Development of nonuniform micropore structure of carbon adsorbents during activation: adsorption and small-angle X-ray scattering studies

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The development of the micropore structure of activated carbons during activation was studied by small-angle X-ray scattering and adsorption methods. A new method for the processing of experimental data was used; this method makes it possible to obtain curves of the dimension distribution of micropores from the intensities of small-angle X-ray scattering and the adsorption isotherm. In the initial stage of activation, up to burnouts $\omega \leq 0.3$, the micropore structure is uniform, micropores with radius of gyration under 0.5—0.6 nm dominate. When activation is more prolonged ($\omega = 0.3 \div 0.67$), a bimodal system with $R_1^{\max} \approx 0.6$ nm and $R_2^{\max} \approx 0.85 \div 1.0$ nm forms, and the volume of large micropores (supermicropores) exceeds that of small ones considerably.

Key words: carbon adsorbents, small-angle X-ray scattering, adsorption, bimodal dimension distribution of micropores.

In recent years, great interest has been expressed in the development of methods for the analysis of the dimension distribution of micropores in carbon adsorbents. The most promising works are those in which data obtained by different methods (in particular, small-angle X-ray scattering and adsorption) are used. In this case, a series of alternatives was proposed for determining the dimension distribution; these methods are based on the Dubinin—Radushkevich equation[1—6] and its modifications.[7, 8]

In the integrated form, the equation of physical adsorption of vapor by nonuniform microporous carbon adsorbents can be written as follows:

$$\omega(y) = \int_0^\infty \upsilon(R)\theta(y,R)\mathrm{d}R, \qquad (1)$$

$y = [(T \cdot \log p/p_s)/\beta)]^2$; $\theta(y,R) = \exp(-bR^2y)$; $b = 1.6 \cdot 10^{-6}$, where R is the radius of inertia, the linear characteristic applicable to micropores of an arbitrary shape; T is temperature, β is the similarity coefficient; p/p_s is relative pressure; $\upsilon(R)$ is the radial distribution function for micropore volumes; $\theta(y,R)$ is the local adsorption isotherm (the adsorption isotherm for the system containing identical micropores with radius of gyration R), which can be expressed by the Dubinin—Radushkevich equation or by its modifications.

Expression (1) is analogous to the integral equation obtained previously[1,4] and differs from the latter only in that instead of the half-width of micropores x, an alternative linear parameter is used, namely, the radius of giration R, related to x by the simple equation $R = 1.23x$. Parameters R and x appear in the equation after substituting $R = 14.8E_0^{-1}$ or, respectively, $x = 12E_0^{-1}$, where E_0 is the characteristic adsorption energy in the Dubinin—Radushkevich equation.[1] The relation between R, x, and E was obtained empirically[2,4,5,9] and only for carbon adsorbents, therefore, application of Eq. (1) is restricted only to this class of materials.

When solving Eq. (1), most authors use the preliminary definition of the form of the dimension-distribution function, reducing thereby the solution to the choice of parameters of the chosen function $\upsilon(R)$ (or $f(x)$). A Gaussian distribution is most often used for this purpose;[1—4] alternative types of unimodal functions are used more rarely.[7,8] However, the actual distribution of micropores in the adsorbent may differ essentially from the given one. Moreover, this distribution may be polymodal rather than unimodal as evidenced by the results of a series of works in which, based on analysis of adsorption isotherms, it was suggested that the micropore structure has a bidispersed character. A number of other drawbacks of the procedure, which involves an *a priori* definition of the distribution of the Gaussian type, were discussed in Ref. 6. The solution proposed in Ref. 6 requires no preliminary definition of the distribution function and is free from the above mentioned drawbacks. This procedure was originally developed for solving the analogous integral equations (Fredholm equation of the first kind) for small-angle X-ray scattering.[10]

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Table 1. Characteristics of the micropore structure of carbon samples of the E series (ω, the volume of micropores v_{1mi} and v_{2mi}, v_{mi}*, the characteristic adsorption energy E_0)

