

ABSTRACT

SEZAKI, TAKAO. Colloidal Behavior of Amphoteric Dry Strength Agents. (Under the direction of Dr. Martin A. Hubbe)

Dry strength additives are essential to produce paper that is strong enough to meet various usage requirements. Recently, amphoteric copolymers have been developed as more effective dry strength agents for addition during the papermaking process. To understand the mechanism of such polyampholytes, the fundamental colloidal behavior of amphoteric polyacrylamide dry strength additives was investigated. The present thesis includes potentiometric titrations, viscometric and turbidimetric measurements, charge analysis using microelectrophoresis and colloidal titration with a streaming current detector, and adsorption of amphoteric polyacrylamides onto bleached kraft hardwood fibers.

The potentiometric titration results for the polyampholytes were in agreement with the theoretical curves except in a range between pH 4 and 6. The charge analysis showed that the total charge of the amphoteric polyacrylamides depended on pH. The total net charge was reversed at the pH value termed the iso-electric point, where the polyampholytes have no net charge. The iso-electric points determined by the two measurements, microelectrophoresis and streaming current, coincided well, but not with the calculated values. Around the iso-electric point, the turbidity of the polyampholyte solution was maximized, while the viscosity was minimized. In this region of pH, addition of salt led to swelling of the polyampholyte chain conformation, which was an opposite effect from what is seen in simple polyelectrolytes (anti-polyelectrolyte effect). Namely, the turbidity was decreased and the viscosity was increased by addition of salt to the polyampholyte solution around the iso-electric point.

A colloidal titration procedure using a streaming current technique was found to be applicable at either pH 3 or 11 in order to determine the concentration of the polyampholytes. The required titration amount for zero charge was found to deviate from a 1:1 stoichiometric relationship, depending on the salt concentration. The adsorption of the amphoteric polyacrylamide dry strength additives onto bleached hardwood fibers was significantly affected by the pH and salt concentration. Also, it was slightly increased with time for adsorption. The stirring rate during adsorption was not an important factor for adsorption. It was found that the polyampholytes with no net charge were also adsorbed on negatively charged fibers. The maximum adsorption of the polyampholytes was achieved around the isoelectric point. This behavior is attributed to a sufficiently low charge density of the polyampholytes around the iso-electric point, which does not allow the polyampholyte chains to lie flat against the charged surfaces because of electrostatic attractions.

COLLOIDAL BEHAVIOR OF AMPHOTERIC DRY STRENGTH AGENTS

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BIOGRAPHY

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1. INTRODUCTION

In the modern papermaking process various kinds of chemicals are added to pulp slurry. Since they can improve the qualities of paper efficiently, they are almost indispensable to the papermaking industry. Dry strength agents, which can increase the dry strength of paper, comprise an important class of these chemicals [Scott, 1996].

Polysaccharides (starches, guar gums, and chitosans) or synthetic polymers (polyacrylamides) are often used as dry strength agents [Reynolds, 1980]. These polymers are usually modified to cationic or amphoteric forms so that they can interact with negatively charged fiber surfaces by attractive electrostatic forces. The mechanism of increasing dry strength is not well understood, but these polymers are believed to increase the area of fiber-to-fiber bonding [Linke, 1968] and/or reinforce the hydrogen bonding per unit area [Howard and Jowsey, 1989].

Cationic starches and cationic polyacrylamides (PAMs) are widely recognized as dry strength agents, and the former ones are the most used because of their economy [Roberts *et al.*, 1986]. For both starches [Yoshizawa *et al.*, 1998] and polyacrylamides [Tanaka *et al.*, 1976], it is often reported that amphoteric polymers are more effective in improving dry strength than conventional cationic ones.

The trend in the papermaking industry has been changing from the point of view of economy and environmental preservation. The basis weight of paper is getting lighter and the addition of fillers is increasing [Tanaka, 1994]. More paper is recycled and the white-water systems in most mills are getting more closed [Tanaka, 1994]. These changes are expected to result in decreases of the paper strength. On the other hand, the trend to faster paper production and high-speed printing requires higher qualities of paper that are strong enough to avoid breakage of the web. It is getting increasingly difficult to meet the quality demands [Tanaka, 1994].

Under such circumstances, more attention has been paid to development of amphoteric dry strength agents. However, the reason that amphoteric polymers have higher ability to increase strength is not clear, although they have been developed for practical use. In practice, dry strength agents are added to the pulp slurry. Most of the interactions between the polymers and fibers occur at this colloidal stage, and the interactions happening here have potential to govern the final properties of the product. Therefore, investigation and understanding of colloidal behavior of amphoteric dry strength agents is of great importance for further developments that will make it possible to cope with future demands on the environment aspects and paper qualities. In this thesis, the fundamentals on the colloidal behavior of amphoteric dry strength agents and the interaction between dry strength agents and cellulose fibers will be discussed. These results will be compared with recent theories of amphoteric polymers and the unique characteristics of amphoteric dry strength agents will be addressed.

2. LITERATURE REVIEW

2.1 General aspects of paper strength and dry strength additives

Most paper products are required have high enough dry strength to resist external stresses occurring in manufacturing processes and end use. The properties related to the dry strength in which people are most interested include tensile strength, tearing resistance, folding endurance, bending resistance, bursting strength, surface strength, internal bonding strength, and compression resistance [Scott, 1996]. Among these properties, some are important and others are not, depending on what the paper is used for. The tensile strength is one of the important properties for most grades, since the paper web is exposed to external forces in the plane of the sheet during the papermaking and printing processes. If the paper does not have high enough tensile strength, it will cause frequent web-breaks that result in considerable economic losses. There are several methods for increasing the tensile strength. These include increasing the degree of refining, applying a higher nip loading in wet pressing, using dry strength additives, and increasing the content of long fibers [Scott, 1996]. An increase of the degree of refining will affect many properties other than the tensile strength [Scott, 1996]. It will slow the drainage, decrease the opacity, brightness, and thickness, and increase the density. Because the refining condition is adjusted to obtain the optimum balance of these properties and the cost, it may be hard to change the refining condition without sacrificing the cost and other properties.

Wet pressing is used in the typical papermaking process to remove the excess water from the wet paper web. Applying high pressure can increase the tensile strength [Howard and Jowsey, 1989], but the pressure condition is usually determined to achieve both good runnability and water removal, and the increase of the tensile strength is considered as a secondary effect. Dry strength additives may cause some changes in other properties such as opacity decrease and poor

formation [Roberts *et al.*, 1986], but this could be the most practical way of increasing the tensile strength effectively and economically [Farley, 1986]. The choice of increasing the content of long fibers in order to enhance the tensile strength is sometimes limited due to economic reasons [Farley, 1986].

A theoretical model for tensile strength was proposed by Page. It was derived from mathematical premises with some assumptions. The equation is given by

$$\frac{1}{T} = \frac{9}{8Z} + \frac{12A\rho g}{bPL(R.B.A.)} \quad [1]$$

where, T is the tensile strength, Z is the zero-span tensile strength, A is the average fiber cross-sectional area, ρ is the density of the fibrous material, g is the acceleration due to gravity, b is the shear bond strength per unit bonded area, P is the perimeter of the fiber cross section, L is the fiber length, and $R.B.A.$ is the relative bonded area [Page, 1969]. The equation states that the tensile strength can be determined by two factors, individual fiber strength and fiber-fiber bond strength to break the paper. The validity of the equation was checked in his report by applying several sets of experimental data, and it was shown that the equation was well-fitted to them.

An addition of dry strength agents is expected to increase tensile strength by increasing the bond strength per unit of bonded area b and/or relative bonded area $R.B.A.$ in the Page equation. The other terms originating from the fiber characteristics (zero-span tensile strength, fiber cross-sectional area, fiber density, fiber perimeter, and fiber length) are not expected to be affected by dry strength additives. In this case, the Page equation could be simplified to

$$\frac{1}{T} = K_1 + \frac{K_2}{b (R.B.A.)} \quad K_1, K_2 : \text{Constants} \quad [2]$$

A plot of $1/T$ against $1/R.B.A.$ will give a straight line, and the bond strength per unit of bonded areas b for starched and non-starched fibers can be compared relative to one another by

calculating their slopes. According to Howard and Jowsey, an addition of cationic starch (0.5 % starch to unbeaten fine-free softwood fibers) did not change the R.B.A., which was calculated from the scattering coefficient measurement, but it increased the bond strength per unit of bonded area [Howard and Jowsey, 1989]. They concluded that the cationic starch increases the tensile strength by increasing the bond strength per unit bonded area b but not the relative bonded area $R.B.A.$ Yamauchi and Hatanaka also found that an improvement of the tensile strength by cationic PAM addition was mainly due to the increase in the bond strength per unit of bonded area [Yamauchi and Hatanaka, 2002]. As the amount of PAM added to fines-free hardwood kraft pulp increased, the relative bonded area also increased. However, this increase in the relative bonded area was too slight to explain the tensile strength development, compared with that achieved by long-time refining. Retulainen and Nieminen reported that an addition of cationic starch (1.2 %) increased the tensile strength without changing the light scattering coefficient for long kraft fibers containing kraft fines (10 %), whereas a decrease of the light scattering coefficient was observed for those containing TMP fines (10 %) [Retulainen and Nieminen, 1996]. Considering these experimental results with regard to strength improvement by dry strength additives, one can say that dry strength additives typically improve the paper strength due to increasing the bond strength per unit bonded area rather than by increasing the relative bonded area.

The enhancement of the bond strength per unit of bonded area can be due to the reinforcement of hydrogen bonding within the bonded area [Scott, 1996]. Cellulosic fibers used to produce papers consist largely of polysaccharides, which have abundant hydroxyl groups. The dry strength of paper is primarily attributed to a large density of hydrogen bonds that are formed between fibers via those hydroxyl groups. Meanwhile, commercially important dry strength additives are also

polymeric materials bearing functional groups that have the abilities to form the hydrogen bonds. Therefore, it is considered that those polymers can help to form extra hydrogen bonding between fibers by acting as mediators. For those pulps which contain a lot of fines, dry strength agents can make the paper consolidate by increasing the fines retention, which in turn increases the relative bonded area (while decreasing the scattering coefficient).

A polyampholyte is a copolymer that has both positively and negatively charged groups in the same chain. It has been shown in some reports and patents that amphoteric dry strength additives such as amphoteric starches and amphoteric polyacrylamides provide a better strength enhancement than conventional cationic additives [Tanaka *et al.*, 1976; Carr *et al.*, 1977; Ghosh, 1994; Glittenberg, 1993]. Tanaka *et al.* developed a new method (modified Hoffmann degradation) of synthesizing amphoteric PAMs, in which the content of the cationic group (primary amine) could be easily controlled [Tanaka *et al.*, 1976]. Using the amphoteric PAMs synthesized according to this method, they found that amphoteric PAMs improved the breaking length effectively compared to cationic PAMs and anionic PAMs when they were added to bleached kraft pulp (1.0 % PAM dosage) along with alum. The amount of cationic groups did not affect the tensile strength. The tensile strength was increased with increasing molecular weight of the PAM, but saturated at degree of polymerization of 1000. Carr *et al.* evaluated starch polyampholytes containing tertiary amine or quaternary ammonium groups as dry strength additives [Carr *et al.*, 1977]. The improvement of the dry strength by these polyampholytes was superior to that of the conventional cationic starches when they were added to unbleached kraft pulp. Glittenberg compared a cationic potato starch and a cationic corn starch in terms of their abilities to improve the dry strength [Glittenberg, 1993]. The results showed that the cationic potato starch, in which a number of anionic phosphate groups are naturally present, increased the

tensile strength more effectively. One of the reasons for this result could be due to the amphoteric characteristics of the potato starch.

2.2 Behavior of polyampholytes in solution

2.2.1 Conformation of a polyampholyte chain

Conformational study of polyampholytes in solution is an important subject to understand the behavior of amphoteric wet-end additives in a papermaking system. Theories related to polyampholyte properties have been developed for twenty years [Kudaibergenov, 2002], but there are still controversial aspects within this area of research. Depending on the characteristics of their charged groups, polyampholytes may be neutral, positive, or negative in net charge at a certain pH. The conformation of polyampholytes is highly affected by the net charge, since the electrostatic force can work as a strong repulsive or attractive force among the charged groups [Higgs and Joanny, 1991]. This electrostatic force can be screened by the presence of salt in solution. Namely, the ionic strength is also an important factor that is considered to affect the conformation of polyampholytes. In addition to these factors, here is another thing to be considered. Linear polyampholytes can be roughly classified under three categories based on the sequence of monomeric units (charge groups) along the chains; they are alternating, random, and block polyampholytes. The differences among these microstructures are also expected to affect the polyampholyte conformation, since one of the main driving forces that determines the conformation is how the charged groups interact within the chain. To sum up, the conformation of polyampholytes is dependent mainly on three conditions, net charge of polyampholytes, ionic strength of solution, and arrangement of charged groups [Higgs and Joanny, 1991]. From the

point of view of free energy, the size and shape of polyampholytes are determined in a balance of the following three potential factors:

- (1) Chain entropy tends to keep the polymer in a random, loosely coiled configuration that is consistent with Gaussian statistics.
- (2) Electrostatic attraction tends to collapse the chain into a globular shape, especially in cases where the net charge is near to zero.
- (3) Overall electrostatic repulsion tends to expand the chain.

The size and conformation settle at the point where the free energy contributed by these three potentials is minimized [Dobrynin and Rubinstein, 1997].

The distribution of charged groups is also an important parameter that has a strong influence on the properties of polyampholytes. A polyampholyte that possesses alternating negatively and positively charged groups tends to be soluble at the iso-electric point, which is the pH where the polymer has no overall net charge, whereas a polyampholyte that contains the same number of oppositely charged groups but randomly distributed along the chain tends to be insoluble [Joanny, 1994]. For a block-like distributed polyampholyte, aggregation tends to take place around the iso-electric point [Goloub *et al.*, 1999]. It is reported that such block-copolymers at the iso-electric point showed similar properties to the complexes between polycations and polyanions [Varoqui *et al.*, 1979]

The first detailed study about the conformation of polyampholytes was done by Edwards *et al.* [Edwards *et al.*, 1980]. It is well known that polyampholytes change their conformation from extended, random forms to collapsed microglobes depending on the nature of polyampholytes and solvent. Edwards *et al.* gave an equation that can predict whether the conformation expands or collapses. It was found that this transition depends on the iso-electric state of polyampholytes

in a theta solvent, where there is no interaction between the solvent and the polymer. The chain collapses if the following condition is met,

$$kT < \frac{e^2 a^2}{\sqrt{L_a l_k}} \quad [3]$$

where, e is the electron charge, a is the monomer length, k is the Boltzman constant, T is the absolute temperature, L_a is the contour end-to-end length of the polymer, and l_k is the Kuhn length that refers to the distance between charged monomers. According to the above equation, if the electrostatic attraction potential between any two charges on the polymer chain is larger than the thermal energy kT , then the conformation of polyampholytes will be collapsed.

Higgs and Joanny developed the Debye-Hückel theory for neutral or nearly neutral polyampholytes by taking into account the third virial term that works against the electrostatic attraction [Higgs and Joanny, 1991]. They neglected the configurational entropy, which Edwards *et al.* considered. This is because the third virial term is always larger than the entropy term, which comes from the confinement of the polymer chain in a globule smaller than its natural radius. According to their theory, a neutral, randomly distributed polyampholyte chain collapses due to the attractive electrostatic interactions. If the salt concentration is larger than the polymeric charge concentration in the collapsed globule, then the blob size is expanded and dependent on the salt concentration. This transitional salt concentration, at which the polyampholyte globule starts to expand, can be expressed using the Debye length κ_{\min}^{-1} . The Debye length is the length scale in which the electrostatic interaction is effective, and it is a function of salt concentration, valence, dielectric constant of media, and temperature. The polyampholyte coil is predicted to start expanding at the Debye length κ_{\min}^{-1}

$$\kappa_{\min} = \frac{l_B f}{a^2} \quad [4]$$

where, l_B is the Bjerrum length, f is the fraction of either positively or negatively charged group, and a is the bond length. The Bjerrum length l_B is defined by

$$l_B = \frac{e^2}{4\pi\epsilon kT} \quad [5]$$

where, e is the electron charge, ϵ is the dielectric constant of the media, k is the Boltzman constant, and T is the absolute temperature. The Bjerrum length is the length scale in which the electrostatic interaction between two electron charges in a media is equal to the thermal energy. They predicted the condition where the chain conformation is collapsed for neutral polyampholytes in no-salt solvent.

$$kT < \frac{N^{1/2} f e^2}{\epsilon a} \quad [6]$$

where N is the degree of polymerization. The inequality 6 states that the polymer chain tends to collapse if the degree of polymerization is sufficiently large. This is contrary to the inequality 3 found by Edward *et al.* [Edward *et al.*, 1980], which predicts that short chains collapse and long chains remain open.

Dobrynin and Rubinstein further developed the understanding of regimes of polyampholyte configurations based on a simple two-parametric Flory theory [Dobrynin and Rubinstein, 1997]. They showed that there are theoretically three possible regimes of chain configuration in the absence of salt, depending on the fraction of positive f_+ and negative f_- charges to the total monomeric units including uncharged groups and the degree of polymerization N (Fig. 1):

(1) *Unperturbed* for polyampholytes with a small number of charged groups:

Both fluctuation-induced attraction and Coulombic repulsion are weak, and the conformation is determined by the solvent quality. The chain is in Gaussian coil

conformation in a theta solvent, expanded in a good solvent, and collapsed in a poor solvent.

(2) *Polyelectrolyte* for asymmetrically, highly charged polyampholytes:

Coulomb repulsion is larger than the fluctuation-induced attraction, and the chain is stretched into an array of electrostatic blobs. The chain has the unperturbed configuration in each blob in the same manner as for the regime (1).

(3) *Necklace* for highly charged polyampholytes in a balance of excess charge:

Fluctuation-induced attraction is balanced with Coulombic repulsion to form a unique, elongated necklace-like shape. The globule is comprised of a lot of small blobs (represented by circles in Fig. 1(b)) in which the chain configuration is unperturbed like the regime (1). The size of each blob is smaller than the Debye length and the blobs form a dense packing.

