# Interfacial Properties of Polyelectrolyte-Cellulose Systems. IV. Electrokinetic Properties of Carboxymethylcellulose Fibers with Adsorbed Multilayers of Cationic Polyelectrolyte

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## Synopsis

Zeta potential measurements by the streaming current method were performed on carboxymethylcellulose (CMC) with and without irreversibly adsorbed multilayers of cationic polyelectrolyte. Factors affecting the electrokinetic properties such as the amount of adsorbed polymer, polymer molecular weights ($M_n$ 50,000 and 200,000), ionic strength ($10^{-5} \sim 10^{-2}M$ KCl), and pH of the streaming medium (KCl solutions) were examined. The negative zeta potential of CMC decreased to the point of monolayer formation and increased from that point to the saturated multilayer formation. The polarity of the zeta potential was negative throughout every adsorption stage. The negative zeta potential increase was attributed to: (a) binding of anions ($Cl^-$ and $OH^-$) to the outermost layer of the multilayer from KCl solutions and (b) change in chemical potentials of counterions in a diffuse double layer due to expansion of the double layer in the presence of the adsorbed multilayer on CMC. The results suggest that the carboxyl groups under the monolayer are undetectable electrokinetically; however, the negative charge, due to unneutralized carboxyl groups under the monolayer, appears to cause further adsorption forming a saturated multilayer. When the effect of unneutralized carboxyls of CMC are shielded at higher levels of adsorption, the outermost layer of the multilayer becomes a potential-determining layer.

## INTRODUCTION

The conditions for monolayer or multilayer formation of the cationic polyelectrolyte poly-DMDAAC on various cellulose fibers were investigated using adsorption, hydrodynamic permeability, and electrokinetic measurements.[1] The various factors affecting the electrokinetic properties of the monolayer-formed DP (dissolving pulp) fibers were also examined.[2] A theoretical model for the electrokinetic behavior of the monolayer-formed DP has been proposed.[3]

Concerning the multilayer formation, it has been shown in part I that adsorption of the polymer on CMC fibers proceeds mainly by electrostatic interaction with polymer chains lying nearly flat on the fiber surface up to the point of monolayer formation and that the number of adsorbed polymer segments at the point of monolayer formation on CMC fibers ($k_1$) is smaller than the number of carboxyl groups on the fiber surface ($k_2$). The monolayer CMC fiber surface in equilibrium with KCl solutions is negatively charged. The excess negative charge of surface leads to further adsorption of the polymer to form a multilayer until all the negative charges of the carboxyl groups of the fibers are neutralized by the quaternary ammonium groups of the adsorbed polymer molecules.

The presence of the excess negative charge, due to the unneutralized carboxyls

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at the point of monolayer formation, is a prerequisite for further adsorption in the formation of a saturated multilayer. Furthermore, a model for the adsorbed polymer chain configuration of the multilayer has been proposed.[1]

This paper investigates the various factors affecting the electrokinetic properties of the multilayer CMC fibers. It correlates the structure of the adsorbed multilayer with surface charge characteristics of the multilayer-formed CMC by measuring the zeta potentials. It is also intended to seek applicability of multilayer formations of cationic polyelectrolytes as a means to surface charge control of negatively charged cellulose fibers.

## EXPERIMENTAL

Zeta potential measurements by the streaming current method were carried out on multilayer CMC fibers. The materials, apparatus, and experimental procedure employed were the same as those described in parts I and II of this series.[1,2] CMC fibers were Whatman's ion exchange cellulose (Type CM1, coarse fibrous sample). The fibers were in Na salt form and were converted to acidic form by pretreatment before use. The CMC fibers were characterized as shown in Table I.

## RESULTS AND DISCUSSION

This section deals with the factors affecting the electrokinetic behavior of the multilayer CMC fibers in equilibrium with streaming solutions of potassium chloride.

### Amount of Adsorbed Polymer Molecules

No significant difference in the amount of adsorption was observed at lower initial concentrations (ca. less than 0.1%) of the polymer (Fig. 1). However, at higher initial concentrations of the polymer (0.5% through 1%), the amount of adsorption was higher for the lower molecular weight polymer ($M_n$ 50,000), and saturation adsorption occurred when the initial concentration of the polymer was between 0.5% and 1%.

