

DETERMINATION OF SURFACE AREA OF MESOPORES

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Dedicated to the 65th anniversary of the late Academician R. Brdička.

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A new method of determining specific surface area of mesopores* of adsorbents containing micropores is described. Adsorption isotherms of benzene on active coals have been analyzed by this method. In order to evaluate the adsorption isotherms, the t -curve of benzene on non-porous carbon black has been measured. The calculated surface areas of active coal mesopores have been compared with the results achieved by the methods used up to now. In contrast to the surface areas determined from the branch of the desorption isotherm by the Pierce method and from the measurements involving intrusion of mercury according to the Dubinin method, the higher values of mesopore surface areas have been explained by a more exact determination of the boundary between micropores and mesopores.

Several classifications of pores in porous materials according to the shape and size have been suggested. Distribution of pores to macropores, mesopores, and micropores, as suggested by Dubinin¹, reflects differences in the mechanism of processes taking place in pores during adsorption and capillary condensation. In the heterogeneous catalytic processes as well, mesopores and micropores can behave quite differently². The determination of surface areas of these individual types of pores is a task which remained unsolved with micropores^{3,4}, and likewise in the case of mesopores it has been solved with only a partial success up to now.

The surface area of mesopores can be primarily established on the basis of the adsorption measurements. Of other methods, the measurements involving intrusion of mercury seem to be the most important. As was shown by Dubinin⁵, the surface area of mesopores can be calculated from equation

$$S = \frac{1}{\sigma \cos \theta} \int_0^V P dV, \quad (1)$$

where V is the volume of pores filled with mercury under the hydrostatic pressure P , σ is the surface energy of mercury, and θ denotes the angle of wetting.

* On recommendation of the IUPAC commission for nomenclature the term mesopores has been used instead of the term transition pores, used up to now.

Most of the methods concerning the measurements of the mesopore surface areas start from the adsorption isotherms in the hysteresis loop region. The principle of the calculation of cumulative surface area of mesopores from the distribution curve obtained on the basis of the Kelvin equation from the desorption or adsorption branch of the hysteresis loop, is well known⁶⁻¹⁰. Likewise the thermodynamic Kiselev method¹¹, according to which surface area S' of the adsorption film on mesopores is equal to

$$S' = \frac{1}{\sigma} \int_{a_0}^{a^*} A da, \quad (2)$$

utilizes the adsorption isotherm in the hysteresis loop region for the calculation of mesopore surface areas. In equation (2), A is the differential molar energy of adsorption $A = RT \ln p_0/p$, a_0 is the value of adsorption at the start of the hysteresis loop under a characteristic relative pressure $x = 1$, and σ is the surface energy of the adsorbate.

The mentioned methods assign the lower limit of mesopore dimensions to the lower joint point of the adsorption and desorption branches of the hysteresis loop under a characteristic relative pressure x_0 . However, results of the study of the adsorption hysteresis show that the characteristic relative pressure x_0 is associated rather with adsorbate properties (with its tensile strength) than with those of the adsorbents¹². The smallest radius of pores in which capillary condensation can occur is dependent on the kind of the adsorbate¹³. The determination of the specific surface area of mesopores from adsorption isotherms measured with various adsorbates may therefore provide different results and the mesopores considered cannot be entirely equal to the mesopores defined on the basis of the diversity in the increase of the adsorption potential in micropores in comparison with mesopores and macropores.

The surface area of mesopores may be likewise determined from a part of the adsorption isotherm preceding the capillary condensation so that the surface area thus determined is independent of the value of the characteristic relative pressure x_0 . This has been enabled by the t -method of Lippens and de Boer^{14,15}, which rests upon plotting adsorbed amount a against thickness of the adsorption layer t on nonporous material under equal relative pressure, under which adsorption is going on. The tangent of a linear section of the a - t curve is proportional to the mesopore surface area. However, if micropores are present, some complications arise, for on the a - t curve some deviations from linearity take place. In this paper, modification of the t -method concerning the determination of mesopores surface areas has been suggested; the method in question removes the quoted shortcoming.

