

# Interfacial Properties of Polyelectrolyte–Cellulose Systems. II. Electrokinetic Properties of Cellulose Fibers with Adsorbed Monolayers of Cationic Polyelectrolyte

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## Synopsis

Zeta potential measurements by the streaming current method were performed on pulp (DP) fibers with or without irreversibly adsorbed monolayers of cationic polyelectrolyte. Factors affecting the electrokinetic properties of these fibers, such as the amount of adsorbed polymer, the polymer molecular weight ( $M_n$  50,000 and 200,000), ionic strength ( $10^{-5} \sim 10^{-2}M$  KCl), and the pH of the streaming medium (KCl solution), were examined. As the amount of adsorbed polymer increased, the negative zeta potential of the fibers decreased until the polarity of the zeta potential was reversed to the positive side. A marked change in the value of zeta potential was not observed when the formation of the saturated monolayer was completed. The zeta potential also varied in proportion to an increase in the amount of polymer adsorbed. Experimental results are interpreted with reference to the origin of the surface charge, the amphoteric nature of the surface, the modes of adsorption, and the adsorbed polymer chain configuration. Possible effects of the adsorbed monolayer formation on the structural change of the electric double layer at the fiber surface are discussed. It is concluded that the formation of a monolayer of cationic polyelectrolytes on the negatively charged cellulose fibers under the condition of  $k_1 > k_2$  (part I) provides a means to arbitrarily control the charge of the fibers until formation of a saturated monolayer.

## INTRODUCTION

It has been demonstrated<sup>1</sup> that formation of the adsorbed polymer layers occurs on the fiber surfaces after treating the cellulose fibers with varying concentrations of the cationic polymer (poly-DMDAAC) followed by repeated washing with demineralized water. Furthermore, it has been suggested that monolayers of the polymer are formed on cotton linter (CT) fibers and pulp (DP) fibers. Since the fibers with saturated monolayers are positively charged, further adsorption of the polymer does not occur. Thus, when the number of adsorbed polymer segments per unit surface area at the point of the saturated monolayer formation ( $k_1$ ) is larger than the number of carboxyl groups on the unit fiber surface area ( $k_2$ ), formation of the adsorbed polymer layers on the surface does not proceed.

This study investigates various factors affecting the electrokinetic properties of monolayer-formed fibers and also provides brief theoretical interpretations for their properties. The zeta potential measurements on human hair keratin treated with polyethyleneimines were carried out by Cook et al.<sup>2</sup>

An additional objective of this paper is to give further support, from the electrokinetic measurements, to the hypothesis of monolayer formation of the polymer (part I) proposed on DP mainly using the polymer adsorption data.

This paper investigates the applicability of the formation of monolayers of cationic polyelectrolytes as a means to surface charge control of the negatively charged cellulose fibers.

## EXPERIMENTAL

Zeta potential measurements by the streaming current method were carried out on the pads of the monolayer-formed acetate-grade dissolving pulp (DP) fibers. Various factors, such as (i) ionic contaminants, (ii) electrode polarization, (iii) nonuniform pad formation, (iv) air bubble entrapment in the pad and in the streaming liquid, and (v) unstable streaming liquid, resulted in fluctuations of the streaming current data.

### Cationic Polyelectrolyte

Poly-DMDAAC<sup>3</sup> is a quaternary ammonium water-soluble polymer (see Fig. 1 in part I for the monomer unit) manufactured by Calgon Corporation, Pittsburgh, Penn. Two kinds of molecular weight samples were used: Conductive Polymer 261 ( $M_n$  50,000)<sup>4</sup> and Cat Flocc ( $M_n$  200,000).<sup>5</sup> Conductive Polymer 261, available in 40% aqueous solution, was developed for use as an electroconductive coating on paper in the electrographic reproduction process.<sup>6</sup>

Cat Flocc, available in 15% aqueous solution, was developed for use as a coagulant in destabilizing colloidal suspensions and in industrial waste water clarification.<sup>7</sup>

Poly-DMDAAC is a homopolymer of dimethyldiallylammonium chloride. It was confirmed both by Kjeldahl nitrogen analysis and titration of the cationic groups of the polymer using an anionic polymer, i.e., poly(vinyl alcohol)-potassium sulfate (PVSK) (the colloid titration technique)<sup>8,9</sup> that each monomer unit of the polymer contains one quaternary ammonium group. It has been demonstrated (part I) that the mono- or multilayers of this polymer were formed irreversibly on the cellulose fibers presumably by tenacious electrostatic bonding between the quaternary ammonium groups of the polymer and the carboxyl groups of the cellulose fibers.

### Demineralized Water

Since trace contaminants, particularly ionic substances, affect the results of electrokinetic measurements, the water obtained through a two-stage clarification, i.e., distillation and demineralization, was used throughout this work.