TABLE I
Characterization of CMC Fibers

| | |
|---|---|
| Specific surface area $(X)$[a] | 5950 cm$^2$/g |
| Specific volume[a] | 1.66 cm$^3$/g |
| Surface area per unit volume[a] | 3584 cm$^2$/cm$^3$ |
| Carboxyl content $(Y)$[b] | 19.6 × 10$^{-5}$ geq/g |
| Density of carboxyl groups $(Y/X)$ | 32.9 × 10$^{-9}$ geq/cm$^2$ |
| The number of carboxyl groups | 197 × 10$^{14}$/cm$^2$ |
| Zeta potential (in 10$^{-4}$M KCl)[c] | −20.5 mV |
| Amount of polymer adsorbed at point of monolayer formation[c] | 1.2 × 10$^{-5}$ geq/g |
| Amount of polymer adsorbed at point of saturated multilayer formation[c] | |
|   For $M_n$ 50,000 | 29 × 10$^{-5}$ geq/g |
|   For $M_n$ 200,000 | 26 × 10$^{-5}$ geq/g |

[a] Obtained by hydrodynamic permeability of fiber pads (see part I[1]).

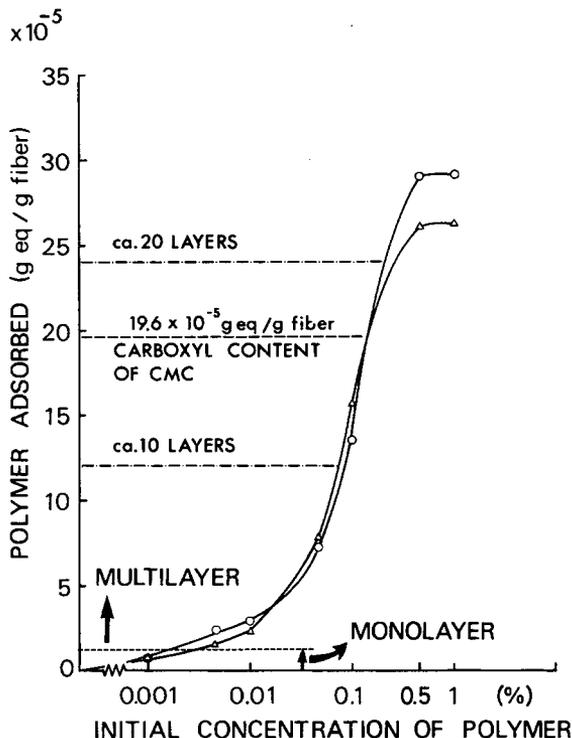[b] Obtained by NaHCO$_3$–NaOH method (see part I[1]).

[c] See part I.[1]

Fig. 1. Adsorption isotherms of polymer on CMC.   Reproduced from Fig. 4 in part I[1] Approximate numbers of adsorbed layers are calculated on the assumption of piled-up monolayers (see Fig. 10 in part I[1]).   One adsorbed layer corresponds to the amount of $1.2 \times 10^{-5}$ geq/g fiber:   (O) $M_n$ = 50,000; (△) $M_n$ = 200,000.

As the initial concentrations of the polymer increased, the negative zeta potentials first decreased and passed the maxima, then continued to increase. However, these maxima were located on the negative side of the zeta potential curves, i.e., the polarity of zeta potentials were not reversed to the positive side over the entire adsorption stages (Fig. 2).

Figure 3 shows that the negative zeta potentials of CMC fibers decreased up to certain levels and then started to increase to the negative side again as adsorption of the polymer proceeded.
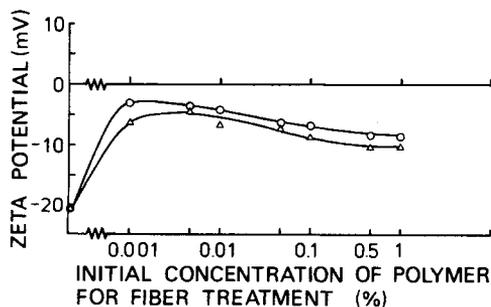


Fig. 2. Initial concentration of polymer for CMC fiber treatment vs. zeta potential.   Medium $10^{-4}M$ KCl aqueous solutions:   (O) $M_n$ = 50,000; (△) $M_n$ = 200,000.
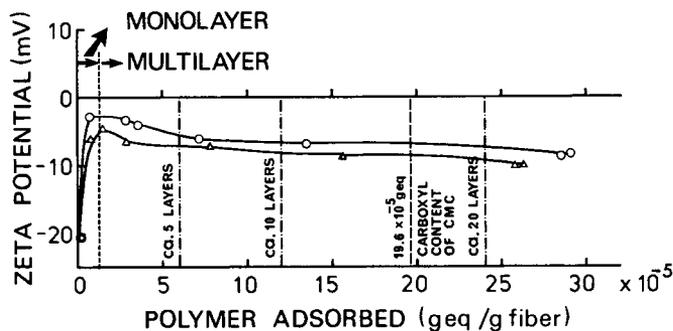
Fig. 3. Effect of amount of polymer adsorbed on zeta potential. Fiber = CMC. For meaning of adsorbed layers, see legend to Fig. 1. Medium = $10^{-4}M$ KCl aqueous solutions: (O) $M_n$ = 50,000; (△) $M_n$ = 200,000.

