Charge Properties of Fibers in the Paper Mill Environment. 1. Effect of Electrical Conductivity

F. Wang and M. A. Hubbe

F. Wang and M. A. Hubbe
Dept. of Wood & Paper Science
North Carolina State University
Box 8005
Raleigh, NC 27695-8005

The electrical conductivity of water used in papermaking tends to increase over time due to water conservation efforts. This study concerns the effect of changes in conductivity on the amounts of highly charged cationic polymers required to neutralize the surfaces, as measured with a fiber-pad streaming potential method. The streaming potential measurements were carried out at relatively high applied pressure to obtain more precise data, especially at the more challenging conditions of increased electrical conductivity. Poly-diallyldimethyl-ammonium chloride was added to vary the observed streaming potential from its initial value to zero. The amount of cationic polymer required for neutralization of bleached hardwood kraft fiber surfaces, determined by this test, increased moderately as the electrical conductivity was increased from 0.5 to 10 mS/cm. The amount of cationic polymer required to reach neutrality increased with increasing contact time and with decreasing molecular mass of the polymer. Results are consistent with the porous nature of kraft fibers and the effects of salt on the effective size of macromolecules in solution.

INTRODUCTION

J. Pulp Paper Science 28 (10) 347-353 (2002).

The electrical charges at the surfaces of fibers in papermaking furnish provide a driving force for adsorption of retention aids, sizing agents, and strength-enhancing chemicals, among other things [1-2]. The situation is complex because of possible interactions among many polymeric, colloidal, and suspended substances present in a typical papermaking system. The present study was undertaken to show how the some of these interactions may be affected by increases in the amount of neutral salts present in the process water of different paper mills. Use of a new design of streaming potential device enabled more accurate analysis of electrokinetic properties of polymer-treated fiber surfaces over a wide range of conductivities, spanning the typical range used for papermaking [3-4].

The conductivity levels used in the experiments spanned the range from “very open” process water systems (0.6 mS/cm) to “highly closed” process water systems (8 mS/cm) [5]. As described in greater detail by others [1-2,6-9] electrokinetic tests involve the relative motion of a fluid phase and either a suspended phase or a fixed phase through which the fluid flows. Electrokinetic data were obtained by fiber-pad streaming potential tests, using an applied positive pressure of 207 kPa (30 psig.) to force the aqueous solutions through fiber plugs that accumulated on a submerged screen [3]. Increased conductivity tends to make it more difficult to evaluate the electrokinetic properties of aqueous mixtures by various other popular methods, including micro-electrophoresis, streaming current, and colorimetric titrations [2,6-11].

Several studies have dealt with the relationship between zeta potentials and streaming potentials [10-15]. Practices regarding the use of streaming potential data to predict zeta potentials have been criticized [11-12], but many workers have assumed a direct proportionality in practical applications [13-15]. The present work shows that these issues can be avoided by titration of fiber slurry samples to the point of zero streaming potential, using a highly charged cationic polyelectrolyte.

Previous Work Related to Fiber Surface Charge and Polymer Adsorption

Factors affecting the surface charge density of papermaking fibers have been reported in many studies, of which several are especially relevant here [16-24]. These factors include the density of charged groups on fiber surfaces [19-21], adsorption of charged multivalent ions or polyelectrolytes [23-26], and dissociation of chemical groups associated with the fiber surfaces [1-2,20,22].

It has been shown, for instance, that the surface charge of fibers is highly dependent on their history of pulping and bleaching [21,27-29]. A relatively high anionic charge density of mechanical pulp fibers and unbleached kraft fibers is consistent with the presence of relatively high levels of resin acids, fatty acids, hemicellulose, and certain degradation products of lignin [29-30]. Increased values of surface charge are sometimes observed following oxidative pulping or bleaching processes, depending on whether those processes result in dissolution and removal of the charged materials from the fibers [27-28]. By contrast, the surface charge density of bleached kraft fibers is much lower, because the charged material has been removed. A typical value for refined bleached hardwood kraft is 30 to 100 μeq per gram of dry fiber [20-21].

Salts are known to affect electrokinetic properties of solid materials in various ways, even if one excludes the effects of strongly adsorbing species and potential-determining ions [20]. For instance, the absolute value of zeta potential tends to decrease with increasing electrolyte concentration [31-33]. This effect has been attributed to a compression of ionic double layers. If one assumes that the position of the hydrodynamic shear plane is fixed, then a thinning of the double layers can be expected to result in a larger proportion of the counter-ions being inside of the shear plane. Recent work indicates that electrical conductivity within the cell walls of fibers also affects electrophoretic mobilities; at low levels of conductivity it is necessary to account for this factor when computing zeta potential values [12].

Salt concentration also is known to affect the dissociation of charged groups, such as the carboxylate groups at fiber surfaces [20,22]. It is well known that dissociation of carboxyl groups in solution is governed by pH, and that it can be predicted in terms of one or more dissociation constants. The situation is similar in the case of surfaces, with the addition requirement that one should take into account the presence of the ionic double layer when figuring the concentration of hydrogen ions at the surface.   In previous studies increasing fiber charge at higher salt concentration has been attributed to decreased mutual interaction of each carboxyl groups with its neighbors [20,34]. By contrast, at very low ionic strength of solution, dissociation or one carboxyl group tends to suppress dissociation of neighboring carboxyl groups so that the fiber has a lower charge in the pH range between about 4 and 8 compared to predictions based on a first dissociation constant of an isolated carboxyl group of the same type [34].

A third way in which salts are known to affect the surface charge of papermaking fibers in suspension is by their effects on adsorption of charged polymers. Studies have shown both positive and negative effects of salt concentration on adsorbed amounts of cationic polyelectrolytes [25,35]. For example, it has been found that a moderate increase in salt concentration may increase the adsorbed amount of cationic starch or polyacrylamide [25]. This effect has been attributed to a less extended conformation of the polyelectrolytes in the dissolved and adsorbed states [26]. At yet higher salt concentrations the adsorption may be suppressed due to a decreased free energy of interaction [25].

Reported Effects of Porosity, pH, and Time

To understand how fiber surfaces will respond to increased electrolyte concentrations it is worth noting some of their surface features. Based on studies of water retention values [36-37] and solvent exclusion [38-39] it can be concluded that kraft fibers are highly porous, however questions have been raised about the interpretation of the data [40]. Results of solute-exclusion tests, using the original assumptions, suggest that kraft pulps have many slit-like pores with characteristic sizes in the range of about 5 to 10 nm [39] or maybe somewhat larger [38]. This conclusion has been questioned [40], based on a study of highly cationic polymer adsorption onto cellulose. Below a certain molecular mass there was no evidence of polymers being excluded from fiber pores, and results could be fit by assuming that the kraft fibers have a relatively narrow distribution of pores having widths of about 40 nm. Some of the apparent disagreement between this estimate of pore size versus the previous estimates depends on assumptions about excluded volumes, polymer deformability, and the possibility of odd-shaped pores, so there is a need for more work in this area.

