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Symposium held April 5-8, 1988, Reno, Nevada, U.S.A.

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particles, it is necessary either to maintain flame temperatures low enough to continuously generate reactive monomer or to use a continuous feed reactor. In either situation, small molecules are always available. So long as small molecules are present, the system will remain in the monomer-cluster growth regime producing large uniformly dense colloidal particles with minimal aggregation.

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LIGHT SCATTERING OF SiO_2 MONODISPERSE MICROSPHERES PREPARED BY THE SOL-GEL ROUTE

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ABSTRACT

SiO_2 microspheres have been prepared from TMOS/Methanol/water sols in basic condition (pH ≃ 12) by the Stöber method and studied by TEM static and dynamic light scattering techniques in order to determine the mean size $\bar{R}$, size distribution, hydrodynamic radius R_H, radius of gyration R_G and translational diffusion coefficient D_t ; the ratio R_H/R_G was found less than 0.55 and the aggregates have a fractal geometry with df ~ 2.3 ± 0,05. The results are compared to previous work on colloidal silica aggregates prepared by other techniques and discussed.

INTRODUCTION

In recent years the concept of fractal geometry has become important and has proved successful for the description of non equilibrium aggregation in colloidal and macro molecular systems. Static and dynamic light scattering, X-ray and neutron scattering, electron microscopy as well as computer simulation are among the best and most used techniques for probing these fractal structures.

In the scattering experiments several quantities can be determined to characterize the physical properties of the clusters : the hydrodynamic radius R_H is obtained from the initial slope of the correlation function (first cumulant) measured in dynamic light scattering (DLS) and allows to determine the diffusion coefficients of the non-interacting particles; the radius of gyration of the primary particles and of the clusters R_G as well as the surface and mass fractal dimensions of the aggregates can be extracted from the static structure factor measured in light, X-ray or neutron scattering experiments.

Small silica particles are commercialy produced under trade names as Cab-O-Sil (Cabot Corporation) or Ludox (Dupont) and have been extensively studied in the last few years [illegible]; in this paper we present original results of transmission electron microscopy, static and dynamic light scattering of almost monodisperse spherical SiO_2 aggregates prepared by a sol-gel process using a technique originally developed by Stöber [9] .

PREPARATION AND CHARACTERIZATION

Sols have been prepared at room temperature by first mixing 65ml of methanol in 34.4ml bidistilled water and adding then 22ml NH_4OH and 3ml of tetramethoxysilante TMOS (Fluka). Such sols have a pH of 12.3. The growth of the SiO_2 particles up to a certain size is extremely fast and aggregation process cannot be followed by one or the other experimental technique. Figure 1 is a typical result of the shape and size distribution of the particles observed by Transmission Electron Microscopy. The particles appear practically spherical with a moderate polydispersity but without aggregation; their mean diameter calculated with 50 particles is $\bar{R}$=150±30nm.

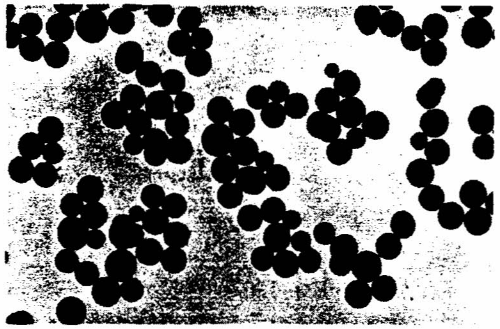

Fig.1 - Typical TEM Micrography of SiO_2 particles.

$\overline{R}$ = 150 ± 30nm

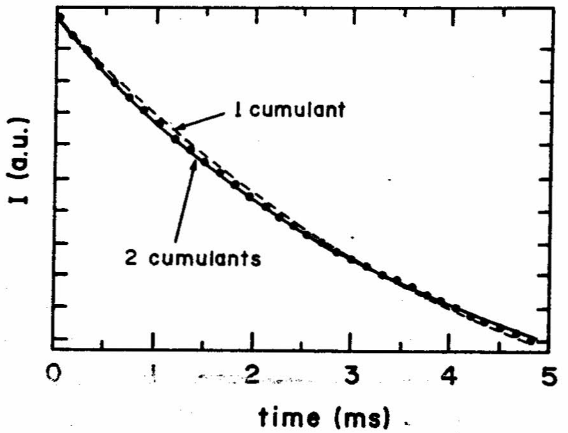

Fig.2 - Fit of a typical dynamic light scattering correlation spectrum taken at Θ=30° using 1 and 2 cumulants.

