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Influence of ionic specificity on the microstructure and the strength of gelled colloidal silica suspensions

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Abstract

The dynamic rheological behavior of gelled Ludox suspensions in the presence of the structure-breaker ammonium counterion and the structure-maker sodium counterion has been investigated. Depending on the nature of the electrolyte and its concentration, the results highlight the crucial effect of the network microstructure on the rheological results. Within the same microstructure, the strength of gelled networks has been found to be greater in the presence of the poorly hydrated ammonium counterions at any Ludox volume fraction. The obtained results were discussed with respect to recent contradictory trends reported in the literature concerning the behavior of silica suspensions.

Keywords: Ionic specificity; Microstructure; Strength; Gelled silica suspensions

1. Introduction

Although it was unsuspected, the nature of a given coagulant 1:1 electrolyte has been found to be important in optimizing desired macroscopic properties of aggregated colloidal suspensions, such as the permeability of filtration cakes during separation processes [1]. As it has been emphasized for many years, the classical DLVO theory was found to present some limitations and failed to adequately represent various experimental results [2,3]. According to this continuum theory, the stability of colloidal suspensions can be predicted through knowledge of the total energy of interaction between two particles resulting from the algebraic sum of two interaction energies [4]: the van der Waals attraction (V_A) and the electrostatic double-layer repulsion (V_R).

Many reasons have been invoked to explain such discrepancies between theory and unexplained experimental findings, especially at high electrolyte concentrations and small separation distances, such as the ionic species being considered as point charges and solvent–surface, surface–ion, and solvent–ion interactions being neglected. However, the development of direct surface force measurement techniques in the past two decades, with the surface force apparatus

(SFA) and the atomic force microscope (AFM), has allowed the discovery of short-range forces, known as solvation (or structural) and steric forces [5,6]. These forces were found to be either attractive or repulsive, depending on the nature of the surfaces (or the particles), the solvent, and the experimental conditions. Starting from the empirical exponential function describing the structural forces and using the Derjaguin approximation for spherical particles of radius a (much greater than the separation distance D between the particles), the following expression for the interaction energy arising from such structural forces was proposed [3],

$$V_S(D) = \pi a K_S \lambda^2 \exp(-D/\lambda), \quad (1)$$

where for 1:1 electrolytes the decay length λ is in the range 0.2–1.1 nm, and it does not vary significantly with ionic strength. The structural force constant K_S , determined experimentally for different hydrophilic solid materials, lies within the range 10^6 – 5×10^8 N/m².

In order to determine the origin of the structural force, experiments were conducted to measure the hydration repulsion between various solid surfaces in the presence of different aqueous electrolyte solutions. Owing to the ability of the ions to structure the water molecules in their vicinity, the cosmotropic (or structure-maker) and chaotropic (or structure-breaker) nature of the ions has been expected to exert a significant influence on the magnitude of the short-

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range repulsion [7]. However, the experimental results were found to exhibit conflicting tendencies according to the studied surfaces. For pyrogenic silica surfaces at pH 5.5, the more hydrated counterions (Li^+ and Na^+), having an electrical charge of sign opposite to that of the surface, produced the weaker force, whereas for mica surfaces it was the reverse [7,8]. The weaker force was recorded in the presence of the poorly hydrated ions Cs^+ and K^+ . Moreover, it was noted that this short-range repulsive force was always present between silica surfaces in pure water with a magnitude greater than that measured with any electrolyte. In the case of mica, it only appeared (as mica surface does not hydrogen-bond to water) once a minimum salt concentration was reached [8]. So the exact origin of the hydration repulsion remains open. It is interpreted either as the energy required to dehydrate the adsorbed ions confined between the approaching surfaces or as the energy associated with the ion-specific disruption of the hydrogen-bonding network of water molecules at the solid surface.

As a consequence, the study of the ionic specificity (Hofmeister effect) in the stability behavior of colloidal suspensions has gained renewed attention. Indirect surface force measurement techniques, such as the yield stress, the viscosity, the storage modulus, the particle packing density, the sedimentation rate, the consolidation behavior, the flow stress of consolidated bodies, and the ζ potential, were recently used at high concentration of varying salts in various aggregated aqueous slurries (alumina, zirconia, rutile, silica) [9–14] and latices (polystyrene, polyNIPAM) [15,16] or proteins (fibrinogen, myoglobin) [17]. The magnitude of all of these physical variables was expected to be related to the strength of attractive particle networks, which is controlled by the depth of the interparticle potential well. The latter results from the balance between the van der Waals attraction and the extent of the short-range repulsion [12].

