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Deswelling Kinetics of Macroporous Poly(*N*-isopropylacrylamide) Gel in Salt Solution

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The deswelling kinetics of a macroporous poly(*N*-isopropylacrylamide) gel in a NaCl solution was investigated. NaCl was used as the probe in order to trace out any hydration from the hydrated polymer chains. In the case of macroporous gel immersed in a NaCl solution, the minimum of the initial deswelling rate ($v = 0.06\ \mathrm{s}^{-1}$) appeared at around 0.2—0.3 M ($1\ \mathrm{M} = 1\ \mathrm{mol\,dm}^{-3}$) when the equilibrated gels (at 22 °C) were heated to 40 °C. The maxima of the apparent activation energy ($E_a = 110\ \mathrm{kJ\,mol}^{-1}$) and the change in the activation entropy ($\Delta S_{313} = 80\ \mathrm{J\,K}^{-1}\,\mathrm{mol}^{-1}$) were at 0.2—0.3 M NaCl. These results indicate that deswelling of the gel in a NaCl solution advanced on the condition of the following two factors. One is an electrostatic repulsion between Cl^- ions below 0.2—0.3 M. Another is a salting-out effect due to NaCl above 0.2—0.3 M. The deswelling kinetics and the lower critical solution temperatures of the gels in other alkalimetal halide solutions were also measured in order to clarify the effect of the species of the cations and the anions on the interaction between the water and polymer chains.

The thermosensitive poly(*N*-isopropylacrylamide) gel, abbreviated as poly(NIPAAm) gel, could deswell 10^2 times faster than a gel having no treatment after a treatment of freeze-dry and hydration; also, the deswelling process was investigated kinetically in connection with the rate-determining step in our previous paper.[1] On the other hand, a conventional gel, which was not treated by freeze-dry and hydration, could deswell during the process of water diffusing through a dehydrated skin layer at the surface of the gel; this diffusion process determined the rate-determining step toward deswelling.[2]

Among the many papers concerning the deswelling mechanism of poly(NIPAAm) gel, the hydrophobic interaction was reported as one of the important problems. The hydrophobic isopropyl groups in poly(NIPAAm) bound with a distinctive structured water, called an "iceberg".[3—8] However, the role of both the hydrophobic and hydrophilic properties of poly(NIPPAm) had not been explained in connection with the deswelling of a macroporous gel; hence, the rate-determining step of deswelling is still unclear.

The lower critical solution temperature (LCST) of the hydrogel or the water-soluble polymer of poly(NIPAAm) was known to decrease in the presence of an alkalimetal halide solution.[9—11] Studies have focused on the interaction between the hydrophobic atmosphere surrounded by polymer chains and coulombically hydrated anions or alkalimetal cations.[5,12]

It was considered that the alkalimetal chlorides were useful for the probe in order to clarify the interaction between the water and polymer chains. This paper presents the results of a kinetic study concerning the deswelling of macroporous poly(NIPAAm) gel with an alkalimetal halide solution in order to resolve any remaining problems.

Experimental

Materials. *N*-Isopropylacrylamide was purchased from Tokyo Kasei Kogyo Co., Ltd. All other chemicals were of guaranteed grade or the best commercially available.

Preparation of Macroporous Poly(NIPAAm) Gel. A macroporous gel of poly(NIPAAm) crosslinked by 4% *N,N′*-methylenediacrylamide was prepared by the freeze-dry and hydration (method 2) treatment, as described in a previous paper.[1] Polymerization was carried out in a silicone tube ($\phi = 2$ mm), from which the gel rod was pulled out. After washing the gel rod by water to remove any unreacted monomer inside the gel, the swollen gel (at 22 °C) was freeze-dried. The dried gel rod was then reswollen in various alkalimetal halide solutions.

