Macromolecules **1996,** *29,* 8391−8397

Ion-Specific Swelling and Deswelling Behaviors of Ampholytic Polymer Gels

Y. Okazaki, K. Ishizuki, S. Kawauchi, M. Satoh,* and J. Komiyama

Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguroku, Tokyo 152, Japan

Received August 1, 1996; Revised Manuscript Received September 30, 1996⊗

ABSTRACT: Ampholytic polymer gels were prepared by γ-ray irradiation to aqueous solutions of two kinds of poly(vinyl alcohol)s containing sulfonate and quaternary ammonium groups, respectively. By adjusting the mixing ratio of the two polymers, three kinds of ampholytic gels were obtained: anion-rich, cation-rich, and 1:1 ampholytic ones. These gel samples were immersed in many kinds of salt solutions and buffers to observe the swelling behavior. The swelling degrees of the cation-rich and the anion-rich gels decreased with the increase in the salt concentration (from 0 to $10^{-3}-10^{-2}$ M), followed by reswelling with a further increase in the ionic strength of the immersing solutions. The initial deswelling is common to ionic gels and the latter swelling may be ascribed to scission of preformed ionic cross-linking. A similar swelling was also observed for the 1:1 gel, which did not show any decrease in the swelling degree in the lower salt concentration region. A remarkable ion-specificity was noted at the highest salt concentration region above 0.1 M; the three kinds of gels significantly deswelled in solutions containing strongly hydrated anions, such as F^-, SO_4^{2-}, HPO_4^{2-}, and citrate anion. The ion-specific swelling behavior is discussed in terms of the compatibility of ionic hydration with the polymer hydroxyl group through the electron pair donation and acceptance abilities of the water molecules.

Introduction

The response of polyion gels to external stimuli, e.g., pH,[1,2] temperature,[3,4] salt concentration,[5,6] solvent composition,[7] has been extensively studied. Their unique properties have been utilized also in an industrial application field such as separation materials.[8] However, when one considers application of a polyion gel as a super absorbent, the sensitivity to surrounding salt concentration and/or pH should be rather disfavored.

Polyampholyte may be a promising candidate for a component polymer in super water absorbent gels which are free from unfavorable influences of concentrated salt in aqueous medium. According to Baker et al.,[9] an acrylamide-based polyampholyte swells by 40% with increasing NaCl concentration in a region from 10^{-2} to 1.0 M, in contrast to deswelling at higher salt concentration observed for common polyion gels.

The initial aim of the present study was preparation of an ampholytic polymer gel which contains strong acidic and basic groups, to ensure its insensitivity to external pH changes, and maintains high degrees of swelling even at the highest salt concentrations. As expected, the gel prepared from two kinds of modified poly(vinyl alcohol)s which contain 10 mol % of sulfonic and quaternary ammonium groups, respectively, showed a significant swelling in an aqueous solution, e.g., of NaSCN, in a higher concentration region, typically 0.1−3 M. At the same salt concentration region, however, we have found a marked ion-specific swelling behavior; the ampholytic polymer gel remarkably deswelled in solutions containing anions such as F^-, SO_4^{2-}, and HPO_4^{2-}. To our knowledge, this kind of ion-specificity on ampholytic gels has not been reported.

In the present study, we have focused our attention on the ion-specific deswelling at the higher salt region. The sequence of anions for deswelling power were obtained as $SCN^- < Cl^- < CH_3COO^- < F^- < SO_4^{2-} < HPO_4^{2-} <$ citrate, which is compared to the Hofmeister series. This empirical rule is still often invoked for summarizing experimental observations on various kinds of salt effects, e.g., for solubilization of polyampholytes in aqueous media,[10,11] and swelling of nonionic polymer gels,[12] as well as salting out of proteins and polysaccharides. However, the mechanism has never been clarified. Thus, through the present investigation, we have proposed one possible mechanism for such salt effects.

Experimental Section

Materials. Two kinds of poly(vinyl alcohol)s, which contain 10 mol % of sodium 2-(acrylamido)-2-methylpropanesulfonate and *N*-(3-(acrylamido)propyl)trimethylammonium chloride as copolymer components, respectively, were kindly supplied by Kuraray Co. Ltd. The chemical details of the samples are given in Figure 1. Since the samples were supplied as two different lots, the respective samples are named as PVA(S)1, PVA(S)2, PVA(N)1, and PVA(N)2, where S means anionic PVA and N the cationic one, and the numbers show the difference in lot.

As solutes for immersing solution, the following salts and buffers were employed (all are of analytical grade from Kanto Chem. Co.): NaF, NaCl, NaSCN, Na_2SO_4, KF, KCl, KSCN, $MgCl_2$, $MgSO_4$, acetate buffer (CH_3COONa[mol]:CH_3COOH[mol] = 2:1), phosphate buffer (KH_2PO_4:K_2 HPO_4 = 1:1), citrate buffer ($KH_2C_6H_5O_7$:NaOH = 1:2). These buffer solutions were employed to adjust the pH to the neutral region (pH = ca. 5.0 for acetate buffer, ca. 7.3 for phosphate and ca. 7.6 for citrate), since in basic or acidic ones amide in the polymer side chain may be hydrolyzed. Urea (Kanto Chem. Co., analytical grade) was also used as a single and/or mixed solute.

