

The role of polyampholyte charge density on its interactions with cellulose

Yun Wang, Martin A. Hubbe, Takao Sezaki, Xingwu Wang, Orlando J. Rojas, and Dimitris S. Argyropoulos, Department of Wood and Paper Science, North Carolina State University, Raleigh, NC, USA, and (*) Harima Chemicals, Inc., Osaka, Japan*

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 in the terpolymers. Analysis by ¹H and ¹³C 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 density of ionizable groups 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 single-charged 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 pK_a values of the respective charged groups.

ADDRESSES OF THE AUTHORS: Yun Wang (wjmwy1129@gmail.com) Martin A. Hubbe (hubbe@ncsu.edu), Xingwu Wang (xwang11@ncsu.edu), Orlando J. Rojas (ojrojas@ncsu.edu) and Dimitris S. Argyropoulos (dimitris.argyropoulos@ncsu.edu): North Carolina State Univ., Department of Wood and Paper Science, Box 8005, Raleigh, NC 27695-8005, USA; Takao Sezaki (sezaki-t@harima.co.jp): Harima Chemicals, Inc., Osaka, Japan.

Corresponding author: Martin A. Hubbe

Introduction

Considerable interest has been shown in recent years for the development of dry-strength additives having improved efficacy (Lorenčák 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. Amphoteric additives also are less likely to disturb the overall balance of ionic charges in a paper machine system (McQueary 1990; Kimura, Hamada 1992), and 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 (van de Steeg et al., 1992; Wågberg 2000) or mineral (Sukhishvili, Granick 1998) surfaces.

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 with 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 water that had been purified by ion exchange 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 added at a 0.04 mole percent level the reaction mixtures (Samples A-D, F, and G) as a cross-linking agent in order to increase the average molecular masses. As shown, the mean weight-averaged molecular masses of the polyampholyte samples were within the range 2.85 to 2.93 x 10⁶ Daltons, and the polyelectrolyte masses also were similar.

Sample	Ionic nature	DMAPAA (mol %)	IA (mol %)	Viscosity* (mPa·s)	M _w ** (10 ⁶ Daltons)
A	Ampho- teric	2.5	1	5300	2.95
B		5	2	4900	2.85
C		10	4	4000	2.90
D		20	8	2400	2.93
F	Cationic	5	0	3600	2.98
G	Anionic	0	2	5300	3.23

* 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 D₂O. Crystals of CrK(SO₄)₂ were added at a concentration of 1.5 mM in order to reduce the spin-lattice relaxation times (T₁). The NMR experiments were performed in a Bruker 300MHz spectrometer equipped with a Quad dedicated probe at room temperature. The quantitative ¹³C 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 ^1H 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, no addition of background electrolyte, 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 Mutek PCD-05pH streaming current detector from BTG. The cationic titrant was 1×10^{-4} N poly-diallyldimethylammonium chloride (poly-DADMAC), Cat. No. AS1C0019 from Nalco Chemical Co. The anionic titrant was 1×10^{-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 1×10^{-4} M.

Elemental chlorine free (ECF) bleached kraft pulp was obtained in dry-lap form from a south-eastern U.S. pulp mill. Fines-free suspensions 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). The device operates by using three conditions of air pressure to alternately force a suspension of fibers or other suspended matter toward a fine screen. Filtrate passes through the screen, and the apparent voltage drop across the mat of collected materials on the screen is measured. The raw streaming potential, which is measured, is corrected by means of a second measurement at zero applied pressure. Before each cycle of testing a low vacuum is applied briefly in order to return all of the filtrate to a continuously stirred vessel within the pressure chamber. In the work reported here, 7.5g of 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 1×10^{-4} M sodium bicarbonate (to stabilize the pH near to the neutral point) and sufficient sodium sulfate to achieve an electrical conductivity of 1000 $\mu\text{S}/\text{cm}$ 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 with the electric conductivity adjusted to 1000 $\mu\text{S}/\text{cm}$, by addition of sodium sulfate. The pH was adjusted to the values shown later in this article. 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 $\mu\text{S}/\text{cm}$, then titrated by 1×10^{-4} N PVSK. This value was then compared with a blank to calculate the adsorbed amount.

