Interfacial Properties of Polyelectrolyte–Cellulose Systems. III. Theoretical Model for the Electrokinetic Behavior of Cellulose Fibers with Adsorbed Monolayers of Cationic Polyelectrolyte

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Synopsis

A theoretical model is proposed to account for the experimental results in part II. The basic assumption is that the total surface charge of the monolayer-formed DP fibers stems from (i) fixed ionized groups on the surface and (ii) adsorbed ions on the surface from surrounding solutions. The fixed ionized groups are the carboxyl groups of the fibers and quaternary ammonium groups of the polymer. The proposed model correlates the amount of adsorbed polymer with the zeta potential of the monolayer-formed DP fibers. Calculations made on the proposed model using the experimental data in part II suggest that a comparison of the charge calculated from zeta potential with that from the amount of adsorbed polymer yields ca. 0.04% of the fixed ionizable groups as effective charged sites, i.e., electrokinetically detectable. This finding is due to the binding of counterions to the fixed ionized sites on the surface. Zeta potentials of the DP with adsorbed monolayers largely stem from the fixed ionized groups with only a minor contribution from the adsorbed ions. The zeta potentials are nearly proportional to the difference between the number of cationic and anionic groups on the surface.

INTRODUCTION

It has been demonstrated that a positively charged saturated monolayer of the polymer poly-DMDAAC is formed on DP fibers.[1] Furthermore, various factors affecting the electrokinetic properties of the monolayer-formed DP fibers have been investigated. The applicability of the monolayer formation of the cationic polymer on the negatively charged cellulose fibers (as a means to surface charge control of the cellulose fibers) was discussed.[2] Increasing amounts of adsorbed polymer cause a decrease in the negative zeta potential of the fibers, and the negative fiber surface charge was ultimately reversed. It was also suggested that the zeta potential varies in proportion to the increase in the amount of adsorbed polymer.

This study develops a theoretical model capable of correlating the amount of adsorbed polymer with the zeta potential. In order to evaluate the data in part II[2] quantitatively, some calculations will be made on the proposed model.

DATA FOR CALCULATIONS

The experimental results of the electrokinetic measurements on the monolayer-formed DP fibers in part II[2] were used for the calculations on the proposed model. The data on CT (cotton linter) fibers that appeared in part I were used for the sake of comparison with DP.

DEVELOPMENT OF THE MODEL

First, an expression for the total surface charge of the monolayer-formed fibers was derived. Then, an expression correlating the total surface charge with the zeta potential at a given ionic strength was derived using the Debye–Hückel approximation[3] for a flat surface with relatively lower potential. A combination of these two expressions provides a model correlating the amount of adsorbed polymer with the zeta potential of the monolayer-formed DP fibers.

Origin of Surface Charge

Most solid materials exposed to water or aqueous electrolyte solutions develop electrically charged surfaces, either by ionization of surface molecules or by adsorption of ions from either water or electrolyte solutions. Therefore, it seems reasonable to assume that the total surface charge of the monolayer-formed fibers stems from (i) fixed ionized groups on the surface, and (ii) adsorption of ions on the surface from surrounding aqueous electrolyte solutions, i.e., streaming current liquid. Thus, it follows that

$$Q_t = Q_i + Q_s \tag{1}$$

where Q_t = total surface charge per unit area (i.e., surface charge density); Q_i = average surface charge density due to both ionized groups on the fibers and adsorbed polymer monolayers; and Q_s = average surface charge density due to adsorption of ions on the fibers or monolayer-formed fibers ($0 < \theta < 1$, where θ is the surface coverage fraction). All the Q values represent surface charge of unit surface area, i.e., surface charge density.

Since both anionic groups on the fibers and cationic groups on the polymer are ionized to a certain extent, we have

$$Q_i = Q_{if} + Q_{ip} \tag{2}$$

where $Q_{if} = Q_i$ due to ionized groups on the fiber surface (i.e., carboxyl groups of cellulose); and $Q_{ip} = Q_i$ due to ionized groups on the monolayer-formed fiber surface (i.e., quaternary ammonium groups of the polymer).

Since small inorganic ions are adsorbed on these fibers and on the mono-layer-formed fibers, we have

$$Q_s = Q_{sf} + Q_{sp} \tag{3}$$

where $Q_{sf} = Q_s$ due to adsorption of ions on the fiber surface and $Q_{sp} = Q_s$ due to adsorption of ions on the monolayer-formed surface.

When the fiber surface is not fully covered with the polymer monolayer, i.e., $0 < \theta < 1$, we have the following expression:

$$Q_s = (1 - \theta)q_{sf} + \theta q_{sp} \tag{4}$$

where q_{sf} = surface charge due to adsorption of ions on a unit surface area of the fibers (i.e., surface charge density) and q_{sp} = surface charge due to adsorption of ions on a unit surface area of the monolayer-formed surface (i.e., surface charge density).

On the other hand, when the fiber surface is fully covered with the polymer monolayer, i.e., $\theta = 1$ (saturated monolayer), we have

$$Q_{sf} = 0 \tag{5}$$

Therefore, Q_s stems only from the monolayer-formed fiber surface, namely,

$$Q_s = Q_{sp} \tag{6}$$

Consequently, overall surface charge per unit surface area of the monolayer-formed fibers may be expressed as

$$\begin{aligned}
Q_t &= Q_i + Q_s \\
&= Q_{if} + Q_{ip} + Q_{sf} + Q_{sp} \\
&= (Q_{if} + Q_{sf}) + (Q_{ip} + Q_{sp})
\end{aligned} \tag{7}$$

Let us now consider a few special cases of eq. (7).
For $\theta = 0$:

$$Q_t = Q_{if} + Q_{sf} = q_{if} + q_{sf} \tag{8}$$

For $0 < \theta < 1$:

$$Q_t = (1 - \theta)(q_{if} + q_{sf}) + \theta(q_{ip} + q_{sp}) \tag{9}$$

For $\theta = 1$:

$$Q_t = Q_{ip} + Q_{sp} = q_{ip} + q_{sp} \tag{10}$$

where q_{if} = surface charge due to ionized groups on a unit surface area of the fibers and q_{ip} = surface charge due to ionized groups on a unit area of the monolayer-formed surface.