Sample	ω	v_{1mi} /cm$^3 \cdot$ g^{-1}	E_{01} /kJ $\cdot$ mol^{-1}	v_{2mi} /cm$^3 \cdot$ g^{-1}	E_{02} /kJ $\cdot$ mol^{-1}	$v_{1mi}+v_{2mi}$ /cm$^3 \cdot$ g^{-1}	v_{mi}* /cm$^3 \cdot$ g^{-1}	v_{me} /cm$^3 \cdot$ g^{-1}
E-0	0	—	—	—	—	—	—	—
E-2	0.32	0.212	24.9	0	—	0.212	0.24	0.029
E-4	0.48	0.236	22.3	0.07	12.3	0.306	0.363	0.039
E-6	0.67	0.22	20.2	0.22	9.26	0.44	0.42	0.079

* Volume of micropores calculated from Eq. (2).

The solution is based on either the application of the Laplace method[11] or the combination of the Laplace method and the method of successive approximations.[10] These methods were used for solving Eq. (1).[5,6] The solution proposed later[6] is more rigorous and accurate. It can be represented as follows:

$$v_n(R) = N_n(R)R^3 \qquad (2)$$

$$N_n(R) = \frac{w(y)N_{n-1}(R)}{\mathrm{A} \cdot N_{n-1}(R)}\;; \quad R = \mathrm{C}_n \cdot \sqrt{\frac{1.5}{b \cdot y}}\;,$$

where $\mathrm{A} \cdot N_n(R) = \int\limits_0^\infty N_{n-1}(R)R^3\exp(-bR^2y)\mathrm{d}R$ is the linear integral operator, $N(R)$ is the number of micropores with radius of gyration R, C_n is a constant dependent on the order number of the approximation n. As the calculations for model systems showed,[6] solution (2) is reasonably accurate, even in the case of an intricate bimodal distribution.

In this work, data on the development of the micropore structure of carbon adsorbents during activation is presented; this data was obtained by small-angle X-ray scattering and adsorption methods.

Experimental

We studied samples prepared from granulated coal based on anthracite and resin and activated with water vapor at 900 °C to different burnouts (ω), the values of which are given in Table 1. Table 1 also shows the volumes of micro- and mesopores, and the parameters E_{01} and E_{02} calculated from the adsorption isotherms for benzene at 20 °C in the p/p_s range $1 \cdot 10^{-5}$ to 1. Conditions of sample preparation and the procedure for processing the adsorption data have been described in more detail previously.[12]

Intensities of small-angle X-ray scattering were measured on a KRM-1 instrument using nickel-monochromated Cu $K\alpha$ radiation. Measurements were carried out in the angle range $h = 4.7 \cdot 10^{-3}$ to $6.0 \cdot 10^{-1}$ Å^{-1} ($h = 4\pi\sin\theta/\lambda$, 2θ is the angle of scattering, λ is the wavelength of characteristic radiation).

To eliminate collimation distortions, the scattering curves were corrected for the height and width of the collimating slit using a program developed at the Institute of Crystallography of the Russian Academy of Sciences.[13] For processing the data of small-angle X-ray scattering, the form-factor suitable for roughly equiaxial particles (pores) of arbitrary form was used.[14] Therefore, it was not necessary to specify any definite form of micropores. Distortions of the distribution function caused by the finite extent of the range of measurements were eliminated by applying a correcting multiplier[15] ("temperature" multiplier) in the form of the function $(1 + \gamma h^2)^{-1}$, where γ is a constant chosen in the process of calculations.

The program for processing the adsorption measurements, in which the algorithm of solution (2) was used,[6] includes a unit allowing extrapolation of the adsorption isotherm to the region of lower filling. Thus, we managed to avoid the effect of "break waves", *i.e.*, distortions resulting from termination of the $w(y)$ function after integral transformations.

