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USING THE THEORY OF THE VOLUMETRIC FILLING OF MICROPORES TO CALCULATE THE SORPTION OF ELECTRICALLY INSULATING CELLULOSE MATERIALS

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It is shown that the theory of the volumetric filling of micropores may be used to calculate sorption isotherms and the specific isothermal moisture capacity of electrically insulating cellulose materials.

In [1, 2] values of the equilibrium moisture content of electrically insulating cellulose materials were given for a wide range of sorption parameters — temperature and pressure. As noted in [1, 2], the sorption isotherms of cellulose materials for water-vapor pressures in the range of practical importance for the vacuum drying of electrical insulation ($P/P_S < 0.3$) are described by an equation of Freundlich type

$$W_e = cP^n, \tag{1}$$

where c and n are temperature-dependent constants characterizing the given material.

The sorption-isotherm equation of Freundlich type may be regarded as a particular case of the generalized absorption-isotherm equation for microporous sorbents based on the theory of volume filling, which in energy form, is written as follows [3-5]

$$W_e = W_0 \exp[-(A/E)^m], \tag{2}$$

where W_0 is a certain value of the adsorption, called the limiting value of the adsorption; A, differential work of adsorption ($A = RT\ln P_S/P$); E, characteristic adsorption energy determined at the characteristic point for a filling of $W_e/W_0 = \Theta = \exp(-1) = 0.368$; m, power index or the rank of the distribution. Together, m and E characterize the mechanism of the sorption interaction. When $m = 1$, Eq. (2) may be written in the Freundlich form in Eq. (1), and the empirical coefficients n and c in Eq. (1) are then [4]

$$n = RT/E, \tag{3}$$

$$c = W_0 P_s^{-n}. \tag{4}$$

Equation (2) provides a good description of the sorption equilibrium of various gases and vapors on microporous sorbents: active charcoals of various types, zeolites [3-5].

With a view to broadening the class of adsorbate—adsorbent systems for which the engineering method of equilibrium-adsorption proposed in [5] may be used, it is of interest to analyze experimental data on the equilibrium moisture content of electrically insulating cellulose materials. The interaction of water with these materials is a complex process whose mechanism is by no means fully understood, especially at low moisture contents. According to one viewpoint, the cellulose—water system should be regarded as the interaction of a polymer with the vapors of low-molecular solubility of water in cellulose [7]. Real cellulose systems — especially those which are electrically conducting — constitute complex fiber—porous systems, which may contain not only dissolved and adsorption-bound water, but also moisture bound by capillary and osmotic forces.

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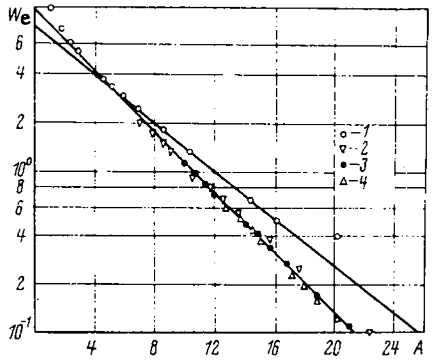

Fig. 1. Sorption isotherm for K-120 cable paper, $W_e = f(A)$, for different temperatures: 1) 302°K; 2) 343°K; 3) 363°K; 4) 383°K. W_e, %; A, kJ/mole.

TABLE 1. Values of W_0 and E for Electrically Insulating Cellulose Materials

Material	W_0,g/g ·100%	E, J/mole
K-120 cable paper		
(T=343—383 °K)	9,6	4650
K-120 cable paper		
(T=296—302 °K)	7,7	5900
EMTs cardboard	8,4	5700
A and B cardboard	8,4	5020

Electrically insulating cellulose materials, which contain not only large pores on the order of 10^{-4} cm but also pores and microcapillaries with an equivalent diameter of order 10^{-6}-10^{-7} cm, should evidently be regarded as adsorbents of transitional-porous type; their specific surface for water is 140-150 m^2/g [6].

Note that for such materials the specific surface is the conventional characteristic of their sorption capacity with respect to water. Another conventional notion, characterizing the fraction of water that is most strongly bound for cellulose materials, is the "monomolecular-layer moisture," since in sorption the filling of micropores by polymolecular adsorption of "island" type and even the filling of microcapillaries by water may occur before the formation of the monomolecular layer is complete.

