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Abstract

Full Text

PHYSICAL CHEMISTRY

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REVERSIBLE ISOTHERMS OF WATER ADSORPTION ON QUARTZ

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The adsorption of water vapor on quartz was studied in works (^1-3). The water adsorption isotherms obtained in these investigations are shown in Fig. 1. Although in all cases the adsorption is referred to a unit surface area of quartz, the adsorption isotherms in Fig. 1 do not coincide, but diverge very strongly, beginning from the smallest values of p/p_s. The results of these investigations were not compared and were not discussed; however, the observed noncoincidence of the "absolute" isotherms of water adsorption on quartz is of fundamental interest, especially in connection with the fact that the adsorption isotherms of water vapor on different silica gels, as shown in work (^4), coincide in the initial region of relative pressures if the adsorption is referred to a unit surface area. In the present work we report the results of a study of the adsorption of water vapor on four samples of various quartz powders, differing in the magnitude of their specific surface area and in origin. Three samples were prepared by crushing crystals of rock crystal of different origin, followed by treatment of the powders with HCl and thorough washing with water to remove traces of Cl′. The fourth, most finely dispersed powder, was obtained from crystals of nontransparent quartz in an analogous way, but in order to isolate the finest fraction the powder was elutriated in water for a long time.

Fig. 1. Comparison of water adsorption isotherms on quartz described in the literature.
1—Livingston (^1), 2—Sarakov (^2), 3—Stober—desorption (^3).

The specific surface areas were determined by the Brunauer, Emmett and Teller method from the adsorption isotherms of nitrogen, argon, and methyl alcohol. The following values were taken for the area (ω) occupied by adsorbed molecules in the monolayer: $\omega_{\mathrm{N}_2} = 16.2\ \text{Å}^2$, $\omega_{\mathrm{Ar}} = 15.4\ \text{Å}^2$, and $\omega_{\mathrm{CH_3OH}} = 25\ \text{Å}^2$.

The calculated values of the specific surface areas of the investigated quartz

Fig. 2

Figure 2: Fig. 2

powders are given in Table 1.

Table 1

Samples and pumping conditions	S, m^2/g N_2	S, m^2/g Ar	S, m^2/g CH_3OH	Adopted value
Rock crystal I, 200°	–	0.195	0.195	0.195
Rock crystal II, 200°	–	0.290	–	0.290
Rock crystal III, 20°	0.57	–	–	0.57
Rock crystal III, 200°	0.56	–	–	0.56
Nontransparent quartz, 20°	5.15	–	4.85	5.15
Nontransparent quartz, 200°	5.4	–	–	5.4

The isotherms of adsorption of water vapor, obtained on the investigated quartz samples by the volumetric method, are shown in Fig. 2A. All these isotherms, except isotherm 5, are reversible. For two of them this is seen directly, and the reversibility of the other two follows from the coincidence of the isotherm recorded after heating the sample at 200° with the repeated one obtained without heating. This latter circumstance indicates that neither as a result of heating nor as a result of the first adsorption did the properties of the surface, like its total magnitude, change. Heating the powder of nontransparent quartz ⋯

evacuating quartz in vacuum at 200° led to a sharp increase in the adsorption of water and to irreversibility of the isotherm (curve 5). As in the case of the isotherms in Fig. 1, the isotherms shown in Fig. 2A represent a series of curves diverging from the origin, although here too the adsorption is referred to unit surface area of quartz.

Fig. 2. A —Isotherms of water adsorption on various quartz samples, referred to unit surface area; B —absolute isotherm of water adsorption on quartz. 1 —Rock crystal I: a —first adsorption on a sample heated in vacuum at 200°, —repeated adsorption without heating. 2 —Rock crystal II; —first adsorption on a sample heated in vacuum at 200°, —repeated adsorption without heating. 3 —Rock crystal III, evacuated without heating; —adsorption, —desorption. 4 —opaque quartz, evacuated without heating; —adsorption, —desorption. 5 —the same sample, but evacuated at 200°; —adsorption, —desorption

These results, at first glance, may be interpreted as evidence of the nonidentity of the properties of unit surface areas of different quartz samples. From the isotherms of Figs. 1 and 2A, which give straight lines in the coordinates

$$\frac{p/p_s}{a(1-p/p_s)};\ p/p_s,$$

one can calculate the areas occupied by a water molecule in the adsorption monolayer (ω_{H_2O}). These quantities vary within the limits from 10.6 to 30 Å^2. Hence it would seem to follow that the packing density of water molecules in the first adsorption layer, directly associated with the surface, is different for different quartz samples. There are works known$^{(5-9)}$ in which, from isotherms of water adsorption on silica gels, aluminosilicates, and porous glasses, very different values of ω_{H_2O} were obtained—from 10.8 to 55 Å^2—some of which can be brought into agreement with surface areas calculated from water and from nitrogen.

Owing to the sharply pronounced sensitivity of water adsorption to the state of the surface of silica adsorbents$^{(10-15,4)}$, the above-noted nonconstancy of the calculated values of ω_{H_2O} might be connected with the nonidentity of the surface state and the different nature of the adsorbents investigated. However, isotherms 1, 2, 3, 4, and 5 of Fig. 2A were obtained on one and the same crystalline substance—low-temperature quartz—and under identical and comparable evacuation conditions. The reversibility of the first four isotherms directly indicates that in all these cases water adsorption occurred on the SiO_2 surface in the state of its maximum hydration. Adsorption of water molecules on a silica surface at small p/p_s, as shown in works$^{(10-15)}$, occurs primarily on surface hydroxyls, and the magnitude of adsorption is related to the degree of hydration of the surface. The number of hydroxyls on the quartz surface in the state of its maximum hydration must be

