

Article

# Inhibition of Cationic Polymer-Induced Colloid Flocculation by Polyacrylic Acid

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**Abstract:** Although the dosage of cationic flocculants used for water treatment is well known to increase in the presence of natural organic matter (NOM), the underlying reasons for this increase are not properly understood. Herein, we studied the flocculation behavior of polystyrene latex (PSL) particles in the presence and absence of polyacrylic acid (PAA5K) as an NOM analogue using an end-over-end rotation apparatus for standardized flow mixing. In the absence of PAA5K, the initial rate of cationic flocculant (PAM5M)-induced flocculation was enhanced, as reflected by the size of flocculant in solution. Additionally, flocculation experiments were performed in the presence of 0.5 mg/L PAA5K for five concentrations of PAM5M and two ionic strengths, and the increase of the initial rate of PAM5M-induced flocculation was suppressed by PAA5K immediately after mixing, with the most pronounced suppression obtained at a PAM5M concentration similar to PAA5K. Based on the above insights and the results of viscosity measurements, the inhibitory effect of PAA on flocculation was ascribed to (1) the reduction of PAM charge and the concomitant shrinkage via electrostatic association with PAA and (2) the termination of polycation adsorption on PSL caused by polyion complex formation when the charge ratio of PAM:PAA is close to unity.

**Keywords:** polymer flocculation; polystyrene latex; initial flocculation rate; cationic polyelectrolyte; inhibition of flocculation by natural organic matter

## 1. Introduction

The affinity of polyelectrolytes to oppositely charged surfaces is used to promote flocculation in numerous practical applications such as water purification [1], soil conditioning [2], mineral processing [3], and papermaking [4]. In the case of water treatment, the utilization of polyelectrolytes in the coagulation-flocculation process facilitates the control of floc structure and enhances the rate of solid/liquid separation. In addition, polymeric coagulants exhibit a range of advantages (e.g., lower dosage, decreased sludge production, cost-effectiveness, and decreased increment of ionic load and amount of Al in treated water) over the commonly used alum [5]. In general, polymer-induced flocculation is thought to proceed via two mechanisms involving (1) the neutralization of colloidal particle charge by patches of adsorbed polyelectrolyte [6,7] or/and (2) the formation of bridges between colloidal particles by simultaneous adsorption of polyelectrolyte chains onto more than two particles [8,9].

The improvement of flocculation efficiency requires a deep understanding of polyelectrolyte adsorption onto the surface of colloidal particles, and considerable efforts have therefore been directed at deepening our theoretical and experimental understanding of polymer behavior at the interface of thermodynamically well defined surfaces [10–13]. However, despite the large number of corresponding

studies, the exact mechanism of polymer-induced flocculation has not been clarified yet. For instance, in numerous engineering flocculation practices, it can be easily imagined that systems experience far-from-equilibrium conditions just after the onset of flocculation. That is, the progress and results of flocculation are strongly influenced by non-equilibrium aspects such as the transportation of polymer flocculants from bulk solution to surface of colloidal particles that is followed by a transition from a coil-like solution-phase conformation to a more or less flattened adsorbed-phase conformation [13–15]. To evaluate the transient states of polymer coagulants, we have previously developed a procedure of fluid mixing normalization in terms of colloidal particle collision frequency equivalent to the rate of rapid coagulation [16] and applied the developed technique to the analysis of polymer adsorption-induced flocculation of colloidal particles. One of the most remarkable results obtained from polymer-induced flocculation is that the maximum rate of flocculation in the beginning stage reflects the size of the polymer in solution [17–19].

Most of the recent flocculation investigations were performed under single-flocculant conditions [20–22]. However, real-life water treatment is commonly performed in the presence of naturally-occurring polymers, i.e., natural organic matter (NOM), which are opposite in charge to the flocculants employed [23,24]. The presence of such polymers complicates water treatment by deteriorating water quality and promoting the formation of strongly toxic disinfection by-products such as trihalomethanes. Among the numerous components of NOM, the most abundant ones belong to the class of humic substances and can be further categorized into fulvic and humic acids [25,26], which account for the anionic charge of humic substances and are considered to play an important role in flocculation processes because of their tendency to interact with cationic flocculants. Similar effects are found in the addition of anionic surfactant in the latex flocculation with polycation, where cationic flocculant appeared to be less competent and induces bridging or patch flocculation in low concentration of anionic surfactant [27]. Although the above interaction explains why higher flocculant dosages are required to treat NOM-containing water in the coagulation-flocculation process [28,29], only few studies have investigated the underlying reasons of this behavior.

