Adsorption of Ammonia on Graphitized Soot

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Abstract

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Adsorption of Ammonia on Graphitized Soot

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As is known, the adsorption of water vapor on carbon adsorbents has a number of specific features, manifested in the distinctive shape of the adsorption isotherm. A systematic study of this question (1) led to the conclusion that these features are due to the ability of adsorbed water molecules to form associative complexes as a result of the formation of hydrogen bonds. If this conception is correct, then one may expect that other substances as well, for which, as for water, the binding energy upon adsorption on carbon adsorbents is small, while tangential interactions in the adsorption layer, owing to the manifestation of hydrogen bonds, are very significant, will be characterized by an analogous form of the adsorption isotherm. In connection with this, several years ago our laboratory undertook a study of the adsorption of ammonia vapor on carbon adsorbents at temperatures close to its boiling point. Preliminary experiments carried out with calcined soot made it possible to establish the presence in this case of a concave adsorption isotherm and thus, in the main, confirmed the correctness of this point of view. A similar conclusion is also reached in the work of Beebe and Dell (2). However, whereas, in accordance with the cited concepts, the magnitudes of adsorption and the forms of the adsorption isotherms of water on carbon adsorbents depend sharply on the degree of oxidation of the surface of the latter, in the case of ammonia adsorption reversible, concave isotherms are observed only on soots calcined at high temperature. Thus, according to the data of Beebe and Dell (2), the adsorption of ammonia on Spheron-6 soot calcined at 1000° is irreversible: in the initial part the desorption branch of the isotherm lies above the adsorption branch; on the contrary, the adsorption of ammonia on the same soot calcined at 2700° proceeds reversibly over the entire range of relative pressures. From all that has been said it follows that a simple transfer of the ideas developed for the adsorption of water to the case of ammonia adsorption on carbon adsorbents is impossible.

Below are presented the results of measuring the adsorption of ammonia vapor at a temperature of $-36.3°$ on channel Ukhta soot, preliminarily calcined for 2 hours at a temperature of 1700° in a stream of hydrogen. The choice of the soot and of the conditions of its preliminary treatment was dictated by the aim of obtaining a carbon adsorbent with a comparatively homogeneous surface. The specific surface of the prepared soot was measured by the method of low-temperature nitrogen adsorption and was found to be 100 m^2/g. All measurements were carried out on the standard volumetric apparatus used in

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

our laboratory. The temperature of the adsorbent was maintained constant to within ±0.1° by means of a cryostat described by G. G. Muttik (3). The ammonia was obtained by repeated low-temperature distillation of a concentrated aqueous solution of ammonia, followed by drying over metallic sodium.

Figure 1 shows the ammonia adsorption isotherm obtained by us on

channel carbon black at a temperature of -36.3°. In the upper left corner the initial portion of the same isotherm is shown on an enlarged scale. Over the entire range of relative pressures the adsorption is completely reversible.

Taking for ammonia the area per molecule $\omega = 13.1$ Å^2, we obtain the monolayer capacity $a_m = 1.27$ mM/g. In other words, up to point A in Fig. 1 the adsorption, apparently, is monomolecular, and point A approximately corresponds to the transition to polymolecular adsorption.

Comparison of the isotherm obtained in Fig. 1 with adsorption isotherms of water vapor on analogous adsorbents that are well known from the literature leads to the following conclusions.

Although in both cases the adsorption isotherms in the monomolecular region are concave, there are also substantial differences in their form. The adsorption isotherms of water are characterized by the presence of a region of very steep rise, which is absent on the ammonia adsorption isotherms. In the case of water, with a decrease in the degree of oxidation of the surface, the region of steep rise shifts in the direction of increasing relative pressure, while the adsorption values at lower pressures remain extremely small. As has already been indicated, in the adsorption of ammonia on carbon blacks with different degrees of oxidation, no shift of the isotherm toward higher relative pressures is observed with a decrease in the number of surface oxides, which are the primary adsorption centers for adsorption of water molecules (4). Moreover, as is seen from Fig. 1, in the adsorption of ammonia on carbon adsorbents, even at comparatively low pressures the adsorption values prove to be already rather appreciable. These features may be explained by the fact that, owing to the greater polarizability of the ammonia molecule in comparison with the water molecule, the energy of interaction with the surface of the graphite lattice is greater for ammonia than for water, whereas the hydrogen-bond energy is greater for water.

