Distinct mechanisms of particle aggregation induced by alum and PACl: Floc structure and DLVO evaluation

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ABSTRACT

Interactions of silica microspheres were examined by light scattering in presence of alum and polyaluminum chloride (PACl) with various OH/Al ratios. The coagulation behaviors were investigated using different coagulant dosages at constant pH (6.5) and salt concentration (0.01 mol/L). Based on the measurement of size distribution and zeta potential, charge neutralization was proposed to be the primary coagulation step for all the coagulants while other distinct coagulation steps were also involved depending on in situ formed or preformed hydrolyzing products. Precipitate coverage and sweep flocculation were induced for alum, contrasted to polycation patch and bridge aggregation for PACl. Based on simplified DLVO theory, particle aggregation was explained in terms of interaction forces. It was demonstrated that PACl outperformed alum in particle agglomeration at lower concentration (1–2 $\mu\text{mol/L}$), owing mainly to the considerable energy barrier reduction and deeper secondary minimum at longer distance induced by high positive polycations. The role of secondary minimum was found to be significant when secondary depth exceeded 12 kT. The interaction energy calculations coincided well with coagulation result for PACl, especially PACl22 with high content Al_{13} . However, other interaction forces prevailed over the electrical repulsion for alum and PACl containing other aluminum species.

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1. Introduction

Particle aggregation in aquatic systems can be achieved by coagulation and flocculation process through altering interactive forces between particles [1,2]. In water treatment practice, hydrolysis products of metal coagulants of Al or Fe are often responsible for the particle interaction, aggregation and subsequent removal. Many coagulation models, mainly for traditional alum, have been proposed; these generally describe the mechanism as a sequence of physicochemical reactions, e.g. hydrolysis, precipitation, adsorption, charge neutralization, coherence and enmeshment. The reactions may be described as progressing in various pathways, depending upon the composition of the aquatic systems [3–6].

Although the use of inorganic pre-polymerized flocculants (IPFs) has significantly increased, studies of the coagulation process using polyaluminum chloride (PACl) have not been well linked with the earlier conceptual models. Several authors have indicated that the chemical species of PACl and their activities lead it to be more effective in coagulation in some cases [7–10]. However, a coagulation mechanism and a model for IPFs have not been as well established as for alum, though some studies have provided useful

guidelines on PACl use [9,10]. The comparative behaviors of traditional metal coagulants such as alum, versus tailor-made IPFs such as PACl, should be more clearly related to mechanism and model in both qualitative and quantitative respects, yet few papers have been published [11–13]. Recently, two distinct adsorption isotherms on microsphere SiO_2 at pH 6.5 have been assigned to alum and PACl with high content Al_{13} , suggesting that the chemical species and their adsorptive behaviors determine the coagulation process [14]. To date, a rigorous theoretical understanding based on interaction force calculations has not been completed, even though Derjaguin–Landau–Verwey–Overbeek (DLVO) theory and model [15,16] have long been applied to more conventional coagulation chemicals and processes.

The DLVO theory primarily addresses electrical double layer and physical interactions. Chemical aspects of coagulation have been integrated with the model based on the chemical behaviors of soluble or insoluble hydroxide species, in these cases, the DLVO theory has generally been treated as a qualitative background for the coagulation model [3–6,17]. Other papers have described the efficiency of particle aggregation in water treatment by applying the DLVO principle with the secondary energy minimum, which have been mainly concerned with the water filtration process [18,19]. Few papers have applied the DLVO model quantitatively to this particle aggregation process when it follows charge-neutralization. Such an approach might be advantageous because the model might describe the loose structure of agglomerated flocs if formed by the trapping

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effect of the secondary energy minimum, which arise from long range van der Waals attraction.

Thus, in this study, particle aggregation under different coagulants at various dosages was monitored by small angle static light scattering technique (SASLS). The in situ measured size and zeta potential of aggregated particles were used to calculate the interaction energy profile consequently. A qualitative/semi-quantitative comparison of the different coagulation mechanisms of alum and PACl are provided accordingly.

