A small-angle X-ray scattering study of aggregation and gelation of colloidal silica

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Abstract

Aggregation and gelation in colloidal silica dispersions have been studied by time-resolved, small-angle X-ray scattering. Two different ways of raising the ionic strength, leading to destabilization of the dispersions, have been examined. *In situ* destabilization by urease-catalyzed hydrolysis of urea has been used as well as an approach with simple mixing of sols with salt solutions. For concentrated dispersions different structures result from the two destabilization methods. Structures differ also in the gelled state, with essentially no fractal scattering from the directly mixed samples whereas fractal scattering on intermediate length scales is observed for the *in situ* destabilized samples. In contrast, for more dilute particle concentrations, similar structures are generated in both cases and at gelation structures are in close agreement. However, gel times differ drastically in some cases for the two methods, as do the conditions for gelation. These differences are tentatively rationalized by some degree of irreversible aggregation occurring in the mixing stage that, given sufficient time, leads to gelation.
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1. Introduction

Colloidal aggregation and gelation are of great scientific and technological interest. They play important roles in applications, including the colloidal processing of ceramics [1–4], solid–liquid separations [5], polymer dispersions processing [6], and processing of food stuffs [7,8]. Loss of stability is many times detrimental but is at other times induced deliberately by producing physico-chemical conditions that reduce the stabilizing forces among colloids so that aggregation can proceed. As aggregates grow, they often assemble into sample-spanning networks that impart solid-like properties to the system at the gel point. In such cases, controlling and predicting rates of aggregation and gel times are imperative, something for which kinetic models have been developed [9–11].

It is well established that rapid colloidal aggregation proceeds by fractal growth and cluster aggregation [12–14]. Less

is known about aggregation in more concentrated dispersions, where gelation follows, even though this is highly relevant from an applications point of view. This can in part be ascribed to the difficulty in reproducibly destabilizing concentrated systems. Simply adding salt or acid/base in the form of concentrated solutions, as is done in many cases, may lead to irreversible aggregation before uniform distribution of ions has been reached. Nonetheless, the structural evolution has been tracked by, for instance, time-resolved static scattering [15–18], which is well suited to extracting information on fractal aggregates [19–22] provided the aggregation kinetics is sufficiently slow. In such cases, however, it is difficult to ascertain whether permanent structures are created in the mixing stage and whether the gels formed have inherited some inhomogeneity as a result.

Methods have been devised to remedy this situation, of which the so-called *in situ* destabilization [1–3] has elicited much interest of late (see also [23]). In this method, a chemical reaction in the solvent produces inert or potential-determining ions gradually and uniformly. It has opened up the possibility of studying homogeneously induced, irreversible aggregation in concentrated systems by combining with, e.g., time-resolved

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static scattering [24,25], diffusing wave spectroscopy [26–28], rheology [25,27,29], and cryo-SEM [30,31].

Given that destabilization of dispersions by direct addition of salt solutions is widely used, it is of interest to compare the aggregation and gelation processes resulting in this case with those from *in situ* destabilization. To this end, we use time-resolved small-angle X-ray scattering (SAXS) in this study and focus on the gelation step in converting silica sols into solid gel bodies initiated by both destabilization methods. The study is motivated by results obtained in previous work [32], where gelation caused by raising the ionic strength at constant pH was found to depend on both silica particle concentration and ionic strength, something that has been noted also in work on other irreversibly aggregating colloids [23]. In addition, different conditions for gelation were identified depending on how the ionic strength was raised. The enzymatic hydrolysis of urea in the solvent produced gel transitions at substantially higher ionic strengths than did direct addition of moderately concentrated salt solutions. A plausible explanation is that the two methods produce very different aggregates that may well result in different structures at the gel point.

In this work, we follow structures resulting from both destabilization methods by SAXS. Intermediate-range structures, accessible with SAXS, do indeed evolve differently for concentrated systems, but they remain qualitatively similar for more dilute systems, yet they gel under very different conditions and on different time scales. The results are tentatively rationalized in terms of the concentration dependence of the crossover between reversible and irreversible aggregation.