Fig. 1

Fig. 2

As was shown by Bering and Serpiński (^{5}), the predominance of tangential attractive forces in the adsorption layer, independent of the specific mechanism of interaction, must always lead to adsorption isotherms that are concave in the initial region. To describe the concave part of the adsorption isotherm of water vapor on carbon adsorbents, Dubinin and Serpiński (^{4}) derived the equation

$$a = \frac{a_0 ch}{1 - ch}, \tag{1}$$

in which a is adsorption, h is the relative pressure of water vapor, and c and a_0 are constants, with a_0 denoting the number of "primary" adsorption centers, which are molecules of chemisorbed oxygen.

It is seen in Fig. 2 that in the interval of relative pressures from 0.1 to 0.45

our data can be described by an equation of the form (1), although, as indicated above, the adsorption of ammonia on carbon adsorbents is insensitive to the amount of chemisorbed oxygen. Therefore, below we shall attempt to show that the same type of dependence between a and h as in equation (1) can be arrived at without making the assumption that primary adsorption centers are present on the surface of the adsorbent.

We shall proceed from the assumption that, even on a completely homogeneous surface, in the monomolecular adsorption layer, two-dimensional adsorption complexes of different sizes are formed as a result of the manifestation of hydrogen bonds. In other words, let us assume that, as a result of adsorption, individual unassociated molecules can form complexes of two molecules, double complexes can pass into triple ones, etc.

Let θ denote the total fraction of the surface filled by the adsorbed substance, and let $\theta_1, \theta_2, \theta_3, \ldots$ denote the degrees of filling of the surface by complexes of one, two, three, etc. molecules. It is evident that

$$\theta = \theta_1 + \theta_2 + \theta_3 + \cdots + \theta_n + \cdots \tag{2}$$

Let k_n' denote the rate constant for the formation (by adsorption) of a complex of n molecules, and let k_n'', respectively, denote the rate constant for the decomposition (by desorption) of such a complex. We shall further assume that $k_2' = k_3' = k_4' = \cdots$ and that $k_2'' = k_3'' = k_4'' = \cdots$; from general physical considerations it is evident that $k_1' \neq k_2'$ and that $k_1'' \neq k_2''$.

If it is assumed, as is usually done in analogous cases, that at equilibrium the rate of adsorption on complexes of $(n-1)$ molecules is equal to the rate of desorption from complexes of n molecules, then it is easy to obtain

$$\theta_1 = \frac{k_1'}{k_1''}(1 - \theta)h,$$

$$\theta_2 = \frac{k_n'}{k_n''}\theta_1 h = \frac{k_1'}{k_1''}\frac{k_n'}{k_n''}(1-\theta)h^2,$$

$$\theta_3 = \frac{k_n'}{k_n''}\theta_2 h = \frac{k_1'}{k_1''}\left(\frac{k_n'}{k_n''}\right)^2(1-\theta)h^3,$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \tag{3}$$

$$\theta_p = \frac{k_n'}{k_n''}\theta_{n-1} h = \frac{k_1'}{k_1''}\left(\frac{k_n'}{k_n''}\right)^{n-1}(1-\theta)h^n$$

Introducing, for brevity, the notations $k_1'/k_1'' = c'$ and $k_n'/k_n'' = c''$, and adding equations (3) term by term, we obtain

$$\theta = \Sigma\theta_i = c'(1-\theta)h\left[1 + c''h + (c''h)^2 + \cdots + (c''h)^n\right] \tag{4}$$

Carrying out the summation of the geometric progression on the right-hand side of equation (4) for $n \to \infty$, we arrive at the final expression

$$\theta = \frac{a}{a_m} = \frac{c'h}{1-(c''-c')h}, \tag{5}$$

where a_m is the capacity of the monolayer. It is evident that equation (5), whose derivation is not based on the assumption that primary adsorption centers are present on the surface of the adsorbent, is formally analogous to equation (1).

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CITED LITERATURE

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