

Effects of monovalent and multivalent ions on the stability of a polyelectrolyte complex with entrapped surfactants

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ABSTRACT: In this article, we report the effects of nine different monovalent and multivalent salts on the particle size and stability of refined, positively charged polyelectrolyte complexes (PECs) with entrapped surfactant. Dynamic light scattering and ζ potential measurements of these polymeric particles as a function of various salt concentrations showed that both counter ions and co-ions induced a concentration-dependent increase in the particle size and a decrease in the ζ potential. We found that the anion concentration where the particle size doubled and the maximum anion concentration beyond which particle precipitation occurred ($C_{a,max}$) demonstrated a power law dependence on the anion valence. Moreover, for anions of the same valence but different hydration ratio, $C_{a,max}$ decreased in the following order: $\text{NO}_3^- \rightarrow \text{Cl}^- \rightarrow \text{HPO}_4^{2-} > \text{SO}_4^{2-} > \text{PO}_4^{3-}$. However, unlike the case of hard colloids where co-ions have relatively little effect on particle interactions, the co-ions also increased the hydrodynamic radii of our PECs in the following order: $\text{K}^+ \approx \text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Al}^{3+}$. Furthermore, we found that the entrapped surfactants were shielded from the adverse effect of multivalent ions; this established that the monovalent and multivalent ions interacted with the polyelectrolyte shells of the PEC. This behavior was in contrast with the effect of salts on mixtures containing the polyelectrolyte and surfactant components, where the addition of salts typically causes an interaction with the individual components. Because several biomedical and technological applications involving PECs require saline environments, our studies provide insight into how small ions influence the PEC stability in applications involving varying salinities. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42099.

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INTRODUCTION

Self-assembled polyelectrolyte complexes (PECs) are becoming increasingly important in various industrial, biological, and commercial applications.^{1–5} The ease of assembly and disassembly of these PECs make them attractive as potential drug-delivery vehicles that enable controlled release of drugs and small molecules and also as nonviral gene-delivery vectors.^{3,6–8} Some of us have extended the use of these PECs to enhanced oil recovery as well and used PECs to control the release of oil-field chemical agents, including surfactants.² In recent applications, the advantages of using self-assembled PECs without any excess surfactant or polyelectrolytes over the use of polyelectrolyte–surfactant mixtures have been highlighted.^{9,10} Muller *et al.*⁹ termed such complexes *refined polyelectrolyte complexes* and demonstrated that the behavior of these PECs was significantly different from that of polyelectrolyte surfactant mixtures or aggregates with free excess polyions. It is important to note that these permeable polymeric particles are trapped in a nonequilibrium state;^{11,12} this makes

them sensitive to their environment, particularly to changes in the pH or salinity. For example, during use as drug-delivery vehicles, refined PEC particles are expected to encounter salt concentrations as high as 0.5M while encountering variations in the pH in the early and late endosomes in cells. Similarly, applications in the oil industry can expose PECs to salt solutions with concentrations that can even be higher than that of regular seawater ($\sim 0.5M$).¹³

In a recent publication, we reported the interfacial and bulk properties of such a polyelectrolyte-based system with entrapped surfactant and demonstrated that these PECs displayed a uniform size of 110–120 nm and remained extremely stable in bulk water solutions over several months.¹⁴ In this article, we focus on the effects of the addition of monovalent and multivalent ions on the stability of our PEC system.

The effect of salts on the stability of polyelectrolyte–surfactant mixtures and the formation of polyelectrolyte–surfactant

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complexes has been studied extensively over the past few years.^{15–24} What is currently known about the formation of polyelectrolyte–surfactant complexes in mixtures containing free excess components in the presence of salts may be summarized as follows: it has been reported that the addition of salts can alter the electrostatic and nonelectrostatic interactions that control the binding of oppositely charged surfactants and polyelectrolytes. This leads to different phases, including the formation of soluble mixtures, insoluble complexes, or dissociation of the complex systems in the presence of excess polyelectrolyte or surfactants. For example, using mixtures with various concentrations of poly(ethylene imine) (PEI) and sodium dodecyl sulfate (SDS), Mészáros *et al.*²⁵ showed that the addition of a moderate concentration of sodium chloride (NaCl) caused a decrease in the kinetic stability of PEI/SDS particles, which was due to the suppression of free SDS on the PEI/SDS particles triggered by NaCl. In a more recent publication, Pojjak *et al.*²⁶ showed that “at small and moderate NaCl concentrations,” these electrolytes caused a “reduction of the kinetically stable composition range” in the case of PSS/CTAB mixtures, which were found to be trapped in the nonequilibrium colloidal dispersion state. Furthermore, it was shown that the salts interacted with the excess components, rather than the self-assembled particles as a whole, to alter their interactions. The role of hydration of the ions on the formation of these complexes has also been argued.^{22,27} The addition of salt was also shown to influence micellization equilibria or even the morphology of the particles in polyelectrolyte surfactant mixtures.^{22,28}

In contrast to the polyelectrolyte–surfactant mixtures, understanding of the effects of the salinity on the stability of refined PECs without any free excess components is currently limited. In this article, we report monovalent- and multivalent-salt-induced changes in the particle size and stability of refined PECs with entrapped surfactants. We showed previously that these PECs were stable over several months¹⁴ when suspended in water and ascertained that the effects described in this study were a result of the addition of salts. In contrast with the observations for polyelectrolyte–surfactant mixtures, we found that overall for our nanoparticle system without any excess components, the addition of salts caused an increase in the particle size, a decrease in the ζ potential, and ultimately, a decrease in the precipitation. However, under no conditions did we encounter dissociation of the PECs; this indicated that the interactions of the refined PECs were significantly different from those of the PEI/SDS mixtures or PEI/SDS PECs in the presence of excess surfactants. In this article, we discuss our results in more detail and propose that for our PECs, electrostatic interactions and hydration forces between the ions and the permeable polyelectrolyte shell of the PECs together modulated the stability of these systems while also protecting the entrapped surfactant from changes in the environment.

EXPERIMENTAL

Chemicals

The surfactant, SDS (molecular weight = 288.38 g/mol, purity > 99.9%), and branched polyelectrolyte, PEI (molecular weight = 25 kDa), were purchased from Sigma Aldrich and were used without further purification. The inorganic salts, including

NaCl, potassium chloride, sodium nitrate, calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), magnesium chloride ($\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$), aluminum chloride ($\text{AlCl}_3 \cdot 2\text{H}_2\text{O}$), sodium sulfate, disodium phosphate, and sodium phosphate, were used as received from Fisher Scientific. Millipore water with an initial pH of 7.0 was used to make the solution during the experiment.

