Q_0 is the heat of adsorption for zero coverage, L is the heat of condensation of the adsorbate to the standard liquid (on the binodal), $h = p/p_s$ is the relative vapor pressure, p is the equilibrium pressure of the adsorbate vapor, and p_s is the pressure of the saturated water vapor with a planar liquid—vapor interface. At the end of the first stage, at point *l*, the equation for the integral heat takes the form

$$q_1 = Q_1 a_l = a_l[Q_0 - (Q_0 - L)h_l]. \qquad (5)$$

Second stage. The stretched liquid water film is formed on the hydrophilic adsorbent surface. The equation of the adsorption isotherm for this state of the adsorption layer has been obtained[2]

$$\ln h = -4.34(a/a_m)^{-3}, \qquad (6)$$

where a_m is the adsorption in the compact monolayer. The heat of evaporation of the adsorbate from the liquid layer is equal to the differential heat of adsorption and defined by the equation[2]

$$Q_2^* = L - (1 - \alpha T)RT\ln h, \qquad (7)$$

where α is the thermal coefficient of volume extension of the adsorbate. For water in the standard liquid state, $\alpha = 2.07 \cdot 10^{-4}$ deg^{-1}, and the product $\alpha T = 0.06$ for 20 °C is low compared to unity. Assuming that the properties of the stretched liquid film far from the spinodal do not significantly differ from those of the standard liquid, we may neglect the αT value in Eq. (7), which then takes the form

$$Q^*_2 = L - RT\ln h. \qquad (8)$$

Let us determine the specific heat of adsorption for the formation of the liquid film at the condensation stage, which also includes the integral heat at the first stage, by the equation

$$\begin{aligned} q_2 &= (a - a_l)Q_2 + q_1 = \int_{a_l}^{a} Q_2^* \mathrm{d}a + q_1 = \\ &= \int_{a_l}^{a} L\mathrm{d}a + RT\int_{a_l}^{a} \ln h\mathrm{d}a + q_1. \end{aligned} \qquad (9)$$

The integrating interval is defined by the boundaries of the condensation stage (second stage); it starts at point *l* (a_l, h_l) in Fig. 1 and ceases at the saturation pressure $h = 1$ (point *s*). Substituting the integrand $\ln h$ by its expression through a in Eq. (6), after integration within the indicated limits, insertion of the expression for q_1 from Eq. (5), and transformations, we obtain the resulting equation for the integral heat of adsorption at the second stage:

$$\begin{aligned} q_2 = a(L - 0.5RT\ln h) + \\ + a_l[(Q_0 - L)(1 - h_l) + 0.5RT\ln h_l], \end{aligned} \qquad (10)$$

$$\begin{aligned} Q_2 = L - 0.5RT\ln h + [(Q_0 - L)(1 - h_l) + \\ + 0.5RT\ln h_l](a_l/a). \end{aligned} \qquad (11)$$

It is more convenient to express Q_2 in Eq. (11) as a single-valued function of Q on h. Substituting a and a_l by their expressions through h, we obtain after transformations:

$$\begin{aligned} Q_2 = L - 0.5RT\ln h + [(Q_0 - L)(1 - h_l) + \\ + 0.5RT\ln h_l](\ln h/\ln h_l)^{1/3}. \end{aligned} \qquad (12)$$

It should be emphasized that Eqs. (8) and (12) are fulfilled for the second stage of adsorption (in Fig. 1 from point *l* (h_l) to $h = 1$). For the first stage, within the interval from $h = 0$ to h_l, Eqs. (3) and (4) are fulfilled.

Estimation calculations

Let us estimate the integral and differential heats in terms of the model of two-stage adsorption for an entirely hydrophilic surface, using the simplified scheme of interaction of water associates with the adsorbent surface: weak adsorption with the formation of one hydrogen bond and strong adsorption with the formation of two hydrogen bonds. We can estimate the Q_0, h_l, and C parameters in the equations for heats of adsorption of these two stages.

