

Salt concentration influence on the efficiency of two cationic polymeric flocculants

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Received: 15 February 2012 / Revised: 21 March 2012 / Accepted: 28 March 2012 / Published online: 24 April 2012
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Abstract The influence of the increase of the solution ionic strength on the flocculation of charged latex particles in the presence of cationic polymers is reported. Empirical flocculation rate constants are experimentally determined using particle counting and for two cationic polymers, one linear and the second with two branches. Comparisons are made with a solution containing monovalent salt only at different ionic concentrations in the absence of polymers. In all cases, polymer-induced flocculation is significantly more efficient than charge screening effects using salt only. Analysis of zeta potential measurements indicates that the charge neutralization and surface charge variations dictate the stability of the latex suspensions. Moreover, the addition of a small amount of salt in the polymer–particle mixtures results in a dramatic decrease of the polymer efficiency which is more pronounced for the linear polymeric flocculant. By increasing further the ionic strength, the rates of polymer flocculation are found to increase again but remain smaller than in the absence of salt.

Keywords Flocculant efficiency · Latexes · Salt effect · Kinetic rates · Flocculant dosage

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Introduction

Flocculation processes are playing central roles in aquatic systems as well as in water treatment. On the one hand, in aquatic systems, algal and bacterial exudates composed of polysaccharide chains are promoting the flocculation of the suspended colloids and adsorbed pollutants [1, 2]; on the other hand, in many industrial processes, flocculation is used for rapid water clarification or wastewater treatment [3, 4]. For efficient water clarification, flocculation is usually induced by positively charged polyelectrolytes such as organic synthetic polymers to rapidly separate the liquid phase from the solid one and hence obtain a clear filtrate [5–7]. Generally, the use of polymeric flocculant versus other inorganic polyelectrolytes, such as poly-aluminum complexes, gives significant advantages when the water has a high concentration of suspended solids since usually, and in the same conditions, the concentration of the polymeric flocculant is lower, the resulting sludge is more compact, and there is less coagulant left in the water after treatment [4, 8]. Dosing polymeric flocculants to improve phase separation is then a widely practiced method for efficient water treatment and water quality management [9].

Polymeric flocculants are not always used in a rational way for optimal flocculation with regard to the natural fluctuations and heterogeneity of water solution compositions, suspended particle concentrations, and corresponding physicochemical properties (e.g., surface charges, electric double layer). In addition, for a rational use of polymeric flocculants, an improved understanding of the interaction mechanisms between flocculants and the suspended material (colloidal particles) is necessary. From a more prospective point of view, also the design and synthesis of new polymer architectures (linear, branched, dendritic, star) to (1)

increase the flocculation rates and (2) improve the efficiency of the flocculation processes by increasing the polymer concentration range in which polymers remain efficient are important objectives. Another key aspect concerns the physical and chemical character of the formed flocs such as the compactness, fractal dimension, and floc resistance to breakage [10, 11] which were recently considered.

There are many different parameters to take into consideration for the design and rational use of polymeric flocculants. On the one hand, different chemical monomers can be considered to control the polymeric flocculant properties [12]. Natural and promising polyelectrolytes from an environmental point of view, such as chitosan [13], as for example, chitosan glutamate, were also considered and tested for the flocculation of dissolved humic acids and their complexes with metal ions and organic pollutant [14]. In the same area, Libeck [15] found that cationic polyacrylamide chains with high charge density and low molecular weight were the most effective in the removal of humic acids. Chitosan was also tested on kaolinite suspensions [16]. On the other hand, co-polymers were synthesized using two different monomers so as to better control the flocculant hydrophobic or hydrophilic character and thus affinity for non-polar compounds such as oil emulsions [17, 18]. The chain size and molecular weight are also important parameters which are controlling the polymer ability to form aggregates through different flocculation mechanisms. Since most of the flocculation mechanisms are mainly driven by electrostatic interactions, the polymer charge as well as the amount of total charge are important parameters to take into consideration [19]. It should be noted here that there are different manners to determine the polymer charge; the first one is considering the chemical charge amount, usually determined by potentiometric titrations or colloid titration. The second one is considering the effective charge at the double-layer interface and more precisely the charge at the slipping plane of the diffuse layer and the solution. This parameter is usually determined by electrophoretic measurements, and this effective charge is commonly referred to the zeta potential. The polymer branching also plays here a key role since it is largely controlling the polymer interaction behavior with the particles [20–22]. Moreover, the branching also induces important differences in the floc structure, compactness, and fractal dimensions, which are affecting the sedimentation rates and floc strength with regards to filtration processes [7].