Although some contradictory results may be encountered in the literature, general trends have been reported. The number of adsorbed counterions follows the concept of “like adsorbs like” [18,19]. The propensity of counterions with the same electrical charge to be more favorably adsorbed on a surface depends on their own ability to structure the water molecules and on the extent of the hydrogen-bonding water network around the particle surfaces. The degree of hydration of a surface is intimately related to the number density of neutral hydroxyl groups on the surface that are able to create a thick hydration layer through hydrogen bonding with surrounding water molecules. In the case of silica, the pK_a value corresponding to the equilibrium $\text{SiO}^- + \text{H}^+ = \text{SiOH}$ is 7.5 and it is around -4 for the equilibrium $\text{SiOH} + \text{H}^+ = \text{SiOH}_2^+$ [20]. So for pH values greater than 7, the only ionic sites at the silica surface are the SiO^- groups. Under these conditions, the presence of the protonated silanol sites is controlled by the gap between the isoelectric point (iep) of the solid surface and the pH of the aqueous suspension. The high stability of suspensions of silica at its iep value (pH 2) was indeed explained by the presence of such

a protective hydration layer involving a short-range repulsive hydration force, dehydration being energetically unfavorable [3,21]. For the same reason, structure-maker ions are expected to be preferentially adsorbed at a well-hydrated surface, while structure-breaker ions should be more favorably adsorbed at a poorly hydrated surface. Moreover, the number of adsorbed counterions has been assumed to generate an additional attractive ion–ion correlation force between the surfaces [12,14] and to regulate the magnitude of the repulsive hydration force, since some aggregated colloidal suspensions were found to disperse again with a great excess of electrolyte [17].

Owing to its specific properties, a gelled network may be assumed to preserve in its structure the memory trace of its formation. These systems are thus expected to offer the opportunity to study the relation between the internal structure and the rheological response. In the present study, the influence of a representative structure-breaker ion (ammonium) and a structure-maker ion (sodium) on the microstructure and the dynamic rheological behavior of gelled concentrated colloidal silica (Ludox) suspensions has been investigated.

2. Materials and methods

2.1. Materials

Ludox HS-40 suspension (Dupont, Belgium) with a 40% w/w solid content (silica density 2.2 g/ml) was used. The average particle radius and the specific surface area are respectively 12 nm and 220 m²/g, as indicated by the manufacturer. The pH and the density of the stock suspension are respectively 9.8 and 1.29 g/ml. The ζ potential of a dilute suspension, measured with a Zetasizer 5000 apparatus (Malvern Instrument), was found to be -30 mV at pH 9.8. Sodium chloride and ammonium chloride salts were purchased from Fluka (France) and were used as received. Distilled and deionized water was used as a solvent.

2.2. Visual determination of the gelation time

A volume of 4 ml of the gelling Ludox suspensions was prepared by adding 1 ml of a stock aqueous salt solution to 3 ml of a dilute aqueous Ludox suspension of varying Ludox HS-40 content in order to obtain the desired volume fraction. The resulting suspension was then poured into a stoppered borosilicate glass tube (internal diameter 1.1 cm, height 12 cm). The gelation time was determined while the test tube was gently inverted. The time when the sample stopped flowing was taken classically as the gel point. It has to be noted that although the pH of the gelling suspension was slightly different with the studied salt (pH 8.6 with NaCl and pH 7.8 with NH_4Cl), it was found to remain constant during the gelation process.

2.3. Rheological measurements

As prepared previously, 4 ml of the concentrated Ludox suspensions of varying volume fractions were placed in glass beakers (internal diameter 3.5 cm) and stored at rest at 298 K during 24 h before any measurement. Each studied beaker was directly fixed on the plate of the rheometer (Bohlin, France) with a double-face adhesive. Measurements of the viscoelastic properties of the various gelled suspensions were performed in oscillatory mode at 298 K with a parallel geometry (gap 0.8 mm) using a grooved plate (diameter 2.5 cm) to avoid any sliding effect on the gel surface. The level of the strain was checked in order to ensure that all measurements were made within the linear viscoelastic regime. The studied frequency was fixed at 0.5 Hz; the storage modulus G' (measuring the solidlike elasticity of the material) and the loss modulus G'' (measuring the viscous flow properties of the material) were measured at varying shear stresses (linear increase). Both modulus were found to be practically constant throughout the investigated shear stress range, 0.1–100 Pa, and average values were taken. The loss angle δ values ($\tan\delta = G''/G'$) of the gels were found to be lower than 5° (say $G' \gg G''$).

3. Results and discussion

3.1. Qualitative comparison of the repulsive hydration contribution

The critical coagulation concentration (ccc) is referred as the electrolyte concentration for which the transition from a slow (kinetic rate constant k_S) to a rapid (kinetic rate constant k_R) aggregation regime occurs for a given suspension [4]. Classically, the ccc is experimentally determined by adding increasing amounts of electrolyte on several dilute samples of the studied suspension at a constant particle volume fraction. The turbidity of the suspension, τ , is then recorded as a function of time, t . The initial slope of $\tau(t)$ makes it possible to evaluate the kinetic constants. This experimental determination is correlated to the DLVO model through the well-known stability ratio W [4]:

$$W = \frac{k_R}{k_S} = 2a \int_{2a}^{\infty} \frac{\exp(V_{\text{tot}}/k_B T)}{D} dD. \quad (2)$$

