

ABSTRACT

CHEN, JUNHUA. Factors Affecting Interactions of Polyelectrolytes During Charge Analysis. (Under the direction of Dr. Martin A. Hubbe and Dr. John A. Heitmann)

The streaming current method is commonly used for charge analysis in water treatment and the paper industry. The working mechanism of this method is understood to involve polyelectrolyte complex (PEC) formation. Since the formation of PECs is important for many applications, the factors that could affect this complexation have been widely investigated. Studies have found increasing deviations from 1:1 stoichiometry of complexation with increasing salt concentration. The colloidal charge of water recirculated within a paper mill can affect process efficiency and product quality. With increased conductivities due to water recirculation and reuse, the need for accurate and reliable charge measurements at high conductivities has become more important. This research focused on experiments that define the range of sample types and electrical conductivity where it is possible to achieve accurate and reliable results from streaming current titrations.

Other studies related to the theories of polyelectrolyte complexation involved titrations carried out between solutions of a strong poly-acid and a strong poly-base over a range of salt concentrations. The results showed that deviations from 1:1 stoichiometry are consistent with earlier studies. In addition, it was

found that the stoichiometry of PEC complexation depended on the direction of the titration. An excess over the stoichiometric amount was required to achieve a streaming current reading of zero. Theoretical models based on non-equilibrium complexation are proposed to explain the current results. Other tests, such as turbidity and electrophoretic mobility also have been used to evaluate the theoretical models. The results are consistent with those from the streaming current analysis.

Factors that can influence the polyelectrolyte adsorption and PEC formation were studied also. It is thought that the charge density of anionic polyelectrolytes may affect the titration stoichiometry to some extent at high conductivities; however, no clear trend was found in this study with carboxymethylcelluloses. It was also found that the shape of the titration curves indicates the strength of complexation between titrant and sample molecules.

Aluminum ion interferes with the stoichiometry of charge titrations in a different way when compared with other inorganic ions such as Ca^{2+} , Cl^- and Na^+ . It is possible to consider the aluminum ion itself as one kind of cationic sample to be titrated with standard anionic titrant under certain conditions. Turbidity and zeta potential tests indicated that there could be polynuclear species existing under the conditions in which the aluminum ions can be titrated as a cationic sample.

**FACTORS AFFECTING INTERACTIONS OF
POLYELECTROLYTES DURING CHARGE ANALYSIS**

by

JUNHUA CHEN

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Co-chair of Advisory Committee

Co-chair of Advisory Committee

BIOGRAPHY

The author was born in July 1973 in Shanghai, China. She received her Bachelor of Engineering degree in Material Science and Engineering in 1995 from Tianjin University, China. Then she worked for the Inorganic Material Institute in Tianjin China as a process engineer. In May 2000, she obtained a Master of Science degree from the Department of Wood and Paper Science at North Carolina State University. In August 2000, she continued her Ph. D study at North Carolina State University. Her research interested areas are wet-end chemistry and charge analysis in papermaking processes.

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LIST OF SYMBOLS

(-/+)	Ratio of anionic to cationic polyelectrolyte groups
(+/-)	Ratio of cationic to anionic polyelectrolyte groups
Al	The molar amount of aluminum element exist in a solution, despite of the ion species
H	The molar amount of H ⁺ ion exist in a solution
M	mol/l
OH	The molar amount of OH ⁻ ion exist in a solution
(PVSK/Al)	Ratio of the amount of anionic polyelectrolyte groups to the amount of aluminum element

LIST OF ABBREVIATIONS

CCC	Critical concentration of coagulation
CFC	Critical flocculation concentration
CMC	Carboxymethylcellulose
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
NMR	Nuclear magnetic resonance
OFC	Optimum flocculation concentration
PAC	Polyaluminum chloride
PEC	Polyelectrolyte complex
poly-DADMAC	Poly-diallyldimethylammonium chloride
PTFE	Poly-tetrafluoroethylene
PVSK	Poly-vinylsulfate potassium
RSC	Restabilization concentration
SC	Streaming current
SCD	Streaming current detector
WAXS	Wide angle X-ray spectra

Chapter 1

Introduction

With increasing the usage of polyelectrolytes, their behavior in aqueous solution is becoming an active area of research [1-6]. One of the interesting aspects is the interaction between oppositely charged polyelectrolytes. The mechanism of this interaction is also one of fundamentals important to many different applications, such as modifying surface properties with adsorbed polyelectrolytes [4,7], complexation between various polyelectrolytes [8,9], and measurements of colloidal charge [10]. More and more studies have reported that the behavior polyelectrolytes of could be influenced by increasing ionic strength [11-14]. It has been found that increasing conductivities could interfere with stoichiometries between oppositely charge polyelectrolytes [15], and even change the structure of polyelectrolyte complexes [16]. Both the stoichiometry between oppositely charge polyelectrolytes and structure of polyelectrolyte complexes are the important factors that affect colloidal charge measurements.

In the paper industry the conductivity of process water becomes ever higher with increasing closure of water systems [17-24]. The efficiency of polymeric wet-end chemicals is expected to be inhibited by increasing conductivities [17, 23]. In order to add the appropriate dosage of polymeric additives at the wet end, charge measurements and their accuracy become of more important to papermakers with increasing process water system closure.

The purpose of this introductory section is to review past research findings related to various aspects of interactions between polyelectrolytes. In this introduction the mechanisms of polyelectrolyte interaction is one of the most fundamentals and will be discussed first. The methods that can be used to test these mechanisms are also very important and these will be reviewed second. Next to be considered are the factors that can affect polyelectrolyte interaction. The primarily focus is on increasing conductivity and the presence of soluble aluminum compounds.

1. Polyelectrolyte Complexation

1.1 Stoichiometry of Polyelectrolyte Complex Formation

The interactions between polyelectrolytes and oppositely charged polymeric material or colloid particles and their ability to form complexes have been widely investigated [25-29]. The mechanism of polyelectrolyte complexation has become more and more interesting because it helps to explain applications such as microencapsulation or membranes with special separation properties [30-32]. However, the mechanism of polyelectrolytes complexation and the effect of increasing conductivity on this complexation are still not well understood.

In the paper industry dissolved charge is introduced with the charged groups associated with dissolved polyelectrolytes, such as lignins, hemicelluloses, starches, and synthetic polymers employed for various purposes. The stoichiometry of polyelectrolyte complexation could be involved in the mechanism

by which retention and drainage aids work and also in the formation of some unwanted deposits [27, 33]. Fundamental issues of the polyelectrolyte complexation reaction also are critical in order to interpret correctly the results of charge analysis methods. For example, a common assumption during charge titration is 1:1 complexation for linear strong acid and/or base polyelectrolytes with sufficiently high charge density, as shown in Fig 1.1.1 [34]. In this case one anionic group is associated with one cationic group. This assumption appears to be true in most cases involving tap water or deionized water [35].

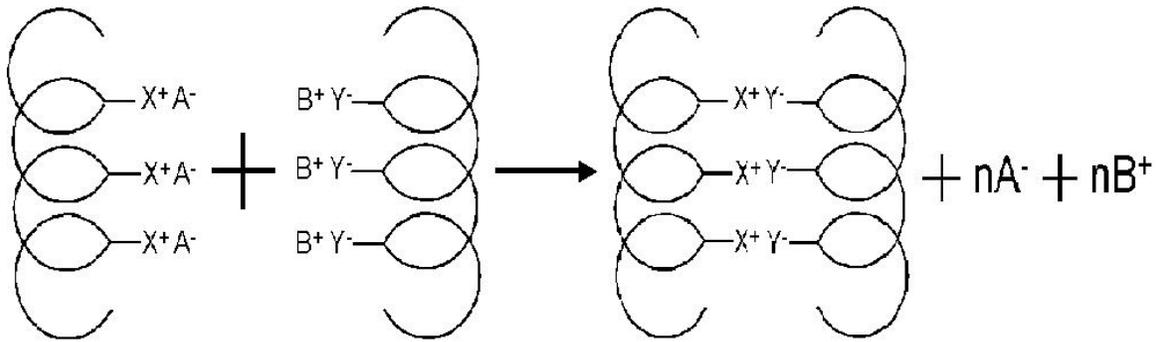


Fig 1.1.1: Schematic illustration of one-to-one charge complex formation (adapted from Keihei Ueno) [34].

According to the Gibbs equation ($\Delta G = \Delta H - T \Delta S$), for a reaction, if ΔG (the change in Gibbs free energy) is negative, then the reaction is favorable and will occur at a specified temperature. If temperature stays the same, the driving force of the polyelectrolyte complexation can involve both electrostatic attraction and the hydrophobic nature of the polyelectrolytes [36]. Increasing hydrophobicity of polyelectrolytes could lower the ΔH (the change in enthalpy) term in the Gibbs equation, when the reaction is carried out in an aqueous solution. It has also been proposed that the driving force of this complexation

reaction could be due to an entropy increase [37], increasing the ΔS term in the Gibbs equation. This increase in entropy can result when ion pairs form between the poly-ions, the smaller ions are allowed to migrate away from the double-layer regions and into the bulk solution.

The stoichiometry of polyelectrolyte complexes can be affected by various factors [12, 38-43]. It has been found that structural and electrophoretic properties of polyelectrolyte complexes are rather sensitive to variations in the ionic strength of the surrounding medium. The salt effects suggest that a higher level of the particles aggregation of the polyelectrolyte complexes (PEC) is achieved in response to an increase in the ionic strength of aqueous solution [44]. In other words, small PEC particles more easily collide with each other and form larger aggregates. (Note: the salt in section 1 and 2 in this chapter refers to monovalent or divalent low molecular mass ions, for example Na^+ , Ca^{2+} , Cl^-) However, it is still not clear if the compositions of the PECs formed at different conductivity values are similar.

Another characteristic that can affect stoichiometry of PEC formation is ionic spacing, which refers to the average distance between two adjacent charged groups on the same polyelectrolyte molecule. It has been reported that the equality of ionic spacing between two oppositely charged interacting polyelectrolytes is essential to the stoichiometry of reactions [38].

Polyelectrolytes with similar ionic spacing have been found to achieve 1:1 stoichiometry more easily. Non-equal ionic spacing of two polyelectrolytes could

cause stoichiometry to deviate from 1:1 in charge group complexation. However, if the interacting polyelectrolytes have the same ionic spacing, then the degree of polymerization of each reacting polyelectrolyte would not be critical to the stoichiometry of polyelectrolyte complexation [38].

In contrast to 1:1 stoichiometric complexation, non-stoichiometric complexation refers to stoichiometry that is not 1:1. This kind of polyelectrolyte complex has been found by researchers all over the world [35, 42, 45]. The formation mechanisms of these PECs, which are believed to account for the deviation from 1:1 polymer complex formation, are also widely investigated using various methods [42, 45, 46].

Studies using layer-by-layer polymer adsorption as an approach often provide information about the stoichiometry of PEC formation [14, 16, 46], though this method was not originally designed for stoichiometric investigation. In this approach a highly charged substrate is normally used for initial adsorption, and then it is sequentially dipped in oppositely charged polyelectrolyte solutions.

1.2 Mechanisms of Layer-By-Layer Polymer Interaction

Dubas and Schlenoff studied stoichiometry of the layer-by-layer adsorption of polyelectrolytes with opposite charges [14]. They proposed the following complexation and adsorption mechanism:



where M represents metal ions and A represents anions. The subscript (aq) stands for an aqueous solution. The subscript (m) indicates that the polyelectrolyte in equation is part of a multilayer film on a solid surface. They found that charged segments of the newly arriving polymers could replace small ions and complex with the charged groups of polyelectrolytes in the multilayer. In the case of low salt concentration, polyelectrolyte segments were very efficient at seeking out uncomplexed groups and forming a near-stoichiometric PEC layer [47]. Unfortunately, it still was not clear whether the polyelectrolyte complexation followed this mechanism at high ionic strength.

In order to investigate the stoichiometry of binding polyelectrolyte complexes during the multilayer formation, a method was developed by using a fluorescent probe [16]. This probe molecule could detect and bond with the un-complexed charge groups when the outermost polyelectrolyte layer is oppositely charged to the probe molecules. It was found that not all charges in the polyelectrolyte multilayer films for about the top 11 layers were involved in the assembly process by forming ion pairs. This indicated that this layer-by-layer multilayer formation was not following 1:1 stoichiometry [16]. It was also found that the last added polyelectrolytes can penetrate into as many as four layers. In other words, the unpaired charged sites can be detected in 11 layers under the outermost layer, but when the multilayer is exposed to new polymer solution, only the unpaired-charged sites in the top 4 layers can become involved in pairing. This observation suggested that the formation of polyelectrolyte layers might not have a perfect 1:1 zipper shape.

1.3 The Effect of Conductivity on Polyelectrolytes

It is well known that the presence of salt can affect polyelectrolyte conformation [48-51]. Viscosity measurements can be used as an indication of the extension of the polyelectrolytes in solution. It has been found that the viscosity of polyelectrolyte solutions could be decreased by increasing the concentration of inorganic salts [50, 51]. Higher salt concentration causes the compression of the electrical double layer, which decreases the repulsion force between charged groups. Therefore the apparent density of polymer becomes higher [51, 52]. In other words, the polymer is less extended, more compacted and the radius of polymer gyration is lower. This might be one aspect that can influence the PEC formation. However it is still unclear whether this change in conformation is the mechanism by which high salt concentrations affect the stoichiometry of PEC formation.

In addition it has been reported that the complexation between oppositely charged polyelectrolytes could be decreased with increasing concentration of low molecular weight ions, such as NaCl [16]. In other words, the unpaired charged sites are increased with increasing salt concentration. This can be partially explained by an electrostatic shielding effect of the salt on the attraction between the charged sites. At high salt concentrations salt ions stay closer to the polyelectrolyte charge sites and block the access of other charged polyelectrolytes. In terms of multilayer assembling, another reason for the decreased interactions involves structural changes in the multilayer films, *i.e.*,

swelling when immersed in NaCl solutions with concentrations higher than 0.02M [53].

With respect to streaming current charge analysis, effects of salt concentration were demonstrated by the inventor of the device, as well as some early researchers [54, 55]. They found that if the conductivity was increased, there were some deviations from 1:1 stoichiometry in the endpoint detection. Later, Tanaka [15] also found a similar effect of inorganic salt on the titration endpoint by colorimetric titration. This change in stoichiometry can be related to geometric fitting of both polyelectrolytes [56]. At low concentrations of salt ions, the thickness of the electrical double layer can be larger than the distance between the charges on a single polymer. Increasing ionic strength will decrease the thickness of the double layers. The constraint of geometric fitting of two oppositely charged ionic groups becomes narrower. As a result, polyelectrolytes with higher charge density are expected to lose more of their complexing ability [56].

Higher conductivity can often affect the adsorption of polymers onto various surfaces as well. One of the important assumptions involved in streaming current charge analysis is that adsorption of polyelectrolytes onto the plastic probe surfaces takes place with high efficiency. However, it has been shown that, when the adsorption process is dominated by an electrostatic mechanism, salt concentrations above a certain level can be sufficient to displace essentially all of the polymers from the surface [14]. This concentration has been reported

to be proportional to $(\alpha\sigma_0)^{0.9}$, where α is the average charge per repeat unit and σ_0 is the surface charge density [57]. This means that the charged polymer has to compete with added salt ions for charged sites on surfaces. For weakly charged polyelectrolytes, desorption might occur much earlier than for high-charge density polyelectrolytes [57].

1.4 Methods for the Investigation of Complex Formation and Structures

At different stages of PEC formation different methods have been used to test their structures. Levine and Friesen proposed a model of flocculation in 1987 [58]. In this model there are three regions of polymer concentrations, a stable region at very low concentrations of flocculants, a flocculation region, and a region of restablization at high concentration. The optimum flocculation concentration (OFC) lies within the boundaries of the flocculation region, which is demarcated by the critical flocculation concentration (CFC) and the restabilization concentration (RSC). Table 1.1 shows a set of testing methods according to Levin's model, as summarized by Phillip *et al.* [59].

Table 1.1: Common methods for investigating polyelectrolyte complex formation and structures.

State of Dispersity	Method
Macroscopic homogeneous systems	Light scattering Viscometry Sedimentation in the ultracentrifuge UV/VIS spectroscopy Colloid titration
Transition to phase separation	Electrophoresis Potentiometry Conductometry Turbidimetry
Precipitated polysalts	Sorption measurements Elemental analysis WAXS (Wide Angle X-ray Spectra) NMR spectroscopy IR spectroscopy DSC (Differential Scanning Calorimetry) DTA (Differential Thermal Analysis) Electron microscopy

2. Development of Charge Measurement Using Polyelectrolytes

Polyelectrolyte complexation is a basic principle of many applications. Charge measurement of colloidal material or surfaces is one of those most widely used applications. Measurements of charge demand of an aqueous solution or a charged surface is especially of interest to papermakers [60]. It is well known in the paper industry that, at a near zero charge demand, the fiber furnish often shows its best drainage and retention. These are critical characteristics for the quality and quantity of production [61]. However, the surfaces of untreated fibers after pulping carry negative charges, as many types of filler particles.

Papermakers use a variety of chemical additives to modify the charge demand of fiber slurry in order to get best retention, drainage rate, and formation of the final product. In order to know how much charged additives need to be applied, charge measurement becomes very important.

2.1 Colloidal Titration

Several charge measurement methods have been developed, such as electrophoresis, electroosmosis, and charge titration. Colloid titration is a term that has been used to describe one of the methods that involves a titration with standard polyelectrolyte titrants to evaluate the colloidal charge content of aqueous samples. The method was first used by Terayama of the University of Tokyo in 1948 [62, 63]. As mentioned earlier, the basic principle is the reaction of oppositely charged polymeric materials or charged surfaces and charged particles. When aqueous solutions of cationic and anionic polymers are mixed, a

neutralization reaction will occur. In most cases 1:1 stoichiometry is assumed for this complexation. Therefore if the charge density and chemical structure of one polymer is known, the charge density of the other polymer can be calculated. An indicator, such as a colorimetric indicator (most common one: Toluidine Blue) or potentiometric detector (in case that there are changes in pH during titration [64]), can detect when the reaction achieves the charge equivalent point.

The charge-equivalence point (end-point) of a colloid titration test can be detected by various methods [60, 65-67]. One such method is to use the aforementioned streaming current charge analysis. The instrument which applies this method is streaming current detector (SCD). It was originally designed for the water treatment industry [54]; however it has become used subsequently for paper industry applications as well. Currently the streaming current detector is widely used in the papermaking industry to measure the net charge of white water on paper machines because of the following advantages:

1. The mechanical parts of the device are simple, durable, and easy to replace.
2. No calibration is needed.
3. The method does not require any visual analysis.
4. The method can be automated.

There are several kinds of steaming current detectors available on the market.

Figure 1.2.1 shows a cutaway view of one kind. Usually the piston is made from

poly-tetrafluoroethylene (PTFE), and the cylinder is made from another piece of plastic, sometimes also PTFE. Both of them are very hydrophobic.

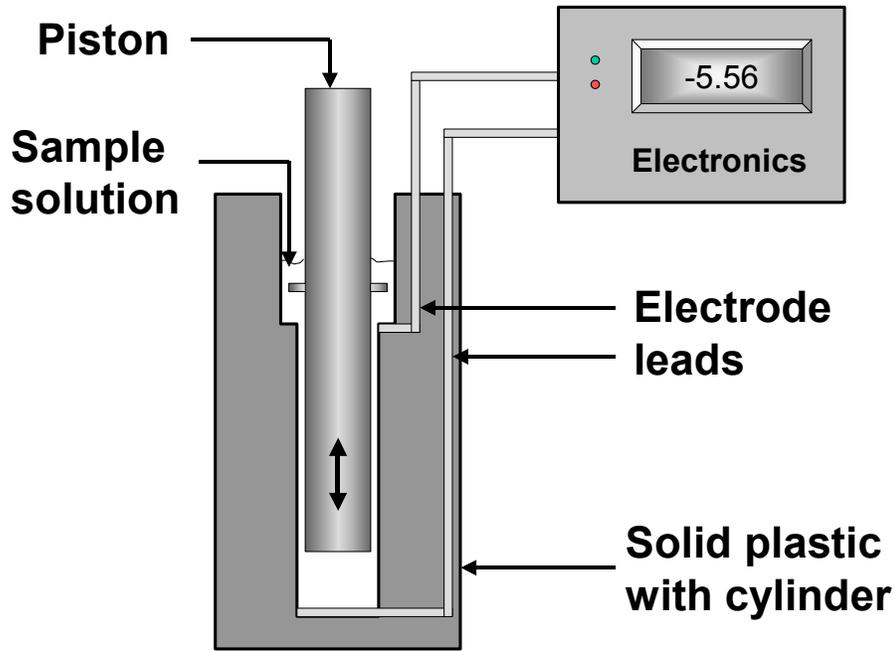


Figure 1.2.1: A cutaway view of a streaming current detector.

2.2 Theoretical Aspects of Streaming Current Device

Dentel and Kingery have studied the theoretical aspects of SCD measurements [68]. During operation of this device the piston goes up and down at a rate of about four times per second. This motion forces the water to go in the opposite direction. According to the movement of the piston, the flow profile and shear force in the apparatus were estimated [68]. The details will be discussed later in this section.

In common practice the wetted surfaces of the SCD probe are not neutral when only deionized water is added. Davison and Cates tested the zeta potential of the probe surfaces of their streaming current device and found that the PTFE surfaces carried a weak anionic charge in the presence of clean water and univalent ions [69]. This finding is consistent with the negative initial reading of streaming current detectors without any polymer present. The general assumption has been made that in the course of a titration either the charged polyelectrolyte complexes or polyelectrolytes molecules adsorb onto the probe surfaces. This adsorption may result in a net charge on the surfaces and the formation of an electrical double layer. Some of the counter-ions will be located outside of the hydrodynamic slip plane where ions will come under the influence of flow. The excess charges in the bulk solution will migrate with the fluid flow up and down the annulus in response to the reciprocating motion of the piston and thus create a current, which can be mathematically related to the electrical potential, the zeta potential. The relationship is [70]:

$$I = \frac{\varepsilon p R^2 \zeta}{4 \mu l} \quad , \quad (1.2)$$

where: I = streaming current,
 p = applied pressure,
 R = passage radius,
 ζ = zeta potential,
 ε = dielectric constant of water,
 μ = viscosity of water, and
 l = length of passage.

This current is an alternating signal, and can be detected by the metal electrodes. The signal obtained is processed by the electronic devices to amplify and rectify it, as follows [70]:

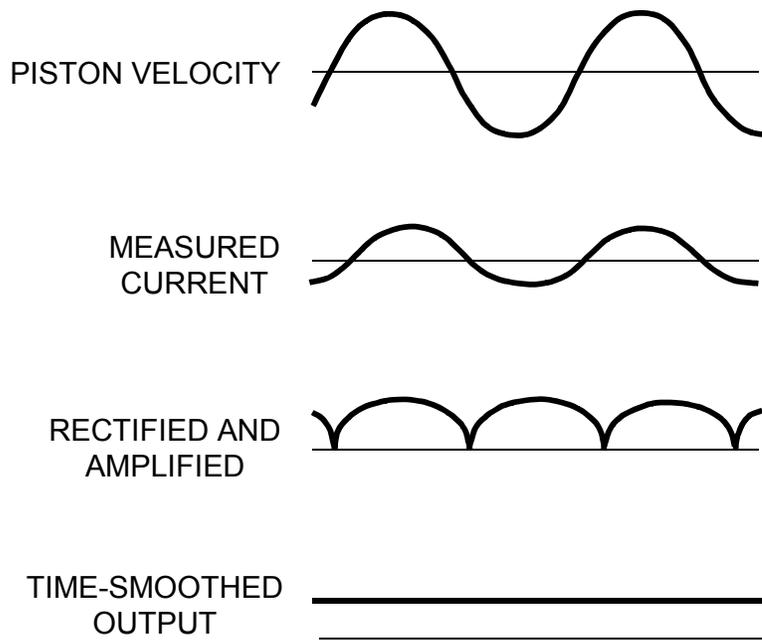


Figure 1.2.2: Streaming current signal processing steps relative to piston velocity.

The instantaneous current has been calculated by Gerdes [54]. The equation he used is:

$$i = dq_1 / dt \tag{1.3}$$

where i = total instantaneous current,

q_1 = total counter-ion charge located above the specified plane, and

t = time

The total counter-ions can be estimated by equation 1.4.

$$q_1 = \sigma_1 pl \tag{1.4}$$

where σ_1 is charge density in the shear planes,

p is the combined perimeter of two cylindrical shear planes, one facing the piston surface and the other facing the cylinder wall of the SCD device, and

l is the length of the cylinders above the specified plane.

$$\text{Therefore } i = dq_1 / dt = \sigma_1 p dl / dt = \sigma_1 p v_1 \quad (1.5)$$

with v_1 = instantaneous velocity of the counter-ion layers

And time average values (indicated with a bar on the top) of the current can be

$$\text{represented as } \bar{i} = \sigma_1 p \bar{v}_1 \quad (1.6)$$

Dentel and Kingery [68] have estimated the magnitude of \bar{v}_1 using the triangular velocity profile. They assume that the velocity at shear plane is zero and Laminar flow exists in the annulus. The velocity distribution at a time t in an annulus of SCD can be calculated as equation 1.7.

$$v(r,t) = \frac{\lambda^2 - 1}{\lambda^2} \left[\frac{1 - (r/R)^2 + (1 + \lambda^2) \ln(r/R)}{1 - \lambda^2 + (1 + \lambda^2) \ln \lambda} \right] (\pi w s) \sin(2\pi w t) \quad (1.7)$$

where r = radial distance from center line of piston and cylinder

t = time

λ = ratio of piston radius to cylinder radius

R = radius of cylinder

w = rotational speed of the driving motor (normally 4 cycles/sec)

s = the piston stroke

Therefore the maximum velocity can be calculated with equation (1.7) by setting the sinusoidal term to $w t = 1$. This velocity profile also makes it possible to estimate the hydrodynamic shear force.

2.3 Other Methods for Endpoint Detection

Turbidity testing is another method that has been used to examine the PEC stoichiometry [12,71-73]. In an aqueous solution with a low conductivity, turbidity changes very slowly as titrant solution is added until close to the neutral point of the titration and then the turbidity increases rapidly. Turbidimetric endpoint determinations show a very good agreement with colorimetric and potential determination at low to medium conductivity ranges. It has an advantage compared to SCD in that polymeric materials do not have to adsorb onto surfaces. However, once again it was found that low mass salts could affect turbidimetric endpoint detection [11]. Different ions affect the formation of polyelectrolyte complexes to different degrees. In general, univalent ions have less effect on the turbidity measurement of PEC formation than divalent and trivalent ions [11].

Another method to determine the endpoint is conductometric titration. This technique involves monitoring the conductivity change pattern during titration. Theoretically if one polyelectrolyte is added to a solution of another polyelectrolyte without changing the volume to any appreciable extent, the conductivity increases at a certain rate as long as the all the ions in the solution do not react with each other. If polyelectrolytes interact with each other and form a slightly dissociated complex, the conductivity of the solution changes at a different rate. In the case that counter-ions have a greater mobility than polyelectrolytes, the conductivity increases [74]. However, in a high conductivity

solution with other high mobility ions present the conductivity changes may not be large enough to be detected.

2.4 Standard Reagents Used in Colloidal Titration

The selection of standard titrants is also very important. Improper selection of standard titrant may cause restrictions of conditions used, such as pH. Highly charged polyelectrolytes are the preferred choice for titrant. Initially glycolchitosan (Gch) or methylglycolchitosan were used as titrants with positive charge. However, Gch carries positive charge only in the acidic range. By contrast, the quaternary amine group is known to carry a positive charge over a wider range of pH [75]. Now a synthetic polymer with a quaternary amine group, poly-dimethyldiallylammonium chloride (poly-DADMAC), is considered more pH-tolerant and a more stable cationic titrant. Among various anionic polyelectrolytes, poly-vinylsulfate potassium salt (PVSK) is found to be the most suitable titrant due to the sharpness of the endpoint color change of Toluidine Blue and high pH tolerance.

3. Interaction between Aluminum Ions and Polyelectrolytes

Studies of inorganic univalent ions and divalent ions and their effect on polymer interactions have been reviewed in a previous section. Aluminum ions are another important class of ions that commonly are found in papermaking process water. They behave differently from other ions that are commonly present in such samples. Due to their highly charged cationic nature at acidic conditions,

soluble aluminum products are commonly used as retention and drainage aids. Originally aluminum ions were introduced to the papermaking process in the form of alum. The major ingredient of alum is $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. With growing interest in neutral and alkaline systems, another aluminum compound – polyaluminum chloride (PAC) has been more widely used. PAC can remain positive in surface charge even at pH values above 6. Therefore, even at neutral and alkaline pH values of papermaking process water, it is possible that there are positively charged aluminum ions present.

It has been reported that aluminum ions can “interfere” with the endpoint of titrations when a polyelectrolyte is used to determine the concentration of another oppositely charged polyelectrolyte in solution either by colorimetric [76-79], or streaming current [80] endpoint detection. To understand what is the “interference” of an aluminum ion, it is worth investigating aluminum ion behavior in aqueous solutions, and whether these aluminum ions can interact with polyelectrolytes consistently.

3.1 Aluminum Ion Chemistry

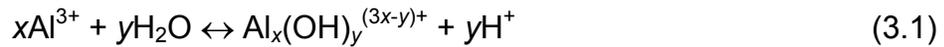
The aqueous chemistry of aluminum ions is very complicated. The aluminum ions undergo various hydrolysis reactions. The reaction equilibriums based on experiments with the aluminum salt of a non-complexing anion (such as Cl^- , NO_3^- , ClO_4^-) solution are listed in Table 1.2.

Table 1.2: Aluminum equilibriums [81].

Reaction	Log K (25°C)
$\text{Al}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})^{2+} + \text{H}^+$	-4.97
$\text{Al}(\text{OH})^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_2^+ + \text{H}^+$	-4.3
$\text{Al}(\text{OH})_2^+ + \text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_3 + \text{H}^+$	-5.7
$\text{Al}(\text{OH})_3 + \text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_4^- + \text{H}^+$	-8.0
$2\text{Al}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Al}_2(\text{OH})_2^{4+} + 2\text{H}^+$	-7.7
$3\text{Al}^{3+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Al}_3(\text{OH})_4^{5+} + 4\text{H}^+$	-13.97
$13\text{Al}^{3+} + 28\text{H}_2\text{O} \rightleftharpoons \text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+} + 2\text{H}^+$	-98.73
$\text{Al}(\text{OH})_3 \text{ (amorphous)} \rightleftharpoons \text{Al}^{3+} + 3\text{OH}^-$	-31.5 (estimated)

Note: K is the stepwise equilibrium hydrolysis constants for the respective reactions.

The overall hydrolysis or polymerization reaction can be summarized as follows:



The overall equilibrium hydrolysis constant β_{xy} can be expressed:

$$\beta_{xy} = \frac{[\text{Al}_x(\text{OH})_y^{(3x-y)+}][\text{H}^+]^y}{[\text{Al}^{3+}]^x} \quad (3.2)$$

In papermaking processes aluminum ions are commonly used to provide anchoring sites for retention of rosin size or other anionic polymers. The structure of the aluminum ion is the key to how it functions. Studies trying to

identify aluminum species responsible for the improvement of retention are still on going [82]. Many species have been proposed to explain the aluminum ion's behavior in water. However, major species reported based on different experimental methods are seemingly inconsistent. This problem will be discussed later. The most commonly reported monomeric ions are $\text{Al}(\text{H}_2\text{O})_6^{3+}$, $\text{Al}(\text{OH})(\text{H}_2\text{O})_5^{2+}$, $\text{Al}(\text{OH})_2(\text{H}_2\text{O})_4^+$, $\text{Al}(\text{OH})_3$, and $\text{Al}(\text{OH})_4^-$. At a certain pH, especially higher pH range in acidic condition, the mononuclear species of aluminum ions are capable of complexing with themselves, leading to the formation of poly-nuclear species, also shown in the row 5, 6 and 7 of Table 1.2. Figure 1.3.1 shows the beginning step of polymerization, and then aluminum ion undergoes a further complexation reaction. The most commonly cited oligomers are $\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_8^{4+}$, $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$, and $\text{Al}_3(\text{OH})_4(\text{H}_2\text{O})_{10}^{5+}$.

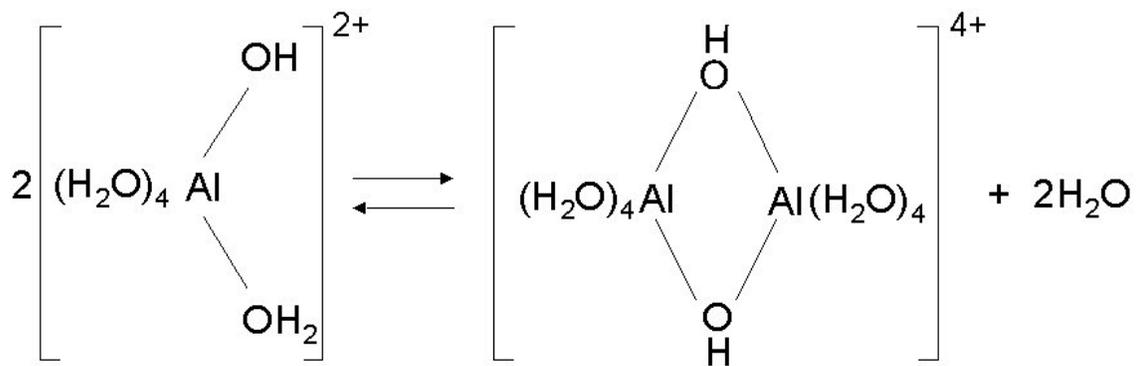


Figure 1.3.1: Aluminum ion dimer formation.

3.2 Proposed Structures of Various Aluminum Hydrolysis Species

Numerous tests have been used to demonstrate the existence of poly-nuclear species of aluminum ions [83-87]. Jander and Winkel [83] were among the first to suggest the existence of polynuclear species. Their experiments were based on

the measurement of diffusion coefficients of aluminum salts in the solution. Studies involving the ferron-orthophenathroline method for aluminum also suggest the existence of polynuclear species [84]. Brosset [85] proposed $[\text{Al}_6(\text{OH})_{15}]^{3+}$ was the predominant species, based on their study of potentiometric titrations of aqueous aluminum solutions. Still later, two other species $[\text{Al}_{13}(\text{OH})_{34}]^{5+}$ and $[\text{Al}_7(\text{OH})_{17}]^{4+}$ were proposed by Biedermann [86].

In a study by Haydin and Rubin [87], based on the results from X-ray and light-scattering tests, the concentrations of different aluminum ion species in solution at different pH were calculated. They supported the existence of the polymeric ion $[\text{Al}_8(\text{OH})_{20}]^{4+}$, which was first used to interpret colloid coagulation data by Matijević and Tezak [88]. At the same time their research also dismissed the probability of the presence of other polynuclear ions.

Hsu and Bates [89] proposed another series of polynuclear complexes with the basic unit of $[\text{Al}_6(\text{OH})_{12}(\text{H}_2\text{O})_{12}]^{6+}$, which has six-member ring structure. Although evidence had indicated that the OH group was predominately in a bridging position, there is no other structural evidence to support the proposed ring structure.

