INTERACTION OF MOISTURE WITH MODEL CAPILLARY-POROUS HYDROPHILIC MATERIALS

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This paper gives the results of an experimental investigation of the interaction of moisture with model capillary-porous materials and the thermodynamic functions of the water retained by them.

An elucidation of the mechanism of interaction of moisture with capillary-porous materials with different porous structure is of fundamental interest for the theory and practice of mass and heat transfer.

Valuable information can be obtained by a combination of sorption and calorimetric methods of investigation. In this way the thermodynamic functions characterizing the binding of moisture can be calculated and the energy of binding of the moisture with the material can also be determined.

We investigated model capillary-porous materials—silica gels: industrial samples KSK-2, KSS-4, and KSM-5, and a sample 5-a prepared in the laboratory. These form a standard series of solvents of the composition $SiO_2 \cdot nH_2O$ of the second (uniform large-pored) and third (uniform small-pored) structural types, according to Kiselev's classification [1].

According to the results of electron-microscopic and sorption investigations [2–4], the framework of silica gels is composed of spherical particles (globules) which coalesce at the points of contact. The gaps between the globules form the pores. Small-pored silica gels consist of small particles packed tightly together, while large-pored gels consist of loosely packed large particles.

Before the experiments the silica gels were pulverized and for each type we selected fractions with grain diameter $0.25 \le d \le 0.5$ mm. To remove foreign ions we kept the samples in concentrated hydrochloric acid for some time, washed them with distilled water until the chlorine ion test was completely negative, and then dried them at 130° C for 60 hr. The water content of silica gels dried in this way was assumed to be zero.

An analysis of the differential water-retaining properties of the silica gels was carried out by independent methods from the van Bemmlen sorption and desorption isotherms by means of a vacuum sorption apparatus with a quartz spring balance, from thermograms of isothermal drying [5], and by Dumanskii's indicator method [6]. As an indicator we used a 5% sugar solution and the change in concentration was determined with an ITR-1 interferometer.

Figure 1-I shows the isotherms for sorption and desorption of water vapor by the silica gels. The amount of adsorbed moisture in the monolayer was determined graphically from the sorption isotherms represented in BET coordinates (Fig. 1-II).

Figure 1-I shows that the investigated set of silica gels have sorption isotherms of different nature. This

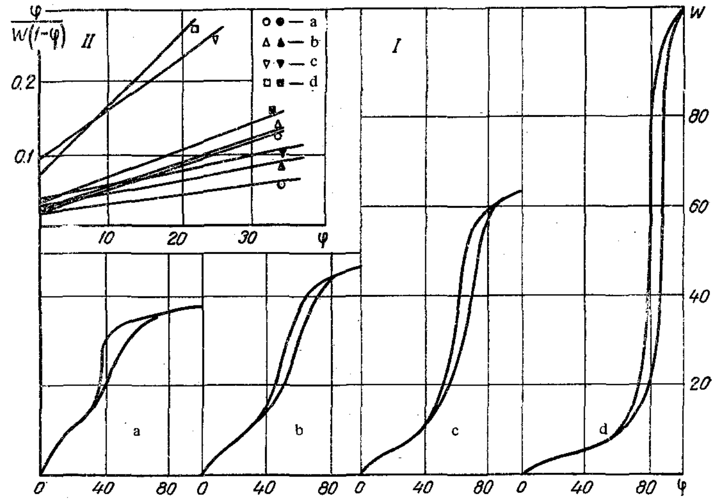

Fig. 1. Isotherms for sorption and desorption of water vapor (I) and isotherms for sorption of water vapor (white symbols) and benzene (black symbols) (II) by silica gels: a) 5-a; b) KSM-5; c) KSS-4; d) KSK-2.

Table 1

Structural Sorption Characteristics of Silica Gels

Silica gel	True density $d \cdot 10^3$, kg/m^3	Limiting sorption pore volume, $V_s \cdot 10^3$, m^3/kg		Micropore volume $V_{mp} \cdot 10^3$, m^3/kg (H_2O)	Intermediate pore volume $V_{ip} \cdot 10^3$, m^3/kg (H_2O)	Specific surface $S \cdot 10^3$, m^2/kg		Effective size of predominant pores $r_{eff} \cdot 10^{-10}$, m (H_2O)
		H_2O	C_6H_6			H_2O	C_6H_6	
5-a	2.255	0.388	0.375	0.165	0.223	1004	840	12
KSM-5	2.250	0.475	0.442	0.152	0.323	772	830	13
KCC-4	2.235	0.636	0.636	0.145	0.491	573	590	20
KSK-2	2.240	1.041	0.990	0.132	0.909	352	430	41

