ANALYSIS OF THE PORE STRUCTURE OF ADSORBENTS AND ITS CHARACTERIZATION BY A NUMERICAL METHOD

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This paper describes the algorithm of numerical evaluation of the parameters of the pore structure of adsorbents (the micro, mezo and macropores). The structure of individual types of pores is described with the equation proposed by one of the present authors and giving the total distribution function of the pores with respect to their radii. The reliability of the suggested algorithm was verified in a number of calculations using a specially developed program. The results of the analysis and characterization of three different specimens of active carbon are shown as an example.

In recent years, it has been possible to observe an extensive development of methods of analysis and characterization of the pore structure of the adsorbents. The described methods are based on application of various experimental techniques. In the case where we are concerned with the analysis of the micropores with dimensions comparable with the size of the molecules (up to radii 1·5 nm), the adsorption methods are still of primary importance. The development of the last mentioned methods has been strongly enhanced by the idea of Dubinin and Radushkevich[1] who resolved to generalize the extended experimental material which was available from the studies of the adsorption isotherms, by expressing the obtained "characteristic" curves in the form of a mathematical function. The "characteristic" curves described the dependence of the differential molar work of adsorption A on volume of the adsorption space $W = av$, where a is the amount adsorbed and v is the molar volume of a substance in adsorbed state. The differential molar work of adsorption $A = RT \ln (p_s/p)$ represents the change of the Gibbs function in the adsorption, taken with a negative sign with respect to the standard state. It is convenient to take as a standard state, a state of the liquid which is at temperature T in equilibrium with saturated vapour at equilibrium pressure p_s. The Polanyi's postulate of the temperature invariance of the characteristic curve $W(A)$ was successfully tested by a large number of authors.

Dubinin and Radushkevich[1] proposed for the function $W(A)$ the expression

$$W = W_0 \exp\left[-(A/E)^n\right], \qquad (1)$$

where W_0 is the limiting adsorption volume, n is a parameter and E (known as "characteristic energy") is the value of quantity A when $W_0/W = e$ (e is the base of natural logarithms). Dubinin and his coworkers generalized further equation (*1*) by introducing the assumption of affinity of the characteristic curves. According to this assumption which was verified in many papers, equation (*1*) has a general validity for any kind of adsorbent if characteristic energy E is substituted with the expression $E = \beta E_0$ (where β is the coefficient of affinity and E_0 is the characteristic energy of the standard substance, for which $\beta = 1$ (benzene)). Experimental evidence has also shown that the coefficient of thermal expansion of the adsorbate α is practically constant within a wide range of temperature. The dependence of the molar volume v on temperature can be therefore written as

$$v = v_0 \exp\left[\alpha(T - T_0)\right], \qquad (2)$$

where v_0 is the molar volume of the adsorbate at temperature of the triple point T_0. For standard adsorbate (benzene) we have $T_0 = 280$ K and $v_0 = 0{\cdot}08669$ cm^3 . . mmol^{-1}. (The adsorbate density is assumed to be equal to the density of liquid benzene, 0·901 g cm^{-3}). Numerous measurements (including direct determination of the density of adsorbed benzene) have led to the value $\alpha = 1{\cdot}178 \,.\, 10^{-3}$ K^{-1}. Parameters v_0, α, p_s and β of equation (*1*) expressed in explicite form (using relation $W = av$ and equation (*2*)) characterize the properties of the adsorbate while parameters W_0, E_0 and n are related to the properties of the adsorbent.

Characteristic curves were originally expressed by means of Gauss function (*i.e.* using Eq. (*1*), for $n = 2$) and generally they fitted quite well the adsorption isotherms of active carbon samples. Later, when it became possible to extent the experimental studies on new types of adsorbents, it has been postulated that parameter n can attain only small, integer values. So, *e.g.*, it was found that for nonporous carbonaceous solids, $n = 1$; for active carbon activated with water vapour (if the degree of burn-off did not exceed 50%), $n = 2$; and for zeolitic and carbon molecular sieves[2], $n = 3$. Equation (*1*) has become the fundamental relation in the theory of volume filling of the micropores (TVFM).

The adsorption isotherms obtained for active carbon samples with a high degree of burn-off (over 50%) and for chemically activated active carbon (using *e.g.* zinc chloride) did not fit any integer value of parameter n in Eq. (*1*). According to Dubinin[2], micropores of these adsorbents consist of two discrete structures – the micropores and the supermicropores. Each of them can be described separately with equation (*1*), for $n = 2$. The equation of the characteristic curve of "bidisperse" type

has then a form

$$W = W_{01} \exp\left[-(A/E_1)^2\right] + W_{02} \exp\left[-(A/E_2)^2\right], \qquad (3)$$

where parameters E and W_0 are the coefficients corresponding to the individual micropore structures. Dubinin and Stoeckli[3] extended the above considerations by assuming that the active carbon structure consists of a polydisperse distribution of primary structures (each of which can be described by Eq. (1)) – given by the relation $f(E_0) = (dW_0/dE_0)$

$$\frac{dW_0}{dE_0} = \frac{W_0^0}{\Delta\sqrt{(2\pi)}} \left[-2(2{\cdot}303R)^2 E_0^{-3}\right] \exp\left\{-(2{\cdot}303R)^4 \left[(E_0^0)^{-2} - E_0^{-2}\right]^2 \frac{\Delta^{-2}}{2}\right\}. \qquad (4)$$