The equation of volumetric filling, based on the assumption that the adsorption space is filled without the formation of a phase interface, may be used for the case of adsorption on transitional-porous and nonporous sorbents. In this case, the rank of the distribution $m = 1$, and adsorption mechanism may be regarded as the accumulation of adsorbate molecules on the pore surface [4].

Sorption isotherms of cable paper are shown in Fig. 1 in the coordinates of Eq. (2) ($m = 1$), for temperatures in the range 302-383°K. As follows from Fig. 1, the curve of $\log W_e = f(A)$ is a straight line over a considerable range of W_e, while experimental values of W_e obtained at 343-383°K are grouped closely about the same straight line. Thus, the equilibrium moisture content of K-120 cable paper may be taken to be

$$W_e = W_0 \exp\left(-RT/E \ln \frac{P_s}{P}\right). \tag{5}$$

The same dependence is obtained for other electrically insulating cellulose materials; values of W_0 and E for some electrically insulating materials are shown in Table 1.

It is also of interest to compare the coefficients n and c of the Freundlich equation obtained empirically [6] for cellulose materials with those calculated from Eqs. (3) and (4); Table 2 shows this comparison for K-120 cable paper.

Thus, it follows from the data in Fig. 1 and in Tables 1 and 2 that the generalized equation of the adsorption isotherm based on the theory of volumetric filling may be used to calculate the equilibrium moisture content of electrically insulating cellulose materials with adequate accuracy for practical purposes. Note that to calculate the hygroscopic properties of these materials at high temperatures it is sufficient to obtain a single experimental isotherm, which considerably shortens the investigation. In this case, it is thought that the basic parameters in the adsorption-isotherm equation of the theory of the volumetric filling of micropores —

TABLE 2. Comparison of Values of c and n Obtained Experimentally [6] and Calculated from Eqs. (3) and (4) for K-120 Cable Paper

T, °K	Experimental [6]		Calculated from Eqs. (3) and (4)	
	n	c, g/g·100%/(mm·Hg)^n	n	c, g/g·100%/(mm·Hg)^n
343	0,56	0,370	0,61	0,383
363	0,63	0,170	0,65	0,166
383	0,69	0,075	0,69	0,08
393	0,73	0,048	0,71	0,055
403	0,76	0,034	0,72	0,041
296	0,40	2,48	0,41	2,19
302	0,42	1,81	0,42	1,84
318	0,48	0,92	0,45	1,12

the limiting adsorption W_0 and the characteristic energy E — take on a rather different meaning: the value of W_0 obtained by linear extrapolation of Eq. (5) when $P/P_s = 1$ is a structural characteristic of the material, and corresponds to the amount of adsorption-bound moisture in the cellulose material.

The difference in the values of W_0 and E in Eq. (5) at high (T = 343-383°K) and room temperatures (T = 296-302°K) may be regarded as indicating an increase in the proportion of purely surface adsorption, as is confirmed by data on the adsorption kinetics of water vapor on electrically insulating cellulose materials [6]. This conclusion is also confirmed by the observation that at lower temperatures there is a certain rise in the characteristic energy E, which in the given case is also some averaged energy characteristic of the adsorbate–adsorbent interaction for the system being considered. Comparison of the value of E with the binding-energy values for cable paper reveals that the result E = 5900 J/mole corresponds to the binding energy of moisture with a material of moisture content 4.5%, i.e., at complete filling of the monomolecular layer at the given temperature (T = 302°K) [6].

It is interesting to note that, for the given description of the equilibrium moisture content, the expression for the specific isothermal moisture capacity, which is an important thermodynamic parameter of moisture transfer, takes the simple form

$$c_m' = W_e / E, \tag{6}$$

i.e., the specific isothermal moisture capacity is equal to the ratio between the equilibrium moisture content and the characteristic energy of the system being considered. If the specific moisture capacity is known, Eq. (6) allows the equilibrium moisture content of the material to be calculated.

The values of the specific isothermal moisture capacity for cable paper obtained from Eq. (6) are in good agreement with the values of c_m' given in [6].

NOTATION

W_e, equilibrium moisture content of material; W_0, limiting value of adsorption; P, water-vapor pressure; P_s, saturated vapor pressure; Θ, degree of filling; A, differential molar work of adsorption; E, characteristic adsorption energy; R, gas constant; T, temperature, °K; c_m', specific isothermal moisture capacity; c, m, n, empirical coefficients.

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