ABSTRACT

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Polyampholytes are polymers that have both positively and negatively charged groups in the same chain. In recent years polyampholytes have started to be used in papermaking applications, as well as in sludge treatment processes. Benefits, in the case of papermaking, have included increased dry-strength and faster removal of water. But the molecular mechanisms by which such benefits are achieved have not been fully understood. This thesis project focused on effects related to polyampholyte charge density. A series of polyampholytes with a fixed charge ratio but different charge density was used for the experiments. Analysis methods included pH titrations, streaming current titrations, and adsorption isotherms. From pH titrations the charge density of cationic and anionic groups under different pH were calculated. From streaming current tests the net apparent charge density under different pH was calculated. And from adsorption tests it was found that the highest adsorbed amounts were achieved in certain cases corresponding to the highest content of ionic groups on the polyampholytes. Adsorption depended strongly on pH. Substantial differences were observed when comparing results obtained with polyampholyte samples versus ordinary polyelectrolyte samples with same charge density of cationic or anionic groups.
Colloidal Behavior of Polyampholytes

by

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1. INTRODUCTION

Synthetic polyampholytes began to be used in the papermaking and sludge dewatering industries just several years ago\textsuperscript{1-3}. In the paper industry, the copolymer-type amphoteric poly(acrylamide) co-AMP-PAM, which is a type of amphoteric PAM, was found to be more effective than poly(acrylamide)(PAM)\textsuperscript{1}. In sludge treatment, a combination of a metal coagulant and an amphoteric polymer was found to produce large and mechanically strong floc\textsuperscript{2}.

Synthetic polyampholytes have acidic and basic monomers along the chain, which makes them have unique properties, including electrochemical, hydrodynamic and conformational properties. The understanding of this kind of polymers is not well advanced, and they are not as widely used, compared to traditional additives. However, knowledge of these properties is important for understanding the function of polyampholytes. The methods developed and used in the present research were intended to add to the needed understanding. For example, theoretical equations related to pH titrations have been found to predict the electrokinetic properties. The conformations of polyampholytes can be simulated by computer, using Monte Carlo theory.

Though the behaviors of polyampholytes are still not totally understood, there is more and more focus on them because of their new fields of application.
2. LITERATURE REVIEW

2.1 Potentiometric behavior of amphoteric polymers

Amphoteric copolymers and terpolymers have both acidic and basic groups on their chain. In general, the acidic and basic degrees of ionization are expected to depend on pH. That means that under different pH values, the net charge densities, due to dissociation of acidic and basic groups, will be different. Under a certain pH, which is called the isoelectric point of the system, the amounts of dissociated acidic and basic groups will be the same, and the net electrokinetic charge will be zero. This isoelectric pH value can be calculated for every amphoteric polymer, if certain coefficients are known and if simplifying assumptions are made.

To calculate the isoelectric pH value of a polyampholyte, it is first necessary to consider the equilibration of an individual dissociable group. The potentiometric behavior of polyampholytes may be expressed as

\[
\text{pH} = pK_a^+ + n \log(\alpha/(1-\alpha)) \quad (1-1)
\]

\[
\text{pH} = pK_b^+ + n \log((1-\beta)/\beta) \quad (1-2)
\]

where \( pK_a^+ \) and \( pK_b^+ \) are the apparent acidic dissociation constants of acid and basic groups, respectively, and \( \alpha \) and \( \beta \) are the degree of ionization of acid and basic groups of the polyampholytes.

To calculate the dissociation constants, some ideas used in the case of polyelectrolytes are borrowed here. For a polyelectrolyte molecule with hydrogen ions in aqueous solution, the
following concept has been found to be useful; that is\textsuperscript{4}, to picture the charges on the molecule as being replaced by a smeared-out potential along the chain. This idea has been successfully applied to protein, which is the basis of the net charge model used in the analysis of protein titrations. Logically, the same idea also should be applicable for synthetic polyampholytes, which share many essential similarities with proteins. In general, the interactions in a polyampholyte solution can be expected to be very complex. But in these interactions, some specific interactions between the chain and the components of the solution, or between the segments of the chain among themselves, or even between close neighbors on the chain, may be neglected, because these interactions such as H-bonding are believed not likely to influence the common run of polyampholyte titrations for common polyampholytes\textsuperscript{4}. Finally, this model only takes into account the electrostatic interactions between different chain segments as well as between ionic groups and low molecular weight electrolytes. This type of theoretical calculation has been found to be in good agreement with experimental results obtained for 2-vinylpyridine-acrylic acid (2VP-AA)\textsuperscript{5}. However, from the experimental results, it is also found that the pK value changes with increasing cationic or anionic charge density. Thus, there is a big deficiency in the original Katchalsky and Gillis model\textsuperscript{5}. This model missed the effect of neighbor interactions. But not all neighbor interactions need to be considered. Only those nearest neighbor interactions between oppositely charged groups are of general significance.

Rice and Harris first considered the nearest-neighbor interaction for copolymers of regularly alternating structure\textsuperscript{6}. Mazur, Silberberg, and Katchalsky in 1959 then found that nearest-neighbor interactions between charges of opposite sign can be quite important, even in the
polymers where ionizable groups of polyampholytes are not close together $^4,^7$. So, besides
the electrostatic interaction, nearest-neighbor effects cannot be neglected.

According to all of the information shown above, the apparent pK’ of the acidic and basic
groups can be expressed as the sum of the intrinsic pK, the nearest neighbor interaction (Ed),
and the long range electrostatic interaction (Er),

$$pK_a' = pK_a + 0.434/kT \left( \frac{\delta E_d}{\delta v} \right) \xi + 0.434/kT \left( \frac{\delta E_r}{\delta v} \right) \xi \quad (1-3)$$

$$pK_b' = pK_b + 0.434/kT \left( \frac{\delta E_d}{\delta \xi} \right) v + 0.434/kT \left( \frac{\delta E_r}{\delta \xi} \right) v \quad (1-4)$$

where $v$ and $\xi$ are respectively the mean number of negative and positive charges on the
macromolecule, $k$ is Boltzmann’s constant, and $T$ is absolute temperature $^3$.

The long range electrostatic energy $E_r$ of the molecule, i.e., the energy due to the randomly
distributed (smeared-out) charges, can be known based on the average shape of the molecule
and the corresponding distribution of the small ions (counterions and neutral salt). At high
ionic strength, $E_r$ equals 0. At low ionic strength this random interaction effect cannot be
neglected. In many cases the titration curve with no added salt is the best we can obtain
experimentally, because one can, in principle, try to correct the titration curve for the
$0.434/kT \left( \frac{\delta E_d}{\delta v} \right) \xi$ or $0.434/kT \left( \frac{\delta E_r}{\delta \xi} \right) v$ term, using one of several theoretical approaches.

But in some particular cases, these terms cannot be corrected even at low ionic strength. For
example, one may not carry out (1) separate determination of the degree of ionization of one
of the groups, e.g. by spectrophotometry, and (2) analysis of the dependence of isoelectric
point of the polyampholytes on the composition ratio.$^4$
The value of $0.434/kT \left( \frac{\delta E_d}{\delta v} \right)_\xi$ or $0.434/kT \left( \frac{\delta E_d}{\delta \xi} \right)_\xi$ is determined by the structure and chemistry of the chain. For the chemical composition factor, increasing the acidic group density enhances ionization of basic group, while increasing the basic group density decreases the ionization of basic group. For the structure factor, the arrangement is important. In a diblock copolymer, there is no nearest-neighbor interaction, and the apparent pK equals the intrinsic pK \textsuperscript{8}.

If in isoelectric pH with high salt, the equation can be written as follows \textsuperscript{3}:

\[
\begin{align*}
\text{pH}_{\text{IEP}} &= \text{pK}_{a0'} + \log \left( \alpha_{\text{IEP}} / (1 - \alpha_{\text{IEP}}) \right) \quad (1-5) \\
\text{pH}_{\text{IEP}} &= \text{pK}_{b0'} + \log \left( (1 - \beta_{\text{IEP}}) / \beta_{\text{IEP}} \right) \quad (1-6)
\end{align*}
\]

If $\text{pK}_{b0'} - \text{pK}_{a0'} > 2$, then $\text{pH}_{\text{IEP}}$ of a polyampholyte which contains an excess of acid monomer ($a > 0.5$) is calculated from:

\[
\text{pH}_{\text{IEP}} = \text{pK}_{a0'} + \log \left( (1 - a) / (2a - 1) \right) \quad (1-7)
\]

And at an excess of base monomer ($a < 0.5$) from:

\[
\text{pH}_{\text{IEP}} = \text{pK}_{b0'} + \log \left( (1 - 2a) / a \right) \quad (1-8)
\]

The equation connecting the IEP of polyampholytes with the acid-to-base molar ratio and with the acid-base dissociation constants was solved by Patrickios, and it can be expressed as follows. For acid-rich ($R > 1$) polyampholytes,

\[
\text{pH}_{\text{IEP}} = \text{pK}_a - \log \left\{ R / 2 \left[ (1 - R) / R + (1 - R / R)^2 + (4 / R)^{10(pK_a - pK_b)} \right] \right\} \quad (1-9)
\]

while for base-rich polyampholyte ($R < 1$)

\[
\text{pH}_{\text{IEP}} = \text{pK}_b - \log \left\{ 1 / 2 \left[ (1 - R) / R + (1 - R / R)^2 + (4 / R)^{10(pK_a - pK_b)} \right] \right\} \quad (1-10)
\]

where $R$ is the molar ratio of acid to base.
But generally from the literature, all of these equations and theory are intended to be used for polyampholytes that contain only one kind of acidic and basic group by pH titration. If there are more than one kind of acidic or basic group, then the interaction forces will be more complex between ionic groups. So whether this kind of method is still suitable is in doubt.

Another thing worth mentioning here is the iso-electric pH (IEP) value. At the IEP, the behavior of polyampholytes is very different, and it also may depend on specific characteristics of polyampholytes. At this point, the amounts of oppositely charged bound ions are almost the same, so the electrostatic attraction forces between oppositely charged groups are very high. This situation makes the polymers condense into a compact globule, squeezing out the solvent. Any low- or high-molecular-weight substances associated with polyampholytes can potentially be released at the IEP. Such release can be used as evidence that materials are behaving as polyampholytes at the IEP. The reason for this phenomenon is that there is a competition between inter- and intramolecular interactions. If the intrachain interactions of acidic and basic groups within a single macromolecule predominate over those interactions between different chains, then the IEP effect phenomenon can be realized. This phenomenon can affect other properties of polyampholytes, such as viscosity and adsorbed amount. In addition, Keotz et al. studied the titration curves of polyampholytes. They found that if the positive and negative groups were titrated separately by sodium poly (styrenesulfonate) (SPSS) and poly (N, N-dimethyldiallylammonium chloride) (PDMDAAC), these two curves would intersect at the IEP, where the addition amount is almost zero.
2.2 Electrokinetic properties of amphoteric polymers

Electrokinetic analysis can be used to estimate the charge on solid surfaces, macroscopic particles, colloidal species, and macromolecular aggregates. Charges on surfaces are important for understanding the behavior of many materials such as colloids, coatings films, films, and fibers\(^{13}\). Four principal electrokinetic processes of interest are electrophoresis, sedimentation potential, electro-osmosis, and streaming potential.

The basic theory of electrokinetics is based on the concept of the double layer. In a simplified view, the double layer is comprises of two parts. One is called the Guoy diffuse layer, and the other is called the Stern condensed layer. A plane of shear is assumed by some researchers to be located somewhere within the Guoy diffuse layer, close to the Stern condensed layer. The actual potential drops from the surface ( \( \delta = 0 \) ) to the bulk solution ( \( \xi = 0 \) ). And the zeta potential is assumed to be determined by the plane of shear.
Electrophoresis is by far the most common method for determining the zeta potential. In this method, mobility is recorded. Electrophoretic mobility is defined as the velocity per unit field

$$\mu_e = \frac{v}{E}$$

Then the zeta potential can be calculated from $\mu_e$ by the following equation, because $\mu_e$ is directly proportional to the zeta potential.

$$Zeta\ potential\ \delta = 4\pi\eta(\nu/E)/\varepsilon$$

where $\eta$ is viscosity, $\nu/E$ is electrophoretic mobility and $\varepsilon$ is dielectric constant.
Another way to determine the zeta potential is by the streaming potential method. Compared to the electrophoresis method, streaming potential has one key advantage; it can be used for undiluted slurries sampled directly from the papermaking process\textsuperscript{15}. Because of this, the method seems more suitable for the papermaking industry. In streaming potential measurements, the solution is made to flow by applying a pressure, and a potential is obtained in units of mV. Under the neglect of conductivity associated with the solids, the relationship between the streaming potential and the zeta potential can be estimated by the following equation:

\[ \zeta = \frac{E_s \eta L}{AR\varepsilon_0 \Delta P} \]  

(2-3)

where \( E_s \) = streaming potential, \( \eta \) = viscosity, \( L \) = length of capillary, \( A \) = cross-sectional area of the chamber perpendicular to the direction of flow, \( R \) = ohmic resistance of electrolyte (which may also include the surface conductance) in the chamber, and \( \Delta P \) = applied pressure drop. This equation is called “Helmholtz-Smoluchowski” relationship.
Based on the principle of streaming potential, different experimental equipment can be used. Unlike electrophoresis, which has the standard equipment for researchers to use, many researchers prefer to setting up their own streaming potential equipment depending on their research purpose \(^\text{16, 17}\). The present work employs a streaming potential device that was designed for repeated tests and high-sensitivity with papermaking fibers. As shown by the work of Wang and Hubbe, the method is efficient and simple, especially in the case of hard wood fiber \(^\text{18}\). In this device, there is no capillary, the fiber slurry flow through the screen to form a fiber pad. Theorists usually consider a fiber pad as being equivalent to a series of interconnecting capillaries. This difference can be seen from the figure 4.
One important factor for electrokinetic analysis is salt, which affects the thickness of the double-layer $\kappa^{-1}$. Besides the salt, van de Ven $^{19}$ found that fiber conductance strongly influences the electrophoretic mobility, streaming potential, and streaming current. Fibers can conduct a significant amount of current, except at very low pH condition or high ionic strength. So the effect of conductivity cannot be neglected in most cases.