According to the DLVO model, the total interaction energy $V_{\text{tot}}(D)$, resulting from the sum $V_A(D) + V_R(D)$, and its derivative as a function of the separation distance ($dV_{\text{tot}}(D)/dD$), are predicted to be zero for a critical separation distance D_c corresponding to the ccc value [4]. In the case of two spherical particles of radius a , separated by a distance D , $V_A = -Aa/12D$, where A is the Hamaker constant of the solid in the suspending medium ($A = 0.83 \times 10^{-20}$ J for silica in water [22]), and $V_R =$

$32\pi\epsilon\epsilon_0 a (k_B T / ez)^2 \gamma^2 \exp(-\kappa D)$, where $\epsilon\epsilon_0$ is the permittivity of the medium, $k_B T$ represents the thermal energy, e is the electronic charge, and z is the ion valency. The term γ corresponds to $\tanh(ze\psi_S/4k_B T)$, where ψ_S is the surface potential. In these relations,

$$\kappa = \left(\frac{e^2 \sum_i \rho_i z_i^2}{\epsilon\epsilon_0 k_B T} \right)^{1/2} = \left(\frac{2.10^3 e^2 z^2 N_A C}{\epsilon\epsilon_0 k_B T} \right)^{1/2}$$

represents the inverse of the Debye length, in which ρ_i is the number density of each electrolyte i , N_A is the Avogadro number, and C is the salt concentration expressed in mol/l.

Thus, the predicted value of the ccc for aqueous suspensions at 298 K may be obtained from the relation

$$\text{ccc} \approx 4 \times 10^{-39} \frac{\gamma^4}{A^2 z^6} \quad (\text{in mol/l}) \quad (3)$$

and W is expected to be equal to 1 when the ccc is reached ($V_{\text{tot}} = 0$) and to remain constant.

However, in many studies relating to various systems, the experimental ccc is often found to be significantly different from the theoretical DLVO value and moreover to depend on the nature of the coagulant used [3,4]. In a preceding article [23] relating to the effect of the ion specificity on the gelation kinetics of colloidal silica suspensions (Ludox HS40), the ccc was found to be 0.45 M with the chaotropic NH_4Cl salt and 0.70 M in the presence of the kosmotropic NaCl salt. These values were at variance with the 0.34 M theoretical value. At pH far away from the iep, the density of silanol sites at the silica surface is low and the extent of the hydration layer around the particles can be assumed to be small. In these conditions the ammonium counterions are preferentially adsorbed at the surface of the Ludox particles. As observed, the ccc of diluted Ludox suspensions is greater and the gelation kinetics of concentrated Ludox is slower in the presence of the sodium ions.

Considering now, in the framework of the DLVO model, that the total interaction energy is given by $V_{\text{tot}}(D) = V_A(D) + V_R(D) + V_S(D)$, the ccc should correspond to the two following conditions:

$$\begin{aligned} V_{\text{tot}}(D) = 0: \\ -\frac{A}{12D} + 32\pi\epsilon\epsilon_0 \left(\frac{k_B T}{ez} \right)^2 \exp(-\kappa D) \\ + \pi K_S \lambda^2 \exp(-D/\lambda) = 0 \end{aligned} \quad (4)$$

and

$$\begin{aligned} \frac{dV_{\text{tot}}(D)}{dD} = 0: \\ \frac{A}{12D^2} - 32\kappa\pi\epsilon\epsilon_0 \left(\frac{k_B T}{ez} \right)^2 \exp(-\kappa D) \\ - \pi K_S \lambda \exp(-D/\lambda) = 0. \end{aligned} \quad (5)$$

This is verified for λ values such that

$$\lambda = \frac{A/12D - 32\pi\epsilon\epsilon_0 (k_B T / ez)^2 \gamma^2 \exp(-\kappa D)}{A/12D^2 - 32\kappa\pi\epsilon\epsilon_0 (k_B T / ez)^2 \gamma^2 \exp(-\kappa D)}$$

$$= \frac{Q_A - Q_R}{Q_A/D - \kappa Q_R} \quad (6)$$

The corresponding K_S values are then given by

$$K_S = \frac{A/12D - 32\pi\epsilon\epsilon_0(k_B T/e z)^2 \gamma^2 \exp(-\kappa D)}{\pi \lambda^2 \exp(-D/\lambda)} \quad (7)$$

$$= \frac{Q_A - Q_R}{\pi \lambda^2 \exp(-D/\lambda)}$$

As the ccc in the presence of both salts has been determined experimentally, the corresponding κ values can be calculated. For a given salt, the D values can thus be varied so that λ and K_S values, obtained through Eqs. (6) and (7), should belong respectively to their expected ranges, say 0.2–1.1 nm and 10^6 – 5×10^8 N/m². The results of numerical calculations are reported in Figs. 1 and 2 for Na⁺ and NH₄⁺ respectively. The variation of the expected λ values as a function of K_S is thus shown in Fig. 3. For the same K_S value (characteristic of the silica/water interface), the obtained $\lambda(\text{Na}^+)$ values are always found to be greater than the $\lambda(\text{NH}_4^+)$ ones. This indicates that whatever the separation distance and for a given K_S value, the repulsive V_S term in the presence of sodium ions is of greater magnitude than that in the presence of the ammonium ions. Taking, for example, the same $K_S = 5 \times 10^6$ N/m², which is represen-

