COMPARISON OF DIFFERENT METHODS FOR STUDY OF PORE STRUCTURE

Dagmar TOMANOVÁ[a], Bořivoj ZBUZEK[b], Karel JEŘÁBEK[a] and Petr SCHNEIDER[a]

[a] *Institute of Chemical Process Fundamentals,*
Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchdol and
[b] *Department of Silicate Technology,*
Institute of Chemical Technology, 166 28 Prague 6

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Samples of controlled pore glass were used as model materials for comparison of pore distributions obtained by low temperature nitrogen adsorption/desorption and by mercury porosimetry. Pore distributions calculated from nitrogen sorption data by means of Broekhoff and de Boer equations seemed to be more reliable than results based on Kelvin equation or those obtained by mercury porosimetry, since the latter predict too narrow pores.

Nitrogen capillary condensation and mercury porosimetry are considered as standard for the study of pore structure. These methods are indirect, *i.e.* are based on theoretical relations through which the measured physical quantities are transformed into geometrical parameters of pore structure. The evaluation of results is, of course, based on the assumption that the actual pore structure can be described by a simple model. The reliability of the obtained results depends therefore both upon the correctness of theoretical assumptions as well as upon the suitability of the applied geometrical model of pore structure. Data obtained by one measurement represent, as a rule, a great number of porous particles and the evaluation of results is independent of subjective factors; the availability of commercial automated instruments for these measurements is of great advantage.

In this paper we would like to compare the results obtained by both mentioned methods with the use of different theoretical assumptions and of different geometrical models of pore structure.

EXPERIMENTAL AND CALCULATIONS

Samples of controlled pore glass CPG-10 (BDH Chemicals, England) were used as model materials. According to the producer they have very narrow pore size distribution with the possibility of wide range of mean pore sizes. We have used samples with the following pore radii: 3·75 nm (CPG-10/75), 12 nm (CPG-10/240), 18·5 nm (CPG-10/370), 35 nm (CPG-10/700), 62·5 nm (CPG-10/1 250) and 100 nm (CPG-10/2 000).

Measurements by mercury porosimetry were made on Erba Science Model 65 automated apparatus (Italy) working up to 100 MPa pressures. Adsorption and desorption isotherms of nitrogen were measured with Sorptomatic, Model 1826 automated apparatus supplied by the same manufacturer. The numerical treatment of results was carried out with the use of computer. We have attempted also to characterize the samples by means of scanning electron microscopy, using JEM 100 instrument (JEOL, Japan); the resulting photographs clearly show their structure (Fig. 1).* The available resolution of the instrument (about 10 nm) did not allow, however, to get clear enough photographs of samples with narrow pores which could be measured by nitrogen capillary condensation (CPG-10/75, CPG-10/240 and CPG-10/370). The qualitative agreement of pore structures for samples with narrow and wide pores was, nevertheless, obvious.

Pore distributions from mercury porosimetry (results denoted as P) were calculated according to the Washburn equation valid for cylindrical pores

$$p = -2\gamma \cos \Theta / r\,, \qquad (1)$$

where p is the pressure needed to force mercury into a cylindrical pore of radius r, γ the surface tension of mercury (calculations were made with $\gamma = 0{\cdot}480$ N/m) and Θ is the wetting angle ($\Theta = 140°$ was used).

Pore distributions from adsorption/desorption data were calculated by several methods. All of them are based essentially on equation (*2*)

$$r - t_e = \frac{n\gamma V_m \cos \Theta}{RT \ln (p_0/p)} + F(r, t_e)\,, \qquad (2)$$

where r is the radius of the widest pore filled with the liquid sorbate at pressure p, γ the surface tension of the liquid sorbate, V_m its molar volume and p_0 is the saturated vapour pressure at temperature T. Θ is the liquid sorbate wetting angle, n the meniscus shape factor ($n = 1$ for slit--shaped pores and for cylindrical pores at adsorption, $n = 2$ for cylindrical pores at desorption and $n = 3$ for "ink-bottle" pores) and t_e is the equilibrium thickness of the adsorbed layer. If the correction term $F(r, t_e)$ (see below) is neglected, relation (*2*) corresponds to the well known Kelvin equation. In this form we used it to analyse the pore distribution on the basis of the model of cylindrical pores, using the procedure reported by Roberts[1].

The thickness of adsorbed layer in dependence upon relative pressure of the sorbate (p/p_0) was calculated according to a relation taken from ref.[2]. The results so obtained are denoted as RA (adsorption) and RD (desorption).

