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Diffusion Phenomena of Small Molecules in Polyelectrolyte Solutions

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SUMMARY

From diffusion data of xylose in poly (acrylic acid) and in poly(sodium acrylate) aqueous solutions, the behaviour of these polymers in solution is discussed. When these polyelectrolytes are ionized and expanded in water, consequently, the diffusion phenomena of xylose in these solutions follows the theory of linear macromolecules in solution. When NaCl is added in poly (acrylic acid) solution, the polymer chain contracts and becomes spherical. Therefore, xylose cannot pass through the polymer domain. With poly(sodium acrylate), however, an effect of salt has not been found. Furthermore, effects of neutralization are discussed.

INTRODUCTION

In general, the diffusion rate of small molecules in solution is inversely proportional to the viscosity of the solvent, but when macromolecules exist in this medium, the diffusion rate does not decrease so much despite remarkable increment of solution viscosity.

Previously we proposed that the diffusion rate of small molecules in solution of linear macromolecules depends on the volume fraction of polymer chain v_p as represented by eq.(1), and that in solution of rigid and spherical macromolecules it depends on the volume fraction of polymer domain ϕ according to eq.(2).

$$D/D_0 = [(1 - v_p)/(1 + v_p)]^2 \qquad (1)$$

$$D/D_0 = (1 - k\phi) \qquad (2)$$

In this paper, the diffusion phenomena of small molecules in polyelectrolyte solutions are discussed.

EXPERIMENTAL

Materials

Poly (acrylic acid) (PAA) and poly (sodium acrylate) (PA-Na) were synthesized. The viscosity average molecular weights were calculated 14.4×10^4 and 15.5×10^4, respectively, from the following equations ;

for PAA in dioxane at 30°C

$$[\eta] = 7.6 \times 10^{-4}\ M^{0.5}$$

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for PA-Na in 2M-NaOH aq. at 25°C

$$[\eta] = 4.22 \times 10^{-4} M^{0.64}$$

Xylose was used as the diffusing substance.

Viscosity Measurements

The viscosity of each solution was measured with Ubbelohde type viscometer.

Diffusivity Measurements

Diffusivity measurements were carried out by HITACHI Tiserius Electrophoresis Apparatus equipped with Schlieren optical system. Polyelectrolyte aqueous solution was injected into the upper layer of Neurath Cell as solvent. Xylose was dissolved in this aqueous solution in 0.5 g/100 ml concentration and the mixture was injected into the lower layer of the cell. The average diffusion coefficient can be calculated from the following equation,

$$D = A^2 / 4\pi H^2 t \qquad (3)$$

where A and H are the area and the maximum height of the diffusion curve, respectively, and t is the diffusion period. Temperature was kept constant at 25°C.

RESULTS AND DISCUSSION

Diffusivity of xylose in PAA aqueous solutions is shown in Fig. 1 and that in PA-Na aqueous solutions in Fig. 2. In these figures, solid lines and broken lines are theoretical curves calculated from eq.(1) and eq.(2), respectively, and open circles are experimental values.

