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Abstract

Full Text

PHYSICAL CHEMISTRY

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DEPENDENCE OF THE DIFFUSION COEFFICIENT ON THE AMOUNT OF ADSORPTION ON ACTIVATED CARBONS

(Presented by Academician M. M. Dubinin, 25 XII 1959)

Diffusion coefficients in porous sorbents change during sorption, and in different ways depending on the degree of filling of the sorption volume, the structure of the sorbent, the nature of the sorbed substance, and certain other factors ([1–7]). The study of this dependence is of interest for questions concerning the calculation of the rates of sorption processes occurring in the intradiffusion region, and also for elucidating the mechanism of mass transfer in porous sorbents. Meanwhile, investigations in this field are few in number, and the results obtained in some cases are contradictory. Least clear are the causes of the decrease in the diffusion coefficient with filling, which has been noted in a number of works ([3,6,7]).

Table 1

Brief characterization of the carbons investigated

Carbons	Pore volume, cm^3/g	Pore volume, cm^3/g	Pore volume, cm^3/g	Granule diameter, mm	Granule length, mm
	micro	transitional	macro		
I	0.33	0.10	0.25	3	5-6
II	0.38	0.05	0.31	1.6	3-3.5
IIa	0.38	0.05	0.31	1.6	1.6
III	0.28	0.40	0.20	1.4-1.6	2.4

The only attempt to explain this phenomenon is found in the works of Barrer ([1,8]). Considering the sorption process on zeolites as diffusion in crystals, Barrer ([8]), in calculating the diffusion coefficient, takes into account the change in the number of vacant sites for the diffusing molecules, which gives a linear decrease of the diffusion coefficient with filling. However, such a concept is hardly applicable to porous sorbents such as activated carbons, silica gels, etc., in which the mechanism of transfer differs substantially from diffusion in crystals.

In this case the decrease in the diffusion coefficient during sorption is apparently connected with the character of the interrelation of different types of pores. This question was partly discussed by us in ([9]) and is considered in somewhat greater detail in the present work.

The experimental part of the study consisted in determining the dependence of the diffusion coefficient of methyl alcohol on the amount of adsorption on activated carbons with different porous structures. Granulated activated carbons were obtained under laboratory conditions by the vapor-gas method from fossil coal and wood resin (carbons I and II) and from hydrolysis lignin and resin (carbon III). The principal data on the porous structure and sorption properties of the carbons are given in Table 1 and in Fig. 1.

Measurements of the sorption kinetics were carried out under vacuum conditions at 20° and at constant vapor pressure of methyl alcohol. The volume of the system, the carbon sample weight, and the intervals of equilibrium pressures in which the measurements were made were selected so that, in the most unfavorable case, the vapor pressure during the experiment decreased as a result of adsorption by no more than 3-4% of the initial value. Before the experiment the carbon was evacuated with a mercury pump for 3 hours at a temperature of 400°. The quantity

the adsorbed methanol was determined from the weight gain of the carbon with the aid of sorption balances. After the operating pressure had been established in the apparatus system, the sorption tube containing the carbon was connected to the system, and then, at definite time intervals, the increase in adsorption was recorded until sorption equilibrium was reached.

The diffusion coefficients for carbon IIa were calculated from the diffusion equation for a cylinder of finite dimensions

$$\gamma = \frac{a - a}{a_\infty - a} = 1 - \frac{32}{\pi^2} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{1}{\mu_n^2 (2m-1)^2} \exp\left[- \left(\frac{\mu_n^2}{R^2} + \frac{(2m-1)\pi^2}{4l^2} \right) Dt \right], \tag{1}$$

where a is the adsorption value at time t; a is the equilibrium adsorption value at the beginning of the experiment (at $t = 0$); a_∞ is the equilibrium adsorption value at the end of the experiment ($t \to \infty$); μ_n are the roots of the Bessel function $J_0(\mu_n)$; D is the effective diffusion coefficient (calculated per unit cross section of the porous medium); R and l are, respectively, the radius and length of the cylinder; $n = 1, 2, 3, \ldots$; $m = 1, 2, 3, \ldots$

At $\gamma = 0.5$, the equation assumes a form identical for the adsorption and desorption processes:

$$\sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{1}{\mu_n^2 (2m-1)^2} \exp\left[- \left(\frac{\mu_n^2}{\pi^2} + \frac{(2m-1)^2}{16} \right) \frac{\pi^2 D t_{0.5}}{R^2} \right] = \frac{\pi^2}{64}. \tag{2}$$

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Fig. 1. Adsorption isotherms of methanol vapor on carbons I, II, III

Figure 1: Fig. 1. Adsorption isotherms of methanol vapor on carbons I, II, III

Fig. 2. Dependence of the diffusion coefficient D and of the quantity $D\Gamma$ on adsorption a on carbon IIa

Figure 2: Fig. 2. Dependence of the diffusion coefficient D and of the quantity $D\Gamma$ on adsorption a on carbon IIa

In equation (2), l has been replaced by $2R$ for the given carbon sample (see Table 1).

