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# THE POSSIBILITY OF USING THE THERMAL EQUATION OF ABSORPTION FROM THE THEORY OF VOLUME FILLING OF MICROPORES FOR CALCULATION OF HOLDING CAPACITY OF BUSOFIT IN THERMAL VACUUM DESORPTION

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*An experimental study was carried out to investigate thermal desorption of organic solvents from activated carbon fiber materials (ACFM) of the busofit type in the temperature range of 293–423 K. Comparison of experimental and calculated holding capacities of ACFM has shown that the thermal equation of absorption from the theory of volume filling of micropores can be used for estimation of the holding capacity.*

Special attention is devoted to the desorption stage in recuperation and cleaning of gaseous industrial effluents. Since this stage largely determines the efficiency of adsorption-desorption processes as a whole, the interest shown in its comprehensive investigation is quite understandable [1-3].

Apart from the adsorbing-carbon method that is widely used for extraction of harmful admixtures from gaseous industrial effluents followed by recuperation of their captured components or their detoxification, some attempts have been made recently to use activated carbon fiber materials in adsorption processes. The unique adsorption and desorption properties of ACFM determine their attractiveness. According to information reported in [4], in the case of ACFM the total mass transfer coefficient is by an order of magnitude larger than in the case of granular carbon, and adsorption and desorption processes are much more intense in the former case. It is known, [4] however, that desorption from microporous adsorbents, including ACFM, is rather difficult. The reason is that the adsorption and, consequently, desorption heats are highest at low saturation. Consequently, desorption increases with temperature. Since heating of carbon adsorbents to high temperatures is always undesirable in practice, a certain amount of adsorbate always remains in the adsorbent, because of which the adsorption capacity decreases in subsequent cycles. In the case of a convex isotherm, which is characteristic of adsorption of most of organic compounds on microporous carbon adsorbents, the rate of desorption rapidly decreases with time and after a certain period it appears to stop. In this case, the amount of material that remains in the adsorbent is interpreted as the holding capacity of the adsorbent, provided that the rate of desorption is lower than the sensitivity of the method of study [5, 6]. There are no consistent experimental or theoretical methods for estimation or calculation of holding capacities of carbon adsorbents. However, all experimental methods used for this purpose are characterized by initial saturation of the adsorbent by organic vapor at a high partial pressure and by subsequent desorption in a gas flow or in vacuum [7].

In what follows results are presented of a study of desorption of organic solvents (acetone, benzene, perchlorethylene, toluene, ethanol, and ethylacetate) from ACFM such as busofit, and the possibility is considered of calculating the holding ability of this compound from the thermal equation of adsorption from the theory of volume filling of micropores as applied to thermal vacuum desorption as a method for obtaining desired components without diluents.

The parameters of the porous structure of the ACFM studied were calculated according to the theory of volume filling of micropores from adsorption isotherms of benzene at 293 K and are given in Table 1.

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TABLE 1. Relative Holding Capacity of ACFM in Adsorption of Benzene Vapor as a Function of Temperature and Parameters of Porous Structure of ACFM

| Specimen No. | $W_0$, cm$^3$/g | $E_0$, kJ/mole | $X$, nm | Temperatures $T$, K | | | |
|---|---|---|---|---|---|---|---|
| | | | | 293 | 323 | 373 | 423 |
| 1 | 0.63 | 18.2 | 0.70 | 0.42 | 0.22 | 0.06 | 0.01 |
| 2 | 0.44 | 24.0 | 0.50 | 0.59 | 0.23 | 0.08 | 0.01 |
| 3 | 0.55 | 21.6 | 0.57 | 0.54 | 0.26 | 0.09 | 0.01 |
| 4 | 0.47 | 23.1 | 0.52 | 0.58 | 0.25 | 0.09 | 0.01 |

Desorption of organic materials from ACFM was studied in a vacuum adsorption setup with a quartz spring balance. The specimen was preevacuated (to a residual pressure of $1.33 \cdot 10^{-2}$ Pa) at 523 K to a constant mass, and then saturated by vapor of the adsorbate at the experiment temperature. After equilibrium was established, the adsorption cell with the specimen was connected to a vacuum system, in which the pressure was kept at about 10 Pa. Changes in mass were recorded by a cathetometer.

