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Ion-specific swelling behavior of uncharged poly(acrylic acid) gel

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Abstract The ion-specific swelling behavior of poly(acrylic acid) (PAA) gel prepared by γ-ray irradiation was investigated as a function of salt concentration in the presence of 0.01 M HCl. The anion specificity for the swelling ratio was similar to that for many kinds of hydrogels, i.e., $Cl^- < Br^- < NO_3^- < I^-$, while the cation specificity proved to be rather unusual, i.e., $Mg^{2+} < Ca^{2+} < Li^+ < Na^+ < K^+ < Cs^+$. In order to find any differences in the hydration of uncharged PAA from that of other polymers having typical polar groups, the hydrogen-bonding hydrations on the relevant polar groups were compared for small molecule analogues with an ab initio molecular orbital calculation. According to the results, the marked deswelling of PAA gel in the presence of strongly hydrated cations was ascribed to the unfavorable hydration to the acidic proton of PAA due to the reduced availability of water oxygen as well as to the destabilization of hydrophobic hydration developing around the uncharged PAA.

Keywords Poly(acrylic acid) · Hydrogel · Ion specificity · Hydrogen-bonding hydration · Hydrophobic hydration

Introduction

Uncharged hydrogels often show significant deswelling in concentrated salt solutions containing strongly hydrated anions such as F^- and SO_4^{2-}, but only slight swelling or deswelling in the presence of strongly hydrated cations such as Li^+ and Mg^{2+} [1, 2, 3, 4, 5]. These ion-specific (de)swelling behaviors have been studied as a kind of Hofmeister series. The elucidation seems to be essentially important for the development of intelligent materials based on hydrogels as well as for fundamental understanding of polymer hydration, which must be a key factor for the spontaneous structuring of biopolymers in water.

When a polymer has no charged sites, the hydration sites consist of polar groups and hydrophobic ones, and the polymer hydration is made up of hydrogen-bonding hydration (HBH) and hydrophobic hydration (HPH). Thus, the ion-specific swelling of uncharged hydrogels may be understood as being caused by direct and indirect interaction of ions with those two kinds of sites or hydrations [6]. Interaction of ions with the latter, HPH, is empirically known as follows; larger anions are bound on the interface of the hydrophobic moiety and water (salting-in) and smaller anions are repelled (salting-out). On the other hand, cations are repelled from the interface irrespective of the ion size (salting-out) and hence the ion specificity is much less significant than that for anions [4, 7, 8]. The specific binding of large anions to polymers has been demonstrated, for example, by NMR studies on I^- and SCN^- binding to poly(vinyl pyrrolidone) (PVP) [9, 10], which is known to have HPH [11].

On the other hand, interaction of ions with HBH has also proved to be essential in determining the swelling behavior of hydrogels. We have so far investigated hydrogel swelling for several kinds of uncharged polymer substrates, i.e., PVP [6, 12], poly(vinyl alcohol) (PVA) [13], poly(allyl amine) (PAlAm) [13], and poly(4-vinyl phenol) (P4VPh) [14] to find significant ion-specificities. For the former three polymer systems, one common feature was found for the ion-specific swelling: significant deswelling in the presence of strongly hydrated anions and slight swelling and/or slight deswelling for strongly hydrated cations. These anion- and cation-specific swelling behaviors have also been found for poly(2-hydroxyethyl methacrylate) (PHEMA) [1], poly(*N*-isopropyl acrylamide) (PNIPA) [2, 3] and poly(ethylene glycol) (PEG) [5] gels. We have successfully explained the ion-specificities by taking into account the changes in water properties through ionic hydration [6, 13]; the electron-pair donation and acceptance abilities [15] (EPD and EPA, respectively) of water are enhanced on hydration to an anion and a cation, respectively [16, 17]. HBH to negative atoms of polar groups may be destabilized by an enhancement of water EPD upon hydration to anions, while it is stabilized by water with enhanced EPA through hydration to cations, resulting in the observed ion-specific swelling behaviors. However, P4VPh gel showed a completely different swelling behavior: no deswelling even in saturated solutions for many kinds of salts, including LiCl, KF, and Na_2SO_4. This unexpected behavior, referred to as "super salt-resistivity", means that both cations and anions favorably interact with the polymer substrate in a hydrogel. Such favorable interactions of ions with P4VPh may be traced to some features of this polymer distinguishable from the other polymers cited previously: an acidic proton on the polar group, and the aromatic ring (or π-electron system) as a hydrophobic moiety. In fact, our ab initio calculation on relevant model systems suggested that the HBH to the former is stabilized by strongly hydrated anions, and that to the latter by strongly hydrated cations [14]. The stabilization of HBH to the π system by cations means that such cations are accessible to the hydrophobic part of the polymer, which may explain the observed disappearance of salting-out effects by cations.