In contrast to the example just cited [40], several previous studies have reported increases in adsorbed amounts of oppositely charged polyelectrolytes with decreasing molecular mass [16,41-42]. A common explanation is that the charged polymers of lower molecular mass are able to penetrate into a greater fraction of the available pores. A study involving poly-diallyldimethylammonium chloride (DADMAC), the same titrant as used in the present work, indicated a decrease in adsorption from 10.5 to 2 μEq/g as the molecular mass of the cationic polymer was increased from 14,000 to 390,000 g/mole [41]. Other workers observed 1:1 stoichiometry of interaction between low-mass polyDADMAC and carboxymethylated kraft fibers, but the adsorption decreased markedly above a molecular mass of about 10,000 g/mole [43]. The degree to which polyelectrolytes can penetrate into the pore structure of fibers is so extensive that one study showed little change in the uptake of cationic polymers when kraft pulp was refined, increasing its external surface area [44].

Paper mill process water may have widely varying values of pH, though there has been a strong trend toward the use of alkaline papermaking within the pH range between about 7 and 9. Studies have shown increasing fiber surface charge with increasing pH, consistent with the expected dissociation of carboxyl groups [20]. In the present study the variation of pH provided a way to vary fiber surface charge independently of the charge of the titrant.

Effects of time on the interactions between fibers and cationic polyelectrolytes have been reviewed [45]. Certain studies have shown a decay of zeta potential following the addition of cationic polyelectrolytes to slurries of fibers [14,46-47]. The rate of zeta potential decay was most rapid in the case of polyelectrolytes having a relatively low molecular mass [14,47].

EXPERIMENTAL

Materials

Pulp used in the study was southern U.S. bleached hardwood kraft pulp (HBKP). It was refined in deionized water at 1.52% consistency using a Valley laboratory beater to 270 ml of Canadian Standard Freeness (see TAPPI Methods T200 and T227). Each pulp sample was disintegrated in deionized water at 0.3% consistency before application of electrokinetic tests. Na_2SO_4 solution was added to the pulp slurry, as needed, to establish desired values of electrical conductivity. A solutions of 0.1 N NaOH or HCl was used to adjust the pH of the furnish. The resulting pH was within the range 5.5 to 5.8 during testing, except where indicated otherwise. Poly-diallyldimethylammonium chloride samples (poly-DADMAC, Aldrich Chemical Co.) of various different mass-average molecular mass were employed to evaluate the changes in fiber charge properties at different conductivity. Since the original source is said to be the same as in a previous study [43], these samples can be assumed to have broad distributions of molecular mass. The polymers were diluted before use with deionized water to a charge concentration of 0.005 N.

Methods

Fiber charge measurements were carried out with an automated fiber pad streaming potential device, the Streaming Potential Jar (SPJ) [3]. In this test 500 ml of 0.3% solids fiber slurry were added to an 800 ml cylindrical plastic pressure vessel, where it was continuously agitated with a magnetic stirrer. The streaming potential was obtained by applying a pressure differential across a 70 mesh of screen opening and measuring the relative electrical potential on each side with electrodes composed of a silver alloy (45% Ag, 30% Cu, 25% Zn).

For a measurement cycle, a high pressure P1 was applied at first, then a low pressure P2, and then the vacuum valve was opened. The applied pressure P1 was 207 kPa (30 psi.), except where noted otherwise. The duration of high pressure P1, zero pressure P2, and vacuum applied was set at 15, 30, and 15 seconds, respectively, and the rest time between successive tests was set at 15 seconds. Voltage information was obtained with a GW GDM-8055 digital multi-meter that had an electrical impedance rating of 1 GΩ over the range of use. In comparison, radio-frequency conductance values of the sample cell, with fibers included, were in the range of 50 to 2000 Ω over the course of the work. Data were collected for 10 seconds and averaged before and after the pressure was changed from its high to zero setting. The streaming potential value was taken as the millivolt reading at 207 kPa (30 psi.) minus the reading at zero applied pressure. LabVIEW® software and hardware were used for valve actuation and data acquisition. In the case of titration with poly-DADMAC, the polymer was added from the inlet of the pressure vessel during the rest time, and the streaming potential before and after polymer addition were measured and recorded respectively.

RESULTS AND DISCUSSION

Untreated Pulp

Results in Fig. 1 show the effect of increasing electrical conductivity on the streaming potential of bleached hardwood kraft pulp (HBKP) dispersed in dilute solutions of Na_2SO_4. The absolute value of streaming potential fell with increasing electrical conductivity. These results are consistent with theory and with previous experimental work involving a variety of surfaces and methods [31-33].

One of the questions raised by results such as those in Fig. 1 involves the precision of the results when the conductivity is relatively high. As was noted in the Experimental section, this concern was partly addressed by the design of the test method. By using pressurized air, rather than vacuum, it was possible to achieve larger voltage signals. The standard deviations of streaming potential values obtained from the HBKP were less than 5% of the corresponding mean values, when tests were carried out at conductivity levels between 0.6 and 20 mS/cm. To give a specific example, a 99% confidence interval of streaming potential values of HBKP at the extreme high conductivity of 20 mS/cm was between –0.13 and –0.61 mV (with 172 kPa applied pressure difference).

This article mainly addresses a second set of questions raised by results such as those shown in Fig. 1. Those questions involve the interactions of polyelectrolytes with fiber surfaces, and the effects of those interactions on streaming potential results when the salt levels are increased, as in the case of a paper machine system in which the usage of fresh water is reduced.

Titrations with High-Charge-Density Cationic Polymer

Figure 2 shows two main effects of Na_2SO_4 concentration on the titration curves obtained with poly-diallyldimethylammonium chloride (poly-DADMAC). As already shown, the absolute magnitude of the signals decreased with increasing salt. In addition, the point of neutralization of the apparent fiber surface charge increased with increasing salt. It is worth noting that the conductivity levels represented in Fig. 2 correspond to those of typical process water samples from paper machine systems that might be described as “very open,” “moderately closed,” and “highly closed” [5]. Also, the vertical scale in Fig. 2 has been amplified by a factor of about ten, compared to Fig. 1.

Various mechanisms can be used to explain the observed shifts in the endpoints with increasing salt, as shown in Fig. 1. First, let us tentatively assume a 1:1 stoichiometry of interaction of the polymer with surface groups [43]. Based on this assumption the direction of the shift is consistent with the change in dissociation of the surface-bound carboxyl groups with increasing salt. However, the expected magnitude of the change in dissociation is not big enough to account for the data. Based on potentiometric studies [20], the relative change in fiber charge is expected to be about a factor of 1.3 or 1.4 over the range of conductivities represented in Fig. 2. By contrast, Fig. 1 indicates an increase by a factor of about 3 in the amount of cationic polymer needed to achieve a zero streaming potential signal when the conductivity was increased from 0.6 to 8.0 mS/cm.

A second hypothesis is that some of the added cationic polymer remains in solution, especially when the concentration of monomeric electrolytes is increased. Previous work supports the assumption that increasing salt concentration can inhibit or even prevent adsorption of oppositely charged polymers onto cellulose [25,32]. Adsorption isotherms would be needed in order to say for sure whether such a mechanism was significant in the case considered.

