

# Swelling of Hydrophilic Polymers. IV

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## SYNOPSIS

The swelling of five types of spherical crosslinked dextrans (Sephadex) that are either nonionic (G) or ionic [carboxymethyl (CM), sulphopropyl (SP), diethylaminoethyl (DEAE), and diethyl-(2-hydroxypropyl)aminoethyl (QAE)] in the same skeleton has been studied in water at different dissolved oxygen concentrations by microscopic observation and by dilatometry. The maximum specific volume,  $V_{\max}/V_0$  obtained by microscopic observation increased with the lowered dissolved oxygen concentration for each Sephadex. The change of the maximum specific volume was closely related to the changes of the dissolved oxygen concentrations. The maximum changes of the total volume took the larger negative values at the lower dissolved oxygen concentration. The effect of the difference in the dissolved oxygen on the change of the total volume with swelling was closely related to the viscosity  $B$  coefficient of the Jones–Dole equation. From these results, we conclude that the structure of water on the inside of the gel differs from that on the outside of the gel. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

This study constitutes the fourth in a series dealing with the swelling of hydrophilic polymers.<sup>1–3</sup> In a previous work, we reported the dilatometrical study on the swelling of crosslinked dextrans (Sephadexes) with water.<sup>3</sup> Our preliminary experiments revealed that changes of total volume, including gel and surrounding bound-water layers, were different when boiled water or deionized water was used. Also in our study on the swelling of dried foods,<sup>4</sup> the volume change of foods and the amounts of elution of the soluble components with swelling were much different when the water contained air or when deaerated water was used. From these results, we presumed that the dissolved air in water greatly affects the swelling of hydrophilic polymers.

The present study was undertaken to discuss the effect of dissolved air on the swelling of Sephadexes by picture analysis with a microscope-videotape recorder (VTR) system and by dilatometry.

## EXPERIMENTAL

Sephadex G-50 (crosslinked dextrans from Pharmacia)<sup>5</sup> for gel filtration (Abb. G) and four ion exchangers containing different dissociable species having different ionic concentrations [carboxymethyl (CM), sulphopropyl (SP), diethylaminoethyl (DEAE), and diethyl-(2-hydroxypropyl)amino-ethyl (QAE)] were used. Details are in our previous work.<sup>2</sup>

Normal water at equilibrium with air contains about 16 mg/L of nitrogen, 7 mg/L of oxygen, and a little of the inert gases. As a criterion of the concentration of dissolved air in water, concentration of the dissolved oxygen,  $c_{DO}$  was measured with a dissolved oxygen meter (HORIBA Co. DO-8F), and the change of the concentration of dissolved oxygen was measured with a DO meter connected to a recorder.

As shown in Figure 1, the principle of the DO meter is to measure the potential of a redox system of an anode (Pb) and a cathode (Ag) in an alkaline electrolyte solution in a glass tube. The cathode (Ag) is in contact with a thin oxygen transfer diaphragm and constitutes the bottom of the glass tube. The potential development at the redox system is proportional to amount of oxygen transferred through

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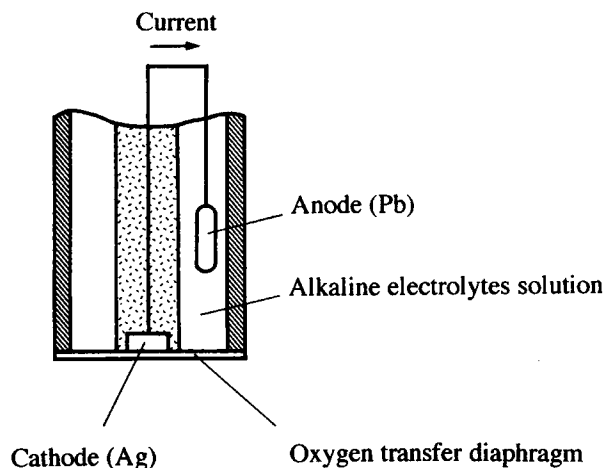


Figure 1 Constitution of dissolved oxygen electrodes.

the diaphragm. Oxygen measured by this method is assumed to be in a molecularly dispersed state, however, detail information of oxygen state in water cannot be discussed at the present time.

The deaerated water was made by boiling water in a Myer flask and storing it sealed with silicone rubber stoppers. The  $c_{DO}$  of deaerated water was  $0.8 \pm 0.1$  mg/L at room temperature. Deionized water in equilibrium with air was used for normal water.

Water having different concentrations of  $c_{DO}$  was obtained by mixing deionized water ( $c_{DO} = 7.0 \pm 1.0$  g/L) and deaerated water in a glass syringe.