Relationship Between Zeta Potential and Surface Charge Density

A correlation of surface charge density with surface potential (ψ_0) is given by the Poisson–Boltzmann equation for a plane interface.[4]   However, since it is normally impossible to obtain surface potential experimentally, the surface potential is usually approximated by the zeta potential ζ, i.e., $\psi_0 \approx \zeta$. Then, we have

$$Q_t = \left(\frac{2DkTC}{\pi}\right)^{1/2} \sinh \frac{Ze\zeta}{2kT} \tag{11}$$

where Z = valency of ions (in the case of a symmetrical binary electrolyte such as KCl, the valency of cation Z^+ is equal to that of anion Z^-, i.e., $Z^+ = Z^- = Z$); D = dielectric constant; C = concentration of ions; ζ = zeta potential; and k = Boltzmann constant.

When the zeta potential is relatively small compared with kT, i.e.,

$$Ze\zeta/kT \ll 1 \tag{12}$$

and the ionic strength is relatively lower, the Debye–Hückel approximation[3] holds. Equation (11) is then reduced to eq. (13):

$$Q_t = \frac{D\kappa}{4\pi} \zeta \tag{13}$$

where κ = Debye–Hückel function associated with the size of the ionic atmosphere around each ion, which is defined by

$$\kappa = \left(\frac{8\pi e^2 NI}{1000DkT}\right)^{1/2} \tag{14}$$

where I = ionic strength. The square of κ is expressed as

$$\kappa^2 = \frac{8\pi e^2 NI}{1000 D k T} = AI \tag{15}$$

The quantity A for aqueous medium ($D = 80$) at 25°C is given by substituting the following quantities into eq. (16): $e = 4.8 \times 10^{-10}$ esu; $N = 6 \times 10^{23}$; $k = 1.38 \times 10^{-16}$ erg/K; $T = 273 + 25 = 298$ (cgs units),

$$A = \frac{8\pi e^2 N}{1000 D k T} = (3.25 \times 10^7)^2 \text{ cm} \tag{16}$$

(For details of calculations, see Appendix I.)   Therefore, the Debye–Hückel function (κ) is expressed as a function of ionic strength (I) as shown in eq. (17):

$$\kappa = A^{1/2} I^{1/2} = (3.25 \times 10^7) \, I^{1/2} \text{ cm}^{-1} \tag{17}$$

Using eq. (13), we obtain a factor correlating surface charge density Q_t with zeta potential ζ:

$$\frac{D\kappa}{4\pi} = (2.069 \times 10^8) \, I^{1/2} \text{ cm}^{-1} \tag{18}$$

(see Appendix I).   Consequently, the formula correlating Q_t with the zeta potential is written as

$$Q_t = (2.069 \times 10^8) \, I^{1/2} \zeta \text{ mV/cm} \tag{19}$$

Let us now consider a special case for $\zeta = 1$ mV; then we obtain

$$Q_t = 690(I)^{1/2} \text{ esu/cm}^2$$
$$= (2.30 \times 10^{-7}) \, I^{1/2} \text{ coulomb/cm}^2 \tag{20}$$

(see units in Appendix II).   Equation (20) correlates surface charge density with zeta potential for arbitrary ionic strength I.   The result of the calculations for Q_t over the experimental range of this study (i.e., $C = 10^{-5}$ through 10^{-2} mole/l.) is shown in Table I.

TABLE I
Surface Charge Density at Various Ionic Strengths of KCl

KCl concn, mole/l.	Square root of ionic Strength $(I^{1/2})$[c]	Surface charge density Q_t[a] corresponding to $\zeta = 1$ mV		Debye length $1/\kappa$,[b] Å
		esu/cm^2	coulomb/cm^2	
10^{-5}	3.16×10^{-3}	2.18	0.727×10^{-9}	973
10^{-4}	1×10^{-2}	6.90	2.30×10^{-9}	308
10^{-3}	3.16×10^{-2}	21.8	7.27×10^{-9}	97.3
10^{-2}	1×10^{-1}	69.0	23.0×10^{-9}	30.8

[a] Q_t is calculated using eq. (20).

[b] Debye length is defined as the reciprocal of the Debye Hückel function κ, which can be calculated using eq. (17).   Debye length is a measure of the dimension of the ionic atmosphere.

[c] Ionic strength I is related to electrolyte concentration as $I = \frac{1}{2} \Sigma m_i z_i^2$, where m_i and z_i are molar concentration of electrolyte and valence of ions, respectively.   Therefore, $I = \frac{1}{2}(M \times 1^2 + M \times 1^2) = M$ for a 1:1 type of electrolyte such as KCl.

Theoretical Model Correlating Amount of Adsorbed Polymer with Zeta Potential

Let X_1 and X_2 be the numbers of adsorbed polymer segments. Then the amount of polymer adsorbed, Ad, on a gram-equivalent basis per unit weight of the fiber, is expressed as

$$Ad = \frac{X_1 + X_2}{N} \sigma \qquad (21)$$

where X_1 = number of polymer segments adsorbed without charge neutralization per unit fiber surface area; X_2 = number of polymer segments adsorbed with charge neutralization per unit fiber surface area; σ = specific surface area of the fibers, in cm^2/g; and N = Avogadro's number (6×10^{23}).