A third hypothesis is that the increase in amount of cationic polymer needed to achieve neutral streaming potential at increased salt levels, as seen in Fig. 2, is due to penetration of polyelectrolyte into the pore structure of fibers. Past work has shown that penetration of polymers into kraft fibers is a strong function of the size of the molecules [16,38,41].

Though the cited studies involved variations in the molecular mass of various soluble polymers, a similar effect can be reasonably expected to result from changes in conductivity. The double layer thickness, as represented by the Debye-Huekel reciprocal length κ^{-1} is expected to decrease by a factor of approximately five as the conductivity is increased over the range shown in Fig. 2. It has been shown that the effective size of polyelectrolytes in solution also decreases with decreasing values of κ^{-1} [48-49]. These considerations are consistent with a hypothesis that the observed shifts in the titration endpoints were due mainly to increased ability of poly-DADMAC molecules to penetrate into the pores of the kraft fiber cell walls was a when the conductivity is increased.

Molecular Mass of the Titrant

Figures 3 through 5 further address the question of pore penetration by the cationic polymers. Here, in addition to considering the electrical conductivity, the molecular mass of the titrant was also varied. Tests with poly-DADMAC of three different molecular mass values were repeated at three levels of conductivity.

As shown in Fig. 3, at a relatively low conductivity of 1.02 mS/cm the amount of poly-DADMAC required to reach at streaming potential value of zero increased with decreasing molecular mass. Over a range of increasing mass-average molecular mass between approximately 150,000 and 1,000,000 g/mole, the poly-DADMAC amount corresponding to the endpoint was approximately doubled. These results can be explained if it is assumed that the lower-mass poly-DADMAC either penetrates to a greater degree into the interior of fibers, thus losing much of its ability to affect the electrokinetic measurements, or if the partition coefficient between the surface and the bulk phase changes significantly. In previous work the radius of gyration of polymers in solution has been taken as an indication of trends in the size of pore into to which a molecule can fit [38]. Based on a random-walk model, the radius of gyration of a high mass, soluble polymer is expected to be proportional to the square-root of molecular mass [50].

Support for the pore-penetration model also comes from a study in which poly-DADMAC adsorption by cellulose fibers was studied as a function of the history of the fibers [41]. It is known that many of the pores in the cell walls of kraft fibers tend to close when paper is dried, and not all of these pores reopen when the paper is placed back into water and disintegrated under moderate agitation. In agreement with the present study, poly-DADMAC uptake by the fibers was relatively high in the case of poly-DADMAC having a relatively low molecular mass of 14,000 g/mole [41]. The adsorption of this same polymer sample onto fiber was decreased from 13 μmoles/g to less than 6 μmoles/g when comparing never-dried kraft fibers with fibers that had been dried and redispersed three times.

As shown in Figs. 4 and 5, corresponding results were obtained at the higher conductivity values of 3.40 and 7.78 mS/cm, respectively. Note that the ordinate and abscissa scales have been adjusted to show each set of data most clearly.

Figure 6 provides a summation of the data presented in Figs. 3-5. The plotted points represent the endpoints of titrations, where the curves crossed the zero value of streaming potential. These results are consistent with an earlier study that also found an increasing apparent surface charge with decreasing molecular mass of cationic titrants [16,51], based on an assumed 1:1 stoichiometry of charged groups.

In the case of the lowest-mass titrant there was a factor of eight change in the amount of polymer required to neutralize the surface over the observed range of conductivity. The large size of the shift suggests that the salt addition is decreasing the radii of gyration of the polymers enough so that they can penetrate the fiber porosity. The data of Wågberg and Ödberg [43] shows a change of similar relative magnitude, except that in that case the independent variable was molecular mass. Adsorption rose most rapidly over a range of molecular mass of 10,000 to 30,000 g/mole, which is much lower than the mean value of polymers used in the present study. Though the salt concentration used in this previous work was not disclosed [43], the direction of the apparent disagreement may be resolved by considering how ionic strength affected molecular size. Based on the work of Lin and Cheng [49] it is possible to estimate that the radius of gyration of the cationic polymer should decrease by a factor of about two for each ten-fold increase in ionic strength. In the present work the large increase in polymer needed to achieve neutrality with increasing salt was observed only for the sample having a mean molecular mass of 150,000 g/mole, the lowest considered. Another possible contributing factor helping to explain the relatively high demand of the surface for this polymer under these conditions is the expected broad distribution of molecular mass.

Effect of pH

As shown in Fig. 7, the amount of cationic polymer needed to reach a zero streaming potential tended to increase with increasing pH of the suspending medium. Changing the pH is not expected to affect the conformation of poly-DADMAC, a compound that contains quaternary ammonium groups [52]. Rather, pH will affect the degree of dissociation of carboxyl groups at the fiber surfaces. Studies have shown a relatively rapid increase in anionic charge of cellulosic surfaces as pH is increased from about 3 to about 5 or more, depending on the salt concentration [20,22].

The observed rapid rise in cationic polymer required to neutralize the surface in Fig. 7 occurs at a lower pH compared to the expected pK_a value of about 4 to 5 for the dissociation of sugar-type carboxyl groups [20,34]. The reason for this has not been determined in this project. However, previous work indicates two likely contributing factors. First, the presence of anionic surfaces of fibers and colloidal material during the measurement is expected to shift the measured pH to lower values compared to a true bulk pH measurement [53]; to overcome this source of error it would be necessary to separate the pH probe liquid junction from the colloidal material by means of a dialysis membrane. This error results because charged surfaces adjacent to the liquid junction of a standard reference electrode affect the relative mobilities of K^+ and Cl^- ions, especially at low conductivity values [53]. The second factor to consider is the affect of the ionic double layers on the surface concentrations of hydrogen ions [1-2]. Since the work represented in Fig. 7 was carried out in the presence of Na_2SO_4 concentrations far exceeding the hydrogen ion concentrations, the second factor is expected to be small.

Also shown in Fig. 7 the amount of cationic polymer needed to neutralize the surfaces increased with increasing conductivity, especially at the highest conductivity level considered. If one assumes that essentially all of the added polymer adsorbs onto the fibers, then Fig. 7 can be interpreted in terms of the charged groups at the surface that are accessible to the titrant molecules. The changes in endpoint values resulting from the pH changes in Fig. 7, are consistent with studies showing an approximately stoichiometric relationship governing the adsorption of highly soluble polyelectrolytes onto fiber surfaces of opposite net charge in aqueous solutions [43,54]. This type of interaction implies that the polyelectrolytes adopt a conformation that allows association with the maximum number of surface-bound charged groups [33]. The influence of electrical conductivity can be interpreted in terms of the amount of surface area that is accessible for such adsorption.