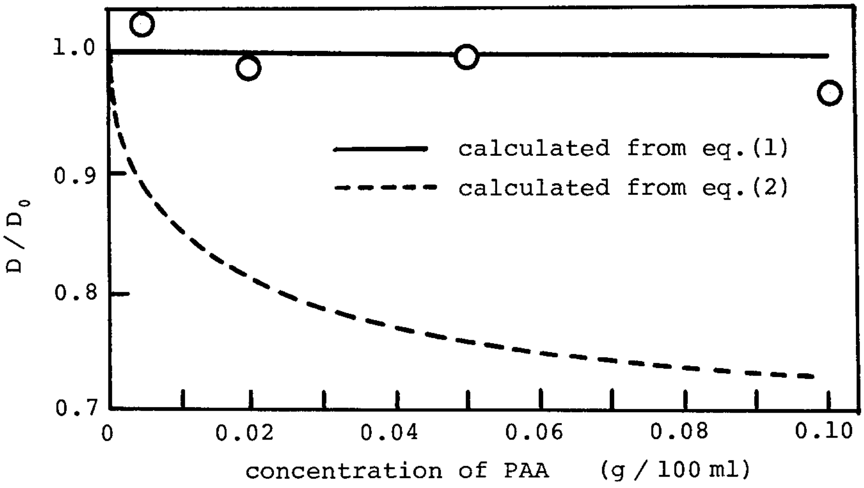

Fig.1 Diffusivity of xylose in PAA aqueous solutions

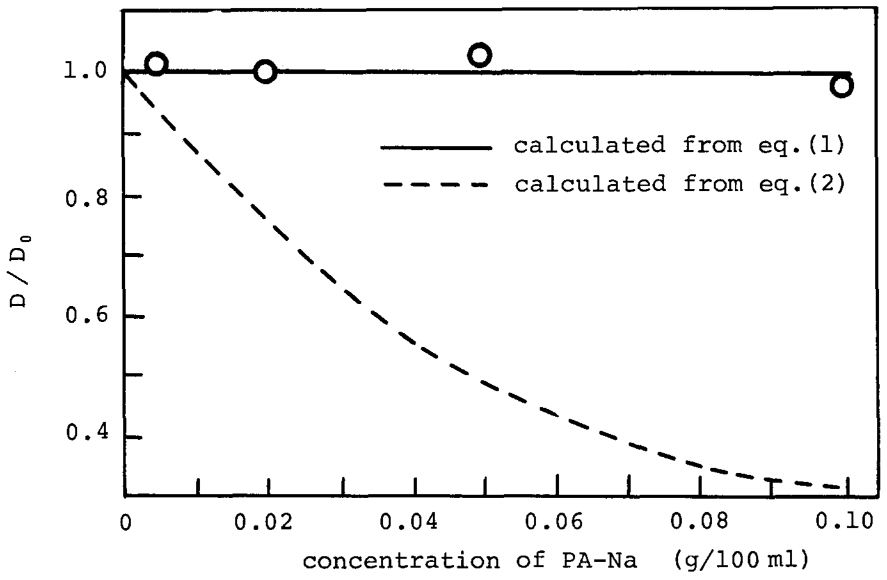

Fig. 2 Diffusivity of xylose in PA-Na aqueous solutions

ϕ in eq.(2) can be obtained from the following equation;

$$c\psi = 100\phi \tag{3}$$

where ψ is the specific volume of polymer in solution and calculated by eq.(4).

$$\eta_{sp} = 2.5\left(\frac{c\psi}{100 - c\psi}\right) + 4.4\left(\frac{c\psi}{100 - c\psi}\right)^2 \tag{4}$$

From these figures, it becomes clear that the diffusion phenomena of xylose follow eq.(1), that is to say, the molecules of polyelectrolytes in water expand similarly to the linear macromolecules in good solvent.

Then a certain amount of NaCl was added into these polyelectrolytes aqueous solutions and the diffusivity of xylose was measured. The results for the solutions in which NaCl was included in 0.01 mol/l concentration are shown in Fig. 3 and Fig. 4. Symbols are the same as Fig. 1 and Fig. 2.

It is known from these results that the diffusivity of xylose in PAA - NaCl aqueous solutions follows eq.(2), and in PA-Na - NaCl aqueous solutions follows eq.(1). That is to say, the molecules of PAA contract and give the same effect as the rigid and spherical macromolecules, but the molecules of PA-Na remain expanded because PA-Na is the strong electrolyte and 0.01 mol/l of NaCl is too small to compensate electric repulsion.

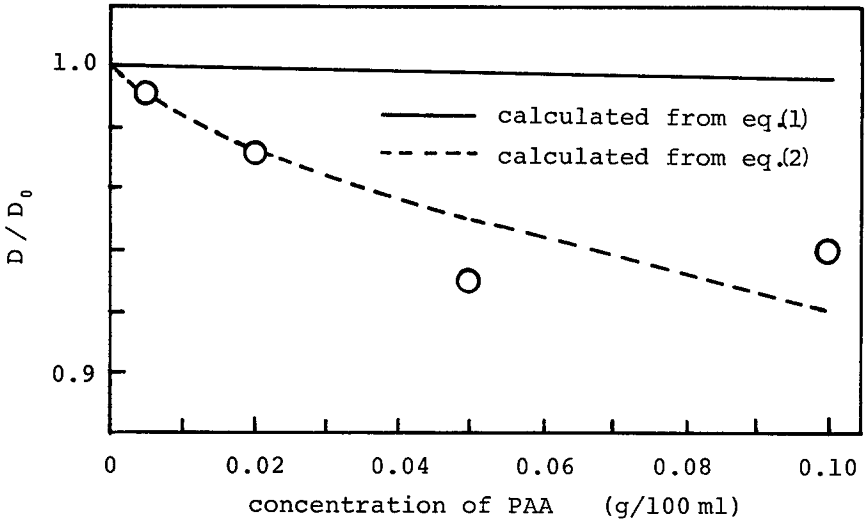

Fig.3 Diffusivity of xylose in PAA - NaCl aqueous solutions (concentration of NaCl : 0.01 mol/l)