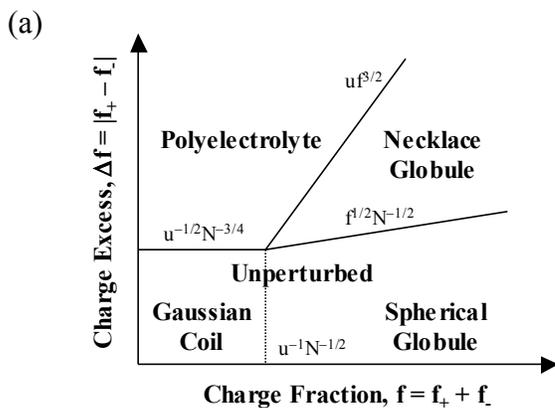
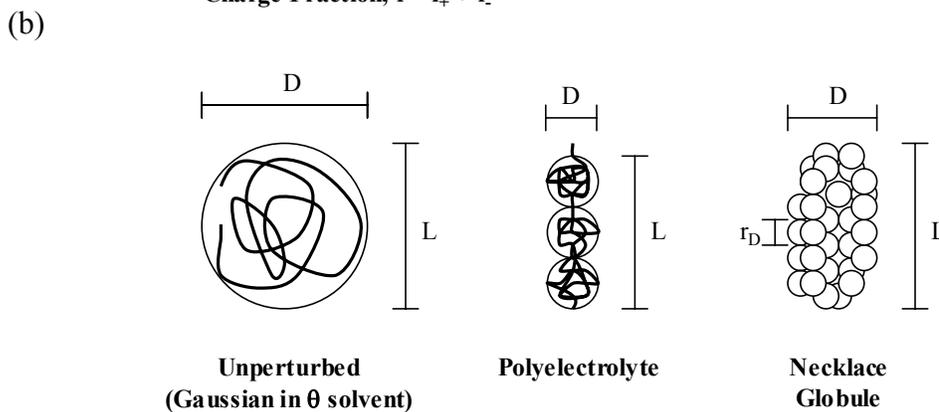


Fig. 1.

(a) Diagram of states of polyampholyte configuration in logarithmic scales

(b) Three regimes of polyampholyte chain configuration

[Dobrynin *et al.*, 1997]



In Fig. 1(a), the coupling constant $u = l_B/a$ is the ratio of the Bjerrum length l_B to the bond length a . These regimes are qualitatively not affected by the quality of solvent. Only the size of both globule and blobs is depending on the solvent quality. The effects of added salt are categorized in three regimes depending on the ratio of the Debye screening length in the solution $r_s = (8\pi l_B C_i)^{-1/2}$ (where C_i : ion concentration) to the chain length L and width D .

(1) No-salt regime ($r_s > L$)

Since the salt concentration is extremely low, the electrostatic interactions between charged groups on the chain are not affected by the existing salt. The configuration is the same as that of no-salt solutions.

(2) Low-salt regime ($D < r_s < L$)

The Debye length due to the salt r_s is larger than the chain width D but smaller than the chain length L . In this case, the configuration within size ranges smaller than r_s is not affected by the salt. However, the electrostatic repulsion is screened at the length scale greater than r_s , and the configuration at scales larger than r_s becomes closer to the self-avoiding random walk theoretical model.

(3) High-salt regime ($r_s < D$)

The salt ions are redistributed inside the polymer coil. In this high salt concentration, the configuration of polyampholyte chain can be treated as the analogy of totally uncharged chains.

All of the theories mentioned above were developed based on the Debye-Huckel or the Flory theories. Therefore, they include some limitations originating from assumptions and approximations made in these theories, as listed below:

- 1) The theories are not quantitatively accurate for concentrated solutions and high salt conditions.
- 2) Nonelectrostatic interactions such as hydrogen bonds, hydrophobic interactions, and van der Waals forces are not taken into account.
- 3) The charged groups must be randomly distributed along the chain. Alternating or block polyampholytes do not follow the theories well.

In most cases, the predictions of these theories can successfully explain the experimental results [Kudaibergenov, 2002]. However, one can say the theories about conformational characteristics of polyampholytes are not well established in detail yet.

2.2.2. Potentiometric titrations and viscometric properties

The acid -base properties of polyampholytes are determined by the nature of their functional groups and the microstructure of the chain [Kudaibergenov, 2002]. The potentiometric titration method can be used to obtain the acid-base properties of polyampholytes. The Henderson-Hasselbach equation can be used to analyze the acid-base equilibrium.

$$pH = pK'_a + n \log \frac{\alpha}{1-\alpha} \quad [7]$$

$$pH = pK'_b + n \log \frac{1-\beta}{\beta} \quad [8]$$

where pK'_a and pK'_b are the apparent dissociation constants of acid and base groups respectively, and α and β are the degree of ionization of acid and base groups. In the acid-base analysis of polyampholytes, the situations are not as simple as those of monomeric acid or base. First, it is reported that near the iso-electric point it is difficult to conduct the exact titration of the functional groups due to the insolubility of polyampholytes [Bekturov *et al.*, 1990]. Second, the

ionization of both acidic and basic groups is strongly affected by the nearest-neighbor interactions. Therefore, the ionization constants for the acid pK_a and base pK_b groups are subtly different, depending on the distribution of the acid and base monomers in an individual molecule [Merle, 1987].

The iso-electric point is of great importance when one considers the electrochemical properties of polyampholytes, because they change drastically around this pH. According to Merle *et al.*, the iso-electric points for polyampholytes are expressed as

For acid-rich polyampholytes:

$$pH_{IEP} = pK_a^{0'} + \log \frac{1-x_a}{2x_a-1} \quad (x_a > 0.5) \quad [9]$$

For base-rich polyampholytes:

$$pH_{IEP} = pK_b^{0'} + \log \frac{1-2x_a}{x_a} \quad (x_a < 0.5) \quad [10]$$

where, x_a is the fraction of acid monomers to the sum of acid and base monomers, and $pK_a^{0'}$ and $pK_b^{0'}$ are the sum of the intrinsic ionization constant and the nearest-neighbor interaction term for acid and base groups, respectively. These equations are valid if the difference between $pK_b^{0'}$ and $pK_a^{0'}$ is greater than 2 [Merle, 1980]. The theoretical formula that defines the isoelectric point of polyampholytes was given by Ehrlich and Doty in 1954 but not solved at that time [Ehrlich and Doty, 1954]. This theoretical formula proposed by Ehrlich and Doty was first solved by Patrickios in 1995 [Patrickios, 1995].

For acid-rich polyampholytes:

$$pH_{IEP} = pK_a - \log \left[\frac{R}{2} \left\{ -\frac{1-R}{R} + \left(\left(\frac{1-R}{R} \right)^2 + \frac{4}{R} 10^{(pK_a-pK_b)} \right)^{1/2} \right\} \right] \quad [11]$$

For base-rich polyampholytes:

$$pH_{IEP} = pK_b + \log \left[\frac{1}{2} \left\{ \frac{1-R}{R} + \left(\left(\frac{1-R}{R} \right)^2 + \frac{4}{R} 10^{(pK_a - pK_b)} \right)^{1/2} \right\} \right] \quad [12]$$

where, R is the molar ratio of acid to base. Equations 11 and 12 are totally equivalent and give the same results, no matter which functional group is more abundant. The calculated iso-electric point using the Merle's Equations 9 or 10 are expected to agree with those of the Patrickios' Equations 11 and 12 as long as a) the difference between the pK_b and pK_a is greater than two, and b) the numbers of acid and base groups are not equal or very close. The calculated iso-electric points are well correlated with those obtained experimentally in many cases [Merle *et al.*, 1980; Patrickios and Yamasaki, 1995; Lowe *et al.*, 1998].

Nagasawa and Noda demonstrated that the iso-electric point was slightly affected by the presence of salt. They used a polyampholyte having both carboxylic acid and amino groups, and found that the iso-ionic pH for the polyampholytes with higher content of amino groups increased with an increase of ionic strength, whereas that of the acid-rich polyampholytes decreased [Nagasawa and Noda, 1968]. Vedikhina *et al.* studied the salt effect on the ionization of the acid and base groups of polyampholytes at the iso-electric point. They found that the addition of salts rendered more acid and base groups ionized at the iso-electric point, and the apparent ionization constant of the base group was shifted to higher values. The shift was proportional to the square root of the ionic strength [Vedikhina *et al.*, 2000].

The viscosity of polyampholytes is well correlated with their charge properties. The viscosities of various polyampholytes are dependent on pH, since their charge properties are affected by pH. The reduced viscosity for random polyampholytes is usually minimized at the iso-electric point in the absence of salt [Koetz *et al.*, 1988]. As the pH shifts away from the iso-electric point, the viscosity is expected to increase. At extremely low or high pH, the viscosity starts to decrease

due to the fact that the electrostatic repulsions between charged groups are screened by the ions. When the ionic strength increases, the viscosity increases around the iso-electric point but decreases as the pH is either increased or decreased away from the iso-electric point. The viscosity change becomes relatively less, compared to no-salt conditions.

2.3 Methods of charge determination

As mentioned above, the charge properties of colloidal materials play an important role in the papermaking process. When a problem arises in the wet-end section of the papermaking process, people may try to understand what is happening by measuring the charge properties of the colloidal materials. Two methods, colloidal titration and microelectrophoresis, are widely used to measure the charge properties of the colloidal materials [Kirbawy, 1992; St. John and Gallagher, 1992]. From the results obtained by colloidal titration, one can know the charge amount of colloidal particles and polyelectrolytes in the aqueous system. The microelectrophoresis method can provide the information about the zeta potential, which is the electrochemical potential on the hydrodynamic slip plane adjacent to the particle surface. It is worth noting that the physical meaning of the charge essentially differs from that of the zeta potential. The charge is an extensive variable, which depends on the sample size, whereas the zeta potential is an intensive property, which is not affected by the sample size. Theoretically, the point of zero zeta potential is supposed to coincide with the zero-charge point, but this is not always true in practice [Davison and Cates, 1975].

The zeta potential is measured based on the principle of the electrophoresis. The term electrophoresis refers to the movement of charged particles in an electric field. The

electrophoretic mobility u is defined as the particle velocity v divided by the electric field strength E .

$$u = \frac{v}{E} \quad [13]$$

Since the electric field strength E is experimentally measurable parameter, the mobility u is calculable by knowing the velocity of the particle v . The zeta potential ζ is related to the particle mobility u as follows:

$$\zeta = \frac{4\pi\eta u}{\varepsilon} \quad [14]$$

where η is the solution viscosity, and ε is the dielectric constant of the medium. A schematic diagram of the apparatus that is used to measure the zeta potential is shown in Fig. 2 (a). The apparatus has a capillary tube in it, and the capillary is filled with the medium in which the target colloidal materials are dispersed. A certain voltage is added through the capillary, and the velocity of particles moving along the stationary layer inside the capillary is measured to calculate the zeta potential. Since the zeta potential is a specific value for each colloidal particle, it sometimes has a distribution in a complicated system like practical papermaking conditions [Sanders and Schaefer, 1995].

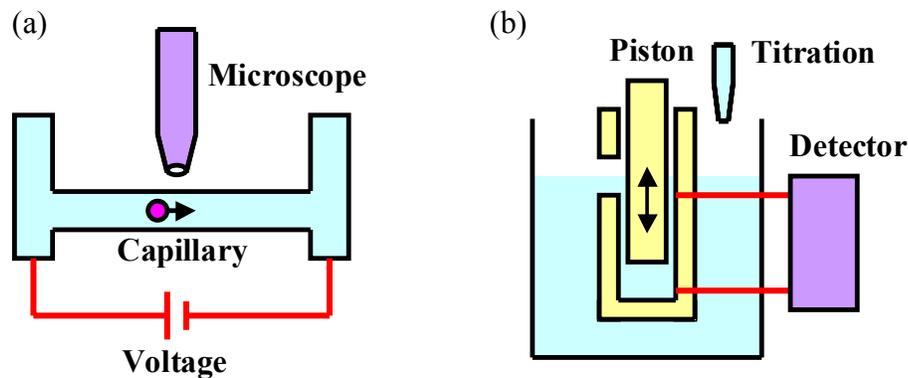


Fig. 2. (a) Microelectrophoresis for zeta potential

(b) Colloidal titration with a streaming current detector for colloidal charge

To measure the charge of colloidal materials, the colloidal titration technique is mostly applied using a streaming current detector. The schematic principal of this technique is shown in Fig. 2 (b). The surfaces of a plastic piston and cylinder are considered to have some charge. The double layer of the piston surfaces is assumed to be in a similar condition to that of the colloidal materials, regardless of the sign of charge. In the case that the plastic surfaces originally have the opposite sign of charge compared to the colloidal materials, the piston surfaces are considered to be covered with oppositely charged colloidal materials, and now this apparent piston surfaces are expected to have a similar double layer state to that of the colloidal materials. When the piston is moving up and down periodically, an alternating current signal induced by the movement of the counterions adjacent to the charged plastic surfaces is detected by electrodes. The sign of the charge of the colloidal materials, which is considered to be the same as that of the apparent piston surfaces, can be recognized by this induced voltage. If the colloidal solution is titrated with the oppositely charged colloidal material (titrant) while the streaming current being monitored, then we can determine the amount of the charged colloidal materials that is necessary to bring the streaming current to zero. This required amount of the titrant to reach zero streaming current is considered to correspond to the colloidal charge of the sample. Polyelectrolytes such as poly(diallyldimethylammonium) chloride and potassium poly(vinylsulfate) are often employed as titrants in this measurement. In many cases 1:1 stoichiometry is met for the complex formation between negatively and positively charged polyelectrolytes [Kam and Gregory, 1999]. However, some deviation from 1:1 stoichiometry was reported in the case of high ionic strength [Chen *et al.*, 2003]. According to their results, as the salt concentration increased, a larger amount of titrant was required to apparently neutralize the polymer charge, regardless of whether the polymer was negatively or positively charged.

2.4 Adsorption of polymers onto charged surfaces

2.4.1 Adsorption of polyelectrolytes

The adsorption of wet-end additives onto fibers is an important issue. Many wet-end additives such as dry strength additives, retention aids, and sizing agents can achieve their expected function by being adsorbed onto fibers. Therefore, a lot of research can be found in this area [Wågberg, 2000]. There are several factors to be considered with regard to polyelectrolyte adsorption onto fibers: (1) surface charge density and surface area of cellulose fibers, (2) characteristics of adsorbed polymers (charge density, molecular weight), (3) ionic strength of the solution, and (4) time effect (adsorption kinetics, penetration of polymers into pores).

Tanaka *et al.* examined the adsorption behavior of many types of cationic polymers such as PEI, poly-DADMAC, PAM, starch, and chitosan. For cationic polymers with primary, secondary, and tertiary amines, the maximum adsorption onto fibers was achieved within a specific, narrow pH range, where a very small amount of amino groups were protonated. Cationic polymers modified with quaternary amines had a wide pH range, covering from acidic to alkaline conditions for the maximum adsorption. Under a high salt concentration ($>0.1\text{M}$), adsorption decreased a lot. This result supports the fact that the primary driving force of adsorption is electrostatic attraction between the pulp surface and cationic polymers [Tanaka *et al.*, 1979]. Durand-Piana *et al.* examined adsorption isotherms of various cationic polyacrylamides onto negatively charged clays [Durand-Piana *et al.*, 1987]. They found that the adsorption was maximized when the cationic copolymer was slightly charged (1 %). As the degree of substitution increased, less of the cationic polymers were adsorbed, since the conformation involved the adsorbed electrolytes lying down on the negatively charged surface.

Nanko *et al.* visualized the conformation of cationic and amphoteric polyacrylamides adsorbed onto pulp fibers by using colloidal gold labeling and the TEM technique. Cationic groups on PAMs were stained with gold particles, which could be seen by TEM. The cationic PAMs seemed to exist as bundles, but not as single chains, after being adsorbed on fibers. It was shown that many of the strands of cationic PAMs with high molecular weight looped back to fibers and the coagulation on the surface became larger. A cationic PAM with a high charge density (2.97) was observed not to extend its chain as far from the surface as a cationic PAM with a low charge density (0.46) did. An amphoteric PAM (Cat. 1.25, An. 0.94) behaved in almost the same manner as the cationic PAMs. The formation of a complicated network structure was observed when a branched amphoteric PAM was used [Nanko *et al.*, 2003].

2.4.2 Adsorption of a single polyampholyte chain

A theory of polyampholyte adsorption onto charged surfaces was proposed by Dobrynin *et al.* [Dobrynin *et al.*, 1997]. They predicted three different regimes in adsorbed state of polyampholytes in the case that a weakly charged polyampholyte chain with equal numbers of positively and negatively charged groups is adsorbed onto an infinite charged plate in salt-free solvent. It is worth noting that such conditions under consideration are quite different from typical papermaking conditions in which salt concentration is significantly higher. However, it will be a good start to take up a simple case. Adsorption behavior in the presence of salt will be discussed later. Under no-salt conditions, most of counter ions are expected to be localized within the Gouy-Chapman length λ apart from the charged surface. The definition of the Gouy-Chapman length λ is given by [Dobrynin *et al.*, 1997]

$$\lambda = \frac{1}{2\pi\sigma l_B} \quad [15]$$

where, σ is the charge density and l_B is the Bjerrum length. According to Dobrynin *et al.*, it is predicted that there are three regimes for adsorbed configuration, depending on the surface charge density σ (Fig. 3):

1) Pole regime: low surface charge density $\sigma_1 < \sigma < \sigma_2$

In this regime, the Gouy-Chapman length λ is expected to be larger than the polyampholyte coil size $aN^{1/2}$. The polyampholyte coil is no longer in the Gaussian shape; rather it is expanded in the direction perpendicular to the charged surface due to the electric field. The functional groups on the polyampholyte chain that have a sign of charge opposite to that of the surface tend to be closer to the surface, and *vice-versa*. As a result, the expanded polyampholyte coil is polarized.

2) Fence regime: medium surface charge density $\sigma_2 < \sigma < \sigma_3$

In this regime, the size of a fully stretched chain is larger than the Gouy-Chapman length λ . However, the chain is located within the Gouy-Chapman length since the chain cannot gain the electrostatic energy outside of this length. As a result, the chain is predicted to have a fence-like configuration inside a layer of the Gouy-Chapman length, and the statistics of the chain is consistent with the model involving a random walk with interactions dominated by the dipole-dipole repulsion between the layer of size λ .

3) Pancake regime: high surface charge density $\sigma > \sigma_3$

In this regime, the Gouy-Chapman length is compressed, and the chain has loops at the mean-square distance between charged monomers $af^{1/2}$, which is larger than the Gouy-Chapman length λ . The thickness of the adsorbed layer is always the same, regardless of the surface charge density.