Silica gel	Mean pore size $r \cdot 10^{-10}$, m		Radius of spherical particle $r \cdot 10^{-10}$, m		$\frac{r}{R}$		$\frac{V_s}{V_s + \frac{1}{d}}$		Coordination number n (H_2O)
	H_2O	C_6H_6	H_2O	C_6H_6	H_2O	C_6H_6	H_2O	C_6H_6	
5-a	8	9	13	13	0.62	0.69	0.466	0.458	6.3
KSM-5	12	11	17	16	0.71	0.69	0.517	0.499	5.3
KSS-4	22	22	23	23	0.95	0.96	0.587	0.587	4.4
KSK-2	59	49	38	31	1.55	1.58	0.700	0.689	3.4

indicates the different porous structure of these adsorbents. A large hysteresis loop shifted to the right indicates the presence of large pores in the adsorbent. This is especially distinct in the case of gels KSS-4 and KSK-2.

Table 1 gives the structural sorption characteristics of the investigated silica gels. It is known that the total pore volume includes the limiting sorption pore volume V_s and the volume of the macropores. For vitreous silica gels the volume of the macropores is always equal to zero. The limiting sorption pore volume is equal in turn to the sum of the volumes of the micropores and intermediate pores, which were determined from the water-vapor sorption isotherms.

The specific surfaces S of the silica gels were determined from the BET polymolecular adsorption equation by means of the formula

$$S = a_m S_0 N.$$

The valus of a_m were calculated from the sorption isotherms plotted in BET coordinates (Fig. 1-II). There is no general agreement in the literature as regards the value of the area occupied by the adsorbate molecule in the monolayer. For benzene we took $S_0 = 49 \cdot 10^{-20}$ m^2 [7], for water we took $S_0 = 20 \cdot 10^{-20}$ m^2 in the case of gels 5-a, KSM-5, and KSS-4 [8], and $25 \cdot 10^{-20}$ m^2 for gel KSK-2 [9].

Figure 2a shows the sorption volume of pores of unit mass of the adsorbent as a function of the effective size of the pores, which was evaluated from the Thomson-Kelvin equation from the desorption branches of the isotherm without introduction of a correction for the thickness of the adsorbed layer. From these curves by graphic differentiation we obtained the effective-size distributions of the pore volumes (Fig. 2b). The distinct maxima, particularly for gels 5-a and KSM-5, indicate that the investigated silica gels are uniformly porous. The values of the predominant r_{eff} form a series 12, 13, 20, and $41 \cdot 10^{-10}$ m, respectively, for silica gels 5-a, KSM-5, KSS-4, and KSK-2.

The mean pore radius was calculated from the formula $r = 2\ V_s/S$ [7]. The density of packing of the primary spherical particles of the gel can be characterized by the ratio of the mean radius of the pores to the radius of these particles. The radius of the spherical particles was determined from the formula $R = 3/dS$.

As Table 1 shows, gels containing large particles (KSS-4 and KSK-2) have a smaller specific surface and larger pores, in which capillary condensation of large amounts of vapor occurs, as is indicated by the large volume of the intermediate pores.

The coordination number, which is a measure of the looseness of the packing of the primary particles, can be evaluated from geometric considerations [10] by taking into account the ratio of the limiting sorption

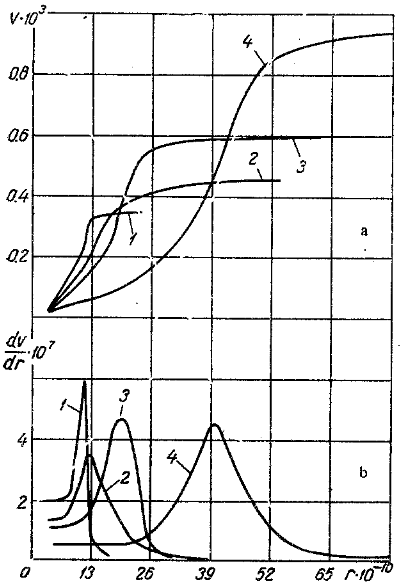

Fig. 2. Sorption volume V (m^3/kg) as a function of effective pore radius r (m) of silica gels (a) and distributions of pore volume dV/dr (m^2/kg) as regards effective radius r (m) (b): 1) 5-a; 2) KSM-5; 3) KSS-4; 4) KSK-2.