Measurement of the Deswelling Rate and the LCST. The initial deswelling rate and the LCST was determined in the same way as described in our previous papers.[1,13] The gel rod equilibrated in an alkalimetal halide solution at 22 °C was transferred to the same solution at the desired temperature ($T = 35$—50 °C). The length (L) of the gel rod was measured with time. Let $(L/L_0)^3$ be the deswelling ratio, where L_0 (= 50—60 mm) is the initial length of the gel rod at 22 °C. The initial deswelling rate, $-\mathrm{d}(L/L_0)^3/\mathrm{d}t$, was determined from the slope of the line obtained by plots of $(L/L_0)^3$ against time. The apparent activation energy (E_a) and the pre-exponential factor (A) were obtained by Arrhenius's equation. The activation entropy change (ΔS_{313}) at 313 K was calculated from A. Depression of the LCST (ΔT) was defined as

$$\Delta T\ \ (\mathrm{K}) = T_\mathrm{L} - 307, \qquad (1)$$

where the LCST in water was 307 K, and T_L (K) expressed each LCST of the gel in different concentrations of salt solution.

Results

Effects of Cations on the Deswelling Rate. After submerging equilibrated poly(NIPAAm) gel rods (in LiCl solution at 22 °C) into a LiCl solution of the same concentration at 40 °C, the change in $(L/L_0)^3$ was measured with time. The results are shown in Fig. 1. The initial deswelling rates, shown as the slopes of the solid line in the inserted figure in Fig. 1, were found to increase with increasing the concentration of LiCl. Figure 2 shows the relationship between $-\mathrm{d}(L/L_0)^3/\mathrm{d}t$ and the concentration (C) of LiCl, NaCl, and KCl, respectively. The minimum $-\mathrm{d}(L/L_0)^3/\mathrm{d}t$ appeared at around 0.1—0.3 M (1 M=1 mol dm^{-3}) of each cation. Arrhenius plots of LiCl, NaCl, and KCl are shown in Fig. 3. The E_a's and ΔS_{313}'s were calculated according to the Arrhenius equation using the slopes of the lines in Fig. 3. The E_a's and ΔS_{313}'s against the alkalimetal halide concentrations are plotted in Figs. 4 and 5. The maxima of the E_a's and ΔS_{313}'s in Figs. 4 and 5 are summarized in Table 1.

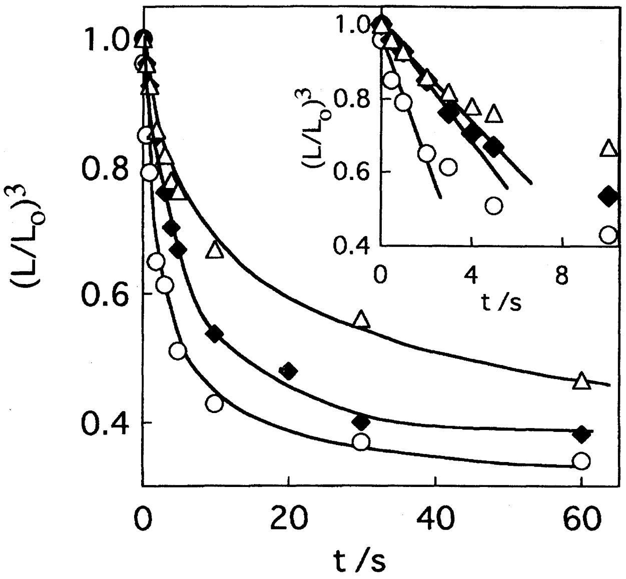

Fig. 1. Deswelling kinetics of macroporous poly(NIPAAm) gel in LiCl solution. The gels equilibrated at 22 °C were submerged into the same concentration of LiCl solution at 40 °C. The slope of the solid line was defined as the initial deswelling rate, $-\mathrm{d}(L/L_0)^3/\mathrm{d}t$: △ 0.05 M, ◆ 0.1 M, ○ 0.5 M LiCl solution.