In more recent work ^{27}Al NMR was found to be sensitive to the aluminum hydrolyzed species, as well as the unhydrolyzed ion $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, in the aqueous solution. This technique has been combined with other test methods, such as spectrophotometric and potentiometric methods, to investigate the structure of these species [90-92]. A typical spectrum is listed in Figure 1.3.2. NMR spectra

can provide much clearer evidence of the existence of different ionic species, and most studies show that an oligomer (tridecamer) comprising 13 aluminum atoms is a particularly stable species existing in the solution. The formula is $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$. The ion's proposed structure is shown in Figure 1.3.3. Among the thirteen aluminum atoms, the central aluminum atom has a tetrahedral coordination, whereas the other twelve are octahedrals. They are joined with common edges. More recently, Exall and her coworkers used ^{27}Al NMR [93] and found similar evidence to prove the existence of the tridecamer at even lower concentrations than that of previously studied [91,94].

$[\text{AlCl}_3] = 0.1 \text{ mol/l}$

Bottero, J-Y, *et al.*,
*Nordic Pulp and Paper
 Research J.*
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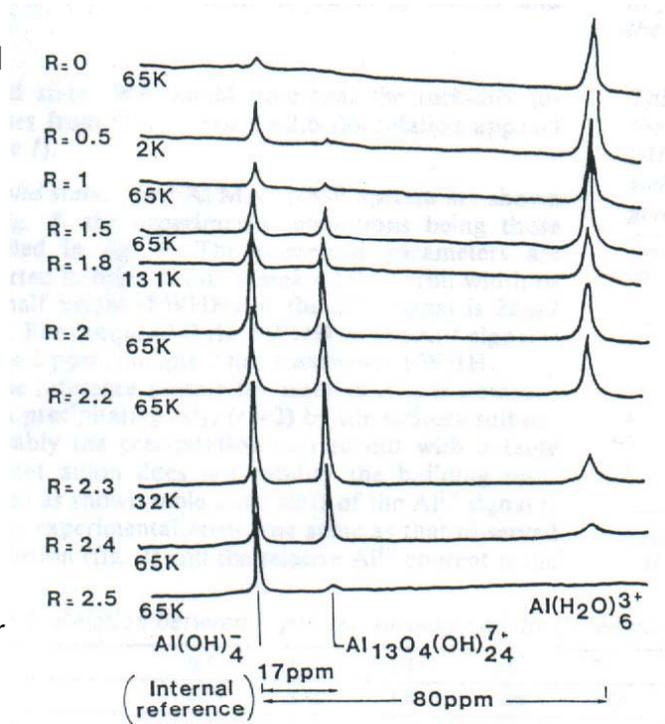


Figure 1.3.2: The Al NMR spectra [94].

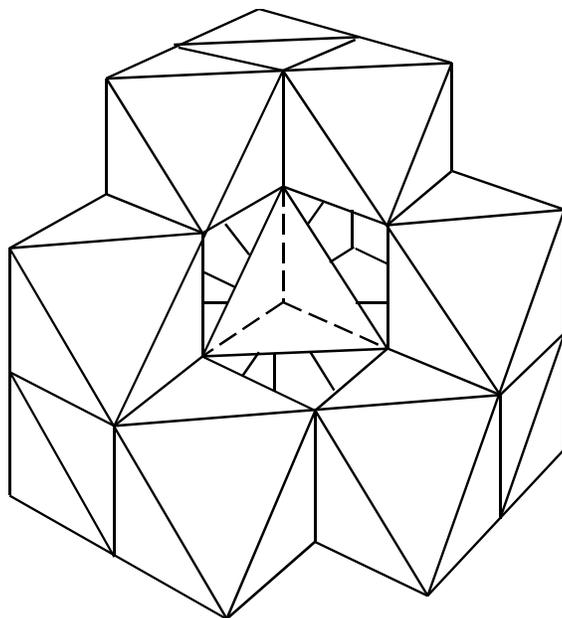


Figure 1.3.3: The proposed structure of tridecamer.

3.3 Aluminum Ion Behavior Relative to pH

For a long time, pH was believed to be one of the most important factors that affect the aluminum species present in the aqueous solution. Various studies have been based on an assumption that pH is the primary factor governing the speciation of aluminum [87, 90]. By assuming that no other stable hydrolyzed cationic species would exist in the presence of precipitate, Haydin and Rubin calculated the effect of the pH on aluminum behavior [87] (as in Figure 1.3.4). For acidic conditions, the distribution of aluminum species as a function of pH is shown in Figure 1.3.5 [95].

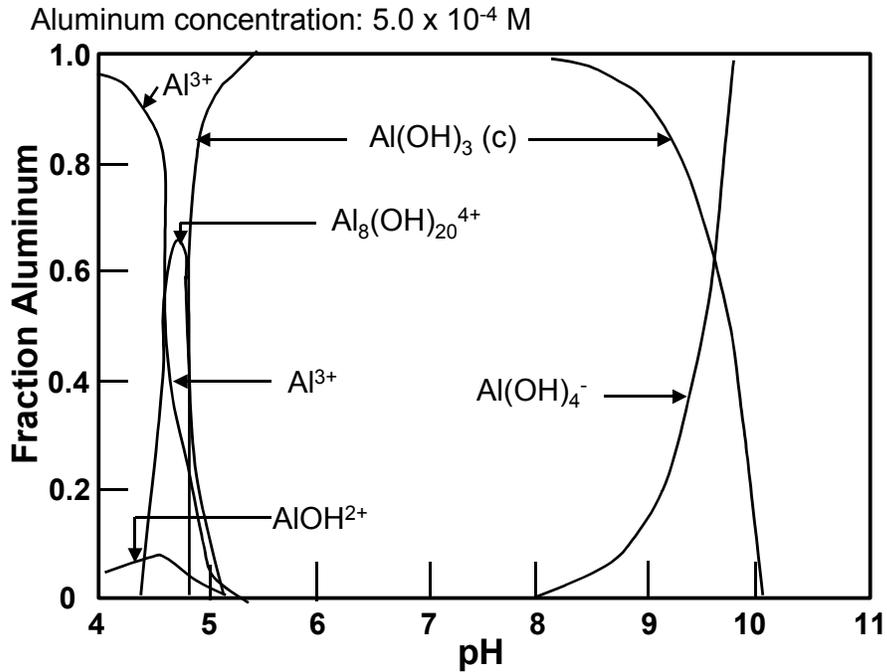


Figure 1.3.4: Distribution of aluminum species as a function of pH for AlCl_3 in both acid and alkaline pH range [84].

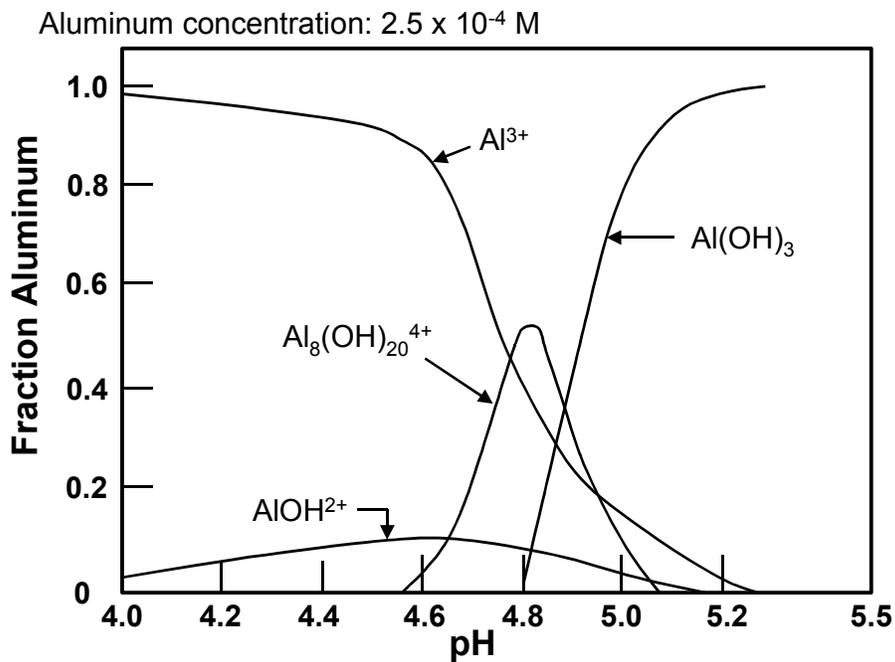


Figure 1.3.5: Distribution of aluminum species as a function of pH for AlCl_3 under acidic conditions [95].

With the use of the NMR technique Bottero *et al.* did a similar study of the pH effect [96]. Figure 1.3.6 shows their result. The 13 oligomer, instead of $[\text{Al}_8(\text{OH})_{20}]^{4+}$, was shown as the predominant polynuclear species. Other species present are $\text{Al}(\text{H}_2\text{O})_6^{3+}$, $\text{Al}(\text{OH})(\text{H}_2\text{O})_5^{2+}$, $\text{Al}(\text{OH})_2(\text{H}_2\text{O})_4^+$, $\text{Al}_2(\text{OH})_x(\text{H}_2\text{O})_{10-x}^{(6-x)+}$.

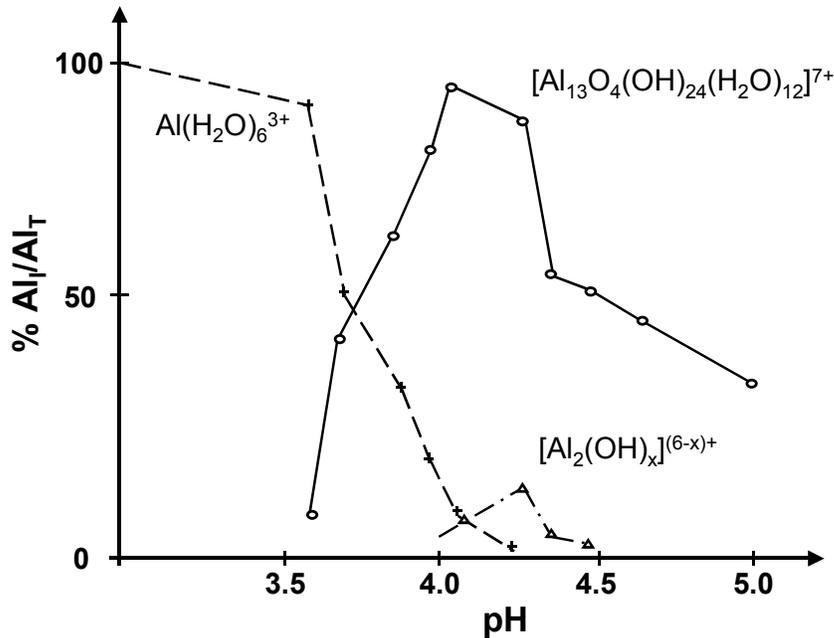


Figure 1.3.6: Aluminum species in the solution measured with high resolution NMR [96].

3.4 Aluminum Ion Behavior Relative to Degree of Neutralization

A study of alum use with an anionic polyacrylamide dry strength resin system found that for two different alum concentrations the maximum tensile strengths were reached at different values of pH [97]. In Arnson's study [95], it was also found that the major aluminum species existing in aqueous solution could be different, even at the same pH with different concentrations, as shown in Figure 1.3.7. Excel studied various factors that could affect the aluminum species, including concentration [93]. According to their study, concentration played an

important role in the aluminum ion hydrolysis process. One of their results (shown in Table 1.3) showed that the proportion of the tridecamer Al_{13} ion was increased with the dilution of the aluminum sample without any pH adjustment, and at the same time the pH values were also increased. The direct reason for increasing proportion of tridecamer was not stated.

Table 1.3: the effect of concentration on the distribution of aluminum species.

Concentration	pH	% Al_1^*	% Al_2^*	% Al_{13}^*
0.5 mol/l	3.5	89	8	5
0.1 mol/l	4.2	79	10	10
0.01 mol/l	4.7	80	1	20

* The number at subscript refers to the number of aluminum ion in species.

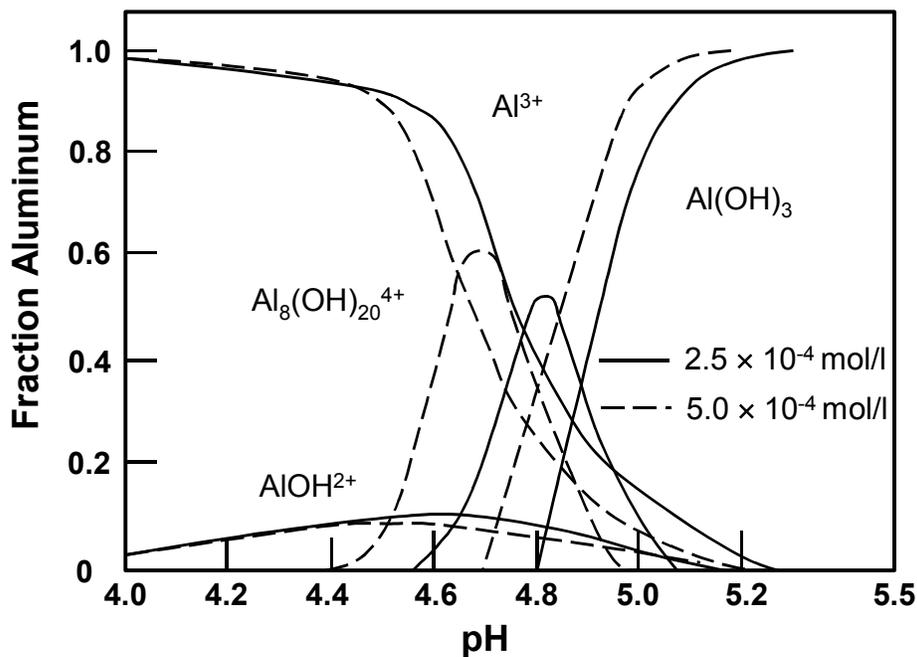


Figure 1.3.7: The effect of total aluminum ion concentration on the distribution of Al species [95].

When Reynolds *et al.* [97] reinterpreted their data by replotting the strength as a function of degree of neutralization, OH/Al. (Note: Al refers to the molar amount of total aluminum ions, regardless of the form in which they are present. OH refers to the molar amount of OH⁻ group in the solution) The maximum tensile strengths were reached at same OH/Al ratio. Therefore, the pH value of a solution may not be the only reason or the direct reason for aluminum species distribution. The degree of neutralization is another important factor to investigate when one studies aluminum chemistry. In Reynolds' study the peak values of various paper strength properties occurred when alum was used in an OH/Al range between 1 and 2. That indicates that the aluminum ions in that range have the highest retention efficiency. Similarly, OH/Al ratio is also one possible explanation for the data in Table 1.3.7, since the OH/Al ratio has been decreased due to the increase amount of OH⁻ with the dilution.

More recently, an increasing number of studies of aluminum ion behavior have considered the aspect of degree of neutralization [98]. Strazdins studied the alum and aluminum chloride chemistry [77, 99] based on the degree of neutralization. He found that alum and aluminum chloride behaved quite differently in terms of titratable charge (the amount of charge can be detected by polymer titration). Alum had much lower titratable charge than aluminum chloride. More particularly, the maximum cationic charge of alum occurred at 1/3 to 1/2 neutralization (OH⁻/Al = 1/3 to 1/2), whereas that of aluminum chloride occurred at around 2/3 neutralization. Although they did not specify the exact

aluminum ion structure at the highest point of titratable charge, based on their experimental results they introduced another factor, shear forces, which played a very important role during the titration. Under low shear conditions aluminum ions had a chance to form large flocs. The results suggested that such chemical floc formation rendered some of the cationic sites inaccessible. High shear conditions appeared to redisperse large flocs [99].

3.5 Adsorption of Aluminum Ions onto Fiber Surfaces

In the paper industry aluminum ions are used as part of a retention aid system, based on the assumption that it can adsorb onto fiber surfaces and work as an anchor site for anionic additives. The adsorption of aluminum ions onto the cellulose surface was found to depend primarily on the pH and concentration of aluminum ions [100]. Simple soluble cations, such as Al^{3+} , do not adsorb onto particles well. According to Arnson and Stratton, only 5-10% of the Al^{3+} is adsorbed onto cellulose fiber [101]. Most of trivalent ions prefer to stay in the diffuse part of the electric double layer [102].

Öhman has also studied the adsorption of aluminum ions onto a cellulose surface [98]. His study is based on the observation that aluminum chloride forms visible flocs upon addition of NaOH, and the flocs grow rapidly during partial neutralization of the aluminum ion. The maximum rate of floc growth has been observed at an OH/Al ratio of 2.9-3.0. The charge balance between polymeric aluminum ions (floc) and celluloses is the factor determining the amount of aluminum can be absorbed onto fibers. At an OH/Al ratio of 3.0-3.1 the

maximum amount of aluminum ions were adsorbed. The adsorbed material has been described as large agglomerates comprised of smaller primary particles [98]. This leads to another common usage of aluminum ion: as a coagulant.

3.6 Coagulation with Aluminum Ion

Before discussing aluminum ion coagulation behavior, the general mechanism of coagulation will be reviewed.

3.6.1 Mechanisms of Coagulation

(a) Stability of colloids

When mineral particles are dispersed in aqueous solution, especially in the absence of organic surface-active or polymeric materials, the major force helping to stabilize colloidal particles is electrostatic repulsion. In cases where the particles have sufficient electrical charge of a given sign, this force can overwhelm the van der Waals' attractive forces, preventing aggregation. For example, Figure 1.3.8 illustrates a case in which the colloidal particles carry a negative charge on their surfaces.

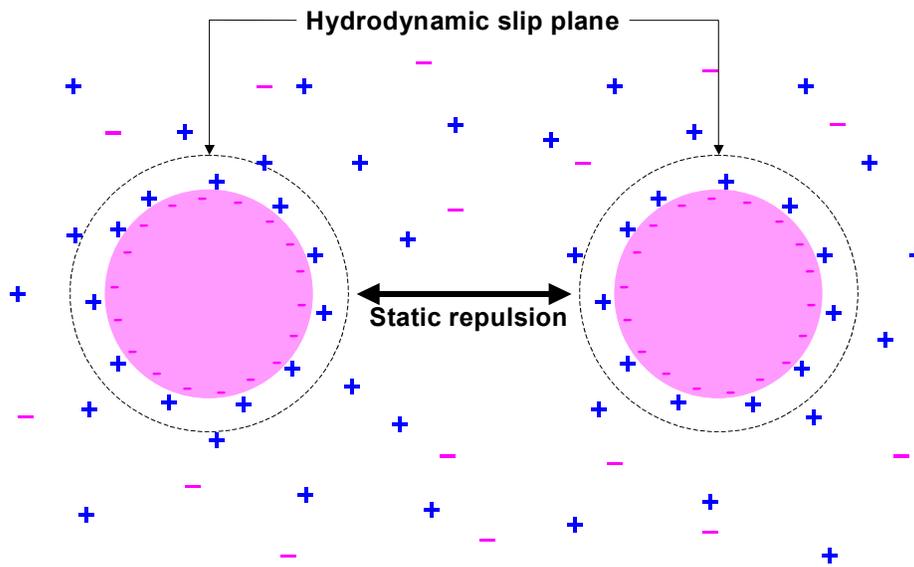


Figure 1.3.8: The mechanisms of the stability of colloids [103].

(b) Destabilizing colloids by adding coagulants

Adding positively charged coagulant ions (such as aluminum or ferric ions) neutralizes the negatively-charged particles, allowing particles to collide and aggregate as flocs. Although in Figure 1.3.9 the coagulants are monovalent, multivalent coagulants are used more commonly. About 100 years ago Schultz and Hardy first summarized the relationship between critical concentration of electrolytic coagulation (CCC) and the charge of the ion that carries opposite sign to the surface charge of colloidal particles. CCC refers to the lowest concentration of a certain ion that will coagulate a sample of suspended solids having opposite net charge. The higher the valence of the counter-ions, the lower the concentration of coagulant required to destabilize the particles. The rule developed by Shultz and Hardy can be expressed as $C = K / Z^6$, where C is

a coagulant concentration which is just sufficient to aggregate a colloidal solution, Z is the valence of the counter-ions, and K is a constant [104].

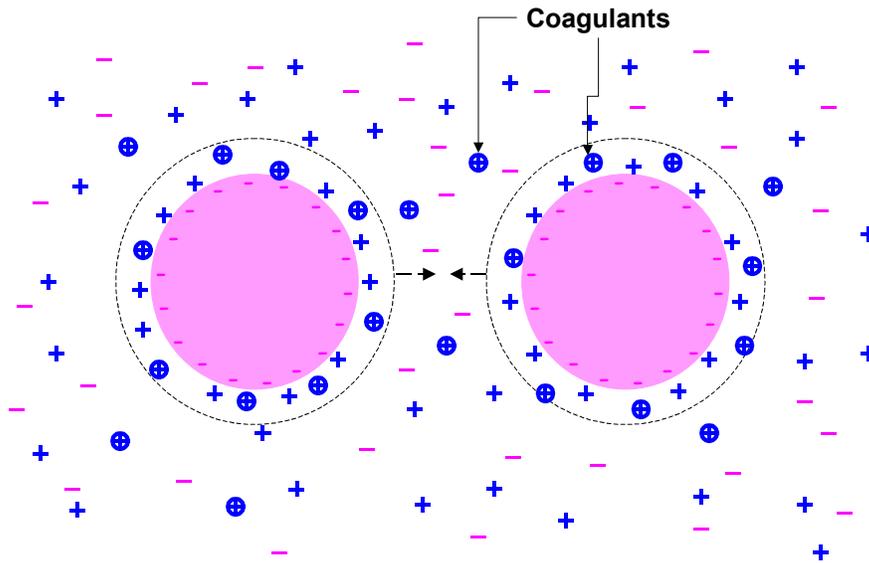


Figure 1.3.9: The mechanism of how a coagulant works.

(c) Coagulation and flocculation

The small flocs formed by coagulation can be built up into larger aggregates by either further collision or by flocculation with the aid of polyelectrolytes. The larger particles formed in this way have higher rates of sedimentation. The process of flocculating with polyelectrolytes involves polymer bridging, in which a polyelectrolyte bound to a floc particle has looped and dangling chains that can attach to nearby particles.

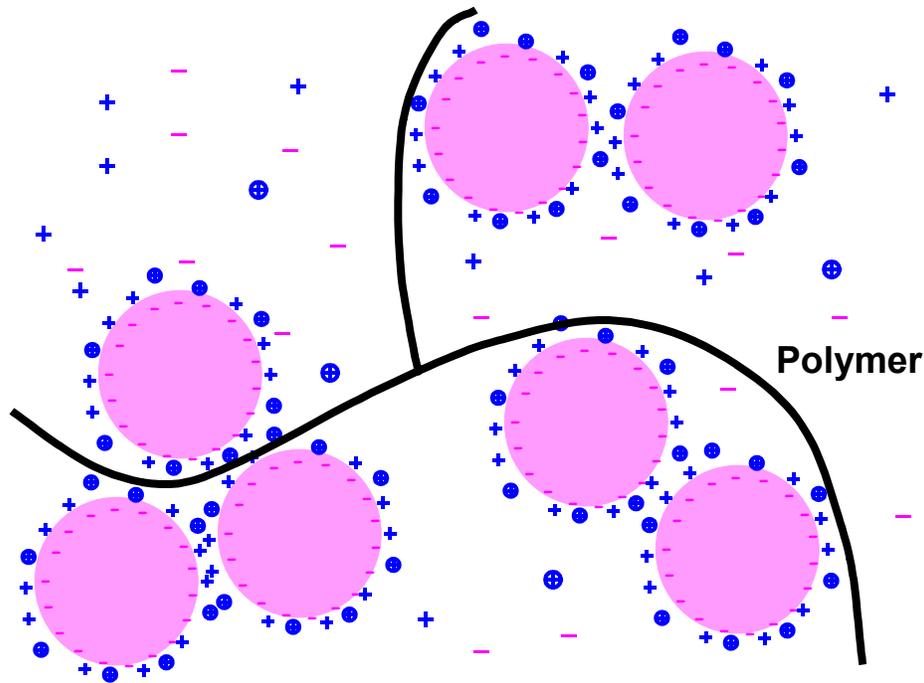


Figure 1.3.10: The formation of aggregates.

A wide variety of different products can be used as coagulants. By far the most common inorganic coagulants are iron and aluminum salts, especially for water and effluent treatments. These include aluminum sulfate, ferric sulfate and polyaluminum chloride. Aluminum compounds are more commonly used in the paper industry, more likely due to the color produced by the iron-containing coagulants. The effectiveness of such additives was originally explained in terms of the positively charged Al^{3+} or Fe^{3+} ions and the Schultz-Hardy rule.

3.6.2 Coagulation with Aluminum Ions

The coagulation performance of aluminum ions depends on several factors, such as coagulant dosage and coagulation pH.

(a) Coagulant dosage

Figure 1.3.11 shows typical coagulation curves, in which the coagulation is increased with the increasing coagulant dosage at different pH. As discussed in a previous section, it is believed that coagulant dosage affects coagulation by neutralizing the surface charges of particles [103,105]. Only values of scattering intensities corresponding to the peak state of coagulation are shown as increasing concentration of coagulation in Figure 1.3.11. At each pH level the turbidity was increased with increasing the concentration of the coagulant. A further study has shown that it is possible to observe the reversal of charge. Matijević *et al.* presented two cases demonstrating the restablization of the coagulated suspension. They observed that with increasing coagulant dosage the turbidity of the sol reached a maximum and then dropped sharply. This is consistent with reversal of charge. The initial stability was attributed to first adsorption of stabilizing ions (counter-ions, such as sodium ions in colloid silica). When increasing the amount of coagulant, colloidal particles start adsorbing oppositely charged ions such as aluminum species, with consequent neutralization of charge. Further adsorption of aluminum ions is expected to reverse the surface charge, which results in the restabilization of colloidal particles.

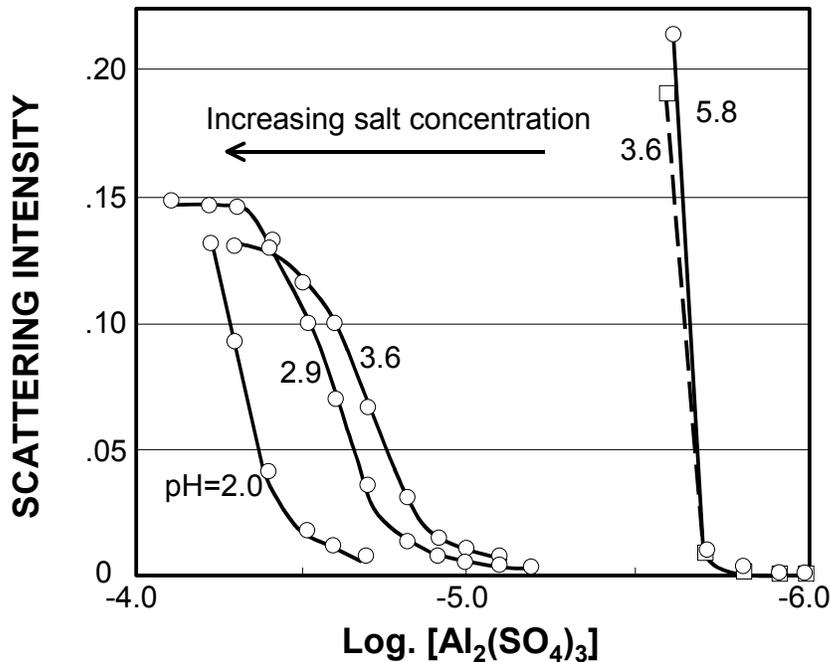


Figure 1.3.11: The coagulation curves of AgI in the presence of various amounts of aluminum sulfate as a function of pH [105].

(b) Coagulation pH

As discussed in earlier sections, various hydrolyzed products are expected to form after adding the aluminum soluble compound to solution, and these are believed to play the most important role in destabilizing any colloidal particles. According to the Shultz-Hardy rule, aluminum species, including highly charged polymeric ions such as $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ and precipitated metal hydroxide, would also play an important role in a colloidal coagulation process. The proportions of different species present in solution are dependent on pH. Matijević and his coworker's studied and reported the effect of pH on the performance of aluminum ions as a coagulant, using silver halide as a coagulation colloid [106]. Figure 1.3.12 shows the result of the coagulation effect over a wide range of pH and critical coagulation concentrations of aluminum

sulfate. There are two stable regions. One is below the circles, which represent the coagulation boundary, and the other one is above the triangles, which gives the stabilization boundary due to reversal of charge of colloidal particles. There are two distinct flat ranges on the coagulation boundary. At higher pH the critical coagulation concentration of aluminum ion is considerably lower than at a lower pH value.

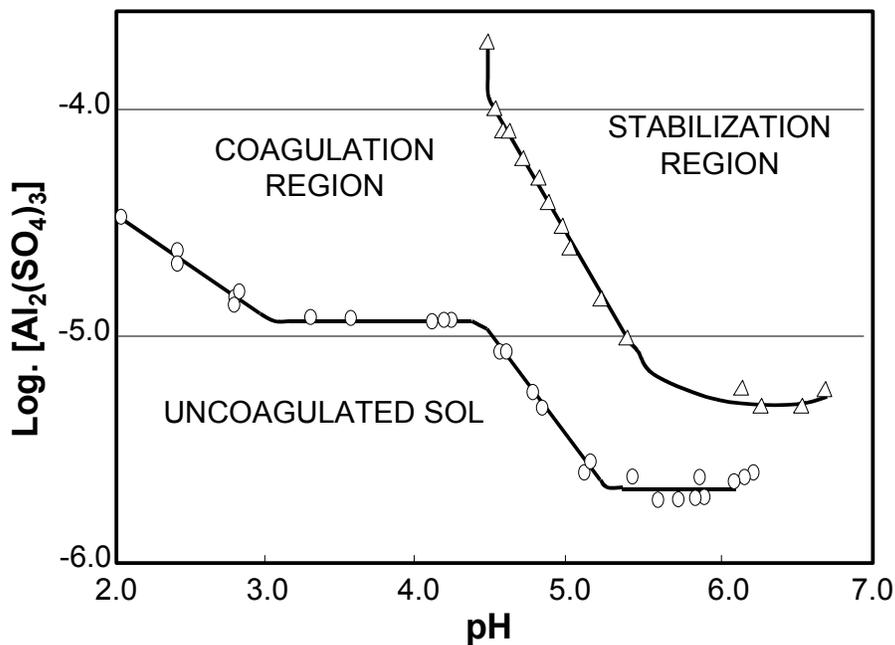


Figure 1.3.12: The entire $\log[\text{Al}_2(\text{SO}_4)_3]$ -pH domain for a silver iodide sol (AgI $1.0 \cdot 10^{-4}$ M, excess KI $4.0 \cdot 10^{-4}$ M) [106].

A nearly constant value of coagulation concentration up to $\text{pH} = 4$ indicated that simple trivalent ions were predominant at the aluminum ion concentrations that were considered. These results agreed with the prediction based on the Schulze-Hardy rule. At pH values between 4 and 7, the coagulation concentration dropped sharply, consistent with the formation of hydrolyzed

species with a charge higher than 3. By converting their pH value to degree of neutralization of aluminum ion, at OH/Al ratio 2.5:1 a highly charged polynuclear hydrolyzed aluminum species was formed and had best agreement with theoretical coagulation values calculated based on $[Al_8(OH)_{20}]^{4+}$ [105]. It is worth noting that their calculation was carried out before the more recent work related to the thirteen aluminum oligomer. It is possible that $[Al_{13}O_4(OH)_{24}]^{7+}$ fits their data better.

(c) Other factors

Besides coagulant dosage and coagulation pH, which are two of the most important factors influencing the types of hydrolysis products, and hence the mechanism of coagulation, there is another factor. “Aging” is particularly important for aluminum coagulants. In other words, the species of aluminum ions existing in the solution is not only dependent on the pH of the solution, but also on the length of time hydrolysis has been taking place [104]. By study of coagulation of silver halide sols, Matijević concluded that the “CCC of aluminum ions depended on the age of the solution.” The pH of these solutions was observed to decrease during aging. A decrease of coagulating concentrations occurred simultaneously with an increase of the hydrogen ion concentration [88]. One proposed explanation for the pH decrease was that the aluminum species were changed during aging, with the formation of a dimer with tetravalent charge or other polynuclear species. Follow up work shown in Figure 1.3.11, showed that the CCC using aged aluminum sulfate solution at pH 3.6 (squares) and fresh

solution at pH 5.8 (circles) were identical. That indicated that aging and rising pH produce essentially the same effect [106].

It has been reported that aluminum ions in nitrate or chloride form behave differently when compared to aluminum ions in the presence of sulfate anions [106]. This directly affects the adsorption and retention behavior. The chemistry of aluminum ion in AlCl_3 or $\text{Al}(\text{NO}_3)_3$ is simpler than that in alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$). It has been reported that a small amount of the sulfate ions show no detectable complexing effect. However when the amount of the sulfate ions increased considerably, coagulation concentration increased significantly [106]. One possible explanation is that the sulfate ion is also a strong complexing agent. It can decrease the positive charge of aluminum species by inner-sphere complexation [99]. In other words, sulfate ion complexes with aluminum ions to form a lower-charge complex.

4. References

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Chapter 2

Research Objectives

Motivations for This Research

It has been observed that (a) the endpoint of a charge titration involving a streaming current titration could be shifted as the conductivity of the solution increases, and (b) aluminum ions may have different interference with a charge titration, compared to other monovalent and divalent ions.

These observations raise significant questions about the reliability of the streaming current charge measurement technique that is widely used within the paper industry to monitor and control the use of charged additives. The range of the conductivity within which the streaming current test can provide a reliable result is important. In addition, these observations may lead to important new insights into the interactions among polyelectrolytes and between polyelectrolytes, their complexes, and solid surfaces.

Other questions derived from the reported observations are (a) whether the critical concentration of monomeric electrolytes sufficient to cause endpoint deviations in streaming current tests depends on the molecular mass of the cationic titrant, (b) whether the endpoint shifting is related to the molecular mass of the anionic polymer if the conductivity is kept constant, (c) whether the order of addition of polyelectrolytes causes the endpoint to shift in the same direction, in the presence of different levels of monomeric ions; and (d) whether the presence

of aluminum ions interferes with the titration endpoint, over a range of pH values within which the streaming current method is frequently practiced.

Hypotheses

From a practical perspective, the following hypotheses provide a basis for the present work: First, it is proposed that as the electrical conductivity of an aqueous polyelectrolyte solution is increased by monomeric or divalent ions, the stoichiometry of a charge titration may be affected by (a) the molecular mass of at least one of the polyelectrolytes, (b) the charge density of the polyelectrolytes, and (c) the direction of charge titrations, in other words, which polyelectrolyte was added first and which was used as the titrant.

When aluminum ions are present in the solution, the hypothesis proposed is that the interference of aluminum ions may depend on (a) pH, and (b) the degree of neutralization. Furthermore, the aluminum ion itself may be titrated as a colloidal sample. The stoichiometry between aluminum ion and PVSK will also be investigated.

From a theoretical perspective, the hypothesis proposed is that the observations of the titration endpoint shifting noted in the previous section can be explained by (a) changes in the adsorption of polyelectrolytes or their complexes onto the plastic surfaces of the streaming current device, and/or (b) changes in the stoichiometry of polyelectrolyte complexes.

With respect to changes in adsorption, it is assumed that polyelectrolytes can significantly affect streaming current output only to the extent that they are able to attach to the plastic surfaces and affect the electrical double layer. Polymer adsorption onto the probe surface is necessary for the analyzer to work properly.

