

Varying the counter ion changes the kinetics, but not the final structure of colloidal gels



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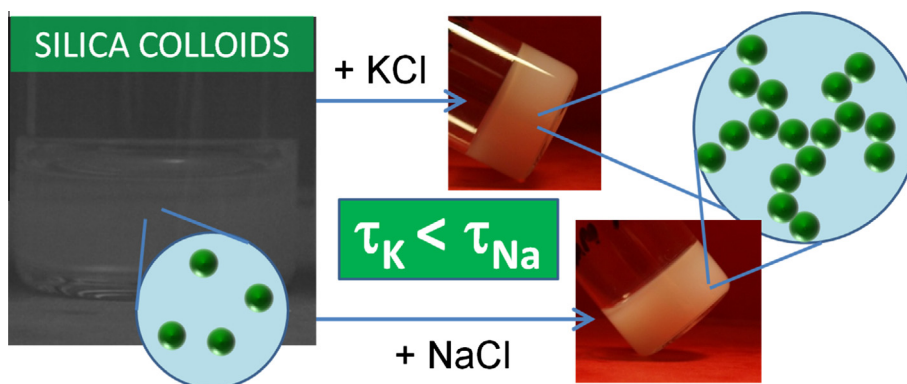
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HIGHLIGHTS

- Colloidal gelation is much faster in the presence of KCl than NaCl.
- The difference in the gels is only kinetic.
- The local structure and the mechanical properties of the final gels are the same.

GRAPHICAL ABSTRACT



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ABSTRACT

We show that, while the gelation of colloidal silica proceeds much faster in the presence of added KCl than NaCl, the final gels are very similar in structure and properties. We have studied the gelation process by visual inspection and by small angle X-ray scattering for a range of salt and silica particle concentrations. The characteristic times of the early aggregation process and the formation of a stress-bearing structure with both salts are shown to collapse onto master curves with single multiplicative constants, linked to the stability ratio of the colloidal suspensions. The influence of the salt type and concentration is confirmed to be mainly kinetic, as the static structure factors and viscoelastic moduli of the gels are shown to be equivalent at normalized times. While there is strong variation in the kinetics, the structure and properties of the gel at long-times are shown to be mainly controlled by the concentration of particles, and hardly influenced by the type or the concentration of salt. This suggests that the differences between gels generated by different salts are only transient in time.

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1. Introduction

In Soft Matter, gels appear when some basic microscopic unit starts to aggregate forming a large solid network that spans macroscopic space [1]. The building blocks can be different, e.g. colloids, nanoparticles, proteins, polymers, but the result is a material that is capable of sustaining mechanical shear stress [2–6]. Gels are important in many applications. In materials science, gelation is a way to obtain materials that have a solid-like response (exhibiting finite yield stress) starting from a small amount of solid material dispersed in a liquid [7]. In food science, a big part of the sensory experience is related to the texture that results from the gel structure formed through protein aggregation [8]. Yogurt, for example, is a gel obtained by the aggregation of casein micelles under acidic conditions [9]. Gels are also found in biological cells through the assembly of actin networks [10]. Here, assembly can produce cell motility and the gelation process is quite distinct from the passive gelation described above [11].

Though gelation has been described in several reviews [1,12,13] many aspects of this process are still not fully understood. To make a gel, the building blocks identified above must aggregate. Aggregation can be induced in a number of ways. For colloidal particles, for example, depletion interactions arising from a polymer in solution can lead to gels that are the result of an arrested phase separation [5,14]. In many food systems, gels are the result of the protein denaturation that precedes aggregation [15,16]. In this case, the loss of stability comes from the interactions between protein domains that are not exposed in the native form [16].

As in most complex fluids, the repulsive electrostatic and the attractive van der Waal forces play an important role in the stability of colloidal and nano-particle dispersions. In this setting, the interaction between these two forces can be qualitatively explained using the theory developed by Derjaguin, Landau, Verwey and Overbeek (DLVO) [17]. In DLVO theory the addition of counter ions to a dispersion lowers the repulsive potential between particles by screening their surface charge and at some critical ion concentration aggregation ensues. In practice, such ions are provided by salts dissolved in solution and the addition of salt is a common method to induce aggregation – particularly in materials science – since it is easy and reliable. Indeed, in the domain of food science, aggregation induced by salt goes under the name of “cold gelation” because heating is not required. The effect of salt is also very important in the domain of nanotoxicity, where the interaction between nanoparticles and cell membranes always occurs in the presence of various salts. Whilst DLVO is one of the few analytical models that can be derived for this problem it has serious limitations. One such limitation is that salt ions of the same valence are considered equivalent and therefore affect the inter-particle potential in the same manner; a consideration that does not reflect reality where systems are sensitive to both a given ion’s valence and its chemical nature.