The methods described above are generally used for electrical potential for charged particles or fibers in aqueous suspension or in packed beds. Though from zeta potential, sometimes the charge density on the surface can be calculated, in most cases there are too many unknown terms in the equation for it to be usefully applied. However, charge density is also very important. In a paper mill, charge demand determines the dosage of polymers that is required to obtain optimum results. So streaming current titrations can be used for this purpose.
The procedures involved in measurement of streaming current are very simple. A titrant, which has the opposite charge relative to the materials in the sample, is added until the streaming current detector displays zero. The amount of polymer added indicates the charge demand of the sample. But it is not possible to interpret the absolute value of the charge density on the surface, because one important assumption for interpretation of titrations is that the interaction is stoichiometric. There are many unknown factors that may influence the stoichiometry of interaction. For example, increases of the salt concentration can increase the deviations from 1:1 stoichiometry. For some particulate materials or inflexible polymers, the charges on the materials are unable to approach sufficiently close to each other to achieve a stoichiometric interaction. As a consequence, the counter-ions have to remain associated with the polymer or surface charges. Deviations of stoichiometry may also be caused by other nonionic interactions. The stoichiometric interaction of polyelectrolyte titrations depends on the nature of the titrant polymer used and whether it can interact with all of the surface and colloidal charge groups present.
2.3 Adsorption of amphoteric polymers on charged surfaces\textsuperscript{23-25}

Though the adsorption of polymers at surfaces and interfaces has been the subject of extensive theoretical and experimental studies during the last four decades, the theory of polyampholyte adsorption has been developed only within the last decade. Compared to the theory of adsorption of other polymers, the theoretical studies of polyampholyte adsorption revealed a new mechanism that is due to the polarization of chains in the external electric field created by charged objects.

Adsorption models

1. Single chain adsorption model

(1) Adsorption of a symmetric polyampholyte chain without salt

![Graph](image)

Fig. 6 Dependence of the absolute value of the adsorption energy $W$ on the surface charge density, Logarithmic scales\textsuperscript{24}
The model is as follows: a weakly charged polyampholyte chain \((N < u^{-2} f^{-2})\) with \(N\) degree of polymerization adsorbs onto an infinite plane from the dilute solution. This chain has equal numbers of positively and negatively charged groups \((f_+ = f_-)\), and the plane has \(\sigma\) charges per unit area. Because the concentration of counter-ions decays with increasing distance from the surface, a significant fraction of counter-ions should be localized within the Gouy-Chapman length \(\lambda = (2\pi L_B \sigma)^{-1}\), and \(L_B\) means the Bjerrum length, in which the electrostatic interactions dominate thermal motions for two charges.

Four regimes can be seen from the figure.

i. \(\sigma < \sigma_1\)

Under these conditions there is no adsorption because the small polarization energy gain (smaller than thermal energy \(kT\)) does not justify the entropy loss.

ii. \(\sigma_1 < \sigma < \sigma_2\)

This regime is called “pole” regime. In this regime, the chain in the direction of the field is elongated by the electric field of the charged surface, while the chain in the perpendicular direction preserves its Gaussian conformation.

iii. \(\sigma_2 < \sigma < \sigma_3\)

Under these conditions the system is in the “fence” regime.

In this regime the size of the chains becomes on the same order of magnitudes as the Gouy-Chapman length \(\lambda\). The chain is confined within the Gouy-Chapman length and is divided into subsections of size \(\lambda\). These subsections are strongly stretched, and the polymer is strongly attracted to the surface.

iv. \(\sigma > \sigma_3\)
Under these conditions the system is in the “pancake” regime. The thickness of a chain in the pancake regime is on the same order of magnitude as the root-mean-square distance between charged monomers and is almost independent on the surface charge density. In this regime, the monomers the charge of which is opposite to surface charge are within distance $\lambda$, while monomers, which has the same as surface charge are in the loops dangling in solution at distances large than $\lambda$.

This model (“pancake”, “fence” and “pole”) has been confirmed experimentally by comparison of the thickness of adsorbed layer $L$ with the gyration radius for betaine type polyampholytes in NaCl solutions $^3$. 
Fig. 7 Conformation of a polyampholyte chain near an adsorbing surface. (a) Pole regime. (b) Fence regime. (c) Pancake regime.
(2) Adsorption of a Charged Polyampholyte Chain on a Similarly Charged Surface

In this situation, the adsorption depends on the Coulombic interaction between the net charge on the chain $\Delta \bar{f}_N = N(f_+ - f_-)e > 0$ and the charged surface. The balance of three forces determines the adsorption results. If the net interaction energy $W$ is negative (attractive) and stronger than the thermal energy $kT$, adsorption would occur. The net interaction is given as follows,

$$W = W_{\text{att}} + W_{\text{rep}} + W_{\text{imag}} < -kT$$

where $W_{\text{att}} + W_{\text{rep}}$ is the total energy of the polyampholyte chain $W$ near the surface, which consists of the attractive part $W_{\text{att}}$ due to the polarization of the chain by the electric field and the repulsive energy $W_{\text{rep}}$ between the net charge on the chain and the field $E$. $W_{\text{imag}}$ is caused by the presence of the dielectric constant (for example, water is dielectric media with $\varepsilon_1$, and silica is the dielectric media with $\varepsilon$). Location of the polyampholyte chain near the surface, with the specified dielectric constant, causes the polarization of both media, which results in the appearance of an image polyampholyte chain. The interaction between this image polyampholyte chain and the polyampholyte chain leads to an additional repulsive force. A three-regime model can be seen from the following figure:
(3) Effect of added salt. At very low salt concentrations (very small $\kappa a$), the inverse screening length $\kappa$ is larger than the Gouy-Chapman length ($\kappa^{-1} > \lambda$), so the screening due to added salt is unimportant, and the adsorption behavior of a polyampholyte chain is almost identical to that in the absence of salt. As the salt concentration increases, the model becomes complex in comparison to the situation with no salt condition. According to the charge density on the surface and the salt concentration, different regimes can be obtained. In the pole regime, the conformation is the same with no salt condition, as well as in the low salt fence regime with chain folding inside the layer of thickness $\lambda$. In the high salt fence regime ($\kappa^{-1} < \lambda$) the chain is localized inside the...
layer of thickness $\kappa^{-1}$. In weak adsorption regime, the chain adsorbs on the surface only if the thickness $R_z$ is smaller than the Gaussian chain size $aN^{1/2}$. In the pancake regime, the adsorbed pancake starts to swell when the screening length becomes smaller than the size of the loop.

Fig. 9 Adsorption diagram of a polyampholyte chain in a salt solution as function of surface charge density and inverse Debye screening length, Logarithmic scales

2. Multichain adsorption model

As in the case of the single chain adsorption, the multichain adsorption model is divided into different conditions.

(1) Adsorption of a Symmetric Polyampholyte Chain without salt

1) Multilayer of stretched chains ($\sigma_1 > \sigma > \sigma_2$). In this regime, polyampholyte chains are polarized and stretched by the external electric filed of the surface. At distances $\lambda < z < \lambda_1$, the polymer density decays as $c = z^{-1}$ in a $\theta$-solvent and as $c = z^{-4/3}$ in a good solvent. The adsorption stops at length scales on the order of $\lambda_1$ because
the external electric field created by surface becomes too weak to polarize the chains. So $\lambda_1$ can be considered as the thickness of the adsorbed layer.

2) Self-similar stretched pseudobrush ($\sigma_2 > \sigma > \sigma_3$). In this regime, the electric field created by the charged surface is almost constant close to the surface at distances $z<\lambda$. The sections of the chains are uniformly stretched up to length scales on the order of $\lambda$. On length scales $z<\lambda$, the polymer density decays as $z^{-1/3}$ in $\theta$-solvent and as $z^{1/2}$ in a good solvent. At length scales larger than $\lambda_2$, the polymer density has the same profile as in the multiplayer of stretched chains.

3) Saturated self-similar stretched pseudobrush ($\sigma > \sigma_3$). In this regime, inside a layer thickness, which is near the wall, the strands of a chain are almost unperturbed by the external electric field and the monomer density is uniform. The surface coverage reaches its maximum value $a^{-2}(fN)^{1/2}\ln(fN)$ in a $\theta$-solvent and as $a^{-2}f^{3/5}N^{2/5}$ in a good solvent and becomes independent of the surface charge density. On length scales between $\lambda_2$ and $\lambda_3$ adsorbed polyampholytes form a self-similar pseudobrush.

This theory of polyampholyte adsorption on charged surfaces was successful in interpretation of experimental results for adsorption of gelatin on polystyene latex and silica particles at various pH and ionic strengths.
(2) Adsorption of a Charged Polyampholyte Chain on a Similarly Charged Surface

The different adsorption regimes depend on the charge density on the surface and the chain charge asymmetry. The graph is showed as follows.

![Adsorption diagram](image)

Fig. 11 Adsorption diagram of polyampholyte chains as a function of the surface charge density and the chain charge asymmetry.

(3) The effect of Added salt
Salt also affects multiplayer adsorption, as shown in the following figure. Compared to adsorption of a single chain, multilayer adsorption is more complex in the presence of salt. Sometimes, only single layer adsorption takes place.

\[
C_{\lambda,1}^s \approx 1/(l_B a_1^2) \approx 1/(l_B a^2 f N^2) \quad (3-2)
\]

\[
C_{\lambda,2}^s \approx 1/(l_B a_1^2) \approx 1/(l_B a^2 f^{1/2} N^{3/2}) \quad (3-3)
\]

\[
C_{R0}^s \approx 1/(l_B D_0^2) \approx 1/(l_B a^2 N) \quad (3-4)
\]

Fig. 12 Adsorption diagram of polyampholyte chains in a salt solution as a function of surface charge density and salt concentration\textsuperscript{28}. Another theoretical approach to study the adsorption of polyampholytes on charged surface is Monte Carlo simulation\textsuperscript{23, 24, 29, 30}. Sometimes the Monte Carlo simulation can be used to verify adsorption models, such as that which is shown above. The following figure is a sample. This is the result of Monte Carlo simulations of adsorption of polyampholyte chains with degrees of polymerization $N = 32, 48, 64, 80, \text{ and } 128$ and with equal numbers of positively and negatively charged monomers at a charged surface from a $\theta$-solvent for the polymer backbone\textsuperscript{23}. It shows three regimes for adsorption and all the regimes are related to the value of $\sigma$. 
But theory remains just theory until it can be applied. Though the models can be calculated by computer, it is still difficult to apply them to real situations, because sometimes there is no way to know all of the parameters in the equation. Also the experimental situations are invariably more complex during the real adsorption experiments. In the real experiments, kinetics and adsorption results are two main topics for research.

If the substrates are fibers, then the adsorption processes can be described as follows: (1) Transport of the polymer from the solution to the fiber surface in general by Brownian motion or turbulent transport; (2) Attachment of the polymers on the fiber surface. The initial conformation is similar to the conformation in solution; (3) Reconformations of the polymers on the fiber surface; (4) Detachment of the polymers from the surface. The desorption is a very slow process in deionized water. However, some factors, such as molecular mass or salt
concentrations can definitely affect the desorption rate. Because the fiber is porous material, so the polymer can sometimes penetrate into fibers, depending the molecular weight of polymer. Wågberg and Hagglund have already used experimental data to show that the low molecular weight polymer can reach all the charges in the fiber wall, while high and medium molecular weight polymers are restricted to the external surfaces of the fibers. The same was shown by Winter and Wågberg. Also their data shows that the kinetics theory of adsorption is more complex for high molecular weight polymer than for low molecular weight polymer. Salt effects also have been researched.

With respect to the adsorbed amount, the charge density of polyampholytes and the charged surface are the two main factors, based on the adsorption models. But many parameters can influence the charge density both on polymer and substrates, such as pH, the substrate properties, and the charge ratio of the polyampholytes. Besides charge density, other factors can also influence the adsorption amount because of the adsorption process kinetics. For example, the molecular weight can affect the accessible area for polymers on the fiber surface because of the pores in the fibers. The structure of polyampholytes can influence the conformation of adsorbed polymers. The salt condition can also affect the conformation. Because a little change of conditions can result a large differences of experimental results, many experiments have been done with different kinds of polyampholytes or different substrates in different conditions. For example, Mishael and Dubin researched the effect of pore size and ionic strength for adsorbing polyelectrolyte on CPG. Mueller researched the pH effect on protein adsorption. Li and Balastre studied the different effects of substrates for polyelectrolyte adsorption. Blokhus and Djurhuus researched the effect of molecular weight for poly(styrene sulfonate) adsorption. Mahltig did a series of experiments...
concerning the adsorption of PMAA-b-PDMAEMA on silicon surface, considering all of these factors. \textsuperscript{38-40} Sezaki\textsuperscript{41} researched the effects of pH, salts, and charge ratio on adsorption of DMAPAA-IA to fines-free hardwood fiber. He found that the maximized adsorption amounts appeared around the IEP of the polyampholytes. Maximum adsorption corresponded to the condition in which the net charge of the polyampholyte was relatively low and opposite in sign to that of the substrate surface. The adsorbed amount increased with increasing conductivity under same pH condition. But more research is needed with respect to the effect of charge density.

