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Note

Interaction of cycloamyloses with polymers

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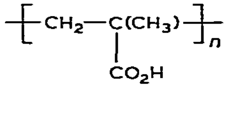
It is well known that cycloamyloses occlude various small molecules[1], such as benzene, naphthalene, and other aromatic compounds.

We reported the diffusion behavior of cyclohexaamylose (**1**) and cycloheptaamylose (**2**) in aqueous poly(methacrylic acid) (**4**), copoly(methacrylic acid–styrene), and poly(styrenesulfonic acid) (**5**) solutions[2]. The diffusion coefficients decreased with the concentration of the polymers, and the descending tendencies were successfully explained by means of (*a*) obstruction, and (*b*) interaction effects. Both of these cycloamyloses interact, for example, **2** interacts with **4**, with a binding constant of ~10 at 25°. In the previous report, we discussed fully the interaction of these systems. In this note, a study on the interaction of cyclooctaamylose (**3**) with **4**, **5** (degree of sulfonation: 100%), and the poly(aminesulfone) (**6**) is presented.

EXPERIMENTAL

Cyclooctaamylose (**3**) was prepared by the action of *Bacillus macerans* cycloamylose glucanotransferase on potato starch. The conventional method[3] was modified slightly to increase the yield of **3**. The method of preparation will be published



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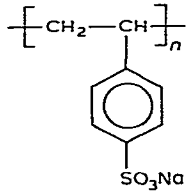

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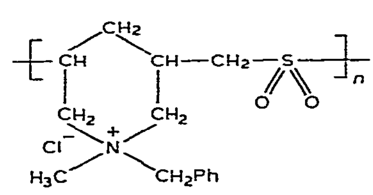

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elsewhere. The polymers used, **4** and **5**, were the same as those in the previous report[2]. Polymer **6** was kindly supplied by Nittohboseki Co., and had a molecular weight of 20,000. The polymer was purified by ultrafiltration through a Diafilter G 10T (Bio-engineering Co.).

The diffusion coefficient of **3** in the polymer solution was determined by means of a Hitachi Tiselius HTB-2 apparatus with a Neurath-type diffusion cell[2]. The initial concentrations of **3** were 7.71, 7.71, and 10.8 mmol/L in aqueous **4**, **5**, and **6** solution, respectively.

RESULTS AND DISCUSSION

The results are shown in Figs. 1, 2, and 3 in comparison with the values for **1** and **2** (ref. 2). Clear evidence for interaction between **3** and the polymers is observed. The descending tendencies of the relative diffusion-coefficients (D/D_0) for **3** with polymer concentration cannot be explained solely by the obstruction effect as expressed[4] by Eq. (*1*),

$$D/D_0 = 1 - \phi C_{po} \quad (1),$$

where D and D_0 are integral diffusion coefficients in aqueous polymer solution and in water, respectively, C_{po} is the polymer concentration, in g/100 mL, and ϕ is a constant, being 0.026 for **4** and 0.025 for **5**.

Here we assume the equilibrium of Eq. (*2*) between a polymer repeating-unit P, and **3**, and determine the equilibrium constant K of the reaction

$$\mathrm{P} + \mathbf{3} \rightleftharpoons \mathrm{P}\cdot\mathbf{3} \quad (2),$$

by means of Eq. (*5*) of the previous report[2], assuming (*a*) only the unbound free species of cycloamylose in Eq. (*2*) can be transported in the medium, and (*b*) that the establishment of the local equilibrium expressed by Eq. (*2*) is much faster than the transport phenomena in this system. The values of K are shown in Table I. The solid lines for **2** and **3** in Figs. 1 and 2, and for **1**, **2**, and **3** in Fig. 3, are the theoretical curves having a constant K.

The order of magnitude of K, namely, **2** > **3** > **1** ~ 0 for **4** and **5** and **1** =

TABLE I

FORMATION CONSTANTS FOR COMPLEXES (L/mol) OF CYCLOAMYLOSES WITH **4**, **5**, AND **6**

Cycloamylose	**4**	**5**[a]	**6**
1 (hexa)	0[b]	0[b]	4.5
2 (hepta)	10.2[b]	6.0[b]	4.5
3 (octa)	7–9	2.2	1.2

[a]Sodium salt. [b]See ref. 2.