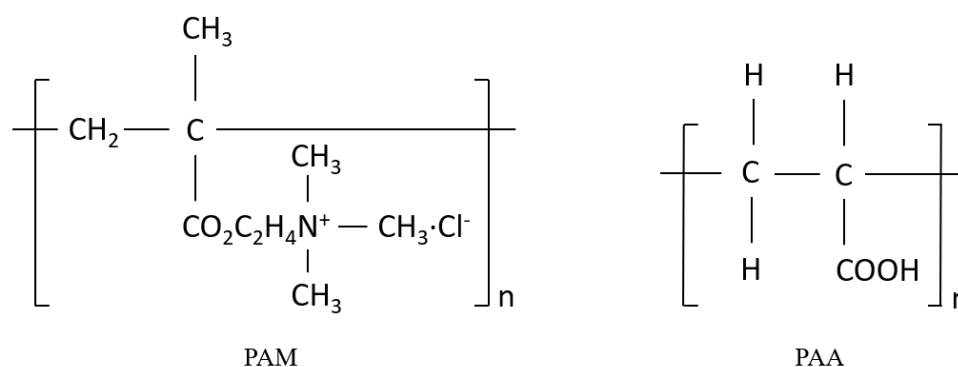
Herein, well-characterized polyacrylic acid (PAA) [30] is used as an NOM analogue with a similar polymer size and effective charge in solution [31,32] to study the inhibitory effect of NOM on the cationic polyelectrolyte-induced flocculation of colloidal particles. Notably, the flocculation rate is shown to be strongly enhanced by the attachment of swollen-chain cationic polyelectrolytes (formed during the transition from the solution-phase coil-like conformation to the adsorbed flattened conformation at the particle interface) to colloidal particles. The behavior of the cationic polyelectrolytes in solution is considered to be most clearly influenced by the presence of PAA at this transient stage.

## 2. Materials and Methods

### 2.1. Materials

A suspension of monodispersed negatively charged polystyrene latex (PSL; Thermo Fisher Scientific Inc., Waltham, MA, USA) was employed as a model colloid. According to the supplier, PSL was synthesized by standard polymerization of styrene in the absence of surfactants, and the diameter of latex particles was determined as  $1.2 \pm 0.01 \mu\text{m}$  by electron microscopy. The initial number concentration of particles,  $N(0)$ , was set to  $5.0 \times 10^7 \text{ cm}^{-3}$ . Prior to flocculation experiments, the PSL suspension was sonicated for 30 min to eliminate aggregates. A linear cationic polyelectrolyte, poly((2-dimethylamino) ethyl methacrylate) methyl chloride quaternary salt (PAM5M; Kaya Flocc Co. Ltd., Tokyo, Japan; nominal molecular weight =  $4.9 \times 10^6 \text{ g/mol}$ ), was used as a flocculant. The charge density of PAM5M, i.e., the ratio of the number of charged segments to the total number of chain segments, equaled 100%. Negatively charged PAA (PAA5K; Wako Pure Chemical Industries Ltd., Osaka, Japan; nominal molecular weight =  $5 \times 10^3 \text{ g/mol}$ ) was employed as a humic substance model. The chemical structures of both polymers are indicated in Figure 1. The stock solution of PAM5M was prepared by dissolving PAM5M in dilute aqueous KCl to the required concentration and was used

up within one week. The stock solution of PAA5K was prepared by dissolving PAA5K in pure water upon 24 h stirring. The prepared polymer solutions were placed in a dark and cold place (5 °C) to avoid light exposure-induced degradation. The ionic strengths of as-prepared solutions were adjusted with 0.1 and 10 mM KCl solutions. KCl solutions and deionized water were filtered through a 0.2 µm cellulose acetate (CA) membrane filter prior to usage. The initial pH of PAA5K was determined as 5.3. Although pH was not strictly controlled, the final pH of mixtures for each ionic strength and polyelectrolyte concentration was measured as 5.2–5.6 by using a glass electrode. Kodama et al. [33] reported that the degree of dissociation of PAA in this range of pH at 10 mM NaCl is ca., 0.35.



**Figure 1.** Chemical structures of monomer unit of poly ((2-dimethylamino)ethyl methacrylate) methyl chloride quaternary salt (PAM) and polyacrylic acid (PAA). Molecular weights of monomer unit for PAM and PAA are 207.5 and 71 g/mol, respectively.

## 2.2. Analytical Principle

The employed analytical principle was based on the rate of collisions between particles in a mixing flow. Notably, the frequency of collisions between colloid particles is equivalent to the rate of rapid coagulation, in which case all collisions result in successful coagulation. For a suspension composed of monodispersed spherical particles with a radius of  $a_0$ , the collision rate can be expressed as the temporary change of the number concentration of colloidal particles,  $N(t)$ , as

$$\frac{dN(t)}{dt} = -\alpha_T \sqrt{\frac{128\pi\varepsilon}{15\nu}} a_0^3 N(t)^2, \quad (1)$$

where  $\varepsilon$  denotes the rate of energy dissipation per unit mass,  $\nu$  is the kinematic viscosity of the fluid, and  $\alpha_T$  is the hydrodynamic interaction-determined capture efficiency of collisions between colloidal particles. Assuming that the concept of effective mixing shear rate is valid,  $\alpha_T$  can be approximately estimated using the approach of Van de Ven et al. [34] as