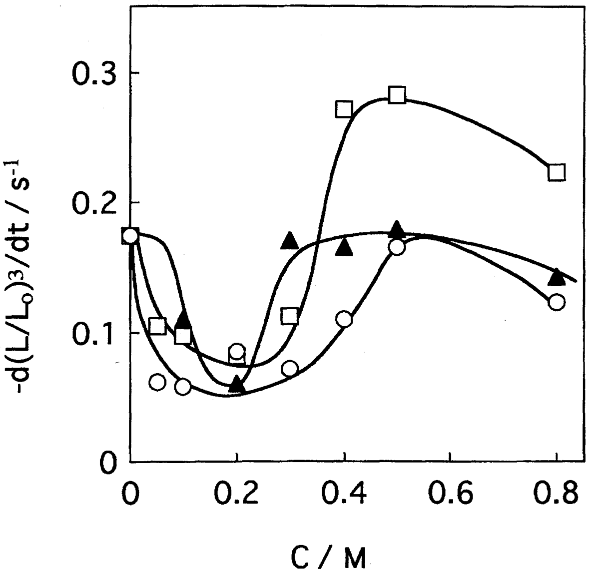

Fig. 2. Cation dependence of the initial deswelling rate. The gel rods were heated in the salt solution at 40 °C: ○ LiCl, ▲ NaCl, □ KCl solution.

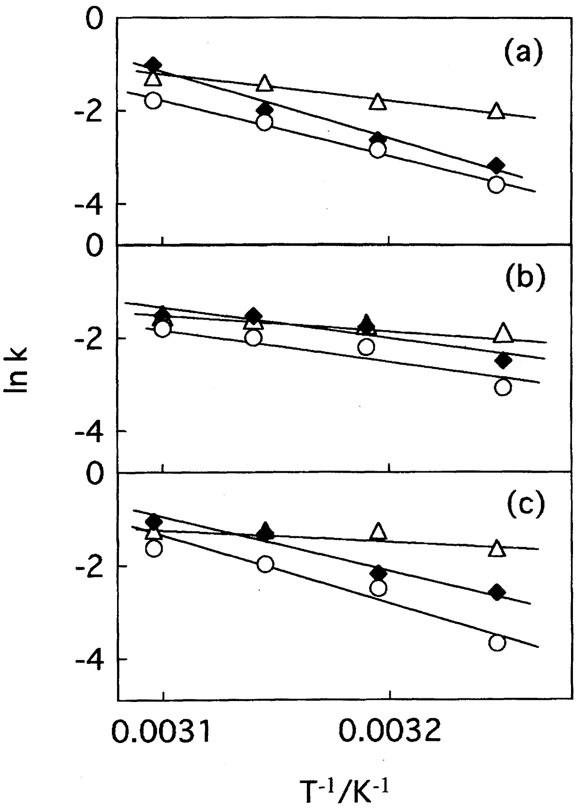

Fig. 3. The Arrhenius plots on the gels in LiCl (a), NaCl (b), and KCl solution (c): ○ 0.1 M, ◆ 0.3 M, △ 0.5 M.

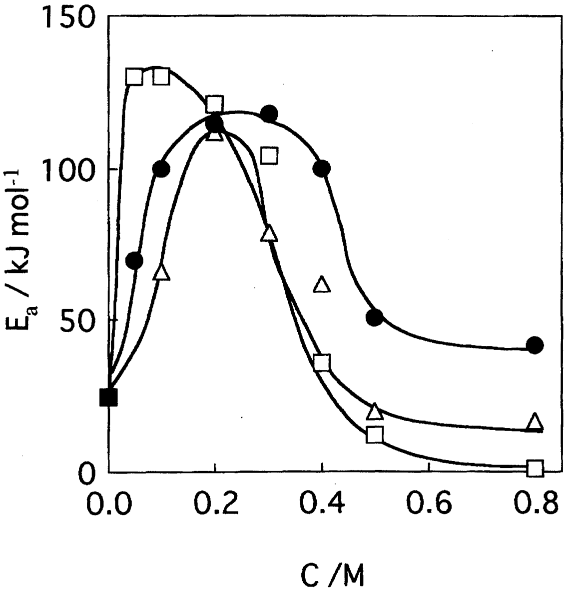

Fig. 4. Cation dependence of the apparent activation energy (E_a) in LiCl (●), NaCl (△), and KCl solution (□). E_a's were calculated according to Arrhenius equation with the slopes in Fig. 3