To achieve a better understanding of adsorption phenomena, different methods have been used. Ellipsometry can be used to measure directly the adsorbed layer and layer thickness on a flat surface. Surface force apparatus (SFA) can be used to research the interaction. Small-angle neutron scattering (SANS) can be used to determine the adsorbed layer structure\textsuperscript{42}. But the problem of these methods is that only very little solution volume can be studied and the experimental situation is not representative of conditions during adsorption in an actual paper mill. So other experimental approaches should be considered. Sezaki found a new procedure for streaming current titration\textsuperscript{41}. With this method the adsorbed amount can be calculated easily.

Having introduced a variety of issues, based on the literature, the next section of this thesis document will describe the key objectives and hypotheses considered in the present work. Following that, the main results of the project will be presented in the form of three research articles, all of which have been submitted for publication. \textless\textless The role of polyampholyte charge density on its interactions with cellulos. Charge and the dry-strength performance of polyampholytes: Part 1. and Part 2\textgreater\textgreater The first of these articles focuses on the effect of
polyampholyte charge density on colloidal phenomena, including electrokinetic and adsorption effects. The second and third articles consider the dry-strength effects of polyamphololytes, and additional effects of polyaluminum chloride (PAC) are considered. Finally, a discussion section, after the three articles, considers the results as a whole and makes comparisons between the present results versus theoretical and practical findings from other investigators.
3. OBJECTIVES

As polyampholytes have received increasing interest in paper manufacture, as well as sludge dewatering and detergency, the properties of polyampholytes used in these industries as additives have received more and more consideration. Because many factors affect the structures of polyampholytes, which leads to the different behavior, these factors should all be researched for any kind of amphoteric samples.

Sezaki studied the effects of the pH, salt and charge ratio of amphoteric samples as strength agent in paper manufacture. So here our purpose is to find the relation between the colloidal behavior of polyampholytes and their charge density with same charge ratio. Also pH, as a main factor responsible for the behavior of polyampholytes, as well as charge density, are key topics of the present investigation.

Through the different experiments, it was our hope to be able to evaluate the following tentative hypotheses:

(1) It is proposed that the behavior of polyampholytes should be pH-dependent, because the charge nature on the polyampholyte chain is expected to be changed with pH.

(2) It is proposed that the iso-electric point (IEPs) of polyampholytes effect also may depend on pH, despite the fact that the ratio of ionizable groups of each charge as a fixed molar ratio. That means that around the IEP, the behavior of polyampholytes should be different compared to other pH conditions, affecting observable phenomena such as streaming titration, adsorption and viscosity. Around the IEP, the
polyampholyte chain prefers to interact with itself, which is tentatively proposed to cause the interaction between the chains of different polyampholyte macromolecules to be very low. Based on this hypothesis it would be expected that in the vicinity of the IEP the polyampholytes should have relatively little interaction with polyelectrolyte titrants (high charge density strong polyacids or polybases); the adsorption amount should reach a maximum; and the solution viscosity should be lowest around IEP.

(3) The behavior of polyampholytes as dry strength agents should be affected by the charge density.

(4) Polyaluminum chloride (PAC) can be used to interact with the anionic polyelectrolytes. So it should interact with the negatively charged groups on the polyampholytes. That means, it should improve the paper strength.
4. PAPERS (EXPERIMENTAL, RESULTS, DISCUSSION)

4.1 Papers-Part 1

The role of polyampholyte charge density on its interactions with cellulose

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Keywords: Polyampholytes, dry strength, streaming potential, adsorption, pH titrations, amphoteric polymers

SUMMARY: Polyampholytes offer considerable promise as dry-strength additives, but the molecular mechanism involved in their adsorption needs to be better understood. Amphoteric terpolymers of acrylamide, itaconic acid, and N-[3-(NN’,N’-dimethylamine)propyl]acrylamide (DMAPAA) with a constant ratio of basic to acidic groups (5:4) were prepared by random polymerization. The basic groups ranged from 2.5 to 20 mole percent. Analysis by $^1$H and $^{13}$C nuclear magnetic resonance revealed near-quantitative agreement with the make up stoichiometry.

Streaming potential tests showed significant effects of polyampholyte adsorption, depending on the charge density of the polyampholyte, its level of addition, the pH, and the background electrolyte. Polyampholytes having higher net charge yielded more positive
streaming potential at low pH values and more negative streaming potentials at high pH values, compared to polyampholytes of lower charge density. At the extremes of pH, e.g. pH=3 and pH=11, the effects of a polyampholyte on streaming potential were similar to those of polyelectrolytes having a matched degree of substitution of charged monomeric groups. Except for the sample having the lowest density of charges, all of the polyampholyte samples showed a broad maximum in adsorbed amount vs. pH within the range of about pH=5 to pH=9, which is intermediate between the pKa values of the respective charged groups.

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Corresponding author: Martin A. Hubbe

**Introduction**

Considerable interest has been shown in recent years for the development of dry-strength additives having improved efficacy (Lorenčak et al. 2000; Kitaoka, Tanaka 2001; Claesson et al 2003; Lindström et al 2005). The present work seeks a greater understanding – and further increases in performance – of certain dry-strength additives that contain cationic and anionic groups on the same macromolecule. These so-called polyampholytes have shown superior
dry-strength capability in certain papermaking applications (Ye et al. 1990; Yoshizawa et al. 1998; Fukunaga 1999; Yoshimoto et al. 2004). Synthetic polyampholytes (Ye et al. 1990), as well as amphoteric starch products (McQueary 1990) also have shown promise for more rapid dewatering of some papermaking furnish types. A further advantage of amphoteric additives is that they are less likely to disturb the over-all balance of ionic charges in a paper machine system (McQueary 1990; Kimura, Hamada 1992), and that the adsorption efficiency onto cellulosic surfaces is observed to be high under a wide variety of conditions (Glittenberg 1993; Yoshizawa et al. 1998; Yoshimoto et al. 2004).

One of the most critical requirements that a chemical additive must satisfy to function effectively in the paper machine wet end as a dry-strength additive is efficient adsorption onto fibers and other solid surfaces (Reynolds, Wasser 1980; Howard, Jowsey 1989). In the case of ordinary polyelectrolytes, those having ionic groups with only a single sign of charge, it has been found that the adsorption efficiency can be explained based on the pH-dependencies of the ionizable groups on the polymer and on the substrate (Wågberg 2000). Other factors affecting adsorption include the ionic strength of the solution (van de Steeg et al, 1992), the molecular mass (Pelton et al. 2003), and the charge densities of the materials (Park, Tanaka 1998; Zhang et al. 2000). An optimum charge density of cationic polyelectrolyte has been observed in some cases, relative to maximizing the adsorbed amount on a negatively charged substrate (Lindström, Wågberg 1983; Rojas et al. 2002). Tests carried out over a range of salt concentrations have revealed a “subtle balance of forces” that determine adsorption of cationic starch and other cationic dry-strength additives onto cellulosic surfaces (van de Steeg et al., 1992; Sukhishvili, Granick 1998; Wågberg 2000).
Though it is reasonable to expect that the dry-strengthening effect of polyampholyte additives also should be highly dependent on their interactions with cellulosic substrates, the charge relationships are expected to be more complex (Bekturov et al. 1990; Higgs, Joanny 1991; Dobrynin et al. 1997; Kudaibergenov 2002). As a working hypothesis, it is tempting to suggest that polyampholyte adsorption can be adequately explained by the net ionic charge of the macromolecule at a given pH and monomeric composition. However, such a hypothesis fails to offer insight into the observed superior performance of this class of dry-strength chemicals. Possible mechanisms that have been considered by others to account for unique capabilities of polyampholyte molecules have included their tendency to self-associate (Kudaibergenov 2002), their tendency to become less soluble in certain pH regions corresponding to self-neutralization (Neyret et al. 1995; Dobrynin et al. 1997; Everaers et al. 1997), and their ability to rearrange their macromolecular conformations, a process that affects their interaction with substrates of either positive or negative charge (Neyret et al. 1995).

In addition to interest in the mechanistic questions cited above, the present work was carried out to shed light on the effect of polyampholyte charge density. That is, if one holds the ratio of basic to acidic monomeric groups constant, is there an advantage, in terms of interactions with cellulose, of having a lower or higher net content of ionic groups in the polyampholyte? Also, we wanted to find out whether the streaming potentials and adsorption behavior resulting from treatment of cellulosic materials with polyampholytes and suitably matched polyacid and polybase samples could be explained in terms of their charge characteristics.
Materials and Methods

Experiments were conducted in deionized water prepared with an ion-exchange system from Pureflow, Inc. Inorganic chemicals all were of reagent grade. Polyampholyte and simple polyelectrolyte samples were prepared by free-radical polymerization, following the molar recipes of charged monomers indicated in Table 1. The cationic monomer was N-[3-(N’,N’-dimethylamino)propyl]acrylamide (DMAPAA), a tertiary amine. The anionic monomer was a dicarboxylic acid, itaconic acid (IA). In each case a sufficient amount of neutral acrylamide monomer was added to comprise 100% on a molar basis.

A typical procedure of synthesis (see G in Table) was as follows: 174 g of 40% acrylamide aqueous solution were added to a reaction vessel, 3.25 g of 80% itaconic acid and 300 g of ion exchange water were placed into a four neck flask provided with a reflux condenser and the mixture was heated to 60 °C in a nitrogen atmosphere. Then 10 g of 1% ammonium persulfate aqueous solution were added to the reaction solution and allowed to react at 85 °C for one hour. After cooling, an anionic polyacrylamide solution (sample G) was obtained. The cationic and amphoteric variants were prepared using the monomer ratios shown in Table 1. Methylenebisacrylamide was employed sparingly as a cross-linking agent in order to achieve molecular masses in the desired range, as shown.
Table 1. Synthesis of acrylamide-based polyampholytes and copolymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ionic nature</th>
<th>DMAPAA (mol %)</th>
<th>IA (mol %)</th>
<th>Viscosity* (mPa⋅s)</th>
<th>$M_w$ ** ($10^6$ Daltons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Amphoteric</td>
<td>2.5</td>
<td>1</td>
<td>5300</td>
<td>2.95</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>5</td>
<td>2</td>
<td>4900</td>
<td>2.85</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>10</td>
<td>4</td>
<td>4000</td>
<td>2.90</td>
</tr>
<tr>
<td>D</td>
<td></td>
<td>20</td>
<td>8</td>
<td>2400</td>
<td>2.93</td>
</tr>
<tr>
<td>F</td>
<td>Cationic</td>
<td>5</td>
<td>0</td>
<td>3600</td>
<td>2.98</td>
</tr>
<tr>
<td>G</td>
<td>Anionic</td>
<td>0</td>
<td>2</td>
<td>5300</td>
<td>3.23</td>
</tr>
</tbody>
</table>

* Evaluated at 25 °C; ** Mass-average molecular mass evaluated by SEC-LALLS-VIS (TDA-302, Viscotek). Note that IA is a dicarboxylic acid and therefore the effective content of anionic (carboxylic) groups is twice the value of the respective IA mol %.

The polymer solution samples described above were first purified by two cycles of dissolution in water and precipitation in methanol; then the pure samples were collected by freeze-drying. Samples for NMR analysis were prepared by making 2-3% polymer solution in D$_2$O. Crystals of CrK(SO$_4$)$_2$ were added at a concentration of 1.5 mM in order to reduce the spin-lattice relaxation times ($T_1$). The NMR experiments were performed in a Bruker 300MHz spectrometer equipped with a Quad dedicated probe at room temperature. The quantitative $^{13}$C spectra were acquired using an inverse gated proton decoupling sequence with a 90° pulse and a relaxation delays of 4.5 s, that was ~5 times of the longest $T_1$ measured for the samples. The $^1$H spectra were measured with 60° pulse and a pulse delay of 3 s.

Potentiometric titrations were carried out with 0.1% and 1% solids solutions of the polymers in deionized water, adjustment of the pH to 3.00 with 0.1N HCl, and then observing the change in pH resulting from incremental addition of 0.1 NaOH. A parallel test was carried out with a blank sample (polymer-free) to account for water’s uptake of base, as well as to compensate for any non-idealities with respect to the pH measurements.
To obtain information related to the effective ionic charge of polyampholytes, titrations were carried out with a Mütek PCD-05pH streaming current detector from BTG. The cationic titrant was 1x10^{-4} N poly-diallyldimethylammonium chloride (poly-DADMAC), Cat. No. AS1C0019 from Nalco Chemical Co. The anionic titrant was 1x10^{-4} N potassium salt of poly-vinylsulfate, Cat. No. AS9S0049 from the same source. Tests were carried out in the presence of NaCl solution having an ionic strength of 1x10^{-4} M.

