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Short Communication

Ion-specific swelling of hydrophilic polymer gels

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Abstract

Ion-specific swelling of poly(allylamine) (PAlAm) gel and poly(vinyl alcohol) (PVA) gel was investigated in various aqueous salt solutions. Both the gels slightly swelled in the presence of small cations (e.g. Li^+) and markedly deswelled in the presence of small anions (e.g. F^-), in a similar way as previously found for poly(*N*-vinylpyrrolidone) (PVP) gel. However, a significant difference was observed among the gels swollen in aqueous NaCl system; only PVA gel showed a remarkable deswelling at the higher NaCl concentration region. These ion-specific swelling behaviors were interpreted in terms of ion effects on the hydrogen-bonding hydration to the pertinent polar groups. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Ion-specific swelling; Hydrophilic polymer gel; Hydrogen-bonding hydration

1. Introduction

Polymeric gels swell or deswell and even show the volume phase transition in response to changes of surrounding conditions, such as temperature [1,2], composition of solvent [1–3], ion concentration [4], and pH [5] of the immersing solution. Various stimuli-induced swelling behaviors, however, still remain to be fully elucidated. Among them, ion-specific swelling behavior observed for polymer gels in aqueous system is an 'old' and 'new' problem. The 'Hofmeister's series' or 'lyotropic series', an order of ability of ions to salt-out proteins [6], has been known for one century as a typical ion-specific phenomenon of polymers in aqueous system. A typical order for anions [7] is $SCN^- < I^- < ClO_4^- < NO_3^- < Br^- < ClO_3^- < Cl^- < BrO_3^- < F^- < SO_4^{2-}$, and for cations [8] $K^+ < Na^+ \ll Li^+ \sim Ca^{2+}$. On the other hand, similar ion-specificities have been recently found for swelling behavior of several kinds of polymer gels [9–12]. For example, Suzuki [9] investigated ion effects on the thermal volume transition of poly(*N*-isopropylacrylamide) gel and found a kind of Hofmeister's series for the transition temperature. The author argued that the origin of the ion-effect comes from changes in water structure around the hydrophobic groups induced by ionic hydration.

In our preceding study [13], we observed that poly(*N*-vinylpyrrolidone) (PVP) hydrogel swells in the presence of small cations, e.g. Mg^{2+} and Li^+, and deswells in the presence of small anions, e.g. F^- and SO_4^{2-}. We interpreted the ion-specific swelling behavior as caused by stabilization or destabilization of the hydrogen-bonding hydration through ionic hydration. Namely, in the case of hydration to anions, positive charge on the water hydrogen decreases and negative charge on the water oxygen increases. These changes in the charges on the water hydrogen and oxygen due to hydration to ions are corresponding to a decrease in the ability of electron-pair acceptance (EPA) [14] and an increase in the ability of electron-pair donation (EPD) [14] of water, respectively. Since the hydrogen-bonding hydration of PVP occurs at the carbonyl oxygen, a decrease in the water EPA would result in destabilization of the hydration. On the contrary, water EPA would be enhanced by hydration to small cations, which would cause stabilization of the hydrogen-bonding hydration. Thus, the observed swelling behavior of PVP gel was successfully explained by considering the changes of water EPA and EPD.

The interpretation for PVP system on the basis of water EPA or EPD was straightforward because PVP has only one type of hydrogen-bonding site, i.e. C=O as acceptor. Since many other polar groups contain both hydrogen-bond acceptor and donor sites, the interpretation of the swelling behavior in terms of the water EPA and EPD, would be more complicated. For example, an amino group consists of two hydrogen-bonding donor sites (two hydrogens) and one acceptor site (N), and a hydroxy group has two hydrogen-bonding acceptor sites (O) and one donor site (one hydrogen). Depending on the relative contributions of the donor

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and acceptor sites to the overall hydrogen-bonding hydration of the polar groups, a unique ion-specific swelling behavior different from that for PVP may be observed for a polymer gel containing such polar groups.

In the present study, in order to test the above possibility, we investigated ion-specific swelling behavior of poly(allylamine) (PAlAm) gel and poly(vinyl alcohol) (PVA) gel in the presence of several kinds of salts. The results are compared with those of PVP gel previously reported [13] and discussed in terms of ion effects on the hydrogen-bonding hydration.