A further hypothesis is that when the ionic strength is high, polyelectrolyte complex formation doesn't follow a 1:1 stoichiometry, because of such factors as (a) unequal spacing of ionic groups on the oppositely charged materials, (b) issues of accessibility of un-complexed, charged groups that may be trapped in the interior of polyelectrolyte complexes, and (c) an excess charge of adsorbed polyelectrolytes surrounding a neutral interior core of polyelectrolyte complexes at the endpoint of a streaming current titration, possibly causing such complexes to be stabilized against coagulation. Details of this hypothesis will be discussed in chapter 4. A related question is what role the low molecular mass ions play during the polymer interactions and whether or not they screen the interaction sites of polyelectrolytes.

When aluminum ions exist in solution, the hypothesis proposed is that the interference with charge titration is due to the presence of certain polynuclear ionic species. This issue will be considered only in Chapter 6.

Chapter 3

Measurement of Colloidal Charge in the Paper Mill by Streaming Current *

Abstract

The colloidal charge of process water within a paper mill can profoundly affect process efficiency and product quality. With increased pressure for productivity and reduced costs the need for accurate and reliable charge measurements has become more urgent. But the paper machine environment presents challenges that may limit the accuracy of such tests. Recently the streaming current method has become the most widely used means of charge analysis. This report presents new data, helping to define the range of sample types and electrical conductivity where it is possible to achieve accurate and reliable results from streaming current titrations. Within the limits of these ranges the results are consistent with a model of polyelectrolyte adsorption onto the plastic probe surfaces of the test instrument. Outside of these limits the results may be unreliable.

* *This chapter has been modified from the following publication: Proc. TAPPI Papermakers Conf., 2001 (Authors Chen, J., Hubbe, M. A., and Heitmann, J. A.).*

1. Introduction

There has been an increasing need for quick and reliable tests of colloidal charge in the process water of paper machines. Papermakers are confronting new issues in paper recycling, reductions in fresh water use, new product objectives, and demands for increased productivity. It has been understood for many years that the charges at surfaces of fibers, fines, and colloidal materials in the furnish play a fundamental role in retention and drainage during formation of the paper web [1]. Several recent studies report progress in understanding the sources of charge variation [2-4]. Other studies report progress in understanding how charge variations can adversely affect process efficiency [1,5-9].

Colloidal charge measurements require two things. First, they require some form of titration. The titrating agent is usually a polyelectrolyte having a colloidal charge opposite to that of the sample. Second, they require some means of detecting the point where the aqueous system has been neutralized to a zero charge or a zero zeta potential [1].

Though other methods of colloidal charge determination are available [1], the streaming current titration method has emerged as the most popular, especially when it comes to online applications in paper mills [5-6].

As illustrated in Figure 3.1, another typical streaming current device, beside that in Figure 1.2.1, involves the reciprocal motion of a plastic piston that is loosely fitted within a closed-ended plastic cylinder [10-14]. The annular space between

the piston and the cylinder wall is filled with the fluid sample of interest. The user makes an implicit assumption that materials from the sample interact with the plastic surfaces and dominate the electrical charge properties of those surfaces [10,15-16]. The charged materials that adsorb onto these probe surfaces may include polyelectrolytes [2,17], surfactants [12], or colloidal particles [18]. Because the annulus is narrow relative to the size of the piston, the reciprocal motion gives rise to a high velocity of the liquid relative to the probe surfaces.

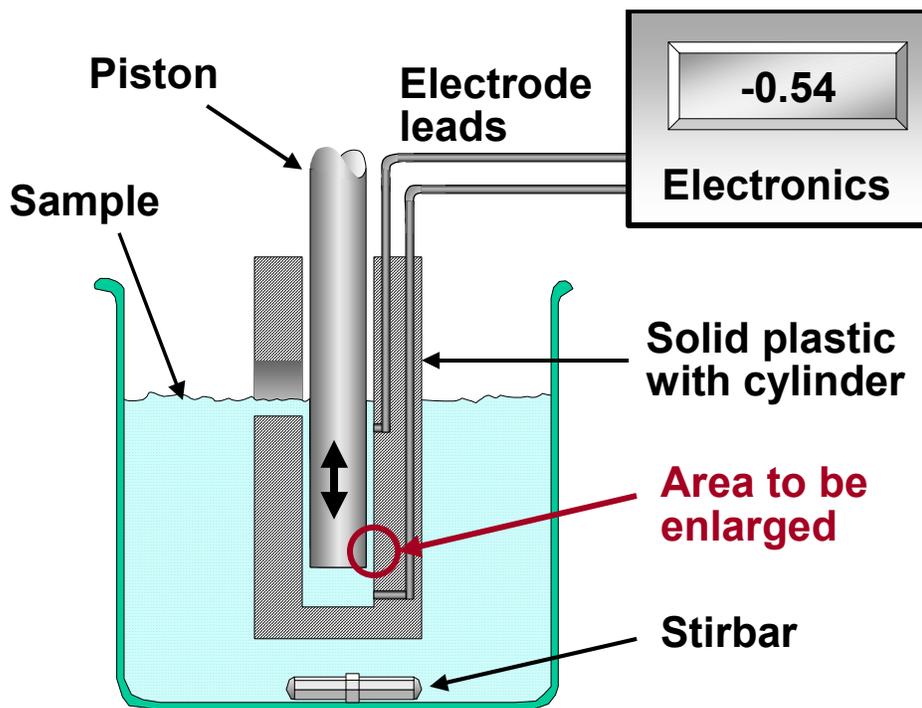


Figure 3.1: Schematic illustration of a streaming current detector used to detect the endpoint of polyelectrolyte titrations.

Figure 3.2 is a schematic enlargement of the circled area in Figure 3.1. It illustrates what happens when the plastic surfaces are in contact with an ionic solution, as in the case of filtrate collected from a paper machine system. As

shown, the net charge of the surface, including the charged materials adsorbed onto that surface, has to be balanced by an equal number of opposite charges of ions in the solution. If the surface has a net negative charge, then the net charge has to be balanced by counter-ions such as sodium or calcium ions.

Electrostatic forces tend to draw such ions towards the surface. Brownian motion due to thermal energy of the system causes the same ions to diffuse in all directions [19]. The resulting distribution of ions is called the “double layer” [1,19]. Some ions in the double layer are far enough away from the surface so that they move with the flow of liquid past the surface, creating an electric current, the “streaming current.” There are two ways in which the circuit for this current can be completed. One way is by conduction of electricity back through the liquid itself. The other is by an external circuit, as illustrated in Figure 3.1. Since the resistance of the external circuit is much lower than the path through the solution, the streaming current can be measured by suitable instruments [10].

Progress has been reported in understanding various aspects of the streaming current method. For instance, Walker *et al.* [15] have developed a more accurate model of fluid flow that includes inertial effects in the device [15]. Others have contributed to an understanding of how the movement of ions adjacent to a surface results in an electrical current [2,10,12,15]. In practice, a low-resistance amplifier circuit detects this current. A rectifier switch and electronic filter convert the alternating signal to a direct-current signal to be viewed by the user. The sign of the rectified and smoothed signal obtained when a sample first is added

to the apparatus indicates the sign of the net charge on the plastic surfaces [12-14].

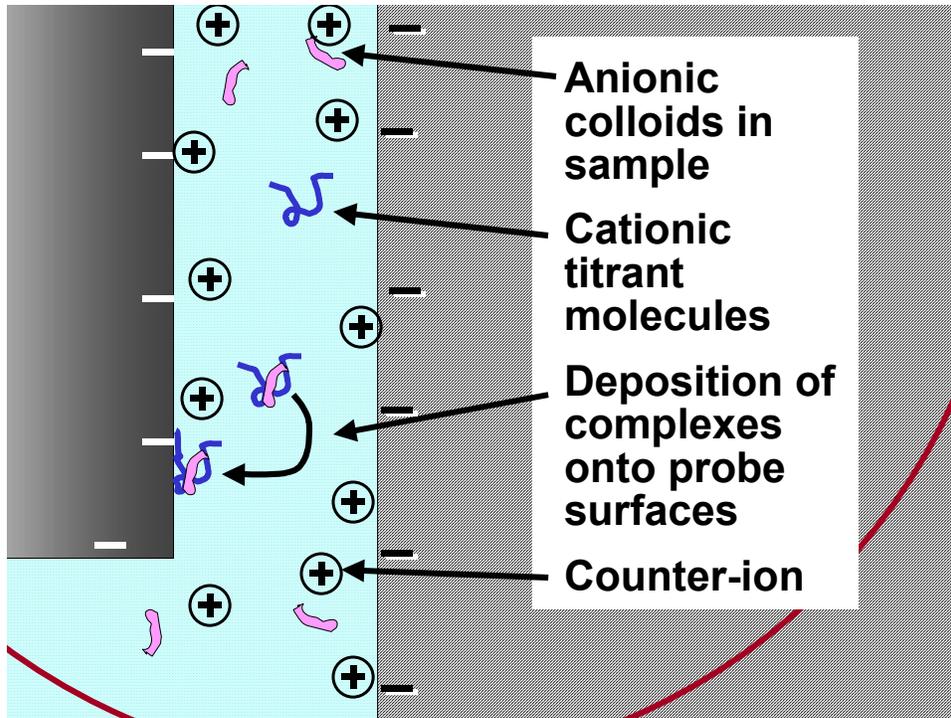


Figure 3.2: Schematic illustration of ions and colloidal material associated with plastic surfaces in a streaming current device exposed to an aqueous sample and titrant.

Experience has shown that the paper machine tends to run steadier, producing a more uniform product, if the colloidal charge is controlled to a steady value [4,5,7,9,20]. In terms of the streaming current method, one can define “colloidal charge” as being equal and opposite to the amount of standard titrant needed to reach an endpoint of zero. The question sometimes arises as to whether it might be sufficient just to use the initial signal, without titration, as the basis for process control decisions. There appear to be two main reasons to rely on the titration endpoints, rather than on the magnitudes of the initial streaming current values.

First, the process of titration is likely to make polyelectrolytes and colloidal materials in the fluid become less soluble, especially when nearing the end-point, because of charge neutralization [4]. This increases the likelihood that the plastic surfaces are well covered with materials that are representative of the sample. Second, a titration procedure provides output that has a simple relationship to the flows of charged additives. For example, a change in the flow of anionic colloidal silica can be expected to produce a linear increase in the amount of cationic titrant needed to reach the endpoint [4,7].

As noted by Walker *et al.* [15], there are three basic assumptions that have to be met, at least partly, for the streaming potential device to give accurate information. First, the plastic surfaces are assumed to be completely covered with materials from the sample. Second, those materials that have adsorbed onto the plastic surfaces are assumed to be representative of all the colloidal materials in the sample. In other words, the system is assumed to be at equilibrium, with exchange of adsorbable material between different surfaces in the sample and with the plastic surfaces. Third, it is assumed that there are no electrical artifacts coming from sources other than the electrical double layers on the plastic surfaces. Several authors have expressed doubt that the plastic surfaces become fully covered by materials from the sample [2,14,16]. Part of the signal is likely to come from the plastic itself, especially at the start of the titration, before materials have become neutralized and precipitated. This source of error is only partly addressed by use of PTFE and other plastics that tend to have a low surface charge [3]. It is an ironic feature of the method that PTFE, a

substance having generally low affinity for other materials, is given the task of collecting colloidal materials on its surface to be evaluated. Justifications for the use of PTFE include the facts that (a) its surface has relatively little charge of its own when exposed to water, (b) it does not have any preference to adsorb either cationic or anionic species, and (c) it is relatively easy to clean.

2. Motivation for Present Work

Recent results reported by Tanaka *et al.* [21] have raised doubts about whether the three assumptions given above are valid over the whole range of electrical conductivities commonly found in paper mill systems. The endpoints of streaming current titrations between pairs of strongly ionized polyelectrolytes were reported to give reliable results up to a sodium chloride level of about 2 mM. At a concentration of 20 mM the report showed a strong, unexplained shift in the titration endpoint, relative to the case of no added salt.

The goal of the present work is to further define and understand the accuracy of the method under conditions of increasing salt or electrical conductivity.

Papermakers need to know under what conditions of electrical conductivity they can expect valid results. Also, they need to know whether the reliability of streaming current results is affected by the type of sample to be tested. This information can help the papermakers use these tests more accurately, since they will know the following:

- When they may accept all of the results as reliable;

- When they should use a more labor-intensive test procedure, such as diluting all the samples by a known factor to keep the conductivities in an acceptable range; or
- Under what conditions of the aqueous samples it is necessary to abandon the streaming current method entirely and to seek other, more reliable strategies to optimize or control the flows of charged additive.

The third alternative, if applied to all samples, would be unfortunate, since the streaming current method is arguably the quickest and most reliable way to monitor and control charge that is widely available within the paper industry [2-9].

To help determine the range of conductivity giving valid streaming current endpoints, experiments were carried out over a wide range of sodium chloride concentration in the presence or absence of 100 ppm calcium chloride (for water hardness). To represent the diversity of negatively charged materials likely to be present in paper mill waters [1], tests were carried out with anionic compounds that spanned a wide range of charge densities and compositions.

3. Experimental

3.1 Materials

De-ionized water having a conductivity of approximately 2 $\mu\text{S}/\text{cm}$ and a pH in the range 5.9 to 6.2 was used to prepare all the aqueous samples. Salts such as

sodium chloride and calcium chloride were reagent grade (Fisher). All were used without further purification.

The poly-diallyldimethylammonium chloride (poly-DADMAC) solution used in the experiments was obtained from Aldrich as a 20% solids solution described as “low molecular mass” (Average MW ca. 100,000-200,000, catalogue no. 40,901-4). It was diluted to a working concentration of 0.001N.

Negatively charged polymers are shown in Table 3.1:

Table 3.1: Anionic polymers.

Type of Polyelectrolyte	Code & Lot. No.	Degree of Substitution	pH
CMC, low mass *	CMC 7L, lot. 70470	0.80	6.02
CMC, medium mass	CMC 7M, lot. 67011	0.72	6.04
CMC, high mass	CMC 7H, lot. 70177	0.85	5.95
CMC, medium charge	CMC 9M8, lot. 69882	0.88	6.05
CMC, high charge	CMC 12M8, lot. 70327	1.33	6.25
Oxidized corn starch	Douglas 3060; Penford	0.022	6.24
Acrylamide-acrylate copol.	Hercobond® 2000	0.08	6.59
Poly-vinylsulfate, K salt	Aldrich, cat. 27,196-9	1.0	6.38
* Note: “CMC” stands for carboxymethylcellulose, a soluble derivative of cellulose.			

The poly-vinylsulfate sample in Table 3.1 had a mass-average molecular mass of 170,000 Daltons.

Anionic polyelectrolyte solutions were prepared by first calculating theoretically how much anionic sample was needed in each case for 100ml of 0.001N solution. Then that amount of material was dissolved in deionized water to make a net volume of 100 ml.

3.2 Instrumentation

Titration tests were conducted using a bench-top streaming current detector ECA 2000 from Chemtrac Systems, Inc. This device employs the kind of geometry that was illustrated schematically in Figures. 3.1 and 3.2. (For purposes of illustrating the principles in two dimensions, the relative position of the electrodes is shown 90 degrees from their true position and one of the openings in the cylinder “boot” is not shown.) The piston, and boot were both composed of PTFE. The piston was approximately 1.25 in diameter, with an annular width of less than 1 mm. The period of reciprocation was approximately 0.25 seconds.

3.3 Procedures

Aliquots of 1.00 ml of anionic polymer were prepared as described under Materials. Each aliquot was then diluted to a final volume of 170 ml with water of a selected hardness and salt content. A period of 20-30 minutes was provided for the streaming current signal to reach a steady value before each titration. Then, the cationic titration solution (poly-DADMAC) was added gradually until the signal reached an endpoint value of zero. Work reported involved a waiting period of 1 minute between addition and measurement until the endpoint was

approached. A waiting period of 3-5 minutes was used in the vicinity of the endpoint.

4. Results and Discussion

4.1 Effects of Time

Gerdes [10] and Phipps [3] reported that between one and five seconds are sufficient for complete mixing of the titrant within the sample solution, even within the confines of the annulus. However, in agreement with earlier studies [3,10,13], we observed that streaming current signals continued to shift for several minutes following each addition of titrant. Thus, the time required for mixing cannot explain the observed time effects. Our observations are consistent with the expected conformational changes of adsorbed polyelectrolytes and competition between different adsorbable species [22]. Indeed, reported hysteresis effects provide further evidence that the adsorption interactions are slow to reach equilibrium [17-18].

Phipps questioned the assumption that papermaking systems are ever at equilibrium with respect to charge [3]. Evidence to the contrary comes from examination of particle motions in an electric field, *i.e.* micro-electrophoresis. Such tests often show distributions in which some particles have a net negative zeta potential and others have a positive zeta potential. If the systems were at equilibrium, then we would anticipate nearly equal values of zeta potential due to

the exchange of polyelectrolytes and colloidal materials between the different surfaces.

4.2 Effects of Temperature

Normally, charge titration tests are carried out at room temperature. However, the temperature in papermaking process may vary from room temperature to near 80°C. Or if tests are running long enough, the temperature of sample solutions will be also increased to certain extent. Therefore the effect of temperature was investigated.

Deionized water was heated up to a desired temperature and used as the aqueous media of charge titration. After sample was added, temperature was measured, and then titration was carried out with poly-DADMAC and PVSK.

The results are shown in Figure 3.3 and Figure 3.4, with PVSK and poly-DADMAC as samples respectively. The vertical axis in Figure 3.3 is the ratio of molar amount of repeated units of poly-DADMAC to that of PVSK. So it is in Figure 3.4, except that the ratio is reversed. From the statistical analysis, the slopes of regression lines for both titration directions are very low. The F-test shows the coefficient of regression line in Figure 3.3 failed to reject the hypothesis that the coefficient was zero. On the other hand the R-square was very low too. Therefore, when PVSK was added as sample, there was no linear relationship between temperature and titration stoichiometry.

Although the F-test rejected the hypothesis that the coefficient of x in the regression line in Figure 3.4 was zero, the absolute value of that coefficient was very small (0.0004). That means the difference in stoichiometry caused by temperature was less than 2% between 70°C and room temperature. However, the R-square value was about 0.65, which was not very high. That means the proposed linear model is not a good model to explain this variation.

From the initial signal of the background solution (before the sample was added), there is a tendency for the signal to become more negative as temperature increased. However, this increase had no significant impact on the titration results.

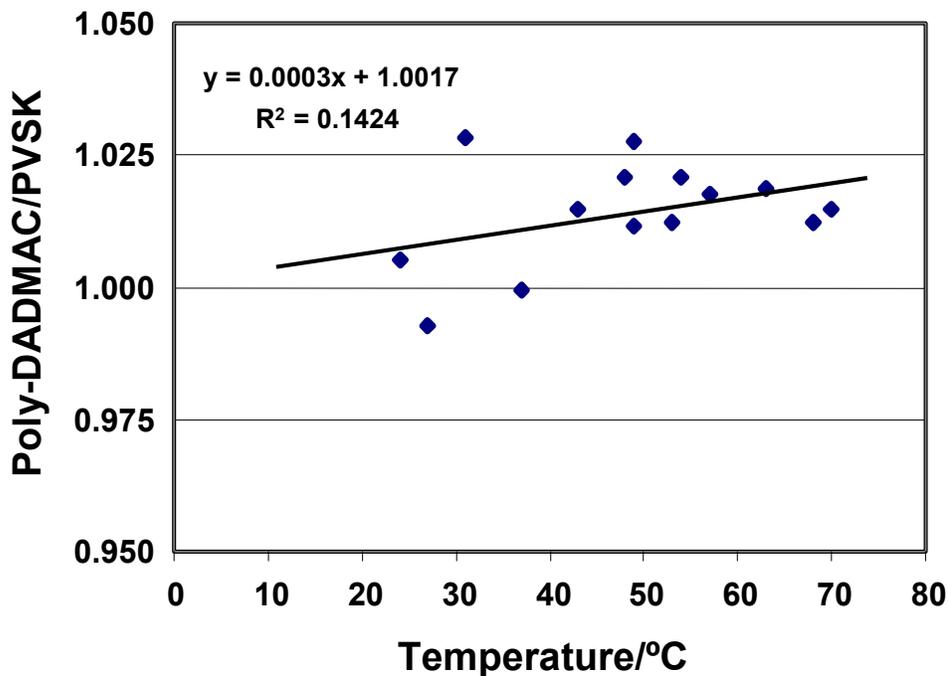


Figure 3.3: The effect of temperature on the stoichiometry of streaming current titration (PVSK as sample).

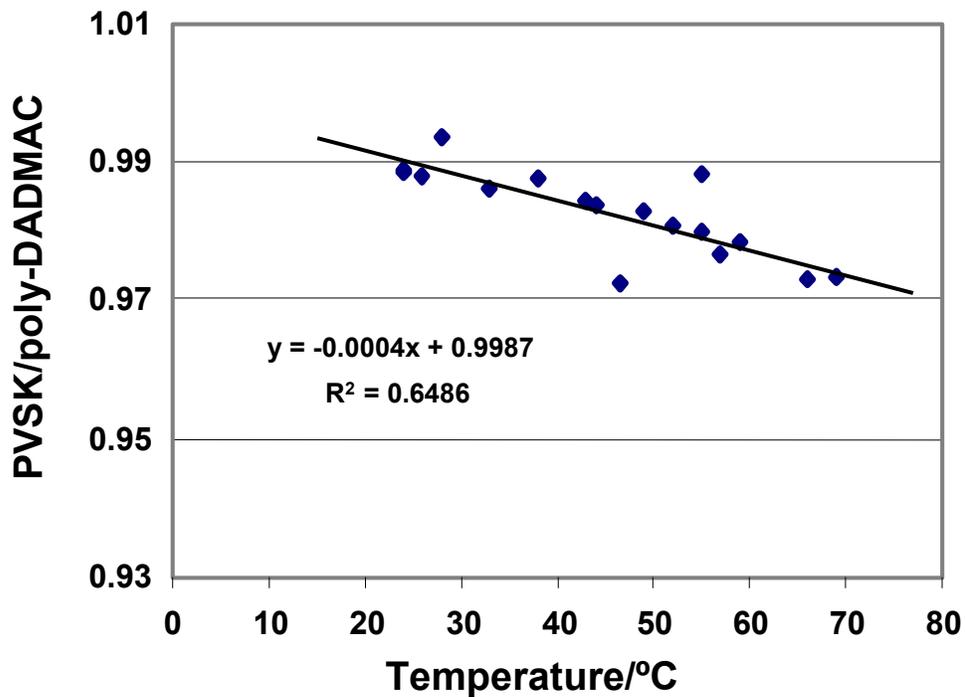


Figure 3.4: The effect of temperature on the stoichiometry of streaming current titration (poly-DADMAC as sample).

4.3 Reproducibility

As shown in Figure 3.5, a titration of carboxymethylcellulose (CMC 12M8) by 0.001 N poly-DADMAC yielded smooth, reproducible curves. Endpoints were relatively sharp and easy to determine by interpolation of the data to zero streaming current signal. Note that the procedure was repeated in deionized water and in artificially hard water with 100 ppm of CaCl₂ added.

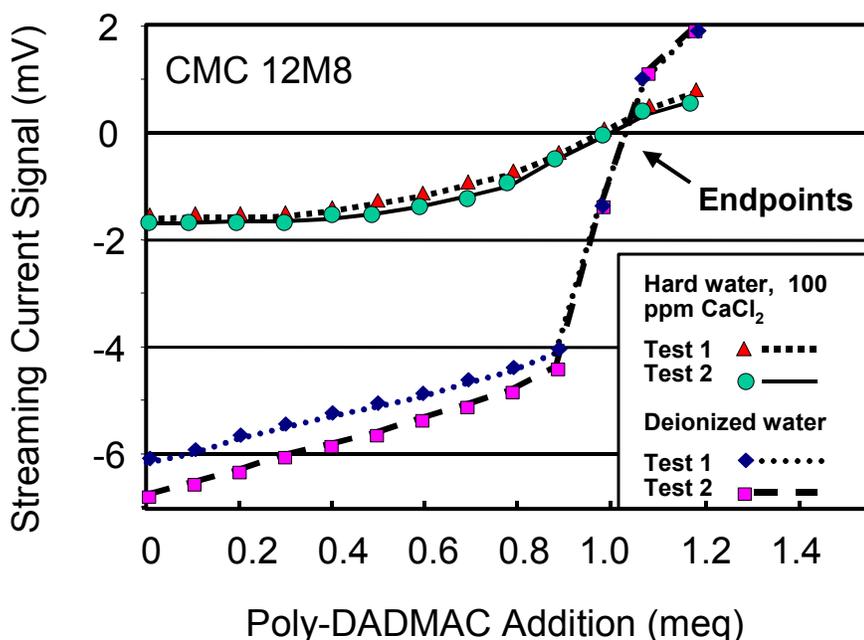


Figure 3.5. Replication of titration curves in hard water and deionized water.

The fact that the streaming current signal decreased gradually, throughout the titration, is consistent with two processes occurring simultaneously. One of these processes is a complexation reaction between the two polyelectrolytes [22]. The other is an adsorption of polyelectrolytes, including polyelectrolyte complexes, onto the plastic surfaces [23]. It is reported both from theoretical [24-25] and experimental [26-28] studies that adsorption of high-mass polymers has the potential to completely mask or reverse any underlying charge of a solid substrate.

4.4 Effects of Increasing Conductivity

Figure 3.6 shows a family of curves obtained with another CMC sample (CMC 7M, see Experimental). The concentration of CaCl₂ was held constant at 100 ppm for the experiments represented in Figures. 3.6-3.8. Experiments were

conducted at increasing levels of NaCl. Each curve shown is the average of two replicate titrations.

Some hypotheses to account for the observed results will be described later. However, some features relating to mechanism are evident already in Figure 3.6. The observed effects of increasing conductivity included (a) a decrease in the absolute magnitude of the initial signal, and (b) a shift in the endpoint.

The reduction in absolute value of the signal with increasing salt content is consistent with theories of ions in aqueous solutions near to interfaces. It is known that the characteristic distance of diffuse counter-ions from a charged surface decreases with increasing ion concentration [19]. For example, an increase in Na_2SO_4 concentration from 0.001 molar (140 ppm) to 0.01 molar (1400 ppm) is expected to decrease the double-layer thickness parameter from about 6 nm to about 2 nm. This change in concentration is consistent with conductivities of about 0.4 and 2.0 mS/cm, respectively. (Note that 0.4 mS/cm is the same as 400 $\mu\text{S/cm}$ or 400 micro-mhos.) These are typical values for “very open” to “intermediate” paper machine water systems. In terms of the streaming current measurements, the compression of the electrical double layer means that a larger amount of the counter-ions reside close enough to the surface that they lie inside of the hydrodynamic slip plane and do not contribute significantly to the streaming current signal [29].

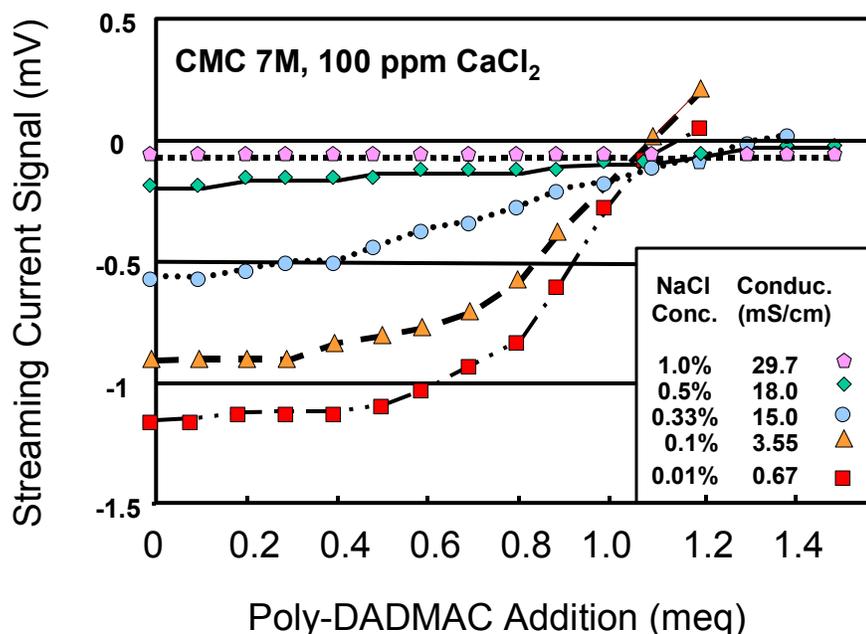


Figure 3.6: Effect of NaCl concentration on titration of CMC solution by poly-DADMAC.

The shift in the titration endpoint is less easy to interpret, since there are several competing explanations, to be described later. Figure 3.6 shows two types of changes in the endpoints with increasing conductivities. For conductivities in a low to moderate range (e.g. 0.2 to 4 mS/cm) the amount of cationic poly-DADMAC needed to reach the endpoint increased moderately with increasing concentration. For concentrations of 18 mS/cm and higher no practical amount of poly-DADMAC titrant was able to reverse the meter output to a positive value.

One preliminary hypothesis to explain the shift in endpoints toward higher amounts of poly-DADMAC with increased electrical conductivity would entail changes in the stoichiometry of complexes formed between the oppositely charged polymers. According to Tanaka *et al.* [22], such changes may be

relatively large. They are certainly large enough to explain the present shifts.

The same cited study also provides a way to test the hypothesis. It is shown that the effect of increased salt is critically dependent on the relative charge densities of the two polyelectrolytes. Accordingly, further tests were performed with anionic polymers covering a wide range of charge density.

4.5 Effects of Charge Density of the Anionic Polymer

As shown in Figure 3.7, titration curves of anionic potassium poly-vinylsulfate (PVSK) solutions with the same poly-DADMAC cationic titrant yielded sharp endpoints. PVSK represents the case of a high-charge-density polymer. Note the strong similarity to Figure 3.6. Once again, increasing salt affected both the initial streaming current signal and the position of the endpoint. A titration endpoint was achieved in the presence of hard water with 0.1% NaCl (3.55 mS/cm), but not with 1.0% NaCl (29.7 mS/cm).

The characteristic shape of the titration curves in Figure 3.7 is consistent with a rapid interaction between the titrant molecules and the PVSK molecules in solution. The streaming current signal did not change markedly during the initial part of each titration. And then it changed more rapidly as the endpoint was approached. This is consistent with the hypothesis that two processes are occurring simultaneously at this period of time. One of these processes is a complexation reaction between the two polyelectrolytes [22]. The other is an adsorption of polyelectrolytes, including polyelectrolyte complexes, onto the plastic surfaces [43]. The results suggest that significant adsorption of poly-

DADMAC onto the plastic surfaces occurred only after most of the dissolved PVSK had become complexed with poly-DADMAC.

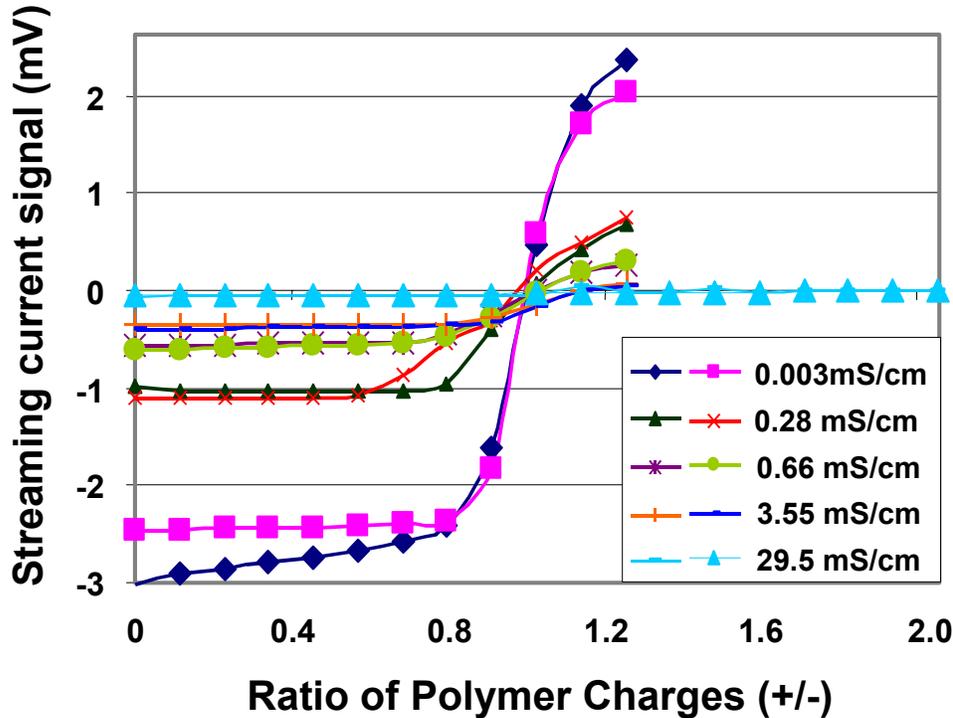


Figure 3.7: Effect of NaCl concentration on titration of highly charged anionic polymer with poly-DADMAC.

Figure 3.8 shows a titration curve for an anionic polymer of much lower charge density, oxidized starch. Colloidal titrations of various kinds are known to work best when carried out with highly charged poly-electrolytes of opposite charge; therefore it is reasonable to assume that weakly charged materials, such as oxidized starch, can be considered as a “worst case” type of sample. The shapes of the titration curves are different, compared to Figure 3.7. The streaming current output began to change right from the start of the titration. The shape of the titration curve suggests that the interaction between poly-DADMAC and the oxidized starch in solution was slow or weak relative to the adsorption of

either poly-DADMAC or complexes between the two polymers onto the plastic surfaces.

As shown in Figure 3.8, titrations of the oxidized starch in the presence of hard water with 100 ppm of NaCl and an electrical conductivity 0.67 mS/cm resulted in a clear, unambiguous endpoint. In fact, all titrations carried out in this work were successful under those conditions of background electrolytes. However, at a higher concentration of 0.1% NaCl (3.55 mS/cm) there was no distinct endpoint, even at addition levels exceeding those shown in the figure. To use round numbers, the method worked on all samples up to a conductivity of about 1 mS/cm, but it depended on the nature of the anionic polymer in the sample when the conductivity was much higher.

Results for several different types of anionic polymers are summarized in Table 3.2. In each case the titration endpoints are expressed as ratios; the amount of poly-DADMAC needed to reach the endpoint is compared to the corresponding value in the absence of both NaCl and CaCl₂.

Before considering effects of increasing conductivity it is worth noting that the method appeared to work well for all of the samples in the presence of hard water without added NaCl. The observations shown in Table 3.2 for low electrical conductivity values are consistent with results reported by Tanaka *et al.* [30], who observed strong adsorption of cationic polymers onto plastic surfaces over a wide range of polymer charge densities. In the present study, however, it

was the charge densities of the anionic polymers that were varied. The cited work was carried out at low electrical conductivity with de-ionized water.

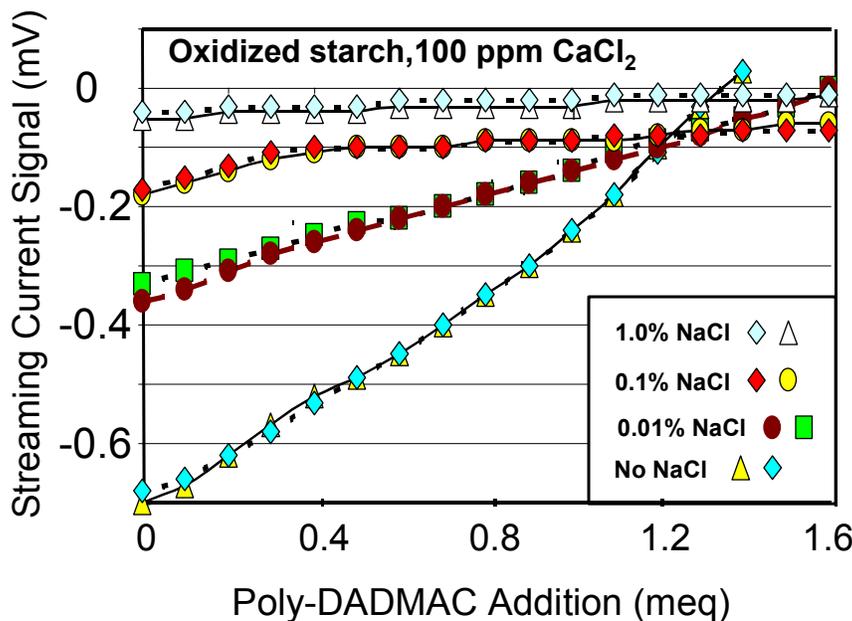


Figure 3.8: Effect of NaCl concentration on titration of low-charge density anionic polymer with poly-DADMAC.