For the visual analysis, small amounts of the Sephadexes were set on glass slides of a microscope (Nikon Microphoto-FX) connected to VTR and 2–3 mL of water were added dropwise on the particles from a hypodermic needle. The volume changes of the particles were videotaped. The details for the analysis are in our previous work.<sup>1</sup> The measurements are volume change of the particle itself and it is represented as gel volume  $V$ .

Total volume changes of the Sephadexes and water system were measured by dilatometry. Details are in our previous study<sup>3</sup> and the total volume change is represented as  $\Delta v$ .

## RESULTS AND DISCUSSION

### Microscopic Observation and Dissolved Oxygen Measurements

Figure 2 shows a typical picture of the swelling states after 30 s in deaerated and normal water. Figure 3 shows a time course of the ratio of the gel volume at time  $t$ ,  $V_t$  to the initial gel volume  $V_0$  for CM.

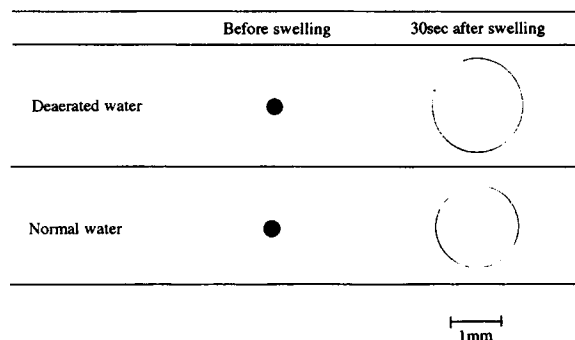


Figure 2 Diagrammatic representation of a CM-Sephadex particle before and 30 s after swelling in deaerated water and in normal water.

$V_t/V_0$  increases with the passage of time in any dissolved-oxygen-containing water and shows simple saturation kinetics. The process for the change in gel volume can be treated as first-order kinetics.

The maximum specific volumes,  $V_{max}/V_0$ , that is, the ratio of the saturation value of  $V_t$ ,  $V_{max}$ , to the initial volume,  $V_0$ , in the different dissolved-oxygen-containing waters and the apparent rate constant of the first-order kinetics  $k$  are listed in Table I. The maximum specific volumes,  $V_{max}/V_0$  increase with the lower dissolved oxygen concentration for each of the Sephadexes. pH of water with Sephadexes did not change for alteration of dissolved oxygen, therefore, volume change of gel in this experiment is not due to a change of pH.

Figure 4 shows a plot of the maximum specific volume  $V_{max}/V_0$  vs. the dissolved oxygen concentration  $c_{DO}$ . The effect of dissolved oxygen on specific volume is greatest for CM and follows for SP, DEAE,

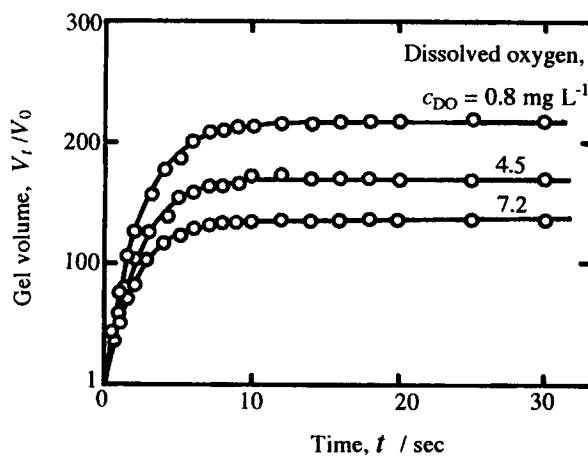


Figure 3 Effect of dissolved oxygen on the time course of the swelling of CM-Sephadex obtained by microscopic observation at 25°C.

**Table I Effect of Dissolved Oxygen on First-Order Kinetic Parameters of the Swelling of Sephadexes**

Sephadex <sup>a</sup>	Dissolved Oxygen Conc. ( $c_{DO}/\text{mg L}^{-1}$ )	Specific Volume ( $V_{\max}/V_0$ )	Rate Constant ( $k/\text{s}^{-1}$ )
G	0.8	$19.1 \pm 6.8$	$0.121 \pm 0.165$
	4.5	$17.1 \pm 5.3$	$0.101 \pm 0.018$
	7.2	$16.4 \pm 2.7$	$0.153 \pm 0.055$
CM	0.8	$217.5 \pm 61.3$	$0.429 \pm 0.221$
	4.5	$171.0 \pm 39.8$	$0.457 \pm 0.071$
	7.2	$136.1 \pm 59.4$	$0.479 \pm 0.139$
SP	0.8	$140.6 \pm 51.2$	$0.256 \pm 0.095$
	4.5	$113.3 \pm 40.4$	$0.276 \pm 0.051$
	7.2	$49.5 \pm 5.9$	$0.281 \pm 0.086$
DEAE	0.8	$78.7 \pm 15.5$	$0.293 \pm 0.133$
	4.5	$65.2 \pm 21.6$	$0.296 \pm 0.103$
	7.2	$48.9 \pm 2.4$	$0.332 \pm 0.152$
QAE	0.8	$100.0 \pm 23.3$	$0.298 \pm 0.160$
	4.5	$78.7 \pm 16.7$	$0.292 \pm 0.074$
	7.2	$68.5 \pm 24.3$	$0.310 \pm 0.121$

