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HEATS AND ENTROPIES OF ADSORPTION OF HEXANE AND BENZENE VAPORS ON AEROSILS WITH A SURFACE CHEMICALLY MODIFIED BY TRIMETHYLSILYL GROUPS

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The study of the adsorption of various vapors on the surface of aerosils modified by reaction with trimethylchlorosilane has shown that a very important characteristic of such modified adsorbents is the degree of coverage of the silica surface by chemically grafted trimethylsilyl groups ([1],[2]). When the layer of these groups is not sufficiently dense, adsorption occurs primarily in the gaps between them, on the unmodified part of the silica surface. Thus, insufficiently complete modification leads to a high heterogeneity of the surface. At the same time, the previously made ([3]) theoretical calculation of the adsorption energy of molecules of *n*-hexane and benzene on modified aerosil refers to the model of a dense layer of trimethylsilyl groups on the silica surface (tridymite). This calculation showed that the displacement of adsorbate molecules away from the silica surface by trimethylsilyl groups leads to a sharp decrease in the adsorption energy. Even in the case of such large hydrocarbon molecules as *n*-hexane and benzene, the theoretically calculated adsorption energy of isolated molecules proved to be less than the heat of condensation. Consequently, one could expect that on aerosil sufficiently densely modified with trimethylsilyl groups the net heats of adsorption of vapors of these hydrocarbons should be negative.

As is seen from work ([2]) and from our measurements of the heats of adsorption on aerosils with a surface modified by only approximately 60 and 85% ([5]), it is very important to obtain the formation of as dense a layer as possible of trimethylsilyl groups, practically eliminating adsorption in the gaps between them on the surface of the silica itself. In order to impart to the aerosil surface, first, greater geometrical uniformity and, second, maximum ability to react with trimethylchlorosilane, we carried out preliminary hydrothermal treatment of the aerosil, as a result of which its particles grew, and their surface became smoothed and was covered with hydroxyl groups to the maximum degree. This ensured good conditions for reaction with trimethylchlorosilane. Table 1 gives the conditions for obtaining various samples of modified aerosils, as well as the average concentration of trimethylsilyl groups on the surface calculated from chemical analyses (after evacuation of the samples at 150°)

Fig. 1

Figure 1: Fig. 1

Table 1

Sample	Autoclave treatment: temp., °C	Autoclave treatment: duration, h	Specific surface before modification, m^2/g	Degree of coverage by Si(CH$_3$)$_3$ groups, %
1	–	–	170	0
2	–	–	170	~60
3	120	8	~165	~85
4	200	19.5	~142	~90
5	265	19.5	~71	~100

groups on the surface (taking the area occupied by this group as equal to 42 Å^2 (2)). The measurements were carried out in a calorimeter (4).

It is seen from Table 1 that the last sample can indeed be regarded as satisfying the model adopted in the theoretical calculation[3].

Figure 1 shows the obtained dependences of the differential heats of adsorption Q_a on the amount adsorbed a (μ-mol/m^2), and Fig. 2 gives the adsorption isotherms a as a function of the relative vapor pressure p/p_s. It is seen from Fig. 1 that, upon modification of the surface, the heat of adsorption of these hydrocarbons decreases; moreover, as the degree of modification increases, the form of the dependence of Q_a on a changes sharply. If, upon modification by 60% and even 85%, the values of Q_a initially remain large and everywhere exceed the heats of condensation L, then, upon modification by approximately 90%, at small a they fall to values somewhat below L; and with the most complete modification (approximately 100%) the heats of adsorption Q_a of n-hexane and benzene become equal to about 7 kcal/mol, i.e., the net heats of adsorption become definitely negative: for n-hexane $Q_a - L = -0.5$, and for benzene $Q_a - L = -1.0$ kcal/mol. At the same time, we were no longer able to observe the initial decrease in the heat of adsorption characteristic of adsorption on heterogeneous surface sites with high adsorption potential. With increasing a, after the surface is covered by molecules of n-hexane and benzene, the heats of adsorption increase by approximately 10% and soon reach the values of the heats of condensation.

Fig. 1. Dependences of the differential heat of adsorption of vapors of n-hexane (a) and benzene (b) on surface coverage of the initial aerosil (1) and of aerosils modified by 60% (2), 85% (3), 90% (4), and 100% (5). The black symbols here and in Fig. 2 denote desorption.

Figure 2

Figure 2: Figure 2

In accordance with such a sharp decrease in the heat of adsorption, the magnitudes of the adsorption itself, a, also decrease (Fig. 2). At $p/p_s = 0.1$, the adsorption of n-hexane, as the degree of modification increases to approximately 100%, decreases by a factor of 12, while the adsorption of benzene decreases by a factor of 35. The relatively stronger decrease in the adsorption and heat of adsorption of benzene is due to the fact that, on the hydroxyl-containing surface of the initial aerosil, benzene molecules are adsorbed both through electrokinetic (dispersion) interactions and through electrostatic interactions of their quadrupoles with the dipoles of the hydroxyl groups on the silica surface[6]. It is seen from Fig. 2 that, in the case of the most completely modified sample, the adsorption isotherm of n-hexane is initially concave, while the adsorption isotherm of benzene is almost linear.