Table 3.2 also shows effects of increasing NaCl. In most cases increasing electrolyte concentration tended to increase the relative amount of cationic polymer needed to reach the endpoint. In regard to the preliminary hypothesis given earlier, it is worth noting that there was a trend that decreasing charge density of anionic polyelectrolytes could increase the degree of endpoint shifting with increased salt concentration. However, the observed trend could be attributed to the difference of backbone structure of different polymers as well as charge density. If one considers only the study of CMCs, there was no consistent trend in the results relative to the charge densities of the anionic polymers.

Table 3.2: Effects of poly-anion charge density and NaCl on the endpoints of streaming current titrations.

Aqueous Electrolyte Conditions					
CaCl ₂ (ppm):		100	100	100	100
NaCl (ppm):		0	100	1000	10,000
Conductivity (mS/cm):		0.277	0.667	3.55	29.7
Anionic Polymer	Charge Density (meq/g)	Poly-DADMAC Required to Achieve Zero Signal (relative amount, compared to tests in de-ionized water)			
PVSK	6.2	0.99	1.04	1.14	2.11
CMC 12M8	5.0	0.95	0.97	1.07	*
CMC 9M8	3.8	0.85	0.87	1.43	*
CMC 7L	3.5	1.00	1.08	1.31	*
CMC 7M	3.3	1.12	1.23	1.30	*
CMC 7H	3.7	0.99	1.00	1.67	*
Copolymer	1.2	1.07	1.23	1.80	*
Oxidized starch	0.14	1.05	1.24	*	*
* The signal remained negative in the presence of excess poly-DADMAC.					

Further work along similar lines showed that there are no significant effects of molecular mass of both cationic and anionic polymer on endpoint shifting during the titration. (See appendix A for more detailed results).

4.6 Possible Explanations for the Endpoints Shift at High Conductivity

Already we have considered one hypothesis that might explain the observed shifts in titration endpoints with increasing NaCl concentration [22]. That hypothesis is re-stated below as the “first hypothesis.” In addition, there are at least two other hypotheses to consider. Figure 3.9 shows simplified schematic representations of the three hypotheses.

First hypothesis: Stoichiometry of Complexes. It is possible that observed shifts in titration endpoints could be due to changes in the stoichiometry of complexes formed between the anionic polyelectrolytes and poly-DADMAC. According to a study by Tanaka [22], increasing conductivity is expected to affect the stoichiometry of polyelectrolyte complexation in the following way: Whichever polyelectrolyte has a higher charge density tends to become shielded to a greater extent, losing its complexing ability at a faster rate than the lower-charged polymer of opposite charge. Although data obtain from PVSK and oxidized starch are consistent with Tanaka’s finding, results in Table 3.2 show no consistent trend *versus* the charge density of the anionic polymer. Therefore, the first hypothesis does not explain the results.

Second hypothesis: Adsorbed Conformations. Another approach is to assume that the shifts in titration endpoints with increasing conductivity are due to changes in adsorbed conformations of polyelectrolytes [17]. When linear polymers are compared under identical solvent conditions, the radius of gyration is expected to increase as the 0.588 power of molecular mass (self-avoiding

random walk model) [31]. Increasing conductivity is expected to reduce the radius of gyration of dissolved polymers due to shielding of intra-molecular repulsive forces [19,32]. Studies have shown that that increasing conductivity can affect polyelectrolyte adsorption either positively or negatively, depending on the circumstances. Moderate increases in salt have been found to increase the amounts of individual polyelectrolytes that can adsorb onto oppositely charged surfaces in certain cases [33-35]. This trend of increasing adsorption with increasing salt is consistent with the transformation from a flat adsorbed conformation to a three-dimensional conformation with loops and tails extending from the surface. Since past studies have been concerned with single adsorbates, rather than the composition of adsorbed polyelectrolyte complexes, it is not possible to predict how this mechanism would be likely to affect streaming current signals.

Third hypothesis: Inhibited Adsorption. A third hypothesis is that the observed shifts are due to decreasing efficiency of adsorption of poly-DADMAC or its complexes as the salt level increases to high levels. Others have reported such effects for different polyelectrolyte systems [33-35]. Two studies involving highly water-soluble polyelectrolytes having relatively low charge densities showed consistent decreases in adsorption with increasing conductivity [36-37]. These studies all support a mechanism in which monomeric ions are able to successfully compete with polymer segments for adsorption sites, while on the other hand, the electrical attractive forces attracting the polyelectrolyte segments towards the surface are weakened and reduced in range. This effect is

consistent with a requirement of increasing amounts of cationic titrant to reverse the charge of a plastic surface as the salt concentration is increased. It is worth noting that Ojala [2] observed a negative streaming current signal in the presence of pure poly-DADMAC solutions if the concentration of NaCl was above 0.45 M.

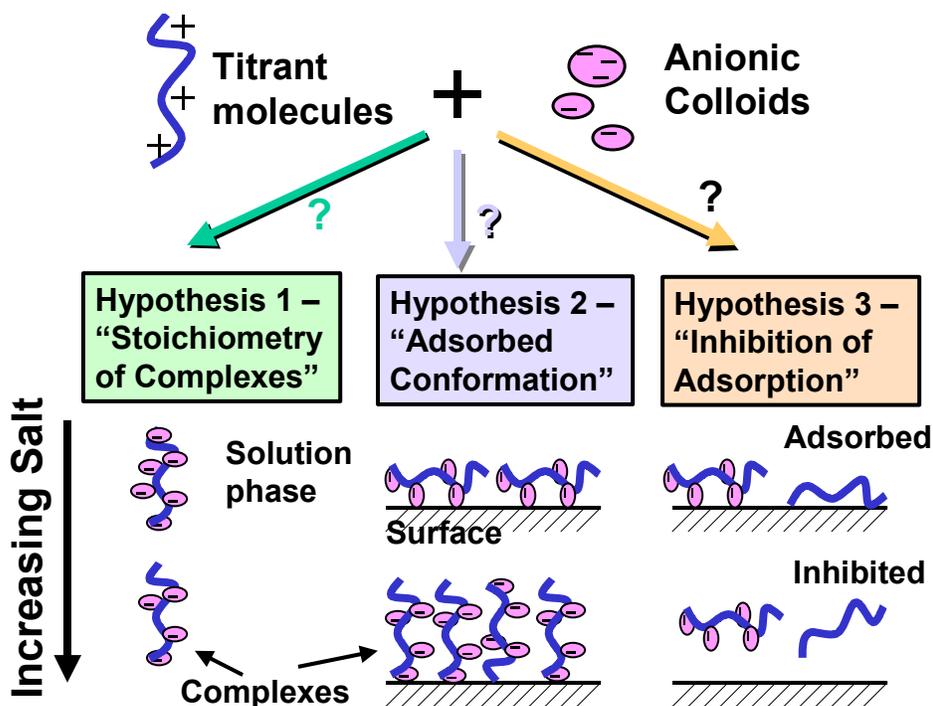


Figure 3.9: Simplified representations of three hypotheses to account for the effect of salt on the endpoints of streaming current titrations.

To confirm the third hypothesis, tests were carried out using chromo-poly-DADMAC, as described by Tanaka *et al.* [21]. This chemical is essentially the same as regular poly-DADMAC, except that it has a deep red color. It was observed that PTFE surfaces acquired a red appearance when exposed to chromo-poly-DADMAC solutions in hard water having low to moderate NaCl concentrations. However, no color was seen after exposure to a similar solution

having a NaCl concentration of 1%. More experiments related to adsorption will be discussed in Chapter 4 and Appendix C. The results were shown similar weakening of polymer adsorption as conductivity increased.

4.7 Possible Alternative Explanations for the Results at High Conductivity

Though the reported observations appear consistent with the chemical mechanisms already described (especially the third hypothesis), other factors might also contribute to difficulties with the use of streaming current methods at high salt levels. Because the absolute magnitudes of streaming current signals all become closer to zero with increasing salt concentration, any offset in the detection of the zero streaming current signal is likely to cause a large relative change in the endpoint value, or even a failure to reach zero [6]. The following factors have the potential to affect streaming current output at high conductivity:

- In theory the electrical conductivity of the liquid in the annulus can become too high relative to that of the external circuit by which the current is evaluated. In such cases the external circuit no longer provides a path of lesser resistance for the return flow of electricity, relative to back-conduction through the liquid phase. As a result there is no basis for interpreting streaming current signals [2]. The instrument used in the present work was adjustable for samples having higher conductivity. However, as was shown in Table 2.1, the streaming current signals remained negative, regardless of the titrant level, for all samples having conductivity levels above 18 mS/cm. Such high conductivity levels are approached only in certain paperboard mills that have near to zero liquid effluent [38].

- Polarization at the electrode surfaces [39] might cause the effective resistance of the measuring circuit to become too high relative to the conductance of liquid in the annulus. Gerdes, the inventor of the streaming current method, reported the use of silver/silver-chloride, reversible electrodes to overcome possible effects of overpotential [10]. Using this approach for the early prototype streaming current devices, he reported successful test results in KCl salt brines having concentrations up to 10% solids. For reasons of low durability and a tendency to foul, reversible electrodes are no longer used on commercially available streaming current devices.
- It is conceivable that the pressure difference between the down-stroke and the up-stroke may affect the redox potential of oxide species at the surfaces of the electrodes in unpredicted ways [10]. It is worth noting that the reciprocating action and rectification of the signal is supposed to continually “zero” the instrument under normal circumstances, but this supposition ignores any possible effects of pressure.
- Gerdes reported that concentrated salt solutions produced a negative signal that did not depend on what else was in the sample [10]. According to Ojala [2], one can expect an offset in observed streaming current signals relative to their true values due to Coehn’s rule [40]. This rule states that if two heterogeneous substances are in contact, then the one with the higher dielectric constant is positively charged with respect to the other. This rule appears to explain why pure water (including tap water) usually gives a strong

negative streaming current signal. However, no publication has attempted to apply this rule to streaming current tests involving other types of samples.

- Dentel [29] demonstrated a phase lag between the expected and the observed (not rectified) streaming current signals. The existence of a phase lag is consistent with the inertial component of flow, especially if the streaming current device has a relatively large annulus [15]. Because electrolytes appear to affect the phase shift of the streaming signals, relative to the motion of the piston, this is a potential source of error if left uncorrected [41].

Kam and Gregory [42] suggested a possible way of dealing with unexplained shifts in the neutralization points of streaming currents titrations. They noted that the titration curve often has an inflection point at neutrality. They suggested that the inflection point might be used as an indication of the endpoint position, especially if there is suspicion that unknown factors have shifted the true endpoint to a non-zero output value of the streaming current meter.

Unfortunately, it would seem impractical to look for an inflection point at salt concentrations above about 15 mS/cm; in the present study such conditions yielded featureless, nearly horizontal curves.

5. Conclusions

1. The present results support the use of the streaming current method for charge determination of process water samples having electrical conductivity

values up to 1 mS/cm. In an intermediate range of conductivities between 1 mS/cm and 10 mS/cm not all samples yielded clear endpoints. Except for a sample consisting of oxidized starch, an anionic polymer having a low charge density, most samples yielded good, clear titration endpoints in solutions having conductivity levels of up to 3.5 mS/cm. However, under the conditions specified in the experimental section, all of the titrations failed to yield reliable endpoints at conductivities of 18 mS/cm and above.

2. Within the low to medium conductivity range given above, the titration method with poly-DADMAC appeared to be tolerant of a very wide range of molecular charge density of the anionic polyelectrolyte solutions tested. The molecular mass of cationic polyelectrolytes did not have clear influence on the titration endpoint shift with increasing conductivities (Appendix A). The poly-anions of relatively high charge density appeared to interact with the titrant as it was added. The streaming current signal remained relatively steady until the endpoint was near. By contrast, in the presence of a poly-anion of relatively low charge density the added poly-DADMAC had an immediate effect on the streaming current output, even at the beginning of a titration. The results were consistent with a model in which the process of neutralization of anionic polymers in the sample to be tested promotes adsorption of polyelectrolyte complexes onto the plastic surfaces.

3. The test results at relatively high electrical conductivity were consistent with a reduced efficiency of poly-DADMAC adsorption. At conductivity levels of 3.5

mS/cm and above it appears likely that adsorption of the cationic titrant onto the probe surfaces was inhibited.

4. In practical terms, temperature did not have a significant effect on streaming current titration results, although at higher temperature plastic surfaces had a tendency to carry slightly more negative charges.

6. Acknowledgements

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Chapter 4

Dependency of Polyelectrolyte Complex Stoichiometry on the Order of Addition Part 1. Effect of Salt Concentration during Streaming Current Titrations with Strong Poly-acid and Poly-base *

Abstract

Titration experiments were carried out between solutions of a strong poly-acid (poly-vinylsulfate, potassium salt) and a strong poly-base (poly-diallyldimethylammonium chloride) over a range of salt concentrations. Streaming current analysis of the titration endpoints appeared to show increasing deviations from 1:1 stoichiometry of complexation with increased salt. The results depended on the direction of the titration, such that a stoichiometric excess of the titrant (second additive) was required to achieve a streaming current reading of zero. These symmetrical results, depending on the order of addition, were obtained despite the fact that the plastic surfaces of the streaming current device had a slight negative charge and differing adsorption tendencies for the two kinds of polymer. A theoretical model based on non-equilibrium entrapment of non-complexed polymer segments was found to be inconsistent with results of tests carried out over a range of initial polymer concentration.

This chapter has been modified from the following publication: Chen, J., Heitmann, J., Hubbe, M., Colloids and Surfaces A: Physicochemical and Engineering Aspects 223(1-3): 215-230 (2003)

Results were better described by a model involving formation of polyelectrolyte complexes (PECs) in solution, in which near-stoichiometric core complexes are stabilized by an excess of the second additive on their surface. Implications of the latter model were compared with the results of turbidimetric tests, aqueous contact angles on polymer-treated plastic surfaces, and microelectrophoresis of PECs. Results of this study have consequences for interpretation of polyelectrolyte titrations, as well as for industrial operations that involve the mixing of oppositely charged polyelectrolytes.

Keywords: ELECTROKINETICS, STREAMING CURRENT, POLYELECTROLYTE COMPLEXATION, TITRATIONS, STOICHIOMETRY

1. Introduction

1.1 Stoichiometry and the Streaming Current Test

The stoichiometry of interactions between water-soluble poly-acids and poly-bases has implications in such fields as wastewater treatment [1-2], papermaking [3-5], and analytical chemistry [6-8]. Though much relevant work suggests a tendency for 1:1 stoichiometry of polyelectrolyte interactions [9-14], some recent publications have identified conditions leading to systematic deviations from 1:1 stoichiometry [8,10,13,15-22]. Such deviations are expected to affect both the efficiency of polyelectrolyte usage in various industrial processes and also the accuracy of certain online and manual analytical tests that are used for process control. The present work was motivated by some unexpected results obtained

during the course of streaming current (SC) titrations [22]. Preliminary tests showed that SC titrations carried out in the presence of salts depended on the order of addition of two polyelectrolyte solutions.

In recent years operators of paper machines have placed increasing reliance on SC titrations to control and optimize addition rates of polyelectrolyte additives. A previous article considered factors affecting the accuracy of such titrations, especially in the presence of low to moderate levels of monomeric salts [22]. Salt levels were found to affect the stoichiometry of polyelectrolyte titration results. These issues are increasingly important to paper technologists, due to increased rates of water reuse and consequent enrichment of ion concentrations.

Though fuller descriptions are given elsewhere [22-27], the SC test procedure can be stated briefly as follows. The wetted parts of the device include a plastic piston loosely fitted within a dead-ended plastic cylinder. A reciprocal motion of the piston within the cylinder causes an aqueous sample placed in the annulus to move back and forth across the plastic surfaces. If the plastic surfaces bear a net charge, usually due to adsorption of colloidal material from the sample, then the fluid motion causes net movement of counter-ions in the diffuse double layer adjacent to the charged surfaces. This motion of ions is detected as a current by means of a pair of electrodes and suitable electronics, which also rectify and smooth the signal [23,27]. A common industrial test involves gradual addition of a polyelectrolyte solution to the sample [28-29]. The titration endpoint usually is identified with the point at which the signal equals zero.

Figure 4.1 provides an example of output from a SC titration, based on previously unpublished data (more data in Appendix A). As noted in the earlier publication [22], an increasing level of sodium chloride produced three kinds of effects on the titration results, of which the second item is the main focus of the present work:

1. The absolute magnitudes of the initial signals were reduced. This is consistent with the known effect of salt on zeta potential values [5,27,30], and in particular on streaming current signals [22-23,31-32].
2. The amount of titrant corresponding to zero streaming current tended to increase with increasing salt. In the earlier publication, all of the titrations were in the same direction. The initial solution always consisted of a poly-acid (an anionic polyelectrolyte), and the titrant was always the high-charge linear cationic polymer.
3. At electrical conductivity levels higher than 2000 to 3550 $\mu\text{S}/\text{cm}$ the endpoints became difficult or impossible to detect. The low end of this range corresponds to low charge density polyelectrolytes. Contributing factors to making SC measurements difficult at high salt levels were considered in the earlier publication [22].

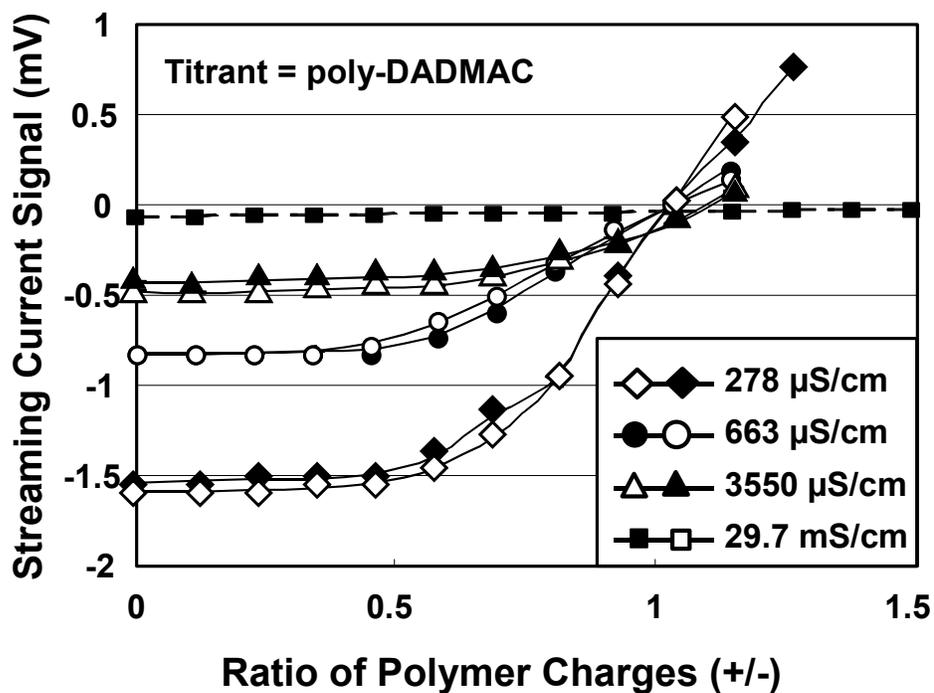


Figure 4.1: Streaming current signal as a function of the stoichiometric ratio at different NaCl levels.

1.2 Theoretical Background

Previous investigators have advanced ideas to explain why or why not to expect a one-to-one pairing of charged groups in the formation of complexes between oppositely charged polyelectrolytes in solution. Two explanations of stoichiometric behavior are the so-called “ladder” and the “scrambled egg” models of polyelectrolyte complexation [33]. The ladder model assumes that the two polyelectrolytes have sufficient flexibility and suitable charge densities that they can zip together in a cooperative fashion [3,12]. An adaptation of the ladder model appears to be successful in explaining behavior of certain PECs formed from a “host” polyelectrolyte and a “guest” polyelectrolytes of much lower molecular mass [16,34]. However, when carrying out titrations or other

complexation reactions between polyelectrolytes both having relatively high molecular mass it may not be reasonable to assume that the polyelectrolyte chains can untangle themselves and line up as a highly regular “ladder.” Thus, a “scrambled egg” model is expected to be a better description under the limiting conditions of high molecular mass, concentration, and/or flow where the rate of irreversible collisions between macromolecules is high relative to their rate of conformational adjustment [35].

The driving force for formation of polyelectrolyte complexation has been described in terms of either (a) attraction of oppositely charged groups [3,16,34,37,39], or (b) an increase in entropy when polyelectrolyte complexation results in release of counter-ions [3,9,33]. These two explanations can be seen as complementary descriptions of the same phenomena. Though entropy considerations alone would lead us to expect irregular structures (possibly with incomplete pairing of charged groups), it is clear that electrostatic effects will tend to drive the system to rearrange itself so that as high a fraction as possible of the charged groups on the respective polyelectrolytes are paired up with their opposites. While it is clear that such rearrangement ought to yield 1:1 stoichiometry in the case of linear polyelectrolytes of similar charge density, previous studies have demonstrated 1:1 stoichiometry over a wide range of charge densities and charge density ratios, especially when the work is carried out in the absence of added low-mass ions, *i.e.* salts [9-14].

The present experimental work was limited to strong, linear, high-mass polyelectrolytes of high charge density. These conditions were selected to avoid certain known complications, as follows. First it has been shown that stable non-stoichiometric complexes can exist in solution in cases where the two polyelectrolytes differ strongly in molecular mass [3,16,36-37]. Other factors tending to produce non-stoichiometric polyelectrolyte interactions include sharply contrasting charge densities [17] and branched molecular structures [38-39].

1.3 Hypothetical Models

Two idealized models will be considered here in anticipation of experimental results to be shown later. Each of these models attempts to explain why titrations between a strong, linear, high-mass poly-acid and a corresponding poly-base ought to depend on the order of addition. In each case we are interested in the relative amounts of charged groups in the two polyelectrolytes that are present in the mixture when the titration has been carried out to a streaming current endpoint of zero.

Figure 4.2 illustrates a “segment entrapment” model. This model emphasizes initial collisions, relatively early in a titration, when each titrant macro-ion is likely to be surrounded by poly-ions of opposite charge. The word “titrant” here refers to whichever of the poly-ions is gradually added to a solution of the oppositely charged polyelectrolyte. For the sake of this model it is assumed that complexation begins at the periphery of a titrant molecule, forming a layer of complexed units surrounding the central portion of the titrant molecule. It is

further assumed that non-complexed segments of the titrant molecule become isolated and protected within the complexed layer. As suggested by Michaels *et al.* [9], a tightly coiled conformation, possibly due to the presence of salt, is expected to make some ionic groups inaccessible for reaction. Under conditions where the segment entrapment model is valid, the model implies deviations from 1:1 stoichiometry. Specifically, the model predicts that titrant will appear “inefficient” in terms the amount needed to fully titrate the sample. It should be noted that the segment-entrapment model is similar in concept, but different in detail from a model proposed by Stamberg *et al.* for the encapsulation of polyelectrolyte solutions [34,40].

Though the segment entrapment model remains to be proven, possible theoretical justifications can be given. The model requires, first of all, that rates of molecular collisions be fast relative to the rates of molecular conformations, factors that can be estimated based on concentrations, molecule sizes, and conditions of flow [35]. A second requirement of the model is that complexation is an essentially irreversible process. It must be reasonable to assume that the polyelectrolytes can remain “stuck” in the kind of non-equilibrium situation envisioned in Figure 4.2. Evidence of such irreversibility has been observed in some other aspects of high-mass polyelectrolyte behavior, including adsorption onto oppositely charged surfaces [41] and formation of polymer bridges [35,42,43].

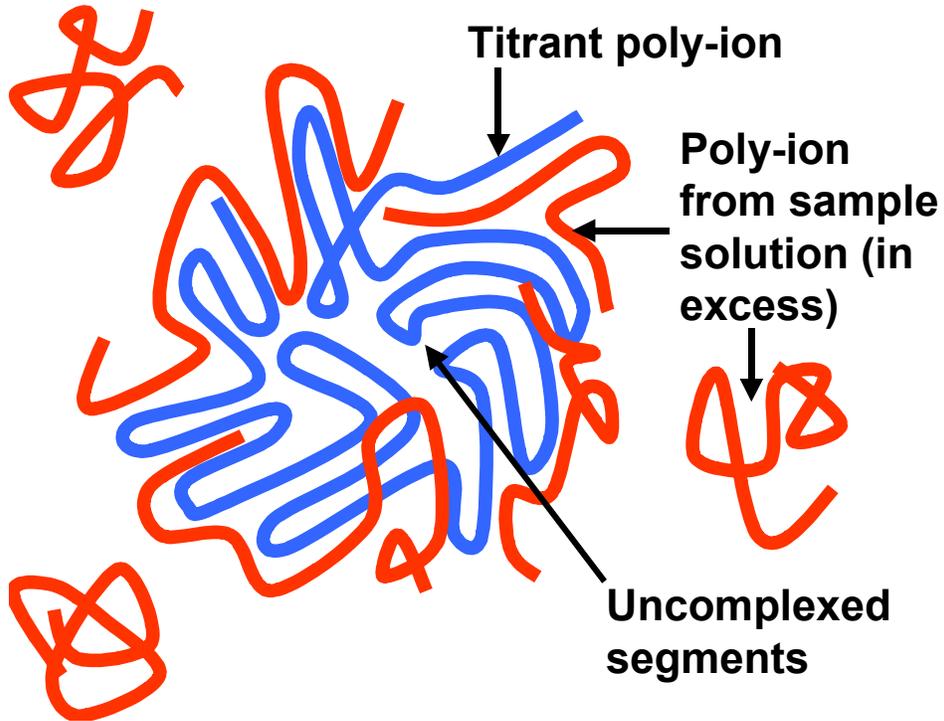


Figure 4.2: "Entrapment" model.

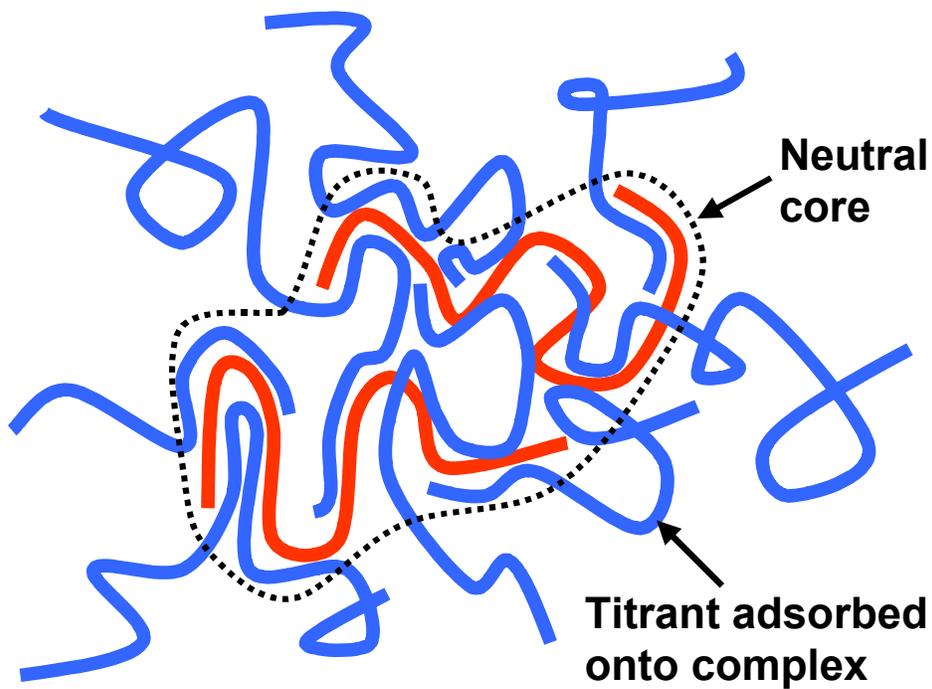


Figure 4.3: "Surface excess" model.

Figure 4.3 illustrates a “surface excess” model to be evaluated as a second idealized explanation for non-stoichiometric endpoints of streaming current titrations. Here it is assumed that 1:1 stoichiometry of complexation prevails during the titration, even in the core regions of each polyelectrolyte. However, the resulting complexes are assumed to be charge-stabilized by whichever of the polyelectrolytes happens to be in excess at different parts of the titration. At the titration endpoint, detected by the streaming current method, it is assumed that tails and loops of the second added polymer (the titrant) extend outward from the surfaces of complexes that remain suspended in the solution [37,44-46].

To justify consideration of the surface excess model, it is proposed that the titrant continues to adsorb onto the surfaces of PECs after the point where a 1:1 stoichiometric endpoint might be expected. Such continued adsorption beyond the point of neutralization is consistent with recent studies of polyelectrolyte adsorption onto oppositely charged surfaces [47-51] or multilayers formed by successive dipping of a solid support surface into polyelectrolyte solutions of opposite charge nature [51-53].

Implications of the two competing models just described are similar in many respects, but there are some key differences. Both models agree with respect to the following predictions for interactions between linear, high-charge polyelectrolytes of similar molecular mass: (a) more titrant should be required to reach an endpoint, compared to 1:1 stoichiometry; (b) the effects ought to be approximately symmetrical, depending on which of two polyelectrolyte is used as

the titrant; and (c) deviations from 1:1 stoichiometry ought to increase with increasing electrical conductivity due to less extended average molecular conformations of the individual poly-ions before they interact [54-55]. On the one hand, a denser conformation is expected to make titrant molecules easier to surround and entrap. Alternatively, denser molecular conformations should allow higher amounts of titrant molecules to be present in a stabilizing layer of a charge-stabilized complex. The latter explanation has been used by others to explain why intermediate levels of salt often increase adsorbed amounts of polyelectrolytes onto surfaces of opposite charge [56-57].

The two idealized models suggest contrasting behavior in certain other respects: (a) the segment entrapment model, which assumes that rates of collisions affect the interaction, ought to depend on the concentrations of both polyelectrolytes during the titration; and (b) the surface-excess model of charge-stabilized polyelectrolyte complexes implies that it should be possible to measure zeta potentials of such complexes that match the charge of the titrant at the point in a titration where the signal equals zero.

2. Experimental

2.1 Materials

Experiments were conducted in solutions prepared from deionized water, to which different levels of salt were added. Table 4.1 shows the series of electrolyte additions and electrical conductivities that were used throughout the study.

Table 4.1: The salt levels and corresponding conductivities.

Salt level	Conductivity ($\mu\text{S}/\text{cm}$)
Deionized water	1.2-5.5*
100 ppm CaCl_2	275-280
100 ppm CaCl_2 and 100 ppm NaCl	663-670
100 ppm CaCl_2 and 0.1% NaCl	3550-3630
100 ppm CaCl_2 and 1% NaCl	29500-29700

* Deionized water conductivity depended on how well the ionic exchanger was working on the day the titration was carried out.

Table 4.2 lists the polyelectrolytes used in this work. All were homopolymers with essentially 100% charged monomeric groups. The abbreviation PVSK stands for the potassium salt of poly-(vinylsulfate). The abbreviation poly-DADMAC stands for poly-(diallyldimethylammonium chloride). Poly-DADMAC having a nominal molecular mass of 400-500 kiloDaltons was used in most experiments, except for turbidity tests reported in Tables 4.5 and 4.6.

Table 4.2: The general properties of polyelectrolytes.

Type of Polyelectrolyte	Supplier	Molecular Mass
poly-DADMAC	Ciba Spec. Chem.	1900k Dalton
poly-DADMAC	Aldrich Co.	400-500k Dalton
poly-DADMAC	Aldrich Co.	100-200k Dalton
poly-DADMAC	Ciba Spec. Chem.	15 k Dalton *
PVSK	Aldrich Co.	170k Dalton

* Calculated from intrinsic viscosity.

2.2 Procedures

Charge titration test: Two streaming current devices were used for polyelectrolyte titrations. Results of tests involving an ECA2000P (Chemtrac Systems, Inc.) are shown in Figures. 4.1 and 4.7. Results of tests involving a PCD 03 pH (Mütek Analytic) are shown in Figures. 4.4-4.6 and 4.8-4.9. In all cases the polyelectrolyte samples were diluted with desired aqueous salt solutions to desired concentrations, then oppositely charged titrant was used to titrate to a zero signal at the endpoint. Titrant was added manually in the case of the ECA2000P, with approximately one minute of equilibration time after each addition. Titrant was added automatically in the case of the PCD 03 pH, using the default settings of a Mütek PCD-T auto-titrator. Calibration of the PVSK titrant was carried out before each set of tests, based on a streaming current endpoint in the absence of added monomeric electrolytes.

Turbidity test: Aliquots of 20 ml solutions with various conductivities were used as background electrolyte. The salt levels and conductivities are listed in Table

4.1. Aliquot of one ml of 0.001 N poly-DADMAC or 0.0008 to 0.0009 N PVSK was added in the preparation of each initial cationic and anionic solution, then the oppositely charged polyelectrolyte was used to titrate it. Titrant was added in 0.1ml steps in the presence of gentle stirring, followed by turbidity analysis with a DRT-15CD Turbidimeter from HF scientific, Inc.

In preparation for zeta potential tests (see next), further turbidity tests were carried out as follows. Replicate samples were prepared, in sets of 7, by adding 100 ml of either deionized water or a selected salt solution. To each beaker, 5.0 ml of 0.001N poly-DADMAC (400-500k Dalton) was added, during gentle agitation, followed by 5.5 ml of PVSK having an approximate strength of 0.0008N. Then, an additional 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, or 0.40 ml of PVSK was added to successive beakers. Turbidity and zeta potential values were determined after 20 min., 5hr., and 24hr.

Electrophoresis test: In order to estimate the zeta potential of polyelectrolyte complexes, electrophoretic mobility was measured with a Charge Analyzer Two (SKS Assoc.) Suspensions of pre-formed polyelectrolyte complexes, taken from the turbidity experiments, were added to the charge analyzer to measure the zeta potential.

Contact angle test: Contact angle measurements on poly-tetrafluoroethylene (PTFE) tape samples were used to sense effects attributable to polymer adsorption. PTFE tape samples were dipped into solutions containing 1.0 ml of either poly-DADMAC or PVSK, plus 100ml of various conductivity solutions.

After 30 minutes the tapes were withdrawn and solution was removed as much as possible by shaking, before measurement of the contact angle. The liquid used in the contact angle measurements was deionized water (about 0.04 ml).