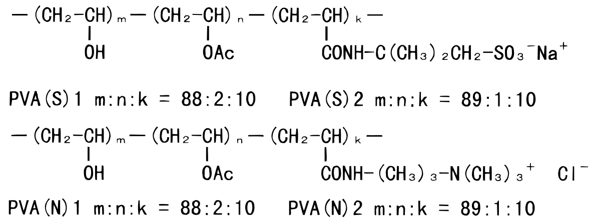
Preparation of Gels. It has been known that vinyl polymers having α-proton such as PVA are easily cross-linked to form gel in aqueous solution.[13] A typical mechanism of cross-linking is considered as follows: α-protons on polymer are abstracted by active species, e.g., hydroxyl radical, which are produced from water under γ-ray irradiation, and such radicals on α-carbons are coupled to form cross-linkings.

Ampholytic gels of different net charges were prepared by irradiating aqueous solutions of PVA(S)1 and PVA(N)1 (or PVA(S)2 and PVA(N)2 with γ-ray (ca. 200 kGy from ^{60}Co at room temperature). Sample solutions of ca. 30 mL were prepared by mixing the two polymers at various ratios with the total concentration kept at 10 wt % in a test tube. The sample solutions thus prepared were slightly opaque, suggest-

---

⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1996.

S0024-9297(96)01155-2 CCC: $12.00



$$-(CH_2\text{-}\underset{OH}{CH})_m-(CH_2\text{-}\underset{OAc}{CH})_n-(CH_2\text{-}\underset{CONH\text{-}C(CH_3)_2CH_2\text{-}SO_3^-Na^+}{CH})_k-$$

PVA(S)1 m:n:k = 88:2:10 PVA(S)2 m:n:k = 89:1:10

$$-(CH_2\text{-}\underset{OH}{CH})_m-(CH_2\text{-}\underset{OAc}{CH})_n-(CH_2\text{-}\underset{CONH\text{-}(CH_3)_3\text{-}N(CH_3)_3^+\ Cl^-}{CH})_k-$$

PVA(N)1 m:n:k = 88:2:10 PVA(N)2 m:n:k = 89:1:10

Figure 1. Nominal chemical structures of the anionic and the cationic PVA's.

ing that microphase separation, probably due to a polyion complex, occurred in the solution before irradiation. This opaque does not seem to affect the gel swelling behavior; according to a preliminary experiment, transparent sample solutions were obtained in the presence of 5 wt % of NaCl. The gels prepared from the transparent solutions showed higher degrees of swelling by ca. 50%, while the qualitative swelling behavior was the same as that of gels prepared in the absence of NaCl.

Gel fractions of the ampholytic gels were estimated from a weight of polymer component in gel as prepared and that of polymer recovered after Soxhlet extraction (9 h with water) of the gel. Almost constant values, 70−80%, were obtained irrespective of the polymer mixing ratios studied here.

Measurements of Swelling Degree. Degree of swelling in distilled water, DS_{aq}, was defined as

$$DS_{aq} = (w_{aq} - w_p)/w_p \tag{1}$$

where w_{aq} and w_p are weights of gels in the swollen and dry states, respectively. w_p was obtained by drying swollen gel samples in a vacuum oven at 100 °C. When the gels were immersed in aqueous solution of the above solutes, the degree of swelling, DS_{sol}, was estimated by using swollen gel weight including solute's weight, w_{sol}, instead of w_{aq} in eq 1. Equilibrium values for these swollen gel weights were obtained after daily exchange of immersing water or solution (usually 7 days for w_{aq} and 5 days for w_{sol}).

Measurements of Solute Distribution Coefficient. Distribution coefficient, K, was determined by a desorption method; a gel in equilibrium with an immersing solution was dipped into distilled water for 3 days with daily exchange of water. By analyzing the total solute amount desorbed, (when the solute was a salt, atomic absorption spectroscopy was applied to the constituting cation; for a buffer, UV absorption at ca. 200 nm was utilized.) K was determined as

$$K = \{g_3/(g_1 + g_2 + g_3)\}/\{g_3^*/(g_1^* + g_3^*)\} \tag{2}$$

where g is the weight in the gel phase and the subscripts 1, 2, and 3 stand for water, polymer, and solute, respectively, and * for immersing solution.

Results and Discussion

Preparation of Ampholytic Gels. In Figure 2, DS_{aq} was plotted against the weight percent of PVA(S)1 or PVA(S)2 in the sample solution for irradiation. The minima in the respective plots show the points where cationic charged groups are completely counterbalanced by anionic ones in the gel, namely, "neutral" gels were obtained. In the following, these neutral gels are named ampholytic gels 1 or 2, which were prepared from aqueous solutions containing 4.6 wt % of PVA(S)1 or 5.2 wt % of PVA(S)2. An anion-rich and a cation-rich gel which were prepared from lot 1 polymers (the compositions of PVA(S)1 were 5.0 and 4.2 wt %, respectively) were also used for measurements of DS_{sol}.