Here, $\sigma_1 = 1 / \{l_B R_0 (fN)^{1/2}\}$ [16]

$\sigma_2 = 1 / \{l_B R_0 (fN)^{1/4}\}$ [17]

$\sigma_3 = f^{1/2} / a l_B$ [18]

where $R_0 \approx aN^{1/2}$ is the radius of the Gaussian chain. If the surface charge density is lower than σ_1 , then no adsorption will occur because the obtained energy due to the chain polarization is smaller than the thermal energy. Under this low surface charge, the polyampholyte chain with equal numbers of positively and negatively charged groups is not polarized and remains neutral with respect to the charged surface. Therefore, there is no driving force for the polyampholyte to be adsorbed. In conclusion, a polyampholyte chain with zero net charge can be adsorbed on charged surfaces at surface charge densities higher than the threshold $\sigma > \sigma_1$

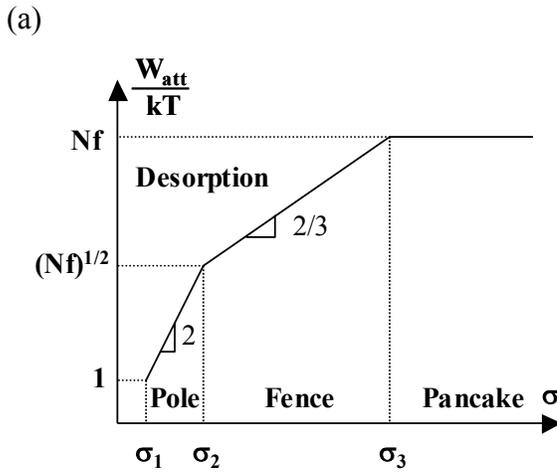
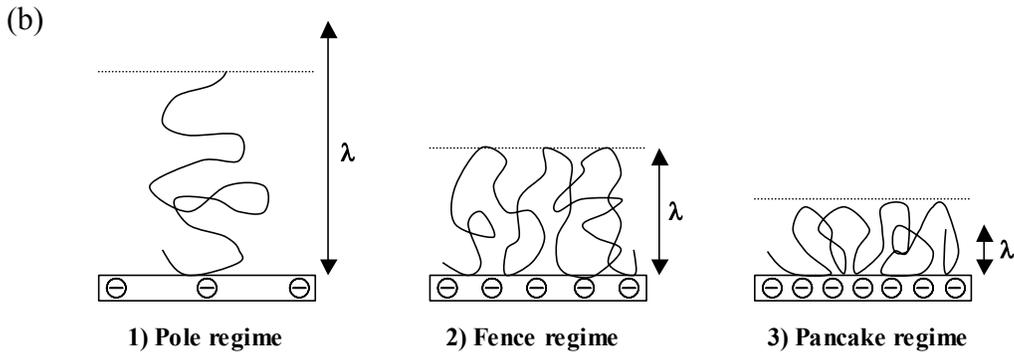


Fig. 3.

(a) Dependency of adsorbed chain configuration on the surface charge density in logarithmic scales

(b) Three regimes of an adsorbed polyampholyte chain with zero net charge

[Dobrynin *et al.*, 1997]



The theory of Dobrynin *et al.* states that polyampholytes with asymmetrically charged groups basically follow the same regimes as those of no net charges. Here, they assumed the polyampholytes with both negative and positive charged groups randomly distributed. Although the regimes are the same, the transitional surface charges (σ_1 , σ_2 , and σ_3) are shifted, depending on the charge balance. If a polyampholyte has a net charge larger than $(f/N)^{1/2}$, then there is no pole regime.

The above-mentioned theory is expected to be valid only in no-salt conditions. In the presence of salt, the regimes of an adsorbed polyampholyte chain are expected to change, depending on the salt concentration as shown in Fig. 4.

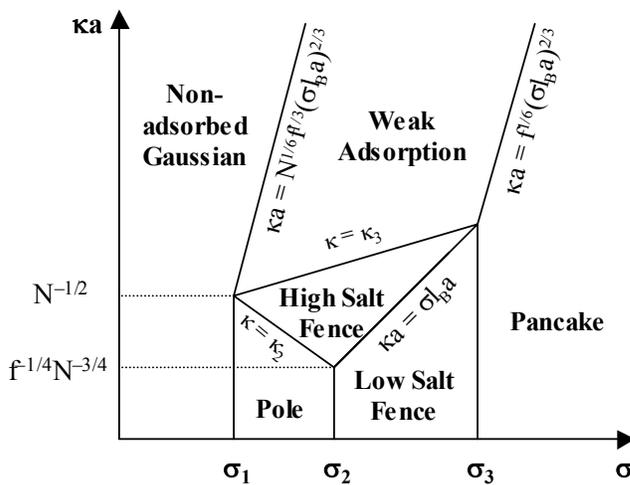


Fig. 4
Adorption diagram of a polyampholyte chain in salt solution as a function of surface charge density σ and Debye screening length κ^{-1} in logarithmic scales
[Dobrynin *et al.*, 1997]

Since the Debye screening length κ^{-1} decreases as the salt concentration increases, the more increased the salt concentration, the larger the value will be on the y-axis in Fig. 4. As the salt concentration becomes higher and higher, the adsorbed configuration is changed from either the pole or the low salt fence regime to the high salt fence regime, and further changed to the weak adsorption regime. The characteristics in terms of configurations for both the low- and high-salt

fences are basically the same. However, the thickness of the adsorbed layer is dominated by the surface charge for low-salt case, while it is determined by the salt concentration for high salt case. Consequently, in the low salt fence regime where the Debye length κ^{-1} is larger than the Gouy-Chapman length λ , the chain is localized inside the layer of the thickness λ . On the other hand, the Debye screening length κ^{-1} is less than the Gouy-Chapman length λ in the high salt concentration, and the chain is located within the layer of the thickness κ^{-1} . In the weak adsorption regime, the polyampholyte is weakly adsorbed on the charged plate in a way that the standard Flory theory explains. Because the attraction between the charged surface and a layer of the chain of size κ^{-1} is less than the thermal energy, no significant change of the chain conformation induced by the charged surface occurs.

2.4.3 Adsorption of multi polyelectrolyte chains

The above theory proposed by Dobrynin *et al.* focuses on adsorption of a single polyampholyte chain onto charged surfaces. They developed the theory further by taking multichains into consideration [Dobrynin *et al.*, 1999]. In this study, they considered a large number of polyampholyte chains existing in a system, which make it possible to form a multi-layer of adsorption. The polymer density in the adsorbed layer is dependent on the balance between the electrostatic attraction to the charged surface and the steric repulsion. Polyampholytes with zero net charges are predicted to have three different regimes in chain adsorption depending on the surface charge density.

1) Multilayer of stretched chains ($\sigma_1 < \sigma < \sigma_2$)

In this regime polyampholyte chains are expected to be polarized and stretched by the electric field. Within the range of distance $\lambda < z < \lambda_1$ the polymer density is expected

to decrease from the charged surface. No adsorption occurs beyond the distance at which the electric field becomes too weak to polarize the polyampholyte chains (Fig. 5 (a)).

2) Self-similar stretched pseudobrush ($\sigma_2 < \sigma < \sigma_3$)

In this regime the polyampholyte chains are expected to be uniformly expanded with the layer of the Gouy-Chapman length λ . In the range of distance $\lambda < z < \lambda_2$ the polyampholytes are stretched. The macromolecules have a configuration that can be described as a self-similar pseudobrush. The density of the polyampholytes decreases with increasing distance of separation from the surfaces. At length scale larger than λ_2 the polymer density change is the same as that of the multilayer of stretched chains (Fig. 5 (b)).

3) Saturated self-similar stretched pseudobrush ($\sigma > \sigma_3$)

In this regime the polymer density is expected to be uniform inside the layer of thickness λ_3 . On the length scale between λ_3 and λ_2 adsorbed polymers follow the same regime as that of the self-similar stretched pseudobrush.

$$\text{Here, } \lambda_1 \approx af^{1/2}N \approx R_0(fN)^{1/2} \quad [19]$$

$$\lambda_2 \approx R_0(fN)^{1/4} = (\lambda_1 R_0)^{1/2} \quad [20]$$

$$\lambda_3 \approx af^{1/2} \approx z \quad [21]$$

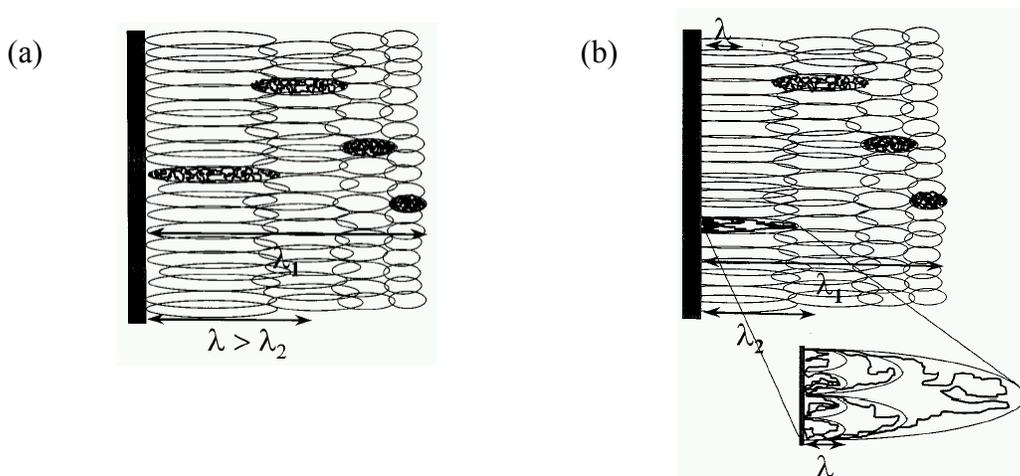


Fig. 5. Schematic sketch of the configurations of adsorbed polyampholyte chains [Dobrynin *et al.*, 1997]
 (a) Multilayer of stretched chains (b) Self-similar stretched pseudobrush

The theory of Dobrynin *et al.* [1997] states that the presence of salt does not affect the thickness of the adsorbed layer as long as the Debye screening length is larger than the Gouy-Chapman length. The Debye length depends on the salt but not the surface charge density, while the Gouy-Chapman length depends on the surface charge density but not the salt. When the Debye length becomes less than the Gouy-Chapman length, in other words, the salt concentration is sufficiently high, the thickness of the adsorbed layer is expected to start to decrease due to the screening effect of polarization-induced attraction. The thickness of the adsorbed layer no longer changes when the Debye length becomes less than the size of the Gaussian chain.

Although the above theory has not yet been fully established experimentally, some experimental results have supported the prediction. Ozon *et al.* examined the loop size distribution of amphoteric polyacrylamides adsorbed onto well-defined charged surfaces using the atomic force microscopy technique [Ozon *et al.*, 2002]. They used several electrically neutral polyampholytes having sulfate and ammonium groups, and the experimental conditions in which the adsorption

was carried out corresponded to the fence regime in the above-mentioned theory that Dobrynin *et al.* proposed [Dobrynin *et al.*, 1997]. They found that the loop size distribution qualitatively agreed with the theoretical projection derived from the Dobrynin's theory under some assumptions.

There is another approach to predict adsorption behavior of a polyampholyte chain onto charged surfaces. Kahn *et al.* investigated the tendency for adsorption of a flexible polyampholyte chain to a charged surface using the Monte Carlo simulation method [Kahn *et al.*, 2001]. The simulation results showed that (1) no adsorption of a neutral polyampholyte occurs when the surface charge density is low, (2) as the surface charge increases, the chain starts to be adsorbed and to expand, and (3) when the Gouy-Chapman length is equal to the Gaussian radius, the chain starts to shrink. These results are in qualitative agreement with a mean-field method presented by Dobrynin *et al.* [Dobrynin *et al.*, 1997]. However, no occurrence of three regimes (pole, fence, and pancake), which are predicted in the mean-field analysis, were found in this simulation. The theories of polyampholyte adsorption to charged surfaces are still open to argument and need to be verified by experiments.

3. OBJECTIVES

Amphoteric polyacrylamides are widely regarded as efficient dry strength agents having the ability to cope with the demand for high product quality and environmental concerns in the papermaking industry. However, the reason for their effectiveness is not well understood. Therefore, further investigation into the fundamental behavior of amphoteric polyacrylamides is important in order to elucidate the mechanism. However, a limited amount of published research related to amphoteric polyacrylamides can be found.

The theories of amphoteric polymers started to be proposed in 1950s but less attention was paid to them in the period between the 1950s and much more recent times. They have again become an intensive field of study since 1990s. Although, it is shown that some theories are consistent with the experimental data, it is still hard to say that the theories have been well supported by experiments.

In this thesis the first goal is to develop a new analytical method for determination of polyampholyte concentration in solution based on principles of colloidal titration, using streaming current for detection of the endpoints. This will be done by carrying out the titrations either at a low or at a high pH condition under which ionized groups of only one sign of charge are present on the polyampholyte.

The following hypotheses will be evaluated:

It is proposed that an analytical method based on principles of colloidal titration for determination of polyelectrolyte concentration is applicable to amphoteric PAMs. This

will be done by carrying out the titrations either at a low or at a high pH condition under which ionized groups of only one sign of charge are present on the polyampholyte.

It is proposed that viscosity behavior of amphoteric polyelectrolytes can be understood in terms of their conformations in solution, including the dependency of conformation on pH. It has been shown that the degree of polymer extension is minimized around the isoelectric point of such polymers.

It is proposed that the adsorption of amphoteric polyacrylamides onto fibers can be maximized at a certain pH that is a little lower than their isoelectric points, where the positive charge on the polyampholytes is sufficiently low as to allow the chains to lie down onto the fiber surface and the electrostatic attractions between negatively charged fibers and polyampholytes permit a significant amount of adsorption to take place.

4. PAPERS (Experimental and Results & Discussion)

“Experimental” and “Results and discussion” sections are replaced with two papers that are intended to submit to scientific journals.

4.1. Papers – Part 1

Colloidal Effects of Amphoteric Acrylamide Copolymers. Part 1. Electrokinetic Behavior

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{{FOOTNOTES}}

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The colloidal and electrokinetic behavior of several commercial amphoteric acrylamide-based polyelectrolytes was elucidated using potentiometric and colloidal titrations as well as microelectrophoresis, viscometry, and turbidity measurements. The independent variables for this investigation were polymer composition, pH and the concentration of salt ions. The shapes of the potentiometric titration curves were found to deviate from the theoretical values at pH's near the isoelectric point, not fully accounting for all the carboxyl groups present on the polymers. The electrophoretic mobility was found to change rapidly with pH near electroneutrality. However, in the case of colloidal titrations there was a wide range of pH's over which most of the polyampholytes showed little tendency to complex with highly charged, linear titrants. The overall results suggest that at pH values relatively close to the isoelectric point, the outer segments of the polyampholyte molecules tend to be enriched in

the charge group present in excess within the chain, with the interior groups being less available for interaction with titrants. Specific viscosity measurements, in the vicinity of the isoelectric point, were found to increase with increasing salt concentration. This is a typical anti-polyelectrolyte behavior. In a similar manner, salt addition suppressed the development of a turbidity maximum at the isoelectric point.

1. Introduction

Polyampholytes, which are polyelectrolytes possessing both positively and negatively charged groups, have received increasing interest in such applications as sludge dewatering [Watanabe *et al.*, 1999], paper manufacture [Tanaka *et al.*, 1976; Ye *et al.*, 1990], and detergency [Hayashi *et al.*, 1997]. Although synthetic polyampholytes have been known for more than 50 years [Alfrey *et al.*, 1950; Alfrey and Morawetz, 1952], their industrial utility has not been as wide as conventional polyelectrolytes. Recently, amphoteric acrylamide copolymers have become commercially available as dry-strength additives for paper [Ghosh, 1994]. It is important to understand the colloidal behavior of such additives in order to maximize the benefits and cost-effectiveness of their use.

Methods to elucidate the colloidal properties of polyampholytes have been demonstrated in previous studies. For example, results of potentiometric titrations have been shown to be consistent with the presence of acidic and basic groups, using reasonable values for the respective dissociation constants [Alfrey and Pinner, 1957; Ascoli and Botre, 1962; Bekturov *et al.*, 1990; Mazur *et al.*, 1959]. Microelectrophoresis has been used to detect the sign of charge of polyampholytes as a function of pH [Alfrey *et al.*, 1950], usually as a means of determining the isoelectric pH [Alfrey and Morawetz, 1952; Ascoli and Botre, 1962; Bekturov *et al.*, 1990; Mahltig *et al.*, 1999]. Recently the streaming current method [Cardwell, 1966] was used,

apparently for the first time, as an evaluation tool for a system involving amphoteric polyelectrolytes [Watanabe *et al.*, 1999]. Other studies have demonstrated a minimum in reduced viscosity of polyampholyte solutions at pH conditions corresponding to near-zero net charge [Alfrey and Morawetz, 1952; Ascoli and Botre, 1962; Lowe and McCormick, 2002].

When characterizing a commercial polyampholyte the following questions are relevant: In what ways is the material different from an ordinary polyelectrolyte? How does this material respond to changes in pH and salt content of the solution, especially within industrially relevant pH ranges? It is questions of this nature that the present fundamental effort attempts to address. The work also is motivated by our desire to comprehend and optimize the solution properties of these polymers. Questions related to the adsorptive behavior, flocculating ability, and paper-strengthening effects of these materials are not considered here but they will be the subjects of future communications.

2. Experimental Section

Polyelectrolyte samples used in this investigation are shown in Table 1. All of the samples were provided by Harima Chemicals, Inc. The numerical value after the letter “C” in the table corresponds to the percentage of cationic monomers and the number after the letter “A” indicates the percentage of anionic charged groups, on a mole basis, in the recipes used for synthesis of the polymers.

Polyelectrolyte sample	Cationic groups mol %	Anionic groups ¹⁾ mol %	Molecular weight 10 ⁶
C3A5	3.0	5.0	2.5
C4A4.4	4.0	4.4	2.7
C5A4	5.0	4.0	3.0
C7A7	7.0	7.0	1.2
C50An	50	-	0.5

1) Diacidic monomers were used.

100 ml of 0.1 % amphoteric polyacrylamide solution was prepared for potentiometric titration. 0.1 N HCl was added until the pH reached to 3.00. Aliquots of 0.02 ml of 0.1 N NaOH were added dropwise to the solution continuously under stirring to pH 11.0. The pH value was recorded after each 0.02 ml of several drops of NaOH was added.

For microelectrophoresis measurements, microcrystalline cellulose powder (max. 20 μ m, Aldrich) was well dispersed in deionized water to 0.01% based on solids. For each analysis involving an acrylamide polymer, 20 ml of 0.02% polymer solution was further diluted to 180 ml in deionized water. The solution was stirred and 20 ml of the cellulose dispersion was added slowly. After the pH reached a desired value using NaOH or HCl, the ionic strength was set to 0.001 M with KCl. After the dispersion was stirred for two minutes, the electrophoretic mobility was measured with an SKS charge analyzer Model II.