2. Experimental

2.1. Preparation of hydrogels

Poly(allylamine)hydrochloride (PAlAm·HCl, $Mw = 6.0 \times 10^4$) was purchased from Nitto Boseki Co., Ltd. PVA was purchased from Nacalai Tesque Co., Ltd (degree of polymerization = 2000, 99–100 mol% hydrolyzed). The respective gels were prepared by γ-ray irradiation to the aqueous solution (10wt% PAlAm or 7.5wt% PVA) in capillaries (ϕ:0.690 mm). Total dose of γ-ray was 200 kGy. pH of the PAlAm·HCl solution was adjusted to 12 with NaOH to neutralize the polymer.

2.2. Measurement of the swelling degree

PAlAm gels thus prepared were first immersed in 0.01 mol/lKOH aqueous solution to keep the polymer neutral. PVA gels were immersed in distilled water. After establishment of equilibrium swelling, gels were immersed in aqueous salt solutions ($MgCl_2$, LiCl, NaCl, KF, and Na_2SO_4). All the immersing solutions for PAlAm gels contained 0.01 mol/lKOH except for $MgCl_2$ system, in which otherwise $Mg(OH)_2$ precipitates. The salt concentration was increased as 0.1, 1, 2, and 4 mol/l in sequence, after the respective equilibrium swellings.

Swelling degree was defined by d/d_0, where d is the gel diameter in salt solutions, and d_0 is that in 0.01 mol/lKOH or in distilled water. d and d_0 were measured by microscope observation (Model SD-ILK, Olympus Optical Co., Ltd).

3. Results and discussion

Figs. 1 and 2 show the swelling behaviors of PAlAm and PVA gels, respectively, in various salt solutions. It should be noted here that the immersing solution of $MgCl_2$ for PAlAm gel does not contain KOH. This means that the amino groups of PAlAm may be protonated. Thus, the marked decrease in d/d_0 obtained for PAlAm/$MgCl_2$ system may be ascribed to a common electrostatic effect, namely, deswelling of a charged gel with increase in the ionic strength of the immersing solution [15].

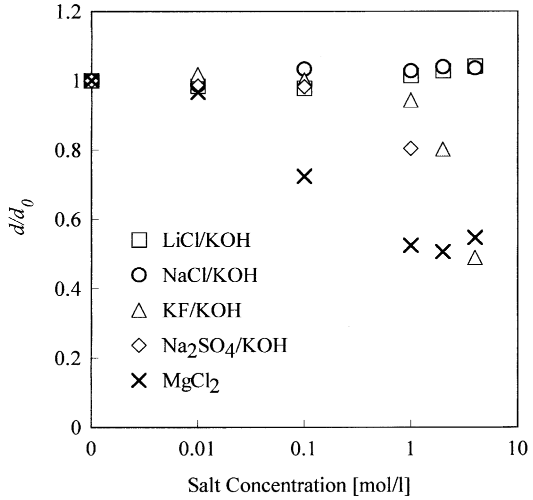


Fig. 1. Swelling behavior of PAlAm gel in aqueous salt solutions. Each solution contains 0.01 mol/lKOH except for $MgCl_2$.

Apart from this exception, the swelling behavior of PAlAm gel seems to be almost comparable with PVA gel. The gels remarkably deswelled by the presence of anions of high charge density as seen for KF and Na_2SO_4 systems, and slightly swelled by the presence of small cation as seen for LiCl system. The d/d_0 values obtained at the highest salt concentrations studied (1 M for Na_2SO_4, 3 M for PVP, 4 M for the other systems) are summarized together with data for PVP on Table 1. As seen from the table, the ion-specificity for the swelling degree does not seem to be dependent on the polymer species, or on the polar groups. This suggests that the number of the hydrogen-bonding acceptor and donor site on the pertinent polar group has only a secondary importance on the ion-specific swelling of polymer gels. This unexpected behavior may be explained in terms of water EPA and EPD as follows. Since the amino group of PAlAm is highly basic (pK_a = ca. 10 for ethylamine), hydrogen bond of water with the

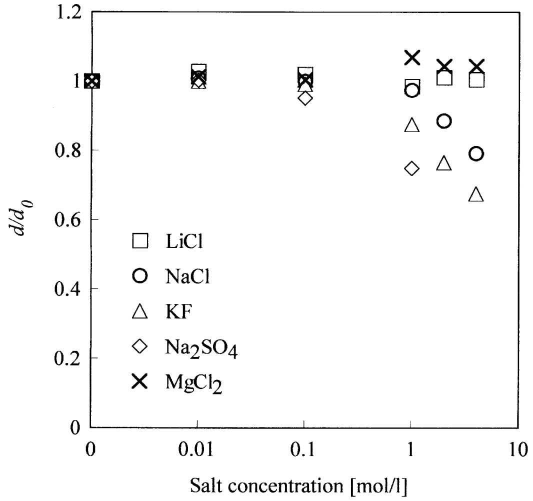


Fig. 2. Swelling behavior of PVA gel in aqueous salt solutions.