The amount of adsorption of the polymer at the point of monolayer formation on CMC fibers is ca. $1.2 \times 10^{-5}$ geq/g.[1] Therefore, the amount of polymer adsorbed exhibiting these two inflection points on the zeta potential curves corresponds to the points of monolayer formation. Monolayer CMC fibers are negatively charged; this negative charge tends to attract positively charged polymer molecules to form a multilayer.

A steep decrease in the zeta potentials occurred up to the monolayer formation. However, gentle slopes for zeta potential variations were observed from the point of monolayer formation up to the multilayer formation. Thus, the zeta potential variations throughout the monolayer formation stages are nearly proportional to the degree of surface coverage of CMC by the polymer.

## Molecular Weight

The effect of molecular weight on the zeta potentials was compared between the two molecular weight samples $M_n$ 200,000 and 50,000 (Figs. 2 and 3). A significant difference in the values of zeta potential was observed for CMC treated with the two molecular weight samples of the polymer (Fig. 3).

Although no significant difference in the amount of adsorption was exhibited between the two samples except for the points near the saturation adsorption (Fig. 1). The lower molecular weight sample is more effective in reducing the negative zeta potential of CMC when the multilayer is formed (Fig. 3). Configurations of the adsorbed polymer chains at the fiber surface differ according to whether or not hydrodynamic shear force, due to the streaming liquid, is applied at the surface of multilayer CMC fibers.

## Ionic Strength

The effect of increasing ionic strength in the case of 1:1 type inorganic salt (KCl) is to reduce absolute values of the negative zeta potential (Figs. 4 and 5). Consequently, the negative zeta potentials of CMC fibers and those with the mono- or multilayers decrease with increasing ionic strength. Furthermore, the zeta potentials over the entire multilayer formation range remained negative, and the polarity was not reversed even at higher concentrations of KCl (e.g., up to $10^{-2}M$).
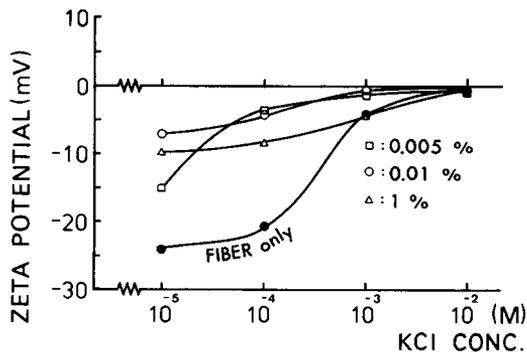
Fig. 4. Effect of ionic strength on zeta potential ($M_n$ = 50,000). Fiber = CMC. Percent shows initial concentrations of the polymer for fiber treatment. The 1% treatment leads to saturated multilayer formation.

In colloidal systems, reversal of surface charge is often observed at increased concentrations of electrolytes when the polarization energy of counterions for interaction with a charged surface is sufficiently high.[4] This suggests that polarization energy of $K^+$ is not high enough to reverse the polarity of the charge of CMC with or without adsorbed layers of the cationic polyelectrolyte.

As for steepness of the zeta potential curves as a function of ionic strength, the fibers with larger amounts of adsorbed polymers (e.g., 0.01% and 1%) exhibited more gentle zeta potential curves, i.e., the fibers with thicker multilayer exhibited a more gentle curve.

The outermost layer of the multilayer is a potential-determining layer for the electrokinetic behavior of the multilayer CMC. Consequently, possible effects of increasing ionic strength of KCl on the zeta potentials can be explained as follows:

Regarding CMC without adsorbed polymer (i.e., Fiber only), the steep zeta potential curve can be attributed to shielding of the negative charge of ionized carboxyl groups of CMC by counterions ($K^+$ and $H^+$) and to change in distribution of counterions and co-ions ($OH^-$ and $Cl^-$) adjacent to CMC.

