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COMPARATIVE STUDY OF GAS ADSORPTION AND SMALL ANGLE X-RAY SCATTERING BY ACTIVE CARBONS, IN RELATION TO HETEROGENEITY

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Abstract—A comparative study of selected active carbons shows that the spread of the structural parameter *B*, implied by the generalized adsorption equation of Stoeckli, is compatible with the spread of the Guinier gyration radii suggested by the small-angle scattering of X-rays. In the case of a molecular-sieve carbon having a large micropore volume, there is no spread for either parameter. It is suggested, that all available SAXS and adsorption data should be reconsidered in terms of continuous distributions.

1. INTRODUCTION

Owing to their high adsorption capacity, active carbons are widely used in the technology of filtration and separation[1]. There exists a direct relation between the adsorption properties of these materials and their texture which consists of micropores. The widths of these cavities are found in the range of 0.4–1.3 nm (4–13 Å) approximately. Depending on the origin of the carbonaceous material and its preparation (carbonization and activation), the micropore size distribution and therefore the adsorptive properties may vary considerably.

The present work is part of a combined study involving a variety of activated carbons. It is based on adsorption measurement of gases and vapours[2,3], on transmission electron microscopy at high resolution[4], and on diffraction experiments. The general aim is to find satisfactory correlations between specific adsorption and structural parameters of selected active carbons, in order to gain a better understanding of their adsorptive properties. The use of small angle X-ray scattering (SAXS) on well defined samples is also justified in view of the relatively small amount of such information available at the present time for active carbons[5,6].

2. ADSORPTION OF GASES AND VAPOURS

Adsorption by microporous solids in general is described by the theory of micropore volume filling, due to Dubinin[7,8]. In its present formulation, the adsorption isotherm is given by the equation of Dubinin–Astakhov,

$$W = W_0 \exp\{-(A/E)^n\}, \tag{1}$$

where $A = RT \ln(p_0/p)$, E is a characteristic free energy depending on the system under investigation, W is the volume of micropores filled at temperature T and relative pressure (p/p_0), and W_0 represents the total micropore volume.

In the case of microporous carbons, n varies approximately between 1.1 and 2.0, depending on the degree of activation[3,9]. The case $n = 2$ corresponds to the classical equation of Dubinin and Radushkevich,

$$W = W_0 \exp\{-B(T/\beta)^2 \log^2(p_0/p)\} \tag{2}$$

widely used in the past. Instead of E, this equation contains the specific parameters B (structural constant) and β (affinity coefficient), which depend respectively on the solid and on the adsorptive. An alternative expression to eqn (1) has recently been suggested by Stoeckli[10]. It is a generalization of eqn (2), based on the observation that this equation is followed over a large range of pressure and temperature in the case of adsorption by carbons with molecular-sieve properties, whereas strongly activated carbons, without such properties, show significant deviations from it[2,3,9].

Postulating that adsorption by a heterogeneous system of micropores consists of a weighted sum of *D-R* equations, each corresponding to a given class of micropores, one obtains the generalized equation

$$W = W_0 \exp\{-B_0 y\} \exp\{y^2\Delta^2/2\}. \quad [1 - \mathrm{erf}(x)]/2, \tag{3}$$

where $y = (T/\beta)^2 \log^2(p_0/p)$ and $x = (y - B_0/\Delta^2)\Delta/\sqrt{2}$.

The quantity Δ is a measure of the spread of B around B_0, if one assumes a simple Gaussian distribution of the micropore volume with B.

In this approach, the emphasis is put on the physical meaning of the structural parameter B, which is related to the texture of the microporous carbon[2,3,5].

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Table 1. Adsorption parameters, according to eqns (1) and (3)[3] S_{mi} and S_{ext} correspond to the equivalent surface area of the micropores and to the external surface area (meso- and macropores)

Carbon	origin	W_o/cm^3g^{-1}	$(S_{mi}$	$S_{ext})/m^2g^{-1}$	$B_o/10^{-6}K^{-2}$	$\Delta/10^{-6}K^{-2}$	n
U-02	anthracite	0.43	1210	93	0.92	0.21	1.65
F-02	coconut	0.64	1800	36	1.03	0.29	1.47
Carbosieve	polymer	0.51	1435	~1	0.57	-	2.0

For the present study, three different carbons were selected. Their specific parameters, listed in Table 1, correspond to the adsorption of N_2, Xe, SF_6, N_2O, CCl_4 and C_6H_6 measured over a large range of temperature and pressure [2, 3].