Effect of Time

The continually changing conformations of dissolved and adsorbed polyelectrolytes make it reasonable to study the effects of time on adsorption and charge. In a paper machine system it is typical for some polymeric additives to remain in contact with the fiber furnish for only a few seconds before the paper is dried. Other polyelectrolytes may remain in contact with wet fibers for many minutes or hours. As shown in Fig. 8, the observed streaming potential tended to decay following each addition of poly-DADMAC to the bleached hardwood kraft fiber slurry at a conductivity of 1.05 mS/cm. Decay curves of this general nature have been reported by others for different fiber slurry conditions [14,46-47]. The most rapid decay of streaming potential was observed immediately after the first aliquot of 0.108 % poly-DADMAC based on fiber mass. Previous workers have attributed this decay not only to pore penetration, but also to a process of reorientation of polyelectrolytes into a flatter adsorbed conformation [45]. In either case the results are consistent with processes in which the polyelectrolyte initially adsorbs in a way that has a relatively large influence on the electrokinetic measurements. Time allows the polyelectrolyte to either move or adopt a different conformation from which it has a lesser effect on the electrokinetic measurements, relative to the original anionic charge of the fiber. Though these assumptions are consistent with the present data, it is not possible to rule out other factors, such as transient gradients of chloride ion concentrations within the fiber wall immediately after addition of the poly-DADMAC.

In the set of tests represented by Fig. 8 it was necessary to add a total of 0.43% poly-DADMAC on fiber mass in order to achieve an asymptotic value near to zero streaming potential. As shown in Fig. 9, an essentially identical asymptotic result was achieved after a contact time of 150 minutes if the entire amount of poly-DADMAC was added at one time.

CONCLUSIONS

Tests with a lab-scale streaming potential device, using an applied pressure of 207 kPa (30 psi.) were used successfully to evaluate the electrokinetic properties of bleached kraft furnish at electrical conductivity values up to 20 mS/cm. The method was found to yield useful titration results with poly-DADMAC at least up to a conductivity of 8 mS/cm. The ability to measure electrokinetic properties and carry out charge titrations in this conductivity range is important in light of continuing efforts to decrease the amount of fresh water used in papermaking systems.

The amount of cationic polymer needed to neutralize the surface of hardwood bleached kraft pulp (BHKP) fibers depended on the electrical conductivity, the molecular mass of the poly-DADMAC, the pH of the aqueous solution, and the time of contact between the polyelectrolyte titrant and the suspension of fibers. Results were consistent with the following hypotheses concerning the interactions between the cationic polymers and the fibers:

1. Increasing salt concentration, as indicated by the conductivity, causes the cationic poly-DADMAC molecules to adopt less extended conformations in solution so that they are able to penetrate to a greater extent into the pores in the cell walls of the fibers. This effect tends to increase the apparent surface charge of the fibers with increasing conductivity.
2. Increasing molecular mass has a similar effect of limiting the extent to which titrant molecules are able to penetrate into fiber pores. This effect is consistent with the expected relationship between molecular mass and radius of gyration.

3. The effect of pH can be explained by dissociation of carboxyl groups at the fiber surfaces.
4. The effect of time is consistent with gradual changes in conformation. One of the expected conformational changes allows polyelectrolytes to reticulate into pores smaller than would be predicted from their average dimensions in bulk solution. The present work cannot rule out the possibility that the impact of a polyelectrolyte on zeta potential is reduced as it lies down flat on a surface to which it is adsorbed.

When all other factors are held constant, papermakers can expect to observe increased cationic demand of fibers with increasing concentrations of salt. However, this conclusion does not necessarily imply that it will be feasible to retain higher amounts of any arbitrarily chosen cationic wet-end additive. As shown by others, retention of charged additives depends not only on charge stoichiometry, but also on other factors affecting the overall free energy of adsorption [25].

REFERENCES

1. LINDSTRÖM, T., “Electrokinetics in the Paper Industry,” in “Paper Chemistry,” Roberts, J. C., Ed., Blackie, London (1991), pp. 25-43.
2. TANAKA, H., “Paper,” in “Electrical Phenomena at Interfaces,” Dekker, New York (1998), Ch. 19, pp. 389-404.
3. WANG, F., and HUBBE, M. A., “Development and Evaluation of an Automated Streaming Potential Measurement Device,” *Colloids Surf. A*, accepted for publication (2001).
4. HUBBE, M. A., and WANG, F., “Where to Add Retention Aid: Issues of Time and Shear,” *TAPPI J.* 84(12), accepted for publication (2001).
5. PIETSCHKER, D. A., “The 100% Closed Water System – What to Expect,” in “Proc. 1996 TAPPI Papermakers Conf.,” TAPPI Press, Atlanta (1996), pp. 521-528.

6. TANAKA, H., “Effect of Salts on Colloid Titration,” *Kami pa Gikyoshi* 37(10), pp. 75-84 or 939-948 (1983).
7. HUBBE, M. A., “Selecting and Interpreting Colloidal Charge Measurements,” in “Proc. Scientific & Technical Advances in Wet End Chemistry*,”* Barcelona, Spain, PIRA Intl., Leatherhead (2000).
8. WINTERS, J. C., “Introduction to the Electrokinetics of Papermaking,” in “Retention of Fines and Fillers During Papermaking,” J. M. Gess, Ed., TAPPI Press, Atlanta (1998), Ch. 3, pp. 29-50.
9. BROUWER, P. H., “The Relationship between Zeta Potential and Ionic Demand and How it Affects Wet-End Retention,” *TAPPI J.* 74(1): 170-179 (1991).
10. SANDERS, N. D., and SCHAEFER, J. H., “Comparing Papermaking Wet-End Charge-Measuring Techniques in Kraft and Groundwood Systems,” *TAPPI J.* 78(11): 142-150 (1995).
11. JAYCOCK, M. J., “Assumptions Made in the Measurement of Zeta-Potential by Streaming Current / Potential Detectors,” *Paper Technol.* 36(6): 35-38 (1995).
12. VAN DE VEN, T. G. M., “Effect of Fiber Conductivity on Zeta Potential Measurements of Pulp Fibers,” *J. Pulp Paper Sci.* 25(7): 243-245 (1999).
13. PENNIMAN, J. G., “Comparison of Pulp Pad Streaming Potential Measurement and Mobility Measurement,” *TAPPI J.* 75(8): 111-115 (1992).
14. KOETHE, J. L., and SCOTT, W. E., “Polyelectrolyte Interactions with Papermaking Fibers: The Mechanism of Surface-Charge Decay,” *Tappi J.* 76(12): 123-133 (1993).
15. VERNHET, A., BELLON-FONTAINE, M. N., and DOREN, A., “Comparison of Three Electrokinetic Methods to Determine the Zeta Potential of Solid Surfaces,” *J. Chim. Phys. Phys.-Chem. Biol.* 91(11/12): 1728-1747 (1994).
16. ÖHMAN, L., WÅGBERG, L., MALMGREN, K., and TJERNSTRÖM, A., *J. Pulp Paper Sci.* 23(10): J467-474 (1997).
17. LINDSTRÖM, T., “Chemical Factors Affecting the Behavior of Fibers during Papermaking,” *Nordic Pulp Paper Res. J.* 7(4): 181-192 (1992).
18. ROUGER, J., and MUTJE PUJOL, P., “Correlation between Cellulose Fiber Beating and Fixation of a Soluble Cationic Polymer,” *Brit. Polymer J.* 16(2): 83-86 (1984).
19. HERRINGTON, T. M., and MIDMORE, B. R., “Adsorption of Ions at the Cellulose / Aqueous Electrolyte Interface. Part 1. Charge / pH Isotherms,” *J. Chem. Soc., Faraday Trans. 1* 80(6): 1525-1537 (1984).
20. HERRINGTON, T. M., and PETZOLD, J. C., “An Investigation into the Nature of Charge on the Surface of Papermaking Woodpulps. 2. Analysis of Potentiometric Titration Data,” *Colloids Surf.* 64: 109-118 (1992).
21. LLOYD, J. A., and HORNE, C. W., “The Determination of Fiber Charge and Acidic Groups of Radiata Pine Pulps,” *Nordic Pulp Paper Res. J.* 8(1): 48-52,67 (1993).
22. FERNANDES DINIZ, J. M. B., “Charge-pH Isotherms of Paper Wood Pulps,” *Holzforschung* 50(1): 37-41 (1996).