THEORETICAL

The principle of the t -method of Lippens and de Boer may be expressed in the following way: With adsorbents containing all three types of pores the total adsorbed amount a is given by a sum of adsorbed amount in micropores a_{micro} and that in mesopores a_{meso}

$$a = a_{\text{micro}} + a_{\text{meso}}. \quad (3)$$

The adsorbed amount in macropores may be, as a rule, neglected, owing to the fact

that their surface area does not exceed $1-2 \text{ m}^2/\text{g}$, i.e. a percentage fraction of total surface area of the adsorbent. By multiplying equation (3) by molar volume v and expressing volume of the adsorption layer on the surface of mesopores $a_{\text{meso}} v$ by a product between the surface area of mesopores S_{meso} and the thickness of adsorption layer t

$$a_{\text{meso}} v = S_{\text{meso}} t, \quad (4)$$

we obtain

$$av = a_{\text{micro}} v + S_{\text{meso}} t. \quad (5)$$

Providing that a_{micro} is independent on the relative pressure and adsorption is not complicated by capillary condensation for which relation (4) is not valid, we obtain a straight line by plotting product av against t , whose tangent denotes surface area of mesopores S_{meso} .

Both assumptions quoted limit the region of relative pressures, where equation (5) can be expressed by linear dependence: for $x > x_0$, capillary condensation occurs, while for $x < x_0$, a_{micro} is not constant. For that reason, it is difficult for adsorbents containing both micropores and mesopores to find linear section on the $av-t$ curve, whose tangent corresponds to the surface area of mesopores. In order to remove this drawback of the t -method of Lippens and de Boer, it is of advantage to express in equation (5) a_{micro} in terms of a function of relative pressure. The experience shows that adsorption in micropores is best described by the Dubinin-Raduškovič¹ equation. On the basis of this equation the adsorbed quantity in micropores can be expressed by

$$a_{\text{micro}} = a_0 F, \quad (6)$$

where

$$F = \exp [(-BT^2/\beta^2) \log^2 (p_0/p)]. \quad (7)$$

In equations (6) and (7), a_0 is the limiting (maximum possible) adsorbed amount in micropores, B is the constant associated with the micropores size, and β denotes the affinity coefficient (for benzene $\beta = 1$). By introducing relation (6) into equation (5) and by further treatment, we obtain equation

$$av/F = a_0 v + S_{\text{meso}} t/F. \quad (8)$$

If we know the value of constant B in equation (7), then by plotting av/F against t/F in the region of relative pressures $x < x_0$, where capillary condensation is not yet applied, we should obtain straight line, whose tangent is equal to the surface area of mesopores. However, it is difficult to obtain independently constant B which corresponds to the given system of micropores. As it is known that value B is for the given adsorbent really constant, we suggest to determine this constant neces-

sary to apply equation (8), by plotting the adsorption isotherm in the region of relative pressures smaller than x_0 in the coordinates $av/F - t/F$ for different values of B . A linear dependence corresponds to the correct value of constant B . The tangent of this dependence is equal to the surface area of mesopores S_{meso} and the section a_0v is identical with the total volume of micropores V_{micro} . This procedure of determining S_{meso} and V_{micro} will be further denoted by us as the t/F method.

EXPERIMENTAL

Samples. The active coal samples were prepared using the method of air separation¹⁶ of granulated active coal Desorex (Chemické závody W. Piecka, Likier, Czechoslovakia) manufactured by activation of carbonized beech-wood material by means of water vapour at 960°C. Since the activation with water vapour does not proceed uniformly, individual samples correspond to vari-

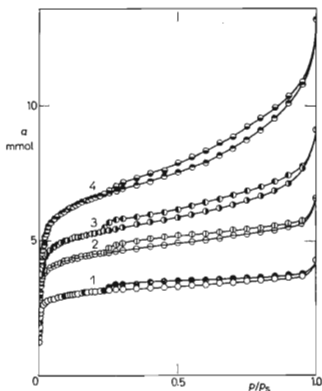


FIG. 1

Adsorption Isotherms of Benzene at 20°C
Numbers of curves correspond to numbers of active coal samples 1–4.

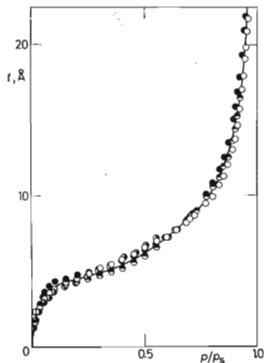


FIG. 2

The t -Curves of Benzene on Nonporous Carbon Black at 20°C

Graphitized Carbon Black Stirling MT \circ , calculation on the basis of the measurement of isotherm using the balance method \bullet , calculation using measurement of the isotherm by means of the volumetric method \ominus , calculation made using the Isirikian and Kiselev²⁰ isotherm \oplus , calculation from the isotherm on thermic carbon black.

ous degrees of activation. The activation degree increases from sample 1 to sample 4. In order to obtain the t -curve of benzene on the nonporous carbon surface, the benzene isotherms on nonporous and graphitized carbon black Stirling MT (U.S.A.) and thermal nonporous carbon black (USSR) were measured gravimetrically and volumetrically.