If we denote the total number of carboxyl groups on a unit fiber surface area by k_2, then we obtain

$$k_2 = Y_1 + Y_2 \qquad (22)$$

where Y_1 = number of carboxyl groups per unit fiber surface area, of which the charge is not neutralized; and Y_2 = number of carboxyl groups per unit fiber surface area, of which the charge is neutralized with quaternary ammonium groups of the polymer. From the definitions of X_2 and Y_2 above, it follows that

$$X_2 = Y_2 \qquad (23)$$

Using eqs. (22) and (23), we obtain

$$\begin{aligned} X_1 - Y_1 &= X_1 + X_2 - Y_2 - Y_1 \\ &= X_1 + X_2 - k_2 \end{aligned} \qquad (24)$$

The above elements (X_1, X_2, Y_1, Y_2) for the development of the model are illustrated in Figure 1. Let k_c and k_a be the fraction of effective charge of the fixed cationic and anionic site, respectively, then we obtain the following expression for Q_i using eq. (2):

$$Q_i = Q_{ip} + Q_{if} = e^+ X_1 k_c + e^- Y_1 k_a \qquad (25)$$

where e^+ and e^- are the charge of one cationic and anionic site, respectively, i.e., $e^- = -e^+ = -4.8 \times 10^{-10}$ esu (e = electron charge).

Since $k_c = k_a$ ($= k_s$) as will be shown in a later section (Theoretical Calculations), eq. (25) may be reduced to
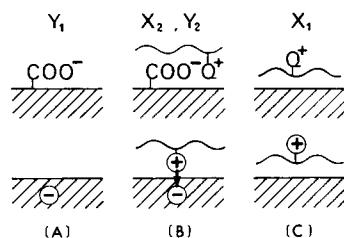

Fig. 1. Elements for the development of the model. For meaning of the elements, refer to eqs. (21) through (23). (A), (C) Fixed ionized groups where the charges are not neutralized; (A) and (C) are the sources of Q_{if} and Q_{ip}, respectively, i.e., they contribute to Q_i. (B) Fixed groups where the charges are neutralized.
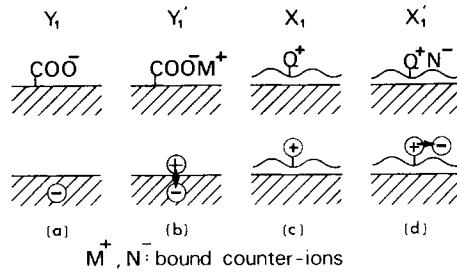
M^+, N^-: bound counter-ions

Fig. 2. Counterion binding to fixed ionized sites. (a), (c) Fixed ionized groups, where the charges are not neutralized. (b) Carboxyl groups bound with counterions. (d) Quaternary ammonium groups bound with counterions. In the case of the monolayer-formed DP fibers in equilibrium with KCl solutions, M^+ is either H^+ or K^+, and N^- is either OH^- or Cl^-.

$$Q_i = e^+(X_1 - Y_1)k_s \qquad (26)$$

where k_s = the fraction of effective charge of the fixed ionic sites and corresponds to the fraction of ionizable groups detected by electrokinetic measurement. Now, by rearranging eq. (21), we obtain

$$X_1 + X_2 = Ad\frac{N}{\sigma} \qquad (27)$$

Substituting eqs. (24) and (27) into eq. (26), we obtain

$$Q_i = e^+\left(Ad\frac{N}{\sigma} - k_2\right)k_s \qquad (28)$$

The surface coverage fraction θ may be approximated by eq. (29):

$$\theta \approx \frac{X_1 + X_2}{k_1} = Ad\frac{N}{\sigma}\frac{1}{k_1} \qquad (29)$$

where k_1 = number of adsorbed polymer segments per unit surface area of the fibers when a saturated monolayer is formed.

Using eqs. (4) and (13), we obtain eqs. (30) and (31):

$$Q_{sf} = (1 - \theta)q_{sf} = \frac{D\kappa}{4\pi}(1 - \theta)\zeta_{sf} \qquad (30)$$

$$Q_{sp} = \theta q_{sp} = \frac{D\kappa}{4\pi}\theta\zeta_{sp} \qquad (31)$$

where ζ_{sf} = zeta potential due to adsorption of ions from electrolyte solutions on the fiber surface and ζ_{sp} = zeta potential due to adsorption of ions from electrolyte solutions on the surface covered with saturated monolayers. Substituting eqs. (30) and (31) into eq. (3), we obtain

$$Q_s = Q_{sf} + Q_{sp}$$

$$= \frac{D\kappa}{4\pi}[(1 - \theta)\zeta_{sf} + \theta\zeta_{sp}]$$

$$= \frac{D\kappa}{4\pi}[(\zeta_{sp} - \zeta_{sf})\theta + \zeta_{sf}] \qquad (32)$$

Therefore, an expression for the total surface charge density Q_t may be written as eq. (33) using eqs. (28), (29) and (32):

$$Q_t = Q_i + Q_s$$

$$= 4.8 \times 10^{-10} \left(Ad\frac{N}{\sigma} - k_2 \right) k_s + 690I^{1/2} \left[(\zeta_{sp} - \zeta_{sf}) Ad\frac{N}{\sigma}\frac{1}{k_1} + \zeta_{sf} \right] \quad (33)$$

in units of esu/cm^2.

Fixed Anionic Sites and Effective Negative Surface Charge

Fixed anionic sites on cellulose fibers stem mainly from carboxyl groups. The total number of carboxyl groups on unit fiber surface area is given by eq. (22):

$$k_2 = Y_1 + Y_2 \quad (22)$$

The number of excess anionic sites calculated from zeta potential data, n_a, is given by

$$n_a = Q_t/e \qquad \text{sites/cm}^2 \quad (34)$$

where Q_t and e have the same polarity of charge and e represents an electron charge, which is equal to the space charge of one fully ionized anionic site.