<sup>a</sup> Crosslinked dextrans G, without ionic group; CM, with sodium carboxymethyl; SP, with sodium sulfopropyl; DEAE, with diethylaminoethyl chloride; QAE, diethyl-(2-hydroxypropyl)aminoethyl chloride

QAE, and is least for G, which has no dissociation groups.

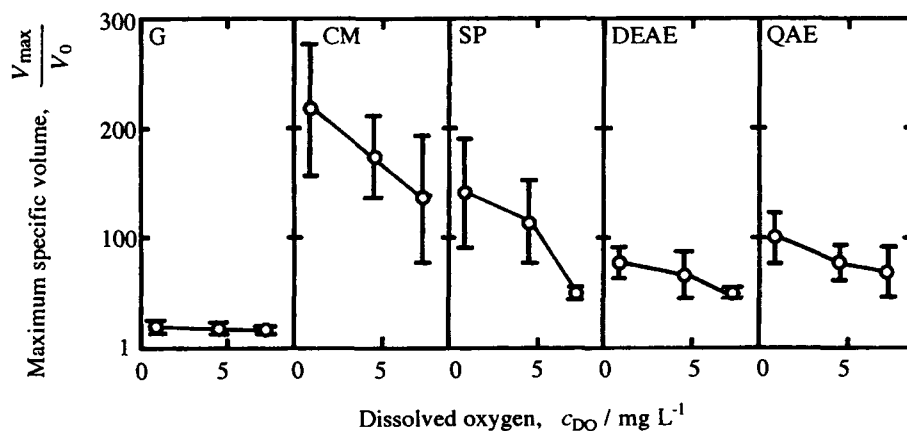
Figure 5 shows the relationship between the rate constant  $k$  and the dissolved oxygen concentration  $c_{DO}$ . The effect of dissolved oxygen  $c_{DO}$  on  $k$  is almost the same as that on the maximum specific volume (see Fig. 4), though the sign differs.

The volume change of the gel with swelling can be divided into two factors; one is the volume change due to dissociation of the substituted dissociation groups and the other is due to the hydration of the dextran molecule itself, in which the volume change

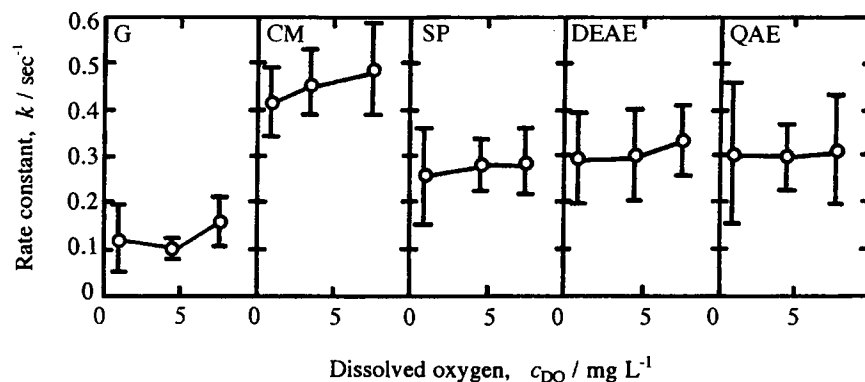
due to the hydration of diminished hydroxyl groups by introduction of ion dissociation groups is included. Accordingly, the maximum specific volume of gel,  $V_{\max}/V_0$  can be formulated as

$$V_{\max}/V_0 = (V_{\max}/V_0)_{\text{sub}} + [(V_{\max}/V_0)_G - (V_{\max}/V_0)_{\text{OH}}] \quad (1)$$

in which  $(V_{\max}/V_0)_G$  is the specific volume for G,  $(V_{\max}/V_0)_{\text{OH}}$  is the specific volume for diminished



**Figure 4** Plot of specific gel volume of Sephadexes vs. dissolved oxygen concentration obtained by microscopic observation at 25°C.



**Figure 5** Effect of dissolved oxygen on the rate constant of the swelling of Sephadexes obtained by microscopic observation at 25°C.

hydroxyl groups, and  $(V_{\max}/V_0)_{\text{sub}}$  is the specific volume for substituted groups.

