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Influence of the Counterion Nature on the Stability Sequence of Hydrophobic Latex Particles

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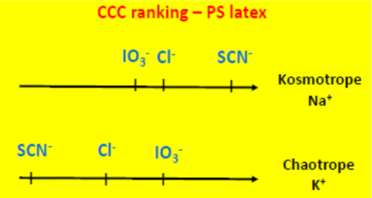
ABSTRACT: The aggregation kinetics of negatively charged polystyrene latex particles in the presence of monovalent electrolytes have been investigated. The inferred coagulation critical concentrations were compared to establish the stability sequence. With the same representative co-ions, this sequence is reversed when using kosmotrope sodium and chaotrope potassium cations. The results have been ascribed to a variable competition of the co-ions toward the hydrophobic surface depending on the lyotropic nature of the associated counterion. They provide new insights into the implication of ionic specificity in the stability behavior of aqueous dispersions of charged colloids.



1. INTRODUCTION

Although Hofmeister (or ion-specific) effects have been known for more than 120 years and were shown to play a significant role in the behavior of many colloidal domains where aqueous salt media are involved, the underlying reasons remain unclear.[1,2] What is remarkable is that they offer the opportunity to modulate the desired properties of a system by simply changing the electrolytes' nature of even the same valency, either the cation or/and the anion.[3]

At the fundamental level, ion-specific effects pose a challenge to the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory,[4] describing the qualitative behavior (stability/aggregation) of colloidal systems through knowledge of the total energy of interaction resulting from the assumed algebraic sum of the van der Waals attraction (U_A) and the electrostatic double-layer repulsion (U_R). Recognized limitations, notably at short separation distances and/or for electrolyte concentrations greater than 0.1 M, were justified since ions are considered as point charges in this theory. Moreover, solvent–surface, surface–ion, and solvent–ion interactions are not taken into account. Additional non-DLVO contributions, such as the dispersion energy (U_{Disp}) and the hydration energy (U_{Hyd}), were thus proposed to interpret the experimental findings, although it is still open to debate.[5−7]

Nevertheless, qualitative trends have been reported when studying the ability of ions to promote aggregation of aqueous dispersions of nanoparticles.[8−12] Various factors such as the hydrophobic/hydrophilic character of the particles, the sign of the particle surface charge, and the kosmotrope/chaotrope (lyotropic) nature of ions were shown to exert an influence.[13−16] Among the different investigated systems, the case of negatively charged hydrophobic particles is particularly representative, as for instance with polystyrene lattices. On the basis of aggregation kinetics experiments, the influence of anions, acting as co-ions, was notably evidenced. The coagulation critical concentration (ccc), representing a stability indicator (or gauge) of a colloidal system, was determined with sodium salts.[17−19] The ranking with monovalent co-ions was as follows

$$IO_3^- \leq F^- < Cl^- < NO_3^- < I^- < SCN^-$$

When the ccc is higher, it reflects that higher amounts of electrolytes are required to definitively suppress any repulsive contribution. This stability sequence was shown to be inverted when the surface charge of the latex was positive (with hydrophobic particles) or when the surface turned hydrophilic (with negatively charged particles).[6]

The above sequence follows what is defined as the indirect Hofmeister series for anions, where chloride Cl^- is usually considered as a reference ion. On the right side of chloride, anions are structure-breaker or chaotrope ions where the immediately adjacent water molecules are weakly attracted to but are sufficiently enough to perturb their organization in the bulk. Anions on the left side of chloride are associated with structure-maker or kosmotrope ions, where the surrounding water molecules are strongly attracted to and are more closely organized among themselves than in pure water. Contrary to the kosmotropes, chaotrope ions have the propensity to easily remove their hydration shell. This kosmotrope or chaotrope nature of the ions can be conveniently distinguished according to the sign of the viscosity B coefficient appearing in the Jones–Dole relationship[20]

$$\frac{\eta}{\eta_w} = 1 + A \times \sqrt{c} + B \times c \tag{1}$$

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 M. 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

Table 1. Representative Parameters of the Studied Ions[a]

ions	SCN^-	Cl^-	IO_3^-	Li^+	Na^+	K^+	NH_4^+
B (M)	−0.103	−0.005	0.138	0.146	0.085	−0.009	−0.008
α_0 (Å^3)	6.61	3.59	8.00	0.03	0.13	0.79	1.86

[a] Viscosity coefficient value (B)[20] and static polarizability (α_0)[2,5,8] of ions.

kosmotrope ions, whereas negative B values correspond to chaotrope ions. The B values of ions are reported in Table 1.

