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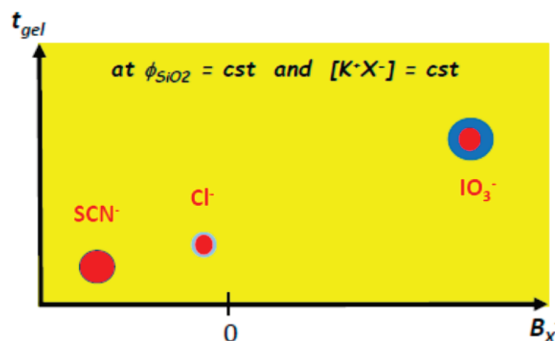
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Influence of Co-Ion Nature on the Gelation Kinetics of Colloidal Silica Suspensions

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ABSTRACT: The influence of the nature of three representative monovalent co-ions on the gelation kinetics of Ludox suspensions has been investigated. At a given Ludox volume fraction and for the same concentration of potassium salt, the gelation time is longer as the studied anion presents a more pronounced kosmotrope character. As the screening of the silica surface charge is similar since the same cationic counterion is taken, these results highlight the unexpected role played by hydration effects imparted by the co-ions when particles are pushed together as gelation proceeds. This reveals that jamming transitions of nanoparticle fluids may be finely tuned by changing the co-ion nature in spite of the fact that the cationic counterion is the same.



1. INTRODUCTION

With the increasing development of novel applications and technologies in which colloidal entities are involved (solid nanoparticles, proteins, polymers, surfactant micelles), ion-specific (or Hofmeister) effects experience a sustained interest since they may offer the opportunity to modulate the desired properties of the system by simply changing the electrolyte nature.¹ Nevertheless, although they have been reported from more than 120 years, the underlying reasons remain still unclear.^{2,3}

Jamming transitions of colloidal fluids are the object of numerous studies since their rheological control is of crucial importance in different domains such as materials science, food technology, cosmetics formulation, and biological media.^{4,5} They refer to the change from liquid-like to solid-like behavior with a sudden arrest of the internal dynamics characterized by dominant elastic properties. In the case of nanoparticles suspension, a simple way to induce gelation is adding an electrolyte to promote aggregation. The gel forms when the strength of attractive interactions between the growing aggregates becomes sufficient to create a network that spans the macroscopic space, allowing it often to withstand its own weight (no more flowing).

Colloidal silica suspensions, such as Ludox, are often used as model systems to study jamming transitions and also as ingredients in some applied processes. In this context, some recent studies^{6–8} have focused on the gelation kinetics of Ludox suspensions in basic media and the corresponding gel structure at the microscopic scale. In agreement with previous works,^{9,10} the gelation time was found to depend on the lyotropic nature of the monovalent counterion of chloride salts, since at any Ludox volume fraction the gelation time decreased as the cation was more chaotropic. However, if the same cationic counterion is taken at the same concentration, it may be interesting to inspect whether the gelation time depends on

co-ion nature; this aspect is relevant since it has not been yet considered in such systems.

In this work, the gelation kinetics of Ludox suspensions have been investigated in the presence of three representative potassium salts where the corresponding anions were chosen according to their variable lyotropic character.

2. EXPERIMENTAL METHODS

2.1. Materials. Commercial Ludox HS-40 sample (Sigma-Aldrich) with a 40% w/w solid content (silica density 2.2 g.mL⁻¹) was used. The density of the suspension is 1.29 g.mL⁻¹ and pH is 9.8 at 25 °C.

Potassium thiocyanate (KSCN), potassium chloride (KCl), and potassium iodate (KIO₃) were purchased from Sigma-Aldrich and were used as received. Deionized water was used as a solvent.

2.2. Methods. After addition of salt solution and Ludox suspension in test tubes, the samples were agitated on a vortex mixer (Fisher Bioblock Scientific) during 10 s at 20 Hz. The gelation time was determined by visual inspection while the test tube was gently inverted at a controlled temperature of 25 °C (the test tubes were placed in a thermostated box). The time when the sample stopped flowing was taken classically as the gel point. The gelation time was estimated by preliminary tests to locate its position before the measurements were repeated twice with a good reproducibility where time uncertainty did not exceed 1 min for each measuring point.