Fines-free suspensions of bleached kraft fibers were prepared from a master batch that was first refined in a laboratory Hollander beater to a Canadian Standard Freeness value of 606 ml. The refined pulp was placed in the final chamber of a Bauer-McNett fractionator, and the “retained” fraction of a 200-mesh screen was used for further testing. The freeness of the fines-free refined hardwood pulp was 708 ml.

Streaming potential tests, to determine the electrokinetic nature of the cellulosic surfaces, were carried out with the SPJ device described elsewhere (Wang, Hubbe 2001). Briefly stated, 7.5g fines-free pulp (oven dry) and a certain amount of 0.1% polyampholyte solution were added to 750ml supporting electrolyte. The pH was adjusted with dilute solutions of HCl or NaOH. The default supporting electrolyte, except where noted otherwise, contained 1x10^{-4} M sodium bicarbonate (to stabilize the pH near to the neutral point) and sufficient sodium sulfate to achieve an electrical conductivity of 1000 µS/cm at about 23 °C (laboratory temperature). Streaming potential measurements were conducted with a pressure differential of 207 kPa across the fiber pad.

To determine the amounts of polymers adsorbed from solution onto cellulosic surfaces, the solution concentrations of polyampholyte (samples A through D) or simple polyelectrolyte (samples F, and G) were adjusted to 0.1%. Aliquots of 1.00 oven-dry grams
of fines-free bleached hardwood kraft fibers at 0.5% consistency were prepared. To each aliquot, 10 ml of polymer solution was added, with continuous stirring for 5 minutes. The slurry was then filtered through a 400-mesh screen. The filtrate was adjusted to pH=3 and a conductivity of 2000 µS/cm, then titrated by 1x10^{-4} N PVSK. This value was then compared with a blank to calculate the adsorbed amount.

**Results**

Figure 1 shows the $^1$H NMR and $^{13}$C NMR spectra of the six samples (see Table 1). The peak assignments indicated in Fig. 1 were made with the help from our previous DEPT and 2-D NMR results (Sezaki et al. 2006).

![Fig. 1. $^1$H NMR spectra (left) and quantitative $^{13}$C NMR spectra (right) of the six copolymer samples. The monomer compositions are summarized in Table 1.](image)

From the peak integrations of the $^{13}$C and $^1$H NMR spectra, the monomer compositions were calculated for the six copolymers and are presented in Table 2. In general there was excellent agreement between the synthesis recipes and the composition of the polymers obtained, which indicates that near-quantitative reactions took place.
Table 2. Composition according to preparation and by NMR analysis. AA – acrylic acid; DMAPAA – N-[3-(N',N’-dimethylamino)propyl]acrylamide; IA – itaconic acid

<table>
<thead>
<tr>
<th>Sample</th>
<th>DMAPAA in Feed (%)</th>
<th>DMAPAA by NMR (%)</th>
<th>IA in Feed (%)</th>
<th>IA by NMR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.5</td>
<td>2.6</td>
<td>1</td>
<td>1.2</td>
</tr>
<tr>
<td>B</td>
<td>5</td>
<td>5</td>
<td>2</td>
<td>2.2</td>
</tr>
<tr>
<td>C</td>
<td>10</td>
<td>9.5</td>
<td>4</td>
<td>4.8</td>
</tr>
<tr>
<td>D</td>
<td>20</td>
<td>18</td>
<td>8</td>
<td>8.4</td>
</tr>
<tr>
<td>F</td>
<td>5</td>
<td>5</td>
<td>0</td>
<td>(0.6)</td>
</tr>
<tr>
<td>G</td>
<td>0</td>
<td>0.5</td>
<td>2</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Ionic Nature of the Polymers

Results of potentiometric titrations are given in Fig. 2a. The plotted lines were calculated based on the known content of monomeric groups in the samples and by fitting the values of the dissociation constants for the two carboxyl groups and the tertiary amine group. The values of the two pK_a and the pK_b constants giving the best overall fit to the data were, respectively, 4.10, 6.82, and 9.82. As shown, the assumed values of dissociation constants yielded good agreement with the observed consumption of base as a function of pH. The agreement not only helps to confirm the values given in Table 1 for the composition of the polyampholytes, but also it is clear that the acidic and basic groups remained accessible to interaction with base throughout the pH range studied.

Because samples A through D have increasing charge densities, it makes sense to consider the expected effects of nearest-neighbor interactions (Mazur et al. 1959). Theoretical and experimental work by Merle (1987) suggests that such interactions would tend to shift the dissociation constants of the acids and bases farther apart with increasing overall charge density of the polyampholytes. This effect is proposed to be due to a higher
statistical probability that oppositely charge groups become neighbors. However, the results in Fig. 2a suggest no such trend, an observation that may be due to the relatively low overall ionic group content of the polymers, compared to the cited work.

Potentiometric titration results corresponding to polyampholyte sample B and two polyelectrolytes having the same density of either cationic or anionic monomer units are shown in Fig. 2b. Excellent agreement with the calculated values was obtained under acidic conditions and up to a pH of 8, based on the same assumed dissociation constants. Deviations at yet higher pH in the case of samples B and G are tentatively attributed to the presence of residual ammonia, a byproduct of the initiator used in the free-radical polymerization. In addition, NMR analysis of sample G showed the presence of 0.5% of the cationic monomeric groups.

![Fig. 2](image)

**Fig. 2.** Results of potentiometric titrations of salt-free 0.001% polymer solutions with 1 mM NaOH. (a) Polyampholyte samples of increasing charge density, but constant ratio of acidic to basic groups. (b) Polyampholyte sample “B” compared to two simple polyelectrolyte samples having the same density of either acidic or basic groups (samples F and G).
Polyelectrolyte Titrations

Another approach to characterizing the ionic nature of a soluble polymer involves evaluation of its interactions with a known polyelectrolyte. Figure 3 shows the results of experiments in which the subject polymer solutions were titrated to a streaming current endpoint of zero, using the standard titrants poly-DADMAC and PVSK (see experimental). The plotted lines were calculated in the same way as those in Fig. 2.

As shown in Fig. 3a, the amounts of the standard titrants required to reach a streaming current endpoint of zero, in the presence of the polyampholyte solutions, tended to be larger than the amounts predicted based on the molar composition of the polyampholytes, especially at the limits of very low or very high pH. The predictions were based on an assumed 1:1 stoichiometry of interaction between the titrant and the net expected charge of the polyampholyte, based on the results in Fig. 2. The lack of fit implies that the standard titrants poly-DADMAC and PVSK were “inefficient” in neutralizing the respective
polyampholytes. This behavior is consistent with the known mis-match in density of the ionic groups (Tse 1979; Tanaka 1983; Laine, Lindström 2000; Chen et al. 2001), noting that each of the standard titrants is fully charged throughout the range of pH studied, with one ionic group per monomeric unit.

A further conclusion can be drawn from Fig. 3a with respect to the middle values of pH. Within a pH “window” between pH values corresponding to the $pK_a$ and that $pK_b$ constants determined by potentiometric titration, the absolute values of the titration endpoints did not exceed the predictions based on the potentiometric titrations and the known compositions. This result might be expected, due to the decreased molecular extension that is predicted for a polyampholyte in solution at a pH value that yields approximately equal amounts of positive and negative charged groups (Bekturov et al. 1990; Higgs, Joanny 1991; Everaers et al. 1997). Thus, within the intermediate window of pH, it is reasonable to expect a reduced interaction between the standard titrants and the polyampholytes, and hence the standard titrants no longer appear “inefficient.”

Figure 3b shows corresponding results for the polyampholyte sample B and the two polyelectrolyte samples sharing the same density of either basic or acidic groups. Here again one can observe deviations from an assumed 1:1 stoichiometry under those conditions where the research samples were most strongly positive or negative in net charge. The fact that the poly-acid, sample G, required more cationic titrant to reach the streaming current endpoint throughout the intermediate range of pH provides further support for the view that the titrants interact inefficiently with charged samples having a substantially lower charge density.
Streaming Potential

Efficient utilization of a strength-enhancing additive requires attention to how the additive affects the electrostatic charge and how much of the additive can be added before the fiber surfaces reach a plateau value of charge. As shown in Fig. 4, addition of increasing amounts of polyampholyte solution to a suspension of de-crilled, bleached hardwood kraft fibers resulted in a progressive change in the measured streaming potential obtained at a pressure differential of 207 kPa (30 psi). These tests were carried out in the presence of sufficient sodium sulfate to give a solution conductivity of 1000 µS/cm, with a 10^{-4} molar concentration of sodium bicarbonate to stabilize the pH near to the neutral point. The results show a leveling off of the streaming potential at polyampholyte addition levels above about 0.1%, based on solid mass.

![Graph showing streaming potential vs. addition level of polymer A](image)

*Fig. 4. Streaming potential vs. addition level of polymer “A,” having 2.5% cationic substitution and 2% anionic substitution*

Figure 5 shows results of streaming potential tests carried out at different pH values with polymer solutions added to microcrystalline cellulose (MCC) at the low level of treatment (0.08% on a dry basis) in the presence of sodium sulfate (1000 µS/cm conductivity). As shown in Fig. 5a, addition of polyampholytes shifted the measured
streaming potential values relative to untreated MCC. At low pH the polyampholyte treatments yielded streaming potential values that were less negative than the untreated fibers (labeled as “blank”), whereas the opposite was true at high pH values. Polyampholytes having higher charge density (increasing in the order A through D) tended to show the greatest deviations of streaming potential relative to untreated MCC.

To place the effects of the polyampholytes in context, Fig. 5b compares the streaming potential results for polyampholyte sample “B” (with 5 mole % basic groups and 4 mole % acidic groups) vs. the two simple polyelectrolytes having the same molar levels of either basic or acidic groups. As shown, the polyelectrolyte treatments resulted in much more significant differences in streaming potential relative to the untreated MCC, especially in the pH range of about 5 to 10. These pH values encompass the approximate range expected between the pK_{a} value of carboxylic acid groups and pK_{b} values of tertiary amine groups present on the polymers. Though results for the polyampholyte “B” were intermediate between those for the respective simple polyelectrolytes, “B” yielded results more similar to the poly-base “F” at pH values below 5 and more similar to the poly-acid “G” at pH=10.
Figure 6 shows results of similar tests carried out in bleached hardwood kraft fibers. The treatment level of polymer on bleached kraft fibers was 0.213%, on a dry basis. Though the same discussion points can be made, as in Fig. 5, the contrasts are yet more distinct, and the differences relative to the untreated fibers tend to be greater. All of the polyampholyte samples shifted the streaming potential to about the same extent when the pH was in the range of about 7 to 9. This range is near to the expected isoelectric point, based on the composition of these polyampholytes (Alfrey, Pinner 1957; Long et al. 1998).

As shown in Fig. 6B, the poly-acid sample “G” had almost no detectable effect relative to the streaming potential of untreated bleached kraft fibers. By contrast, the cationic polyelectrolyte (poly-base) “F” strongly reversed the charge of the fibers up to a pH above 9. The pH-dependency of the streaming potential after treatment with polyampholyte was almost linear with pH, reflecting a progressive change in the ionic nature exposed at the fiber surfaces.

![Fig. 6a. Polyampholyte charge density and pH effects on streaming potential of bleached hardwood kraft fibers](image1)

![Fig. 6b. Polyampholyte effects on streaming potential of bleached hardwood kraft fibers compared with polyelectrolytes having matched charge density](image2)
**Adsorption**

Figure 7a shows the results of tests in which fiber suspensions were mixed with solutions of soluble polymer. To determine the adsorbed amount, filtrate from the suspensions was adjusted to a pH of 3 and then titrated with $1 \times 10^{-4}$ N PVSK to a streaming current endpoint of zero. The total amount of polymer added was 1 g per 100 g of pulp, and tests were carried out in the presence of sodium sulfate, giving a conductivity of 1000 µS/cm. As shown, all of the polyampholytes were found to adsorb efficiently, especially at mid-range pH values of about 5 to 9. Somewhat lower adsorption was observed in the case of the lowest-charge polyampholyte, sample “A”, having a molar concentration of 2.5% basic groups and 2% acidic groups.

As shown in Fig. 7b, the cationic polyelectrolyte, sample F, adsorbed less efficiently, compared to polyampholyte “B,” having the same molar proportion of tertiary amine groups. The observed increase in adsorption of the cationic polyelectrolyte with increasing pH is consistent with expected increases in negative surface charge density, an effect that also can cause the fiber to swell and become more accessible (Grignon, Scallan 1980; Lindström 1992). Superior adsorption efficiency of the cationic polymer, relative to the polyampholyte, was observed only near to pH=9. The severe drop-off in adsorption of the cationic polymer above pH=10 is consistent with the dissociation constant of the tertiary amine group determined earlier, based on the fitting of the potentiometric titration data. Results for sample G (not shown) indicated insignificant adsorption of the anionic polyelectrolyte on the kraft fibers throughout the range of pH tested.
Discussion

Taken as a whole, the present results can help rationalize the reported superior effects of polyampholytes for purposes of dewatering (Ye et al. 1990; McQueary 1990) and dry strength (Tanaka et al. 1976; Ye et al. 1990; Yoshizawa et al. 1998; Fukunaga 1999; Yoshimoto et al. 2004). Rates of gravity drainage of papermaking furnish (Horn, Melzer 1975), as well as the performance of dry-strength agents (McKague et al. 1974; Strazdins 1989) are often maximized when the dosage of a cationic additive is just sufficient to achieve a neutral zeta potential. The results of streaming potential tests shown in Figs. 4-6 suggest that polyampholytes can be used as an unconventional way to shift the zeta potential of a papermaking system towards a lower absolute value. Thus, treatment with the amphoteric polymers yielded streaming potentials that were closer to zero, compared to treatment with polyelectrolytes having similar density of ionizable groups. Unlike what happens in the case of treatment with a high-charge cationic polymer (Horn, Melzer 1975), there is no significant
danger that the sign of charge of the system could be strongly reversed, with possible adverse consequences on paper machine operations.

