ISOTHERMS OF THE SORPTION OF WATER VAPOR BY SWELLING HYDROPHILIC SORBENTS

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On the basis of an equation proposed previously, a method for calculating the isotherms of water-vapor sorption by swelling hydrophilic sorbents is outlined. The construction of the isotherms entails some information on the physicochemical characteristics of the system — for example, the binding energy of the sorbate molecule with the active center, the degree of hydration of the sorbent, the temperature, the sorptional centers and their mutual position, etc. As an example, the calculation of the isotherms of water-vapor sorption by cotton is considered.

As is known, the basic problems of the theory of adsorption and absorption are the description of adsorptional phenomena from a unified viewpoint and the development of methods of calculating the equilibrium characteristics determining these processes. Original contributions were made in these areas in [1-3]. In the present work, a method is outlined for calculating the isotherms of water-vapor sorption by swelling hydrophilic compounds, which are more complex sorbents for the solution of such problems.

In [4, 5], an equation of the isotherm of water-vapor sorption by swelling hydrophilic sorbents was proposed, in the form

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

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

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

It follows from Eqs. (2) and (3) that the coefficients g and d are variable and depend on the water content of the sorbent.

Equation (1) is verified as follows. Experimental sorptional isotherms are plotted in the coordinates $1/W-\ln(p_s/p)$. Then the coefficients g and d are determined from these isotherms and used to calculate a whole series of the most important characteristics: ΔH and ΔS (the change in enthalpy and entropy of the sorbate, respectively) [6], the degree of hydration of the sorbent, the concentration of sorptional centers of the compound, the coordination number of the sorbed water, and the number of sorbate molecules interacting with a single sorption center.

Such verification using NMR methods permits the conclusion that the equation adequately describes the sorption of water vapor by swelling hydrophilic sorbents in a wide range of relative vapor pressure ($0.05 \lesssim p/p_s \lesssim 0.90-0.95$).

Of course, the next logical step is to develop a procedure for calculating the sorption isotherms. A scheme for such calculations is outlined in the present work.

Thus, to solve the given problem using Eq. (1), all the characteristics in Eqs. (2) and (3) must be known; in particular, certain data on the chemical and physical properties of the sorbent must be known.

The following is known about the sorptional system in the present case. Cotton is used as the sorbent. The degree of hydration of the sorbent, i.e., the mass of moisture interacting directly with the sorptional centers of the sorbent (per kg of compound), is W_0 =

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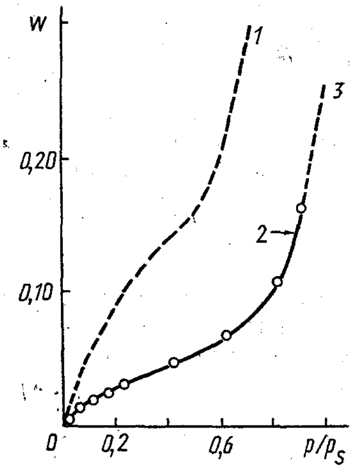

Fig. 1. Isotherms of water-vapor sorption by cotton: 1) T = 293 K, $\overline{\Delta\omega}$ = 0.85 kcal/mole (calculation); 2) 295.5 (experiment); 3) 295.5 K, $\overline{\Delta\omega} = f(W)$ (calculation). W, kg/kg.

0.12 kg/kg. The sorptional centers of the sorbent are OH groups; it is assumed that the maximum number of molecules which may interact with one such group is three [7]. The temperature at which the process occurs is 293 K.

Suppose that, as calculated per mole of adsorbed material, $\overline{\Delta\omega}$ = 0.85 kcal/mole. For the sake of simplicity, assume that $\Delta\omega$ = const, since the principal aim here is simply to illustrate the principle or the scheme for determining the sorption isotherms.

In the calculations, it is taken into account that the coordination number of the water in the free state $z_1 = 4$, while for the sorbed water z_2 will vary in the range 0-4 with increase in water content W.

Then, introducing the parameter α, the proportion of sorbed molecules which are localized directly at the active centers of the sorbent, it is evident that $\alpha = 1$ when $W \leq W_0$ and $\alpha = W_0/W < 1$ when $W > W_0$. Using this characteristic, the concentration x of sorptional centers of the compound which have already participated in the sorption process may be expressed in the form

$$x = \frac{\alpha W N_A}{\mu z_0}. \tag{4}$$

Now Eq. (2) is brought to a form more convenient for calculations

$$g = \frac{RT}{\overline{\Delta\omega}\left(\frac{\text{kcal}}{\text{mole}}\right)\alpha W}. \tag{5}$$

Calculation of the sorption isotherm means that, specifying various values of W, the corresponding values of p/p_S are then calculated.