A NanoZS apparatus (Malvern Instruments, U.K.) was used for zeta potential measurements. The ζ -potential of diluted

Table 1. Viscosity B Coefficient Value and Gibbs Free Energy of Hydration of Some Ions

ion	SCN ⁻	Cl ⁻	IO ₃ ⁻	Cs ⁺	K ⁺	Na ⁺
B (L·mol ⁻¹)	-0.103	-0.005	0.138	-0.047	-0.009	0.085
ΔG_{Hyd} (kJ mol ⁻¹)	-287	-347	-408	-258	-304	-375

Ludox sample in KCl solution at 5 mmol/L was -33 mV at pH 9.8.

The transmittance was recorded during gelation with a spectrophotometer (Jenway, U.K.) at 650 nm wavelength.

A capillary viscosimeter of Ubbelohde type was immersed in a water bath regulated at 25 °C (Lauda, Germany) for viscosity measurements. As the flowing time t (s) was longer than 100 s for all electrolyte solutions, the corresponding dynamic viscosity η (Pa·s) was calculated through: $\eta = K \times t \times \rho$ where K ($4.8 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-2}$) is the viscosimeter constant and ρ ($\text{kg} \cdot \text{m}^{-3}$) is the density of salt solutions measured at 25 °C with a DMA densimeter.

3. RESULTS AND DISCUSSION

3.1. The Lyotropic Character of the Co-ions. At the fundamental level, ion-specific effects pose a challenge to the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory¹¹ describing the behavior of colloidal systems through knowledge of the total energy of interaction resulting from the algebraic sum of the van der Waals attraction (U_A) and the electrostatic double-layer repulsion (U_R). In spite of its successes to predict qualitatively the conditions promoting stability or aggregation, this continuum theory has been shown to present some limitations at short separation distances and/or when electrolyte concentration is greater than 0.1 mol·L⁻¹. Such discrepancies have been justified since ions are considered as point charges; moreover, solvent-surface, surface-ion and solvent–ion interactions are not taken into account.¹² A plethora of studies exhibited the sensitive influence exerted by the nature of ions in aqueous media,^{13–21} but as these Hofmeister effects could not be explained by electrostatic-based theories, additional non-DLVO contributions, such as the hydration energy (U_{Hyd}) or the dispersion energy (U_{Disp}), have been thus proposed to interpret the experimental findings, although it is still open to debate.^{12,16}

Whatever the system, the results suggest that accumulation/exclusion of ionic solutes near surfaces should be a key parameter.¹³ The underlying mechanisms have been expected to depend on the interfacial hydrogen-bonding network of water molecules at the particle surface but also on the water structure around the ions since they are known to interact specifically with water molecules, at least, in the bulk phase. Indeed, the Hofmeister lyotropic sequence reflects the ability of ions to structure the water molecules in their vicinity.²² The kosmotrope and chaotrope nature of the ions can be conveniently distinguished according to the sign of the viscosity B coefficient appearing in the Jones–Dole empirical relationship:²³

$$\frac{\eta}{\eta_w} = 1 + A \times \sqrt{c} + B \times c \quad (1)$$

where η is the viscosity of aqueous salt solution at molar concentration c and η_w is the viscosity of pure water, which is valid usually up to 0.5 mol·L⁻¹. The coefficient A , which is positive for all salts, corresponds to an electrostatic term originating from the interaction between the ions. The value of B which is either positive or negative, is a direct measure of the

strength of ion–water interactions normalized to the strength of the water–water interactions. Positive B values are associated with structure-maker or kosmotrope ions where the surrounding water molecules are strongly attracted and more closely organized among themselves than in pure water. Negative B values correspond to structure-breaker or chaotrope ions where the immediately adjacent water molecules are weakly attracted by these ions but sufficiently enough to perturb their organization in the bulk. Contrarily to the kosmotropes, chaotrope ions have the propensity to remove easily their hydration shell.

