Thermodynamic investigation of the state of water adsorbed by carbonaceous adsorbents

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The state of water adsorbed on active carbons and canal soot was studied using the "chemical potential—entropy—temperature" diagram. In the range of the relative pressures from 0.174 to 1, the state of adsorbed water is similar to the state of a stretched liquid. The molar volume, heat of evaporation, and surface tension of stretched water were calculated at different relative pressures. Near the spinodal, the molar volume of stretched water is 25% higher, and the surface tension is considerably lower compared to water.

Key words: adsorption, carbonaceous adsorbents, chemical potential, entropy, temperature, aggregate state of water.

The primary attention of the majority of the studies performed for the "carbonaceous adsorbents (CA)—water" systems (see, *e.g.*, review[1]) is aimed at revealing the chemical composition of hydrophobic and hydrophilic regions and their arrangement on the surface and in pores of CA. In our opinion, a substantial supplement to the general line of inquiries of these systems should be data on another of their components (water), on the boundaries of the existence of its different aggregate states, including "thermodynamically allowed" highly dispersed states in the form of molecular groups, clusters, minute globules, and films.

The purpose of this work is to determine the state of adsorbed water using the "chemical potential—entropy—temperature" (μ—S—T) diagram. This diagram allows one to determine unambiguously the state of water in the adsorption space. Unlike the common PVT diagram, all parameters of the adsorbed substance used in this case can be determined rather reliably directly from experiments. The chemical potential μ can be determined from the equilibrium pressure of the adsorbate vapor p (which, for simplicity, will be substituted in further discussion by the logarithm of pressure $\ln p$), and entropy (S) can be determined from adsorption calorimetric data.

Experimental

The parameters of the carbonaceous adsorbents used are presented in Table 1. The adsorption isotherms of water and the heats of immersion of two samples of industrial CA (AU-5, AU-5M, and canal soot) in water were determined. The adsorption isotherms of the "graphitized thermal soot (GTB)—water" system were taken from Ref. 2. Carbons AU-5 and AU-5M were obtained from bituminous coal, and ART was obtained from peat by steam activation. Adsorption isotherms of water were measured on a weighting vacuum installation. Heats of immersion were measured on a DAK-1 calorimeter.*

Table 1. Parameters of carbon adsorbents

Adsorbent	W_0 /cm^3 g^{-1}	x_0 /nm	A /m^2 g^{-1}	E_0 /kJ mol^{-1}
AG-3	0.295	0.63	110	19.10
AG-3M	0.296	0.66	110	18.07
ART	0.400	0.42	35	24.40
Canal soot	—	—	120	—
GTB[2]	—	—	7.6	—

Note. A, specific surface; W_0, volume of micropores; x_0, half-width of micropores; E_0, characteristic adsorption energy in the Dubunin—Radushkevich equation

Results and Discussion

Plotting the diagram and determination of the state of adsorbed water

Let us first consider the PVT diagram of water, where P is the external pressure on the phase, V is its molar volume, and T is temperature. This diagram is presented schematically in Fig. 1 as a planar PV diagram. The surfaces of phase equilibria are expressed by the projections on the PV plane (region I is the crystalline phase, II is the liquid, and III is the gas). Lines tl and tl' separate the crystalline state from the liquid

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* The data on the adsorption isotherm and isosteric adsorption heat of steam on the ART carbon were kindly presented by R. Sh. Vartapetyan.