Owing to the very weak adsorbate–adsorbent interaction, very high p/p_s values are already required to retain even very small amounts of these adsorbates on the surface. Under these conditions, the free surface of the modified particles is still covered only by a rarefied film of hydrocarbon molecules; however, in the gaps between aerosil particles, near the points of their contact, capillary condensation is already possible at sufficiently large p/p_s. Correspondingly, the heats of adsorption proper

should be lower than the measured values, since the measured values at $\alpha > 0.1$ μmol/m^2 ($p/p_s > 0.2$) partially include the heats of capillary condensation, close to L. It is also probable that the approximate constancy of the measured heats of adsorption of benzene in the region of small α, evident from curve 5 in Fig. 1, is to some extent the superposition of a decrease in heat associated with residual heterogeneity and an increase in heat associated with adsorbate-adsorbate attraction and with the increasing contribution of capillary condensation. Thus, the true heats of adsorption proper of these hydrocarbons on a completely homogeneous surface of the modifying layer (without capillary condensation) should be still lower, i.e., still closer to the theoretically calculated very small values in (^{3}) (4.3 and 4.0 kcal/mol for vapors of n-hexane and benzene).

Fig. 2. Adsorption isotherms of vapors of n-hexane (a) and benzene (b) on the initial aerosil (1) and on aerosils modified to 60% (2), 85% (3), 90% (4), and 100% (5). **c** –initial portions of the isotherms for the most completely modified sample on an enlarged scale.

Figure labels: α, μmol/m^2; p/p_s; molecules/100 Å^2; C_6H_{14}; C_6H_6. Legend: -1, -2, -3, -4, -5.

Figure 3 presents the differential adsorption entropies of n-hexane and benzene, calculated from the adsorption isotherms and heats of adsorption, as functions of

Figure 3 and Figure 4

Figure 3: Figure 3 and Figure 4

coverage on the initial and the most completely modified aerosil sample. Noteworthy is the transition, upon modification, of the entropy change from the region of negative values to very large positive values (relative to the entropies of the corresponding liquids). This indicates considerable mobility of n-hexane and benzene molecules on the surface of the modifying layer. Such high entropy values, very low adsorption-energy values, and the great homogeneity of the surface allow one to suppose that, at least in the case of the sample with the most completely modified surface, the adsorption of n-hexane and benzene is nonlocalized. In this connection, the adsorption isotherms of vapors of these substances on the most completely modified sample, in the initial region, where capillary condensation between aerosil particles still does not introduce noticeable distortions, are satisfactorily descri-

are described by Hill' s equation of nonlocalized monomolecular adsorption (7), which approximately takes into account adsorbate—adsorbate interactions.

In Fig. 4 the experimental points of the adsorption isotherms shown in the upper part of Fig. 2 are presented in the coordinates of the linear form of this equation (8):

$$W(\theta, p/p_s) = \frac{\theta}{1-\theta} + \ln\frac{\theta}{1-\theta} - \ln p/p_s = \ln K_1 + K_2\theta. \tag{1}$$

Fig. 3. Dependences of the differential entropy of adsorption of benzene vapors (1, 4) and n-hexane (2, 3) on the surface coverage of the initial (1, 2) and the most fully modified (3, 4) aerosil

Fig. 4. Adsorption isotherms of n-hexane (1) and benzene (2) vapors on the most fully modified aerosil in the coordinates of equation (1)

Here θ is the degree of surface coverage, K_1 is the equilibrium constant for adsorbate—adsorbent interactions, and K_2 takes into account adsorbate—adsorbate interactions. The quantity $\theta = \alpha/\alpha_m = \alpha\omega_m$, where α_m is the capacity of a dense monolayer, and $\omega_m = 1/\alpha_m$ is the area occupied in this layer by an adsorbate molecule. For n-hexane $\omega_m = 51$ Å^2, and for benzene $\omega_m = 40$ Å^2 (9).

For the adsorption of n-hexane $K_1 = 0.2$ and $K_2 = 5.0$, and of benzene $K_1 = 0.1$ and $K_2 = 4.3$. The small values of K_1 are associated with weak adsorbate—adsorbent interactions. For benzene K_2 is smaller than for n-hexane, in accordance with weaker adsorbate—adsorbate interactions (10).

Thus, the applied combination of geometric modification of aerosil particles (by hydrothermal treatment) followed by chemical modification of their surface (by reaction with trimethylchlorosilane) led to smoothing of the silica surface and to the formation on it of such a dense layer of grafted trimethylsilyl groups that the surface of this layer becomes very homogeneous; adsorption of hexane and benzene on it occurs nonlocally, and the adsorption energy is so small that the net heats of adsorption of these hydrocarbons are negative.

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CITED LITERATURE

1. Yu. I. Babkin, V. S. Vasil' eva et al., DAN, **129**, 131 (1959).
2. A. V. Kiselev, A. Ya. Korolev et al., Kolloidn. zhurn., **22**, 671 (1960).
3. I. Yu. Babkin, A. V. Kiselev, DAN, **129**, 357 (1959).
4. A. A. Isirikyan, A. V. Kiselev, B. A. Frolov, ZhFKh, **33**, 389 (1959).
5. A. W. Kisselew, K. D. Schtscherbakowa, *Gas-Chromatographie*, 1959, Material zum 2. Symposium über Gas-Chromatographie in Böhlen, Berlin, 1959, S. 198.
6. A. V. Kiselev, D. P. Poshkus, DAN, **120**, 834 (1958).
7. T. H. Hill, J. Chem. Phys., **14**, 441 (1946).
8. S. Ross, W. Winkler, J. Coll. Sci., **10**, 319 (1955).
9. N. N. Avgul' , G. I. Berezin et al., Kolloidn. zhurn., **20**, 298 (1958).
10. A. V. Kiselev, ZhFKh, **35**, No. 2 (1961).

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