W_0^0 signifies the overall volume of the pores, Δ is a parameter depending on the width of the distribution curve and E_0^0 is the characteristic energy corresponding to maximum of the above function (4). The equation of the characteristic curve is given by the integral

$$W = \int_0^\infty f(E_0) \exp\left[-(A/\beta E_0)^2\right] dE_0, \qquad (5)$$

whose solution yields the equation of the characteristic curve in the form

$$W = W_0^0 \exp\left[-2{\cdot}303AR\beta^{-1}E_0^{0\,-2}\right] \exp\left[A^2\beta^{-2}(2{\cdot}303R)^{-2}\,\Delta^2/2\right] \cdot \left[1 - \mathrm{erf}\,(z)\right]/2, \qquad (6)$$

where

$$z = \left[A\beta^{-1}(2{\cdot}303R)^{-1} - (2{\cdot}303R/E_0)^2\,\Delta^{-2}\right] \Delta/2^{1/2}. \qquad (7)$$

Kadlec[4,5] and somewhat later Rand[6] have shown that parameter n in equation (1) can acquire also non-integer values. This result is connected with the fact that curve $W(A)$ carries information on the structure of the pores, where parameter n depends on the width of the distribution function[7] (dispersion). There is no reason why for various adsorbents, the width of the pore distribution could not change continuously – in spite of the fact that the value $n = 2$ is found for *a.c.* samples with a low and middle degree of burn-off, quite frequently. The above interpretation of parameter n permits to describe the adsorption isotherms of chemically activated a.c. samples, with Eq. (1) – regardless whether they were activated chemically or with water vapour up to the high degree of burn-off. The accuracy obtained in this way is roughly comparable with that one obtained by means of Eq. (3) which is using four parameters determined from the adsorption isotherms. In the case when a.c. has been prepared by zinc chloride or phosphoric acid activation, parameter n

is close to 1·5. Dubinin and Stoeckli[3] have shown that the three-parameter equation (*6*) is able to describe quite well the isotherms given by Eq. (*1*) also when parameter n possesses non-integer values. It has been also shown that parameter n is directly proportional to the parameter Δ. This relation can be described with the equation

$$n = 2{\cdot}00 - 1{\cdot}78 \,.\, 10^6 \Delta \,. \tag{8}$$

For $n = 2$, dispersion Δ equals zero and function (*4*) has then a character of delta function. Integral (*5*) is for the above value transformed into Eq. (*1*). It is possible to say that in most cases, equation (*1*) describes with its three parameters W_0, E_0 and n quite well the structure of the micropores.

Thorough studies of the adsorption isotherms carried out in past several years with different microporous adsorbents have shown that Eq. (*1*) is sometimes unable to describe the characteristic curves in the full range of filling of the adsorption volume $\theta = W/W_0$. This disadvantage of Eq. (*1*) can be removed with a more general equation preserving the properties of Eq. (*1*) which has proved to describe reliably the behaviour of a large number of micropore substances and is commonly used for their characterization. The above requirement of a more general equation preserving the properties of Eq. (*1*) is fulfiled by the relation proposed by one of the authors[8].

$$W = W_0 \exp \left[-(A/\beta E_0)^n \exp \varphi(A/\beta E_0) \right] , \tag{9}$$

where function $\varphi(A/\beta E_0)$ has been chosen in such a way that it accounts for the deviations of the experimental function $W(A)$, from equation (*1*). For $A = \beta E_0$, we have $\varphi(A/\beta E_0) = 0$, which means that for the values θ near to $1/e = 0{\cdot}368$, the course of function (*9*) is identical with that one of function (*1*) and the physical meaning of the parameters in Eq. (*1*) remains preserved also in Eq. (*9*). Since Eq. (*9*) describes the adsorption isotherms in a wide range of relative pressures – up to pressures corresponding to the complete filling of the micropores (p/p_s varies in the range from 0·1 to 0·35), the limiting adsorption volume W_0 in Eq. (*9*) has the physical significance of the volume of the micropores. This volume will be further denoted as $V_{0,\text{micro}}$. It is one of the advantages of Eq. (*9*) that the quantity V_0 need not be any more considered as a parameter determined from fitting the above equation with the experimental data found from the adsorption isotherm, since it can be obtained by means of an independent method[9].

Another condition laid down on this supplementary function $\varphi(A/\beta E_0)$ requires this function to be zero – for the zero values of all parameters describing this function – in the full range of values of A. Equation (*9*) is then reduced into equation (*1*). The above requirement can be met with two functions, each of them fitting a different type of distribution. For symmetrical differential distribution functions (if plotted in the coordinates $V'(r) \div \ln r$, where $V'(r) = \mathrm{d}V(r)/\mathrm{d} \ln r$) which appear

quite frequently in the porous structures of a.c., function $\varphi(A/\beta E_0)$ has a form

$$\varphi(A/\beta E_0) = c_1 c_2[1 + (3nc_2)^{-1}] \,.\, |\, R'[1 - (1 + c_2^{-1}|R'|)^{-1}]|\,, \qquad (10)$$

where $R' = 1 - R$ and $R = (A/\beta E_0)^{-1/3}$. In case of strongly asymmetric differential distribution functions which are found *e.g.* in the microporous structures of zeolites, function φ can be best described by the expression

$$\varphi(A/\beta E_0) = s_1 s_2[1 + (3ns_2)^{-1}] \,.\, R'[1 - (1 + s_2^{-1}|R'|)^{-1}]\,. \qquad (11)$$

Dimensionless parameters c_1 and c_2 and s_1 and s_2, respectively, characterize the deviations of the adsorption isotherm from Eq. (*1*). The parameters c_2 and s_2 can have only positive values (exclusion of singularities in Eqs (*10*) and (*11*)).