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(lines of crystallization and melting); line *tbcnm* (binodal) corresponds to the liquid—vapor equilibrium, its left branch (*tbc*) is the liquid, and the right branch (*cnm*) is vapor; *t* is the triple point corresponding to the coexistence of three phases: liquid, solid, and gaseous; *c* is the critical point; lines *sp'spc* and *cg* determine the boundaries of the stability of the liquid water and its vapor (the left and right branches of the spinodal). The largest portion of the left branch of the spinodal near the *t* point is localized in the region of negative pressure. The region of the stretched (metastable) state of water is localized between left branches of the binodal and spinodal. The region above the spinodal determines the labile (unstable) state of water. Metastable and especially labile states of the liquids are poorly studied. Only the temperature range near the critical point, where the spinodal "shifts from depth" and approaches the binodal, is accessible for experimental investigation.[3] A few data on the metastable state of water near the triple point are analyzed in Ref. 4.[4]

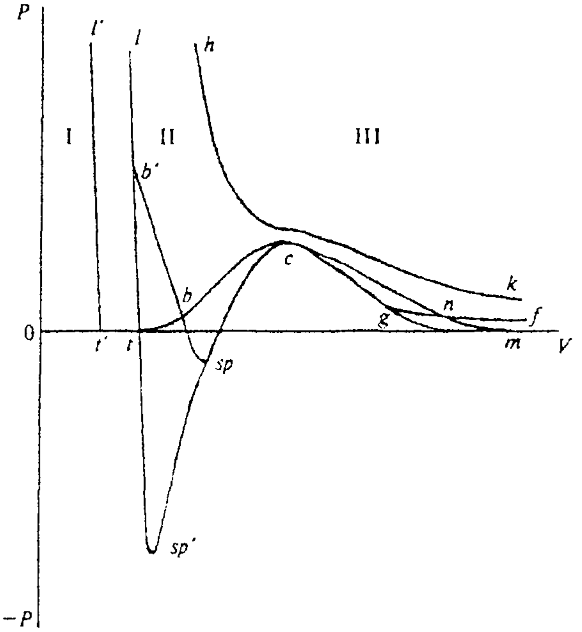

Fig. 1. *PVT* phase diagram of the state of water (schematic sketch).

As has been shown in our studies,[5] the curves describing the state of the adsorbed substance are in the "metastable" and "labile" regions of the phase diagram. However, this adsorption state is thermodynamically stable, and these terms can be applied to it only arbitrarily.

To go from the *PVT* diagram to the ln*p*—*S*—*T* diagram, let us consider the isotherm of liquid water in Fig. 1. In the region of positive pressures, it begins in the *b'* point on the crystallization and melting line, crosses the binodal in point *b*, where the external pressure is equal to the pressure of saturated vapor p_s, and then goes to the region of the negative external pressure that stretches the liquid finishing on the spinodal in point *sp*. Here the stretching pressure attains its maximum value, and the homogeneous liquid phase is destroyed. The isotherm of saturated vapor (line *gnf*) corresponds to the isotherm of the liquid state *b'bsp*. The *gn* region corresponds to "compressed" water, and the *nf* region corresponds to "stretched" water.

Let us determine the first coordinate of the diagram indicated, the logarithm of the pressure of saturated vapor of compressed and stretched water in the whole region of the existence of liquid water at the temperature *T*, using the equation:

$$d\mu^l = d\mu = V^l dp^l = V dp, \qquad (1)$$

where μ is the chemical potential, *V* is the molar volume, and *p* is the pressure applied to the phase. The upper index (*l*) indicates that the substance belongs to the liquid phase, and the index of the gas phase is missing.

Let us first consider the physical meaning of pressures p^l and *p*, for example, for point *b* on the binodal. The external pressure is the pressure of saturated vapor p_s. To determine the physical meaning of *p*, let us divide two latter parts of equality (1) by the product $d\ln V \cdot d\ln V^l$ and transform them taking into account the equation of isothermal compressibility

$$\beta = -\left[\frac{d\ln V}{dp}\right]_T. \qquad (2)$$

After the transformations, we obtain the correlation

$$\frac{dV^l}{\beta^l} - \frac{dV}{\beta} = 0,$$

which determines the work of compression and expansion of the co-existing phases. Under the conditions of isothermal equilibrium, these works are equal and opposite in sign, and pressures *p* and p^l are related to elastic properties of the phases.