Table 2

Differential Water-Retaining Properties of Silica Gels (%)

Silica gel	Monomolecular adsorption			Bound Water			Maximum hygroscopic moisture content	
	from sorption isotherms		from H_2O drying thermograms	from indicator method	from drying thermograms	from sorption isotherms	from sorption isotherms	from drying thermograms
	H_2O	C_6H_6						
5-a	15.0	22.0	14.2	15.7	21.3	16.5	38.8	38.0
KSM-5	11.5	21.7	12.1	14.8	19.3	15.2	47.5	47.4
KSS-4	8.6	15.1	11.8	14.7	18.6	14.5	63.6	60.6
KSK-2	4.2	11.4	7.8	12.4	16.6	13.2	104.1	100,7

pore volume to the total volume of unit mass of the material.

Table 2 gives the differential water-retaining properties of the gels. The monomolecular-adsorption moisture content is directly related to the specific surface of the gels, which depends on their porous structure. The fractional moisture content due to polymolecular adsorption increases with increase in pore size, which is due to the increase in sorptive space in the larger-pored gels. The slightly overestimated moisture contents due to monomolecular adsorption for gels KSS-4 and KSK-2 from the drying thermograms are obviously due to the difficulty of determining the limits of mono- and polymolecular adsorption. The overestimated amounts of bound water obtained from the drying thermograms are obviously due to the difficulty of determining the limits of polymolecular adsorption and capillary condensation. As Table 2 shows, all the methods, based on different methodological principles, show that the differential water-retaining properties of silica gels depend on their porous structure.

According to current ideas, the specific interaction of moisture with the surface of silica gels involves a hydrogen-bond mechanism [11, 12].

A knowledge of the hydrophily of materials and their moisture binding energy is essential for the selection of optimum conditions of hydrothermal treatment. Information about the hydrophily of materials can be obtained by the heat of wetting method.

Figure 3a shows the heats of wetting of wetted silica gels. This figure shows that the investigated silica gels can be arranged in the following order of increasing hydrophily: 5-a, KSM-5, KSS-4, and KSK-2.

The differential moisture binding energies calculated from the sorption isotherms are shown in Fig. 4a in the form of curves $\Delta F_W(W)$. At fixed moisture

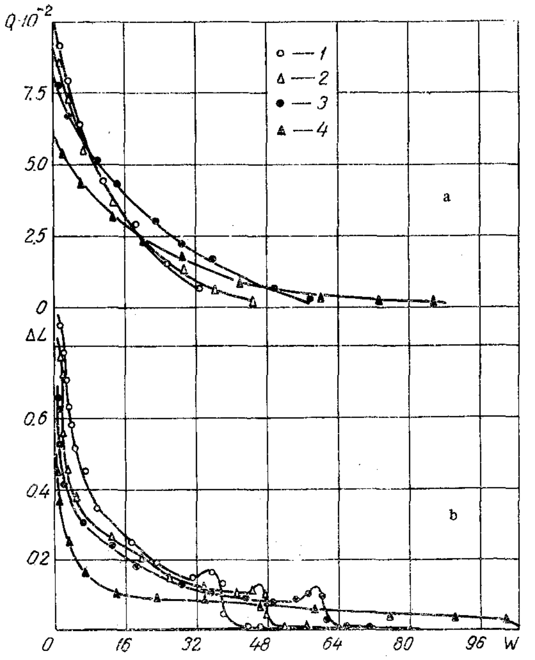

Fig. 3. Heats of wetting Q ($MJ/kg_{dry \cdot sub}$) of silica gels (a) and increase in specific heats of evaporation ΔL of moisture absorbed by gels (b) as functions of their moisture content W (%): 1) 5-a; 2) KSM-5; 3) KSS-4; 4) KSK-2.