Streaming current titration results in Fig. 3a suggest a possible synergistic effect between polyampholyte dry-strength and other charged polymers, such as retention aids. Strong adsorption onto furnish solids is a prerequisite for high retention aid efficiency (Horn, Linhart 1991; Doiron 1998). For example, anionic acrylamide copolymer retention aids are generally ineffective when added to a net-negative suspension of cellulosic fibers in the absence of cationic agents (Hubbe 2001). Results in Fig. 3a show, however, that the polyampholytes were able to interact strongly with polyelectrolytes of either positive or negative charge. This observation is consistent with a possible role of polyampholytes in serving as anchoring points for retention aid polymers.

With respect to the role of polyampholytes in promoting dry strength, the most interesting aspect of the present results involves the relatively wide maxima in the curves of adsorbed amount vs. pH. As mentioned in the introduction, efficient adsorption can be considered as a prerequisite for efficient use as a strength additive for the wet end. As shown in Fig. 7a, efficient adsorption was observed between the pH values of about 5 and 9. According to Fig. 3a, the isoelectric points of the polyampholyte samples were approximately 7.5. The fact that the polyampholytes maintained their efficient adsorption in the range 7.5<pH<9, even when they had a net-negative charge, is consistent with a process of molecular rearrangement, resulting in a higher relative concentration of oppositely charged groups interacting with the net charge of a substrate (Neyret et al. 1995; Mahltig et al. 1999). Efficient adsorption is also consistent with the predicted tendency of polyampholytes to
associate with like macromolecules and to precipitate readily from solution under conditions
in which charges of both sign are present at comparable levels (Everaers et al. 1997).

**Conclusions**

1. The composition of a series of polyampholyte and polyelectrolyte samples synthesized
   for this study showed excellent agreement between the synthesis recipes, NMR analyses,
   and potentiometric titration results.

2. Potentiometric titration data were fitted reasonably well based on a single set of
dissociation constants for the acidic and basic groups of the polymer samples. The \( pK_a \)
values of the two kinds of carboxyl groups in the samples were determined to be 4.1 and
6.8. The \( pK_b \) value of the tertiary amine group was 9.8.

3. Though the polyampholyte samples showed a strong ability to undergo complexation
interactions with high-charge-density, strong polyacid or polybase titrants at the extremes
of pH, streaming current titrations indicated that the samples had less apparent charge
within a “window” of intermediate pH between about 6 and 9, a range in which charged
groups of both sign are present on the macromolecules.

4. Streaming potential tests, by contrast, showed an almost linear response to pH, when
either microcrystalline cellulose (MCC) or bleached kraft fibers had been treated with
polyampholyte solution. This behavior was in contrast to that of polyelectrolytes, for
which the streaming potential of the treated cellulosic surfaces remained almost
independent of pH in the range between about 6 and 9.

5. Adsorption isotherms showed maximum adsorption of the polyampholytes onto bleached
kraft fibers in the case of polyampholyte samples having moderate to high charged
density. Maximum adsorption occurred within the sample pH window over about 6 to 9,
a range where ionic groups of each sign are present at comparable levels. Polybase adsorption, under matched conditions of molecular mass, charge density, and suspension characteristic, was generally lower, compared to the corresponding polyampholyte. A polyacid having the same content of carboxyl groups as one of the polyampholytes failed to show significant adsorption.

**Acknowledgments**

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**Literature**


**4.2 Papers-Part 2**

**Charge and the Dry-Strength Performance of Polyampholytes. Part 1. Handsheets and Bulk Viscosity.**

J. SONG, Y. WANG, M.A. HUBBE, O.J. ROJAS, N.R. SULIĆ, and T. SEZAKI

Paper strength was increased by adding random terpolymers having a fixed ratio of basic to acidic monomeric groups to bleached kraft fiber slurries over a wide range of pH. Subsequent treatment of the fiber slurries with polyaluminum chloride (PAC) further increased tensile breaking length. By contrast, PAC tended to reduce the dry strength contribution of a cationic polyelectrolyte having the same mass and cationic monomer content as one of the polyampholytes. It is proposed that such effects are due to the influence of pH and ionic aluminum species on the molecular conformations, as well as the electrokinetic behavior of solids exposed to the polyampholytes. Results of solution viscosity tests indicated more expanded polyampholyte conformations resulting from PAC addition, especially in those cases where dry strength advantages of PAC addition were observed.

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**INTRODUCTION**

Recent work in our lab has confirmed earlier reports showing superior dry-strength and related effects resulting from wet-end addition of soluble polymers having both positive and negative ionic groups [1-4], the so-called polyampholytes. The present work is intended to clarify the relationship between such strength gains and the charged nature of these polymers.
Any discussion of dry strength effects of papermaking wet-end additives needs to begin with consideration of bond formation between fibers [5]. Work by Howard and Jowsey [6] showed that effects of cationic starch, the most widely used dry-strength additive, are consistent with increased joint strength per unit bonded area. McKenzie [7] and Pelton et al. [8] described dry strength development in terms of a three-dimensional solubilization of the bonding agent with wood-derived macromolecules extending from fiber surfaces. The subject of joint strength and the role of bonding agents has been reviewed recently [9].

Various investigators have proposed that the effectiveness of polyelectrolytes as agents of inter-fiber bonding ought to be related to their molecular mass or their average size in solution [10-12]. Due to the relatively short processing times in the wet end of a paper machine, one cannot assume that adsorbed conformations reach an equilibrium state. The initial adsorbed polymer conformation is expected to resemble the bulk conformation, at least in the case of high-mass polyelectrolytes [13-15]. The degree to which the polymer adopts a flattened conformation, or otherwise rearranges itself, is expected to depend on time, molecular mass, the charge density of the polymer, the strength of interactions between molecular segments and the substrate, the degree of solubility of the polymer in the solution, the existence of branching or cross-linking within the polymer, and the ionic strength of the solution [16-18]. The molecular extension of polyampholytes is expected to depend on the same factors, and also on the ratio of monomeric charged groups of each sign [19-22]. The adsorption of polyampholytes also has been considered by others [23-24]. Viscosity tests have been found to be a convenient way to study factors that affect molecular extension [19,25-27].
Soluble aluminum compounds have been of great interest to paper technologists [28-30], as well as to scientists investigating the ionic speciation [31-33] or optimization of aluminum compounds for coagulation of suspensions [34-38]. Complexation can be expected when aluminum compounds are added to solutions of anionic polyelectrolytes [29,39-40]. Recent results suggest that certain ionic species of aluminum can maximize interactions with anionic polyelectrolytes [41], as well as coagulation of suspensions of negatively charged particles [38]. The present work is aimed at elucidating the effect of polyampholyte overall charge density and charge ratio on the development of dry strength and the synergies that occur in the presence of aluminum ions.

**EXPERIMENTAL**

Experiments were conducted in deionized water prepared with an ion-exchange system from Pureflow, Inc. The poly-aluminum chloride (PAC) was Compozil Eka ATC 8210 from Eka Chemicals, Paper Chemicals Div. The product was added on an as-received basis. Other inorganic chemicals all were of reagent grade.

**Polymer Preparation and Characterization**

Polyampholyte and polyelectrolyte samples were prepared by free-radical polymerization, following the molar content of charged monomers indicated in Table 1. The cationic monomer was N-[3-(N’,N’-dimethylamino)propyl]acrylamide (DMAPAA), a tertiary amine. The anionic monomer was a dicarboxylic acid, itaconic acid (IA). In each case a sufficient amount of neutral acrylamide monomer was added to adjust the total molar content to a fixed value and the mole ratio of cationic to anionic groups was also kept constant (5:4 for samples A through D). The mol % of DMAPAA and IA was corroborated...
by $^1$H and $^{13}$C nuclear magnetic resonance (NMR). Solution viscosities, as shown, were obtained with a Brookfield Model B8L viscometer (Tokimec, Inc.) at approximately 15% solids at 25 °C.

Table 1. Synthesis of acrylamide-based polyampholytes and simple copolymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polymer type</th>
<th>DMAPAA (mol %)</th>
<th>IA (mol %)</th>
<th>Viscosity* (mPa.s)</th>
<th>$M_w$ ** (10$^6$ Daltons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Amphoteric</td>
<td>2.5</td>
<td>1</td>
<td>5300</td>
<td>2.95</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>5</td>
<td>2</td>
<td>4900</td>
<td>2.85</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>10</td>
<td>4</td>
<td>4000</td>
<td>2.90</td>
</tr>
<tr>
<td>D</td>
<td></td>
<td>20</td>
<td>8</td>
<td>2400</td>
<td>2.93</td>
</tr>
<tr>
<td>F</td>
<td>Cationic</td>
<td>5</td>
<td>0</td>
<td>3600</td>
<td>2.98</td>
</tr>
<tr>
<td>G</td>
<td>Anionic</td>
<td>0</td>
<td>2</td>
<td>5300</td>
<td>3.23</td>
</tr>
</tbody>
</table>

* 25 °C and 100 s$^{-1}$. ** SEC-LALLS-VIS (TDA-302, Viscotek).

**Handsheet Preparation**

Tests involving handsheets were carried out with bleached hardwood kraft fibers that had been beaten for 5.6 minutes with a laboratory Hollander refiner (Valley Machinery Co., Appleton, WI) to a Canadian Standard Freeness value (TAPPI Test T227) of 440 ml. The refined fibers were then placed in a 200-mesh screen chamber of a Bauer-McNett classifier apparatus (see TAPPI Method T233). The classifier was run for 15 minutes, per batch, to substantially remove fiber fines from the suspension. The decrilling procedure was carried out to simplify interpretation of results to be presented later, since any polymer becoming adsorbed onto fibers is to be retained in the final paper. The decrilled suspension had a freeness of approximately 600 ml CSF.

The fibers then were resuspended as a 0.5% slurry in 10$^{-4}$ M sodium bicarbonate solution, to which sufficient sodium sulfate had been added to reach an electrical conductivity of 1000 µS/cm at 23 °C. Polyampholyte solutions were added at selected levels and with constant stirring to the fiber suspension. In order to maintain the same salt concentration during formation of the paper, a calibrated amount of sodium sulfate solution
was added to the a British sheet mold just before fiber slurry was added to make the handsheets, following TAPPI Method T205.

In the case of tests involving PAC, NaOH or H$_2$SO$_4$ was first added to the fiber slurry to adjust the pH followed by polyampholyte (or polyelectrolyte), and final PAC addition. The pH of the fiber slurry was pre-adjusted in such a way that the suspension’s pH reached the reported value upon addition of PAC. Sufficient sodium sulfate and either NaOH or H$_2$SO$_4$ were added to the handsheet mold so that the same pH and electrical conductivity were maintained throughout the forming process.

**Viscosity Tests**

Viscosities of 0.1% solids aqueous polymer solutions were measured with an Ubbelohde viscometer in a thermostated water bath at 25.0 °C with the addition of sufficient NaCl so that the resulting ionic strength at different pH values remained at 0.01 moles per liter. The pH was adjusted with HCl or NaOH.

**RESULTS AND DISCUSSION**

Figure 1 shows the results of a series of handsheet tests carried out with various polymer solutions added to a slurry of decrilled bleached hardwood kraft fibers at pH=5 and with sufficient sodium sulfate added to achieve an electrical conductivity of 1000 µS/cm. In cases where the stock was then treated with poly-aluminum chloride (PAC) at the levels shown, the pH was pre-adjusted to ensure the final pH stated in each case (see Experimental). Results labeled as “A” through “G” correspond to the employed polymers (see Table 1). Note again that samples A through D were polyampholytes having a fixed ratio of 5:4 basic to acidic ionizable groups and an increasing overall content of ionizable monomeric groups in the ratio 1:2:4:8, respectively. Sample F was a cationic polyelectrolyte having the same
density of tertiary amine groups as B. Likewise, sample G was an anionic polyelectrolyte having the same density of carboxyl groups as B. As shown in Fig. 1, treatment with the polyampholytes generally resulted in strength gains that were far superior to those achieved by the polyelectrolytes.

Results shown in Fig. 1 raise various questions involving effects of electrical charges. For example, why, in the absence of PAC, was the highest strength achieved at an intermediate charge density of the polyampholyte, sample C, which had a molar content of 10% tertiary amine groups and 8% carboxyl groups? And why was the highest strength achieved when a small amount of the highly cationic aluminum-based additive PAC was added to the polyampholyte sample having the lowest density of ionizable groups?