Then let us take the vapor to obey the ideal gas law $Vp = RT$. Inserting the *V* value for vapor in Eq. (1), we obtain

$$V^l dp^l = RT d\ln p. \qquad (3)$$

The dependence of V^l on p^l should be known for integrating the equation obtained. The equation, which agrees well with the experiment in the ranges of 0—100 °C and 0—100 MPa, was suggested in Ref. 4:

$$1 - p^l/p^l_{sp} = \mathrm{B}\,(V_{sp}^l/V^l - 1)^2, \qquad (4)$$

where B is constant; V_{sp} and p_{sp} are the molar volume and pressure of expansion of water on the spinodal. The values of these parameters at different temperatures are listed in Table 2. Let us differentiate Eq. (4) and insert

Table 2. Parameters of the spinodal of water in liquid state and values of the B constant in Eq. (4) from the data in Ref. 5

T/K	$p_{sp}{}^l$ /MPa	$V_{sp}{}^l$ /cm^3 mol^{-1}	V
273	180	22.067	19.623
283	198	22.228	18.174
293	208	22.302	17.829
303	212.4	22.336	18.025
313	211.2	22.332	18.838
323	206.9	22.303	19.889
333	200.2	22.285	21.188
343	192.2	22.283	22.585
353	182.7	22.285	24.235
363	172.5	22.303	26.010
373	162.1	22.339	27.879

* $p_{sp}{}^l$ is pressure, $V_{sp}{}^l$ is molar volume.

the resulting expression dp^l in Eq. (3). For integration, let us take points b and n on the binodal as a reference point (Fig. 1). Let us indicate their values by the lower index s. After integrating, we obtain the final equation for the first coordinate:

$$\ln p = \ln p_s + \frac{2\mathrm{B}V_{sp}^l \cdot p_{sp}^l}{RT}\left[\frac{V_{sp}^l}{V^l} - \frac{V_{sp}^l}{V_s^l} - \ln\frac{V^l}{V_s^l}\right]. \qquad (5)$$

The second coordinate of the diagram is entropy of water. For its determination, let us use the known thermodynamic correlation that is valid for any state of the substance:

$$\left[\frac{dS}{dp}\right]_T = -V\alpha_p,$$

where α_p is the isobaric thermal coefficient of expansion of a substance. Let us write Eq. (6) for the isotherm of the liquid in the form

$$dS^l = -V^l\alpha_{pl} \cdot dp^l \qquad (7)$$

and integrate it using the reference point indicated above (points b and n). In the first approximation we assume that the product $V^l\alpha_{pl}$ is independent of the pressure. After integrating, we obtain the equation for the second coordinate:

$$S^l = S_s{}^l - V^l\alpha_{pl}(p_s - p^l). \qquad (8)$$

where $S_s{}^l$ is the entropy of water on the binodal.

The fragment of the ln$p$—S—T-diagram of water in the region of temperatures close to room temperature is shown in Fig. 2. It was plotted using Eqs. (5) and (8) and the data in Refs. 4 and 6. As can be seen, the liquid state of water lies in a narrow region of the diagram between lines lt and $cspsp'$. The main surface area is occupied by the region of the labile state of water. It is restricted from the right by the region of the metastable (superheated) vapor. It is not shown in Fig. 2 because the data for its plotting are scarce. Only the right branch of the binodal (line nm) plotted by the tabulated data[6] is presented. Its slope $d\ln p/dS$ is close to that of the isotherm of ideal gas $(d\ln p/dS)_T = 1/R$.