As already mentioned, the use of charged synthetic polymers involves different flocculation mechanisms [4, 23]. When the polymer radius of gyration is small in comparison to the particle size, flocculation is mainly promoted by local polymer adsorption and local inversion of the sign of the

surface charge. Thus, oppositely charged patches are then created at the particle surface which can interact with oppositely charged surfaces. Depending on the flocculant dosage, complete charge neutralization can also be achieved so that van der Waals forces, which are always attractive, induce particle aggregation [24]. However, if flocculant dosage is not properly controlled, an excess of polymers will re-disperse the particle suspension by charge inversion or steric stabilization. Usually, from a practical point of view, three different regimes must be considered: (1) when flocculant concentration is too low to induce rapid flocculation, (2) flocculant dosage is optimal for rapid destabilization, and (3) flocculant concentration is too high and results in particle restabilization [7].

Among the aforementioned factors, there is an important one which concerns the potential impact of the solution ionic strength due to the presence of dissolved ions or simple electrolyte (salt) in the solution [21, 25]. Owing to the multiple effects of an increase (or decrease) of the solution ionic strength, (monovalent) salt influence is not trivial to estimate. Indeed, salt is expected to screen the electrostatic repulsive forces between the charged particles in solution and thus via short-range van der Waals interactions to promote the rate of particle coagulation [26]. On the other hand, it is also expected by screening effects to reduce the electro-attractive interactions between the charged flocculant and the oppositely charged particles and thus strongly affect the flocculation rate and polymer efficiency. The presence of salt is also expected to play a role on the flocculant conformations by promoting, for example, polymer folding and collapse [27–30].

In this study, positively charged linear chains as well as positively charged branched polymers having two branches are used as flocculants. The influence of the polyelectrolyte branching and polymer dosage on the kinetics of flocculation and changes of the electrostatic properties of well-characterized micrometric particles are addressed here. The polymer efficiency is evaluated by considering the flocculation rates of solutions containing well-defined negatively charged and monodisperse latex particles. The impact of the presence of salt at various concentrations is also investigated at optimal and non-optimal flocculation concentration conditions (flocculant dosage), and empirical kinetics constants are determined by adjusting the salt concentration. The electrokinetic properties of the particles are calculated to obtain an insight into the possible parameters governing the flocculation processes and polymer efficiency. In all cases, flocculation rates, optimal polymer dosage, and stability ratio, which are key topics in the colloid and polymer science, are compared with salt-induced particle destabilization only (simple coagulation) to elucidate the impact of the ionic strength influence on the flocculant efficiency.

Materials and methods

Colloidal particle properties

A well-characterized monodisperse aqueous suspension containing 81 g/L of negatively charged latex spheres having a diameter equal to 1 μm and provided by Interfacial Dynamics Corporation (IDC) was used. The TEM diameter was found to be equal to $0.99 \pm 0.03 \mu\text{m}$. The particle number, per milliliter of solution, was equal to 1.5×10^{11} and the specific surface area to $5.7 \times 10^4 \text{ cm}^2/\text{g}$. The presence of sulfate groups at the surface resulted in a constant charge density value equal to $3.9 \mu\text{C}/\text{cm}^2$ for pH values above 4. The zeta potential determined with a Malvern Zetasizer Nano ZS was found to be equal to $-100 \pm 3 \text{ mV}$ [7]. The Zetasizer Nano Series uses a combination of laser Doppler velocimetry and phase analysis light scattering (PALS) in a patented technique called M3-PALS to measure particle electrophoretic mobility. This allows the measurement of high-conductivity samples, plus the ability to accurately measure samples that have low particle mobilities. Stock solutions were prepared at 1 g/L and stored. All experiments were conducted with 0.5 g/L latex suspensions under perikinetic conditions. Gentle mixing of the electrolyte solution and latex suspension was performed in order to eliminate particle sedimentation which sets in slowly owing to the latex density (1.055 g/mL).

