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## A SAXS STUDY OF SILICA AEROGELS

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**Résumé** - La diffusion des Rayons X aux petits angles et la microscopie électronique en transmission, sont utilisées pour étudier la fractalité d'aérogels de silice. On a montré l'existence dans des aérogels obtenus en milieu basique, d'unités structurales dont les dimensions dépendent de la densité de l'aérogel. L'extension du domaine fractal est limitée à la taille des particules constituant le squelette de l'aérogel

**Abstract** - X-ray small angle scattering (SAXS) and transmission electron microscopy (TEM) are used to characterise the fractal properties of base catalysed silical aerogels: observation of change over points in the X-rays scattering curves confirms the existence of structural units, like building blocks or beads forming the network. The fractal behavior exists only in the beads or building blocks.

Scattering techniques provide a straightforward method for solving fractal features (1) (2) (3). In this work we use small angle X-rays scattering, that is the technique of choice to probe in the 10 - 1000 Å range random structures, associated with thermoporometry, low frequency Raman scattering and TEM for study the structure of silica aerogels.

The silica aerogels used in these experiments are obtained from Airglass AB Sjobo Sweden. The material is prepared (4) by base catalysed hydrolysis and condensation of silicon t etramethoxide (TMOS) in alcohol. The gel obtained is hypercritically dried to remove the solvent. The aerogels used in these experiments have density between  $7,5 \cdot 10^{-2} \text{ g/cm}^3$  and  $2,5 \cdot 10^{-1} \text{ g/cm}^3$  and are nearly transparent.

The small angle X-rays scattering (SAXS) measurements are performed on a Rigaku high power rotating anode generator (12 KW) with a position sensitive detector. A multichannel analyser connected to a microcomputer allows fast measurements.

The X rays beam of wavelength  $1,5405 \text{ Å}$  (Cu  $K\alpha_1$ ) is focused on the detector plane by curved monochromator. Both the sample and X-ray beam are held under vacuum in order to reduce air scattering. Point like slit conditions with an irradiated cross section of about  $1 \text{ mm}^2$  is used. Scattering curves are obtained in the range of scattering vector  $q = 4 \pi \sin \theta / \lambda$  where  $\lambda$  is the x-rays wavelength and  $2 \theta$  the scattering angle from  $10^{-2} \text{ Å}^{-1}$  to  $5 \cdot 10^{-1} \text{ Å}^{-1}$  and are corrected from the background scattering and the absorption.

For fractals the intensity  $I(q)$  of X-rays scattered at low angle (5) (6) can be analysed in terms of a power-law using  $\log I(q)$  vs  $\log q$  plots

$$I(q) \sim q^{-\alpha} \quad (1)$$

The regime where (1) applies is called Porod region and  $\alpha$  is the Porod exponent. The interpretation of  $\alpha$  depends on the origin of the scattering and can be related to fractal characteristics of the particles.

Two classes of fractal objects can be distinguished according to the observed slope of the scattering curves in the Porod regime.

- For a mass fractal of dimension  $1 \leq D \leq 3$  the exponent  $\alpha$  is simply  $D$ .
- For surface fractals of dimension  $2 \leq D_s \leq 3$  the exponent  $\alpha = 6 - D_s$ .

Note that volume fractals can be observed for intermediate size smaller than a correlation length  $\xi$  and larger than a mean particle diameter  $r$ . At a given  $q$  one probes length scales of order  $q^{-1}$ .

For a particle with a smooth surface (non fractal)  $\alpha = 4$  and  $D_s = 2$ .

The scattering curves for silica aerogels of apparent densities  $a = 0,075 \text{ g/cm}^3$ ,  $b = 0,1 \text{ g/cm}^3$ ,  $c = 0,2 \text{ g/cm}^3$  and  $d = 0,25 \text{ g/cm}^3$  are shown in figure 1 in double logarithmic plots.

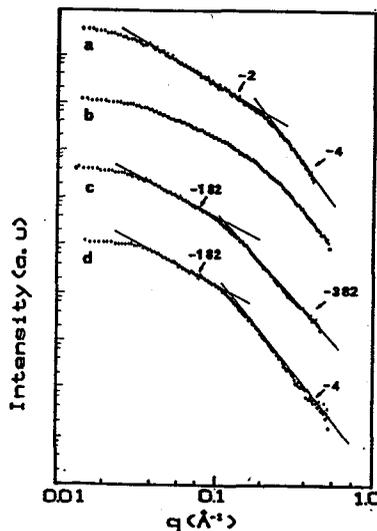


Fig. 1 - Small angle x-ray scattering results plotted as  $\log I$  vs  $\log q$  for silica aerogels of various apparent densities curve a  $\rho = 0,075 \text{ g/cm}^3$ , curve b  $\rho = 0,1 \text{ g/cm}^3$ , curve c  $\rho = 0,2 \text{ g/cm}^3$  and curve d  $\rho = 0,25 \text{ g/cm}^3$

Three distinct regimes are apparent for sample a, c, d. For  $q < 0,03 \text{ \AA}^{-1}$  the data are  $q$ -independent: this is consistent with a uniform non fractal long range structure. For  $q > 0,03$

the SAXS intensities exhibit two linear regions with different slopes. This type of curves can be analysed in terms of the power law (1)

with  $|\alpha| = 2$  ;  $0,03 \leq q < 0,2$  curve a and  $|\alpha| = 1,82$  ;  $0,03 \leq q < 0,11$  curve c and d

for  $q > 0,2$  or  $0,1$   $|\alpha| = 4$  for aerogels a and c, d.