Further questions related to how polyampholytes function as dry-strength agents arise from the results of tests at different pH values, as shown in Fig. 2. Comparing the results obtained at pH 4 (Fig. 2A) vs. pH 8.5 (Fig. 2B), it is apparent that the PAC addition
promoted the dry-strengthening effect with all of the polyampholytes at the higher pH of 8.5, but such treatment with PAC had less benefit to strength at pH=4. Also, it is worth questioning why the dry-strength performance of the cationic polyelectrolyte F was hurt by PAC addition and why the dry-strength performance of the anionic polyelectrolyte G was favored by lower pH.

**Viscosity Analysis**

To account for the tensile strength results presented above, a series of experiments was carried out to evaluate the bulk properties of the polymer solutions. As shown in Fig. 3A, the relative viscosity of each of the polymer solutions was strongly affected by pH in the absence of salt. First considering the polyampholytes, samples A through D, there was a broad minimum in relative viscosity centered at about 6<pH<7. The viscosity of the polyampholytes generally increased with increasing difference in pH relative to neutrality, except that the viscosity fell again at the extremes of pH, below about pH=3 and above about pH=11. The initial increase in viscosity with increasing difference of pH relative to the neutral region is consistent with an expected increase in net ionic charge of the polymers,
noting that the degree of dissociation of both the acidic and the basic groups on the polyampholytes will be a function of pH [19,42]. An increase in net charge is expected to increase the degree of expansion of the molecular conformations in solution [16,43-44]. The subsequent decreases in viscosity of polyampholyte solutions as the extreme values of pH are approached are consistent with the increase in ionic strength of solution resulting from addition of large amounts of acid or base. In these cases the counterions screen the electrostatic and osmotic forces, collapsing the charged polymers.

Results corresponding to the polyelectrolyte samples F and G in Fig. 3 can be accounted for in a similar manner. Separate pH titrations showed that the cationic polyelectrolyte F had a $pK_b$ value of 9.8, and that the anionic polyelectrolyte G had $pK_a$ values of 4.1 and 6.8 for the two adjacent carboxyl groups [45]. Thus, one would expect the molecules in sample F to have a relatively expanded conformation at relatively low pH values corresponding to the charged, protonated form of the tertiary amine groups. Then, with increasing pH above a value of 8 it is reasonable to expect a drop in viscosity, consistent with a reduced molecular extension. Considerations in the case of the anionic polymer G are similar, except that decreasing the pH is expected to increase the proportion of protonated, uncharged carboxylic acid groups relative to charged carboxylate groups on the polymer.

Results shown in Fig. 3B, corresponding to an electrical conductivity of 1000 $\mu$S/cm, generally show lower values of relative viscosity, consistent with screening of electrical charge interactions within the macromolecular chain. The general pattern of the results, however, was similar to what was observed in the absence of salt. One effect that becomes more evident in Fig. 3B is the differentiation between sample A, the lowest-charge polyampholyte, vs. those of higher density of ionic groups. Near to neutral pH, the solution
of sample A was considerably more viscous than the other samples. This observation suggests that the macromolecules in sample A did not have a sufficient density of oppositely charged ionic groups in order to contract the molecules to the same extent as the other polyampholyte solutions at pH=7.

![Fig. 3A. Relative viscosity of 0.1% polymer solutions in water as a function of pH in the absence of added salt](image)

![Fig. 3B. Relative viscosity of 0.1% polymer solutions in 0.01 M ionic strength solution as a function of pH.](image)

As shown in Fig. 4A, addition of a low level of PAC (0.01% in solution, on an as-received basis) consistently increased the relative viscosities of polyampholyte solutions in the absence of added salt, both at pH=4 and pH=5. The opposite was seen in the case of polyelectrolytes, for which increasing PAC monotonically decreased relative viscosity. A higher level of PAC (0.1%) was no longer effective in increasing the relative viscosity of the polyampholyte solutions.

Though there may be various interpretations to account for the results in Fig. 4, it is apparent, first of all, that there exists a specific interaction between PAC and the polyampholytes. It is proposed that the increase in viscosity upon addition of PAC at the 0.01% level is due to complexation between cationic aluminum ionic species and carboxylate groups on the polyampholytes. Since all of the results in Fig. 4 pertain to pH values below
the isoelectric points of the polyampholytes, such complexation would be expected to increase the net positive charge in each case, resulting in a more extended conformation. The reversion of the trend at higher PAC is again consistent with increasing ionic strength of the solution.

![Graphs showing relative viscosity changes with PAC addition at pH 4 and pH 5](image)

Fig. 4A. Effects of polyampholyte charge density and PAC addition on relative viscosities at pH=4

Fig. 4B. Effects of polyampholyte charge density and PAC addition on relative viscosities at pH=5

As indicated by the present results, the conformation of polyampholytes in bulk solution, in the presence and in absence of PAC, is a key factor to explain the development in dry strength. This is logical if one considers that the behavior of the macromolecules in the bulk solution has an important impact on the adsorbed state. For example, when the polymer is in a more “contracted” state in solution (lower viscosities) or in cases of lower solvency, the adsorbed amount on fiber surfaces is expected to increase, and better bonding is expected as a result.

Support to the foregoing explanation is found in our attempt to answer the first question made in relation to Fig. 1. At pH 5 sample C, used in the absence of PAC, produced the highest strength. Results for polyampholytes A and B are comparable, especially in the conditions used in Fig 2A for breaking length measured for slurries prepared at pH 4.
Nevertheless, it is shown consistently that at pH 4 and 5 the purely cationic polyelectrolyte (sample F) performed more poorly than the polyampholyte counterparts. The explanation to this observation lies in the fact that at lower pH (1) the polyampholyte molecules have a smaller hydrodynamic radius (lower viscosity) which allows a more effective diffusion and adsorption on the adsorption sites and, (2) they have a net, higher positive charge, that favors electrostatic interactions with the substrate (better adsorption). This explanation is also supported by direct measurement of polymer adsorbed amount via quartz crystal microbalance (QCM) piezoelectric sensors (data not shown). In fact, sample C showed the highest adsorbed amount at pH 4.

Polyelectrolyte F, which is purely cationic, showed a more extended conformation at pH 4 and 5 due to intra-chain repulsion (see viscosity data in Fig. 4B) and therefore is not expected to adsorb as effectively as polyampholyte B, C, or D. This was also confirmed by measurements of the adsorbed amount on cellulose via QCM. In this condition polyelectrolyte F produced relatively small improvement in fiber bonding.

Our results also point to the fact that at low pH the polyampholytes of intermediate cationic charge worked better than the other ones. In fact, electrostatic bridging between the polymer-coated surfaces, which is an important contribution in the development of paper strength, also reaches a maximum value at an intermediate value of charge density [46]. In the present case this optimum situation occurred for sample C.

At high pH (pH of 8.5) the addition of polymer G produced paper sheets of low breaking length. This is easily explained by the fact that in this condition the polyelectrolyte is effectively anionic and therefore electrostatic repulsion with cellulose surface charges prevents adsorption. Note that paper formation below the pKa of polyelectrolyte G
(suspensions of pH 4 or 5), the breaking length of the sheet was higher than at pH 8. This is as expected, since at low pH the negative charge is suppressed (less dissociation) and the polymer is able to adsorb.

At pH 4 or 5 it is interesting to note the synergetic effect that occurs upon addition of the highly cationic PAC additive to the polyampholyte solutions (A-D) This effect is augmented in the case of polyampholytes of low overall charge density, when the pH is low, while it seems that at higher pH (8.5) this synergy occurs more markedly for polyampholytes of higher charge density. The reason for these effects is not obvious, since PAC and the polyampholytes bear the same sign of net charges. This is evident in the case of purely cationic polyelectrolyte F that produced paper with low breaking length. A plausible phenomenon that could explain the above effects is that PAC interacts with the carboxylate moieties of the polyampholyte chains, rendering a net higher cationic character to the polymer that facilitates adsorption. Experimental evidence supports the observed effects [47-48]. On the other hand, the application of PAC with the anionic polyelectrolyte showed the lowest results, due to the fact that complexation and charge compensation occurs between the anionic polyelectrolyte and PAC and the effective charge (of PAC) is reduced.

CONCLUSIONS
1. Charge effects, pH, and the addition of polyaluminum chloride (PAC) significantly affected the dry strength resulting from treatment of bleached kraft fibers with polymers that contained both positively and negatively charged ionic groups. These polyampholytes yielded higher increases in dry strength, compared to polyelectrolytes having ionic groups with only one sign of charge. PAC addition generally benefited paper strength in cases where the fiber slurry had been treated with polyampholytes, but
the opposite was true if the fibers had been treated with either a cationic or an anionic polyelectrolyte.

2. Results of viscosity tests suggested that multivalent positive ions of aluminum form complexes with the carboxylate groups of polyampholytes, making them more cationic, and thus more expanded in solution.

3. Although it was generally the case that dry strength increases were maximized under pH conditions not far from those where the solution viscosities of polyampholytes were minimized, the optimum dry-strength resulted from a combination of various effects, most importantly a minimum molecular extension and an optimization of electrical charge interactions.

ACKNOWLEDGMENTS

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FIGURE CAPTIONS

Fig. 1. Tensile test resulting from treatment of a slurry (pH 5) of bleached hardwood kraft at the levels of PAC as shown following treatment with polymer samples (see Table 1) at the 1% level.

Fig. 2A. Results of tests similar to those in Fig. 1, except that the final pH of the slurry, before sheet forming, was 4.0.

Fig. 2B. Results of tests similar to those in Fig. 1, except that the final pH of the slurry, before sheet forming, was 8.5.

Fig. 3A. Relative viscosity of 0.1% polymer solutions in water as a function of pH in the absence of added salt

Fig. 3B. Relative viscosity of 0.1% polymer solutions in 0.01 M ionic strength solution as a function of pH.

Fig. 4A. Effects of polyampholyte charge density and PAC addition on relative viscosities at pH=4

Fig. 4B. Effects of polyampholyte charge density and PAC addition on relative viscosities at pH=5
4.3 Papers-Part 3

Charge and the Dry-Strength Performance of Polyampholytes. Part 2. Streaming Potential Analysis

Y. WANG, M.A. HUBBE, O.J. ROJAS, D.S. ARGYROPOULOS, X. WANG, and T. SEZAKI

Results reported in Part 1 of this series showed that paper strength improvements could be optimized by varying pH and the overall content of ionic groups in random terpolymers containing a fixed molar ratio of acidic and basic monomeric groups. In the present study it is shown that further treatment of kraft fiber slurries with polyaluminum chloride (PAC), after polyampholyte addition, can yield significant strength benefits under experimental conditions for which synergistic effects are favored, depending on the balance of charges and pH. Experiments with non-porous glass fibers showed that polyampholyte treatments can be used to achieve low absolute values of electrokinetic potential, with little chance of over-charging the system at high dosage levels. The relative effects of PAC on streaming potential and resulting paper strength were significant in the case of polyampholyte-treated fibers.

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INTRODUCTION

In Part 1 of this series it was shown that treatment of a bleached kraft fiber slurry with terpolymers containing both cationic and anionic functional groups, so-called
polyampholytes, resulted in greater dry-strength, compared with treatment of the same fiber slurry with the respective polyelectrolytes having a single charge [1]. Also it was reported that addition of low amounts of polyaluminum chloride (PAC) was generally beneficial to the performance of the polyampholytes as dry-strength agents. By contrast, such treatment reduced the dry-strength when used in conjunction with ordinary polyelectrolytes of either sign of charge. It was proposed that a subtle balance of complexation phenomena, hydrodynamic size, and effective electrokinetic charge might account for some of these observations. In the present article we report results of complementary experiments that help to explain these effects, based on results from model substrates as well as fiber systems as employed in Part 1.

Streaming potential (SP) measurements provide a powerful tool with which to study electrokinetic effects of polymer adsorption onto particles or fibers in aqueous suspension. Relative to some other kinds of electrokinetic measurements, SP tests in fiber suspensions are quick and direct, being based on signals that originate at the surfaces of the filterable solids [2-5]. When applying such tests to the case of polyampholyte molecules adsorbing onto cellulosic surfaces, various issues ought to be considered: If the adsorbing polyelectrolyte has near-equal numbers of positive and negative groups, can it still be effective in altering the measured streaming potential of the solids? Will coverage of the solid surfaces by polyampholytes tend to drive the streaming potential toward lower absolute values? Is it possible to detect evidence of molecular rearrangement, with time, so that segments having higher density of positive groups eventually are enriched at the polyampholyte-substrate interface?
Despite the fact that aluminum compounds are widely used in combination with polyampholytes for enhancing the dry strength of paper and to promote dewatering during the forming process [6-8], little is known about how the presence of aluminum compounds affects either the bulk solution behavior or the electrokinetic effects resulting from polyampholyte treatment of fibers in suspension. Therefore, the synergistic effects of PAC with polyampholytes were also investigated.

Based on past work [9-11] it is reasonable to expect that adsorbed high-mass polymers will have a dominant effect on the electrokinetic properties of suspended particles or fibers. Such a dominant influence is consistent with the high affinity of many high molecular mass water-soluble polymers with surfaces, over a wide range of conditions [12-13]. Because ion-containing polymers of high molecular mass adsorb in the form of trains and, most importantly, with loops and tails projecting outwards from the surfaces [14-15], their effect on the electrostatic potential at the plane of shear (zeta potential) can be quite large as compared not only with the original, uncovered surfaces but also to the case of lower molecular weight polymers [10-12]. Past studies have suggested that treatment levels in the range of 1%, based on solid mass, may be sufficient to completely obscure the original electrokinetic nature of suspended solids [16-18].