Coagulant and flocculant properties

To adjust the solution ionic strength sodium chloride 99.5 % from Acros Organics was used. Two solutions of NaCl of 1 and 5 M were prepared as stock solutions. Colloidal particles were flocculated by positively charged linear (BHMW) or two-branched (B1^{++}) polyacrylamide polymers synthesized, characterized, and supplied by Aqua+Tech Specialities S.A (Switzerland) [7, 12, 31]. These polymers have charges which are 55 mol%, equivalent to approximately 80 wt%. The charges have been measured using a long-established colloid titration method. The charges can be also estimated, with much less precision, by FTIR. In general, the two methods agree within the expected precision, or approximately $\pm 3 \%$. The degree of branching has been estimated based on the mass balance of multifunctional and monofunctional monomers. Branching was also be indirectly assessed by analytical ultracentrifugation as the sedimentation velocity of branched molecules differs slightly. BHMW and B1^{++} have respectively both a charge density of 80 % (in weight percent), a molecular weight of 7.2×10^6 and 1.2×10^7 (in grams per mole), an intrinsic viscosity of 1,720 and 2,636 (in liters per milligram), hydrodynamic radii of 311 ± 11 and $252 \pm 21 \text{ nm}$, and zeta potential values of $+72 \pm 3$ and $+78 \pm 3 \text{ mV}$ [7]. Stock solutions of the linear BHMW polymer and two-branched B1^{++}

polymer were prepared at 1 g/L. Daily fresh solutions of these two polymers were prepared at $5 \times 10^{-3} \text{ g/L}$ and stirred during 30 min at 800 RPM.

Size distribution determination

The decay of the number of IDC[®] free latex particles (monomers) with time was measured using a Coulter[®] Counter Multisizer II[™]. Through 256 channels, this device measures the equivalent particle diameter (from 1 to 30 μm) and counts the number of particles or aggregates passing through an aperture orifice of 50 μm . Each measurement was performed during 30 s corresponding to 287 μL of solution. Isoton[™] IIA was used as a support electrolyte but was pre-filtered with a 0.22 μm Millipore[®] ISOPORE[™] GTTP filter to reduce the background noise. A solution of 200 μL was placed into 100 mL of isoton IIA and gently mixed to homogenize the solution without breaking aggregates before the measurement. As mentioned above, the diameter given by the Coulter[®] Counter corresponds to the diameter of the sphere equivalent to the aggregate as if all the latex monomers were collapsed in one compact volume. In our study, kinetics aggregation rates, K_S , were determined by the increase with time of the inverse of monomer number given in the 1 μm channel, so as to take into consideration only non-flocculated particles [7].

Zeta potential determination

The zeta potential ζ is related to the electric potential at the boundary surface of the hydrodynamic shear which corresponds to the potential at the slipping plane of the diffuse layer with the bulk solution. The zeta potential considers the contribution of the counterions and coions at the double-layer surface [24, 32]. Normally, 1 mL of the solution to analyze is diluted in a solution containing 20 mL of MilliQ water and 200 μL of Isoton IIA. Then, 1 mL of this secondary solution is analyzed in a zeta potential cell with one Zetasizer Nano ZS.

Results and discussion

Aggregation and flocculation kinetic rates

In Fig. 1 are presented the variations of the inverse free latex particle concentration with time ($1/N_1$) at optimal flocculant concentration. The kinetic flocculation rates were experimentally found here as well as in [7] to follow a second-order law according to:

$$\frac{dN_1}{dt} = -K_S |N_1|^2$$

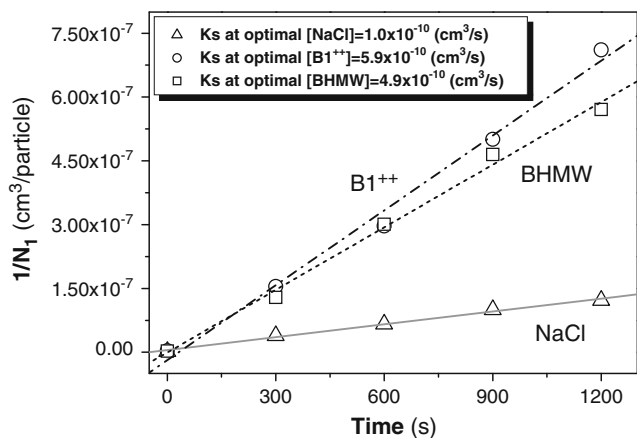


Fig. 1 Inverse of the free particle number variation ($1/N_1$) with time at optimal BHMW, B1⁺⁺ dosage, and NaCl concentration above the critical coagulation concentration, showing that the solution destabilization is much more efficient with the use of polymers (linear and two-branched) than using simple monovalent salt