2. Methods and experimental

2.1. Floc structure determination by static light scattering

Generally, aggregates of colloidal particles or micron-sized flocs have been shown to be mass fractal objects, as fractal dimension represents a structure which should show up at any length scale. With further application of fractal dimension in water and wastewater treatment, static light scattering is thought to be the rapid and straightforward method in gaining insight of floc structure during treatment processes [20,21]. However, when considering the practical objects in water treatment practice, there always exists a lower limiting characteristic length below which the object cannot be described as a mass fractal [20]. Cautions have been put forward to take care of the results of light scattering, when it is used to derive structure information of flocs from complex systems [20]. Nevertheless, for micron size particles of narrow size distribution, static light scattering has been extensively and successfully applied to probe the fractal nature of aggregates [20–22]. In a scattering experiment, a beam of light is directed onto a sample and the scattering intensity I is measured as a function of wave vector, Q , shown as the following:

$$I(Q) \propto Q^{-D_f} \quad (1)$$

where the magnitude of wave vector can be approximated as follows:

$$Q = \frac{4\pi n \sin(\theta/2)}{\lambda} \quad (2)$$

where n is the refractive index of the medium, λ is the wavelength of the incident light in vacuum, and θ is the scattering angle. The information of floc structure was obtained by plotting $\log I$ versus $\log Q$, provided that the Rayleigh–Gans–Debye [RGD] approximation can be applied in this study; the power law region is distinct from the Guinier and Porod regions and polydispersity effects are insignificant [21]. All these factors can be satisfied not only from investigation of literature but also the experimental results in this study, and will be discussed later.

2.2. DLVO calculation

The DLVO theory assumes that the interaction forces between colloids can be regarded as the sum of two contributions, i.e. van der Waals forces and electrical double layer forces [15,16]. For two identical particles, these forces are always defined as attraction and repulsion, respectively. Dispersed particles will aggregate or remain stable depending on whether attraction or repulsion predominates. For years, methods have been reported to calculate the forces under various conditions. Considering spherical particles in a liquid medium at a sufficiently high electrolyte concentration, a simple but well-documented model is applicable in this study. For the van der Waals force, the well-known Hamaker approach can be applied for two spheres of equal radius as given by [23]:

$$V_A = -\frac{A}{6} \left[\frac{2R^2}{H^2 + 4RH} + \frac{2R^2}{(H + 2R)^2} + \ln \left(1 - \frac{4R^2}{(H + 2R)^2} \right) \right] \quad (3)$$

where A is the Hamaker constant of the interacting media (silica–water–silica), R is the particle radius and H is the separation distance. As the model silica particle is produced artificially with purity above 99.95%, Hamaker constant can be obtained from the calculation and direct measurement. Two values, such as 0.83×10^{-20} J (measured) and 0.61×10^{-20} J (calculated), are available for silica in water [24]. The calculated one was chosen in this study in case of the density variation during coagulation process. Since particle radius ($3.0 \mu\text{m}$) in this study is much larger than the separation distance, $R \gg H$; Eq. (5) can be simplified as

$$V_A = -\frac{AR}{12H} \quad (4)$$

The related electrostatic interaction is proposed to be Eq. (5):

$$V_R = \frac{64\pi R n^0 k T \gamma_0^2}{\kappa^2} \exp(-\kappa H) \quad (5)$$

with γ_0 is calculated by

$$\gamma_0 = \frac{e^{ze\psi_0/2kT-1}}{e^{ze\psi_0/2kT+1}} \quad (6)$$

where n^0 is the bulk ion concentration, z the ion valence, k the Boltzmann constant (1.38×10^{-23} J/K), T the temperature (298 K), and e is the electro charge (1.60×10^{-19} C). ψ_0 is the surface potential of particles and is replaced by the measured zeta potential. The Debye–Hückel parameter, κ , is computed in the usual manner as

$$\kappa^{-1} = \left(\frac{\epsilon \epsilon_0 k_B T}{2e^2 z^2 c_s} \right)^{1/2} \quad (7)$$

where ϵ_0 and ϵ are the permittivity of free space and the relative permittivity, respectively ($\epsilon_0 \epsilon = 6.95 \times 10^{-10}$ C/V m).

