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DIFFERENTIAL HEATS OF ADSORPTION OF WATER VAPOR ON SILICA GELS OF DIFFERENT HYDRATION

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In works ([1]-[3]) it was shown that the magnitudes of adsorption of water and methanol vapors, as well as the heats of wetting by these liquids, are in direct dependence on the degree of hydration of the surface of the samples studied. It seemed of interest to clarify the influence of hydration of the silica-gel surface on the differential heats of adsorption, since the latter determine the interaction energy of adsorbed molecules at different stages of surface filling, which is important for studying the mechanism of the elementary adsorption act. Differential heats of adsorption can be determined either by direct calorimetric measurements, or by differentiating the curve of the dependence of the heats of wetting of samples on the amount of vapor previously adsorbed on them, and, finally, can be calculated from the results of adsorption measurements ([5]).

The dependence of the heat of wetting Q on the previously adsorbed amount a is expressed ([4]) by the formula

$$Q = \int_a^{a_s} (Q_a - L)\, da + \varepsilon s', \tag{1}$$

Since the adsorption value a_s, corresponding to saturation, is constant at a given temperature, and the surface energy of the film $\varepsilon s'$ (where ε is the surface energy of the liquid, and s' is the surface of the saturated film) does not depend on a, the differential heat of vapor adsorption is

$$Q_a = \frac{\partial Q}{\partial a} + L.$$

The few works devoted to the study of the heats of wetting of silica gels containing previously adsorbed water (a critical review of them is given in ([4])) were carried out on various samples whose principal characteristics and, in particular, the values of the specific surface areas are unknown, which does not allow these data to be compared with one another or with the results of other works. The comparison made in (^{4}) of the indicated data by calculating the specific surface area of silica gel from the "absolute" heat of wetting may lead to substantial errors, as was shown in (^{1}). In work (^{4}), the dependence of the heats of wetting of silica gel on the amount of water previously adsorbed on it was measured, and the dependence of the differential heats on the adsorbed amount was calculated. However, the initial region of this dependence was not studied by the authors. The values of the differential heats are given in the table of work (^{4}), beginning from 2.5 μmol/m^2 and higher, although the corresponding heats of wetting were measured at considerably smaller adsorption values (from 0.24 μmol/m^2 and higher). The value calculated by us

from these data, the initial part of the differential-heat curve lies above this same section, obtained in (^{4}) by extrapolation. Direct calorimetric measurements of the heats of adsorption of water vapor on silica gel were carried out in (^{6}), but the authors give only the dependence of integral quantities on the amount adsorbed; moreover, the work lacks data on the specific surface area of the sample studied. Thus, there are still no reliable data in the literature on the dependence of the differential heats of adsorption of water vapor on surface coverage.

In the present work, silica gels K-2 and KSK-3 were used; their preparation conditions were the same as in (^{1},^{2}). The adsorption characteristics of the samples are given in Table 1.

Table 1

Adsorption characteristics of the silica gels used

Silica-gel sample	Calcination temperature, °C	Specific surface, m^2/g	Heat of wetting, erg/cm^2	Structural water, μmol/m^2
K-2	300	695	141	3.01
K-2	700	550	108.7	1.17
K-2r*	700	550	129.9	2.6
KSK-3	300	340	181	4.13

* Obtained by keeping silica gel K-2, previously calcined at 700°, in water for 1 month.

Measurements of the heats of wetting were carried out in a calorimeter with constant heat exchange (^{1}); measurements of the heats of adsorption of vapor –in a calorimeter analogous to that described in (^{7}). Preparation of silica-gel samples containing various amounts of adsorbed water was carried out in parallel with measurement of the adsorption isotherm; for this purpose, a comb with calorimetric ampoules for determining the heats of wetting was soldered to

Figure 2 and Figure 3

Figure 1: Figure 2 and Figure 3

the adsorption apparatus with spring balances. Adsorption of water vapor was carried out at a constant vapor pressure, maintained in the apparatus with the aid of a cryostat. Dosing of water vapor into the gas calorimeter was performed by the method of independent weighing (8).

