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ζ-POTENTIAL MEASUREMENTS OF FIBER IN THE PRESENCE OF POLYMER SOLUTION

By

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INTRODUCTION

The so-called ζ-potential measurements of fibers have been made by a number of works.[1)2)3)] Neale *et al.*[4)] and Mason *et al.*[5)] reported to measure the stream potential and stream current by a cell in which the distance between electrodes can be changed to adjust the fiber concentrations. This is named stream compression method. The method has been developed by applying the Kozeny-Carman permeability equation[6)7)] to determine the specific surface of swollen fibers. The method is suitable for the swollen fibers such as cotton fiber in aqueous solution, because both the ζ-potential and the swollen specific volume of fiber can in principle be determined by measuring a electro-kinetic function over a range of the porosities of fiber bed.

ζ-potential measurements of fiber in the presence of polymer solution have been hardly done except for the preliminary examination by Stackelberg *et al.*[8)] In a previous paper,[9)] stream potential measurements of fiber in the presence of polymer solution have been carried out by the method. The permeabilities of solution passing through the fiber bed have also been examined. It is found from the results that the stream potential relate closely to the permeability characterized by the kinds of polymer solution.

The present paper reports a considerable point caused by applying both stream compression method and permeability equation, which is the underlying principle of the method, to the polymer solutions.

PRINCIPLE OF THE METHODS

1) Electrokinetic Equation for Porous Media

The stream current i generated when a liquid undergoes viscous flow through a single capillary of uniform cross section in an electrically charged solid, by the application of a pressure P, is given by the relation

$$i=\frac{PDa\zeta}{4\pi\eta L'} \tag{1}$$

where ζ is the electrokinetic potential, a and L' are the cross sectional area and length of the capillary, and D and η are the dielectric constant and viscosity of the flowing

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liquid.

In a cylindrical bed of unconsolidated particles such as fibers, the pore structure consists of a complex network of interconnecting and tortuous pores of various sizes and shapes. Considering a layer of thickness dL in a bed of thickness L. The total streaming current I can be written by simple addition as

$$I = \frac{D\zeta}{4\pi\eta} \Sigma a \frac{dP}{dL'} \tag{2}$$

If θ is the angle between the direction of a capillary and the axis of the bed

$$\frac{dP}{dL'} = \frac{dp}{dL} \cos\theta \tag{3}$$

If the bed is uniformly packed dP/dL can be replaced by P/L.

$$I = \frac{PD\zeta}{4\pi\eta L} \Sigma a \cos\theta \tag{4}$$

When no charge is withdrawn from the system a stream potential E is established through the bed structure such that the leakback current through the bed balances the stream current. Thus from Equation (4)

$$E = \frac{PDR\zeta}{4\pi\eta L} \Sigma a \cos\theta \tag{5}$$

where R is the electrical resistance of the bed, $\Sigma a \cos\theta$ referred to as the "pore factor". Purely geometrical considerations carried out by Mason et al.[5] are as follows. Let v be the volume of a capillary per unit thickness of bed. Thus

$$a = v \cos\theta \tag{6}$$

If it is assume that the distribution functions of pore size and pore orientation are independent of one another, it can be then write

$$\Sigma a \cos\theta = S\varepsilon \overline{\cos^2\theta} \tag{7}$$

where S is the cross sectional area of the bed, ε is the void fraction $\Sigma v/S$ and $\overline{\cos^2\theta}$ is averaged over all pores. The void fraction ε can be written $(1-\alpha c)$, where α is the swollen specific volume of the fibers and C is the concentration of solids in the porous bed. The pore factor thus becomes

$$\Sigma a \cos\theta = S(1-\alpha c)\overline{\cos^2\theta} = S(1-\alpha c)\tau \tag{8}$$

$$\text{where} \quad \tau = \overline{\cos^2\theta}$$

using this notation, Equation (5) may therefore be written as below

$$\frac{E\eta L}{PSR} = \frac{D\zeta}{4\pi} (1-\alpha c)\tau \tag{9}$$

For flow through beds of randomly packed cylindrical particles, Mason⁶⁾ calculate τ to be 1/2. The value which auther adopts here is 1/1.2 as described in previous paper.⁹⁾

In using Equation (9) to calculate ζ, all quantities are known or can be determined experimentally except the swollen volume α. If this equation is applicable, and stream potential is measured over a range of bed concentrations, ζ and α can be calculated from the intercepts of the straight line plotted $E\eta L/PRS$ against the pad concentration C.

2) Permeability Equation for Porous Media

The rate of viscous flow of a fluid through a bed of porous material under the action of a hydrostatic pressure whose gradient is directed across the bed is given by Darcy's law

$$Q=\frac{KSP}{\eta L} \tag{10}$$

where Q is the volume rate of flow through the bed, K is permeability coefficient of the bed.