Distilled water was fed into a Barnstead D0809 mixed bed ion exchanger for further demineralization. Conductivity of the demineralized water was checked and the water with specific conductance less than  $10^{-6}$  mho/cm was used. Furthermore, the demineralized water was deaerated by suction using an aspirator pump prior to use.

### Cellulose Fibers

For the fiber pretreatment and characterization, see details in part I.

## Electrolyte

Dilute electrolyte solutions for the streaming liquids were prepared using C.P.-grade potassium chloride.

## Streaming Current Cell

The streaming current measurements were made in a compression-type cell with reversible Ag–AgCl electrodes similar in principle to that described by Goring,<sup>10</sup> Biefer,<sup>11</sup> Mason,<sup>10,11</sup> and Chang and Robertson.<sup>12-14</sup>

The compression-type cell, compression device, and electrodes originally designed by Chang and Robertson<sup>12</sup> were employed in combination with a flow system of the author's own design.<sup>15</sup>

The streaming current cell and the experimental system are described in part I.

## Electrodes

Two Ag–AgCl electrodes were prepared by chloridizing perforated disks of a pure silver sheet having a thickness of 0.15 cm. The disks were perforated by drilling ca. 380 of  $\frac{1}{16}$ -in. (in diameter) holes evenly through the silver plate to permit the liquid to flow through the electrodes. They were supported by a plastic base reinforced internally by a steel tube. A rigid support for the silver disk was provided by a plastic tube (acrylic resin) reinforced with a steel tube.

A silver wire fused to the back of the electrode was extended through the plastic inner tube as a connection to the electrical measuring system.

During assembly of the electrodes the plastic supports were inserted through the rubber stoppers which held it concentric with the cell and provide a liquid tight seal at the end of the cell. The length of the pad was altered by sliding the electrodes through the stoppers.

In order to obtain reversible Ag–AgCl electrodes, the perforated silver electrodes were chloridized by electrolysis in 0.1M HCl solution using a platinum cathode at a current density of 10 mA/electrode. A dc power source for the electrolysis was 3 V (1.5 V  $\times$  2) dry battery. The current direction was reversed three times at intervals of 15 min and a final 30-min chloridization occurred. The electrodes were then thoroughly rinsed with distilled water. Since the chloridized electrodes thus prepared were highly polarized, they were submerged in deaerated  $1 \times 10^{-4}$ M KCl solution with two electrodes shorted together to eliminate the residual current between them (depolarization process). To eliminate variations of ionic concentrations around the electrodes with elapsed time during the depolarization process, the KCl solution was agitated for 10 sec at 30-min intervals. This treatment facilitates depolarization and was repeated for the first 3 hr. The residual current between the electrodes fell to 0.01  $\mu$ A or less within 20 hr. The silver chloride layers deposited in this manner were sufficiently thin and the electrodes were stable for more than 30 measurements.

## Requirement for Reversible Ag–AgCl Electrodes

The presence of  $\text{Cl}^-$  ions in the streaming liquids is a prerequisite to maintain reversibility of Ag–AgCl electrodes throughout the electrokinetic measurements. It has been reported<sup>16</sup> that concentrations of KCl greater than  $1 \times 10^{-5}M$  were sufficient to give reliable data with Ag–AgCl electrodes. The concentration range of KCl in this investigation was  $10^{-5}$  to  $10^{-2}M$ .

### Electrical Measuring System

The streaming current generated from the pad was measured with a microvolt-ammeter (Keithley's Model 150A). The input resistance of a Keithley instrument is 1000 and 100 ohms for 1 and  $10 \mu\text{A}$  full-scale ranges, respectively, when used as an ammeter. The 1, 3, and  $10 \mu\text{A}$  full-scale ranges were used for the measurements. The fiber pad conductivity was measured concurrently using a conductivity meter (Radiometer Model CDM-2). The conductivity data will appear in a later publication of this series.

### Flow System

The streaming current and permeability measurements<sup>17</sup> were carried out at a constant operating pressure of 50-cm  $\text{H}_2\text{O}$  produced by the difference in levels of the two liquid reservoirs in the flow system. This flow circuit permits continuous operation of the cell.<sup>15</sup> The basic feature of the flow circuit is to convey overflow from the lower to the upper liquid reservoir by a water pump. The volume of streaming liquid in the flow circuit for each run was 2 liters, including the liquid in the cell and the pad.

### Pad Formation

The fibers with or without adsorbed layers of the polymer were soaked in KCl solutions prepared in deaerated distilled water.

