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Abstract

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ADSORPTION OF NITROGEN VAPORS ON MODIFIED ACTIVATED CARBON

The introduction into the sorption space of an adsorbent of molecules of various substances, firmly bound to its surface, can change its sorption properties over wide limits. Such "modification" of an adsorbent is achieved either by chemically altering its surface (for example, by introducing chemically bound radicals), or by physical adsorption of "modifiers," i.e., substances which, at the temperature of the experiment, have an extremely small vapor pressure above the adsorbent. Below we shall speak only of phenomena associated with "physical" modification. By observing the change in the principal characteristics of the adsorption equilibrium of some substance (for example, nitrogen) with an adsorbent containing a gradually increasing amount of modifier, one can determine the change in the parameters of the adsorption-isotherm equations, trace the gradual change in the pore-volume distribution curves with respect to size, ascertain the character of the change in the differential heats of adsorption, and form an idea of certain properties of the substance in the adsorbed state. It should be noted that sorption of the vapors of some substance on such a modified adsorbent is a peculiar special case of sorption of a mixture of two substances, in which the vapor pressure of one of the adsorbed substances above the adsorbent is always practically equal to zero.

The first study of nitrogen-vapor adsorption at −195° on activated carbon modified with adsorbed water was carried out by American authors (^1). The conclusions of this work seem to us not very convincing, since the formal determination of the specific surface of activated carbons by BET in this case can hardly be theoretically justified (^2). Almost simultaneously with work (^1), an attempt was made to study adsorption of water vapor on activated carbon modified with dibutyl phthalate (^3); however, this work made it possible to draw only qualitative conclusions. Later Barrer and Rees (^4) studied the adsorption of a number of gases at low temperatures on zeolites modified with water, ammonia, or methylamine, and showed that in this way the parameters of the "molecular sieves" used for separating inert gases can be smoothly varied. We also note the work of Singleton and Halsey (^5), in which the adsorption of argon on adsorbents modified with xenon was studied.

In the present article the results are reported of a study of nitrogen-vapor ad-

Fig. 1

Figure 1: Fig. 1

sorption at −195° on activated carbon modified with various amounts of water, methyl alcohol, or benzene. In contrast to the method of very slow cooling (sometimes lasting whole days) of an adsorbent initially in equilibrium with the vapors of the modifier at a higher temperature, we developed a method of rapid cooling of the adsorbent in a helium atmosphere in order to fix, or in a sense "quench,"the state of adsorption equilibrium previously attained at 20°. To carry out the experiments we used the apparatus described earlier (ˆ6) for measuring nitrogen-vapor adsorption by the gravimetric method, introducing into it minor changes—

ments. To accelerate cooling, the thickness of the gas layer between the adsorbent and the cooled wall of the lower part of the balance tube was reduced to about 3 mm. The internal diameter of this tube was reduced to 10 mm, and the coal granules (total weight about 100 mg) were placed in a cylindrical spiral, 3 mm in diameter, suspended vertically from the balance and made of nichrome wire 0.1 mm in diameter. To obtain coal with a specified amount of adsorbed modifier, the adsorbent was first evacuated at 450° and then kept in an atmosphere of modifier vapor at 20° until adsorption equilibrium was established, after which helium was introduced into the vessel containing the balance at a pressure of about 10 mm Hg. Immediately after this the lower end of the tube surrounding the adsorbent was rapidly immersed in a Dewar vessel with liquid nitrogen. Owing to the high thermal conductivity of helium and the low rate of diffusion of modifier vapors through the gas, no desorption of the modifier was observed at all during cooling to the temperature of liquid nitrogen. Half an hour after the start of cooling, the main part of the helium was returned to the cylinder by means of a Toepler mercury pump, and the vessel containing the balance was pumped down to a pressure of about $1 \cdot 10^{-6}$ mm Hg.