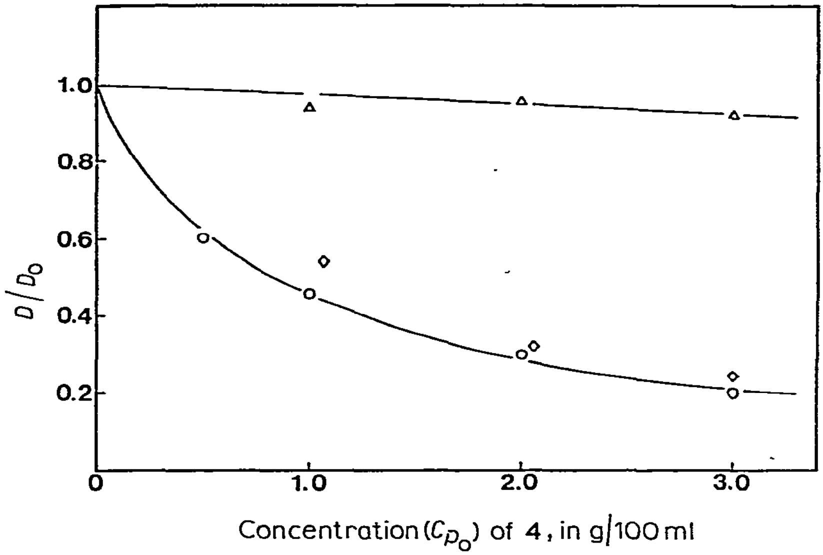

Fig. 1. Relative diffusion-coefficients *vs.* concentration of **4** at 25°. △: **1**; ○: **2**; and ◇: **3**; degree of neutralization of **4** = 0.

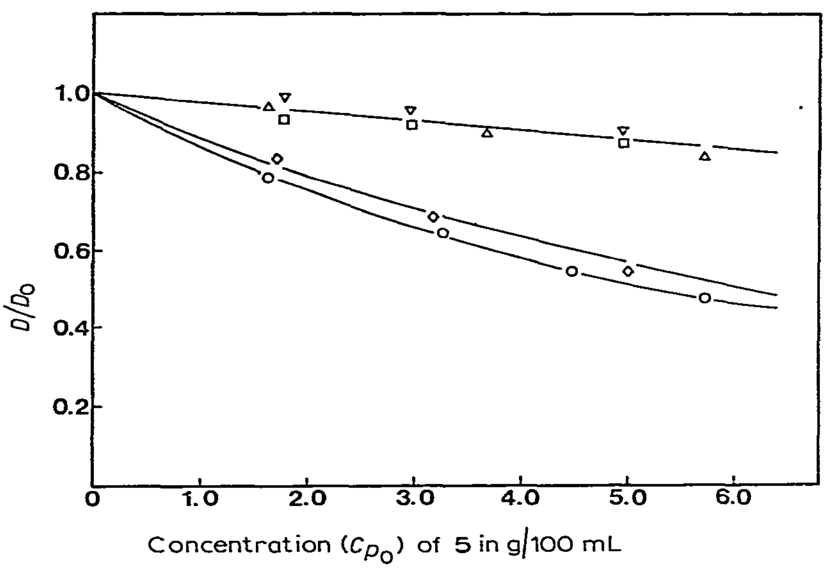

Fig. 2. Relative diffusion-coefficients *vs.* sodium **5** (degree of sulfonation = 100%) at 25°. △: **1**; ○: **2**; and ◇: **3**; ▽: 2-acetamido-2-deoxy-D-glucose; and □: raffinose.

2 > **3** for **6**, suggests a complicated mechanism for the interaction in the individual system. The possibility of an inclusion-type interaction with specific groups of the polymer in relation to the cavity size of a cycloamylose is a matter of great interest.

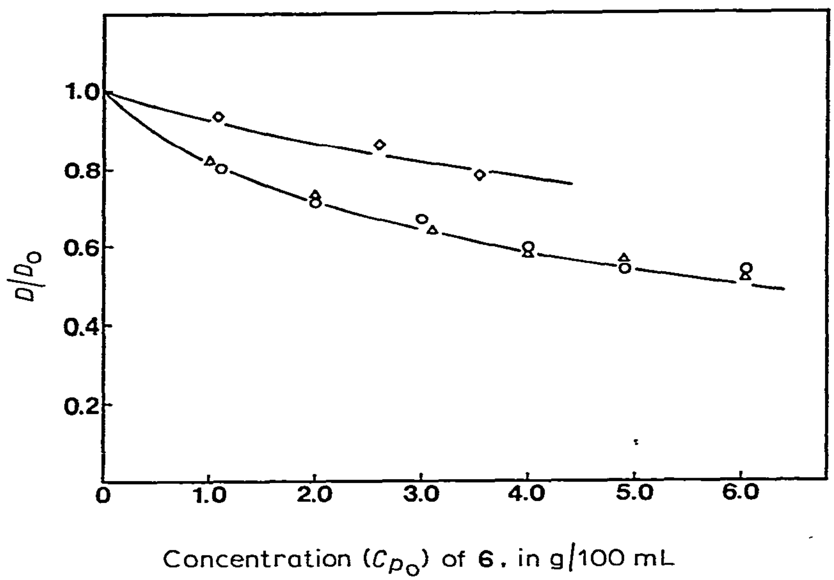

Fig. 3. Relative diffusion-coefficients *vs.* concentration of **6** at 25°. △; **1**: ○: **2**; and ◇: **3**.

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