Mainly two factors contribute to the initial heat of adsorption of water Q_0. One of them is related to the dispersion interaction of a water molecule with the atomic lattice of the adsorbent, and the second factor is defined by the energy of formation of a hydrogen bond with the adsorption center on its surface. The heat of dispersion interaction of water molecules with a basis face of graphite determined from the critical parameters of liquid water (temperature T_c and pressure p_c) by the equation[6]

$$Q_0 = 0.44T_c/(p_c)^{1/2} \quad (13)$$

is close to 19 kJ mol^{-1}. The energies of one and two hydrogen bonds are 17 and 34 kJ mol^{-1}, respectively. Then in the examples under consideration, for the formation of one hydrogen bond, Q_0 = 19 + 17 = 36 kJ mol^{-1}, and for two hydrogen bonds, Q_0 = 19 + 34 = 53 kJ mol^{-1} (the latter is close to the heat of ice sublimation: 50.578 kJ mol^{-1} at 273.2 K). The heat of water evaporation L is accepted to be equal to 44 kJ mol^{-1} (44.163 kJ mol^{-1} at 293 K [7]). Let us find h_l values corresponding to these heats. For this purpose, let us determine approximately the C constant values. The rigid thermodynamic expression of the C constant as a constant of quasi-chemical interaction of molecules of the adsorbate vapor with the adsorbent surface is determined by the general equation

$$RT\ln C = (S_0 - S_L)T + Q_0 - L. \quad (14)$$

Here S_0 is the molar entropy for the initial interaction of a single adsorbate molecule with the adsorption center on the adsorbent surface, and S_L is the entropy in the final state. The state of standard liquid with a planar liquid—vapor interface is taken in the BET theory as the final state of the adsorption layer. This state is independent of the chemical nature of the adsorbent. Let us use this assumption and consider standard liquid water as the adsorption system in the final state for hypothetical water adsorption on the water surface (autoadsorption) with the formation of a "thick" polymolecular layer[8] at h = 1. Its characteristic feature is that the "adsorbate—adsorbent" and "adsorbate—adsorbate" interactions are the same. It is shown[8] that for autoadsorption the C value is related to the molar volume V and the coefficient of isothermic compressibility β by the following equation:

$$C = V/(RT\beta).$$

Water at T = 293 K is characterized by the following coefficients: $\beta = 49.1 \cdot 10^{-6}$ and C = 15.3. In the autoadsorption model, $Q_0 = L$. Inserting these C and Q values in Eq. (14), we obtain the change in entropy in the system under study: $(S_0 - S_L)/R = 2.72$. Let us accept for estimation calculations that this change in entropy is retained for different Q_0 values. Then for the formation of one hydrogen bond, $C' \approx 0.6$, and for two hydrogen bonds, $C' \approx 600$. Finally, using the equation for the beginning of formation of the liquid water phase[3]

$$\ln h_l = -4.34[(1 - h_l)(1/Ch_l + (C - 1)/C)]^3,$$

we obtain h_l values for the formation of one (0.74) and two hydrogen bonds (0.42). Note that for most of the real systems studied by us,[3] the C constant varied in a more narrow interval, from 20 to 1.

The dependences of the molar heats of adsorption calculated by Eqs. (3) and (8) for the differential heat of adsorption (solid lines) and from Eqs. (4) and (12) for the integral heats of adsorption (dashed lines) are presented in Fig. 2. For the formation of one hydrogen bond of a water molecule with an adsorption surface center during the whole first stage, the values of the Q and Q^* heats are

