Journal of Engineering Physics and Thermophysics, Vol. 83, No. 5, 2010

THEORETICAL AND EXPERIMENTAL STUDIES OF THE POROUS STRUCTURE AND ADSORPTION PROPERTIES OF CARBOFIBROUS MATERIALS

A. F. Dolidovich and G. S. Akhremkova

UDC 541.183

We have made theoretical and experimental studies of the porous structure and adsorption properties of activated carbon fibrous materials and granular activated carbon with respect to vapors of benzene, toluene, ethylacetate, and acetone. The parameters of the porous structure of adsorbents have been determined by the adsorption by them of the standard substance — benzene — and used to calculate their adsorption characteristics with respect to the investigated organic solvents. A good agreement between the calculated and experimental characteristics for all investigated adsorbents has been obtained. The dependence of adsorption properties of activated carbon fibrous adsorbents and granular activated carbon on the volume and size of adsorbing pores, as well as on the molecular polarizability of the adsorptive, has been established.

Keywords: *adsorption, granular activated carbon, activated carbon fiber, vaporous volatile organic substance, isotherm.*

Introduction. The most popular methods for decontaminating volatile organic substances (VOSs) are their thermal and catalytic oxidation, absorption by aqueous or chemical solutions, and adsorption by porous carbon materials, mainly by activated carbons [1].

Compared to the methods of oxidation of VOSs, the adsorption of these substances by activated carbons is especially effective in technological processes connected with the extraction, separation, and purification of substances, since it potentially provides the possibility of reusing them upon regeneration as well returning valuable VOSs into production processes [2].

Along with activated carbons, in adsorbers and recuperators of organic solvents, in air cleaning and odor-absorbing systems, and in systems for cleaning process solutions and waste waters from organic impurities, activated carbon fibers (ACFs) are finding ever increasing use since, due to their high adsorption and kinetic characteristics and effective action in the region of low concentrations [3], they make it possible to decrease the mass of the adsorbent used and create convenient-to-use filters of specified density and form.

Samples and Experimental Procedure. In this paper, we present the results of investigating the porous structure and adsorption properties of commercial carbon fibrous adsorbents — woven Busofit-T material (WM) and unwoven (carbofelt) Carbopone-Active material (UM), as well as AR-3 granular activated carbon (GAC) used as a comparison sample.

In the general case, activated carbon adsorbents may contain all kinds of pores: micro-, meso-, and macropores. However, their role in the process of vapor absorption is different. According to multiple experimental data [4, 5], in typical practical events, the adsorption of gases and volatile organic substances is concentrated mainly in micro- and mesopores classified with adsorbing pores. The larger pores — macropores — play the role of transport channels for molecules of adsorbed substances and their adsorption can be neglected [4]. Therefore, the present study considers only the parameters of adsorbing pores. To determine the volume of the pores of the investigated adsorbents, the isotherms of adsorption by them of vapors of the standard adsorptive — benzene — were measured. The adsorption properties of ACFs and GACs were determined with respect to toluene, ethylacetate, isobutanol, and acetone, which were chosen for their volatility limits, polarizability, and molecular mass.

A. V. Luikov Heat and Mass Transfer Institute, National Academy of Sciences of Belarus, 15 P. Brovka Str., Minsk, 220072, Belarus; email: adol@hmti.by. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 83, No. 5, pp. 861–865, September–October, 2010. Original article submitted November 26, 2009.

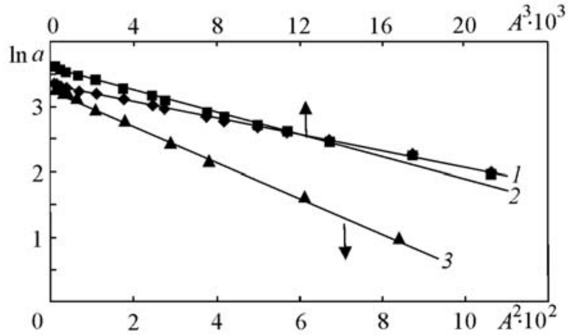

Fig. 1. Isotherms of benzene adsorption by different materials: 1) WM; 2) UM; 3) GAC. A, kJ/mole.

