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HEATS OF WETTING OF AEROSIL BY ALIPHATIC ALCOHOLS

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Systematic investigations of the heats of adsorption of substances of a homologous series are of considerable interest for elucidating the relationship between the structure of adsorbed molecules and the energy of their adsorption. Measurements of differential heats of adsorption of vapors for higher alcohols, which have relatively low vapor pressures, involve considerable methodological difficulties. Simpler in this respect are measurements of integral heats of adsorption, in particular heats of wetting. Measurements of the heats of wetting of ionic crystals and oxidized carbon black by aliphatic alcohols were carried out in our laboratory in works ([1–4]); however, in these investigations we had no data on the chemical nature of the surface of these adsorbents. The state of the surface can exert a substantial influence on the adsorption and energetic properties of a unit surface of an adsorbent. It was of interest to carry out analogous investigations on samples of silica, the nature of whose surface had been studied in detail in works ([5–7]).

The object of the investigation was nonporous silica—Aerosil (white carbon black), obtained in our laboratory by combustion of ethyl orthosilicate ([8]). Separate portions of the initial sample, for the purpose of surface modification, were calcined in air for 24 hours at each of the selected temperatures. The specific surface areas of all the samples obtained were calculated from adsorption isotherms of nitrogen vapors at its boiling temperature by the BET method. The content of structural water was determined from the loss in weight upon calcination. The data obtained are given in Table 1.

Table 1

Adsorption characteristics of Aerosil BS-2 samples

Calcination temperature, °C	Specific surface area, m^2/g	Amount of structural water, $\mu M/m^2$
300	156	6.3
500	143	3.1

Figure 1

Figure 1: Figure 1

Calcination temperature, °C	Specific surface area, m^2/g	Amount of structural water, $\mu M/m^2$
700	120	1.8
900	112	1.5

The method of preparing samples for calorimetric measurements to determine structural water was described in works ($^{5-7}$). The alcohols used in the work were carefully absolutized and distilled on a rectification column. Measurement of the heats of wetting was carried out in a calorimeter with constant heat exchange, which before the experiment was purged for many hours with dry air. Since even negligible impurities of water affect the heat of wetting by organic liquids, the calculation used the constant values of the heats obtained upon successive breaking of a series of ampoules with the sample in one and the same calorimetric liquid.

As is evident from Fig. 1A, the heats of wetting of all samples decrease with increasing hydrocarbon radical of the alcohol, and, beginning with amyl alcohol, remain practically constant. The specific heat of wetting is proportional to the binding energy of the molecules with the adsorption centers and to the concentration of adsorbed molecules on the surface. The latter is determined by the value of the limiting adsorption a_m of the alcohol from a nonpolar solvent, since adsorption of the solvent in this case, as was shown in (9, 10), is negligibly small. The decrease in the heat of wetting for the lower alcohols is probably connected mainly with a decrease in the concentration of adsorbed molecules (Fig. 1B). For the higher alcohols, the decrease in a_m with increasing length of the hydrocarbon radical becomes smaller (Fig. 1B), since the adsorbed molecules apparently are oriented obliquely to the surface (9, 10). On the other hand, the energy of interaction of alcohol molecules may increase with increasing length of the hydrocarbon radical both because of an increase in dispersion interaction with the surface and because of tangential attractive forces between the hydrocarbon radicals of neighboring molecules. The constancy of the heats of wetting by higher alcohols is apparently due to the opposing action of these factors.

Fig. 1. Dependence of the heats of wetting (A) and limiting adsorption $(B)^{(10)}$ for the homologous series of n-alcohols on BS-2 samples: $t = 300°$ (1), BS-2 $t = 500°$ (2), BS-2 $t = 700°$ (3).

Earlier (5, 7) it was shown that, for silica gels, the heats of wetting by water and methanol depend practically linearly on the degree of surface hydration. As is evident from Fig. 2, the heats of wetting of nonporous silica BS-2 by water and methanol fall satisfactorily on the straight lines obtained earlier (5) for silica gels. This once again indicates the absence of any appreciable influence of the pores of the silica gels studied in (5) on the heat of wetting by methanol. On going to *n*-propyl alcohol, the straight line corresponding to the heats of wetting of silica gels with effective pore diameters $d = 65$ and 60 Å lies close to the straight line for nonporous silica. The small difference in the slopes of the straight lines is connected with some strengthening of the adsorption interaction of hydrocarbon radicals in narrow pores. The straight line for the more finely porous sample ($d = 44$ Å) is shifted into the region of lower values of the heat of wetting because of the increasing influence of the pores.