The fiber suspension was deaerated by suction for 1 hr using an aspirator pump and placed overnight under reduced pressure. To form the pad, the cell was clamped vertically with the lower electrode in position and with the water pressure gauge openings closed by stopcocks. A 2-liter suspension containing about 4 g (oven-dry weight) of the fibers (i.e., 0.2% solid consistency) was formed into a pad by filtering through the lower electrode. The flow circuit was designed to convey the filtrate to the upper liquid reservoir by a water pump to be used as the streaming liquid. When the pad was formed, the second electrode was inserted giving the two electrode surfaces direct contact with the pad. The cell was then placed horizontally, and the entire flow circuit and the pressure gauges were connected. However, the flow circuit was still closed at this point and the liquid could not flow through the pad. These steps should be done carefully to prevent air bubbles from being introduced into the pad, cell, and flow circuit.

The distance between the two electrodes was adjusted to 1.7 cm, and this pad thickness was used as the first reading for the run.

The flow circuit was then opened allowing the streaming liquid to fill the cell as well as the entire flow circuit. The liquid was allowed to flow through the pad for 15 min to equilibrate with the pad.

The circuit was closed again and the two electrodes were shorted together in order to reduce polarization interference. The residual current falls substantially to  $0 \mu\text{A}$  and this depolarization process normally takes 1 to 3 hr. A longer time is required for the solutions of higher KCl concentrations (e.g.,  $10^{-2}M$  or above).

### Electrokinetic Measurements

When the residual current of the electrodes holding the pad decayed substantially to  $0 \mu\text{A}$ , the two electrodes were connected to the ammeter, and hydrodynamic pressure was applied by opening the stop cocks in the flow circuit. The direction of the streaming liquid was opposite to that used in the pad formation. After equilibration of the streaming current was achieved a streaming current reading was taken. The streaming liquid temperature increased slightly with elapsed time, and therefore the liquid viscosity was corrected for the temperature change.

The water pressure gauges on both sides of the cell were read to determine the pressure drop across the pad. The flow rate of the liquid across the pad was measured from a point in the flow circuit using a volumetric cylinder.

The streaming liquid was stopped and the streaming current fell to  $0 \mu\text{A}$  in a few seconds. The streaming current does not always decay back to zero, and a small residual current due to electrode polarization was observed, particularly at higher KCl concentrations (e.g.,  $10^{-2}M$  or above). In this case, an "observed" streaming current was corrected for the residual electrode polarization current to give a "true" streaming current.

The pad was then compressed to the second compression level, i.e., 1.4 cm. The thickness of the pad was measured by a micrometer connected to the compression device. Two electrodes were then shorted together for 10 min to eliminate a weak polarization current of the electrodes, which occurred in the measurement of the preceding compression stage. The same measurements were taken for the other four compression stages. At the end of each run, the KCl solution was drained from the cell, the pad was removed, dried at  $105^\circ\text{C}$ , and weighed. Two electrodes were washed with distilled water and then submerged in  $10^{-4}M$  KCl solution with two electrodes shorted together so that the residual current fell down to  $0 \mu\text{A}$ .

The solid concentration of the pad at each compression stage was calculated from the known cross sectional area of the cell, the dry pad weight and the thickness of the pad.

### Computation

The data, consisting of the five compression stages obtained from each run, was arranged in a  $(6 \times 7)$  matrix form and processed by computers at McGill University (IBM 360) and the University of Tokyo (Hitachi's HITAC 8700). The computer program<sup>15</sup> is designed to provide several regression lines from the data on the five compression stages using the least squares method. The exponential form of the streaming current equation proposed by Chang and Robertson<sup>14</sup>, which appears in part I, was employed for computing the zeta potentials.

## RESULTS AND DISCUSSION

### Amount of Adsorbed Polymer Molecules

Figure 1 shows the effect of the initial concentrations of the polymer on the amount of adsorbed polymer on DP. These two adsorption isotherms resemble closely the adsorption isotherms of the polymer on CT.<sup>1</sup> Stepwise regions appear on the isotherms, and the amount of adsorption is higher for the higher molecular weight sample of the polymer. Furthermore, the amount of adsorption is almost independent of the polymer molecular weight when a saturated monolayer formation is completed.

Figure 2 shows the effect of the initial concentrations of the polymer for treatment of the fibers on the value of zeta potential. As the polymer adsorption proceeds, the polarity of the zeta potential reverses from the negative to the positive (Fig. 2).

The shapes of the zeta potential curves as a function of the initial concentration of the polymer closely resemble the adsorption isotherms.<sup>1</sup>

Since free quaternary ammonium groups of the polymer are the source of the positive charge of the monolayer-formed fiber surface, the positive zeta potential at the second plateau illustrates that the positive charges are in excess when the fiber surfaces are saturated with the polymer monolayers.

Figure 3 is a plot of the zeta potential against the amount of polymer adsorbed.

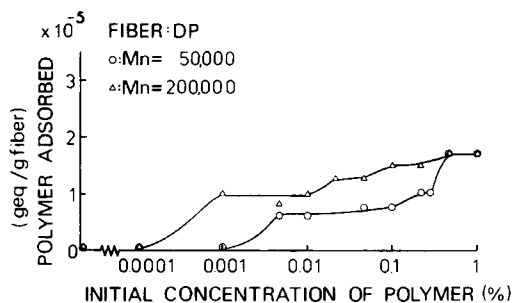


Fig. 1. Adsorption isotherms of the polymer on DP.