To interpret the above trends, an accumulation/exclusion mechanism of ions near surfaces has been proposed.[6,8] It corresponds to a parallel approach of the previous concept "like adsorbs like".[21,22] It is related to the microscopic water structure around both the hydrated ions and particle surfaces. It predicts qualitative attraction/accumulation between ions and surfaces when they have similar water arrangements or repulsion/exclusion between them when they have dissimilar water arrangements.

Nevertheless, it has to be remarked that the previous trends with polymer lattices were inferred from the comparative behavior of monovalent salts where the counterion was restricted to kosmotrope sodium cations. The influence of ionic specificity on many colloidal systems has been often investigated by either changing the anion nature of a same cation (often sodium or potassium) or the cation nature of a same anion (very often chloride).[23−29] However, the crossover study with co-ions and counterions of different lyotropic nature has been scarcely reported in the literature.[17,30] Following the accumulation/exclusion mechanism and as polystyrene lattices are assumed to be model hydrophobic colloids, it may be interesting to examine whether the kosmotrope/chaotrope character of the counterion exerts a sensitive influence in the presence of representative co-ions with a different lyotropic nature.

In this study, the comparative stability behavior of negatively charged polystyrene lattices in the presence of monovalent electrolytes with potassium, ammonium, and sodium counterions has been investigated.

2. EXPERIMENTAL SECTION

2.1. Materials. Sodium thiocyanate (NaSCN), sodium chloride (NaCl), sodium iodate ($NaIO_3$), potassium thiocyanate (KSCN), potassium chloride (KCl), potassium iodate (KIO_3), ammonium thiocyanate (NH_4SCN), ammonium chloride (NH_4Cl), and lithium chloride (LiCl) were purchased from Sigma-Aldrich or Prolabo and were used as received. Deionized water (18.2 MΩ·cm) was used as a solvent to prepare the electrolyte solutions, whose pH values ranged between 6 and 7.

2.2. Synthesis of Polystyrene Latex. Stable polystyrene lattices were synthesized from surfactant-free emulsion polymerization according to classical methods reported in the literature.[31,32] Nitrogen gas was bubbled during 10 min into a solution containing 0.0347 g of potassium persulfate ($K_2S_2O_8$, 270 g·mol^{-1}) dissolved in 100 mL of deionized water. The sample was placed into a double-jacked reactor thermostated at 70 °C through a regulator bath (Lauda Eco Silver), and the solution was moderately agitated (300 rpm) with a magnetic stirrer. The inhibitor present in liquid styrene was removed by filtration across a bed of activated alumina powder. Then, 1.5 mL of purified styrene (C_8H_8, 104.15 g·mol^{-1}, density: 0.906 g·mL^{-1}) was added into the previous solution, and the reaction was stopped after 24 h.

After synthesis, 30 mL of the obtained latex was poured in a dialysis bag (12−14 kDa, regenerated cellulose) that was immersed in 1.8 L of deionized water under gentle agitation. The conductivity of the contact water was checked over time, and deionized water was changed until the conductivity of contact water reached 1 μS·cm^{-1}.

The conductivity, pH value, and dry content of the latex sample passed, respectively, from 1.1 mS·cm^{-1}, pH 4, and 1.22% before dialysis to 59 μS·cm^{-1}, pH 5.2, and 1.07% after dialysis. The density of the dialyzed sample was 0.9981 g·mL^{-1} at 25 °C, corresponding to a particle volume fraction of 0.01 (density of polystyrene: 1.055 g·mL^{-1}).