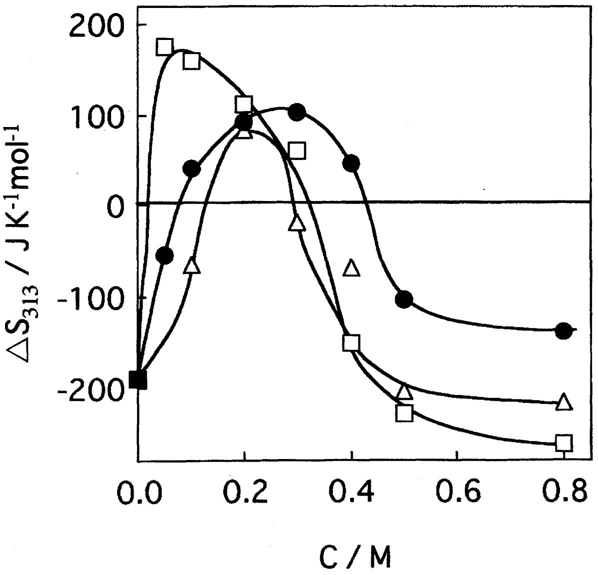

Fig. 5. Cation dependence of the activation entropy change (ΔS_{313}) in LiCl (●), NaCl (△), and KCl solution (□). ΔS_{313}'s were obtained from the pre-exponential factors which were calculated according to Arrhenius equation.

Table 1. The Values for E_a's and ΔS_{313}'s at the Maxima in Figs. 4 and 5

	C / M	E_a / kJ mol^{-1}	ΔS_{313} / J K^{-1} mol^{-1}
LiCl	0.3	120±20	100±30
NaCl	0.2	110±20	80±20
KCl	0.1	130±20	180±40

Effect of Halide Ions on the Deswelling Rate. The initial deswelling rates were measured with various concentrations of every halide ion in order to investigate the anion dependence of the initial deswelling rates. The results are given in Fig. 6. The initial deswelling rates in a solution containing halide ions were smaller than that in water. A minimum was observed at around 0—0.3 M in the case of NaF and NaCl. Arrhenius plots of NaF, NaBr, and NaI are shown in Fig. 7, respectively. The E_a's and ΔS_{313}'s were calculated according to the Arrhenius equation, with the slopes of the lines in Fig. 7. The E_a's and ΔS_{313}'s against the halide-ion concentrations are plotted in Figs. 8 and 9. The maxima or the minima of the E_a's and ΔS_{313}'s in Figs. 8 and 9 are summarized in Table 2.

Effect of Salt Addition on the LCST. The plots of ΔT's against the concentrations of LiCl, NaCl, and KCl in Eq. 1 fell on straight lines, as shown in Fig. 10. The slope of LiCl was different from those of NaCl and KCl. Like Fig. 10, the ΔT's were plotted against the concentration of sodium halides and potassium halides, as shown in Fig. 11. The result of the present study showed a similar response compared with that of the conventional gel.[5] The effect of the anions on ΔT increased in the order F^-, Cl^-, Br^- and I^-.