As is known, the pressure drop between the volume of micropores and in the evacuated volume is a motive force of vacuum desorption. A quasi-equilibrium state is established as the pressure decreases and the temperature is leveled. In this case, the residual amount of adsorbate is determined by its partial pressure in the system. On the basis of experimental data an attempt was made to use the thermal equation of adsorption from the theory of volume filling of micropores for calculation of the residual amount of the compound [8]:

$$a = a_0 \exp\left\{-\left[\left(\frac{A}{\beta E_0}\right)^n + \alpha (T - T_0)\right]\right\}, \tag{1}$$

where $a_0$, $E_0$, and $n$ are parameters to be determined from the adsorption isotherm of standard benzene vapor at $T_0$. In view of the fact that for the ACFM studied $n = 2$, by expressing the adsorption in dimensionless form $\theta = a/a_0$ and substituting the differential molar work $A = RT \ln (P_s/P_c)$ into Eq. (1), for the general case of desorption of organic materials, the relative residual filling of micropores can be expressed as

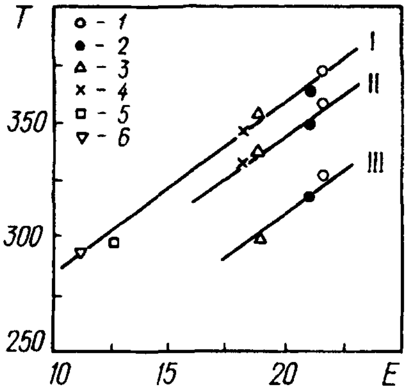
$$\theta = \exp\left\{-\left[\left(\frac{RT \ln P_s/P_c}{E}\right)^2 + \alpha (T - T_0)\right]\right\} \tag{2}$$

or in logarithmic form

$$\ln \theta = -\left[\left(\frac{RT}{E_0} \frac{\ln P_s/P_c}{\beta}\right)^2 + \alpha (T - T_0)\right], \tag{3}$$

where $R$ is the gas constant; $P_s$ and $P_c$ are the saturated-vapor pressure and the residual pressure of the adsorbate in the system at temperature $T$; $E = E_0\beta$ is the characteristic energy of adsorption; $\alpha$ is the thenrmal coefficient of limiting adsorption; $\beta$ is the similarity factor for the vapor considered.

From analysis of Eq. (3) the following conclusions can be drawn about the relationship between the structure of the ACFM and its holding capacity. It is known [8] that the coefficient $\alpha$ is almost constant in a wide temperature range. Then, under the same experimental conditions, if the residual pressure $P_c$ and temperature $T$ in the system are equal for different ACFM and the same adsorbate, $\theta = f(E)$, i.e., the relative residual adsorption, which characterizes the holding capacity of the adsorbent, is a function of the characteristic energy of adsorption. It is also known [9] that for carbon adsorbents there exists a certain relationship between the prevailing micropore dimension and the characteristic energy of adsorption. For example, for a slot micropore model, the half-width of the slot $X$ is related to the characteristic energy $E_0$ by the semiempirical equation [10].



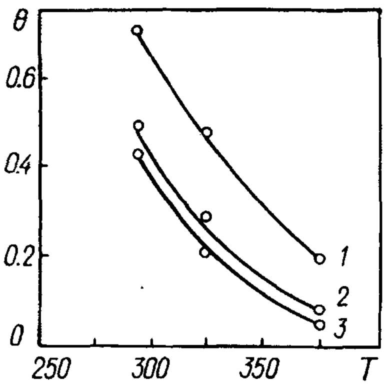


Fig. 1. Plot of temperature of vacuum desorption of organic solvents from ACFM-1 versus characteristic energy of adsorption for relative holding capacities of 0.2 (I), 0.3 (II), and 0.5 (III): 1) toluene, 2) perchlorethylene, 3) ethylacetate, 4) benzene, 5) acetone, 6) ethanol. $T$, K; $E$, kJ/mole.