A Malvern NanoZS model was used for size and zeta potential measurements. Scanning electron microscopy (SEM) micrographs were obtained with a JEOL JSM 7100F model operating at 10 kV.

2.3. Kinetics Measurements. The dialyzed polystyrene latex was diluted with deionized water at a 1:8 ratio, and then 0.2 mL of the diluted sample was added into a quartz cell (1 cm in length) containing 2 mL of aqueous salt solution to obtain the desired electrolyte concentration (whole volume of 2.2 mL). In these conditions, the volume fraction of polystyrene particles corresponds to 114×10^{-6}; the pH value of the resulting dispersions remains the same as that of the prepared electrolyte solutions (i.e., between 6 and 7). As described in other studies,[8,14] the aggregation kinetics of the latex particles were followed at 25 °C with a spectrophotometer (Shimadzu) by recording the variation of the absorbance A at 600 nm wavelength as a function of time t. In each experiment, the initial slope k during the first 40 s was determined. For a given electrolyte, the slope increases with concentration until a maximum value k_f is reached, corresponding to the coagulation critical concentration (ccc). This indicates the onset of the fast or diffusion-limited aggregation regime (DLA), whereas for concentrations lower than the ccc, the slow or reaction-limited aggregation regime (RLA) is characterized by an increasing slope k_s with salt concentration. The stability behavior of a colloidal system is classically assessed through the stability ratio W. It reflects the collision efficiency, that is, the ratio of the number of collisions to the number of efficient collisions, and it is conveniently obtained from the slope measurements through

$$W = \frac{k_{fast}(\text{at } c \geq \text{ccc})}{k_{slow}(\text{at } c < \text{ccc})} = \frac{\left(\frac{dA}{dt}\right)_f}{\left(\frac{dA}{dt}\right)_s} \quad (2)$$

The determination of initial slopes at increasing concentrations enables ccc detection. W was then calculated by dividing the highest slope (corresponding to the ccc) to the slope at each concentration, and it was further plotted in a log scale as a function of salt concentration. The concentration where $W = 1$ corresponds to the ccc (a horizontal line at $W = 1$ is drawn on the plots to locate easily its position). Below the ccc (i.e., RLA regime), there is a repulsive energy barrier so that $W > 1$: each collision between particles does not result in