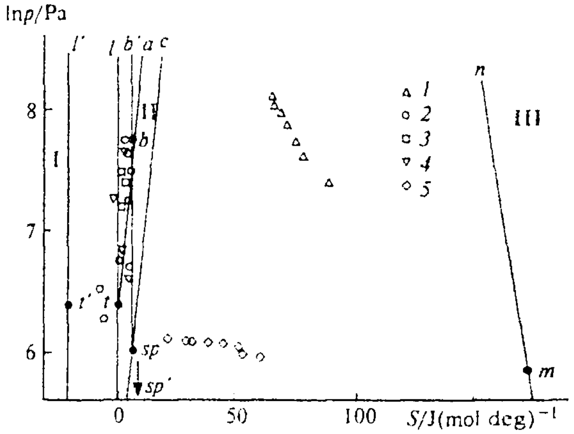

Fig. 2. Diagram "vapor pressure (ln$p$)—entropy (S)—temperature (T)." I, crystalline phase; II, liquid; III, vapor. Designations of lines and regions of metastable and labile states correspond to Fig. 1 and are presented in the text. Points are the result of the experimental determination of the adsorption of water on different adsorbents at 293 K: *1*, graphitized soot; *2*, AU-5; *3*, AU-5M; *4*, canal soot; *5*, ART.

Let us determine the state of water adsorbed on CA.

The points in Fig. 2 are experimental data for different adsorption systems. The ordinate ln$p$ was determined by direct measurement of the equilibrium pressure of water adsorbed on CA at the temperature T and the adsorption a. The entropy of adsorbed water was calculated by the equation

$$S = S_s^l + R\ln p_s/p - \frac{L-Q}{T}, \qquad (9)$$

where $S_s{}^l$ and L are the entropy and heat of evaporation of water on the binodal, respectively, and Q is the integral adsorption heat. It was determined from the heats of immersion q of CA samples on which a moles of water were preliminarily adsorbed according to the equation

$$Q = \frac{q_0 - q}{a}. \qquad (10)$$

where q_0 is the heat of immersion of the "dry" adsorbent.

For the GTB—water and ART—water systems with the known isosteric adsorption heats (q_{st}), the integral heat was calculated from the equation

$$Q = \frac{1}{a}\int_0^a q_{st}da. \qquad (11)$$

The initial adsorption heats at $a = 0$ for GTB and ART were determined by the linear extrapolation of the dependence of q_{st} on a. They are equal to 17 and 34 kJ mol^{-1}, respectively.

As can be seen from Fig. 2, the state of adsorbed water for the majority of the systems studied (points *2*—*5*) is related to the region of the "stretched" liquid, between the binodal (line *ta*) and isothermal (line *bsp*), passing near spinodal point *sp* to the region of the labile state of water. Below spinodal point *sp*, water does not exist in the liquid form at this temperature (293 K).

The state of water adsorbed on graphitized soot (Fig. 2, points *1*) differs substantially from the state of the stretched liquid and conventionally corresponds to the labile state of water.

Let us consider the region of the stretched liquid in more detail and compare the "stretched liquid—vapor" and "adsorbate—vapor" system from the viewpoint of the size of the phase of liquid water and the pressure applied to the system.

"Stretched liquid—vapor" system. It should be mentioned that the biphase system consisting of microscopic stretched water with the planar liquid—vapor interface cannot be obtained under real conditions. This hypothetical state can be presented as the result of the action of the external uniform and isotropic field upon a closed vessel containing water in the form of a liquid in equilibrium with vapor. The field is directed against the action of molecular attraction forces. It results in an increase in the distance between water molecules and a related change in the physical and thermodynamic properties of water.

The action of the field is equivalent to the action of the all-round external stretching pressure p^l applied to the external liquid surface and is the same in any point of its volume. All properties of the stretched liquid far from the critical temperature are determined by the calculation using the extrapolation equations, whose correctness is proved by the experimental data in the region of positive pressures. They were not subjected to experimental testing, especially near the spinodal. The comparison of the experimental data of adsorbed water with the calculated data for the bulk stretched water is of interest independently as the first attempt at experimental checking of the calculations performed.