As for the fibers treated with 0.005% and 0.01% polymers (corresponding to mono- to bimolecular layer and bimolecular layer, respectively), which exhibited intermediate steepness in the zeta potential curves, the change in zeta potential is mainly due to reduction in the thickness of the double layer adjacent to the
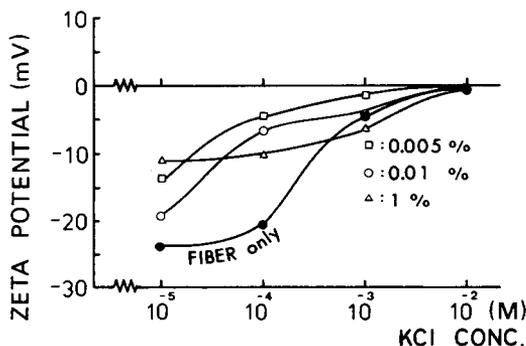


Fig. 5. Effect of ionic strength on zeta potential (Mn = 200,000). See legend to Fig. 4.

surface.  Although it is suggested from the adsorption data that the monolayer or bimolecular layers are adsorbed flat on the surface, a possibility of binding of counterions to the unneutralized carboxyl groups beneath the adsorbed polymer layer can not be ruled out.  Presumably, the change in distribution of counterions and coions also contributes to the change in zeta potentials.

As for the fibers treated with 1% polymer (corresponding to the saturated multilayer formation), which exhibited the least steepness in the zeta potential curves, the change in zeta potential may be partly due to shielding of the positive charge of quaternary ammonium groups of the outermost layer of the adsorbed multilayer.

It seems reasonable to assume that the negative charge of the fibers with the saturated multilayer is nearly neutralized with the quarternary ammonium groups of the polymer.  The change in distribution of counterions and coions adjacent to the outermost layer of the saturated multilayer also contributes to the zeta potential variations.

### pH of Streaming Solutions

Zeta potentials of CMC with or without adsorbed polymer layers at the different levels of adsorption were measured as a function of pH of the streaming solutions (Fig. 6).  The pH of the streaming solutions was controlled by addition of either HCl or NaOH to the KCl solutions.

With regard to the isoelectric points (I.E.P.), the fibers treated with 0.005% and 1% polymer exhibited an I.E.P. in the acidic region (Fig. 6).  However, the charge of the fibers without polymer treatment and those treated with 0.01% polymer were not reversed to positive even under extreme acidic conditions.

The fiber surfaces covered with the saturated multilayer (as with the case of 1% polymer treatment) has the highest I.E.P., pH ca. 4.7, and developed positive zeta potentials in the acidic region.  However, the zeta potentials increased on the negative side when pH was increased.

Since the charge of the carboxyl groups beneath the saturated multilayer is already neutralized, the negative charge in the alkaline region may be due to increased adsorption of hydroxyl ions on the outermost layer of the saturated multilayer.

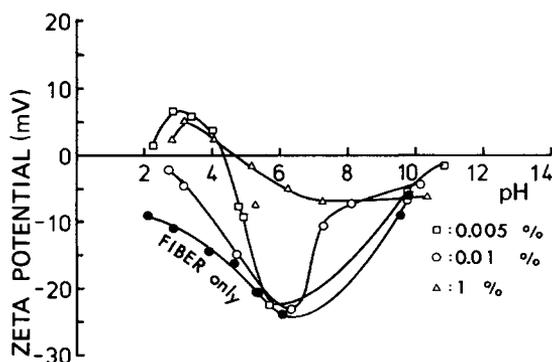At intermediate polymer concentrations which are less than required for



Fig. 6.  Effect of pH on zeta potential.  Fiber = CMC; $M_n$ = 50,000; [KCl] = $10^{-4}M$.  See legend to Fig. 4.

saturated multilayer formation, i.e., 0.01% and 0.005%, the zeta potentials exhibited minima at pH ca. 6 and decreased with increasing or decreasing pH. The fibers treated with 0.005% polymer had an I.E.P., but those treated with 0.01% did not.

CMC exhibited negative zeta potentials over the entire pH region, indicating an extremely high negative surface charge density and hydrophilicity of the fibers. The density of carboxyl groups of CMC is higher than those of CT and DP (part I). Experimental data have shown that the pH of the KCl solutions in equilibrium with CMC is shifted to the acidic region compared with those for CT and DP, probably due to liberation of hydrogen ions of the carboxyl groups to bulk KCl solutions.

The origin of the surface charge of the multilayer CMC is presumably due to the ionized quaternary ammonium groups of the polymer located on the outermost layer and adsorption of inorganic ions to the outermost layer of the multilayer. Hence, zeta potential variations of the multilayer CMC as a function of pH may arise from adsorption of proton ($H^+$) or hydroxyl ions ($OH^-$) to the outermost layer, with minor contribution of the change in degree of ionization of the CMC carboxyl groups.

Since the zeta potential curves for the fibers treated with 0.005% and 0.01% polymer are similar to those for CMC in that the minima appeared at pH ca. 6, ionization of the carboxyls affects the appearance of these minima. Inorganic ions ($H^+$, $OH^-$, $K^+$, and $Cl^-$) are capable of penetrating to a certain extent into the condensed multilayer, leading to a variation in the degree of ionization of the carboxyls beneath the multilayer.