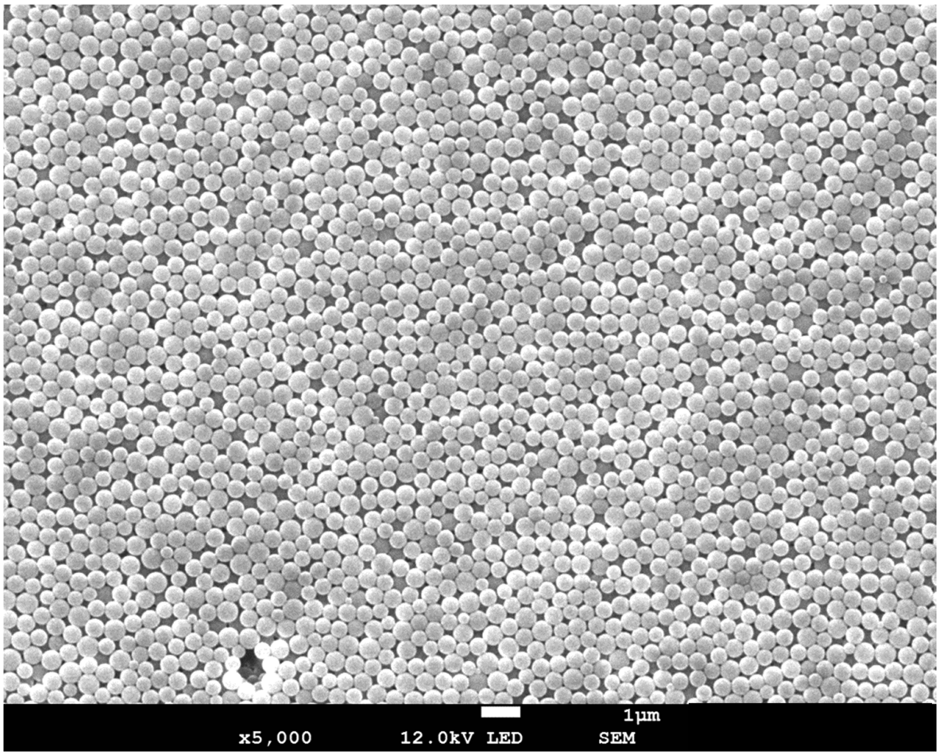


Figure 1. SEM micrograph of a dried sample of the synthesized polystyrene latex.

sticking. The kinetics measurements were repeated twice and were focused to accurately determine the ccc values (average values were taken).

3. RESULTS AND DISCUSSION

3.1. Latex Characterization. Within the synthesis conditions, the molar ratio of monomer styrene (0.1286 M) to initiator potassium persulfate (12.66×10^{-4} M) is 102, ensuring the hydrophobic character of the latex particles. The stability of polystyrene particles originates from their electrostatic repulsion due to the negative charges carried on the hydrophobic surface. They result from the sulfate free radicals ($SO_4{}^{*-}$) generated consecutively to the thermal decomposition of persulfate anions. In the following step, the radical entity is transferred to the styrene monomer through chemical bonding from which the polymerization reaction then propagates. It has been reported in the literature that some sulfate groups may transform in carboxyl groups, owing to eventual differences in preparative, cleaning, or characterization procedures, although there is some conflicting evidence.[33]

Once dialysis was performed (see Section 2.2), the zeta potential and *z*-average diameter of polystyrene particles of diluted sample in 10^{-3} M NaCl were, respectively, −53 mV and 468 nm with a 0.08 polydispersity index (given from the cumulants method). As an indication, a SEM micrograph of the polystyrene latex is shown in Figure 1. The average diameter and polydispersity index (i.e., [standard deviation/average diameter]^2) evaluated from the picture are, respectively, 451 nm and 0.02. The difference originates from the used procedure; analysis from light scattering technique is based on an intensity response, whereas analysis from SEM picture is based on a number response, giving higher emphasis on the smallest components.

3.2. Effect of the Lyotropic Nature of Counterions. In the classical description of the interface between a negatively charged solid surface and an aqueous phase, the ionic atmosphere surrounding the charged surface is composed of cationic counterions that are favorably attracted, whereas the anionic co-ions are repelled. This distribution and random thermal motion of ions lead to the formation of an electric double layer:[4] an inner (Stern) layer rich in cations in the immediate vicinity of the negatively charged surface and an outer (diffuse) layer where some cations and a majority of anions are present, whose thickness, the Debye length κ^{-1}, represents the range of electrostatic repulsion. When enough salt is added, the extent of diffuse layers is sufficiently reduced so that the attractive van der Waals contribution becomes dominant. The aggregation kinetics are related to the total energy of interaction; the more attractive the total interaction, the faster the aggregation. When the ccc is reached, the aggregation regime is fully attractive (i.e., there is no more repulsive contribution).

The influence of the nature of the counterion on the colloidal stability of the synthesized latex was investigated by using chloride electrolytes with monovalent cations exhibiting a different kosmotrope/chaotrope character (see Table 1). The aggregation kinetics were carried out at different electrolyte concentrations to appreciate the slope variation until the ccc was reached, that is, the concentration where the slope remains the highest. As an example, the case with a LiCl electrolyte is shown in Figure 2.