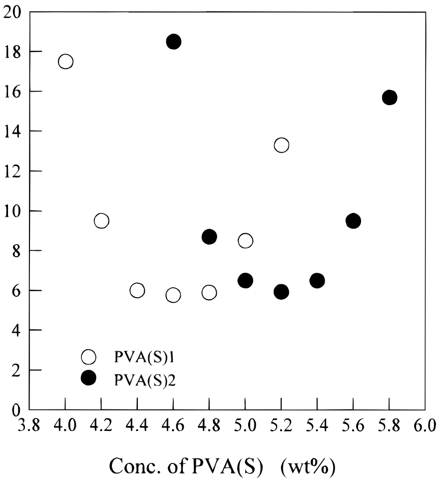


Figure 2. Dependence of DS_{aq} on PVA(S) composition. The total weight percent of the polymers (PVA(S) + PVA(N)) was kept at 10 wt %.

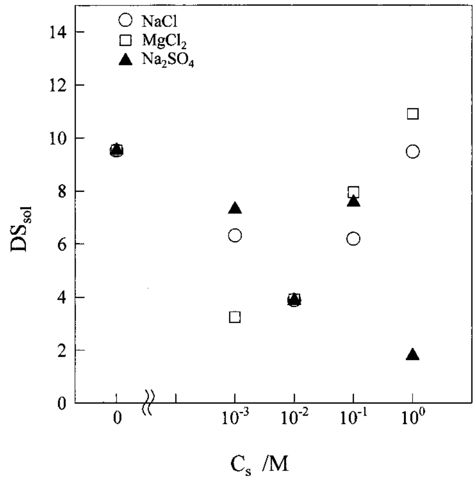


Figure 3. Dependence of DS_{sol} of the anion-rich gel on the salt concentration of the immersing solution.

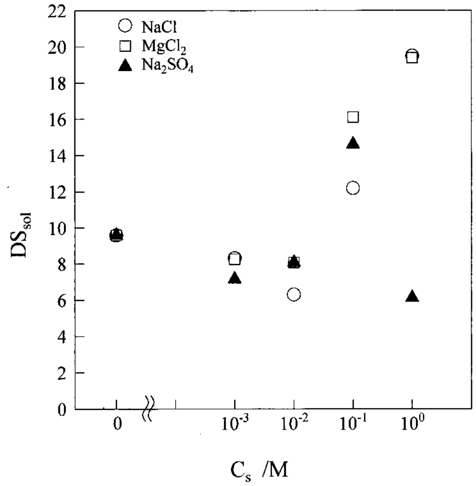


Figure 4. Dependence of DS_{sol} of the cation-rich gel on the salt concentration of the immersing solution.

In the following, we discuss an ion-specific swelling behavior observed for ampholytic gels 1 and 2 which are prepared from polymers of different lots. This may be rationalized because the DS_{aq} values are almost the same (5.76 and 5.93 for gels 1 and 2, respectively), suggesting that the compositions of the respective polymer gels are comparable.

DS_{sol} of Anion- and Cation-Rich Gels. Figures 3 and 4 show the dependence of DS_{sol} on salt concentration (C_s) of immersing solution for the anion-rich and cation-rich gels, respectively. Here one may note a