Results

Figure 1 shows the ^1H 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 analysis involving distortionless enhancement by polarization transfer (DEPT) and 2-dimensional nuclear magnetic resonance (NMR) (Sezaki et al. 2006).

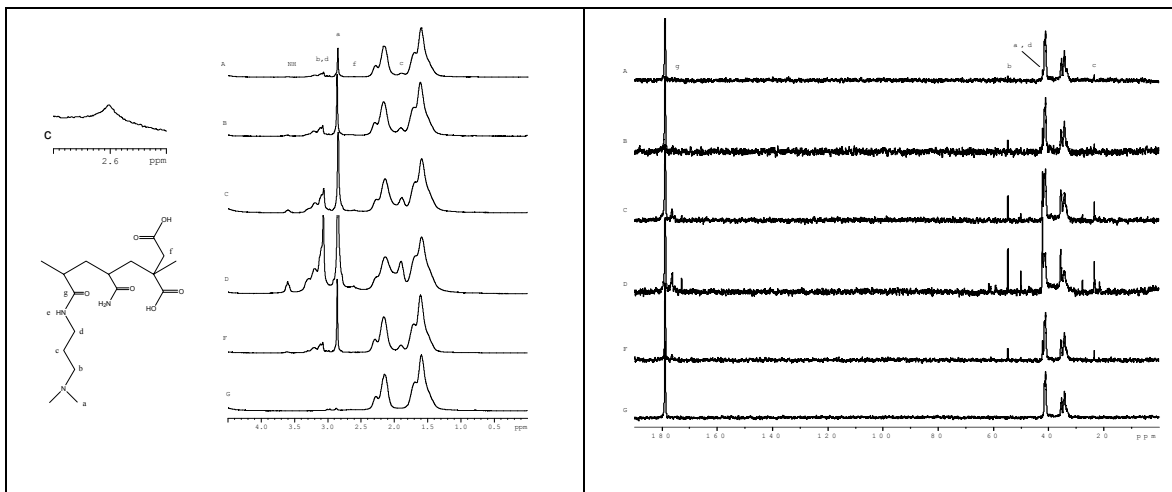


Fig. 1. ^1H NMR spectra (left) and quantitative ^{13}C NMR spectra (right) of the six copolymer samples. The monomer compositions are summarized in Table 1.

From the peak integrations of the ^{13}C and ^1H 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. Even though the average compositions matched very well with the added amounts of reagents, it is still possible that significant compositional differences existed between those polymer segments produced during different stages of the reaction. The apparent presence of cationic monomer in sample G, according to NMR, remains unexplained.

Table 2. Composition according to preparation and by NMR analysis. AA – acrylic acid; DMAPAA – N-[3-(N',N'-dimethylamino)propyl]acrylamide; IA – itaconic acid

Sample	DMAPAA in Feed (%)	DMAPAA by NMR (%)	IA in Feed (%)	IA by NMR (%)
A	2.5	2.6	1	1.2
B	5	5	2	2.2
C	10	9.5	4	4.8
D	20	18	8	8.4
F	5	5	0	(0.6)
G	0	0.5	2	1.8

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. Iterative data fitting yielded acceptable model adjustment as shown in Fig. 2a. 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 support 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). As in the systems discussed by Horn (1980), similar shifts would be expected to arise for polyampholyte molecules interacting with strong polyelectrolytes. 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.

