

Functions Defining Capillary Structure of Microporous Adsorbents

ROMAN WOJSZ and MICHAŁ ROZWADOWSKI*
Institute of Chemistry, N. Copernicus University, 87–100 Toruń, Poland

(Received: 6 February 1987; in final form: 8 May 1987)

Abstract. The applicability of earlier derived equations for adsorption isotherms for the determination of differential curves characterizing the approximate distribution of micropore volumes in relation to their radii is studied. It is concluded that besides the Gaussian distribution, the Rayleigh and exponential distributions also possess a physical sense.

Key words: Adsorption, carbon microporous adsorbent, distribution of micropore volumes.

1. Introduction

The porous structure of adsorbents is best characterized by the distributions of volume and surface area of pores in relation to their radii [1–4]. Using adsorption research methods, those distributions can be determined from the Kelvin equation on the basis of the part of the isotherm corresponding to the process of capillary condensation of vapours. In the cases of micro- and supermicropores, as opposed to mesopores, the distribution curves cannot be determined experimentally because there is no method with which one could determine volumes corresponding to particular ranges of pores sizes.

We have previously derived the adsorption isotherm [5]

$$W(A) = W_0 \exp \left[\frac{\Delta^2}{2} \left(\frac{A}{\beta} \right)^{2n} - \left(\frac{A}{\beta E_\infty} \right)^n \right] \frac{\operatorname{erfc} \left[\frac{\Delta}{\sqrt{2}} \left(\frac{A}{\beta} \right)^n - \frac{1}{E_\infty^n \Delta \sqrt{2}} \right]}{\operatorname{erfc} \left(-\frac{1}{E_\infty^n \Delta \sqrt{2}} \right)} \quad (1)$$

where W is the volume of the liquid-like adsorbate filling micro- and supermicropores at a relative pressure p/p_s and temperature T ; W_0 is the total volume of micro- and supermicropores; $A = RT \ln(p_s/p)$ is the differential molar work of adsorption; Δ is a parameter characterizing the structural heterogeneity of microporous adsorbents; β is a constant characterizing the adsorbate (affinity coefficient of the characteristic curves); n is a constant parameter equal to 2 or 3 in the case of very small micropores; E_∞ is a distribution parameter and erfc is an error function complement.

We have derived the differential equation [6] for the distribution of the micropore volumes according to the characteristic dimension x of the pores for the slit-like model of micropores

* Author for correspondence.

$$f(x) = \frac{n x^{n-1} W_0 \sqrt{2}}{\Delta x^n \sqrt{\pi} \operatorname{erfc}\left(-\frac{x_0^n}{x^n \Delta \sqrt{2}}\right)} \exp\left[-\frac{(x^n - x_0^n)^2}{2 \Delta^2 x^{2n}}\right] \quad (2)$$

where: $x = xE_0$; E_0 is the characteristic energy of adsorption and x_0 is a distribution parameter.

In the case of Equation (2) [6] we postulate, to a good first approximation, that the distribution of the micropore volume W_0 with respect to E_0 is given by the normalized quasi-Gaussian distribution of half-width Δ :

$$f(E_0) = \frac{n W_0 \sqrt{2}}{\Delta E_0^{n+1} \sqrt{\pi} \operatorname{erfc}\left(-\frac{1}{E_0^n \Delta \sqrt{2}}\right)} \exp\left[-\frac{(E_0^{-n} - E_\infty^{-n})^2}{2 \Delta^2}\right] \quad (3)$$

As the Gaussian distribution is only one [7, 8] of many possible solutions for the general equation

$$W = \int_0^\infty f(E_0) \exp\left[-\left(\frac{A}{\beta E_0}\right)^n\right] dE_0 \quad (4)$$

characterizing adsorption on microporous adsorbents of a heterogeneous pore system it is advisable to present how other structural distributions characterize the function $f(x)$. In this way, one should obtain other alternative solutions of Equation (4) which will also approximately characterize the distribution of micropores according to their radii x .

2. Discussion

The results obtained are related to the adsorption of spectrally pure benzene and methanol as well as chemically pure methylamine on active carbon D as described previously [6, 9–11]. The quasi-Gaussian shape of the $f(E_0)$ function assumed in Equation (3) is only one of many possible cases for the solution of the integral Equation (4) determining the global adsorption isotherm $W(A)$. The quasi-Rayleigh and quasi-exponential distributions are also real from the physical viewpoint.