Results and Discussion

The curves of the dimension distribution of micropore volumes, which represent the results of processing the adsorption isotherms and the intensities of small-angle X-ray scattering, are shown in Fig. 1. For the initial sample E-0, only the small-angle distribution is given. We failed to obtain reliable adsorption data because a high proportion of micropores appears to be inaccessible to benzene molecules owing to the blocking of entries. However, for small-angle X-ray scattering these blocked pores virtually do not differ from the open pores. This effect has been discussed in more detail previously.[16]

The curves calculated from adsorption data were not normalized, therefore, areas under the curves correspond to the volumes of the micropores in the samples. These volumes in the interval $R \approx 0.2 \div 1.6$ nm (1.6 nm is the upper limit of validity of the theory of volume filling[1]) are given in Table 2. These values agree well with micropore volumes calculated from adsorption isotherms by the conventional method;[12] the latter values are also given in Table 2. For convenience of comparison, the distributions calculated from data on small-angle X-ray scattering were normalized with respect to the corresponding adsorption distributions, so that the heights of their major maxima were equal.

Changes in the distribution curves reflect changes in the micropore structure during activation. In the initial sample, the micropore structure is characterized by a rather narrow uniform distribution with an average radius gyration of ~0.5 nm. This uniform structure is substantially retained in the ω range $0 \div 0.3$. However, at ω ~0.3, the distribution becomes broader; the average

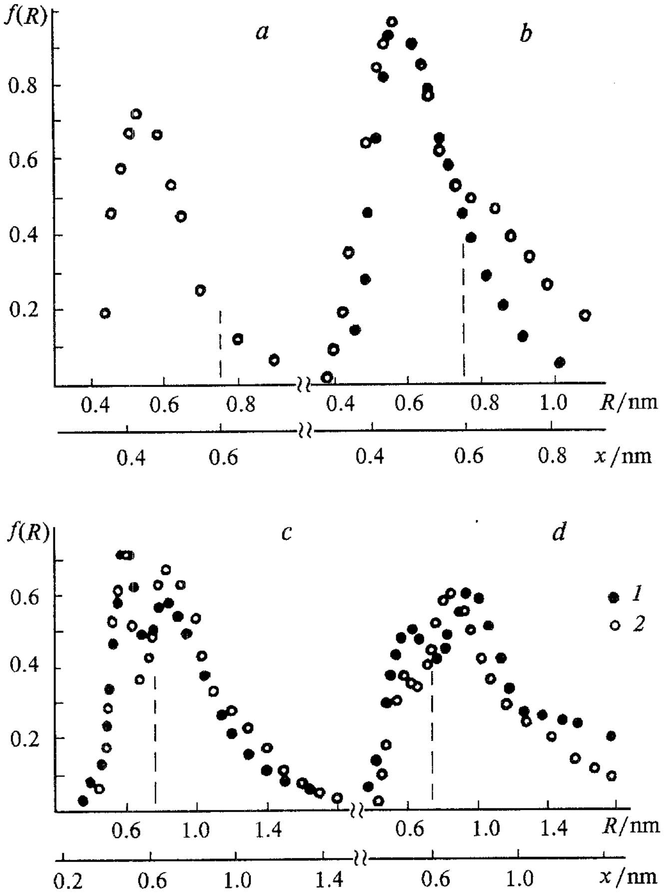

Fig. 1. Dimension distribution curves of micropore volumes for samples: E-0 (*a*), E-2 (*b*), E-4 (*c*), and E-6 (*d*); (*1*) adsorption data, (*2*) small-angle X-ray scattering data.

dimension R, which corresponds to the position of the maximum of curves in Fig. 1, *b*, increases to ~0.6 nm, both distributions (X-ray and adsorption) are nearly the same at $R < 0.8$ nm. In the interval of $R > 0.8$ nm, the small-angle X-ray scattering method is more sensitive to large micropores, the appearance of which manifests itself clearly in the right-hand part of the curve in Fig. 1, *b*. It should be mentioned that in the ω range 0÷0.3 not only are the entries of the micropores unblocked, which makes the micropores available for adsorption of benzene molecules, but also the total volume of micropores increases by a factor of ~2—2.5, as follows from small-angle X-ray scattering data. Because their average dimension changes only slightly (<20 %), it could be suggested that the increase in the volume is mainly due to the formation of new micropores.