The influence of the co-ion nature was thus investigated by using three representative anions covering a wide range of B values to detect eventual differences. According to the corresponding B values^{23,24} reported in Table 1, thiocyanate (SCN⁻) is a well-recognized chaotrope anion, chloride (Cl⁻) is a slightly chaotrope anion which is considered as a reference ion in the Hofmeister series, and iodate (IO₃⁻) is a quite kosmotrope anion. Iodate anion is chosen since recent studies^{25,26} have confirmed its remarkable kosmotrope characteristics. In iodate, the I atom was shown to be sufficiently electropositive to interact directly with three water molecules through their O atoms, and about 2–3 water molecules hydrate each O atom of iodate through hydrogen bonding with their H atoms. As information, the Gibbs free energy of hydration of the ions (ΔG_{Hyd}) has been indicated in Table 1. As expected, it is more negative as B increases (increased kosmotrope character) for each type of ions.

3.2. Counterion-Specific Effects on Gelation Kinetics.

To better apprehend the influence of the lyotropic character of the co-ions on gelation kinetics, it seems useful to summarize the peculiar properties of the silica–water interface and the two main arguments that were invoked to interpret why gelation kinetics of Ludox suspensions was found to depend on the lyotropic nature of the counterion.

As the isoelectric point (iep) of silica is around 2 (pH value for which the zeta potential is zero), the amount of neutral SiOH silanol groups and negatively charged SiO⁻ groups at the silica surface depends on the gap between the iep and the pH of the aqueous suspension above the iep. This relative proportion influences the degree of hydration of the silica surface since silanol groups are able to create a thick hydration layer through hydrogen bonding with surrounding water molecules. Two populations of silanol groups were shown to exist, each one interacting with weakly and strongly hydrogen-bonded water molecules.²⁷ For pH values much greater than 2, silica presents numerous negative sites at its surface, so that cationic counterions are attracted whereas anionic co-ions are repelled. This distribution and the random thermal motion of ions lead to formation of an electric double layer^{11,28} with an inner layer rich in cations and a diffuse layer where cations and a majority of anions are present, this has to be noted. Far away from the surface, the number density of counterions and co-ions is the same to satisfy electroneutrality. The thickness of the diffuse layer, the Debye length κ^{-1} , representing the range of electrostatic repulsion between charged surfaces, is related to

the ionic concentration.¹¹ Its value, expressed in nm, at 25 °C in water is given by

$$\kappa^{-1} = \left(\frac{\varepsilon \varepsilon_0 k_B T}{2 \times 10^3 N_A e^2 I} \right)^{1/2} \approx \frac{0.307}{\sqrt{I}} \quad (2)$$

where ε and ε_0 are, respectively, the medium dielectric permittivity and the dielectric constant of vacuum, $k_B T$ is the thermal energy, N_A is the Avogadro number, e is the electronic charge, and I is the ionic strength ($I = \frac{1}{2} \sum c_i \times z_i^2$ in which c_i and z_i are, respectively, the molar concentration and the ionic valence of the ion i).

Therefore, when nanoparticles approach from one another at low or moderate electrolyte concentration, their long-ranged diffuse layers first begin to overlap. The electrostatic repulsion originates from the increased concentration of ions locally that gives rise to a repulsion due to the osmotic pressure of the ions, so allowing the particles to separate. When enough salt is added, the extent of diffuse layers is sufficiently reduced so that the attractive van der Waals contribution becomes dominant and the particles aggregate into growing clusters over time. The gelation kinetics is related to the total energy of interaction, the more attractive the total interaction the shorter the gelation time. However, at the same ionic strength gelation was faster when the cationic counterion of chloride salts was more chaotrope.⁶

The first proposed argument has been ascribed to charge screening effects. For pH conditions much greater than the pI of silica, the interfacial hydrogen-bonding network of water molecules at the negatively charged silica surface is not well developed. Following the concept of “like adsorbs like”, the structure-breaker cations are preferentially attracted in this favorable environment than the structure-maker cations.^{29,30} Moreover, as the cations interact with the silica surface through electrostatic interaction they perturb the water structure at the solid–liquid interface; this effect was shown to be enhanced with chaotrope cations.^{27,31} As such, the screening of the surface charge is better in the case of chaotrope cations, so that gelation is more rapid. On the basis of recent electrophoretic measurements,¹⁹ the differences in the aggregation rates of latex suspensions were shown to depend on the influence of the counterion nature on the decrease of the surface charge; i.e., poorly hydrated cationic counterions adsorbed more strongly on the oppositely charged hydrophobic latex surfaces.