As a characteristic parameter in aggregation kinetics studies, the half-time of aggregation $t_{1/2}$ may be evaluated. According to Smoluchowski's theory,[4] it is given by $t_{1/2} = \frac{1}{k_r \times N_0}$, where N_0 is the initial number of particles per unit volume, and k_r is the second-order rate constant for diffusion-controlled aggregation that corresponds to 5.48×10^{-18} $m^3 \cdot s^{-1}$ in the

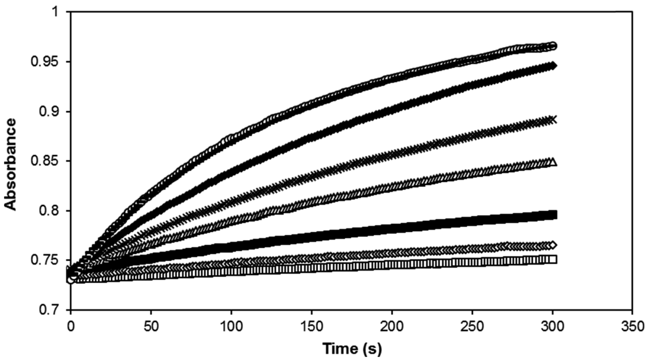


Figure 2. Variation of the absorbance at 600 nm as a function of time during aggregation kinetics at 25 °C of polystyrene particles in the presence of LiCl electrolyte at 0.1 M (open box), 0.15 M (open diamond), 0.2 M (solid box), 0.25 M (open triangle), 0.3 M (times sign), 0.32 M (solid diamond), 0.35 M (open circle), and 0.375 M (minus sign).

dilute aqueous phase at 25 °C. As the particle volume fraction in aggregation kinetics measurement is 114 × 10^{-6} and the average diameter of a spherical particle is taken as 468 nm, it gives $N_0 = 2.1 \times 10^{15}$ particles/m^3. The corresponding half-time of aggregation $t_{1/2}$ is about 80 s, accrediting that kinetics measurements are carried out in the early stages of aggregation during the first 40 s (see Section 2.3).

As an indication, the variation of the absorbance during the first 40 s in the case of LiCl at each concentration is reported in Figure 3. The highest initial slope corresponding to the ccc value occurs at 0.35 M; the initial slopes allow the stability ratio W to be calculated at each concentration from eq 2 (see Section 2.3).

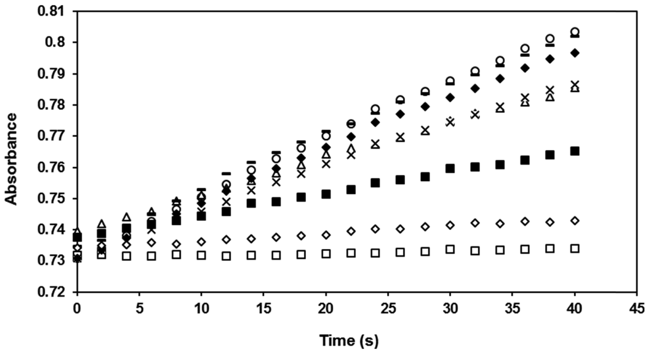


Figure 3. Variation of the absorbance at 600 nm during the first 40 s at 25 °C in the presence of LiCl electrolyte at 0.1 M (open box), 0.15 M (open diamond), 0.2 M (solid box), 0.25 M (times sign), 0.3 M (open triangle), 0.32 M (solid diamond), 0.35 M (open circle), and 0.375 M (minus sign).

The plot of the stability ratio W as a function of electrolyte concentration is presented in Figure 4. The corresponding ccc values are, respectively, 0.35, 0.32, 0.27, and 0.25 M for Li^+, Na^+, K^+, and NH_4^+ cations.

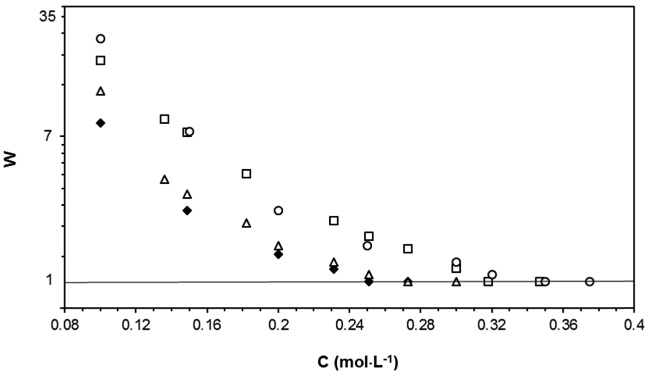


Figure 4. Plot of the stability ratio (log scale) as a function of concentration with LiCl (open circle), NaCl (open square), KCl (open triangle), and NH_4Cl (solid diamond) electrolytes.

