

LIGHT SCATTERING OF SILICA PARTICLES IN SOLUTION

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Static and dynamic light scattering techniques were used to study aggregation of monodisperse silica microspheres prepared by the Stoeber process. The results show that the Stoeber particles form spheroidal aggregates when dispersed in water solutions. In acidic conditions these aggregates tend to coalesce in polydisperse collections of aggregates. These observations are compared with previous works on silica aggregates prepared by different techniques.

1. Introduction

Static and dynamic light scattering techniques have been used extensively in recent years to investigate processes of non-equilibrium aggregation of colloidal systems [1-3]. The range of values of the modulus of the light scattering vector q is very convenient for observing features due both to the individual silica particles and to any aggregation that occurs with these particles. Some of the relevant physical quantities that can be easily determined by these techniques are: the radius of gyration, R_g , of the individual particles; the hydrodynamic radius, R_h , of the particles; the mean mass fractal dimension of the aggregates; the mass fractal dimension of the aggregates when they are fractals and the surface dimension of the particles, if their surface is fractal [2]. Also the diffusion coefficient of particles and aggregates can be directly obtained from dynamic light scattering experiments.

In this paper, we present results from light scattering experiments on SiO_2 microspheres prepared from solutions of tetramethoxysilane (TMOS) in highly basic conditions. It was observed that the particles aggregate rapidly when dispersed in water. These aggregates are very stable when in normal or basic solutions. In acidic conditions, the aggregates grow to large sizes and become unstable. The influence of changes in the conditions of preparation of the solutions was tested by allowing the aggregates to form in a

large range of different viscosities. The velocity of aggregation is only slightly decreased and the physical properties of interest are not significantly affected by these changes in viscosity.

2. Preparation and characterization

Monodisperse silica particles are prepared by the sol-gel technique using the so-called Stoeber process [4]. Solutions are prepared at room temperature by mixing 65 ml methanol in 34.4 ml bidistilled water, adding 22 ml NH_4OH and 3 ml TMOS. A highly basic (pH \approx 12) colloidal solution with a milky hue is obtained. The growth of the silica particles is extremely fast. The sol is dried in vacuum, a liquid nitrogen temperature. The powder product (0.11 g) is dispersed in 15 ml bidistilled water and filtered. The resulting solution is usually quite transparent for visible light but scatters laser light effectively. Some solutions were prepared by dispersing the powder in 0.1N water solutions of HNO_3 or NH_4OH to study the aggregation process in different pH conditions. To other solutions the viscosity was modified by adding saccharose before filtering.

The light scattering experiments were done using the 4965 Å line of an argon ion laser (Spectra Physics Model 171) and a Malvern K7023 autocorrelator. By changing the geometry of scattering a range of values of the scattering vec-

tor q , from 2.5 to $0.5 \times 10^{-3} \text{ \AA}^{-1}$ could be covered. This range allows the observation of scattering from the individual Stoeber particles and the aggregates. Static and dynamic light scattering parameters were obtained simultaneously for each run.

3. Results and discussion

Typical results from static and dynamic light scattering experiments are shown in figs. 1 and 2, respectively. These data were obtained with a pure water solution of silica particles, in normal conditions. At least two regimes are seen in the curve of fig. 1. For values of q greater than about $1.9 \times 10^{-3} \text{ \AA}^{-1}$, the S vs. q curve shows features due to the individual Stoeber particles with a diameter of about 7 nm [5]. For values of $q < 1.9 \times 10^{-3} \text{ \AA}^{-1}$, the scattering curve is mainly due to aggregates of these particles. The mean radius and the size dispersity of these aggregates can be estimated by the dynamic light scattering experiments (fig. 2). From the correlation curves, the mean hydrodynamic radius, R_h , can be obtained by using the Stokes-Einstein relation:

$$\langle R_h \rangle = k_B T / 6\pi\eta \langle D \rangle, \quad (1)$$

where η is the viscosity of the solution and $\langle D \rangle$ is

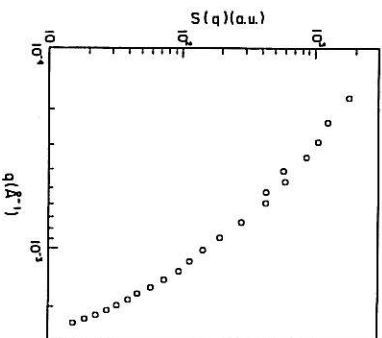


Fig. 1. Double-log Porod-plot of the static light scattering intensity $S(q)$ versus the modulus of the wavevector q .

