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THE ζ-POTENTIAL MEASUREMENTS OF FIBER IN THE PRESENCE OF POLYELECTROLYTES

By

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INTRODUCTION

In the previous paper, [1] the ζ-potential measurements of fiber in the presence of polymer solution have been carried out by the stream compression method which have been developed by Neale *et al.* [2] and Mason *et al.* [3] and the relation between the streaming potential and permeability has been discussed.

The purpose of this paper is to examine an application of the stream compression method (streaming potential) for the determination of ζ-potential of fiber in the presence of polyelectrolytes. The polyelectrolytes have two characteristic properties ; that is, polymeric and electrolytic characters. A number of ions fixed on polymer chain forms a large electrostatic field around polymer molecules. Consequently, it should be noted that a overlap of the Gouy-Chapman diffuse layers on both the solid surface and the polyion occurs, and it gives erroneous results for the determination of ζ-potential. In addition, it may also be considered that the information on the activity coefficient of polyelectrolyties is not sufficient to account for a quantitative discussion of ζ-potential. The discussion in the present paper is limited to the interaction between the diffuse layers which are formed by both the solid surface and the polyion.

EXPERIMENTAL

1) Materials

The fiber sample employed for the stream compression method was cotton about 2mm long and 20μ wide. For electrophoretic method, the fibers were put on a glass plate and cut to 10∼20μ in length with a razor. Both fiber samples were purified with alcohol-benzol (1 : 2) mixture by a Soxhlet extractor, and then with ethyl ether. The samples after extracting were washed with conductivity water of 1×10^{-6} mho. cm^{-1}. and stored in desicator until used for measurements.

The polyelectrolytes used were sodium polyacrylate (NaPAA) shown in Table 1. The sodium salt of the polymers was converted to acid form by passing through a ion-exchange-resin column of Amberlite IR-120 and 400, and then acid form was returned to salt by potentiometric titration. The polymer concentrations were determined from these titration curves.

2) ζ-potential measurements

The ζ-potential measurement by the stream compression method was made as previously described[1]. Electrophoretic measurement was carried out with a micro-

Table 1. Molecular Weights of Sodium Polyacrylate

Sign	$[\eta]$ (dl/g)	Molecular Weight
NaPAA−1	2.5[a)]	1.05×10^6
NaPAA−2	4.1[a)]	2.22×10^6
NaPAA−3	6.3[a)]	4.40×10^6

a) $[\eta] = 6.52\times10^{-3}\ P^{0.64}$ in 2N−NaOH at 25°C[4)]

electrophoretic apparatus of Mitamura Riken Kogyo. Co., Ltd. Measurements were made at the stationary level and at two other levels in order that the value at the stationary level could be checked by interpolation. The mobility values used for the calculation of ζ-potential were the average of twenty readings of the velocities of the powdered fiber.

Potassium chloride of 1×10^{-5} moles per liter was always added to all the measuring solution except the defined cases.

3) Permeability measurements

The permeability of solution passing through fiber bed was measured by the same cell as used for stream compression method. Further details of the measurement was reported in previous paper. [1)5)]

RESULTS

Equation (1) is applied to the calculation of the ζ-potential (ζ_s) from the results of the stream compression method.

$$\frac{E\eta L}{PSR} = \frac{D\zeta}{4\pi}(1-\alpha C)\tau \tag{1}$$

where E is stream potential, P is pressure difference at both ends of fiber bed, D and η are the dielectric constant and the viscosity of flowing liquid, L, S and R are the thickness, cross sectional area and electrical resistance of the bed, α is the swollen specific volume of fiber, C is fiber concentration in the bed, and τ is pore orientation factor in the bed.

ζ and α can be calculated from the intercepts of the straight line plotted $E\eta L/PSR$ against C.

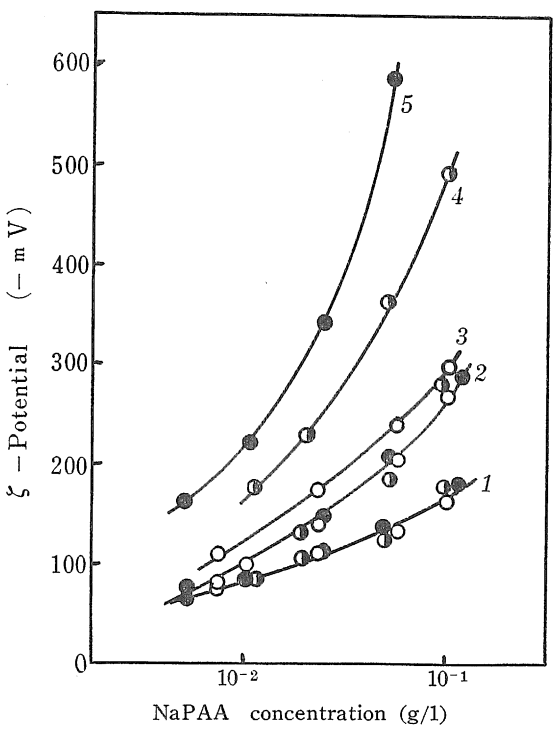
Equation (2) also provides the ζ-potential (ζ_p) from the results of electrophoretic method.

