

Swelling of Hydrophilic Polymers. II*

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SYNOPSIS

The swelling of five types of Sephadex that are either nonionic (G) or possess one of four different ionic groups [sodium carboxymethyl (CM), sodium sulfopropyl (SP), diethyl-aminoethyl chloride (DEAE), diethyl-(2-hydroxypropyl)aminoethyl chloride (QAE)] in the same skeleton of the molecule has been studied by picture analysis and by calorimetry. Inducing dissociation of the ionic group in the polymer skeleton increased the water swelling. By the addition of sodium chloride, the maximum swelling volume of nonionic Sephadex was only slightly decreased. However, that of ionic polymers was considerably decreased. The variation of the apparent first-order rate constant of the swelling and that of the maximum swelling volume show the same tendency. The maximum heats of swelling were $93.2 \pm 7.1 \text{ J g}^{-1}$ for G, $128.8 \pm 9.1 \text{ J g}^{-1}$ for CM, $92.3 \pm 8.0 \text{ J g}^{-1}$ for SP, $68.8 \pm 10.5 \text{ J g}^{-1}$ for DEAE, and $67.0 \pm 7.2 \text{ J g}^{-1}$ for QAE and did not depend on the concentration of sodium chloride. From the results obtained, we conclude that the nonionic Sephadex swells only by hydration but that ionic Sephadexes swell mainly by the osmotic pressure due to the counterions of the ionic groups and that the swelling ratio is not dependent on the kinds of ions but on the ionic concentration. Most of the water in the gels of ionic Sephadexes is free water that does not interact with the Sephadexes. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Practical applications in many fields have been advanced for use of hydrophilic polymers because of their outstanding characteristics for water absorption and water retentivity. Rapid volume changes of hydrophilic polymers have been treated as phase transitions, and the rates of their swelling and shrinking are of interest in many fields of engineering and medicine.²⁻⁵

In the first paper¹ of this series, attention was drawn to the rate of the swelling of sodium polyacrylate. Picture analysis with a microscope-VTR system and calorimetry were used to determine the kinetics of swelling, from which information about a mechanism of the swelling was obtained.

The present investigation was undertaken to discuss the relation between the structure of the hy-

drophilic polymers that have either a nonionic or one of four different ionic groups in the same polymer skeleton and their swelling using the previous methods.¹

EXPERIMENTAL

Sephadex G-60 (cross-linked dextrans from Pharmacia) used for gel filtration (Abb. G) and four ion exchangers containing different dissociable species having different ionic concentrations⁶ are listed in Table I.

The picture analysis was rather simple because of the disappearance of the transient patterns^{7,8} on the surface of these polymer gels, which are otherwise difficult to analyze kinetically. The details for the measurements of the heats of swelling and the picture analysis with the microscope-VTR system are in our previous paper.¹

RESULTS AND DISCUSSION

Figure 1 shows the swelling ratio V_t/V_0 obtained by microscopic observation; V_t is the volume at time t

* Our previous paper entitled "Rate of Swelling of Sodium Polyacrylate"¹ is referred to as "Swelling of Hydrophilic Polymers. I."

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Table I Characteristics of the Sephadex Used

Type	Dissociable Group	Counter Ion	Ionic Concentration f (meq g ⁻¹)
Sephadex G	None	—	—
CM Sephadex C-50	Carboxymethyl	Na ⁺	4.5 ± 0.5
SP Sephadex C-50	Sulfopropyl	Na ⁺	2.3 ± 0.3
DEAE Sephadex C-50	Diethylaminoethyl	Cl ⁻	3.5 ± 0.5
QAE Sephadex A-50	Diethyl-(2-hydroxy-propyl)aminoethyl	Cl ⁻	3.0 ± 0.4

and V_0 is the volume before swelling. The bars show the standard deviations.

The swelling ratio V_t/V_0 of sodium carboxymethyl (CM) is the highest and followed by diethyl-(2-hydroxypropyl) aminoethyl chloride (QAE), sodium sulfopropyl (SP), and diethylaminoethyl chloride (DEAE), respectively. The ratios of these four polymers are much higher than that of nonionic Sephadex (G). Thus, inducing dissociation of the ionic groups in the polymer skeleton increases the water swelling.

If V_t at infinity time is taken as the maximum swelling volume, V_{max} , the semilogarithmic plots of $(V_{max} - V_0)/(V_t - V_0)$ against time t show a straight line as illustrated in Figure 2. Therefore, the process of the swelling may be dealt with by apparent first-order kinetics. When the polymers were swollen in sodium chloride solution, a straight line was also obtained identical to that for water.