Solids U-02 and F-02 are strongly activated (large burn-off) and show large deviations from the original D-R eqn (2). Sample U is also mesoporous. In all cases the external surface is small compared to the equivalent surface area of the micropores (Table 1). Transmission electron microscopy at high resolution carried out by Fryer [4] has also shown that carbon U-02 has a heterogeneous microporosity with a maximum of micropore sizes (widths) near 7 Å. On the other hand, the sample with marked molecular-sieve properties (carbosieve), appears to be homogeneous and has pores in the range of 5 Å approx. Calculations based on the limiting ergergies of adsorption of gases [3, 11], suggest widths of 6–8 Å, for the model of slit-shaped micropores in the case of the present carbons and others.

3. EXPERIMENTAL

The small-angle scattering experiments were carried out with a Kratky camera supplied by Anton Parr Ltd. (Graz), mounted on a Philips PW 1130 generator fitted with a Philips 2253/11 Kratky tube of 2 × 12 mm focus. The generator was operated at 50 kV and 30 mA. Other relevant characteristics were:

—a Ni filter for the Cu-β radiation,

—entrance and counter slits of 150 and 375 μ respectively, and

—a sample holder, 3 mm thick, fitted with a "Mylar" foil window. The latter was filled with the powdered sample and shaken until it packed homogeneously. The absence of preferential graphitic 00l orientation was checked by a conventional Bragg exposure on film. The scattered intensity was already reduced to a few hundredths of the original intensity for values of $s = 2 \sin \theta/\lambda$ smaller than 0.1 Å^{-1}, so that the primary beam could be regarded as infinitely long. This approximation simplifies the treatment of the experimental data.

The measurements were made with a proportional counter linked to a Philips PW 42 counting unit (pulse-height discriminator), and a printer. A step-scanning device [12] allowed the exact repetition of the measurements (5 times in the present experiments).

The inner part of the diffusion curve could only be completed reliably for the sample "Carbosieve", by using the linearity of the Guinier representation. In the case of samples U and F, mathematical difficulties arise in the correction of the collimation effect.

For an infinitely long primary beam, however, it is possible to replace the so-called desmearing procedure by a Hankel transform [13, 14]. This method yields desmeared real-space data starting with smeared data in reciprocal space.

The transformed and normalized curve is usually known as the $\gamma(0)$ curve, and it corresponds to the distribution of all the distances in the sample under investigation (the so-called correlation function of Porod, or one-dimensional Patterson function). According to Porod [15], the Hankel transform carried out on smeared data should lead to a complete agreement with the parameters derived from the $\gamma(0)$ curve.

The parasitic scattering of the sample holder window, as well as the background caused by the short-range fluctuations in the electronic density of the samples, were eliminated.

4. RESULTS AND DISCUSSION

Figure 1 shows the general increase of the intensities towards small values of the quantity $s = 2 \sin \theta/\lambda$, predominantly due to multiple scattering. However, for $s \gtrsim 0.003$ Å^{-1}, this effect may be neglected.

The experimental data and their subsequent analysis show that there exist significant differences between

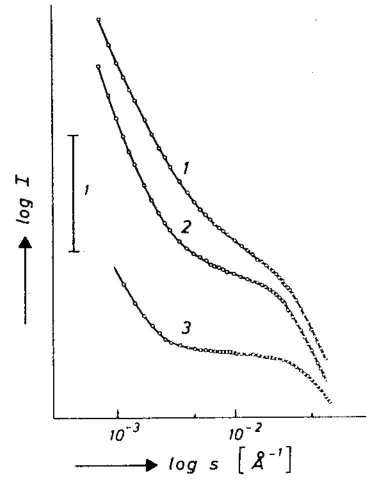


Fig. 1. Plots of log I vs log s ($s = 2 \sin \theta/\lambda$) for samples U (1), F (2) and carbosieve (3).