$$u = \frac{\zeta DX}{4\pi\eta} \tag{2}$$

u is the velocity of suspended fibers, and X is electric field applied externally. Taking into account the condition that the fiber diameter (2a) is about 10 micron and the electrical diffuse double layer thicknees (κ^{-1}) is 1000 Å in 10^{-5} moles/1 potassium chloride solution at 25°C, κa is larger than fifty in all measurements. Therefore, Henry's correction[6)] is not applied to the calculation of ζ-potential.

In the calculation of ζ_s and ζ_p, the viscosities adopted are obtained with a Ostwald type viscometer having shear stress of 21 dyn/cm^2 at the capillary wall. The viscosity of NaPAA solutions is dependent on shear stress. Consequently, the actual viscosity of the polymer solutions in the fiber bed must be employed for the calculation of ζ_s. For this purpose, the viscosity may be determined from a comparison of the permeation rates in the bed of water and NaPAA solutions.

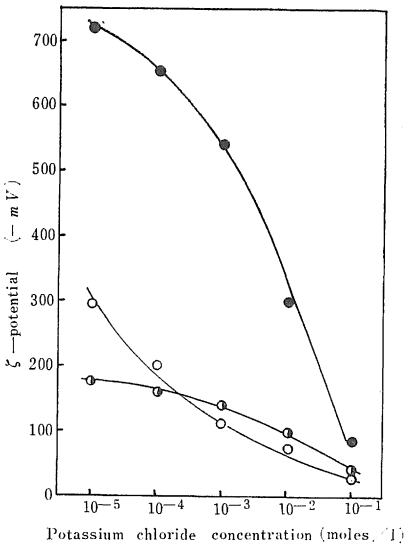
ζ_{sc} is given by applying the viscosity obtained by such a method to Eqation (1). These three groups of ζ-potential are plotted against the concentrations of NaPAA in Fig. 1. All curves rise with an increase in the concentrations of NaPAA, but the influence of molecular weight appeares only in ζ_{sc}. The variations of ζ-potential with the addition of potassium chloride are shown in Fig. 2 and 3. A plot of the relative viscosities of NaPAA solutions against the added potassium chloride concentrations is also shown in Fig. 4. Both the ζ-potential and the relative viscosity decrease with the increase in the added salt concentration. For convenience to compare with the preceding papers[1)5)], potassium chloride was used as the added ion.



1 : ζ_s 2 : ζ_p 3, 4, 5 : ζ_{sc}

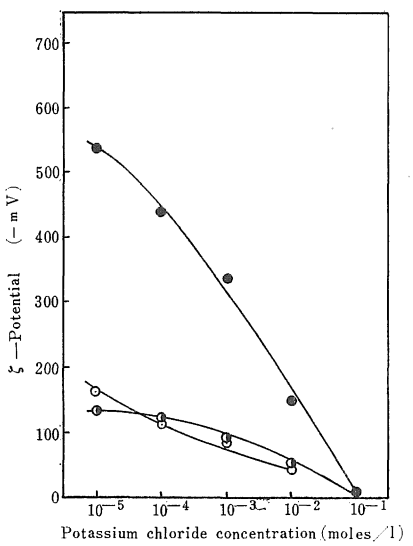
○ : NaPAA−1 ◑NaPAA−2 ◉NaPAA−3

Fig. 1 ζ-potential of cotton in NaPAA solutions containing 1×10^{-5} moles/l potassium chloride.



◑ : ζ_s ● : ζ_{sc} ○ : ζ_p

Fig. 2 The effects of potassium chloride on ζ-potential of cotton in 0.1018g/l solution of NaPAA−3.



◑ : ζ_s ● : ζ_{sc} ○ : ζ_p

Fig. 3. The effects of potassium chloride on ζ-potential of cotton in 0.0512g/l solution of NaPAA−3.

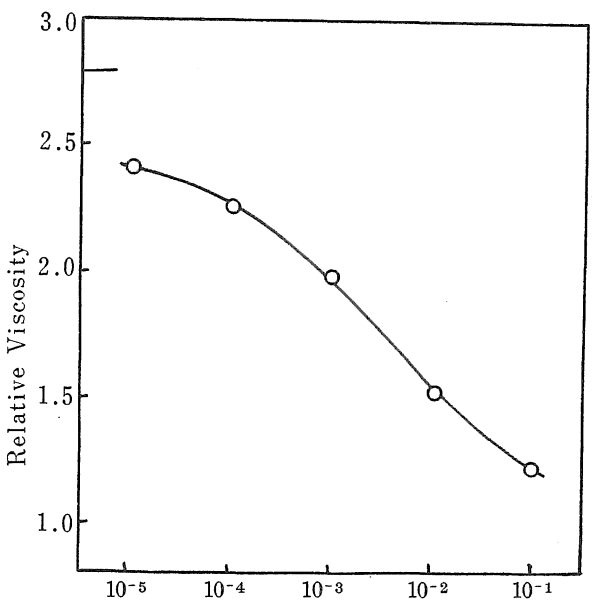


Fig. 4. Plots of viscosity of NaPAA−3 solution against potassium chloride concentration.
NaPAA concentration : 0.102g/l
Temperature : 25°C