Without taking account of the limiting water saturation of cotton, the following water-content values are chosen for the calculations: 0.04, 0.08, 0.12, 0.16, 0.20, 0.25, 0.30 kg/kg. If the degree of hydration of the sorbent W_0 = 0.12 kg/kg and at this water content each of the OH groups participating in the process interacts with three sorbate molecules ($z_0 = 3$), it is found that $z_0 = 1$ when W = 0.04 kg/kg, taking account of the uniform distribution of H_2O molecules over the sorption centers, and $z_0 = 2$ and $z_2 = 1$ when W = 0.08 kg/kg (two molecules at the same active center interact with one another). It follows that a fairly developed spatial grid of hydrogen bonds appears in the formation of the hydrate shells around the sorptional centers of the water molecule; NMR data on water vapor sorbed by cotton lead to the same conclusion [8]. Therefore, in calculations with $W > W_0$, beginning at W = 0.16 kg/kg, z_2 is taken to be four.

The theoretical sorption isotherm is shown in Fig. 1 (curve 1). One criterion of cor-

TABLE 1. Parameters Determining the Form of the Sorption Isotherm (Fig. 1, curve 3)

W, kg/kg	α	z_0	z_1	z_2	$\overline{\Delta\omega}$, kcal/mole	g	d	p/p_s
0,010	1	1	4	0	1,20	48,9	—46,8	0,050
0,020	1	1	4	0	0,75	39,1	—37,5	0,107
0,038	1	1	4	0	0,15	102,9	—98,6	0,297
0,075	1	2	4	1	0,08	97,8	—25,9	0,670
0,113	1	3	4	2	0,25	20,8	4,9	0,828
0,150	0,753	3	4	4	0,44	11,8	5,3	0,891
0,200	0,565	3	4	4	0,40	13,0	4,4	0,953
0,250	0,452	3	4	4	0,36	14,4	3,9	0,993

rect calculation for the given sorptional systems is a sigmoid form of the isotherm. The curve in Fig. 1 is of this form.

Note, in conclusion, that reliable and complete information on the sorbent is required for thorough construction of the isotherms. It is necessary to know the mutual position of the sorptional centers, their energy distribution, i.e., the degree of inhomogeneity of the sorbent, etc. For example, the experimental isotherm of water-vapor absorption by cotton (with a degree of hydration $W_0 = 0.113$ kg/kg) at T = 295.5 K (Fig. 1, curve 2) completely coincides with the theoretical curve (Fig. 1, curve 3), assuming in the calculations that $\overline{\Delta\omega}$ is a function of the water content W (Table 1). The dependence of the isosteric heat on W for the cotton–water-vapor system is of precisely this form [9]. Decrease in $\Delta\omega$ at small p/p_s is explained by inhomogeneity of the sorptional centers or sections of the sorbent. Even the intermolecular interaction ($z_2 = 1$) appearing at W = 0.075 kg/kg is simply "suppressed" by the inhomogeneity of the sorbent, and $\Delta\omega$ continues to fall. Further increase in this parameter is associated with increase in the lateral interaction of the sorbed molecules; the decline at high water contents is explained by the influence of the increasing second fraction of the water, the molecules of which do not interact directly with the sorptional centers of the compound.

Note also that, in the present work, fairly complex sorbents whose sorptional power depends largely on their physical properties – in particular, on the degree of crystallinity – are considered. The degree of hydration of the compound W_0 essentially takes account of the supermolecular structure of the sorbent and determines the maximum concentration of sorptional centers involved in the absorption of the sorbate; this parameter characterizes the specific features of the sorbent and has a definite value for each compound.

It may be concluded that the example considered by the new method – the calculation of the isotherm of water-vapor sorption by cotton – indicates agreement of the theoretical and experimental data on this system. The given approach may be a possible means of determining the macroscopic equilibrium characteristics of the process on the basis of molecular data on the sorbate and sorbent.