On the other hand, the permeability coefficient K of a porous bed is given by the generalized form of the Kozeny-Carman equation :

$$K=\frac{\overline{\cos^2\theta}}{k_0\,S_0^2}\frac{\varepsilon^3}{(1-\varepsilon)^2}=\frac{1}{kS_0^2}\frac{\varepsilon^3}{(1-\varepsilon)^2} \tag{11}$$

where k_0 is a shape factor characteristic of the channels, S_0 is the surface area presented to the flowing liquid per unit volum of bed material. The shape factor and orientation factor $\overline{\cos^2\theta}$ are considered to bo constant and are combined as a single factor $k=k_0/\overline{\cos^2\theta}$.

Substituting ε described above in Equation (11), we have

$$K=\frac{1}{kS_0^2}\frac{(1-\alpha c)^3}{\alpha^2c^2} \tag{12}$$

It will be noted that $\alpha S_0=\sigma$, where σ is the external surface area per gram of fibrous material. Equation (12) becomes

$$(Kc^2)^{1/3}=\frac{1}{(k\sigma^2)^{1/3}}(1-\alpha c) \tag{13}$$

For flow through beds of randomly packed plugs of cotton, wool, rayon and glass wool fibers, Fowler and Hertel obtained k to be 5.55.

Measurements of K at different concentrations C can be used to determine α, in addition to σ, and the α thus computed should be identical with that in Equation (9).

EXPERIMENTAL

1) Materials

The fiber sample was vinylon of 1 denier and 1.5 mm length. The fiber was exracted with alcohol-benzol (1 : 2) mixture by a Soxhlet extractor, and then with ethyl ether. The sample after extracting was washed with conductivity water of 1×10^{-6} mho. cm^{-1} and was stored in desiccator until used for measurements. Water-soluble polymers used are shown in Table 1. polyethylene oxide (PEO) and sodium polyacrylate (SPA) were purified with acetone containing 5% of water and methanol containing 10% of water, respectively. Tororo-aoi mucilage (TA) was prepared by conventional method with water from a root of Tororo-aoi, and was not purified.

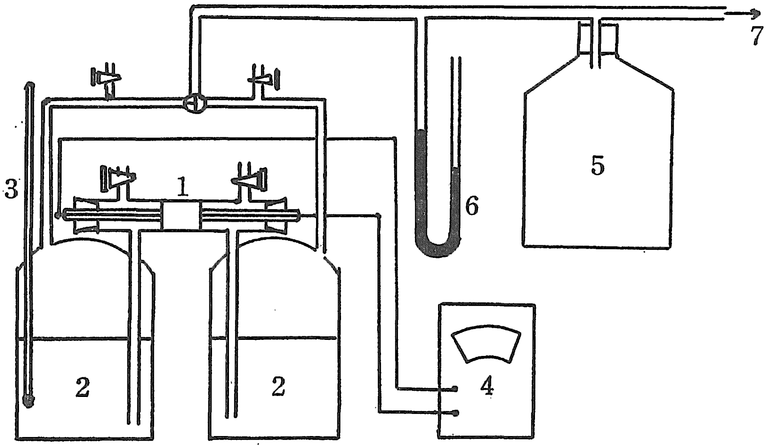
Table 1. Molecular Weight of Polymers.

Polymer	Sign	$[\eta]$ (dl/g)	Molecular weight
Polyethylene oxide	PEO	15.0[a)]	3.54×10^6
Sodium polyacrylate	SPA	6.3[b)]	4.40×10^6
Tororo-aoi	TA	—	—

a) $[\eta]=6.4\times10^{-5}M^{0.82}$ in water at 35°C[10)]
b) $[\eta]=6.52\times10^{-3}P^{0.64}$ in 2N-NaOH at 25°C[11)]

2) ζ-potential Measurements by the Stream Compression Method

The apparatus used for measurement was shown in Fig. 1. The fiber to be examined was packed into the cell, 2. 4 cm in diameter, with two platinum electrodes whose



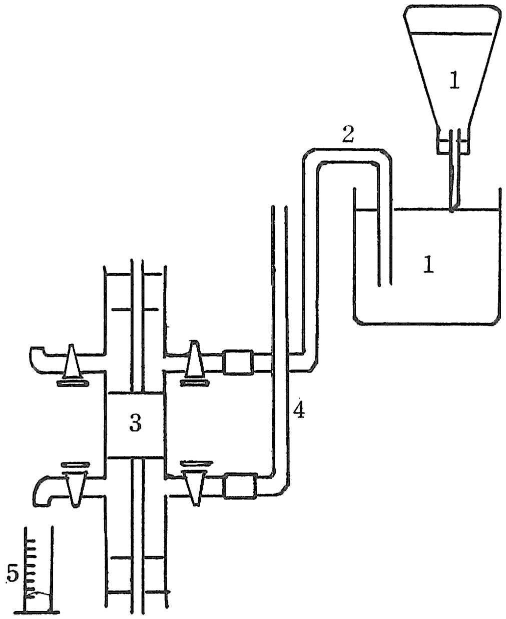
1. Cell, 2. Reservoir, 3. Thermometer, 4. Voltammeter,
5. Buffer-jar, 6. Manometer, 7. Aspirator