For streaming current measurement, after the pH of amphoteric polyacrylamide solution (0.001 %) had been adjusted to a certain value, the ionic strength was set to 0.001 M with KCl. The streaming current value of the polyacrylamide solution was measured with an ECA 2000P instrument from Chemtrac Systems, Inc. The solution was titrated with 0.001 N of poly(diallyldimethylammonium) chloride or potassium poly(vinylsulfate) until the streaming current reached zero.

For viscosity and turbidity measurement, each amphoteric polyacrylamide solution (0.002 % solids for C5A4, 0.01% for C3A5) was prepared and the pH was set to a certain value with NaOH or H₂SO₄. For experiments involving salt addition, the conductivity was adjusted to 1500 μ S/cm by adding 0.1 N Na₂SO₄. The turbidity of such polyacrylamide solutions was measured with HF turbidimeter Model DRT-100B. Then 10 ml of the solution was put into a Cannon-Ubbelohde viscometer and the viscometer was allowed to stand in a water bath

(25.0 °C) for 20 minutes. The efflux times were measured 3 times for each polymer solution. The specific viscosity was calculated by (solution efflux time – solvent efflux time) / solvent efflux time.

3. Results and Discussion

Potentiometric Titration

Figure 1 shows the results of potentiometric titrations, based on addition of NaOH to either deionized water or to a solution of amphoteric polyacrylamide (am-PAM, type C5A4) in deionized water. See Table 1 for monomeric compositions of the polyelectrolytes evaluated. In Fig. 1, the curves were normalized so that the test curve intersects the blank curve at a pH of approximately 6. It will be shown later in this article that this pH corresponds to the iso-electric point of this sample, *i.e.* a condition where the net charge of the polyelectrolyte is zero.

As expected in the case of a polyelectrolyte bearing either weak acid or base groups with dissociation constants within the range of pH tested [Lifson, 1957], there was significant difference between the titration curve for the polyampholyte sample *vs.* the blank.

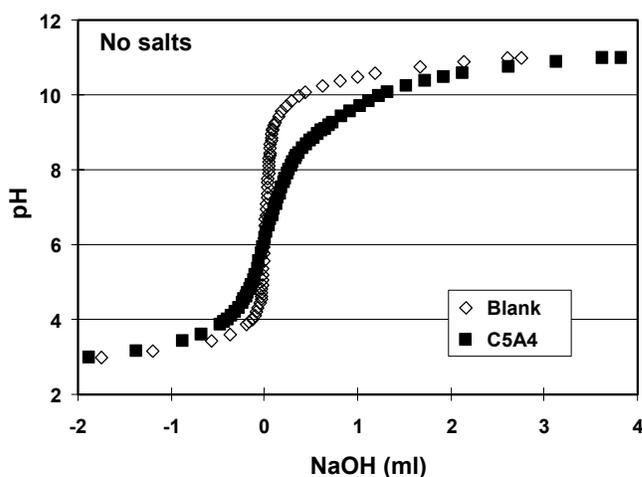


Fig. 1. Potentiometric titration data shown in normalized form such that the curves cross at the isoelectric pH. The amount of NaOH is also set to zero at the isoelectric point.

As shown in Fig. 1., the differences in the amount of NaOH between the test and the blank are related to the net ionic charge of the polyampholyte, as a function of pH. Below pH 6 the differences in consumed NaOH correspond to net positive charge, while differences in consumed NaOH amount *above* the zero point correspond to net negative charge on the polymer.

The next step was to take such differences in NaOH amount, comparing test curves with their corresponding polymer-free blank solution curves, and to plot the data versus pH. Figure 2 shows results for three samples of amphoteric polyacrylamide that differ in monomer ratio. Again the zero point of the curve was defined based on isoelectric points determined by microelectrophoresis and streaming current measurements (see Table 2).

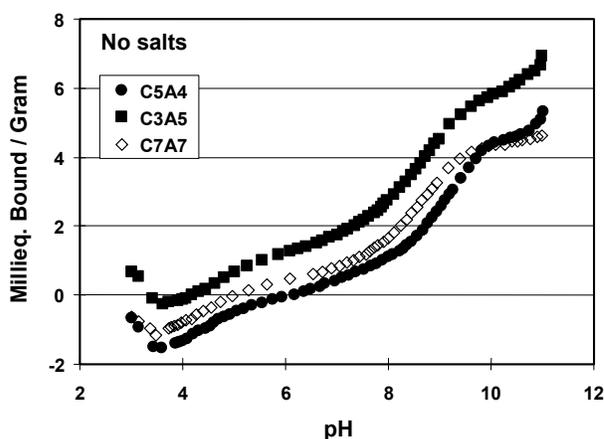


Fig. 2. Potentiometric titration curves for three amphoteric PAM products. Polyacrylamide composition is shown in Table 1.

Accounting for the Potentiometric Titration Data

In an effort to account for the general shape of the curves in Fig. 2., calculations were carried out in two ways, focusing on sample C5A4. A preliminary attempt was made to accurately fit the observed base-consumption vs. pH behavior by treating the acidic and basic groups as independent from each other. The amounts of acidic and basic groups, the dissociation constants, and another fitting parameter were adjusted. As will be shown, despite

the fact that a good fit was obtained, the determined values of acidic and basic groups did not match the actual composition of C5A4. Consequently, an alternate analysis was carried out based on the known composition (see later).

Treating acidic and basic dissociations as independent: To simplify the analysis it was assumed that all of the carboxyl groups in sample C5A4 were governed by a single dissociation constant, and that the same situation held true for the amine groups. As an approximation it was assumed that essentially all of the base consumed by the polyelectrolyte *below* the microelectrophoretic isoelectric pH value was related to the carboxyl groups, and that essentially all of the base consumed *above* the isoelectric point was due to the amine groups. The pH was calculated, based on various assumed values of monomeric group concentrations and dissociation constants, using the following forms of the Henderson-Hasselbach equation [Bekturov *et al.*, 1990],

$$\text{pH} = \text{p}K_a' + n \log [\alpha / (1 - \alpha)] \quad (1)$$

$$\text{pH} = \text{p}K_b' + m \log [(1 - \beta) / \beta] \quad (2)$$

where $\text{p}K_a'$ is the negative logarithm of the apparent dissociation constant of the acidic groups (carboxyl), n is a term introduced by Alfrey and Pinner [Alfrey and Pinner, 1957] to account for neighbor-group effects, and $\text{p}K_b'$ and m are analogous quantities corresponding to the amine groups.

Figure 3 shows the results of calculations with the following assumed values of the fitting parameters: $\text{p}K_a' = 4.5$; $\text{p}K_b' = 9.0$; $n = 1$; $m = 1.7$; and effective monomeric group concentrations of 1.5 and 5.2 meq/g for the acidic and basic groups, respectively, in a given dry

mass of polyampholyte. The filled circles in Fig. 3 correspond to data from tests with polymer sample C5A4 (see also Fig. 2.). The open diamonds correspond to the calculated fit.

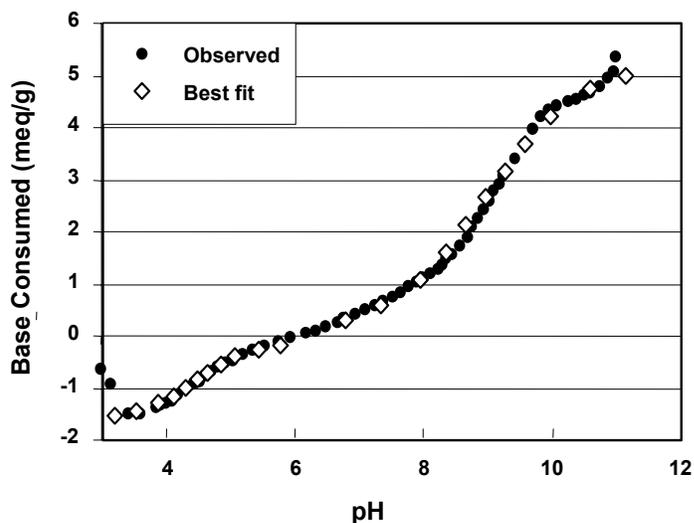


Fig. 3. Henderson-Hasselbalch fit of titration data for polymer C5A4 based on selected values for dissociation constants, monomeric group concentrations, and neighbor-group effects

It should be noted that in order to achieve the excellent fit of Fig. 3 between the experimental and the calculated values it was necessary to assume an unrealistic ratio of amine to carboxyl groups of approximately 3.5. The actual nominal ratio (based on synthesis) was however only 1.25. This difference was considered to be too large to be accounted by experimental error. It also seems suspicious that the fit required such a large value of the fitting parameter m , despite the relatively low charge density of amine groups (5%) in the polyampholyte [Alfrey and Pinner, 1957]. For these reasons the preliminary analysis was rejected.

Analysis based on the known amounts of acidic and basic groups: The analysis was repeated, using the same values of pK_a' and pK_b' , and both of the fitting parameters n and m were set equal to one. The ratio of basic to acidic groups was set to 1.25, based on the known

composition. To ensure self-consistent results, the data were forced to conform to the following equations:

$$\text{pH} = \text{p}K_a' + \log [\alpha / (1 - \alpha)] = \text{p}K_b' + \log [(1 - \beta) / \beta] \quad (3)$$

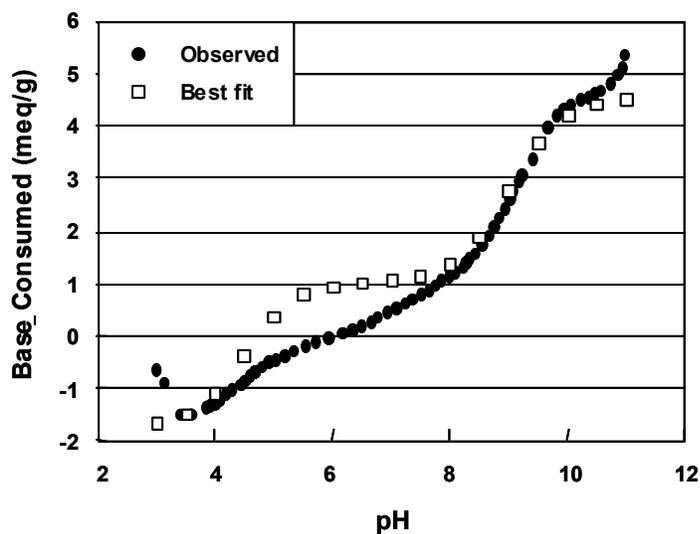


Fig. 4. Potentiometric data compared with results of calculations based on Eq. (3) and the known ratio of amine to carboxyl groups

As shown in Fig. 4 there was substantial difference between the predicted and the actual amount of consumed base within the pH range between about 4 and 8. Two explanations are possible. First, in these pH ranges, ionic groups of both signs of charge are expected to be present within the polyampholyte. Under such conditions polyampholyte molecules in solution are expected to be denser, less soluble, and less capable of equilibrating with the surrounding solution [Higgs and Joanny, 1991]. It is not known whether the microenvironment within a dense, semi-soluble polyampholyte would be likely to shift a potentiometric titration curve as significantly as that of Fig. 4. A more conventional explanation is that the assumption of a single dissociation constant for the carboxyl groups is inappropriate due to neighbor group effects [Merle, 1987]. When ionizable groups are closely spaced, the microenvironment created by the

dissociation of one group increases the effective pK_a of the adjacent group [Merle, 1987]. Since the polyampholyte samples are known to contain di-acid monomeric units, this more conventional explanation probably is sufficient to account for all of the deviation shown in Fig. 4.

Before leaving Fig. 4, it is worth taking note of an alternative explanation that has been used to explain various anomalous behavior of polyampholytes in the neighborhood of their isoelectric points [Bekturov *et al.*, 1990]. This rationalization involves the existence of stable ion pairs between charged acidic and basic groups. Though such an explanation cannot be ruled out entirely by the present results, the deviations shown in Fig. 4 are in the opposite direction of what might be expected from an ion-pair hypothesis. In other words, ion-pairing would be expected to favor the existence of carboxylate species, whereas results in Fig. 4 showed that the pH had to be raised to about 8 before the charge of most of the carboxyl groups had been accounted for. It is worth noting that Ehrlich disputed the ion pair hypothesis based on results of infrared analysis that showed most of the carboxylic acid groups of the polyampholytes were ionized at the iso-electric point [Ehrlich, 1954].

Microelectrophoresis Measurements

The presence of amphoteric PAM in solution was found to have a profound influence on the electrophoretic mobility of microcrystalline cellulose particles (Fig.5). The lowest curve (open circles) corresponds to the mobility of the cellulose in the absence of the copolymers. In agreement with earlier studies [Springer and Taggart, 1986], cellulose is seen to have a negative mobility throughout the observed pH range of 3 to 11, and the absolute magnitude increased with increasing pH. The results are consistent with the presence of some carboxyl groups on the

particle surfaces. Independent conductometric titrations of microcrystalline cellulose may confirm this rationalization.

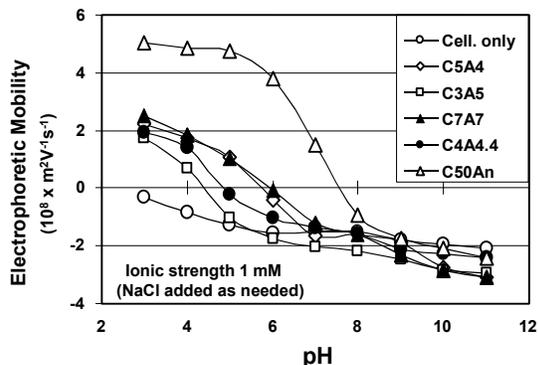


Fig. 5. Electrophoretic mobility of microcrystalline cellulose in solutions containing an excess of amphoteric PAM (PAM/cellulose = 2/1) of various monomer mole ratios (see Table 1 for compositions).

Since the mass of polyelectrolyte added to each mixture represented in Fig. 5 was twice that of the cellulose, it is reasonable to assume that adsorption of the polyelectrolyte leads to essentially complete coverage of the cellulose particles. In actual fact, data by Sandell and Luner implies that approximately 1% cationic poly-ionene halides, based on microcrystalline cellulose solids, was enough to fully reverse the charge [Sandell and Luner, 1973]. Similar levels of adsorbed polymer, at saturation, were achieved with two different charge densities of polyelectrolyte. Likewise, between 0.3% and 2.4% poly-DADMAC by mass has been found to reverse the charge of bleached kraft cellulose fibers [Wang and Hubbe, 2002].

It is worth noting in Fig. 5 that in the presence of polyampholyte solutions the electrophoretic mobility tended to change relatively rapidly, as a function of pH, as the sign of charge was reversed. To interpret these data one needs to consider that polymer segments located towards the outer edges of a dissolved polyelectrolyte molecule are expected to have the greatest impact on electrokinetic effects [Varoqui, R., 1982; Ohshima, H., 1997; Bauer, D., *et al.*,

1998]. Thus, though a positive electrophoretic mobility is expected when there is an excess of ionized amine groups in these outer loops and tails of the polyelectrolyte, the data do not provide as much information about the state of charge in the interior regions of polyampholyte molecules in solution. Long *et al.* proposed that the electrophoretic mobility of polyampholytes in solution is affected by changes in molecular conformation, including the distribution of charged groups within the coiled structure [Long *et al.*, 1998]

By assuming essentially complete coverage of the microcrystalline cellulose particles in the present instance, iso-electric points of the polymers were estimated from Fig. 5 and are shown in the first numerical column of Table 2.

Table 2. Iso-electric pH values estimated from the electrophoretic mobilities (Fig. 5) and streaming current test results (Fig. 6)			
Polyelectrolyte sample	Iso-electric pH		
	From Fig. 5	From Fig. 6	Calculated
C3A5	4.4	4.1	4.7
C4A4.4	4.9	4.5	5.5
C5A4	5.8	6.0	8.4
C7A7	5.9	5.7	6.8 *
C50An	7.6	-	-

* Based on the midpoint of the half-dissociation points for the acid and basic groups, assuming equal activities.

Streaming Current Titration Results vs. pH

Streaming current titration is widely used to detect the colloidal charge. In this method, a polymer sample is titrated with an oppositely charged titrant until the streaming current reaches zero. As shown in Fig. 6, pH also affected the amounts of two fully charged, linear polyelectrolytes that were required to titrate amphoteric PAM solutions to a streaming current (SC) endpoint. Poly-diallyldimethylammonium chloride (poly-DADMAC) was used for all

titrations in which the initial SC signal was negative. Poly-vinylsulfate (PVSK) was used for titrations in which the initial signal was positive.

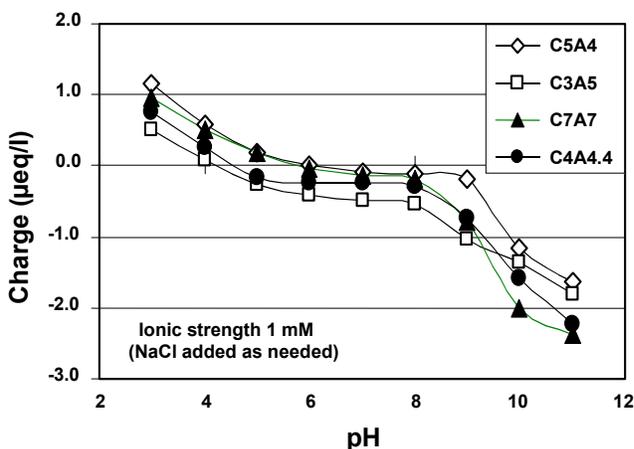


Fig. 6. Polyelectrolyte titration endpoint vs. pH for amphoteric PAM samples of differing monomer role ratio.

The first thing to note in Fig. 6 is the presence of a relatively flat plateau of apparent charge over a pH range of approximately 5 to 8. The relative flatness of these curves, near to the point of charge neutrality, is in contrast to the electrophoretic results just shown. The implication is that, despite the evident change in electric potential on the outside segments of the dissolved molecules, the polyampholytes had relatively low tendency to complex with the high-charge linear titrant molecules in the plateau region, especially poly-diallyldimethylammonium chloride, up to a pH of about 8. Such behavior is consistent with an expected tendency toward globular conformation of polyampholytes when charged groups of both sign are present within the same molecule [Higgs and Joanny, 1991]. Another factor to consider is whether there is a significant effect of ion pairs forming between carboxylate and ammonium groups within individual polyampholyte molecules within the intermediate pH range noted. It has been suggested that such ion-pairing can render such groups unavailable for interaction with

polyelectrolytes [Gruber and Ott, 1995]. Questions concerning whether oppositely charged groups exist as pairs or as free ions require further research [Bekturov *et al.*, 1990].