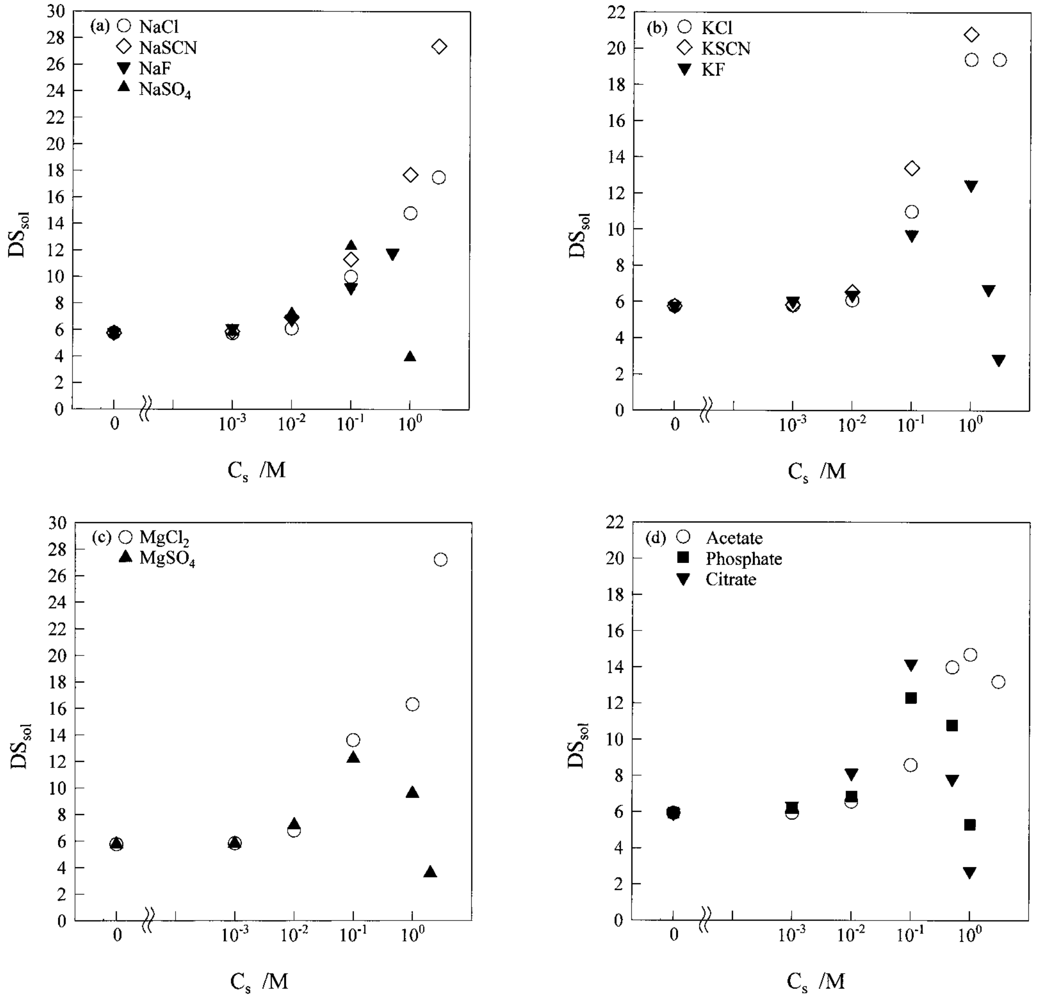


Figure 5. Dependence of DS_{sol} of the ampholytic gel on salt or buffer concentration of the immersing solution. (a) Sodium salts and ampholytic gel 1 were used. (b) Potassium salts and ampholytic gel 1. (c) Magnesium salts and ampholytic gel 1. (d) Buffers and ampholytic gel 2.

general trend, initial decrease in DS_{sol} followed by an increase with the increased in C_s. The former is commonly observed for ionic gels and ascribed to excess anionic or cationic charges in the pertinent gels. The increase in DS_{sol} above $C_s = 10^{-3}-10^{-2}$ M is also typical of ampholytic gels[9] and may be attributed to scission of ionic cross-linkage due to an increase in the ionic strength and interaction of charged groups and counterions.

As a most unusual swelling behavior in the figures, one should note that DS_{sol} significantly decreases only for Na_2SO_4 systems above $C_s = 0.1$ M. Since the second decrease in DS_{sol} is observed for both of anion-rich and cation-rich gels, it is unlikely that a specific interaction of the divalent ion, SO_4^{2-}, with the polymer charges causes the deswelling. A possible mechanism for the unique swelling behavior will be suggested at a later section.

DS_{sol} of Ampholytic Gels. As shown in Figure 5a–c, a similar swelling behavior was observed also for ampholytic gels, although the initial decrease in DS_{sol} was not seen in the plot because the gels have no excess charges. A distinct decrease in DS_{sol} at the higher C_s region is noted for the KF system as well as in Na_2SO_4 solution. This fact suggests that anions of strong hydration induce the deswelling, which reminds us of the Hofmeister series. Thus we investigated effects of other anions of strong hydration, i.e., acetate, phosphate, and citrate anion. The results were shown in Figure 5d. As expected, a significant deswelling was found for phosphate and citrate buffers, while DS_{sol} for acetate buffer slightly decreased at the highest C_s. Since the constituent anions for the respective buffers at the highest concentrations studied are CH_3COO^- (ca. 30% as CH_3COOH), HPO_4^{2-} (ca. 45%), $H_2PO_4^-$ (ca. 55%), citrate trianion (ca. 98%), the following sequence may be considered as an order of deswelling power of anions to the pertinent ampholytic gel:

$$SCN^- < Cl^- < CH_3COO^- < F^- < SO_4^{2-} \sim HPO_4^{2-}(H_2PO_4^-) < \text{citrate trianion}$$

Here we compared DS_{sol} values above $C_s = 1.0$ M and neglected the samll difference in the original DS_{aq} values for gels 1 and 2.

This ion specificity cannot result from a decrease in the water activity, because cations of strong hydration such as Mg^{2+} (when added as chloride) seem to keep the swelling with an increase in C_s. The effect of cations for decreasing DS_{sol}, much less apparent than that of the anions, is in the order

$$Mg^{2+} \leq K^+ \leq Na^+ \tag{4}$$

These two sequences seem to be much the same as Hofmeister's lyotropic series, the mechanism of which has not been elucidated.