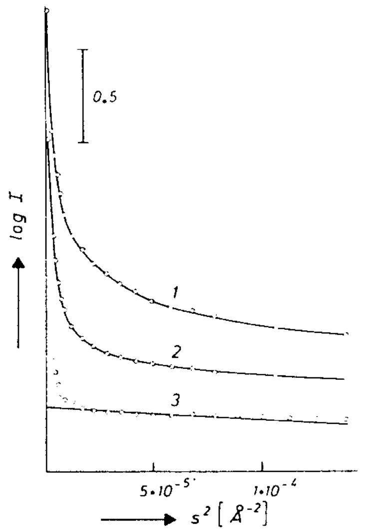


Fig. 2. Plots of log I vs s^2 (Guinier-plot) for samples U (1), F (2) and carbosieve (3).

samples U and F on one hand, and the molecular-sieve carbon on the other. As shown in Fig. 2, a definite Guinier range only exists for the latter sample, characterized by the linearity in the log I vs s^2 plot [16]. The corresponding value of the Guinier gyration radius R_g is slightly higher that the accepted value of 7 Å obtained from the $\gamma_0(r)$ curve, following the Hankel transform method [13, 14]. This value is also in agreement with other parameters derived from the scattering curve (Table 2).

The linearity observed in Fig. 2 for the molecular-sieve carbon implies that the material contains a relatively homogeneous type of void, in spite of its large micropore volume W_0. The absence of linearity for carbon U and F, on the other hand, suggests the existence of a range of R_g values. These observations are in agreement with the findings from adsorption measurements, based on eqn (3), and imply a correlation between the spreads of B and of the gyration radii R_g. It must also be pointed out that the three samples have similar micropore volumes W_0 (Table 1), which makes a comparison of the Guinier plots even more reliable.

Various mathematical techniques can be applied to calculate the distribution function of R_g, as discussed by Guinier [16] and more recently by Plavnik [6]. As shown by the latter author, one observes a considerable increase in the spread with increasing activation (coals AK-0 and AK-4).

The present data for samples U and F suggest a similar spread. Since the earlier approach of Dubinin and Plavnik [5] rests on the concept of a strictly bi-modal type of microporosity, the results of adsorption and SAXS measurements were analyzed accordingly, except in [6], and two sets of average B and R_g values were thus obtained. As found independently by Stoeckli [3, 17] and by Dubinin [8], these quantities are linked by the empirical relation

$$\bar{R}_g = (62 \cdot B \cdot 10^6)^{1/2}. \tag{4}$$

It follows that a spread in B, as implied by the generalized adsorption eqn (3), also implies a spread of the gyration radii R_g. This is already suggested by Plavnik's treatment [6].

Therefore, it seems, that a new evaluation of all data available simultaneously from SAXS and adsorption experiments, would be welcome. The resulting analysis would provide a more accurate relation that eqn (4), and strengthen the physical meaning of the generalized eqn (3). Moreover, the development of microporosity could also be followed directly from SAXS measurements.

Besides the absence of a linear range in the Guinier plot, the heterogeneity of carbons U-02 and F-02 is also revealed by the deviation from Porod's law [16, 18, 19] which normally predicts a decrease of $I(s)$ proportional to s^{-3} at larger values of s. As illustrated by Fig. 3, plots of $s^3 I(s)$ vs s^2, also known as Porod plots, suggest the following relations:

$$I(s) = 6.46\ s^{-1} + 5.1 \cdot 10^{-2}\ s^{-3} \qquad \text{(sample U)}$$

Table 2. Parameters for solids U-02, F-02 and carbosieve, obtained from small angle scattering measurements

Parameter	U-02	F-02	carbosieve
volumic porosity P	0.732	0.752	0.6442
gyration radius R_g [Å]	no Guinier range		7.0 Å
length of coherence ℓ_c [Å]	~18	~14	12.4
range of inhomogeneity $\bar{\ell}$ [Å]	5.10	4.40	2.94
ℓ_p (in pores) [Å]	19.02	17.15	8.23
ℓ_m (in matter) [Å]	6.97	5.86	4.54
Form factor $\ell_c/2\bar{\ell}$	1.7	1.6	2.1
specific area S_p [m^2/g]	684	752	1393
experimental value (table 1)	1300	1836	1435

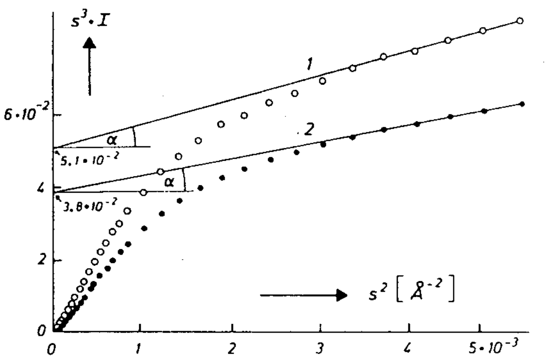


Fig. 3. Plots of $s^3.I$ vs s^2 for samples U (1) and F (2).