where N_1 represents the monomer (single particle) number, and K_S corresponds to the kinetics flocculation rate. This formula is used to calculate K_S values at early stages of flocculation where most of the particles are still single or as small aggregates. As shown in Fig. 1, a significant difference is found between the K_S values obtained in the presence of NaCl only at a corresponding ionic strength equal to 1 M (i.e., above the critical coagulation concentration) and those obtained by the linear BHMW or two-branched B1⁺⁺ polymers in the absence of NaCl, at their optimal concentrations. K_S values are found equal to 1.0×10^{-10} , 4.9×10^{-10} , and $5.9 \times 10^{-10} \text{ cm}^3/\text{s}$ for the linear and branched flocculants and NaCl, respectively. Therefore, the coagulation rate obtained with salt only is found smaller than the values obtained with the polymeric flocculants which are found more efficient than salt only. Moreover, the linear polymer corresponding K_S value is found lower than the two-branched one, hence denoting less efficiency. On the other hand, as shown in Fig. 2, (1) the polymer dosage which is needed to reach the optimal flocculation dosage range is two times lower for the linear one and (2) the effective optimal polymer dosage window is broader when using the two-branched polymer. Such results clearly demonstrate the advantages and disadvantages of both flocculants related to their optimal concentration dosage and range of efficiency as well as their better performances over monovalent salt.

Salt influence at optimal polymer dosage

To investigate the impact of an increase of the ionic strength on the polymer flocculant efficiency, additional experiments were then realized at optimum polymer dosage and at NaCl

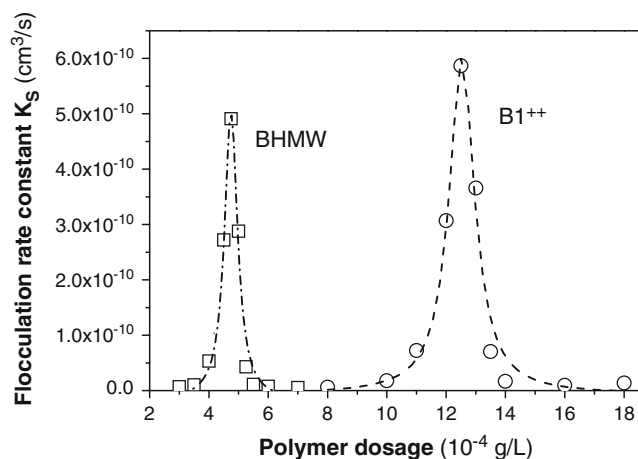


Fig. 2 Kinetic aggregation rates K_S values obtained as a function of polymer flocculant dosage (in the absence of salt). The branched flocculant exhibits a significant larger dosage concentration domain and kinetic flocculation rate whereas the linear one is active at lower concentrations

salt concentration equal to 0.05 M. Such a salt concentration is less than the salt critical concentration conditions (equal to 0.25 M) and not expected here to induce rapid particle coagulation due to charge screening effects [7]. Nonetheless, as shown in Fig. 3, the presence of a small amount of salt is found to decrease significantly the overall efficiency of the two flocculants by a factor of 7.3 for the linear and 5.5 for the two-branched flocculant. The presence of salt and increase of the ionic strength clearly modifies the polymer efficiency in a way which depends on the flocculant branching. In our case,

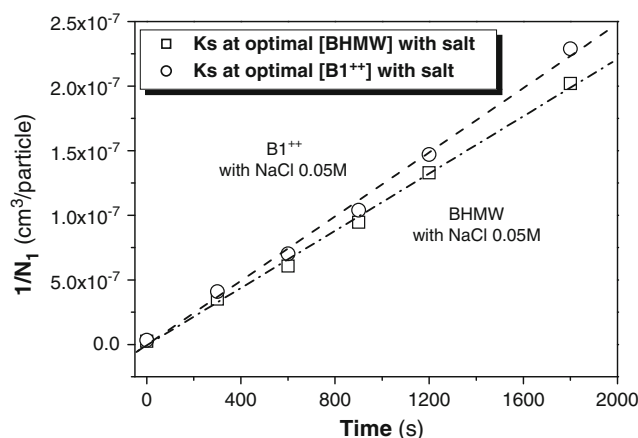


Fig. 3 Inverse monomer number ($1/N_1$) with time at optimal BHMW and B1⁺⁺ dosage in the presence of NaCl (0.05 M). A significant decrease of the polymer efficiency is observed when comparison is made between the different flocculation rates with and without the presence of salt: the K_S values decrease for the linear polymer from 4.91×10^{-10} to $6.65 \times 10^{-11} \text{ cm}^3/\text{s}$ and for the two-branched from 5.87×10^{-10} to $1.06 \times 10^{-10} \text{ cm}^3/\text{s}$

this effect is significantly more pronounced for the linear polymer.

