Dependency of polyelectrolyte complex stoichiometry on the order of addition
2. Aluminum chloride and poly-vinylsulfate

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Abstract

In the first part of this series it was shown that the stoichiometry of complexation between oppositely charged polyelectrolytes became increasingly dependent on the order of addition as the concentrations of monovalent and divalent ions were increased. This study considers the effect of aluminum ions on titrations between solutions of a strong poly-acid and a strong poly-base. In addition, the titratable charge of aluminum ion itself was also investigated. It was found that aluminum ions can interfere with the results of charge titrations, in the sense that the titration results became unpredictable. Stoichiometric relationships between the amount of aluminum present and the amount of titrant required to achieve streaming current values of zero were obtained only at pH values associated with a maximum in the amount of titrant needed to neutralize a given concentration of dissolved aluminum. The results are consistent with complexation between the anionic titrant and polynuclear species of aluminum, where the relative proportion of such species depends strongly on the molar ratio of OH to Al.
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1. Introduction

In the first part of this series [1] it was shown that endpoints of titrations between a strong poly-acid and poly-base, when detected by the streaming current method, depended on the order of addition. It was observed that this dependency became more pronounced with increasing 1:1 or 1:2 electrolyte concentration. The present investigation involves similar systems except for the use of aluminum chloride instead of simpler salts.

Interactions between aluminum ions and polyelectrolytes play major roles in such applications as water and wastewater treatment [2–4], and papermaking [5–8]. In these applica-

tions the streaming current method has emerged as a useful tool to monitor complexation and neutralization phenomena during process optimization [9,10]. There is a need to further improve the measurement protocols, and therefore it is important to understand the principles involved in the streaming current method and also to elucidate the role of soluble aluminum compounds as interfering species.

According to St. John [10], aluminum ions "interfere with" titrations involving oppositely-charged polyelectrolytes. In support of this statement, aluminum ions have been shown to affect the endpoints of such titrations that were carried out with either colorimetric [7,10–13], or streaming current [14] detection of the endpoints. In another study, aluminum ions caused a systematic deviation from a roughly linear relationship between streaming current and electrophoretic mobility [15].

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In seeking a definition for the word "interfere," it is worth considering the conditions under which accurate and reproducible polyelectrolyte titrations can be expected. These conditions include rapid and complete complexation between the respective polyelectrolytes to result in no residual (uncomplexed) polymer in solution at the equivalence point of the titration. A substance "interferes" in a polyelectrolyte titration if it has the capability to complex with either one of the titrants with sufficient strength as to affect the endpoint. The most troublesome types of interferences would be those that cause deviations that cannot be explained by clear-cut stoichiometric arguments.

Trivalent aluminum can be classified as a hard Lewis acid, having an exceptionally small ionic radius relative to its charge [16]. As such, the aluminum ion has a very strong tendency to complex with such ligands as water, OH^-, sulfate, and many other anions that are ubiquitous in industrial applications [16]. In addition, partially hydroxylated aluminum ions have a strong tendency to associate into dimers and certain other multi-aluminum ionic species [3,17–21].

The relative abundance of the different aluminum species in solution has been found to depend on such variables as pH, total aluminum concentration, and time of equilibration. Most notable in this work was the identification of conditions leading to formation of polynuclear ionic species of aluminum [22–25]. The presence of such polynuclear ions was confirmed by colloidal chemical analyses, based on the superior coagulating ability of large, multivalent ions [26]. Akitt et al. [22], Crawford and Flood [25], and Bottéro et al. [23] carried out important work by ^{27}Al nuclear magnetic resonance (NMR) to identify $[AlO_4Al_{12}(OH)_4(H_2O)_{12}]^{7+}$ as the most stable of these polynuclear ions within a pH range of about 4–5 at $AlCl_3$ concentrations of 0.1 M or higher. In the literature this species has been called the Al_{13} ion. In general the proportion of the Al_{13} ion in a solution tends to increase with hydroxylation up to a ratio of approximately 2.3 OHs per Al, followed by a sharp decline in favor of $Al(OH)_3$ with further increases in addition of base, relative to the amount of aluminum present. In addition, significant amounts of the ions $Al(OH)^{2+}$ and $Al(OH)_2^+$ are known to exist in solution, though the concentrations of these two ions tend to be relatively low within the pH ranges and total concentrations considered in the present work [17].