23. MARTON, J., and MARTON, T., "Wet End Starch: Adsorption of Starch on Cellulosic Fibers," *Tappi* 59(12): 121-124 (1976).

24. GILL, R. I. S., "Interaction of Three Different Polyamines with Various Pulps and its Importance in the Control of Contaminants," *Nordic Pulp Paper Res. J.* 8(1): 208-210,231 (1993).

25. VAN DE STEEG, H. G. M., COHEN STUART, M. A., DE KEIZER, A., and BIJSTERBOSCH, B. H., "Polyelectrolyte Adsorption: A Subtle Balance of Forces," *Langmuir* 8(10): 2838-2546 (1992).

26. VERMÖHLEN, K., LEWANDOWSKI, H., NARRES, H. D., AND SCHWUGER, M. J., "Adsorption of Polyelectrolytes onto Oxides – the Influence of Ionic Strength, Molar Mass, and Ca^{2+} ions," Colloids Surf. A – Physicochem. Eng. Aspects 163(1), pp. 45-53 (2000).

27. GOULET, M. T., and STRATTON, R. A., "The Effect of Pulping, Bleaching, and Refining Operations on the Electrokinetic Properties of Wood Fines," *Nordic Pulp Paper Res. J.* 5(3): 118-125 (1990).

28. LAINE, J., and STENIUS, P., "Effect of Effect of ECF and TCF Bleaching on the Charge Properties of Kraft Pulp," *Paperi Puu* 79(8): 551-559 (1997).

29. THORNTON, J., EKMAN, R., HOLMBOM, B., and ECKERMAN, C., "Release of Potential 'Anionic Trash' in Peroxide Bleaching of Mechanical Pulp," *Paperi Puu* 75(6): 426-431 (1993).

30. DONG, D., FRICKE, A. L., HOUDGIL, B. M., and JOHNSON, H., "Electrokinetic Study of Kraft Lignin," *TAPPI J.* 79(7): 191-197 (1996).

31. HUNTER, R. J., "The Electrokinetic Effects," in "Foundations of Colloid Science," Vol. 2, Carendon Press, Oxford, 1989.

32. LINDSTRÖM, T., and SÖREMARK, C., "Zeta Potential Measurements in Paper Manufacture," *Papier* 29(12): 519-525 (1975).

33. ONABE, F., "Studies of Interfacial Properties of Polyelectrolyte-cellulose Systems. I. Formation and Structure of Adsorbed Layers of Cationic Polyelectrolyte-(Poly-DMDAAC) on Cellulose Fibers," *J. Appl. Polymer Sci.* 22: 3495-3510 (1978).

34. BYGRAVE, G., and ENGLEZOS, P., "Fiber Charge from Potentiometric Titration of Kraft Pulp and Donnan Equilibrium Theory," *Nordic Pulp Paper Res. J.* 13(2): 220-224 (1998).

35. LINDSTRÖM, T., and WÅGBERG, L., "Effects of pH and Electrolyte Concentration on the Adsorption of Cationic Polyacrylamides on Cellulose," *Tappi J.* 66(6): 83-85 (1983).

36. THODE, E. F., BERGOMI, J. G., and UNSON, R. E., "The Application of a Centrifugal Water-Retention Test to Pulp Evaluation," Tappi 43(5): 505 (1960).

37. TAPPI, "Water Retention Value," TAPPI Useful Method UM 256, 1981.

38. STONE, J. E. AND SCALLAN, A. M., “A Structural Model for the Cell Wall of Water-Swollen Wood Pulp Fibers Based on their Accessibility to Macromolecules,” *Cellulose Chem. Technol.* 2(3): 343-358 (1968).

39. BERTHOLD, J., and SALMÉN, L., “Effects of Mechanical and Chemical Treatments on the Pore Size Distribution in Wood Pulps Examined by Inverse Size-Exclusion Chromatography,” *J. Pulp Paper Sci.* 23(6): J245-253 (1997).

40. ALINCE, B., and Van de Ven, T. G. M., “Porosity of Swollen Fibers Evaluated by Polymer Adsorption,” in *The Fundamentals of Papermaking Materials*, Trans. 11th Fund. Res. Symp., Cambridge, 771-788 (1997).

41. GRUBER, E., GROSSMAN, K., AND SCHEMPP, W., “Interactions of Synthetic Cationic Polymers with Fibers and Fillers; Influence on Adsorption,” *Wochbl. Papierfabr.* 124(1): 4-11 (1996).

42. HORN, D., and MELZER, J., “Electrostatic and Steric Effects of Cationic Polymers Adsorbed on Cellulose Fibers,” in *Trans. BPBIF Symp. Fiber-Water Interactions in Papermaking*, Oxford, 135-150 (1977).

43. WÅGBERG, L., and ÖDBERG, L., “Polymer Adsorption on Cellulosic Fibers,” *Nordic Pulp Paper Res. J.* 4(2): 135-140 (1989).

44. ROUGER, J., and MUTJE PUJOL, P., “Correlation between Cellulose Fiber Beating and Fixation of a Soluble Cationic Polymer,” *Brit. Polymer J.* 16(2): 83-86 (1984).

45. SWERIN, A., and ÖDBERG, L., “Some Aspects of Retention Aids,” in “The Fundamentals of Papermaking Materials,” C. F. Baker, Ed., Trans 11th Fundam. Res. Symp. at Cambridge, PIRA Intl., Leatherhead, England (1997), Vol. 1, pp. 265-351.

46. STRAZDINS, E., “Optimization of the Papermaking Process by Electrophoresis,” *Tappi* 60(7): 113-114 (1977).

47. FARLEY, C. E., “Factors Influencing the Rate of Charge Decay,” *Tappi J.* 80(10): 177-183 (1997).

48. YANG, J. Y, SOHN, D., KIM, N. J., “Conformations of Anionic and Cationic Polyelectrolytes in Various Salt Concentration Solutions,” Polymer-Korea 23(5): 708-716 (1999).