Figure 3 shows the maximum swelling volume ratio, V_{max}/V_0 , of each Sephadex obtained by picture analysis at different concentrations of sodium chlo-

ride, c . The maximum swelling volume ratio, V_{max}/V_0 , of G was slightly decreased by the addition of sodium chloride. However, the ionic polymers swelled greatly with water, but V_{max}/V_0 were considerably decreased by the addition of sodium chloride.

The decreased V_{max}/V_0 values by the addition of sodium chloride may be due to differences of the osmotic pressure between the external ions and the internal counterions of the ionic polymer gels.⁹ G is a nonionic polymer; thus, G was not essentially affected by the addition of sodium chloride. However, some carboxyl groups may remain in G.⁶ Therefore, the V_{max}/V_0 of G should decrease slightly by the addition of sodium chloride.

The above results are consistent with the following hypothesis based on results in the thesis⁸⁻¹³: A nonionic polymer gel is insensitive to the addition of sodium chloride. However, an ionic polymer gel shrinks sensitively due to decreasing osmotic pres-

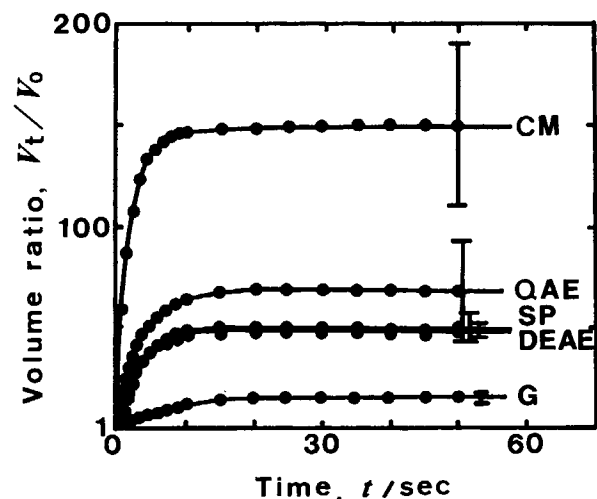


Figure 1 Time course of the volume ratio of swelling of Sephadex obtained by microscopic observation at 25°C.

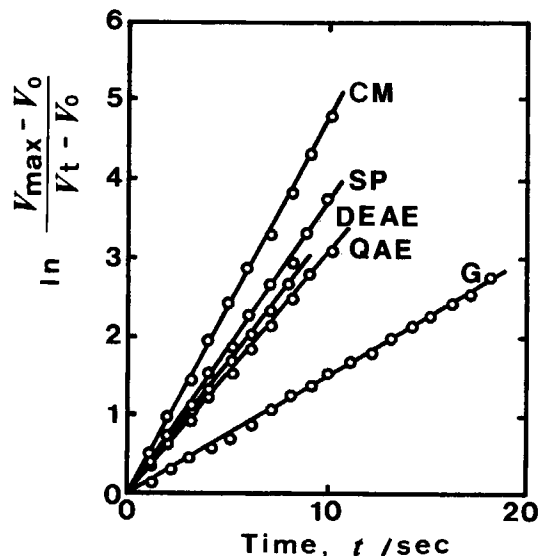


Figure 2 Semilogarithmic plot of volume change vs. time obtained by microscopic observation at 25°C.

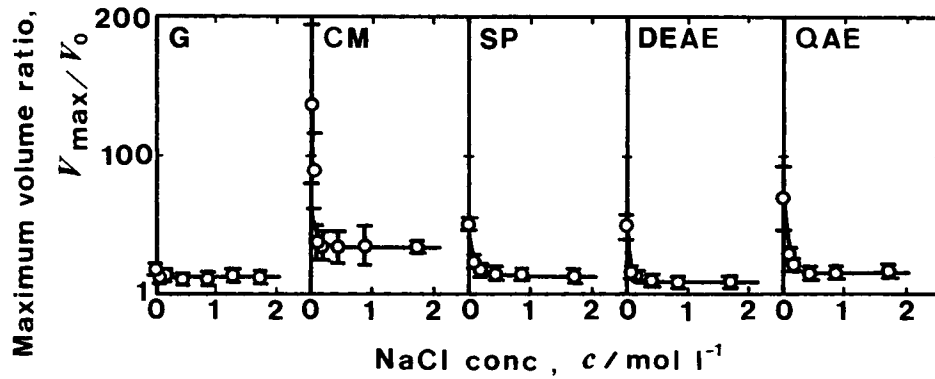


Figure 3 Effect of sodium chloride on the maximum volume of swelling of Sephadex obtained by microscopic observation at 25°C.

sure change with increasing sodium chloride concentration. Thus, the phase transition of a nonionic and an ionic polymer show different phenomena.