Although one might expect, due to its high valency [26], that trivalent aluminum ion ought to form strong complexes with negatively charged polymers, results of various studies suggest that the impact of the polynuclear ions is much more important [3,24,27–30]. For instance, Exall and van Loon [24] found a high correlation between the concentration of Al_{13} present in solutions and their ability to coagulate raw water samples and remove tannins from the solution phase. In papermaking applications, Strazdins [7] found sharp maxima, as a function of the ratio of added OH^- ions to Al, in the ability of aluminum-containing mixtures to complex with an anionic polymer titrant. Also it was found that pH values corresponding to these maxima tended to decrease with in-

creasing aluminum concentration, a finding that is consistent with conditions that would be expected to maximize the proportion of polynuclear ions [7].

Since the present work aims to understand interferences to polyelectrolyte titrations by aluminum ions, it is worth noting factors that affect the proportion of different aluminum species in solution. Crawford and Flood [25] were apparently the first to show that the sulfate ion can interfere with the formation of Al_{13}, an effect that is consistent with sulfate's role as a ligand. Such complexation helps to explain, for instance, the fact that aluminum sulfate has a much lower tendency to reverse the zeta potential of negatively charged particles in suspension, compared to solutions of aluminum chloride, after suitable adjustment of pH [7,27,29]. Strazdins [7] and Trksak [8] showed that the coagulating ability of aluminum sulfate or polyaluminum chloride solutions decreased with aging of the solution. Strazdins [31] showed that the "charge decay" of aluminum sulfate solutions was accelerated at high temperature, but that part of the decay could be partially overcome by mixing under conditions of high shear. The effect of shear was attributed to the entrapment of positively charged aluminum species within an impervious coating of gelatinous $Al(OH)_3$ floc.

To provide focus for the present investigation, two hypotheses are considered, as follows.

First it is proposed that the effects of aluminum ions can be understood as a sum of interactions involving the various aluminum species that are present. Different aluminum ionic species are known to differ in terms of formal charge, and these charges represent a theoretical maximum in the amount of anionic titrant polymer that would be needed to complex with the aluminum-containing solution to reach an electrokinetic endpoint of zero.

The second hypothesis is that complexation of aluminum species with polyelectrolytes of opposite charge may deviate strongly from a stoichiometric relationship. Such deviations could be attributed to such factors as (a) weaker complexation, (b) slower or interrupted progress towards equilibrium due to the slow dynamics of polymeric rearrangements, (c) a loss of soluble aluminum species in favor of $Al(OH)_3$, and (d) the possible entrapment of positively charged aluminum species within layers of less reactive aluminum hydroxide [7]. A systematic investigation was undertaken to test these hypotheses by looking at the effects of changes in the order of addition for titrations involving aluminum chloride and polyvinyl sulfate (PVSK).

2. Experimental

2.1. Materials

Similar to the study in the first part of this series [1], the polyelectrolytes used consisted of poly-diallyldimethylammonium chloride (poly-DADMAC), a highly charged poly-base of 400–500 kDa molecular mass (Aldrich) and

polyvinyl sulfate, a poly-acid of 170 kDa molecular mass (Aldrich). Aluminum chloride (AlCl$_3$·6H$_2$O) was purchased from Fisher Chemicals. Ludox® TM-50 colloidal silica of 22 nm radius (Aldrich) was also used in electrokinetic experiments.

2.2. Titrations to evaluate interference by Al ions

The titrations were carried out using a PCD 03 pH streaming current instrument (Mütek Analytic). In these experiments two levels PVSK in 6 ml of solution were added to 30 ml quantities of either 1 or 10 mM solutions of aluminum chloride. The lower level involved 0.87 μeq. of PVSK and the higher level involved twice that amount. The total pretitration volume was 36 ml in each case. These initial samples were then titrated with poly-DADMAC (0.928 mN).

2.3. Titrations with adjustment of pH

The effect of pH on the titration of aluminum ions with PVSK was first investigated by using pH values of 4.5 and 5. These pH levels are common in acidic papermaking systems. Because of limitations inherent to the streaming current device, at least 10 ml volume of aqueous solution was required for reliable results. Two procedures were followed, one in which PVSK was used as the sample to be titrated with AlCl$_3$ solution and the other in which PVSK was used as titrant. When PVSK was used as sample, it was first diluted with 15 ml of deionized water (DW). In the case of samples containing aluminum ions, aliquots of 15 ml aluminum chloride solution were used directly without any dilution. In all cases the pH of the system was adjusted by addition of 0.01 M NaOH and 0.01 M HCl solutions.