If we define "effective surface charge" as the charge calculated from zeta potential (i.e., electrokinetically detectable charge Q_t), the ratio of the effective negative surface charge to the charge calculated from the total number of carboxyl groups is given by

$$\frac{Q_t}{k_2 e} = \frac{en_a}{k_2 e} = \frac{n_a}{k_2} = \left(\frac{D\kappa}{4\pi} \zeta \frac{1}{e} \right) / k_2 = \frac{D\kappa\zeta}{4\pi e k_2} \quad (35)$$

The average charge of one fixed anionic site is given by

$$Q_t/k_2 \quad (36)$$

Fixed Cationic Sites and Effective Positive Surface Charge

Fixed cationic sites on monolayer-formed fibers stem from quaternary ammonium groups of the polymer, and the total number of adsorbed polymer segments per unit area of saturated monolayer is given by

$$k_1 = X_1 + X_2 \quad (37)$$

Substituting eq. (37) into eq. (24), we obtain

$$X_1 - Y_1 = k_1 - k_2 \quad (38)$$

The number of excess cationic sites calculated from zeta potential data, n_c, is given by

$$n_c = Q_t/e \text{ sites/cm}^2 \quad (39)$$

The ratio of the effective positive surface charge to the charge calculated from the number of excess positive sites is given by

$$\frac{Q_t}{(k_1 - k_2)e} = \frac{en_c}{(k_1 - k_2)e} = \frac{n_c}{k_1 - k_2} = \left(\frac{D\kappa}{4\pi} \zeta \frac{1}{e} \right) / (k_1 - k_2) = \frac{D\kappa\zeta}{4\pi e(k_1 - k_2)} \quad (40)$$

The average charge of one fixed cationic site is given by

$$Q_t/(k_1 - k_2) \quad (41)$$

Expression of Zeta Potential for Particular Cases

In eq. (33), the total surface charge density is expressed as the summation of the surface charge due to the fixed ionized sites and that due to adsorption of ions on the surface. Let us now consider two special cases for the expression of zeta potential.

By rearranging eq. (13), we obtain eq. (42) using eq. (1):

$$\zeta = \frac{4\pi}{D\kappa} Q_t = \frac{4\pi}{D\kappa} (Q_i + Q_s) \tag{42}$$

(i) $\theta = 0$, i.e., without adsorbed polymer layer:
Using eqs. (28) and (29), we obtain

$$Q_i = Q_{if} = -ek_2k_s \tag{43}$$

Using eq. (30), we obtain

$$Q_s = Q_{sf} = \frac{D\kappa}{4\pi} \zeta_{sf} \tag{44}$$

Substituting eqs. (43) and (44) into eq. (42), we obtain

$$\zeta = \zeta_{if} + \zeta_{sf} = -\frac{4\pi}{D\kappa} ek_2k_s + \zeta_{sf} \tag{45}$$

(ii) $\theta = 1$, i.e., with saturated polymer monolayer:
Using eqs. (26) and (38), we obtain

$$Q_i = Q_{ip} = e(k_1 - k_2)k_s \tag{46}$$

Using eq. (31), we obtain

$$Q_s = Q_{sp} = \frac{D\kappa}{4\pi} \zeta_{sp} \tag{47}$$

Substituting eqs. (46) and (47) into eq. (42), we obtain

$$\zeta = \zeta_{ip} + \zeta_{sp} = \frac{4\pi}{D\kappa} e(k_1 - k_2)k_s + \zeta_{sp} \tag{48}$$

In the above two expressions for zeta potential, i.e., eqs. (45) and (48), the first term corresponds to the zeta potential due to ionized groups and the second term, to the zeta potential due to adsorption of ions to the surface. These expressions will be used in the next section (Theoretical Calculations) to calculate zeta potentials due to the fixed ionized sites and those due to adsorption of ions to the surface.

THEORETICAL CALCULATIONS

The following calculations give support to the assumptions made in the development of the theoretical model and also provide a quantitative evaluation of the experimental data in part II. The discrepancy between the surface charge calculated from the zeta potential and that calculated from the amount of adsorbed polymer will be demonstrated.

Effective Ionic Sites

Let us consider two special cases for calculating the surface charge from zeta potential data.

(i) Effective charge of the anionic sites in the absence of adsorbed polymer, i.e., $\theta = 0$:

From Table II, we obtain $k_2 = 3.60 \times 10^{14}$ sites/cm^2, $I = 10^{-4}$, $I^{1/2} = 10^{-2}$, and $\zeta = -10.0$ mV. Using eqs. (20) and (34), the number of anionic sites per unit area of the fiber surface is obtained by

$$n_a = \frac{Q_t}{e} = \frac{(690 \times 10^{-2}) \times 10.0}{4.8 \times 10^{-10}} = 14.4 \times 10^{10}$$

Using eq. (34), the ratio of the effective excess anionic sites to the total carboxyl groups is given by

$$k_a = \frac{n_a}{k_2} = \frac{14.4 \times 10^{10}}{3.60 \times 10^{14}} = 4.00 \times 10^{-4}$$

Using eq. (36), the average charge of one fixed anionic site can be obtained by

$$\frac{Q_t}{k_2} = \frac{(690 \times 10^{-2}) \times 10.0}{3.60 \times 10^{14}} = -19.2 \times 10^{-14} \text{ esu}$$

(ii) Effective charge of the cationic sites in the presence of saturated monolayer, i.e., $\theta = 1$:

From Table II, we obtain $k_1 - k_2 = 8.60 \times 10^{14}$ sites/cm^2, $I = 10^{-4}$, $I^{1/2} = 10^{-2}$, and $\zeta = 22.5$ mV. Using eq. (39), the number of cationic sites per unit area of the surface covered with saturated monolayer is obtained by

$$n_c = \frac{Q_t}{e} = \frac{(690 \times 10^{-2}) \times 22.5}{4.8 \times 10^{-10}} = 32.3 \times 10^{10}$$

Again using eq. (39), the ratio of the effective excess cationic sites to the total excess cationic sites is given by

$$k_c = \frac{n_c}{k_1 - k_2} = \frac{32.3 \times 10^{10}}{8.60 \times 10^{14}} = 3.76 \times 10^{-4}$$

Using eq. (41), the average charge of one fixed cationic site can be obtained by

$$\frac{Q_t}{k_1 - k_2} = \frac{(690 \times 10^{-2}) \times 22.5}{8.60 \times 10^{14}} = 18.1 \times 10^{-14}$$

In the case of partial coverage of fiber surface with the monolayer, i.e., $0 < \theta < 1$, we may reproduce eq. (25) as:

$$Q_i = Q_{ip} + Q_{if} = e^+ X_1 k_c + e^- Y_1 k_a \tag{25}$$

There is no significant difference between k_a and k_c. Therefore, $k_a \approx k_c = 4.0 \times 10^{-4}$ ($= k_s$) and eq. (25) may be written as

$$Q_i = e^+ (X_1 - Y_1) k_s \tag{26}$$

The values of k_a and k_c are far smaller than unity, indicating that only some of the charges of the ionized groups are effective surface charges (i.e., electrokinetically detectable).

TABLE II
Zeta Potential Values Due to Adsorbed Ions and Fixed Ionized Sites

| Fiber | No. of adsorbed polymer segments in saturated monolayer (k_1),[a] $\times 10^{14}$/cm² | No. of carboxyl groups (k_2),[a] $\times 10^{14}$/cm² | Excess charged groups ($k_1 - k_2$), $\times 10^{14}$/cm² | Zeta potential in $10^{-4}M$ KCl aq. soln. | | Zeta potential of fibers due to | | Zeta potential of fibers with saturated monolayer due to | |
				Fiber only (ζ_f[a] = ζ_{sf} + ζ_{if}), mV	Fiber with saturated monolayer (M_n 50,000) (ζ_p[a] = ζ_{sp} + ζ_{ip}), mV	Adsorbed ions (ζ_{sf}[b]), mV	Ionized sites (ζ_{if}), mV	Adsorbed ions (ζ_{sp}[c]), mV	Ionized sites (ζ_{ip}), mV
CT	12.2	1.98	k_1 = 10.2	−18.1	+23.7	−13.5	−4.6	≈0	+23.7
DP	12.2	3.60	k_1 = 8.60	−10.0	+22.5	− 0.6	−9.4	≈0	+22.5

[a] $k_1, k_2, \zeta_f,$ and ζ_p are reproduced from Table III in part I.[1]
[b] Refer to eqs. (57) and (58).
[c] Refer to eq. (52).

Zeta Potential Due to Adsorption of Ions from Aqueous Solutions

We write K for the quantity $(4\pi/D\kappa)ek_s$ in eq. (42):

$$\frac{4\pi}{D\kappa}ek_s = K \tag{49}$$

Then, eq. (45) may be written as

$$\zeta = -Kk_2 + \zeta_{sf} = \zeta_{if} + \zeta_{sf} \tag{50}$$

and eq. (48) may be written as

$$\zeta = K(k_1 - k_2) + \zeta_{sp} = \zeta_{ip} + \zeta_{sp} \tag{51}$$

The zeta potential data in Table II show that the fiber surfaces with saturated monolayer are positively charged. In view of the molecular structure of the monomer (see Fig. 1 of part I), the surface with saturated monolayer other than ionic groups may be hydrophobic in nature. Hence, although it may be practically impossible to separate the two contributions (i.e., the ionized groups and absorbed ions), it seems reasonable to assume that the zeta potential due to the monolayer-covered surface (ζ_{sp}) is negligible compared with that due to the ionized positive groups on the surface (ζ_{ip}). That is,

$$\zeta_{sp} \approx 0 \tag{52}$$

The calculations below using the data in Table II for the two cases give the values of ζ_{sf} for DP.

(i)   Case I—Surface with saturated monolayer, i.e., $\theta = 1$:
   Using eq. (51), we obtain eqs. (53) and (54).

$$\text{For CT: } K_{CT}(10.2 \times 10^{14}) = +23.7 \text{ mV}$$

$$\text{For DP: } K_{DP}(8.60 \times 10^{14}) = +22.5 \text{ mV}$$

The two values of K can be obtained by solving the above equations:

$$K_{CT} = 2.32 \times 10^{-14} \tag{53}$$

$$K_{DP} = 2.62 \times 10^{-14} \tag{54}$$

(ii)   Case II—Surface without adsorbed layer, i.e., $\theta = 0$:

   Using eq. (50), we obtain eqs. (55) and (56):

$$\text{For CT: } -K_{CT}(1.98 \times 10^{14}) + \zeta_{sf} = -18.1 \text{ mV} \tag{55}$$

$$\text{For DP: } -K_{DP}(3.60 \times 10^{14}) + \zeta_{sf} = -10.0 \text{ mV} \tag{56}$$

Substituting K_{CT} and K_{DP} values into eqs. (55) and (56) we obtain eqs. (57) and (58):

$$\text{For CT: } \zeta_{sf} = -13.5 \text{ mV, therefore } \zeta_{if} = -4.6 \text{ mV} \tag{57}$$

$$\text{For DP: } \zeta_{sf} = -0.6 \text{ mV, therefore } \zeta_{if} = -9.4 \text{ mV} \tag{58}$$

This suggests that the zeta potential of DP bare fiber (i.e., no adsorbed polymer layers) is generally due to the ionized carboxyl groups. This also indicates that the CT surface is more hydrophilic than that of DP, since the contribution of the surface to the zeta potential (ζ_{sf}) is higher for CT.