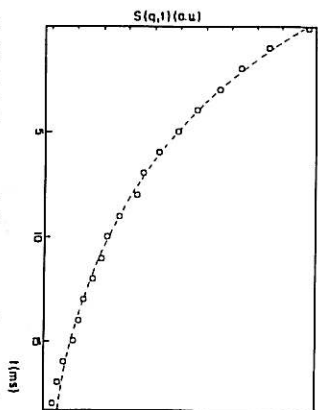


Fig. 2. Typical time correlation curve of a normal water solution of aggregates of Stoeber silica particles fitted to a two-cumulant expansion. For this sample the hydrodynamic radius was 1300 nm.

the mean translational diffusion coefficient which is given by

$$\langle D \rangle = 1/\tau_c q^2. \quad (2)$$

Here τ_c is the optical time of coherence, obtained from the fitting of the correlation curves $S(q, t)$, after subtracting the baseline A , to a multicutant expansion [6]:

$$S(q, t) = [I(0)I(t)] - A]^{1/2} \\ = \exp\left(\sum K_n (-t)^n / n!\right). \quad (3)$$

The optical time of coherence τ_c is given by the inverse of the first cumulant K_1 :

$$K_1 = \tau_c^{-1} = - (d \ln S(q, t = 0)) / dt. \quad (4)$$

For a normal aqueous solution the correlation curve is very well fitted to an exponential (one cumulant) curve. This indicates an essentially monodisperse spheroidal aggregate of Stoeber particles. The mean value $\langle R_h \rangle$ for these aggregates is 180 nm. This value is in excellent agreement with electron microscopy measurements [5].

Normal or basic solutions are very stable, retaining the above described characteristics for a long time. Decreasing the pH of a normal solution leads to further aggregation of these spheroidal aggregates. Figure 3 shows the variation of the mean hydrodynamic radius of the light scatterers with time, as calculated from the correlation

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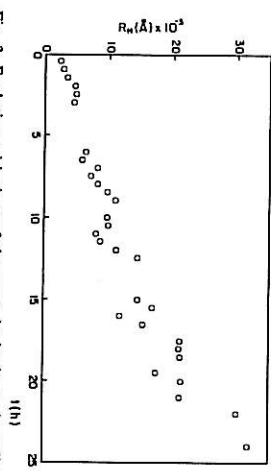


Fig. 3. Evolution with time of the mean hydrodynamic radius R_H of the aggregates of Stober silica particles in 0.1N HNO_3 aqueous solution.

curves. For $R_H < 1000$ nm, one can fit the correlation data using only one cumulant, showing that these aggregates are still approximately monodisperse. However, bigger aggregates give correlation curves that need two or three cumulants to yield a successful fitting. This is also reflected in the increased error range for the measured value of $\langle R_H \rangle$. After about 2 days the aggregates are very large ($R_H > 3000$ nm) and polydisperse. These large aggregates are also unstable and tend to disaggregate, probably back to the individual Stober particles measuring around 7 nm. The solution becomes totally transparent to visible light, showing only a very feebly scattering.

In normal conditions the aggregation takes place very rapidly. It is not possible to follow the aggregation of the Stober particles with the light scattering observations. An attempt to slow down

the aggregation process was made by increasing the viscosity of the solvent adding saccharose before dispersing the silica particles in water. In this way, the viscosity of the final solution could be varied from 1.002 to 6.12 cP. The diffusion coefficient was strongly affected by this variation in viscosity. However the aggregation process was still too rapid to be followed by the experiments. In addition no modification in the physical parameters could be observed compared to a pure water solution. This seems to be an interesting result since the viscosity is an important parameter in any theoretical model of aggregation.

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