Assuming the quasi-Rayleigh distribution [7, 12] of the $f(E_0)$ function, one should consider the two following cases:

(a) the structural heterogeneity distribution with a widening at the right-hand side

$$\begin{cases} f(x) = \frac{2n x^{n-1} \Delta^2 W_0}{x^{2n}} (x^n - x_0^n) \exp\left[-\frac{\Delta^2}{x^{2n}} (x^n - x_0^n)^2\right]; & x_0 \geq 0 \quad \text{and} \quad x \geq x_0 \\ f(x) = 0 & x < x_0 \end{cases} \quad (5)$$

where x_0 is a parameter of the $f(x)$ distribution,

(b) the distribution with a widening at the left-hand side

$$\left\{ \begin{array}{l} f(x) = \frac{2n x^{n-1} \Delta^2 W_0 (x_0^n - x^n) \exp\left[-\frac{\Delta^2}{x^{2n}} (x_0^n - x^n)^2\right]}{x^{2n} \left[1 - \exp\left(-\frac{\Delta^2 x_0^{2n}}{x^{2n}}\right)\right]}; \quad 0 \leq x \leq x_0 \\ f(x) = 0 \quad \quad \quad x > x_0 \quad \text{or} \quad x < 0 \end{array} \right. \quad (6)$$

Assuming the quasi-exponential distribution of the $f(E_0)$ function, one should also consider two cases.

(a) the distribution for the decreasing quasi-exponential function

$$\left\{ \begin{array}{l} f(x) = \frac{n x^{n-1} W_0}{x^n \Delta} \exp\left(-\frac{x^n - x_0^n}{x^n \Delta}\right); \quad x_0 \geq 0 \quad \text{and} \quad x \geq x_0 \\ f(x) = 0 \quad \quad \quad x < x_0 \end{array} \right. \quad (7)$$

(b) the distribution for the increasing quasi-exponential function $f(E_0)$

$$\left\{ \begin{array}{l} f(x) = \frac{n x^{n-1} W_0 \exp\left(-\frac{x_0^n - x^n}{x^n \Delta}\right)}{x^n \Delta \left[1 - \exp\left(-\frac{x_0^n}{x^n \Delta}\right)\right]} \quad ; \quad 0 \leq x \leq x_0 \\ f(x) = 0 \quad \quad \quad x > x_0 \quad \text{or} \quad x < 0 \end{array} \right. \quad (8)$$

The differential curves $f(x)$ for the distribution of the micropore volume with respect to the characteristic dimensions of micropores calculated for active carbon D from Equations (2), (5–8) are given in Figs. 1–3.

These values have been obtained using the method of least squares for the experimental data. It should be stated in spite of assumed differences in the shape of $f(E_0)$ functions that the distribution curves obtained from these Equations (curves 1 and 2 in Figs. 1–3) contain a broad common range of x values. The distribution obtained from Equation (8) is relatively the least probable one while the other distributions do not exclude each other and they can be accepted as the curves characterizing approximately the volumes of micropores occurring in the active carbon used in this study.

Acknowledgement

This work was partially supported by the Ministry of Science and Higher Education program CPBP.01.06.