"Adsorbate—vapor" system. The field of molecular forces of the adsorbent applied to the adsorbate is the external field in adsorption systems. This field is nonuniform: it decreases rapidly along the normal to the surface. It creates tangential forces parallel to the surface, which depend on the relief and chemical nature of the surface and space of pores.

The real adsorption phase is a totality of a great number of microphases of the adsorbate with different volumes and geometry. The overall properties of nonuniform systems are characterized by average values of such magnitudes as, *e.g.*, the density and heat capacity. The other parameters of the system (temperature, chemical potential, equilibrium pressure in the gas phase) are the same at any point, but the local pressures on the microphases differ. The latter is caused by the fact that the pressure on the microphases is related to their molar volume (V^l) and compressibility (β^l) by Eqs. (1) and (2). According to these equations, some effective pressure p^l and the average isothermal compressibility correspond to the average value of the molar volume.

The average thickness of the adsorption phase is equal to one or several molecular diameters. By their physical nature, liquid layers of this thickness are intermediate layers at the interface with vapor or solid, and their properties differ from those of bulk water layers.

It can be seen from Fig. 2 that as the equilibrium pressure of adsorbed water decreases, the experimental points are located in the region of the metastable state of water near the isotherm (line *bsp*). Some systematic deviation from the isotherm can be caused by the aforementioned difference of the properties of the transition layers from the properties of bulk water. Near the spinodal on the isotherm (point *sp*), the experimental points remove sharply from the region of the stretched liquid to the region of the labile state of water. It is noteworthy that, according to the published data,[4] the discontinuity of the properties of liquid water (destruction of the liquid phase) takes place at the relative pressure p/p_s = 0.184 (T = 293 K). The high dispersity of the adsorption phase probably exerts some effect on the value of the pressure of the "discontinuity," shifting or expanding it by some interval of the transition pressure.

At the same time, the comparison we performed shows that the differences between the highly dispersed adsorption phase and stretched microscopic water are insignificant. Therefore, in the first approximation, the properties of adsorbed water can be equalized to those of stretched water. Let us determine some of them.

Molar volume. As the stretching pressure increases, the molar volume of water increases, reaching the limiting value on the spinodal. It can be seen from Table 1 that the limiting volume of stretched water is not greater than 25% of the volume of water on the binodal. The limit of the possible expansion of the water volume is the molar ratio of 57.03 mL mol^{-1} at the critical temperature, which is more than 3 times higher than the water volume near the triple point.

The dependence of the molar volume of stretched water on the pressure of saturated vapor calculated from Eq. (5) is shown in Fig. 3, *a*. A sharp increase in the molar volume is observed when it approaches the limiting volume V_{sp}^l. In point *sp*, the derivative $(dp/dV^l)_T$ is equal to zero.

Heat of evaporation. Let us consider two heats of evaporation of the stretched liquid: isobaric Q_p and isothermal Q_T. The isobaric heat is determined from a change in the pressure of saturated water vapor at the constant stretching pressure:

$$Q_p = -R\left[\frac{\partial \ln p}{\partial T^{-1}}\right]_{p^l}. \qquad (12)$$

The method for determination of the isobaric heat of evaporation, using V^l as the independent variable, is