Measurement of benzene adsorption. Adsorption isotherms of benzene on active coals were measured gravimetrically using quartz spiral balance³ of sensitivities 5–7 mg/mm and 1 g load. Extension of spirals and pressure of the Hg U-manometer were read off by a cathetometer with an accuracy within ± 0.01 mm. In addition to the gravimetric method, also the volumetric one¹⁷ was used to measure adsorption isotherms on graphitized carbon black. Prior to the measurement of the adsorption isotherms, the samples were heated to 400°C and evacuated to a pressure of 10^{-5} Torr for a period of 24 hours.

Measurement by means of mercury intrusion. The measurement was accomplished with use of a high-pressure mercury porosimeter PA-5 (ref.¹⁸) from 1 to 4000 atm. Mercury was distilled to the sample in dilatometer, which was evacuated and heated to 350°C for 12 hours.

RESULTS

The adsorption isotherms of benzene, measured on active coals 1–4 at 20°C, are graphically presented in Fig. 1. A particular attention has been paid to the exact and detailed measuring the adsorption isotherms in the region of relative pressures lower than x_0 , which is necessary to determine the surface area of mesopores by the t/F method. By using the measurement of the adsorption isotherms of benzene on nonporous carbon black at 20°C, the t -curves were calculated (Fig. 2). The value of 41 Å (ref.¹⁹) was used for the molecular surface of benzene molecule in the filled monolayer (ω). In Fig. 3, the a - t graphs of benzene isotherms of the quoted four

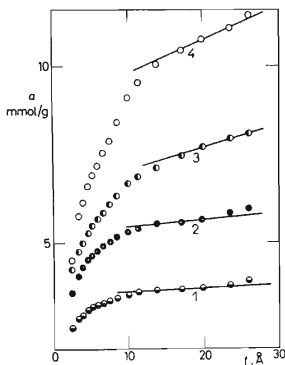


FIG. 3

Plot of the Adsorbed Quantity of Benzene a against Thickness of the Benzene Adsorption Layer t for Active Coal Samples 1–4

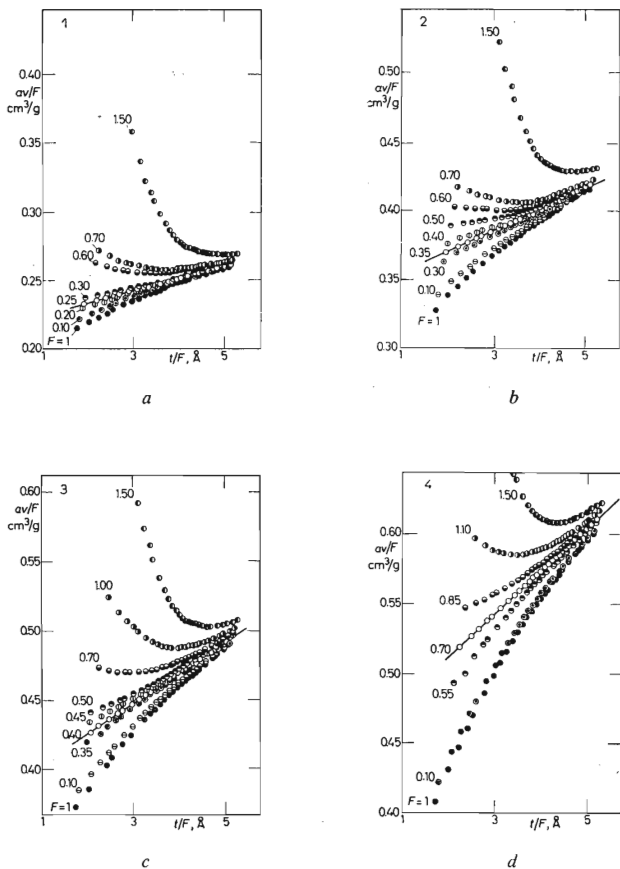


FIG. 4

The $av/F-t/F$ Dependences of Benzene Isotherms for Various Values of the B Constant of Active Coal Samples 1-4

Values of Constants $B \cdot 10^6$ are given near individual curves.

samples of active coal are plotted. The tangents of linear sections in these plots correspond to 7.5, 15, 57, and 80 m²/g for samples 1–4, respectively.