TABLE 1. Parameters of the Porous Structure of the Adsorbents Determined by Benzene

Adsorbent	n	W_0, cm^3/g	E_0, kJ/mole	X, nm	V_{me}, cm^3/g	V_s, cm^3/g	S_{me}, m^2/g
WM	3	0.417	22.8	0.53	0.168	0.585	84
UM	3	0.336	26.5	0.44	0.124	0.460	53
GAC	2	0.308	18.4	0.67	0.046	0.354	18

Measurements of adsorption isotherms were made on a gravimetric vacuum assembly [5] under static conditions at 293 K in the range of equilibrium relative pressures P/P_s from 10^{-4} to 0.995. The adsorbent was preliminarily vacuum-degassed at 523 K to a constant mass.

Results and Discussion. The experimental data obtained were processed by means of the calculation apparatus of the theory of volume filling of micropores (TVFM) [6], in particular, by the Dubinin–Radushkevich–Astakhov equation [7], written in general form as

$$a = a_0 \exp\left[-\left(\frac{A}{E}\right)^n\right] = W_0 \rho \exp\left[-\left(\frac{A}{E_0 \beta}\right)^n\right]. \tag{1}$$

The quantity $A = RT \ln (P/P_s)$ is the molar work of substance compression from the equilibrium pressure P to the pressure of saturated vapors of the liquid P_s at the experimental temperature T. The characteristic adsorption energy $E = E_0\beta$ is equal numerically to A at $a = 0.368a_0$. It should be noted that the use of Eq. (1) for determining the microporous structure parameters W_0, E_0, and n for benzene is determined in a specific instance by the linearity of the dependence of ln a on A^n. The selection of a reliable value of n by the experimental data has shown that at $n = 2$ for GACs and at $n = 3$ for ACFs the dependence ln $a = f(A^n)$ is linearized in a fairly wide range of relative pressures (Fig. 1). The adsorption isotherms of benzene on GACS and UMs are linear in the range of equilibrium relative pressures P/P_s from 10^{-5} to 0.1, which points to the high homogeneity of micropores and permits estimating the microporous structure of these adsorbents with a high degree of accuracy. At the same time, for WMs in the range of relative pressures $P/P_s < 10^{-4}$, a deviation from linearity is observed, which is explained, apparently, by the presence in them, apart from micropores, of submicropores as well.

The porous microstructure parameters of ACFs and GACs — the total volume of micropores W_0, the characteristic adsorption energy E_0, the micropore half-width X, the volume of mesopores V_{me}, and the limiting volume of the adsorption space V_s determined by the standard vapor – benzene – are given in Table 1.

As is seen from Table 1, the main volume of the adsorption space of the investigated adsorbents falls on micropores. Granular activated carbon contains an insignificant amount of mesopores, about 13%, while in activated carbofibrous materials the volume of mesopores constitutes, on average, 28% of the total adsorption volume of the pores. Comparison of the adsorption characteristics of the investigated ACFs and GACs shows that the UM has a minimum size of micropores and a maximum characteristic adsorption energy, and also that such adsorption-structural characteristics as the volume of micropores, the specific surface, and the volume of macropores are lower in it than in the WM but higher than in the GAC.