Although other interactions between particles in electrolyte suspension might be considered, such as hydration, hydrophobic and steric forces, it was assumed that the predominant, competing forces governing particle aggregation were those quantified above. In fact, as charge–neutralization dominate the particle destabilization and aggregation for both alum and PACl, electrostatic force outweighs other forces in coagulation with inorganic coagulants. To simplify the calculation and establish rather a practical method for coagulants comparison and selection, other forces were neglected in this study. As a result, the total interaction energy was calculated by the following equation:

$$V_{TOT} = V_A + V_R \quad (8)$$

2.3. Silica microspheres and coagulants

Silica microspheres with mean diameter of $3.0 \mu\text{m}$ were used in the coagulation experiment (Suaier Company, China). Particle size distribution and characteristics were determined using a Mastersizer 2000 (Malvern Co., UK). The volume-weighted diameter was used in the interaction energy calculations as the most appropriate value. The surface potential of silica particle was replaced by zeta potential, measured by Zetasizer 2000 (Malvern Co., UK). The prepared coagulants included conventional alum and PACl. The preparation and characterization followed the same method as our previous study reported [14]. From Table 1 and Fig. 1, it can be seen that all the PACl coagulants holds various portions of keggin- Al_{13} , whereas no keggin- Al_{13} can be observed for alum. The portion of monomer decreases with increasing basicity (B) values owing to the injected hydroxyl during pre-hydrolyzation.

2.4. Coagulation test

Silica suspensions were prepared using NaNO_3 (0.01 M) and NaHCO_3 (0.001 M) to provide the desired ionic strength and pH

Table 1
Characterization and speciation of coagulants.

Coagulants	Al _T (mol/L)	Ferron assay			²⁷ Al NMR	
		Al _a (%)	Al _b (%)	Al _c (%)	Al ₁₃ (%)	Al ₁ (%)
Alum	0.1	96.3	2.0	1.7	0	79.2
PACl 1.0	0.104	56.2	42.9	0.9	41.8	43.5
PACl 2.2	0.101	9.4	83.8	6.8	76.7	5.9
PACl 2.5	0.100	1.8	48.6	49.6	37.9	0

buffer. The concentration of the silica suspension was 0.5 g/L. The pH was adjusted to pH 6.5 prior to each coagulation test. Preliminary experiments had demonstrated a pH range of 6.5±0.3 over the range of aluminum concentrations used, and consequently no pH adjustment was performed during the coagulation process. The initial turbidity and zeta potential of working suspension were 130±5NTU and −72±0.5 mv. Jar tests were conducted in a 1L beaker connected to the Mastersizer 2000 (Malvern Co., UK). After injection, suspensions were rapidly mixed at 200rpm for 1min and stirred slowly at 40rpm for 20 min. At the same time, a peristaltic pump (BT00-300M, China) drew the suspension out of the jar continuously to the sample cell for aggregates size and structure measurements. The flow rate was maintained at 2.0mL/s to ensure an integrated floc size distribution. Moreover, zeta potential and residual turbidity were measured after rapid mixing and 10 min sedimentation with Zetasizer 2000 (Malvern Co., UK) and HACH 2100N turbid meter.

2.5. Size distribution and structure analysis

Size distributions and structure information of aggregated particles were determined by small-angle static light scattering with Malvern Mastersizer 2000. The instrument determined the scattered intensity at measuring angles ranging from 0° to 46° with a He–Ne laser light of 632.8 nm. An integration time of 35 s per curve was chosen as a compromise between measuring speed and data quality. The size information of aggregated particle was collected simultaneously during the coagulation process. As a result, fractal information could be calculated by plotting log intensity versus logQ of the scattering wave vector. It should be noted that the absolute aggregate size cannot be obtained, as the observed data are deduced assuming solid spheres rather than porous objects. However, the trend of particle size evolution will be exhibited correctly. The morphology of aggregated particle (floc) was also examined with a HITACHI S-570 scanning electron microscopy. After rapid mixing, a small drop of suspension was placed on the copper tab, which was attached to an aluminum pin stub and allowed to dry at room temperature. In addition, the prepared substrate was sputter coated with gold in case of charging.

Fig. 1. ²⁷Al NMR analysis of PACl at various *B* values.