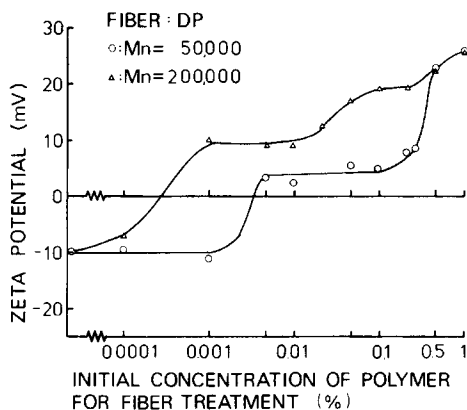


Fig. 2. Zeta potential of monolayer-formed DP, reproduced from Fig. 8 of part I. Medium  $10^{-4}M$  KCl aqueous solutions.

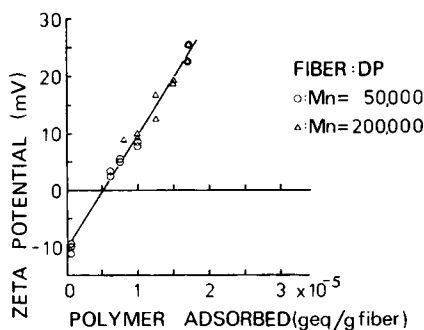


Fig. 3. Effect of the amount of polymer adsorbed on the value of zeta potential for monolayer-formed DP.

The zeta potential values are almost independent of the molecular weight when the equal amounts of the two molecular weight samples are adsorbed (Fig. 3).

Consider the isoelectric points (IEP) of the monolayer-formed fibers: as the polymer adsorption proceeds, the isoelectric points shift to an alkaline region (Fig. 5). This shift is due to the amphoteric surface characteristics.

### Polymer Molecular Weight

The effect of the polymer molecular weights on the zeta potential values was compared between the two molecular weight samples, i.e.,  $M_n$  200,000 and 50,000. The zeta potential curves, as a function of the initial concentration of the polymer, are stepwise (Fig. 2). The values of the zeta potential are higher for the higher molecular weight sample at a given concentration less than that required for saturated monolayer formation. In contrast, however, when the fibers were treated with the polymer solutions having concentrations in excess of those required for the saturated adsorption, no significant difference between the two molecular weight samples of the polymer was observed in the values of the zeta potential. The molecular weight dependence of zeta potential is consistent with the idea that the number of extended polymer segments on the fiber surface is higher for the fibers treated with the higher molecular weight sample of the polymer; at the point of saturation, nearly all the segments lie almost flat on the fiber surface (Fig. 6).

### Ionic Strength

The effect of ionic strength of the streaming solutions on the value of zeta potential is shown in Figure 4. Increasing ionic strength in the case of 1:1 type inorganic salt (KCl) reduces the absolute values of zeta potential (Fig. 4). The negative zeta potentials of the bare fibers (i.e., without adsorbed polymer layers) and the positive zeta potentials of the fibers with the saturated monolayers decrease with increasing ionic strength. However, reversal of the polarity of the zeta potential was not observed even at higher concentrations of KCl (e.g.,  $10^{-2}M$ ).

Possible effects of an increasing ionic strength of the streaming solutions on the values of zeta potential of the fibers may be (1) shielding of the charges of ionic groups on the surface, (2) change in distributions of the counterions and

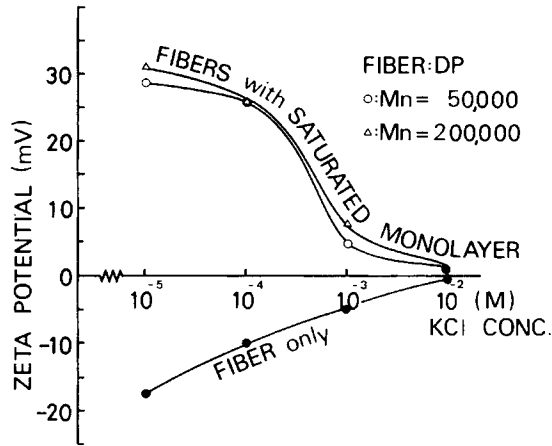


Fig. 4. Effect of ionic strength on the value of zeta potential. Fibers were treated with 1% polymer solutions, whereby saturated monolayer formation is assumed.

the coions in the electric double layer, and (3) decrease in the thickness of the electric double layer adjacent to the surface.