In the present work, the initial portions of the isotherms and of the differential heats of adsorption of water vapor on different silica gels were investigated by two independent methods. Figure 1 gives the heats of wetting, calculated per unit surface area (i.e., specific values), as a function of the amount of water previously adsorbed.

Fig. 1. Dependence of the specific heats of wetting on the amount of water previously adsorbed for silica gels KSK-3-300° (1), K-2-300° (2), K-2-700° r (3), K-2-700° (4).

In the case of a nonporous hydrophilic adsorbent with a practically homogeneous surface, the specific heats of wetting decrease with increasing adsorbed amount and, as a approaches a_s, tend toward the value of the total surface energy of the liquid ε (for water, 118 erg/cm^2), as was shown in (9) for the TiO_2—H_2O system*. For the heterogeneous surface of silica, the adsorption of water, as follows from (2), proceeds mainly on the silanol surface, whose magnitude may be considerably smaller than the total surface area of the skeleton s, determined, for example, from nitrogen adsorption data. Owing to the presence on the silica surface of regions with different wetting energies (1), the values of the heats wetting, according to formula (1), will be different for them during filling. The heat of wetting of the siloxane surface will apparently increase with increasing a, as was observed for a hydrophobic surface (12), whereas for the silanol surface it will decrease. In the experiment we determine the total heat over the entire heterogeneous surface; therefore the heat curve (Fig. 1) reaching the value $\varepsilon = 118$ erg/cm^2 does not yet unambiguously indicate the presence, over the whole surface, of a saturated film of adsorbed water. In the case of porous adsorbents it is also necessary to take into account the reduction of the film surface s' as a result of capillary condensation.

Fig. 2. Initial portions of the water adsorption isotherms on silica gels KSK-3-300° (1), K-2-300° (2), K-2-700° g (3), K-2-700° (4)

Fig. 3. Dependence of the differential heat of adsorption of water on the amount preadsorbed for silica gels KSK-3-300° (1), K-2-300° (2), K2-700° g (3);

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* In works (10, 11), incorrect graphs are presented to illustrate these data; according to them, the heat of wetting increases with increasing amount of adsorbed water.

the solid curves were obtained from the data of Fig. 1, the points on curve 2 are the result of direct measurements

In the present work we dealt with uniformly macroporous adsorbents and considered the adsorption region up to the onset of capillary condensation, when the film surface s' is practically equal to s (4). As is seen from Fig. 1, all the heat curves are arranged in such a way that, at equal preadsorbed amounts of water, the heats of wetting decrease as the hydration of the surface of the initial samples decreases. An analogous dependence is also observed for the initial portions of the adsorption isotherms of water vapor (Fig. 2). Despite the fact that, when the dehydrated silica gel K-2-700° is wetted, in addition to the "physical" heat of wetting, the heat of hydration is also evolved (1), the total heat, owing to the low hydration of the surface (Table 1), nevertheless lies considerably below the heat curve for the secondarily hydrated sample K-2-700° g.

The results of calculating the differential heats of adsorption as a function of the specific amounts of adsorption are given in Fig. 3. As is seen from the figure, the heats of adsorption on silica gel K-2-300°, obtained by direct calorimetric measurements, agree well with the curve calculated from the data of Fig. 1. The initial values of the heats of adsorption of water for silica gel KSK-3 lie in the range 15–20 kcal/mole; apparently, at small degrees of filling the adsorbed molecules form 3 and even 4 hydrogen bonds with the hydroxyls of the surface*; it is possible that some fraction of the molecules in this region is adsorbed on centers with a higher energy (3). As the surface is filled, the heat of adsorption decreases, which can apparently be explained by a decrease in the number of hydrogen bonds with surface hydroxyls falling, on average, to one adsorbed water molecule. The role of repulsive forces between the dipoles of the adsorbed molecules (4) is small. The estimate, made according to (13), of the energy of tangential interactions

* As is the case in the association of water molecules (14).

for the idealized case of complete filling of the hydrated surface with a monomolecular layer of identically oriented water dipoles shows that this value does not exceed 1 kcal/mole. In the case of a real, i.e., partially dehydrated, silica surface, this value will be still smaller.