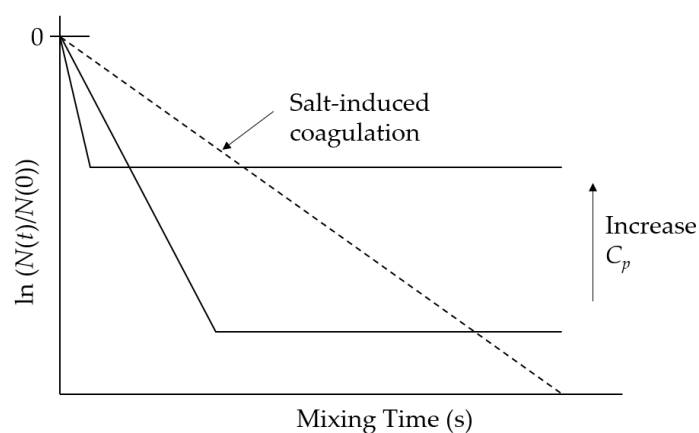
$$\alpha_T = \left( \frac{A}{36\mu\pi\sqrt{(4\varepsilon/15\pi\nu)}a_0^3} \right)^{0.18}, \quad (2)$$

where  $A$  and  $\mu$  denote the Hamaker constant and fluid viscosity, respectively. If we limit our discussion to the initial stage of flocculation, when the majority of clusters or particles can be regarded as monomers, Equation 1 can be reduced to a first-order expression, and an approximate solution for temporal number concentration variation can be expressed as

$$\ln\left(\frac{N(t)}{N(0)}\right) = -\alpha_T(a_0 + \delta)^3 Kt, \quad (3)$$

where  $K$  is a constant determined by the mechanical setup of the experiment and  $\delta$  denotes the protruding length of attached polymers on colloidal particles. Figure 2 shows the typical patterns of flocculation in the presence and absence of a polymer flocculant under a polymer concentration,  $C_p$ ,

above the optimal dosage. The solid lines represent polymer-induced flocculation, while the dashed line represents salt-induced rapid coagulation.



**Figure 2.** Schematic diagram of progressive polymer-induced flocculation.

Association of colloidal particles with polymeric coagulants increases the effective collision radius by the protruding length of attached polymers and therefore significantly increases the collision frequency. Assuming that the attached polymer structure is completely permeable, i.e., that the correction for hydrodynamic interaction is negligibly small, the flocculation of polymer-coated particles can be described as

$$\ln\left(\frac{N(t)}{N(0)}\right) = -\alpha_T a_0^3 Kt. \quad (4)$$

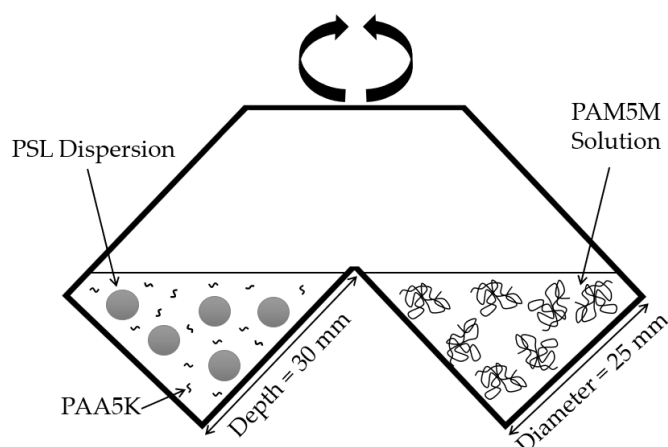
Therefore, the enhancement factor  $\zeta$ , which defines the ratio of the initial polymer-induced flocculation rate and the rate of salt-induced rapid coagulation under polymer-free conditions, can be expressed as

$$\zeta = \frac{(a_0 + \delta)^3}{\alpha_T a_0^3}. \quad (5)$$

In our previous studies, the value of  $\delta$  was confirmed to be correlated with the size of solution-phase polymer molecules rather than with the thickness of the adsorbed polymer in the equilibrium state. This finding implies that a remarkable behavior is expected in the extreme case when the bare surfaces of colloidal particles are exposed to an excess dosage of polymer flocculant. That is, the enhancement factor initially increases with increasing polymer concentration, whereas flocculation progress is abruptly terminated when the particle surface becomes saturated with the polymer (Figure 2). The duration of the enhanced stage is shorter for the case of higher polymer concentrations. This is due to saturation of the attached polymer on colloidal surfaces that induces steric stabilization.

### 2.3. Particle Aggregation Analysis

Colloid mixing was induced by the turbulent flow generated by the rocking motion of a forked flask installed on an end-over-end rotation shaker, as illustrated in Figure 3. The detail information can be found elsewhere [35]. In the beginning, 5 mL of the PSL dispersion was placed into one side of flask, and the other end was filled with 5 mL of PAM5M solution or KCl solution. The PAM5M solution and the PSL dispersion with/without PAA5K were mixed using the end-over-end rotation apparatus at a rotation frequency of 1 Hz until the predetermined number of mixing times was reached. The degree of coagulation/flocculation was monitored by determining the total number of clusters,  $N(t)$ , using a Coulter counter (Multisizers 4e, Beckman Coulter Inc., Brea, CA, USA). In order to evaluate the effects of the polymer swelling degree in solution, experiments were carried out at two different ionic strengths.