3. Results And Discussion

3.1 Streaming Current Titrations – Order of Addition

Titration were carried out between poly-(diallyldimethylammonium chloride) (poly-DADMAC) and the potassium salt of poly-(vinylsulfate) (PVSK) in deionized water, in the presence of hardness (100 ppm CaCl_2), or in hard water (also 100 ppm) to which different amounts of NaCl had been added. In the first case to be considered, the initial solution consisted of poly-DADMAC at a concentration of 47.6 $\mu\text{eq/L}$ after dilution, and the titrant consisted of about 0.0008-0.0009N PVSK. The PVSK concentration was recalibrated before each titration because of its limited stability. As shown in Figure 4.4, the amount of titrant required in order to reach the endpoint of zero streaming current increased with increasing salt addition. Water hardness caused the volume of titrant required to reach the endpoint to increase by a factor of about 5% relative to titrations carried out in deionized water. The presence of 100 ppm or 0.1% NaCl concentration, in addition to the hardness ions, caused the endpoints to be shifted by about 12% to 16%, respectively, compared to deionized water. The light- and dark-shaded histogram bars represent replicate experiments.

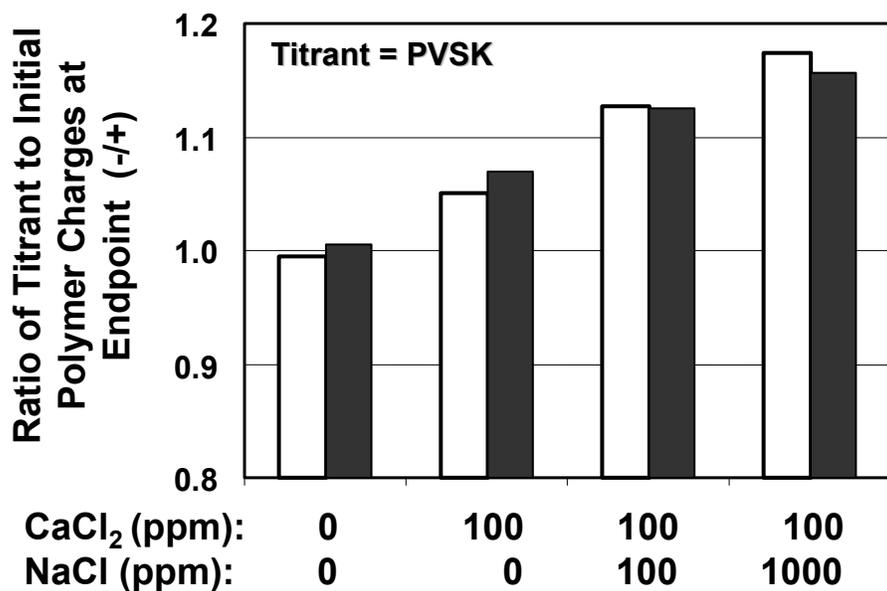


Figure 4.4: Stoichiometric ratio in the presence of various salt concentrations (poly-DADMAC: 400 - 500 k).

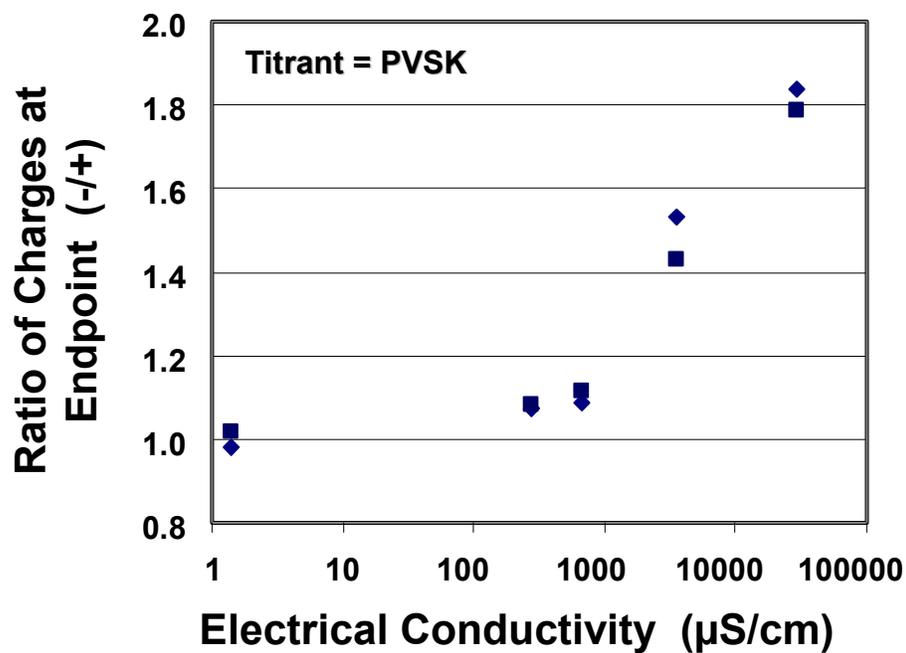


Figure 4.5: Stoichiometric ratio in the presence of various salt concentrations (poly-DADMAC: 100-200 k).

To allow for more convenient comparison, results of the form shown in Figure 4.4 were converted to a “+/-“ format, following a convention used by others [37]. In this article the ratio always is expressed with the amount of titrant (second additive) in the numerator. The value of +/- or -/+ can be taken as the stoichiometric ratio of titrant polymer groups to initially present polymer groups at the streaming current endpoint of the titration. Results shown in Figure 4.5 correspond to a different set of titrations involving initial addition of poly-DADMAC having a molecular mass in the range 400 ~ 500k Dalton. The initial concentration, after dilution, was 6.0 $\mu\text{eq/L}$. Once again, addition of salt tended to increase the relative amount of titrant corresponding to zero output of the streaming current meter. While the results shown in Figures. 4.4 and 4.5 appear similar in nature to endpoint shifts reported earlier [22], it is worth noting that these new results involved the opposite direction of titration. (See Appendix A for the complete study about the effect of molecular mass on the titration endpoint shift.)

To confirm the earlier results, Figure 4.6 shows additional results of tests in which the poly-anion (PVSK) was the initial solution and in which the poly-cation (poly-DADMAC) was the titrant. Again, increasing conductivity tended to make the titrant appear less effective in reaching the endpoint.

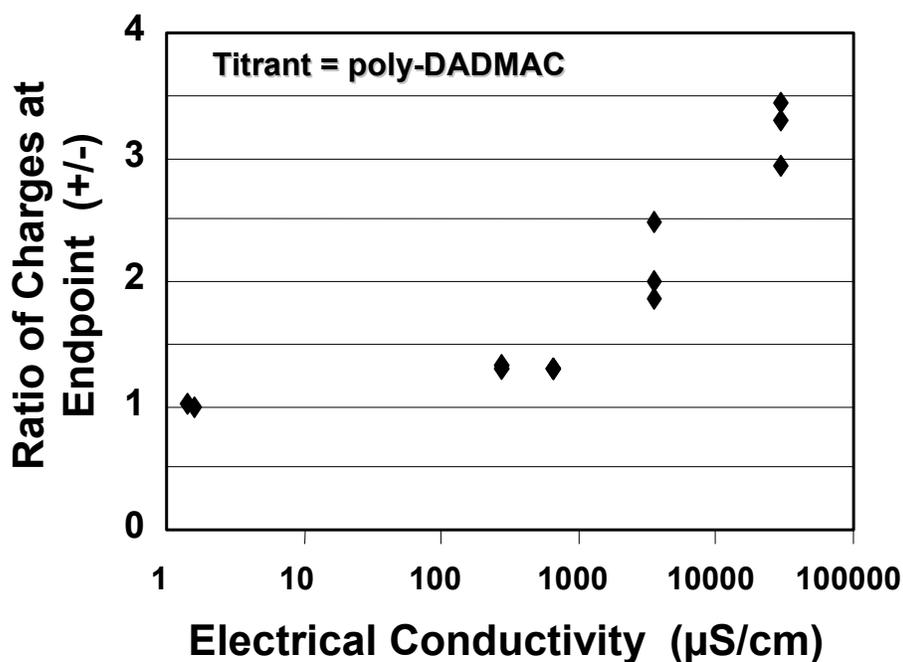


Figure 4.6: Stoichiometric ratio in the presence of various salt concentrations when poly-DADMAC used as titrant.

Further confirmation of the effect was obtained with different brand of streaming current detector (see Experimental). The direction of titration corresponds to Figure 4.5. As shown in Figure 4.7 the same shift to higher +/- values at the streaming current endpoint were evident with increasing electrical conductivity up to about 1000 $\mu\text{S/cm}$. Above that point the +/- values declined again. Possible reasons for unreliable SC output at very high conductivity were reviewed elsewhere [22].

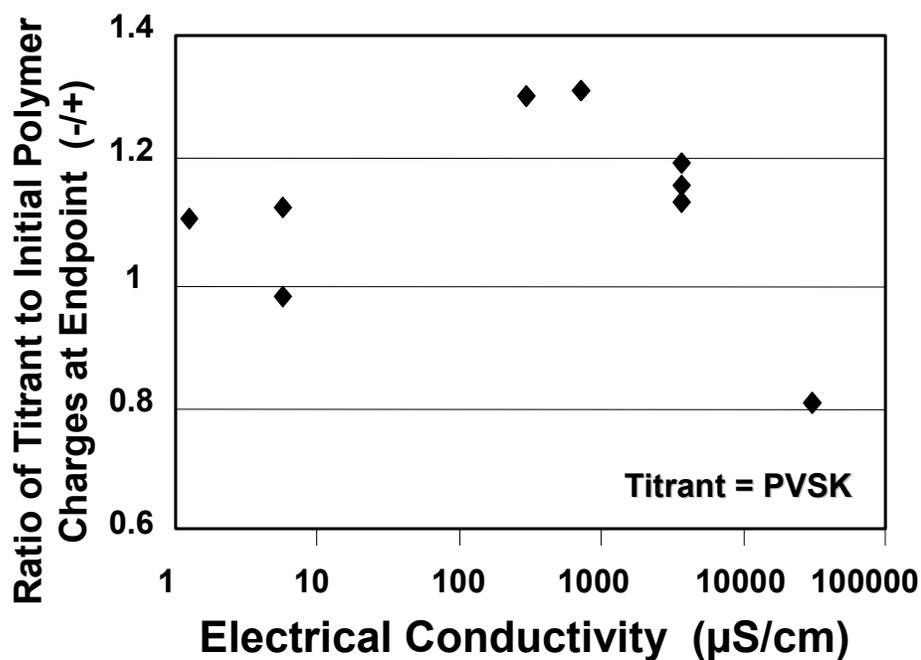


Figure 4.7: Stoichiometric ratio in the presence of various salt concentrations using the other SC device.

3.2 Baseline Tests of Streaming Current Output

Before judging the appropriateness of either of the idealized models described earlier it is worth considering the results of some baseline tests. The first area of concern was a possible influence of the initial apparent charge of the plastic surfaces within the sensing areas of a streaming current apparatus. Though the poly-tetrafluoroethylene and other hard plastics used in fabrication of streaming current devices are usually described as “uncharged” and oleophilic, experience suggests that these surfaces develop a negative surface charge when exposed to water [23-24,31-32].

Figure 4.8 shows the results of tests carried out in the absence of any polyelectrolytes, but with the same saline solutions used in the other examples that have been shown. These results confirm the negative character of the plastic surfaces of the streaming current device, as sensed by the apparatus in the absence of polyelectrolytes. The results also show a simple diminution in signal with increasing ionic strength, as shown by others [5,30]. Similar tests carried out over a range of pH values were consistent with the presence of anionic groups on the plastic surfaces being the main contribution to the apparent charge.

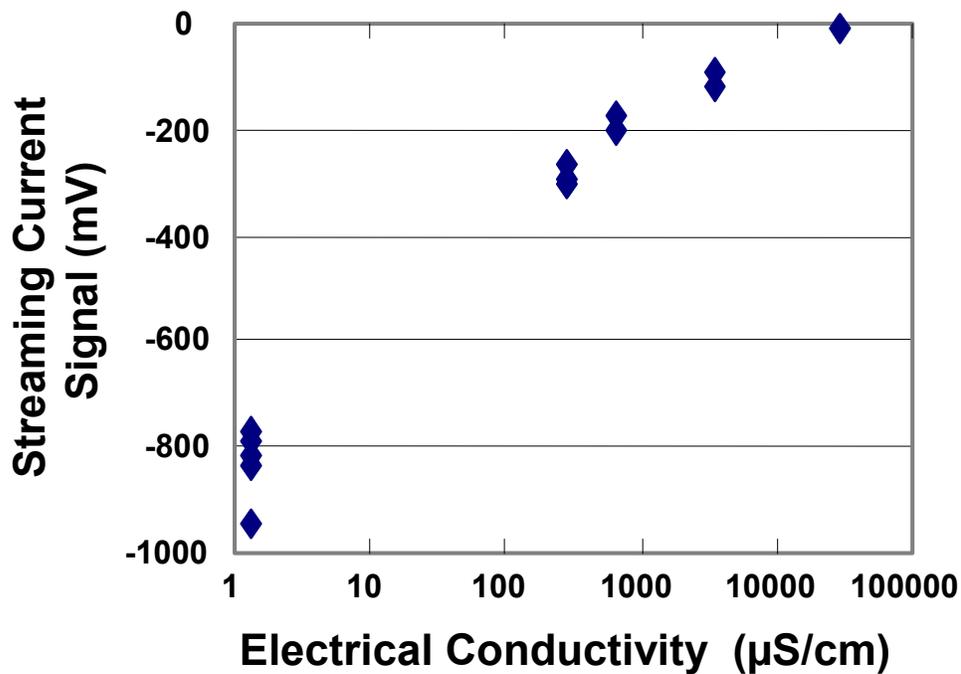


Figure 4.8: Effect of salts on SC output in the absence of polyelectrolytes.

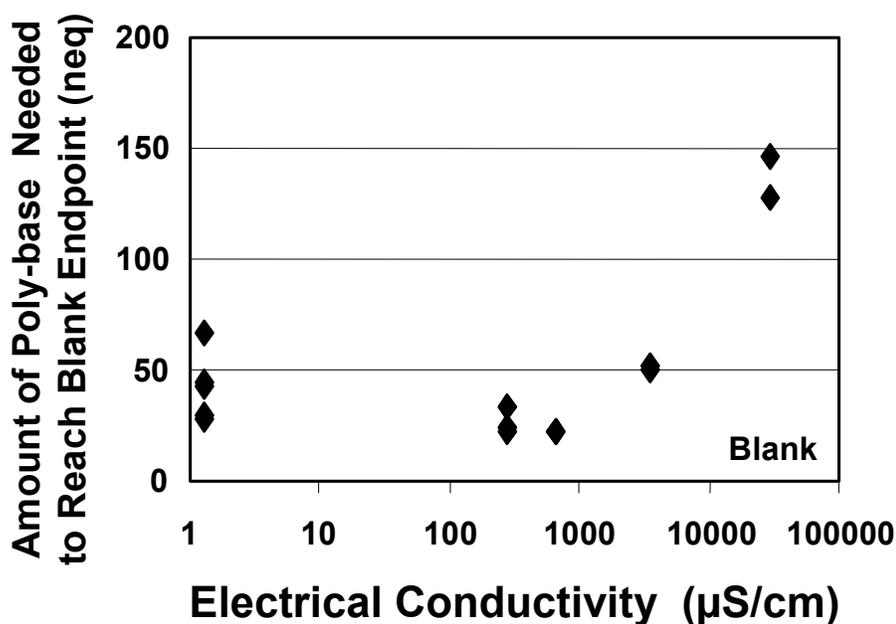


Figure 4.9: Amount of poly-DADMAC needed to reach zero SC signal in the absence of poly-acid.

Though the SC signal values shown in Figure 4.8 appear relatively large, that does not imply that a large amount of cationic polymer was needed to reach a titration endpoint of zero. Figure 4.9 shows the results of a series of “titrations” starting with a cleaned apparatus and samples consisting of deionized water and various salt additions as outlined earlier. Within a conductivity range from near 0 up to 29700 $\mu\text{S/cm}$, the amount of poly-DADMAC needed to reach zero SC signal was 0.02 to 0.05 μeq , which amounts to 2-5% relative to the starting amount of polymer used during tests such as that shown in Figure 4.4. Increasing amounts of titrant required to reach the zero SC endpoint at yet higher conductivity are consistent with a suppression of adsorption of the poly-DADMAC, as discussed previously [22]. At the highest conductivity levels tested

the apparent deviations can be expected due to the decreased magnitudes of the signals and sensing limitations of the devices [22].

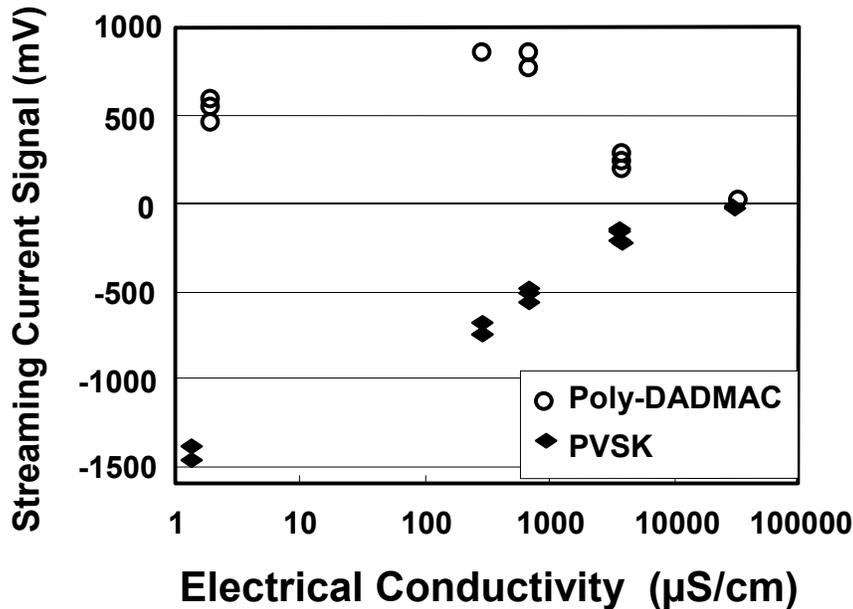


Figure 4.10: Initial SC signal in the presence of 6.0 µeq/L poly-DADMAC (upper curve) or 4.8-5.4 µeq/L PVSK (lower curve) at different salt levels.

Figure 4.10 shows results of two series of tests in which SC signals were evaluated in the presence of single solutions of polyelectrolytes with different levels of monovalent ions. Results of tests carried out in the presence of PVSK (lower curve) were similar in their basic trend to those obtained in the absence of polyelectrolytes, except that the absolute magnitudes were approximately twice as large. This difference is consistent with adsorption of at least some of the PVSK onto the plastic surfaces. However, the present results do not provide sufficient information to demonstrate complete coverage of the plastic surfaces by the anionic polyelectrolyte.

The upper curve in Figure 4.10, corresponding to saline solutions of poly-DADMAC, shows a maximum in positive signal within a conductivity range between 2 and about 1000 $\mu\text{S}/\text{cm}$. Though the reason for this maximum has not been determined in this study, the trend appears consistent with known effects of salt levels on adsorbed amounts of cationic polymers onto negative surfaces in solution [56-58]. Such studies often show maxima in adsorbed amounts at intermediate salt levels, followed by partial or complete suppression of adsorption at the highest levels of salt considered by the investigators.

To summarize the baseline tests, the plastic probe surfaces behaved as if they had a weakly negative surface charge. The amounts of cationic polyelectrolyte to neutralize the charges of the bare surfaces of the apparatus, in the absence of anionic polyelectrolyte, were too small to account for the observed shifts in apparent stoichiometry of the complexation interactions, as sensed by the streaming current tests.

3.3 Contact Angle Tests Related to Baseline Conditions

Contact angle of a surface is one of the factors that can be a reflection of the hydrophobicity of that surface. If hydrophilic polymers are adsorbed on a hydrophobic surface, the hydrophobicity of that surface may be changed. The objective of the contact angle tests was to evaluate the validity of the hypothesis that salt essentially prevented adsorption of poly-DADMAC at the high level of the conductivity range considered.

Results of contact angle tests are listed in Tables 4.3 and 4.4. The measurements before adsorption represents blank experiments in which the poly-tetrafluoroethylene (PTFE) tape was dipped into salt solution without polymer added. This tape was considered similar to the surfaces used in the probe construction. The contact angle of PTFE samples that were never dipped in any solution was 116.4 ± 1.8 degree. Ranges show plus or minus one standard deviation from the mean. It should be noted that within each row of data the PTFE tape samples were obtained from the same roll. Differences in “before adsorption” values between the first two rows of Table 4.3, and the remaining rows of Tables 4.3 and 4.4 can be attributed to a switch to a fresh roll of PTFE tape.

Table 4.3: Contact angle for PTFE tape before and after adsorption of poly-DADMAC.

Conductivity ($\mu\text{S}/\text{cm}$)	Before adsorption	After adsorption
278	$112.5^\circ \pm 2.2^\circ$ *	$106.3^\circ \pm 2.6^\circ$ *
667	$112.0^\circ \pm 2.2^\circ$ *	$106.6^\circ \pm 2.3^\circ$ *
3550	$115.1^\circ \pm 1.6^\circ$ *	$115.6^\circ \pm 1.8^\circ$ *
29500	$115.6^\circ \pm 1.8^\circ$ *	$115.3^\circ \pm 1.6^\circ$ *
Notes: * = plus or minus one standard deviation from the mean		

As shown in Table 4.3, contact angle differences between the conditions of before and after adsorption were apparent only at relatively low conductivities. This is consistent with an ability of the cationic polymer to adsorb at low

conductivity onto the PTFE tapes, but not at high salt levels. PTFE has a negatively charged surface, whereas poly-DADMAC is cationic. Poly-DADMAC is hydrophilic, and PTFE is hydrophobic. It follows that the contact angle of PTFE will be decreased if poly-DADMAC is adsorbed. High conductivity is expected to repress the adsorption tendency [56-58].

Table 4.4: Contact angle for PTFE tape before and after adsorption of PVSK.

Conductivity ($\mu\text{S}/\text{cm}$)	Before adsorption	After adsorption
278	$114.0^\circ \pm 2.0^\circ *$	$109.1^\circ \pm 2.7^\circ *$
667	$115.6^\circ \pm 1.6^\circ *$	$112.0^\circ \pm 1.6^\circ *$
3550	$115.1^\circ \pm 1.6^\circ *$	$113.8^\circ \pm 1.6^\circ *$
29500	$115.6^\circ \pm 1.8^\circ *$	$114.8^\circ \pm 2.7^\circ *$
Notes: * = plus or minus one standard deviation from the mean		

In the case of PVSK the difference of the contact angle was not as significant as in the case of poly-DADMAC. That is expected because PVSK carries negative charges, reducing its tendency to adsorb onto the negative surface of the PTFE.

In addition an adsorption test was carried out on the probe of the streaming current detector. This study found that the initial signal from SC device before titrations carried out could remain negative at extremely high conductivity even the polyelectrolyte added was poly-DADMAC. (See Appendix C)

The present results also are consistent with previous tests with adsorption of chromo-poly-DADMAC onto PTFE powder [22]. Chromo-poly-DADMAC had

been provided to us by Tanaka [21] as a copolymer with a bright red chromophoric group to render it highly visible. A PTFE surface appeared red after its exposure to chromo-poly-DADMAC in low to medium conductivity solutions, whereas no red color could be seen for high conductivity solutions.

3.4 Tests at Different Polyelectrolyte Concentrations in the Initial Solution

There is one difference between the two idealized models discussed earlier in this chapter. Because of its structural nature, the “segment entrapment” model is concentration dependent, whereas the “surface excess” model is not. Figure 4.11 shows the results of tests carried out with different amounts of PVSK added to the initial solution. All of these tests were carried out in the presence of 100 ppm CaCl_2 and no NaCl (conductivity = 280 $\mu\text{S}/\text{cm}$). In each case the concentration of poly-DADMAC in the mixture, at the zero SC endpoint, was plotted relative to the initial concentration of PVSK. The plotted line is based on a linear regression of the data. The coefficient of determination (R^2) had a value of over 0.999. Similarly, Figure 4.12 shows the results with reversed the titration direction, in which different levels of poly-DADMAC were used as the initial samples. Same as Figure 4.11, the coefficient of determination is over 0.999. In both cases, the slopes are close to 1.0. This indicates that the ratio of polyelectrolytes at the streaming current endpoint was independent of the concentration, over the range considered, despite of the titration direction. It also indicates that at low salt concentration polymer complexation still follows 1:1 stoichiometry from either titration direction.

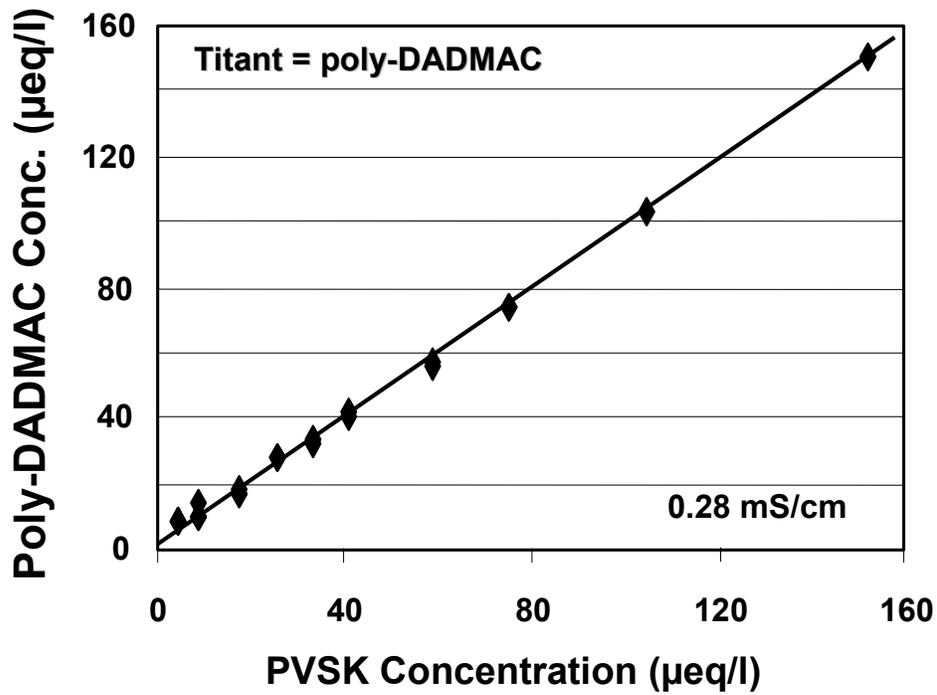


Figure 4.11: Corresponding concentrations of poly-DADMAC in the SC endpoint mixture to different concentrations of PVSK.

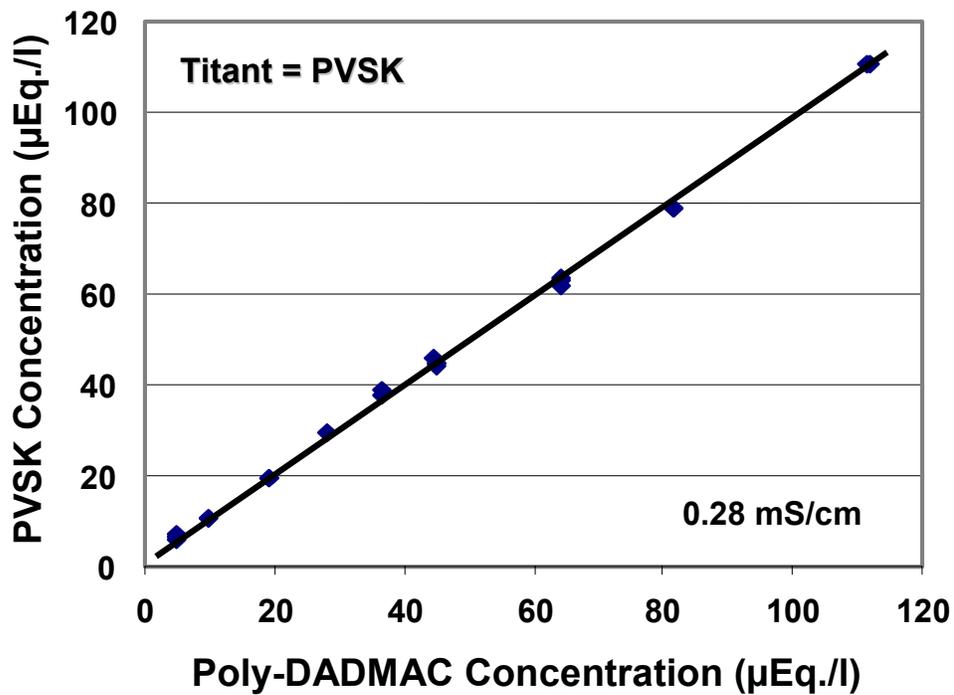


Figure 4.12: Corresponding concentrations of PVSK in the SC endpoint mixture to different concentrations of poly-DADMAC.

Figure 4.13 shows corresponding results in the case of poly-DADMAC solutions of differing concentration that were titrated with PVSK at a high salt concentration (100 ppm CaCl_2 and 1% NaCl). Once again, the regression line ($R^2 = 0.96$) showed no significant dependency of the ratio of polyelectrolytes on the concentration of the starting solution. However, the stoichiometry does not follow 1:1 any more. The slope of the regression line is about 1.14. It takes more of the second added polyelectrolyte to reach endpoint. To further test the hypothesis of 1:1 stoichiometry of interaction, the slope of regression line was forced to have a value of 1.0 and the intercept was treated as a fitting parameter. The resulting coefficient of determination was to about 0.75. In other words, this model did not predict the data well. Base on that, the proposed linear regression model was rejected.

In all three cases above, there are positive intercepts in the linear regression model. One possibility is that the second added polyelectrolyte needs to reach excess in order to affect the output from the charge detector. This deviation from zero became larger at higher conductivity.

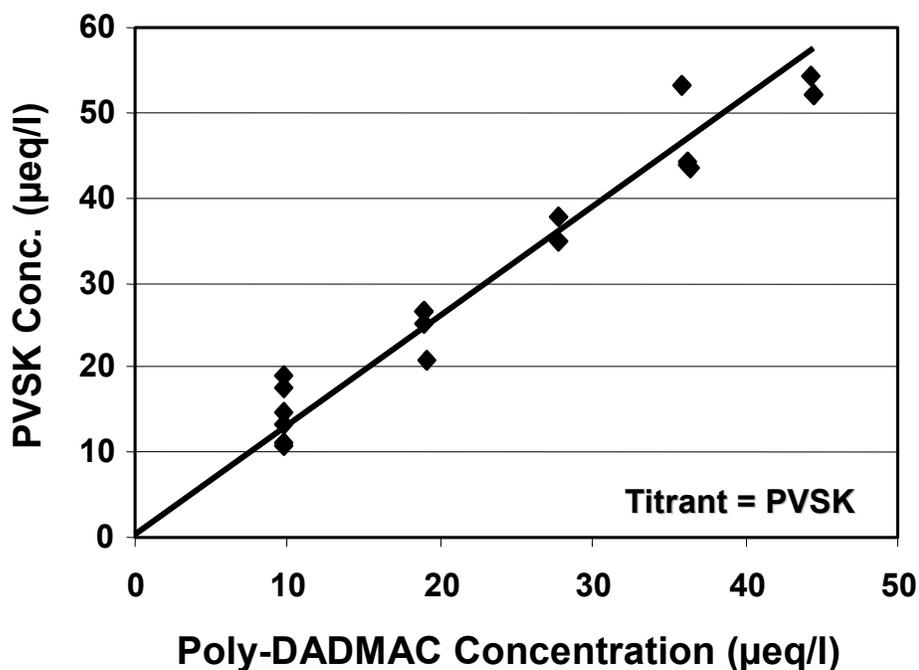


Figure 4.13: Corresponding concentrations of PVSK in the SC endpoint mixture to different concentrations of poly-DADMAC at highest conductivities.

The lack of concentration-dependency in Figure 4.13 at high conductivity appears to conflict with the segment-entrapment model outlined earlier in this article. In other words, if the non-stoichiometric endpoints had been due to polyelectrolytes becoming “stuck” in non-equilibrium situations, then one would expect such effects to become more prominent with increasing concentrations. This was not observed.

Elementary calculations of collision rates in gently stirred solutions [35], when applied to the polymer types and concentrations used in the present work, suggest collision half-lives within the range of 0.2 to 5 seconds over the concentration range of 5 to 150 µeq/L of the polyelectrolytes. Values assumed for these calculations included polymer radii of 50 nm, a temperature of 25 °C, a

shear rate of 100 s^{-1} , and molecular mass near to 200,000 Daltons. The corresponding calculations for Brownian collisions, disregarding flow, yielded collision half-lives in the range of 0.7 to 20 seconds over the same concentration range. In comparison, it has been suggested that the conformation of a polyelectrolyte of several hundred thousand g/mole may be of the order of magnitude of 1 second [35]. Based on these estimates one would expect to see a dependency of the endpoint ratio on concentration, if in fact the process were dominated by kinetic factors related to collisions, as in the case of the segment entrapment model.

3.5 Results of Turbidity Tests

Turbidity tests were used in the manner of earlier investigators [36,45] to detect the onset of precipitation of polyelectrolyte complexes during titrations carried out as already described. The purpose of these tests used in this study was to demonstrate the results from streaming current tests with an independent experimental approach. Representative results are shown in Figures. 4.14-4.17 for cases in which the default poly-DADMAC of intermediate mass was used as the initial solution. Figure 4.14 shows results corresponding to low to moderate levels of monomeric electrolytes. The turbidity values under these conditions remained very low, almost up to the point of charge-equivalence between the poly-DADMAC and the PVSK titrant. Thereafter, the turbidity rapidly increased and remained high with further increases in the amount of PVSK.

One way to explain the results in Figure 4.14 is to envision that nascent complexes, formed well before the equivalence point, have sufficient net positive charge so that coagulation is inhibited by electrostatic repulsion. Near the equivalence point the repulsion falls rapidly, so that particles grow large enough to scatter light effectively. The lack of further change in turbidity, upon further addition of titrant beyond the endpoint in Figure 4.14, suggests that the buildup of polyelectrolyte complex particles big enough to scatter light is not easily reversible.

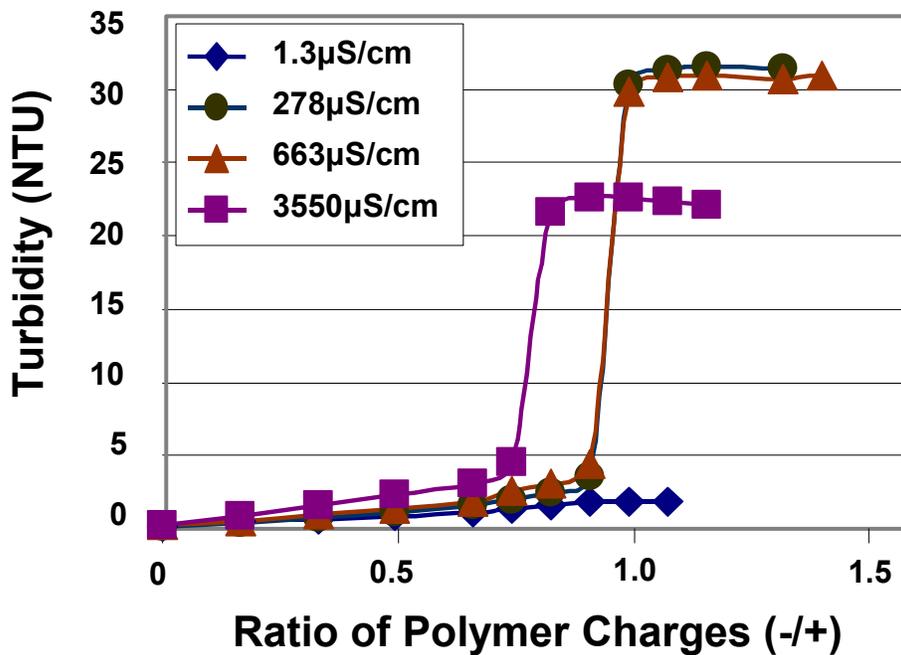


Figure 4.14: Turbidity as a function of the ratio of charged groups at various salt levels (from low to medium).