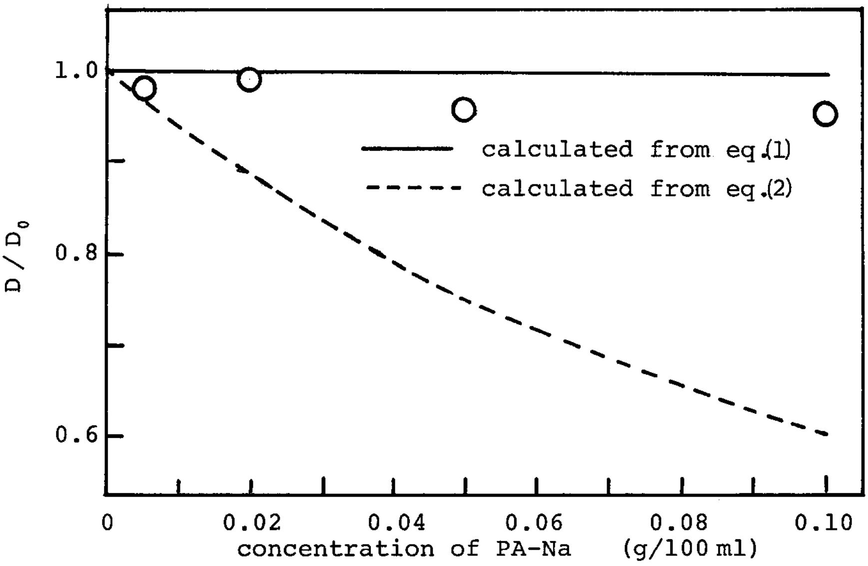

Fig.4 Diffusivity of xylose in PA-Na - NaCl aqueous solutions (concentration of NaCl : 0.01 mol/l)

A certain amount of NaOH was added into each PAA aqueous solution to control the degree of neutralization (DN). In this paper, the percent of the amount of carboxyl group which corresponds to added NaOH in solution is defined as the DN. In Fig.5, diffusivity of xylose in the neutralized PAA aqueous solutions is plotted against DN.

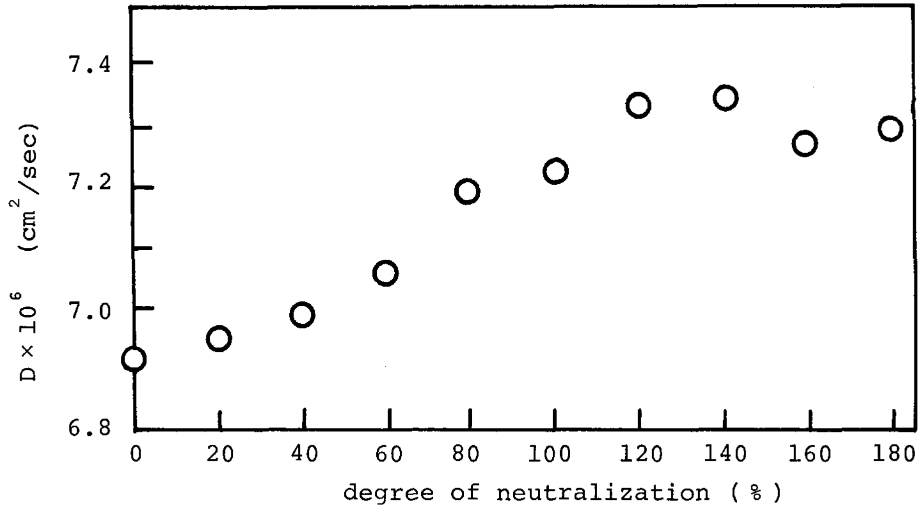

Fig. 5 Diffusivity of xylose in neutralized PAA aqueous solutions (Concentration of PAA : 0.02 g/100 ml)

As polyelectrolyte molecules expand by neutralization, the diffusion coefficient of xylose increases with increment of DN. Above 100 % DN, however, the conformation of polymer molecules becomes stationary and the diffusion coefficient of xylose does not change remarkably.

REFFERENCES

BRANDRUP,J. and IMMERGUT,E.H. (Edit) : Polymer Handbook (2nd ed.), New York, London, Sydney, Toronto : John Wiley & Sons 1974.
KANEKO,K. : Kogyo Kagaku Zasshi, 44, 471 (1941).
NAKAGAWA,M., ISHIDA,S. and KANEKO,K. : Kobunshi Kagaku 29, 661 (1972).

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