It is normally accepted in colloidal systems that the charge reversal phenomena occur at higher concentrations of inorganic electrolyte when the polarization energy of counterions for the interaction with the fixed charged species is sufficiently high.<sup>18</sup> In view of this, the polarization energy of counterions in KCl (i.e., K<sup>+</sup> or Cl<sup>-</sup>) is not high enough to reverse the polarity of the charge of the fibers with or without saturated monolayers even at higher concentrations of KCl.

**pH of Streaming Solutions**

The zeta potentials of the fibers, with or without adsorbed polymer layers at different levels of adsorption, were measured as a function of the pH of the streaming solution (Fig. 5). The pH of the streaming solutions were controlled by the addition of either HCl or NaOH to the KCl solutions. The fiber surface covered with the saturated monolayer (as with the case of the treatment with 1% polymer solution) develops a positive zeta potential at an intermediate pH (Fig. 5).

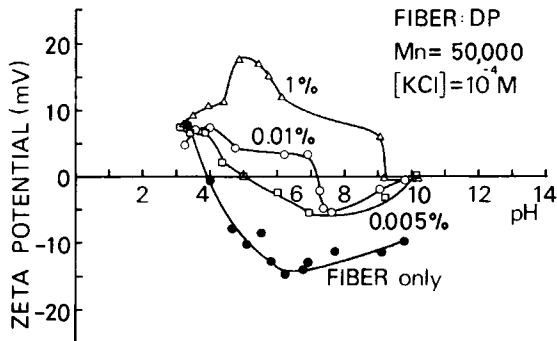


Fig. 5. Effect of pH of streaming solutions on the value of zeta potential. % shows initial concentrations of the polymer for the fiber treatment. pH was controlled by adding either HCl or NaOH.



However, the zeta potential was on the decreasing tendency and the polarity of the zeta potential was reversed to the negative side at higher alkalinity (above pH 9.2). At the intermediate polymer concentrations, which are less than required for the saturated monolayer formation, i.e., 0.01% and 0.005%, the zeta potentials decreased with increasing pH and the polarity was reversed from the positive side to the negative side (Fig. 5). The isoelectric points (IEP) were shifted to the higher pH values by increasing the initial concentrations of the polymer for the treatment of the fibers, i.e., the amount of adsorbed polymer. The IEP for the fiber samples were 4.0, 5.0, 7.2, and 9.2 corresponding to the polymer concentrations for the treatment of the fibers of 0%, 0.005%, 0.01%, and 1%, respectively.

The main origins of the surface charge of the polymer-treated fibers may be (i) the ionized carboxyl groups of the fibers, and (ii) the free quaternary ammonium groups of the polymer. The degree to which these potentially ionizable groups are ionized depends upon the pH of the surrounding electrolyte solutions (i.e., KCl). Consequently, both the free carboxyl and the quaternary ammonium

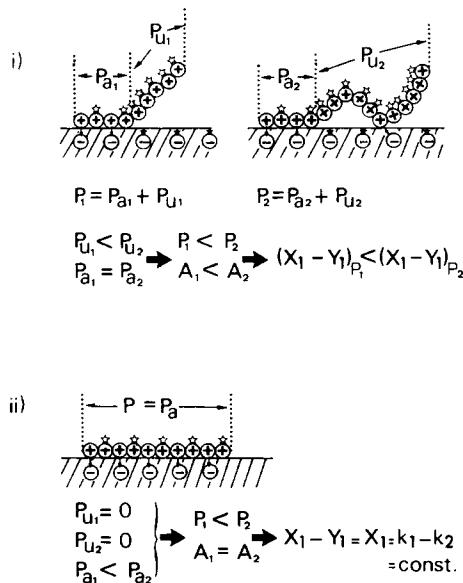


Fig. 6. Schematic representation of molecular weight dependence of zeta potential. (i) Before saturated adsorption ( $0 < \theta < 1$ ). The amount of adsorption is molecular weight dependent, i.e.,  $A_1$  is not equal to  $A_2$  when compared on the equal initial concentrations. (ii) At saturated adsorption ( $\theta = 1$ ). The amount of adsorption is independent of the molecular weight, i.e.,  $A_1$  is equal to  $A_2$ , when compared on the equal initial concentrations.  $P_1$  is the degree of polymerization of the lower molecular weight sample ( $M_n$  50,000);  $P_2$  the degree of polymerization of the higher molecular weight sample ( $M_n$  200,000);  $A_1$  the amount of polymer adsorbed for  $P = P_1$ ;  $A_2$  the amount of polymer adsorbed for  $P = P_2$ ;  $P_a$  the number of adsorbed segments per one adsorbed chain;  $P_u$  the number of unadsorbed polymer segments per one adsorbed chain. Small circles with plus ( $\oplus$ ) or minus ( $\ominus$ ) sign inside represent quaternary ammonium and carboxyl groups, respectively. The circles with a star denote the groups in which the charges are not neutralized. Those with arrows denote the groups in which the charges are neutralized.  $X_1$  is the number of unneutralized polymer segments per unit area of fiber surface;  $Y_1$  the number of unneutralized carboxyl groups per unit area of fiber surface;  $X_1 - Y_1$  is the source of effective surface charge due to ionized groups on the surface;  $k_1$  is the number of adsorbed segments per unit area of fiber surface at saturated monolayer formation;  $k_2$  the number of carboxyl groups on unit fiber surface area.

groups are present on the fiber surfaces that are partially covered with the polymer ( $0 < \theta < 1$ ;  $\theta$ -surface coverage fraction).