Equation (*9*) describes correctly the adsorption isotherms in the full range of θ ($\theta = V/V_0$). For example, the parameters of this equation, $V_{0,\text{micro}}$, E_0, n, c_1 and c_2 characterize completely, for the case of active carbon, the course of the adsorption isotherm. On the basis of these parameters, it is possible to calculate the isotherms for any adsorbate at arbitrary temperature. The characteristic function $W(A/\beta)$ thus contains great amount of information. Since this function is independent of the type of adsorbate, it must depend only on the properties of the micropore structure of the adsorbent. It is a very important task of the theory to find a relation between the above function and the structure of the micropores, for a given adsorbent. One of the first attempts to analyse the micropore structure on basis of the adsorption isotherms of vapours was described by one of the present authors[4,5,7–13]. This analysis is based on evaluation of the function $A(r)$, where r is the value of the radii of the micropores which have their volumes filled at equilibrium vapour pressure p. Substituting expression $A(r)$ into Eq. (*9*), one can find the integral distribution function of the micropore volumes according to their radii, $V(r)$. This function represents the dependence of the total volume of pores with radii r (or smaller) on radius r. The expression for the function $A(r)$ will be shown in the next section.

Besides the micropores which play a dominant role in the adsorption process, we can find nearly always in the adsorbents and catalysts, systems of pores which have much larger dimensions and which are responsible for transport of the adsorbate. These pores form two groups: the mezopores (with radii in the range 1·5 to 100 nm) and the macropores (with $r > 100$ nm). In order to characterize fully the pore structure of the adsorbents, it was found useful to describe the different types of pores, with one identical function $V(r)$. The function $V(r)$ describing the structure of the different types of adsorbents was suggested in the form[8]

$$V(r) = V_0 \exp\left[-R^{-h} \exp \varphi(r)\right], \qquad (12)$$

where V_0 is the total volume of the pores of a given structure, $R = r/r_m$ is the reduced radius of the pores, r_m is the characteristic radius of the pores (corresponding to $V_0/V(r) = e = 2{\cdot}718$), h is a parameter describing the width of the differential distribution function $V'(r)$. Expression $\varphi(r)$, similarly as expression $\varphi(A/\beta E_0)$ in Eq. (*9*) constitutes of two functions

$$\varphi(r) = c_1 c_2[1 + (c_2 h)^{-1}]\,|R'[1 - (1 + c_2^{-1}|R'|)^{-1}]| \qquad (13)$$

and

$$\varphi(r) = s_1 s_2[1 + (s_2 h)^{-1}]\,R'[1 - (1 + s_2^{-1}|R'|)^{-1}]\,. \qquad (14)$$

Application of these equations depends on a type of symmetry of the differential distribution function. Parameters c_1 and c_2 (respectively s_1 and s_2) describe the form of the above functions (their symmetry, narrowness). The values c_2 and s_2 can have, like in Eqs (*10*) and (*11*) only positive values. If we substitute function $A(r)$ with an approximate relation[4,7] $A = k_A/r^3$ (where k_A is a constant), then parameters c and s in Eqs (*9*) and (*12*) characterizing the micropores are identical and parameter $h = 3n$.

It has to be emphasized that the possibility to use equation (*12*) for the description of individual structures of pores (the micro, mezo and macropores – the size of which differs by several orders of magnitude and the formation of which is affected by entirely different processes) is not based on the fact that equation (*12*) was in some way connected with the mechanism of formation of these pores. Eqs (*9*) and (*12*) have not been derived based on the ideas concerning a way in which the porous structure was formed. The fundamental property of these equations is their ability to characterize properly the basic parameters of the distribution functions, as are the total volume of the pores, their characteristic radii, *etc.* Equation (*12*) is thus a statistical distribution function which can be used for description of the various statistical systems, as *e.g.* the distribution of particles, the tensile strength of fibres, *etc.* The preference of Eq. (*12*) is related with the fact that unlike, *e.g.* in the method of statistical moments, it permits to describe the integral and the differential distribution function with the same parameters. Both the above functions can be easily evaluated from the explicite expressions[8] if we know the parameters V_0, r_m, h, c_1 and c_2 (or s_1 and s_2). With these parameters, it is also possible to evaluate the integral and the differential distributions of pore surfaces according to their size, as well as, the total specific surface of the individual pore structures. Equation (*12*) enables therefore a complete characterization of the pore structure of solid substances.

The suggested method seems to be the most suitable approach to a complete pore analysis. This does not mean that a calculation of the parameters of the integral distribution function $V(r)$ is a simple and easy task. For its solution, we propose in the present paper an algorithm of numerical calculation of the parameters of pore structure which is based on the experimental adsorption isotherms and porosi-

metric data. In order to test the above procedure, we have developed a program in ALGOL and in a number of calculations of the parameters of integral distribution function $V(r)$ (carried out on an ODRA 1305 computer) we have proved correct functioning of the proposed algorithm. Some of these results of evaluation of the above parameters are given for the adsorbents with different pore structures in the next section of this paper.

EXPERIMENTAL

The adsorption isotherms of benzene were measured at 293·2 K by means of the gravimetric method. Porosimetric measuremets were carried out on Carlo Erba porosimeters. The active carbon HS-43 (which was described in detail in paper[11]) is an industrial active carbon product activated with zinc chloride, prepared in Moravské chemické závody, Czechoslovakia. Active carbon M-22 (described in detail in paper[14]) was prepared by carbonization and subsequent activation of appricot kernels. Active carbon AG-50 (described in detail in paper[15]) was prepared from black coal. The obtained adsorption isotherms are shown in Fig. 1. Fig. 2 gives the results of measurements performed with the high-pressure porosimeters.