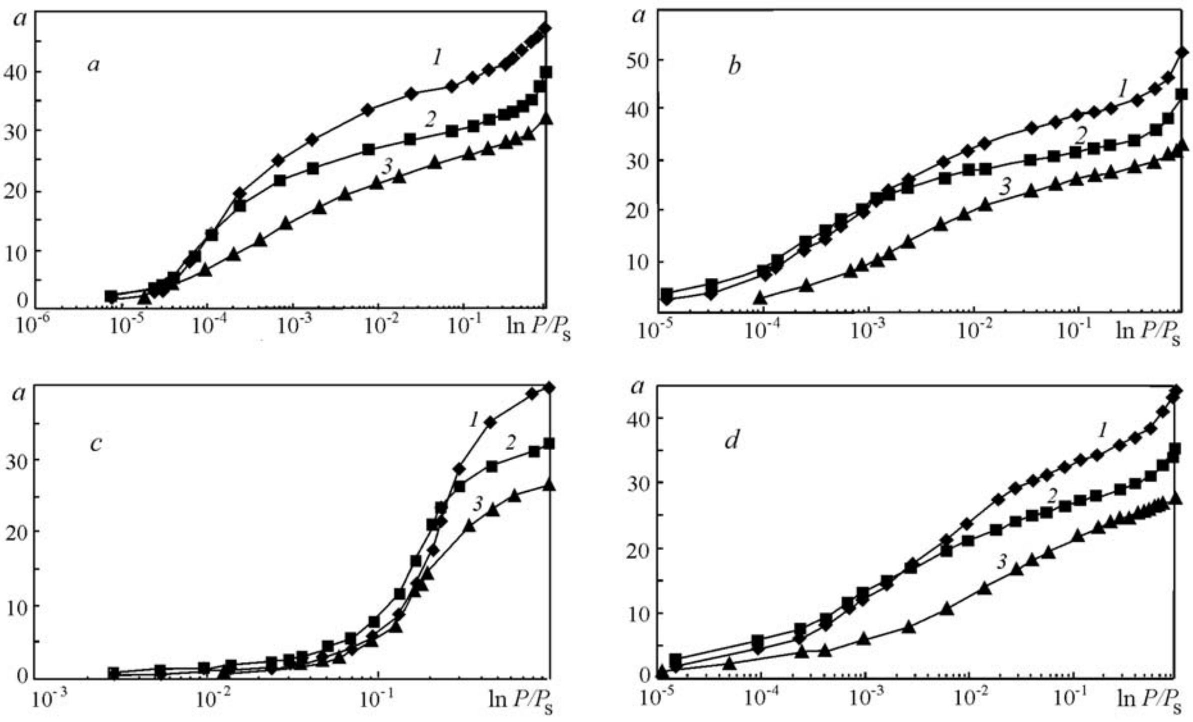

Fig. 2. Adsorption isotherms of toluene (a), acetylacetate (b), isobutanol (c), and acetone (d) on activated carbon fibers and granular activated carbon. Designations 1–3) same as in Fig. 1. *a*, mass %.

The experimental adsorption isotherms of toluene, ethylacetate, isobutanol, and acetone vapors by the ACFs and GAC are presented in Fig. 2. On their basis a comparison of the adsorptivity of the investigated adsorbents at various relative pressures has been made. As seen from Fig. 2, for each substance in the range of low pressures ln $P/P_s < 10^{-3}$, the adsorption on the woven and unwoven materials is practically equal. Obviously, this corresponds to the filling of micropores close in size present in the porous structure of the given adsorbents. At higher pressures the adsorption on the woven material is more active. The maximum pressure below which equality of adsorption on ACFs is observed for all VOSs is different and correlates well with the change in the structural characteristics, namely: the larger the size of the micropores, the higher the region of relative pressures in which the filling of micropores close in size is observed. As compared to the GAC, the adsorption capacity of the ACFs is higher throughout the investigated range of pressures.

Analysis of the curves of the adsorption isotherms of VOSs in the region of low relative pressures illustrates some of their differences. This shows up most vividly in the case of the adsorption of isobutanol. For both the ACFs and the GAC, the adsorption isotherms of isobutanol differ in the concave portion in the region of ln $P/P_s < 0.2$ (Fig. 2a), which is due to the stronger intermolecular interaction of adsorbate molecules with one another compared to the interaction of adsorbate molecules with the adsorbent.

The calculation apparatus of the TVFM makes it possible to calculate by the parameters of the porous structure of the ACFs and GAC determined by the adsorption of benzene by them the adsorption characteristics of these adsorbents with respect to the other VOSs [6, 7]. Some of them (the limiting quantity of the adsorbent in micropores a_{mi} and in the volume of adsorbing pores a_s and the characteristic adsorption energy E) determined from the experimental adsorption isotherms of the VOSs (Fig. 2) and calculated by the porous-structure parameters of the investigated adsorbents (Table 1) are given in Table 2.