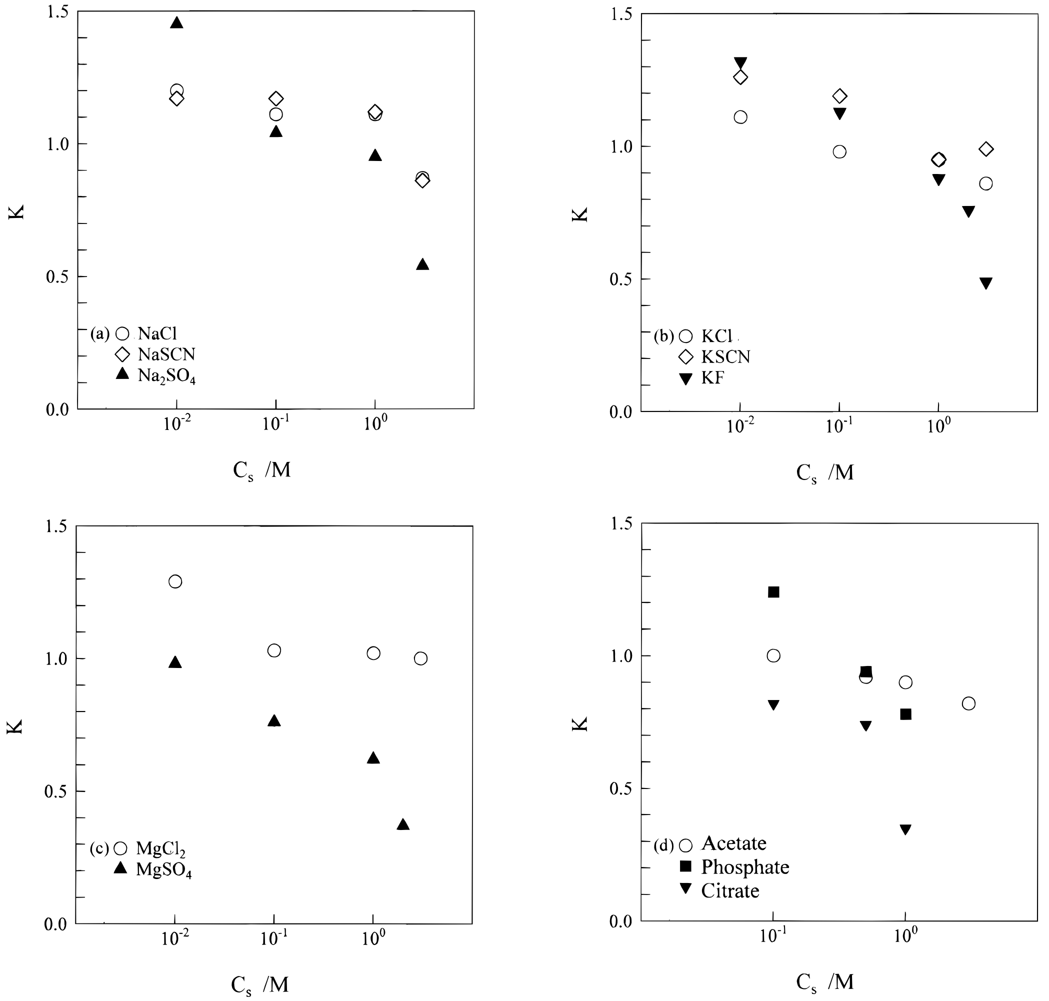


Figure 6. Dependence of the distribution coefficient for the ampholytic gel on the salt or buffer concentration of the immersing solution. (a−d): see Figure 5.

Several workers have reported "specific binding" of anions to polymers in aqueous solution, which may explain the salting-in effect of the relevant anions. According to Dušek et al.,[12] poly(2-hydroxyethyl methacrylate) (PHEMA) binds ClO_4^- and SCN^- even in the dilute solutions. Song et al.[14] also found with NMR spectroscopy that anions of weak hydration, such as SCN^- and I^-, are bound to poly(vinylpyrrolidone) in aqueous solutions. Thus, specific ion binding of SCN^- to the present ampholytic gels, if any, may explain its salting-in behavior. We have investigated the possibility by measuring the salt distribution coefficient, K.

Correlation of K and the (De)Swelling Behavior. In Figure 6a−d, estimated K values are plotted against C_s for sodium, potassium, magnesium salts and buffers, respectively. As a general trend, K decreases with increasing C_s; we could not find any extra absorption of SCN^- salts, which might explain the highest DS_{sol}, when compared with Cl^- salts. On the other hand, for salts and buffers which showed marked deswelling in the higher C_s region, a characteristic decrease in K is seen in the corresponding C_s regions. For example, the K value in the KF system decreases from 0.88 at 1 M to 0.49 at 3 M. This experimental observation strongly suggests that deswelling of the gel is coupled with a decrease in K. The pertinent salts or anions seem to be repelled from the vicinity of the polymer segment.

A Mechanism for the Gel Collapse. Here we consider a mechanism for the anion-specific gel collapse. From the experimental results on K, we suppose that the deswelling was induced by an incompatibility of hydration (structure) of the polymer segment or network and that of anion. In order to proceed with the discussion and to confine to a qualitative one, we introduce the following assumptions: (1) The hydration of polymer network is dominated by hydration to the hydroxyl group rather than that to the ionic groups and/or hydrophobic groups. (2) The hydration to the hydroxyl group is characterized as hydrogen-bonding between lone-pair electrons on the oxygen of the hydroxyl group and the proton of water. (3) The stability of the hydrogen-bonding hydration is dependent upon electron pair donation (EPD)[15] and acceptance (EPA)[15] abilities of the water molecule. These properties are enhanced or reduced via hydration to solutes, in the present case, cations and anions.

These assumptions may be justified as follows.

Assumption 1: Since the respective charged groups amount only to ca. 10 mol %, ionic hydration seems to be a minor contributor to the number of hydrating water molecules compared to those of hydrogen-bonding hydration to the hydroxyl group. The same may be said for hydrophobic hydration in the case of the present polymer network.