Fig. 2. Plot of relative holding capacity of ACFM-1 in vacuum versus temperature (curves, calculation; points, experiment): 1) toluene, 2) benzene, 3) ethylacetate.

$$X = \frac{13.028 - 1.53 \cdot 10^{-5} E_0^{3.5}}{E_0}. \tag{4}$$

As can be seen from the experimental data for benzene at 293 K given in Table 1, the relative holding capacity of ACFM depends not on the limiting adsorption volume of micropores ($W_0$), but only on their dimension; a decrease in the half-width of micropores ($X$) results in an increase in the relative holding capacity. At higher temperatures, $\theta$ is almost independent of the micropore dimension as well. Thus, for ACFM with a higher $E_0$, i.e., with a smaller micropore dimension, the holding capacity is higher.

It is also known that holding capacity is not a property of the adsorbent alone, but also depends on the properties of the adsorbed material. In Eq. (3), the nature of the absorbate is taken into account by the constants $P_s$ and $\beta$. The effect of the characteristic energy of adsorption of acetone, benzene, perchlorethylene, toluene, ethanol, and ethylacetate ($E = \beta E_0$) on the relative holding capacity can be followed from experimental data given in Fig. 1, which is a plot of the temperature of ACFM-1 for $\theta$ equal to 0.2, 0.3, and 0.5 versus the characteristic energy of adsorption. As can be seen, the experimental curve is well approximated by a straight line, which indicates that as the characteristic energy of adsorption decreases, the relative holding capacity and the temperature of desorption also decrease. Similar curves are found for other ACFM specimens.

For the compounds enumerated above, the ACFM holding capacity was found in the temperature range 293–373 K from Eq. (2). The calculated and experimental curves of the residual adsorption of benzene, toluene, and ethylacetate for ACFM-1 are shown in Fig. 2. Comparison of the holding capacities determined experimentally and calculated from Eq. (2) shows that the behavior of $\theta$ as a function of temperature is the same, which indicates that the thermal equation of adsorption from the theory of volume filling of micropores can be used for description of thermal vacuum desorption.

The applicability of this equation for estimation of the holding capacity of ACFM-1 is also illustrated by Fig. 3, where experimental and calculated residual adsorptions of acetone, benzene, perchlorethylene, toluene, ethanol, and ethylacetate at 293 K are plotted versus the characteristic energy of adsorption in the coordinates of Eq. (3). As can be seen, the curves are linear. The experimental points fall fairly well on the calculated straight line. The maximum difference between the experimental and calculated ACFM holding capacities presented in Figs. 2 and 3 is within ±10%.

Thus, the study of the effect of the parameters of the porous structure of activated carbon fiber materials of the busofit type and the physicochemical properties of adsorptives on the residual adsorption at different

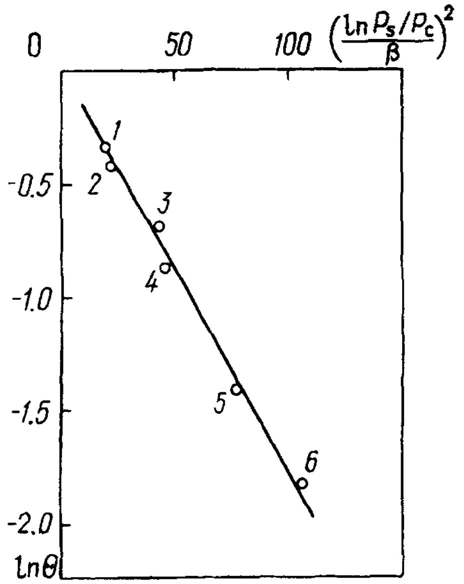


Fig. 3. Holding capacity of ACFM-1 at 293 K for organic solvents in coordinates of thermal equation of adsorption (curve, calculation; points, experiment): 1) toluene, 2) perchlorethylene, 3) ethylacetate, 4) benzene, 5) acetone, 6) ethanol.

temperatures has shown that the state that is established at a constant temperature and falling pressure can be considered as quasi-equilibrium state. The fair agreement of the calculated and experimental residual desorptions as a function of temperature confirms that the thermal equation of desorption from the theory of volume filling of micropores can be used for description of this quasi-equilibrium state. The present results indicate that this equation provides ±10% accuracy for ACFM holding capacity in the case of thermal vacuum desorption of organic solvents with various physicochemical properties in the presence of experimental information only about the adsorption isotherm of standard benzene vapor for a particular adsorbent.

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