Fig. 1 Apparatus for stream potential measurement.

mutual distance can freely be changed. The cell was so constructed that it was easily obtained various fiber concentrations by changing a distance between electrodes. The potential measurement was carried out with the alternate supply of solution from both reservoirs (2)under the pressure at 25°C. Potassium chloride of 1×10^{-5} moles per liter was added to all the measuring solutions. D. C. Voltammeter (PM-18C) of Toa Denpa Kogyo Co., Ltd. was used to measure the stream potential. The electrical resistance measurement of the fiber bed was carried out with 800 cycle conductance (MY-7) of Yanagimoto Co., Ltd.

3) Permeability Measurement

The permeability of solution passing through fiber bed was measured by the same cell as used for stream potential measurements. The apparatus was set up as illustrated in Fig. 2. The solution was made to flow through bed out of reservoirs (1). Permeability coefficents were also obtained in various fiber concentrations as described above.

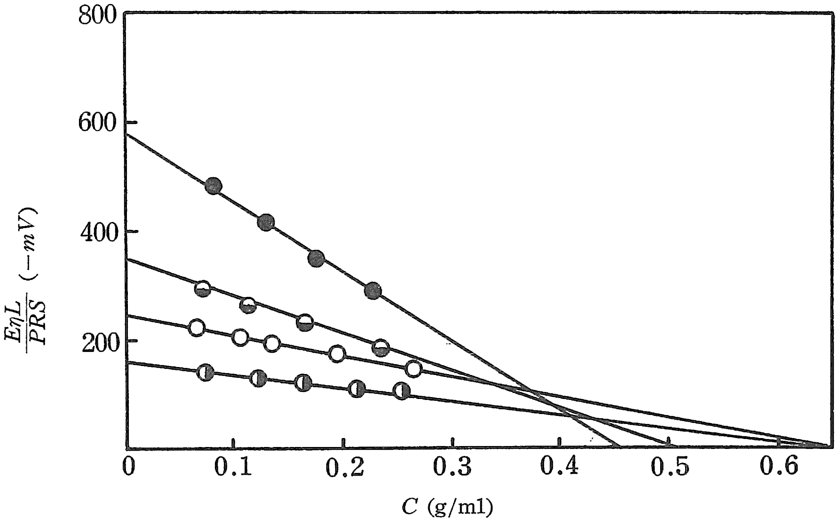


1. Reservoir, 2. Syphon, 3. Cell, (Bed)
4. Manometer, 5. Measuring-flask.

Fig. 2 Apparatus for permeability measurement.

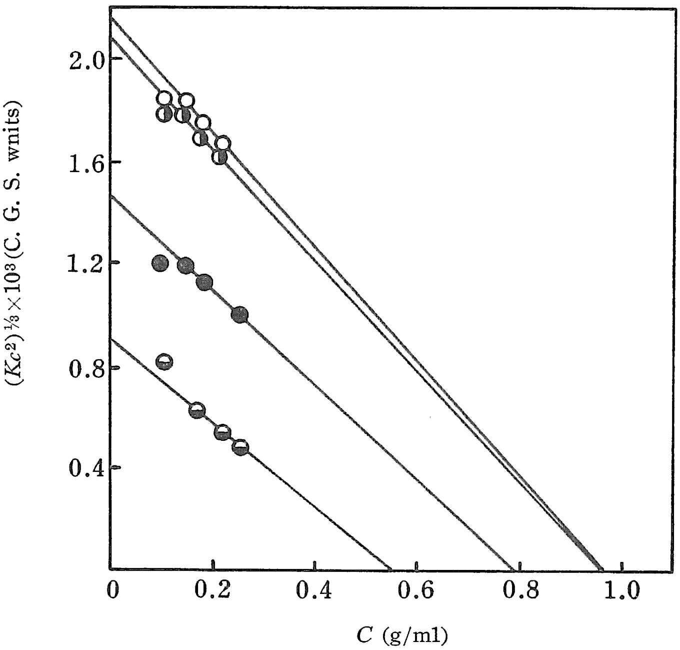
RESULTS

Stream potential and permeability measurement were carried out on the bed of vinylon fiber of various concentrations. Table 2 summarizes the results obtained. Plots of $E\eta L/PRS$ against the bed concentration C yield straight lines. Plots of $(Kc^2)^{1/3}$ against C also give straight lines. Fig. 3 shows the plots for $E\eta L/PRS$ vs. C, and Fig, 4 for $(Kc^2)^{1/3}$ vs. C. From these plots, values of ζ, specific surfaces and specific volume, α, of the swollen fiber were obtained by the intercept method.