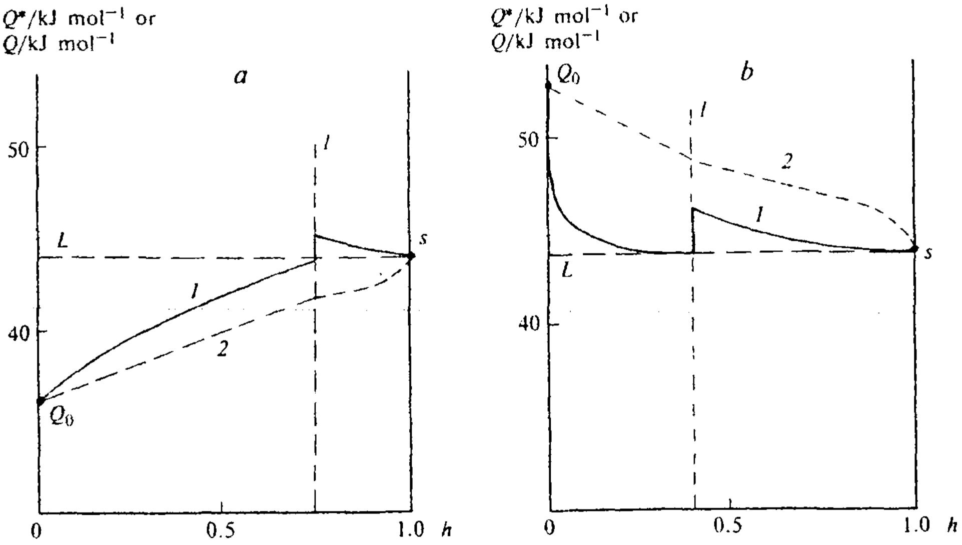

Fig. 2. Theoretical curves of the differential (Q^*) (*1*) and integral Q (*2*) heats of adsorption for weak (*a*) and strong (*b*) interactions of the water molecule with the adsorption center. Horizontal dashed line indicates the heat of evaporation L of pure water; vertical dashed line shows the beginning of formation of the liquid film (point *l* in Fig. 1); Q_0 is the initial heat of adsorption.

lower than the heat L, and for the transition to the second stage (at point l), the differential heat Q^* changes jumpwise. The integral heat of adsorption Q in the whole adsorption region is lower than the heat L, and the curve of Q has an inflection at point l. The formation of two hydrogen bonds of adsorbed molecules with adsorption surface centers results in the transposition of the heats of adsorption Q and Q^* to the region localized above the L level. At point l, the differential heat of adsorption also undergoes a break, and an inflection appears on the curve of the integral heat of adsorption.

Thus, at point l, as on the adsorption isotherm, the model of two-stage adsorption assumes an inflection on the curve of the integral heat of adsorption and a jump in the values of the differential heat of adsorption. The inflection on the curve of the dependence $Q = f(h)$ is weakly pronounced and, most likely, inaccessible for direct calorimetric determinations. The change in the differential heat of adsorption is more pronounced. In the region of the beginning of formation of the liquid stretched layer, this heat undergoes a break for an idealized system and, probably, passes through a maximum for real adsorbents. According to the estimations performed, the value of the maximum is not higher than RT.

Transition point in real systems

A maximum on the isotherm of the differential heat of adsorption in the region of polymolecular adsorption has been observed in several works[9] that used precision calorimeters with continuous injection of the adsorbate vapor into a calorimeter. A sharp maximum was found for the transition from mono- to polymolecular adsorption, and smooth maxima were observed for the formation of the second, third, and subsequent layers in the case of the step adsorption isotherm.

It is difficult to study the differential heat of water adsorption by precision methods because of specific features of its physical properties: a low vapor pressure and the ability to retain strongly dissolved gases. For example, in calorimeters with continuous injection of the adsorbate vapor into the calorimetric cell, the results can be erroneous because of traces of air (dissolved in the liquid adsorptive and hardly removed by evacuation) that entered the cell. Perhaps, only a few experimental studies of the differential heat of water adsorption on carbon adsorbents were carried out because of these methodological difficulties. The available data on the isosteric heat of adsorption indicate that its value passes through a maximum for many systems.[10] However, the accuracy of determination of these heats is low.

To verify the conclusions of the theory about the presence of the transition point on the curve of a changing differential heat of adsorption, which is valid in the general case for any nonporous adsorption systems, let us consider two examples (Fig. 3) with detailed and sufficiently exactly measured differential heats of adsorption[11,12] of methanol (a) and n-hexane (b) on graphitized thermal carbon black (GTC). They can be used for illustrating the behavior of the differential heat of adsorption with weak and strong adsorbate—adsorbent interactions, respectively, and have a break at point l.