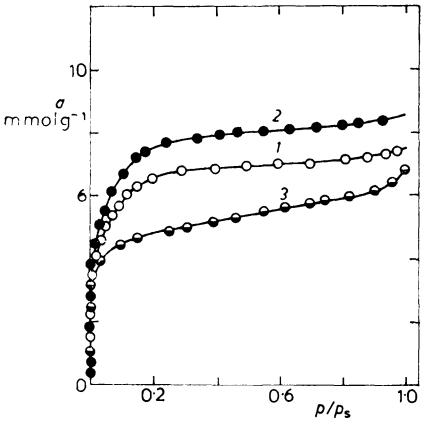

FIG. 1

The adsorption isotherms of benzene at temperature 293·2 K obtained on active carbon; a adsorbed amount in mmol g^{-1}, p/p_s relative pressure; *1* HS-43; *2* M-22 and *3* AG-50

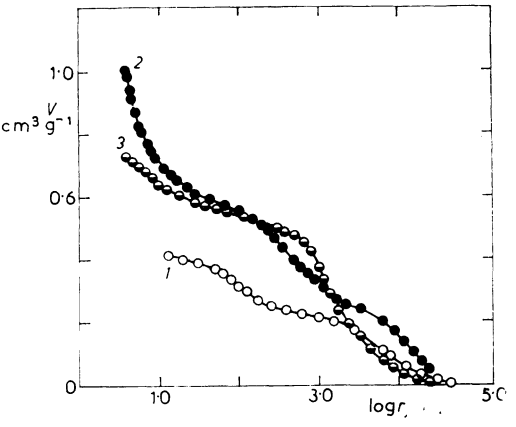

FIG. 2

Experimental dependence of the volume of intruded mercury V ($cm^3\ g^{-1}$) on the logarithm of minimum value of radius r (nm) of the filled pores. The dependence was obtained with high-pressure mercury porosimetry on samples of active carbon. *1* HS-43; *2* M-22 and *3* AG-50

THEORETICAL

If we want to evaluate the parameters of the distribution function $V(r)$ of all three main pore structures (*12*) from the experimental adsorption isotherms of benzene vapour (Fig. 1) and porosimetric data (Fig. 2), we must transform the data so that they can be expressed by one and the same function. To obtain one united function $V(r)$, the evaluation has to be implemented in a following way. The adsorbed amount a determines the volume of the filled up micropores ($V = av$) with radii r (or smaller). The radius of the pores is related to the equilibrium pressure p at which the pore volume has been filled. In the case of the mezopores, this dependence is defined by the well known Kelvin equation based on the theory of capillary condensation. For the mezopores, with the radii between 5–6 nm, the above mechanism is already affected by the dispersion forces at the walls of the pores. The Kelvin equation for the pores open at one side, with a hemispherical meniscus can be written (after the correction for the effect of the force field) in the form[4,11]

$$-A = RT \ln (p/p_s) = \frac{-2v\sigma}{r - t(p/p_s)} - \frac{k_A}{r^3} + \frac{k_B}{r^9}, \qquad (15)$$

where σ signifies the surface tension of the adsorbate and k_A, k_B are constants depending on the shape of the pores[13] and proportional to the known Kirkwood–Müller constant C_A. For the active carbon–benzene system (with a cylindrical form of the pores), $k_A = 6{\cdot}664$ kJ nm^3 mol^{-1} and $k_B = 2{\cdot}46 \cdot 10^{-3}$ kJ nm^9 mol^{-1}. In the case that we apply for the analysis of micropores the slit–like model, we can determine the half–width d of the slits by means of the corresponding parameters k_A and k_B in eqs. (*15*) and (*16*) from paper[13]. Function $t(p/p_s)$ represents the dependence of the

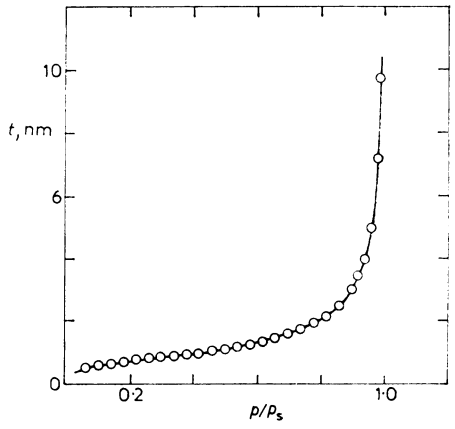

FIG. 3

The dependence of the thickness t of the adsorption layer of benzene on carbonaceous adsorbents; calculation takes into account the effect of the meniscus curvature in mezopores on surface tension of the adsorbate; evaluation of the function $t(p/p_s)$ is analogous to paper[16]

thickness t of the adsorption layer at the surface of the unfilled pores on relative pressure p/p_s. The calculation of this dependence for benzene (which took into account the effect of the size of the pores, on σ) was performed in the same way as it was described for nitrogen in paper[16]. The course of this dependence is shown for the carbon adsorbents in Fig. 3.

For the micropores, the expression for A is given by Eq. (*15*) in which the first term at the right-hand side has been omitted because, in this case, the capillary condensation mechanism is no more significant (the concept of the meniscus has lost its physical meaning). This is true only for such types of adsorbates the structure of which is only slightly affected by the force field and steric hindrances (*e.g.* of formation of associated particles). It is therefore impossible to apply the above function for the analysis of the isotherms of associating compounds (like water, alcohols, amines, mercury, *etc.*). The implemented theoretical and experimental studies[5,17] have shown that the above expression can be used with convenience for the micropore analysis of non-associating adsorbates.