All these examples, together with many other studies, strongly suggest that ion effects on uncharged hydrogel swelling consist of contributions from the respective interactions of cations and anions with HPH and HBH. In this context, poly(acrylic acid) (PAA) must be an interesting object to research the ion-specific swelling behavior of the corresponding gel, because PAA in the uncharged state has an acidic proton like P4VPh but no πsystem as a hydrophobic moiety. From the combination of the acidic proton and the nonaromatic hydrophobic moiety, one may expect HBH like that of P4VPh and HPHs similar to those of the common hydrogels such as PVA and PVP. The coexistence of these hydrations for a polymer is unique for PAA and its analogues. Thus, in the present study, we investigated how cations and anions affect the hydrations of PAA hydrogel, through observation of the swelling behavior as a function of salt concentration, to find an unexpectedly significant deswelling for systems containing strongly hydrated cations, for example, Mg^{2+} and Li^{+}.

Experimental

Materials and preparation of PAA gel

PAA ($M_w = 90{,}000$, 25 wt% aqueous solution) was purchased from Polysciences. Salts of analytical grade were purchased from Kanto Chemical Co. or Nakalai Tesque Co. All materials were used as received. Deionized and then distilled water was used throughout the experiments.

PAA gel was prepared by γ-ray irradiation. It is known that polymer gels prepared by γ-ray irradiation have a more homogeneous network than the corresponding ones prepared by chemical cross-linking [18]. Further, the PAA gel samples prepared in the present study were transparent except for those in the most deswollen state in concentrated salt solutions. Thus, the present PAA gels seem to be suitable for the study of ion effects on the polymer hydration (molecular level interaction) on the basis of the degree of swelling (macroscopic observation).

The concentration and the pH of PAA aqueous solution for γ-ray irradiation were adjusted to 10 wt% and 2.0 by adding distilled water and concentrated aqueous HCl. Glass capillaries (Drummond Scientific Co., 25 µl, diameter 0.690 mm) were set in the acidic PAA solution to prepare rod-type gels, and the solution was irradiated with γ-rays. The total dose of γ-rays was 30 kGy. The water fraction of the PAA gel was calculated by $(w_g - w_p)/ w_g$, where w_g is the weight of the swelling gels in 0.01 M aqueous HCl and w_p is the weight of dried gel under vacuum (120 °C, 48 h). The water fractions thus estimated were in a range of 0.985–0.990 for all the gel samples prepared.

Measurement of degree of swelling

The PAA gels obtained were first immersed in 0.01 M aqueous HCl solution for 1 week to remove noncross-linked substances. After the establishment of equilibrium swelling, the gels were immersed in 0.01 M aqueous salt solutions (LiCl, NaCl, KCl, CsCl, $MgCl_2$, $CaCl_2$, KBr, KNO_3, KI, Na_2SO_4) containing 0.01 M HCl to keep PAA in the uncharged state. Then, the salt concentration was increased to 0.1, 1, 2 and 4 mol/l, after the respective equilibrium swellings. For KNO_3 and Na_2SO_4, the concentrations were increased up to 2 and 1 mol/l, respectively, because of their limited solubilities. Na_2SO_4 was chosen as a sulfate because of the lower solubility of the potassium salt. The degree of swelling was defined by d / d_0, where d is the gel diameter in the salt solutions, and d_0 is that in 0.01 M aqueous HCl solution. d and d_0 were measured by microscope observation. (model SD-ILK, Olympus Optical Co.)

Ab initio calculation for hydration on polar groups

In order to estimate the hydration property for typical polar groups, ab initio calculations were carried out at the Hartree–Fock level with the 6-31 + G(d) basis set [19, 20, 21, 22, 23, 24] for cyclic trimer systems consisting of one organic molecule (acetic acid, methanol, phenol, methylamine, or aniline) and two water molecules. For acetic acid, a cyclic dimer including one water molecule was also calculated. These cyclic dimer and trimers were utilized as simple models for hydration on polymer polar groups; PAA, PVA, P4VPh, PAlAm, and poly(4-vinyl aniline). (Except for the last one, ion-specific swelling data for the corresponding hydrogels are available.) Atomic charges were calculated by natural population analysis [25]. The approximate amount of electron transfer from lone pair(s) to the O(N)–H antibonding orbital was estimated by natural bond orbital analysis according to the second-order perturbation method proposed by Weinhold [26]. The approximate quantity of transferred charge, q_{CT}, can be estimated as follows:

$$q_{\mathrm{CT}} = 2[<n|F|\sigma * > /(\varepsilon_{\sigma *} - \varepsilon_n)]^2,$$

where $< n \mid F \mid \sigma^* >$ is the Fock operator, $\epsilon_{\sigma^*} - \epsilon_n$ is the orbital energy difference for σ^* (O–H antibonding orbital) and n (lone pair or π orbital). These two values can be obtained by natural bond orbital analysis results.