The second argument has been ascribed to hydration effects. Whatever the variable screening of the surface charge by cationic counterions, a supplementary and concomitant contribution has been assumed to arise when particles arrive at close surface to surface separation. As the cationic counterions are confined when aggregation proceeds, a non-DLVO and ion-specific hydration repulsion may manifest since energy is required to dehydrate these counterions.^{6,32} As the kosmotrope cations have a thicker hydration shell than the chaotropes, and which is held more strongly, the magnitude of this hydration repulsion is expected to be higher than in the case with chaotrope cations. The gelation time was effectively found to increase with the increasing kosmotrope character of the cations.⁶ As indication for the cations listed in Table 1, the gelation time increased significantly in the sequence $\text{Na}^+ > \text{K}^+ > \text{Cs}^+$.

3.3. Influence of the Co-Ion Nature on Gelation Kinetics. As information, the solubility of KSCN, KCl and

KIO_3 corresponds respectively to 23.09, 4.77, and 0.43 mol·kg⁻¹ of water (molality units) at 25 °C. This affects the range of the investigated salt concentrations since solubility has to be guaranteed, all experiments were thus performed at 25 °C and with potassium iodate solutions never higher than 0.42 mol·L⁻¹ (molarity units).

The stability behavior of Ludox suspensions in the presence of the different potassium electrolytes was appreciated by comparing the aspect of samples containing 0.2 mL of Ludox with 10 mL of aqueous salt solution at varying concentrations. Whatever the potassium electrolyte, the final aspect is similar, the three cases are illustrated in parts A–C of Figure 1. At 0.20 mol·L⁻¹ the samples resemble that with no salt, so indicating no distinguishable aggregation at the macroscopic scale. At 0.25 mol·L⁻¹ the samples are turbid owing to aggregates formation. At 0.3 mol·L⁻¹ the turbidity is increased and from 0.35 mol·L⁻¹ the turbidity (transmittance) remains the same. The critical coagulation concentration (ccc), characterizing the occurrence of a concentration-independent aggregation regime, is often ascribed to the concentration for which there is invariance of turbidity. The ccc may thus be assumed to be comprised between 0.3 and 0.35 mol·L⁻¹ with this same potassium counterion, so indicating no significant co-ion specific effect in the ccc values. This expected behavior has been already reported in the case of negatively charged hydrophilic particles in the presence of different co-ions of the same cationic counterion.³³

First comparative gelation experiments were carried out by adding in identical glass test tubes 0.5 mL of Ludox to 3.5 mL of each aqueous salt solution at 0.4 mol·L⁻¹. The corresponding Ludox volume fraction is $\phi = 0.0295$ with a 0.35 mol·L⁻¹ salt concentration. The pH values of the resulting suspensions with KSCN, KCl, and KIO_3 , are 9.1, 9.0, and 9.4, respectively. As information the ζ potential of diluted Ludox suspensions with KSCN, KCl, and KIO_3 at 0.35 mol·L⁻¹ concentration, corresponds to -16.2, -17.8, and -16.7 mV, respectively. Within these conditions, it may be assumed that gelation of silica nanoparticles operates in a similar way in each sample. The gelation times were 65, 90, and nearly 300 min with KSCN, KCl, and KIO_3 , respectively. These unexpected differences were confirmed when adding 0.2 mL of Ludox to 2.8 mL of solution at 0.42 mol·L⁻¹, corresponding to $\phi \approx 0.0158$ and 0.392 mol·L⁻¹ salt concentration, since the gelation times were 97, 115, and about 480 min with KSCN, KCl, and KIO_3 , respectively.