3. Results and discussion

3.1. Mechanisms interpretation during coagulation

3.1.1. Zeta potential and particle removal

Generally, colloidal particles are thought to be coagulated and aggregated through the actions of charge neutralization, patch aggregation, bridge connection and sweep flocculation in series or synchronously. Although difficulties exist in distinguishing these mechanisms throughout the aggregation process, some insight can be expected in examining the zeta potential variation and particle removal as a function of coagulants dosage. As Fig. 2 indicates, the coagulation region can be divided into two parts according to the zeta potential, for which part I refer to the negative zone and part II positive zone, respectively. Although similar charge properties of silica particles can be observed upon the injection of the four coagulants, turbidity variation exhibits reversely between alum and PACl. For PACl, residual turbidity of suspension decreases rapidly and lower than that of alum in part I, whereas remarkable increase of turbidity observed in the part II with increasing dosage. Correspondingly, the alum keeps a relatively low turbidity level in the part II. Clearly, the dominant mechanisms for alum and PACl in part I and II are rather distinct due to their dominant species during the coagulation. It was generally accepted that the positively charged keggin–Al₁₃ of PACl cause efficient charge compensation and result in effective particle aggregation at the lower dosage [10,11]. Hence, strong charge-neutralization and electro-patch coagulation are

Fig. 2. Zeta potential and residual turbidity as a function of coagulant dosage: (a) zeta potential and (b) residual turbidity ([Al]_T equals to the total aluminum concentration added in).

Fig. 3. Floc size as a function of time at different coagulant dosages: (a) $[Al]_T = 10^{-6}$ mol/L and (b) $[Al]_T = 10^{-5}$ mol/L.

thought to be the dominant mechanisms for PACI in part I. This kind of electro-patch coagulation differs from that of alum, with polycations adsorbing and complexing on the particle's surface rather than precipitates [13]. On the other hand, bridge-connection can also be included since aggregated Al_{13} and other polymeric species formed during pre-hydrolyzation [14]. More evidence can be seen from the following floc size distribution and floc structure. In part II, particles are coated with more positive polycations leading to a strong repulsion and no aggregation at higher dosages. It should be noted that a slow turbidity increase is observed for the PACI25 due to the great portions of larger polymers (Table 1). In this regard, bridge-connection enables particle linkage in spite of strong repulsions. For alum, the coagulation behavior agrees well with previous study and the main mechanisms are charge-neutralization and precipitate patch coagulation in part I, and sweep flocculation in part II, respectively. Although the coagulation I mechanisms of such PACI

and alum have been studied and summarized extensively [9–12], a quantitative description has not been achieved yet. The following part will discuss the floc structure for both alum and PACI coagulants, particle interaction profiles will be summarized quantitatively later based on the floc size distribution and charge variations.

3.1.2. Floc size distribution and floc structure

The rate of particle aggregation is significantly influenced by the coagulation mechanisms. With different mechanisms dominate the coagulation process at part I and part II, floc size during the coagulation process and size distributions for coagulants under various dosages are shown in Figs. 3 and 4. For alum and PACI coagulants, the size increasing curves are indicated in Fig. 3(a) and (b). At lower aluminum concentration, flocs size increased to $\sim 200 \mu m$ for PACI. For alum, the floc diameter began to increase at $10 \mu mol/L$ ($\sim 50 \mu m$) and reached to hundreds micrometers at much

Fig. 4. Floc size distribution at the end of coagulation process for different coagulants under various dosages.

