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Abstract

Full Text

PHYSICAL CHEMISTRY

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HEAT OF ADSORPTION OF BENZENE AND HEXANE VAPORS ON QUARTZ

(Presented by Academician M. M. Dubinin, August 10, 1957)

The study of the adsorption properties of quartz is of interest in connection with the similarity of its surface chemical structure to that of a broad class of highly dispersed porous adsorbents—silica gels ([1–4]). The study of the adsorption of benzene and hexane vapors on quartz, as on other nonporous hydroxides, is of interest because the adsorption energy of benzene apparently represents not only the energy of van der Waals interaction but also the energy of an additional hydrogen bond with the hydroxyl groups of the surface, whereas the adsorption energy of hexane represents only the energy of van der Waals interactions ([5–7]). Investigation of the adsorption and heats of adsorption of vapors on quartz is also of interest for determining the dependence of the thickness of a polymolecular film on the relative vapor pressure p/p_s, as well as the dependence of the adsorption energy on the thickness of the adsorption film, since for such studies it is necessary to use comparatively coarsely dispersed nonporous adsorbents so that the adsorption process is not complicated by capillary condensation up to high p/p_s.

Direct measurements of the heats of adsorption of these hydrocarbons on quartz have not been carried out. In works ([8,9]), calculations were made of the isosteric heats of adsorption of benzene vapor on quartz. However, these are difficult to compare, both because of their inaccuracy, associated with the small specific surfaces of the quartz samples used, and because of the different conditions of their preparation and preliminary heat treatment.

In the present work, in an adsorption-calorimetric apparatus ([10]), adsorption isotherms and differential heats of adsorption of benzene and *n*-hexane vapors on quartz powder were measured up to saturation. The quartz powder had a specific surface area of 6.0 m^2/g, determined from the adsorption of nitrogen vapor ([11]). On this quartz sample we had previously studied the heats of adsorption of methanol vapor ([12]). In order to remove the products of the reaction of methanol with the quartz surface, the latter was washed for a long time with water with decantation and heated in the moist state at 130° until dry, after which the quartz powder was placed in the calorimetric sleeve and evacuated in the adsorption-calorimetric apparatus at 200°. The hydrocarbons used were

Fig. 1

Figure 1: Fig. 1

the same as in ([10,13]).

Figure 1 gives the obtained isotherms of the absolute values of adsorption a (per unit surface area) for hexane and benzene vapors. In the case of benzene the isotherm was taken up to complete saturation. The isotherms are reversible up to $p/p_s \approx 0.9$ and have the S-shaped form typical of adsorption on non-porous adsorbents. At higher p/p_s a quite clearly reproducible hysteresis was obtained, associated with capillary condensation in the gaps between particles of the quartz powder, which had stuck together during drying and were compacted on the trays of the calorimetric sleeve. The distribution curve shown in the upper part of this figure, calculated from the desorption branch of the isotherm, shows that between the quartz particles in the compacted powder there were gaps with sizes predominantly from 1000 to 7000 Å. These sizes approximately correspond to the sizes

particle sizes of the quartz powder, obtained from electron-microscope photographs. As p/p_s increases from the onset of hysteresis to saturation, the surface of the adsorption film disappears ([14,15]), $s' \approx 4$ m^2/g, i.e., about $0.7s$. Thus, before the onset of hysteresis, the decrease in s' due to the reversible stage of capillary condensation ([14,16]) amounts to no more than $0.3s$, and adsorption in the middle region of p/p_s may be regarded as not complicated by capillary condensation.

Fig. 1. Absolute adsorption isotherms of vapors of n-hexane on quartz (1), silica gel KSK-2, 650° (2), silica aerogel (3), and benzene on quartz (4) and silica aerogel (5). Black points denote desorption. Isotherms without points are for hexane (6) and benzene (7) on silica gel KSK-2, 200°. Upper right: curve of the distribution of the volume of voids in quartz powder according to their sizes.

In Fig. 1, for comparison, the adsorption isotherms of the same vapors on homogeneous wide-pore silica gel KSK-2 ([10,13]) are plotted. It is seen from the figure that the desorption branch begins to descend steeply near $p/p_s = 0.7$. In this region, adsorption on quartz is not yet complicated to any significant extent by capillary condensation in the voids between particles; therefore, from the absolute adsorption isotherm of benzene and hexane vapors on quartz one can find the corresponding thicknesses of the adsorption layers needed for introducing corrections into the pore sizes of silica gels obtained from the Thomson formula ([15,17]). In the case of homogeneous porous silica gels, the fall of the desorption branch occurs in such a narrow interval of p/p_s that the thickness of the adsorption film on quartz changes only slightly. Therefore, to find the true throat sizes ([16]) of silica-gel pores possessing a homogeneous globular skeleton structure, it is sufficient to add to the diameter found from the Thomson for-

Fig. 2. Dependence of the heat of adsorption of benzene vapor on quartz on coverage.

Figure 2: Fig. 2. Dependence of the heat of adsorption of benzene vapor on quartz on coverage.

Fig. 3. Dependence of the heat of adsorption of n-hexane vapor on coverage on quartz and silicas.