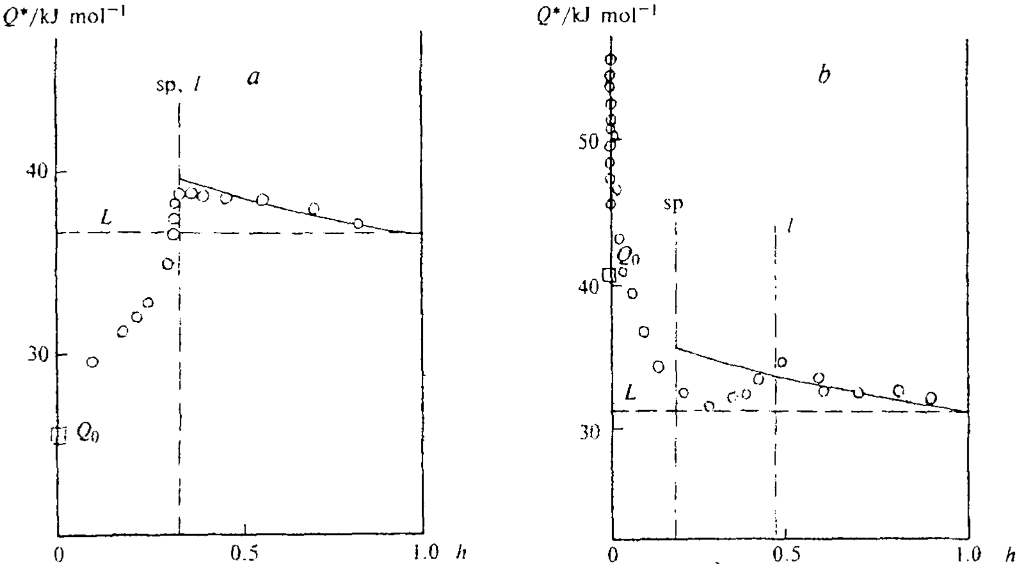

Fig. 3. Differential heat of adsorption (Q^*) of methanol (a) and n-hexane (b) on graphitized thermal carbon black according to the data in Ref. 10, illustrating the break of Q^* at point l (designations are presented in Fig. 1) for weak and strong adsorbate—adsorbent interactions. Points indicate experiment; square is the Q_0 value calculated by Eq. (14). Horizontal dashed line indicates the heat of condensation (L) of the liquid adsorbate; vertical dashed line: sp is the oriented boundary of the limiting stretched state of the liquid adsorbate (spinodal), l is the beginning of formation of the liquid layer; solid curve shows the theoretical heat Q^* for the liquid layer calculated from Eq. (8).

As can be seen in Fig. 3, *a*, the curve of the differential heat of methanol adsorption[11] begins with a Q_0 value that is much lower than L (the square is the Q_0 value calculated from Eq. (14)). When h increases, the Q^* heat increases, reaches L values, passes through a maximum, and then decreases monotonically to the L value. The solid curve was calculated by Eq. (8) for a stretched liquid film of methanol (L = 38.15 kJ mol^{-1}, T = 293 K), which coincides well with the experimental points within the whole range of the monotonic decrease in Q^*. The spinodal parameters for methanol are unknown. The estimation calculation of the spinodal pressure from its surface tension[13] gives $p_{sp} = -65$ MPa. When the specific volume of methanol (V = 40.43 cm^3 mol^{-1}) is accepted to be independent of the pressure, the relative pressure of its vapor on the spinodal (h_{sp}) calculated using the equation $RT\ln h_{sp} = p_{sp}V$ is ~0.33. As can be seen in Fig. 3, Q^* changes sharply near this h_{sp} value (it is likely that points sp and *l* are very close for this system).

The differential heat of adsorption of *n*-hexane[12] on GTC (see Fig. 3, *b*) changes from a Q_0 value much higher than L. Adsorption of *n*-hexane in the region of formation of the monolayer corresponds to low h values; therefore, the curve corresponding to Q^* is almost adjacent to the ordinate in this region. The decrease in the Q^* curve determines the transition from mono- to polymolecular adsorption, where it passes through a smooth maximum and then decreases monotonically to the L value. The solid curve was calculated by Eq. (8). It is close to the experimental points within the range from h = 1 to the top of the maximum ($h \approx 0.5$). Point *l* is probably localized near h = 0.5. The h_{sp} value for *n*-hexane calculated similarly to that for methanol from its surface tension and molar volume is equal to 0.19.

Comparison of Fig. 2 with Fig. 3 shows a satisfactory agreement between the theoretical and experimental data about the presence and position of the break on the curve of the differential heat of adsorption for the systems with weak and strong adsorbate—adsorbent interactions.

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