Broekhoff and de Boer[3] introduced into the classical Kelvin equation for capillary condensation and spontaneous evaporation of the sorbate in pores a semiempirical correction for the effect of pore walls, which is expressed in equation (*2*) by the function $F(r, t_e)$. In addition, they considered the thickness of adsorbed layer t_e to depend not upon only the relative pressure of the sorbate but also upon the shape of the pore and its radius. In the treatment of our experimental data we used the procedures set forth by Broekhoff and de Boer for the model of cylindrical pores and an adsorption branch of isotherm[2] (results denoted as CA), cylindrical pores and a desorption branch of isotherm[4] (CD), ink-bottle pores and adsorption branch of isotherm[5] (IA) and for slit-shaped pores and desorption branch of isotherm[6] (SD).

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* See insert facing p. 2066.

In addition to the mentioned corrections, Dubinin[7] introduced also correction for surface tension of sorbate at extreme curvature of its meniscus in narrow pores. Since this phenomenon plays a role only in very narrow pores ($r < 5$ nm) which were not present in our samples, this correction has not been used.

RESULTS AND DISCUSSION

According to the classification due to de Boer[8], the sorption isotherms for all the samples measured (Fig. 2) were of the A-type with narrow and high hysteresis loop. This type of isotherm is ascribed by de Boer to cylindrical capillaries, eventually to locally narrowed spherical cavities with narrower necks. Isotherms of this type do not comport with the model of slit-shaped pores.

Pore distributions obtained by all the methods employed (P, RA, RD, CA, CD, IA and SD) showed only one maximum (Fig. 3) and differed from one another mainly by its location. Pore radii of these maxima are summarized in Table I. Of the methods based on cylindrical pores, the mercury porosimetry and the treatment of sorption data according to the classical Kelvin equation (P, RA and RD) give the smallest mean pore radii. Introduction of corrections according to Broekhoff and de Boer shifts the maxima of pore distributions to the right (CA, CD). Markedly different results for the model of ink-bottle pores (IA) and of slit-shaped pores (SD) are mainly due to changes in the values of the shape factor n in equation (*2*).

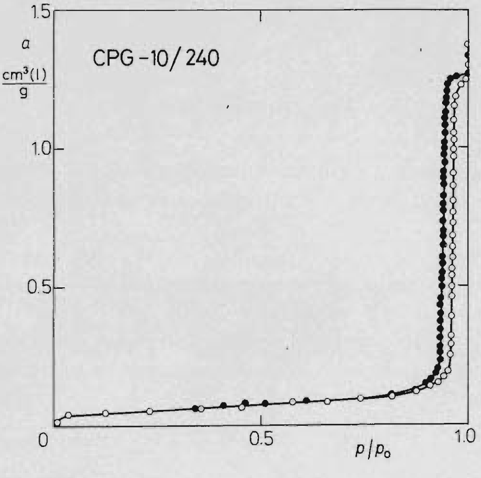

Fig. 2

Nitrogen isotherm for sample CPG-10/240

TABLE I

Mean pore radii (in nm)

Method	CPG-10/75	CPG-10/140	CPG-10/370	CPG-10/700	CPG-10/1 250	CPG-10/2 000
According to producer	4	12·1	17·7	34·7	59·8	99·5
P		14·1	19·7	39·3	67·6	105·6
RA	4·2	14·3	23·7	—	—	—
RD	5·6	18·1	25·3	—	—	—
CA	6·7	21·4	34·0	—	—	—
CD	7·2	21·8	30·4	—	—	—
IA	10·7	35·5	57·5	—	—	—
SD	43	12·0	16·9	—	—	—