To gain insight into the effect of charge screening, the ionic strength of the solution containing the flocculants was adjusted with NaCl, and K_S values obtained at optimal polymer dosage with the linear and two-branched polymers were determined. They are presented in Fig. 4. K_S values, corresponding to NaCl salt variations only, are also presented for comparison. Using salt only, the fast aggregation rate regime is obtained when NaCl concentration is greater than the critical coagulation concentration (CCC) which is found here equal to 0.25 M. Using NaCl only, ions resulting from salt dissolution are screening the charges at the particle surface, hence leading to the decrease of the double-layer thickness. When the double-layer thickness is so low that the van der Waals interactions can overcome the Coulomb electrostatic repulsive forces (at the CCC), then fast aggregation occurs, and a plateau is obtained with regard to the coagulation rate constants. As shown in Fig. 4, there is still a significant difference between the K_S values obtained with NaCl only and those obtained with the flocculants even in the presence of salt. Polymers are found more efficient than salt coagulation whatever the final solution ionic strength. This is an important result from a practical and fundamental point of view.

It is also shown that upon the addition of a small amount of salt (5×10^{-3} M), the polymer flocculation rates are found to rapidly decrease first. This effect is more pronounced for the linear flocculant. Then, by increasing further the salt concentration, kinetics flocculation rates are then increasing again to reach plateau values. It is important to note here

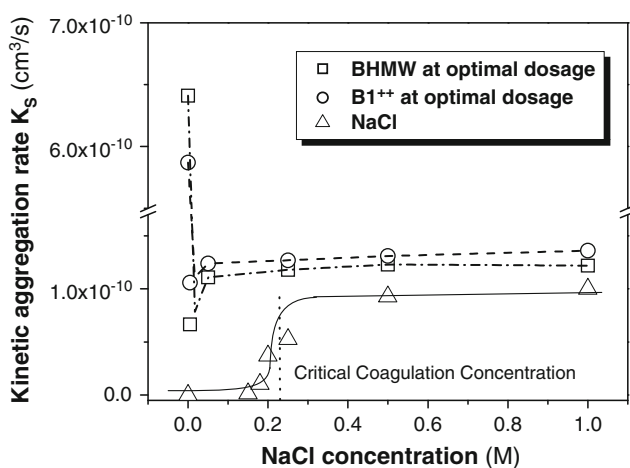


Fig. 4 K_S variations as a function of NaCl concentration at BHMW and B1⁺⁺ optimal dosage. Polymer efficiency is rapidly reduced and reaches a plateau value at high salt concentration. It is also shown that the presence of flocculants above the critical coagulation concentration still improves the coagulation rates of the particles

that, for both polymers, the K_S plateau values which are obtained are significantly higher than the values corresponding to the situation where only NaCl is used at variable concentrations. This points out that even if the polymer efficiency is reduced by the increase of the ionic strength, the polymer remains active not only below the CCC but also at high NaCl concentration. It is also noteworthy to observe here that the kinetics flocculation rates are surprisingly low when NaCl concentration is equal to 5×10^{-3} M. This occurs for both polymers but is emphasized when using the linear polymer. This point will be discussed later.

Ionic strength influence below and above optimal polymer dosage

K_S variations at variable salt concentrations obtained with linear BHMW and two-branched B1⁺⁺ polymers, below and above optimal dosage (respectively at 4×10^{-4} and 5.25×10^{-4} g/L for the linear and 1.1×10^{-3} and 1.35×10^{-3} g/L for the two-branched) are now presented and discussed in Fig. 5a and b. In the two cases, when NaCl concentration is equal to zero, it is found that the linear flocculant efficiency is less than the two-branched one. It is shown here that by increasing the ionic strength, the kinetic aggregation rates are rapidly increasing to reach plateau values which are significantly higher than the values obtained with NaCl only and close to the values obtained at optimum polymer dosage in the presence of NaCl. Thus, below an above optimal polymer dosage, the increase of ionic strength is clearly found to increase the flocculation rates.