For calculations with an accuracy of about 1%, the equation may be transformed to the form

$$D = 0.318 \frac{R^2}{\pi^2 t_{0.5}}, \tag{3}$$

where $t_{0.5}$ is the time, in seconds, in which the adsorption value $\gamma = 0.5$ is reached; D is in sq. centimeters per second and R is in centimeters.

Fig. 1. Adsorption isotherms of methanol vapor on carbons I, II, III

The dependence of D on filling for carbons I, II, and III was determined from the relation [(10)]

$$\frac{D_2}{D_1} = \frac{t'_{0.5}}{t''_{0.5}}, \tag{4}$$

where the quantities with subscripts 1 and 2 refer respectively to two different ranges of filling. The diffusion coefficient for the adsorption value a_0, corresponding to the filled volume of the micropores, is taken as unity.

The experimental data satisfy the root law fairly well up to $\gamma = 0.6$–0.8. Curves of the dependence of the diffusion coefficient D and of the quantity $D\Gamma$ (Γ is Henry' s constant) on filling for the carbon samples studied are given in Figs. 2 and 3.

If one assumes that active carbon contains conglomerates of elementary carbon crystallites with more or less compact packing, so that the free spaces between crystallites are micropores connected with one another (see Fig. 4), then the simultaneous decrease of D and $D\Gamma$ with filling can be explained as follows. The path of molecular motion from the surface into the interior of the grain to the adsorption centers passes through wide and narrow channels, in which the diffusion coefficients are different. The wide channels are the free spaces between conglomerates of crystallites, and the narrow channels are micropores. The overall coef-

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Fig. 3. Dependence of the ratio of diffusion coefficients D_2/D_1 and $D_2\Gamma_2/D_1\Gamma_1$ on adsorption a on carbons I, II, and III

Figure 3: Fig. 3. Dependence of the ratio of diffusion coefficients D_2/D_1 and $D_2\Gamma_2/D_1\Gamma_1$ on adsorption a on carbons I, II, and III

Fig. 4. Schematic representation of the porous structure of activated carbon (a) and of an element of the porous structure (b)

Figure 4: Fig. 4. Schematic representation of the porous structure of activated carbon (a) and of an element of the porous structure (b)

Fig. 2. Dependence of the diffusion coefficient D and of the quantity $D\Gamma$ on adsorption a on carbon IIa

Fig. 3. Dependence of the ratio of the diffusion coefficients D_2/D_1 and $D_2\Gamma_2/D_1\Gamma_1$ on adsorption a on carbons I, II, and III

ficient of diffusion depends on the partial values of the diffusion coefficients in the wide and narrow pores. For the path element shown in Fig. 4b, the overall diffusion coefficient may be written in the form

$$D = \frac{D_{\text{I}} D_{\text{II}}}{\alpha D_{\text{I}} + (1-\alpha) D_{\text{II}}}, \tag{5}$$

where D_{I} is the diffusion coefficient in a wide pore; D_{II} is the diffusion coefficient in the microporous zone; $\alpha = \dfrac{l_{\text{II}}}{l_{\text{I}} + l_{\text{II}}}$ is the fraction of the path of the diffusing molecules through the micropores.

In the course of adsorption, the micropores are filled with the adsorbed substance; at the same time the free space between the carbon crystallites decreases and, consequently, the diffusion coefficient in the microporous zone decreases. The diffusion coefficients in the wide pores remain practically unchanged during this process. A decrease in D_{II}, according to (5), leads to a decrease in the overall diffusion coefficient. A more general expression for D can be obtained if one takes into account

distribution of pores by radii, the presence of parallel channels, and other qualifying circumstances, but the qualitative picture does not change.

Fig. 4. Schematic representation of the porous structure of activated carbon (a) and of an element of the porous structure (b)

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