If we assume that the substituted quantity is sufficiently smaller than that of total hydroxyl groups in the molecule, that is,

$$(V_{\max}/V_0)_G \gg (V_{\max}/V_0)_{\text{OH}}$$

and the volume change due to the diminished hydroxyl groups is assumed to be negligible, Eq. (1) can be altered to Eq. (2):

$$(V_{\max}/V_0)_{\text{sub}} = V_{\max}/V_0 - (V_{\max}/V_0)_G \quad (2)$$

From Eq. (2), the volume change due to the modified ion dissociation groups of CM, SP, DEAE, and QAE can be calculated; they are listed in Table II. To discuss the effect of the dissolved air on the volume change of the gel, we define the difference of the maximum specific volume per ion dissociation group with the swelling in normal water ( $c_{\text{DO}} = 7.2$  mg/L) and in the deaerated water ( $c_{\text{DO}} = 0.8$  mg/L),

in which  $f$  is the number of dissociation groups<sup>5</sup> as follows:

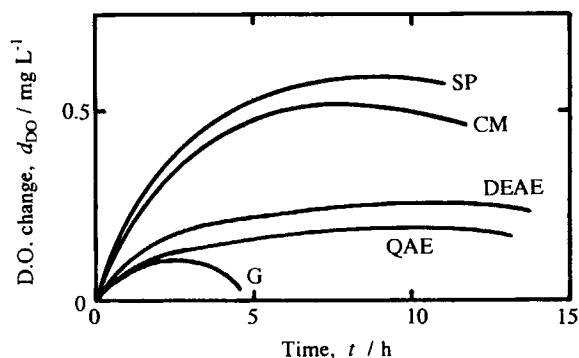
$$d(V_{\max}/V_0)_{\text{sub}}/f = [(V_{\max}/V_0)_{\text{sub}}^{\text{DO}=7.2} - (V_{\max}/V_0)_{\text{sub}}^{\text{DO}=0.8}]/f \quad (3)$$

This value signifies variation of the maximum volume change by substituent groups to the dissolved oxygen. The calculated values are listed in Table II. SP takes on a large negative value and  $\text{SP} < \text{CM} < \text{QAE} \approx \text{DEAE}$  in that order.

To see the change of the dissolved oxygen in the deaerated water ( $c_{\text{DO}} \approx 0.8$  mg/L) with the swelling of Sephadexes in the closed system, the changes of the dissolved oxygen with time were measured. Figure 6 shows the time course of  $d_{\text{DO}}$ , that is, the difference in the amounts of the dissolved oxygen at time  $t$  and that at time zero. The dissolved oxygen in water increases with the swelling of the Sephadexes, and after reaching maximum values, the dissolved oxygen decreases. The adsorbed or the adhering oxygen with Sephadexes may be transferred to water and adsorbed by Sephadexes again. The dissolved oxygen in normal water with the swelling of Sephadexes, however, simply decreased with time.

The relationship between the maximum change of dissolved oxygen concentration and amounts of the added Sephadexes in the deaerated water in the closed system is linear, as shown in Figure 7.

The maximum rise in the dissolved oxygen per gram of Sephadex,  $d_{\text{max}}$ , can be divided into two factors, one is the rise in the ion dissociable groups and the other is the hydroxyl groups of dextran in which the diminished hydroxyl groups are replaced with the substituted groups. Accordingly, the following equation applies:



**Figure 6** Time course of dissolved oxygen in deaerated water during the swelling of Sephadexes.

**Table II** Effect of Dissolved Oxygen on First-Order Kinetic Parameters of the Increasing of Gel Volume with the Swelling of Sephadexes Obtained by Microscopic Observation at 25°C

Sephadex	Dissolved Oxygen Conc. (c <sub>DO</sub> /mg L <sup>-1</sup> )	(V <sub>max</sub> /V <sub>0</sub> ) <sub>sub</sub> <sup>a</sup>	d(V <sub>max</sub> /V <sub>0</sub> ) <sub>sub</sub> <sup>b</sup>	Ionic Conc <sup>c</sup> (f/mmol g <sup>-1</sup> )	d(V <sub>max</sub> /V <sub>0</sub> ) <sub>sub</sub> /f (g mmol <sup>-1</sup> )
CM	0.8	198.4 ± 61.7			
	4.5	153.9 ± 40.2	-78.7 ± 85.7	4.5 ± 0.5	-17.5 ± 19.1
	7.2	119.7 ± 59.5			
SP	0.8	121.5 ± 51.6			
	4.5	96.2 ± 40.7	-88.4 ± 46.2	2.3 ± 0.3	-38.4 ± 5.4
	7.2	33.1 ± 6.5			
DEAE	0.8	59.6 ± 16.9			
	4.5	48.1 ± 22.2	-27.1 ± 17.3	3.5 ± 0.5	-7.7 ± 5.1
	7.2	32.5 ± 3.6			
QAE	0.8	80.9 ± 24.3			
	4.5	61.6 ± 17.5	-28.8 ± 38.1	3.0 ± 0.4	-9.6 ± 12.8
	7.2	52.1 ± 29.3			

<sup>a</sup> V<sub>max</sub>/V<sub>0</sub> - (V<sub>max</sub>/V<sub>0</sub>)<sub>G</sub>.