In agreement with the assumption according to which the concept of the meniscus loses its physical meaning for the radii of the pores approaching the value r_k, relation $A(r)$ can be expressed in the general form which is valid both for the mesopores and for the micropores:

$$A = RT \ln \left(\frac{p_s}{p} \right) = \frac{2v\sigma}{r - t(p/p_s)} \gamma(r) + \frac{k_A}{r^3} - \frac{k_B}{r^9} . \qquad (16)$$

In this case, $\gamma(r)$ is an empirical function which shows whether and to which extent the mechanism of capillary condensation participates in the filling of the pore volumes with the pore radii r. It can be expected that function $\gamma(r)$ (ranging between 0 and 1) does not change its value in the neighborhood of r_k discontinuously, though this dependence might be quite steep. The above function can be therefore approximated with the expression

$$\gamma(r) = \exp \left[-(r_k/r)^\tau \right] , \qquad (17)$$

where the values $r_k = 1{\cdot}15$ nm and $\tau = 18$ were estimated from the condition that $\gamma(r) = 0$ for $r < 1$ nm and $\gamma(r) = 1$ for $r > 1{\cdot}5$ nm. The parameter values used in the calculations ought to be considered as purely qualitative and more precise values have to be found in the future. If in the pores with the radii 0·8 nm the mechanism of capillary condensation plays, at least partially, a significant role then parameter τ has the value 6 and $r_k = 0{\cdot}9$ nm.

The solution of Eq. (*16*), for the given values of relative pressure corresponding to the experimental points at the isotherm, enables – along with the data obtained by high-pressure mercury porosimetry – to express the experimental function $V = V(\log r)$ (Fig. 4), which is fundamental for the evaluation of the parameters of the pore structure for a given adsorbent.

Calculation of the Total Volume of the Micropores, Mezopores, and Macropores

In order to evaluate the volume of the micro, mezo and macropores, we must transform the experimental values ($V = V(\log r)$) into the analytical form. Simultaneously, we must smooth out the data to eliminate the inevitable errors of measurement. In principle, we must find the equation of a curve which is passing sufficiently close to the experimental points and which is reasonably smooth (the "approximation" curve).

For approximation of the function of one variable, we have used the method of a cubic spline[18]. Function $V(r)$, defined directly in u points $r_i \in [a, b]$ $(i = 1, \ldots, u)$ has been substituted with a complex function $g(r)$, having in the intervals (r_{i-1}, r_i) $(i = 2, \ldots, u)$ a form of the polynomial of third order. It is required function $g(r)$ be continuous at the points r_i and have a continuous derivation up to the second order. To fulfil such a requirement, function $g(r)$ in the range (r_{i-1}, r_i) ought to be expressed in the form

$$g(r) = \frac{1}{6}\frac{y_{i-1}}{h_i}(r_i - r)^3 + \frac{1}{6}\frac{y_i}{h_i}(r - r_{i-1})^3 + \left(\frac{g_i}{h_i} - \frac{1}{6}y_i h_i\right)(r - r_{i-1}) + \left(\frac{g_{i-1}}{h_i} - \frac{1}{6}y_{i-1}h_i\right)(r_i - r), \tag{18}$$

where $h_i = r_i - r_{i-1}$ and $y_i = g''(r_i)$. Should function $g(r)$ approximate reasonably well the function $V(r)$, it must minimize the following functional

$$\phi(g) = (b - a)^3 \int_a^b [g''(r)]\,\mathrm{d}r + \sum_{i=1}^{u} \frac{1}{2} p_i (g_i - V_i)^2 . \tag{19}$$

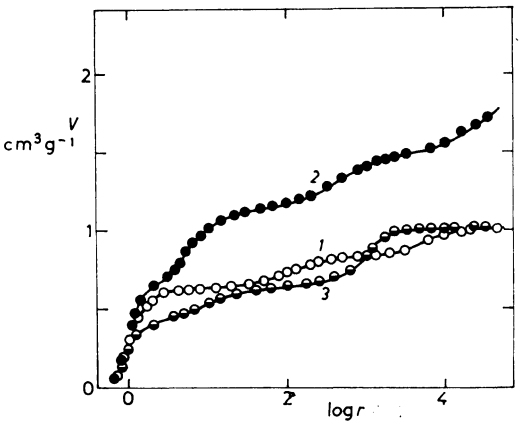

FIG. 4

Integral curve of pore volume distribution according to pore radii, V ($\log r$); the curves were obtained from the adsorption and porosimetric measurements on active carbon samples (r in nm); *1* HS-43, *2* M-22 and *3* AG-50

There, $a = r_1$, $b = r_u$ and p_i are the statistical weights. If the above function is identical with the function $V(r)$ in all nodes r_i (in this case function $g(r)$ represents the interpolation spline), then the second term of the functional $\phi(g)$ is equal to zero.

The experimental function $V(r)$ is illustrated in Fig. 5 with dots while the approximation curve $g(r)$ is shown with a dashed line. The total volumes of the micro, mezo and macropores were evaluated from the approximation function and they relate to the points inside the interval forming a distinct plateau. These points were determined by examination of the reversion of a sign of the 2nd derivation of the function $V(r)$ when passing across these points. The course of the dependence of the 2nd derivation of the function $V(r)$ with respect to ln r, on log r is given in Fig. 5 with a full line. Proceeding along the abscissa in positive direction, we find the values for $V_{O,micro}$, $V_{O,mezo}$ and $V_{O,macro}$ at the points where the second derivation equals to zero and the sign of this derivation changes in the neighborhood of the given point from negative to positive. The values of the total volumes of the micro, mezo and macropores are marked in Fig. 5 with arrows.