NOTATION

W, water content of sorbent; p/p_s, relative vapor pressure of sorbate; T, temperature; R, universal gas constant; μ, molar mass of sorbate; $\Delta\omega = \omega_{12} - \omega_{11}$, where ω_{12} is the binding energy per molecule directly interacting with a sorptional center of the sorbent; ω_{11} is the energy of molecular interaction per molecule for water in the free state; z_0 is the number of sorbate molecules (averaged over the number of sorptional centers bound with sorbate molecules up to a definite moment in the process) interacting with the active center; x is the concentration of sorptional centers of the compound participating in the process; α is the proportion of sorbed molecules directly localized at active centers of the sorbent; $c_1 = z_1 + 1$, $c_2 = z_2 + 1$ (z_1 and z_2 are the coordination numbers of the sorbate in the free and bound states, respectively); H is the enthalpy; S is the entropy; W_0 is the degree of hydration of the sorbent.

LITERATURE CITED

1. B. P. Bering and V. V. Serpinskii, Izv. Akad. Nauk SSSR, Ser. Khim., No. 11, 2427-2440 (1974).
2. B. P. Bering, V. V. Serpinskii, and T. S. Yakubov, Adsorbents, Their Preparation, Properties, and Application [in Russian], Leningrad (1978).
3. Yu. K. Tovbin, Theory of Physicochemical Processes at a Gas—Solid Boundary [in Russian], Moscow (1990).
4. N. I. Gamayunov and A. V. Tvardovskii, Inzh.-Fiz. Zh., 41, No. 5, 854-858 (1981).
5. N. I. Gamayunov and A. V. Tvardovskii, Zh. Fiz. Khim., 60, No. 12, 3011-3015 (1986).
6. N. I. Gamayunov and A. V. Tvardovskii, Inzh.-Fiz. Zh., 51, No. 4, 533-536 (1986).
7. V. I. Kasatochkin and A. G. Pasynskii, Physical and Colloidal Chemistry [in Russian], Moscow (1960).
8. N. I. Gamayunov and A. V. Tverdovskii, Zh. Fiz. Khim., 55, No. 6, 1599-1601 (1981).
9. N. I. Gamayunov and B. V. Evdokimov, in: Physicochemical Mechanics and Lyophilic Character of Disperse Systems [in Russian], No. 11, 55-62 (1979).

FLOW OF FREEZING WATER AND AQUEOUS SALT SOLUTIONS THROUGH TUBES

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The problem of internal freezing of pipes is formulated and results of numerical studies presented.

Transport of freezing liquids, including water, various suspensions, and aqueous solutions of salts under conditions of reduced ambient temperature may be accompanied by internal icing of lines [1], which leads to an increase in the pressure head required to pump the liquid, or complete closing of the "live" line section and impossibility of further use.

We will consider the process of ice freezing on the inner wall of a tube when aqueous solutions of certain salts, for example, sodium chloride, flow therein. We will assume that the salt concentration in the water is less than eutectic (for sodium chloride the eutectic concentration in water is approximately 30% by weight [2]).

In freezing of a subeutectic composition only the solvent goes through a phase transition. The concentration of the dissolved material will then increase near the phase transition boundary. Due to the difference between concentrations near the phase transition boundary and the remaining part of the solution which thus develops the dissolved substance will be removed from the phase transition zone by diffusion.

Thus, the salt concentration at the phase transition boundary and the related freezing temperature will be variables, and the process of salt water freezing during flow in a tube must be described by combined heat and mass transport equations. The formulation of the problem will be analogous to that of [3].

For flow of an incompressible liquid in a tube of varying section the continuity equation can be written in the following form:

$$\frac{\partial S_w}{\partial t}+\frac{\partial (VS_w)}{\partial x}=\frac{\rho_{\text{т}}}{\rho_{\ell}}\,\frac{\partial S_w}{\partial t}. \tag{1}$$

In the case under consideration the equation of motion has the form

$$\frac{\partial V}{\partial t}+V\frac{\partial V}{\partial x}=-\frac{1}{\rho_{\ell}}\,\frac{\partial P}{\partial x}-\frac{\sqrt{\pi}\,\xi V^2}{4\sqrt{S_w}}-g\sin\gamma-\frac{\rho_{\text{т}}}{\rho_{\ell}}\,\frac{V}{S_w}\,\frac{\partial S_w}{\partial t}. \tag{2}$$

The energy equation can be written as

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