and

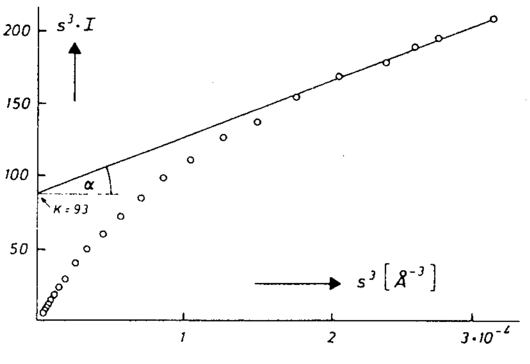
$$I(s) = 4.31\,s^{-1} + 3.8 \cdot 10^{-2}\,s^{-3} \qquad \text{(sample F)}$$

For the molecular-sieve, on the other hand, one finds a normal behaviour (Fig. 4) and

$$I(s) = 3.8 \cdot 10^5 + 93\,s^{-3}.$$

According to Schiller and Méring [18], the term in s^{-1}, observed for samples U and F, is directly related to the fluctuations in the electronic density in the $00l$ direction of the carbonaceous material. This means that the d_{002} spacings show a non-negligible fluctuation around the average value obtained from Bragg's Law. Similar observations have been reported by Perret and Ruland [19], for other carbonaceous materials. In the case of the molecular-sieve, on the other hand, the results suggest that there is homogeneity not only in the voids, but also in the surrounding material.

The spread in the d_{002} spacings can also be observed by means of the dark-field technique developed by Oberlin *et al.* [20]. A semi-quantitative analysis carried out on the molecular-sieve [3] shows relatively narrow distributions of the d_{002} spacings above 3.4 Å, and in the region of 5.5–6.5 Å. The latter can be ascribed to the pores themselves. However, it should be kept in mind that these d_{002} spacings and the gyration radii R_g of the pores are different quantities and should not be confused, even if they are numerically similar.



Further characteristic parameters, given in Table 2, were also determined. First the length of coherence, or correlation distance l_c, [16, 21] defined as

$$l_c = \int_0^\infty I(s)\,ds \Big/ \left(\pi \int_0^\infty sI(s)\,ds\right) = 2\int_0^\infty \gamma(r)\,dr. \tag{5}$$

This quantity should be similar to the average "crystallite" size obtained from a Debye-Scherrer picture.

Secondly the range of inhomogeneity $\bar{l}$ [16, 17], also called mean intersect, defined by

$$\bar{l} = \int_0^\infty sI(s)\,ds \Big/ 2\pi \lim_{s\to\infty} s^3 I(s). \tag{6}$$

The quantity represents the average length of all segments drawn across the solid, in all directions. For a two-phase system (matter and voids), the reduced inhomogeneity lengths in each phase, l_p and l_m, can be derived from it through the relations

$$l_p = \bar{l}/(1-P) \quad \text{(pores)} \tag{7}$$

and

$$l_m = \bar{l}/P \quad \text{(matter)} \tag{8}$$

P is the volumic fraction of the pores present in the sample, usually calculated from the absolute intensity of the primary beam. This intensity was measured by means of a calibrated probe (lupolen), as described in Ref. [22].

The relatively high value of the form factor $l_c/2\bar{l}$ [23] suggests the presence of a lamellar structure, in particular for the molecular-sieve material. This is in agreement with the picture of predominantly slit-shaped micropores [11].

Finally, the specific surface S_p (in m²/g) is given by [16]

$$S_p = 4 \cdot 10^4 P(1-P)/\bar{l} \cdot \rho, \tag{9}$$

ρ being the density of the solid [16, 21].

The lack of agreement between the calculated and experimental values of S_p in the case of samples U and F may be ascribed, partly at least, to the absence of a true Porod limit and to the importance of the inner part of the scattering curve, which appears in the calculation of $\bar{l}$ and S_p [16].

5. CONCLUSIONS

The present study shows that the small angle scattering of X-rays leads to a general picture for the heterogeneity of activated carbons which is compatible with the physical assumptions on which the generalized adsorption eqn (3) of Stoeckli is based. Further experimental data is still needed in order to establish the exact relation between the spreads of the structural parameter B and of the Guinier gyration radii R_g of the micropores. As a consequence, it should be possible to follow the development of microporosity during activation by adsorption and SAXS measurements. The present work also shows that a linear Guinier range can still be found in the case of a high volumic porosity, when the pores are no longer diluted in the solid matrix.

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