Since the quaternary ammonium groups are normally almost fully ionized over the entire pH region it seems reasonable to assume that the quaternary ammonium groups of the polymer are ionized. Therefore, an increase in the negative value of the zeta potential with an increase in the pH of the streaming solution is probably due to ionization of the unneutralized carboxyl groups on the fibers.

The decrease in the positive zeta potential for the fiber treated with 1% polymer solutions when the pH was varied from 5 to 3 was partially due to a reduction in the double layer thickness with an increase in the ionic strength. This was accompanied by shielding of the charge of the fixed positive sites by the counterions.

The characteristic electrokinetic behavior of the fibers with a polymer monolayer (i.e., shifting of IEP with polymer adsorption) resembles that of amphoteric colloids. This is due to the presence of both the negatively and the positively charged groups on the polymer-treated fiber surface. As the pH was lowered to an acidic region, the fixed anionic sites on the fibers with or without the adsorbed layers become nonionic to some extent by conversion of  $\text{COO}^-$  to  $\text{COOH}$  form. At the isoelectric points, the number of fixed positive sites (the quaternary ammonium groups) is close to the number of fixed negative sites (the ionized carboxyl groups).

### Origin of Surface Charge and Electrokinetic Potential

It is generally accepted that the polarity and the magnitude of the electrokinetic potential of a solid determined by an electrokinetic measurement depend upon the chemical nature of the surface of a solid and the ionic composition of surrounding electrolytes in equilibrium with a solid.<sup>20</sup> In this connection, wood pulp fibers in aqueous electrolyte solutions are negatively charged. This is mainly caused by the ionizable groups present on cellulose fibers, residual lignin, and carbohydrate,<sup>21</sup> with minor contributions from both dissociation of water molecules and adsorption of ions from water.<sup>22,23</sup>

In the case of cellulose fibers with adsorbed monolayers of the cationic polyelectrolyte (poly-DMDAAC), the ionized groups on the surface are the carboxyl groups of the fibers and the quaternary ammonium groups of the polymer. Furthermore, the charge due to adsorption of inorganic ions ( $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{H}^+$ , and  $\text{OH}^-$ ) from aqueous electrolyte (KCl) solutions to the bare fibers or the monolayer-formed fibers may also contribute to the overall surface charge.

### Amphoteric Nature of Monolayer-Formed Fiber Surfaces

Cellulose fibers with monolayers of cationic polyelectrolyte (poly-DMDAAC) on the surface may be classified as solid amphotelytes: both acidic (carboxyl) and basic (quaternary ammonium) groups are present on the surface. The amphoteric nature of the monolayer-formed fibers may be characterized by the model shown in Figure 7. The degree to which these functional groups are ionized determines their contribution to the overall surface charge of the monolayer-formed fibers.

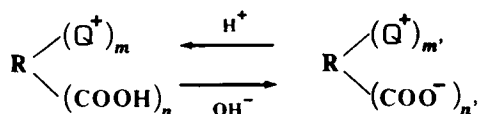


Fig. 7. Amphoteric nature of monolayer-formed fiber surface.  $\text{Q}^+$  denotes quaternary ammonium group of the polymer in ionized state.  $\text{COOH}$  and  $\text{COO}^-$  denote unionized and ionized carboxyl groups, respectively.

In amphoteric solid systems, ionizable groups of one sign usually predominate at extremely low pH and a solid carries a positive charge. However, with an increase in pH there appears an isoelectric point, and then reversal of the polarity of the charge occurs. Hence, the surface of the monolayer-formed fibers carries a positive charge at comparatively lower pH region. With an increase in pH, there appears an isoelectric point. Then the polarity of the charge of the monolayer-formed fibers is reversed since the effect of the ionized carboxyl groups predominates that of the quaternary ammonium groups.

### Electric Double Layer of Monolayer-Formed Fibers

The zeta potentials were measured by the streaming current method. The streaming current observed, when the streaming electrolyte solution is forced to flow past the surface of the monolayer-formed fibers, originates from the electric double layer existing at the monolayer-formed fibers/electrolyte solution interface.