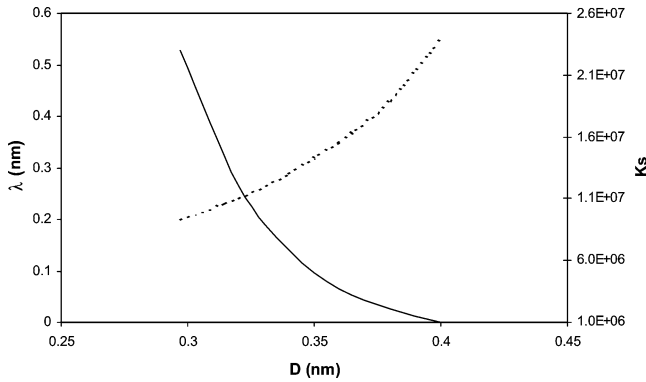


Fig. 1. Results of the numerical calculations of λ (dotted line) and K_S (continuous line) as a function of the separation distance D with ccc (NaCl) = 0.70 M.

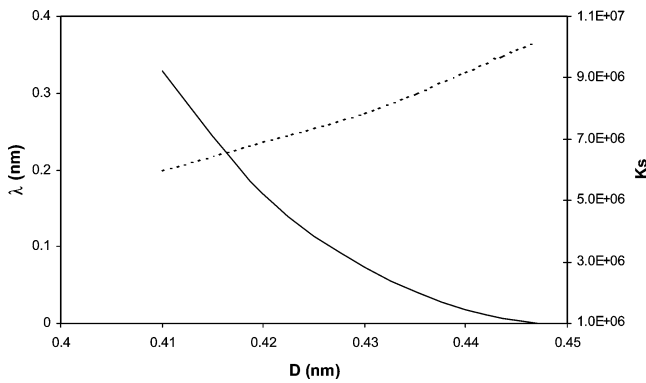


Fig. 2. Results of the numerical calculations of λ (dotted line) and K_S (continuous line) as a function of the separation distance D with ccc (NH₄Cl) = 0.45 M.

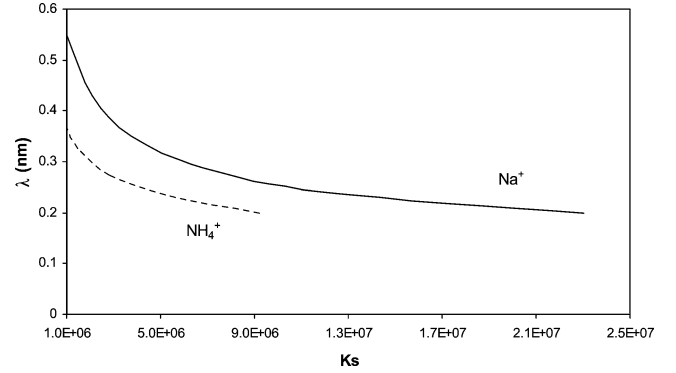


Fig. 3. Variation of the expected λ values as a function of the K_S values with NaCl (continuous line) and NH₄Cl (dotted line).

tative of a poorly hydrated silica surface (as in the studied case where the pH is much greater than the iep), one obtains $\lambda(\text{Na}^+) = 0.32$ nm and $\lambda(\text{NH}_4^+) = 0.21$ nm.

This qualitative analysis, which is based on the existence of the V_S term to explain the origin in the different ccc values, suggests that for a given electrolyte concentration the more hydrated (cosmotropic) ions generate a stronger repulsive hydration energy between the Ludox silica surfaces at pH well above the iep. This result may have an influence on the strength of the particle networks, since it is related to the depth of the attractive potential well. This aspect is discussed later. However, this conclusion is in contradiction to a previous work relating to SFA measurements between silica surfaces [8]. Nevertheless, it has to be noted that the use of flame (pyrogenic) silica in SFA experiments was highly questioned to make relevant comparison with the colloidal stability of silica particles (precipitate silica or Ludox) [10,13]. Moreover, the studied pH was different, pH 5.5. It is probable that the charging effects and the resulting environment of the water network around the surfaces are not the same.

3.2. Influence of the ion specificity on the rheological behavior

In the present study, dynamic rheological measurements were performed on gelled Ludox suspensions in order to determine the magnitude of the storage (or elastic) modulus, say G' , in the presence of both salts. The elastic modulus is related to the strength of the interparticle attraction, the solids volume fraction, the particle size, and the microstructure of the particle network [12,24]. Although the volume fraction and the particle size can be easily imposed, the microstructure of the aggregated suspension is more difficult to control. However, knowledge of it is very important in order to make relevant quantitative analysis.