**Figure 3.** Schematic diagram of the employed end-over-end rotation shaker.

The effect of the transient state was analyzed by performing experiments at two different PAM5M concentrations. Based on our previous studies of the same polycation [19], PAM5M concentrations of 2.5 and 0.5 mg/L were selected. The concentration of PAA5K was set to 0.5 mg/L, and the inhibitory effect was analyzed for five different PAM5M concentrations (2.5, 1.5, 0.6, 0.5, and 0.4 mg/L). The obtained results were compared with those of the corresponding blank experiments. For experiments conducted in the presence of PAA5K, 4 mL of the PSL dispersion was mixed with 1 mL of the PAA5K solution beforehand, whereas in blank experiments, the PAA5K solution was replaced by an equal volume of deionized water. All sets of experiments were repeated at least twice to confirm the reproducibility of the obtained results.

#### 2.4. Viscosity Measurements

The viscosities of polymer-only solutions were measured by a capillary viscometer and used to determine the size of polymer aggregates employing Einstein's viscosity equation and nominal molecular weights provided by suppliers, with the results obtained for each ionic strength summarized in Table 1. When two polymers were present, viscosity measurements were employed to confirm the formation of polyion complexes [36,37]. Specifically, PAA5K and PAM5M solutions were mixed to afford the desired concentration ratios and gently shaken for 60 times. The resulting mixtures were centrifuged (Model 3520, Kubota Corp., Osaka, Japan) for 5 min at 150 rpm, and the supernatants were sampled and used for viscosity measurements. To reduce the influence of human error and ensure the reliability of acquired data, all measurements were conducted at high polymer concentrations (50 mg/L PAA5K and 50–250 mg/L PAM5M).

**Table 1.** Hydrodynamic diameters ( $a_p$ ) of polymers estimated by the Einstein's viscosity equation. All measurements were conducted at a controlled temperature of 20 °C and initial PAA5K and PAM5M concentrations of 50 mg/L.

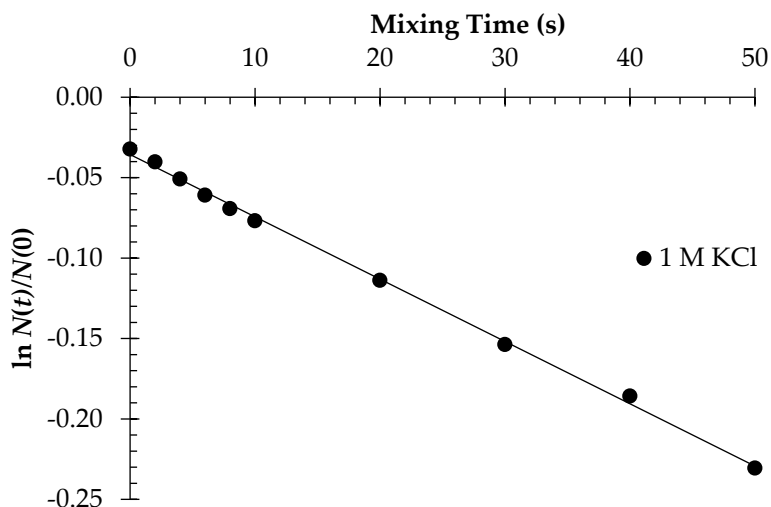
Sample	$a_p$ (nm)	
	10 mM KCl	0.1 mM KCl
PAA5K	6.4	7.2
PAM5M	277	341

## 3. Results

### 3.1. Polycation-Induced Flocculation

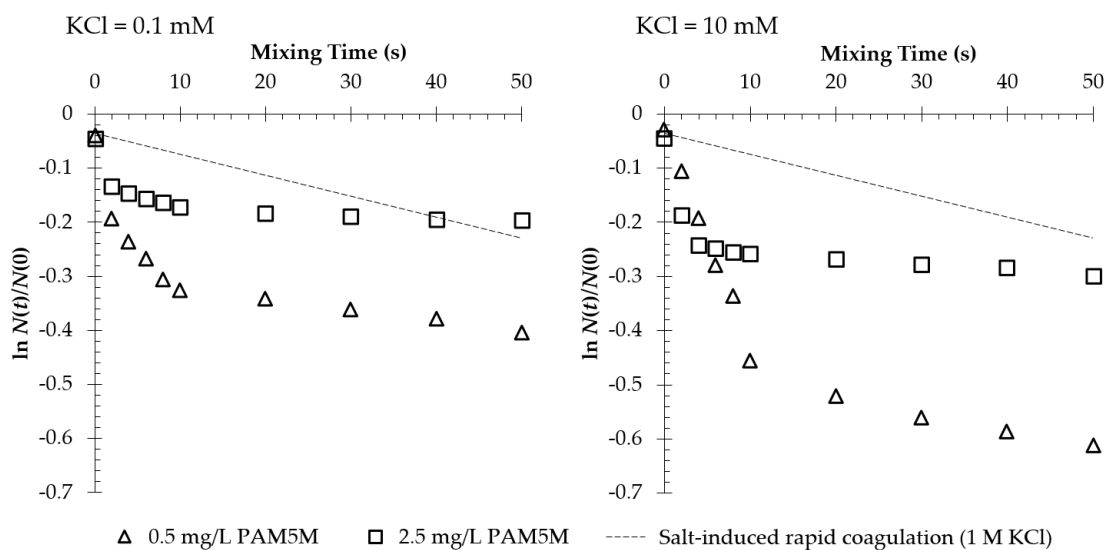
Figure 4 depicts the results of salt-induced rapid coagulation experiments, showing that  $\ln(N(t)/N(0))$  was linearly dependent on the mixing time (s), which verified the validity of the

applied method. The slope of the above plot was used in the subsequent analysis of data obtained for numerous conditions.