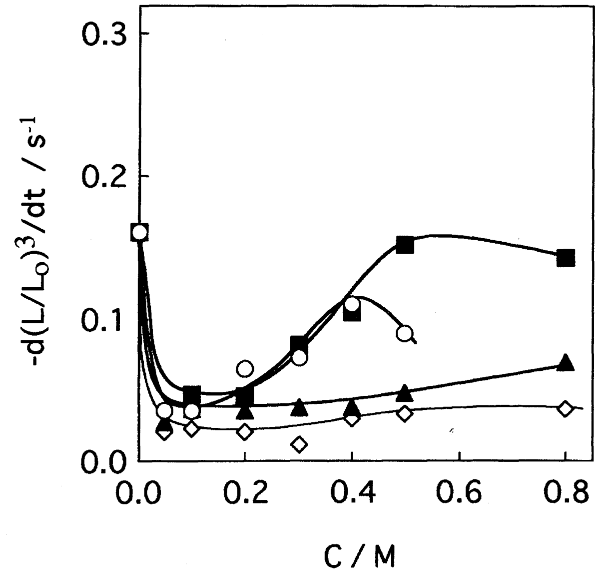

Fig. 6. Anion dependence of the initial deswelling rate. The gel rods were heated to 35 °C in NaF (○), NaCl (■), NaBr (▲), and NaI solution (◇).

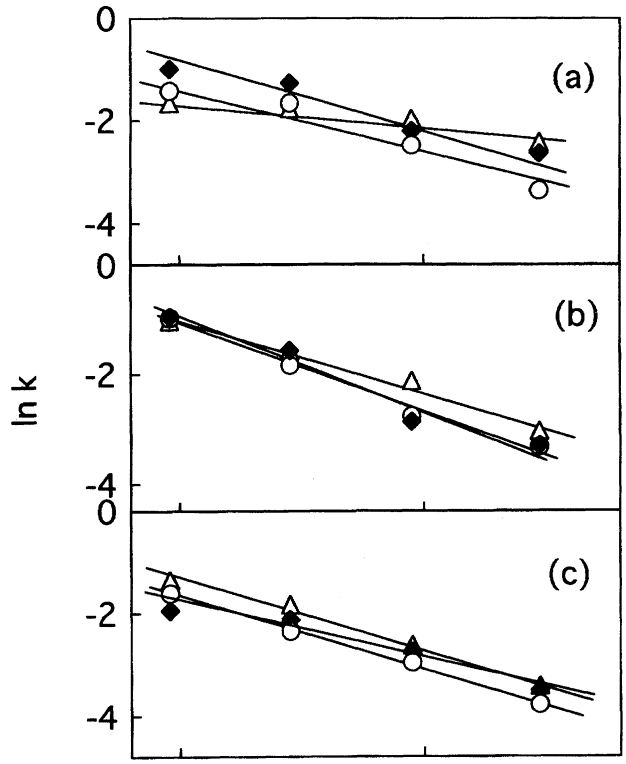

Fig. 7. The Arrhenius plots on the gels in NaF (a), NaBr (b), and NaI solution (c): ○ 0.1 M, ◆ 0.3 M, △ 0.5 M.

The slopes of the solid lines were obtained based on an extrapolation to zero mol kg^{-1}. The LCST depressing constants (K_d's) were calculated by the following equation:

$$\Delta T\ (\mathrm{K}) = -K_d \times C, \tag{2}$$

where C is defined as the concentration of alkalimetal halide.

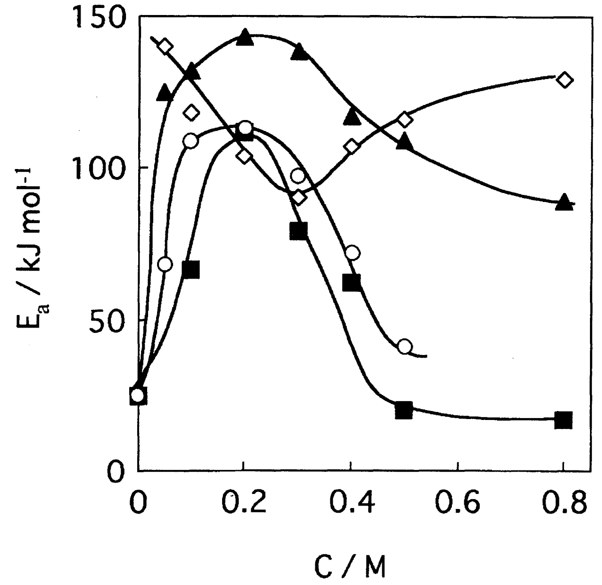

Fig. 8. Anion dependence of the apparent activation energy (E_a) in NaF (○), NaCl (■), NaBr (▲), and NaI solution (◇). E_a's were calculated according to Arrhenius equation with the slopes in Fig. 7.