Although there is still a lot of uncertainty as to the structure of the electric double layer, it has been accepted that a mechanism of formation of the electric double layer is linked with dissociation of the surface ionogenic groups under the effect of a polar dispersion medium.<sup>20</sup> As for the structure of the electric double layer, it is predicted that in the presence of an adsorbed neutral polymer, the double layer of certain cell substances expands due to the excluded volume effect.<sup>24</sup> Adsorption of the positively charged polymer to the fiber surface bearing the fixed anionic charge causes the double layer to expand somewhat and alters the charge characteristics of the fiber surface. Expansion of the double layer caused by the adsorbed monolayer affects (i) the thickness of adsorbed layers, (ii) the location of shear plane, and (iii) the velocity profile of the streaming flow. Furthermore, a potential-determining layer due to the positive charge of the adsorbed monolayer will probably be formed adjacent to the fixed ionic layer of the double layer. As for the charge characteristics of the double layer, introduction of the fixed cationic groups by the adsorbed monolayer may lead to a change in the surface charge. The change in the surface charge will in turn alter distribution of counterions and coions in the double layer. A possible potential variation in the electric double layer on the monolayer-formed DP fibers is illustrated in Figure 8.

### Stepwise Zeta Potential Curves and Modes of Adsorption

Stepwise zeta potential curves (Fig. 2) are consistent with the idea that two kinds of forces of interaction are involved in the monolayer formation process. Similarity of the shape of zeta potential curves to the adsorption isotherms for DP (Fig. 1) is interpreted with reference to polymer chain configurations and

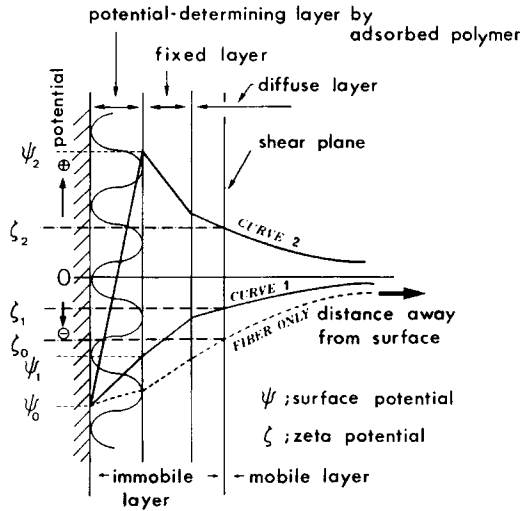


Fig. 8. An electric double layer model for the monolayer-formed DP fiber/KCl aq. soln. interface. This model is set up from the ordinary Stern double layer model, where potential varies at the fixed layer and the diffuse layer. This proposed model applies only to the case where a charge is not reversed at higher concentrations of electrolytes (e.g., KCl). Since the thickness of the adsorbed monolayer is ca.  $2.86 \text{ \AA}$  (see Fig. 9 in part I), a potential-determining layer by adsorbed polymer layer may be assumed to exist inside the fixed layer. Broken curve refers to the potential variation in the absence of adsorbed polymer layer. Curve 1 symbolizes the case in which zeta potential is not reversed by adsorbed polymer layer (e.g., 0.005% treatment). Curve 2 depicts the case in which zeta potential is reversed by adsorbed polymer layer (e.g., 0.01% and 1% treatments). Streaming current is produced by relative motion between solid (fiber) and liquid interface. The potential at the shear plane is the zeta potential.

polymer charge neutralization at the fiber surface. The zeta potential curves suggest that, up to the first plateau, the adsorption proceeds mainly by ionic interaction between the quaternary ammonium groups of the polymer and the carboxyl groups of the fiber surface.

Beyond this first plateau, up to the point of saturation, further adsorption proceeds mainly by van der Waals force between the polymer molecules and the fiber surfaces until a saturated monolayer formation is completed. The first plateau is located on the positive side of the zeta potential curves suggesting that the interaction between the positive groups of the polymer and the negative groups of the fibers does not proceed stoichiometrically.

### Polymer Chain Configurations and Zeta Potential

Both  $X_1$  and  $Y_1$  contribute to the effective surface charge of the monolayer-formed DP fibers (Fig. 6). Before the fiber surface is fully covered with the polymer segments, the positive charge of the fiber surface increases as the amount of unneutralized polymer segments ( $X_1$ ) increases.

When the zeta potential values are compared on the same initial concentration of the polymer, the fibers treated with the higher molecular weight polymer exhibit a higher positive zeta potential. This suggests that the number of loops or tails present on the fiber surface is higher for the higher molecular weight polymer.

In polymer chain configurations, the polymer chains adsorbed as loops or tails all contribute to an increase in the positive charge. Those adsorbed as trains contribute partly to neutralize the negative charge of the carboxyl groups on the fiber surface and partly to increase the positive charge on the fiber surface.

### Monolayer Formation as a Means to Surface Charge Control of Cellulose Fibers

Under the condition of  $k_1 > k_2$ , progressive formation of the monolayer of the cationic polyelectrolyte on the negatively charged cellulose fibers permits reversal of the charge of the fibers to the positive side. Whether or not the  $k_1 > k_2$  relationship holds depends upon the relative magnitudes of the specific surface area of the fibers, the carboxyl contents of the fibers, the molecular area of one adsorbed polymer segment, and the cationic charge of the positively charged groups of the polymer.