**Figure 4.** Variation of the total number of clusters per unit volume  $N(t)$  with the number of mixing time (s) for salt-induced coagulation ( $N(0) = 5 \times 10^7 \text{ cm}^{-3}$ ).

Figure 5 shows the results obtained for polycation-induced flocculation at different ionic strengths (0.1 and 10 mM), demonstrating that the enhancement factor for the PAA5K-free case is consistent with values reported elsewhere [17,19]. The calculated enhancement factors are shown in Table 2.



**Figure 5.** Temporal variation of polycation-induced flocculation rate in 0.1 and 10 mM KCl.

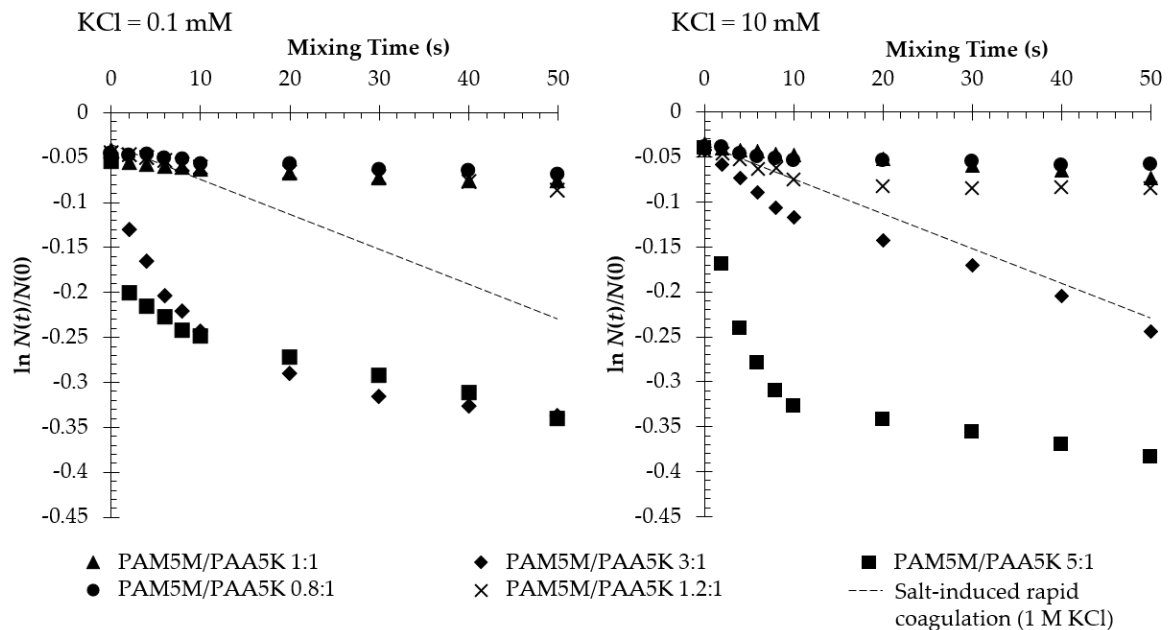
**Table 2.** Enhancement factors obtained for polymer-induced flocculation under different conditions.

Sample	$\xi$	
	10 mM KCl	0.1 mM KCl
0.5 mg/L PAM5M	8.76	10.54
2.5 mg/L PAM5M	10.64	N/A