Application of the t/F method is illustrated in Fig. 4, where $av/F - t/F$ dependences of the adsorption isotherms of benzene on samples 1–4 are presented for different values of constant B . The mesopore surface areas calculated from the tangents are listed in Table I, where they are compared with the mesopore surface areas determined from adsorption isotherms using the Pierce⁷ and Kiselev¹¹ methods, and with the values of surface areas determined on the basis of mercury intrusion measurements. Integral curves of the size distribution of macropores and mesopores, determined by mercury intrusion measurements are depicted in Fig. 5.

DISCUSSION

The value of mesopore surface areas, determined by the Pierce method and summarized in Table I are in relative good accordance with the values determined using the Dubinin method of mercury intrusion. The maximum pressure applied in the mercury porosimetry was 4 000 atm., which corresponds to the filling of pores having effective radii of 19 Å. The capillary radius, which at 20°C corresponds according to the Kelvin scale to the characteristic relative pressure of benzene $x_0 = 0.23$, is 14.3 Å. If the adsorption layer is 4.6 Å thick under the pressure x_0 , then the smallest pore radius determined by the Pierce method is 18.9 Å. Both methods, however, apply the same assumption on the cylindrical shape of pores to the calculation of mesopore surface areas and for that reason, an approximate agreement of surface areas determined by the Pierce method and the method of mercury intrusion may be considered a demonstration of their mutual consistence. The adsorption film surface areas in mesopores determined by the Kiselev method are considerably smaller.

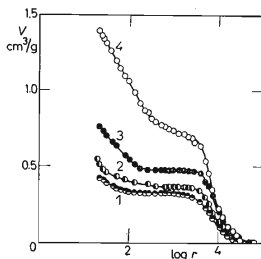


FIG. 5

Integral Distribution Curves of Macropores and Mesopores of Active Coals 1–4 from the Mercury Intrusion Measurements

Pore radius r in Å.

TABLE I

Values of Mesopore Surface Areas Determined by Various Methods

Sample No	Pierce m^2/g	Kiselev according to relation (1) m^2/g	Dubinin according to relation (2) m^2/g	t/F Method m^2/g
1	67	44	73	90
2	92	64	98	153
3	136	98	148	223
4	195	158	216	310

This is, according to Brunauer and coworkers⁹, in accordance with the fact that the surface area achieved by this method is not a true surface area of pore walls, but rather a surface area of the interface between the layer adsorbed on the pore walls and the gaseous phase, the so-called core surface area.

When determining the cumulative surface area of mesopores from the desorption branch of the isotherm using the Pierce method, the application of the Kelvin equation up to the lower joint of the hysteresis loop is assumed to be possible. This assumption, however, is, as a rule, not fulfilled, for the course of the desorption branch in the vicinity of characteristic relative pressure x_0 is defined by the tensile strength of adsorbate and does not connect with structure of pores¹². Therefore, in values of the mesopore surface areas achieved by this method as well as by that of Kiselev, certain error may be involved.

There is a problem, whether the pore radius of 19 Å really corresponds to the boundary between micropores and mesopores according to the Dubinin classification¹. As was shown by Burgess and Everett¹³, the value of the meniscus radius in pores of this limiting size (this radius is associated with the characteristic relative pressure x_0 at which adsorption and desorption branches of the isotherm are connected) differs for individual adsorbates from 11 to 22 Å. The characteristic relative pressure x_0 which defines boundary between micropores and mesopores for methods of calculating surface areas, based on the application of the Kelvin equation, does not connect with the considerable difference between micropores and mesopores, which results in the increase of adsorption potential in micropores. The boundary between micropores and mesopores is therefore not exactly determined by the characteristic relative pressure x_0 .

This fundamental difference between micropores and mesopores according to the Dubinin classification¹, is properly characterized by the t -method, because it considers diversity in the course of isotherms on a smooth surface and in micropores. The

t -method, however, appeared to be inapplicable for the determination of mesopore surface areas of active coals. As apparent from Fig. 3 in which the $a-t$ dependence of benzene on active coals 1–4 is presented, such linear section, whose tangent would equal the surface area of mesopores, cannot be found on the given graphs. Linear sections on the curves obviously correspond even to the region of capillary condensation, for the surface areas calculated from the tangents lie for specimens 1–4 between 7.5 and 80 m²/g, these being obviously not correct, values as follows from Table I. Inapplicability of the t -method to the determination of the mesopore surface areas of active coals is due to the fact that for active coals, no region of relative pressures exists, in which the adsorbed amount in micropores would be independent on the relative pressure already (higher x values), and at the same time any capillary condensation would not take place yet.