As for irreversibility of adsorbed polymer segments, polymer chains are normally adsorbed to a solid substrate with their multiple bondings, therefore, polymer segments once adsorbed are not readily desorbable from a solid surface.<sup>25</sup> This interpretation appears to hold particularly for cellulose fiber/cationic polyelectrolyte systems. An irreversibly adsorbed monolayer by tenacious electrostatic bonding may be formed on the DP surface by poly-DMDAAC.

In the present study, the fibers with the saturated monolayer ( $\theta = 1$ ) exhibit a maximum positive charge which is a function of the excess positive charge at saturation.

A polymer with stronger basic groups provides a higher positive charge at the point of saturated monolayer formation. In the case of polymers having amines as ionic groups, quaternary ammonium groups are more effective to convert the negative charge of the fibers to the positive side.

A multilayer of the polymer (poly-DMDAAC) is formed on the CMC fiber surface under the condition of  $k_1 < k_2$ . However, contrary to the monolayer formation on DP, the negative charge of CMC is not reversed to the positive side by increasing the amount of adsorbed polymer.

Although the problems regarding the selection of the condition of the  $k_1 > k_2$  still remain to be solved, cationic polyelectrolyte/cellulose systems under this condition provide a means of controlling the surface charge of cellulose fibers.

### CONCLUDING REMARKS

Fibers, the polymer, and surrounding medium (KCl solution) affect the electrokinetic behavior of the monolayer-formed DP fibers. The zeta potential variation is proportional to an increase in the amount of polymer adsorbed.

The results thus far suggest that formation of the monolayer of cationic polyelectrolytes on the negatively charged cellulose fibers under the condition of  $k_1 > k_2$  appears to provide a means to arbitrarily control the charge of the fibers within a range of  $0 \leq \theta \leq 1$  until a saturated monolayer is completed.

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## References

1. F. Onabe, *J. Appl. Polymer Sci.*, **22**, 3495 (1978).
2. H. D. Cook and I. T. Smith, *Appl. Polym. Symp.*, **No. 18**, 663 (1971).
3. M. F. Hoover, *J. Macromol. Sci., Chem. Ed. A*, **4**, 1327 (1970).
4. *Calgon Chemical Product Bulletin*, Calgon Co., Pittsburgh, Penn., 1966, 7-22.
5. *Calgon Chemical Product Bulletin*, Calgon Co., 1967, 12-24b.
6. M. F. Hoover and H. E. Carr, *Tappi*, **51**(12), 552 (1968).
7. J. P. Kleber, *Water Wastes Eng.*, **6**(6), 42 (1969).
8. R. Senju and I. Sakata, *J. Jpn. Tappi*, **7**, 166 (1953).
9. L. S. Sandell and P. Luner, *ESPRI Rep.*, **58**, 131 (1973), Empire State Paper Res. Inst., Syracuse.
10. D. A. I. Goring and S. G. Mason, *Can. J. Res.*, **28B**, 323 (1950).
11. G. J. Biefer and S. G. Mason, *J. Colloid Sci.*, **9**, 20 (1954).
12. M. Y. Chang, Ph.D. Thesis, McGill University, 1966.
13. M. Y. Chang and A. A. Robertson, *Pulp Paper Mag. Can.*, **68**, T438 (1967).
14. M. Y. Chang and A. A. Robertson, *Can. J. Chem. Eng.*, **45**(4), 66 (1967).
15. F. Onabe, unpublished.
16. J. A. Ciriacks and D. G. Williams, *J. Colloid Interface Sci.*, **26**, 446 (1968).
17. A. A. Robertson and S. G. Mason, *Pulp Paper Mag. Can.*, **50**(13), 103 (1949).
18. J. T. Davies and E. K. Rideal, *Interfacial Phenomena*, 2nd ed., Academic, New York, 1963, p. 84.
19. F. Onabe, unpublished data.
20. S. S. Dukhin and B. V. Derjaguin, *Surface and Colloid Science*, Vol. 7, E. Matijević, Ed., Wiley-Interscience, New York, 1974, p. 20.
21. J. W. Swanson, *Consolidation of the Paper Web*, Vol. 2, F. Bolam, Ed., B.P. & B.M.A., London, 1966, p. 741.
22. S. G. Mason, *Tappi*, **33**(8), 413 (1950).
23. S. M. Neale and R. H. Peters, *Trans. Faraday Soc.*, **41**, 478 (1946).
24. D. E. Brooks, *J. Colloid Interfac. Sci.*, **43**, 687 (1973).
25. J. J. Kipling, *Adsorption from Solutions of Non-electrolytes*, Academic, New York, 1965, p. 134.

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