The surface of silica is heterogeneous and consists of silanol and siloxane regions. In the course of thermal dehydration, not only the ratio between these regions changes, but also their properties. At low treatment temperatures of the sample, in addition to structural water, physically adsorbed water may also be present on its surface. The question of the presence on the surface of coordinatively bound water, the existence of which Weil (11) admits on the basis of consideration of the screening of surface Si atoms, is still controversial. Existing methods for determining structural water give the total water content in the sample and do not make it possible to separate water bound to the surface in different ways. The question of establishing the exact conditions and temperatures of sample treatment at which water bound in one way or another is removed is at present

time remains open ([6],[14],[17]). At a sufficiently high concentration of hydroxyl groups on the surface, the latter can form hydrogen bonds with one another, which may lead to a decrease in the energetic properties of the silanol surface ([6],[7]). The same conclusions were drawn in interpreting the infrared spectra of the surface layer of silica gel ([12],[13]). As the calcination temperature of the sample increases, dehydration of the surface occurs, associated with rotation of part of the surface silicon-oxygen tetrahedra ([10]). In this process, evidently, the tetrahedra bound to the bulk by one bond will rotate first, then those bound by two bonds, and finally by three bonds. Thus, in the process of dehydration not only the concentration of hydroxyl groups on the surface changes, but also their topography. In samples treated at high temperatures, the silanol part of the surface will probably consist mainly of isolated OH groups ([14]).

The siloxane part of the surface is also apparently heterogeneous. The irreversibility of the rehydration process of a silica-gel surface dehydrated at high temperatures, which we found in ([6]), indicates that such a surface includes regions with at least two different types of packing of SiO_4 tetrahedra: tetrahedra turned toward the bulk with all four corners ([6]), and tetrahedra joined by edges, forming strained oxygen bridges capable of hydration. Thus, as silica gel is calcined, not only the degree of hydration of the surface changes, but also the properties of the silanol surface; moreover, these changes may affect the adsorption of different molecules in different ways.

Fig. 2. Heats of wetting by alcohols of aerosil samples (*a*), silica gel K-2 (*b*), KSK-1 (*v*), KSK-2 (*g*) as a function of the degree of surface hydration. The numbers next to the straight lines denote the number of carbon atoms in the alcohol molecule. In the upper plot, the dotted line gives the straight line for

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In the case of water molecules, which are capable of forming from four to one bond with the hydroxyls of the surface, the number of bonds may change both in the process of filling the surface (15) and as a result of its dehydration (6,14), which leads to a change in the topography of the adsorption centers on the surface.

Alcohol molecules bind to hydroxyls through a single hydrogen bond (10,14). The linear dependence of the heats of wetting on the degree of hydration (Fig. 2) shows that, within the range of changes in the degree of hydration of the samples studied, the heat of wetting is determined mainly by the ratio between the silanol and siloxane regions of the surface, while changes in the properties of these regions in the present case do not play a substantial role. A decrease in the degree of surface hydration has the strongest effect on the heat of wetting by methanol. With increasing length of the hydrocarbon radical and of the molecular landing area (Fig. 1B), the molecules of the higher alcohols probably screen part of the hydroxyl groups of the surface. In this connection, a decrease in the degree of surface hydration begins to have little effect on the magnitude of the adsorption limit (10), i.e., the concentration of adsorbed molecules changes little upon dehydration of the surface. In this case it must be taken into account that alcohol molecules can interact—

also interact with the siloxane part of the surface. On passing to higher alcohols, the slope of the straight lines for the heats of wetting changes. As the length of the hydrocarbon radical increases, its role in the adsorption interaction increases, and the heats of wetting by higher alcohols approach the corresponding values for hydrocarbons, the adsorption and adsorption energy of which are only slightly sensitive to changes in the state of the silica surface (5,16).

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