Figure 3: Fig. 3. Dependence of the heat of adsorption of n-hexane vapor on coverage on quartz and silicas.

mula at the maximum of the silica-gel distribution curve twice the thickness of the adsorption film on quartz, determined from the isotherms in Fig. 1 at the corresponding p/p_s (15).

In the initial region of monomolecular filling, adsorption on quartz is greater than adsorption on silica gel KSK-2 heated at 200° (13), which is connected mainly with the lower skeleton density of such silica gel. It is seen from Fig. 1 that the adsorption of hexane on this silica gel after its calcination at 650° (7), and on silica aerogel obtained by combustion of organosilicon compounds (6), is already very close to adsorption on quartz. The adsorption of benzene also depends strongly on the degree of hydration of the silica-aerogel surface (6,7). It is seen from Fig. 1 that adsorption of benzene vapor on

on calcined silica from organosilicon compounds after hydration of the surface of this silica gel (6) nearly coincides with the adsorption on quartz. The adsorption isotherm of benzene vapor on quartz is well obeyed by the BET equation, whence the capacity of a dense monolayer is $\alpha_m = 3.35$ μmol/m^2, which corresponds to an area $\omega_0 = 1/\alpha_m = 49$ Å^2 per benzene molecule, as also in adsorption on silica gel (10, 7).

Fig. 2. Dependence of the heat of adsorption of benzene vapor on quartz on coverage. Black points—desorption. Horizontal dashed line—heat of condensation L. Vertical dashed line—monolayer capacity α_m.

Fig. 3. Dependence of the heat of adsorption of *n*-hexane vapor on coverage on quartz (1) and silicas (2) and (3). Black points—desorption, dashed line—heat of condensation.

Figure 2 gives the dependence of the heat of adsorption of benzene vapor Q_a on the absolute amount of adsorption on quartz α. It is seen from the figure that, after the first two layers have been filled, the heat of adsorption exceeds the heat of condensation by only 3%, and after adsorption of four layers by 1%. The further decrease in the heat of adsorption proceeds very slowly; its cause is both the decrease in the adsorption energy with distance from the surface (with increasing film thickness) and a certain unavoidable reduction of the film surface at the points of contact of quartz particles. The heat of adsorption on

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Fig. 4

Figure 4: Fig. 4

a smooth quartz surface can only be less than that indicated in Fig. 2 in this region.

Figure 3 gives the dependence of the heat of adsorption on quartz of n-hexane vapor. Here too a gradual decrease in the heat of adsorption is observed. The heat of adsorption of hexane on silica gel obtained by burning organosilicon compounds (^{6}) is close to the heat of adsorption on quartz. A more exact and detailed study of the dependence of the heat of adsorption on coverage in the monomolecular region in a calorimeter (^{1}) for powders with a surface area of less than 10 m^2/g is difficult. We hope to carry out a detailed investigation of this region of coverage on quartz in the future.

Integration of the curve of the dependence of the pure heat of adsorption of benzene vapor $Q_a - L$ on α gives about 50-90 erg/cm^{2}*. Adding the full surface energy of benzene, 68 erg/cm^{2}, we obtain for the heat of wetting of quartz by benzene 120-160 erg/cm^{2}, which is greater than the heat of wetting of silica gel (^{13}) by no more than 1.1-1.5 times**.

It is also seen from Fig. 2 that the curve of the differential heat of adsorption on quartz, in contrast to homogeneous-pore silica gels (^{10,13,18}), does not end in a maximum, since the adsorption isotherm increases continuously, the adsorbed liquid is not stretched by capillary forces, and its properties gradually approach those of a normal liquid. The difference in the heat of adsorption on approaching saturation for adsorbents of all four structural types (^{15}) is clearly seen in Fig. 4, in which, for ease of comparison, the dependences are given both for the differential heats of adsorption Q_a and for the adsorption a itself on p/p_s.

Fig. 4. Dependences of the heats of adsorption (top) and adsorption (bottom) of benzene vapor on relative pressure for quartz (*1*), coarse-porous silica gel (*2*), fine-porous silica gel (*3*), and heterogeneous-pore silica (*4*). Horizontal dashed line—heat of condensation

In the case of uncomplicated polymolecular adsorption on an adsorbent of the first structural type—nonporous quartz—the heat of adsorption asymptotically approaches the heat of condensation. On an adsorbent of the second structural type—coarse-porous silica gel—owing to the action of menisci at the pore mouths, maxima of the heat of compression of the capillary-condensed liquid appear (^{10,13,18}). On an adsorbent of the third structural type—fine-porous sil-

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* Integration in the region of large α introduces inaccuracy into this calculation.

** It is possible that the obtained heat of wetting of quartz is even somewhat overestimated owing to the liberation of the heat of evaporation of part of the surface of the adsorption film.

ica gel—owing to the large curvature of the menisci that lock the liquid in the pores, the maxima of the heats of adsorption and desorption are expressed especially sharply ([10,13,18]). Finally, on an adsorbent of the fourth structural type —heterogeneous-pore silica—the heat of compression of the liquid in the pores is gradually superposed on the heat of disappearance of the adsorption film in them; the heat of adsorption over the entire range of fillings is noticeably greater than the heat of condensation, but maxima do not appear sharply ([6]).

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