<sup>b</sup> (V<sub>max</sub>/V<sub>0</sub>)<sub>sub</sub><sup>DO=7.2</sup> - (V<sub>max</sub>/V<sub>0</sub>)<sub>sub</sub><sup>DO=0.8</sup>.

<sup>c</sup> Cited from Ref. 5.

$$d_{\max} = (d_{\max})_{\text{sub}} + [(d_{\max})_{\text{G}} - (d_{\max})_{\text{OH}}] \quad (4)$$

We assume that the number of diminished hydroxyl groups by substitution of ion dissociable groups are much fewer than the total number of hydroxyl groups in skeleton:

$$(d_{\max})_{\text{G}} \gg (d_{\max})_{\text{OH}} \approx 0$$

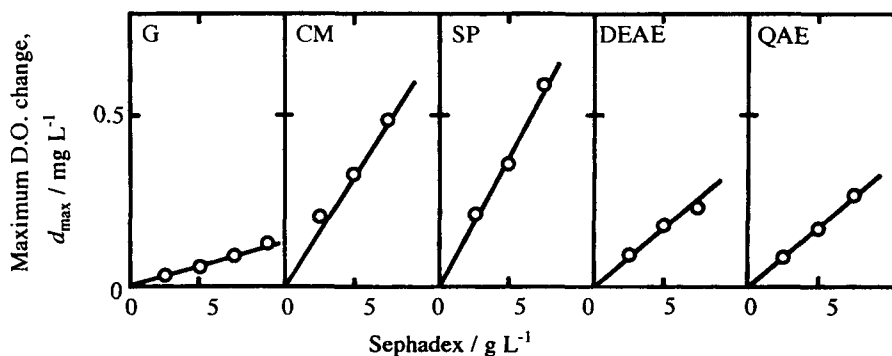
thereby,

$$(d_{\max})_{\text{sub}} = d_{\max} - (d_{\max})_{\text{G}} \quad (5)$$

Table III lists the increases in dissolved oxygen per ion dissociable group of Sephadexes, (d<sub>max</sub>)<sub>sub</sub>/f. All of the calculated values are positive and the

order of their magnitude is SP > CM > QAE ≈ DEAE.

The relationships between the differences of the maximum specific volume per ion dissociable group with normal and various deaerated waters, d(V<sub>max</sub>/V<sub>0</sub>)<sub>sub</sub>/f and the rise of the dissolved oxygen per ion dissociable group, (d<sub>max</sub>)<sub>sub</sub>/f are plotted in Figure 8. A straight line through zero is obtained. For those gels in which the maximum specific volume increases, oxygen connected with the gels transfers largely to water when the gels are swollen in water at lower dissolved oxygen concentrations. The maximum specific volume of ionic gels is determined by the difference of the osmotic pressure of the counterions in and out of the gels and the repulsion force of the dissociable groups.<sup>2,6</sup> When the dissolved oxygen is lower, the air connected with gels will largely


**Figure 7** Maximum change of dissolved oxygen concentration in deaerated water with the swelling of Sephadexes.

**Table III** Maximum Change of Dissolved Oxygen Concentration by the Swelling of Sephadexes

Sephadex	$d_{\max}$ (mg L <sup>-1</sup> g <sup>-1</sup> )	$(d_{\max})_{\text{sub}}^a$ (mg L <sup>-13</sup> g <sup>-1</sup> )	$f^b$ (mmol g <sup>-1</sup> )	$(d_{\max})_{\text{sub}}/f$ (mg L <sup>-1</sup> mmol <sup>-1</sup> )
G	0.124 ± 0.004	—	—	—
CM	0.709 ± 0.073	0.545 ± 0.073	4.5 ± 0.5	0.121 ± 0.021
SP	0.786 ± 0.052	0.662 ± 0.052	2.3 ± 0.3	0.288 ± 0.044
DEAE	0.344 ± 0.025	0.220 ± 0.025	3.5 ± 0.5	0.063 ± 0.016
QAE	0.347 ± 0.009	0.228 ± 0.010	3.0 ± 0.4	0.076 ± 0.011