Fig. 1

For the experiments a laboratory sample was taken of granulated, ash-free activated carbon, activated with carbon dioxide at 950° to 50% burn-off. From the adsorption isotherm of nitrogen vapors it was found that, for this carbon, the micropore volume is 0.480 cm^3/g, and the volume of transitional pores is 0.190 cm^3/g. All measurements were carried out with one and the same sample of this carbon, successively modified with different amounts of water, methyl alcohol, or benzene. The experimental data obtained were analyzed from the standpoint of the concepts of the potential theory of adsorption developed in our laboratory ([7,8]). It was found that the isotherms of adsorption of nitrogen vapor measured in each of the three series of experiments over a wide range of relative pressures h are well described by the equation for adsorbents of the first structural type ([1]):

$$a = \frac{W_0}{v} e^{-\frac{BT^2}{\beta^2} \lg^2 h}, \tag{1}$$

where W_0 is the limiting volume of the sorption space, v is the molar volume of the adsorbed substance (for liquid nitrogen, equal to 34.7 cm^3/mol), B is a constant depending on the dimensions of the micropores, which determine the effect of enhancement of the adsorption potentials, and on the nature of the adsorbent surface, and β is the affinity coefficient of the characteristic curve.

As an illustration of the experimental data, Fig. 1 gives isotherms of adsorption of nitrogen vapor on carbon modified with methyl alcohol, plotted in coordinates corresponding to the linear form of equation (1). The numbers placed near the isotherms indicate the amount of adsorption of CH_3OH in mmol/g. Similar families of linear isotherms of nitrogen adsorption were obtained by us for carbon modified with water and for carbon modified with benzene. From the intercepts on the ordinate axis and the slopes of the linear isotherms, the parameters W_0 and B were calculated for the families of adsorption isotherms corresponding to each modifier, and the values obtained for these parameters were presented as functions of the magnitude of adsorption of the modifier a_2.

Figure 2 shows the dependence of the limiting micropore volume W_0 on a_2 for water (curve 1), methyl alcohol (curve 2), and benzene (curve 3).

In all three cases W_0 decreases linearly with increasing a_2, and only after the volume W_0 has been filled by 70-80% are deviations from the linear dependence observed. The angular coefficient of the linear part of each of the curves in Fig. 2 is evidently equal to the molar volume of the modifier, and the reciprocal value to the effective density of the substance in the adsorbed state. We shall call this density effective in order to emphasize its difference from the normal density of the bulk phase. In the present case we are dealing with the density of a solid substance in an exceptionally highly dispersed state (in micropores of dimensions on the order of 10 Å), and therefore there is no reason to expect that this value will be equal to the normal density of the bulk solid phase. Table 1 gives the values of the effective density d_e of solid water, methyl alcohol, and benzene in the micropores of activated carbon at -195°. The same table gives, for these substances, the values of the normal density d_n of the bulk solid phase at -195°, measured by us by the method of hydrostatic weighing in liquid nitrogen. From a comparison of these numbers it follows that, for all three substances, the density d_e is 30-40% lower than the normal density. We are inclined to think that the anomalously low density values found for solid adsorption phases in the micropores of carbon

Table 1

Substance	d_e, g/cm^3	d_n, g/cm^3
H_2O	0.62	0.89
CH_3OH	0.55	0.95

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

Substance	d_e, g/cm^3	d_n, g/cm^3
C_6H_6	0.67	1.14

Fig. 2

Fig. 3

characterize the real properties of these phases. The reduced density values may be caused by the extremely high degree of dispersion of the solid modifier, a consequence of which is a very considerable increase in the fraction of molecules located on the surfaces of submicrocrystals or of some quasi-crystalline formations in the micropores. It is also possible that in such highly dispersed solid phases formed in the micropores of carbon, the normal crystal lattice is distorted by the adsorption field of the adsorbent itself.

In Fig. 3, for water (curve 1), methyl alcohol (curve 2), and benzene (curve 3), the dependence of the parameter B on the value of the volume $a_2 v_2$ filled by the modifier, in cm^3/g, or on the volumetric degree of filling $\theta = a_2 v_2 / W_0$, is shown. In constructing this graph, the values of the molar volume of the modifier v_2 were calculated from the densities d_e. For all three substances the parameter B at first increases very slowly and practically linearly, and begins to increase rapidly only at large values of θ. It should be noted that the increase in B and the linear decrease in W_0 with increasing a_2 were found earlier in our laboratory in analyzing the results of adsorption measurements

mixtures of water and ethyl chloride on active carbon (9,10). The increase in B may be regarded as the result of at least three factors: a change in the pore-size distribution function, caused by the gradual exclusion of the smallest pores during adsorption of increasing amounts of the modifier; a change in the sizes of the pores accessible to nitrogen when the modifier is adsorbed on their walls; and, finally, a change in the nature of the adsorbent surface caused by adsorption of the modifier.

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