More prolonged activation (Figs. 1, *c*, *d*; samples E-4 and E-6) results not only in the broadening of the distribution curve, but also in the appearance of a second maximum on the curve; the height of this maximum for E-4 is comparable with that of the first maximum, for E-6 the height of the second maximum exceeds that of the first one. These changes are caused by the formation of a fraction of larger micropores, supermicropores,[1,12] the dimensions of which are 1.5—2 times larger than those of the small initial ones (E-0 and E-2). The position of the first maximum on the distribution curve is virtually unchanged, *i.e.*, the dimensions of the small micropores remain unchanged. This is most evident in Fig. 1, *c*, in which the distribution curves calculated from the X-ray and adsorption data coincide; in Fig. 1, *d* (E-6) the slight shift of the first maximum to greater values of R is evidently caused by the effect of the superposition of the distribution of supermicropores rather than by an increase in dimensions.

To analyze the bimodal structure in more detail, we arbitrarily partitioned the areas under the curves into two parts (see Fig. 1, dashed line): the region of smaller pores with $R \le 0.75$ nm and the region of larger micropores with $0.75 \le R < 1.6$ nm. We chose the interval of $R \le 0.75$ nm according to Figs. 1, *a*, *b*; the region of small initial micropores is clearly defined in this interval. The volumes v_1 and v_2 (see Table 2) for each fraction were calculated from the adsorption distribution curves, because the volumes in curves of small-angle X-ray scattering are expressed in relative rather than absolute units. As is evident from the data given in Table 2, the decrease in volume $-\Delta v_1$ in the range $\omega = 0.32 \div 0.67$ is considerably smaller (by a factor of ~4) than the increase in volume Δv_2. Two versions of the mechanism of the development of the bimodal structure are possible, namely: (1) supermicropores are formed owing to the burnout of separate large sections of the

Table 2. Radius of gyration of micropores (nm) calculated from positions of maxima of the distributions ($R_1^{\max}$ and $R_2^{\max}$) and by the tangent method (R_1^{t} and R_2^{t})

Sample	Small-angle X-ray scattering				Adsorption				v_1*	v_2*
	$R_1^{\max}$	R_1^{t}	$R_2^{\max}$	R_2^{t}	$R_1^{\max}$	R_1^{t}	$R_2^{\max}$	R_2^{t}	$R \le 0.75$	$0.75 \le R \le 1.6$
E-0	0.55	0.55	—							
E-2	0.60	0.65	—	1.15	0.58	0.60	—	—	0.180	0.060
E-4	0.60	0.70	0.85	1.20	0.60	0.66	0.84	1.2	0.136	0.226
E-6	0.60	0.70	0.85	1.35	0.65	0.73	1.00	1.6	0.122	0.297
									$-\Delta v_1 = 0.058$	$\Delta v_2 = 0.237$

* Values are given in $cm^3 g^{-1}$.

solid phase, rather than at the expense of small micropores (which is unlikely); (2) supermicropores are formed by enlarging small micropores while small micropores continue to be generated. The second version seems to be more reliable, or, at least, prevailing. This version is confirmed by the fact that the position of the first distribution maximum is virtually unchanged; the constancy of $R_1^{\max}$ also indicates that the dimension of the small pores generated is the same as that of the pores present in the initial stage (E-0 and E-2).

The supermicropores are formed largely through coalescence of small micropores due to burnout of the walls separating the micropores. This is evident from the ratio $R_2^{\max}/R_1^{\max} \approx 1.5$ and the approximately constant position of the second maximum (see Table 2).

The distributions presented in Figs. 1, *c*, *d* can be interpreted in terms of two mutually overlapped distributions of different fractions of micropores (a bidispersed structure according to the previously accepted nomenclature) or in terms of a bimodal broad distribution. In our opinion, the last alternative is more general and correct.