Since $\zeta_{sp} \approx 0$ and $\zeta_{sf} \approx 0$ for DP, it follows that $\zeta_s \approx 0$. Therefore,

$$\zeta = \zeta_s + \zeta_i \approx \zeta_i \tag{59}$$

Using eq. (42), we obtain

$$Q_t = Q_i + Q_s \approx Q_i \tag{60}$$

Therefore, using eq. (26) we may say that the zeta potential of DP with an adsorbed monolayer ($0 \leq \theta \leq 1$) is nearly proportional to $X_1 - Y_1$:

$$\zeta \propto X_1 - Y_1 \tag{61}$$

Surface Charge Density from Zeta Potential Data: $Q_t(ZP)$

Surface charge density can be calculated from zeta potential data using eq. (20) for ionic strength of $10^{-4}M$ KCl:

$$Q_t = 690 \times (10^{-4})^{1/2}\zeta \text{ esu/cm}^2 = 6.90\zeta \text{ esu/cm}^2 \tag{62}$$

$$= 2.30 \times 10^{-9}\zeta \text{ coulomb/cm}^2$$

where the unit for ζ is mV. The total number of effective ionic sites is given by

$$n_t = Q_t/e \tag{63}$$

The results of the calculations are shown in Table III and IV.

Surface Charge Density from Polymer Adsorption Data: $Q_t(Ad)$

The surface charge density at various levels of polymer adsorption can be calculated from the adsorption isotherms using eqs. (21)–(33). The values

TABLE III
Surface Charge Density from Zeta Potential Data: $Q_t(ZP)$ (M_n 50,000)

Initial concn of polymer for fiber treatment, %	Zeta potential in $10^{-4}M$ KCl aq. soln. (ζ^a), mV	Surface charge density $Q_t(ZP)^b$		Total no. of effective ionic sites ($n_t{}^c$), $\times 10^{10}$ sites/cm^2	Excess charged groups A (anionic) or C (cationic)
		esu/cm^2	$\times 10^{-9}$ coulomb/cm^2		
	-10.0	-69.0	-23.0	14.4	A
0.0001	-9.8	-67.6	-22.5	14.1	A
0.001	-11.2	-77.3	-25.8	16.1	A
0.005	$+3.4$	$+23.4$	$+7.8$	4.9	C
0.01	$+2.5$	$+17.3$	$+5.8$	3.6	C
0.05	$+5.5$	$+38.0$	$+12.7$	7.9	C
0.1	$+4.9$	$+33.8$	$+11.3$	7.0	C
0.2	$+7.7$	$+53.1$	$+17.7$	11.1	C
0.25	$+8.5$	$+58.7$	$+19.6$	12.2	C
0.5	$+22.5$	$+155.3$	$+51.8$	32.4	C
1.0	$+25.8$	$+178.0$	$+59.3$	37.1	C

[a] Data of Fig. 2 in part II.[2]
[b] $Q_t(ZP)$ is calculated using eq. (62).
[c] n_t is calculated using eq. (63).

TABLE IV
Surface Charge Density from Zeta Potential Data: $Q_t(ZP)$ (M_n 200,000)

Initial concn of polymer for fiber treatment %	Zeta potential in $10^{-4}M$ KCl aq. soln. (ζ^a), mV	Surface charge density $Q_t(ZP)^b$		Total no. of effective ionic sites ($n_t{}^c$), $\times 10^{10}$ sites/cm^2	Excess charged groups A (anionic) or C (cationic)
		esu/cm^2	$\times 10^{-9}$ coulomb/cm^2		
0	−10.0	−69.0	−23.0	14.4	A
0.0001	−7.3	−50.4	−16.8	10.5	A
0.001	+9.7	+66.9	+22.3	14.0	C
0.005	+8.7	+60.0	+20.0	12.5	C
0.01	+8.6	+59.3	+19.8	12.4	C
0.02	+12.4	+85.6	+28.5	17.9	C
0.05	+16.8	+115.9	+38.6	24.2	C
0.1	+18.7	+129.0	+43.0	26.9	C
0.2	+18.9	+130.4	+43.4	27.2	C
0.5	+22.1	+152.5	+50.8	31.8	C
1.0	+25.2	+173.9	+58.0	36.3	C

[a] Data of Fig. 2 in Part II.[2]

[b] $Q_t(ZP)$ is calculated using eq. (62).

[c] n_t is calculated using eq. (63).

(Tables V and VI) correspond to the surface charge density when the surface is exposed to air ($D = 1$), i.e., space charge density in the absence of counterion binding.

TABLE V
Surface Charge Density from Polymer Adsorption Data: $Q_t(Ad)$ (M_n 50,000)

Initial concn of polymer for fiber treatment, %	Amount of polymer adsorbed[a] $\left(Ad = \dfrac{X_1 + X_2}{N}\sigma\right)$, $\times 10^{-5}$ g-eq/g	No. of adsorbed polymer segments $(X_1 + X_2)$, $\times 10^{14}$/cm^2	No. of effective ionic sites $(X_1 - Y_1 = X_1 + X_2 - k_2{}^b)$, $\times 10^{14}$ sites/cm^2	Surface charge density due to ionic sites $(Q_t(Ad) = Q_i{}^c = (X_1 - Y_1)e)$, $\times 10^4$ esu/cm^2
0	0	0	−3.60	−17.3
0.0001	0	0	−3.60	−17.3
0.001	0	0	−3.60	−17.3
0.005	0.65	4.59	+0.99	+4.75
0.01	0.65	4.59	+0.99	+4.75
0.05	0.75	5.30	+1.70	+8.14
0.1	0.75	5.30	+1.70	+8.14
0.2	1.0	7.06	+3.46	+16.6
0.25	1.0	7.06	+3.46	+16.6
0.5	1.7	12.0	+8.40	+40.3
1.0	1.7	12.0	+8.40	+40.3

[a] See eq. (21); $\sigma = 8,500$ cm^2/g (from Table I in part I).