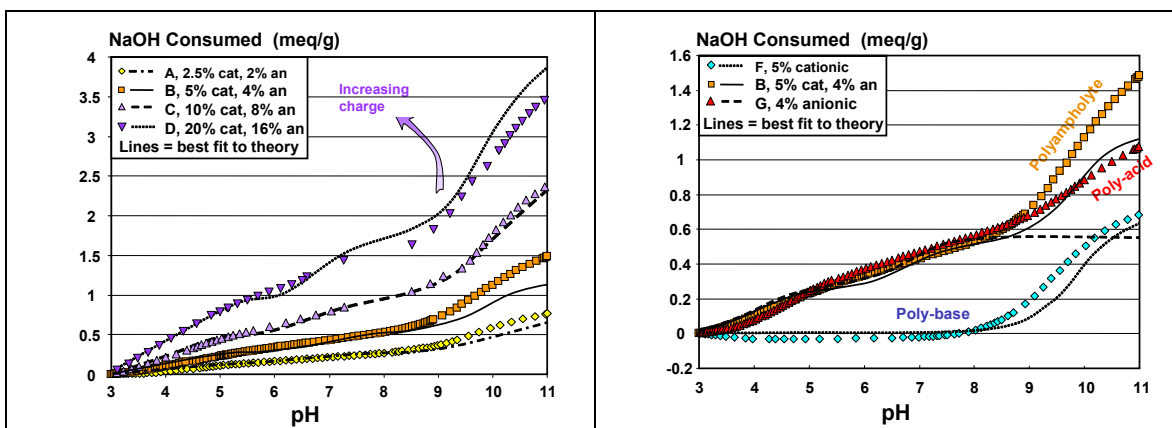


Fig. 2. Results of potentiometric titrations of salt-free 0.001% polymer solutions with 1 mM NaOH. (a) Polyampholyte samples of increasing charge density, but constant ratio of acidic to basic groups. (b) Polyampholyte sample "B" compared

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 PVSJ (see experimental). The plotted lines were calculated using the same equations and coefficients as in Fig. 2. In other words, this analysis uses the same fixed values for the two pK_a constants and the pK_b constant.

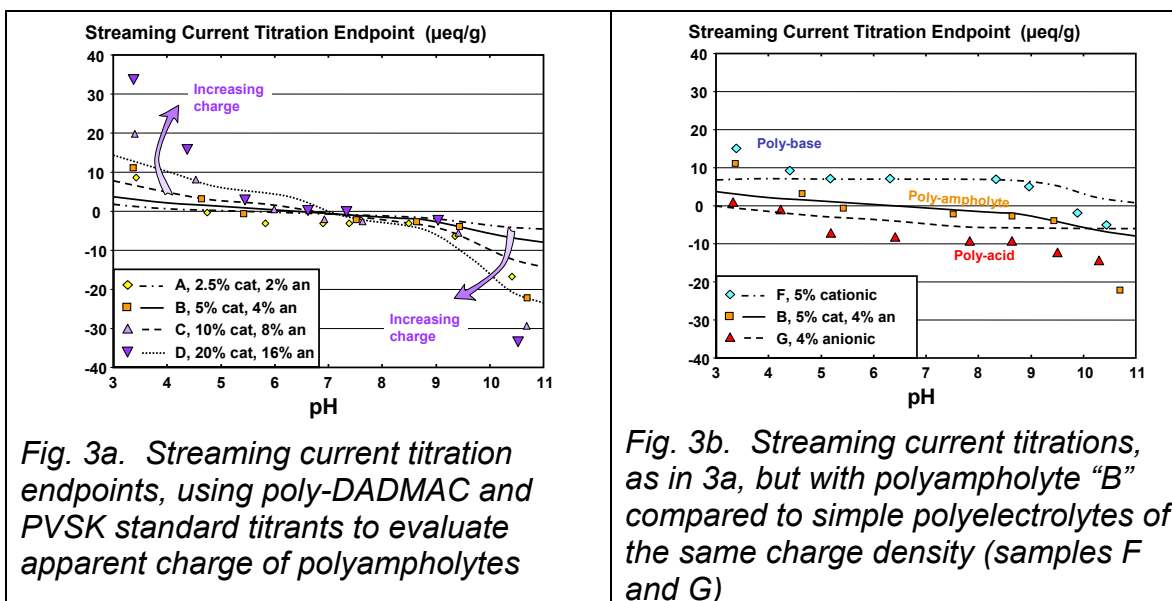


Fig. 3a. Streaming current titration endpoints, using poly-DADMAC and PVSJ standard titrants to evaluate apparent charge of polyampholytes

Fig. 3b. Streaming current titrations, as in 3a, but with polyampholyte "B" compared to simple polyelectrolytes of the same charge density (samples F and G)

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 PVSJ were "inefficient" in neutralizing the respective polyampholytes, if one employs the same dissociation constants as determined by the potentiometric titrations. 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. Another way to explain the deviations of the experimental points from the plotted lines is that the presence of either poly-DADMAC or PVSJ titrant molecules resulted in substantial shifts of the dissociation constants of the polyampholytes. This latter explanation is weakened by the fact that the largest deviations of the experimental points

from the calculated lines were at the extremes of pH, where either the acidic or the basic groups of the polyampholytes would be expected to be fully dissociated.