higher dosage of 100 $\mu\text{mol/L}$ (not shown). Particle aggregation occurs initially due to the particle–particle collisions, which leads to small aggregates (microflocs) and later particle–aggregate and aggregate–aggregate collisions. As a result, larger aggregates (flocs) formed as porous objects with highly irregular and open structure. As can be seen from Fig. 4(a) and (b), PACI coagulants exhibit a wider size range of larger flocs at the lower dosages of 1–2 $\mu\text{mol/L}$. While for alum, there are almost no particle aggregation occurred at 1 $\mu\text{mol/L}$, and aggregates with larger size formed till dosage of 5 $\mu\text{mol/L}$. It can be suggested that the Al_{13} of PACI enhanced the particle collision and resulted in aggregates size increase at lower dosage. With high content Al_{13} and larger size hydroxyl aluminum polymers, microflocs of 20–30 μm and flocs of 200–300 μm were formed for PACI22 and PACI25 at dosage of 1 $\mu\text{mol/L}$, respectively. However, higher dosages of 5–10 and 100 $\mu\text{mol/L}$ were required to achieve the same size increase for alum as Fig. 4(b–d) indicates. On the other side, no aggregation occurred for PACI at higher dosages due to the strong repulsion between positively charged particles, coinciding with the re-destabilization area in Fig. 3. Generally, the adsorption of positively charged polynuclear species onto the negatively charged particles is responsible for the charge neutralization coagulation [17]. As the coagulant dosage would affect the conformation of polynuclear species and subsequent adsorption, different mechanisms are involved for alum and PACI. With stable and high positively charged keggins- Al_{13} , PACI can easily adsorb and neutralize more than one of the negatively charged silica particles. Due to the strong electrostatic attraction and inorganic polymer bridging, they may bind together to form the primary aggregates. In virtue of the open surface structure and residual positive charge, these primary aggregate can continue to agglomerate each other so as to form micro-flocs through self-assembling. Accordingly, particle aggregation mechanisms as polycation-patch coagulation and bridge connection are thought to be operative besides charge neutralization for PACI. As coagulant dosage increased, negatively charged particles transferred to be positively polymer-coated aggregates. This kind of aggregate would repel each other and aggregation would be impaired consequently. For alum, with in situ hydrolyzed species of lower positive charge, particle destabilization can also be viewed as an adsorption process. However, owing to the species transformation of such in situ formed polynuclear species, precipitates would appear on the surface and result in precipitate coverage on the charged surface. As dosages increase, more precipitates formed not only on the particle surface but also in the solution, particle collisions expanded from particle–particle to particle–precipitate and precipitate–precipitate, leading to larger flocs at the higher dosage. Obviously, the structure of such flocs is different from that of PACI, owing to their distinct particle aggregation mechanisms induced.

Table 2
Mass fractal dimension at the end of coagulation process for all coagulants under various dosages.

Dose ($\mu\text{mol/L}$)	Alum	PACI10	PACI22	PACI25
1	–	2.16	2.07	2.03
2	–	1.91	1.98	2.02
5	2.05	2.04	–	1.95
10	2.07	2.13	–	2.05
100	1.88	–	–	–

The corresponding mass fractal dimensions of all the coagulants under various dosages are presented in Table 2. The D_f value of initial silica suspension was also measured and was about 2.2. It should be noted that silica particles experienced stabilization–aggregation–restabilization along the increasing dosage of coagulants. In this regard, the scattering exponent of power-law region was extracted as mass fractal dimension when floc grows rapidly. Comparing the D_f values between alum and PACI, for optimal dosage, it is possible to observe that PACI produce denser flocs than alum, due to the more pronounced polycation-patch coagulation at the lower concentration for PACI (part I). However, looser flocs formed at the dosage of 100 $\mu\text{mol/L}$ for alum, $D_f \sim 1.88$, owing much to the sweep flocculation then. In addition, the mass fractal dimension variation during the coagulation process is also shown in Fig. 5, for PACI and alum under different concentrations. For PACI and alum, the D_f decreases abruptly during the first minutes of coagulation because single silica particles were aggregated into porous aggregates with addition of coagulants. For alum, D_f decreases and then increases slightly, because the formed flocs are rather loose and would break down more easily with the turbulent environment. Whereas for PACI, the D_f values change with the coagulant dosages as different mechanisms are competing depend on coagulants speciation. For PACI22 (higher dosage of 2 $\mu\text{mol/L}$) and PACI10 (higher dosage of 5 $\mu\text{mol/L}$), denser flocs formed as patch-coagulation mechanism is more pronounced associating with higher positive charge density then. On the other side, with certain degree of bridge connection occurred for PACI25, PACI22 (lower dosage of 1 $\mu\text{mol/L}$) and PACI10 (lower dosage of 2 $\mu\text{mol/L}$), the mass fractal dimension decreases and increases slightly, since these flocs are more porous and become denser with further mixing. Compared with the coagulation test results, coagulation mechanisms deduced from the floc structure variation correspond well with that from zeta potential and residual turbidity.

3.2. DLVO calculation

3.2.1. Interaction energy profile

Given the condition of DLVO theory for predicting particle stability as summarized earlier, the total interaction energy was

Fig. 5. Mass fractal dimension during coagulation for alum and PACI under several dosages.