Concerning silica suspensions, controversial results have been encountered in the literature. Colic et al. [10] have reported that the viscosity of silica (Nissan Chemicals) slurries at any pH was greater in the presence of the more hydrated counterions. It was inferred that deeper attractive potential

wells, resulting from a lesser extent of the short-range repulsive force, were obtained in this case than in that with the poorly hydrated ions. However, little information was given on the preparation of the silica suspensions before viscosity measurements and the aspect relative to the aggregated microstructures was not treated. On the other hand, Franks [14] reported that the magnitude of the yield stress of two types of silica (Geltech amorphous silica and Sigma ground quartz) suspensions at $\text{pH} > 6$ was found to increase with the number of adsorbed ions. The greatest yield stresses were observed with the least hydrated counterions. In this study, special care was taken to maintain, a priori, the same structure of particle networks by preshearing the suspensions prior to the yield stress measurements with the vane technique.

According to fractal models of viscoelastic properties [26,27], a convenient way to appreciate the network microstructure is to examine the volume fraction dependence of the elastic modulus. Similar network structures are expected to generate the same scaling behavior. The power law behavior of the elastic modulus is expressed as

$$G' = G'_0 \phi^x, \quad (8)$$

where G'_0 is the preexponential factor characterizing the elasticity of the interparticle bonds and the exponent x is related to the network structure through the fractal dimension. The x value was predicted to be 4.5 for reaction-limited cluster aggregation (RLCA) and 3.5 for diffusion-limited cluster aggregation (DLCA) [25].

In a previous study [23], it was shown that the microstructure of gelled concentrated Ludox suspensions could be assessed from the scaling of the gelation time (t_{gel}) as a function of the volume fraction (ϕ) through [28]

$$t_{\text{gel}} \sim \phi^{3/(D_f-3)}, \quad (9)$$

where D_f represents the fractal dimension. For the two limiting regimes RLCA and DLCA, the fractal dimensions, calculated from lattice models and in agreement with scattering experiments, have been reported to be respectively 1.8 and 2.2 [29]. The previous results have emphasized that the microstructure of the networks was similar in the presence of ammonium and sodium ions, provided that the electrolyte concentration used to destabilize the suspensions was higher or lower than the ccc for both investigated counterions. Indeed, at 0.45 M (corresponding to the ccc in the presence of ammonium), the D value was found to be 1.5 ± 0.1 for NH_4^+ , whereas $D = 2.1 \pm 0.1$ in the presence of Na^+ , indicating that at this concentration an RLCA regime was still prevailing with sodium.

In order to confirm these results at the rheological level, the storage (G') and loss (G'') modulus were measured, as described in the experimental section, on gelled suspensions at varying Ludox volume fractions at the same 0.45 M ionic strength for both counterions. As an example, the invariance of the modulus as a function of the shear stress range is

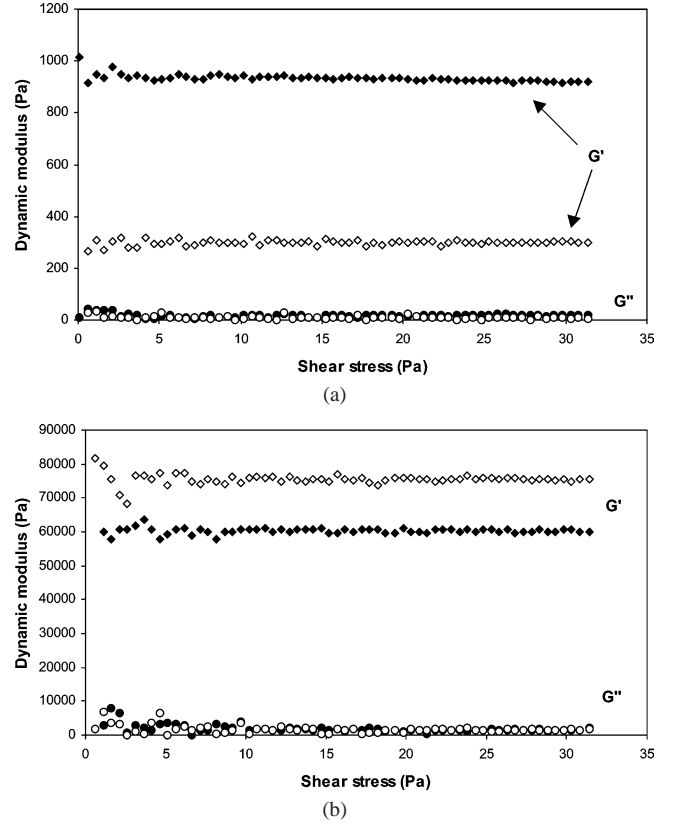


Fig. 4. Variation of the elastic (diamond) and viscous (circle) modulus as a function of the shear stress for NH_4Cl (black diamond and circle) and NaCl (open diamond and circle) at 0.45 M and $\phi_{\text{Ludox}} = 0.023$ (a) and 0.07 (b).