Assumption 2: A hydroxyl group affords three hydrogen bonds, one with the proton and two with the two lone-pairs on the oxygen. Thus we simply consider that the latter two sites for hydrogen bonding will control the total hydration. (If this is the case, one may explain the asymmetric ion-specificity on the deswelling. See below.) Assumption 3: For example, fluoride ion in aqueous solution is coordinated by water molecules through one of their hydrogen atoms. According to Gutmann,[15] the negative charge on the fluoride ion is partially transferred through the hydrogen atom to the oxygen atom, and also to the other hydrogen through the oxygen. This means that EPA of water in the hydration shell decreases and EPD increases to lead to an unfavorable condition for hydrogen-bond formation with the oxygen atom of the hydroxyl group. The inverse may be said for water which hydrates cations such as Mg^{2+}.

On the basis of these assumptions, we consider what happens to the hydration of the present polymer network with increasing salt concentration.

First of all, as for nonspecific effects of C_s on the swelling of ampholytic polymer gels, two opposite ones should be in operation; one is scission of ionic cross-linkage, as observed, to swell the gels, and the other is dehydration of gels due to reduced water activity. The latter in fact has been often cited as one explanation for the Hofmeister series. These two effects should be enhanced for ions of higher valency.

On the other hand, an ion-specific effect may be deduced based on the above assumptions. Anions of higher charge density (e.g., F^-, SO_4^{2-}, HPO_4^{2-}) are hydrated through hydrogen bonding with protons of water, leading to an increase in EPD and a decrease in EPA of the hydrating water molecules. The higher EPD (the lower EPA) of water is unfavorable for hydration of the pertinent polymer network (assumptions 1 and 2). Then, immersion of the gel into aqueous solution containing high concentration of anions of strong hydration will promote repelling of the unfavorable water together with ions, to result in the total deswelling of gel. The deswollen state may be stabilized by hydrogen bonding between hydroxyl groups on the polymer network as well as re-formation of ionic cross-linking.

As for cations, the very inverse of the anion's effect may be the case; the higher the charge density, the more enhanced the EPA of hydration water is. Thus, Mg^{2+} ions, for example, make a hydration shell around themselves, in which water molecules may be favorably hydrogen-bonded to the oxygen of OH through the proton having a higher partial positive charge. In fact, DS_{sol}'s in 3 M $MgCl_2$ and 1 M $MgSO_4$ are appreciably larger than those in the respective corresponding Na salt solutions. (However, the higher DS_{sol} for Mg salt may be partially contributed by the stronger scission of ionic cross-linking with the divalent cation.)

A puzzle left is the asymmetry in the ion-specificity between anions and cations, namely, why that marked deswelling is observed for the $MgSO_4$ system or why the anion's effect seems more pronounced. An answer may be obtained from one of the nonspecific effects cited above, the dehydration effect of ions. Since the ion-specificity for the gel swelling becomes appreciable only in the higher C_s region, where the dehydration of polymer should be also effective, the favorable polymer hydration imparted through hydration water of cations may be partially cancelled by the nonspecific effect. Here it seems necessary to consider some contribution from hydration of the ionic groups and hydrophobic ones which was first neglected (assumption 1) as a class of hydration which should be subject to the dehydration effect.

Effects of Urea on DS_{sol} and *K*. As discussed above, the observed ion-specificity for the gel swelling seems to be resulted from (de)stabilization of hydrogen-bonding onto the polymer hydroxyl groups through subtle modification of EPD and EPA of water molecules effected by small ions. If the hydrogen-bonding has an essential contribution to the whole polymer hydration, it would be significantly affected by addition of urea of high concentration. In fact, Ilmain et al.[3] reported that a discontinuous volume transition of an interpenetrating network of poly(acrylamide) and poly(acrylic acid) was not observed in the presence of 1 M urea, which was attributed to the well-known ability of urea to disrupt hydrogen bonding, in this case, between the two polymers. In the present study, too, the effect of urea on DS_{sol} and K was checked as shown in Figure 7a,b. Here 1 M NaCl and 3 M KF were used as a cosolute of urea, respectively. DS_{sol} in the absence and in the presence of cosolute increases with the increase in urea concentration. This may be ascribed to "disruption" of the hydrogen bonding of polymer hydroxyl groups. Although the true mechanism of the scission of inter- and/or intrapolymer hydrogen bonding by urea cannot be given at the present stage, if it is effected by a direct interaction of urea with the OH group, then the hydrogen-bonding sites on polymer may be largely occupied by urea. If it is the case, incompatibility of the polymer hydration with that of small anions may be weakened. As a matter of fact, as seen in Figure 7b, K_{co}, K of the cosolute, also increases with urea concentration. The slight increase of K_{co} of NaCl and the significant one for KF seem to support this speculation.