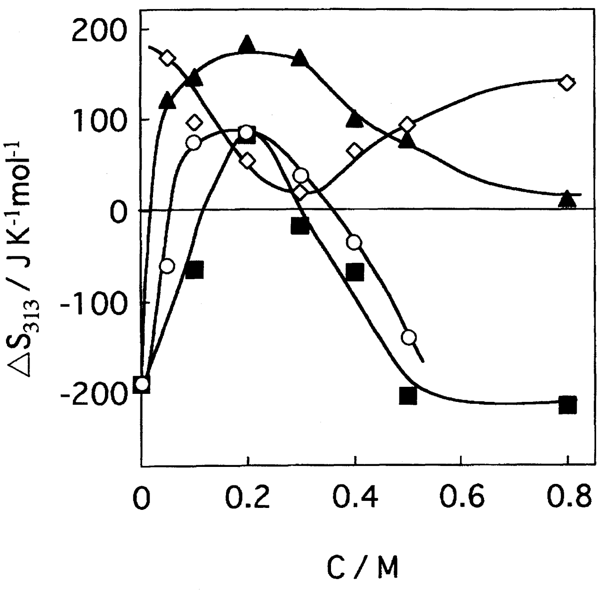

Fig. 9. Anion dependence of the activation entropy change (ΔS_{313}) in NaF (○), NaCl (■), NaBr (▲), and NaI solution (◇). ΔS_{313}'s were obtained from the pre-exponential factors which were calculated according to Arrehenius equation.

Table 2. The Values for E_a's and ΔS_{313}'s at the Maxima or Minima in Figs. 8 and 9

	C	E_a	ΔS_{313}
	M	kJ mol^{-1}	J K^{-1} mol^{-1}
NaF	0.2	110±20	80±20
NaCl	0.2	110±20	80±20
NaBr	0.2	140±20	180±20
NaI	0.3	90±30	20±30

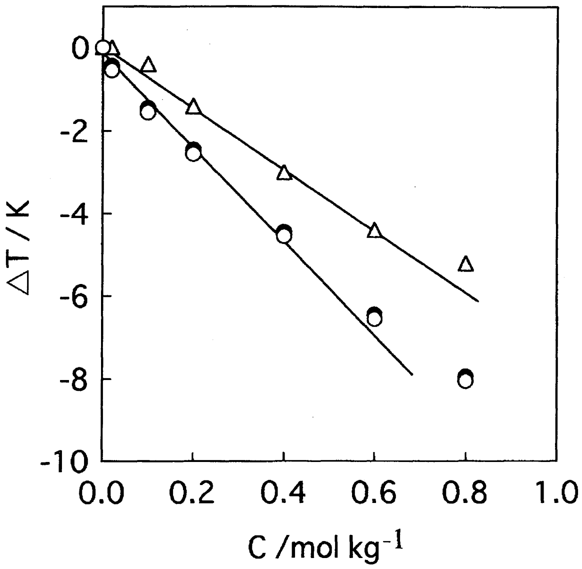

Fig. 10. Relationship between ΔT and concentrations of LiCl (△), NaCl (●), and KCl (○) solution. ΔT was calculated with Eq. 1.