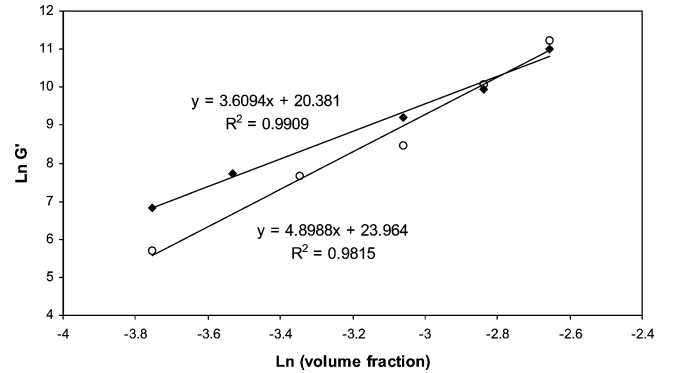


Fig. 5. Double logarithmic plot of the elastic modulus with the Ludox volume fraction for NH_4Cl (◆) and NaCl (○) at 0.45 M.

illustrated in Figs. 4a and 4b for two different Ludox volume fractions in the presence of both salts. A double logarithmic plot of the scaling of the elastic modulus with the volume fraction at 0.45 M is reported in Fig. 5. In the case of NH_4Cl and NaCl , the exponents are found to be respectively $x = 3.6 \pm 0.2$ and $x = 4.9 \pm 0.4$. These results are in agreement with the theoretically predicted exponent values. However, the difference between the G' values for the two electrolytes decreases as the volume fraction increases. More importantly, as a result of a different network structure, the elastic modulus with the cosmotropic Na^+ ion becomes

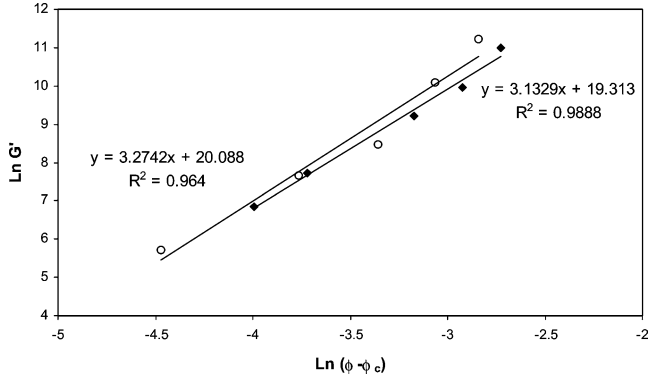


Fig. 6. Double logarithmic plot of the elastic modulus with the distance to the gelation threshold for NH_4Cl (◆) and NaCl (○) at 0.45 M.

greater than that in the presence of the NH_4^+ ion at higher ϕ values. Therefore, direct quantitative comparison appears to be irrelevant in such a case.

As was also proposed in the literature [24,30,31], the generic mechanical behavior of particle gels has been assumed to follow the relation

$$G' = G'_0(\phi - \phi_c)^s, \quad (10)$$

in which the difference $(\phi - \phi_c)$ is the distance to the gelation threshold, where ϕ_c corresponds to the critical volume fraction. The exponent s is expected to relate to the structure of the network, although its value has not been predicted by any existing theory. The ϕ_c values in the presence of both salts at the same 0.45 M concentration were determined. For that purpose, suspensions at the same salt concentration and with varying Ludox volume fractions were prepared. The lowest particle volume fraction in suspension for which a gel was formed has been taken as the ϕ_c value. The experiments indicated that, for the same 0.45 M concentration, the ϕ_c were significantly different: $\phi_c(\text{Na}^+) = 0.012$ and $\phi_c(\text{NH}_4^+) = 5 \times 10^{-3}$. This result suggests that the higher the attractive interaction, the lower the critical volume fraction. It may be interpreted as confirming that stronger attraction leads to faster aggregation processes that generate more loosely packed aggregates, so that the gelation threshold is attained for lower volume fractions [32,33]. The scaling of G' as a function of $(\phi - \phi_c)$ is presented in Fig. 6. The linear regressions are not so good as in the case of the previous scaling of G' versus ϕ ; the s exponent is found to be of the same order, say 3.2 ± 0.3 .