Experiments were organized into two series according to the way the pH was adjusted. In the first series the pH was adjusted during the course of the titrations. In other words, either HCl or NaOH was added dropwise, after each 0.1–0.3 ml addition of titrant, to keep the pH as constant as possible. In the second series, the pH was adjusted before the titrations, allowed to change during the titrations, and then adjusted back to the selected value of pH, if necessary, after a zero value of streaming potential was reached. Additional titrant was added in those cases where adjustment of the pH caused a change in the streaming current signal (such shifts in signal always required additional titrant to reach an output value of zero). The titrant volume was taken as the sum of all of titrant added until the pH adjustment did not affect the sign of the streaming current.

Additional experiments were carried out in order to examine the charge of the aluminum ions, which could be detected by titration with PVSK over a wider range of pH values. In each experiment 15 ml of AlCl$_3$ solutions of three different concentrations (0.1, 1 and 5 mM) were used as the initial sample, and the pH was adjusted before and during the titrations. The titrations were carried out using a Mütek PCD-T auto-titrator.

2.4. Zeta potential

Colloidal silica was used as the dispersed phase to make the electrokinetic measurements possible. Aluminum chloride solution concentrations were 0.1 and 1 mM. In each experiment 2 ml of 1 wt.% silica was added to 30 ml aluminum chloride solution, which was previously adjusted to the desired pH. A Laser Zee Meter Model 501 was used to measure the electrophoretic mobility of well-mixed dispersions of colloidal silica and the zeta potential was calculated according to the Henry equation [32].

2.5. Turbidity

Turbidity tests were carried out with a series of test tubes, with the samples prepared in a manner similar to the zeta potential experiments. After the addition of colloidal silica, the turbidities were measured by means of a DRT-15CE Turbidimeter from HF Scientific Inc. The final concentration of colloidal silica was 909 ppm in each case. After mixing, the measurements were carried out periodically, at specific time intervals, within a period of 24 h.

3. Results and discussion

3.1. Aluminum interference

Table 1 shows experimental results that support the assertion that aluminum ions interfere with titrations that are carried out between polyelectrolytes of opposite charge [10]. In this discussion, the word "interfere" implies an unpredictable scatter in the data, and that the problem cannot be overcome simply by accounting for the stoichiometry of charged groups on the substances under consideration. In the set of experiments corresponding to Table 1, poly-vinylsulfate was added to two different concentrations of aluminum chloride solution as the samples. The mixtures were then back-titrated with poly-diallyldimethylammonium chloride to a streaming current endpoint of zero. Results were repeated at two levels of PVSK addition, as noted in Section 2.

As shown, addition of the aluminum chloride decreased the amount of poly-DADMAC needed to reach a streaming current output signal of zero. This finding is consistent with an assumption that one or more aluminum species had at least some ability to form a complex with negatively charged groups on the PVSK macromolecules and block the charged sites from access to poly-DADMAC. However, in line with our use of the term "interfere", there was no simple relationship between the amount of aluminum compound added and the degree of shift of the titration between PVSK and poly-DADMAC. Especially troubling, from this perspective, was the fact that in at least one case a higher amount of aluminum chloride resulted in less interference with the titration between PVSK and poly-DADMAC.

Table 1
Effect of aluminum chloride on the amount of poly-DADMAC required to titrate PVSK solution to a streaming current endpoint of zero

	$AlCl_3$ concentration (mM)		
	0	1	0.1
Poly-DADMAC at endpoint (μeq.) (0.87 μeq. of PVSK)	0.87 ± 0.01^a	0.19 ± 0.05^a	0.37 ± 0.18^a
Poly-DADMAC at endpoint (μeq.) (1.71 μeq. of PVSK)	1.71 ± 0.01^a	0.40 ± 0.03^a	0.43 ± 0.08^a
PH at start of titration	6–7	4.10	3.69

[a] 95% confidence intervals of the measurement results.