Generally, the swelling and the shrinking of polymer gels have been explained by the osmotic pressure of the gel. The osmotic pressure π is defined by the following equation based on the Flory-Huggins equation^{11,14}:

$$\pi = \pi_1 + \pi_2 + \pi_3 + \pi_4 \quad (1)$$

where π_1 is the pressure of rubber elasticity; π_2 , the pressure of interaction of the polymer with the solvent; π_3 , the pressure of the counterions of the polymer network; and π_4 , the pressure of entropy by the mixing of the polymer network with the solvent.

Of the above factors, for the swelling of the ionic polymers, the pressure of the counterions of the polymers is largely responsible for the osmotic pressure and is in proportion to the number of the dissociated counterions, f , per polymer chain¹⁴:

$$\pi_3 = f \cdot \nu \cdot k \cdot T \cdot (\phi / \phi_0) \quad (2)$$

where f is the number of the counterions per polymer chain; ν , the number of polymers per unit volume; k , the Boltzman constant; ϕ , the volume fraction of a polymer chain; ϕ_0 , the volume fraction when the polymer chain is in random conformation; and T , the absolute temperature.

When we consider the swelling that has taken place only by the osmotic pressure due to the counterions, and if we assume that π_3 is constant and the reaction is at equilibrium, i.e., π is zero, then

$$f \cdot \nu \cdot k \cdot T \frac{\phi}{\phi_0} = \text{const.} \quad (3)$$

$$\frac{\phi_0}{\phi} = \frac{\nu \cdot k \cdot T}{\text{const.}} \cdot f \quad (4)$$

thereby, $V_{\max}/V_0 \sim \phi_0/\phi$,

$$V_{\max}/V_0 = \frac{\nu \cdot k \cdot T}{\text{const.}} \cdot f \quad (5)$$

When the concentration of sodium chloride, c , is zero and infinity, V_{\max}/V_0 is taken as $(V_{\max}/V_0)_{c=0}$ and $(V_{\max}/V_0)_{c=\infty}$, respectively, and the following equation can be expected to hold:

$$\frac{V_{\max}}{V_0} = \left(\frac{V_{\max}}{V_0} \right)_{c=0} - \left(\frac{V_{\max}}{V_0} \right)_{c=\infty} \quad (6)$$

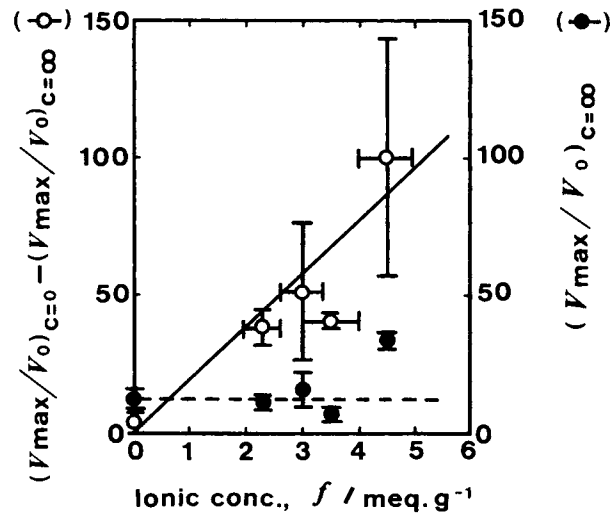


Figure 4 Effect of the ionic concentration of the polymer on the amounts of the swelling with the osmotic pressure of the counterions of the polymer network and the swelling from other causes.

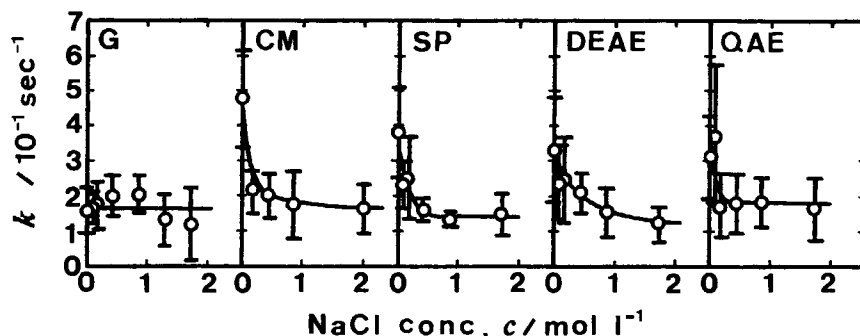


Figure 5 Effect of sodium chloride on the apparent first-order rate constant of swelling of Sephadex obtained by microscopic observation at 25°C.