Figure 1 gives a schematic representation of how a high-mass polyampholyte might be expected to rearrange after it is adsorbed on a substrate having a negative charge. Even if the ordering of monomer groups along the macromolecular chain is completely random, one still can expect there to be segments that happen to be enriched in either positive or negative charged groups [19-20]. Any differences in the reactivities of monomeric groups with each other or with contrasting monomeric groups will favor further enrichment of charged groups
within different segments [21]. While there is a need for methods capable of detecting non-uniform distributions of charged groups within charged polymers, it is reasonable to look for evidence of such distributions by practical experiments. Thus, in Fig. 1, one can expect segments rich in positively charged ionic groups to become enriched close to a substrate of opposite charge [22-23]. As shown in the figure, such reconformation can be expected to result in a gradual depletion of positive groups, on average, on segments that are extending away from the surface. If the model shown in Fig. 1 is valid, then one ought to expect a decay in streaming potential to less positive or more negative values, relative to the initial SP values achieved following treatment of the negative surfaces with polyampholyte molecules.

**EXPERIMENTAL**

Experiments were conducted in deionized water prepared with an ion-exchange system from Pureflow, Inc. The poly-aluminumchloride (PAC) was Compozil Eka ATC 8210 from Eka Chemicals, Paper Chemicals Div. The product was added on an as-received basis. Other inorganic chemicals all were of reagent grade.
Polymer Preparation and Characterization

The compositions of polyampholyte and simple polyelectrolyte samples synthesized for this study are shown in Table 1. The preparation and analysis of samples A through D, F, and G were described in Part 1 of this series [1]. Preparation and analysis of polyampholyte samples H-1 and H-2 likewise were described elsewhere [24]. Briefly stated, both of these sets of research materials were prepared by free-radical polymerization, using ammonium persulfate as a radical initiator. Reactions were carried out at 60 °C with stirring under a nitrogen atmosphere.

Polyampholytes FR-1 and FR-2 were prepared in our laboratories by free-radical polymerization with the monomer compositions shown in Table 1. The monomers were first dissolved in 100ml deionized water in a three-necked flask equipped with a reflux condenser and a bubble sparger, that was used to inject argon at room temperature for 60 min. After adding ammonium persulfate, the reaction was allowed to proceed at 85°C for one hour. After cooling, the viscous polymer solution was precipitated in excess methanol. The polymer was collected by filtration and dried under vacuum at 40°C for 2 days. The chemical structures of the polymers obtained were confirmed using NMR in D₂O solution.
Table 1. Synthesis of acrylamide-based polyampholytes and simple copolymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polymer type</th>
<th>Basic group * (if any)</th>
<th>Acidic group * (if any)</th>
<th>Basic group molar content (%)</th>
<th>Carboxylic (acidic) group molar content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Amphoteric</td>
<td>DMAPAA</td>
<td>IA</td>
<td>2.5</td>
<td>2</td>
</tr>
<tr>
<td>B</td>
<td>Amphoteric</td>
<td>DMAPAA</td>
<td>IA</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>C</td>
<td>Amphoteric</td>
<td>DMAPAA</td>
<td>IA</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>D</td>
<td>Amphoteric</td>
<td>DMAPAA</td>
<td>IA</td>
<td>20</td>
<td>16</td>
</tr>
<tr>
<td>F</td>
<td>Cationic</td>
<td>DMAPAA</td>
<td>-</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>G</td>
<td>Anionic</td>
<td>-</td>
<td>IA</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td>H-1</td>
<td>Amphoteric</td>
<td>DMAEA</td>
<td>IA</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>H-2</td>
<td>Amphoteric</td>
<td>DMAEA</td>
<td>IA</td>
<td>3.8</td>
<td>9</td>
</tr>
<tr>
<td>FR-1</td>
<td>Amphoteric</td>
<td>DMAEMA</td>
<td>IA</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>FR-2</td>
<td></td>
<td>DMAEMA</td>
<td>AA</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

DMAPAA = N-[3-(N',N'-dimethylamino)propyl]acrylamide; IA = itaconic acid; DMAEA = 2-(dimethylamino)ethyl acrylate; DMAEMA = 2-(dimethylamino)ethyl methacrylate; AA = acrylic acid

Streaming Potential Tests

Streaming potential experiments, to determine the effects of polyampholytes on the electrokinetic nature of the fiber surfaces, were carried out with the SPJ device described elsewhere [25]. Briefly stated, 7.5g of fibers and a certain amount of polyampholyte solution (0.1%) were added to 750ml water with background electrolyte. The pH was adjusted with dilute solutions of HCl or NaOH. The background electrolyte, except where noted otherwise, was sodium bicarbonate ($10^{-4}$ M) (to stabilize the pH near to the neutral point) and sodium sulfate to achieve an electrical conductivity of 1000 $\mu$S/cm (23 °C). “Salt-free” conditions were similarly prepared, but without sodium sulfate. Streaming potentials were evaluated with an applied pressure of 207 kPa.

To avoid complications involving the nanoporous nature of cellulosic fibers, all of the streaming potential reported here were obtained with suspensions of glass micro-fibers, product C-50-R from Lauscha Fibre International of Sommerville, SC. The fibers had a nominal thickness of about 4 $\mu$m and were 4 mm in length. Though such fibers have a
negative surface charge, as do cellulosic fibers, the surfaces are not fibrillated and the fines content in aqueous suspension is negligible. Previous work showed advantages of using such fibers to study the mode of action of dual-polymer dry-strength systems [26].

RESULTS AND DISCUSSION

Effect of Polyampholytes on Streaming Potential of Glass Fibers

Figure 2 shows the results of an initial test carried out to determine the range of treatment levels over which one of the polyampholytes (B) had significant effects on streaming potential. As shown, the untreated fibers at pH=11 had a negative charge, which is consistent with previous findings [26-27]. Addition of a solution of the moderately low-charge polyampholyte B yielded significant changes in SP over the dosage range 0.001 to about 0.03%, based on the dry mass of fibers. Further increases in treatment yielded little further change, which suggests a saturated condition of the surfaces [28].

The results in Fig. 2 reveal how adsorption of a net-negative polyampholyte at high pH, where fibers also have a net-negative charge, may actually reduce the absolute value of streaming potential (SP). The reduction in the absolute value of SP was achieved despite the fact that negative carboxylate groups are expected to dominate the charged nature of the polyampholyte, for instance at pH=11. The effect on SP is tentatively attributed to the coverage of the substrate by polymer segments that have a lower net charge density, compared to that of glass, and also due to the presence of tails and loops of polymer extending outwards from the substrate into the solution phase [10-11].

Figure 3 shows how polyampholyte treatment at different levels affected the SP of glass fibers at different values of pH. Results for the “blank” confirm the expectation that the glass surfaces in aqueous solution is strongly negative above a pH of about 3. As the pH is decreased below 3, the remaining silanol groups are expected to become protonated,
achieving neutrality at about 2.5 [27]. The family of curves corresponding to treatment with
the moderately low-charge polyampholyte B shows a progressive shift in SP values with
increasing dosage. It appears that a treatment level of 0.6%, based on fiber mass, was
enough to achieve a limiting value. It is notable that intermediate pH values of
polyampholyte addition tended to neutralize the apparent charge of the surfaces, achieving
near-zero value of SP at high levels of treatment. Addition of polyampholyte in acidic
conditions showed greater effectiveness for neutralization of the surface charge of the
oppositely charged fiber, due to a stronger electrostatic attraction.

Previous work has shown various instances in which drainage, retention, sizing, or
dry-strength results were maximized when the zeta potential of the fiber furnish was near to
zero, due to adjustments in the amounts of added chemicals [29-33]. The present results
suggest that the reported effectiveness of polyampholytes as dewatering aids [6, 34-36] also
may be associated with their tendency to reduce absolute values of the zeta potential in the
papermaking systems to which they are added.

Fig. 2. Effect polyampholyte B dosage, as percent by mass on solids, on the
streaming potential of glass fibers.

Fig. 3. Effect of pH on streaming potential for glass fiber suspensions
treated with different levels of polyampholyte B.
Figure 4 shows a series of results all obtained at the treatment level of 0.2% polymer, based on the mass of glass microfibers. Results for polyampholyte samples of increasing charge density are shown in Fig. 4A. Despite an eight-fold increase in charge density, based on monomeric groups within the series of polyampholytes A through D, it is clear that all of the polyampholytes produced similar changes in the streaming potential of the glass microfibers. Nevertheless, the highest-charge polyampholyte, sample D, yielded SP values that were more positive below pH=8 and more negative above about pH=9, compared to the lesser-charged polyampholytes. The opposite was true for polyampholyte A, the lowest-charge polyampholyte, still noting that the ratio of basic to acidic groups on this series of polyampholytes was held constant.

Part B of Fig. 4 shows comparative results for polyampholyte sample B and the single polyelectrolytes having the same molar proportions of either acidic or basic functional groups. In contrast to treatment with the polyampholyte, the cationic and anionic polyelectrolytes (F and G, respectively) yielded streaming potential values that were almost independent of pH in the range of about 5 to 9. Thus, sample F, the cationic copolymer, yielded positive SP values at pH values below about 10. At yet higher pH it is expected that most of the tertiary amine groups are not charged. The anionic polyelectrolyte G yielded SP values less negative than that of the untreated glass. Again, the most likely explanation is that polymer segments extending outwards from the glass surface tend to dominate the electrokinetic properties, almost completely obscuring the original electrokinetic nature of the bare substrate.
Synergistic Effects of PAC and Polyampholytes

The effects on streaming potential of the addition of PAC are illustrated in Fig. 5 for pH=5, considering the same polymer solutions discussed before. As a generalization, the streaming potentials of polyampholyte solutions were affected to a greater extent by the PAC addition, compared to those of the single polyelectrolyte solutions. Thus, in Fig. 5A, increasing PAC addition caused a change from negative to positive streaming potential for systems treated with polyampholytes A through D. At pH=5 the polyampholytes of higher density of ionic groups (increasing by factors of 2 in the order A through D) tended to start out with less negative streaming potentials and end up at higher positive streaming potentials, even exceeding the streaming potential resulting from the addition of the cationic polyelectrolyte. By contrast, the system with the cationic polyelectrolyte, sample F, appeared unaffected by PAC addition. The system involving sample G, the anionic polyelectrolyte, became somewhat less negative with increasing addition of PAC, but the net sign of potential remained negative.
Results in Fig. 5B pertain to tests carried out with sufficient sodium sulfate so that the conductivity was 1000 µS/cm. The screening effect of the added salt is evident in the much smaller range of values on the vertical axis scale. Though the results generally are consistent with the same explanations given in the previous paragraph, there is one puzzling feature. That is, at zero PAC addition the system treated with the cationic polyelectrolyte F had a negative value of streaming potential. The best explanation for this observation is that aluminum species were able to interact with silanol groups at uncovered areas on the fiber surfaces, making the system more positive. This interpretation is consistent with supplementary tests carried out with glass fibers and PAC addition in the absence of organic polymers.

Results similar to those shown in Fig. 5 also were obtained in solutions having a pH of 4. Briefly stated, the effects due to PAC addition were less important. A likely explanation is that there aluminum species have a lower tendency to polymerize and adsorb onto fiber surfaces at the lower value of pH [37-40].

Fig. 5A. Effect of PAC addition at increasing levels to salt-free glass fiber suspensions treated at the 0.02% level with ionic polymers at pH=5.

Fig. 5B. Effect of PAC addition at increasing levels of salt-containing glass fiber suspensions (1000 µS/cm) treated at 0.02% with ionic polymers at pH=5.
Results shown in Fig. 6 help to answer one of the questions that was raised in the introduction, namely, whether there is evidence of molecular rearrangement following initial adsorption of polyampholytes onto fibers. As shown in Fig. 6A, the streaming potentials of systems treated with polyampholyte B through D in the absence of salt all showed decays of streaming potential toward more negative values with increasing time. Such results are consistent with a rearrangement favoring more of the cationic ionic groups facing the fiber surfaces. Such a rearrangement is expected to result in a disproportionate density of negatively charged macromolecular groups facing outwards, consistent with the experimental results. No significant decay in streaming potential was observable in the case of the cationic polyelectrolyte F, or the lowest-charge polyampholyte A. Results in Fig. 6B of the figure show the same general trends in the case of tests carried out in the presence of sodium sulfate.

Figure 7 shows results of a follow-up test in which the ratio of acidic to basic groups was varied. The molar compositions of these polyampholytes are shown in Table 1. Polyampholyte H-1 with a ratio of 5 amine groups to 8 carboxyl groups was compared with
polyampholyte H-2 with a ratio of 3.8 amine groups to 9 carboxyl groups. As shown, the largest differences in charge effects were encountered at relatively low pH. Thus, below about pH=6, the sample that was richer in amine groups yielded SP values that were less negative.