The values of R_H=140±10nm

Quasielastic light scattering experiments using a 50mW, λ =4965 Å Ar laser (Spectra Physics 170) and a 48 channels Malvern K7023 autocorrelator confirm these results. Fig.2 shows a fit of a typical correlation spectrum taken at Θ=30° using 1 and 2 cumulants (ratio of the cumulants K_2/K_1^2=0.46) The cumulants analysis shows that the mean decay rate or Rayleigh linewidth Γ as well as the ratio of the first two cumulants are independent of the scattering vector q in the range $0,3.10^4 < q < 3.10^5 cm^{-1}$(figure 3). As discussed below the system can be perfectly described as a dilute solution of almost monodisperse but optically isotropic and rigid spherical particles; the first cumulant contains only contribution from the translational degree of freedom $\Gamma = D_t q^2$, where D_t is the translational diffusion coefficient, its mean value being $\overline{D_t}$ = 1.6 10^{-8} cm^2/s, $\overline{D}_t$ in turn is related to a hydrodynamic radius R_H via the Einstein Stokes relation $D_t = K_B T/6\pi\eta R_H$ where K_B is the Boltzmann constant, T the temperature and η the solvent viscosity. The value obtained for R_H for the data of Figure 3 is 140 ± 10nm.

A typical result of static light scattering experiment measured with the same instrument is presented in figure 4. The data are fitted using a Fisher-Burford type approximant [8] .

$$S(q) = \frac{S(q=0)}{\left(1 + \frac{2q^2}{3d_f} R_G^2\right)^{d_f/2}} \qquad (1)$$

where d_f is the mass fractal dimension of the SiO_2 particles. The data analysis of this figure give : d_f = 2,26 ± 0,05 and R_G = 285 ± 10nm, showing that the aggregates are indeed mass fractals.

DISCUSSION

According to Martin and Leyvraz [10] the Rayleigh linewidth obtained from the DLS first cumulant analysis is given by $\Gamma = D_t q^2 h(qR)$ where h (qR)= 1 for qR<< 1 (insensitivity of the linewidth to internal degrees of freedom) and $h(qR) \sim (qR)^{\omega}$ for qR >> 1 with ω=0 for rigid bodies, ω=d-2 for flexible particles with strong hydrodynamic interaction and $\omega = d_f$ for flexible particles with weak hydrodynamic interaction. Moreover, taking in account a polydispersity in power law form $N(M)= M^{-\tau} g(M/M_z)$, they showed that for τ <3, $\Gamma = q^2 D_z F(qR_z)$ where $F(qR_z) \sim 1$ for qR_z << 1 and $F(qR_z) \sim (qR_z)^{\alpha -2}$ and consequently $\Gamma \sim q^{\alpha}$ for qR_z >> 1. Our data shows that $\Gamma \sim q^2$ for all values of qR_z up to 6 confirming that our particles are rigid bodies and that ω=0 . For mass fractal an upper limit of the polydispersity exponent τ can then be estimated as $\tau = 1 + \omega/d_f$ = 1 for no hydrodynamic interaction and $\tau = 2-(d-2-\omega)/d_f$ = 1,56 for strong hydrodynamic interaction. This indicates that our experimental value of the Hausdorf dimension d_f = 2,26, calculated from the static structure factor is correct since already for τ < 2, the static structure factor for mass fractals scales as $(qR_z)^{-d_f}$. The surface fractal dimension d_s of our particles may be obtained at large q by small angle X-ray scattering (measurements are underway). According to Martin et al [10] the static structure factor should scale as 2d - d_s for 0 < τ < 1 + d_s/d . The lowest superior limit of τ will be obtained for d_s = 2 (smooth particles) and its value 1.66 is already larger than the maximum experimental value τ = 1,56 as calculated above. Polydispersity is therefore irrelevant in our case. The determination of the exponent τ of these sol-gel aggregates is not possible but an upper limit can be given : $\tau \leq$ 1,56.

Another interesting result is the value found for the ratio R_H/R_G. For silica particles this ratio has been only determined during the aggregation of LUDOX Particles [7] and found equal to 0,72, a value close to the value obtained for linear flexible random-walk chain polymer in solution R_H/R_G = 0,79 but in disagreement with other aggregation models such as the reaction-

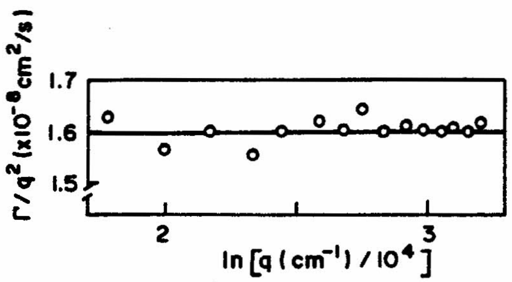

Fig.3 - Rayleigh linewidth Γ as a function of the scattering vector $q = 4\pi \frac{n}{\lambda}$ sen $\theta/2$. Γ/q^2 is constant over the whole q range.