3.3. Comparative rheological behavior at 0.80 M

In order to verify the microstructure, gelled suspensions at varying Ludox volume fraction were prepared with the same 0.80 M salt concentration of both salts (greater than the highest ccc, say 0.70 M for NaCl) and the gelation time was measured by visual determination [34]. The results are reported in Fig. 7. A continuous decrease of the gelation time as a function of the volume fraction is observed in the presence of both electrolytes. However, for the same ionic

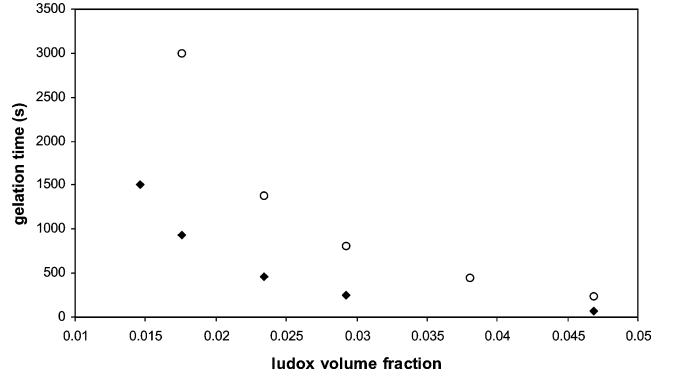


Fig. 7. Variation of the gelation time as a function of the Ludox volume fraction for NH_4Cl (◆) and NaCl (○) at 0.80 M.

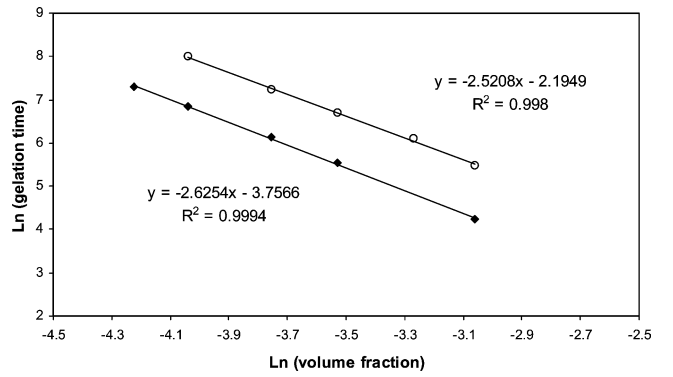


Fig. 8. Double logarithmic plot of the gelation time with the Ludox volume fraction for NH_4Cl (◆) and NaCl (○) at 0.80 M.

strength, the gelation kinetics are faster with the ammonium counterion at any volume fraction. According to the expected scaling relationship, the double logarithm plots are shown on Fig. 8. The linear regressions are very good and the obtained exponent values are very similar: -2.52 ± 0.07 for sodium ions and -2.63 ± 0.04 for ammonium ions. These values correspond to $D = 1.81 \pm 0.04$ for gelled networks in the presence of Na^+ and $D = 1.86 \pm 0.02$ in the presence of NH_4^+ . As expected, the order of magnitude of the D value is similar to that of a DLCA aggregation regime, confirming the reliability of visual determination to evaluate of the microstructure of gelled systems.

To investigate the ion-specific effect on the rheological behavior within the same microstructure, G' and G'' were measured for gelled suspensions at varying Ludox volume fractions at the same 0.80 M ionic strength for both counterions. As an example, Fig. 9 illustrates the variation of the dynamic modulus with the shear stress in the presence of both salts for the same volume fraction. The variation of G' as a function of the volume fraction is shown in Fig. 10. As observed, the G' values are always greater, at any volume fraction, in the presence of the chaotropic ammonium ion. The corresponding scaling of G' versus ϕ is represented in Fig. 11. The exponent values are found to be 3.1 ± 0.3 and 3.5 ± 0.2 for NH_4Cl and NaCl salts, respectively, and are on the same order as that characteristic of a DLCA aggregation

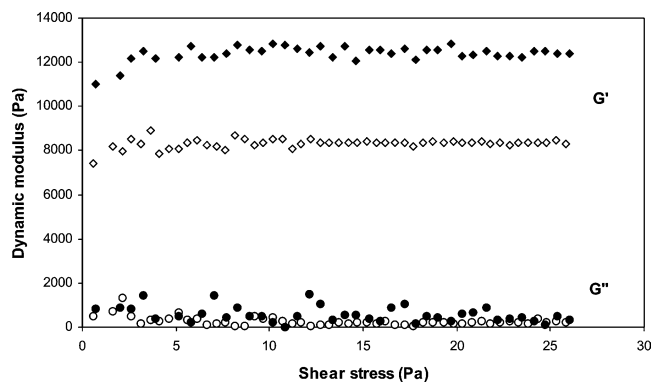


Fig. 9. Variation of the elastic (diamond) and viscous (circle) modulus as a function of the shear stress for NH_4Cl (black diamond and circle) and NaCl (open diamond and circle) at 0.80 M and $\phi_{\text{Ludox}} = 0.047$.

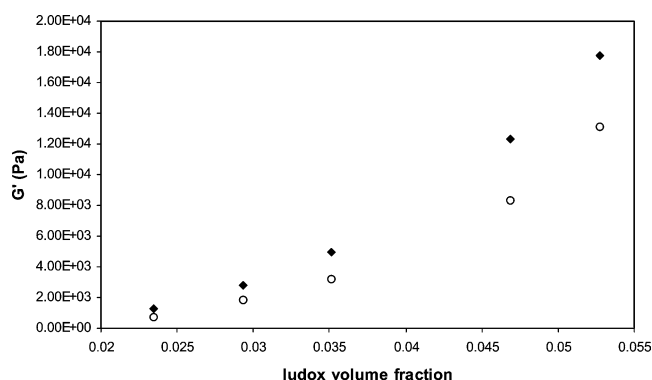


Fig. 10. Variation of the elastic modulus as a function of the Ludox volume fraction for NH_4Cl (◆) and NaCl (○) at 0.80 M.