49. LIN, K.-F., and Cheng, H.-L., “A Simple Method to Estimate Chain Conformations of Polyelectrolytes in the Semidilute Regime,” *Macromol.* 33(13): 4961-4965 (2000).

50. BILLMEYER, F. W., JR., “Textbook of Polymer Science,” Second Ed., Wiley-Interscience, New York (1971).

51. SWERIN, A., and WÅGBERG, L., “Size-Exclusion Chromatography for Characterization of Cationic Polyelectrolytes Use in Papermaking,” *Nordic Pulp Paper Res. J.* 9(1): 18-25 (1994).

52. NICKE, R., PENSOLD, S., TAPPE, M., and HARTMANN, H.-J., “Poly-diallyldimethylammonium Chloride Used as a Flocculant,” *Wochenbl. Papierfabr.* 120(14): 559-564 (1992).

53. JENNY, H., NIELSEN, T. R., COLEMAN, N. T., and WILLIAMS, D. E., "Concerning the Measurement of pH, Ion Activities, and Membrane Potentials in Colloidal Systems," *Science* 112(2902): 164-167 (1950).

54. WINTER, L., WÅGBERG, L., ÖDBERG, L., and LINDSTRÖM, T., "Polyelectrolytes Adsorbed on the Surface of Cellulosic Materials," *J. Colloid Interface Sci.* 111(2): 537-543 (1986).

CAPTIONS

Fig. 1. Variation of streaming potential of hardwood bleached kraft pulp (HBKP) fibers as a function of electrical conductivity.

Fig. 2. Effect of electrical conductivity on the titration endpoint of HBKP.

Fig. 3. Titration curve of HBKP with different molecular mass of poly-DADMAC at a conductivity of 1.01 mS/cm.

Fig. 4. Titration curves of HBKP with different molecular mass of poly-DADMAC at a conductivity of 3.41 mS/cm.

Fig. 5. Titration curves of HBKP with different molecular mass of poly-DADMAC at a conductivity of 7.78 mS/cm.

Fig. 6. Variation of apparent surface charge of pulp derived from titrations with poly-DADMAC of different molecular mass as a function of electrical conductivity, assuming that all added polymer adsorbs.

Fig. 7. Relationships between the amount of cationic polymer at the endpoint for HBKP fibers, pH, and conductivity.

Fig. 8. Streaming potential decay of HBKP fibers after adsorption of high molecular mass poly-DADMAC.

Fig. 9. Time dependence of fiber streaming potential after neutralization with high molecular mass poly-DADMAC.

FIGURES

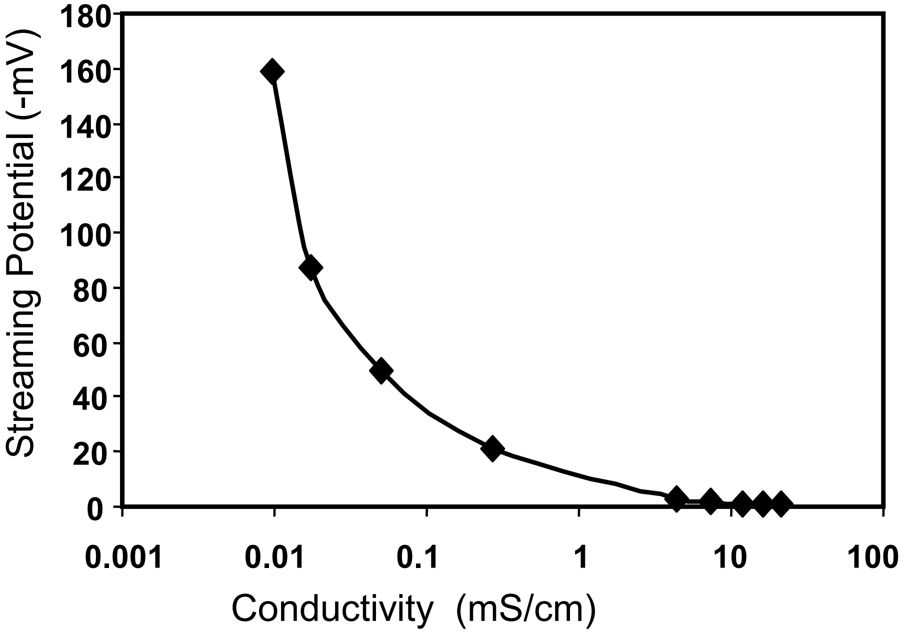


Fig. 1. Variation of streaming potential of hardwood bleached kraft pulp (HBKP) fibers as a function of electrical conductivity.

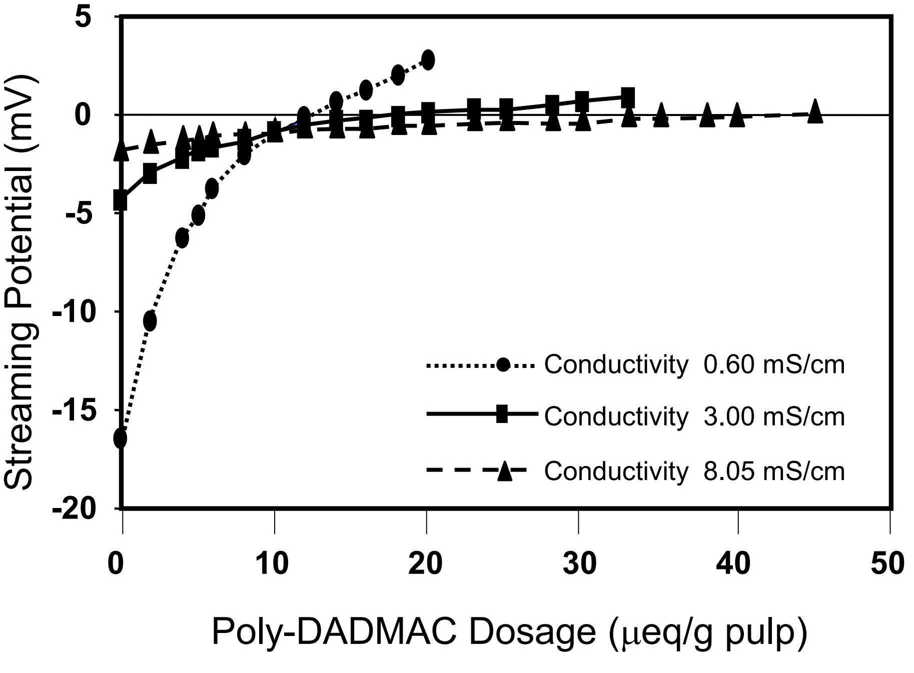


Fig. 2. Effect of electrical conductivity on the titration endpoint of HBKP.