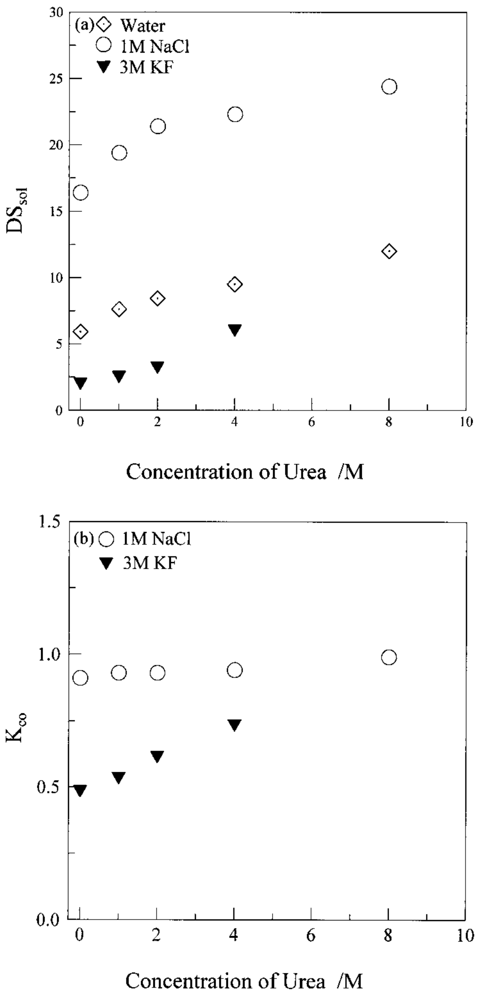


Figure 7. Dependence of DS_{sol} (a) and the distribution coefficient of cosolute (b) for ampholytic gel 2 on the urea concentration of the immersing solution.

Comparison with Other Studies. Since the above discussion is based on many assumptions and speculations, the validity or generality of the proposed mechanism for the gel collapse should be examined by referring to other studies. In the following, we describe a reinterpretation of typical ion specificities, which have been found in polymer gel and solution systems, in terms of the ion effect on the water EPD and EPA.

It seems most appropriate to compare the present experimental results with those for other ampholytic polymer systems. However, in most studies, polymers which have a zwitterionic sulfobetaine group have been employed, and few studies have been reported for salt effects on the gel swelling; several studies are available only for the solution systems. For example, Salamone et al.[11] investigated solubility of poly(vinyl imidazolium sulfobetaine) in water in the presence of various kinds of salts and found the following ionic effects for the polymer solubility: $F^- < Cl^- < NO_3^- < Br^- < I^- < ClO_4^-$ and $NH_4^+ < Li^+ < Na^+ < K^+$. These sequences seem to be consistent with those in the present study for the gel swelling. However, the coincidence may be apparent because the hydration of the ampholytic polymer must be determined largely by those onto the charged groups or ionic hydration. Therefore the above ion specificity should reflect any specificity in interaction between the respective counterions and the zwitterionic group. The same may be said also for ampholytic polymers which have positive and negative charged groups on separate side chains in a rather high density.

A most comparable study to the present study may be that reported by Baker et al.,[9] who prepared ampholytic gels by copolymerizing acrylamide with a cationic monomer containing a quaternary ammonium group and styrene sulfonate as an anionic monomer with the total monomer content kept at 4.7 mol %. The authors investigated the swelling ratio as a function of NaCl concentration and found a qualitatively identical dependence as those in Figures 3−5. Unfortunately, they used NaCl only as added salt, hence it is not certain whether a similar collapse appears for a higher concentration of, for example, Na_2SO_4.

A more relevant comparison may be made for nonionic gels. Dušek et al.[12] extensively studied the salting-in and salting-out effects on the swelling of poly(2-hydroxyethyl methacrylate) (PHEMA) gel in water and reported that ClO_4^-, SCN^-, and I^- as the salting-in anions restrict hydrophobic association of the polymer through the specific binding. Thus, the authors obtained qualitatively the same result as ours while a contrastive explanation as that in the present study was proposed. As far as the gel of PHEMA is concerned, the importance of hydrophobic association and/or anion binding for determination of the swelling behavior may not be denied. However, such a specific anion binding or substantial hydrophobic interaction is unlikely for the present system. Therefore, the salting-in effect of those anions in the study by Dušek et al. may have also resulted, at least partly, from relative stabilization of hydration onto the polymer polar groups, i.e., −COO− and OH, through hydration on the added ions.

On the other hand, Kesting[16] found a lyotropic swelling of a cellulose acetate membrane and attempted to explain it in terms of complex formation between small cations and the hydroxyl and the acetate groups. In his explanation, the swelling effect by large anions such as ClO_4^- was attributed to the water structure breaking ability; the more destroyed the water structure is, the more hydrated the bound cations such as Mg^{2+} are, leading to gel swelling. Further, the observed ineffectiveness of fluoride for gel swelling was ascribed to ion-pair formation with effective cations, which reduces the cation's hydratability. Thus, a possibility proposed in the present study that small anions destabilize the hydrogen-bonding hydration onto the polymer polar groups was not considered in Kesting's study, although it could explain the experimental results. The ion-pair formation between salt constituting anion and cation, which was suggested by Kesting, should also be contributing to the present system. However, it may not be in a way that ion-pair formation impairs the cation's contribution to the gel swelling. For example, in the case of $MgSO_4$, the respective effects for swelling and deswelling may be partially cancelled out by the ion-pairing.