[b] See eq. (24); $k_2 = 3.60 \times 10^{14}$ (from Table I in part I). Negative and positive signs mean cationic and anionic sites are in excess, respectively.

[c] See eq. (26).

TABLE VI
Surface Charge Density from Polymer Adsorption Data: $Q_t(Ad)$ (M_n 200,000)

Initial concn of polymer for fiber treatment, %	Amount of polymer adsorbed[a] $\left(Ad = \dfrac{X_1 + X_2}{N} \sigma\right)$, $\times 10^{-5}$ g-eq/g	No. of adsorbed polymer segments $(X_1 + X_2)$, $\times 10^{14}$/cm^2	No. of effective ionic sites $(X_1 - Y_1 = X_1 + X_2 - k_2{}^b)$, $\times 10^{14}$ sites/cm^2	Surface charge density due to ionic sites $(Q_t(Ad) = Q_i{}^c = (X_1 - Y_1)e)$, $\times 10^4$ esu/cm^2
0	0	0	-3.60	-17.3
0.0001	0	0	-3.60	-17.3
0.001	1.0	7.06	$+3.46$	$+16.6$
0.005	0.8	5.65	$+2.05$	$+9.83$
0.01	1.0	7.06	$+3.46$	$+16.6$
0.02	1.25	8.83	$+5.23$	$+25.1$
0.05	1.25	8.83	$+5.23$	$+25.1$
0.1	1.5	10.6	$+7.00$	$+33.6$
0.2	1.5	10.6	$+7.00$	$+33.6$
0.5	1.7	12.0	$+8.40$	$+40.3$
1.0	1.7	12.0	$+8.40$	$+40.3$

[a] See eq. (21); $\sigma = 8500$ cm^2/g (from Table I in part I).

[b] See eq. (24); $k_2 = 3.60 \times 10^{14}$ (from Table I in part I).   Negative and positive signs mean cationic and anionic sites are in excess, respectively.

[c] See eq. (26).

Comparison of $Q_t(ZP)$ with $Q_t(Ad)$

$Q_t(ZP)$ was compared with $Q_t(Ad)$, and the effective surface charge density is expressed as the ratio of these two quantities:

$$\frac{Q_t(ZP)}{Q_t(Ad)} \times 100 \ (\%) \tag{64}$$

The results are shown in Tables VII and VIII.

DISCUSSION OF THEORETICAL CALCULATIONS

Fiber Surface Affinity and Zeta Potential

Comparison of ζ_{sf} for CT (-13.5 mV) with ζ_{sf} for DP (-0.6 mV) indicates that fibers with a higher hydrophilic nature tend to attract OH$^-$ ions from aqueous electrolyte solutions to their surface.   This trend may in turn lead to a higher relative contribution of the surface (ζ_s) to the total zeta potential (ζ).

Counterion Binding and Effective Surface Charge

Comparison of $Q_t(ZP)$ with $Q_t(Ad)$ (Tables VII and VIII) suggests that only ca. 0.04% of the fixed ionizable groups of both fibers and polymers appears to be detectable by zeta potential measurement.   In the system under investigation, ionization of carboxyl groups on the cellulose fibers places negative charges on the surface and positive charges in the surrounding medium, whereas ionization of adsorbed quaternary ammonium groups places positive charges on the monolayer-formed surface and negative charges in the surrounding medium.

TABLE VII
Comparison of $Q_t(ZP)$ with $Q_t(Ad)$ (Mn = 50,000)

Initial concn of polymer for fiber treatment, %	Surface charge density from zeta potential $Q_t(ZP)$, esu/cm^2	Surface charge density from polymer adsorption Data $Q_t(Ad)$, $\times 10^4$ esu/cm^2	Effective surface charge density $\dfrac{Q_t(ZP)}{Q_t(Ad)} \times 100$, $\times 10^{-2}$ %
0	−69.0	−17.3	3.99
0.0001	−67.6	−17.3	3.91
0.001	−77.3	−17.3	4.47
0.005	+23.4	+4.75	4.93
0.01	+17.3	+4.75	3.64
0.05	+38.0	+8.14	4.67
0.1	+33.8	+8.14	4.15
0.2	+53.1	+16.6	3.20
0.25	+58.7	+16.6	3.54
0.5	+155.3	+40.3	3.85
1.0	+178.0	+40.3	4.42
		average:	4.07

TABLE VIII
Comparison of $Q_t(ZP)$ with $Q_t(Ad)$ (M_n = 200,000)

Initial concn of polymer for fiber treatment, %	Surface charge density from zeta potential $Q_t(ZP)$, esu/cm^2	Surface charge density from polymer adsorption data $Q_t(Ad)$, $\times 10^4$ esu/cm^2	Effective surface charge density $\dfrac{Q_t(ZP)}{Q_t(Ad)} \times 100$, $\times 10^{-2}$ %
0	−69.0	−17.3	3.99
0.0001	−50.4	−17.3	2.91
0.001	+66.9	+16.6	4.03
0.005	+60.0	+9.83	6.10
0.01	+59.3	+16.6	3.57
0.02	+85.6	+25.1	3.41
0.05	+115.9	+25.1	4.62
0.1	+129.0	+33.6	3.84
0.2	+130.4	+33.6	3.88
0.5	+152.5	+40.3	3.78
1.0	+173.9	+40.3	4.32
		average:	4.04

However, small ions of a sign opposite to that of fixed ionized groups are constrained to some extent by electrostatic attraction. They remain close to the fixed ionized groups and balance the surface charge; hence, the law of electric neutrality pertains to this system. These small ions, referred to as "counterions," have low activities and behave differently from similar ions in solution.[5] The fact that $Q_t(ZP)$ is far smaller than $Q_t(Ad)$ indicates that only a small portion of the fixed ionized sites are free from counterion binding, and these sites will become effective charged sites detectable by zeta potential measurements. Thus, the discrepancy between $Q_t(ZP)$ and $Q_t(Ad)$ reflects the extent to which coun-

terions are bound to the fixed ionized sites and the degree of counterion activity.