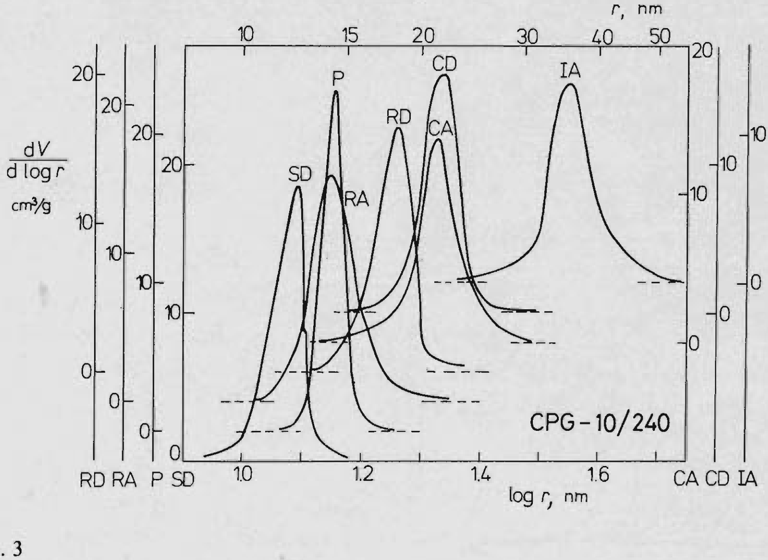

FIG. 3

Pore size distribution for sample CPG-10/240

Comparison of the specific surface area measured by the independent BET method (S_{BET}) with those calculated from the pore distribution (cumulative surface area S_{cumul}) has been often used as a suitability criterion of methods of pore distribution construction. These data are presented in Table II and Fig. 4; it is seen that the greatest differences arise for mercury porosimetry and for evaluation of sorption data from both branches of isotherm on the basis of classical Kelvin equation (P, RA and RD). Procedures proposed by Broekhoff and de Boer lead to better agreement between S_{BET} and S_{cumul} (CA, CD, IA and SD). It can be seen that in these cases S_{cumul} is not too sensitive to the shape of the pores. Since the expression

$$S = nV/r\,, \tag{3}$$

which describes the dependence of the surface of the pore (S) of radius r upon its volume (V) includes the same shape factor n as does the equation (2) for calculation of the critical pore radius, their influence largely cancells out. Differences in S_{cumul} for individual models are mainly due to difference in values of the correction function $F(r, t_{\mathrm{e}})$.

Sometimes a comparison of the cumulative volume of pores and the total volume adsorbed is recommended as a method for the detection if the sample contents flat surface in addition to the surface of pores. In our case examination of those values revealed differences in the range of experimental error only, so probably no significant flat areas outside pores are present.

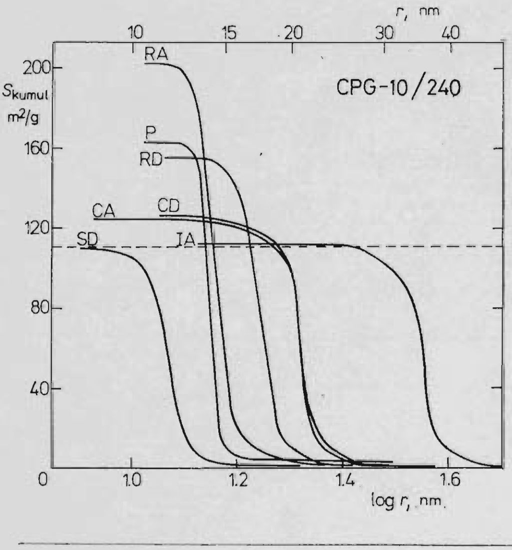

FIG. 4

Cumulative distribution of specific surfaces of sample CPG-10/240

For our samples the treatment of sorption measurements according to Broekhoff and de Boer gives seemingly more realistic results than the other methods. The same conclusion has been arrived at by de Wit and Scholten[9,10] in a study of cylindrical crystals of synthetic chrysotile and by Ihm and Ruckenstein[11] who measured alumina deposited electrochemically on a metal surface. However, also in these cases the resulting pore distributions depend strongly upon the choice of the pore structure model.

It is difficult to asses which of the pore shapes describes the real situation best. The shape of the hysteresis loop of the sorption isotherm has frequently served as a clue. In our case, however, the difference in the shape of the adsorption and desorption branches of isotherm can be explained equally well by differences in condensation and evaporation of sorbate in cylindrical pores (agreement between pore distributions CA and CD) as well as in spherical pores with narrower necks (ink-bottle pores – IA). Based on scanning electron microscopy, the slit-shaped pores can be exluded, but no unequivocal decision can be made between the model of cylin-

TABLE II

Pore volumes and specific surface areas

Sample		CPG-10/75	CPG-10/240	CPG-10/370	CPG-10/700	CPG-10/1 250	CPG-10/2 000
			Pore volume, cm^3/g				
According to producer		0·52	1·08	1·30	0·87	0·85	1·00
Hg porosimetry		—	1·18	1·31	0·77	0·85	1·03
Sorption method		0·83	1·28	1·30	—	—	—
			Specific surface, m^2/g				
S_{BET}		231	111	88	27·4	15·5	10·2
S_{cumul} according to	P	—	167	133	39·2	25·1	18·9
	RA	459	202	121	—	—	—
	RD	300	153	110	—	—	—
	CA	288	125	80	—	—	—
	CD	233	126	93	—	—	—
	IA	266	112	71	—	—	—
	SD	189	109	81	—	—	—

drical and ink-bottle pores. If the model of ink-bottle pores were valid, the structure of porous glass adsorbents would be formed by spherical cavities – with radii determined by the method IA – which are interconnected by narrower necks (whose sizes correspond approximately to the CD results). Based on the model of cylindrical pores, the pore structure should be formed by capillaries with radii corresponding to CA and CD results.