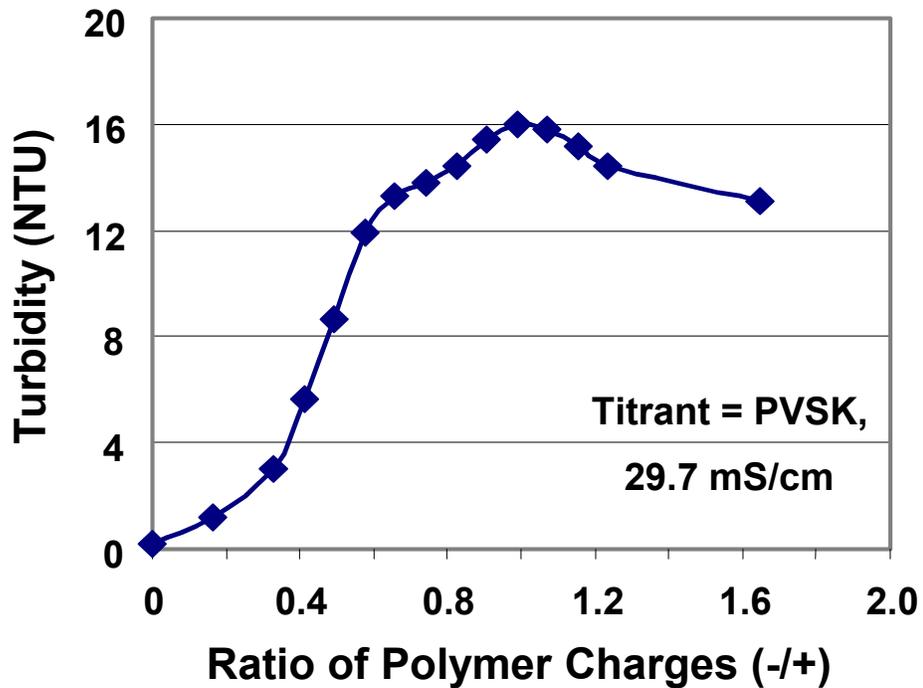


Figure 4.15: Turbidity as a function of the ratio of charged groups at high salt level.

A subtle aspect in Figure 4.14 requires further explanation. There were many individual experiments, such as this one, in which turbidity failed to show an anticipated increase in the absence of added salts (CaCl_2 and NaCl).

Subsequent tests showed that it was possible to observe strong increases in turbidity, even in the absence of salts, only if the titration was carried out very slowly in the vicinity of the equivalence point. Such results suggest the existence of a very narrow coagulation domain at very low ionic strength. In other words, it was possible to skip quickly past the point where coagulation could occur and restabilize the nascent complex particles in a form too small to scatter light effectively. However, this increase in turbidity occurred much more slowly,

compared to tests in the presence of salt. Normally hours passed before the turbidity could be detected by naked eye.

Figure 4.15 shows a much broader coagulation range in the corresponding titration carried out at the highest level of salt considered (100 ppm CaCl_2 and 1% NaCl). This observation is consistent with coagulation of charged, suspended particles [5]. A gradual dip in the turbidity at the highest levels of titrant addition, beyond the equivalence point, is tentatively attributed to a weakening of complexation interactions at high salt levels [59-60]. According to that interpretation, the system would be expected to be more reversible and capable of becoming restabilized upon addition of excess titrant, in comparison with similar tests at relatively low levels of monomeric electrolytes.

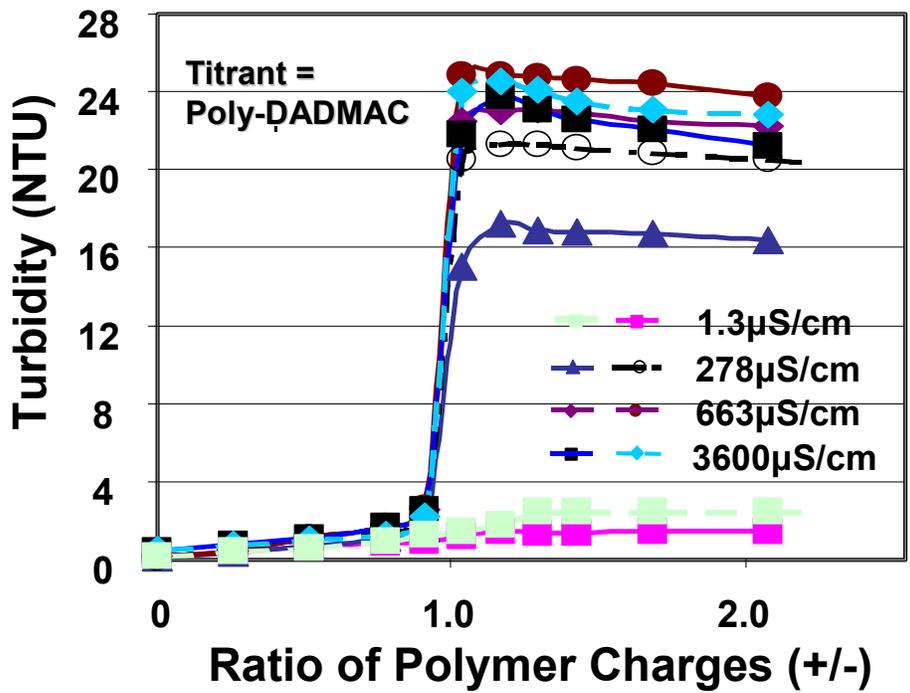


Figure 4.16: Turbidity as a function of the ratio of charged groups when poly-DADMAC was used as titrant at various salt levels.

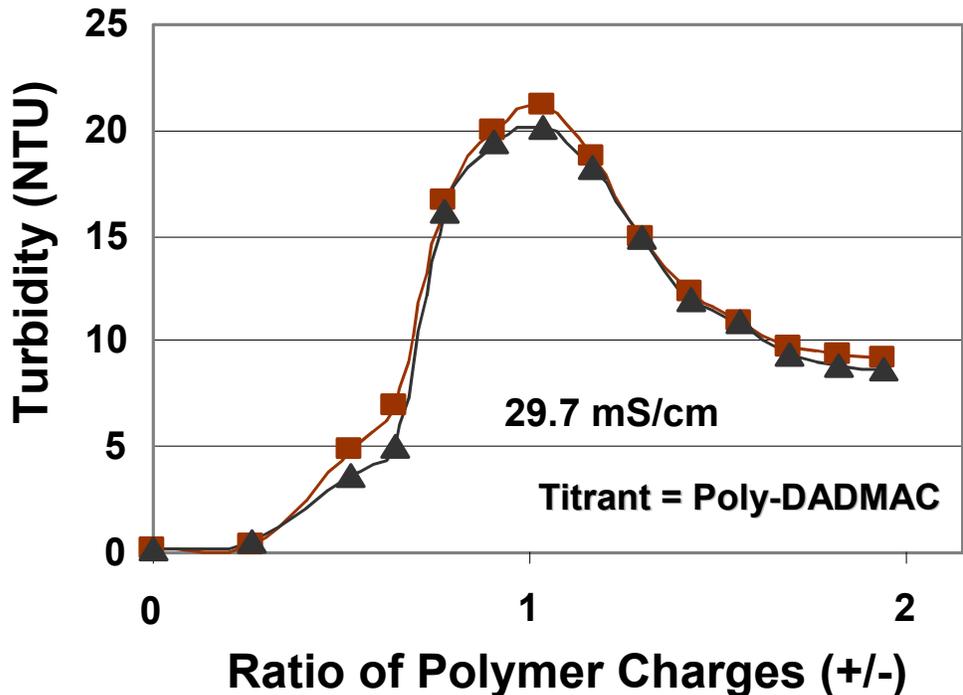


Figure 4.17: Turbidity as a function of the ratio of charged groups when poly-DADMAC was used as titrant at highest salt level.

Figure 4.16 shows related results in which the anionic polymer (PVSK) constituted the initial solution, and poly-DADMAC served as the titrant. Once again, turbidity values tended to remain very low until the equivalence point was approached. Thereafter, the turbidities either remained high or gradually declined with further increases in titrant amount. Again, it was possible to skip past the point of destabilization, when titrations were carried out at the normal rate in the absence of added salts. The fact that the results in Figure 4.14 and 4.16 are very similar is consistent with the symmetry shown earlier in Figures. 4.4 through 4.7 for streaming current titrations carried out in opposite directions.

Figure 4.17 shows corresponding results in the case of the highest salt level considered (100 ppm CaCl_2 and 1% NaCl). Here the appearance of a maximum in turbidity, near to the equivalence point, is most pronounced.

Table 4.5 summarizes results of similar turbidimetric titrations carried out under the same range of salt conditions, but with the initial polymer consisting of poly-DADMAC samples having three different average molecular masses. The values of $-/+$ at the point of most rapid turbidity rise were determined from graphs by observing the abscissa values of the rising curves at one-half of the turbidity maxima. As shown, effects due to increasing salt concentration were apparent for all three cases, not just with the intermediate poly-DADMAC mass represented in Figures. 4.14-4.15. However at each salt level the point of most rapid turbidity rise depended upon molecular mass of the poly-DADMAC. In the case of the lowest-mass poly-DADMAC, addition of PVSK titrant resulted in colloidal instability already at relatively low values of the titration ratio ($-/+$), especially at the two highest levels of salt. In the case of the highest-mass poly-DADMAC, the same titration conditions did not result in colloidal instability until the PVSK titrant addition was much closer to the stoichiometric point. While the present work does not provide enough evidence to reach a firm conclusion, such behavior is consistent with an increasing ability of the larger poly-DADMAC molecules to act as “hosts” for the smaller PVSK “guests” in colloiddally stable complexes [16,36].

Table 4.5. Ratio of anionic to cationic polyelectrolyte groups (-/+) at the point of rapid turbidity rise when titrating poly-DADMAC solutions of different molecular mass with PVSK.

Poly-DADMAC mass	Low (15 k Daltons)	Medium (400-500 k Daltons)	High (1900 k Daltons)
Hard water (100 ppm CaCl ₂)	0.865	0.948	1.030
Hard + 100 ppm NaCl	0.783	0.948	1.030
Hard + 0.1% NaCl	0.330	0.783	0.947
Hard + 1.0% NaCl	0.288	0.494	0.660

No consistent trends relative to molecular mass were observed when a parallel set of tests was carried out with poly-DADMAC samples of differing molecular mass used to titrate PVSK solutions, at various salt concentrations. This lack of dependency on molecular mass tends to cast doubt on the “entrapment” model in Figure 4.2. Molecular mass would be expected to affect whether a titrant molecule can untangle itself rapidly enough to avoid isolation of non-complexed segments.

The completed results and discussion about the shape of each titration curve when various molecular mass of poly-DADMAC used are shown in Appendix B.

3.6 Results of Microelectrophoresis Tests

One of the idealized models implies a non-zero zeta potential of PECs at the neutral point of an SC titration. Microelectrophoresis tests were carried to examine this possibility. Results (Table 4.6) of microelectrophoresis tests indicated that during titrations the suspended matter in the colloidal phase reached zero zeta

potential long before achievement of a zero streaming current endpoint. In these tests PVSK was added as a titrant to solutions of poly-DADMAC. Tests in the absence of CaCl₂ or NaCl yielded positive zeta potential values in the range of +20mV to +26mV when the mixture became turbid at ratios (-/+) of PVSK ionic groups to poly-DADMAC groups between 0.93 and 0.95. Zero mobility was observed in the suspended matter upon further addition of PVSK when the ratio (-/+) had reached 0.978. The SC endpoint was at 1.000 (see Experimental).

Table 4.6: Zeta potential of polyelectrolyte complexes formed with various charge ratios in deionized water.

Ratio of Charged Groups (-/+) *	Average Zeta Potential (mV)	
	5 hrs	24 hr
0.929 / 1	+ 22.6	+ 25.63
0.937 / 1	+ 21.5	+ 20.69
0.945 / 1	+ 20.4	+ 23.62
0.953 / 1	+ 20.2	+ 21.46
0.962 / 1	+ 7.3	0
0.970 / 1	+ 11.5	+ 11.43
0.978 / 1	0 **	0

* The ratio is based on calibration of the polyelectrolytes by titration in deionized water.

** Particles moving in both directions, about equally, were observed.

Visual and turbidimetric observations from the tests just described were consistent with a mechanism of charge stabilization of the polyelectrolyte complex particles in suspension. The particle size after 24hrs aggregation was

generally larger than that after 5hrs, consistent with ongoing coagulation. A drop in turbidity (Table 4.7) was noted in the case of those mixtures for which the measured zeta potential was near zero. Such behavior is consistent with the disappearance of charge repulsion under those conditions, allowing particles to approach each other, stick together efficiently, form large aggregates, and settle [61].

Table 4.7: Turbidities of polyelectrolyte complexes formed with various charge ratios in deionized water.

Ratio of Charged Groups (-/+) *	5hrs	24hrs
0.929 / 1	18.6	17.8
0.937 / 1	20.5	19.5
0.945 / 1	21.8	21.2
0.953 / 1	22.7	21.2
0.962 / 1	23.3	7.55
0.970 / 1	22.0	18.7
0.978 / 1	17.7	8.02

* The ratio is based on calibration of the polyelectrolytes by titration in deionized water.

A series of additional tests was carried out with PVSK gradually added to poly-DADMAC solutions at different salt levels, but always with the same ratio of anionic to cationic polyelectrolyte groups (Table 4.8 is the zeta potential results and Table 4.9 is the corresponding turbidity data). It was found that polyelectrolyte additions at a ratio (-/+) equal to 0.962 yielded negative zeta potentials of the polyelectrolyte complexes for all samples that contained at least

100 ppm of NaCl in addition to the standard 100 ppm of hardness. However, Figure 4.5 shows that the corresponding streaming current endpoint was not reached until the ratio (-/+) was either about 1.08 or higher, depending on the level of salt. This phenomenon becomes more significant as the conductivity increases. This observation again supports the existence at the SC endpoint of charge-stabilized complexes of the type illustrated in Figure 4.3. In other words, the “surface excess” model of polyelectrolyte complexes in colloidal suspension appeared to be most consistent with the present observations regarding the stoichiometry of streaming current titrations.

Table 4.8: Zeta potentials of polyelectrolyte complexes when (-/+) = 0.962 in various salt solutions.

Salt level	5hrs	24hrs
100ppm CaCl ₂	14.95	Positive
100ppm CaCl ₂ +100ppm NaCl	-3.939	Particles do not move
100ppm CaCl ₂ +0.1% NaCl	-14.13	Negative
100ppm CaCl ₂ +1% NaCl*	Negative *	Negative *

* Conductivity is too high to measure accurate zeta potential.

Table 4.9: Turbidities of the solutions when (-/+) = 0.962 at various salt levels.

Salt level	20 min	5hrs	24hrs
100ppm CaCl ₂	19.3	19.5	15.2
100ppm CaCl ₂ +100ppm NaCl	21.5	10.9	5.28
100ppm CaCl ₂ +0.1% NaCl	24.9	17.6	13.0
100ppm CaCl ₂ +1% NaCl	24.6	16.0	13.7

4. Conclusions

1. In the presence of CaCl_2 and NaCl the endpoint of titrations between strong, linear, high-charge polyelectrolyte solutions, using a streaming current endpoint, depended on which of the two solutions was used as the titrant. Deviations from 1:1 stoichiometry increased with increasing NaCl concentration.
2. Results were consistent with the existence, during the titrations, of charge-stabilized polyelectrolyte complexes in which charge-stability involves an excess of one of the polyelectrolytes at the surface of each particle. These particles continue to take up titrant even after their zeta potential has been reversed.
3. The present study helps to explain some apparent shifts in polyelectrolyte complexation stoichiometry in earlier studies involving streaming current endpoints. The results also reinforce earlier recommendations to minimize errors in endpoint determination by diluting high-conductivity samples with known ratios of distilled water to bring the electrical conductivity below about $1000 \mu\text{S}/\text{cm}$ [22].

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Chapter 5

Dependency of Polyelectrolyte Complex Stoichiometry on the Order of Addition. Part 2. Aluminum Chloride and Potassium Poly-vinylsulfate

Abstract

The dependency of polyelectrolyte complex stoichiometry on the order of addition with increasing monomeric and divalent ion concentrations has been addressed in an earlier study that focused on the effects of concentration of monomeric and divalent ions. Besides sodium and calcium ions, aluminum ions are also common in the process water during papermaking. In this study the effect of aluminum ions on titrations between solutions of a strong poly-acid (polyvinyl sulfate, potassium salt) and a strong poly-base (poly-diallyldimethylammonium chloride) was investigated. 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, and not all of the results can be predicted by stoichiometric relationships. Several factors could affect this “interference”. However, with a careful control of pH and degree of neutralization of aluminum ion, the titratable charge of aluminum ions could be estimated by SC titration. This study also showed an indication of the existence of aluminum polynuclear species when the highest titratable charge was reached.

1. Introduction

In Chapter 4 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, and that this dependency became more pronounced with increasing salt concentration. The present investigation involves similar titrations in which aluminum chloride was one of the charged entities. Interactions between aluminum ions and polyelectrolytes play major roles in such applications as water and wastewater treatment [1-3], and papermaking [4-7]. In both of these areas of application the streaming current method has emerged as a major tool for process control [8, 9]. Therefore, to further improve process efficiency it is important to understand not only the streaming current method in general, but also how the results of the tests may be affected by the presence of soluble aluminum compounds.

According to St. John [9], aluminum ions “interfere with” titrations that use polyelectrolytes of opposite charge to determine the solution concentrations of a certain polyelectrolyte of interest. In support of this statement, aluminum ions have been shown to affect the endpoints of such titrations that were carried out with either colorimetric [6, 9-12], or streaming current [13] detection of the endpoints. To understand what is meant by the word “interfere,” it is worth considering the conditions under which accurate and reproducible polyelectrolyte titrations can be expected. These conditions include prompt complexation between the respective polyelectrolytes, at a fixed ratio, leaving essentially a

zero net concentration of either polymer in solution at the equivalence point of the titration. A substance would be said to interfere with a polyelectrolyte titration if it had the capability to complex with either one of the titrants with sufficient strength as to affect the endpoint. The most troublesome type of interference would be one that causes unpredictable deviations, not related in a clear stoichiometric way to the amount of the substance present.

Trivalent aluminum can be classed as a hard Lewis acid, having an exceptionally small ionic radius relative to its charge [14]. As such, the aluminum ion has a very strong tendency to complex with such ligands as water, OH^- , sulfate, and many other anions of industrial importance [14]. In addition, partially hydroxylated aluminum ions have a strong tendency to associate into dimers and certain other multi-aluminum ionic species [2,15-19]. The relative abundance of 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 [20-23]. The presence of such polynuclear ions was confirmed also by colloidal chemical analyses, based on the superior coagulating ability of large, multivalent ions [24]. Akitt [20], Crawford [23], and Bottero *et al.* [21] carried out important work by ^{27}Al nuclear magnetic resonance (NMR) to identify $[\text{AlO}_4\text{Al}_{12}(\text{OH})_4(\text{H}_2\text{O})_{12}]^{7+}$ as the most stable of these polynuclear ions. 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 OH's per Al, followed by a sharp decline in favor of $\text{Al}(\text{OH})_3$ with further increases in hydroxylation of the solution.

Although one might expect, based on the Shultz-Hardy rule [24], that trivalent aluminum ions 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 [2, 22, 25-28]. For instance, Exall and van Loon [22] 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. With respect to papermaking applications, Strazdins [6] was the first to show sharp maxima, as a function of the degree of hydroxylation, 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 increasing aluminum concentration, a finding that is consistent with conditions that would be expected to maximize the proportion of polynuclear ions [6].

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 [23] was 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 [6, 25, 27].

Strazdins [6] and Trksak [7] showed that the coagulating ability of aluminum sulfate or polyaluminum chloride solutions decreased with aging of the solution.

Strazdins [29] showed that the “charge decay” of aluminum sulfate solutions was accelerated at high temperature, but part of the decay could be recovered if the solution was subsequently exposed to high shears.

To provide focus for the present investigation, two hypotheses were considered, as follows:

First it is proposed that the effects of aluminum ions can be understood as a linear combination of interactions involving various aluminum species that are present, with the understanding that both the quantity of colloidal charge and the degree of affinity for the anionic titrant would be expected to differ, according to the aluminum species under consideration.

The second hypothesis is that aluminum species may deviate strongly from a stoichiometric relationship with polyelectrolytes of opposite charge. Such deviations could be attributed to such factors as (a) relatively weak complexation, (b) slow or interrupted progress towards thermodynamic equilibrium, due to the difficulties of polymeric rearrangement, and (c) the possible isolation of positively charged aluminum species that may have become coated by an impermeable layer of aluminum hydroxide [6]. Hypotheses (b) and (c), if true, imply that the order of addition of aluminum chloride vs. PVSK ought to affect the titration endpoints between the two solutions.

2. Experimental

2.1 Materials:

Similar to the study in Chapter 4, the polyelectrolytes used were highly charged strong poly-acids and poly-bases. Table 5.1 lists the major chemicals used in this study.

Table 5.1: General properties of the polyelectrolytes.

Type of Polyelectrolyte	Supplier	Properties
AlCl_3	Fisher Chemicals	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$
poly-DADMAC	Aldrich Co.	MW=400-500k Dalton
Colloidal silica	Aldrich Co.	R=22 nm
PVSK	Aldrich Co.	MW=170k Dalton

2.2 Titration Method to Evaluate Interference

The titrations were carried out using a PCD 03 pH streaming current instrument (Mütek Analytic) in the presence of various concentrations of aluminum ion. In these experiments two different amounts of PVSK (0.866 mN) were added to two different concentrations of aluminum chloride solution as initial samples, then poly-DADMAC (0.928 mN) was used to titrate the mixtures. The corresponding concentrations of aluminum ion were 0.01 mol/l and 0.001 mol/l.

2.3 Titration Method with pH Adjustment

In order to investigate the effect of the pH of solutions on the titration between aluminum ions and PVSK, two pH values, which are common in acid

papermaking, were chosen: 4.5 and 5.0. Because of the restrictions of the streaming current device, at least 10 ml of aqueous solution was required to get reliable results. When PVSK served as sample, PVSK was added to 15 ml of deionized water (DW) as the initial sample, whereas when aluminum ion was used as sample, aliquots of 15 ml of aluminum chloride solution were used directly without any dilution. NaOH and HCl were used to adjust the desired pH.

Experiments were organized into two series according to how the pH was maintained. During one series the pH was adjusted in the course of titrations, and final results were reported. In the other series, the pH was adjusted before the titrations, allowed to float during the titrations, and then adjusted back to the target value after the titrations, if necessary. Further titrant was added in those cases where adjustment of the pH caused a change in the streaming current signal (such shifts in signal always requiring additional titrant to reach an output value of zero). The final result was reported as the sum of all of the titrations until the pH adjustment did not affect the sign of the streaming current reading.

Additional experiments were carried out in order to examine the amount of charge of the aluminum ions which could be detected by titration with PVSK over a wider range of pH values. Three different concentrations of aluminum chloride, 0.001 mol/l, 0.005 mol/l and 0.0001 mol/l were used. In each experiment 15 ml of AlCl_3 was used as the initial sample, and the pH values were adjusted only before and during the titrations. Titrations were carried out using PCD 03 pH with a Mutek PCD-T auto-titrator.

2.4 Zeta Potential

Ludox® TM-50 colloidal silica from Aldrich was used as the dispersed phase, making electrokinetic measurements possible. Aluminum chloride with two different concentrations, 0.001 mol/l and 0.0001 mol/l, were used as coagulants. In each experiment 2.0 ml of 1 wt% of silica was added to 30 ml aluminum chloride solution, which had been adjusted to desired pH. The zeta potential of colloidal silica, based on the Henry equation [30], was measured with a Laser Zee Meter Model 501, after mixing.

2.5 Turbidity

Turbidity tests were carried out in 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. Measurements were carried out periodically, at specified points in time following mixing, within a period of 24 hours.

3. Results and Discussion

3.1 Aluminum as an Interference

Table 5.2 shows experimental results that help to support an assertion that aluminum ions can “interfere” with titrations that are carried out between polyelectrolytes of opposite charge [9]. 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

substance under consideration. In the set of experiments represented by Table 5.2, two different amounts of poly-vinylsulfate (PVSK) were added to two different concentrations of aluminum chloride solution as the samples. The mixtures were then back-titrated with poly-diallyldimethylammonium chloride (poly-DADMAC) to a streaming current endpoint of zero. Results were repeated at two levels of PVSK addition.

Table 5.2: Effect of aluminum chloride on the amount of poly-DADMAC required to titrate PVSK solution to a streaming current endpoint of zero.

Amount of AlCl ₃	None	1.01 x 10 ⁻³ M	1.01 x 10 ⁻² M
Poly-DADMAC amount (μeq), lower PVSK series	0.87 ± 0.01*	0.19 ± 0.05*	0.37 ± 0.18*
Poly-DADMAC amount (μeq), higher PVSK ser.	1.71 ± 0.01*	0.40 ± 0.03*	0.43 ± 0.08*
Notes: * = 95% confidence intervals of the measurement results			

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 aluminum species had at least some ability to form a complex with negatively charged groups of the PVSK and block the charged sites from the access of 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.

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 (Al), neglecting the existence of other stable ionic species. In other words, the titration data were compared to the theoretical efficiencies that one would anticipate based on a model of one hexa-hydrated Al^{3+} ion 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 5.2, the apparent equivalents of PVSK complexing with each mole of aluminum were scattered between 0.003 and 0.09. This means that the effect of the aluminum compound was highly inefficient relative to the idealized stoichiometric model based on the unhydrolyzed aqueous aluminum ions. Also, there was no clear pattern to 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 nonstoichiometric results in Table 5.2 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 [31-33]. 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 Chapter 4 of this thesis, the order of addition of the interacting compounds also was varied.

3.2 Direct Titrations at Controlled pH

PVSK First: 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.

Table 5.3: Ratio of PVSK negative groups per aluminum atom at the streaming current endpoint when adding aluminum chloride solutions to PVSK solution.

Conditions	Aluminum concentration before addition (moles/liter)	
	0.001	0.0001
Ratio of PVSK equivalents per mole of Al at pH 4.5	0.27 ± 0.16 *	< 0.25 **
Ratio of PVSK equivalents per mole of Al at pH 5.0	0.64 ± 0.05 *	0.50 ± 0.03 *
Notes: * = 95% confidence intervals of the measurement results ** = Overflow precluded continuation of experiment beyond this point at the higher dilution.		

As shown in Table 5.3, 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 to 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 solutions (aluminum chloride solution).

To account for the general trend of data in Table 5.3, calculations were carried out based on a working hypothesis that all of the aluminum was present in the form of the $[\text{AlO}_4\text{Al}_{12}(\text{OH})_4(\text{H}_2\text{O})_{12}]^{7+}$ (Al_{13}) ion proposed by others [19]. The ratio of seven charges per 13 aluminum atoms, as implied by 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 5.3 obtained at $\text{pH} = 5$ could be fortuitous, the results are consistent with an efficient, high-affinity interaction mainly between this ionic species and PVSK.

AlCl_3 First: In the next set of tests to be discussed, the order of addition was reversed. Aluminum solution was placed first in the testing vessel, and the PVSK served as the titrant. 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 the experimental section. Results are given in Table 5.4.

Table 5.4: Ratio of PVSK negative groups per aluminum atom at the streaming current endpoint when adding PVSK to aluminum chloride solutions, comparing two methods for pH control.

Method of pH control	pH	Aluminum concentration in initial solution (moles/liter)	
		0.001	0.0001
After each aliquot	4.5	0.56 ± 0.04 *	0.10 ± 0.06 *
Simultaneous	4.5	0.48 ± 0.03 *	0.21 ± 0.05 *
After each aliquot	5.0	0.27 ± 0.01 *	0.48 ± 0.01 *
Simultaneous	5.0	0.26 ± 0.01 *	0.48 ± 0.01 *

Notes: * = 95% confidence intervals of the measurement results

Results in Table 5.4 show an apparent conflict. At the higher initial concentration of aluminum chloride solution, the most efficient complexing ability, as indicated by the higher values, were 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 are also different from the results of experiments shown earlier in which PVSK served as the sample.

To interpret the results in Table 5.4 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 [33]. 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 of PVSK titrated with 0.001 mol/l AlCl_3 were fairly close to those for 0.0001 mol/l AlCl_3 titrated with PVSK. With a careful calculation, the final concentrations of AlCl_3 after titration in both cases were very close. The finding suggests that the complexation between PVSK and AlCl_3 may be a function of the concentration of AlCl_3 in the final solution.

To further test the explanation given above, experiments were carried out over a wider range of pH values and initial concentrations. 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.

3.3 Apparent Charge as a Function of pH

To reinforce the findings shown in the previous section, a series of titrations was carried out with aluminum chloride solutions of selected concentrations (see experimental). 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 Figure 5.1, the apparent charge of the aluminum chloride solutions 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 about 3.5 or above 8.

At each of the three concentrations of aluminum considered, the effective charge approached a maximum of about 0.5 equivalents per mole of aluminum ($\text{OH}/\text{Al} = 0.52, 0.53, 0.52$ with aluminum concentration $1.01 \text{ mmol/l}, 0.507 \text{ mmol/l},$ and 0.101 mmol/l respectively). This value is reasonably close to the theoretical value 0.538 for the polynuclear ion $[\text{AlO}_4\text{Al}_{12}(\text{OH})_4(\text{H}_2\text{O})_{12}]^{7+}$, as noted earlier.

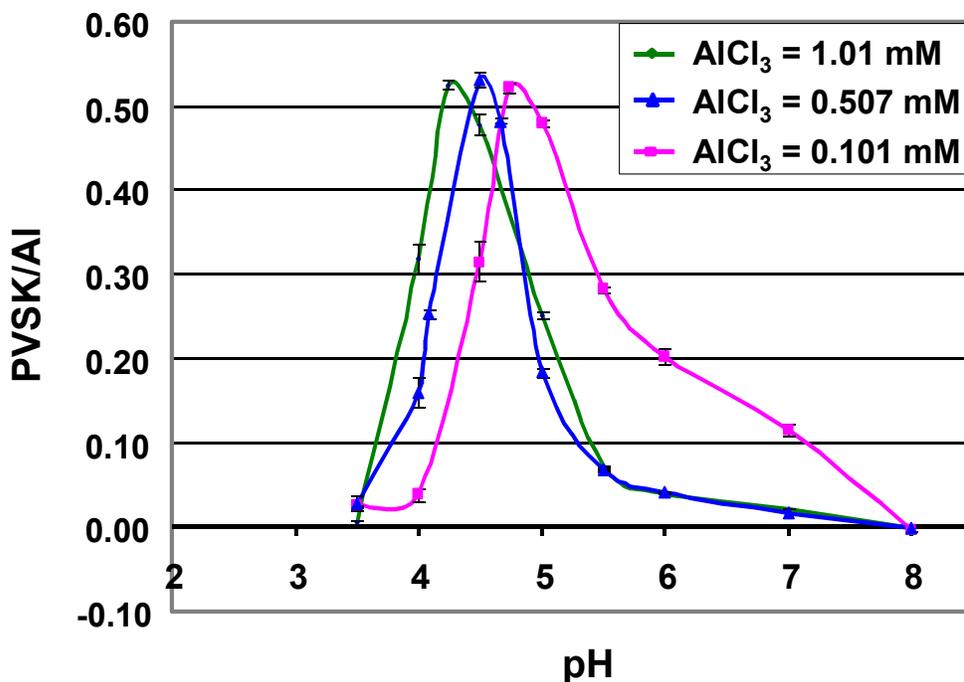


Figure 5.1: Equivalents of PVSK required to titrate AlCl_3 solutions to a zero streaming current endpoint as a function of pH

One way to interpret the results in Figure 5.1 is to propose a model in which the aluminum tridecamer (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 Figure 5.2.

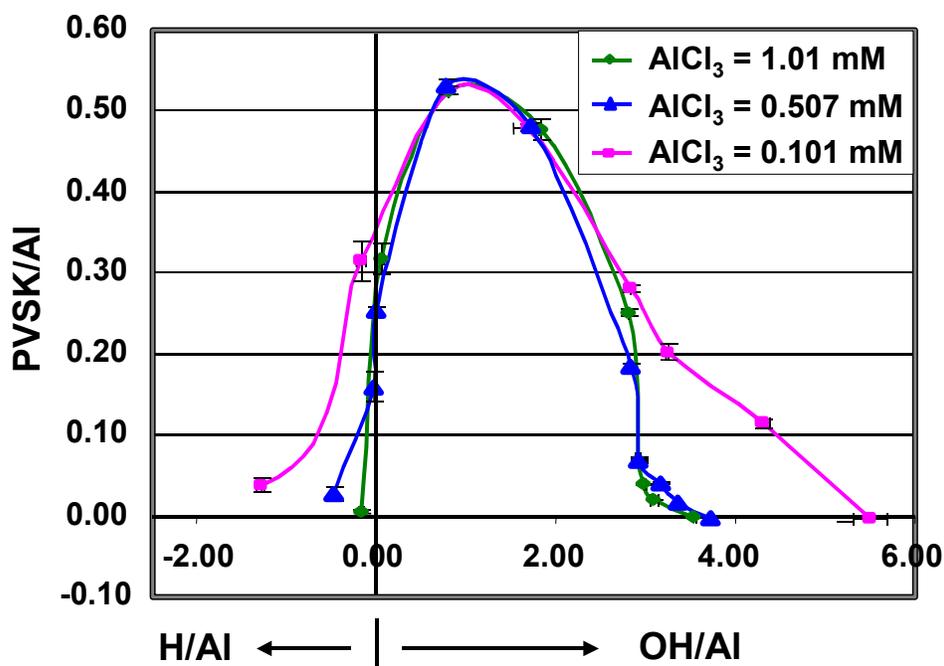


Figure 5.2: Equivalents of PVSK required to titrate AlCl_3 solutions to a zero streaming current endpoint as a function of OH-to-aluminum ratio (degree of hydroxylation)

As shown, results in Figure 5.2 allowed most of the data points to 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 of 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 complex ability with PVS-K at similar ratio of OH to Al (degree of neutralization), which is about 1. These results are similar to Reynolds' study that was related to dry strength resins used with alum [34], as discussed earlier in Chapter one. The peak areas of the curves are relatively broad in Figure 5.2, compared with those in Figure 5.1 when they are plotted against pH. This is to be expected, since aluminum solution itself is a good pH buffer. It takes a lot of base to change the pH (Figure 5.3).