As a means of defining the efficiency with which soluble aluminum ions form complexes with the anionic polyelectrolyte, calculations first were carried out in terms of the Al^{3+} ion, neglecting the existence of other stable ionic species. The titration data were compared to the theoretical efficiencies that one would anticipate based on a model of hexa-hydrated Al^{3+} ions interacting with the sulfate groups of the PVSK. If such an interaction were to take place with 100% efficiency, then the expected stoichiometry would be three equivalents of charge of the poly-acid for each one mole of aluminum. However, when this model is applied to the numbers in Table 1, the apparent equivalents of PVSK complexing with each mole of aluminum were scattered between 0.003 and 0.09. In other words the aluminum-containing solution was highly inefficient relative to the idealized stoichiometric model based on strong complexation of the unhydrolyzed aqueous aluminum ions with PVSK. Also, there was no clear pattern in the data. Another possibility is that aluminum ions were in a much lower charged form instead of hexa-hydrated Al^{3+} ion.

One suspected contributing cause of the non-stoichiometric results in Table 1 was the fact that the pH was not held constant. Aluminum ionic species are known to depend on pH, which affects their degree of hydrolysis [36–38]. Also, it is to be expected that the complexation interaction between poly-DADMAC and PVSK should be much stronger, compared to a competing interaction between aluminum species and PVSK. To address these issues, the remaining work was carried out with direct titrations between PVSK and aluminum ion solutions, with the pH being controlled in different ways. In addition, following the practice introduced in part 1 of this series [1], the order of addition of the interacting compounds also was varied.

3.2. Direct titrations at controlled pH — PVSK as sample

This set of experiments was carried out with PVSK solution initially present in a beaker, adjustment of the pH to either 4.5 or 5.0, and then gradual titration with aluminum chloride solution. The pH was adjusted to its starting value after addition of each aliquot of titrant. The initial concentration of PVSK solution was 5.4×10^{-5} N in terms of charged groups, and aluminum was added in the form of a 0.1 mM or 1 mM solution of aluminum chloride.

As shown in Table 2, the aluminum compounds acted as a more efficient complexing agent at pH 5.0, compared to 4.5, for both concentration levels. At pH 5.0 the apparent charge of the aluminum species was 0.5–0.65 equivalents per mole of aluminum. By contrast, at pH 4.5 the apparent charge, in terms of the streaming current endpoint, was about 0.25 equivalents per mole of aluminum. Before attempting to interpret these findings it is also worth noting that the results depended to a significant extent on the concentration of the titrant (aluminum chloride solution).

To account for the general trend of data in Table 2, calculations were carried out based on a working hypothesis that all of the aluminum was present in the form of the $[AlO_4Al_{12}(OH)_4(H_2O)_{12}]^{7+}$ (or "Al_{13}") ion proposed by others [21]. The ratio of seven charges per 13 aluminum atoms, corresponding to the ion's valence, implies a theoretical charge contribution of 0.538 charge equivalents per mole of aluminum. Though the approximate agreement of this number with the values in Table 2 obtained at pH = 5 could be fortuitous, the results are consistent with an efficient, high-affinity interaction mainly between this ionic species and PVSK. The fact that the titratable charge of the aluminum-containing solutions fell rapidly at lower ratios of OH to Al, where one would expect monomeric species such as $Al(OH)^{2+}$ and $Al(OH)^{2+}$ [17] having higher ratios of formal charge per aluminum, suggests that such species do not complex strongly with PVSK.

3.3. Direct titrations at controlled pH — $AlCl_3$ as sample

In the next set of tests to be discussed, the order of addition was reversed. Aluminum solution was placed first in the testing vessel (as sample), and the PVSK served as the titrant.

Table 2
Ratio of PVSK negative groups per aluminum atom at the streaming current endpoint in titrations of PVSK solutions with $AlCl_3$ as titrant (PVSK as sample)

Conditions	Aluminum concentration in titrant solution(mM)	
	1	0.1
Ratio of PVSK equivalents per mole of Al at pH 4.5	0.27 ± 0.16^a	$<0.25^b$
Ratio of PVSK equivalents per mole of Al at pH 5.0	0.64 ± 0.05^a	0.50 ± 0.03^b

[a] 95% confidence intervals of the measurement results.

[b] Overflow of the sample reservoir in the streaming current device precluded continuation of experiment beyond this point at the higher dilution.

Table 3
Ratio of PVSK negative groups per aluminum atom at the streaming current endpoint when adding PVSK (titrant) to aluminum chloride solutions (sample)

pH	Method of pH control	Aluminum concentration in initial solution (mM)	
		1	0.1
4.5	After each aliquot	0.56 ± 0.04[a]	0.10 ± 0.06[a]
	Simultaneous	0.48 ± 0.03[a]	0.21 ± 0.05[a]
5.0	After each aliquot	0.27 ± 0.01[a]	0.48 ± 0.01[a]
	Simultaneous	0.26 ± 0.01[a]	0.48 ± 0.01[a]

Two methods for pH control are compared: (1) adjustment of pH during the course of experiments and, (2) pH and end point adjusted simultaneously at the end of titration.

