METHODS OF CALCULATING THE THERMODYNAMIC PARAMETERS OF WATER SORBED BY A SWELLING HYDROPHILIC SORBENT

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A sorbtion-isotherm equation is derived, which is used with the observed isotherms in the method of calculating the thermodynamic parameters of water sorbed by a swelling hydrophilic sorbent.

We have previously [1, 2] derived an equation for the sorption isotherm for water vapor on a swelling hydrophilic sorbent by means of methods from thermodynamics and statistical physics

$$1/W = g \ln\left(\frac{p_s}{p}\right) + d, \tag{1}$$

$$g = RT/(\mu\Delta\omega z_0 x), \tag{2}$$

$$d = g\left[\frac{\alpha}{z_0}\ln(z_0!) + \frac{1}{c_2}\ln(c_2!) - \frac{1}{c_1}\ln(c_1!)\right]. \tag{3}$$

Here g and d are coefficients dependent on numerous parameters.

Equation (1) was derived by calculating the changes in Gibbs energy ΔG, enthalpy ΔH, and entropy ΔS for the sorbed water with allowance for sorbent reaction, while a standard thermodynamic relation was used for the isothermal process:

$$\Delta G = \Delta H - T\Delta S. \tag{4}$$

The changes were considered relative to unbound water.

Tests on (1) showed that it describes the sorption in these systems for wide ranges in the relative vapor pressure (at least up to $p/p_s \sim 0.90$-0.95) and gives good scope for determining the thermodynamic parameters.

Figure 1 shows room-temperature water-vapor sorption isotherms for some swelling hydrophilic sorbents; the slopes of the parts give g, while extrapolation gives d. There g and d have been used with set α, z_0, and z_1 in (3) to calculate the coordination numbers z_g for the sorbate in the sorbed state. The values of z_0 as functions of W were in the range 1-4 for different parts of the curve, since these are most characteristic of polar groups in macromolecular materials such as $-\mathrm{OH}$, $-\mathrm{COOH}$ $>\mathrm{CO}$, $>\mathrm{NH_2}$, $>\mathrm{COH}$, $-\mathrm{NH_2}$, $-\mathrm{CONH}-$ (in proteins) which interact with numbers of water molecules correspondingly 3, 4, 2, 2, 2, 2-3, 1 [3] as indicated by the speed of ultrasound in solutions. The range in z_0 is naturally related to the properties of the particular sorbent. For example, Table 1 gives forms of relation between α, z_0, z_1, and z_2 for the cotton-sorbed water system that satisfy the observed g and d. The data show that the calculated values correspond to physical concepts on the state of bound water. Also, nuclear magnetic resonance spin-echo data confirm the calculated α [4], which in essence characterized the sorbent hydration. The calculation and experiments were performed on systems with the sorbents consisting of cotton, wool, starch, and gelatin. The concepts also correspond to the concentrations of sorption centers given by the formulas:

$$x = \frac{RT}{g\mu\Delta\omega z_0}, \tag{5}$$

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TABLE 1. Values of Parameters Determining Form of Water-Vapor Sorption Isotherm for Cotton (z_1 = 4)

p/p_s	g	d	$d:g$	α	z_0	z_2
[0,068 — 0,113)	34,6	—25,4	—0,73	1	1	1
				1	2	—
[0,113 — 0,237)	25,0	—4,5	—0,18	1	1	3
[0,237 — 0,619)	17,9	5,7	0,32	1	2	4
[0,619 — 0,806)	19,3	5,0	0,26	1	3	2
				0,71	3	3
				0,44	3	4
[0,806 — 0,894]	29,3	2,8	0,10	0,17	3	4

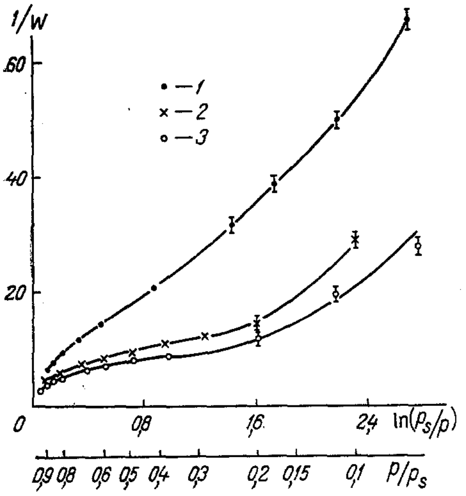

Fig. 1. Water-vapor sorption isotherms: 1) cotton (T = 295.5°K); 2) potato starch (T = 293°K); 3) wool (T = 293.5°K); 1/W in kg/kg.

as well as the enthalpy changes

$$\Delta H = -\frac{RT}{gW} \tag{6}$$

and the entropy changes

$$\Delta S = -\frac{d}{g} R \tag{7}$$

per mole of sorbed water; Fig. 2 shows the W dependence of ΔH and ΔS typical of these systems.