The values of the differential heats at one and the same filling decrease with decreasing degree of hydration of the surface of the samples (Table 1). In contrast to (4), we did not obtain a single "absolute" dependence of the differential heat of adsorption of water vapor in the case of the coarse-pore silica-gel samples studied. Adsorption of water molecules upon filling of the silanol part of the surface is apparently due mainly to the interaction of water molecules with two hydroxyl groups (2). With a decrease in the concentration of hydroxyl groups on the surface and an increase in the mean distance between them, the probability of formation of such paired interactions will decrease; the adsorption interaction may then be determined by one hydrogen bond of the adsorbed molecule with one hydroxyl of the surface. In this case the differential heat of adsorption will be less than the heat of condensation. At high relative pressures, as a result of gradual filling of the siloxane part of the surface, the differential heat will assume the value of the heat of condensation. Investigation of adsorption and of the differential heats of adsorption in this range of relative pressures on substantially dehydrated silica samples can be carried out only on nonporous or very coarse-pore objects, for which the phenomenon of capillary condensation may be neglected, i.e., under the condition that $s' \approx s$.

Our estimate of the differential entropy of adsorption of water vapor ΔS shows that it decreases with increasing hydration of the surface of the silica gels. When the liquid state of water is chosen as its standard state, the curves of differential entropy lie in the region of negative values (thus, for example, at $a = 1$ mole/m^2 the value of ΔS for silica gels K-2-300° and KSK-3-300° is, respectively, -0.3 and -7.3 cal/g-mole). As the surface is dehydrated, i.e., as the number of adsorption centers decreases, the mobility of the adsorbed water molecules increases, but for the samples studied it nevertheless remains below the mobility of molecules in liquid water, i.e., in this sense the surface becomes more homogeneous.

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CITED LITERATURE

[1] M. M. Egorov, K. G. Krasil' nikov, E. A. Sysoev, DAN, **108**, 103 (1956).
[2] B. V. Ilyin, V. F. Kiselev, K. G. Krasil' nikov, Vestn. MGU, No. 6, 35 (1957).
[3] K. G. Krasil' nikov, V. F. Kiselev, E. A. Sysoev, DAN, **116**, 990 (1957).
[4] A. V. Kiselev, K. G. Krasil' nikov and others, ZhFKh, **26**, 986 (1952).
[5] B. P. Bering, V. V. Serpinskii, DAN, **114**, 1254 (1957).
[6] W. H. Patrick, C. E. Greider, J. Phys. Chem., **29**, 1031 (1925).
[7] A. V. Kiselev, V. F. Kiselev and others, ZhFKh, **23**, 577 (1949).
[8] B. P. Bering, V. V. Serpinskii, DAN, **55**, 741 (1947).
[9] W. Harkins, G. Jura, J. Am. Chem. Soc., **66**, 919 (1944).
[10] A. V. Kiselev, Usp. khim., **15**, 456 (1946).
[11] A. V. Kiselev, Appendix to the book by S. Brunauer, *Adsorption of Gases and Vapors*, 1948, p. 714.
[12] G. J. Young, J. Chessick, E. H. Healy, A. C. Zettlemayer, J. Phys. Chem., **58**, 313 (1954).
[13] J. J. Topping, Proc. Roy. Soc., A, **114**, 67 (1927).
[14] D. Bernal, R. Fowler, Usp. fiz. nauk, **14**, 586 (1934).

Note: Figure translations are in progress. See original paper for figures.