[a] 95% confidence intervals of the measurement results.

Results of preliminary tests showed that even after initial pH adjustment of the aluminum chloride solutions, subsequent addition of PVSK caused substantial shifts in pH. To overcome such shifts, experiments were repeated under two different methods of pH control as described in Section 2. Results are given in Table 3.

Results in Table 3 show agreement between the two methods employed to adjust pH. Most importantly, an apparent conflict is observed with regards to the ratio of negative groups per Al atom. At the higher initial concentration of aluminum chloride solution the most efficient complexing ability, as indicated by the higher values, was obtained at pH = 4.5. However, at the lower initial concentration of aluminum the highest values of the ratio were obtained at pH = 5.0. The values also were different from the results of experiments shown earlier in which PVSK served as the sample.

To interpret the results in Table 3 it is important to note that the relative abundance of aluminum species in solution is expected to be a function of overall aluminum concentration, in addition to pH [38]. In particular, increasing aluminum concentration is expected to decrease the value of pH at which the polynuclear aluminum ion species has its greatest relative abundance. Though this circumstance does not prove the mechanism, it is at least consistent with the finding that higher efficiency of the aluminum chloride solution was observed at a higher pH in the case of the lower initial concentration. It is worth noting that the results for PVSK titrated with 0.1 mM $AlCl_3$ were fairly close to those for 0.1 mM $AlCl_3$ titrated with PVSK. The ratios of PVSK negative groups per aluminum atom in both cases were very close. At this low aluminum concentration the order of addition was found to be irrelevant with respect to the neutralization of charge. However, at high $AlCl_3$ concentrations, i.e., when Al polymeric species are more likely to be present, the order of addition played a role, as judged by the different results attained for the results for the two different orders of addition involving 1 mM $AlCl_3$ concentration. This phenomenon is consistent with the presence of trapped non-equilibrium complexes between Al-species and PVSK. The entrapment of charged aluminum species within a protective sheath of $Al(OH)_3$ floc [7],

at least under the conditions used in the present experiments, can be also a contributing factor.

To further test the explanation given above, experiments were carried out over a wider range of pH and initial concentrations. It was of interest to consider lower values of pH where different species of aluminum can be expected to predominate. Due to the relatively good agreement between tests with the two different pH control methods, all further work to be reported was obtained with pH adjustments being made to the initial solutions and during the course of the titrant additions by the automatic titrator.

3.4. Apparent charge as a function of pH

To reinforce the findings shown in the previous section, a series of titrations were carried out with aluminum chloride solutions of selected concentrations (see Section 2). The pH was adjusted before the titrations, and then adjusted back to the target value, if necessary, along with the titrant addition. As shown in Fig. 1, the ratio of PVSK to aluminum required to achieve a zero endpoint of the streaming current test depended on pH. At any given value of aluminum concentration in the initial solution, the apparent charge of the aluminum rose to a maximum with increasing pH and then decreased again. For each aluminum concentration the maximum was achieved at a different pH value. The higher the aluminum concentration was, the lower the pH at which the aluminum achieved its maximum ability to complex with PVSK. Notably, under the conditions of testing there was essentially no apparent ability to complex with the PVSK titrant when the pH of the aluminum-containing solution was either below 3.5 or above 8. Because hydrated Al^{3+} species are expected to account for most of the aluminum at pH < 3 [17], the present results showed no significant complexing ability of these species with PVSK.

At each of the three concentrations of aluminum considered, the effective charge approached a maximum of about 0.5 equivalents per mole of aluminum (OH/Al = 0.52, 0.53, 0.52 with aluminum concentration 1.01, 0.507,
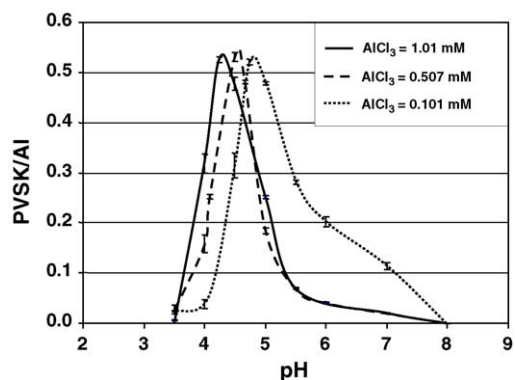