Table 1
Swelling degrees (d/d_0) of PAlAm, PAA and PVP gels in concentrated salt solutions

Salts	PAlAm[a]	PVA[a]	PVP[b]
$MgCl_2$	0.54	1.04	1.05
LiCl	1.04	1.01	1.04
NaCl	1.04	0.79	0.99
KF	0.49	0.67	0.63
Na_2SO_4[c]	0.85	0.75	0.70

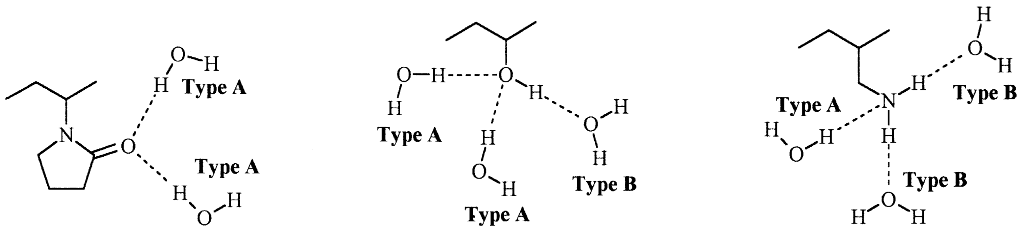
[a] At 4 M except for Na_2SO_4.
[b] At 3 M except for Na_2SO_4, from Takano et al. [13].
[c] At 1 M.

basic site, i.e. lone-pair on nitrogen of the amino group, may be preferred to hydrogen bond to the two hydrogens on the amino group. The former hydrogen bond is to be destabilized by enhancement of EPD of the water through ionic hydration of F^- and SO_4^{2-}, and stabilized by enhancement of EPA of the water through ionic hydration to small cations like Li^+.

To illustrate the ion-specificity in more detail, we employ a simple hydrogen-bonding hydration model of polymer side chains shown in Fig. 3, where two different types of hydrogen-bonding hydration are considered. One is 'type A', where water molecule serves as a hydrogen-bond donor. Hydrogen-bonding hydration of type A is stabilized or destabilized through hydration to cation or anion, respectively. In the former case, water EPA increases and in the latter EPD (EPA) increases (decreases). The other is 'type B', where water molecule serves as a hydrogen-bond acceptor. Hydrogen-bonding hydration of type B is stabilized through hydration to anion because of enhancement of water EPD.

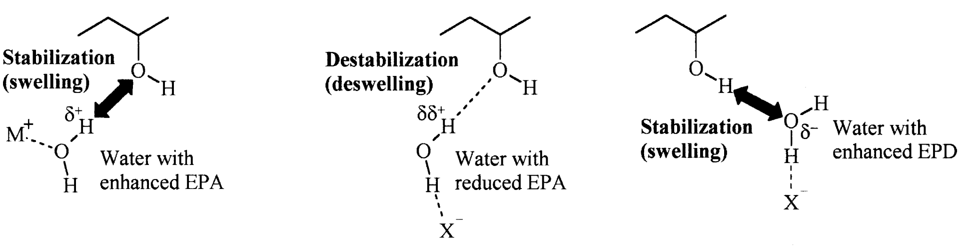
For example, in KF system, both PAlAm and PVA gels largely deswelled. This can be ascribed to destabilization of type A hydration by F^-. Although stabilization of type A hydration by K^+ and stabilization of type B hydration by F^- should occur at the same time, they may be significantly lower than type A destabilization. On the other hand, in LiCl system, both PAlAm and PVA gels slightly swelled. This may be interpreted as follows; stabilization of type A hydration by Li^+ should be larger than K^+ and destabilization of type A hydration by Cl^- is weaker than F^-. Further, stabilization of type B hydration by Cl^-, though weaker than that by F^-, should contribute at the same time. As a result of the total balance of these stabilization and destabilization of hydrogen-bonding hydration, the slight swelling observed for both gels should be explained.

