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Section 3. Gel Formation

A SAXS STUDY OF KINETICS OF AGGREGATION OF SILICA SOLS

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SAXS in situ experiments on the evolution of TMOS solutions during hydrolysis and polycondensation lead to power laws with scaling exponents  $\alpha \sim 2$ . It is suggested that this could be the result of the polydispersity of the samples and that only an apparent fractal dimension can be obtained in this way. Kinetic studies tend to indicate that agglomeration in the sol is the result of a diffusion-controlled process.

1. Introduction

Recent SAXS experiments [1,2] on silica sols obtained by hydrolysis and polycondensation of  $\text{Si}(\text{OC}_2\text{H}_5)_4$  (TEOS) solution led to the conclusion that the resulting sol was formed of particles which could be described in terms of mass or surface fractals.

We have undertaken systematic studies in order to obtain more detailed information about the kinetics of the process using  $\text{Si}(\text{OCH}_3)_4$  (TMOS) which undergoes faster hydrolysis and thus permits an in situ study of the evolution of the sol. The first results of this work are presented here.

The intensity of X-rays scattered at low angles by a system of identical particles can be approximated by Guinier's law:

$$I(q) = N(\Delta\rho)^2 v^2 \exp\left(-\frac{1}{3}R_G^2 q^2\right),$$

where  $I(q)$  is the SAXS intensity as a function of the modulus of the scattering vector  $q = 4\pi(\sin \theta)/\lambda$ ,  $2\theta$  being the scattering angle,  $\lambda$  the X-ray wavelength,  $N$  the number of particles of volume  $v$ ,  $R_G$  the electronic radius of gyration and  $\Delta\rho$  the difference of electronic densities of the scattering particles and of the background (solvent). This law holds for  $qR_G < 1$ .

For a polydispersed system  $R_G$  is heavily weighted towards larger particles. An average value  $\langle R_G \rangle$  can be obtained from SAXS measurements on a relative scale from a  $\log I(q)$  versus  $q^2$  plot. The intensity scattered at higher angles for  $qR_G \gg 1$  can be analysed in terms of a power law  $I(q) \sim q^{-\alpha}$

using  $\log I(q)$  versus  $\log(q)$  plots. It has been shown [1-3] that  $\alpha$  is simply related to the fractal characteristics of the particles.

For mass fractals of dimension  $1 < D < 3$

$$\alpha = D$$

and for surface fractals of dimension  $2 < D_s < 3$

$$\alpha = 6 - D_s.$$

When a particle has a smooth surface, (that means it is not a fractal)  $D_s = 2$  and  $\alpha = 4$  which corresponds to the classic Porod's behaviour:

$$\lim_{q \rightarrow \infty} |I(q)q^4| = Cte.$$

2. Preparation of the samples

Samples were prepared from solutions of tetramethoxysilane (TMOS) (Fluka) dissolved in

methanol; the composition was uniformly fixed at 50% vol. TMOS. To this solution varied amounts of bidistilled water were added. The molar ratio  $R = \text{H}_2\text{O}/\text{TMOS}$  was either  $R = 1, 2$  or  $4$ .

Two distinct series were studied. In the acid-catalysed series  $\text{HNO}_3$  was added with  $\text{pH} = 2$ ; in the base-catalysed series  $\text{NH}_4\text{OH}$  was used with  $\text{pH} = 9$ .

The initial TMOS-alcohol mixture was thoroughly stirred at  $25^\circ\text{C}$  then the prescribed amount of water + catalyst was added under constant stirring. The end of the addition corresponds to the origin of time  $t_0$  in the kinetic studies described.

Lindemann-glass capillaries of 1 mm diameter were filled with the solution; the tips of the tubes were then carefully flame-sealed taking care not to affect the middle solution-filled portion. The filled capillary was placed horizontally in the sample holder of the SAXS device and the run started immediately.

### 3. Experimental

The SAXS experiments were carried out using synchrotron radiation at LURE (Orsay, France). The white beam of the storage ring is monochromatized by a double-crystal monochromator of Si tuned for 8 keV. The resulting X-ray wavelength was  $\lambda = 1.55 \text{ \AA}$ . Two sets of slits define the beam cross-section and reduce the parasitic scattering. This point-like type of geometry of collimation avoids the troublesome necessity of mathematical data desmearing for the slit-height effects unavoidable in systems using "infinite height" slits and which may affect the precision of results used for testing the possible fractal behaviour.

A one-dimensional position-sensitive detector was used to record the scattered X-ray intensity from the sample contained in a capillary. The parasitic background scattering from the capillary and slits was subtracted using a "blank" capillary filled with undehydrated 50% vol. TMOS-50% vol. methyl alcohol solution.