As is seen, for each adsorbent–adsorbate system the calculated limiting value of adsorption in the volume of micropores is close to that determined directly from the experimental isotherm and differs by no more than 5%. The limiting value of adsorption of toluene, ethylacetate, and acetone in the total volume of the adsorption space is also close to the calculated one, whereas for isobutanol it is smaller than the calculated one, on average, by 14% and 9%

TABLE 2. Adsorption Characteristics of the Adsorbents with Respect to the Vapors of Volatile Organic Substances

Adsorbent	a_{mi}, mass %		E, kJ/mole		a_s, mass %	
	Calculation	Experiment	Calculation	Experiment	Calculation	Experiment
			Toluene C_7H_8			
WM	36.15	37.37	27.2	24.4	50.72	47.16
UM	29.13	29.39	31.7	28.2	39.88	39.80
GAC	26.70	27.48	22.0	20.4	30.69	32.08
			Ethylacetate $C_4H_8O_2$			
WM	37.55	37.82	23.9	20.3	52.68	51.24
UM	30.26	30.44	27.7	23.8	41.42	42.95
GAC	27.74	28.46	19.3	16.5	31.88	32.87
			Isobutanol $C_4H_{10}O$			
WM	33.49	32.05	22.8	2.0	46.98	39.91
UM	26.98	26.98	26.5	2.2	36.94	32.12
GAC	24.73	23.62	18.4	2.2	28.43	25.46
			Acetate C_3H_6O			
WM	32.96	32.96	17.7	17.9	46.24	44.26
UM	26.56	25.48	20.5	19.6	36.36	35.08
GAC	24.35	25.30	14.3	13.5	27.98	27.15

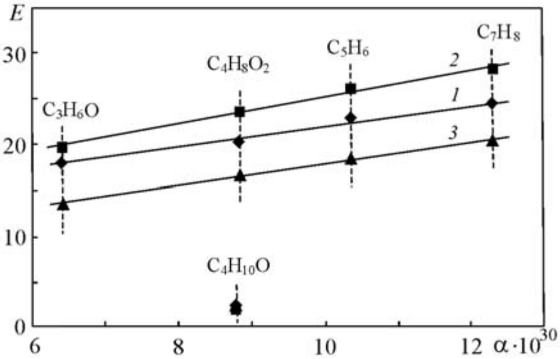

Fig. 3. Dependence of the characteristic adsorption energy on the molecular polarizability of the adsorptive. Designations 1–3) same as in Fig. 1. E, kJ/mole; α, m^3/molecule.

for the ACFs and the GAC, respectively. This points to the fact that the density of adsorbed isobutanol is much lower than the density of the liquid adsorptive. The experimental and calculated values of the characteristic adsorption energy of the investigated substances are also in good agreement with each other. The E value therewith is independent of the volume of micropores and depends only on their size and the adsorptive's properties: it is maximal for all VOSs in the case of adsorption on the unwoven activated material having a minimum micropore width and decreases with increasing micropore size. This conclusion holds for all substances except isobutanol, for which the experimental value of the characteristic adsorption energy is much smaller than the calculated one and is practically independent of the size of adsorbent micropores. This is likely due to the lower surface-tension coefficient and the wettability of the carbon surface with alcohols.

In estimating the adsorptive interaction energy of volatile organic substances with carbon adsorbents, the influence of the dispersion forces is taken into account first of all. As one of the factors determining the dispersive interaction potential, the molecular polarizability of the investigated substances can be considered. Figure 3 shows the dependence of the characteristic adsorption energy on the molecular polarizability of the investigated substances increasing in the following sequence: $C_3H_6O < C_4H_{10}O < C_4H_8O_2 < C_7H_8$ [8]. As is seen, the characteristic adsorption energy increases in an analogous sequence and, in so doing, for each adsorbent a practically linear dependence between the characteristic adsorption energy and the molecular polarizability of the adsorptive is observed.