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. It is worth noting that there was a consistent offset of the calculated line from the data in the case of sample G in Fig. 3b; this offset lends some support to the hypothesis that the degree of dissociation of the polyacids was substantially increased due to the presence of the strong polybase titrant. It is suggested that future work might be done in order to clarify the relative importance of such shifts in dissociation constants relative to the adsorption or complexation reactions of weak polyampholytes.

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 at neutral pH to a suspension of decrilled, 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 $\mu\text{S}/\text{cm}$, 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.

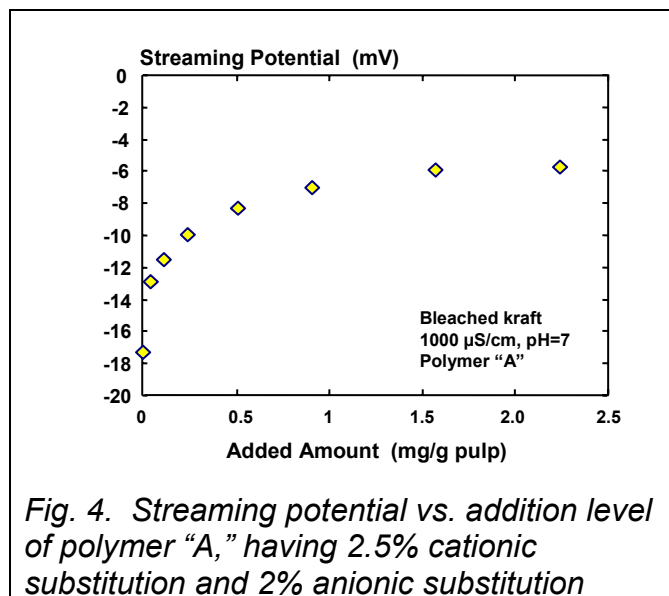


Figure 5 shows results of streaming potential tests carried out at different pH values with polymer solutions added to microcrystalline cellulose (MCC) at the low level of treatment (0.08% on a dry basis) in the presence of sodium sulfate (1000 $\mu\text{S}/\text{cm}$ conductivity). The same SPJ method (see Experimental) was used, as in the case of tests with cellulosic fibers. 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.