identical for different quartz samples, since it is determined by the crystallographic structure of quartz (^{11}). Therefore, it is unlikely that the divergence of the isotherms in Fig. 2A was caused by nonidentity of the properties of a unit surface of different quartz samples and by a different packing density of water molecules in the first adsorption layer. The most probable reason for this divergence is the inaccessibility to nitrogen molecules of some fraction of the surface that is accessible to the smaller water molecules. Such a phenomenon is well known for ultraporous crystalline aluminosilicates—zeolites ([16]). In the case of quartz this may be due to the presence of submicroscopic cracks in the crystals. Apparently, all the quartz samples investigated in the present work, except for rock crystal I, contain such cracks. There should be especially many of them in crystals of opaque quartz. This is confirmed by the release of a large quantity of water by the powder of this quartz when it is heated in vacuum in the temperature interval 100—200°, as well as by the anomalously high quantity of structural water released on ignition from a unit surface of quartz in the interval 200—1000° (about 25μ M/m^2), if the surface is determined from nitrogen. The latter was also observed by Stöber ([3]) on some quartz samples investigated by him; however, he did not associate this with the presence of cracks in the crystals, but attributed it to the influence of clay impurities in the quartz. It is known that mineralogists consider strongly developed fissuring to be one of the causes of the opacity of quartz crystals from some deposits ([17]).

Obviously, for constructing an absolute isotherm of water adsorption, values of surfaces determined from nitrogen and from other substances with molecular sizes larger than the size of the water molecule are suitable only under the condition that the surface accessible to water molecules is equally accessible to those molecules which are used for measuring the surface. Rock crystal I, as can be concluded from the position of isotherm 1 in Fig. 2A, meets these conditions more than all the other quartz samples investigated.

The value of ω_{H_2O}, calculated from isotherm 1 in Fig. 2A, proved to be equal to 26 Å^2. This value is very close to the value 25 Å^2, found for silica gels in work ([4]). It agrees with the value 13.4 Å^2, obtained for the area corresponding to one hydroxyl on the hydrated surface of low-temperature α-quartz in work ([11]), if it is assumed that the primary adsorption centers with respect to water molecules are not individual hydroxyls, but their pairs. Such a mechanism of water adsorption follows from the observed quantitative correspondence between the decrease in the number of pairs of hydroxyls on the surface of porous glass during its dehydration and the decrease in water adsorption in the region of monolayer filling ([13,14]). The authors of work ([4]) also arrive at a similar mechanism of adsorption of water molecules on the hydrated surface of silica gels.

If the values of the specific surfaces of the quartz samples investigated are calculated from the water adsorption isotherms using the value $\omega_{H_2O} = 26\ \text{Å}^2$, and the values obtained are used for constructing absolute isotherms, then all the reversible isotherms of Fig. 2A, within the possible errors of measurement, lie on one common curve (Fig. 2B).

Comparison of the isotherm in Fig. 2B with the absolute isotherms of water adsorption on silica gels ([4]) and porous glass ([14]) shows that in the region $\theta \leq 1$ the absolute isotherms in all these cases can be represented by one curve, if adsorption occurs on a surface in the state of its limiting hydration. Reversibility of the isotherm in the monomolecular region is one of the indications of such a state.

The observed discrepancies of the absolute isotherms of water adsorption obtained by other investigators on quartz ($^{1-3}$), silica gels (^{5,9}), and porous glasses (^{18}) in the region of small p/p_s, and the consequent insuffi-

The constancy of the values of ω_{H_2O} is connected with two circumstances not taken into account in these works: 1) the possible ultraporosity of the objects studied, which in some cases manifests itself even in nitrogen adsorption, and 2) the sharply expressed sensitivity of water adsorption to the state of the surface of siliceous adsorbents and to the degree of its hydration.

In the case of sharply expressed ultraporosity, estimation of the surface from nitrogen adsorption isotherms leads to the obtaining of underestimated values. This may be the reason for an overestimate of the adsorption of water calculated per unit surface area and, correspondingly, for an underestimate of the values of ω_{H_2O} ($^{1,2,5-8,18}$). One of the signs of such ultraporosity is the liberation of a considerable amount of water adsorbed in the finest pores and cracks upon heating to 200°, which leads to a sharply expressed irreversibility of the adsorption isotherm (isotherm 5 in Fig. 2A). However, on the surface of some of the pores exhibiting ultraporosity toward nitrogen, water may adsorb quite reversibly (isotherms 3 and 4 in Fig. 2A).

The obtaining of overestimated values of ω_{H_2O} in works ($^{5-9}$) is due to the fact that in these works water adsorption was studied on silica gels that had been dehydrated to a considerable degree. In connection with the features noted above of the mechanism of water adsorption, the formation of a dense adsorbed monomolecular layer on a dehydrated surface of SiO_2 in the usual range of p/p_s cannot occur, and therefore calculations of ω_{H_2O} in such cases have no real meaning.

Thus, the properties of a unit surface of different samples of quartz, and equally of other siliceous adsorbents, may be identical with respect to water adsorption only in the case when adsorption occurs on a maximally hydrated surface. In the presence of irreversible adsorption, the properties of a unit surface are not comparable. Identity of the heating conditions before the adsorption experiment is not a sufficient guarantee of obtaining an SiO_2 surface with identical adsorption properties with respect to water.

The presence of the finest cracks, inaccessible even to nitrogen molecules but detected in water adsorption, in such a nonporous material as quartz had been considered to be, compels one to treat with some caution the values of surfaces measured by nitrogen in other cases, especially when data obtained from water and from nitrogen are used to calculate the area occupied by a water molecule in an adsorbed monomolecular layer (^{1,19}).

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