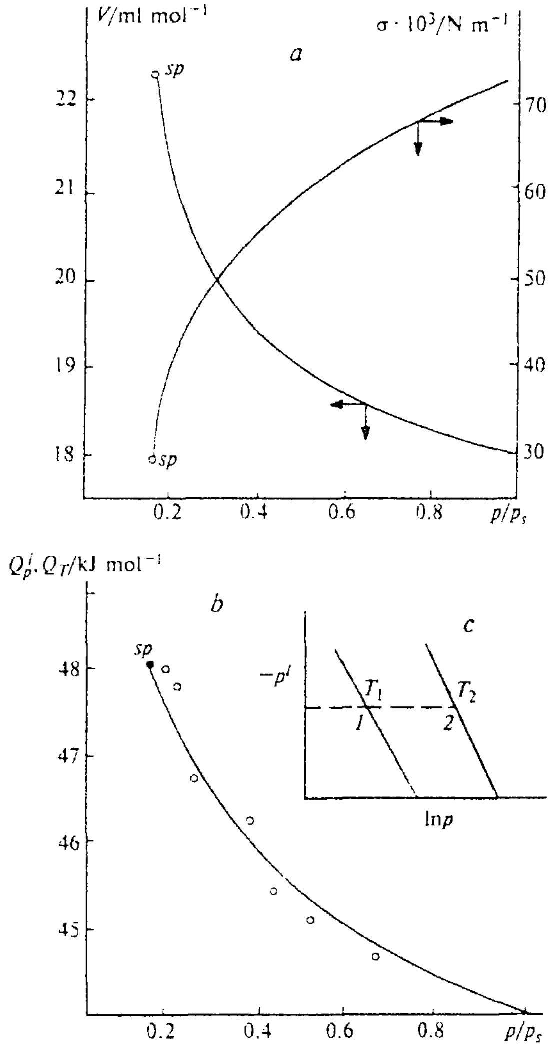

Fig. 3. Physical properties of stretched water at 293 K: *a*, molar volume (V) and surface tension (σ); *b*, isobaric Q_p (points) and isothermal Q_T (solid lines) of heats of evaporation of water calculated from Eqs. (12) and (14); *c*, scheme of the graphic calculation of the isobaric heat of evaporation.

shown schematically in Fig. 3, *c*. The dependences $p^l = f_1(V^l)$ and $\ln p = f_2(V^l)$ were calculated from Eqs. (4) and (5) for two temperatures (curves T_1 and T_2). Then the isobaric heat of evaporation of stretched water was determined by substitution of the differentials in Eq. (12) by the final increments $\Delta \ln p$ and ΔT^{-1} (points 1 and 2 in Fig. 3, *c*).

The isothermal heat of evaporation is determined as a change in the enthalpy of water (H) in the isothermal transition from the state of the stretched liquid to the vapor in equilibrium with water:

$$Q_T = H - H^l$$

or as a change in entropy in this transition

$$Q_T = T(S - S^l). \qquad (13)$$

Using Eqs. (8) and (13), the equation of the isothermal heat of evaporation of the stretched liquid was obtained in Ref. 7

$$Q_T = L + (1 - \alpha^l T)RT \cdot \ln(p_s/p), \qquad (14)$$

where L is the heat of evaporation of the liquid on the binodal. The dependence of Q_T on p/p_s calculated from Eq. (14) is shown as a solid curve in Fig. 3, *b*. As can be seen from Fig. 3, *b*, the isobaric and isothermal heats are similar and increase, reaching the final maximum value at point *sp* as the pressure of saturated vapor decreases (as the stretching pressure increases).

Surface tension. To calculate the surface tension of stretched water, the McLeod—Sagden empirical equation was used[8]

$$\sigma^{1/4} = [P]\left[\frac{1}{V^l} - \frac{1}{V}\right], \qquad (15)$$

where $[P]$ is constant (parachor). It was determined by the known values of the surface tension and molar volumes on the binodal and is equal to 4.037. As can be seen from Fig. 3, *a*, as p/p_s decreases, the surface tension decreases especially sharply approaching point *sp*. It is difficult to determine the σ value on the spinodal; perhaps, it tends to zero.[4]

Comparative analysis of the state of water adsorbed, *e.g.*, on GTB (points *1* in Fig. 2) is difficult in the labile region of the diagram in Fig. 2, because it is difficult to make analogies between the state of the adsorbate and known aggregate states of water. This state can be indirectly estimated by the slope of the curve $\ln p = f(S)$. It is close to $0.3/R$ and $0.05/R$ for the GTS—water and ART—water systems, respectively. Gases in the temperature region close to supercritical possess similar properties (curve *hk* near point *c* in Fig. 1).

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