Otake et al.[17] studied effects of small substances such as alcohols, DMSO, and salts on the phase transition temperatures, T_m, of poly(*N*-isopropylacrylamide) (PNIPA) gel and solution. They observed that addition of a structure-maker anion decreased T_m and interpreted it as resulting from promotion of hydrophobic interaction. The viscosity B coefficient, which was employed in their study as a measure of structure-making ability of solutes, seems to be correlated also with EPD of water hydrating onto anions. Thus, it may be reasonable to consider some additional contribution of hydrogen-bonding hydration to the amide group to the observed decrement of T_m upon addition of the pertinent solutes. In fact, Hirotsu[7] pointed out that hydrogen-bond formation between water molecules and the amide groups may explain thermodynamic parameters, ΔH and ΔS, in Flory's χ parameter, which were analyzed for the gel volume transition of PNIPA in the presence of small amounts of alcohols.

Further, the hydrogen-bonding hydration onto the polar group may also explain one of the experimental observations by Otake et al.[18] that the molar heat for the solution phase transition of PNIPA decreases in the presence of a small amount of DMSO (3−7%). This organic solvent has a rather higher EPD, as suggested by the donor number[15] (29.8), than ethanol (20), which effected no appreciable decrement of the molar transition heat. Namely, relative destabilization of amide solvation would lead to interamide group interaction, which should contribute to the total heat of transition as an exothermic component.

In conclusion, we have proposed an interpretation for Hofmeister series or ion-specificity observed for gel's swelling−collapse behavior in terms of hydrogen-bonding hydration to polymer polar groups. Since the stability of such hydration should be controlled by EPD and EPA properties of water molecules, it seems to be reasonable to assume that variation of the two properties through hydration to added ions is responsible for the ion-specific behavior of gels. Although there have been a few interpretations for the ion-specificity for gels, e.g., (de)stabilization of hydrophobic hydration for thermosensitive polymer gels, and anion- or cation-binding to hydrophilic polymers, no explicit consideration has ever been made for the effect on gel's swelling through water's EPD and EPA depending on added ion species, at least to our knowledge.

In the present study, the cation effect seems to be less marked compared with that by anions, as often observed in other examples on Hofmeister series. However, a definite conclusion must wait for further investigation because larger cations of lower charge densities, the hydration energies of which are comparable to that of SCN^-, e.g. Cs^+, have not been tested. In fact, it has been found that the distribution coefficient of CsCl to poly(vinyl alcohol) hydrogel membranes markedly decreases upon decreasing the water content while that of LiCl shows only a slight decrease.[19] This suggests that CsCl is incompatible with hydration of the polymer matrix.

It is evident that elucidation of the true mechanism for the "Hofmeister series" is a tough task, which, however, would be assisted by quantum mechanical, e.g., ab initio, calculation on hydrogen-bonding properties of water molecules under the influence of small ions. An attempt for such an approach is now in progress, as well as an investigation on cation effects.

Acknowledgment. We are grateful to Professor S. Tsunashima, Department of Applied Physics, for providing us every convenience in γ-ray irradiation.

References and Notes

(1) Tanaka, T.; Fillmore, D.; Sun, S. T.; Nishio, I.; Swislow, G.; Shah, A. *Phys. Rev. Lett.* **1980**, *45*, 1636.
(2) Batich, C. D.; Yan, J.; Bucaria, C., Jr.; Elsabee, M. *Macromolecules* **1993**, *26*, 4675.
(3) Ilmain, F.; Tanaka, T.; Kokufuta, E. *Nature* **1991**, *349*, 400.
(4) Kokufuta, E.; Tanaka, T.; Ito, S.; Hirasa, O.; Fujishige, S.; Yamauchi, I. *Phase Trans.* **1993**, *44*, 217.
(5) Ohmine, I.; Tanaka, T. *J. Chem. Phys.* **1982**, *77*, 5725.
(6) Tasaki, I.; Byrne, P. M. *Biopolymers* **1992**, *32*, 1019.
(7) Hirotsu, S. *J. Phys. Soc. Jpn.* **1987**, *56*, 233.
(8) Freitas, R. F. S.; Cussler, E. S. *Chem. Eng. Sci.* **1987**, *42*, 97.
(9) Baker, J. P.; Stephens, D. R.; Blanch, H. W.; Prausnitz, J. M. *Macromolecules* **1992**, *25*, 1955.
(10) Lee, W. F.; Tsai, C. C. *Polymer* **1995**, *36*, 357.
(11) Salamone, J. C.; Volksen, W.; Olson, A. P.; Israel, S. C. *Polymer* **1978**, *19*, 1157.
(12) Dušek, K.; Bohdanecký, M.; Vošický, V. *Collect. Czech. Chem. Commun.* **1977**, *42*, 1599.
(13) Swallow, A. J. *Radiation Chemistry*; Longman Group LTD: London, 1973.
(14) Song, J. D.; Ryoo, R.; Jhon, M. S. *Macromolecules* **1991**, *24*, 1727.
(15) Gutmann, V.; Schmid, R. *Coor. Chem. Rev.* **1974**, *12*, 263.
(16) Kesting, R. E. *J. Appl. Polym. Sci.* **1965**, *9*, 663.
(17) Inomata, H.; Goto, S.; Otake, K.; Saito, S. *Langmuir* **1992**, *8*, 687.
(18) Otake, K.; Inomata, H.; Konno, M.; Saito, S. *Macromolecules* **1990**, *23*, 283.
(19) Zhang, W. Z.; Nodera, A.; Satoh, M.; Komiyama, J. *J. Membr. Sci.* **1988**, *35*, 311.

MA961155N