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Evidence of structural reorganization during aggregation of silica nanoparticles

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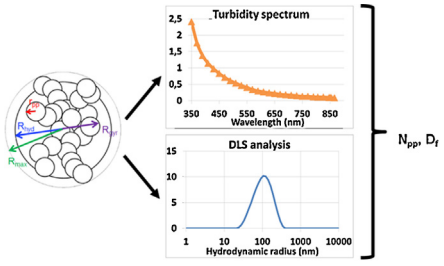
HIGHLIGHTS

- We monitored aggregation of silica particles thanks to turbidity and DLS analyses.
- We developed an optical model to quantitatively interpret the turbidity spectra.
- Analysis of the data evidenced aggregate restructuring.

GRAPHICAL ABSTRACT



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ABSTRACT

Silica nanoparticles have been produced by neutralization of sodium silicate. The obtained suspension was unstable because of the high value of the ionic strength of the medium. Aggregation of the particles has been monitored thanks to a combination of in situ turbidity and dynamic light scattering (DLS) measurements. An optical model has been developed to extract both fractal dimension D_f and primary particle radius r_{pp} of the formed aggregates from these data. The obtained results clearly indicate a densification of the clusters as aggregation proceeds. A correlation between our experimental turbidity values and hydrodynamic radii was found. Comparison with calculated dimensionless numbers showed that a constant D_f could not explain the observed trend. A fractal dimension dependent on the number of particles inside the aggregate N_{pp} is thus suggested.

1. Introduction

Colloidal systems are currently used in many fields of application and the potential of such materials is still to be fully explored. As far as silica is concerned, fields of application include controlled abrasion, elastomer reinforcement, whiteness improvement, coating, etc. [1] Very lately, colloidal suspensions of silica nanoparticles have been highlighted as potential tools for organ repair [2]. When silica is produced from TEOS (tetraethylorthosilicate) using Stöber's method [3], monodisperse isolated particles are obtained. However, when silica is industrially manufactured by neutralization of a silicate solution with acid (precipitated silica) or by hydrolysis of silicon tetrachloride $SiCl_4$ in vapor phase (pyrogenic silica), the resulting powder is made of strong aggregates. These aggregates pile to form large agglomerates. The presence of such structural organization is a prerequisite for certain of the previously mentioned applications. Typically, it has been shown that the hierarchical structures of precipitated silica and carbon black are very similar [4], which explains why the former has progressively replaced the latter as a reinforcing filler in rubbers over the years. However, no consensus exists regarding the morphological properties of the ideal filler [5]. Investigations are thus still conducted to gain control over the morphology of the silica aggregates [6–10].

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Nomenclature

C_{sca}	scattering cross section (m^2)
D_f	fractal dimension
$D_f^{h,t}$	hydrodynamic dimension of translation
$D_p(r)$	pair distribution density
$F(\theta)$	shape factor
$I(\lambda)$	intensity of the transmitted beam
$I_0(\lambda)$	intensity of the incident beam
L_{opt}	optical path length
N_{pp}	number of primary particles in an aggregate
R_{adim}	dimensionless radius
R_{hyd}	hydrodynamic radius of aggregate (nm)
R_{max}	radius of the circumscribed sphere on the aggregate (nm)
$S(\theta)$	structure factor
BET	Brunauer–Emmet–Teller (method used to determine the specific surface area of a powder for N_2 physisorption data)
BJH	Barrett–Joyner–Halenda (method used to determine the distribution of mesopore sizes of a powder for N_2 physisorption data)
DLS	dynamic light scattering
RDG	Rayleigh–Debye–Gans (approximation of the exact Mie scattering theory)
b	$D_f - 3$
k	wavenumber
k_f	fractal prefactor
$k_f^{h,t}$	fractal prefactor of translation
m	relative refractive index
n_{SiO_2}	refractive index of amorphous silica (1.44)
n_{water}	refractive index of water (1.33)
r	dimensionless distance
r_{pp}	radius of primary particle (nm)
λ	wavelength (nm)
$\rho(r)$	radial number density
τ	turbidity (cm^{-1})
τ_{adim}	dimensionless turbidity
θ	scattering angle (°)
ϕ_{SiO_2}	volume fraction of solid

As with many colloids, the aggregates formed by coagulation of silica particles are known to be fractal [11]. This model of aggregate structure [12] is based on the existence of a parameter called the fractal dimension D_f, which varies between 1 and 3 according to the density of the aggregate. Usual values of D_f are associated with the mechanism of aggregation: 1.8 when aggregation is fast and limited by diffusion of the particles in the suspension and 2.1 when aggregation is slow and limited by the low collision efficiency of the particles. In the case of silica, fractal aggregates can sometimes undergo some restructuring. Aubert and Cannel [13] could form aggregates with fractal dimensions of either 1.75 or 2.05 depending on the conditions of the experiment. The authors also observed that, given enough time, D_f would naturally increase from 1.75 to 2.05 and that the speed of restructuring was a function of pH.