These aerogels are thought to be mass fractal with dimensionality  $D = 1,82$  or  $2$  over one decade in length scale only.

The  $q$  values associated with cross over points at high  $q$  range from  $r = 5 \text{ \AA}$  for a, to  $r = 9 \text{ \AA}$  for c. and d. This should represent the approximate average size of smooth structural units ( non fractal ) which build up the volume fractal structure of aerogels.

The approximately constant value of  $I(q)$  over the small angle side of the studied  $q$  domain for samples a, c, d implies that the structures of the aerogels have low correlation length. The cross over between the constant intensity region and the domain where  $I(q) \propto q^{-\alpha}$  defines the correlation length. This represents the upper limit of fractal scaling of the studied aerogels. The value obtained is approximately the same for sample a, c, d,  $\zeta = 35 \text{ \AA}$ . The length is smaller than the sizes of the particles deduced from TEM. Electron microscope observations performed at 120 KV on a Jeol 1200 EX microscope show ( figure 2 ) that the backbone network of aerogels a, c, d is formed of rods entangled in nodes. The rods are chains of sticked beads (7) (8). The chains or beads diameter increases with the apparent densities of aerogels and ranges from  $\sim 40 \text{ \AA}$  for (a) to  $\sim 80 \text{ \AA}$  for (c) and (d).

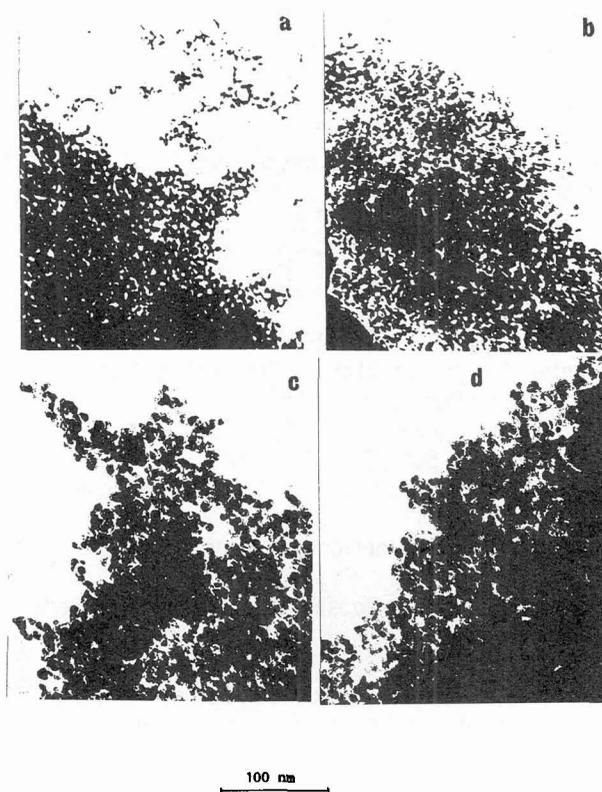


Fig. 2 - Structure of the network in aerogels for a density  
 a)  $\rho = 0,075 \text{ g/cm}^3$ , b)  $\rho = 0,1 \text{ g/cm}^3$ , c)  $\rho = 0,2 \text{ g/cm}^3$  and d)  $\rho = 0,25 \text{ g/cm}^3$

The difference between the size of beads observed by TEM and the single correlation length obtained by SAXS is due to the limited range ( $q \geq 0,01$ ) of the measurements. That implies a great error on the determination of  $\xi$ .

It is reasonable to consider that the size of chains or beads deduced from electron microscope observations and confirmed by low frequency Raman scattering (9) is 55 Å for aerogels (a) and 82 Å for aerogels (c) and (d) is the upper limit of the fractal scaling.

It should be noted that for the aerogel of density 0,1 g/cm<sup>3</sup> no well defined exponent can be deduced from the curve b figure 1. This can be consistent with a polydispersed system or non fractal structure (10).

Electron microscope observations show (fig. 2b) an inhomogeneous texture of the aerogel b. Thermoporometry measurements performed (7) on the sample a, b, c, d show microporous volume for the sample b, only. This microporosity is consistent with pores surface roughness or polydispersity of the beads.

However, despite these characteristics of the b sample, low frequency Raman scattering (7) has shown the fractal character of the internal structure of the beads.

## CONCLUSION

The most reasonable texture consistent with SAXS and TEM data is a backbone of branched chains of beads. Our analysis suggests that it is the beads of the backbone and not the pore space which are fractal. The domain of self similarity extend approximately on one order of magnitude. The mass fractals are observed over sizes increasing with apparent densities. The size ranges from 40 Å to 80 Å that corresponds to the size of beads or building blocks. These observations are in good agreement with an early observation on a same aerogel (3), with low frequency Raman scattering (7) thermoporometry (9) and what is known on the chemistry of the gelation process (11).

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