The spectra were taken automatically at 10 min intervals, the acquisition time was of the order of 1 min.

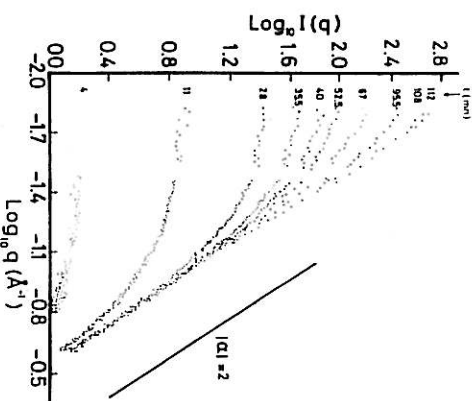


Fig. 1.  $\text{Log } I(q)$  versus  $\text{log } q$  plots for an acid-catalysed solution with  $R = 1$  observed for increasing time values indicated.

The data were stored and computer processed for correction and display.

### 4. Results

Fig. 1 shows the sequence observed for an acid-catalysed solution with  $R = 1$ . It can be seen

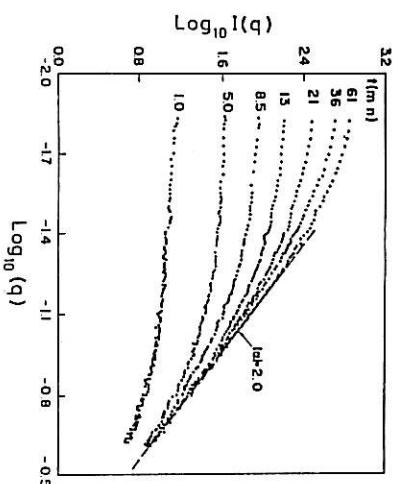


Fig. 2.  $\text{Log } I(q)$  versus  $\text{log } q$  plots for an acid-catalysed solution with  $R = 2$  observed for increasing time values indicated.

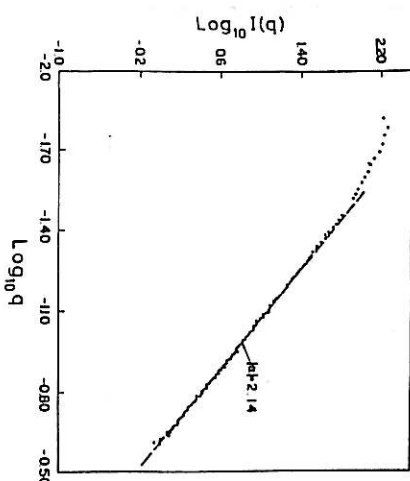


Fig. 3.  $\text{Log } I(q)$  versus  $\text{log } q$  plots for an acid-catalysed solution with  $R = 4$  observed between 50 and 115 min.

that the curves tend progressively towards a limiting slope, corresponding to  $|\alpha| = 2.09$ .

For  $R = 2$  (fig. 2), the limiting value is  $|\alpha| = 2.0$  while, for  $R = 4$ , the value  $|\alpha| = 2.14$  was systematically observed, between 50 and 115 min (fig. 3).

For the basic series for  $R = 1$ , two linear regions were observed with a cross-over for  $q \sim 0.066 \text{ \AA}^{-1}$ , corresponding to a particle size of  $15 \text{ \AA}$  (fig. 4). For  $R = 2$  and  $4$ , however, the plots show a

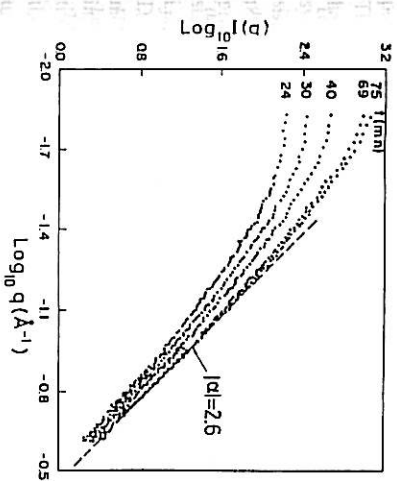


Fig. 4.  $\text{Log } I(q)$  versus  $\text{log } q$  plots for a base-catalysed solution with  $R = 1$ .