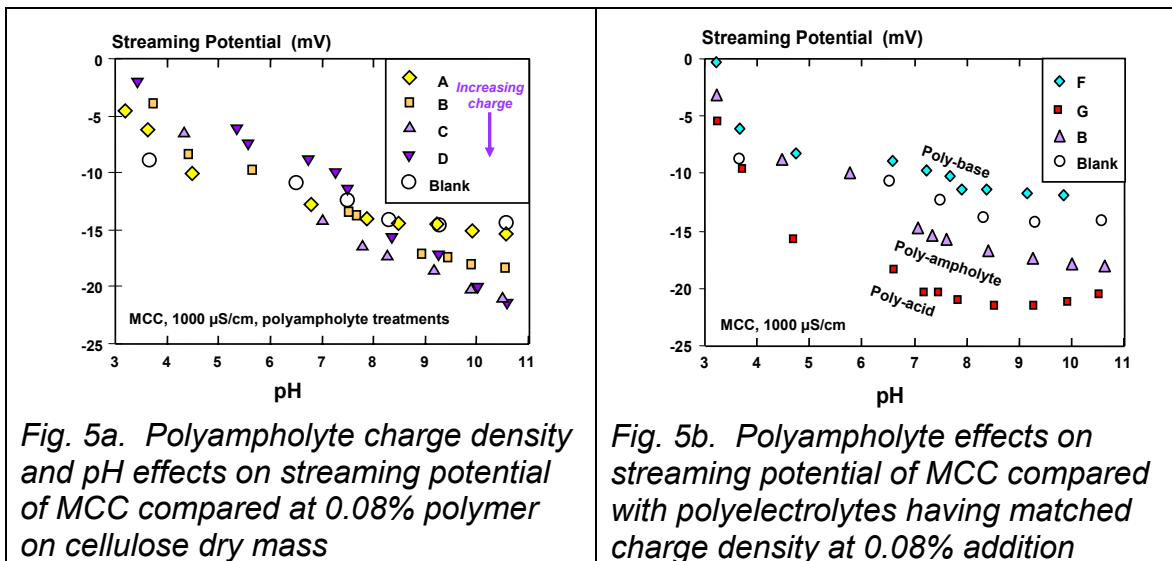
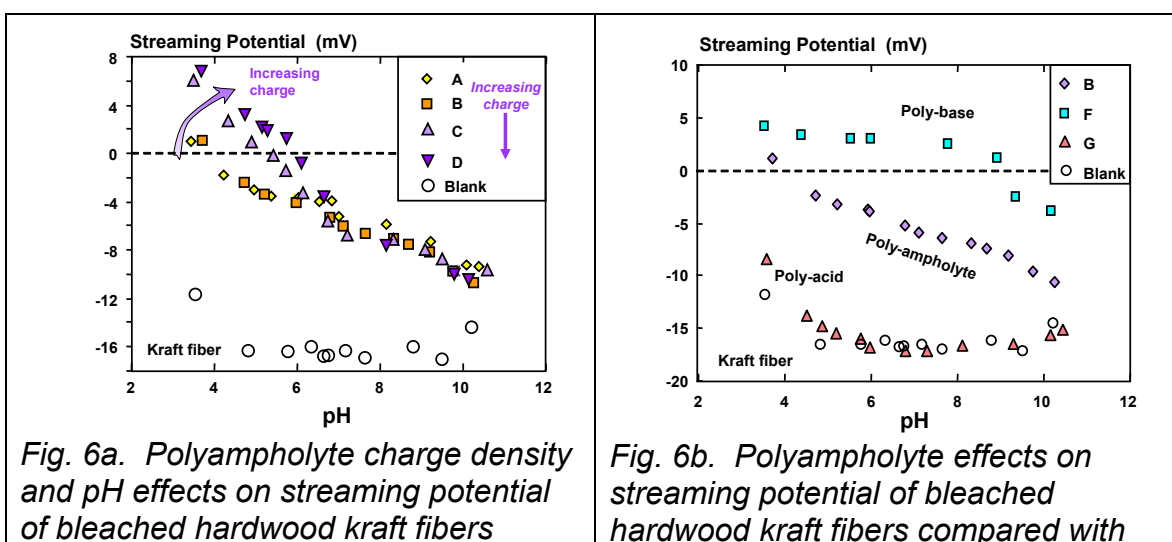


Figure 6 shows results of similar tests carried out in bleached hardwood kraft fibers. The treatment level of polymer on bleached kraft fibers was 0.213%, on a dry basis. Though the same discussion points can be made, as in Fig. 5, the contrasts are yet more distinct, and the differences relative to 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).