Methods

Nanoparticle Synthesis. The PEI/SDS mixtures were prepared according to the same procedure described in a previous work.¹⁴ The positively charged PEI/SDS nanoparticles were prepared by the mixture and constant stirring of 0.25% PEI and 26.6 mM SDS stock solutions at a weight ratio of 3 : 1. After 5 min of mixing, the free surfactants and PEI were eliminated from the freshly prepared PEC dispersions by repeated centrifugation at 15,000 rpm for 1.5 h; this caused the free polyelectrolytes and surfactants to separate into the supernatant, whereas the desired PECs were contained in the coarcescent phase. These desired PECs were collected and resuspended with Millipore water after the removal of the supernatant, and the pH of the suspension was recorded and adjusted if needed to ensure that the final pH of the refined PEC solution was maintained at 7.0. The final concentration of the entrapped surfactant (SDS) in the PEI/SDS PECs was calculated from the entrapment efficiency with the UV absorbance at 650 nm, as described in ref. 14. Because no absorbance of the PEI solution at the same wavelength was observed, we concluded that PEI had no effect on the measurement of the SDS concentration during the entrapment efficiency test. The initial stock PEC solution with entrapped SDS was at a concentration of 30 mM and was then diluted to different concentrations by Millipore water. All results are reported in terms of this entrapped SDS concentration, which in turn is used as a measure of increases or decreases in the PEC concentration.

Addition of Salts. The salt solutions were prepared at different concentrations. The PEI/SDS nanoparticle stock solutions with different entrapped SDS concentrations were mixed in vials with salt solutions of different concentrations in equivalent volumes. The final concentrations of the salts in the suspensions were in the range 0–1M, depending on the stability of the suspension, that is, when the particles started precipitating. In addition to the particle size and ζ potential, the pH of the solution was also monitored for each experiment.

Nanoparticle Characterization. The particle size and particle size distribution of the nanoparticles were measured by dynamic light scattering with a Brookhaven 90 Plus/BI-MAS instrument (Brookhaven Instruments Corp., Holtsville, NY). A volume of 0.8 mL of the nanoparticle samples was placed in polystyrene cuvettes and then diluted with deionized water. A detector positioned at 90° was used to measure the scattered light. The fluctuation of the light intensity was fitted by an autocorrelation function, and the diffusion coefficient obtained by second-order cumulant fitting was then used to calculate the particle size. The ζ potential of the nanoparticles was determined with a ZetaPlus instrument (Brookhaven Instruments Corp., Holtsville, NY). We measured the ζ potential by analyzing the electrophoretic mobility of our PEC using the Smoluchowski model. The particle size and ζ potential are both reported as averages of three different recordings noted within a minute of each other.

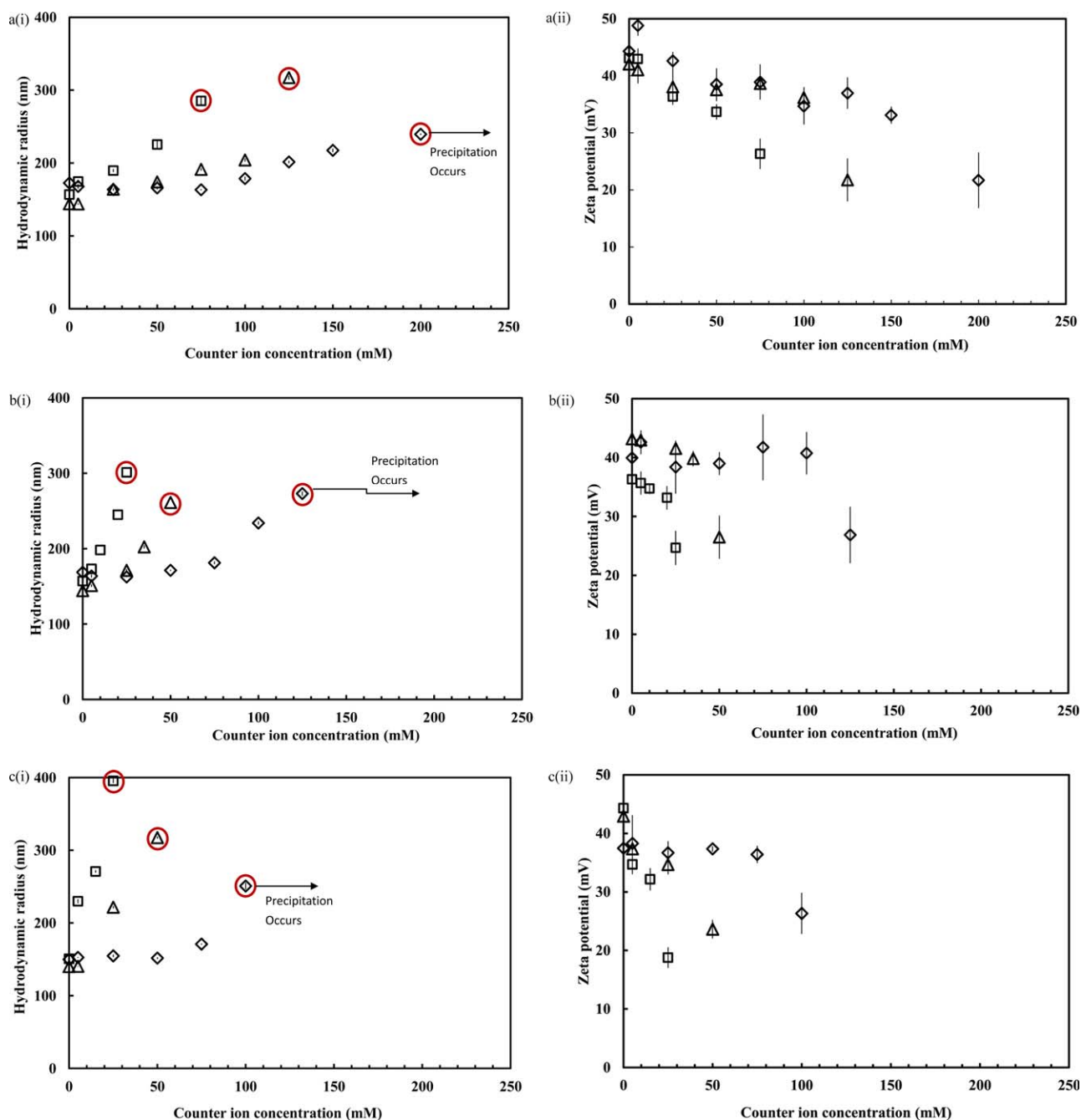


Figure 1. (i) Hydrodynamic radius and (ii) ζ potential values of the positively charged PEI/SDS nanoparticles as function of the anion (counter ion) concentration at different entrapped SDS concentrations: (a) 1.4, (b) 4, and (c) 6 mM SDS. At each SDS concentration, three anions were compared: (\diamond) Cl⁻, (Δ) SO₄²⁻, and (\square) PO₄³⁻. The results show that for each SDS concentration, multivalent anions were more efficient at increasing the particle size. The points in red circles show the maximum measured particle size before the suspension was destabilized. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

Previous results in our laboratory have shown the formation of self-assembled cationic complex nanoparticles (~ 120 nm) composed of PEI with entrapped SDS in deionized water, that formed stable colloidal complexes for up to 6 months (now for more than a year). The PEI/SDS PECs were formed as a result of strong electrostatic interactions between the branched cati-

onic PEI of high molecular weight and SDS in a ratio of 3 : 1 w/w.¹⁴ This stoichiometry implies that in our system of nanoparticles, there was originally an excess of PEI. Dautzenberg and Kriz²⁹ proposed that polyelectrolyte–surfactant complexes exist as highly compact, almost spherical particles with a charge-neutralized core, surrounded by chains of the polyelectrolyte that is in excess. In our case, this would mean a charge-

neutralized core of PEI and SDS with a shell of the cationic PEI; this resulted in net positive values of ζ potential for our complexes and prevented further aggregation. Moreover, as expected, we have previously shown that centrifugation and resuspension of the complexes and removal of the free excess components did not affect the stability or pH of our complexes. However, to the best of our knowledge, how monovalent and multivalent salts affect the stability of our refined PECs, once formed, has been less explored, especially in the absence of any free surfactant and/or surfactant components.