In this connection, $H^+$ or $OH^-$ are often effective "potential-determining ions" in colloidal systems, and they can reverse the charge of colloids at increased or decreased pH of the suspending medium.[2] However, amphoteric colloidal nature was observed only for the fibers treated with 0.005% and 1%, i.e., isoelectric points were exhibited.

### Correlation of Zeta Potential with Configuration of Multilayer Polymers on CMC

Configuration of adsorbed polymer chains at the fiber surface over the entire multilayer formation stages differs according to each adsorption stage. The hypothetical configurations illustrated in Figure 7 affect the zeta potentials of the multilayer CMC.

The polymer chains are adsorbed flat on the fiber surfaces when the amount of adsorption is independent of the molecular weight of the polymer in the case of monolayer formations on CT and DP.[1] Furthermore, in the case of multilayer formation, it has been demonstrated that the adsorbed polymer chains are lying almost flat on the fiber surface at the lower level of adsorption; however, after all the carboxyls on CMC are neutralized, configurations of the adsorbed chains deviate slightly from the flat chain formation by partly forming loops or tails on the outermost layers at relatively higher levels of adsorption. Interpretations for the chain configurations at each adsorption stage of the multilayer formation will be given in terms of the above concept.

*Unsaturated Monolayer Formation (0 < θ < 1).* This level of adsorption corresponds to the treatment with initial concentrations of 0 through ca. 0.001%
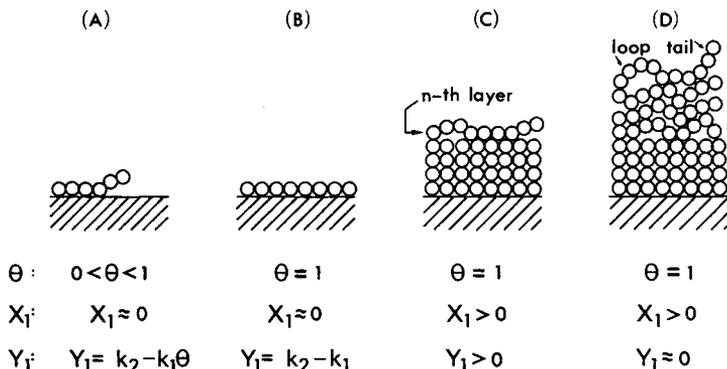
Fig. 7. Schematic representation of hypothetical adsorbed polymer chain configurations: (A) unsaturated monolayer formation; (B) saturated monolayer formation; (C) $n$th multilayer formation (unsaturated multilayer); (D) saturated multilayer formation; $\theta$ = fraction of fiber surface covered with polymer chains; $X_1$ = number of unneutralized polymer segments per unit area of fiber surface; $Y_1$ = number of unneutralized carboxyl groups per unit area of fiber surface; $k_1$ = number of adsorbed segments per unit area of fiber surface at saturated monolayer formation; $k_2$ = number of carboxyl groups on unit fiber surface area.

polymer. Although no significant difference in the amount of adsorption was observed between the two molecular weight samples when compared at the same initial concentrations of the polymer, the zeta potential was slightly molecular weight dependent (Fig. 2). This dependency suggests that: (1) a part of the adsorbed polymer chain exists as loops or tails during the zeta potential measurements, and (2) hydrodynamic shear force by streaming liquid applied to the adsorbed flat monolayer may cause the configurations.

*Saturated Monolayer Formation* ($\theta = 1$). The amount of adsorption for this case was slightly molecular weight dependent, and the negative zeta potential was lower for the lower molecular weight polymer. These results also suggest that adsorbed chain configurations deviate slightly from flat saturated monolayer while streaming liquid flows past through the surface.

*nth Multilayer Formation (Unsaturated Multilayer).* Up to $n = 20$ (a multilayer consisting of 20 layers), the amount of adsorption was almost independent of the molecular weight, however, the zeta potential was significantly lower for the fibers treated with the lower molecular weight polymer (Fig. 1). This suggests that up to ca. $n = 20$, the polymer chains are mostly adsorbed as piled-up flat monolayers (Fig. 10 in part I[1]). However, configurations of the chains in the outermost layers changed to form loops or tails probably because of hydrodynamic shear force of the streaming liquid. Additional adsorption by van der Waals force takes place to some extent after all the negatively charged groups of the fibers are neutralized.

