WATER VAPOR ADSORPTION AND MICROPOROUS STRUCTURE
OF CARBON ADSORBENTS.

17. ANALYSIS OF EXPERIMENTAL ISOTHERMS FOR WATER VAPOR ADSORPTION

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Water vapor adsorption for various activated carbons with narrow and wide micropore volume distributions and mesopore surface areas between 40 and 300 m²/g have been investigated. For all the isotherms the point of inflection was determined, which can be taken as the point characterizing the formation of a water adsorption layer on the pore wall surface of carbon adsorbents. To do this the adsorption and desorption branches of the isotherms were approximated according to Weibull's distribution. A good correlation was obtained between values for the water monolayer capacity, calculated from the porous structure parameters of the carbons, and the adsorption values corresponding to the isotherm inflection points $a_{inf}$. For the group of carbons studied the values of relative pressure at the inflection point of the isotherms fell within the range 0.5-0.72.

It has been shown [1] that during adsorption of water vapor on graphitized soot formation of a continuous adsorption layer of water molecules occurs at $p/p_0 = 0.6$. Analogous results were obtained for a series of activated carbons (AC) [2], which enabled us to put forward a method of determining microporous structure parameters of AC from the water vapor adsorption isotherms. However, the application of this method is limited to AC possessing a "normally" oxidized surface with a narrow micropore volume distribution. As numerous experiments have shown, a change in the degree of oxidation of the adsorbent surface leads to displacement of water vapor adsorption isotherms along the $p/p_0$ axis. During this the microporous structure parameters determined from benzene adsorption hardly change [3]. Generally the porous structure parameters of AC have a significant effect on the type of water vapor adsorption isotherm and its displacement along the $p/p_0$ axis [4, 5].

The aim of this study was to determine the adsorption value corresponding to the formation of the calculated water monolayer on the pore surface of adsorbents with different porous structures, mesopore distributions, and surface chemical composition, and also to determine the corresponding $p/p_0$ value on the isotherm.

EXPERIMENTAL

Water vapor adsorption isotherms were studied on various AC with both narrow (AC-2, AC-5) and wide (AC-1, AC-3, AC-4, AC-6, AC-7, and AC-8) micropore volume distributions and with a mesopore structure distribution having a wide range of $S_{mes}$ from 40 to 300 m²/g. The samples differed in their source materials and method of production.

Water vapor adsorption isotherms were determined at 293 K in a vacuum sorption apparatus which worked on the principle of MacBain's sorption balance in the relative pressure range $h = p/p_0$ from 0.1 to 1.0. The sample had been previously evacuated to constant weight at 673 K and $10^{-4}$ Pa. Water vapor adsorption isotherms for the AC are shown in Figs. 1 and 2.

The microporous structure parameters for the AC were determined from benzene vapor adsorption isotherms measured in the same apparatus at 293 K in the $p/p_0$ range from $1 \times 10^{-6}$ to 1.0. Before the measurements the samples were evacuated to constant weight at 673 K and 1.0.

RESULTS AND DISCUSSION

The connection between the particular form of the isotherm and the mechanism of water vapor adsorption was noted in [8, 9]. The inflection point of the S-shaped isotherm can be taken as the point characterizing the formation of a water adsorption layer on the pore wall surface of carbon adsorbents.

Arising from this an attempt was made to determine the inflection point approximating the S-shaped curve of the isotherm according to the equation [10]

$$y = 1 - \exp \left[ -\left( \frac{x}{b} \right)^n \right].$$

When applied to water vapor adsorption (1) it is more convenient to use it in the form

$$a = a_s \left\{ 1 - \exp \left[ -\left( \frac{h + \alpha}{b} \right)^n \right] \right\},$$

where $a$ is the adsorption value mmole/g; $a_s$ is the adsorption value at $h = 1$; $n$ is the shape parameter; $b$ is the scale factor and $\alpha$ is the displacement parameter.

The point of inflection of curve (2) corresponds to the maximum of the first differential and can be determined by putting the second differential equal to zero:

$$\frac{d^2a}{dh^2} = \frac{n \cdot a_s}{b^n} \left( h + \alpha \right)^{n-2} \left\{ n \left[ 1 - \left( \frac{h + \alpha}{b} \right)^n \right] - 1 \right\} e^{-\left( \frac{h + \alpha}{b} \right)^n} = 0.$$