An example of the latter are the “salting in” and “salting out” effects observed in protein solutions. Here, counter ions of the same valence may either stabilize (salting in) or de-stabilize (salting out) the system depending on their elemental nature [18]. There is, however, some systematic behavior and the ions can be ordered in a sequence according to the effects they have on solubility in the so-called Hofmeister series. It has been found that this series tallies with the respective water affinities of the ions [18] and recent work has related the size of an ions’ hydration shell to its position in the series [19]. Further, it has been shown that it is possible to predict the critical coagulation concentration with different salts when the specific absorption of the ions on the surface of the colloids, is accounted for. Specifically, chaotropic ions, i.e. those that can easily lose their hydration shell, tend to be

adsorbed on the colloidal surface while kosmotropic ones are not [20,21] decreasing and increasing stability respectively.

Whilst there is an obvious connection with the hydration phenomena described above and an ion’s capacity to coagulate colloidal systems [21], there have been less studies on how such phenomena influence the kinetics and the structure of the gels. Colloidal silica has been extensively studied, mainly in the presence of NaCl. The fractal nature of the gels has been shown to form through a reaction limited cluster aggregation process (RLCA) [22–25]. The peculiar influence of salt on the coagulation concentration of silica was demonstrated almost 50 years ago [26], when this influence was shown to depend strongly on the pH of the silica stock solution. Silica gels have been shown to form much more quickly in the presence of chaotropic ions (such as NH_4^+ or K^+) rather than kosmotropic ones, such as Na^+ [27–30]. The changes in the critical coagulation concentrations of silica particles with a range of salts was recently shown to correlate very well with the change in the surface charge arising from differences in ionic adsorption [30]. The gelation times have been measured by eye-inspection, turbidity measurements or rheology all of which focus on larger length-scales. However, there has not been, to our knowledge, a comparison between the aggregation kinetics at the microscopic and macroscopic scales. With this aim in mind, we have used time resolved small angle X-ray scattering (SAXS) for two different types and a range of concentrations of salt, and for several particle densities. In doing so, we are able to define a *microscopic* transition time in addition to the macroscopic one defined by traditional eye inspection. In this way, the chain of events leading to gelation at the microscopic and macroscopic length-scales can be compared. Moreover, the question of the mechanical properties of the different gels and their relations to the nature of the salt and the time elapsed from preparation is addressed.

2. Materials and methods

2.1. Materials

Silica particles (Ludox TMA from Sigma Aldrich (TMA in the following)) with a particle diameter of 27 nm (from SAXS measurements) and a stock concentration of 34 wt% were used. The pH of the stock solution was measured as 7.0 and the residual ionic strength of the stock solution is below 9.5 mM (see [Supplementary Fig. S1](#) for further information). Sodium chloride (NaCl , $\geq 99.5\%$) and potassium chloride (KCl , $\geq 99.0\%$) (both from Sigma Aldrich) were used without further purification. Milli-Q water (18.2 M Ω cm) was used for the preparation of the samples.

2.2. Methods

2.2.1. Sample preparation

Various amounts of silica, expressed in terms of volume fraction ϕ_{TMA} , were added to salt solutions ranging from 0 to 500 mM in concentration (c_s) and immediately agitated with a vortex mixer for 10 s to ensure homogeneous mixing. Samples were then sealed to avoid solvent evaporation and stored for observation – save for those samples prepared for SAXS and rheological experiments. These were immediately transferred into SAXS capillaries (see below) and into folded paper containers respectively, both of which were sealed and stored until the measurements. The paper containers allowed transfer of the samples into the rheometer with minimal perturbation. After ageing, the samples were transferred into a rheometer (Rheoplus, Anton Paar, France) and the storage (G') and loss moduli (G'') were measured at a fixed frequency of 10 Hz and with varying strain from 1% to 100% with a cone plate geometry.

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