Keeping in mind the issues concerning the shapes of the curves, the cross points of the curves in Fig. 6 provide an alternative means to estimate the isoelectric pH values of the polymer samples. Such estimates are shown in the final column of Table 2. Caution should be used in the interpretation of these data in light of the shallow slope of some the curves where they cross the zero charge horizontal line; it is evident that only a minor shift in the vertical position of the line would have a major effect on the resulting estimate of iso-electric point. Placed in this context it is worth noting in Table 2 that the iso-electric pH values estimated from the streaming current tests were generally similar, and in the same sequence, as those obtained by the microelectrophoresis measurements.

To further interpret the data of Fig. 6, as a first approximation it is assumed that the titrants poly-DADMAC (for pH values below the iso-electric point of a given sample) and PVS₂K (for pH values above the iso-electric point) form 1:1 complexes with the charged groups on the polymers. This assumption has been found to be generally valid for linear polyelectrolytes having charged groups of just one sign, as long as the salt concentration is sufficiently low and the charge density is sufficiently high [Chen *et al.*, 2003]. Since amphoteric polyelectrolytes offer chances for intra-molecular interactions, it can be assumed that the standard titrants complex with the *net* charge of each amphoteric polyelectrolyte, at a given pH.

Results of these assumptions are shown in Fig. 7. As shown, the absolute value of the apparent charge, based on the polyelectrolyte titration endpoints, generally exceeded the predicted charge. Such behavior is consistent with the much higher charge density of the titrants compared to the polyampholyte [Chen *et al.*, 2003], and the known effect of order of addition

during polyelectrolyte titrations with a streaming current endpoint [Chen *et al.*, 2003]. The greater deviations observed at the extreme pH's are consistent with the higher ionic strengths of these values.

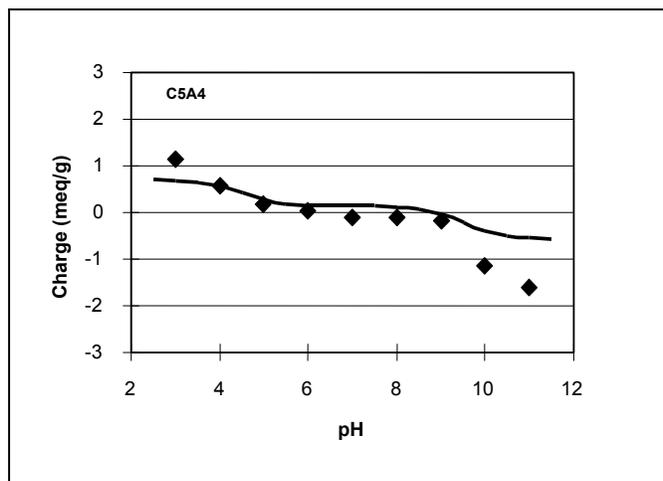


Fig. 7. Charge titration data, based on polyelectrolyte titrations of sample C5A4, compared with predictions based on an assumed 1:1 stoichiometry

Streaming current data for the more highly charged, net cationic polyelectrolyte C50An is shown in Fig.8. While the general shape of the curve is similar to those that were shown in Fig. 6, it is worth keeping in mind that the scale of the Y-axis is increased. The higher apparent cationic charge of the C50An polymer is consistent with its nominal content of 50% cationic groups. Despite the fact that the detailed structures of these polymers have not been disclosed, it is known that the mass per cationic monomer unit was larger than the corresponding masses of neutral or anionic monomer units. This explains why (Fig. 6 for polymer C5A4 at pH=3) the polyelectrolyte titration endpoint implied a charge density of positive 1.2 $\mu\text{eq/g}$, whereas the apparent charge density was only about seven times larger, despite having ten times the number concentration of cationic groups. The titrated values at the high end of the pH scale, *e.g.* at pH=11, imply a carboxyl content in the neighborhood of 10 %.

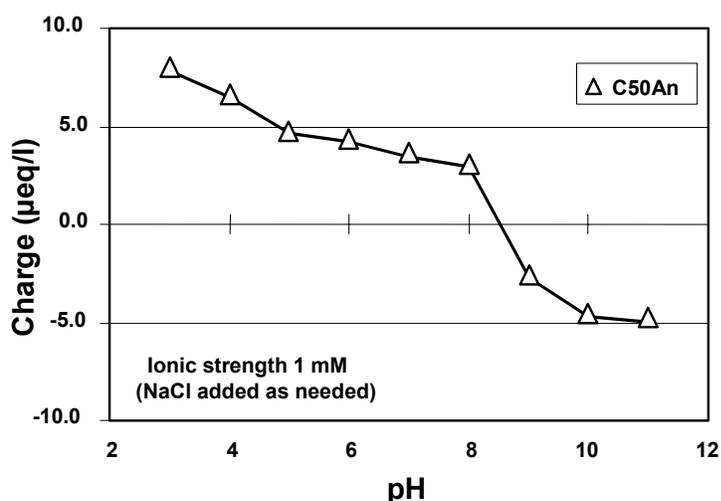


Fig. 8. Polyelectrolyte titration endpoint vs. pH for a high-cationic, amphoteric PAM sample (C50An).

Accounting for Isoelectric pH Values

According to Merle *et al.* [Merle *et al.*, 1980], the iso-electric pH of a polyampholyte having an excess of acid groups can be estimated from the following expression,

$$\text{pH}_{\text{is}} = \text{p}K_{\text{a}}^{\text{0}'} + \log [(1 - a) / (2a - 1)] \quad (4)$$

and in the case where base groups are in excess,

$$\text{pH}_{\text{is}} = \text{p}K_{\text{b}}^{\text{0}'} + \log [(1 - 2a) / a] \quad (5)$$

where a is the mole fraction of acidic to total ionizable groups. These expressions were used to calculate the expected isoelectric pH values for the first three samples represented in the final column of Table 2. At first glance the agreement of this estimate to the data appears poor.

However, it should be noted in Fig. 5 the streaming current endpoints, for samples other than C3A5, tended to remain close to zero as the pH was raised above the point where charge reversal was first evident. The calculated estimates of isoelectric points are in better agreement with the break points of the curves, where the measured charge density began to become significantly more negative with increasing pH. This level of agreement seems reasonable in light of various

factors that can affect the endpoint values of streaming current titrations [Chen *et al.*, 2001; Chen *et al.*, 2003]

It is more difficult to reconcile the calculated isoelectric points (last column of Table 2) with the corresponding values determined by microelectrophoresis. The fact that microelectrophoresis consistently yielded lower values for the isoelectric pH, compared to the calculated values, suggests that carboxyl groups tended to be enriched towards the outside of the adsorbed layer under the conditions of testing. It could be argued that potentiometric titrations are more reflective of bulk phenomena, whereas the microelectrophoresis and streaming current results are more influenced by surface conformation details. Further work is required to clarify this and other aspects of the structure of adsorbed layers of polyampholytes.

Viscosity Measurements

Results of solution viscosity tests (capillary method) are shown in Fig. 9 (A) for one of the amphoteric PAM solutions (C5A4). The following features, seen in Fig. 9 (A), have been previously described as characteristic for amphoteric polymers [Lowe and McCormick, 2002]: (a) the viscosity approached a minimum near the known isoelectric pH, and (b) the viscosity rose with increasing difference in pH relative to the iso-electric point (c) the viscosity was suppressed at the extremes pH's values. The initial rise in viscosity, with increasing pH difference from the iso-electric point is consistent with the mechanisms of intra-molecular charge repulsion [Lowe and McCormick, 2002]. The suppression of viscosity at extreme pH's has been attributed to shielding of electrical double layers at the higher electrolyte concentrations associated with pH value at increasing distances from the neutral point. It is also worth noting that the minimum viscosity, in this case, coincided with the iso-electric point of the C5A4 polymer (see Table 2).

The unfilled square symbols in Fig. 9 (A) correspond to sufficient sodium sulfate to reach a final electrical conductivity of 1500 $\mu\text{S}/\text{cm}$. The fact that the viscosity at pH 7 increased with increasing salt has been called an example of “anti-polyelectrolyte” behavior [Lowe *et al.*, 1999]. Such behavior has been attributed to the tendency of amphoteric polyelectrolytes to uncoil, approaching unperturbed coil dimensions in solution, similar to what an uncharged, soluble polymer would be expected to have. However the more important effect of salt appears to be the suppression of substantial viscosity contribution with increasing distance from the iso-electric point.

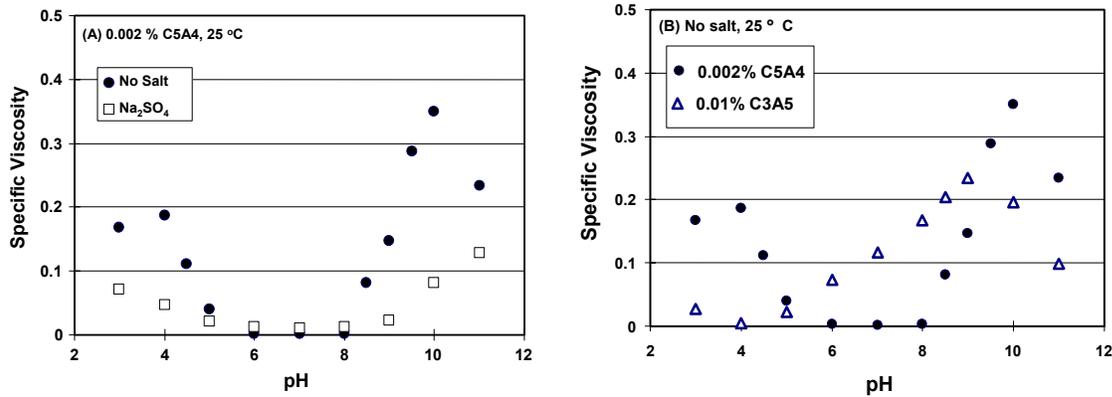


Fig. 9. (A) Specific viscosity of a 0.002% solution of amphoteric PAM (sample C5A4) as a function of pH in the presence or absence of sodium sulfate (used to adjust the electrical conductivity to 1500 $\mu\text{S}/\text{cm}$ throughout the pH range). (B) Specific viscosity of two amphoteric PAM solutions (C5A4 and C3A5) differing in monomer ratio, as a function of pH in the absence of added salt.

Figure 9 (B) shows related data, comparing cases of different amphoteric PAM samples. It should be noted that the minima in specific viscosity correspond roughly to the iso-electric points shown in Table 2. Based on these results it is reasonable to expect that products C5A4 and C3A5 might have very different optimum pH values when they are used as strength additives in papermaking operations.

Turbidity

A further manifestation of the amphoteric character of one of the polyampholyte samples is shown in Fig. 10. It will be noted that the position of the turbidity maximum, near to pH 6 or 7, coincided approximately with the iso-electric pH values shown earlier. The higher turbidity is consistent with decreased solubility of the polyampholyte molecules, such that they coagulate, forming a suspension of particles large enough to scatter light. A tendency for such insolubility at the neutral point is strongly predicted by thermodynamic considerations [Everaers *et al.*, 1997]. The high turbidity near to the point charge equivalency is analogous to what is sometimes observed during of titrations between oppositely charged polyelectrolytes, each bearing only one sign of charge [Chen *et al.*, 2003].

Interestingly, although salt generally suppressed the development of turbidity, there was increased turbidity at the higher salt level at pH values more than about 1 or 1.5 units away from the isoelectric point. This effect is tentatively attributed to a generalized coagulating effect of increased salt content, regardless of the detailed charge makeup of the polymers.

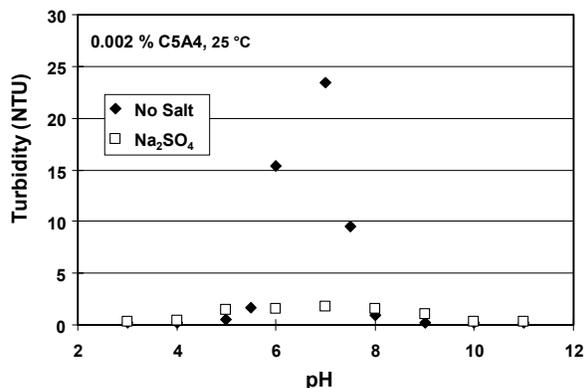


Fig. 10. Turbidity as a function of pH for a 0.002% solution of amphoteric PAM (C5A4) as a function of pH in the presence of absence of sodium sulfate (used to adjust the electrical conductivity to 1500 $\mu\text{S}/\text{cm}$ throughout the pH range).

Industrial Implications

Results of this study have shown that some of the most characteristic features of the amphoteric polyelectrolytes under study were manifested at or near the iso-electric pH values of the samples. Consequently, one strategy of implementing these materials industrially, and seeking unique effects, would involve selecting the polymers having suitable iso-electric pH values near those of industrial streams, *e.g.* in papermaking or water treatment. Despite the fact that the present results suggest that the isoelectric condition minimizes the molecular extension of the polyampholytes, it needs to be seen whether the same condition maximize their adsorption onto papermaking solids. Further work from our laboratory will report on the results of this effort in which the same amphoteric polyelectrolytes are added to a papermaking furnish.

4. Conclusions

1. The amphoteric acrylamide-based polyelectrolytes described showed many colloid-chemical features that are common to their class of compounds. These included evidence of two different kinds of dissociable groups in the potentiometric data, iso-electric pH values that appear related to monomeric compositions, pH-dependent behavior that included increasing positive and negative electrophoretic mobility with distance from the iso-electric point, minimum solution viscosity in the vicinity of the iso-electric point, and maximum turbidity when the isoelectric point was achieved at a low salt content of the solution.
2. It was not possible to interpret potentiometric data based solely on assumed values of dissociation constants K_a and K_b . Rather it was necessary also to assume either a delayed dissociation of carboxyl groups or a significant effect of neighbor carboxyl groups on the progress of dissociation.

3. The electrophoretic mobilities of the polyampholytes changed relatively rapidly with pH in the neighborhood of the isoelectric pH values, consistent with a tendency of any excess of charged groups to express itself at the surface of a polyampholyte molecule in solution.
4. Results of colloidal titration tests with poly-diallyldimethylammonium chloride and the potassium salt of poly-vinylsulfate, using streaming current to detect the endpoints, revealed a range of pH, usually between about 5 and 8, over which the polyampholytes had relatively little apparent charge density.
5. Viscometric and turbidimetric test results showed evidence of anti-polyelectrolyte behavior. Addition of salt to polyampholyte solution near to the isoelectric pH value increased the observed specific viscosity and suppressed the tendency for development of high turbidity.

Acknowledgement. The amphoteric acrylamide copolymer samples were provided by Harima Chemical Co., Ltd. Financial support by Harima for graduate educational support is gratefully acknowledged.

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4.2. Papers – Part 2

Colloidal Effects of Amphoteric Acrylamide Copolymers. 2. Adsorption onto Cellulosic Fibers

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{{FOOTNOTES}}

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A colloidal titration of several commercial amphoteric acrylamide-based polyelectrolytes using a streaming current technique was performed at either pH 3 or 11, where the polyampholytes are considered to be fully in their respective cationic or anionic forms and to act as simple polyelectrolytes. This method was found to be useful in order to determine the concentration of polyampholytes. The titration endpoint to reach the zero streaming current (SC) signal deviated from a 1:1 stoichiometry, depending on the salt concentration. It was also dependent on titration methods, indicating that rate of forming equilibrated poly-ion complexes between polyampholytes and titrants was relatively slow. Adsorption of the amphoteric polyacrylamide copolymers onto bleached hardwood fibers was found to be significantly affected by pH. The adsorption of the polyampholytes was maximized around the isoelectric point, and it was reduced as the pH shifted from the iso-electric pH to either the acidic or alkaline side. It was found that net neutral and negatively charged polyampholytes also adsorbed onto the negatively charged fibers. Addition of salt tended to increase the adsorption up to a conductivity of 1000 $\mu\text{S}/\text{cm}$. Also, the adsorption was slightly increased with increasing time for adsorption, but its

increase leveled off after a certain time. The stirring rate during adsorption was not an important factor for adsorption under the conditions used in the present work.

1. Introduction

Part 1 of this series considered the colloidal nature of certain amphoteric acrylamide copolymer products that have become used within the paper industry as a means of increasing the strength of fiber-to-fiber bonding. It was shown that the charged nature and other colloidal attributes of the copolymers depended on conditions of pH, salt concentration, and molar ratio of cationic and anionic groups. The present article goes one step further and considers how changes in these aqueous conditions affect the copolymers' ability to adsorb onto cellulosic fibers.

A motivating question for the present work has been whether or not adsorption of the amphoteric polymers under study generally follow the adsorption behavior associated with polyelectrolytes having ionized groups of just one sign of charge, or whether it is necessary to consider both the negative and positive groups in order to adequately describe their adsorptive behavior. In addition to the scientific importance of this question, the work also is motivated by a need to increase the efficiency of chemical treatments designed to increase the dry-strength characteristics of paper [Tanaka, 1994], a need which becomes increasingly important with increases in the amount of paper that is recycled. Various polyelectrolytes, including cationic starch [Howard and Jowsey, 1989; Glittenberg, 1993], copolymers of acrylamide [Carlsson *et al.*, 1977; Farley, 1986], and sequential addition of positively and negatively charged additives [Carr *et al.*, 1977] have been used to overcome deficiencies in the wetted fibers' ability to bond to each other when the paper is dried. Amphoteric copolymers, which also can be added to the fibrous

suspension in a paper mill [Tanaka *et al.*, 1976], represent an additional option for papermakers to increase paper strength.

Aspects of polyelectrolyte adsorption onto cellulosic fibers recently were reviewed by Wågberg [Wågberg, 2000], who paid particular attention to some recent advances [Böhmer *et al.*, 1990; Fleer *et al.*, 1993]. Though the reader is directed to these sources for full descriptions, the key point is that there has been reasonable success in accounting for effects of charge densities, salt concentrations, pH, and other variables on the adsorbed amounts and conformations of polyelectrolytes, especially those which contain only a single type of charged group. For example, it has been shown that adsorption of polyelectrolytes onto surfaces of opposite charge frequently are maximized when the charge density of the polyelectrolyte is quite low [Davison and Cates, 1975], a circumstance that often favors a three-dimensional conformation of the polyelectrolyte in the adsorbed state [Fleer *et al.*, 1993; Ödberg *et al.*, 1995; Sukhishvili and Granick, 1998; Vermohlen, 2000]. Increased levels of salt addition typically result in increased adsorbed amounts, though adsorption usually falls again or is effectively eliminated at very high levels of electrical conductivity in the solution [Lindström and Wågberg, 1983]

Adsorption characteristics of amphoteric polyelectrolytes have been considered in various theoretical [Joanny, 1994; Dobrynin *et al.*, 1997; Dobrynin *et al.*, 1999; Khan *et al.*, 2001] and experimental [Ozon *et al.*, 2002] studies. Although the theoretical studies using a mean-field approach [Dobrynin *et al.*, 1997] have come to conclusions that are slightly different from the results treated by Monte Carlo simulations [Khan *et al.*, 2001], most of the predictions are in agreement with experimental results. Their predictions coincide with the fact that polyampholyte chains tend to collapse and precipitate at iso-electric pH, and addition of salt can

lead to the expansion of the collapsed state. Also, the predictions state that even neutral and similarly charged polyampholytes can adsorb onto charged surfaces. These characteristics are unique to polyampholytes and cannot be seen in simple polyelectrolytes.

