Swelling of Hydrophilic Polymers. III

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SYNOPSIS

The total volume change included gel and surrounded water with the swelling of five types of spherical cross-linked dextran (Sephadex) that are either nonionic (G) or possess one of four different ionic groups in the same molecular skeleton: CM: sodium carboxymethyl, SP: sodium sulphopropyl, DEAE: diethylaminoethyl chloride, and QAE: diethyl-(2-hydroxypropyl) aminoethyl chloride. All have been studied by dilatometry. The total volume decreased with the swelling of all Sephadexes. The maximum changes of total volume with the swelling in water were all negatives of CM, G, SP, (DEAE, QAE), which decrease in that order. These values did not depend on the concentration of sodium chloride and were closely related to the maximum heats of swelling. Total volume changes occurred by the dissociation of the ionic group of dextran derivatives that subtracted the total volume change due to hydration of Sephadex skeleton from the total volume change: -21.6 ± 3.1 μL mmol^{-1} for CM, -2.8 ± 8.0 μL mmol^{-1} for SP, $+13.2 \pm 4.4$ μL mmol^{-1} for DEAE, and $+15.4 \pm 4.6$ μL mmol^{-1} for QAE. These values are assumed to be reflected in the quantities of ions-water interaction of Sephadexes. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

This paper constitutes the third in a series of articles dealing with the swelling of hydrophilic polymers.[1,2]

In the previous paper,[2] nonionic and four ionic cross-linked dextrans (Sephadex) were used for measurement of (a) the gel volume by picture analysis with a VTR system and (b) the heats of swelling by calorimetry. In swelling of nonionic Sephadex in water and in saline solution, the final volume changes of the gel itself and the heat of swelling showed no influence. However, in swelling of ionic Sephadexes, the final volume in water was greater than that in saline solution, but the heat of swelling did not change.

From these results, we pointed out that the swelling mechanism of nonionic and ionic gels may differ.

To discuss the interaction of water and gel, it may be necessary to measure not only the volume change of gel itself but also the total volume change, including gel and surrounding water.

The present investigation was undertaken to discuss the interaction of nonionic and ionic Sephadexes with water by measurement of the total volume change using a dilatometer.

EXPERIMENTAL

Spherical and typical hydrophilic polymers, Sephadex G-60 (cross-linked dextrans from Pharmacia) used in gel filtration (Abb. G), and four ion exchangers containing different dissociable species having different ionic concentrations were employed. They are listed in Table I.[3] Details are described in the previous paper.[2]

For dilatometry, air-free water was used to avoid errors caused by dissolved air. Boiling distilled water was cooled in a rubber-stoppered glass container.

About 250 mg of Sephadex and a small bar for a stirrer were set in the lower cell (about 60 cm^3), and the graduated capillary glass tube (maximum volume 100 μL) was mounted at the neck of the cell. A reservoir syringe filled with air-free water was connected to the cell by silicone tubing, then placed in the thermostat (25.000 ± 0.001°C).

When the system reached thermoequilibrium, the stopcock of the cell was opened and sufficient water

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Table I   Characteristics of the Sephadex Used[3]

Type	Dissociable Group	Counterion	Ionic Concentration f/mmol g^{-1}
Sephadex G	None	—	—
CM Sephadex C-50	Carboxymethyl	Na$^+$	4.5 ± 0.5
SP Sephadex C-50	Sulphopropyl	Na$^+$	2.3 ± 0.3
DEAE Sephadex C-50	Diethylaminoethyl	Cl$^-$	3.5 ± 0.5
QAE Sephadex A-50	Diethyl-(2-hydroxypropyl)aminoethyl	Cl$^-$	3.0 ± 0.4

was introduced into the cell to reach the center of the capillary. Then the stopcock was closed.

The sample was continuously stirred by a magnetic stirrer in the thermostat, and the volume change of the system was measured by reading a meniscus.

As one and one-half minutes were needed to introduce the water into the cell, the measurement of the dilatometry was started when the stopcock was closed.

RESULTS AND DISCUSSION

Figure 1 shows the forms of Sephadex gels before and after swelling. All are spherical. Accordingly, they can be treated as homogeneous systems with regard to total volume change.

Figure 2 shows the time course for the total volume change, ΔV_t, of the swelling of Sephadex with water. The total volume, v_t, decreased with the passage of time, t.