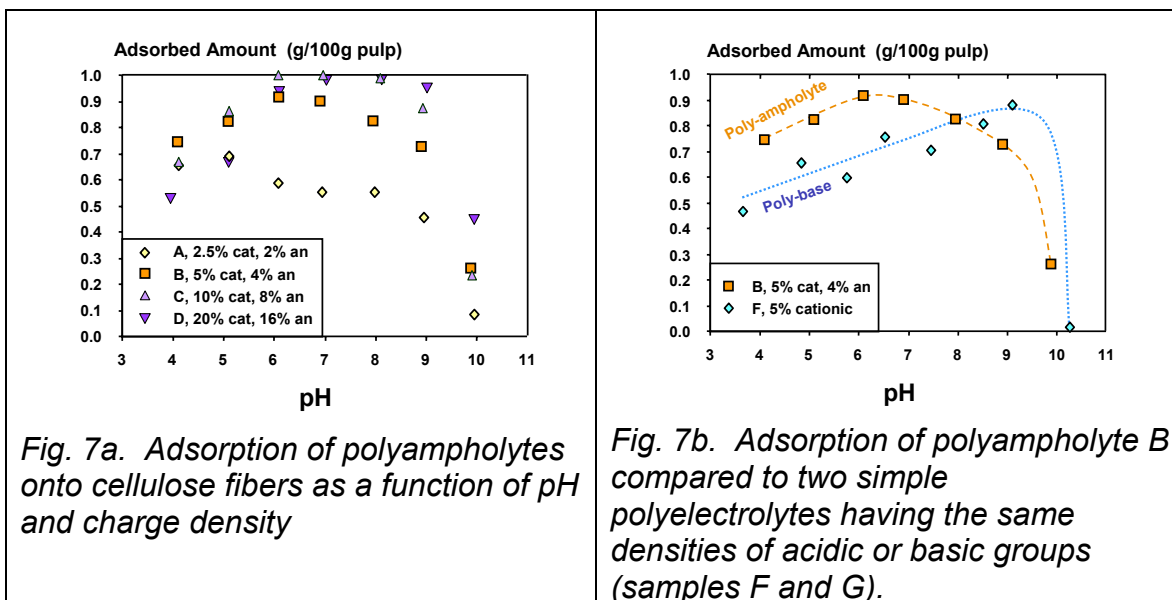
As shown in Fig. 6B, the poly-acid sample “G” had almost no detectable effect relative to the streaming potential of untreated bleached kraft fibers. By contrast, the cationic polyelectrolyte (poly-base) “F” strongly reversed the charge of the fibers up to a pH above 9. The pH-dependency of the streaming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



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 1×10^{-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 $1000 \mu\text{S}/\text{cm}$. 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; Wågberg 2000). 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 single-charged 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 by polyampholyte addition, 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 $7.5 < \text{pH} < 9$, 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).

Issues related to the regulation of surface charges can be expected to play a role in complex systems such as those considered in the present study. As noted by Shubin and Linse (1997), numerical investigations of polyelectrolyte adsorption onto oppositely charged surfaces, under the assumption of charge regulation, have shown agreement between theoretical predictions and experimental trends. The surfaces and polyelectrolytes studied here bear dissociable functional groups whose degree of dissociation depends on the conditions in the solution, as well as the proximity and charged nature of neighboring species. In this case, neither surface charge nor surface potential remains constant. Therefore the exact nature of charges becomes more difficult to predict. The quantification of the degree of dissociation of discrete surface functional

groups and specific adsorption of electrolyte ions on particular surface sites, along with mass-action rules for polyelectrolyte adsorption equilibria, would help to elucidate a more comprehensive description of the systems investigated here.

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 assumed dissociation constants for the acidic and basic groups of the polymer samples. The best-fit pK_a values of the two kinds of carboxyl groups in the samples were 4.1 and 6.8. The pK_b value of the tertiary amine group was assumed to be 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. Experiments at various pH levels showed maximum adsorption of polyampholytes onto bleached kraft fibers in the case of samples having moderate to high charge 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

The authors wish to acknowledge the support of the National Research Initiative of the USDA Cooperative State Research, Education and Extension Service, grant number 2004-35504-14655. In-kind support provided by Harima Chemicals, Inc. is also gratefully acknowledged.

Literature

- Alfrey, T. and Pinner, H.* (1957): Preparation and titration of amphoteric polyelectrolytes, *J. Poly. Sci.* 23(104), 533.
- Bekturov, E.A., Kudaibergenov, S.E. and Rafikov, S.R.* (1990): Synthetic polymeric ampholytes in solution, *Rev. Macromol. Chem. Phys.* C30(2), 233.

Chen, J., Hubbe, M.A. and Heitmann, J.A. (2001): Measurement of colloidal charge in the paper mill by streaming current, Proc. TAPPI Papermakers Conf.

Claesson, P.M., Dedinaite, A. and Rojas, O.J. (2003): Polyelectrolytes as adhesion modifiers, Adv. Colloid Interface Sci. 104(1-3), 53.

Dobrynin, A.V., Rubinstein, M. and Joanny, J.-F. (1997): Adsorption of a polyampholyte chain on a charged surface, Macromolecules 30, 4332.

Doiron, B.E. (1998): Retention aid systems, in "Retention of Fines and Fillers during Papermaking," Edited J.M. Gess, TAPPI Press, Atlanta, pp. 159-176.