Flocculation mechanisms in the presence of salt

Zeta potential measurements were performed to help elucidate the possible flocculation mechanisms by considering the particle surface charge modifications due to polymer adsorption and salt effects. Zeta potential measurements allow the determination of the effective charge at the particle surface and thus can give useful indirect information on the amount of polymer adsorbed as well as charge evolution of the particles with flocculant dosage. In Fig. 6, the latex particle zeta potential evolution is presented as a function of NaCl concentration at optimal linear and two-branched polymer dosages.

In the absence of salt and at optimal polymer dosage, it is important to note that the particle zeta potentials are close to -20 mV, due to the adsorption of the positively charged polymers at the negatively charged particle surfaces. In that case, the zeta potential value is decreasing from -100 mV for bare particles to -20 mV showing that the two flocculants, in the absence of salt, exhibit a strong affinity with the particle surfaces. Charge neutralization is not completely

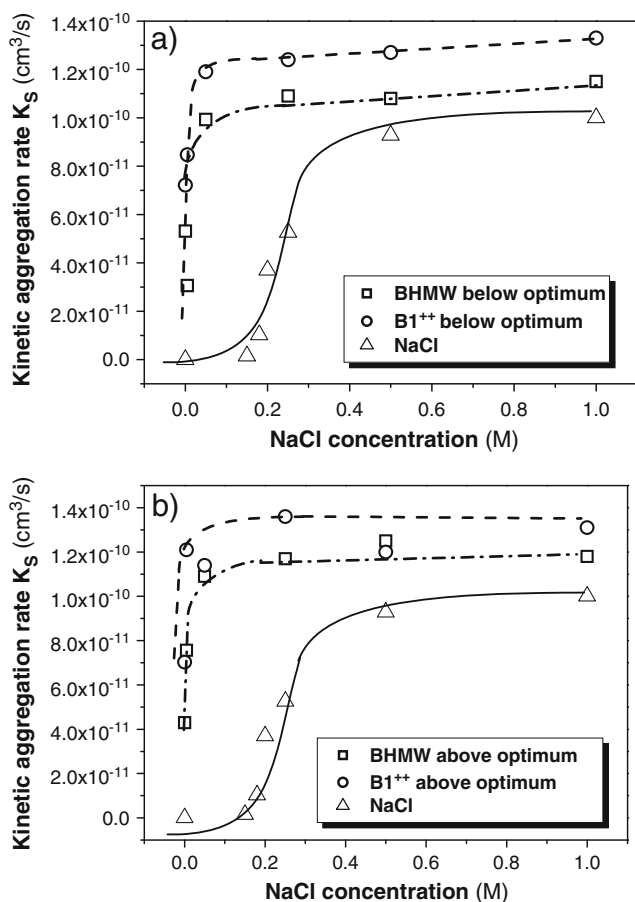


Fig. 5 **a** K_S evolution as a function of NaCl concentration below optimal BHMW and B1⁺⁺ dosage (respectively, 4×10^{-4} and 1.1×10^{-3} g/L). **b** K_S evolution as a function of NaCl concentration above optimal BHMW and B1⁺⁺ dosage (respectively, 5.25×10^{-4} and 1.35×10^{-3} g/L). In all cases, the increase of the ionic strength is improving the kinetic aggregation rates

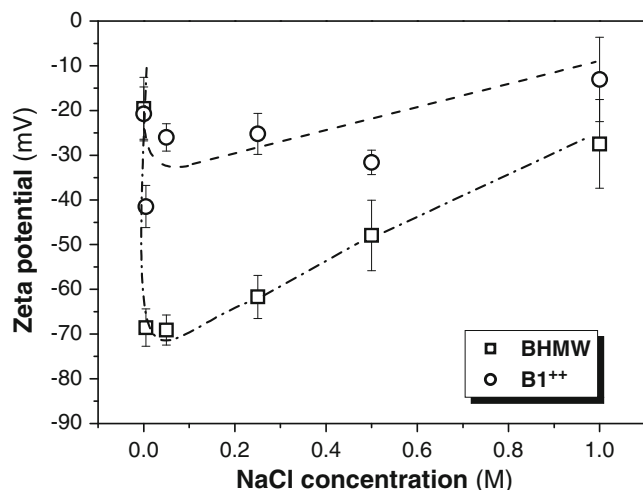


Fig. 6 Latex particle zeta potential variations with NaCl concentration in the presence of the BHMW and B1⁺⁺ at optimal concentration. The presence of salt is significantly decreasing the zeta potential values. It should be noted that the initial zeta potential of the bare latex particles is equal to -100 mV