2. Experimental Section

The polyelectrolytes considered in this work (Table 1) were the same as those used in Part 1. All the samples were provided by Harima Chemicals, Inc.

Polyelectrolyte sample	Cationic groups mol %	Anionic groups ¹⁾ mol %	Molecular weight 10 ⁶	Iso-electric point ²⁾
C3A5	3.0	5.0	2.5	4.1
C5A4	5.0	4.0	3.0	4.5
C7A7	7.0	7.0	1.2	6.0

1) Diacidic monomers were used.

2) Iso-electric points were determined by colloidal titrations.

The cellulosic fibers used in the experiments to be described were obtained from conventional bleached hardwood (HW) kraft pulp, which was supplied in the form of dry-lap sheets. Pulp disintegration and refining were carried out according to TAPPI Method T248. A batch of 30.0 oven-dry grams of HW pulp sheet was soaked in 2000 ml of deionized water for more than 4 hours. The soaked sheet was disintegrated for 15000 revolutions. The slurry was drained and the total mass was adjusted to 300 g (10% consistency). It was refined with a PFI mill for 5000 revs. The refined pulp was diluted to 2000 ml with deionized water and disintegrated for 15000 revs (CSF 400 ml).

Fines removal was accomplished with a modification of TAPPI Test Method T233. Different conditions (sample amount, flow rate, and time) were used. Each 30 g oven-dry sub-batch of pulp was put in the final container of the Bauer-McNett classifier, which was fitted with

a 100-mesh screen. Tap water was allowed to flow at 6 l/min for 30 min. The fines-free fibers (72 % retained, percent fines measured by the Fiber Quality Analyzer (FQA): 2.5 % based on arithmetic amounts, 0.4 % based on length-weighted amounts) were taken from the container. The selected criterion for fines, when running tests with the FQA, was anything smaller than 0.2 mm that still was detectable by the equipment. The tap water was replaced with deionized water. The resulting Canadian Standard Freeness of the fines-free suspension was 680 ml. The consistency was adjusted to 0.5 % with deionized water.

The procedure used to determine adsorbed amounts of adsorbed amphoteric polyelectrolyte was based on the principles of colloidal titration [Terayama, 1952] and streaming current analysis [Cardwell, 1966]. However, drawing on results that were shown in Part 1, the new procedure also involved pH adjustments to convert the polyampholytes into either their fully cationic or fully anionic forms.

Both pH and conductivity of the fines-free pulp slurry (consistency 0.5 %) were adjusted by addition of NaOH or H₂SO₄. The same procedures were used to adjust the 0.1 % PAM solution to the same values of pH and conductivity as the slurry. 200 g of the slurry was placed in a 250 ml glass beaker. The slurry was stirred with a mechanical stirrer at a given speed (500 rpm). A given amount of PAM solution was added to the slurry (1 % of fiber). The mixture was stirred for a given time (5 min). The slurry was filtered with a 400-mesh screen.

The amount of PAM copolymer in the filtrate was determined by colloidal titration as follows. The pH of the filtrate was adjusted to 3.0, and the conductivity was set to 2000 μ S/cm with Na₂SO₄. Ten ml of the sample was put in the measuring cell of a Müttek particle Charge Detector (PCD 03 pH). PVSK solution (0.001 N) was added slowly until the streaming current value reached to zero and the amount of the titrant added was recorded. This value was

compared with that of a blank test, in which no fiber was used, to calculate the adsorbed amount of PAM.

3. Results and Discussion

Method Development.

The adsorption experiments to be described in this report were based on determination of solution concentrations of amphoteric polymers. In other words, the adsorbed amounts were determined by difference, based on analysis of the concentrations remaining in solution.

Therefore, results related to development of the needed test procedure will be shown first.

An example of a baseline calibration between the two main analytical titrants used in this work is shown in Fig. 1. The data points indicate the endpoint of the titrations between an initial poly-vinylsulfate, potassium salt (PVSK) solution by addition of poly-diallyldimethylammonium chloride (poly-DADMAC).

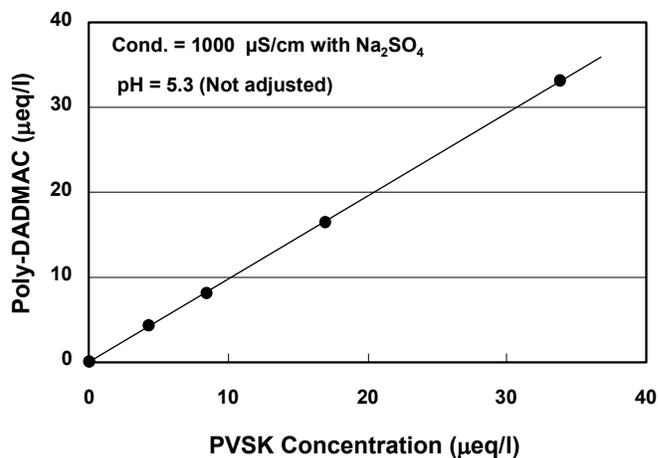


Fig. 1. Concentrations of poly-DADMAC at the titration endpoint corresponding to the initial PVSK concentrations.

Results shown in Fig. 1 are consistent with previous work, showing an approximately 1:1 stoichiometry of charged groups, especially under conditions of relatively low ionic strength [Chen *et al.*, 2003]. More importantly, the stoichiometry of the endpoints did not depend on the initial concentration, within the range of study.

The next set of results to consider involved titration of the polyampholyte sample “C5A4,” noting that the label indicates a content 5% cationic groups and 4% anionic groups on a molar basis. In this experiment that solution was adjusted to a pH value of 11 in order to make sure that essentially all of the carboxyl groups were present in their dissociated, carboxylate form, and that essentially all of the amine groups were uncharged. As shown in Fig. 2, it was found that the ratio of poly-DADMAC to polyampholyte at the streaming current endpoints depended on the concentration of monomeric electrolytes. The results in the case where no additional salts had been added, other than those already in the polyelectrolyte products, showed better repeatability, and also the endpoint values increased linearly with increasing concentration of C5A4 in the initial solution. By contrast, results were more scattered when considering tests carried out in the presence of an additional 100 ppm calcium chloride plus sufficient sodium sulfate to bring the final electrical conductivity to 1760 $\mu\text{S}/\text{cm}$ after the pH adjustment.

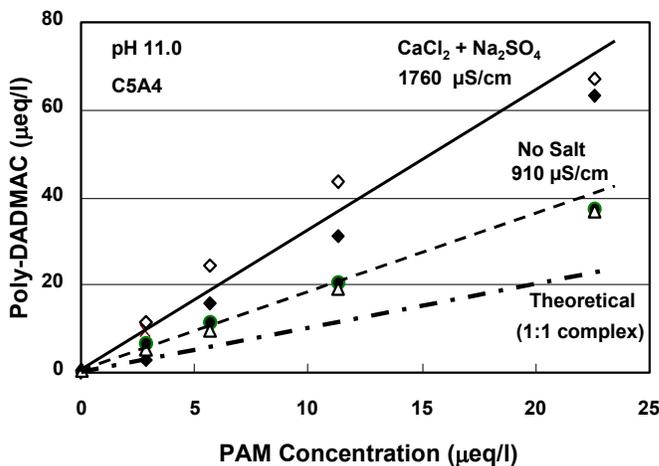


Fig. 2. Concentrations of poly-DADMAC at the titration endpoint corresponding to the initial amphoteric polyacrylamide (sample C4A4) concentrations at pH 11 in different salt concentrations.

The dashed line in Fig. 2 represents an expected value if it were assumed that each negative group on the polyampholyte effectively forms an ion pair with a corresponding positive group on the titrant molecule. In addition, any remaining amine groups still in their positively charged state at pH 11, were ignored. Relative to this line the poly-DADMAC appears to interact inefficiently with the polyampholyte, so that more than the expected amount was required to reach a streaming current endpoint. The ratio of actual to expected amounts of poly-DADMAC required to reach the endpoint was calculated as 1.8 based on Fig.2 and 1.5 based on Fig. 4 for titrations in the absence of added salt, and approximately 3 in the presence of the added salts. The general trend of these deviations from the dashed line agree with two different contributing factors that have been described in earlier work. On the one hand there is an expectation that one-to-one stoichiometry will become difficult to achieve when titrations involve polyelectrolytes of very different charge density; it is expected in such cases that not all of the groups on the more highly charged polymer will be engaged in the complexation [Tse, 1979; Haronska *et al.*, 1989]. In addition, it recently was shown that results of titrations between strong polyelectrolyte of high charge density can depend on the direction of titration, especially when the level of background electrolyte is increased [Chen *et al.*, 2003]. The effect was attributed to the presence of charge-stabilized polyelectrolyte complexes in the solution phase when the streaming current endpoint was reached. The same mechanism provides a reason to expect that the poly-DADMAC would appear even more inefficient, in terms of charge interactions, at the higher electrical conductivity.

Calibration Tests at pH 11

Results of some preliminary tests suggested that some of the scatter of data shown in Fig. 2 may have been due to a kinetic effect, related to the time needed to obtain a steady streaming current signal. This possibility was evaluated by comparing results of relatively rapid titration, using an auto-titrator, with manual tests in which streaming current signals were observed 5 minutes after each addition of titrant. A typical automatic titration took approximately 1 to 2 minutes after each addition of titrant. A typical automatic titration took approximately 1 to 2 minutes to complete, whereas a typical manual titration took 20 to 40 minutes. Figure 3 shows a new series of experiments in which the slower rate of titration yielded results closer to the theoretical line. For reasons of relatively high linearity and repeatability, the manual titration method was selected for further work involving adjustment of the pH to 11.

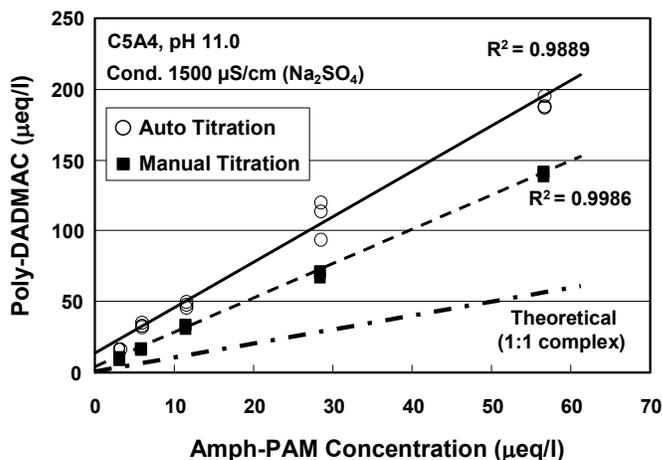


Fig. 3. Concentrations of poly-DADMAC at the titration endpoint corresponding to the initial amphoteric polyacrylamide (sample C4A4) concentrations at pH 11 in different titration procedures.

The fact that the slower titration came closer to the line representing 1:1 pairing suggests a process in which the polyelectrolytes gradually adjust their respective conformations in order to enable a more and more efficient usage of the titrant groups already present at each stage of a

titration. Periods of conformational adjustment in the range of almost zero to 30 seconds have been suggested in a recent review [Swerin and Ödberg, 1997].

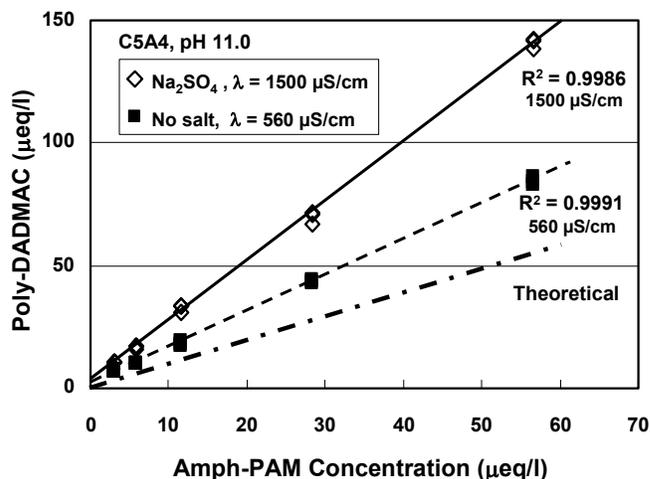


Fig. 4. Concentrations of poly-DADMAC at the titration endpoint corresponding to the initial amphoteric polyacrylamide (sample C4A4) concentrations at pH 11 in different salt concentrations using the manual titration method

Using the manual method demonstrated in Fig. 3, the conditions represented in Fig. 2 were then repeated. As shown in Fig. 4 the main trends agreed with Fig. 2, but the repeatability was improved, as indicated by the high values for coefficients of determination.

Calibration Tests at pH 3

Figure 5 shows the results of automatic and manual titrations with PVSU carried out at pH 3, conditions intended to convert the polyampholytes into their most fully cationic form. It is interesting that the results from auto-titration showed some of the same non-linear tendency as was apparent in the upper curve of Fig. 2. Again, the manual titration involved more efficient utilization of the titrant.

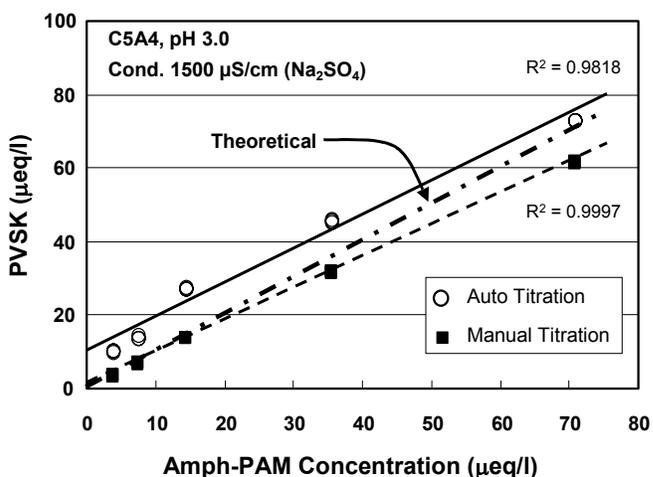


Fig. 5. Concentrations of PVS-K at the titration endpoint corresponding to the initial amphoteric polyacrylamide (sample C4A4) concentrations at pH 3 in different titration procedures.

As shown in Fig. 6, titrations carried out at pH 3 were much less affected by salt, compared to the pH 11 results that were shown in Figs. 2 and 4. Based on the high linearity and repeatability of these results, the condition represented by the upper curve was selected for all of the adsorption experiments to be described. The reason for adding background electrolyte was to reduce the relative change in ionic strength of solution, during titrations, that results from ions that enter the mixture with the titrant solution.

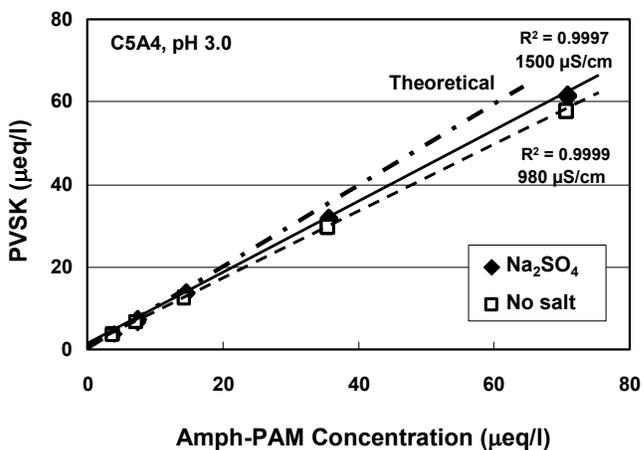


Fig. 6. Concentrations of PVS_K at the titration endpoint corresponding to the initial amphoteric polyacrylamide (sample C4A4) concentrations at pH 3 in different salt concentrations

It is worth noting that in Fig. 6 the data points fell quite close to or below the theoretical line (dashed) based on 1:1 stoichiometry. This contrasts with the situation in Figs. 2 through 5, which dealt with poly-DADMAC titrations at pH 3. The reasons for this difference have not been determined. Likely contributing factors include possible hydrolysis of amine groups in the copolymer [Caulfield *et al.*, 2003] and the proximity of the pK_a of the polyacid groups to the titration pH [Alfry and Pinner, 1957; Bekturov, 1990; Lowe and McCormick, 2002].

Up to this point, all of the results shown have involved just one of the three polyampholyte samples considered in this work. Figure 7 compares the calibration curves for polyampholytes having three different monomeric compositions. Since the titrations represented in the figure were carried out at a pH of 3, one would anticipate the results to depend on the content of amine groups in each product. However, it was not expected that the highest demand for the anionic PVS_K would be observed in the case of a polyelectrolyte having 5% amine groups, compared to sample C7A7 that had 7% amine groups. Although these results have not been explained, it is worth emphasizing that the PVS_K titrant acted inefficiently, in terms of ion pairing, in all of these cases. Therefore it is reasonable to expect kinetic factors, as mentioned earlier, to interfere with expectations based solely on stoichiometric relationships.

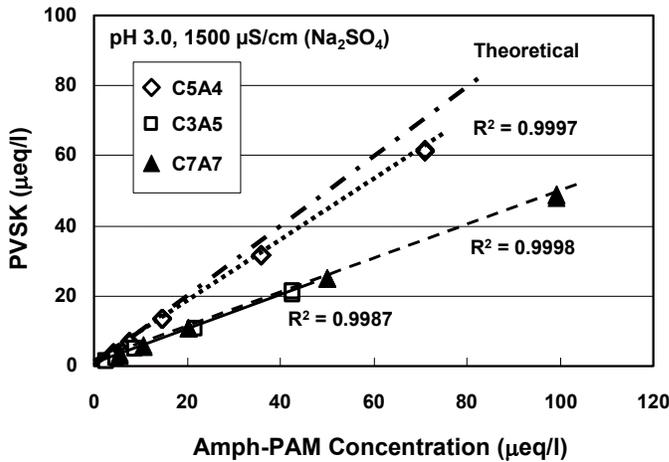


Fig. 7. Concentrations of PVSK at the titration endpoint corresponding to the initial amphoteric polyacrylamide concentrations at pH 3 using different polyacrylamide products.