As the same potassium counterion is used in these preliminary experiments and as the Debye length is significantly reduced at such ionic strengths (κ^{-1} is around 0.5 nm in both cases), this suggests existence of an enhanced repulsive contribution as the anion has a more pronounced kosmotrope (or less chaotrope) character.

In light of these results, the variation of the gelation time as a function of the salt concentration for the same $\phi = 0.059$ in a whole volume of 4 mL, has been investigated, see Figure 2. As expected the gelation time decreases as the concentration increases. Although gelation is much longer with iodate, the gap between the gelation times of the three salts decreases as concentration increases. For solubility reasons the sample at 0.4 mol·L⁻¹ with potassium iodate could not be prepared at this Ludox volume fraction, however the difference in gelation times between KSCN and KCl is still noticeable at such electrolyte concentration, i.e., 8.5 and 11.5 min, respectively.

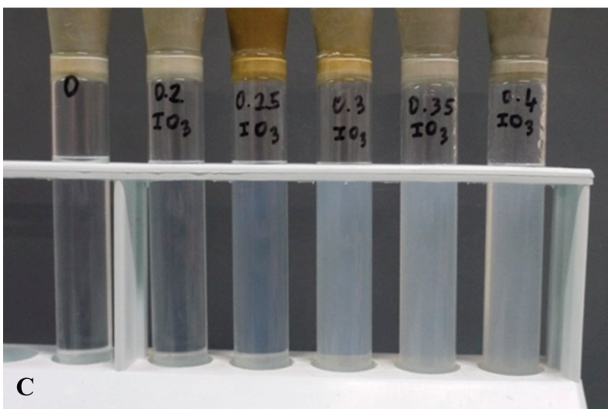
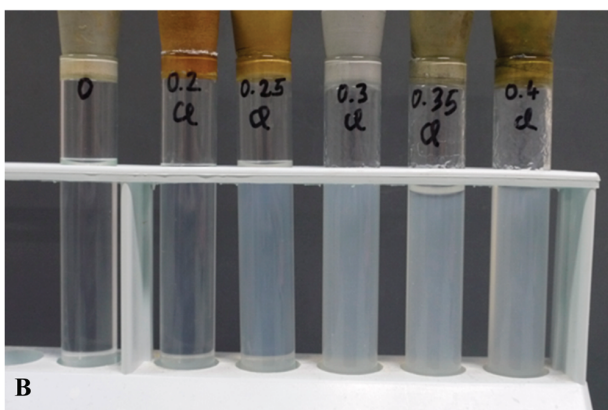
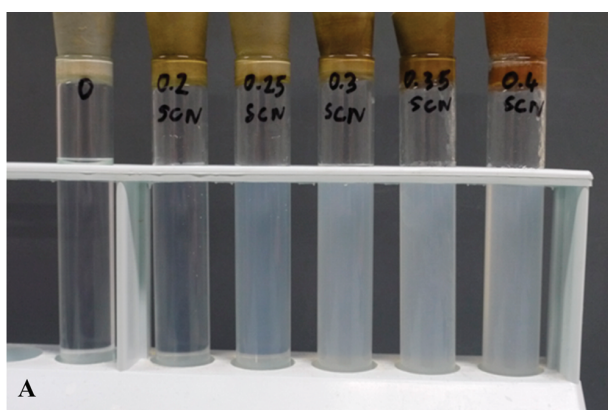


Figure 1. Comparative aspect of diluted Ludox samples at varying (A) KSCN, (B) KCl, and (C) KIO₃ concentrations.

As an indication, the variation of the transmittance was recorded as a function of time for the three suspensions at 0.3 mol·L⁻¹; see Figure 3. The curves with KSCN and KCl diverge from one another from 10 min and the decrease of the transmittance is more pronounced in the case of KSCN. The decrease of the transmittance starts to level off in the inflection zone of the curves where is located the measured gelation time (indicated by an arrow). In the case of KIO₃ the situation is drastically different since the transmittance decreases very slowly from the beginning.