Therefore, the results described and discussed later focus on the elucidation of the effects of various monovalent and multivalent salts on the interparticle interactions that controlled the stability of these positively charged PECs in bulk solutions.

Effect of Monovalent and Multivalent Anions

The effects of different anions (Cl^- , NO_3^- , HPO_4^{2-} , SO_4^{2-} , and PO_4^{3-}) on the particle size and particle stability were illustrated by through a comparison of the hydrodynamic radii of these PECs in different sodium salts at different concentrations of salt and nanoparticles. In Figure 1, we present the effect of the addition of salts with different anion valences (Z_s) on the hydrodynamic radius and ζ potential of cationic PECs with three different entrapped SDS concentrations. Figure 1(a-i-c-i) shows the hydrodynamic radius as a function of NaCl, sodium sulfate, and sodium phosphate, whereas Figure 1(a-ii-c-ii) represents observed changes in the ζ potential at the same salt concentrations. We found that for monovalent Cl^- ions at low SDS concentration [Fig.1(a-i)], the particle size remained almost constant (hydrodynamic radius ≈ 120 nm) up to 75 mM $[\text{Cl}^-]$. At higher anion concentrations, the particle size increased gradually but increased nonlinearly with the anion concentration; this ultimately resulted in precipitation when the anion concentration exceeded 200 mM $[\text{Cl}^-]$. We define the maximum anion concentration at the onset of this precipitation as $C_{a,\text{max}}$. This concentration was verified to within an accuracy of 10 mM above and below $C_{a,\text{max}}$, as shown by the data points near $C_{a,\text{max}}$. As shown in Figure 1(a-ii), the ζ potential data showed that particles were positively charged. Furthermore, Figure 1(a-ii) shows that the ζ potential decreased slightly with the concentration of Cl^- up to a concentration of about 125 mM, beyond which it sharply reduced from 37 to 21 mV. We also found the increase in particle size and decrease in ζ potential to be higher for multivalent ions. Figure 1(a-i) shows that the particle size almost doubled at concentrations ($C_{a,\text{doubled}}$'s) of 200 mM for Cl^- , 125 mM for SO_4^{2-} , and 75 mM for PO_4^{3-} ; a sharp decrease in the ζ potential was also observed. Similarly, our results also show that in the presence of different salts, $C_{a,\text{max}}$ decreased drastically with increasing Z [Figure 1(a-c)]. Furthermore, our results show that with increasing bulk SDS concentration [Figure 1(b,c)], the increase in the particle size and the anion concentrations at which precipitation was observed were also lower. For example, as shown in Figure 1(b-i), for an entrapped SDS concentration of 4.0 mM, $C_{a,\text{doubled}}$ was found to be 110 mM for Cl^- , 50 mM for SO_4^{2-} , and 20 mM for PO_4^{3-} . Figure 1(c-i) shows that for an entrapped SDS concentration of 6.0 mM, $C_{a,\text{doubled}}$ was 100 mM for Cl^- , 40 mM for SO_4^{2-} , and 10 mM for PO_4^{3-} .

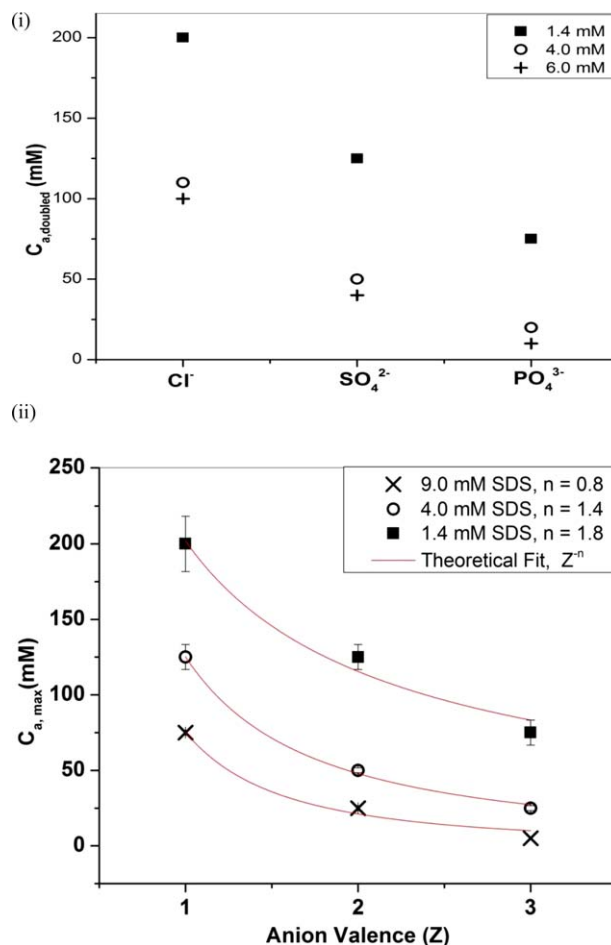


Figure 2. (i) $C_{a,\text{doubled}}$ as a function of Z at different SDS concentrations: (■) 1.4, (○) 4, and (+) 6 mM. (ii) $C_{a,\text{max}}$ as a function of Z at different SDS concentrations: (■) 1.4, (○) 4, and (×) 9 mM. The anion concentration decreased with increasing Z and SDS concentration. The power-fitting results are shown for each set of experimental data that could be rationalized with the Shultz–Hardy rule: Z^{-n} . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The dependence of $C_{a,\text{doubled}}$ and $C_{a,\text{max}}$ on the anion concentration is further illustrated in Figure 2, where we plotted $C_{a,\text{doubled}}$ and $C_{a,\text{max}}$ as a function of the anion concentration for three different concentrations of PEI/SDS nanoparticles (1.4, 4.0, and 9.0 mM). With increasing counter-ion valence, $C_{a,\text{doubled}}$ and $C_{a,\text{max}}$ followed a power law dependence on Z in the form Z^{-n} , where n increased with entrapped SDS concentration. We explained this behavior by reviewing the colloidal interactions in this PEC solution. From a basic knowledge of intermolecular forces between colloidal particles, one can assume that the positive surface charge on these particles would cause an electric double layer (the Debye layer) to form.³⁰ Upon addition of salts, the anions (counter ions for this charged system) screened the charge on the PECs; this explained the decrease in the ζ potential with increasing counter-ion concentration. Such a decrease could induce strong interparticle attractions and ultimately lead to coagulation, flocculation, or precipitation. This interparticle attraction due to a decrease in