Fig. 6. Calculated DLVO interaction energy profiles between silica particles upon the addition of coagulants at the dosage of 10^{-6} mol/L (a) and 10^{-4} mol/L (b). The depth and location of the secondary minimum are highlighted in the (a)-1 and (b)-1, respectively. The net attraction occurs at different dosages for alum, PACI10 and PACI22 as indicated in (c).

calculated using Eqs. (4)–(8), and particle diameter was chosen at the moment immediately after rapid mixing of 1 min. Based on the floc size distribution, it can be suggested that compact aggregates close to spherical occupy the suspension at that time, and calculations can be carried out assuming identical spherical particles. Parameters such as Hamaker constants were chosen disregarding the surface roughness, and the ζ -potential was taken as the surface potential. Although the DLVO theory might not be strictly applicable, a qualitative/semi-quantitative interpretation is attempted to indicate the relative changes in the interaction energy during coagulation for different coagulants.

Fig. 6 shows the potential curves calculated from the simplified DLVO theory for silica microspheres upon the addition of coagulants at the dosages of 10^{-6} mol/L and 10^{-4} mol/L. Although interaction energy profiles under other dosages were calculated, we choose

these two dosages in part I and part II corresponding to the before-mentioned coagulation mechanisms. Apparently, the interaction energy barrier reduces greatly for PACI22 at the low dosage of 10^{-6} mol/L, owing to the adsorbing polycations to decrease the negative charges on the surface, and lead to a sharp reduction of electrical repulsion later. However, the same reduction occurred for alum at high dosage of 10^{-4} mol/L. Although an relative high interaction energy of ~ 1000 kT holds between particles coated with polycation or precipitates, effective coagulation can still be observed in Fig. 2 for PACI22 and alum, respectively. Based on the theory, such a high-energy barrier would prevent particle aggregation and this deviation may attribute much to the assumption which only two interaction forces were considered. Nevertheless, the relative low energy barriers at these conditions coincide with the low turbidity in coagulation tests. In this regard, the simple interaction energy calculation can be viewed as a practical method for dosage prediction in water treatment, whereas some modifications need to be made beforehand. For PACI containing keggins- Al_{13} with high positive charge, electrostatic force is the driving force to create effective particle collisions and later particle aggregation. The interaction energy calculations show that a much lower dosage is needed for PACI than that of alum to produce a favorable condition, when no repulsion exists between particles (Fig. 6(c)). In fact, such optimum dosage of PACI10 and PACI22 proportions to the content of keggins- Al_{13} in this study. Although other forces may prevail over the electrostatic repulsion that fast coagulation occurred for PACI25 without any favorable conditions, a stoichiometry relationship between keggins- Al_{13} concentration and optimum dosage can be deduced based on the coagulation results and calculation data. However, study on this issue pays much less attention on the aspect of interaction calculation due to the complexity and transformation of aluminum species. By virtue of its stability and convenient confirmation, keggins- Al_{13} can be used not only to evaluate the coagulation efficiency, but also predict the optimum dosage of PACI. Further work on the bridging force of Al_{13} is required, as bridge connection was one of the dominant mechanisms for PACI in part I accounting for the deviation of PACI25 in interaction energy profile.

3.2.2. Particle aggregation trapped at the secondary energy minimum

It is well known that particles should be held together in the deep primary minimum on curves where the potential energy barrier is overcome at close separation distances. However, owing to the different distance dependences of the attractive and repulsive forces, a shallow secondary minimum also arise at larger distance, with the attractive force again predominating. This secondary minimum is mainly related to the particle size and ionic strength, which determine the value of κ , and hence the repulsion range. Particles of $1\ \mu\text{m}$ or larger may have a deep secondary minimum of a few kT to initiate reversible particle aggregation [24]. Table 3 indicates the depth and corresponding distance of the secondary minimum. It can be seen that the secondary well depth of silica particles changes with the dosage for different coagulants. On the whole, the deepest well for PACI appears at low dosages of $1\text{--}2 \times 10^{-6}$ mol/L and a relatively high dosage of 5×10^{-6} mol/L for alum. Previous reports stated that “As the height of the potential energy barrier increase, for a given value of the depth of the secondary minimum, the fraction of particles that coagulating in the primary minimum becomes negligible and secondary minimum coagulation dominates” [25]. In addition, the importance of reversible attachment of colloidal particles in secondary energy minimum has been well proved by the deposition and reentrainment through porous media [18,19]. Based on the discussion of coagulation mechanisms in the former section, patch coagulation and bridge connection are thought to prevail over charge neutralization when particle surfaces have charges of the same sign. For PACI22 with high content of Al_{13} , the deepest

Table 3
Calculated depth and distance of secondary minimum.