The Calculation of the Characteristic Radius of the Pores r_m *and of the Parameter* h *of the Width of the Differential Distribution Function*

The parameters r and h for the individual pore structures were evaluated from the dependence ln ln (V_0/V) on ln r. The procedure for evaluation of these parameters

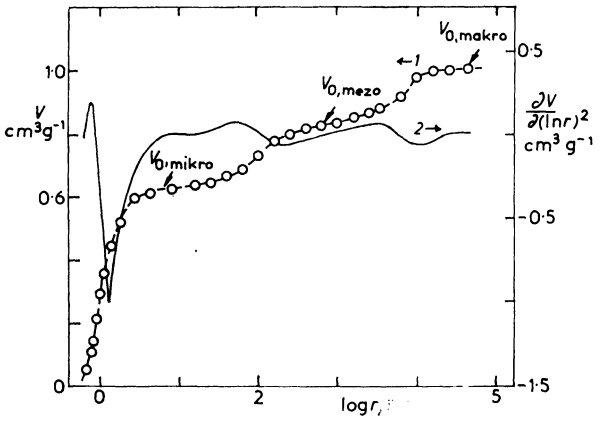

FIG. 5

Graphical illustration of the way of determination of the total volume of micropores $V_{O,micro}$, mezopores $V_{O,mezo}$ and macropores $V_{O,macro}$, for active carbon HS-43. The values of $V_{O,micro}$, $V_{O,mezo}$ and $V_{O,macro}$ are denoted with arrows (V, cm^3 g^{-1}, r, nm); O experimental values V (log r), *1* approximation function, *2* the course of second derivation

is illustrated in Fig. 6. The experimental points correspond to the micropores of active carbon M-22. The full line represents the approximation spline. A slope of the tangent drawn at the point with the coordinates $\ln \ln (V_0/V) = 0$ and $\ln r = \ln r_m$ represents (if taken with a negative sign) the parameter h, giving the width of the differential distribution function. Using the approximation spline, we have calculated by means of Eq. (*16*) the value of $\ln r$ corresponding to the coordinate $\ln \ln (V_0/V) = 0$ (denoted as $\ln r_m$).

The Calculation of Parameters c_1 *and* c_2

Parameters c_1 and c_2 characterize the asymmetry of the differential distribution function $V'(r)$ and they permit to describe with precision the experimental data. The above parameters have been calculated from a set of pairs with the radii r_1 and r_2, using the expressions

$$c_1 = \frac{\varphi(r_1)}{c_2} \frac{1}{[1 + (c_2 h)^{-1}] \, |1 - (r_1/r_m)| \, [1 - (1 + c_2^{-1} \, |1 - (r_1/r_m)|)^{-1}]} \qquad (20)$$

and

$$c_2 = \frac{\dfrac{\varphi(r_2)}{\varphi(r_1)} - \dfrac{|1 - (r_2/r_m)|}{|1 - (r_1/r_m)|}}{\dfrac{|1 - (r_2/r_m)|}{|1 - (r_1/r_m)|} - \dfrac{\varphi(r_2)}{\varphi(r_1) \, |1 - (r_2/r_m)|}} \qquad (21)$$

(where $\varphi(r) = \ln \ln (V_0/V(r)) - h \ln r_m + h \ln r$).

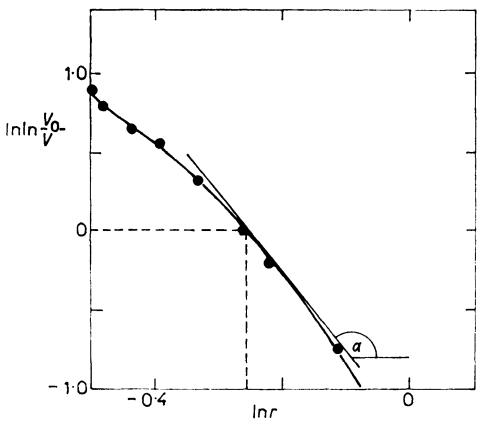

FIG. 6

Graphical illustration of the numerical evaluation of the value of characteristic pore radius r_m and of the parameter h describing the width of the differential distribution function — for the micropore structure of active carbon M-22; the dots represent the experimental data, full line gives the approximation function and the straight line is a tangent to the point with the coordinates $\ln \ln (V_0/V) = 0$ and $\ln r = \ln r_m$, (r, nm)

In this calculation we have minimized the mean square deviation δ given by the expression

$$\delta = \sum_{i=1}^{N} [V(r)_{calc} - V(r)_{exper}]_i/(N - 1) \qquad (22)$$

where N is the number of experimental points, $V(r)_{calc}$ function value calculated from Eq. (*12*) by means of the obtained parameters V_O, r_m, h, c_1 and c_2; $V(r)_{exper}$ is the value of the above function determined experimentally.

Determination of the Specific Surface of the Pores S

The numerical method permits a simple and accurate evaluation of the specific surface of the individual pore structures from Eq. (*12*) and its parameters found from the experimental isotherms and porosimetric curves. The specific surface of the pores of the given structure with radii $r \in \langle r_a, r_b \rangle$ and volume $V(r) \in \langle V_a, V_b \rangle$ is given by the expression

$$S_{ab} = B \int_{V_a}^{V_b} \frac{1}{r} \, dV = B \int_{r_a}^{r_b} \frac{1}{r} \, \omega(r) \, dr \,, \qquad (23)$$

where $\omega(r) = dV(r)/dr$ and B is a constant depending on the form of the pores. For cylindrical pores open at both ends, B is equal to 2. For evaluation of the value of the integrals in Eq. (*23*), we have used the trapezoid method[19] based on the expression

$$\int_a^b f(x) \, dx = \frac{b - a}{2m} [f_0 + 2(f_1 + f_2 + \ldots + f_{m-1}) + f_m] - \frac{(b - a)^3}{12m^2} f''(\vartheta) \,, \qquad (24)$$

where $a \leqq \vartheta \leqq b$, $f_k = f(x_k)$, $x_k = a + k(b - a)/m$, $k = 0, 2, 1, \ldots, m$.