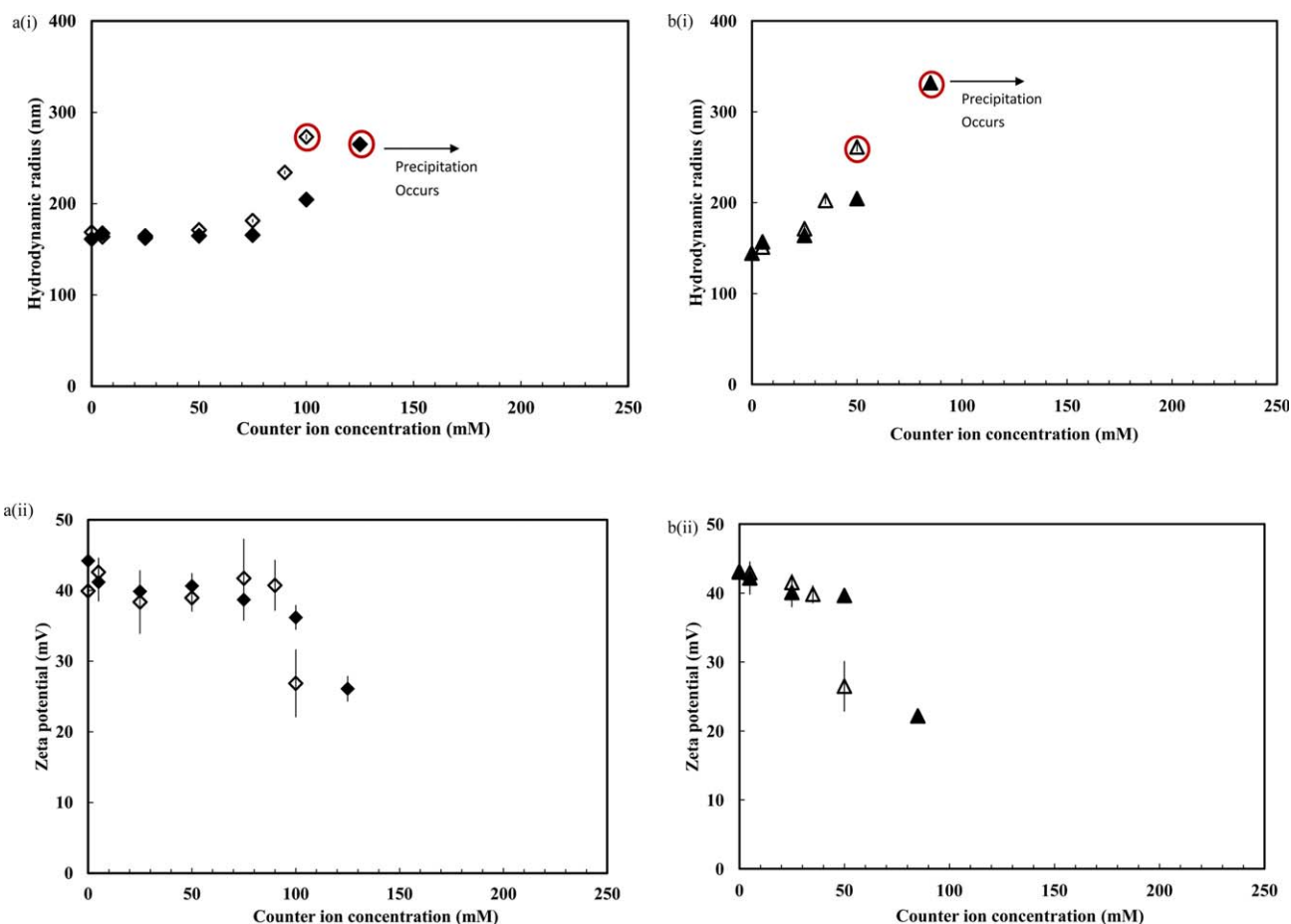


Figure 3. (i) Hydrodynamic radius and (ii) ζ potential of the positively charged PEI/SDS nanoparticle suspensions as function of the anion concentration at 4 mM SDS: (a) monovalent anions [(\diamond) Cl^- and (\blacklozenge) NO_3^-] and (b) divalent ions [(\triangle) SO_4^{2-} and (\blacktriangle) HPO_4^{2-}]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the electric double layer around the PECs could be a possible explanation for the observed anion-concentration-dependent increase in the particle size, which ultimately resulted in the precipitation of our PECs. The power law dependence of the PEC particle size on the anion concentration presented in Figure 2 could be further explained in terms of the Schulze–Hardy rule, which is mostly used to qualitatively describe the interparticle forces between colloidal particles in the presence of salts. The Schulze–Hardy rule, derived from Derjaguin–Landau–Verwey–Overbeek theory, states that the counter ion of a colloidal particle plays a decisive role in determining the coagulation behavior of charged particles. The critical coagulation concentration is scaled as z^{-6} , where z is the counter ion valence.^{31,32} However, such a correlation is only valid for symmetric electrolytes and colloids with a high surface charge density (>1000 mC/m^2).^{30,33} In many practical examples of charged colloids, the surface charge of the particles cannot reach such a high value. In such cases, the critical coagulation concentration is expected to demonstrate a weaker dependence on the valence of counter ions, Z^{-n} , where $n \cong 1.6$ – 4.5 is expected.^{34–37} Borkovec *et al.*³⁸ recently reported that for weakly charged colloids, this dependence could be weaker and could also be system dependent.³⁸

However, at the same ion valence, $C_{a,\text{max}}$ was found to be significantly higher for 1.4 mM SDS compared to 9 mM SDS; this suggested that the Derjaguin–Landau–Verwey–Overbeek theory alone could not accurately describe interparticle interactions in the case of our PECs. The screening of the Debye length could also have caused more ions to interact directly with the PEI shells of our PECs and caused an increase in the thickness of the shell and, therefore, an increase in the particle hydrodynamic radius. Because multivalent ions cause a greater decrease in the Debye length, this effect was more pronounced for the multivalent salts, as summarized in Figure 2.