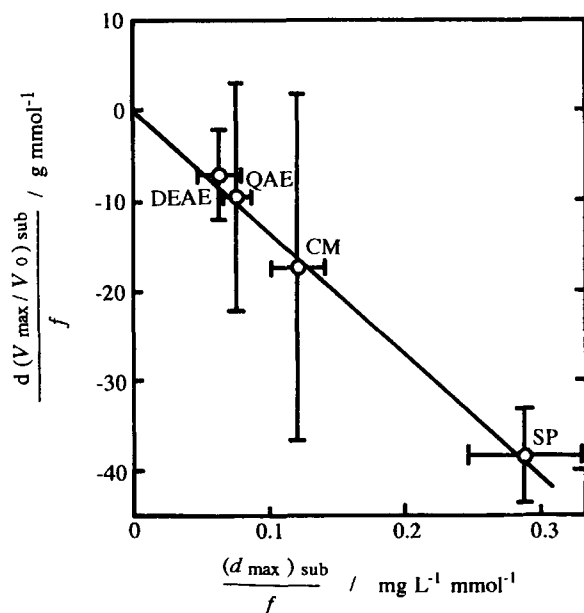
<sup>a</sup>  $d_{\max} - (d_{\max})_G$ .<sup>b</sup> Cited from Ref. 5.

transfer to water, so that the repulsive force by dissociable groups and the osmotic pressure of the counterions due to proceeding of the dissociation of Sephadexes may increase.

### Dilatometric measurements

Figure 9 shows the changes of the total volumes of CM in water at different dissolved oxygen concentrations with time by dilatometry. The total volumes decrease with time and show single saturation curves. The maximum change of the total volume  $\Delta v_{\max}$  is more negative at lower dissolved oxygen concentration.

Similar relationships are found for the other Sephadexes, which show sigmoid curves; see Figure



**Figure 8** Relationship between the difference of the maximum specific volume with normal and deaerated waters and the increase in dissolved oxygen in deaerated water.

10 and Figure 11. The difference of the upper and lower values of the sigmoid curves of Figure 10,  $d\Delta v_{\max}$ , is listed in Table IV.

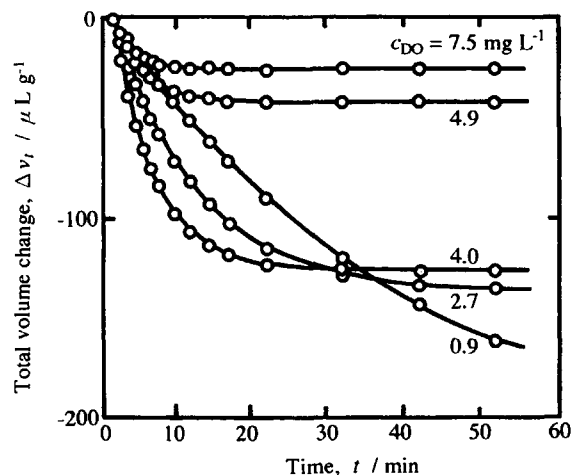
The maximum change of the total volume can be assumed to be the sum of the change of the total volumes of hydration of the dextran molecule and the hydration of the ion dissociable groups.

If we consider the hydration of —OH groups which were diminished by the introduction of the ionic groups in the molecule, the following equation can be obtained:

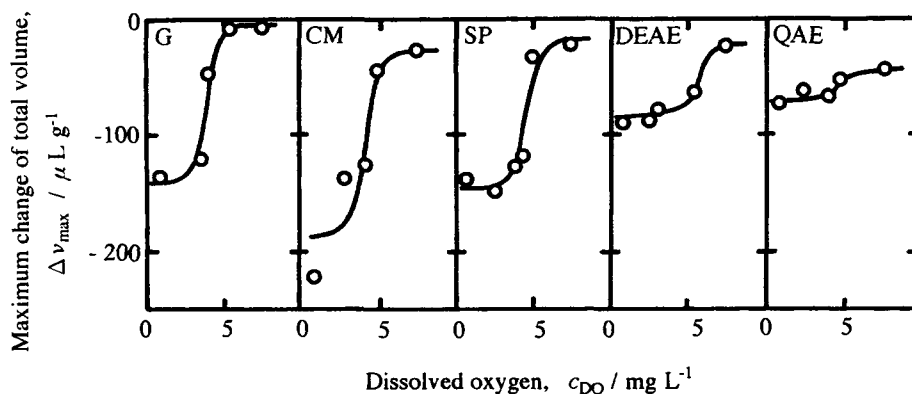
$$d\Delta v_{\max} = (d\Delta v_{\max})_G + (d\Delta v_{\max})_{\text{sub}} \quad (6)$$

in which,  $d\Delta v_{\max}$  is the maximum change in the total volume of the ionic gel,  $(d\Delta v_{\max})_G$  is the maximum change of the total volume of the hydration of dextran molecule,  $(d\Delta v_{\max})_{\text{sub}}$  is the hydration of the ion dissociable groups.