Determination of the Differential Function of Pore Distribution

By derivation of the integral distribution function (*12*) with respect to ln r, we may obtain the explicite expression[8] for the differential distribution function $V'(r) = dV(r)/d \ln r$, which depends on the parameters of Eq. (*12*), V_O, r_m, h, c_1 and c_2. As an example, Fig. 7 illustrates the calculated differential function of pore distribution for a.c. HS-43.

RESULTS AND DISCUSSION

In order to verify the reliability and convergency of the proposed algorithm, we have carried out a number of calculations of the parameters of pore structure of three different specimens of active carbon which were described in the experimental part.

The values of the parameters of pore structure in Eq. (*12*), obtained with the described algorithm are presented in Table I. These parameters can serve as the basis for the evaluation of the function $V(r)$, the differential distribution function $V'(r)$ and the specific surface of the individual pore structures S. In Table II. shown as an example, we compare the values of the function $V(r)$ which were evaluated from Eq. (*12*) (denoted as $V(r)_{calc}$), with the experimental values $V(r)_{exper}$ obtained for the micropores of a.c. HS-43. From this table it is obvious that with the parameters of Eq. (*12*), function $V(r)$ can be calculated with an accuracy which deviates

TABLE I

The values of parameters characterizing the pore structure of studied samples of active carbon

Denotation of adsorbent	Type of pores	V_0 $cm^3\ g^{-1}$	r_m nm	h	c_1	c_2	S $m^2\ g^{-1}$
HS-43	micropores	0·636	0·769	3·87	0·910	0·408	1 544
	mezopores	0·190	74·3	1·23	−0·180	0·049	5·09
	macropores	0·225	4 158	1·13	0	0	0·11
M-22	micropores	0·642	0·770	4·52	−4·910	2·222	1 606
	mezopores	0·505	4·79	2·14	0·450	0·051	181·0
	macropores	0·586	653·2	0·51	0	0	2·61
AG-50	micropores	0·457	0·717	5·23	2·890	0·408	1 108
	mezopores	0·187	7·74	0·89	−0·110	0·051	30·9
	macropores	0·552	1 168	1·01	−0·060	0·049	1·02

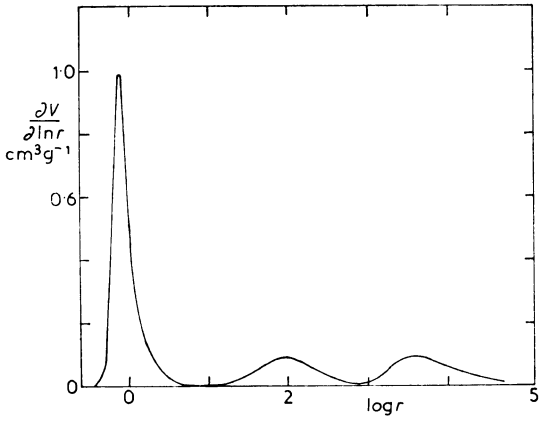

FIG. 7

The differential curve of pore volume distribution according to the pore radii of active carbon HS-43; the curve was calculated from the parameters of Eq. (*12*) listed in Table I (r, nm)

from the experimental data by less than ±3%. Also as an example, Fig. 7 illustrates the differential function of the pore distribution for a.c. HS-43 which was calculated using the parameters listed in Table I. This figure clearly demonstrates the typical structure of chemically activated active carbon.

Table I shows also the specific surface of the micro, mezo and macropores of the individual a.c. samples. It is evident that the surface of the mezopores and macropores forms only a small part of the total surface of the adsorbents; for sample HS-43 it does not exceed 0·4%, for sample AG it is less than 3%. Only in case of the active carbon prepared from appricot kernels, the discussed value is 10% of the total surface. This is due to the fact that the value $V_{O,mezo}$ of this sample is 0·50 $cm^3 . g^{-1}$ and the value of r_m for the mezopores (4·8 nm) is the lowest value of all adsorbents studied in the present work.

For the application of the adsorbents as catalyst supports, it is quite important to have pores with defined dimensions which are optimal for that which catalytic process. The fact that it is possible to calculate the volumes and specific surfaces of the pores which have their radii in the range $\langle r_a, r_b \rangle$ can be of importance in the studies on the supported catalysts. It is also possible to evaluate in this type of studies, the integral and the differential distribution function of the pore surfaces by means of the characteristic parameters of Eq. (*12*) for a.c. HS-43.