In the same way, the variation of the gelation time as a function of the Ludox volume fraction was studied at the same

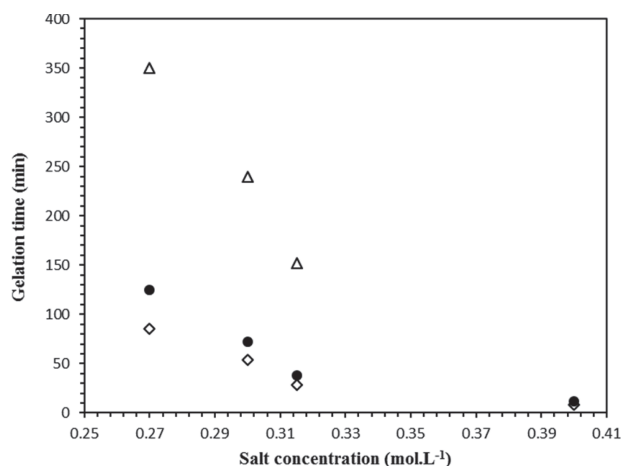


Figure 2. Variation of the gelation time as a function of salt concentration at 0.059 Ludox volume fraction: KSCN (◇), KCl (●), KIO₃ (△).

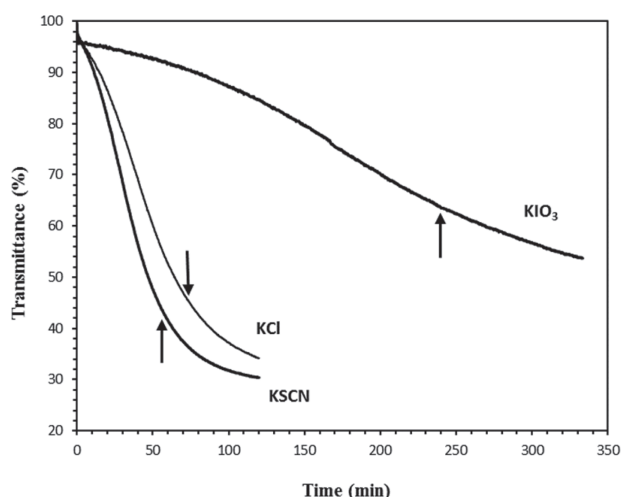


Figure 3. Variation of the transmittance as a function of time at 0.059 Ludox volume fraction and 0.3 mol·L⁻¹ salt concentration.

0.27 mol·L⁻¹ salt concentration in a whole volume of 4 mL, see Figure 4. As expected, the gelation time is longer as the volume fraction decreases, moreover the differences increase when the content of silica nanoparticles is more diluted. These results are found to depend intimately on the lyotropic character since for the two chaotrope anions, i.e. SCN⁻ and Cl⁻, the difference remains quite appreciable and it is exacerbated in the presence of the kosmotrope IO₃⁻ anion. Although it was unsuspected,^{6,7,9} the reported trends evidence that the gelation time can be modulated by changing the nature of the co-ion in spite the cationic counterion concentration is the same.

Since it may have an influence on the kinetics, the viscosity of the continuous phase was determined in the investigated salt concentration range at 25 °C, see Figure 5. As expected from the lyotropic character of the anions, the viscosity of KSCN solutions decreases slightly with salt concentration; that of KCl solutions remains practically unchanged whereas it increases with concentration for KIO₃ solutions. Nevertheless, the main conclusion is that as the viscosity level varies only from 0.88 to 0.95 mPa.s, the effect of solution viscosity on the presumed

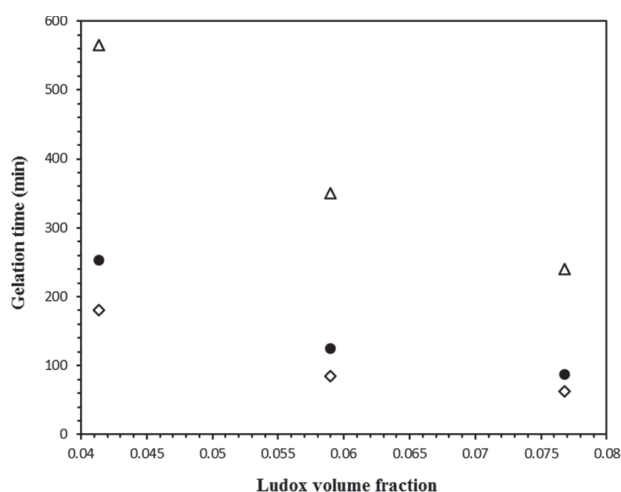


Figure 4. Variation of the gelation time as a function of the Ludox volume fraction at $0.27 \text{ mol}\cdot\text{L}^{-1}$ salt concentration: KSCN (◇), KCl (●), and KIO_3 (△).