achieved, and charge inversion (i.e., charge reversal of the particles) is not observed at optimal polymer dosage. This denotes that charge neutralization is not the only mechanism of latex destabilization.

As shown in Fig. 6, the addition of a small amount of salt results in a significant decrease of the zeta potentials (-70 mV for BHMW and -40 mV for B1⁺⁺) and a decrease of the kinetic aggregation rates as previously observed in Fig. 4. Then, by increasing the salt concentration further, the zeta potential value is found to increase again concomitantly with the aggregation rates. Such a complex behavior can be explained by the fact that the presence of salt is expected to influence at least three important parameters. The first one is related to the flocculant conformation at low salt concentration; to reduce the intra-chain electrostatic interactions, the positively charged flocculants are expected to adopt extended conformations and as a result to promote the formation of bridges between the latex particles (Fig. 7a) concomitantly to partial charge neutralization. This could also explain the presence of slightly negative species at the optimum flocculation rates. The second one is dealing with the changes related to the flocculant conformations and the total amount of adsorbed flocculant in the presence of salt. Increasing the salt concentration may result, through electrostatic screening, in the formation of more folded polymeric structures and the concomitant reduction of the amount of adsorbed polymer at the particle surface due to the

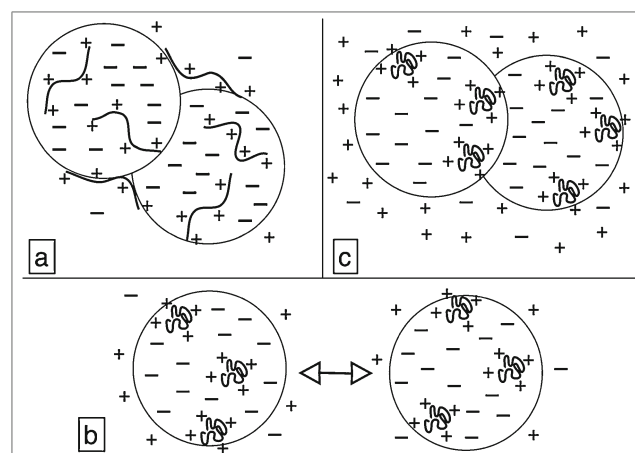


Fig. 7 Possible mode of adsorption and flocculation processes by the cationic polymeric flocculants (linear) on the negatively charged particles and influence of the salt concentration on the flocculant conformation and flocculation mechanisms. **a** In the absence of salt, **b** with salt at 5×10^{-3} M, and **c** with salt at 0.15 M (importance of charge screening between the latex particles). Salt is proposed to have significant impacts on the flocculant conformation and flocculation mechanisms

decrease of the electro-attractive interactions between the flocculants and the latex particles (Fig. 7b) [33]. This would explain a rapid decrease of the particle zeta potential as well as the rapid decrease of the flocculation rates and flocculant efficiency (less charge neutralization and less polymer bridging). The third one is related to the importance of the latex–latex particle charge screening by increasing further the salt concentration. This effect is expected to increase the aggregation rate between the latex particles (Fig. 7c). The large decrease of the zeta potential of the latex particles as the salt concentration increases from 5 mM may be also due to electrokinetic effect since it has often been found that the zeta potential of the latex particles decreases with increasing salt concentration.

To obtain additional insight into the behavior of our polymer/particle mixtures, the zeta potential values as a function of the NaCl concentrations for the linear and two-branched polymer, respectively, (a) below and (b) above optimal flocculant dosage but still in the effective flocculation concentration window (respectively 4×10^{-4} and 5.25×10^{-4} g/L for the linear and 1.1×10^{-3} and 1.35×10^{-3} g/L for the two-branched) were determined (Fig. 8). Compared to the optimal dosage situation, similar trends are observed, i.e., a rapid decrease of the zeta potential values and flocculation rates followed by a decrease of the zeta potentials and increase of the flocculation rates. It is interesting to note here that the linear flocculant is much more affected by an increase of the ionic strength. Indeed, larger changes in the linear polymer dimensions by charge monomer screening are expected in comparison to the branched conformations, hence demonstrating that the polymer branching in our case is an important parameter to take into consideration.