For both these pore structure models the results of mercury porosimetry should correspond to results of the CD method. However, pore distributions P are distinctly shifted to smaller radii. This may be caused by the fact that mercury porosimetry is most influenced by the narrowest passages on the way to the center of particles. In such a case the shift toward smaller radii can be easily understood. It is of interest, however, that approximately the same relative differences between the results from mercury porosimetry and those obtained by the treatment of sorption data by the Broekhoff and de Boer method have been found also by de Wit and Scholten[10] for several samples of different porous materials. Among others also for tubular crystals of synthetic chrysotile for which narrower passages, which could prevented the mercury penetration, have not been detected by electron microscopy. De Wit and Scholten ascribe the too small pore radii obtained by mercury porosimetry to the change in the wetting angle and the surface tension due to the strong curvature of the mercury meniscus in narrow pores. It seems, however, likely that Washburn equation (*1*) is only a very simplified description of the penetration of mercury through very narrow capillaries. In order to describe better the real situation, an approach similar to that employed by Broekhoff and de Boer for the calculation of pore distribution from sorption measurements, should be probably used also in mercury porosimetry.

In comparison with usual samples of porous materials (catalysts, adsorbents *etc.*) the structure of porous glasses is relatively very simple; nevertheless, even in this model case it was impossible to denote a single distribution curve as representing true pore dimension and to determine unequivocally the best model of pore structure. Thus, the physical meaning of results of the pore structure determinations has to be considered as limited. This nevertheless leaves the results as valuable for comparative purposes – in these cases the results should be always accompanied by detailed information about the experimental method and the processing procedures.

REFERENCES

1. Roberts B. F.: J. Colloid Interface Sci. *23*, 266 (1967).
2. Broekhoff J. C. P. de Boer J. H.: J. Catal. *9*, 15 (1967).
3. Broekhoff J. C. P., de Boer J. H.: J. Catal. *9*, 8 (1967).
4. Broekhoff J. C. P., de Boer J. H.: J. Catal. *10*, 377 (1968).
5. Broekhoff J. C. P., de Boer J. H.: J. Catal. *10*, 153 (1968).
6. Broekhoff J. C. P., de Boer J. H.: J. Catal. *10*, 391 (1968).

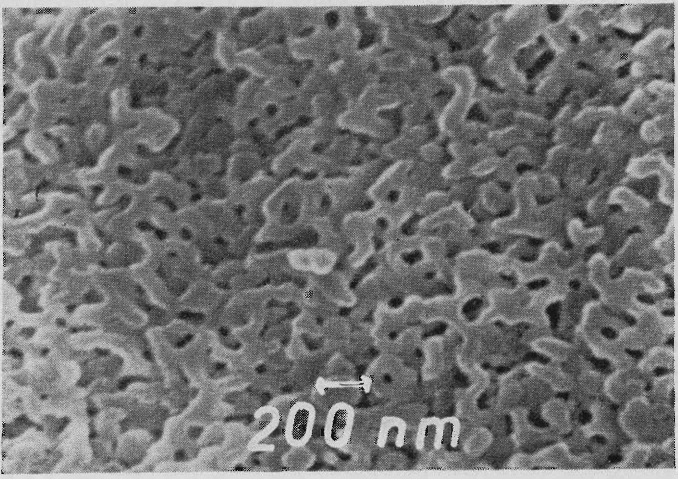

FIG. 1
Scanning electron micrograph of sample CPG-10/700

7. Dubinin M. M., Kaiajeva L. I., Ulin V. I.: Izv. Akad. Nauk SSSR, Ser. Khim. *1977*, 510.
8. de Boer J. H. in the book: *Structure and Properties of Porous Materials* (D. H. Everett, F. S. Stone, Eds). Butterworth, London 1958.
9. de Wit L. A., Scholten J. J. F.: J. Catal. *36*, 30 (1975).
10. de Wit L. A., Scholten J. J. F.: J. Catal. *36*, 36 (1975).
11. Ihm S. K., Ruckenstein E.: J. Colloid Interface Sci. *61*, 146 (1977).