The origin of such restructuring is still unclear. A possible explanation would be that the aggregated particles are in a shallow secondary potential minimum [14–16]. Aggregation would then be reversible: Martin et al. [17] triggered aggregation of silica nanoparticles by addition of salts to their suspension and dispersion of the formed aggregates by dilution. The reversibility of aggregation would allow the primary particles to diffuse inside the aggregates and form denser structures over time. Schlomach and Kind [18], out of their simulations, suggested an Arrhenius-type mechanism for intra-aggregate diffusion. Another theory is based on the nature of the bonds between silica particles: at first, two particles are linked by inter-particle hydroxo bridges between silanols groups [19]. These bonds are easily broken and flexible which gives mobility to the particles inside the aggregate. The hydroxo bridges later evolve into covalent bonds, thus making the aggregation irreversible.

Turbidity is one of the widest-spread techniques to monitor the aggregation of a suspension [20]. It has, unsurprisingly, been applied to study aggregation of silica [21,22]. In this paper, turbidity is used not only to monitor the aggregation of destabilized nanoparticles but also to get structural information about the formed aggregates. An optical model, based on scattering of fractal aggregates, has been built to extract both the fractal dimension and the primary particle size of the aggregates from the experimental turbidity spectra. Evolution of the calculated fractal dimension with time would evidence structural rearrangement of our aggregates. Section 2 deals with the method of preparation of our silica nanoparticles suspensions and with the characterization techniques employed during this work. The optical model and the associated fitting software we developed are introduced in Section 3. In Section 4, some of our experimental results are presented and analyzed thanks to our program. Finally, in Section 5, the correlation observed between our experimental data is confronted to theoretical considerations.

2. Material and methods

2.1. Experimental set-up

Suspensions of silica nanoparticles have been prepared by neutralization of a SiO_2 sodium silicate solution (3.55 SiO_2:Na_2O ratio) with 8 wt% sulfuric acid. These solutions have been prepared by dilution of commercially available solutions of 19 wt% SiO_2 sodium silicate and 72 wt% sulfuric acid (Chimie Plus) with deionized water. The mixing of reactants has been performed in a 3 L stirred tank reactor. The temperature has been maintained to 85 °C during the whole experiment.

The first suspension prepared according to this protocol presented, at the end of the neutralization, a final volume of 1.3 L and a volume fraction of solid ϕ_{SiO_2} of 7.5×10^{-3}. The pH and the ionic strength in solution were respectively 7.5 and 0.23 M (the ionic strength of the solution has been calculated from the total concentrations of sodium and sulfate ions.). The second one presented a final volume of 1.6 L and a volume fraction of solid ϕ_{SiO_2} of 1.22×10^{-2}. In this case, the pH and the ionic strength in solution were respectively 8.5 and 0.36 M. Once the mixing was over, aggregation of the particles was monitored by a combination of in situ turbidity and DLS measurements until the system gelled. The pH of the medium did not deviate from its original value during the time of the experiment.

2.2. Turbidity measurements

The turbidity measurements were carried out with a set-up comprising three elements: a light source, a turbidity probe and a commercial spectrometer (Fig. 1). A halogen-deuterium lamp (L7893, Hamamatsu) provides a polychromatic signal in the working range of 350–900 nm, which is passed through an optical fiber (600 μm in diameter, T58-457, Edmund Optics) to the probe. The probe has been designed according to Crawley's recommendations [23]: two plano-convex spherical lenses (LPX-5.0-5.2-C, Melles-Griot) insure the parallelism of the light beam across the probe cavity. The length of this cavity sets the optical path length L_{opt}, which is used in the determination of experimental turbidity. The transmitted signal is passed through a second optical fiber to the spectrometer (USB Red Tide USB650, Ocean Optics). Its wavelength