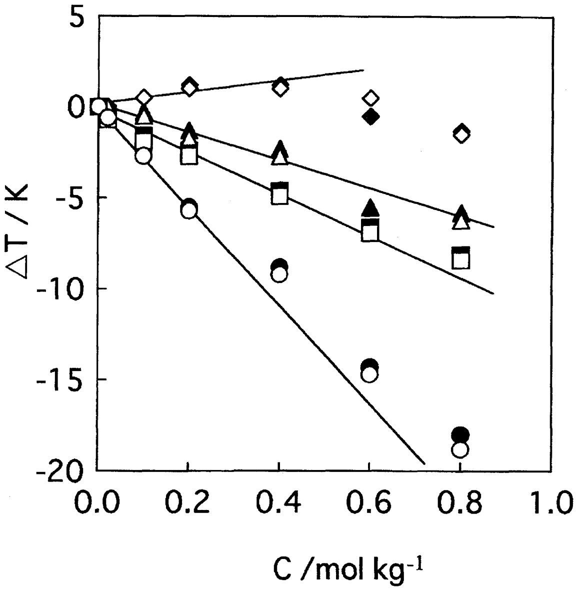

Fig. 11. Relationship between ΔT and concentrations of sodium halides and potassium halides: NaF (●), NaCl (■), NaBr (▲), NaI (◆), KF (○), KCl (□), KBr (△), KI (◇). ΔT was calculated with Eq. 1.

The results of K_d in various salt solution are summarized in Table 3.

Discussion

The Initial Deswelling Rate. Since the plots of $(L/L_0)^3$ against time fell on straight lines during an early stage of the deswelling process illustrated in Fig. 1, it was assumed that the deswelling rate could be determined as a zero-order reaction with respect to $(L/L_0)^3$. In that case, the initial deswelling rate should be equal to the deswelling rate constant (k) as follows:

Table 3. The LCST Depressing Constants (K_d)[a]

	Na^+	K^+	Li^+
F^-	27	27	
Cl^-	12	12	7.8
Br^-	4.6	4.6	
I^-	−2.7	−2.7	

a) K_d (K kgmol^{-1}) was obtained from Figs. 10 and 11 with using Eq. 2.

$$\lim_{t\to 0}[-\mathrm{d}(L/L_0)^3/\mathrm{d}t] = [-\mathrm{d}(L/L_0)^3/\mathrm{d}t]_0 = k. \qquad (3)$$

The deswelling rate was considered to be a function of the pore size, because the contact surface area between the water and polymer matrix is changed by the pore size. We could assume

$$[\text{Volume change}] : [\text{Area change}] = (L/L_0)^3 : (L/L_0)^2 = L : L_0$$

when the pore size was regarded as constant, the deswelling rate of the gel (the volume change) was considered to be approximately a zero-order reaction. We could discuss E_a and ΔS_{313} obtained by the Arrhenius equation.

Deswelling in Alkalimetal Chloride Solution. It was reported in our previous paper that an expansion of the diffusion area of water and a decrease in the thickness of the surface layer for a macroporous gel could be the reason for the increase in the deswelling rate, and that there was no speculation on the rate-determining step in the deswelling process of a macroporous gel.[1] The E_a's of the deswelling process of a macroporous gel containing 0.1—0.3 M alkalimetal chloride were roughly the same as that of the conventional gel without NaCl. However, these results could not be explained in connection with the water-diffusion area in the gel.

Lithium, sodium, and potassium had a similar effect on the deswelling rate given in Fig. 2. Therefore, it was considered that there was no essential difference with respect to the effect of the cation on the deswelling rate.

The Effect of Cl^- Ions. Park and Hoffman speculated in connection with lowering the LCST in their paper, that Cl^- ions might bind specifically to a certain portion (perhaps polar amide groups) of the polymer segment and/or might interact with hydrated water molecules which were associated with polar or hydrophobic polymer segments.[12] On the other hand, the salting-out effect was well known for the sedimentation of proteins and polymers.[14,15]

We obtained peculiar results, as presented in Figs. 2 and 6, which showed bottoms in the curves. These results were studied by separating into two regions of lower and higher than 0.1—0.3 M aklalimetal chloride.

After immersion in a 0.2 M NaCl solution at 22 °C, the amount of Cl^- ions inside the gel was given as follows:

$$0.2\ (\mathrm{M}) \times V_0\ (\mathrm{ml}) \times 0.9 = 0.034\ (\mathrm{mmol}),$$

where the gel volume was $V_0 = 0.19$ ml ($\phi = 2$ mm, 60 mm long) and 90% of the gel volume was occupied by the solvent. Figure 2 shows the bottoms at about a four- or six-times higher concentration of the NIPAAm unit than that of Cl^- ions on the initial deswelling rate, because the amount of the NIPAAm unit inside the gel ($V_0 = 0.19$ ml) was 0.21 mmol.