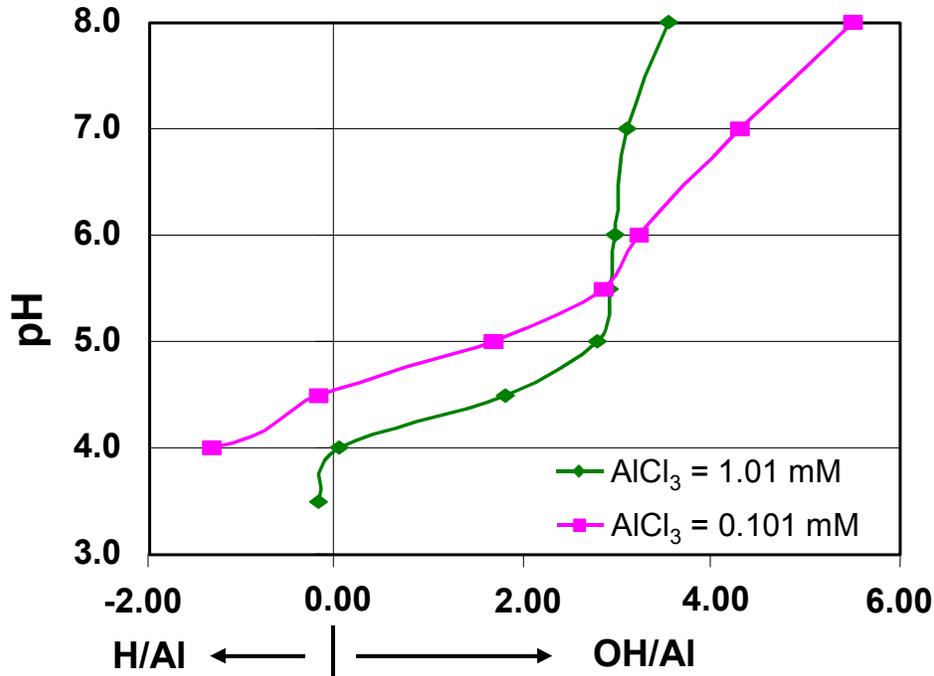


Figure 5.3: The relationship between pH and degree of neutralization.

3.4 Zeta Potential Test

Because the explanation given in the previous section assumed the existence of the Al_{13} ion in solution within a certain concentration range, further tests were carried out to test this assumption. Accurate analysis of aluminum species usually requires higher solution concentrations than those used in the present work [20-23]. Therefore, colloidal chemical tests were carried out to obtain further evidence of the existence of polynuclear aluminum species within the range of conditions employed in the streaming current titration experiments.

Figure 5.4 shows results of tests in which 1.00 mM and 0.10 mM aluminum chloride solutions, to which different amounts of NaOH had been added to adjust pH, and the calculated zeta potential was observed. At the higher concentration there were sufficient amounts of aluminum ions in the solution, since silica particles had positive zeta potential even at low pH end over the range of this study. It is worth noting that the zeta potential became increasingly positive as the pH was increased within a range between 4 and 5. In this respect our results are consistent with those of Brace and Matijević [35], who observed positive zeta potentials at similar pH values during work with somewhat more concentrated solutions (3 mmol/l $Al(NO_3)_3$). 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 [22, 26], where Figure 5.4 shows a lesser positive zeta potential.

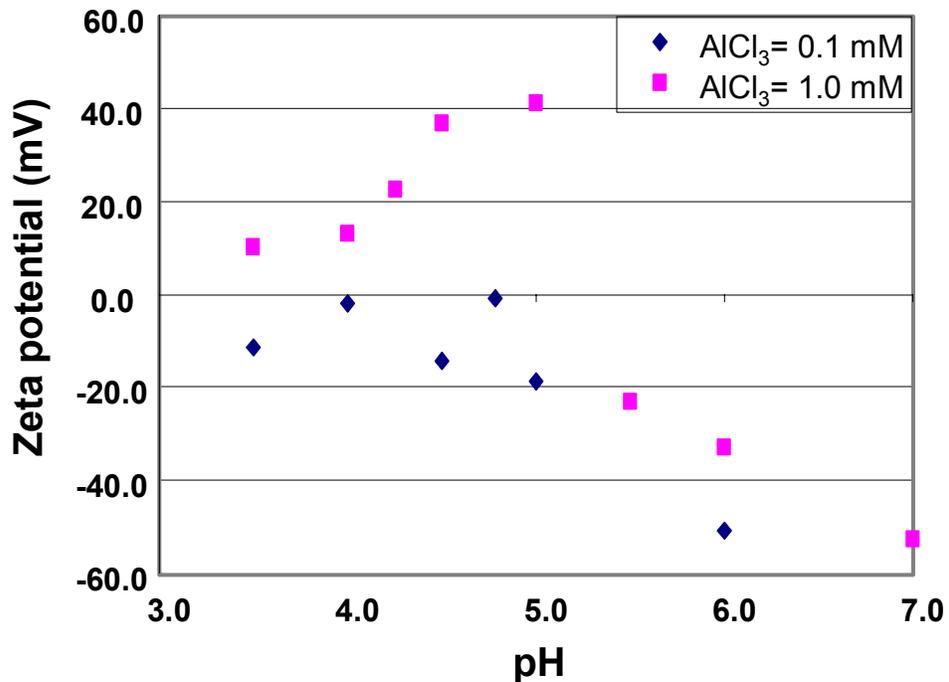


Figure 5.4: Zeta potential of silica particles in presence of 1 mM $AlCl_3$ solutions to which NaOH was added to adjust the pH.

At the lower concentration of aluminum ions considered, there was only one-tenth the amount of aluminum ions in the solution, compared with that of the higher concentration. In this case, there were two peak values over the pH range studied. Several replicate experiments were carried out to confirm that this result was not due to experimental errors. One possible explanation for this unexpected result is that there may not have been sufficient aluminum in the solution for coagulation, since at most pH values the colloidal silica remained negative. Only highly charged aluminum polynuclear species have a possibility to neutralize the surface charges of colloidal silica. Similar results also have been found in the study of the critical coagulation concentration when aluminum chloride used as coagulant [36].

3.5 Turbidimetric Tests

To further confirm the presence of polynuclear aluminum species under some of the aqueous conditions used in this study, Table 5.5 shows the results of turbidity measurements. In each case 0.001 mol/l aluminum chloride was used as the coagulant. 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 added amount of NaOH, or equivalently, on the pH.

Especially it is worth noting the results corresponding to pH values of 4.25 and 4.49, where the suspension not only reached a high initial value of turbidity after mixing, but also the turbidity remained high after 24 hours. It is worth noting that the measured zeta potentials were strongly positive for these two samples, 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 hours fell to very low levels, consistent with the precipitation of agglomerated material. The results shown in Table 5.5 are generally consistent with studies by Matijević *et al.* [37] and by Rubin and Hayden [15], in which polynuclear species were proposed to explain results of nephelometric studies with 1 mM aluminum nitrate solutions.

Table 5.5: Turbidity of colloidal silica dispersions after partial neutralization of 1.01 mM AlCl₃ 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 hours	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	-----

Table 5.6 shows results of tests involving 0.1 mM AlCl₃ solutions, which is about a factor of ten less concentrated than was considered in the cited previous work [22]. As shown, the lower concentration conditions yielded results that were very different from those shown in Table 5.5. 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 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 range from 4 to 5. 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 hours. 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 ($4 < \text{pH} < 5$) where it would be reasonable to expect the presence of polynuclear aluminum species.

Table 5.6: Turbidity of colloidal silica dispersions after partial neutralization of 0.101 mM AlCl_3 solutions.

OH^- added per Al	-	-	-	0.79	1.68	2.84	3.24	4.31	5.50
H_3O^+ 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 hours	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	-----	-----

More turbidity tests were carried out with PVSK as the first added polymer. In order to distinguish the turbidity increase due to aluminum flocs, no base was used to adjust pH. Results showed that PVSK and aluminum chloride can form visible complex flocs over pH range from 2.0 to 3.5. However, no turbidity increases were detectable when the pH was lower than 2.0. This experiment

may show some coagulating ability of aluminum ions at low pH. However, further study needs to be done to fully understand those results (see Appendix D).

4. Conclusions

1. Aluminum ions interfered with the stoichiometry of titrations between poly(diallyldimethylammonium chloride) (poly-DADMAC) and potassium poly(vinyl sulfate) (PVSK), even when their concentration was very low compared to the concentration of other inorganic ions in the experiments carried out in Chapters 3 and 4.
2. Titrations between PVSK and aluminum ions failed to show a consistent stoichiometry of interactions when the direction of titration was varied, even when the pH was held constant. In other words, different results were obtained, depending on whether PVSK or aluminum ions were used as the titrant or the sample. Results were consistent with an explanation involving the concentration of aluminum ions in the final solution. According to Arnson, the aluminum species present in the solution could be affected by the concentration of the dissolved aluminum compound [33], and these species can be one of the factors affecting the stoichiometry of the titration. When the concentrations of aluminum ions were similar, the stoichiometry was fairly close from both directions.
3. It is possible to titrate the apparent charges of aluminum ions with PVSK under specified conditions of pH, the amount of base added, and a rough estimate of the initial aluminum compound concentration. However, the

stoichiometry depended on pH and degree of charge neutralization of aluminum ions.

4. The highest titratable charge occurred within the range of 0.5 to 2 of the OH/Al ratio. The highest titratable charge was about 0.5, when expressed as the ratio of the negative charge in moles used to titrate to the endpoint vs. the total moles of aluminum element in the solution. This value was consistent with the action of the polynuclear species $[AlO_4Al_{12}(OH)_4(H_2O)_{12}]^{7+}$.
5. The zeta potential and turbidity results indicated the presence of aluminum polynuclear species, possibly $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ in the pH range between 4 and 5. This thirteen-oligomer has been identified by previous researchers as the most stable polynuclear species [2]. 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 this “interference”.

5. References

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Chapter 6

Summary of Conclusions

In summary, this thesis research documented how various factors affect the results of titrations between polyelectrolyte species. The primary focus was on the use of streaming current (SC) as an endpoint-detection method. Other methods were used to provide information to confirm the mechanism. Effects of salt ions, polyelectrolyte properties, the order of polymer addition, and the presence of multivalent aluminum ions were evaluated. Both adsorption and the complexation behavior of polyelectrolytes were investigated to understand the titration behavior of polymers.

With respect to salt addition, the current work showed that the results of streaming current tests at relatively high electrical conductivity were consistent with a reduced efficiency of poly-DADMAC adsorption. There is a maximum level of conductivity for this instrument beyond which it is more difficult to get a reliable result. This range was found to have some dependency on the charge density of the anionic polymer used as a sample. The approximate range of conductivity that is expected to get reliable results for all anionic polyelectrolytes is up to 1.0 mS/cm. For most anionic polyelectrolytes clear and reasonable titration results could be achieved up to 3.6 mS/cm, whereas when the conductivity went up to as high as 10mS/cm, only highly charged anionic polyelectrolytes could give acceptable results. The present experimental results showed no significant impact of molecular weight of cationic polymer on both the

shape of the charge titration and turbidity test curves. The shapes of titration curves for anionic starch (low DS) and CMC (high DS) were quite different. This may indicate that the shape of the titration curve could suggest the charge density of anionic polyelectrolytes. At low salt concentrations the titration curve of low DS anionic polymer was more like a linear relationship between titrant addition and the signal output; whereas the titration curves of high DS anionic polymer had a relatively flat region at the beginning of the titrations, and a sharp change near to the charge equivalent point. As salt concentration was increased, this sharp change became less significant even for highly charged anionic polyelectrolyte. The changing in shape of titration curves is more sensitive to salt concentration for low DS anionic polyelectrolytes.

In the second main part of the work it was found that the deviation from 1:1 stoichiometry becomes more and more severe as the conductivity increases. For the first time it was demonstrated that this shift from 1:1 stoichiometry is related to the direction of the titrations. It was observed that it took more titrant (second added polymer) to get to the endpoint. The shift from 1:1 stoichiometry with increasing conductivity could be due to the following reasons: (1) polyelectrolytes have less ability to adsorb onto the surface of streaming current probe when large amounts of low molecular mass salt ions are present; (2) the incomplete pairing of polyelectrolyte charged groups.

This dissertation presented the experiments that provided possible explanations of the observations about the shift of polyelectrolyte complex stoichiometry. The

results from contact angle measurements showed that the difference in contact angle between polymer treated and un-treated PTFE tapes was decreased with increasing conductivities. Additionally, the adsorption test was carried out with chromo-poly-DADMAC (red color) onto PTFE powder. No color was seen on PTFE powders after exposure to a chromo-poly-DADMAC solution having a NaCl concentration of 1%, whereas there was a red appearance after being treated with a similar solution with a low hardness. The adsorption tests related to streaming current devices also showed that increasing conductivity could reverse a positive initial reading to negative eventually. Since it is possible to use PTFE powders and tapes to simulate the probe surface of SCD, all of the experiments above indicated a decreasing ability of polyelectrolytes to adsorb onto PTFE surfaces with increasing salt concentration.

With respect to the mechanism of incomplete pairing, two theoretical models were proposed. One was a segment entrapment model (Figure 4.2), in which incomplete pairing occurred in the core area of a PEC. The other was a surface excess model (Figure 4.3), in which the incomplete pairing happened at surfaces of PECs. Lack of concentration-dependency at high conductivity appeared to be inconsistent with the segment-entrapment model in Figure 4.2. Turbidity values were dramatically increased at the charge equivalent point, and stayed high even after the equivalent point. This indicated that it was possible that there were unpaired groups on the surfaces of PECs to keep them from further aggregating. At the same time electrophoretic mobility tests showed that it took slightly more titrant to reach the endpoint in the case of the SCD method than that using the

zeta potential method. This indicated that more second added polyelectrolytes were needed to reverse the reading of a SCD. In general most of the results favor the “surface excess” model (Figure 4.3).

This study has also demonstrated the “interference” of aluminum ions with respect to the stoichiometry of titrations between poly-DADMAC and PVSK, even when their concentration is very low compared to the concentration of other monomeric and divalent ions studied in Chapters 3 and 4. When titrations only involve PVSK and aluminum ions, the stoichiometry is related to the direction of titrations, even at the same pH. However, in cases where the concentrations of aluminum ions of the final solution are similar, the stoichiometry is fairly close from both directions. When such factors as pH and the degree of charge neutralization of aluminum ions are constant, the stoichiometry can be determined. The highest titratable charges (PVSK/Al) occur at a similar ratio of OH to Al from 0.5 to 2.0 despite of the concentration of aluminum chloride sample. However, these highest titratable charges occur at different pH values with different aluminum chloride concentrations. All the values of the highest titratable charges are about 0.5, which is fairly close to the theoretical value of $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$, if it is assumed that Al_{13} is the only species present in the solution. Further results from zeta potential and turbidity tests also indicated the presence of aluminum polynuclear species.

Chapter 7

Proposed Future Research

This dissertation focused on various factors affecting the formation of polyelectrolyte complex (PEC), including the interaction of polyelectrolytes with aluminum ions. Some unique findings of the present study appear to be prime areas of future research. There are both practical and theoretical aspects that are worth of further investigation.

Practical Aspects:

Many of the results from present work have potential to be applied in practical situations, such as analysis or control of industrial processes that involve polyelectrolyte interactions. However, the aqueous environments in the common practice of several industries will be more complicated in terms of the presence of varieties of inorganic ions and polymeric materials, when compared to the conditions considered in this study. The present work concentrated mainly on pair-wise interactions between polyelectrolyte and ions or polyelectrolytes in the presence of a single kind of interference. It is not certain to what extent the current results can be directly applied in such complicated environments. It would be logical to continue the research on the following aspects to enhance potential for the practical application of current works.

This study considered mainly the separate effects of Ca^{2+} , Cl^- , Na^+ , and aluminum ions on polyelectrolyte charge interactions and titrations.

Combinations of ions of different valence were generally neglected. Aluminum ion itself can be considered as one of the “titratable samples” under a certain range of pH and degree of neutralizations. However, the stoichiometry of titration, in which the combination of aluminum ions with other salt ions is used as sample, may be different.

Additionally in the parts of this study that dealt with aluminum ions only the stoichiometry of Al^{3+} itself and PVSK were studied. The combination of aluminum ions and other polyelectrolytes (both cationic and anionic, even nonionic) as a sample at a given condition (with and without monomeric and divalent ions presence, such as Ca^{2+} , Cl^- , Na^+ , SO_4^{2-}) is worth further investigation. Although the situation will be much more complicated, it is common in papermaking processes.

Some other future work may include determining the dependency of the deviations from 1:1 stoichiometry on molecular masses of the anionic standard titrant (PVSK) and the speed of addition during the titration. If it is possible that polyelectrolytes can rearrange themselves during the formation of a PEC; then the titration speed may have some influence on the stoichiometry of the PEC.

Another important aspect is to study the interaction between weakly charged polycations and polyanions, and the effect of monomeric and divalent or aluminum ions on the interactions of these polymers.

The interaction of aluminum ions and PVSK only was studied (Appendix D) in the low pH range (0.5-3.5). A study of this interaction over a full pH range would be interesting. A different aluminum PVSK coagulation behavior in terms of turbidity was found below and above pH 2 in acid conditions. More study is needed to understand this difference.

Theoretical Aspects:

One of the very big challenges with respect to the study of polyelectrolyte interactions is how to analyze the composition and structure of formed PECs. Some of the current results provide a reason to suspect that free ions are possibly present within the core areas of polyelectrolyte complexes. However, in this study there was no direct evidence to prove that. The complexation structure of a PEC is very important for their practical application, such as the adsorption ability of a polymer onto a surface. Some surface analysis or elemental analysis methods, such as SEM, X-ray, or fluorescent probes, could be used to find evidence related to pairing or non-pairing of ionic groups within the PEC.

A further experiment derived from the turbidity test is to examine excess polyelectrolytes in the supernatants after removal of PEC aggregates. Chromo-poly-DADMAC may be used in this test to analyze the composition of the supernatant. Similarly, it is also possible to measure the weight of aggregates that are generated during the turbidity test to see the composition of the aggregates and to be able to evaluate the completeness of this reaction.

Regarding the two ideal models discussed in Chapter 4, there is another possibility, that is, the combinations of these two models. For example, at the very beginning of the titration, a segment entrapment phenomenon may be the more accurate description of what is happening, and then as titration goes on, the surface excess model may gradually take over and become dominant. Further study can also examine this possibility.

Another big challenge is to analyze which aluminum ion species actually exist at the concentrations of the titration carried out between aluminum chloride and PVSK. ^{27}Al NMR is a promising technique to do that.

Appendix

The contents of this section are some detail results and discussions of experiments that were not included in the chapters that were intended for publication due to the limitation of space. However, these data could be useful to the extending research of current work.

A. Effect of Charge Density of Anionic Polymers on Endpoint Shift

Two important characteristics of a polyelectrolyte used in the papermaking process are charge density and molecular mass. In order to test the effect of those two factors of polyelectrolytes on endpoint shift, a series of anionic polymers was selected, as listed in Table 3.1. First factor considered was the molecular mass of anionic polyelectrolytes.

Effect of Molecular Mass of Anionic Polymer on Titration Endpoint.

The anionic polyelectrolytes used in this study were carboxyl-methyl-cellulose (CMC). The number seven shown in Figures 8.1.1-8.1.3 refers to the degree of substitutions are about 0.7, and L, M, H refer to low, medium, and high molecular mass. In each experiment the concentrations of anionic polymers were calibrated with standard poly-DADMAC, which was provided by Ondeo Nalco Chemicals, in deionized water, and used as samples to be titrated. The results are listed in Figures 8.1.1-3.

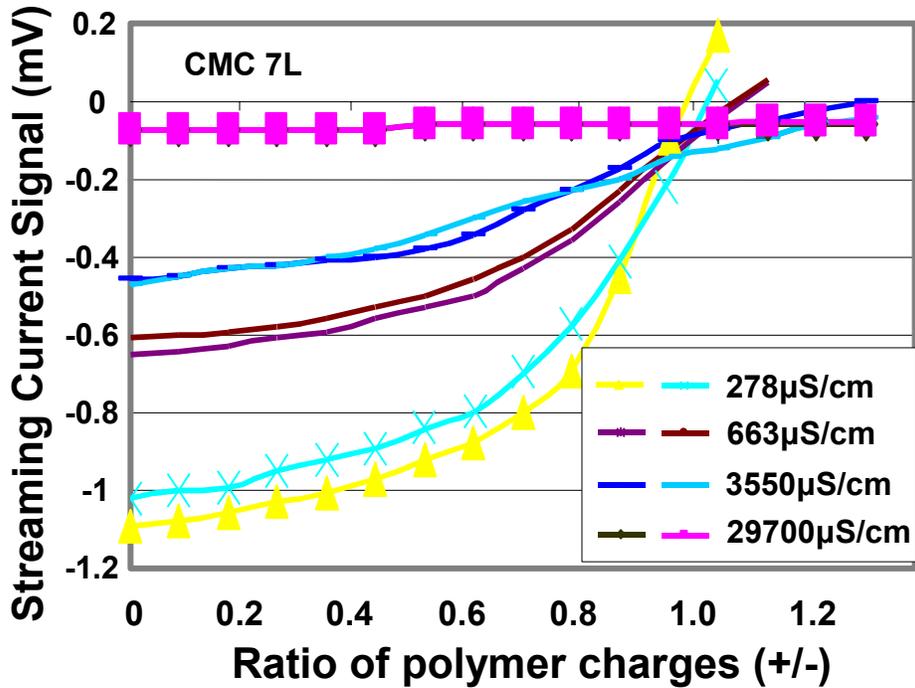


Figure 8.1.1: Effect of NaCl concentration on titration of CMC 7L with poly-DADMAC.

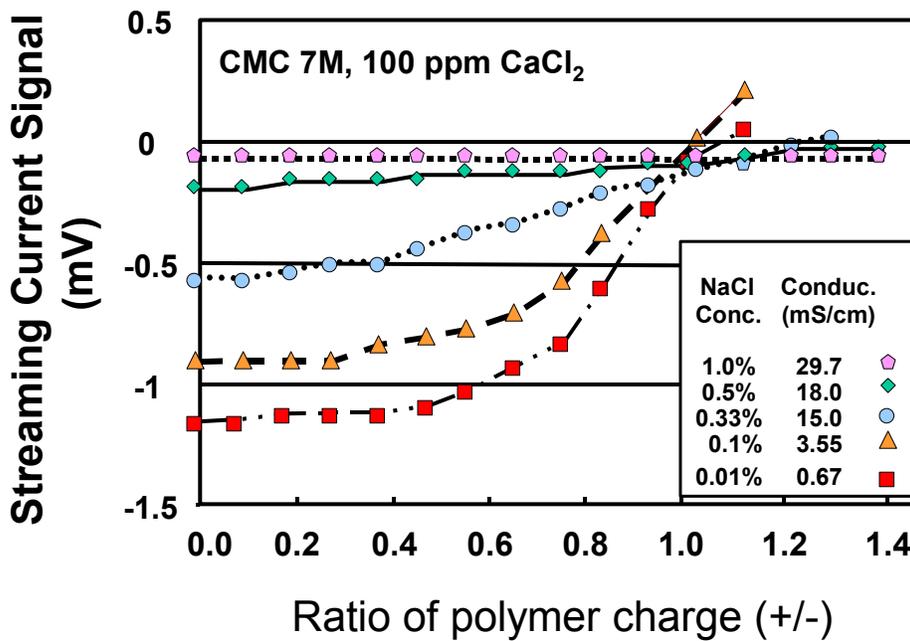


Figure 8.1.2: Effect of NaCl concentration on titration of CMC 7L with poly-DADMAC.

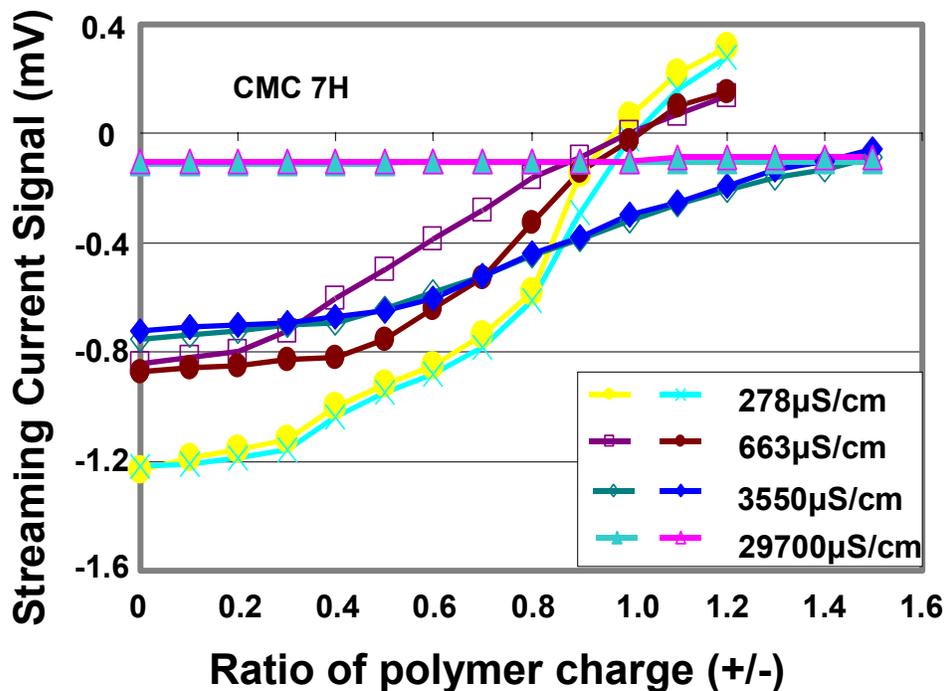


Figure 8.1.3: Effect of NaCl concentration of titration of CMC 7H with poly-DADMAC.

As shown in all three figures, the characteristic shape of titration curves is consistent with a rapid interaction between the titrant molecules and PVSK molecules in solutions. However, all three CMCs showed some degree of shift in titration endpoint, no matter how large was the CMC molecule. The endpoint shift pattern between low and medium molecular mass CMC was very similar. The salt level had a bigger effect on high molecular mass CMC than the other two, especially at high conductivities.

In general, there was no significant difference between the three different CMCs with respect to the trend of titration endpoint shifting. Increasing conductivity shifts the titration endpoint for all three CMC samples.

Effect of Molecular Weight of Cationic Polymer on Titration Endpoint.

In this section the investigation was carried out by varying the molecular mass of cationic polyelectrolytes.

The cationic polyelectrolyte was poly-DADMAC with 100-200 kilo Dalton to 1.9 million Dalton, and PVSK (molecular weight is 170k) with strength around 0.001 N used as anionic polyelectrolyte. The titrations were carried out at various inorganic salt levels.

As shown in Figures 3.7, 8.1.4, and 8.1.5 there were no significant differences between the shifts of titration endpoints at the same conductivities. Figure 3.7 showed results from an experiment of the same type with 400-500 kilo Dalton poly-DADMAC as titrant. A summary of the endpoints was listed in Table 8.1.1. However, the lower molecular mass poly-DADMAC had a longer flat portion at the beginning of the titration, and the drop in magnitude of the potential output occurred more sharply. One probability is that the molecular length of the poly-DADMAC was quite similar to that of the PVSK (the DP of the PVSK was around 1056 and that of low MW poly-DADMAC was about 1000). This may have made it easier for the charged groups on the cationic polymer to react completely with those on the anionic polymer to form a neutral complex.

Table 8.1.1: Effects of poly-cation molecular weight and NaCl on the endpoints of streaming current titrations.

Aqueous Electrolyte Conditions					
CaCl ₂ (ppm):		100	100	100	100
NaCl (ppm):		0	100	1000	10,000
Conductivity (mS/cm):		0.277	0.667	3.55	29.7
Cationic Polymer	MW (K Dalton)	PVSK Required to Achieve Zero Signal (Compared to tests in deionized water)			
DADMAC	400-500	0.99	1.04	1.14	2.11
DADMAC	100-200	1.01	0.99	1.07	2.25
DADMAC	1900	1.00	1.01	1.07	1.90

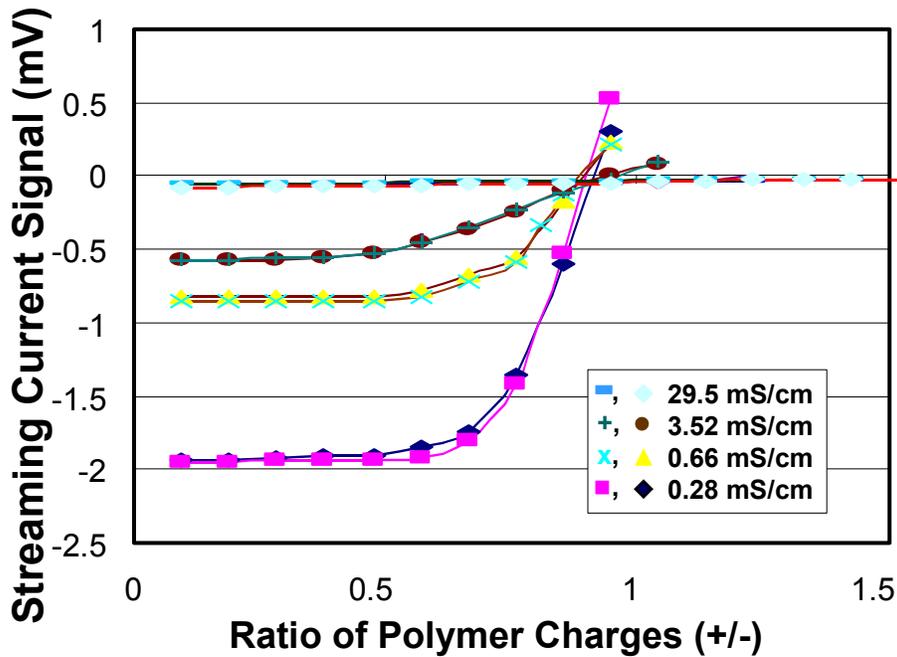


Figure 8.1.4: Charge titration curves with 100-200k DADMAC as titrant.

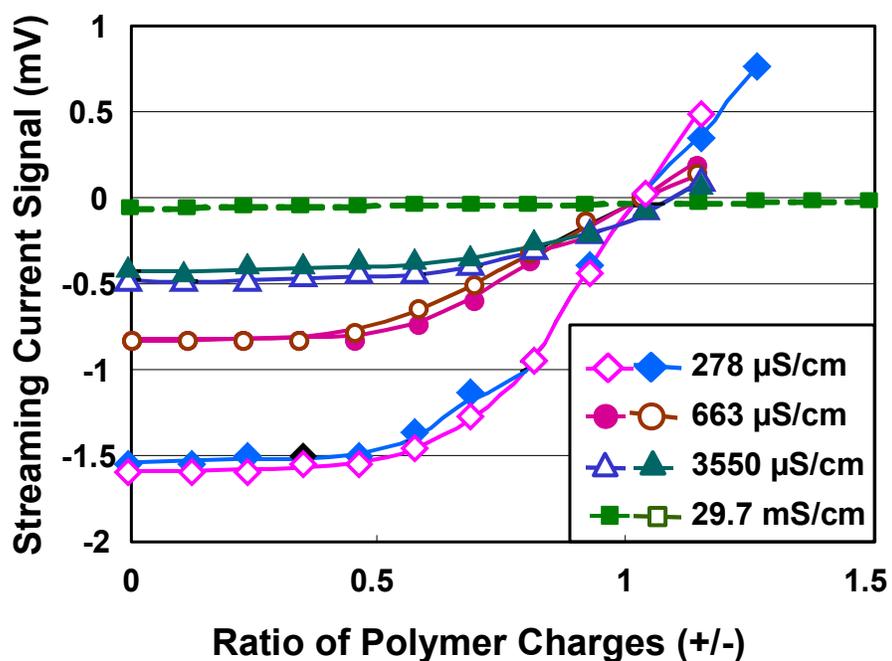


Figure 8.1.5: Charge titration curves with 1.9M DADMAC as titrant.

Effect of Charge Density of Anionic Polymer on Titration Endpoint.

For easy composition, the rest of the titration curves corresponding to the results listed in Table 3.2 are shown in Figures. 8.1.6-8.

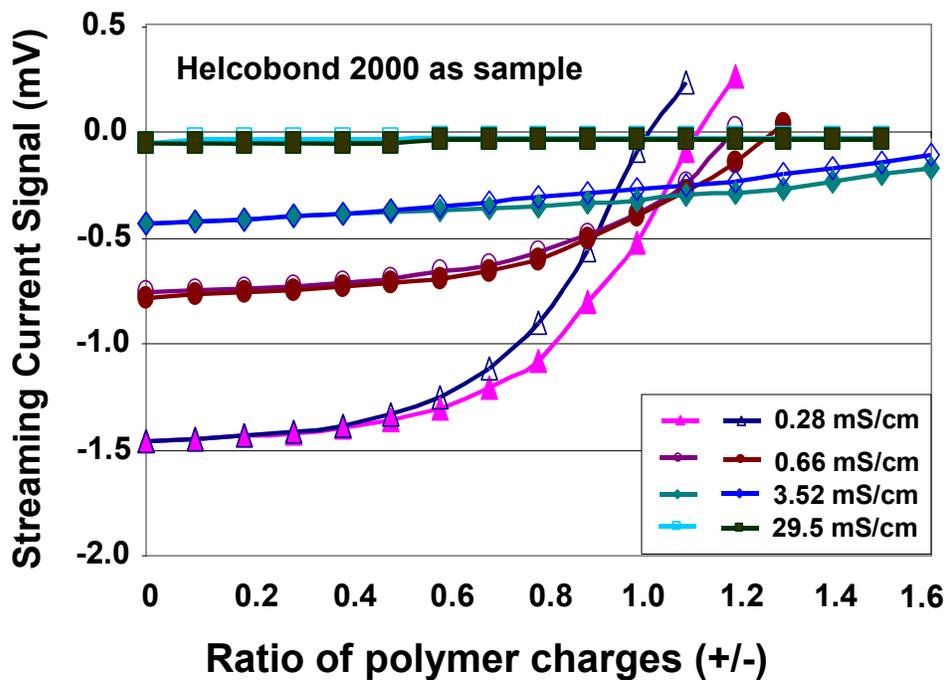


Figure 8.1.6: Charge titration with polyacrylamide (Hercobond® 2000) as sample.

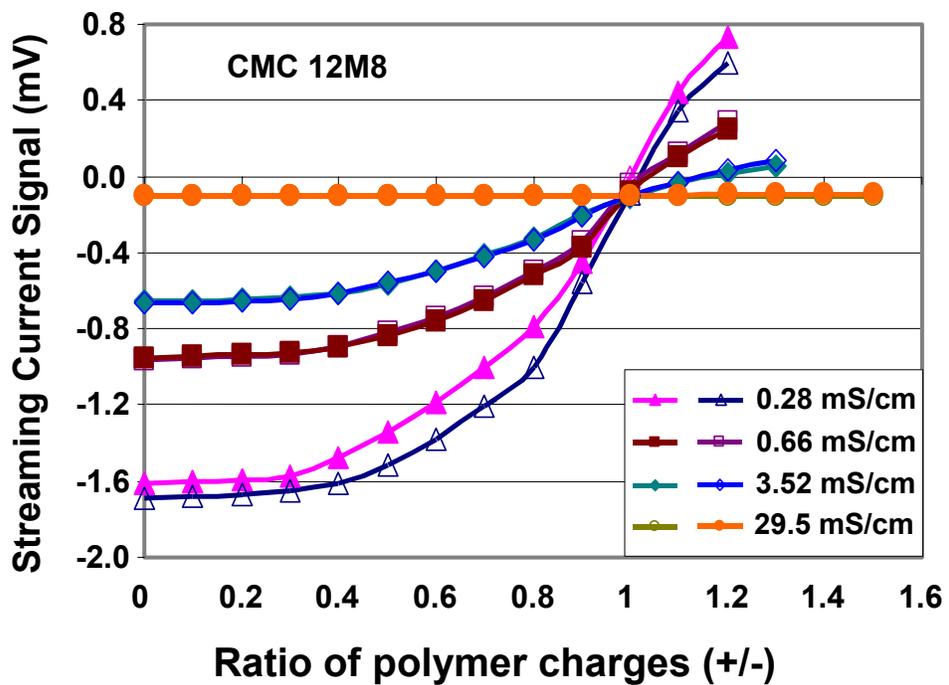


Figure 8.1.7: Charge titration with CMC 12M8 as sample.