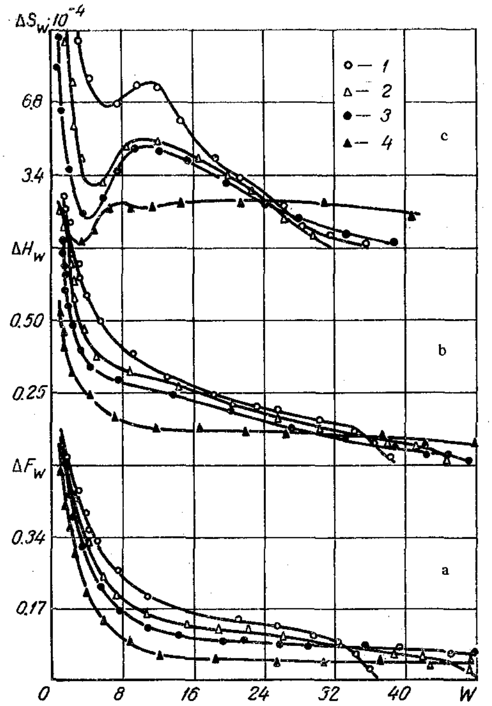

Fig. 4. Differential free energies ΔF_W (MJ/kg) (a), differential enthalpies ΔH_W (MJ/kg) (b), and differential entropies ΔS_W (MJ/kg · deg) (c) of bound moisture as functions of moisture content W(%) of gels: 1) 5-a; 2) KSM-5; 3) KSS-4; 4) KSK-2.

contents the values of ΔF_W and, hence, the energy of binding of moisture with the surface of the investigated gels are arranged in the same order as the heats of wetting Q for them.

Figure 3b shows the differences between the specific heats of isothermic evaporation ΔL for moisture bound by silica gels and free water. These results were obtained with the isothermic calorimeter [13] at 30° C.

The course of these curves and the curves $\Delta H_W(W)$ (Fig. 4b) is similar.

The position of the curves of $\Delta F_W(W)$, $\Delta H_W(W)$, and $\Delta L(W)$ for the investigated gels in the region of hygroscopic moisture contents shows that the free and internal binding energy depend on the structure and hydrophily of the materials.

High values of ΔH_W and ΔL correspond to the first batches of bound water. Hence, sorption in this region of moisture contents occurs on the most active sorption centers, which are the free hydroxyl groups on the surface of the gels. The reduction of ΔH_W and ΔL in the region of monomolecular adsorption is due to filling of the less active sorption centers. This is obviously due either to energetic difference between the free hydroxyl groups on the surface, or to reduction in the number of bonds of water molecules with them, or to adsorption of the latter on bound hydroxyl groups [14], since interactions of adsorbed molecules with one another in this region of moisture contents are absent or have no appreciable effect [15].

The further gradual reduction of ΔH_W and ΔL is due to the formation of polymolecular layers of moisture.

The values of ΔL for the region of the moist state of the materials are zero within the limits of experimental error. When the micropores open there is an increase in ΔL due to the sharp increase in the evaporation area, and also to the change in the pressure of vapor and liquid in them. The curves of $\Delta H_W(W)$ do not illustrate these features of filling of the micropores of silica gels. Hence, we can assume that the values of ΔL provide a better energy description of the removal of microcapillary moisture.

The interaction of moisture with the surface of silica gels is illustrated most distinctly by the curves of differential entropies of the sorbed moisture $\Delta S_W(W)$ (Fig. 4c), which characterize the change in the degree of order of adsorbed water molecules. The standard state of water at 20° C was selected as the zero level.

The first batches of water are bound most energetically, which leads to almost complete stoppage of the molecules. The greatest degree of order of the bound water molecules and the lowest value of ΔS_W correspond to these states. Reduction of the values of ΔH_W and ΔL corresponds to an increase in the entropy of the bound moisture.

Special physical investigations will be required to explain the minima on the curves $\Delta S_W(W)$. With further increase in moisture content due to the formation of monomolecular layers the entropy of the bound water increases.

As Fig. 4 shows, in the region of capillary moisture for all the silica gels the entropy of the bound water approaches that of free water, but still remains less than it at a given temperature. This indicates that the state of the water molecules of capillary moisture in the fine pores of the adsorbent due to the action of molecular forces of the phase interface is more ordered in comparison with free liquid and agrees with the conclusions of other authors [6].

This comprehensive investigation shows that the thermodynamic functions of bound moisture, like the hydrophilic properties of model capillary-porous materials, depend largely on the porous structure of the materials and indicates that bound water is a special phase characterized by an ordered state of the molecules.

NOTATION

Q is the heat of wetting of dry material; a_m is the monomolecular absorption; S_0 is the area occupied by adsorbate molecules; N is Avogardro's number.

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