These weak but noticeable variations are in accordance with the accumulation/exclusion mechanism, which is based on hydration state compatibilities between ions and surfaces. It can be assumed that the interfacial hydrogen-bonding network of water molecules at the hydrophobic polystyrene surface is poorly developed so that the structure-breaker cations (that disrupt the water structure around them) are preferentially attracted in this favorable environment than the structure-maker cations, contributing to an enhanced screening of the electrostatic repulsions between particles. This is also consistent when the dispersion energy U_{Disp} is considered. It is expected to be attractive when the refractive index n of the substrate is larger than that of water ($n = 1.3325$), which is the case for polystyrene particles since $n = 1.5916$, and its magnitude should increase as the static polarizability of ion in water, α_0, is higher[1,8] (see the reported values in Table 1). A better screening of the surface charge, and thus a promoted destabilizing effect, is therefore expected as the counterions are chaotropes and are more polarizable. The ccc value increases effectively according to the Hofmeister series of cations: $NH_4^+ < K^+ < Na^+ < Li^+$. This is in agreement with earlier studies on negatively charged hydrophobic latex surfaces.[13] The same trends have been also reported in the presence of negatively charged silica nanoparticles at pH values much greater than the isoelectric point (IEP), that is, 2 (pH value for which the zeta potential is zero). Within these conditions, where fewer neutral SiOH silanol groups are present at the silica surface, the adjacent aqueous layers are not well structured so that an enhanced accumulation of alkali cations with increasing chaotrope character was observed.[28]

3.3. Comparative Effect of Co-Ions with Counterions of Different Lyotropic Nature. The comparative colloidal stability of the polystyrene latex has been investigated through aggregation kinetics measurements with sodium, potassium, and ammonium salts of identical anions. The three chosen co-ions were the same as those in a previous study[34] since they correspond to representative anions covering a wide range of B values. Thiocyanate (SCN^-) is a well-recognized chaotrope anion of high polarizability, chloride (Cl^-) is a slightly chaotrope anion that is considered as a central ion in the Hofmeister series, and iodate (IO_3^-) is a quite kosmotrope anion,[35] however, with a large polarizability (see Table 1).

It has to be mentioned that, owing to solubility considerations, the study of colloidal stability in aqueous electrolyte solutions at 25 °C is limited to concentrations lower than 0.478 and 0.428 M, respectively, for $NaIO_3$ and KIO_3 salts. That for ammonium iodate (NH_4IO_3) is precluded since its solubility is too low (i.e., 0.155 M). Because of the experimental procedure described in Section 2.3, the tested concentrations could not exceed 0.42 and 0.38 M, respectively, for $NaIO_3$ and KIO_3. As a consequence, the charge density of the synthesized particles should not be too high to allow the study in the authorized concentration range of these salts. This was achieved when disposing of stable polystyrene latex particles with a zeta potential in the range −50 to −60 mV.

The results obtained with the sodium salts are presented in Figure 5.

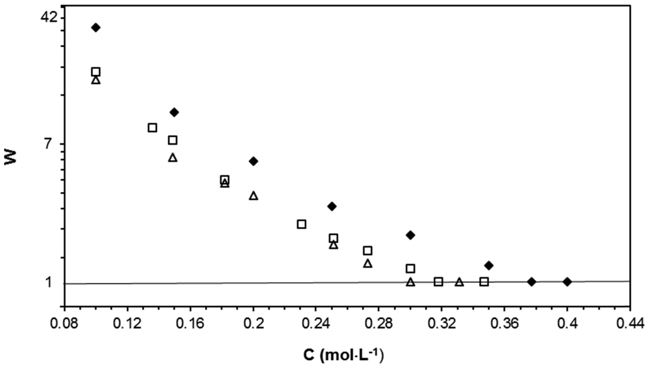


Figure 5. Plot of the stability ratio (log scale) as a function of concentration with NaSCN (solid diamond), NaCl (open square), and $NaIO_3$ (open triangle) electrolytes.

