THE ADSORPTION AND HEAT OF ADSORPTION OF NORMAL ALCOHOLS ON GRAPHITIZED CARBON BLACK

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In [1-5] we studied the heat of adsorption of a number of hydrocarbons (normal and isoalkanes, cyclanes, and aromatics) and the regular features governing the adsorption of these substances on the uniform surface of graphitized carbon black. In the present work in this series we have studied the adsorption and heat of adsorption of hydrocarbon derivatives—the normal alcohols: methanol, ethanol, propanol, and butanol, and have also made a tentative determination of the heat of adsorption of water vapor at high degrees of covering of the surface of channel black.

The adsorption of methanol on graphitized channel black and graphite has already been studied [6-10]. In [10] it was shown that the adsorption of methanol is the same on graphite and on graphitized channel and thermal blacks, within the limits of possible accuracy of the graphs given in the literature; the methanol adsorption isotherm has an undulating shape with two inflections, starting with a sharply concave section. This isotherm shape is characteristic of relatively strong adsorbate–adsorbate interaction [11, 9]. The differential heat of adsorption of methanol on graphitized channel black was measured only in [7], but the data must apparently be regarded as tentative, since the authors of [7] do not give the experimental points. In [6] the heat of adsorption of methanol on graphite was calculated from the isosteres.

The isotherms for the adsorption of water vapor on graphitized carbon black and graphite have been studied in a number of works (see for example [8-10, 12-14]); they have been studied in detail in [10]: It was shown that the adsorption of water on graphitized carbon black is negligibly small, the isotherm is concave throughout the whole range of relative pressures \( P/P_s \) and even at values of \( P/P_s \) close to unity a compact monolayer is not formed. This was attributed to a particularly weak bond between the water molecules and the graphite surface. The differential heat of adsorption of water on graphitized channel black was studied in [13, 14], and contradictory data were obtained. In [13], high negative values were obtained for the pure heat of adsorption, like the heats of adsorption of water on carbon, determined in [15].

EXPERIMENTAL

The main adsorbent used was "sferon-6" carbon black, as used in [5], i.e., graphitized in an atmosphere of helium at 2800°C for 10 min; its specific surface, determined by the BET method from the adsorption of nitrogen vapor, was \( s = 89 \, \text{m}^2/\text{g} \). A separate study was carried out with T-1 thermal black obtained from Tesner, graphitized at 3000°C for 45 min in an atmosphere of CO; its specific surface, determined by the BET method from the adsorption of nitrogen vapor [16], was 29.0 m²/g. Twice-distilled water was used in the experiments. The constants of the purified alcohols used are given in Table 1.

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>( d^2 )</th>
<th>( n_D )</th>
<th>Vapor pressure ( P_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.7917</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ethanol</td>
<td>—</td>
<td>1.3615 (20°)</td>
<td>34.6 (16°)</td>
</tr>
<tr>
<td>n-Propanol</td>
<td>0.8059</td>
<td>1.3860 (20°)</td>
<td>12.4 (18°)</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>—</td>
<td>1.3990 (21°)</td>
<td>3.65 (16°)</td>
</tr>
</tbody>
</table>
As in [1-5], the differential heat of adsorption was measured in a calorimeter with constant heat capacity (1953 model) and the magnitude of the adsorption of the alcohols was measured by means of vacuum liquid capillary microburets [17]. The adsorption of water vapor was measured by the gas volume method [18]. The experiments were carried out at 20°; the determination of the isotherm for butanol adsorption was also carried out at 41.5°.

Fig. 1. Isotherms for the adsorption of the vapor of water (1), methanol (2), ethanol (3), propanol (4), and butanol (5) on "sferon-6" graphitized carbon black at 20° (the crosses denote data for the adsorption of butanol at 41.5°; the black symbols give the desorption data).

Fig. 2. Relationship between the differential heat of adsorption of the vapor of methanol (1), ethanol (2), n-propanol (3), and n-butanol (4) and the quantity adsorbed on "sferon-6" graphitized carbon black at 20° (the points on curve (1), marked with circles, refer to the heat of adsorption of methanol vapor on graphitized thermal carbon black; the horizontal lines on the right mark the values of the latent heat of condensation of the corresponding alcohols; the black points give the heat of desorption).

Figure 1 shows the isotherms obtained for the adsorption of the vapor of water, methanol, ethanol, propanol, and butanol on "sferon-6" graphitized carbon black. Several series of experiments were carried out for each vapor and good agreement was obtained. The adsorption isotherms are completely reversible up to very small values of p. In addition to the relative scale of values of the adsorption a (mM per 1 g), Figure 1 gives the absolute scale α (µM per 1 m² of surface).

The adsorption of water is negligibly small and the isotherm is concave throughout. On going from water to methanol the adsorption increases sharply and the isotherm changes shape: remaining concave at first, it subsequently shows two points of inflection. The same isotherm shape is retained for the adsorption of ethanol and propanol (we have not yet established the exact shape of the initial section of the isotherm for butanol, due to the very low values of p). Thus in the alcohol series there is an increase in the adsorption in the initial section of the isotherm with increase in the number n of carbon atoms in the molecule. In the central region the adsorption isotherms cross one another and afterwards the reverse order of values of the adsorption is observed.

Figure 2 shows the relationship between the differential heat of adsorption Qₐ and α for the vapors of methanol, ethanol, propanol, and butanol. In the case of ethanol, propanol, and butanol, only "sferon-6" graphitized carbon