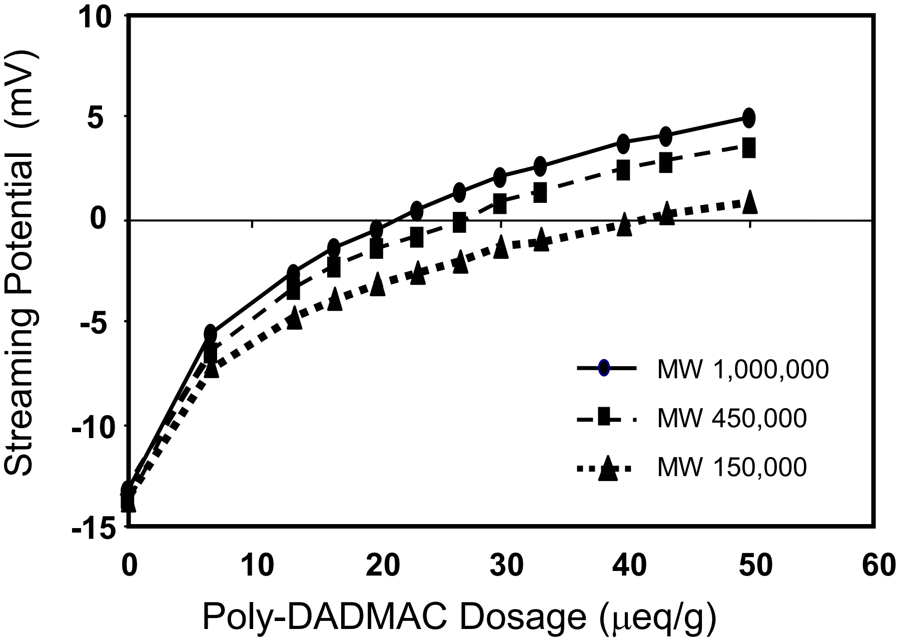


Fig. 3. Titration curve of HBKP with different molecular mass of poly-DADMAC at a conductivity of 1.01 mS/cm.

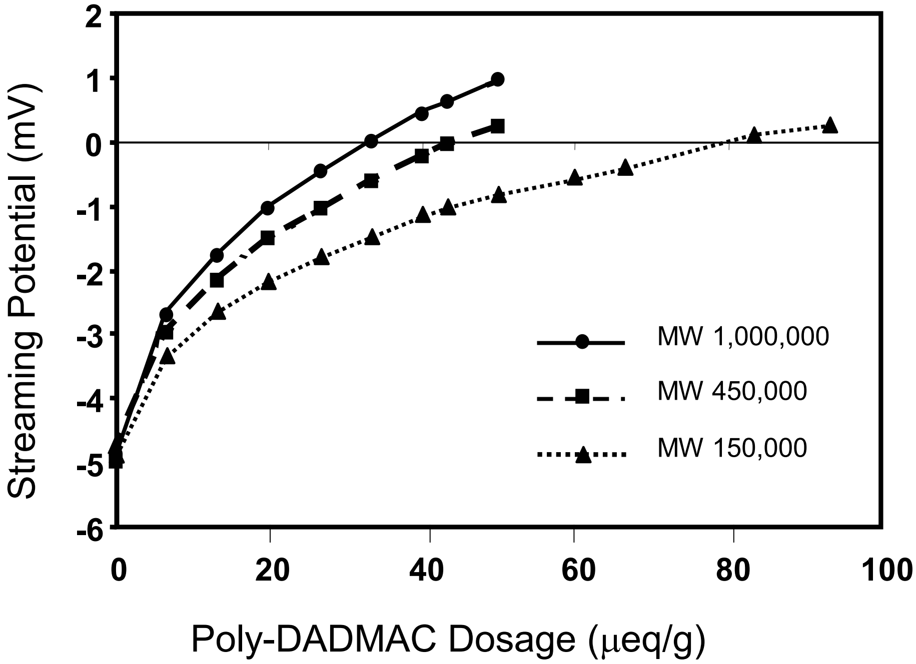


Fig. 4. Titration curves of HBKP with different molecular mass of poly-DADMAC at a conductivity of 3.41 mS/cm.

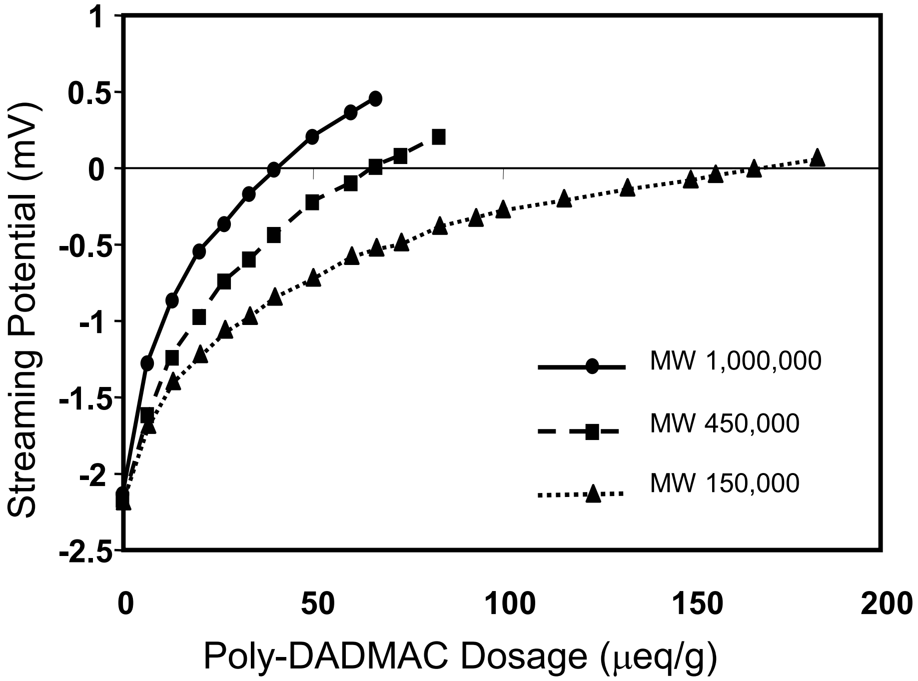
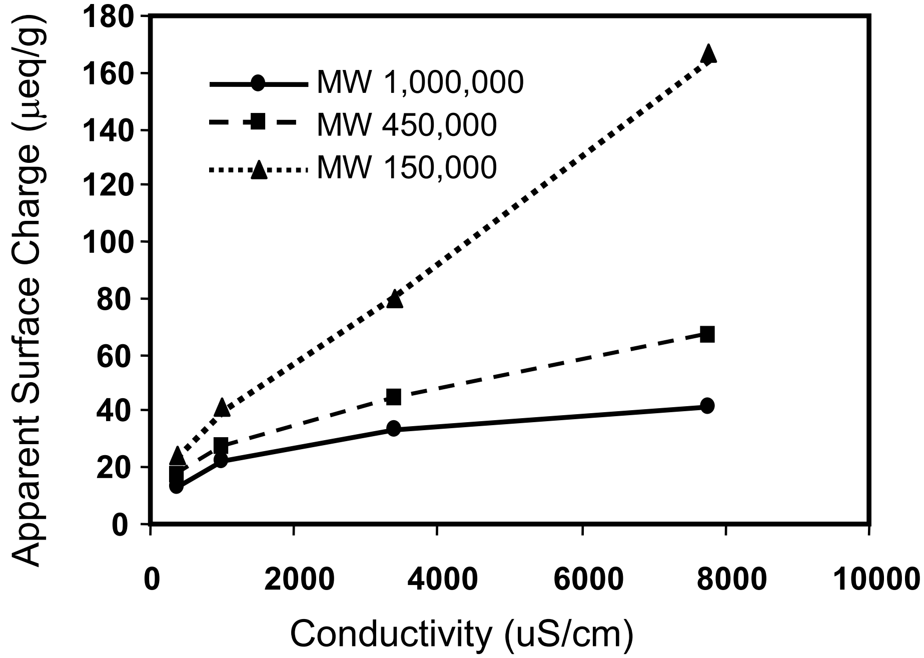


Fig. 5. Titration curves of HBKP with different molecular mass of poly-DADMAC at a conductivity of 7.78 mS/cm.