○ : Water, ◑ : PEO (0.03g/1), ● : SPA (0.03g/1) ◒ : TA (0.018g/1)

Fig. 3 Plots of $E\eta L/PRS$ against fiber concentration C



○ : Water, ◑ : PEO (0.03g/1), ● : SPA (0.03g/1),
◒ : TA (0.018g/1)

Fig. 4 Plots of $(KC^2)^{1/3}$ against fiber concentration C

It is noted from the results in Table 2 that the stream potential data in all solutions yield α values which are significantly greater than those caluculated from permeability data. According fo the theory these values should be identical.

Table 2. Discrepancy between the α Values from Stream and Permeability methods.

Permeant	ζ (-mV)	α from Stream Potential (ml/g)	α from Permeability (ml/g)
KCl (10^{-5}M/1)	49.5	1.57	1.06
PEO (0.03g/1) + KCl (10^{-5}M/1)	30.1	1.57	1.06
SPA (0.03g/1) + KCl (10^{-5}M/1)	110.2	2.22	1.30
TA (0.018g/1) + KCl (10^{-5}M/1)	61.5	1.96	1.81

DISCUSSION

The discrepancy between the α values from stream and permeability methods must be explained.

The "permeability" α value for vinylon in water containing 10^{-5} moles KCl per liter in Table 2 shows considerably agreement with swollen volume, 1.2ml/g, computed from thh another experiment,[12] using a weight method.[13] It is resonably certain that the true swollen volume of vinylon in bed in water is 1.06ml/g.

The "permeability" α values for vinylon in PEO, SPA and TA solutions are greater than that in water. The fact is due to the decrease of the permeability of polymer solutions passing through the bed. The permeability decrease arises from the adsorption and the non-Newtonian flow of polymer solutions, because it is impossibly considered that the swollen volumes of vinylon in the polymer solutions are greater than that in water. Thus it must be explained that the α values from stream measurements are greater than true swollen volume of the fiber.

An assumption involved in deriving the Equation (9) is that the dimensions of the space charge are negligible compared with the diameter of the capillaries through which flow occurs. This is valid in the bed as is described in previous paper.[9] that is to say, the equivalent pore radius computed from permeability data is about 1.38×10^{-3} at a bed concentration of 0.23g/ml. Whereas, the thickness of the Gouy-Chapman diffuse layer in 10^{-5} moles/1 KCl solution is 1×10^{-5} cm. The distortion of the space charge distribution of single isolated layer is caused by bringing a similar layer within a distance of five times.[14] Consequently, the large α value from stream measurement cannot be attributed to the layer thickness effect. This discrepancy of α was recognized by Mason et al. for sulphite pulp and cotton in water, and they interpreted it in terms of a diffuse boundary of considerable thickness called the β-layer, in which partially dissolved molecules and groups of molecules, bearing an electrical charge, extend into the liquid. The presence of the layer consisting of partially dissolved molecules such as β-layer can also be expected for vinylon fiber, since the discrepancy is recognized even in water which is free from polymers.

It is interesting that in the examined solutions the order of the magnitude of α from streaming measurement is the same as that from permeability. The fact shows that the large α values in polymer solutions are attributed to the neglect of viscosity change resulted from increasing non-Nwetonian flow with increase of fiber concentrations, and that the effect of polymer adsorption may be underestimate. It can therefore be presumed that if the correction of viscosity is applicable, both the stream compression and permeability methods are valid for the determination of ζ, α and surface area of fiber in the polymer solutions.

SUMMARY

ζ-potential measurements of vinylon fiber in the presence of polymer solutions were carried out by the stream compression method. The polymers used were polyethylene oxide (PEO), sodium polyacrylate (SPA) and Tororo-aoi mucilage (TA). The relation between the stream compression method and permeability equation which is the underlying principle of the method was discussed. The stream potential data in all solutions yielded the swollen specific volums of fiber, α, which were significantly greater than those calculated from permeability data. The discrepancy between the α values from stream and permeability methods was interpreted by the β-layer, in which partially dissolved molecules of fiber, bearing an electrical charge, extend into the liquid. Futhermore, the α values from both methods for vinylon in polymer solutions were greater than that in water. It is presumed that the large α values in polymer solutions arise from the non-Newtonian flow of the solutions, and that with viscosity correction both the stream compression and permeability methods are valid for the determination of ζ, α and surface area of fiber in polymer solutions.

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