*Saturated Multilayer Formation.* The amount of adsorption at saturated multilayer formation was higher for the lower molecular weight polymer (Fig. 1). The zeta potential was slightly lower for the lower molecular weight polymer (Fig. 2). Some of the polymer chains, probably those at the outermost layers, are adsorbed as loops or tails, even in the absence of applied hydrodynamic shear force, due to streaming liquid. In this connection, the fact that the amount of adsorbed polymer at saturation (0.5% through 1% initial concentration) is higher than the value predicted from the carboxyl content suggests that not all the polymer chains lie almost flat on the fiber surface.

## Source of Negative Zeta Potential of Multilayer CMC

The polarity of zeta potentials of the polymer-adsorbed CMC is negative over the entire multilayer formation stages (Fig. 3). The main source[2] of the negative zeta potential of wood pulp fibers are the ionized groups present on cellulose fibers, with minor contributions from adsorbed water molecules and adsorbed inorganic ions from aqueous solutions.[5–7]

In general, zeta potential is proportional to surface charge density, i.e., the number of charged sites and adsorbed ions. Thus, possible sources of the negative charge of CMC in equilibrium with KCl solutions are ionized carboxyl groups and adsorbed inorganic ions ($K^+$, $Cl^-$, $H^+$, and $OH^-$) on the surface.

The zeta potentials of CMC decreased drastically up to the formation of a monolayer (Fig. 3). However, the zeta potentials increased from the point of monolayer formation up to the saturated multilayer. A significant increase in the zeta potential was observed from the point of monolayer formation up to ca. 10 multilayers (corresponding to the amount of adsorption of $12 \times 10^{-5}$ geq/g fiber). However, after this point (ca. 10 multilayers) up to the point of saturated multilayer formation, only a slight zeta potential increase was observed. The negative charge due to unneutralized carboxyl groups beneath the adsorbed polymer layers may affect adsorption of inorganic ions on the outermost layer of the multilayer at an initial stage of the multilayer formation process (up to ca. 10 layers). However, from the 10th layer up to the saturated multilayer, the charge due to the carboxyls is shielded by the adsorbed multilayer. Further adsorption after the 10th layer does not cause a significant change in the zeta potential.

Let us now consider the sources of the negative zeta potentials at each adsorption stage (Fig. 7):

*Unsaturated Monolayer Formation ($0 < \theta < 1$).* Most of the positive charge of the adsorbed polymer chains throughout the adsorption process is neutralized; therefore, no excess positively charged groups are present on the surface of the adsorbed monolayer. The source of the negative zeta potentials of CMC with an unsaturated monolayer is presumably ionized carboxyl groups of CMC and adsorbed inorganic ions on the monolayer CMC.

*Saturated Monolayer Formation ($\theta = 1$).* CMC with a saturated monolayer has no excess positive charge due to unneutralized quaternary ammonium groups of the polymer. The number of unneutralized carboxyls is far in excess at the point of saturated monolayer formation, and this excess negative charge attracts inorganic ions on the surface of a saturated monolayer. Adsorbed ions on a saturated monolayer are the main source of the negative zeta potential. The number of anions adsorbed must be larger than the cations adsorbed.

*nth Multilayer Formation (Unsaturated Multilayer).* This applies to the unsaturated multilayer formation, where the multilayer consists of $n$ layers with more or less unneutralized carboxyl groups. The negative charge due to unneutralized carboxyls is not strong enough to attract all of the adsorbed chains to form flat monolayers. Therefore, loops or tails exist in the outermost layers of the multilayer, and some of the positive charge of these layers tends to attract inorganic ions to their surface. Unneutralized positive charges on the outermost layer of the multilayer and adsorbed inorganic ions of the multilayer are the source of the charge. However, the negative charge, due to adsorbed anions, predominates the charge due to the unneutralized fixed positive groups (quar-

ternary ammonium groups) and adsorbed cations on the outermost layer, which results in the negative zeta potential.

*Saturated Multilayer Formation.*    This applies to the case of saturated multilayer formation, where the fixed negative groups (carboxyl groups) on CMC are neutralized.   Since no electrostatic force, due to the carboxyl groups, functions over the outermost layer of the multilayer, the number of loops or tails for (D) is larger than the case for (C).   Unneutralized fixed positive groups on the outermost layer and the adsorbed ions on the outermost layer are the source of the charge.   Predominance of the negative charge (due to adsorbed anions on the outermost layer) due to unneutralized quaternary ammonium groups and adsorbed cations on the outermost layer results in the negative zeta potential.