Coagulant	Coagulant dosage($\mu\text{mol/L}$)									
	1		2		5		10		100	
	V_T (kT)	h (nm)	V_T (kT)	h (nm)	V_T (kT)	h (nm)	V_T (kT)	h (nm)	V_T (kT)	h (nm)
Alum	10.10	26	12.35	21	14.65	19	–	–	13.04	20
PACIB10	8.64	27	17.39	21	–	–	10.26	22	8.77	26
PACIB22	16.28	20	–	–	10.85	22	9.20	25	8.62	25
PACIB25	9.73	26	13.63	24	12.24	19	10.10	21	9.22	24

Fig. 7. The secondary energy minimum as a function of distance for silica particles added with (a) alum and (b) PACI22 under different dosages.

Fig. 8. SEM images of aggregated silica particles with addition of alum and PACI22 under the dosage of 10^{-6} mol/L (a) and (c), and 10^{-4} mol/L (b) and (d).

secondary well appeared and significant particle removal reached at the same time. For alum and other PACl with different content Al_{13} , particle aggregation stepped into critical coagulation when secondary well depth exceeded 12 kT. However, the secondary minimum depth decreases after charge neutralization with increasing dosage for all the coagulants, whereas minor reduction of less than 2 kT for alum. In this regard, the secondary well is important for PACl to trap more particles at rather lower dosages, and increasing electrostatic forces would pull away particles of same positive charge at the high dosages. On the contrary, the secondary well would still contribute to the particle aggregation with the addition of alum, as other forces like complexation would be the controlling forces at higher dosages (Fig. 7).

3.3. Floc morphology

Observation of floc morphology was performed by SEM to provide more evidence for the distinct particle aggregation mechanisms induced by alum and PACl. It should be noted that images were taken after 24 h air-drying, which means species may have experienced transformation. Nevertheless, the observed floc morphology can provide valuable information on particle interactions and allow inferences regarding coagulation mechanisms. Selected images were taken at 1×10^{-6} mol/L and 1×10^{-4} mol/L for alum and PACl22, respectively, highlighting the significance of keggings- Al_{13} in this regard. At the low dosage, as seen in Fig. 8(a) and (c), silica particles form primary aggregates for alum (Fig. 8(a)) and micro-flocs for PACl22 (Fig. 8(c)), respectively. The corresponding floc sizes increase from ~ 10 to ~ 30 μm , which are similar to the results by light scattering. According to the coagulation results and interaction energy calculations, the relatively larger floc formed by PACl22 attribute much to the high positively charged Al_{13} and the deeper secondary well between polycation-patched particles. Although hydrolyzing species of alum would also absorb on the negative particle forming positive patches, this relatively low positive patches can attract few particles prevented by high-energy barriers. With further coagulant addition, those hydrolyzing species increased and transformed into most amorphous precipitates. Consequently, particles with positive patches cannot only aggregate through attraction, but also be wrapped by those amorphous precipitates forming larger flocs of ~ 100 μm (Fig. 8(b)). On the other side, further hydrolyzation of PACl was postponed by virtue of its stability. Thus few precipitates formed and polycation-patched particles repel to each other when they were completely positively charged, as Fig. 8(d) indicates. In this regard, the floc morphology allows the aggregation pathways induced by different coagulants to be distinguished. It may also be predicted that the voluminous flocs produced by heavy alum dosage would be advantageous in processes utilizing gravity sedimentation, and the lesser dosages of PACl22 inducing micro-aggregates would be optimal for contact coagulation technologies such as microfloc or membrane filtration, flotation, etc.

4. Conclusion

Particle aggregation induced by alum and PACl can be interpreted through jar test, light scattering and interaction energy calculation. As a result, distinct coagulation mechanisms were demonstrated by variations of zeta potential, mass fractal dimensions and interaction energy profiles. Charge neutralization and polycation-patch coagulation are suggested to be the main coagulation mechanisms for PACl, coupled with bridge connection when

larger polymer species formed in situ or in advance. On the other side, charge neutralization and sweep flocculation are involved for alum due to the hydrolyzing species in the solution. Water treatment technologies such as micro-floc filtration and flotation would be better employed for PACl application, as their coagulation pathways and formed structure are distinct from alum.

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