DISCUSSION

The fact that the absolute value of ζ_p are larger than that of ζ_s are due to that the overlap of the electrical double layers produced from fiber surface and NaPAA molecule occurs more easily in stream compression method in comparison with the electrophoretic method, and that in spite of the difference of the actual viscosities in both the methods, the same viscosity is employed for the calculation of ζ-potentials. It is well known that the increase of ionic strength in a solution compresses the electrical double layer. Furthermore, in the case of polyelectrolytes, the addition of a low molecular salt accompanies the contraction in the volume of polyions, because the replusion among the ions fixed on polymer chain is shielded by the added salt ion. Thus, the increase of ionic strength tends to decrease the viscosity and the shear stress dependence of the viscosity. An information on the overlap of the electrical double layers may be obtained by measuring ζ_s and ζ_p in the various concentrations of added ions. The validity of such a correction of viscosity in the calculation of ζ_{sc} is further examined by the measurement. The results of Fig. 2 and 3 are summarized in Table 2. The difference between ζ_s and ζ_p decrease with an increase of potassium

Table 2. The Effects of Potassium Chloride on ζ-potential of Cotton in Sodium Polyacrylate Solutions.

NaPAA−3 Conc. (g/l)	KCl Conc. (mol/l)	ζ_s (−mV)	ζ_{sc} (−mV)	ζ_p (−mV)	ζ_p/ζ_s	ζ_{sc}/ζ_s
0.0512	1×10^{-5}	133.2	538.1	164.9	1.24	4.04
〃	1×10^{-4}	112.5	440.1	123.3	1.10	3.91
〃	1×10^{-3}	95.7	337.8	80.0	0.84	3.53
〃	1×10^{-2}	52.6	150.2	40.1	0.76	2.86
〃	1×10^{-1}	5.0	8.8	—	—	1.76
0.1018	1×10^{-5}	175.2	720.3	295.0	1.68	4.11
〃	1×10^{-4}	160.0	654.7	200.1	1.25	4.09
〃	1×10^{-3}	139.8	548.2	115.0	0.82	3.92
〃	1×10^{-2}	99.3	300.6	74.5	0.75	3.03
〃	1×10^{-1}	35.5	80.1	25.3	0.71	2.26
—	1×10^{-5}	44.1	44.1	42.5	0.96	1.00
—	1×10^{-4}	38.2	38.2	36.8	0.96	1.00
—	1×10^{-3}	25.2	25.2	24.0	0.95	1.00

chloride concentration. The relation of $\zeta_s<\zeta_p$ in potassium chloride concentration 1×10^{-5} moles/1 changes to $\zeta_s>\zeta_p$ in 1×10^{-3} moles/1. Accordingly, it is also concluded that the overlap of the electrical double layers occurs more easily in the stream compression method than in the electrophoresis. The viscosity correction used for the calculation of ζ_{sc} is examined next. The values of ζ_{sc}/ζ_s are almost constant when the measurements are made on 0.1g/1 NaPAA solution ranging in potassium concentration from 1×10^{-5} to 1×10^{-3} moles/1. The ζ_{sc}/ζ_s is also altered slightly by the variation in concentration of NaPAA solutions containing a constant amount of potassium chloride. Consequently, the corrected viscosity given for the calcuration of ζ_{sc} is found to be not valid as a viscosity of polymer solution flowed through fiber bed. It can be

presumed, therefore, that the flow resistance which arise from a adsorption of polymer on capillary wall or a macromolecule produced by the counter ion binding of polyelectrolytes[7] are involved in the corrected viscosity. It is further concluded from these results that ζ_p is adopted as optimum for the ζ-potential of fiber in the presence of polyelectrolytes.

SUMMARY

Stream potential and permeability measurements were made on vinylon fiber in the presence of sodium polyacrylate (NaPAA). Stream potential was measured by the so-called stream compression mathod. Electrophretic measurement was also carried out on the powdered vinylon fiber. The ζ-potential calculated by these measurements differed from each other. In particularly, the difference was remarkable, when the viscosity corrected by the permeability measurement of NaPAA solution passing through the fiber bed was employed for the results of stream potential.

It was found that the overrap of the electrical double layers produced from fiber surface and NaPAA molecule occured more easily in the stream potential than in the electrophoresis, and that such a corrected viscosity for stream potential was not valid. The electrophoretic method was well suited for the ζ-potential measurement of fiber in the presence of polyelectrolytes.

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