and substituting eq. (5):

$$\left(\frac{V_{\max}}{V_0}\right)_{c=0} - \left(\frac{V_{\max}}{V_0}\right)_{c=\infty} = \frac{\nu \cdot k \cdot T}{\text{const.}} \cdot f \quad (7)$$

Figure 4 shows the plot of eq. (7) and that at $(V_{\max}/V_0)_{c=\infty}$ together, which can be considered as the swelling ratio V_{\max}/V_0 when no repulsion by counterions takes place. The relation between the amounts of the swelling by the osmotic pressure caused by the counterions and the ionic concentration is proportional. Consequently, the above assumption should be appropriate and is reasonable when applied in eq. (7) to the osmotic pressure caused by the different kinds of counterions. The swelling caused by factors other than the counterions becomes almost equal. This result is consistent with the fact that these Sephadexes have the same skeleton.

Hirose et al.¹⁵ reported that when the same dissociation group was introduced to the gels the volume changes increased the ionic concentration. Our results show that the swelling with the osmotic pressure caused by the counterions depends only on the ionic concentration and is independent of both the charge and the kinds of counterions.

Figure 5 shows the rate constant k of the apparent first-order reaction of the swelling obtained by microscopic observation against the concentration of sodium chloride, c . Sephadex G is not affected by sodium chloride. However, k of the other ionic Sephadexes is large with water and is decreased by the addition of sodium chloride. The relation between the rate constant k and V_{\max}/V_0 of the swelling of the five Sephadexes was plotted as shown in Figure 6. Good correlation is indicated in the correlation coefficient, $\gamma = 0.911$, i.e., the variation of the rate constant k and that of V_{\max}/V_0 show the

same tendency. This result agrees with that found for sodium polyacrylate in our previous paper.¹

Figure 7 shows the heat of the swelling of Sephadex, Q_i , with water and Figure 8 depicts the relation of the maximum heat of swelling, Q_{\max} , and the concentration of sodium chloride. The maximum heat of swelling, Q_{\max} , does not depend on the concentration of sodium chloride. The maximum heats of the swelling were $93.2 \pm 7.1 \text{ J g}^{-1}$ for G, $128.8 \pm 9.1 \text{ J g}^{-1}$ for CM, $92.3 \pm 8.0 \text{ J g}^{-1}$ for SP, $68.8 \pm 10.5 \text{ J g}^{-1}$ for DEAE, and $67.0 \pm 7.2 \text{ J g}^{-1}$ for QAE. This result differs from the results of Figure 3, in which it was shown that the maximum swelling ratio $V_{\max}/$

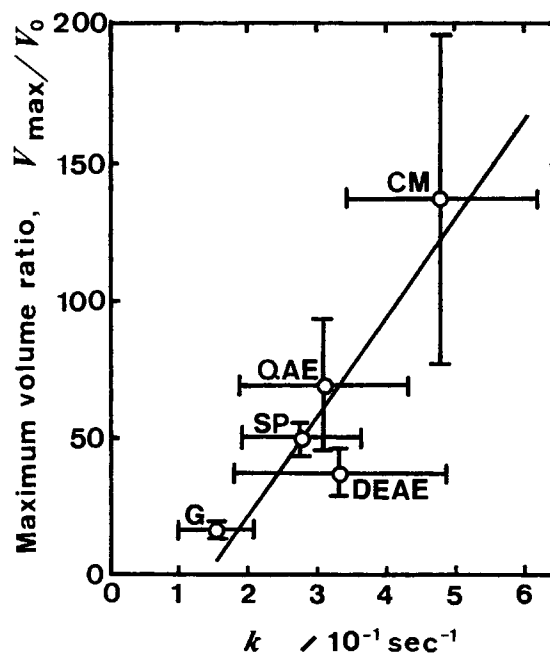


Figure 6 Relationship between apparent first-order rate constant k of swelling of Sephadex and the maximum volume ratio obtained by microscopic observation at 25°C.

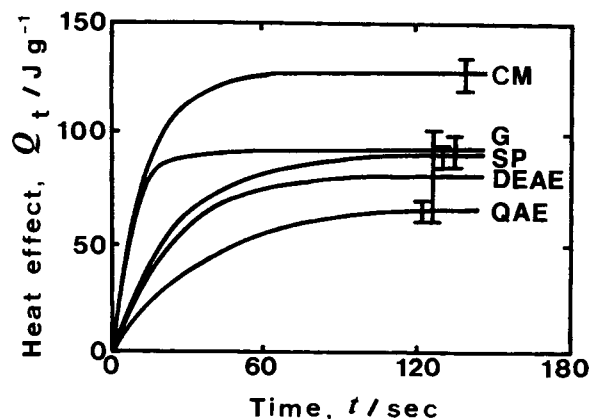


Figure 7 Time course of the heat effect of Sephadex swelling obtained by calorimetry at 25°C.