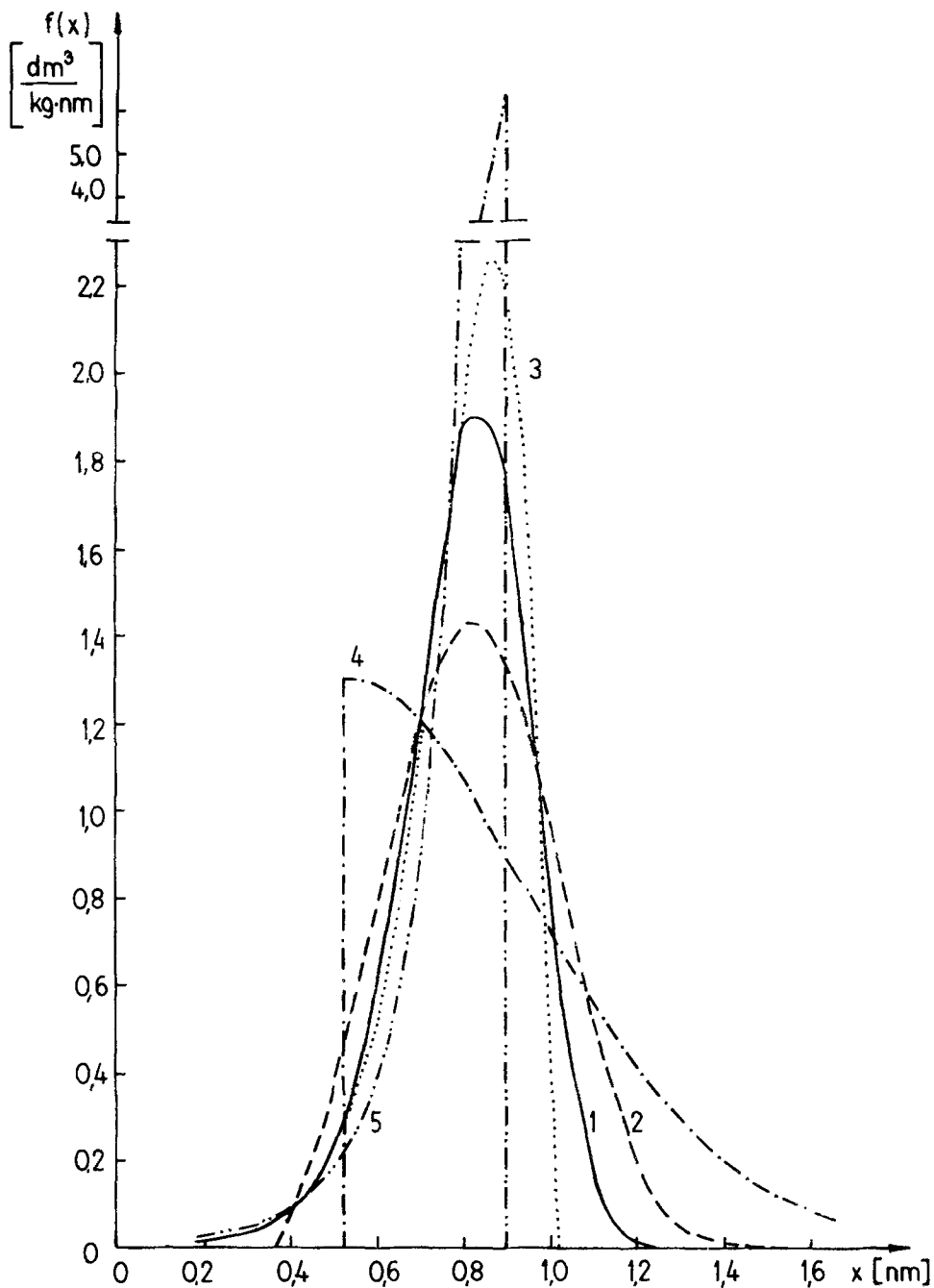


Fig. 1. Differential curves for the distribution of the micropore volume according to the characteristic dimension of the micropores for benzene adsorption. 1 - calculated from Equation (2), 2 - calculated from Equation (5), 3 - calculated from Equation (6), 4 - calculated from Equation (7), 5 - calculated from Equation (8).