This drawback of the t -method is removed by the t/F method which allows to use the adsorption isotherm in the region in which the capillary condensation ($x < x_0$) does not take place as yet. It can be seen from Fig. 4 that for a properly selected value of the B constant, linear $av/F - t/F$ dependences may be obtained. For samples 1–4, values of the B constants, corresponding to linear dependences, increase from 0.25 to 0.70 · 10⁻⁶. This is in accordance with the fact that starting from sample 1 to sample 4, the size of micropores increases due to the increasing extent of the burn-off. At $F = 1$, the t/F method is reduced to the t -method. As shown in Fig. 4, the dependence $av/F - t/F$, i.e. $av - t$, becomes nonlinear for this case.

The surface areas of mesopores, determined by the t/F method are by as much as 66% larger than those determined by the Pierce method and on the basis of the mercury intrusion measurements according to Dubinin. This means that the boundary between micropores and mesopores, based upon the idea of the increase of the adsorption potential in micropores does not lie at the value of 19 Å, but at smaller pores. A characteristic feature of the t/F method is that it is not based on the capillary effects and does not use either the Kelvin or Washburn equation. It cannot be excluded that the found differences in the value of mesopore surface areas are caused, to a certain extent, by the fact that for a meniscus of small radius of curvature, the assumptions on which the Kelvin as well as Washburn equations are based, cease to hold.

Results of the t/F method are dependent on the proper determination of thickness t which was established on the basis of measuring the surface area of nonporous material of similar composition using the BET method. A delicate point is here the choice of effective surface of the molecule of the measured substance in the adsorbed state. For benzene, the ω values from 30 to 50 Å^{2,20,21} have been reported in the literature. For that reason, absolute precision of the surface area determination using this method is given by the limits from ±10%²² to ±30%²³.

The t/F method further assumes validity of the Dubinin–Raduškavič adsorption isotherm for the adsorption of micropores. Even small deviations from the validity

of this equation can introduce a considerable error into the calculation of mesopore surface area. Even though the Dubinin-Raduškovič equation proved to be useful for the description of adsorption equilibria on microporous adsorbents, it will be of advantage to pay attention to the study of adsorption equilibria for high fillings of microporous adsorbents containing no mesopores.

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REFERENCES

1. Dubinin M. M.: *Pure Appl. Chem.* 10, 309 (1965).
2. Broekhoff J. C. P., de Boer J. H.: *Symposium on Surface Area Determination, Bristol 1969.*
3. Kadlec O., Daneš V.: *This Journal* 32, 693 (1967).
4. Dubinin M. M.: *J. Colloid. Interface Sci.* 23, 787 (1967).
5. Dubinin M. M.: *Symposium on Surface Area Determination, Bristol 1969.*
6. Barrett E. P., Joyner L. P., Holenda P.P.: *J. Am. Chem. Soc.* 73, 373 (1951).
7. Pierce C.: *J. Phys. Chem.* 57, 149 (1953).
8. Cranston R. W., Inkley F. A.: *Advan. Catalysis* 9, 143 (1957).
9. Brunauer S., Mikkail R. S., Bodor E. E.: *J. Colloid Interface Sci.* 24, 451 (1967).
10. Dubinin M. M.: *Ž. Phys. Chim.* 30, 1652 (1956).
11. Kiselev A. V.: *Proceedings on the Second International Congress of Surface Activity, Vol. 2,* p. 183. Butterworths, London 1957.
12. Kadlec O., Dubinin M. M.: *J. Colloid Interface Sci.* 31, 479 (1969).
13. Burgess C. G. V., Everett D. H.: *J. Colloid Interface Sci.* 33, 611 (1970).
14. Lippens B. C., de Boer J. H.: *J. Catalysis* 4, 319 (1965).
15. de Boer J. H., Linsen B. G., Plas T., Zonderzan G. J.: *J. Catalysis* 4, 649 (1965).
16. Smíšek M., Černý S., Minářová J.: *Chem. průmysl* 12, 237 (1962).
17. Zukal A., Dubinin G. G., Kadlec O.: *Izv. Akad. Nauk SSSR* 1967, 2148.
18. Platchenov T. G.: *Mercury Porosimeter, P-5M.* Leningrad Technological Institute, Leningrad 1961.
19. Smith R. N., Pierce C., Cordes H.: *J. Am. Chem. Soc.* 72, 5595 (1950).
20. Isirikian A. A., Kiselev A. V.: *Ž. Phys. Chem.* 36, 1162 (1962).
21. McClellan A. L., Harnsberger H. F.: *J. Colloid Interface Sci.* 23, 577 (1967).
22. Pierce C., Ewins B.: *J. Phys. Chem.* 68, 2562 (1964).
23. Emmet P. H.: *J. Phys. Chem.* 63, 449 (1959).

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