The amount of the ion dissociable groups introduced in a molecule is small. Therefore Eq. (7) can be applied:



**Figure 9** Time course of total volume change of the swelling of CM-Sephadex obtained by dilatometry at 25°C.



**Figure 10** Effect of dissolved oxygen in water on the maximum change of total volume with the swelling of Sephadexes obtained by dilatometry at 25°C.

$$(d\Delta v_{\max})_{\text{sub}} = d\Delta v_{\max} - (d\Delta v_{\max})_G \quad (7)$$

$$\frac{\eta}{\eta_0} = 1 + AC^{1/2} + BC \quad (8)$$

From Eq. (7), the maximum change of the total volume by dissociation of dissociable groups in CM, SP, DEAE, and QAE can be calculated. They are listed in Table IV. These values are the maximum volume changes of all dissociable groups originating from the difference in the amount of the dissolved oxygen.

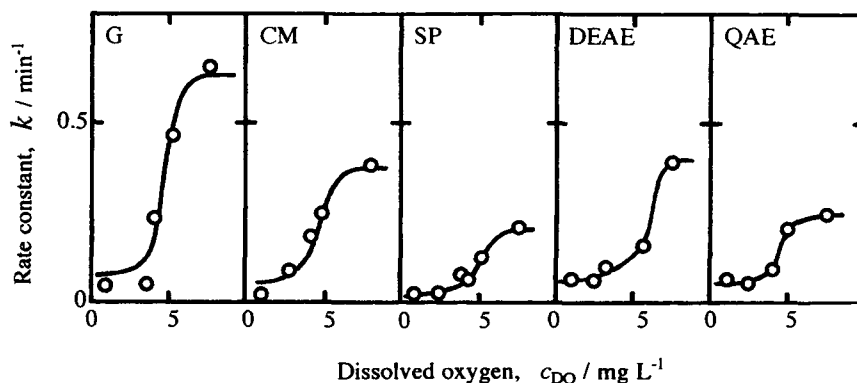
Furthermore, the amounts of the dissociable groups of each Sephadex ion  $(d\Delta v_{\max})_{\text{sub}}/f$  are calculated. These values show the order of the change in total volume with the difference in the amount of dissolved oxygen.

As indicated previously,<sup>3</sup> when an ion dissociable group is dissociated in water, the structure of water surrounding the polymer changes. Contribution to changes of water structure by ionic polymers is represented by the viscosity  $B$  coefficient in the Jones-Dole equation<sup>7</sup> for the viscosity  $\eta$  of aqueous electrolyte solutions:

where  $\eta_0$  is the viscosity of water,  $C$  is the concentration (molarity),  $A$  is the constant relating to cation-anion interaction, and  $B$  is the viscosity  $B$  coefficient.

Coefficient  $B$  is the factor related to ion-water interaction and is applied as the additive property. When  $B > 0$ , the interaction between ion and water is enhanced and the ion is a "structure maker," The water goes into hardly movable, so that the total volume may be decreased.<sup>8-16</sup> On the other hand, when  $B < 0$ , the water-ion interaction weakens, that is, the ion is a "structure breaker," and the total volume may be increased.<sup>8-16</sup>

The calculated values of the viscosity  $B$  coefficient for CM, SP, DEAE, and QAE are 0.098, -0.087, -0.124, and -0.124, respectively.<sup>3</sup> The positive value for CM means that of the promotion of the water structure and total volume will decrease with hy-



**Figure 11** Effect of dissolved oxygen in water on the first-order rate constant of the swelling of Sephadexes obtained by dilatometry at 25°C.

**Table IV** Effect of Dissolved Oxygen on the Maximum Change of Total Volume

Sephadex	$d\Delta\nu_{\max}^a$ ( $\mu\text{L g}^{-1}$ )	$(d\Delta\nu_{\max})_{\text{sub}}^b$ ( $\mu\text{L g}^{-1}$ )	$f^c$ ( $\text{mmol g}^{-1}$ )	$(d\Delta\nu_{\max})_{\text{sub}}/f$ ( $\mu\text{L mmol}^{-1}$ )
G	140.0 $\pm$ 27.2	—	—	—
CM	161.4 $\pm$ 44.5	21.4 $\pm$ 51.2	4.5 $\pm$ 0.5	4.8 $\pm$ 11.5
SP	128.6 $\pm$ 13.5	-11.8 $\pm$ 27.2	2.3 $\pm$ 0.3	-5.0 $\pm$ 11.9
DEAE	63.3 $\pm$ 8.3	-76.7 $\pm$ 31.2	3.5 $\pm$ 0.5	-21.9 $\pm$ 10.0
QAE	23.6 $\pm$ 11.1	-116.4 $\pm$ 29.4	3.0 $\pm$ 0.4	-38.8 $\pm$ 11.7