The corresponding ccc values are, respectively, 0.38, 0.32, and 0.3 M for SCN^-, Cl^-, and IO_3^-. This sequence is similar with that reported in previous studies using polystyrene particles,[14] and the accumulation/exclusion mechanism allowed interpretation of this stability sequence.[6] When the surface is hydrophobic, interfacial water molecules experience a peculiar arrangement at its contact so that adjacent aqueous layers exhibit a lower density than that in the bulk. Therefore, chaotrope anions with larger polarizability are more favorably accumulated even on these negatively charged hydrophobic surfaces than the kosmotrope anions. As a result, the effective negative charge on the particles' surface is increased so that stability is enhanced and higher concentrations of salts are thus required to reach the ccc from IO_3^- to SCN^-. Even though the polarizability of iodate anion (IO_3^-) is large, this co-ion should not accumulate to the hydrophobic particle surface, owing to its pronounced kosmotrope character[14] (see Table 1). This indicated, in fact, that hydration state compatibilities between ions and surfaces prevailed over polarizability (dispersive energy) considerations.[8,14]

The results obtained with potassium and ammonium salts are presented, respectively, in Figures 6 and 7.

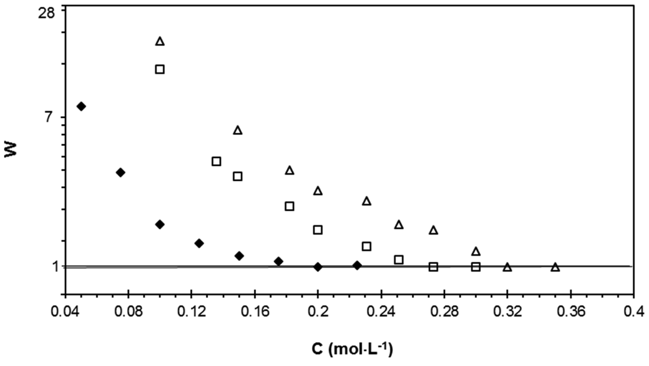


Figure 6. Plot of the stability ratio (log scale) as a function of concentration with KSCN (solid diamond), KCl (open square), and KIO_3 (solid triangle) electrolytes.

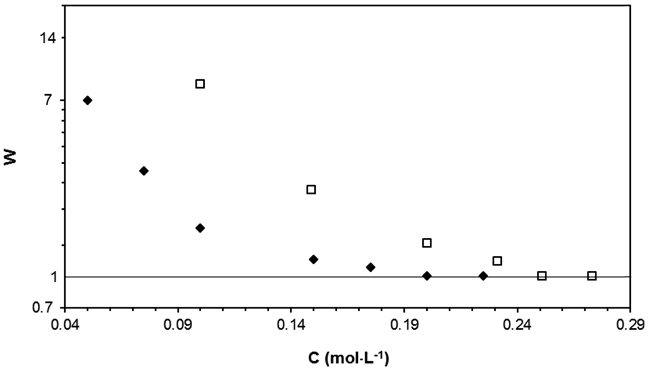


Figure 7. Plot of the stability ratio (log scale) as a function of concentration with NH_4SCN (solid diamond) and NH_4Cl (open square) electrolytes.

With potassium, the corresponding ccc values are, respectively, 0.2, 0.27, and 0.32 M for SCN^-, Cl^-, and IO_3^-. This sequence is the opposite from that of sodium cations. The same ccc was obtained with NH_4SCN and KSCN (i.e., 0.2 M), and that with NH_4Cl was 0.25 M. The comparative ccc values for the studied salts are summarized in Table 2.