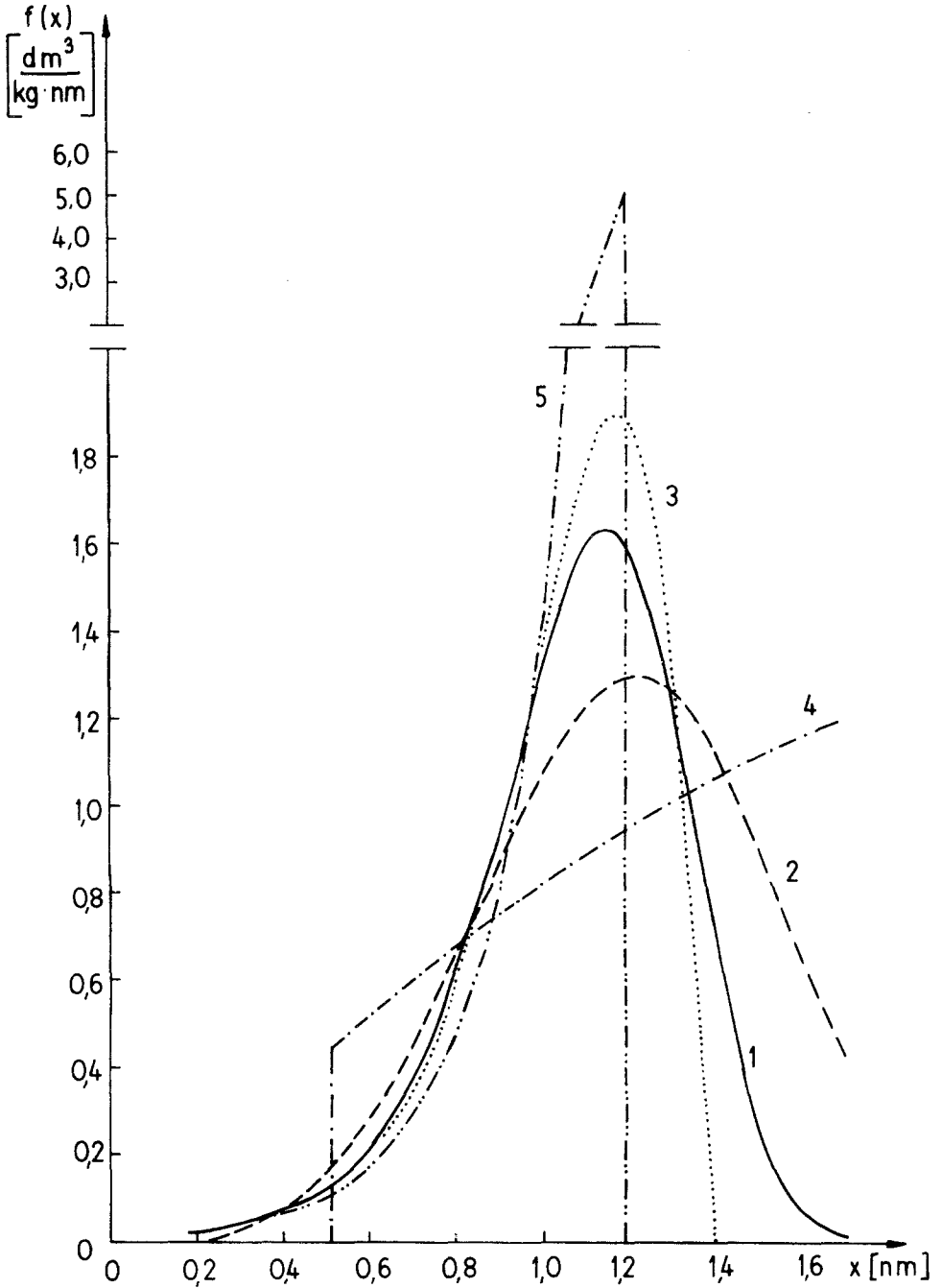


Fig. 2. Differential curves for the distribution of the micropore volume according to the characteristic dimension of the micropores for methanol adsorption. 1 - calculated from Equation (2), 2 - calculated from Equation (5), 3 - calculated from Equation (6), 4 - calculated from Equation (7), 5 - calculated from Equation (8).