In addition to the long-range electrostatic interactions discussed previously, short-range forces, such as solvation forces, may also influence the PEC particle size. To check the validity of short-range forces^{39–41} on the stability of our PECs, additional experiments were carried out with different anions of the same valence but different sizes, which resulted from a difference in their hydration. Figure 3 represents the effect of salts with the same Z but different hydration radii on the hydrodynamic radius and ζ potential for the PEI/SDS nanoparticles at a representative concentration of 4.0 mM entrapped SDS. Figure 3(a-i) shows a slightly larger increase in the particle size and ζ

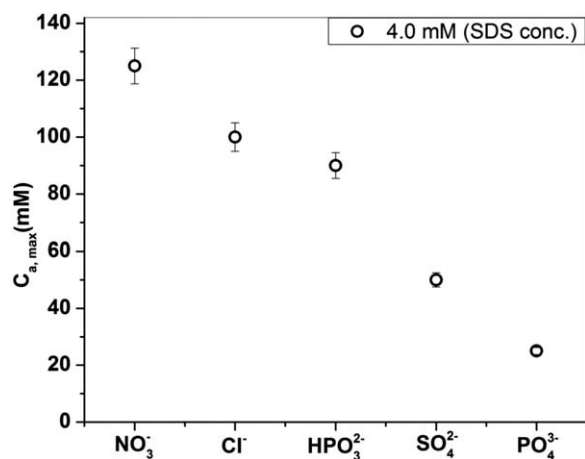


Figure 4. $C_{a,max}$ for all of the anions studied. The results show that the ability of anions to induce precipitation increased in the order $\text{NO}_3^- < \text{Cl}^- < \text{HPO}_4^{2-} < \text{SO}_4^{2-} < \text{PO}_4^{3-}$. The results show that electrostatic forces played a role in determining the order of ability of anions to induce precipitation; higher valence anions led to more precipitation. However, for anions with the same valence, the ability of anions to induce precipitation was similar to the salting-out effects of anions in the Hofmeister series.

potential of the PEI/SDS nanoparticles in the presence of Cl^- as compared to NO_3^- . Similarly, we found that SO_4^{2-} yielded PECs of larger size than did HPO_4^{2-} at the same anion concentration [Figure 3(b-i)]. $C_{a,max}$ depended on the specific anion, as summarized in Figure 4 for five different anions. As shown in Figure 4, we found that the anion concentration where precipitation occurred in the case of Cl^- was 100 mM, whereas it was 125 mM for NO_3^- . Similarly, the concentration of SO_4^{2-} beyond which precipitation occurred was significantly less (~50 mM) compared with HPO_4^{2-} (85 mM). The results from the plot in Figure 4 indicate that the ability of small anions to induce instability in these PEI/SDS PECs increased in the order $\text{NO}_3^- < \text{Cl}^- < \text{HPO}_4^{2-} < \text{SO}_4^{2-} < \text{PO}_4^{3-}$. These observations indicate that the interparticle interactions in these systems were not just related to long-range electrostatic interactions. As proposed by Borkovec *et al.*,⁴² when the only forces acting on these PECs were the long-range electrostatic forces; then, the particle size and onset of precipitation depended only on the valence of ion and not on the chemical nature of the ions. Instead, our observations could be explained by the influence of solvation forces and the law of matching water affinity. This law states that oppositely charged ions in solution will only form ion pairs when they have the same water affinity. Collins^{40,42} suggested that anions follow the order $\text{NO}_3^- < \text{Cl}^- < \text{SO}_4^{2-} < \text{HPO}_4^{2-}$ in the number of bound water molecules. NO_3^- and Cl^- are weakly hydrated with less than one water molecule; SO_4^{2-} is moderately hydrated with two water molecules, and HPO_4^{2-} is highly hydrated with four water molecules. At the same time, the positively charged amine group in PEI is bound to two water molecules on average.⁴³ Therefore, the law of matching water affinity dictates that SO_4^{2-} , with two water molecules, was bound the most strongly with the amine groups on the PEI shell (also hydrated with two water molecules) when compared with HPO_4^{2-} , and this increased the particle size.

Effect of the Monovalent and Multivalent Co-Ions

In addition to the effect of the counter ions, we also used salts with the same anion, Cl^- , but different cations, Na^+ , Ca^{2+} , Mg^{2+} and Al^{3+} , to analyze the contribution of co-ions to the stability and size of the refined PEI/SDS PECs in solution. In Figure 5(a–c), the hydrodynamic radius and ζ potential of PEI/SDS PECs versus the Cl^- concentration are plotted for three different cations (Na^+ , Ca^{2+} , and Al^{3+}). Figure 5(a–i) shows that at low SDS concentrations [1.4 mM; Figure 5(a)] for Na^+ salts, the particle size remained constant up to 75 mM $[\text{Cl}^-]$, then increased steadily until the particle size almost doubled at 200 mM $[\text{Cl}^-]$, and precipitated with further increases in $[\text{Cl}^-]$. The ζ potential at 200 mM $[\text{Cl}^-]$ decreased below 20 mV. In contrast, for Ca^{2+} , the particle size increase was found to be slower than for Na^+ . For Ca^{2+} , the particle size remained constant until a $[\text{Cl}^-]$ of 160 mM and then increased nonlinearly. The chlorine ion concentration at which the particle size doubled ($C_{\text{Cl,doubled}}$) was found to be about 320 mM $[\text{Cl}^-]$, and the particles continued to increase in size until precipitation occurred at $[\text{Cl}^-]$ values beyond 500 mM. For Al^{3+} , the particle sizes did not change until 740 mM. Beyond this concentration, the particle size continued to increase until the particles precipitated at a $[\text{Cl}^-]$ of 1.2M or higher. Furthermore, the multivalent cations increased the stability of PEI/SDS nanoparticles against precipitation. The particle ζ potentials decreased with increasing hydrodynamic radius, with the ζ potential decreasing to nearly half the value (from 40 to 20 mV) at a $[\text{Cl}^-]$ of 200 mM for Na^+ , 400 mM for Ca^{2+} , and 850 mM for Al^{3+} for an entrapped SDS concentration of 1.4 mM.

Figure 5(b,c) shows that the increase in the hydrodynamic radius of nanoparticles due to cations also depended on the entrapped SDS concentration. In Figure 5(b–i), for particles with entrapped SDS concentrations of 4.0 mM, the particle size remained nearly constant until a $[\text{Cl}^-]$ of 50 mM in the presence of NaCl, beyond which the particle size continued to increase until precipitation occurred at concentrations beyond 110 mM. For Ca^{2+} , this change was slower: the hydrodynamic radius of the particles was constant up to a $[\text{Cl}^-]$ of 50 mM but increased steadily thereafter until a $[\text{Cl}^-]$ 200 mM, beyond which precipitation occurred. For Al^{3+} , the particles were able to maintain their hydrodynamic radius until a $[\text{Cl}^-]$ of 400 mM, increased in size beyond this concentration, and finally precipitated at concentrations higher than 800 mM. The particle ζ potentials were also found to decrease with increasing $[\text{Cl}^-]$. Figure 5(b–ii) shows that the ζ potential decreased from 40 to 25 mV at a $[\text{Cl}^-]$ of 120 mM for the NaCl solution and from 40 to 20 mV at a $[\text{Cl}^-]$ of 200 mM for CaCl_2 solution and 900 mM for AlCl_3 . Similar results were also observed for an entrapped SDS concentration of 6.0 mM.