## Negative Zeta Potential Increase by Progressive Formation of Multilayer on CMC

The negative zeta potentials of the polymer-adsorbed CMC increased as formation of the multilayer proceeded from the point of saturated monolayer formation up to the point of saturated multilayer formation (Fig. 3).   In this connection, Brooks[8] observed a negative zeta potential increase in the presence of adsorbed neutral polymer layers on biologic cells and other charged particles.

Phenomena similar to this have been observed by several workers, and three different explanations for this effect have been presented[8].   (i) dielectric constant change, (ii) rearrangement of the interfacial region, and (iii) ion adsorption to an adsorbed polymer layer.   Brooks[8] has concluded that none of these could satisfactorily explain the effect of adsorbed neutral polymers on the electrokinetic properties.   In addition, Brooks has proposed a model[9] for this zeta potential increase based on the effect an adsorbed layer of a neutral polymer would have on the chemical potentials of counterions in a diffuse layer.   In the presence of adsorbed neutral polymer, the double layer is predicted to expand due to generalized excluded volume effects.[9]   The expansion alters the relationship between the surface charge and surface potential so that if the surface charge density remains constant, the surface potential is increased.   Brooks has concluded that as long as the shear plane is not shifted too far from the particle surface, the zeta potential increases in the presence of adsorbed neutral polymer.

Consider applicability of each of these explanations and a model to the negative zeta potential increase by progressive formation of the multilayer on CMC.

*Change of Dielectric Constant in the Interfacial Region.*    Aqueous neutral polymer solutions have an apparently higher bulk dielectric constant than water and the adsorbed polymer layer.   The dielectric constant increases near the shear plane of the cell.   Such an increased dielectric constant should decrease the electrostatic attraction between the fixed surface charge of the particle and the counterions to that charge.   The double layer would therefore expand and the surface potential increase.   In contrast, however, the fixed positive groups on the multilayer CMC are almost neutralized at each adsorbed layer and the local dielectric constant could not be altered by the adsorbed multilayer.   Furthermore, polymer molecules are irreversibly adsorbed on CMC; therefore, multilayers will not change the dielectric constant of the bulk medium (KCl solutions).

*Rearrangement of the Interfacial Region to Expose Additional Charged*

*Groups.* Interaction of adsorbed polymers with a surface causes a rearrangement of the interfacial region. Such a rearrangement might expose previously undetected charged groups at the shear plane, thus increasing the surface charge density and, consequently, the zeta potential. In the case of the multilayer CMC, the negative charge of the carboxyl will be neutralized by a progressive multilayer formation. There is no possibility that previously undetected negatively charged groups would be exposed to give an increased negative zeta potential.

*Ion Adsorption or Ion Binding to an Adsorbed Polymer Layer.* If an adsorbed polymer layer at the solid–solution interface could acquire a negative charge by binding anions from a solution, the charge density in the interfacial region could be increased, thus increasing the negative zeta potential.

The charge increase was attributed to anion binding to the neutral polymer. In the case of the multilayer CMC, the fixed positive groups will remain on the outermost layer of the multilayer. Therefore, the surface might acquire a negative charge by binding anions ($Cl^-$ and $OH^-$) from KCl solutions.

*Change in Chemical Potentials of Counterions in a Diffuse Double Layer.* This explanation proposed by Brooks presumes that the conditions under which the zeta potential increases are:  (1) the adsorbed layer should be free draining, and (2) the charge density of the surface should be unaffected by the presence of adsorbed polymer. The free-draining polymer chains on the outermost layers of the multilayer CMC fibers are partially adsorbed as loops or tails.

Since the fixed positive charge of each adsorbed layer is neutralized during the process of multilayer formation, they are present to a lesser extent on the outermost layer. There will be an appreciable increase in the number of positive groups on the outermost layer with an increase in the number of layers. This indicates that the charge density of the potential-determining layer, i.e., the outermost layer of the multilayer, is nearly unaffected from the point of monolayer formation up to the point of saturated multilayer formation.

It is suggested from the analogy of Brooks's neutral polymers–cell systems that the negative zeta potential increase due to progressive multilayer formation occurs because an adsorbed multilayer affects distribution of ions in the diffuse double layer adjacent to the CMC surface. The double layer is predicted to expand in the presence of the adsorbed multilayer, thus altering the relationship between the fixed surface charge and potential, and causing the increase observed.

Since the thickness of the saturated multilayer is ca. 62–69 Å,[1] the shift of shear plane in the presence of the multilayer is at most 62–69 Å. Incidentally, the thickness of the ionic atmosphere, $1/\kappa$, (see Table I) in part III[3] at $10^{-4}M$ KCl is ca. 308 Å. This suggests that maximum shift of shear plane by the multilayer is smaller than the thickness of the ionic atmosphere.