Everaers, R., Johner, A. and Joanny, J.-F. (1997): Polyampholytes: From single chains to solutions, Macromolecules 30(26), 8478.

Fukunaga, Y. (1999): New application method of dry strength agents by effective utilization of amphoteric polyacrylamide and aluminum sulfate, Proc. Japan TAPPI Ann. Mtg., 349.

Glittenberg, D. (1993): Starch alternatives for improved strength, retention, and sizing, Tappi J. 76(11), 215.

Grignon, J. and Scallan, A.M. (1980): Effect of pH and neutral salts upon the swelling of cellulose gels, J. Appl. Poly. Sci. 25(12), 2829.

Higgs, P.G. and Joanny, J.-F. (1991): Theory of polyampholyte solutions, J. Chem. Phys. 94(2), 1543.

Horn, D. and Linhart, F. (1991): Retention aids, in "Paper Chemistry," Edited J.C. Roberts, Blackie, Glasgow, UK, pp. 44-62.

Horn, D. (1980): Polyethylenimine – physicochemical properties and applications, in "Polymeric Amines and Ammonium Salts," Edited E. J. Goethals, Pergamon Press, Oxford, UK, pp. 333-355.

Horn, D. and Melzer, J. (1975): Effect of high molecular mass cationic dewatering aids on the electrokinetic properties of cellulosic fibers, Wochenbl. Papierfabr. 29(12), 534.

Howard, R.C. and Jowsey, C.J. (1989): The effect of cationic starch on the tensile strength of paper, J. Pulp Paper Sci. 15 (6), J225.

Hubbe, M.A. (2001): Reversibility of polymer-induced fiber flocculation by shear. 2. Multi-component chemical treatments, Nord. Pulp Paper Res. J. 16(4), 369.

Kimura, Y. and Hamada, M. (1992): Wet-end paper chemicals in secondary fiber system, Proc. 1992 Pan-Pacific Pulp & Paper Tech. Conf., Part B, Japan TAPPI, 83.

Kitaoka, T. and Tanaka, H. (2001): Novel paper strength additive containing cellulose-bonding domain of cellulase, J. Wood Sci. 47(4), 322.

Kudaibergenov, S.E. (2002): "Polyampholytes Synthesis, Characterization and Application," Kluwer Academic/Plenum Publ., New York.

Laine, J. and Lindström, T. (2000): The colloid/polyelectrolyte titration technique – A review and an appraisal of the technique, ED/COST E14 Workshop: New Measurement Techniques for Monitoring White Water Chemistry In Papermaking, Lisbon.

Lindström, T. (1992): Chemical factors affecting the behavior of fibers during papermaking, Nordic Pulp Paper Res. J. 7(4), 181.

Lindström, T. and Wågberg, L. (1983): Effects of pH and electrolyte concentration on adsorption of cationic polyacrylamides on cellulose, Tappi J. 66(6), 83.

Lindström, T., Wågberg, L. and Larsson, T. (2005): On the nature of joint strength in paper – A review of dry and wet strength resins used in paper manufacturing, 13th Fundamental Res. Symp., Cambridge, UK., pp. 457-562.