Fig. 1. Equivalents of PVSK required to titrate $AlCl_3$ solutions to a zero streaming current endpoint as a function of pH. The inset shows the amount of $AlCl_3$ used as initial sample to be titrated (based on total volume).

and 0.101 mM, respectively). This value is reasonably close to the theoretical value 0.538 for the polynuclear ion $[AlO_4Al_{12}(OH)_4(H_2O)_{12}]^{7+}$, as noted earlier. These results, which imply a predominance of the Al_{13} ion under the conditions of testing, are in general agreement with the conclusions of Boudot et al. [39] and Furrer et al. [40,41].

One way to interpret the results in Fig. 1 is to propose that the Al_{13} ion is the only ionic species capable of forming a complex with PVSK. If this hypothesis is true, then the maximum efficiency of the titration ought to correspond, at least approximately, to a fixed ratio of OH to Al, consistent with the presence of this ion. To test this hypothesis, the results were recalculated and replotted, as shown in Fig. 2.

In Fig. 2 most of the data points converge as a single curve. Deviations at the lowest concentration of aluminum tested are tentatively attributed to the expected drift of the streaming current signal that is observed when an aqueous sample contains a very low value of charged colloidal material. Negative values on the plot correspond to cases in which acid, rather than base, had to be added to the aqueous system to achieve a certain target pH. The three curves corresponding to different aluminum concentrations are fairly close in the range of OH/Al from 0 to 3. Aluminum ions reach the maximum complexing ability with PVSK at ratio of OH to Al (degree of neutralization) of approximately 1 in each case. The strong relationship between this ratio and the ability of the aluminum species present to complex with the anionic titrant provides further support that species of aluminum, other than the hydrated Al^{3+} ion, are responsible for the observed interaction with PVSK. In the pH range of 4–5, which is typical of acid papermaking, the most likely specie, as pointed out before, is Al_{13} ion [REF].

It is worth noting that the results in Fig. 2 are similar to Reynolds' study that was related to dry strength resins used with alum [33]. The peak areas of the curves are relatively broad in Fig. 2, compared with those in Fig. 1 when they are plotted against pH. This is to be expected, since aluminum solution itself is a good pH buffer. Fig. 3 shows the consumption of base versus pH.
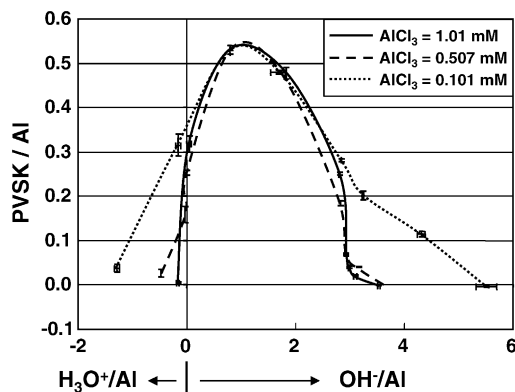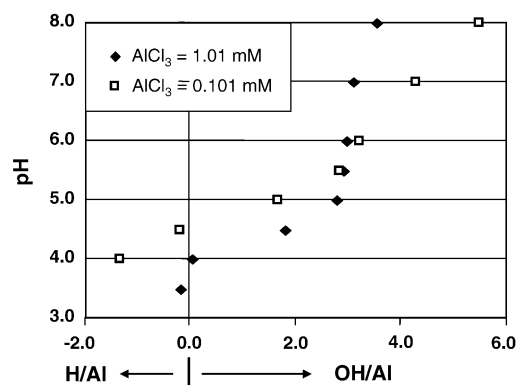

Fig. 3. The relationship between pH and degree of neutralization. The horizontal axis indicates the molar amount of either acid or base added, based on the aluminum molar concentration.

To further test the hypothesis that only one species of aluminum ion undergoes significant complexation with PVSK under the conditions of testing, the titration results were compared with literature values for the speciation of aluminum chloride solutions [5,17]. Remarkable agreement was found between Hayden and Rubin's calculated estimates of the proportion of polynuclear species [17] and the present titration results versus pH as shown in Fig. 1 for the 1 mM solution. If an ionic species such as $Al(OH)^{2+}$ were to play a significant role in the titrations, the calculations suggest that Fig. 1 ought to show sub-peaks or tails of the curves at pH values of 0.2–0.5 units below the maximum of each curve. While no such evidence was found, it is worth bearing in mind that the present results say nothing about whether the divalent ion $Al(OH)^{2+}$ is present. Rather, it appears that the low-valent ion, presumed to be present within part of the pH range considered, did not affect the titration results.