The shortest and longest times to reach equilibrium were 30 min. for SP and 180 min. for CM. These times are extremely long when compared to the several minutes required to reach the maximum gel volume change observed for swelling of Sephadexes as shown in the previous paper.[2]

With all Sephadexes, when the concentration of sodium chloride, c, was changed, total volume change, Δv_t, against time, t, decreased. Also, the relationship between the maximum decreasing value of total volume, Δv_{max}, and the concentration of sodium chloride, c, showed almost constant values, as indicated in Figure 3.

Figure 1   Microscope graphs of Sephadexes before and after swelling.
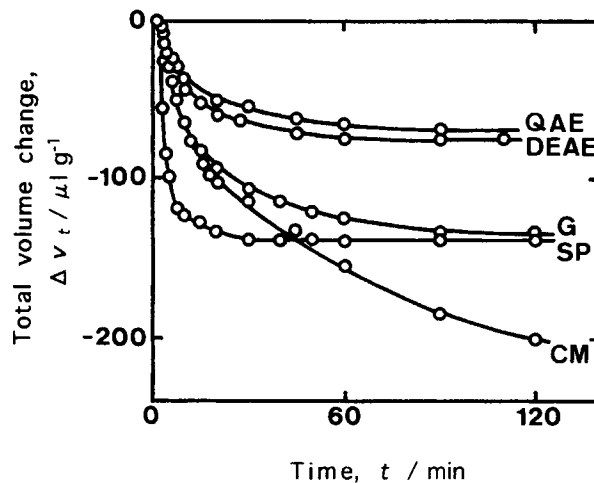
Figure 2   Time course of total volume change for the swelling of Sephadex at 25°C.
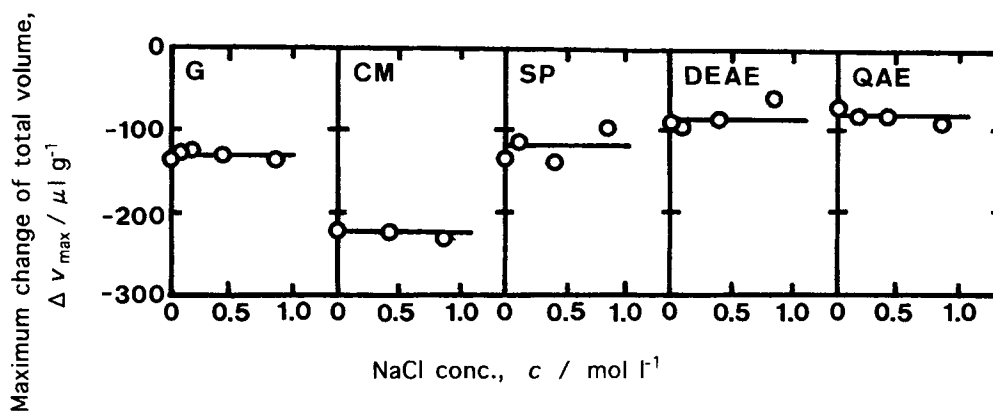
Figure 3 Effect of sodium chloride concentration of the maximum change of total volume of the swelling of Sephadex obtained by dilatometry at 25°C.

The maximum gel volume ratio of the swelling, V_{max}/V_o; the heats of swelling, Q_{max} (which were shown in the previous paper[2]); and the values of ΔV_{max} at c = zero and 0.856 molL^{-1} at 25°C are listed in Table II.

Plots of Δv_{max} and Q_{max} at c = zero are shown in Figure 4, and at c = 0.856 molL^{-1} are shown in Figure 5.

As shown in Figures 4 and 5, Δv_{max} is closely related to Q_{max}. Both Q_{max} and Δv_{max} are assumed to be constant values with no dependence on c; although, as shown in Table II, the maximum gel volume, V_{max}/V_o, was greatly dependent on the concentration of sodium chloride, c.

From the above results, we can say that the volume change of the gel itself and the total volume change of the gel and surrounded water are assumed to be reflected in the different phenomena.

We can separate the total volume change of the swelling of ionic Sephadex, Δv_{obs}, into two elements. One is the total volume change by the dissociation of ionic groups, Δv_{mod}; and the other is the total volume change by the hydration of dextran molecules, Δv_G, in which the total volume change of the

imaginary hydration of $-$OH groups substituted, Δv_{OH}, may be included.