Figure 6 summarizes the $[\text{Cl}^-]$ where the particle size increased to 250 nm (it nearly doubled in size compared to the original size), $C_{\text{Cl},250\text{nm}}$ for different cations (Na^+ , Ca^{2+} , and Al^{3+}) and the maximum chlorine ion concentration beyond which the suspension became unstable and precipitation occurred ($C_{\text{Cl,max}}$) at three different concentrations of trapped SDS. The $C_{\text{Cl,max}}$ values were found to be (1) 150 mM for Na^+ , 250 mM for Ca^{2+} , and 1.0M for Al^{3+} for an entrapped SDS

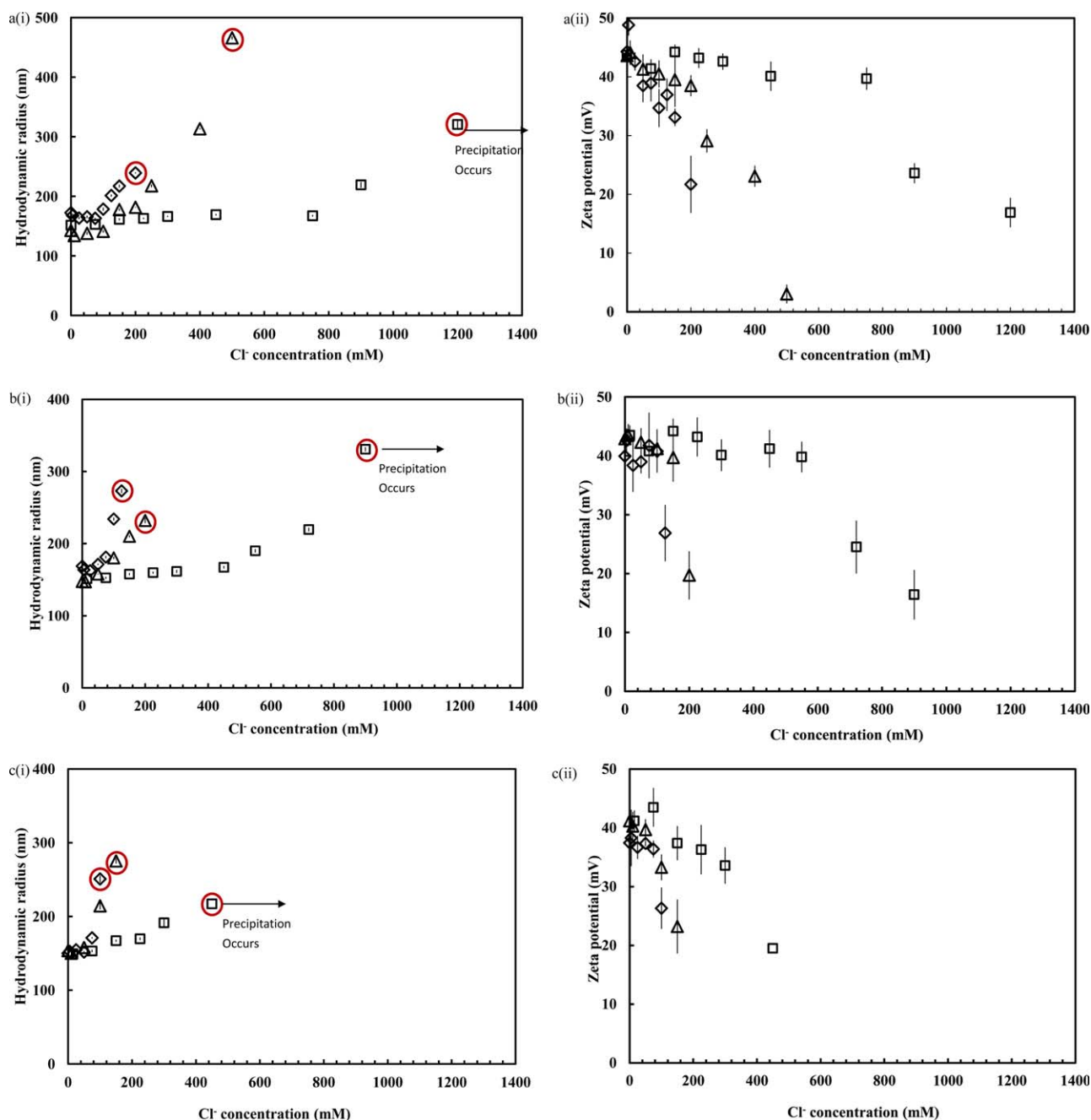


Figure 5. Effect of different cations (co-ions) on the (i) hydrodynamic radius and (ii) ζ potential of positively charged PEI/SDS nanoparticle suspensions: (a) 1.4, (b) 4, and (c) 6 mM SDS. At each SDS concentration, three cations were compared: (\diamond) Na^+ , (\triangle) Ca^{2+} , and (\square) Al^{3+} . Similarly to Figure 1, the points in red circles for each salt correspond to the maximum $[\text{Cl}^-]$ beyond which the solution became unstable and precipitation occurred. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

concentration of 1.4 mM; (2) 110 mN for Na^+ , 200 mN for Ca^{2+} , and 800 mN for Al^{3+} for an entrapped SDS concentration of 4.0 mM; and (3) 100 mN for Na^+ , 150 mN for Ca^{2+} , and 400 mN for Al^{3+} for an entrapped SDS concentration of 6.0 mM. Similarly, $C_{\text{Cl},\text{max}}$ was found to increase with increasing ion valence for all of the entrapped SDS concentrations studied.

On the basis of the results outlined in Figures 5 and 6, we concluded that the multivalent cations showed a stronger ability to

eliminate precipitation compared to monovalent ions; $C_{\text{Cl},\text{max}}$ for different cations followed the order $\text{Na}^+ < \text{Ca}^{2+} < \text{Al}^{3+}$. These observations were in contrast to the suggestions of Haya-kawat and Kwak,⁴⁴ who showed that cations of higher valence interfered more with polyelectrolyte–surfactant binding than the cations of lower valence. One possible explanation for the current observations was that even though the PEI/SDS PECs were positively charged, once the Debye layer was screened, the