The parameter values in Eq. (*12*) given for a.c. HS-43 in Table I are somewhat different from those ones described in paper[11]. The reason for that is connected

TABLE II

Comparison of the values of $V(r)_{calc}$ obtained from Eq. (*11*) (using parameters listed in Table I) with the experimental values $V(r)_{exper}$ from the integral curve of micropore distribution, for a.c. HS-43

log *r* *r*, nm	$V(r)_{exper}$ $cm^3 g^{-1}$	$V(r)_{calc}$ $cm^3 g^{-1}$	relative error Δ_r %
−0·1624	0·136	0·134	1·5
−0·1524	0·155	0·154	0·6
−0·1403	0·179	0·179	0
−0·1284	0·203	0·204	−0·5
−0·1075	0·250	0·252	−0·8
−0·0857	0·294	0·292	0·7
−0·0526	0·361	0·352	2·6
0·4363	0·602	0·618	−2·6
0·5367	0·612	0·623	−1·8
0·7436	0·624	0·626	−0·3

with the application of more recent values in the dependence of the thickness of the adsorption layer on the mezopore surfaces on relative pressure $t(p/p_s)$, which is used in Eq. (*16*). The parameters of the micropore structures of the investigated active carbon samples which are presented in Table I have quite reasonable values and, as it will be shown in the next paper, they are in good agreement with the values obtained by independent methods (high-resolution electron microscopy, X-ray diffraction, *etc.*).

It is the advantage of application of Eq. (*16*) that it enables to evaluate in one run the adsorption and the porosimetric measurements, with one integral function of pore distribution according to their radii, $V(r)$. As one can see from the evaluated parameters of Eq. (*12*), these parameters describe quite well the pore structure of the adsorbents. The preference of the application of these parameters lies in their quite simple physical meaning. The elaborated program allows to obtain quickly reasonably accurate values of the fundamental parameters of the pore structure.

It may be expected that the described way of characterization of the pore structure of solid substances, which is intended to be developed further, will become a base for the rational classification of the industrial adsorbents and catalysts.

LIST OF SYMBOLS

A	differential molar work of adsorption [kJ mol^{-1}]
a	adsorbed amount [mmol g^{-1}]
B	a constant depending on the form of the pores (equal 2 for cylindrical pores)
C_A	Kirkwood–Müller constant [kJ nm^6 mol^{-1}]
c_1, c_2	parameters of Eq. (*9*) and (*12*)
E	characteristic energy — a parameter of Eq. (*1*) [kJ mol^{-1}]
E_0	characteristic energy of the standard adsorbate (benzene) [kJ mol^{-1}]
E_0^0	parameter of Eq. (*4*) [kJ mol^{-1}]
E_1, E_2	characteristic energy corresponding to the individual pore structures (micro and supermicropores) [kJ mol^{-1}]
e	base of natural logarithms
$g(r)$	approximation function [cm^3 g^{-1}]
h	parameter of Eq. (*12*) characterizing the width of the differential distribution function $V'(r)$ (for micropores $h = 3n$)
k_A	constant of Eq. (*15*) [kJ nm^3 mol^{-1}]
k_B	constant of Eq. (*15*) [kJ nm^9 mol^{-1}]
n	parameter of Eq. (*1*)
p	equilibrium pressure of adsorbate vapour above the adsorbent [Pa]
p_s	saturated pressure of adsorbate vapour at temperature T [Pa]
p/p_s	relative pressure
$R = r/r_m$	reduced pore radius (for micropores also $R = r/r_m = (A/\beta E_0)^{-1/3}$
$R' = 1 - R$	
$\boldsymbol{R}$	gas constant [kJ mol^{-1} K^{-1}]
r	pore radius [nm]

r_k	radius of the micropores characterizing the limits of applicability of Kelvin equation [nm]
r_m	characteristic radius of the pores — a parameter of Eq. (*12*) [nm]
S	specific surface [$m^2\ g^{-1}$]
s_1, s_2	parameters of Eq. (*9*) and (*12*)
T	temperature of measurement of the adsorption isotherm [K]
T_0	temperature of triple point of the adsorbate [K]
t	thickness of adsorption layer at the surface of mezopores [nm]
$t(p/p_s)$	dependence t on relative pressure [nm]
$V(r)$	integral function of pore distribution — dependence of the total volume of pores with radii r and less, on r [$cm^3\ g^{-1}$]
$V'(r)$	differential function of pore distribution ($= dV(r)/d \ln r$) [$cm^3\ g^{-1}$]
$V_{O,micro}$	total volume of the micropores [$cm^3\ g^{-1}$]
$V_{O,mezo}$	total volume of the mezopores [$cm^3\ g^{-1}$]
$V_{O,macro}$	total volume of the macropores [$cm^3\ g^{-1}$]
v	molar volume of the adsorbate [$cm^3\ mol^{-1}$]
v_0	molar volume of the adsorbate at temperature T_0 [$cm^3\ mol^{-1}$]
W	volume of the adsorption space [$cm^3\ g^{-1}$]
$W(A)$	characteristic curve [$cm^3\ g^{-1}$]
W_0	limiting adsorption volume — a parameter of Eq. (*1*) [$cm^3\ g^{-1}$]
W_0^0	total volume of the micropores of the polydisperse structure [$cm^3\ g^{-1}$]
W_{01}, W_{02}	limiting adsorption volumes corresponding to the individual micropore structure [$cm^3\ g^{-1}$]
$\alpha = \frac{1}{v}\frac{dv}{dT}$	temperature coefficient of volume expansion of the adsorbate [K^{-1}]
β	coefficient of affinity of the characteristic curves
$\gamma(r)$	a function defining the range of applicability of Kelvin equation
Δ	parameter of the distribution function (*4*) giving its width (dispersion)
Δ_r	relative error
δ	mean quadratic deviation
$\theta = W/W_0$	degree of filling of the adsorption space
ϑ	variable of equation (*24*)
$\pi = 3{\cdot}1416$	
σ	surface tension of the adsorbate [N/m]
τ	parameter of function $\gamma(r)$
$\phi(g)$	functional
$\varphi(A/\beta E_0)$	supplementary function of Eq. (*9*)
$\varphi(r)$	supplementary function of Eq. (*12*)
$\omega(r) = dV(r)/dr$	

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