3.5. Zeta potential results

Evidence that strongly complexing aluminum species exist even at concentrations of 0.1 mM aluminum concentration and below was provided by the coagulation studies of Matijević et al. [35]. Because the explanation given in the pre-

Fig. 2. Equivalents of PVSK required to titrate $AlCl_3$ solutions to a zero streaming current endpoint as a function of OH-to-aluminum ratio (degree of hydroxylation).
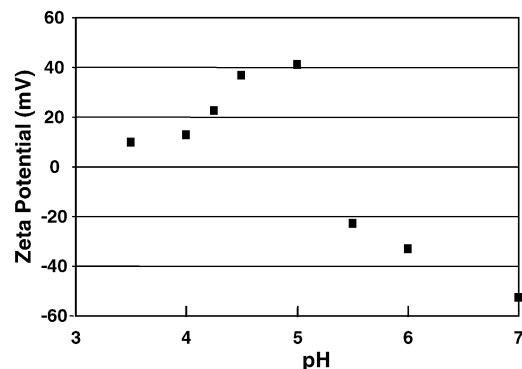

Fig. 4. Zeta potential of silica particles in presence of 1 mM $AlCl_3$ solutions to which NaOH was added to adjust the pH.

Table 4
Turbidity of colloidal silica dispersions after partial neutralization with 1 mM AlCl$_3$ solutions

OH$^-$ added per Al	–	0.04	0.79	1.82	2.80	2.92	2.98	3.10	3.53
H$_3$O$^+$ added/Al	0.17	–	–	–	–	–	–	–	–
pH	3.50	4.00	4.25	4.49	5.07	5.52	6.00	7.00	8.00
Turbidity (NTU)									
Initial	17.5	39.8	37.1	50.1	46.9	42.0	37.4	32.3	6.08
Maximum	64.0	60.3	40.0	50.3	61.9	48.2	43.6	37.1	6.08
After 24 h	2.8	2.38	40.0	49.6	0.31	44.2	36.9	24.3	4.41
Time/max (min)	150	150	150	3	3	60	90	30	1
ζ (mV)	9.9	12.8	22.4	36.7	41.1	−23.0	−33.0	−52.6	–

vious section assumed the existence of the Al$_{13}$ ion in solution within a certain concentration range, further experiments were carried out to test this assumption. Accurate analysis of aluminum species usually requires higher solution concentrations that those used in the present work [22–25]. Therefore, colloidal chemical tests were conducted to confirm the existence of polynuclear aluminum species within the range of conditions employed in the streaming current titration experiments.

Fig. 4 shows results of tests with 1 mM aluminum chloride solutions, to which different amounts of NaOH had been added to adjust pH. The concentration of aluminum ions was sufficient to cause charge reversal of the colloidal silica indicator particles between pH 3.5 and 5. It is worth noting that the zeta potential became increasingly positive as the pH was increased between 4 and 5. In this respect our results are consistent with those of Brace and Matijević [34], who observed positive zeta potentials at similar pH values during work with somewhat more concentrated solutions (3 mM Al(NO$_3$)$_3$). Both sets of results are consistent with the higher expected adsorption tendency of the Al$_{13}$ ion, compared to hydrated Al^{3+}. There appears to be a consensus in the literature that the latter species is the dominant ionic form of aluminum below a pH of about 4 [24,28], where Fig. 4 shows a lesser positive zeta potential. Despite the fact that in general the results point out to the predominance of the Al$_{13}$ ion in the studied conditions, involvement of other ionic species, such as Al(OH)$_2^+$ and Al(OH)$^{2+}$, cannot be ruled out.

3.6. Turbidimetric tests

To corroborate the presence of polynuclear aluminum species, turbidity measurements were performed for colloidal silica dispersions treated with 1 mM AlCl$_3$ as coagulant at various pHs (see Table 4). For sake of comparison, the measured turbidity of an untreated, stable suspension of the colloidal silica at the same solids level was 3.1 NTU. As shown in the table, the turbidity of the aluminum-treated suspensions was strongly dependent on the ratio of OH$^-$/Al (or H$_3$O$^+$/Al), or equivalently, on the pH.