In a further confirmation of the explained effect of the charge balance, a series of two polyampholyte samples was prepared with the level of tertiary amine groups held constant, but with a two-fold difference in the proportion of carboxyl groups. As shown in Fig. 8, a doubling of the carboxyl group content so that it was twice the level of amine groups shifted the resulting streaming potentials to lower values, especially at pHs above 6. As in the case of the polyelectrolyte F (see Fig. 3B), the polyampholyte FR-2 yielded SP values that were almost pH-independent in the pH range between about 5 and 9. By contrast, FR-1, the polyampholyte having the high level of carboxyl groups, yielded strongly pH-dependent streaming potential values over the same pH range.
CONCLUSIONS

3. Depending on the details of monomeric composition, adsorption in aqueous suspension of random polyampholytes onto glass microfibers generally resulted in streaming potentials that were less negative or more positive than that of the bare substrate at the given levels of pH, but not as positive as when the fibers were exposed to a cationic polyelectrolyte having similar density of amine groups. This tendency of the polyampholytes to reduce absolute values of streaming potentials is consistent with the fact that gains in dry-strength, fine-particle retention, and the rate of dewatering are achieved as the electrokinetic potential of furnish solids is reduced towards zero.

4. Polyampholytes having a fixed ratio of basic to acidic groups showed a remarkable degree of similarity, with respect to streaming potentials, despite an eight-fold difference in the overall molar content of charged groups. Subtle trends within the family group included a tendency of the higher-charged polyampholytes to shift the streaming potential to more positive values at low pH and more negative values at pH above the isoelectric point.
5. Addition of polyaluminum chloride (PAC) to polyampholyte-treated glass fiber suspensions had a disproportionately large effect, compared to similar addition to fibers suspensions that had been treated with polyelectrolytes of similar charge density and molecular mass. The effect of PAC raising the streaming potential to less negative or more positive values was greatest in the case of polyampholytes having the highest charge density. The effect is attributed to complex formation between aluminum ionic species and carboxylate groups within the polyampholytes.

6. The change with time of the streaming potential of glass microfibers, following their treatment with polyampholytes, supports a hypothesis that the macromolecules rearrange themselves in response to the original net charge of the substrate. An enrichment of cationic groups at the polyampholyte-substrate interface results in a net depletion of cationic groups facing outwards towards the solution phase, consistent with a shift towards less positive or more negative streaming potentials with time.

7. By varying the ratio of basic to acidic groups in polyampholytes it was possible to shift the streaming potential-pH responses in predictable ways. In many, but not all cases, the streaming potentials of fiber systems following treatment with polyampholytes were almost linearly dependent on pH throughout most of the pH range between the pKₐ values of the acidic groups and the pKₐ value of the basic group. Though the significance of this finding is not yet fully understood, it is clear that charge ratios can be used as an additional tool for the optimization of these chemicals in papermaking systems.

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LITERATURE CITED


FIGURE CAPTIONS

Fig. 1. Schematic representation of expected conformational change following adsorption of a high-mass, linear polyampholyte in which the distribution of charged groups is segregated.

Fig. 2. Effect polyampholyte B dosage, as percent by mass on solids, on the streaming potential of glass fibers.

Fig. 3. Effect of pH on streaming potential for glass fiber suspensions treated with different levels of polyampholyte B.

Fig. 4A. Effect of the density of ionic groups in polyampholytes on the streaming potential of glass microfibers (0.2 % polymer dosage) at 1000 µS/cm conductivity. The polyampholytes have a constant molar ratio of acidic to basic groups.

Fig. 4B. Contrast between the effects of polyampholyte B versus poly-base F and poly-acid G having the same molar content of either positive or negative groups. Tests were performed at 1000 µS/cm conductivity.

Fig. 5A. Effect of PAC addition at increasing levels to salt-free glass fiber suspensions treated at the 0.02% level with ionic polymers at pH=5.

Fig. 5B. Effect of PAC addition at increasing levels of salt-containing glass fiber suspensions (1000 µS/cm) treated at 0.02% with ionic polymers at pH=5.

Fig. 6A. Effect of time on the streaming potential of glass fibers freshly treated with ionic polymers at pH=5 in the absence of sodium sulfate.

Fig. 6B. Effect of time on the streaming potential of glass fibers freshly treated with ionic polymers at pH=5 in the presence of sodium sulfate (1000 µS/cm).

Fig. 7. Streaming potentials vs. pH for glass fibers treated with polyampholytes having different ratios of monomeric groups: Polyampholytes H-1 and H-2 with a ratio of amine groups to carboxyl groups of 5:8 and 3.8:9, respectively.

Fig. 8A. Streaming potential – pH behavior of glass fibers treated with a polyampholyte having equal amounts of cationic and anionic groups

Fig. 8B. Streaming potential – pH behavior of glass fibers treated with polyampholytes in which the anionic groups were doubled by use of a di-functional carboxylic monomer
DISCUSSION

1. Ionic Nature of the Polymers

As has been discussed throughout this document, pH titrations can be used to characterize the ionic nature of a polymer as a function of pH. Besides the experimental curves, theoretical curves can be drawn, using equations 1-1 and 1-2.

If one compares the experimental and theoretical curves, the dissociation constants for charged groups can be determined. For our polyampholyte samples, the dissociation constants are 4.10, 6.82, and 9.82, respectively, for the two carboxyl groups and the tertiary amine group. Compared to the dissociation constant values from the references, these dissociation constants are reasonable.

It is notable that the dissociation constants used to fit the experimental data remain the same, even though the charge densities are different among the polyampholyte samples. Mazur\textsuperscript{4} has researched the potentiometric titration of 2-vinylpyridine-methacrylic acid (2VP-MAA) with different composition. His results reveal that at low MAA content the curve is analogous to that of polyvinylpyridine alone, but upon increasing the acid content, the shape of the titration curves changes. When Schiesset and Mosalova\textsuperscript{43, 44} studied the titration of 2-methyl-5-vinylpyridine-acrylic acid (2M5VP-AA), they found similar results. The change is attributable to the inductive influence of neighboring groups. However, the polyampholyte samples considered in the present work have relatively low charge density, such that the nearest-neighbor interaction can be neglected. If one compares the curve of our
polyampholyte sample and our polyelectrolyte sample with the same positive or negative charge density, the shape is similar, which can be taken as further evidence that the charge density of our polyampholyte samples is low enough to neglect the nearest neighboring interactions.

2. Polyelectrolyte Titrations

The streaming current titration method also is used to find the charge density of polyampholytes as a function of pH. But the difference from pH titration is that the streaming titration results show the net charge, while the pH titration shows the carboxyl group charge density. For the polyampholytes, the former method is not efficient, especially around the IEP\textsuperscript{3}. That means that it is difficult to titrate the functional groups of polyampholytes in the vicinity of the IEP, as has been proved in Tanford’s paper\textsuperscript{45}. Results of the present study show a flat stage at pH values around the iso-electric pH for each polyampholyte sample, demonstrating this kind of behavior. Kulagina’s work also shows the similar results\textsuperscript{11}. It appears that such behavior is characteristic of polyampholytes having different polybase or polyacid. If one compares the titration curves of our polyampholyte relative to simple polyacid or polybase copolymer samples, this difference is significant. This specific behavior is called the IEP effect. This effect is important for the applications of polyampholytes, such as the recovery metal ions. Also in the present project, the importance will be seen in adsorption and viscosity. Here, because of the IEP effect, the IEP value can be narrowed to fall within a certain range, based on the streaming current titration.
Another thing worth mentioning here is 1:1 stoichiometry, which is a fundamental assumption for ordinary polyelectrolyte titrations, including those in which the endpoint is determined by streaming current tests. However, from our results, this assumption is not justified. This is another reason that this method is not valid for our samples as a means to research the charged nature as a function of pH. In fact, the titration depends on the accessible nature of the polymers. It is important that the titrant can interact with all the surface and colloidal charge groups present. But for our polyampholyte samples, its charged groups appear to be difficult to totally access. In the vicinity of the IEP, the polyampholyte macromolecules form a compact globule, squeezing out the solvent. So, in Phipps’s paper\textsuperscript{21}, he mentioned that the macromolecular or colloidal cationic and anionic species did not appear to coexist, based on results from the streaming current titration method.

3. Streaming potential results

Streaming potential results can show changes of electrokinetic properties of cellulosic fibers after adding the polyampholytes. This parameter is important especially in the real papermaking process\textsuperscript{15}. In the real mill, many additives are added to the stock, and if an excess of cationic or anionic additives is added, the production is expected to become less efficient in terms of such parameters as dewatering rates, retention of fine particles, and rates of deposit formation. To use the streaming potential method to research the effect of polyampholytes has not been described before.

And from the present results, we can see that a key effect of the polyampholytes is to increase the zeta potential of the stock to less negative or positive values. But compared to
the cationic polyelectrolytes, the polyampholytes are not efficient. That means, adding a little more polyampholyte than the optimum amount will not be expected to lead to as significant a worsening of paper quality or paper machine operations as the cationic polyampholytes. This is consistent with Akihiro’s results, and in his paper, the polyampholyte sample co-AMP-PAM doesn’t become less effective as dosage increases, compared to other chemical additives¹.

If one compares the effect of polyampholyte samples on the streaming potential, the higher the charge density is, the more efficient is the effect on streaming potential. This is consistent with the adsorption results, which will be described next.

4. Adsorption

Adsorption results show how much polyampholytes can be adsorbed on the fiber surface. The present results indicate that the adsorption amount is influenced by the pH and the charge density.

Mahltig’s work shows the importance of pH³⁸. In agreement with the present results, he also found that the highest adsorption amount appears in the neighborhood of the IEP. Kamiyama, Shubin and Cohen’s results likewise show the maximum of adsorbed polymer was obtained at the IEP of the polymer³⁸,⁴⁶. Though these researchers used different samples and substrates, their conclusion are similar, and they are also consistent with our results. This is explained by the fact that the net amount of charge in the polyampholyte decreases, and this
decrease leads to a screening in electrostatic repulsion between the polyelectrolyte segments\textsuperscript{38}. Therefore, in the vicinity of the IEP, the adsorbed amount is at its maximum.

For the effect of charge density, our results show that higher charge density results in a higher adsorbed amount. Though many papers have considered the adsorption of polyampholytes, very few papers have considers this factor. In fact, the interaction between the fiber and polyampholyte is mainly governed by the electrostatic forces. More cationic charge density means more available points on the polymer chain to interact with fiber surface. At the limit of low positive charge density, this leads to more adsorption. The fact that above pH 10, the adsorption amount decreases rapidly and the polyacid cannot attach to the fiber surface proves the importance of cationic charge density for adsorption as an anchor.

Like other cationic dry-strength agents\textsuperscript{47}, the cationic polyelectrolytes’s adsorption depends on the charge density on the fiber surface, so it is reasonable to see an adsorption amount increase before pH 10.

But all these results just discussed are only experimental results. Though the adsorption amount is known, the real conformation and the layer structures are not known. From the perspective of the adsorption models that were introduced in the literature review section, conformation as fundamental. Theoretical calculations, which can involve both direct calculations and the Monte Carlo simulations, can be used to predict adsorbed conformations, depending on the capabilities of software. Presently it is still difficult to predict real adsorbed conformational structures. However, software is becoming more and more capable. It can be
expected that researchers will make increased use of simulations in futures studies of polyampholyte behavior.
GENERAL CONCLUSIONS FROM THE THESIS PROJECT

In addition to the more specific conclusions provided in the preceding three main sections, corresponding to submitted research articles, it is possible to summarize some of the main conclusions as follows:

1. From the pH titration experiment, the association constant of ionic groups can be calculated. The determined pKa values were, respectively, 4.10, 6.82, and 9.82 separately for the two carboxyl groups and the tertiary amine group. The pH titration curves corresponding to polyampholytes are consistent with the theoretical predictions, as well as with the results of tests with the cationic polyelectrolytes.

2. The streaming potential curves showed that the amount of titrant required to reach zero streaming potential was almost zero around the iso-electric pH point. This means that the conformation of polyampholytes near to the IEP makes the ionic groups on the titrant difficult to attach the oppositely charged ionic groups on the polyampholytes. Also because of an expected contraction of the conformation of polyampholytes near to the IEP, it is difficult to reach the expected 1:1 stoichiometry.

3. The streaming potential results demonstrate that adsorption of polyampholyte samples can affect the electrokinetic properties of fibers in a suspension. Unlike cationic polyelectrolytes, which increase the streaming potential of the fibers, and unlike anionic polyelectrolytes, which decrease the streaming potential, polyampholyte samples behave like poly-base below pH=6 and like poly-acid above this pH. Also the efficiency of polyampholyte sample, in terms of streaming potential, is between that of a
corresponding poly-base and poly-acid when they have the same basic group density or acidic group density.

4. Adsorption results show, for each polyampholyte sample, that the maximum adsorption amount appears near to the IEP. And above pH=10, the adsorption amount decreases significantly compared to other pH conditions. Adsorption amount also increases with increasing charge density. The cationic polyelectrolytes can also adsorb on the fiber surface. Its efficiency, in terms of adsorption amount, is larger than that of a polyampholyte with same charge density below a certain pH but less above this pH. However the results also show that the anionic polyelectrolytes cannot adsorb on the fiber surface.

5. Though the addition of PAC can affect the dry-strength of paper, there are other effects that simultaneously influence the dry strength of paper. Thus, pH affects the electrical charge interactions and the viscosity, consistent with expected changes in the conformation of polyampholytes. Whether the dry strength increases or decreases depends on the effects of all these factors.

6. Polyampholytes can make the streaming potential of glass fiber less negative. But with respect to such changes, the polyampholytes are not as efficient as cationic polymers. Also in comparison to the cationic polymers, time effects for polyampholytes are more significant. The addition of PAC can make this time effect more significant, especially in the case of the high charge density polyampholytes.
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