So, Δv_{mod} is defined by the following equation:

$$\Delta v_{mod} = \Delta v_{obs} - (\Delta v_G - \Delta v_{OH}) \qquad (1)$$

and the following relations are valid,

$$\Delta v_G \gg \Delta v_{OH} \text{ and } \Delta c_{OH} \simeq 0$$

We then modify equation (1) to (2)

$$\Delta v_{mod} = \Delta v_{obs} - \Delta v_G \qquad (2)$$

The values of Δv_{mod} calculated for CM, SP, DEAE, and QAE are listed in Table III.

Generally, the behavior of ions in water has been attributed to the structural change in water upon the introduction of ions into water.[5–13] In solutions of electrolytes with small ions, such as Na$^+$ and Li$^+$ ions, these ions increase the extent of intermolecular hydrogen-bonding of water in the vicinity of the ions; thus, they are "electrostrictive structure-makers."[5] On the other hand, in solutions of electrolytes with

Table II   The Maximum Change of Total Volume, Heat,[2] and Gel Volume Ratio[2] at Two Different Concentrations of Sodium Chloride at 25°C

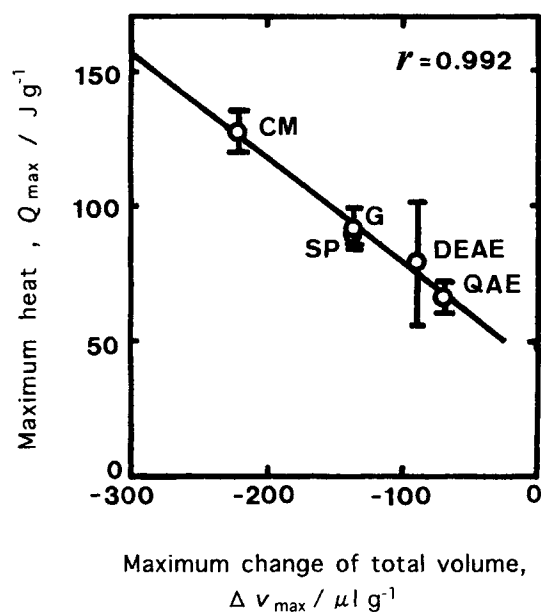| c/mol L^{-1}	$\Delta v_{max}/\mu$ L g^{-1}		$Q_{max}/$Jg^{-1}		V_{max}/V_0	
	0	0.856	0	0.856	0	0.856
G	−136.9	−136.6	91.4 ± 6.9	94.6 ± 10.3	16.4 ± 2.7	12.3 ± 2.7
CM	−221.6	−232.0	127.2 ± 8.2	128.0 ± 3.8	136.1 ± 59.4	39.1 ± 14.4
SP	−136.4	−89.9	89.3 ± 5.4	99.4 ± 5.7	49.5 ± 5.9	12.6 ± 2.1
DEAE	−90.3	−58.8	79.0 ± 22.8	69.1 ± 7.7	48.9 ± 2.4	9.1 ± 1.6
QAE	−70.2	−92.3	66.2 ± 5.4	69.3 ± 6.7	68.5 ± 24.3	16.0 ± 6.9

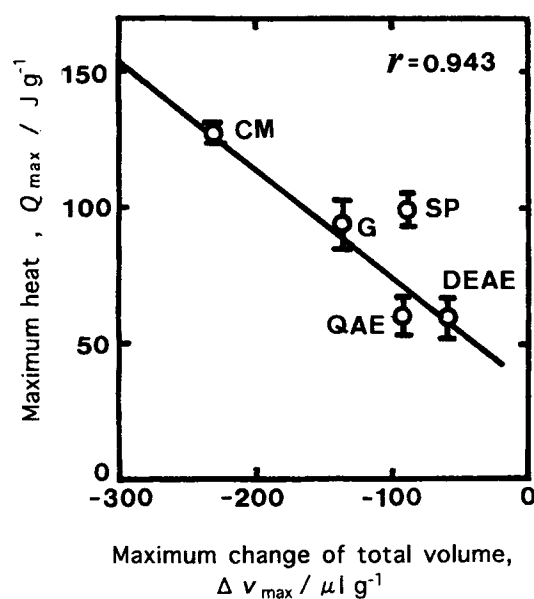**Figure 4** Relationship between maximum change of total volume and maximum heat[2] without sodium chloride at 25°C.

Figure 5 Relationship between maximum change of total volume and maximum heat[2] with sodium chloride, 0.856 molL^{-1} at 25°C.

large ions, such as K^+, Cl^-, and Br^- ions, these ions decrease the extent of intermolecular hydrogen-bonding of water in the vicinity of the ions; thus, they are "electrostrictive structure-breakers."