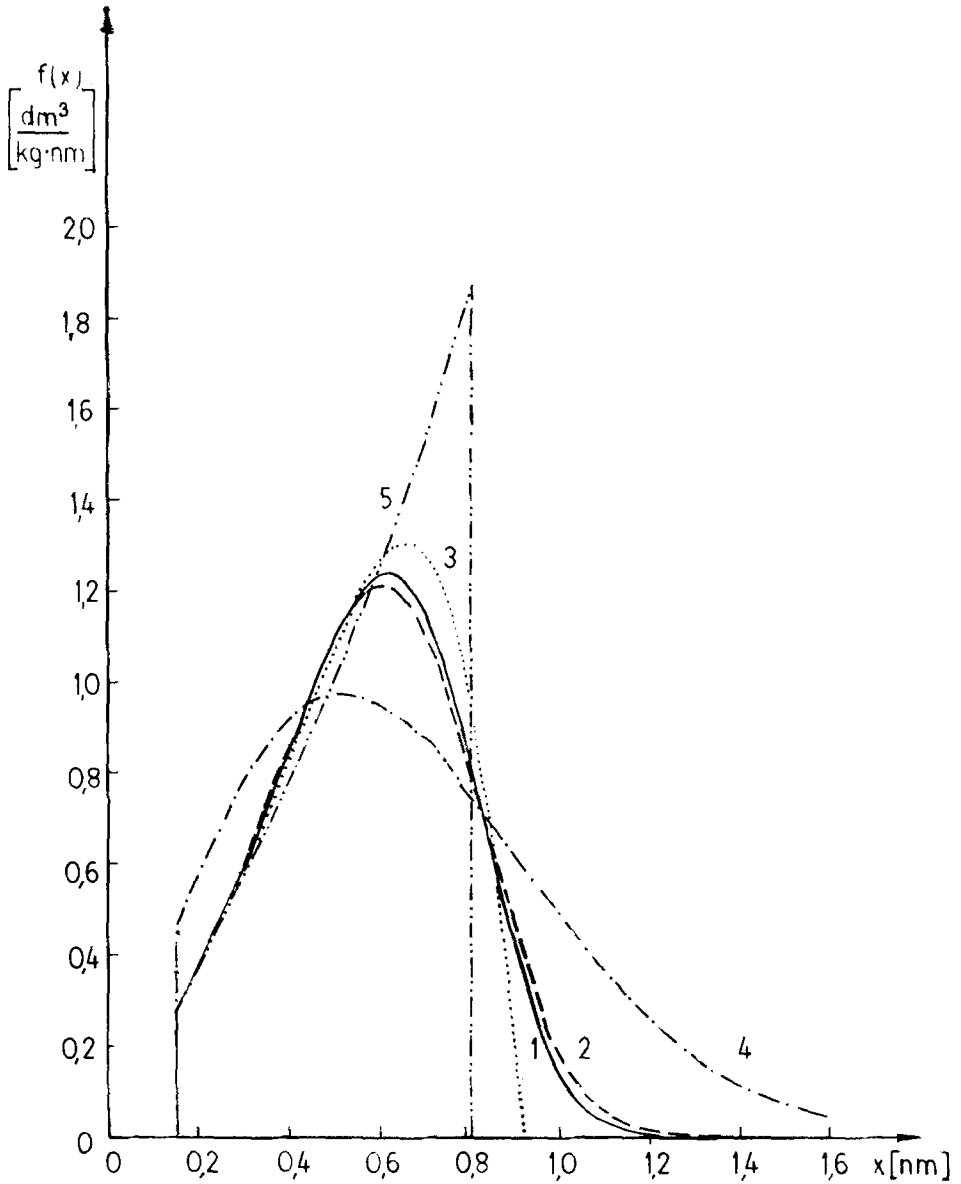


Fig. 3. Differential curves for the distribution of the micropore volume according to the characteristic dimension of the micropores for methylamine adsorption. 1 - calculated from Equation (2), 2 - calculated from Equation (5), 3 - calculated from Equation (6), 4 - calculated from Equation (7), 5 - calculated from Equation (8).

References

1. M. M. Dubinin and H. F. Stoeckli: *J. Colloid Interface Sci.* **75**, 34 (1980).
2. M. M. Dubinin: *Dokl. Akad. Nauk SSSR* **275**, 1442 (1984).
3. M. M. Dubinin, S. N. Efremov, L. J. Kamaeva, and E. A. Ustinov: *Izv. Akad. Nauk SSSR, Ser. Khim.* **255** (1985).
4. M. M. Dubinin and N. S. Polakov: *Izv. Akad. Nauk, Ser. Khim.* 1943 (1985).
5. M. Rozwadowski and R. Wojsz: *Carbon* **22**, 363 (1984).
6. R. Wojsz and M. Rozwadowski: *Chem. Eng. Sci.* **42**, (1987).
7. M. Rozwadowski and R. Wojsz: *Pol. J. Chem.* **58**, 837 (1984).
8. R. Wojsz and M. Rozwadowski: *Monatsh. Chem.* **117**, 453 (1986).
9. M. Rozwadowski: *Sorption of Aliphatic Alcohols in Active Carbons*, UMK, Toruń (1977).
10. M. Rozwadowski and R. Wojsz: *Carbon* **19**, 383 (1981).
11. R. Wojsz and M. Rozwadowski: *Pol. J. Chem.* **55**, 1895 (1981).
12. J. Bass: *Elements of Probability Theory*, New York, Academic Press (1966).