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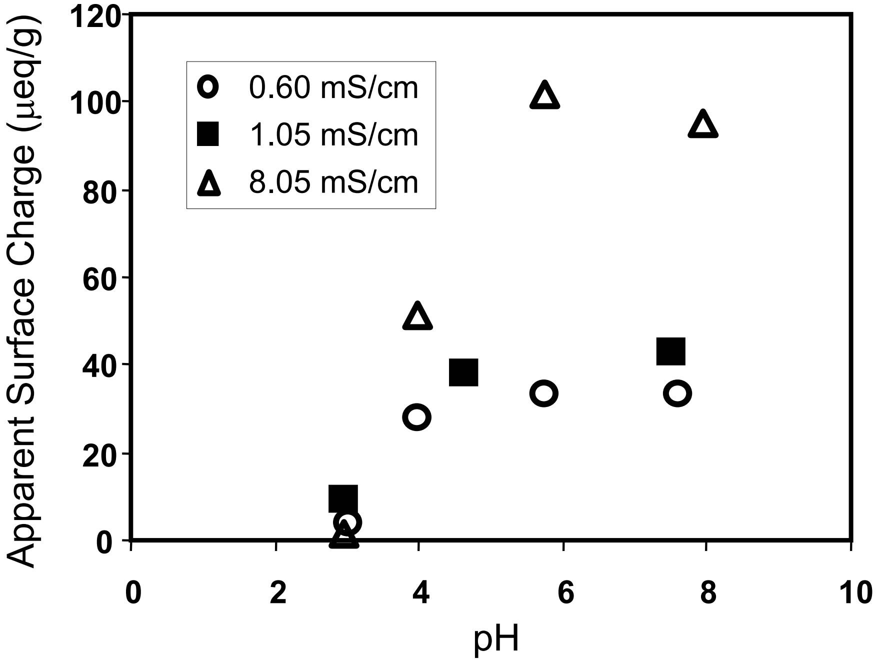

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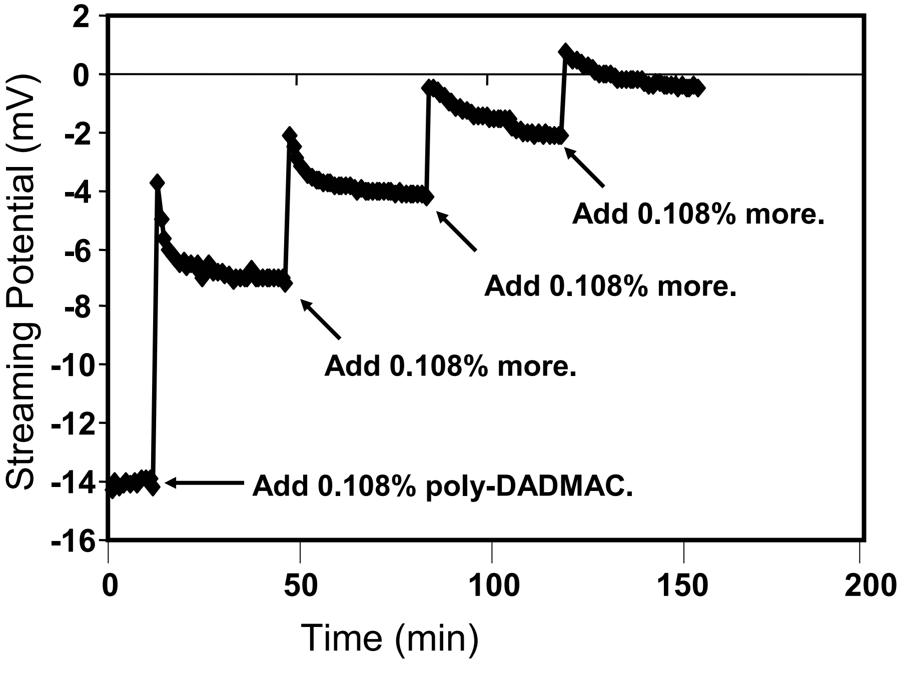
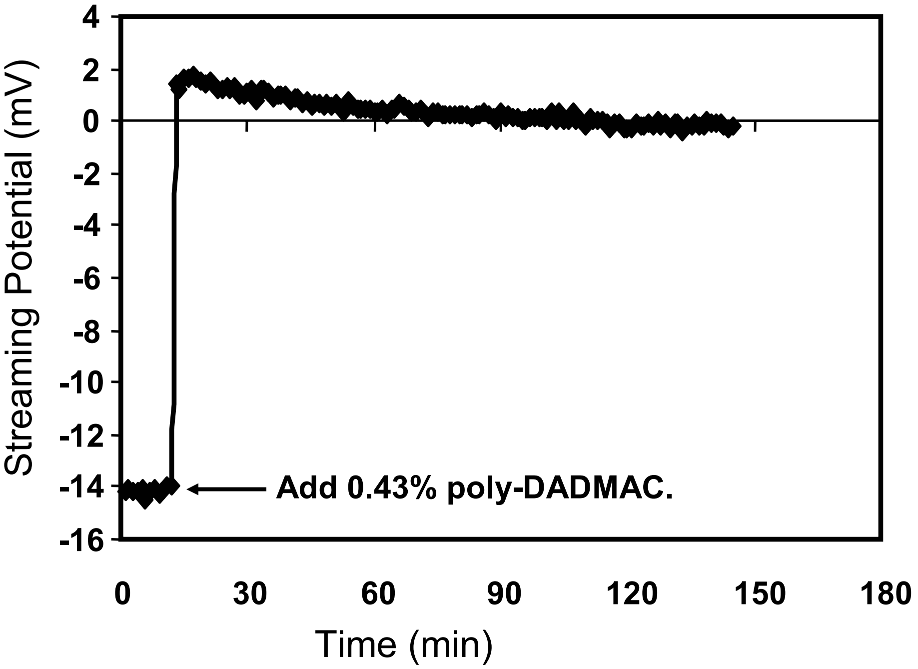


Fig. 8. Streaming potential decay of HBKP fibers after adsorption of high molecular mass poly-DADMAC.



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