To estimate such interaction between ions and water, refer to Jones–Dole equation[14] for the viscosity, η, of aqueous electrolyte solutions:

$$\eta/\eta_0 = 1 + AC^{1/2} + BC \tag{3}$$

where η_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.

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 a hardly movable state, so that the total volume may be decreased.[6,15] 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.[6,15]

Viscosity B coefficient of the counterions, B_i, and the dissociable groups which are approximate dissociable groups of Sephadexes, B_d, are listed in Table IV.

As for CM, B values of both the counterion, Na^+, and the dissociation group, COO^-, are positive; that is, they are "structure-makers." By dissociation, the ion and dissociable group contribute to decreasing the total volume. On the other hand, B values of both the counterions and the dissociable groups of DEAE and QAE are negative; that is, they are "structure-breakers." So, by dissociation, the total volume may be increased. As for SP, the counterion Na^+ is a "structure-maker" and the dissociable group, sulfopropyl, is a "structure-breaker." Here, the total volume change might be small.

Table III Estimation of the Total Volume Change by Dissociation of Ionic Groups

	$\dfrac{\Delta v_{obs}}{\mu L \ g^{-1}}$	$\dfrac{\Delta v_{obs} - \Delta v_G}{\mu L \ g^{-1}}$	$\dfrac{f}{mmol \ g^{-1}}$	$\dfrac{\Delta v_{mod}/f}{\mu L \ mmol^{-1}}$
G	$-129.5 \pm 8.1 \ (\Delta v_G)$	0	0	—
CM	-226.8 ± 4.2	-97.3 ± 9.1	4.5 ± 0.5	-21.6 ± 3.1
SP	-123.1 ± 16.5	-6.4 ± 18.4	2.3 ± 0.3	-2.8 ± 8.0
DEAE	-83.0 ± 11.4	$+46.5 \pm 14.0$	3.5 ± 0.5	$+13.2 \pm 4.4$
QAE	-83.3 ± 9.4	$+46.2 \pm 12.4$	3.0 ± 0.4	$+15.4 \pm 4.6$

Table IV   Viscosity B Coefficients of Counterions and Dissociable Groups which are Approximate to Those of Sephadexes

	Counterion	B_i^{16}	Dissociable Group	$B_d^{6,13}$	$B_i + B_d$
CM	Na^+	0.086	COO^-	0.012	0.098
SP	Na^+	0.086	SO_3^-	−0.173	−0.087
DEAE	Cl^-	−0.007	NH_3^+	−0.117	−0.124
QAE	Cl^-	−0.007	NH_3^+	−0.117	−0.124

The results show the total volume change, $\Delta v_{mod}/f$, of CM is large negative values: -21.6 ± 3.1 $\mu L\ mmol^{-1}$; that of SP is a small negative value: $-2.8 \pm 8.0\ \mu L\ mmol^{-1}$; and that of DEAE and QAE are large positive values: $+13.2 \pm 4.4\ \mu L\ mmol^{-1}$ and $+15.4 \pm 4.6\ \mu L\ mmol^{-1}$, respectively. These data agree with the above theory and the values $B_i + B_d$ in Table IV.

The above results should imply that the maximum change of the total volume of ionic Sephadex reflects the interaction quantities between the counterion and the dissociation groups with surrounding water.

Our previous papers[1,2] did not find the correlation between the volume change of the gel itself and the change of enthalpy. Accordingly, it is difficult to explain the result by Flory's theory. However, the total volume change of gel and included surrounding water is highly correlated with the change of enthalpy. This results is in agreement with Flory's theory. Accordingly, whether or not a gel is spherical, to study the swelling phenomena of polymers it is important to discuss the total volume change, and the dilatometrical study might also be useful.

CONCLUSIONS

From the results of dilatometrical study of the swelling of five types of cross-linked dextran (Sephadex), we concluded that the total volume change of all Sephadexes decreases; and that the values of the maximum total volume change are related to the maximum heat of swelling, even though the volume changes of the gel itself are not related to enthalpy change as shown in our previous papers.

Accordingly, Flory's theory for enthalpy and polymer-solvent interaction can be applied between the total volume change of Sephadex and enthalpy

change. Thus, to obtain detailed information about the swelling of hydrophilic polymers, it is necessary to measure the total volume change. For this the dilatometrical study might be a useful tool.

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