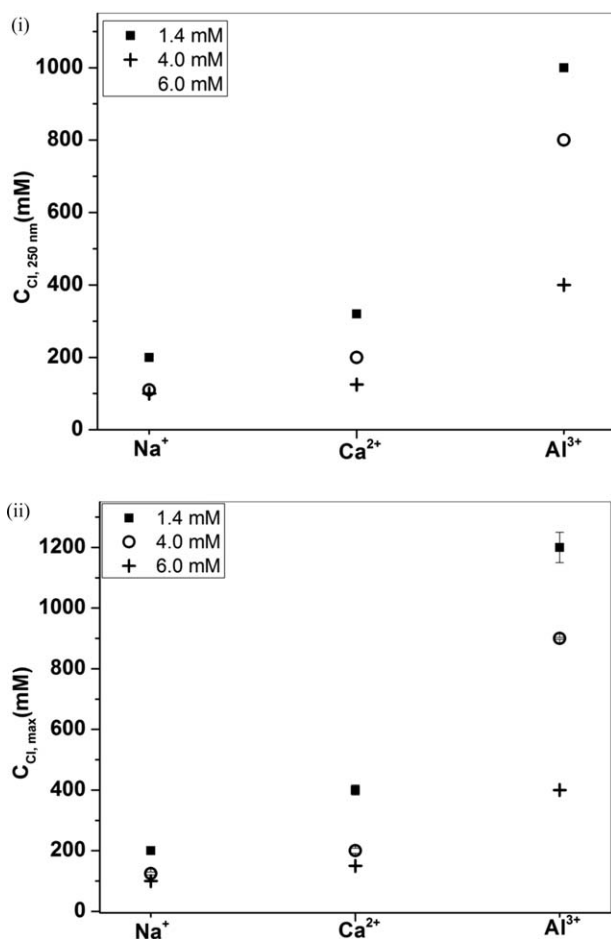


Figure 6. (i) Chlorine ion concentration at which the hydrodynamic particle radius increased to 250 nm (nearly double the original particle size) and (ii) $C_{a, \text{max}}$ as a function of the co-ion valence for three different concentrations of entrapped SDS. Unlike hard colloids, the hydrodynamic particle size and the stability of the suspension depended on the co-ion valence.

cations could diffuse into the PEC system and interact with either the PEI shell or SDS micelles entrapped in the PEC or both; this led to particle swelling and precipitation.

To understand this mechanism in further detail, let us first focus on the possible interaction of the cations with the SDS micelles. Sammalkorpi and Haataja⁴⁵ provided molecular dynamics simulation results showing that Ca²⁺ yielded stronger salt bridges between charged SDS head groups and Na⁺ showed no specific binding to micelles and stayed highly mobile on the micellar surface.⁴⁶ Our results (Supporting Information, Figure S1) show that Ca²⁺ destabilizes pure SDS solutions at 25 mM, whereas up to 0.5M concentration of Na⁺ did not. If indeed the cations were able to interact with the SDS micelles in the PEC core, we expected that Na⁺ would lead to a more stable solution; this was contrary to our results. Furthermore, if there was a weakening of the PEI/SDS bond due to competitive binding between the salt and SDS, we would expect a dissociation of our PECs. However, no dissociation was observed, even when a 1.0M concentration of salt was added. Rather, we observed an

increase in the size before precipitation, which may have been due to the swelling of the PEC. Therefore, interactions of the cations with the SDS micelles in the core could be ruled out in case of our PECs.

Next, we focus on the possible interactions of the cations with the PEI shell. The increase in the particle size due to addition of salts could have been due to the indirect hydration effect of the cations with the hydrated PEI shells. Using NMR and light-scattering studies, Dautzenberg and Kriz²⁹ showed that interactions between multivalent cations and a positively charged polyelectrolyte could lead to a conformational change in PEC and to the formation of a thicker stabilizing shell. This thicker stabilizing shell then protected the complex from further aggregation and led to a more stable system. Figure 5 suggests that similar to the observation by Dautzenberg and Kriz, in our system, the multivalent cations stabilized the PECs by interacting with the PEI chains. Al³⁺, with the largest hydration radius, possibly stabilized the PECs more than the monovalent ions. To further prove this hypothesis, we recorded the effect of the addition of a small concentration of Ca²⁺ (10 mM) followed by addition of Na⁺ to our PEC system (Supporting Information, Figure S2). Surprisingly, even when a small amount of Ca²⁺ was added, the PECs were able to resist precipitation at twice the original Na⁺ concentration. This implied that the larger Ca²⁺ blocked further interactions with Na⁺ and stabilized the system. Additionally, Al³⁺ was acidic and could lower the local pH; this was not reflected in the overall pH of the mixture. A lower local pH would cause an increase in the surface charge of the polyelectrolyte and further improve the resistance to aggregation.²⁹

To further explore the role of the chemical nature of the cation on PEC stabilization, we studied the effect of the addition of two monovalent and two divalent salts on the PEC stability. Figure 7 shows the dependence of the particle size and ζ potential on the concentration of [Cl⁻] for different monovalent and divalent cations. Figure 7(a) shows that the different monovalent cations (Na⁺ and K⁺) had very similar effects on both the particle size and ζ potentials. Figure 7(b) shows that for the two divalent cations (Ca²⁺ and Mg²⁺), the addition of Mg²⁺ caused a greater increase in the particle size compared to Ca²⁺ [Figure 7(b-i)], although the ζ potentials were found to be comparable [Figure 7(b-ii)]. This was possibly because Mg²⁺ showed a relative higher water affinity than Ca²⁺; therefore, Mg²⁺ easily formed hydrogen bonds with water molecules around the polyelectrolyte, which caused quicker swelling and, ultimately, the salting out of the particles.⁴²

Finally, Figure 8 shows the concentration of each cation required to reach an arbitrarily chosen hydrodynamic radius of 250 nm (nearly double the initial particle size). We found that the ability of cations to increase the particle hydrodynamic radius followed the order Na⁺ \approx K⁺ < Ca²⁺ < Mg²⁺ < Al³⁺. Furthermore, a comparison with Figure 4 revealed that, overall, the anions had a larger influence on the particle size and ζ potential in our nanoparticle system than the cations. This observation suggested that the anions played a more significant role than the cations in maintaining the stability of this positively charged PEC. Taken together, our results establish that