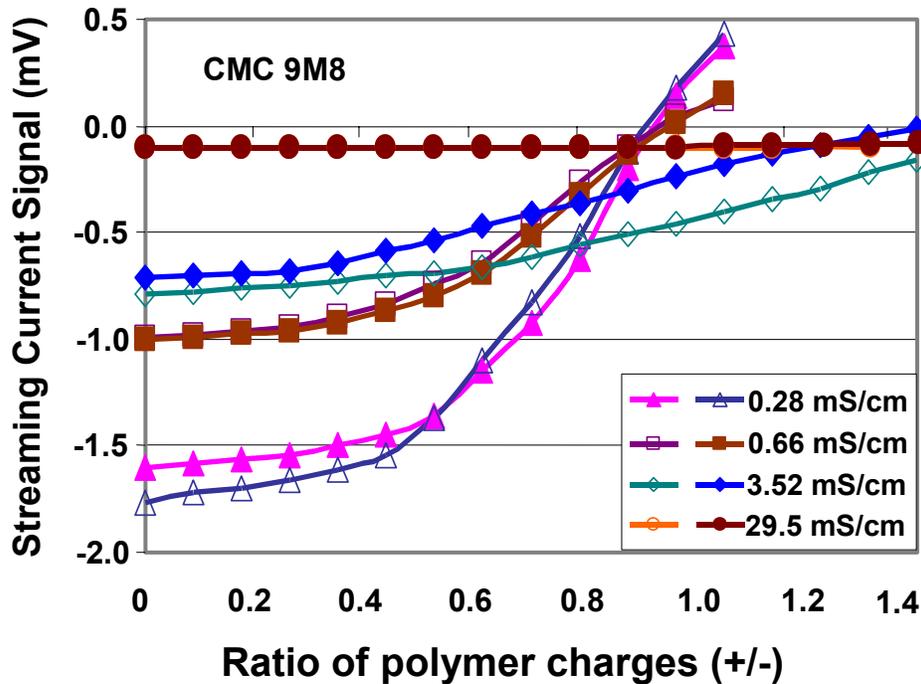


Figure 8.1.8: Charge titration with CMC 9M8 as sample.

B. Effect of Molecular Mass of Poly-DADMAC on Turbidity Test

Results shown in Figures. 4.14-17 are from experiments using 400-500 kilo Dalton poly-DADMAC either as the titrant or as the sample. For a more complete study, an investigation was carried out to see if changing the molecular mass of poly-DADMAC would affect the phenomena related to turbidity titrations, which was discussed earlier in Chapter 4.

Once again a tentative explanation for the results shown in Figures. 4.14-17 is that cationic and anionic polymers are forming polyelectrolyte complexes. When the titration approaches its neutral point, the PECs start collapsing and coagulating together, forming larger-size aggregates. In the deionized water, this PEC aggregation may be very sensitive to the extra charge. A small amount of

extra charge can restablize PECs and prevent them from continuing to “grow”. High salt level reduces this sensitivity. This turbidity-raising pattern was observed similarly when the titration started from either side.

Two more poly-DADMACs, one a very low molecular mass poly-DADMAC (MW=15k) and the other a high-mass poly-DADMAC (Alcofix® 109 from CIBA), were used in this study. Aliquots of 20ml solutions with various conductivities were used as the testing background. The salt levels, conductivities and experimental procedure followed the description provided in the experimental section in Chapter 4.

The results are shown in Figures. 8.2.1-8. The information pertaining to the cationic polymers is listed in Table 4.2. In cases where PVSK was added first, the basic patterns of turbidity increases of both poly-DADMACs were very similar to those of the poly-DADMAC with average molecular masses in the range of 400 to 500 kg/mole.

At lower conductivities the solutions became turbid as the titration approached the “neutral” point. As even more poly-DADMAC was added, the turbidities of these solutions stayed high, whereas, in the case of the highest conductivity, the turbidity dropped with increasing amount of poly-DADMAC above the equivalence point.

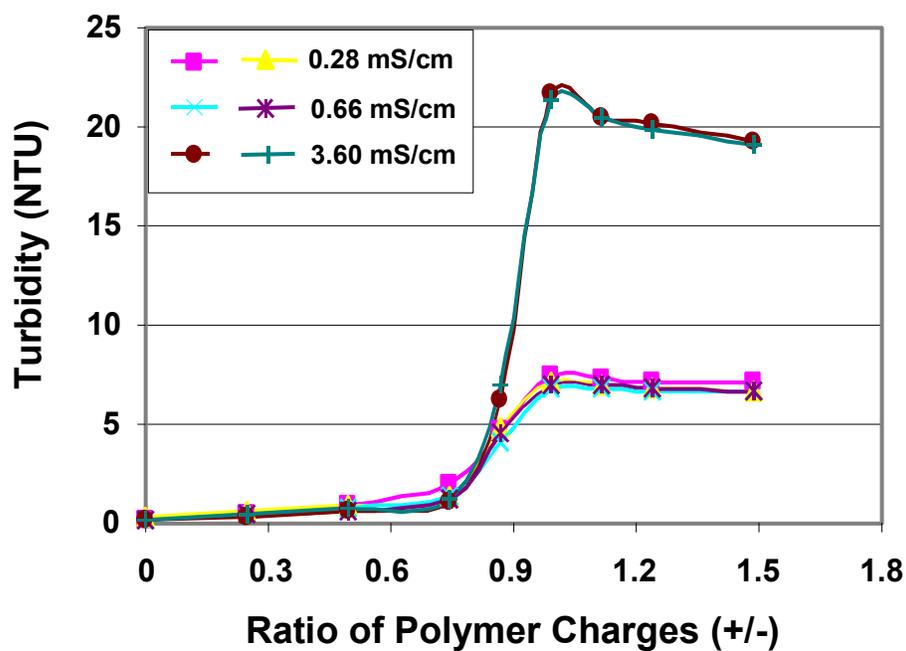


Figure 8.2.1: Results of turbidity tests with DADMAC (Alcofix® 109) serving as sample at lower conductivities.

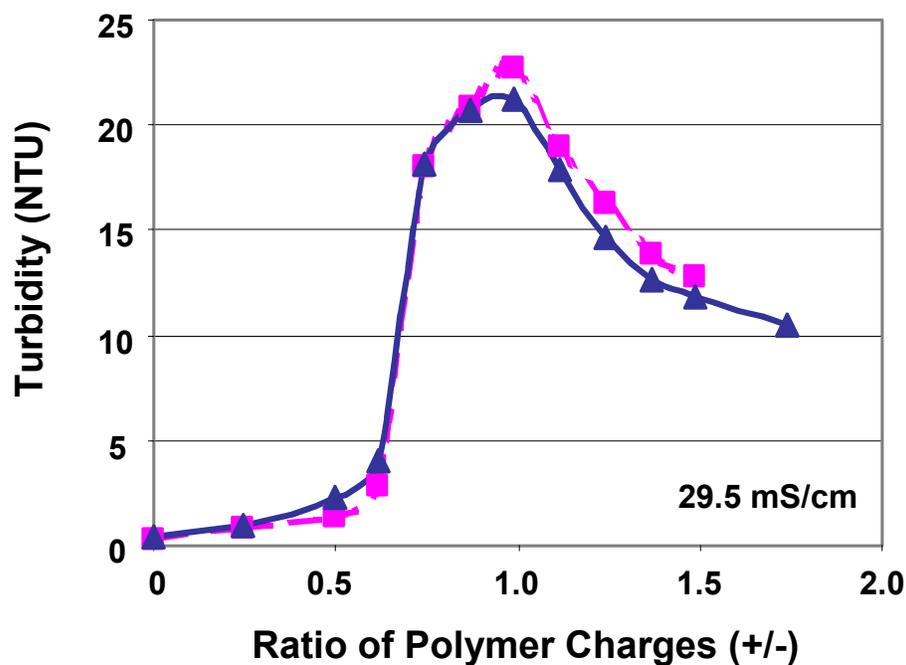


Figure 8.2.2: The result of the turbidity test with poly-DADMAC (Alcofix® 109) serving as titrant at highest conductivities.

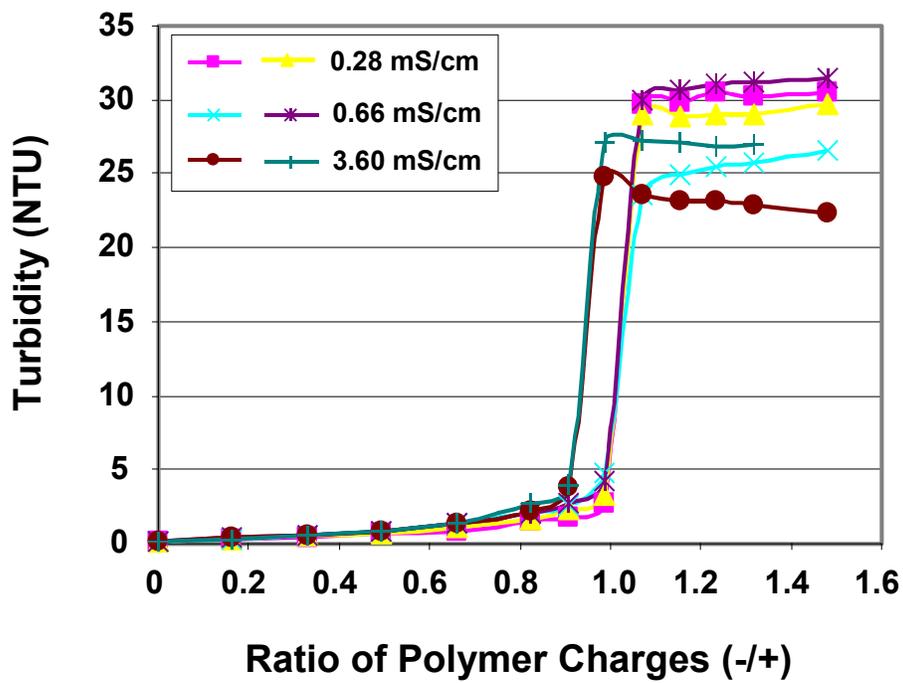


Figure 8.2.3: The result of the turbidity test with poly-DADMAC (Alcofix® 109) serving as sample at low to medium conductivities.

In the case of DADMAC added first, Alcofix® 109 had a similar titration curve to poly-DADMAC (400-500k).

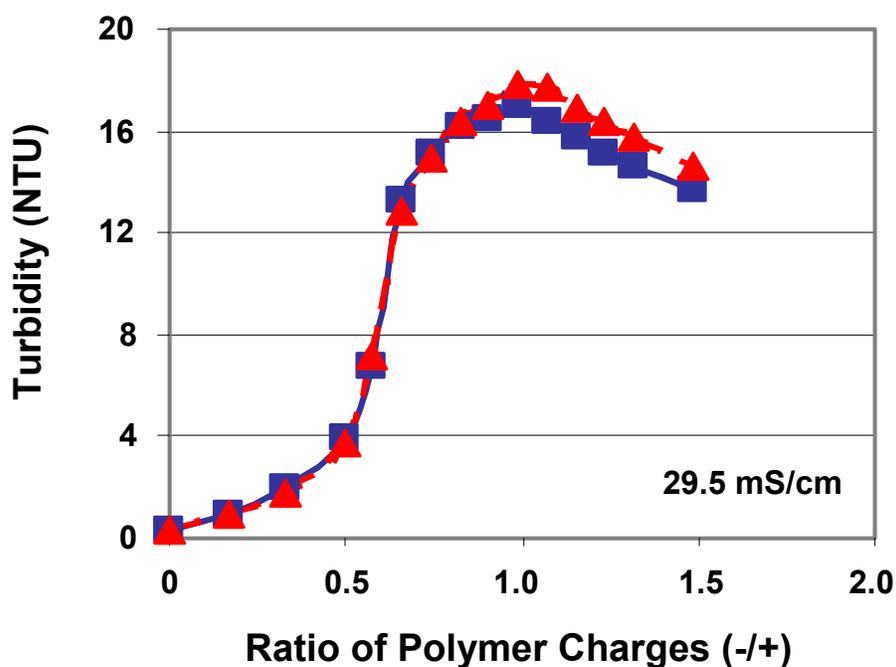


Figure 8.2.4: The result of the turbidity test with poly-DADMAC (Alcofix® 109) serving as sample at highest conductivities.

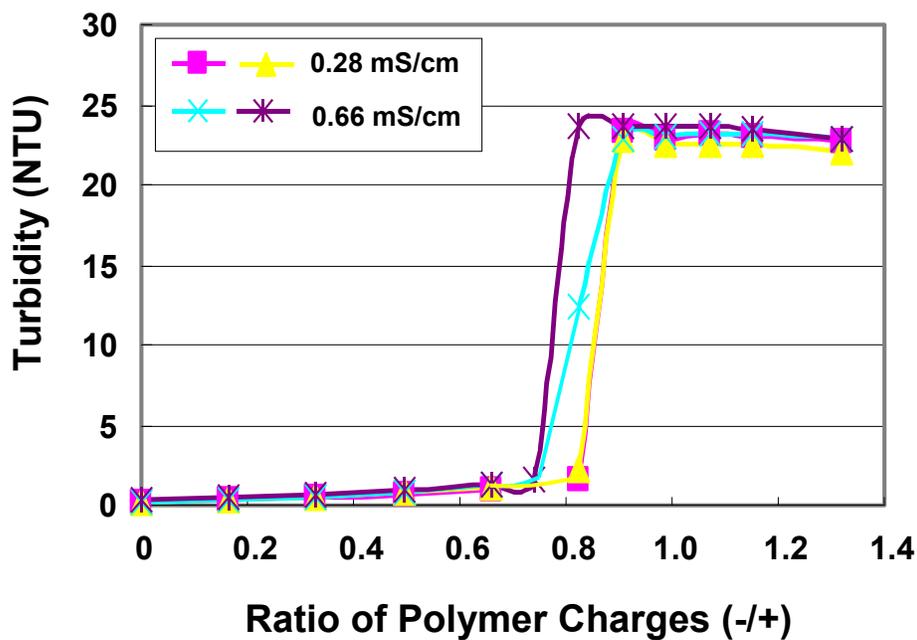


Figure 8.2.5: The result of the turbidity test with poly-DADMAC (MW=15k) serving as sample at low conductivities.

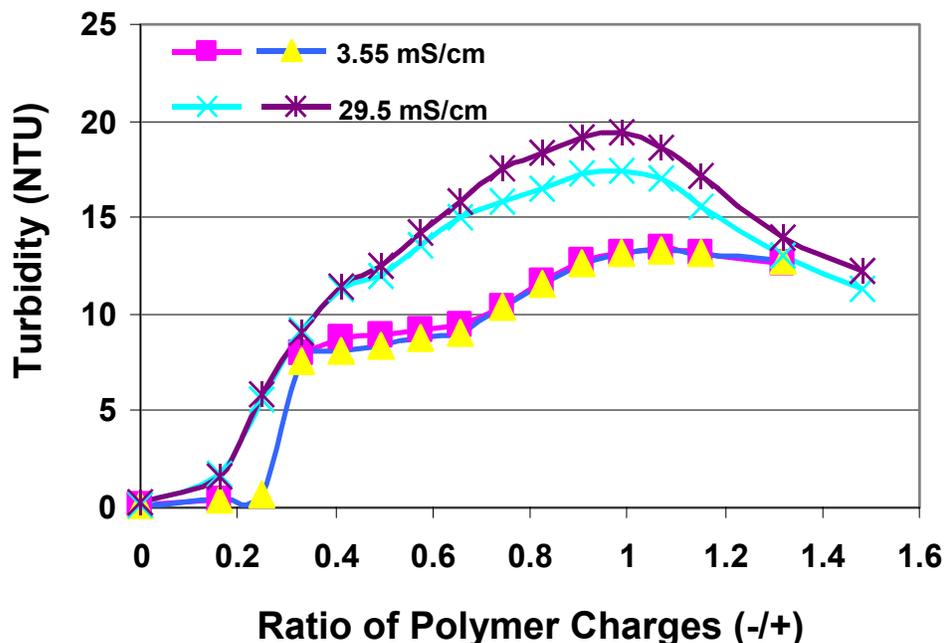


Figure 8.2.6: The result of the turbidity test with poly-DADMAC (MW=15k) serving as sample at higher conductivities.

The only difference between low molecular mass poly-DADMAC and other poly-DADMACs in term of the shape of titration curve is shown in Figure 8.2.6 above. The titration curve at a conductivity of 3550 $\mu\text{S}/\text{cm}$ in the case of DADMAC (MW=15k) had a sudden rise at a titrant vs. sample ratio of 0.3. Though there is not sufficient experimental evidence to fully explain this observation, the following hypothetical mechanism might be considered: The small rise might be because the interaction proceeds by a patch mechanism. The molecular mass of poly-DADMAC is very low in this case, and the length of the molecules is relatively short. Therefore, they are more successful in achieving alignment with the PVSK chain (have a better alignment with PVSK chain) and have a better opportunity to form a zipper-like partially charged complex. However, the size of the PECs is

expected to be smaller than those formed by polyelectrolytes of higher molecular weight. PVSK is still in the minority, so the excess charges on the complex prevent the continued growth of the PECs. For other PECs' formation in the present work, PVSK was the smaller molecule of the two.

When the titration direction was changed (in Figures 8.2.7 and 8.2.8, this phenomenon was no longer apparent. However, at a conductivity of 3550 $\mu\text{S}/\text{cm}$, the turbidity decreased significantly after the charge equivalence point, which is similar to what happened at the highest conductivity. This could indicate that the complex formed by low molecular mass poly-DADMAC was more sensitive to the increasing conductivities.

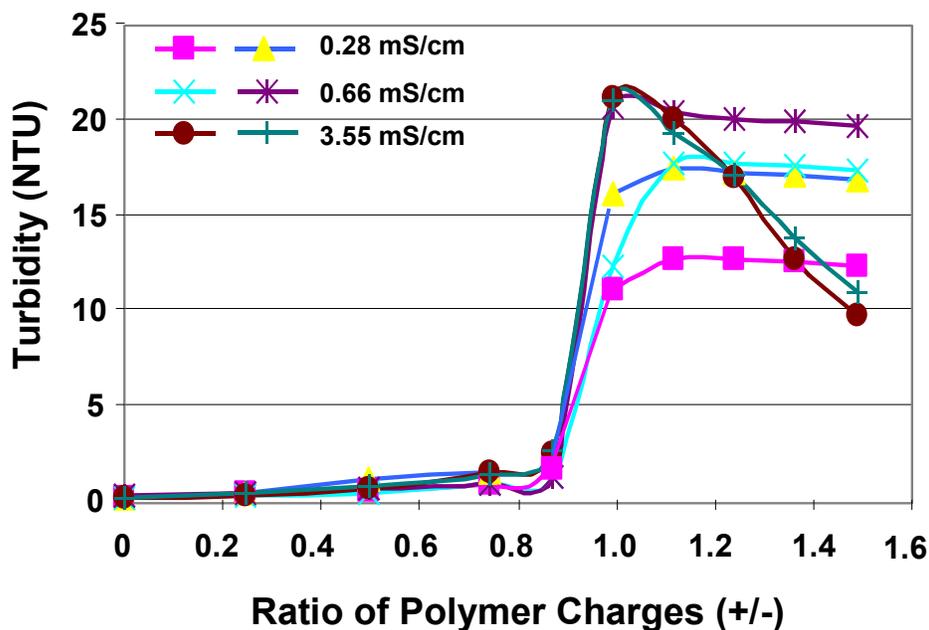


Figure 8.2.7: The result of the turbidity test with poly-DADMAC (MW=15k) serving as titrant at low to medium conductivities.

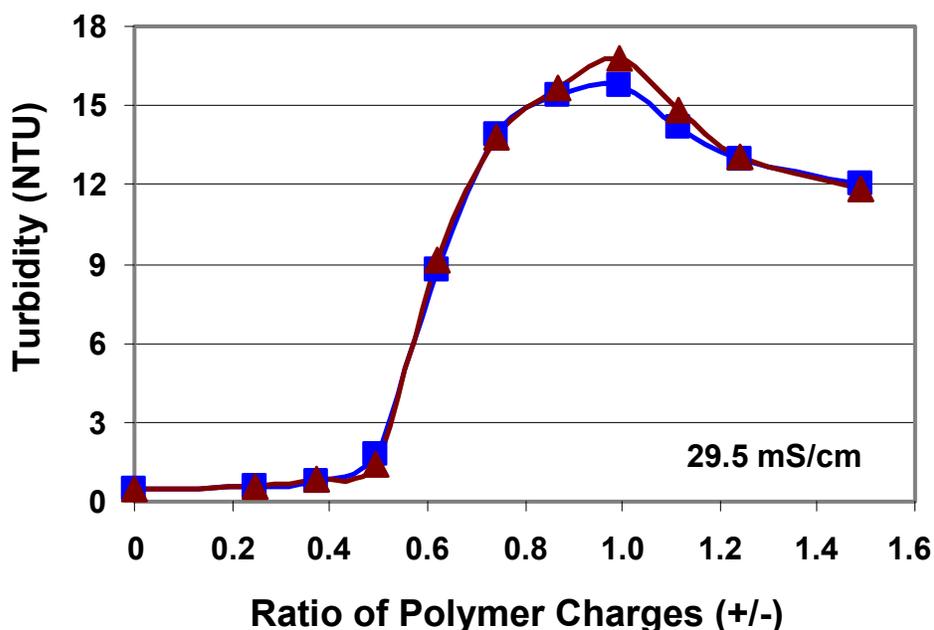


Figure 8.2.8: The result of the turbidity test with poly-DADMAC (MW=15k) serving as titrant at higher conductivities.

The turbidity drop after the neutral point at high conductivities could be due to either breakage of the PEC or the growth and settling of the PEC. The following further experiment was carried out to test these two possibilities.

In order to further examine the polyelectrolytes complexation, the turbidities were measured in different time periods. In each of these experiments 1.0 ml of 0.001 N DADMAC (MW=15k) was added first, then each of the samples was titrated by PVSK until reaching the desired ratio of cationic to anionic charges. The results are listed in Table 8.2.1 and Table 8.2.2.

The results in Table 8.2.1 show that the only one case that did not have a turbidity drop was the one that had not reached the neutral point. This is probably because the PECs start growing but they still remain charged.

Therefore, the extra charge can stabilize the PECs. However, in Table 8.2.2 the only turbidity drop is near the equivalence point. One possible explanation is that at the higher conductivity, PECs is not stable after the equivalence point. The turbidity drop could be due to the redispersal of the PECs.

Table 8.2.1: The turbidities of various samples in 100ppm CaCl₂ + 1%NaCl at different times.

Sample	+/-	1 min	30 min	5 hrs
1	1/0.330	6.33	9.67	9.36
2	1/0.906	17.2	9.70	6.65
3	1/0.989	17.1	10.16	7.24
4	1/1.071	16.1	10.28	7.26
5	1/1.153	13.4	8.98	6.22

Table 8.2.2: The turbidities of various samples in 100ppm CaCl₂ at different time.

Sample	+/-	1 min	30 min	5hrs
1	1/0.906	5.21	14.1	6.51
2	1/0.989	15.0	25.3	18.7
3	1/1.071	19.3	19.4	19.4
4	1/1.153	19.5	19.1	19.2

C. Adsorption Test of Polyelectrolytes onto PTFE

Contact angle measurement, as discussed in Chapter 4 is one of the indirect tests of polyelectrolytes adsorption onto PTFE. Another test related to

polyelectrolytes adsorption onto plastic surface of streaming current device is directly measuring the signal during the addition of polyelectrolytes. In this experiment standard titrant PVSK or poly-DADMAC was gradually added to the streaming current apparatus, and the values of signals from streaming current were recorded. The results are shown in Figure 8.3.1.

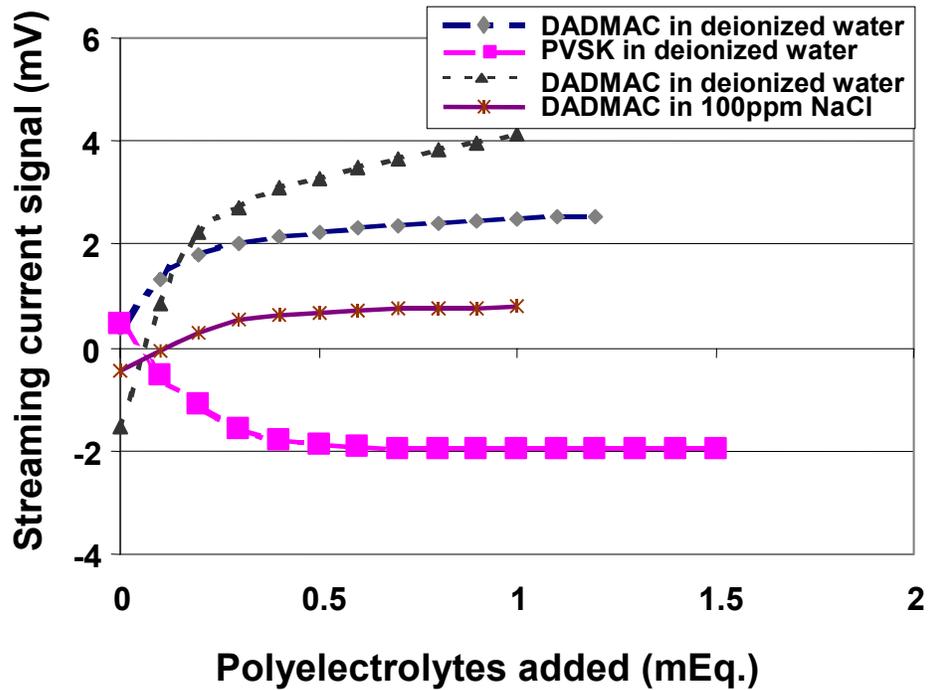


Figure 8.3.1: Adsorption of polyelectrolytes on SC probe surface.

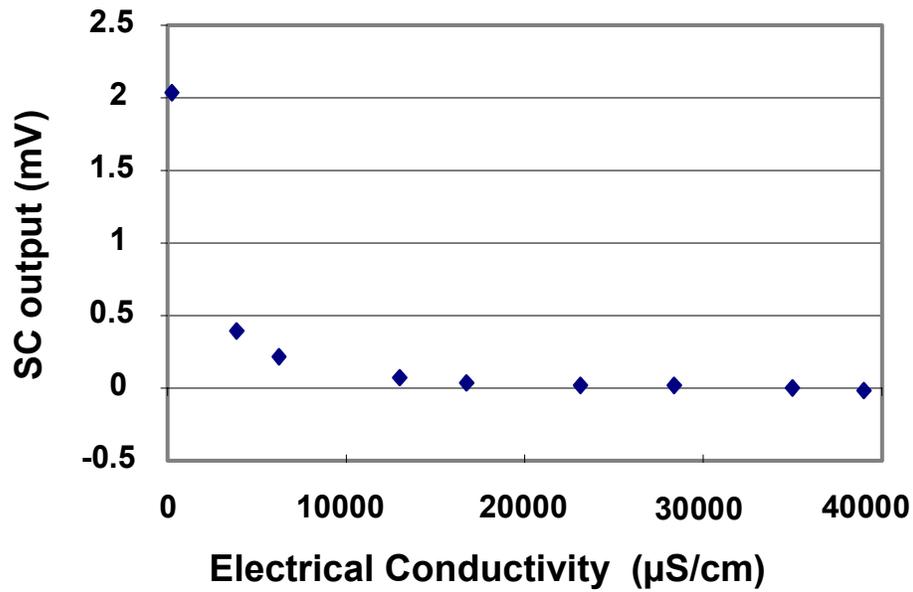


Figure 8.3.2: The effect of ionic strength on streaming current output.

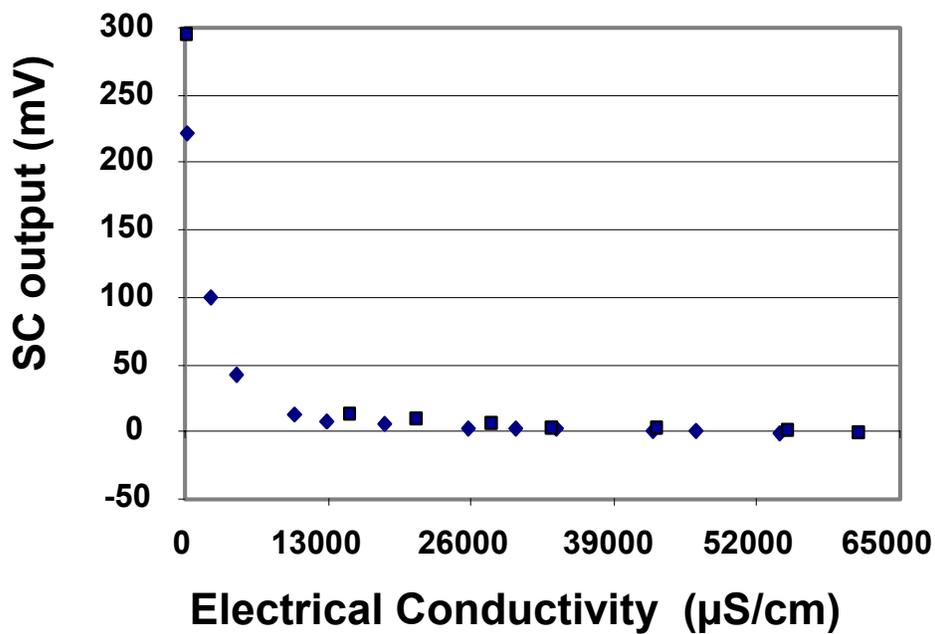


Figure 8.3.3: The effect of ionic strength on streaming current output. (alternative SC device).

In this experiment only one polyelectrolyte was added, and there was no other treatment. All the curves in Figure 8.3.1 show the relationship between the amount of polyelectrolytes added and the streaming current output. The curves have common character, which is that at the beginning the output changes more rapidly, then approaches a relatively steady state. The point when they reach the steady state was pretty close for both polyelectrolytes in both conductivity conditions. This is probably due to polymer adsorption reaching a maximum. In other words the surfaces of SC probe were saturated with polymers when the slope of the curves changed.

Another experiment which may give us some hints about the effect of ionic strength on the adsorption of polyelectrolytes onto the probe surface was that the cationic polymer solution was added to the streaming current devices at low conductivities, and then salt such as NaCl was gradually added. The results were shown in following two figures (Figures 8.3.2 and 8.3.3).

As expected, the SC readings decreased as the conductivity increased. One possible explanation may involve the compression of the electrical double layers of the surfaces of a SC detector, and then lower amounts of polyelectrolytes were located within these electrical double layers. However, at extremely high conductivities, the SC output became negative. This could be an indication that the low molecular weight ions inhibited the adsorption of polyelectrolytes.

D. Interaction between Aluminum and PVSK

In order to further investigate the interaction between aluminum ions and potassium polyvinyl sulfate, a turbidity test was used to determine whether aluminum ions will cause any cross-linking between PVSK polymer chains. Aluminum chloride and PVSK solutions were adjusted to the desired pH value, and then they were mixed with certain ratios in test tubes to measure their turbidities. The results are shown in Table 8.4.1, and Figure 8.4.1 is the plot with the values from Table 8.4.1.

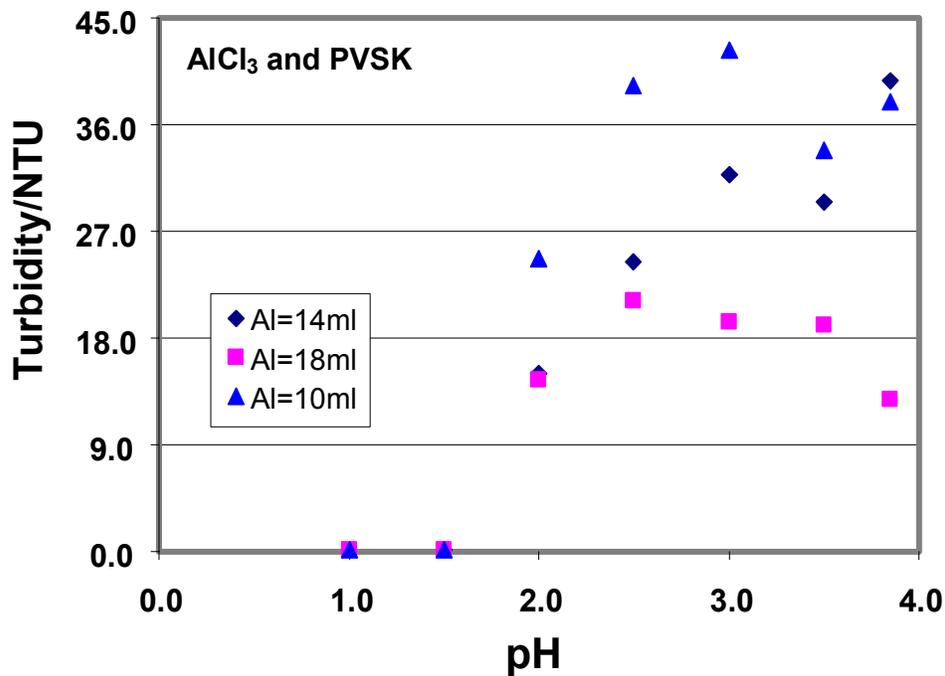


Figure 8.4.1 Turbidities of different pH of aluminum ions and PVSK combinations.

Table 8.4.1 Turbidities of aluminum chloride and PVSK mixture at different pH.

pH	Control (Turbidity)		Sample		
	PVSK	AlCl ₃	PVSK/ml	AlCl ₃ /ml	Turbidity
1	0.09	0.05	20	10	0.11
			10	18	0.10
1.5	0.10	0.04	14	14	0.08
			10	18	0.10
			18	10	0.09
2	0.08	0.07	14	14	15.0
			10	18	14.5
			18	10	24.7
2.5	0.09	0.06	14	14	24.4
			10	18	21.2
			18	10	39.3
3	0.06	0.04	14	14	31.8
			10	18	19.4
			18	10	42.3
3.5	0.08	0.05	14	14	29.4
			10	18	19.1
			18	10	33.8
3.85	0.10	0.04	14	14	39.7
Natural			10	18	12.8
			18	10	37.9

In Table 8.4.1, the controls were the turbidities of PVSK and AlCl_3 solution after they were adjusted to the desired pH and before being mixed each other. Figure 8.4.1 shows a clear trend. At very low pH values, between 1-2, there was no turbidity increase after mixing. At that pH range most references agree that aluminum ions are in the Al^{3+} form. There are two possible reasons for this behavior: one is that the trivalent aluminum ion does not have a very strong affinity to interact with PVSK, and therefore no coagulation has occurred; the other is that PVSK cannot remain negatively charged within such a low pH range. With increasing pH, the turbidity of mixed solutions was also increased regardless of the mixed ratios. In that pH range PVSK is known to carry negative charges [1]. This indicates that an aluminum ion has an interaction with PVSK. However there is no direct evidence shown which form of aluminum ion existed in that solution when that interaction was taking place. In this experiment only three aluminum to PVSK ratios were tested. In these three ratios the higher the PVSK/Al was, the higher the turbidities were. This could indicate that the ratio of PVSK/Al is more important in determining turbidities. Further study over a wider range of ratios of Al to PVSK is needed to understand this phenomenon.

References

1. Toei, K., and Kawada, K., "Investigation on Colloid Titration Reagents - (Fundamental Studies on Colloid Titration)," *Japan Analyst*, 21 (11): 1510, 1972.