Conclusions

Kinetic flocculation rates and electrophoretic mobility measurements were used to investigate the influence of the solution ionic strength on the floc formation between negatively charged latex particles and two oppositely charged polymeric flocculants with different branching (linear and two-branched). The role of polymer dosage on the flocculation rate constants was also investigated, and a systematic comparison was made with salt-induced particle aggregation processes for a better estimation of polymer efficiency and optimal dosage concentration range. Our results point out (1) the differences between the flocculation and the salt-induced destabilization mechanisms; at optimal polymer dosage, the flocculation rate constants are significantly higher than the aggregation rate constant obtained with salt

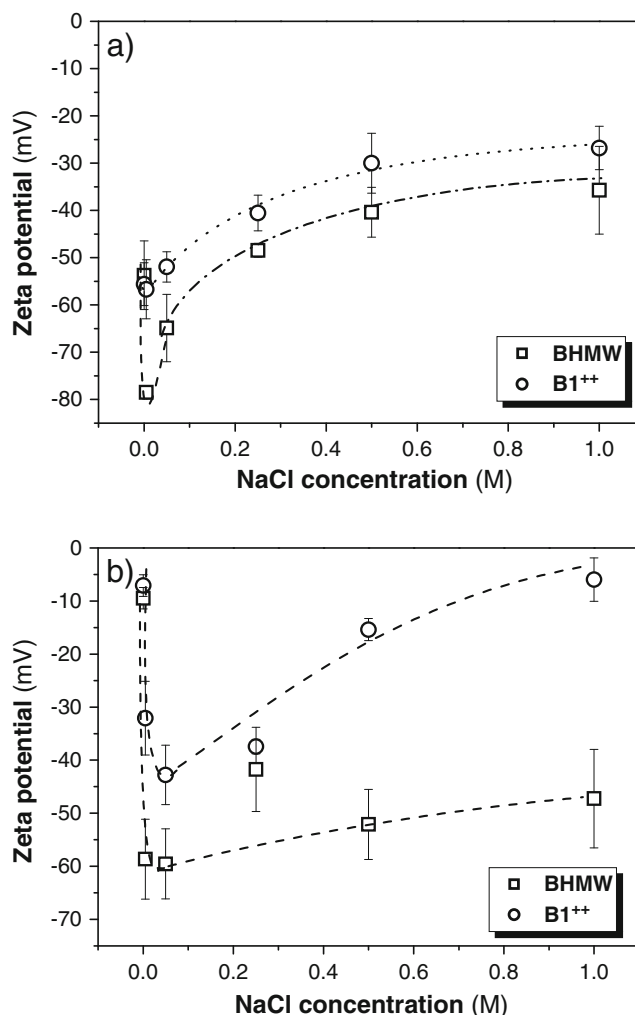


Fig. 8 a Zeta potential evolution with [NaCl] below optimal BHMW and B1⁺⁺ dosage. b Zeta potential evolution with [NaCl] above optimal BHMW and B1⁺⁺ dosage

only, i.e., when charge screening has reached its optimal effect, (2) the branching of the polymer is shown to play a significant role on the kinetics of flocculation and the range of concentration over which flocculation occurs. Our findings suggest (3) that charge neutralization and, to a lesser extent, bridging dictate here the stability of the charged latex particle suspension. (4) The dramatic effect of even small amounts of salt on flocculation efficiency, which is a result of paramount importance in colloid and polymer science, is here demonstrated. Indeed, by increasing the suspension ionic strength, our results indicate that the polymer efficiency is strongly reduced. Another interesting result of this study (5) is the fact that the analysis of the kinetics flocculation rates clearly demonstrates the efficiency of the branched flocculant is less affected by large changes in the solution ionic strength.

Acknowledgments The authors are grateful to F. Carnal for useful discussions and comments. We gratefully acknowledge the financial support received from the Swiss National Science Foundation, Research Project 200021–135240. The authors also acknowledge Aqua+Tech Specialties SA (La Plaine, Geneva, Switzerland) for supplying the flocculant samples.

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