Table 2. Coagulation Critical Concentration (in M) of the Corresponding Electrolytes

ions	SCN^-	Cl^-	IO_3^-
Na^+	0.38	0.32	0.30
K^+	0.20	0.27	0.32
NH_4^+	0.20	0.25	

From the accumulation/exclusion mechanism, it is difficult to consider that the higher ccc value with iodate anion (IO_3^-) in the presence of potassium cation would result now from a better accumulation of this kosmotrope co-ion to the hydrophobic polystyrene surface (so as to increase significantly the negative surface charge). In the case with thiocyanate anion (SCN^-), there is a striking difference in the ccc values: it corresponds to the highest with Na^+ (i.e. 0.38 M), whereas it corresponds to the lowest with K^+ or NH_4^+ cations, that is, 0.2 M. As it was confirmed that accumulation of chaotrope counterions (potassium or ammonium) is enhanced when compared to the kosmotrope counterion (sodium), it suggests that chaotrope thiocyanate anions may experience a quite different accumulation toward the hydrophobic surface, depending on the lyotropic nature of the counterion. Assuming that accumulation of both chaotrope counterions and co-ions should be promoted near a hydrophobic surface, this leads to consider a possible competition between ions within the inner layer to interpret the obtained results.

It has to be emphasized at this level that the knowledge of the precise solution structure near charged interfaces is a difficult task. The concentration profiles of counterions and co-ions are clearly dependent on the surface chemistry (nature and extent of electrical charge and hydrophobic/hydrophilic character of the surface) and the bulk ionic strength. Moreover, the water molecules have a paramount role in establishing this solution structure, owing to their very large number and their ability to promote or inhibit hydrogen bonds around surfaces and ions depending on their nature. Nevertheless, qualitative trends may be assumed to interpret the results.

It may be suggested that, when co-ions have a marked chaotrope character, together with an appreciable polarizability such as thiocyanates, they may significantly compete with the kosmotrope sodium counterions within the inner layer close to the hydrophobic surface. The kosmotrope cations may be seen as being permissive to such co-ions in this case. As a result, the screening of the negative surface charge should be effectively decreased, and higher amounts of sodium salts are required to reach the ccc. With chloride, which is slightly chaotrope, and with a lower polarizability, this competitive aspect should be less pronounced. As iodate anions (IO_3^-) are quite kosmotropes, they should reside preferably in the diffuse (outer) layer.

When the counterions have a chaotrope nature, the inner layer near the hydrophobic surface is expected to be more densely constituted by such cations such as potassium or ammonium. They may be seen as being much less permissive to the co-ions, inhibiting their accumulation close to the hydrophobic surface. As a result, the screening of the negative surface charge is enhanced by these counterions, and a large majority of co-ions should remain in the diffuse layer where they experience however a distinct affinity with the solvent water molecules. The observed differences in ccc values may originate in this situation from variable repulsive hydration effects (U_{Hyd}) depending on the lyotropic character of the co-ions. When the ionic concentration is not negligible, the presence of strongly hydrated co-ions such as the iodates should exert a more enhanced water ordering and cohesiveness within the contracted diffuse layer when compared to the case with the chaotrope chloride and thiocyanate co-ions. As a result, more energy should be supplied upon closer approach (aggregation) of the nanoparticles to disrupt this outer interfacial water structure stabilized by the confined kosmotrope iodate anions, aiming at minimizing the extent of broken hydrogen bonds. When the contracted diffuse layer is populated by chaotrope co-ions, the magnitude of this repulsive dehydration contribution is expected to be significantly reduced as aggregation proceeds so that the electrolyte concentration required to reach the ccc should be lowered, especially as the co-ion has a marked chaotrope character such as thiocyanate. These trends seem to coincide with the reported influence of the same co-ions of potassium electrolytes on the gelation kinetics of silica nanoparticles at pH much higher than the IEP.[34]

4. CONCLUSIONS

In this study, the influence of the lyotropic nature of monovalent counterions on the inversion of the stability sequence of negatively charged hydrophobic latex particles has been evidenced. For the same representative co-ions, the ordering of the ccc values has been found to be reversed when using comparatively the kosmotrope sodium and the chaotrope potassium or ammonium counterions. This result advocates in favor of a competitive behavior of the implied co-ions and counterions within the inner layer at the hydrophobic particle−aqueous solution interface.

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Notes

The authors declare no competing financial interest.

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