Conclusions. It has been shown that by the porous-structure parameters of the investigated adsorbents determined by the adsorption by them of the standard vapor – benzene – their adsorptivity with respect to the vapors of the other organic substances can be determined with a fair accuracy. The calculated values of the limiting adsorption of toluene, ethylacetate, isobutanol, and acetone vapors in the volume of micropores and in the total volume of the adsorbing pores of ACFs and GACs are in good agreement with the corresponding characteristics of these substances obtained from the experimental adsorption isotherms.

The experiments and calculations performed have shown that the adsorptivity of the ACFs and GACs with respect to VOSs depends, as would be expected, on the volume of adsorbed pores, while their energy characteristics depend on the pore size and the polarizability of adsorbing molecules. It has also been revealed that the adsorption of all the investigated VOSs by the activated carbon fibers in woven and unwoven forms in the region of low relative pressures ln $P/P_s < 10^{-3}$ is practically the same, whereas at ln P/P_s close to unity the adsorptivity of unwoven materials is somewhat lower: on average by 18% with respect to toluene and ethylacetate and by 25% with respect to isobutanol and acetone. It has been established that the adsorptivity of the ACFs with respect to the above VOSs is much higher (by 3.0–1.2 times, on average) compared to the GACs throughout the investigated range of pressures.

The data obtained confirm the possibility of successful use of ACFs in gas purification systems for scrubbing gas flows. These data can be useful in calculating and designing adsorption equipment for gas purification and technological systems.

NOTATION

A, molar work of adsorption, kg/mole; a, quantity of adsorbate, mass %; a_{mi}, quantity of adsorbate in micropores, mass %; a_0, quantity of benzene in micropores, mass %; a_s, limiting quantity of adsorbate in the volume of adsorbing pores, mass %; E_0, characteristic adsorption energy for benzene, kJ/mole; E, characteristic adsorption energy, kJ/mole; n, constant; P, pressure of adsorptive vapors, Pa; P_s, pressure of adsorptive saturated vapors at a temperature of 293 K, Pa; R, universal gas constant; S_{me}, specific surface of mesopores, m^2/g; V_{me}, volume of mesopores, cm^3/g; V_s, limiting volume of the adsorption space, cm^3/g; T, experimental temperature, K; W_0, adsorption volume of micropores for benzene, cm^3/g; X, micropore half-width, nm; α, molecular polarizability, m^3/molecule; β, affinity coefficient; ρ, adsorbate density in micropores equal to the liquid adsorptive density, g/cm^3. Subscripts: me, mesopores; mi, micropores; n, exponent; 0, characteristics for benzene; s, saturated, limiting.

REFERENCES

1. A. F. Dolidovich and G. S. Akhremkova, Innovative gas cleaning technologies preventing the environmental contamination by heat and CO_2, *Proc. 2nd EUROENVIRONMENT-2000 Conf.*, 18–20 October 2000, Denmark, Aalborg (2000), pp. 48–51.
2. V. Ya. Varshavskii, *Carbon Fibers* [in Russian], Khimiya, Moscow (2005).
3. I. N. Ermolenko, I. P. Lyubliner, and N. V. Gul'ko, *Element-Containing Carbon Fibrous Materials* [in Russian], Nauka i Tekhnika, Minsk (1982).
4. N. V. Kel'tsev, *Principles of the Adsorption Technique* [in Russian], Khimiya, Moscow (1984).
5. M. M. Dubinin, *Adsorption and Porosity* [in Russian], Voen. Akad. Khim. Zashchity, Moscow (1972).
6. A. F. Dolidovich and G. S. Akhremkova, Novel technologies of VOC decontamination in fixed, moving, and fluidized catalyst-adsorbent beds, *Canadian J. Chem. Eng.*, **77**, No. 2, 253–258 (1999).
7. M. M. Dubinin and V. A. Astakhov, Development of notions on the volumetric filling of micropores in the process of adsorption of gases and vapors by microporous adsorbents, *Izv. Akad. Nauk SSSR, Ser. Khimicheskaya*, No. 1, 5–11 (1978).
8. E. A. Melvin-Hughes, *Physical Chemistry* [Russian translation], Vol. 1, IL, Moscow (1962).