Previously, the tangent method has been used for studying the micropore structure of activated carbons (among them, carbons of the E series).[1,2,12] This method is equally appropriate for processing the experimental small-angle X-ray scattering and adsorption data owing to the formal analogy between Guinier's exponential equations (small-angle scattering)[13] and the Dubinin—Radushkevich equation.[1] Both equations can be written in logarithmic coordinates in the form:

$$\ln I = \ln I_0 - (hR)^2/3 \qquad (3a)$$

$$\ln a = \ln a_0 - (1/E_0)^2 \cdot \mathrm{A}^2, \qquad (3b)$$

$$\mathrm{A} = R_c T \ln (p/p_s),\ R = 14.8/E_0,$$

where I is the intensity of small-angle X-ray scattering, h is the scattering vector, a is the value of sorption at p/p_s and temperature T, and R_c is the gas constant.

Only discrete values of dimensions and the corresponding volumes are determined by the tangent method from Eqs. (3a) and (3b). Specifically, in microporous carbons as few as one (uniform micropore structures) or two (nonuniform structures) dimensions are usually calculated. In the latter case, it cannot be unambiguously determined from these discrete values whether they characterize two fractions of micropores of a broad unimodal distribution or two different distributions. This refers equally to the small-angle X-ray scattering and adsorption data. The procedure used in this work gives more detailed information (see Figs. 1, *c, d*).

Data given in Table 2 attest to close agreement between $R_1^{\max}$, which corresponds to the position of the distribution maxima, and R_1^{t} calculated by the tangent method (for X-ray and adsorption data). For R_2, the agreement is significantly worse: the values calculated from tangents are 1.5 times larger than $R_2^{\max}$. This is because the larger micropores with $R > R_2^{\max}$ and considerable volume contribute significantly to these values, though they are averaged (see Figs. 1, *c*, *d*). It has been mentioned above that in Fig. 1, *b* in the interval $R > 0.8$, the distribution curve calculated from small-angle X-ray scattering data passes considerably above the adsorption curve, thus pointing to the higher sensitivity of small-angle X-ray scattering to larger micropores. This distinction remains when the data are processed by the tangent method, that is, we managed to determine the R_2^{t} parameter corresponding to supermicropores in E-2 only from the small-angle X-ray scattering data. Figure 1, *b* indicates that the appearance of this parameter does not signify the formation of a bidispersed structure, but reflects broadening of the initial distribution at the expense of the larger micropores.

Comparison of v_1 and v_2 revealed significant differences. The v_2 values calculated by the tangent method are substantially smaller than the v_1 values, whereas from the distributions presented in Figs. 1, *c*, *d*, the opposite is true. As the tangent method is essentially a rough approximate solution of integral Eq. (1), and solution (2) is more rigorous and accurate (both in the cases of small-angle X-ray scattering and adsorption), the results calculated using solution (2) must be considered more reliable. Estimates obtained by the tangent method including the two-term expression for the adsorption isotherm[1,12] are rougher and carry less information; when the micropore structure of carbons is analyzed, these estimates can be used as a first approximation. In this work, we did not compare the results obtained from solution (2) with those obtained by an *a priori* definition of the form of the distribution function. As was previously demonstrated,[6] in the case of the unimodal narrow distributions, the results obtained by these methods are similar. In the case of bimodal systems, comparison with the unimodal distribution makes no sense.

Therefore, this study demonstrated that the use of the solutions of the integral equations for small-angle X-ray scattering and adsorption proposed in Refs. 6 and 10 enables one to obtain more detailed and reliable information on the nonuniform micropore structure of carbon adsorbents than that obtained by the tangent method or by an *a priori* definition of the form of the distribution function. The results obtained indicate that on prolonged activation a bimodal system is formed, in which primarily supermicropores are formed owing to coalescence of micropores due to burnout of walls separating micropores.

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