According to the same reasoning above, swelling degrees in NaCl system are expected to be between those of LiCl and KF systems because the degree of stabilization of type A hydration by Na^+ should be between Li^+ and K^+. As seen from Table 1, it is the case. However, only PVA gel shows a marked deswelling, while PAlAm and PVP gels keep their swelling state even at the highest salt concentration studied. This contrastive swelling behavior observed for NaCl system may be ascribed to the subtle balance of stabilization and destabilization of type A hydration by Na^+ and Cl^-, and also to ability of the polar groups to form a stable intramolecular hydrogen bond. As it is well known, the ability of



(i) PVP (ii) PVA (iii) PAlAm

(a) Hydration model for the respective polar groups.



(i) Stabilization of type A (ii) Destabilization of type A (iii) Stabilization of type B

(b) Mechanism of (de)stabilization of hydrogen-bonding hydration through ionic hydration.

Fig. 3. Hydrogen-bonding hydration model of polymer side chains.

amino groups to form intramolecular hydrogen bond is generally much lower than that of alcohols. Therefore, intramolecular hydrogen bond in PAlAm gel, if any, would not favor deswelling as much as in PVA gel. Thus, the intramolecular hydrogen bond in PVA gel seems to help the significant deswelling in NaCl system, in which the hydrogen-bonding hydration is less stabilized than in LiCl system.

In order to justify the above interpretation made on the basis of our model for the ion effects on the hydrogen-bonding hydration, observation of the hydrogen-bonding hydration by any spectroscopic methods and other sophisticated experiments would be necessary. In fact, these have been partly performed. In a previous study [13], we demonstrated that hydrogen bond strength of water in PVP gel estimated through FTIR spectroscopy is actually enhanced in the presence of cations, e.g. Li^+ and Mg^{2+}, and reduced in the presence of anions such as F^- and SO_4^{2-}. Furthermore, in a separate study [16] we have estimated hydrogen bond energies between methanol or *N*-methylpyrrolidone (*N*-MePy) as a model for PVA or PVP, respectively, and a hydrated ion cluster of Na^+ or F^- by ab initio molecular orbital calculation. The results are consistent with the above interpretation. The calculated hydrogen bond energies for Na^+ ion clusters were higher (more stable) than that for F^-. Further, destabilization of type A hydration for methanol by F^- was sufficiently large to cancel out the stabilization of type B hydration. For example, the calculated hydrogen bond energies with $[Na(H_2O)_4]^+$ at the HF/6-31G(d,p) level are −83.6 kJ/mol for *N*-MePy, −51.1 kJ/mol for methanol. Typical values of calculated hydrogen bond energies with $[F(H_2O)_4]^-$ at the same level are −18.3 kJ/mol for *N*-MePy, −48.7 kJ/mol for methanol. Since the organic molecules are bound to water molecules of the hydrated ion clusters in all cases, the above changes in hydrogen bond energies can be ascribed to the changes in properties of water molecules bound to ions, i.e. water EPA and EPD. In fact, calculated atomic charges of water hydrogens of hydrated ion cluster bound to carbonyl oxygen in the above case of *N*-MePy are 0.542 and 0.543 for $[Na(H_2O)_4]^+$ case, while they are reduced to 0.494 for $[F(H_2O)_4]^-$. The same trend was also observed for methanol; 0.535 for $[Na(H_2O)_4]^+$ and 0.491 for $[F(H_2O)_4]^-$. These estimations support our model that ionic hydration to cations (anions) enhances (reduces) water EPA since higher positive atomic charges of water hydrogens are corresponding to higher EPA.

4. Conclusions

In the present study, we investigated ion-specific swelling behaviors of PAlAm and PVA gels in several kinds of aqueous salt solutions. The ion-specificities were qualitatively interpreted in terms of perturbation of water EPA and EPD through ionic hydration. PAlAm gels showed a common (de)swelling behavior with those of PVA and PVP irrespective of the difference in the number of hydrogen bond acceptor and donor sites on the respective polar groups. This suggests that strength of basicity or acidity at the hydrogen-bonding site is more essential than the number of the site. A more detailed investigation by ab initio calculation will be reported in a forthcoming paper, where effects of the basicity of the polar groups and the number of hydrogen bond sites are also examined for complexes between various organic molecules as model compounds of polymers and hydrated ion clusters.

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