In the case of multilayer CMC, formation of the polymer layers proceeds mainly by electrostatic interaction. In this connection, the negative charge due to unneutralized carboxyl groups beneath the multilayer is the source of an electrostatic potential through the surface phase.

As for the multilayer CMC, an electrostatic potential throughout the surface phase may affect distribution of counterions and coions in adjacent fixed or diffuse layers. This potential on the multilayer tends to attract positive ions on the outermost layer. Fixed positive groups on the loops or tails tend to attract negatively charged ions to neutralize the fixed positive charge. Thus, the cause

for the negative zeta potential increase by progressive formation of the multilayer on CMC is (1) binding of anions (Cl$^-$ and OH$^-$) to the outermost layer of the multilayer from KCl solutions, and (2) change in chemical potentials of counterions in a diffuse double layer.

## Sensitivity of Zeta Potential Variations to Polymer Adsorption

Figure 3 shows steep variations in the zeta potential over the monolayer formation stage and slight variations from the point of monolayer formation up to the saturated multilayer. Table II shows the variation of zeta potential with sequential increase in the number of adsorbed polymer layers in the multilayer formation process.

Change in zeta potential per each adsorbed layer reveals that a drastic change in the value of zeta potential took place up to the monolayer formation. The table also shows that as the number of adsorbed layers increases, the change in zeta potential per adsorbed layer decreases. This finding is consistent with the hypothesis that the negative charge due to unneutralized carboxyls beneath the multilayer may affect adsorption of ions up to a certain level of adsorption (ca. 10 layers). However, from this level up to the saturated multilayer the negative charge does not affect adsorption of ions on the outermost layer of the multilayer. This means that the charge of multilayer CMC with 10 layers to saturation, is a function of the charge of the outermost layer. The outermost layer is a potential-determining layer of the multilayer CMC. This also suggests that the electrokinetic measurements by the streaming current method do not permit detection of even an approximate number of adsorbed layers external to the monolayer on CMC.

TABLE II
Sensitivity of Zeta Potential Variations to Polymer Adsorption

| Stage of adsorbed layer formation | Zeta potential variation,[a] mV | increment (+) or decrement (−), mV | Zeta potential change per one adsorbed layer, mV |
|---|---|---|---|
| *M*$_n$ 50,000 | | | |
| Up to saturated monolayer formation | −20.5 → −3.4 | +17.1 | +17.1 |
| Monolayer to 5th layer | −3.4 → −5.5 | −2.1 | −0.53 |
| 5th layer to 10th layer | −5.5 → −7.0 | −1.5 | −0.30 |
| 10th layer to 24th layer[b] | −7.0 → −8.7 | −1.7 | −0.12 |
| *M*$_n$ 200,000 | | | |
| Up to saturated monolayer formation | −20.5 → −4.7 | +15.8 | +15.8 |
| Monolayer to 5th layer | −4.7 → −7.2 | −2.5 | −0.63 |
| 5th layer to 10th layer | −7.2 → −8.3 | −1.1 | −0.22 |
| 10th layer to 22th layer[b] | −8.3 → −10.3 | −2.0 | −0.17 |

[a] Zeta potential in 10$^{-4}$*M* KCl aq. solutions.

[b] Saturated multilayers.

## Multilayer Formation as a Means to Control Surface Charge on Cellulose Fibers

It has been suggested that formation of the multilayer under the condition of $k_1 < k_2$ does not permit reversal of the polarity of the charge of CMC. Strong electrostatic force functions to form a tenacious irreversible bond up to monolayer formation. However, from the point of monolayer formation up to the point of saturated multilayer formation, the electrostatic force functions to a lesser extent due to increased neutralization of the CMC carboxyl groups. Therefore, it is expected that tenacious irreversible adsorbed layers may be formed on the lower part of the multilayer and the layers formed on the upper part of the multilayer may be due to weaker bonding.

If multilayer formation of cationic polymers significantly enhances the negative zeta potentials of certain solid particles, they might also be expected to enhance the stability of these particles. The multilayer formation may have stabilizing action for colloidal dispersions on the negative side of the zeta potential.

## Conclusions

Electrokinetic properties of the multilayer CMC differ from the monolayer DP. The zeta potential variations were not proportional to an increase in the amount of polymer adsorbed, and the negative zeta potential of CMC was not reversed to the positive even at the saturated multilayer. Throughout all of the adsorption levels (monolayer and multilayer formations), the outermost layer of adsorbed layers is a potential-determining one. The negative zeta potential increases with an increase in the number of layers in multilayer formation. Therefore, the multilayer formation under the condition of $k_1 < k_2$ may have a stabilizing action for colloidal dispersions on the negative side of the zeta potential.

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