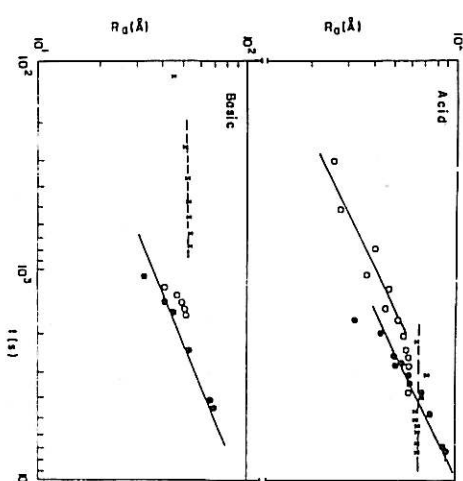


Fig. 5. Variation of  $\langle R_G \rangle_z$  with time for the acid and basic series:  $\bullet$ ,  $R = 1$ ;  $\circ$ ,  $R = 2$ ;  $\times$ ,  $R = 4$ .

progressive curvature without well-defined linear portions; the average intermediate slope is around 2.2 while the limiting slopes for high  $q$  values exceed 3.

The corresponding Guinier plots show a marked curvature which increases with time; from the limiting slopes the average gyration radii  $\langle R_G \rangle_z$  were calculated: their variation with time is shown in fig. 5 for acid and basic series.

### 5. Discussion and interpretation

If the interpretation of  $|\alpha|$  in terms of fractals is to be adopted, the preceding results seem to indicate that the particles are indeed mass fractals for the acid series, the fractal dimension being simply  $D = |\alpha|$ .

The problem is seen to be more complex for the basic series, where a transition towards surface fractals would have to be admitted for  $|\alpha|$  values greater than 3.

However, it seems to us that another explanation is possible if the expected high polydispersity of these solutions is taken into account.

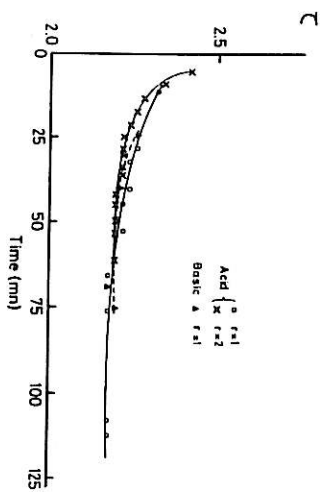


Fig. 6. Polydispersity  $\tau$  as a function of time for acid series ( $R=1$ ) and  $R=2$ ) and for the basic series ( $R=1$ ). The value  $D=2.5$  has been assumed.

It has recently been shown [4] that for a polydisperse fractal solution the exponent  $|\alpha|$  of the power law is given by the relation:

$$|\alpha| = D(3 - \tau),$$

where  $D$  is the fractal dimension and  $\tau$  the classic scaling exponent of the mass distribution law:

$$N(M) \sim M^{-\tau}.$$

The exponent  $|\alpha|$  thus represents only a polydispersity-smearred fractal dimension and to extract  $D$  a separate determination of  $\tau$  would be necessary.

For the acid series, if we admit the classic values  $D=2.5$  and  $\tau=2.2$  given by the percolation theory,  $|\alpha|=2$  is found, which is indeed close to the experimental final slope.

From the variations of  $|\alpha|$  with time the evolution of polydispersity  $\tau$  can be estimated if  $D$  is considered constant; it can be seen (fig. 6) that in all cases there is an increase of polydispersity, but the final value  $\tau=2.2$  is reached earlier for  $R=2$  than for  $R=1$ .

For the basic series for  $R=1$  the cross-over between two power-laws indicates a hierarchical fractal structure of elementary fractal particles agglomerated into larger fractal units [5]. The above polydispersity argument can be applied here to the intermediate slope  $|\alpha| \sim 2.2$ ; the resulting

polydispersity  $\tau$  values of the clusters are shown in fig. 6.

For higher  $R$  values the curvature of the plot precludes a straightforward interpretation. A more refined fitting of the whole curves would be needed.

The slope of the graphs relating the variations of  $\langle R_G \rangle_z$  with time (fig. 5) indicate a scaling law,  $\langle R_G \rangle_z \sim t^\beta$  with  $\beta \sim \frac{1}{2} - 1/D$ ; this should be indicative of a diffusion-controlled agglomeration process [6].

## 6. Conclusion

SAXS measurements of kinetics of agglomeration of a silica sol show for acid-catalysed solutions an apparent fractal dimension of 2. This, however, could be an effect of the polydispersity of the sample and to extract the real fractal dimension independent evaluation of the mass distribution scaling exponent would be needed. For basic solutions no simple fractal coefficient could be extracted from the data. The agglomeration seems to be controlled in all cases by a diffusion process.

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