Results of Adsorption Experiments

In light of the observed importance of titration rate, it is reasonable to expect that the adsorbed amount of polyampholyte onto cellulosic fibers should depend on the time of mixing. Figure 8 shows such an effect, but it also shows that the adsorbed amount already had reached about 90% of its plateau value after 5 minutes. Subsequent tests were carried out at the same five-minute mixing condition.

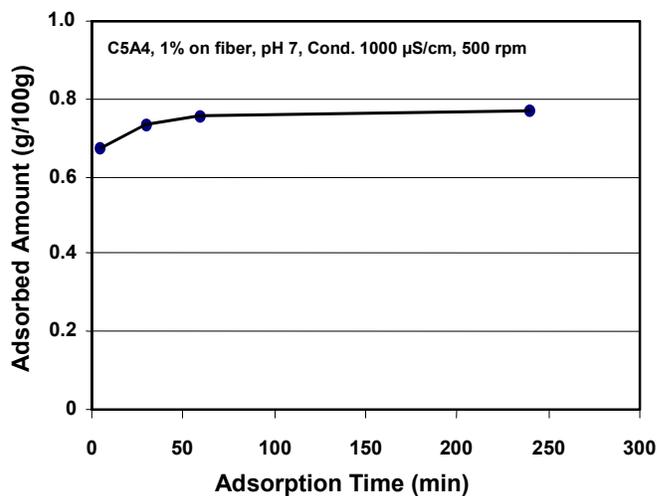


Fig. 8. Adsorption of the amphoteric polyacrylamide onto cellulosic fibers: Effect of adsorption time.

Rates of adsorption from solution sometimes are limited slow convection or diffusion from the bulk solution onto the surfaces [Swerin and Ödberg, 1997]. To test this possibility, experiments were repeated at different rates of agitation with an impeller stirrer. As shown in Fig. 9, such variations in stirring rate did not affect the adsorbed amounts under the conditions used in the present work.

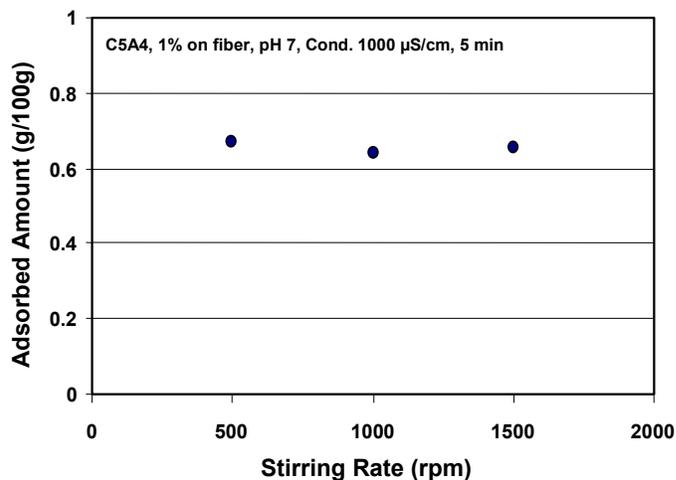


Fig. 9. Adsorption of the amphoteric polyacrylamide onto cellulosic fibers: Effect of stirring rates.

Effect of Salt

Effects of increasing salt (sodium sulfate) are shown in Fig. 10. The fact that adsorption increased with increasing electrical conductivity is an example of what has been called “ordinary polyelectrolyte behavior” [Lindström and Wågberg, 1983]. In other words, the results are consistent with a trend towards less extended molecular conformations with increasing shielding of charged groups within polyelectrolytes by monomeric ions. It is worth noting that under some conditions polyampholytes swell with increasing salt, presumably due to a weakening of intra-

molecular associations between charged groups [Lowe *et al.*, 1999], an effect that is especially anticipated in the case of interactions of block copolymer polyampholytes. The fact that the present results are better described by ordinary polyelectrolyte considerations suggests that the degree of ion pairing within a given molecule did not change greatly within the range of conditions considered in this work. Though it has been suggested that ions pairs within a polyampholyte molecule may be effectively unavailable for interaction [Gruber and Ott, 1995], the present results do not provide a sufficient basis to judge this issue.

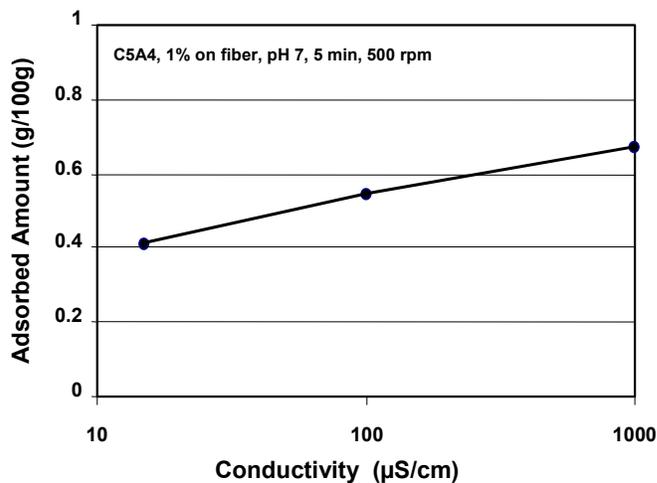


Fig. 10. Adsorption of the amphoteric polyacrylamide onto cellulosic fibers: Effect of conductivity.

Effects of pH

Figure 11 shows raw data from experiments carried out at different pH values. The results were based on titrations carried out at pH 3 with poly-DADMAC. Adsorbed amounts ranged from near zero up to almost 100% of the added amount in various cases, though the efficiency of adsorption generally declined with increasing levels of addition. The greatest adsorption was observed at pH 5. With the exception of a few results corresponding to pH

values of 7 and 9, the adsorbed amount generally declined as the pH became more and more different from 5.

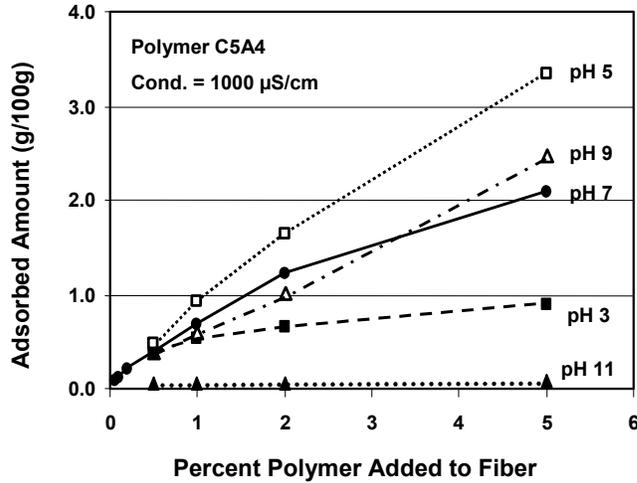


Fig. 11. Adsorption of the amphoteric polyacrylamide onto cellulosic fibers in various pH values: Percent polymer added to fiber basis.

To show a different aspect of the results, Fig. 12 presents the adsorbed amounts relative to the final concentrations in solution. From this perspective it is apparent that the plateau values of adsorption were not yet reached, except possibly at the extreme pH values of 3 and 11. Values of adsorbed amounts above 2% are noteworthy in light of the fact that fiber fines had been removed from the fiber suspension (see Experimental), a procedure that is expected to reduce the overall surface area per unit mass of cellulosic materials [Marton, 1980, 1991]. Even in the presence of fiber fines, other papermaking additives such as cationic starch usually do not adsorb efficiently onto fibers at quantities greater than 2% [Marton, J. and Marton, T., 1976].

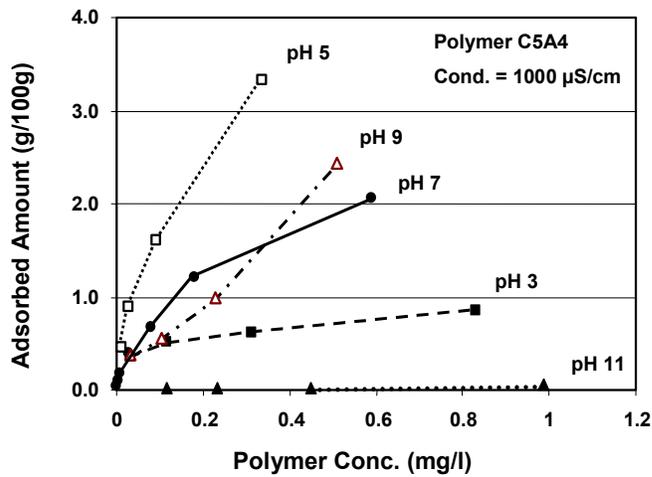


Fig. 12. Adsorption of the amphoteric polyacrylamide onto cellulosic fibers in various pH values: Polymer concentration basis.

Figure 13 shows results of numerous adsorption tests carried out with the same polyampholyte sample over a range of different pH values. As shown, the maximum adsorption took place at a pH of 5, which was a little lower than the iso-electric pH. As the pH was increased, the adsorbed amount decreased gradually up to about pH 9, and then fell rapidly. The decrease in adsorbed amount also was relatively abrupt as the pH was decreased below 5 to yet lower values.

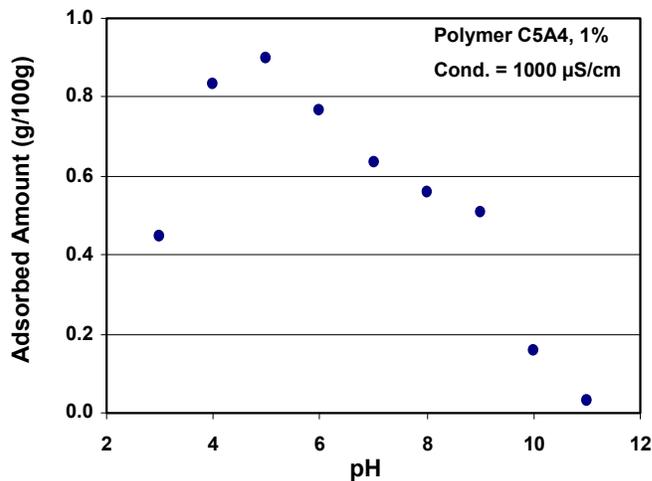


Fig. 13. Adsorption of the amphoteric polyacrylamide onto cellulosic fibers: Effect of pH.

To understand the results in Fig. 13 it is worth noting that three different types of charged groups are expected to govern adsorption under such circumstances. In addition to the carboxyl and amino groups on the polyampholyte molecules, one also needs to consider carboxyl groups that mainly determine the charged nature of bleached kraft fibers in aqueous solution [Bygrave and Englezos, 1998]. The latter provide a net negative charge suitable for adsorption of net cationic polymers. However, the pK_a value of such surface-bound carboxyl groups is expected to be near to 4.4. Since even the maximum charge density at the surfaces of bleached kraft fibers already is quite low [Lloyd and Horne, 1993], it is reasonable to expect the charge density of the fibers to become a limiting factor in adsorption, especially as the pH is decreased below the pK_a value of those groups. On the other hand, as pH is increased above 5, the majority of carboxyl groups already are expected to be in their negative, carboxylate form. As shown in Part 1 of this series, the predominant pK_b value of the amine groups in the polyampholytes under consideration was approximately 9. Thus, a steep fall-off in adsorption at pH values higher than 9 is consistent with increasing neutralization of the amine groups on the polyampholyte. The iso-electric point of the polyampholyte examined here was 6.0, as measured in the previous study. In a pH range above 6.0, both the polyampholyte and fibers are expected to be negative in net charge. However, the polyampholyte still had an ability to adsorb onto similarly charged fibers. This result coincides with recent theoretical study with regard to adsorption of polyampholytes on charged surfaces [Dobrynin *et al.*, 1999].

Figure 14 shows results that are closely related to those in Fig. 13, except that a fresh batch of hardwood fibers was used. First it is worth noting the excellent agreement between the results shown for the C5A4 sample in Figs. 14 and 13. For the other two polyampholyte samples

no results are shown above a pH value of 7 because the streaming current endpoints were not sufficiently distinct. The most important differences between the respective polyampholyte samples were observed at a pH value of 3. Surprisingly, the adsorbed amounts did not correspond in a clear way to the respective cationic charge densities of the adsorbing polymers. Rather, the trend is roughly consistent with how the polymers interacted with PVSF at pH 3, as was shown in Fig. 7. Again, such results suggest that charge interactions are not the only factor governing the stoichiometry of interaction. Rather, future work also should consider detailed structural factors such as the randomness or blockiness of different polyampholyte samples.

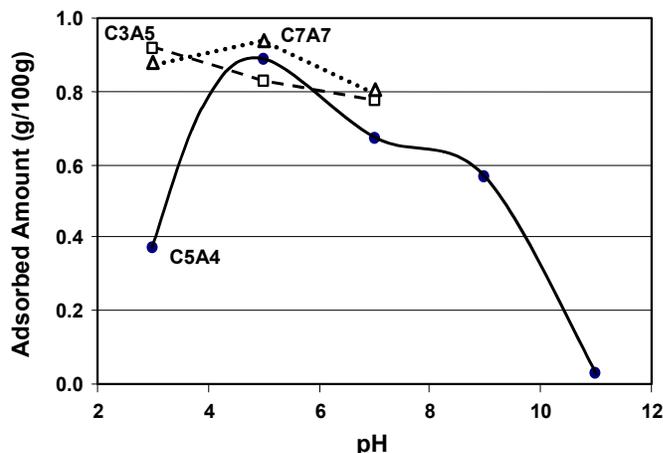


Fig. 14. Adsorption of the amphoteric polyacrylamide onto cellulosic fibers using different polyampholytes.

4. Conclusions

1. SC titration method was demonstrated as a means of quantifying the concentration in solution. Results at high pH (to sense only the carboxyl functional groups) and low pH (to sense only the amine functional groups) agreed with each other precisely.

2. It is beneficial to allow more equilibration time, rather than to use a typical automatic titration rate. Modified SC titration procedure yielded linear calibration curves with coefficients of determination close to 1.
3. Adsorption amounts of amphoteric polyacrylamides onto cellulose tended to be maximized around their iso-electric points, but maximal adsorption also favored conditions where the net charge of the polyelectrolyte was opposite to that of the substrate surface.
4. Adsorption amounts onto cellulose showed a similar tendency to polyelectrolyte behavior with respect to salt concentration up to the medium level of electrical conductivity examined in this study.
5. Amphoteric polyacrylamides with negative net charge had an ability to adsorb onto negatively charged fibers. Adsorption amounts of amphoteric polyacrylamides were greater than those of typical cationic polyelectrolytes.

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5. CONCLUSIONS

The potentiometric titration curves for the polyampholyte samples showed a good agreement with the theoretical calculation, except within the pH range from 4 to 8. The reasons that the theoretical curves did not match the experimental curves only in this range may be that (1) the pK_a was not a single value as was originally assumed, because diacidic monomers were used to synthesize the polyampholytes, or (2) some precipitation was observed in this range, which might disturb the accuracy of the potentiometry.

The iso-electric points, which were determined from the results of two methods, microelectrophoresis and colloidal titration using the streaming current technique, were almost in agreement with each other. For the microelectrophoresis, microcrystalline cellulose powder was used as cores for colloidal particles. This agreement of the iso-electric point using two methods is consistent with an assumption that the microcrystalline cellulose surfaces were totally covered with the polyacrylamides and the outer layer of the covering polyacrylamides dominated the electrophoretic behaviors. The experimental iso-electric points were different from the theoretical ones. The gaps between theory and experiment may be attributed to (1) molar ratios of the acidic and basic groups were changed from the provided data due to unexpected hydrolysis or decomposition, or (2) the pK_a and/or pK_b for the acidic and basic groups of the polyampholytes were different from the assumed values due to nearest neighbor interactions caused by the close proximity of the same functional groups.

The viscosity of amphoteric PAMs was minimized around the iso-electric point. In the case of no salt, the viscosity increased as the pH was adjusted to be increasingly removed from the iso-

electric point towards either the acidic or alkaline side. This increase leveled off and started to decrease when the pH was yet further away from the iso-electric point. This could be explained due to the fact that electrostatic repulsions between the charged groups are screened when the ionic strength is high. In the presence of salt, the screening effect of salt ions was so significant that the viscosity did not change a lot throughout a wide pH range. Consequently, the viscosity under high salt conditions was greater than that of no salt conditions around the iso-electric point, while this relationship was reversed in low and high pH regions. These results are consistent with those reported for random polyampholytes. The turbidity curve of polyampholyte solution as a function of the solution pH revealed the maximum adsorption around the iso-electric point. In the same manner as the viscometric behavior, the turbidity was not affected a lot by the pH. The turbidimetric behavior was consistent with the viscometric behavior from the point of view of how a polymer chain stretches in solution.

Colloidal titrations of amphoteric polyacrylamides possessing weak acid and base groups were carried out at pH 3 or 11, where one of the acidic and basic functional groups was almost completely ionized, and the other remained neutral. A plot of the polyampholyte concentration against the required amount of the oppositely charged polyelectrolyte that brought the streaming current signal to zero gave a linear regression with a coefficient of determination close to 1. This result brings us to conclude that the colloidal titration technique with streaming current measurement is applicable to determine the concentration of amphoteric polyacrylamides. The titration should be carried out carefully, since time for the conformational equilibration of the poly-ion complexes between the polyampholyte sample and the titrant is needed in order to obtain stable streaming current signals compared to polyelectrolytes possessing strong base or

acid groups. For a precise measurement, streaming current signals are recommended to be observed when they become stable after each aliquot of titrant is added (5 minutes for the present experiment). This method is quite useful when adsorption of polyampholytes onto fibers is investigated in up to medium salt concentrations (0 - 10mS/cm).

Adsorption of the amphoteric polyacrylamides onto fibers was strongly affected by pH. Unlike uncharged polymers, the polyampholytes in the neutral state were adsorbed onto charged fibers. Even the polyampholytes with negative net charge, which were in solution at pH higher than the iso-electric point, were adsorbed. This behavior cannot be seen in the case of polyelectrolytes. This might be because polyampholytes can be polarized by the electric field caused by the charged surface when they are close enough to the surface, as predicted in the theory by Dobrynin *et al.* [Dobrynin *et al.*, 1997]

The adsorption increased as the conductivity increased up to 1000 $\mu\text{S}/\text{cm}$. At values of conductivity more than 10 mS/cm it was difficult to apply the colloidal titration method, since the absolute signal from a streaming current detector became too low to obtain the accurate titration endpoint. The longer the adsorption time, the greater were the amounts of polyampholytes that tended to be adsorbed. However, this time effect was slight, and the adsorption was almost leveled off in 10 minutes. Stirring speeds of 500, 1000, and 1500 rpm during the adsorbing stage did not make a significant difference to the adsorption.