In addition to the effect of counterion binding, reasons for the discrepancy may be the following: (1) some of the carboxyl groups are located inside the porous structure of the fibers and are not detectable by zeta potential measurement; i.e., electrokinetically "ineffective" ionized sites may be present on the fiber surface. (2) Fixed ionized sites may be normally hydrated with water molecules; then hydration of these sites leads to the reduction of the effective surface charge.

Conclusions

The proposed model permits quantitative evaluation of the experimental results in part II[2] and also provides new information concerning the surface charge characteristics of the monolayer-formed DP fibers.

Results indicate that (1) there is a discrepancy between the surface charge theoretically predicted using the adsorption data and that calculated from zeta potential data; (2) the zeta potential is nearly proportional to the difference between the number of cationic and anionic groups on the surface; (3) the surface charge stems largely from the fixed ionized groups with only a minor contribution from the adsorbed ions; and (4) the surfaces with higher affinity for water tend to have a higher relative contribution of the adsorbed ions to the total surface charge.

Explanations are offered for the discrepancy in terms of counterion binding, the presence of electrokinetically undetectable carboxyl groups within the porous structure of the fibers, and hydration of ionized sites on the surface.

Although only a small portion of the ionized groups are electrokinetically detectable, a linear relationship has been established between the amount of adsorbed polymer and the value of the zeta potential. The proposed model will be helpful in designing a system with $k_1 > k_2$, the condition yielding a positively charged saturated monolayer of the polymer.

Appendix I. Details of Calculations

Calculation for Eq. (16)

$$A = \frac{8\pi e^2 N}{1000DkT} = \frac{8 \times 3.1416 \times (4.8 \times 10^{-10})^2 \times (6 \times 10^{23})}{1000 \times 80 \times (1.38 \times 10^{-16}) \times 298}$$

$$= 10.561 \times 10^{14} \div (3.25 \times 10^7)^2 \text{ cm}$$

Calculation for Eq. (18)

$$\frac{D\kappa}{4\pi} = \frac{80 \times (3.25 \times 10^7) \times I^{1/2}}{4 \times 3.1416}$$

$$= (2.069 \times 10^8) \times I^{1/2} \text{ cm}^{-1}$$

Calculation for Eq. (20)

$$Q_t = (2.069 \times 10^8) \times I^{1/2} \times \frac{1}{3 \times 10^5} \text{ esu/cm}^2$$

$$= 690 \times I^{1/2} \text{ esu/cm}^2 \ (\because 1 \text{ mV/cm} = \frac{1}{3 \times 10^5} \text{ esu/cm}^2)$$

Appendix II. Unit Systems

Unit Systems for Electric Charge and Electric Potential

	mksa unit	cgs esu
Electric charge	coulomb	$c \times 10^{-1}$ stat-coulomb (= 3×10^9)
Electric potential	volt	$c^{-1} \times 10^8$ stat-volt (= 1/300)

where $c = 3 \times 10^{10}$ cm/sec (velocity of light).

Conversion of Units

$$\text{Electric charge: stat-coulomb} = \text{cm}^{3/2} \text{ g}^{1/2} \text{ sec}^{-1}$$

$$\text{Electrical potential: stat-volt} = \text{cm}^{1/2} \text{ g}^{1/2} \text{ sec}^{-1}$$

Therefore,

$$1 \text{ coulomb} = 3 \times 10^9 \text{ cm}^{3/2} \text{ g}^{1/2} \text{ sec}^{-1}$$

$$1 \text{ volt} = \frac{1}{300} \text{ cm}^{1/2} \text{ g}^{1/2} \text{ sec}^{-1}$$

Zeta Potential Versus Surface Charge Density Relationship

For zeta potential:

$$\zeta = 1 \text{ mV} = 10^{-3} \times \frac{1}{300} \text{ cm}^{1/2} \text{ g}^{1/2} \text{ sec}^{-1}$$

$$= \frac{1}{3 \times 10^5} \text{ cm}^{1/2} \text{ g}^{1/2} \text{ sec}^{-1}$$

For surface charge density:

$$Q_t = 1 \text{ coulomb/cm}^2 = (3 \times 10^9) \text{ cm}^{-1/2} \text{ g}^{1/2} \text{ sec}^{-1}$$

$$1 \text{ mV/cm} = \frac{1}{3 \times 10^5} \text{ cm}^{-1/2} \text{ g}^{1/2} \text{ sec}^{-1}$$

The above calculations show that Q_t and $(D\kappa/4\pi) \zeta$ have the same dimension. That is to say,

$$[Q_t] = [L^{-1/2} M^{1/2} T^{-1}]$$

$$\left[\frac{D\kappa}{4\pi} \zeta\right] = [L^{-1}][L^{1/2} M^{1/2} T^{-1}] = [L^{-1/2} M^{1/2} T^{-1}]$$

Finally, we obtain

$$(3 \times 10^5) \text{ mV/cm} = \frac{1}{3 \times 10^9} \text{ coulomb/cm}^2 = 1 \text{ esu/cm}^2$$

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