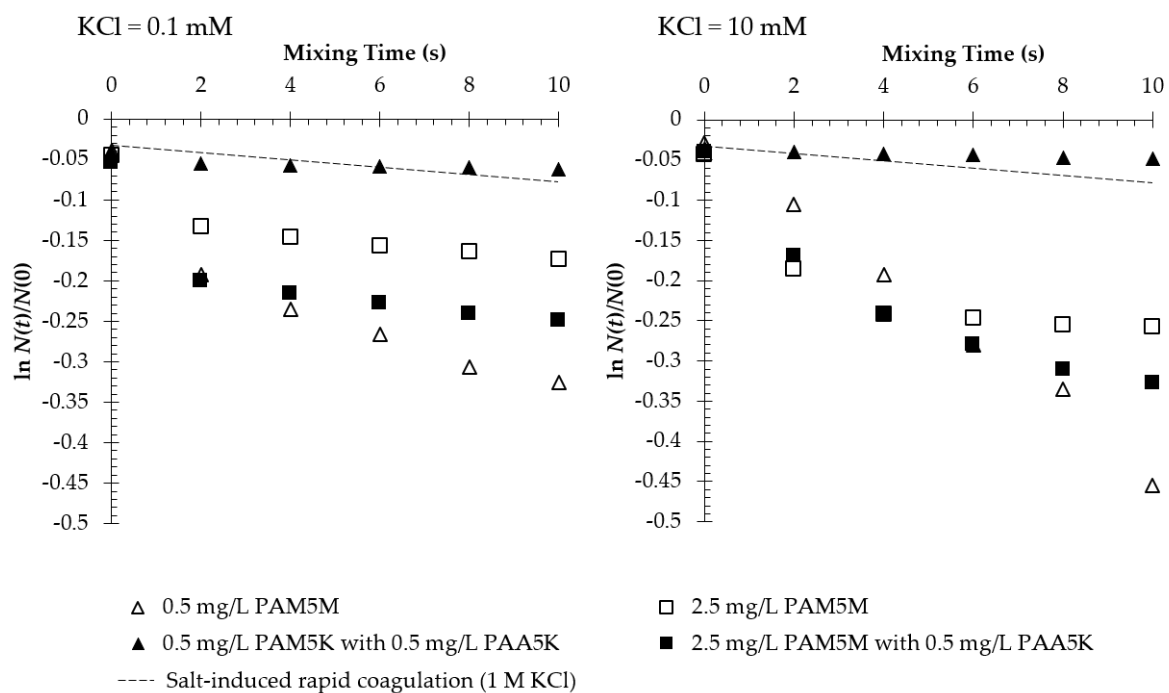
### 3.2. Flocculation in the Presence of Two Oppositely Charged Polymers

Figure 6 shows the influence of PAA5K on the PAM5M-induced flocculation of PSL at two different ionic strengths, demonstrating that the PAA5K significantly inhibits flocculation. This inhibitory

effect was most pronounced when the concentration of PAM5M was equal or less than that of PAA5K, in which case flocculation was essentially stopped. Moreover, the enhancement of the initial flocculation rate was disturbed by the presence of PAA5K, and this disturbance became more pronounced with increasing PAM5M/PAA5K concentration ratio. Figure 7 shows the initial flocculation rates (0 to 10 s) observed under different conditions, revealing that the rates were clearly reduced in the presence of PAA5K under the same concentration ratio. Conversely, at an excess dosage of PAM5M (2.5 mg/L), a slight enhancement in the rate of flocculation can be observed in the presence of PAA5K.



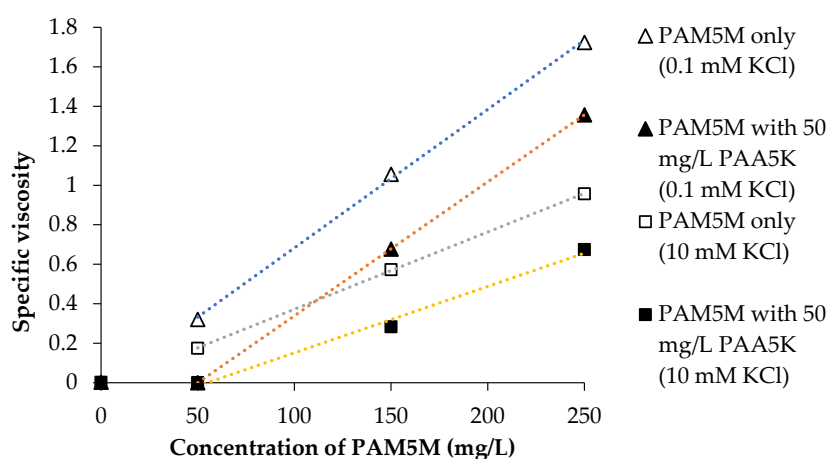
**Figure 6.** Temporal variation of polycation-induced flocculation rate in 0.1 mM and 10 mM KCl determined in the presence of 0.5 mg/L PAA5K.



**Figure 7.** Temporal variation of the rate of polycation-induced flocculation in 0.1 mM and 10 mM KCl with/without PAA5K.

### 3.3. Reduction of PAM5M Viscosity

Figure 8 shows that the viscosity of PAM5M solutions increased with increasing polymer concentration at all ionic strengths. Notably, the viscosities of 50 mg/L PAA5K solutions approximately equaled that of the solvent since the molecular weight of this polymer was much less than that of PAM5M. On the other hand, data obtained for the PAM5M-PAA5K supernatant solutions confirmed that the presence of PAA5K reduces the viscosity of PAM5M solutions. It should be noted that the viscosity of PAM5M solutions decreased to approximately that of PAA5K solutions when the concentrations of both polymers were equal, at which point PAM5M was completely neutralized by PAA5K to form solid complexes that were removed by centrifugation, in agreement with the results of flocculation rate measurements.



**Figure 8.** Specific viscosities of PAM5M and PAM5M-PAA5K supernatant solutions as functions of PAM5M concentration at KCl = 0.1 mM and 10 mM.