V_0 was depressed by sodium chloride. The large swelling ratio of the ionic Sephadexes with water indicates that this swelling is not attended by a heat change, i.e., the polymers swell with free water that does not interact with the polymer. Most of the water in the swollen gel of the ionic polymers is thought to be free water that does not interact with the polymer.¹⁶⁻¹⁹ Thus, the results of Figure 8 seem reasonable.

We assume that the heat of the swelling of G is the heat of hydration of the hydroxyl groups in G and that the heats of the other ionic Sephadexes are the sum of the hydration of hydroxyl groups that remained in the molecules and the heat of the dissolution of the ionic dissociable groups. The heat of the ionization of the substituent group is represented in the following equation:

$$Q_{\text{ion}} = Q_{\text{obs}} - (Q_{\text{G}} - Q_{\text{OH}}) \quad (8)$$

where Q_{ion} is the heat of ionization of the substituent group; Q_{obs} , the heat of the swelling of the ionic

Sephadex; Q_{G} , the heat of G; and Q_{OH} , the heat of the hydration of hydroxyl groups that would be substituted.

From the literature,²⁰ $-\Delta H_{\text{soln}}^0$ of β -D-glucose, α -D-glucose, and lactose are +3.3, +2.3, and +3.2 kJeq^{-1} , respectively. Consequently, it is reasonable to take the value of 3.0 kJeq^{-1} for Q_{OH} .

The heat of the ionization of the substituted groups, Q_{ion} , can be calculated from the difference of the heats of the swelling of ionic Sephadex, Q_{obs} , and the difference of the heat of G, Q_{G} , and the heat of the hydration of hydroxyl groups that would be substituted, Q_{OH} .

We calculate the Q_{ion} values of +11.0 kJeq^{-1} for CM, +2.1 kJeq^{-1} for SP, -0.5 kJeq^{-1} for DEAE, and -5.4 kJeq^{-1} for QAE. The values of the standard heat of dissolution ($-\Delta H_{\text{soln}}^0$) of the approximate salts in the literature²⁰ are +17.3 kJ mol^{-1} for sodium acetate, 0 to -2.5 kJ mol^{-1} for ethylene sulfonic acid, -2.5 kJ mol^{-1} for diethylamine hydrochloride, and -2.1 kJ mol^{-1} for triethylenamine hydrochloride. These values agree closely with our results, i.e., the heat of swelling of Sephadex is the sum of the heats of hydration of hydroxyl groups in the Sephadex skeletons and the heat of the dissociation of ionic group in the molecules.

CONCLUSIONS

The swelling of Sephadexes that are either nonionic or that contain one of different ionic groups in the same skeleton of the molecule have been studied by picture analysis and by calorimetry. We conclude that the nonionic Sephadex swells only by hydration, but that ionic Sephadexes swell mainly from the osmotic pressure due to the counterion of the ionic group. The swelling ratio is not dependent on the

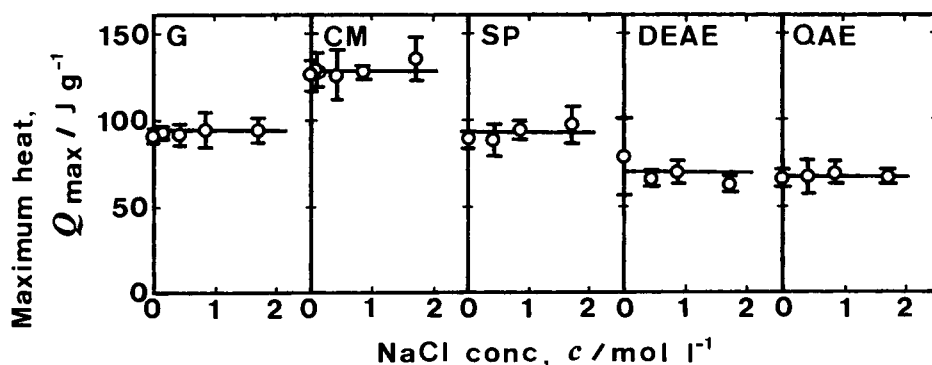


Figure 8 Relationship between the maximum heat effect of swelling of Sephadex and sodium chloride concentration obtained by calorimetry.

kind of ion but on the ionic concentration. Most of the water in the gels of ionic Sephadexes is free water that does not interact with the Sephadexes.

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