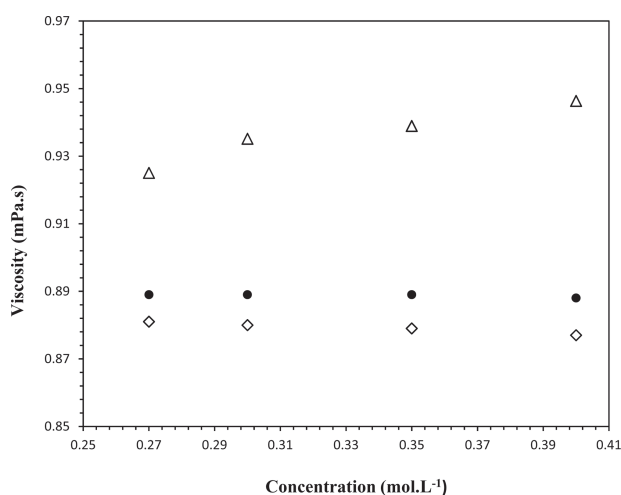


Figure 5. Variation of the viscosity as a function of salt concentration: KSCN (◇), KCl (●), and KIO_3 (△).

slowing down of the kinetics cannot reasonably justify the significant differences of the gelation times.

As the same concentration of potassium is used in the presented experiments, the screening of the surface charge is expected to be the same and/or the repulsive dehydration contribution of this counterion may be assumed to be similar. Thus, the observed differences in gelation times advocate in favor of the specific role played by the co-ions when particles are pushed together as aggregation proceeds. This is at variance with the common picture of aggregation phenomena since the co-ions have been often assumed to be squeezed out from the interfacial region during closer approach and to have a negligible influence. As the main difference between the studied co-ions is their lyotropic character it may be assumed that the reported trends originate from hydration effects.

The obtained results suggest that when the ionic atmosphere is formed around charged solid surfaces, the specific ionic composition of this atmosphere has a marked influence on the interfacial hydrogen-bonding network of water molecules and particularly in the case of hydrophilic surfaces such as silica.¹³ In

the studied cases, the inner layer is densely constituted by the chaotrope potassium counterions whereas the diffuse layer is composed of a large majority of co-ions presenting a distinct affinity with the solvent water molecules. When the ionic concentration is not negligible, the presence of strongly and completely hydrated co-ions such as the iodates should contribute to exert a much more enhanced water ordering and cohesiveness within the interfacial region when compared to the case with the chaotrope co-ions such as chlorides and thiocyanates. As a result, more energy should be supplied upon closer approach of the hydrophilic silica nanoparticles to disrupt the interfacial water structure which is stabilized by the confined kosmotrope iodate anions aiming at minimizing the extent of broken hydrogen bonds. When the silica surface–solution interface is populated by both chaotrope counterions and co-ions, the magnitude of this repulsive dehydration contribution during aggregation is expected to be significantly reduced so that the gelation kinetics should be faster, especially as the co-ion has a marked chaotrope character, such as thiocyanate. This is supported by the obtained results.

4. CONCLUSIONS

Through relatively simple experiments and carried out with care, this study reports the unsuspected influence of the co-ion nature on the gelation kinetics of nanoparticles suspension. The main result is that jamming protocols of nanoparticles fluids can be finely tuned by changing the co-ion although the cationic counterion is the same. From a more fundamental point of view, these results contribute to shed more light on the presumed ion-specific disruption of the hydrogen-bonding network of water molecules at the solid–liquid interface during nanoparticles crowding, so emphasizing that the structuring of water at interfaces (i.e., around surfaces and ions) should play a decisive role.

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Notes

The author declares no competing financial interest.

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