## 4. Discussion

### 4.1. Enhancement of Initial Flocculation Rate by PAM5M

Detailed analysis of the acquired data reveals some minor deviations. Figure 5 shows that at low ionic strength, the initial flocculation rate was significantly enhanced in the presence of 2.5 mg/L PAM5M, with an even more pronounced enhancement observed for a PAM5M concentration of 0.5 mg/L. This scenario can be explained by enhancement factor and polymer adsorption rates as illustrated in Figure 2. In high  $C_p$  condition, adsorption of polymers on colloidal particles are fast, which induces saturation in low dosage. However, in this case, the duration of the initial flocculation rate enhancement stage was too short in view of the swollen conformation of PAM5M chains, which corresponds to the case of low  $C_p$ . Meanwhile, in low  $C_p$ , adsorption is continuously taking place until flocculation is essentially stopped. In contrast, the result obtained at high ionic strength was consistent with that predicted in Figure 2. Adachi et al. [7] reported that both flocculation mechanisms; bridging and charge neutralization can be distinguished by the slope (the rate) of flocculation. Remarkable enhancement accompanied by abrupt termination of flocculation indicates that flocculation is taking place through bridging, which is observed in Figure 5 and illustrated in Figure 2. This behavior is contrast with the latter mechanism, where flocculation incessantly occurs with a rate similar to salt-induced rapid coagulation.

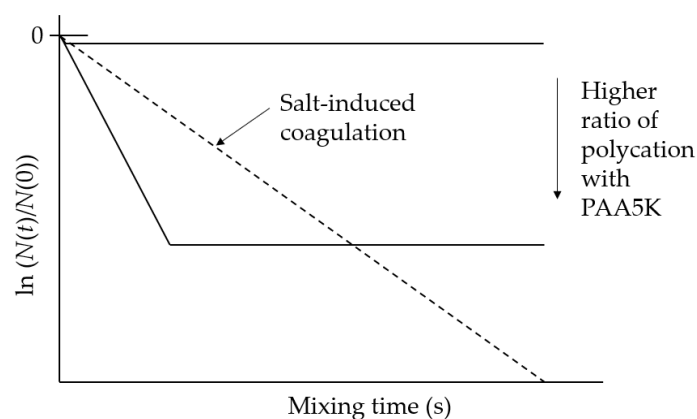
Comparison of flocculation rates observed for both ionic strengths indicated that (1) the most pronounced increase of the initial flocculation rate was observed at low ionic strength and (2) the highest maximum flocculation rate was observed at high ionic strength. The first finding can be explained by the incubation of electrolyte concentrations. At low ionic strength, PAM5M molecules exhibit an elongated form rather than a coiled form because of the strong repulsion between ionic groups in the polymer chain, which increases the collision size of the polyelectrolyte and hence promotes the



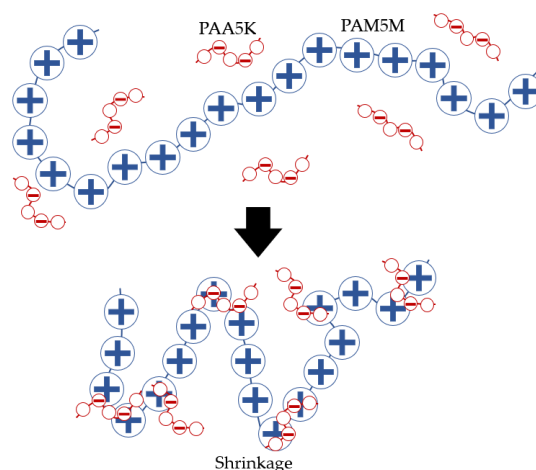
collisions of the polyelectrolyte and particles. On the other hand, the reduction of the above repulsion at high ionic strength leads to the accumulation of counter-ions and results in the adoption of coil-like conformations. This explanation is consistent with the results of viscosity measurements (Figure 8), where a steeper slope was observed at low ionic strength. Furthermore, Table 1 confirms that the size of polyelectrolyte molecules decreases with increasing ionic strength. Finally, the increase of the maximum flocculation rate with increasing ionic strength can be explained by the concomitant reduction of Debye length,  $K^{-1}$ , which is inversely proportional to salt concentration. At low ionic strength, the repulsion between polyelectrolytes is long ranged due to the swollen conformation and induces saturation of the particle surface at lower adsorbed amounts. When the salt level was increased, coil-like conformation of polyelectrolytes owing to screening of the intramolecular electrostatic repulsion between charged segments resulted in local accumulation of positive charge on the negatively charged particle. The tail of adsorbed polyelectrolytes would then attach to neighboring bare particles due to electrostatic attraction. As a result, larger amounts of polyelectrolytes are needed to induce saturation of the particles while particle-to-particle collision that leads to flocculation is proceeding.