2. Experimental

2.1. Materials

An aqueous dispersion of colloidal silica spheres with initially ~40 wt% solids, Ludox HS-40 (Aldrich), was used in this work. Ammonium hydrogen carbonate, NH_4HCO_3, from Scharlau was used as received. The commercial stock dispersion was dialyzed for five days against 20 mM NH_4HCO_3 before use. After the dialysis, in order to remove any aggregates and unknown components of the initial stock dispersion, the colloidal silica dispersion was centrifuged in a mild fashion for five hours. Milli-Q water was used throughout the study. Urea and urease (from Jack beans) were both obtained from Sigma and were used as received. Concentration series were obtained by dilution of the stock dispersion with 20 mM aqueous solutions of ammonium hydrogen carbonate. The average weight fraction of the dialyzed and centrifuged stock dispersion (36.0 ± 0.1 wt%) was determined by drying three different samples from the same batch in an oven at $100\,^\circ$C until constant weight was obtained for each sample.

2.2. Methods

In this study, colloidal dispersions of silica spheres are destabilized by the addition of the salt ammonium hydrogen carbonate, NH_4HCO_3. This is done by two separate methods, referred to as the *in situ* and the direct addition methods. In direct addition, moderately concentrated aqueous solutions of the salt, NH_4HCO_3, were added to the particle dispersions (with particle concentrations above the targeted ones). In the *in situ* method, NH_4HCO_3 is 'added' through the enzymatically catalyzed hydrolysis of urea by urease [3]. The internal formation of the salt NH_4HCO_3 occurs at a constant (buffer) pH of ~9.2. Prior to every experiment, an aqueous stock solution consisting of 1 wt% urease was prepared. Urea was added to a dispersion with the targeted concentration of silica particles. The hydrolysis was initiated by an addition of a small portion of the aqueous stock solution containing the enzyme. In all experiments the ratio between urease and urea was kept constant. As in Ref. [32], consideration was given to the volume occupied by the particles in determining concentrations and the concentration of urea in the solvent of the dispersion was kept constant at 1.0 M in all experiments. In this study, most results concern two particle concentrations, 5 and 17 wt%, which correpond to particle volume fractions of 0.024 and 0.086, respectively.

2.3. Small-angle X-ray scattering (SAXS)

Small-angle X-ray scattering measurements were performed using the pinhole SAXS instrument at the University of Aarhus. The instrument consists of an X-ray camera (NanoSTAR, Bruker AXS) with a rotating anode X-ray (Cu Kα radiation) source, cross-coupled Göbel mirrors, collimation using three pinholes and an evacuated beam path, and a 2D position-sensitive gas detector (HiSTAR). The set-up has been modified and optimized for scattering investigations of solutions as described in detail in Ref. [33]. In the current experiments the sample-to-detector distance was kept at 107 cm, and small pinholes were used, giving a range of scattering vectors as $0.0037 \leq q(\text{Å}^{-1}) \leq 0.22$, where $q = (4\pi/\lambda)\sin(\theta/2)$ is the modulus of the wave vector, θ is the scattering angle, and $\lambda = 1.542$ Å is the X-ray wavelength. Samples were gently transfered into borosilicate glass mark tubes with an outside- Ø of 2.0 mm and a wall thickness of 0.01 mm (Hilgenberg). The mark tubes were then flame sealed at the time of preparation in order to withstand the vacuum inside the camera. Also, some samples were stored in this state during aggregation for long times, thus minimizing the disturbance of the aggregation process. Measurements were made at room temperature and the data were corrected for detector efficiency and for spatial distortions, and azimuthally averaged. The scattering from salt solutions was measured as backgrounds and were subsequently subtracted from scattering spectra recorded for particle dispersions. The scattering data have not been converted to obtain an absolute scale for the intensity.

3. Results and discussion

3.1. Summary of previous results

In Ref. [32], two different methods of destabilizing initially stable silica dispersions were used. The enzymatic hydrolysis of urea by urease was used to raise the ionic strength gradually