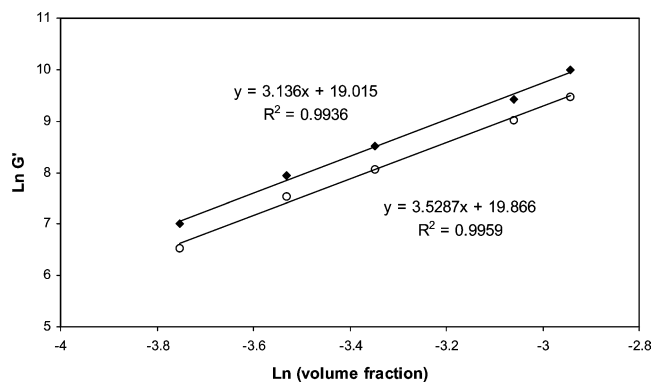


Fig. 11. Double logarithmic plot of the elastic modulus with the Ludox volume fraction for NH_4Cl (◆) and NaCl (○) at 0.80 M.

regime. Moreover, it has to be noted that the G' values are slightly stronger, with a greater amount of ammonium salt (0.45 and 0.80 M) for a similar microstructure.

To make the comparison with the scaling of G' with the distance to the gelation threshold, the ϕ_c values in the presence of a 0.8 M concentration of both salts were determined. The ϕ_c value was found to be the same for sodium and ammonium salts, and moreover it was hard to distinguish from that obtained with NH_4Cl at 0.45 M, say $\phi_c = 0.005$. This observation is expected to result from the fact that these salt

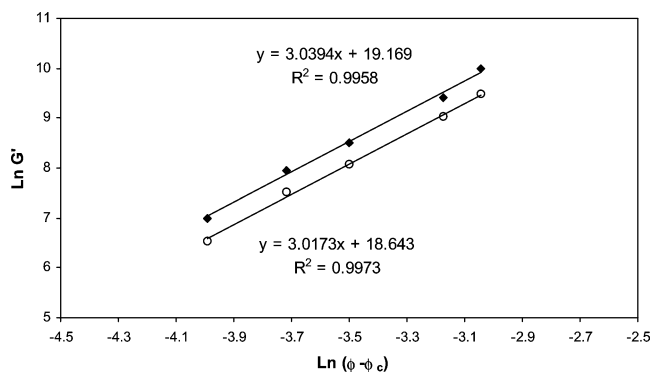


Fig. 12. Double logarithmic plot of the elastic modulus with the distance to the gelation threshold for NH_4Cl (◆) and NaCl (○) at 0.80 M.

concentrations are greater than the ccc, indicating the occurrence of a DLCA aggregation regime characterized by strong attractive interactions. The double logarithm plot of G' with $(\phi - \phi_c)$ at 0.8 M is presented in Fig. 12. The linear regressions are satisfactory; the s exponent is found to be similar, say $s = 3.0 \pm 0.1$, and on the same order as that obtained for a 0.45 M salt concentration (see Fig. 7). This emphasizes the generic character of this scaling, although no comprehensive model has been proposed.

Nevertheless, the results indicate that attractive silica-gelled networks at pH above the iep are stronger in the presence of the chaotropic counterion. This is consistent with the results of Ref. [14] but in contradiction to those of Ref. [10]. It may be interpreted as a consequence of a greater number of chaotropic ions that are preferentially adsorbed on the silica surface at high pH. Very thin and dense polarizable counterion clouds have been assumed to result from the high concentration of adsorbed ions between the surfaces. The correlated fluctuations of the counterion clouds are expected to generate an additional van der Waals-like attraction called the ion-ion correlation force [12]. On the other hand, the results may also be ascribed to a lesser magnitude of the short-range repulsive hydration force in the presence of the chaotropic ions. The observation that at such a 0.80 M ionic strength the gelation time is still longer at any volume fraction, and also that the ccc is much greater in the presence of Na^+ ions, may be seen as indicating the presence of a stronger repulsive contribution due to hydration effects during the irreversible aggregation process.

4. Conclusion

The obtained results were shown to exhibit complementary aspects between the gelation kinetics study and the rheological behavior of gelled Ludox suspensions to assess the microstructure of the network. Within the same microstructure, the strength of the resulting silica networks at pH well above the iep has been found to be definitively greater in the presence of the more adsorbed and poorly hydrated counterion. The combined influence of an ion-ion correlation force

together with a repulsive hydration force is suggested to explain the comparative strength of the gels.

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