#### 4.2. Shrinkage of PAM5M in the Presence of PAA5K

One of the most significant results of the present study is the disturbing effect of PAA5K on the large flocculation rate increase observed in the presence of PAM5M. Notably, this disturbance becomes more pronounced with decreasing PAM5M:PAA5K concentration ratio (Figure 9). The above behavior was explained by the regulatory effect of PAA5K adsorption on the conformation of PAM5M chains exhibiting electrostatic repulsion-induced swelling, i.e., neutralized parts of the latter chains are no longer involved in repulsive interactions, and the persistence length of the polymer is therefore considerably decreased (Figure 10). Therefore, the charge density of the excess PAM5M dosage (2.5 mg/L) was reduced to the charge density in a lower dosage condition, which resulted in a slight increase of the flocculation rate. In-depth analysis of Figure 6 provides an insight of the flocculation mechanisms involved. In the initial stage of flocculation (0 to 10 s), the rate of flocculation of the 2.5 mg/L PAM5M was enhanced by the increment of collision radius by protruding chain of PAM5M attached to the surface of colloidal particle and gradually terminated in the later stage (10 to 50 s). Flocculation in this condition can be interpreted as bridging flocculation. With the exception of PAM5M:PAA5K concentration ratio of 3:1, flocculation proceeds persistently at high ionic strength, which is an effect of charge neutralization by patch interaction [7]. Notably, inhibition of the initial flocculation rate was most pronounced at high ionic strength in view of the counter-ion screening effects and the reduction of PAM5M charge density by PAA5K. The subsequently observed flocculation behavior at a PAM5M:PAA5K concentration ratio of 3:1 resembled that of salt-induced coagulation at high ionic strength, whereas no such similarity was observed at low ionic strength. Such trend can be explained by Aoki and Adachi [19], where the presence of counter-ions and smaller polyelectrolytes prolongs the time required for PSL particles to reach saturation.



**Figure 9.** Schematic diagram of progressive polycation-induced flocculation in the presence of PAA5K.



**Figure 10.** Schematic representation of conformational changes of PAM5M upon the adsorption of PAA5K.

#### 4.3. Polyion Complex Formation

The results of viscosity measurements demonstrated that at a constant concentration ratio, the attraction between two oppositely charged polyelectrolytes resulted in the formation of solid complexes, which decreased the content of soluble polymer molecules in the suspension and its viscosity. The nature of solid complexes formation can be explained by considering the total charge concentrations of the polymers in solution. Izumrudov and Sybachin [38] reported that non-equimolar mixture of quaternary polyamines and polycarboxylates in a salt solution makes an insoluble polyelectrolyte complex in a certain range of ratio of the molar concentrations of charged groups of polycation and polyanion and demonstrates a maximum turbidity when the ratio is close to unity. The molar concentrations of charged groups of PAM5M and PAA5K in solution can be estimated by multiplying the molar concentration of monomer unit by the degree of dissociation. At 0.5 mg/L of polymers, molar concentrations of the monomer unit of PAM5M and PAA5K are  $2.36 \times 10^{-6}$  mol/L and  $7.04 \times 10^{-6}$  mol/L, respectively. Therefore, the charge concentrations of PAM5M and PAA5K are  $2.41 \times 10^{-6}$  mol/L and  $2.45 \times 10^{-6}$  mol/L by adopting the values of 1.0 and 0.35 [33] as the degree of dissociation of PAM5M and PAA5K, respectively. In the case of a concentration ratio of 1:1, the respective distribution of charge in solution of polyanion and polycation are approximate, which gives rise to complete charge neutralization through electrostatic interactions. Hence, the formation of polyion complexes was concluded to terminate the adsorption of polycations on PSL and thus inhibit flocculation.

## 5. Conclusions

The large enhancement of the initial flocculation rate observed at excess dosages of a cationic polymer flocculant was remarkably inhibited in the presence of an oppositely charged small polymer. This phenomenon was attributed to the adsorption of this oppositely charged polymer onto the cationic flocculant, which resulted in electrostatic neutralization of certain chain parts and therefore decreased the degree of swelling. Subsequently, decreased the net charge of cationic flocculant and effective collision radius of particles. This effect was more significant in high ionic strength due to the presence of counter-ions, and hence induced patch flocculation at specific concentration ratio of PAM5M:PAA5K. Therefore, it was concluded that the same electrostatic attraction can occur between negatively charged NOM and the positively charged polymer flocculant backbone, which, at a charge ratio close to unity, caused complete neutralization to occur to form solid complexes. Thus, flocculation of colloidal particles occurred only when the demand of PAA5K for the cationic flocculant charge was satisfied. In the present study, we have conducted experiments under only weakly acidic conditions. Similar experiments over a wider range of pH conditions will lead to more comprehensive knowledge.

**Author Contributions:** Conceptualization, Y.Y. and Y.A.; Methodology, Y.Y. and Y.A.; Validation, V.H.L. and Y.T.H.D.; Formal Analysis, Y.Y. and Y.A.; Investigation, V.H.L. and Y.T.H.D.; Resources, Y.Y. and Y.A.; Data Curation, Y.Y.; Writing-Original Draft Preparation, V.H.L.; Writing-Review & Editing, Y.Y., Y.T.H.D. and Y.A.; Visualization, V.H.L.; Supervision, Y.A.; Project Administration, Y.Y.; Funding Acquisition, Y.Y. and Y.A.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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