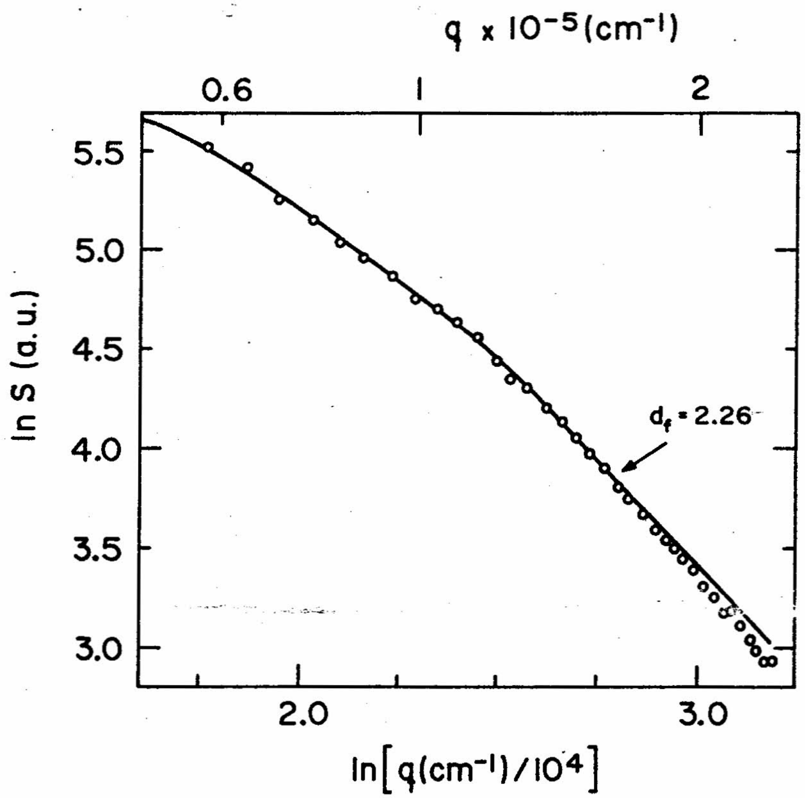

Figure 4 - Static light scattering intensity S versus q and fitting using the Fisher -Burford approximant : R_G = 290 ± 10nm and d_f = 2.26 ± 0,05

limited aggregation $R_H/R_G \sim 0{,}97$ [11] . Pusey et al [11] showed however that the values determined experimentaly are in fact average radius $\langle R_H \rangle$ and $\langle R_G^2 \rangle^{1/2}$ and reflect different moments of the cluster mass distribution. They define consequently $\langle R_H \rangle / \langle R_G^2 \rangle^{1/2} = \gamma R_H/R_G = \gamma \beta$ where γ is a correcting factor strongly dependent of the form of the cut-off function of the power-law distribution, the polydispersity exponent τ and the mass fractal dimension d_f.

On the other hand R_H is a parameter calculated from the Einstein-Stokes relation and which envolves an experimental parameter of difficult access and most of the time not known with precision: the solvent viscosity η. A wrong estimation may therefore lead to erroneous determination of R_H / R_G. We also found in our experiments that the measured parameters R, R_G and d_f are not universal; their values may change from run to run by up to 15%. The systematic study of the influence of some parameters such as temperature, slight variation in the starting composition, quality of the starting components (especially NH_4OH) aging of the sols etc is underway. With the most recent and better controlled sols for which SLS and DLS have been performed on the same samples and in sequence within one hour we encountered the following results.

Test A : SiO_2 particles prepared as above, dried by solvent evaporation and washed several times in water. SLS and DLS performed with SiO_2 agglomerates dispersed in bidistilled water T = 22°C η H_2O = 0.97 cp.

Test B : SiO_2 particles prepared as above and measured in situ. The sol has then been diluted in methanol. Solvent used for viscosity measurement: amount of methanol + water + NH_4OH, η = 1.02 cp.

	R_H (nm)	R_G (nm)	d_f	R_H / R_g
Test A	228	408	2.34	0.54
Test B	112	349	2.02	0.32

These preliminary results show that the values of R_H / R_G are even lower than those found by Wiltzius [7] and not in agreement with theoretical models [12,13]. However we think that it is too early to make a clear and honest comparison and more work are necessary to elucidate this interesting problem.

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