Approximate calculations have been made on the active-center concentrations x for cotton, wool, and potato and maize starches, as well as silk, jute, and gelatin from (5) for the range $p/p_s \sim 0.1$-0.2 on the assumption that $\Delta\omega = 6.3$ kJ/mole (the mean energy difference between hydrogen bonds for the usual range [5]), which with the experimental isotherms give correspondingly the values 0.6, 1.5, 1.0, 3.3, 0.8, 0.9, 4.5 mol/kg. These are only approximate estimates because the choice $\Delta\omega = 6.3$ kJ/mol is arbitrary, as the characteristic will have some definite value for each particular case, although the results agree at least as regards order of magnitude with the calculations previously performed by another method [6].

From the physical viewpoint, the mode of variation in ΔS (Fig. 2b) can be explained as follows. At low sorptions, the water molecules are discretely distributed over the centers and are not linked together. Then the state of the bound sorbate resembles that of a gas in

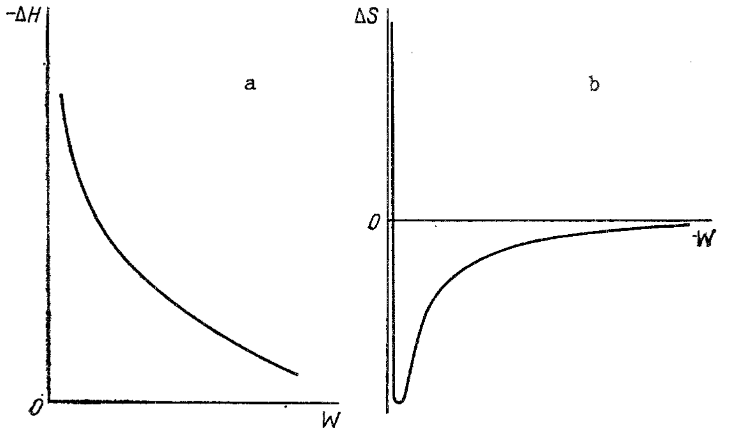

Fig. 2. Typical dependence on W for the changes in enthalpy ΔH and entropy ΔS for sorbed water in the systems used.

the field of the sorbent, and $\Delta S > 0$. As the amount of sorbate increases, the numbers of bonds between the molecules themselves increase. The molecular mobility falls, and ΔS changes from + to − in a certain range. The entropy of a mole of sorbed material continues to decrease (ΔS increases in absolute value) down to a certain minimal value, after which ΔS falls in absolute value to the limit of 0 at high uptakes, since there is an increase in the proportion of sorbate molecules not interacting directly with the sorption centers.

The ΔS have been compared with the changes in the spin-spin relaxation times T_2 for the sorbed water as determined by spin-echo methods [4]. The conclusion was that the trends and rates of change in T_2 and ΔS coincide for all these systems, where the sorbents were cotton, wool, gelatin, and starch.

NOTATION

G, Gibbs energy; H, enthalpy; S, entropy; T, temperature; W, moist content of sorbent; p/p_S, relative vapor pressure of sorbed substance; R, universal gas constant; μ, molar mass of sorbed substance; Δω, energy difference (mean over the number of bonds of the sorbate-sorbent type) for the interaction of a liquid molecule with an active site after absorption and a liquid molecule with its surrounding molecules before the start of the process; z_0, number of sorbate molecules (averaged over the number of the sorption sites interacting with sorbate molecules at a certain point) interacting with an active site; x, concentration of compound sorption sites; α, fraction of the total number of molecules sorbed immediately localized at the active sites; $c_1 = z_1 + 1$ and $c_2 = z_2 + 1$ where z_1 and z_2 are the coordination numbers of the sorbate in the free and sorbed states respectively; T_2, spin-spin relaxation time of sorbed substance.

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