<sup>a</sup>  $d\Delta\nu_{\max} = (d\Delta\nu_{\max})_{\text{DO=setu.}} - (d\Delta\nu_{\max})_{\text{DO=0.}}$

<sup>b</sup>  $(d\Delta\nu_{\max})_{\text{sub}} = d\Delta\nu_{\max} - (d\Delta\nu_{\max})_{\text{G.}}$

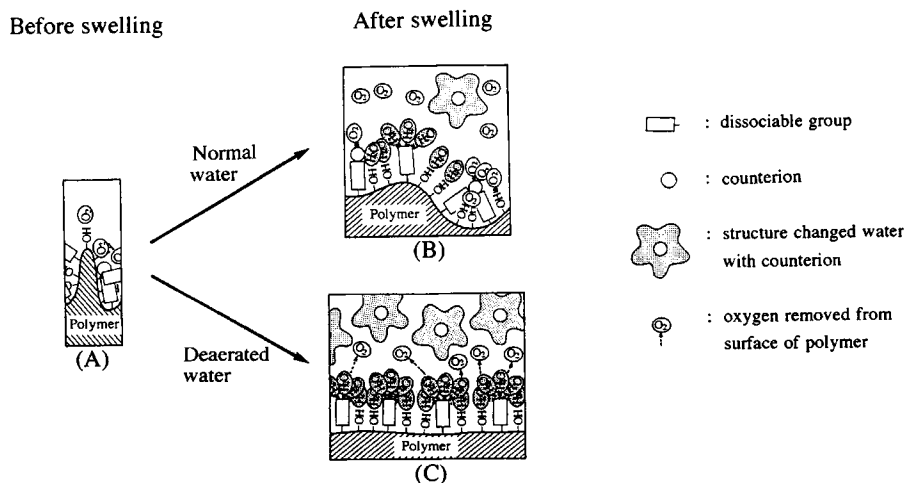
<sup>c</sup> Cited from Ref. 5.

dration. Conversely, the ion having negative values as in DEAE and QAE indicate the destruction of the water structure, and the total volume increases with hydration.

These values are compared with those for the difference in the maximum change of total volume per ion dissociable group  $(d\Delta\nu_{\max})_{\text{sub}}/f$ , the dissociable groups of CM are structure makers and when the dissociation occurred, total volume should decrease.

From the value of the maximum change of total volume per ion dissociable group of CM, the lower the dissolved oxygen, the more the acceleration of the hydration of the dissociable group. The dissociable groups of DEAE and QAE, however, are structure breakers: the total volumes increase with the dissociation of the dissociable groups. When the dissolved oxygen decreases, the total volume should increase. That is, when the dissolved oxygen decreases, the hydration of the dissociable group should be accelerated.

From these results and discussion, we can show a hypothetical mechanistic sketch on the effect of dissolved oxygen on the swelling of Sephadexes (see Fig. 12). The adsorbed or the adhering oxygen with Sephadexes at the dry state (A) may be dissolved into the water introduced, therefore, the amount of oxygen transferred from the surface of Sephadexes to water depends on the concentration of oxygen in the water introduced (B). When the dissolved oxygen in water decreases, the place bare of oxygen in the surface of Sephadexes increase, so that the dissociation of the ion-dissociable groups are accelerated (C), the repulsion force by dissociated groups is increased, therefore, the volume of gel itself increases. And also the water structure surrounding the ions may be changed according to the varieties of ions. That is, the water structure becomes tighter or weakens. The dilatometrical results reveal these phenomena. In Figure 12, the dissolved air is shown as only oxygen, however, nitrogen and inert gases



**Figure 12** Hypothetical sketch for the swelling of ionic Sephadexes with normal and deaerated water.



must effect on the swelling. From present results, it is difficult to discuss these problems.

## CONCLUSIONS

The results obtained by microscopic observation and the measurement of changes of the dissolved oxygen in water with the swelling of Sephadexes show that amounts of dissolved oxygen in water and the change of the maximum specific volume are closely related. And the results obtained by the dilatometrical measurement for the swelling show that the effect of the difference of the dissolved oxygen on the change of the total volume with the swelling is closely related with the viscosity  $B$  coefficient. If the water structures in and out of gels of Sephadexes having different substituent group are in the same state, the effect of the dissolved oxygen revealed by microscopic observations and dilatometrical measurement should have same tendency for swelling. However, the results obtained by microscopic observation and dilatometrical measurements were different. The water structures of the inside of the gel should differ from that outside the gel.

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