In the case of 0.2—0.3 M alkalimetal chloride, it was assumed according to Hoffman's explanation that Cl^- ions might interact with water molecules bound to a polymer segment. Some of the Cl^- ions might be placed around polymer segments, despite the fact that the concentration was too low to dissociate hydrated water to polymer segments. Consequently, the electrostatic repulsion between Cl^- ions might disturb the intermolecular interaction between polymer segments, and might give rise to a decrease in the deswelling rate and, in turn, increase the E_a's and ΔS_{313}'s in Figs. 4 and 5.

In the case of higher than 0.2—0.3 M alkalimetal chloride, the acceleration of the deswelling rate and the decrease in the E_a's and ΔS_{313}'s might result from a salting-out effect. It is plausible that the presence of excess Cl^- ions in bulk water might drown the electrostatic repulsion between the Cl^- ions around polymer chains, and facilitate the dissociation of hydrated water to polymer segments. On the other hand, that the hydrophobic aggregation force might be strengthened with increasing the temperature above that of the LCST was also considered in addition to the salting-out effect.

Deswelling in Other Salt Solutions. Other halide ions might bind to hydrated water molecules around the polymer chains in the same way as Cl^-.

The curves of E_a and ΔS_{313} of I^- were different from those of other halide ions in Figs. 8 and 9. Although the effect of additive I^- ions was not clearly known, this peculiar behavior was supposed to have originated from the strong structure-breaking properties of I^-.

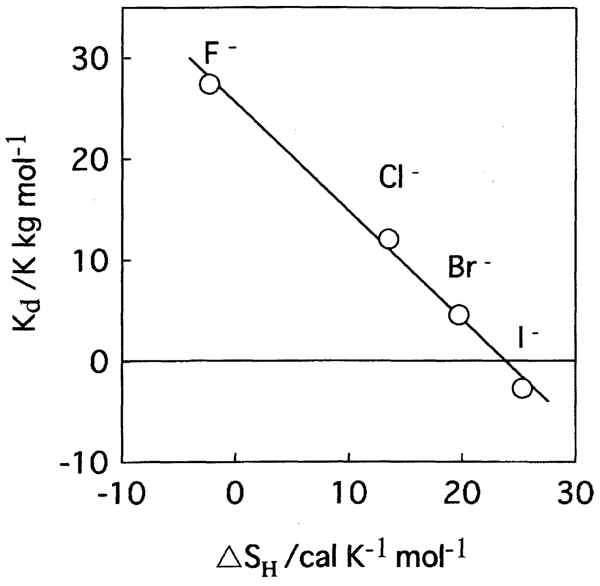

Fig. 12. Relationship between the entropy of hydration (ΔS_H) and the LCST depressing constant (K_d). K_d's were calculated with Eq. 2. ΔS_H's were cited from the previous literature.[16]

E_a and ΔS_{313}. The maxima of the E_a's and ΔS_{313} in the curves in Figs. 4, 5, 8, and 9 were explained using two factors: One is the effect of an increase due to the repulsion between the halide ions; the other is that of a decrease due to the salting-out effect.

The Relationship between K_d and ΔS_H. By using the K_d's (summarized in Table 3) and ΔS_H referred from Latimer et al.,16) the relationship between K_d and ΔS_H was obtained (Fig. 12) in which ΔS_H was defined as the entropy of hydration for each anion at 298.1 K. It is indicative from Fig. 12 that halide ions broke the structure of water around the polymer segments. The decrease in the LCST might be responsible for the decrease in the interaction between the polymer and water due to the hydration properties of the halide ions. On the other hand, there was a significant difference of the K_d's in the solution between LiCl and NaCl (Fig. 10). This result also indicated that both anions and cations could affect the poly(NIPAAm) polymer chains cooperatively and alter the interaction between polymer and water.

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