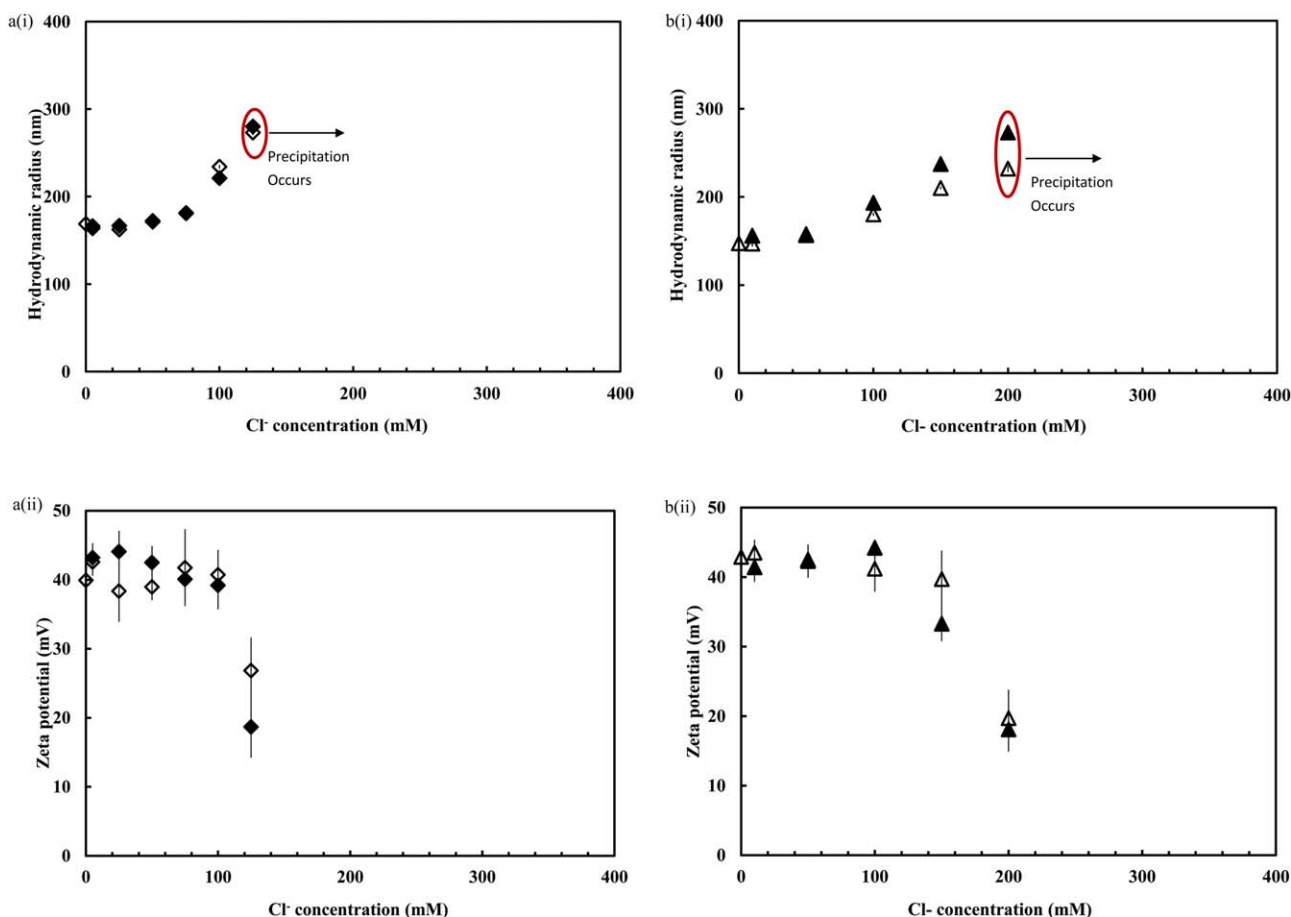


Figure 7. (i) Hydrodynamic radius and (ii) ζ potential of the positively charged PEI/SDS nanoparticle suspensions as function of the $[\text{Cl}^-]$ at 4 mM SDS: (a) monovalent cations [(\diamond) Na^+ and (\blacklozenge) K^+] and (b) divalent cations [(\triangle) Ca^{2+} and (\blacktriangle) Mg^{2+}]. The results show that for monovalent cations, the particle size and ζ potential change in very similar ways for both cations. However, for divalent cations, Mg^{2+} was more efficient than Ca^{2+} in increasing the particle size of these soft systems. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

although the primary effect of the addition of salts to the refined PEI/SDS PEC with entrapped molecules was due to electrostatic interactions with the charged PEI shell, secondary effects, such as hydration effects, also control the interactions of these polyelectrolyte-based colloidal particles with monovalent and multivalent salts.

CONCLUSIONS

In conclusion, we showed that the stability of refined positively charged PECs with entrapped surfactant acted as soft colloidal particles, where the PEC interactions with salts depended on the interactions of the salts with the polyelectrolyte shell. These results are in contrast with literature reports on the effect of salts on polyelectrolyte surfactant mixtures or polyelectrolyte surfactant complexes in the presence of excess surfactant components, which have typically resulted in the growth of micelles due to increased salts.^{16,25,47–50} We found that the PECs could be influenced by the valence of both the anions and cations and the chemical nature of these ions. We established a power law dependence of the particle size and particle precipitation on counter-ion valence, which could be explained by the Shultz–

Hardy rule. To the best of our knowledge, such an effect has not been described for polyelectrolyte surfactant mixtures or refined PECs. In addition, we found that nonelectrostatic hydration forces also controlled the stability of these PECs, as expected for other hard colloidal particles. Furthermore, anions with increased hydration radius induced instability of the PEI/SDS PECs and followed the order $\text{NO}_3^- < \text{Cl}^- < \text{HPO}_4^{2-} < \text{SO}_4^{2-} < \text{PO}_4^{3-}$, as expected for salts in the Hofmeister series, which follow the law of matching water affinity.^{40,42} Furthermore, unlike solid colloidal dispersions, cations also influenced the stability of the PEC system. We showed that the cations caused an increase in the particle radius in the following order: $\text{Na}^+ \approx \text{K}^+ < \text{Ca}^{2+} < \text{Mg}^{2+} < \text{Al}^{3+}$. This behavior could be explained by interactions of the salts with the permeable PEI shell. Moreover, the effects of salts on free surfactant micelles did not hold for this system; this suggested that the encapsulated surfactant molecules were shielded from the effect of salts. In contrast, in case of polyelectrolyte surfactant mixtures, the salts were found to interact with the individual components; this altered the association behavior of the polyelectrolyte surfactant aggregates and often led to dissociation of the aggregates at very high salt concentrations.^{18,21,22} Our PECs did not dissociate, even at very high ($\sim 1\text{M}$) salt

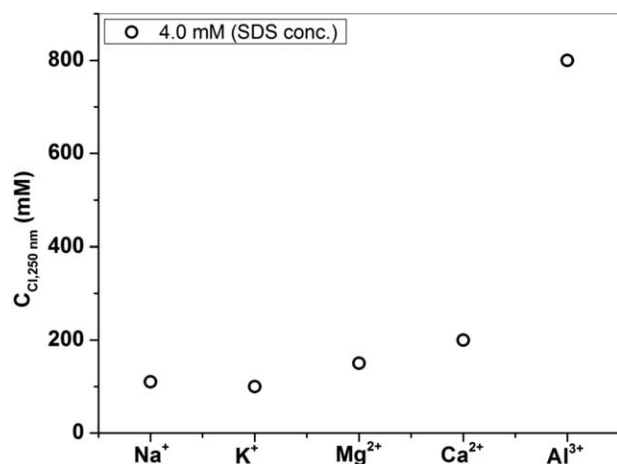


Figure 8. Effect of co-ions on nanoparticle swelling: the concentration of cations required to reach a hydrodynamic radius of 250 nm for the PEI/SDS nanoparticles with an original size around 125 nm. The results show that the ability of cations to increase the nanoparticle size increased in the order $\text{Na}^+ \cong \text{K}^+ < \text{Mg}^{2+} < \text{Ca}^{2+} < \text{Al}^{3+}$. Although multivalent cations showed an increase in their ability to increase the particle size, for cations with the same valence, the ions with higher water affinity induced more swelling. This trend followed the law of matching water affinity, which was mainly due to solvation forces.

concentrations. Therefore, our results suggest that when one considers the effect of salts on the stability of these soft PECs after their formation, interactions of the particles as a whole with both cations (co-ions) and anions (counter ions) should be considered. In our system, in addition to electrostatic forces, we showed that solvation forces also played a significant role in maintaining the particle size and stability. These fundamental results are important polyelectrolyte-based nanocarriers that can protect encapsulated components from environmental effects in several commercial and biomedical applications.

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