- Long, D., Dobrynin, A.V., Rubinsteain, M. and Ajdari, A.** (1998): Electrophoresis of polyampholytes, *J. Chem. Phys.* 108(3), 1234.
- Lorenčák, P., Stange, A., Neißner, M. and Esser, A.** (2000): Polyvinylamine – A new polymer for increasing paper strength, *Wochenbl. Papierfabr.* 128(1/2), 14.
- Mahltig, B., Walter, H., Harrats, C., Müller-Buschbaum, P., Jérôme, R. and Stamm, M.** (1999): Adsorption of polyampholyte copolymers at the solid/liquid interface: the influence of pH and salt on the adsorption behavior, *Phys. Chem. Chem. Phys.* 1, 3853.
- Mazur, J., Siberberg, A. and Katchalsky, A.** (1959): Potentiometric behavior of polyampholytes, *J. Polymer Sci.* 35(128), 43.
- McKague, J.F., Etter, D.O., Pilgrim, J.O. and Griggs, W.H.** (1974): Practical applications of the electrokinetics of papermaking, *Tappi* 57(12), 101.
- McQueary, R.T.** (1990): Wet end waxy amphoteric starch impacts drainage, retention, and strength, *Proc. TAPPI 1990 Papermakers Conf.*, pp. 137-142.
- Merle, Y.** (187): Synthetic polyampholytes. 5. Influence of nearest-neighbor interactions on potentiometric curves, *J. Phys. Chem.* 91(11), 3092.
- Neyret, S., Ouali, L., Candau, F. and Pefferkorn, E.** (1995): Adsorption of polyampholytes on polystyrene latex: Effect on colloid stability, *J. Colloid Interface Sci.* 176(1), 86.
- Park, S.-B., Tanaka, H.** (1998): Effects of charge densities of cationic polyacrylamides on strength properties of handsheets, *Mokusai Gakkaishi* 44(3), 199.
- Pelton, R., Zhang, J., Chen, N. and Moghaddamzadeh, A.** (2003): The influence of dextran molecular weight on the dry strength of dextran-impregnated paper, *Tappi J.* 2(4), 15.
- Reynolds, W.F. and Wasser, R.B.** (1980): Dry-strength resins, in “Pulp and Paper Chemistry and Chemical Technology,” 3rd Ed., Edited J. P. Casey, Wiley-Interscience, New York, Vol. 3, Ch. 13, pp. 1447-1474.
- Rojas, O.J., Ernstsson, M., Neuman, R.D. and Claesson, P.M.** (2002): Effect of polyelectrolyte charge density on the adsorption and desorption behavior on mica, *Langmuir* 18, 1604.
- Sezaki, T., Hubbe, M.A., Heitmann, J.A., Argyropoulos, D.S. and Wang, X.** (2006): Colloidal effects of acrylamide polyampholytes Part 1. Electrokinetic behavior, *Colloids Surf. A*, 281(1-3), 74.
- Shubin, V., and Linse, P.** (1997): Self-consistent-field modeling of polyelectrolyte adsorption on charge-regulating surfaces, *Macromolecules* 30(19), 5944.
- Strazdins, E.** (1989): Theoretical and practical aspects of alum use in papermaking, *Nordic Pulp Paper Res. J.* 4(2), 128.
- Sukhishvili, S.A. and Granick, S.** (1998): Polyelectrolyte adsorption onto an initially-bare solid surface of opposite electrical charge, *J. Chem. Phys.* 109(16), 6861.
- Tanaka, H.** (1983): Effects of salts on colloid titration, *Japan Tappi (Kami pa Gikyoshi)* 37(10), 75.
- Tse, S.H.** (1979): The effects of ionic spacing and degree of polymerization on the stoichiometry of polyelectrolyte interaction in dilute aqueous solutions, PhD Thesis, Inst. Paper Chem., Appleton, WI.
- Van de Steeg, H.G.M., Cohen Stuart, M.A., de Kaizer, A. and Bijsterbosch, B.** (1992): Polyelectrolyte adsorption – A subtle balance of forces, *Langmuir* 8(10), 2538.

- Wågberg, L.** (2000): Polyelectrolyte adsorption onto cellulose fibers – a review, *Nordic Pulp Paper Res. J.* 15(5), 586.
- Wang, F. and Hubbe, M.** (2001): Development and evaluation of an automated streaming potential measurement device, *Colloids Surf. A* 194(1-3), 221.
- Ye, X.C., Tanaka, H. and Sumimoto, M.** (1990): Effects of network-type polyacrylamides on the drainage and retention of wheat straw pulp, *Mokuzai Gakkaishi* 36, 64.
- Yoshimoto, Y., Iwasa, Y. and Fujiwara, T.** (2004): Study on the mechanism of PAMs as dry strength agents, *Proc. 2004(71st) Pulp Paper Res. Conf.*, pp. 126-129.
- Yoshizawa, J., Isogai, A. and Onabe, F.** (1998): Analysis and retention behavior of cationic and amphoteric starches on handsheets, *J. Pulp Paper Sci.* 24(7), 213.
- Zhang, J., Pelton, R., Wågberg, L. and Rundlöf, M.** (2000): The effect of charge density and hydrophobic modification on dextran-based paper strength enhancing polymers, *Nord. Pulp Paper Res. J.* 15(5), 440.