The maximum adsorption of polyampholytes was achieved when the pH was a little lower than the iso-electric point. When the pH is shifted to the acidic side from the iso-electric pH, two

effects on adsorption will occur: (1) the positive charge on polyampholyte chains increases, which increases the electrostatic attractions between polyampholytes and fibers, and (2) the negative charge on fiber surface decreases, which decrease the attractions. In addition, considering the fact that slightly charged polyelectrolytes are more adsorbed on oppositely charged materials than strongly charged polyampholytes, the pH that was a little lower than iso-electric point was appropriate for the maximum adsorption.

6. SUGGESTED WORK

In this study, basic colloidal behaviors of amphoteric dry strength additives were investigated. To make a connection between these colloidal and the strength properties of paper, it is worth measuring the drainage, flocculation, and strength properties using the amphoteric polyacrylamides. These experiments are suggested to be carried out under the same conditions as the adsorption experiments. In the present work, it was shown that the charge balance of the polyampholytes played an important role in colloidal behaviors. The iso-electric point was considered as a specific pH at which polyampholytes can attain a unique properties, which cannot be seen in polyelectrolytes. Based on this knowledge, it is of interesting to see whether or not the drainage, flocculation, and strength properties are maximized around the iso-electric point. By adjusting the adsorbed amount of polyampholytes onto fibers over a range of pH using the adsorption isotherms, it may be found how the polyampholyte conformations affect the strength properties. Since the pH itself in papermaking conditions will also affect the strength properties of paper, the control strength properties should be measured for each pH.

It was found that the experimental iso-electric points of amphoteric polyacrylamides differed from those calculated from the information about charge groups that was provided by the supplier. These differences may be attributed to 1) some amide groups were hydrolyzed or some functional groups were decomposed to change the molar ratio of charged groups, or 2) some charged groups were strongly localized in close proximity on the chains so that the nearest neighbor interactions were predominant strong enough to shift the theoretical iso-electric points. In order to confirm this, it is suggested that the molar ratio of functional groups is be determined by experiments. The nuclear magnetic resonance (NMR) technique is applicable to determine

the exact ratio of the functional groups. To do this, the polyacrylamides are can be freeze-dried, dissolved in deuterated solvent, and molar ratio is can be calculated by taking the ratio of the partial integration of the NMR signal for the functional groups to the total integration.

In this study, bleached hard wood fibers were used as charged adsorbents for a practical purpose. Adsorption is affected by the adsorbent properties, surface charge density and surface area. These characteristics were not determined in the present work. To understand the adsorption behavior, it is important to know these characteristics of the adsorbent. However, as a matter of fact, it is not simple to determine these values due to the issues of pH dependence of charge and definition of the surface. First, the charge density of fibers are is variable, depending on the pH, since the charge of fibers is originatesd from dissociation of carboxylic groups. The dissociation of carboxylic acids is affected by the pH. Therefore, it is necessary to obtain the pH – charge curves. Second, as is known, there are internal and external surfaces since fibers have pore structures. As long as the polymer adsorption is concerned, only the external surfaces should come to a discussion under an assumption that the polymer molecules are too large to penetrate into the fiber pores. In addition to this problem, the roughness of the fiber surface is also a factor that makes it difficult to determine the exact surface area. As a matter of fact, there are several methods to determine the surface area of fibers, but they are not always in agreement. To avoid these problems, it is possible to use the well-defined charged surfaces as adsorbents if it is assumed that only the electrostatic interaction is significant for adsorption.

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APPENDICES

A. Normalization of potentiometric titration curves

According to the procedure mentioned in the section titled PAPER, potentiometric titration curves for amphoteric PAMs and a control (deionized water) were obtained as shown in Fig. A-1. Then, Fig. A-1 was converted into Fig. 1 shown in “PAPERS – part 1” section based on the following procedure. The curve for the amphoteric PAM was shifted horizontally so that the iso-electric pH of the amphoteric PAM was located just above zero in the horizontal axis. In this case, the iso-electric point was 6.0, which was determined by colloidal titration (see Table 2 in the PAPERS – part 1 section). The curve for the control was also shifted parallel to the horizontal axis so that it intersected the curve for the sample at zero on the horizontal axis.

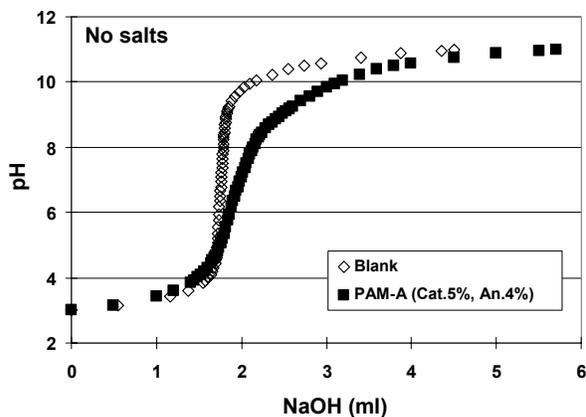


Fig. A-1. Potentiometric titration of amphoteric PAM solution in comparison with blank titration.

B. Comparison between theory and experiments

In this section, experimental results with regard to polyampholyte behavior will be compared with recent theoretical predictions. Before stating the comparison, it is worth noting that the theoretical predictions here are not expected to be quantitatively accurate, due to the facts that 1) some of critical parameters required for calculations were not determined in the present work, and 2) the theory is valid under ideal conditions with several approximations, which are not quite practical in a certain case, e.g. ignoring effects of hydrogen bonding. However, it is considered that one can still obtain some ideas to interpret the experimental results.

B-1 . Conformation of a polyampholyte chain in a solvent

According to the theory proposed by Dobrynin *et al.* [1997], a polyampholyte chain in solvent can take three possible regimes of configurations, unperturbed, polyelectrolyte, and necklace. The configurations are determined by charge fractions of the polyampholyte chain and degree of polymerization. To estimate the polyampholyte configuration, the following values are used for the polyacrylamide products examined in the project:

Dielectric constant of media (water) $\epsilon = 78.5$ [-]

Temperature $T = 298$ [K]

Monomer length $a = 2.8 \times 10^{-10}$ [m]

Charge fractions $f^+ = 0.05$ and $f^- = 0.04$

Degree of polymerization $N = 40000$ [-]

The following parameters are calculated:

Bjerrum length $l_B = e^2/(4\pi\epsilon_0\epsilon kT) = 7.14 \times 10^{-10}$ [m]

Coupling constant $u = l_B/a = 2.55$ [-]

Using the above data, the diagram for predicted configuration in aqueous solvent without salt is calculated as shown in Fig. B-1 based on Fig. 1 in the “LITERATURE REVIEW” section. In Fig. B-1, the charge fraction and charge excess of the polyampholyte product C5A4 at various pH values, which were obtained from charge analysis using the colloidal titration measurements, are also plotted.

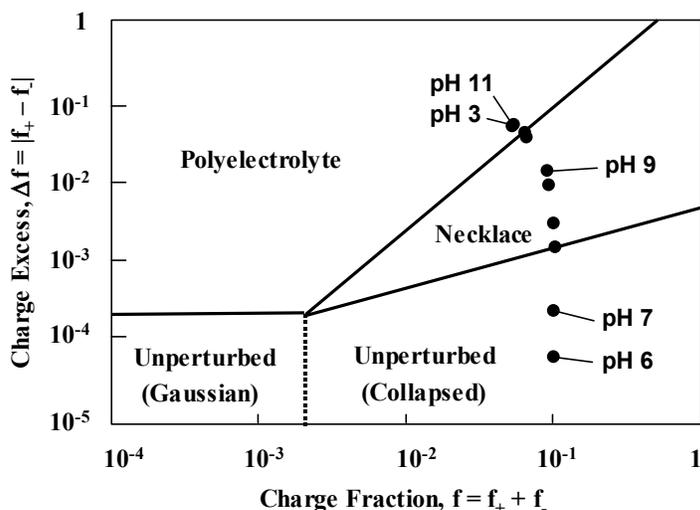


Fig. B-1. Diagram of configuration for the amphoteric polyacryamide product C5A4 in water without salt

As shown in Fig. B-1, the polyampholyte sample C5A4 is expected to form all of the three configurations in no-salt conditions within a pH range between 3 and 11. Over a wide range of pH, the chain configuration is in the regime of necklace globule, which is unique to polyampholytes. Around the iso-electric point, the theory states that the chain conformation is expected to be in a collapsed state but not in a Gaussian state, which is in agreement with the turbidimetric observation as shown in Fig. 10 in the “PAPERS – part 1” section.

B-2. Anti-polyelectrolyte behavior

According to Higgs and Joanny [1990], a neutral polyampholyte chain in collapsed state starts to swell by addition of a certain amount of salt. This behavior is called “anti-polyelectrolyte” effect.

The Debye length corresponding to this minimum salt concentration, at which the collapsed chain starts to expand, is given by $\kappa_{\min}^{-1} = a^2/fl_B$. For the polyampholyte product C5A4 in water,

$$\text{Monomer length } a = 2.8 \times 10^{-10} \text{ [m]}$$

$$\text{Charge fraction at iso-electric point } f = 0.05$$

$$\text{Bjerrum length } l_B = 7.14 \times 10^{-10} \text{ [m]}$$

The Debye length corresponding to the minimum salt concentration κ_{\min}^{-1} is calculated as

$$\kappa_{\min}^{-1} = a^2/fl_B = 2.20 \times 10^{-9} \text{ [m]}$$

This scale of the Debye length corresponds to Na_2SO_4 solution at concentration of $6.4 \times 10^{-3} \text{ M}$ or Na_2SO_4 solution at conductivity of approximate $1400 \text{ }\mu\text{S/cm}$. Namely, the collapsed polyampholyte (C5A4) chain at the iso-electric point is expected to swell at Na_2SO_4 concentration greater than $6.4 \times 10^{-3} \text{ M}$ or at conductivity greater than $1400 \text{ }\mu\text{S/cm}$ of Na_2SO_4 solution. This theoretical estimate agrees with the results of viscometric measurements shown in Fig. 9 (a) in “PAPERS – Part 1” section. In Fig. 9 (a), the viscosity is slightly increased around the iso-electric point by addition of Na_2SO_4 to the conductivity value of $1500 \text{ }\mu\text{S/cm}$.

B-3. Adsorption of a single polyampholyte chain onto a charged surface

According to Dobrynin *et al.* [1997], if a neutral polyampholyte chain can be adsorbed on charged surfaces, the adsorbed chain has one of three regimes of configurations, pole, fence and pancake, depending on surface charge density of the charged surfaces. A question here is what regime of configuration for an adsorbed chain is expected under the conditions used in the present thesis. The problem here is that the surface charge density of bleached kraft fibers that

were used in the experiments is not known. To calculate the surface charge density, it is necessary to measure the fiber charge and the fiber surface area. For the sake of discussion, both values are taken from earlier work [Lloyd and Horne, 1993; Marton *et al.*, 1976], although both of them are significantly dependent on several factors such as wood species, pulping, bleaching, and refining conditions, solution properties, and methods of determination.

Lloyd and Horne determined charge of bleached kraft fibers in a pH range from 3 to 11 by using a polybrene adsorption method [Lloyd and Horne, 1993]. According to their result, the charge for bleached kraft fibers was increased from 20 to 40 mmol/kg as the pH was moved from 3 to 11. To simplify the calculation, it is assumed that the fiber charge increases linearly as the pH increases. Fiber charge can be also determined by potentiometric titration methods, but it is considered to be appropriate to use the value determined by cationic electrolyte adsorption methods, since adsorption of a polyampholyte chain on charged surfaces is now under discussion. Specific surface area of fibers is dependent significantly on refining conditions and methods of determination. It will also change depending on pH due to swelling. However, for simplicity, it is assumed that the specific surface area is approximate 1.0 m²/g, according to Marton *et al.*, regardless of pH [Marton *et al.*, 1976].

Under the above assumptions, the surface charge density of fibers σ is

$$\sigma = 1.20 \times 10^{19} \sim 2.41 \times 10^{19} \text{ [m}^{-2}\text{]} \text{ (pH 3} \sim \text{11)}$$

In addition, the following values are used for calculation:

$$\text{Monomer length } a = 2.8 \times 10^{-10} \text{ [m]}$$

$$\text{Total charge fraction at iso-electric point } f = 0.1$$

$$\text{Degree of polymerization } N = 40000$$

$$\text{Bjerrum length } l_B = 7.14 \times 10^{-10} \text{ [m]}$$

The transitional surface charge densities σ_1 , σ_2 , and σ_3 in theta solvent are calculated in order to predict the configuration of the adsorbed polyampholyte chain as

$$\sigma_1 = 1 / \{l_B(aN^{1/2})(fN)^{1/2}\} = 3.95 \times 10^{14} \text{ [m}^{-2}\text{]}$$

$$\sigma_2 = 1 / \{l_B(aN^{1/2})(fN)^{1/4}\} = 3.14 \times 10^{15} \text{ [m}^{-2}\text{]}$$

$$\sigma_3 = f^{1/2} / al_B = 1.58 \times 10^{18} \text{ [m}^{-2}\text{]}$$

The surface charge density of fibers $\sigma = 1.20 \times 10^{19} \sim 2.41 \times 10^{19} \text{ [m}^{-2}\text{]}$ is greater than the transitional surface charge density $\sigma_3 = 1.58 \times 10^{18} \text{ [m}^{-2}\text{]}$. Therefore, according to the theory, it is expected that the polyampholyte chain (C5A4) at iso-electric pH in theta solvent has an ability to adsorb on the charged fiber surfaces (If $\sigma < \sigma_1$, no adsorption is expected to take place). The adsorbed chain has the configuration of “pancake” regime (because $\sigma > \sigma_3$) as shown in Fig. 3 (b) in the “LITERATURE REVIEW” section. This configuration is expected to be affected by the presence of salt. Fig. B-2 shows the effect of salt addition on the configuration.

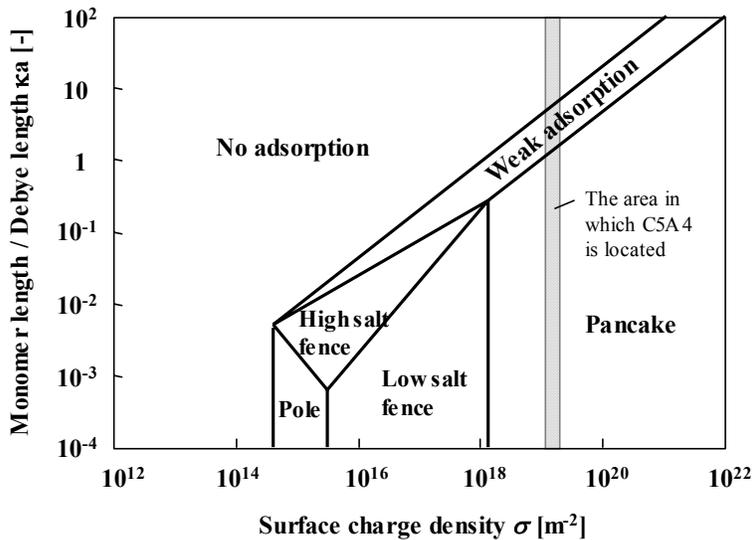


Fig. B-2. Diagram of configuration for an adsorbed chain of the amphoteric polyacryamide product C5A4 onto bleached kraft fibers in water

In Fig. B-2, the ratio of the monomer length to the Debye length increases as the salt concentration increases. In the conditions used for the adsorption experiments, where the conductivity was adjusted to 1000 $\mu\text{S}/\text{cm}$ by adding Na_2SO_4 , the ratio of the monomer length to the Debye length is about 0.1. At this level of salt concentration, the configuration of the adsorbed chain is expected to remain in the pancake regime. If Na_2SO_4 is added to the concentration level more than 1.5 M, where the ratio of the monomer length to the Debye length is greater than 2.0, then the configuration is expected to change to the “weak adsorption.” If Na_2SO_4 is further added until the ratio of the monomer length to the Debye length is greater than 7.8, that is, the Na_2SO_4 concentration is higher than 23.7 M, then no adsorption is expected to occur. In fact, however, Na_2SO_4 solution of such high concentration cannot exist, since it exceeds the saturation level (19.4g / 100ml at 20°C).

B-4. Adsorption of multi-polyampholyte chains onto a charged surface

Dobrynin *et al.* proposed a theory on multi-chain adsorption of polyampholytes [Dobrynin *et al.*, 1999]. According to the theory, the maximum adsorption of similarly charged polyampholytes onto charged surfaces Γ_{max} is given by

$$\Gamma_{\text{max}} \approx (f / a^2 \Delta f) [1 - \Delta f (\lambda / af)^{2/3}]^{3/2} \quad \text{for } (f / N)^{1/2} < \Delta f < (af / \lambda)^{2/3}$$

Polyampholytes are expected to have similar charge to cellulosic fibers above the iso-electric pH. Thus, in the case of the polyampholyte product C5A4, the theory can predict the adsorption behavior above pH 6.

Here, the same assumptions mentioned above are made in terms of the surface charge density of fibers, and the same values with regard to a , N , and l_B are used as well. The calculated results for the maximum adsorption are shown in Fig. B-3, along with the experimental results.

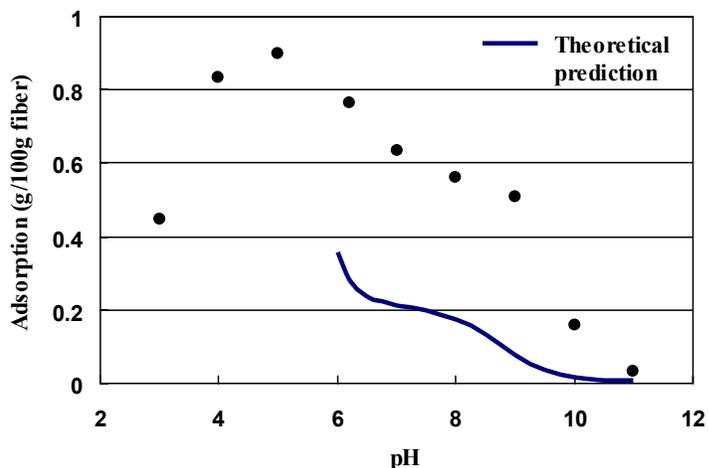


Fig. B-3. Theoretical prediction for adsorption of polyampholytes onto charged surfaces

The experimental data shown in Fig. B-3 do not correspond to the maximum adsorption, but they exceed the maximum adsorption predicted by the theory. This may be due to a) the inaccurate data for surface charge density of fibers, b) difference in solvent condition between calculations and experiments, and c) the limitation of the theory. Although the theory does not predict the adsorption behavior of the polyampholytes quantitatively, the trend of the adsorption curve is similar to the experiment results.