At pH values of 4.25 and 4.49 the suspension not only reached a high initial value of turbidity after mixing, but also the turbidity remained high after 24 h. It is worth noting that the measured zeta potentials were strongly positive for these two conditions, consistent with charge-stabilization of any agglomerates formed during the initial mixing or of any individually dispersed particles. By contrast, unstable suspensions were obtained at OH$^-$ addition levels both lower and higher than these two samples. The colloidal instability is particularly evident in those samples in which the turbidity after 24 h fell to very low levels, consistent with the precipitation of agglomerated material. The results shown in Table 4 are generally consistent with studies by Matijević et al. [35] and by Hayden and Rubin [17], in which polynuclear species were proposed to explain results of nephelometric studies with 1 mM aluminum nitrate solutions.

Table 5 shows results of similar of tests as reported before but involving 0.1 mM AlCl$_3$ solutions. This Al concentration is about 10-fold lower than was considered in the cited previous work [24]. As shown, the lower concentration conditions yielded results that were very different from those shown in Table 4. Most notably, there was no region of strong charge reversal leading to colloidal stability of the initially-formed agglomerates of particles. Rather, coagulation was maximized at those levels of OH$^-$ addition (4 < pH < 5) where it would be reasonable to expect the

Table 5
Turbidity of colloidal silica dispersions after partial neutralization of 0.1 mM AlCl$_3$ solutions

OH$^-$ added per Al	–	–	–	0.79	1.68	2.84	3.24	4.31	5.50
H$_3$O$^+$ added/Al	6.50	1.29	0.17	–	–	–	–	–	–
pH	3.47	4.08	4.58	4.80	4.98	5.50	5.94	6.90	7.91
Turbidity (NTU)									
Initial	2.48	22.4	54.1	55.9	33.6	2.91	2.70	2.81	2.38
Maximum	2.48	51.8	53.9	56.0	33.6	2.93	2.78	2.81	2.38
After 24 h	2.29	16.3	0.51	0.67	31.8	2.85	2.65	2.63	2.34
Time/max (min)	1	180	10	5	1	5	5	1	1
ζ (mV)	−11.3	−2.0	−14.3	−0.8	−18.6	–	−50.7	–	–

presence of polynuclear aluminum species. Outside of this range the soluble aluminum species had less impact on the original strongly negative zeta potential and high colloidal stability of the dispersions. In summary, at this lower concentration of aluminum ions, the results were consistent with the presence of polynuclear species at pH values of 4.08 and 4.58. The results suggest that these ions were almost sufficient to neutralize the surface charge of the solid phase, as evidenced by the initial rise in turbidity, plus the very low values after 24 h. There was no region of strong charge reversal leading to colloidal stability of the initially-formed agglomerates of particles. Rather, coagulation was maximized at those levels of OH^- addition ($4 < pH < 5$) where it would be reasonable to expect the presence of polynuclear aluminum species.

4. Conclusions

Aluminum ions interfered with the stoichiometry of titrations between poly(diallyldimethylammonium chloride) and potassium polyvinyl sulfate, even when their concentration was very low compared to the concentration of other inorganic ions present during related experiments described earlier [1,42].

Titrations between PVSK and aluminum ions failed to show a consistent stoichiometry of interaction when the starting concentration of sample was varied, even when the pH was held constant during the titrations. Results depended on the order of addition, i.e. whether PVSK or aluminum ions were used as the titrant or the sample.

The highest titratable charge occurred when the OH/Al ratio was within the range of 0.5–2. The highest titratable charge was about 0.5, when expressed as the ratio of the negative charge-equivalent end point versus the total moles of aluminum in the solution. This value was consistent with the action of the polynuclear species $[AlO_4Al_{12}(OH)_4(H_2O)_{12}]^{7+}$ as the dominant ionic species. It was not necessary to assume significant complexing ability of other aluminum species in order to explain the results.

The zeta potential and turbidity results also indicated the presence of aluminum polynuclear species, possibly $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ in the pH range of 4–5. However, current results could not completely explain the interference effect of aluminum ions on the titration stoichiometry between poly-DADMAC and PVSK. More study would be needed to quantitatively understand the relationship between aluminum ionic species in solution relative to adsorbed aluminum species and their contributions to surface charge.

Acknowledgements

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