Geometry optimization and frequency calculation were carried out with Gaussian 98 [27], and natural bond orbital and natural population analyses were performed with the NBO 3.1 program implemented in Gaussian 98.

Results and discussion

Cation specificity

The swelling behavior of PAA gels in various aqueous salt solutions containing 0.01 M HCl is shown in Fig. 1. The swelling behavior of PAA gel is essentially different, especially for the cation specificity, from those of other common hydrogels, for example, PHEMA, PNIPA, PEG, PVP, PVA and PAlAm gels; PAA gel deswelled quite significantly in aqueous solutions containing strongly hydrated cations such as Li^+ and Mg^{2+}.

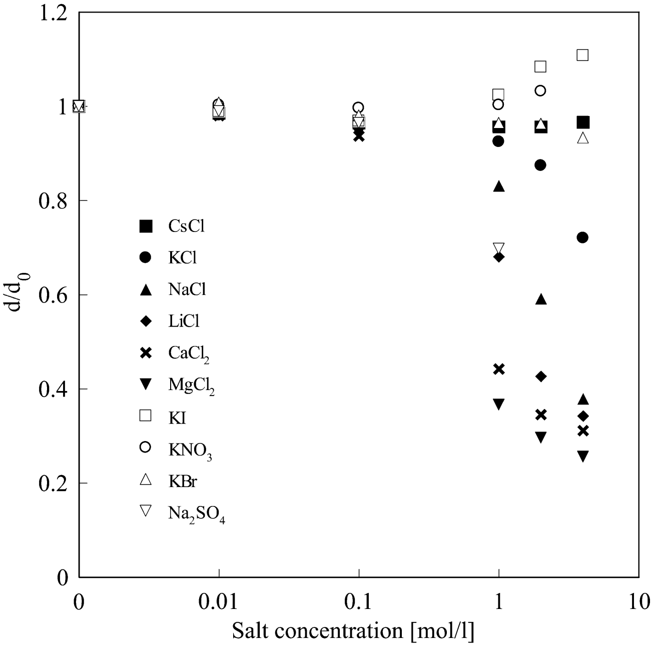

Fig. 1 Swelling behavior of poly(acrylic acid) gel in various aqueous salt solutions containing 0.01 M HCl

When compared within the common anion (Cl^-) system, the order of the degree of swelling is $\mathrm{Cs}^+ > \mathrm{K}^+ > \mathrm{Na}^+ > \mathrm{Li}^+ > \mathrm{Ca}^{2+} > \mathrm{Mg}^{2+}$. This order conforms inversely to the hydration energy of the cations, namely strongly hydrated cations show more significant salting-out for uncharged PAA gel. This cation-specific deswelling is parallel to the salting-out effects for PAA solution in the presence of 0.01 M HCl reported by Ikegami and Imai [28]. As a possible cause for the cation specificity, one may consider cross-linking of –COOH or $\mathrm{–COO^-}$ (if any) by a cation. However, this is most unlikely, because it is known that Mg^{2+}, which showed the most striking deswelling, forms 1:1 type binding ($\mathrm{–COO^-Mg^{2+}}$) with the carboxyl anion of PAA, but not 1:2 type ($\mathrm{–COO^-Mg^{2+}\,^-OOC–}$) in the lower dissociation region [28]. The unfavorable 1:2 binding for Mg^{2+} may be ascribed to the large (de)hydration energy [28] and its small size [29], which hamper stable binding enthalpically and entropically, respectively. In the present system, much weaker interactions with cations can only be expected because most of the carboxyl groups remain undissociated. Therefore, the significant deswelling observed for small cation systems may not be explained by cross-linking of PAA carboxyl groups by cations.

As discussed earlier, direct interactions of cations with –COOH groups do not seem to be the main cause for the observed cation-specific (de)swelling of PAA gel. Then, any indirect interaction must be essentially involved, i.e., cation effects on the HBH of the carboxyl group or interaction between cations and –COOH via hydration water. On the basis of this speculation, we first estimated hydration properties for several polar groups including –COOH to find any feature distinguishable from the other polar groups (R –OH, ϕ–OH, R –$\mathrm{NH_2}$, ϕ–$\mathrm{NH_2}$). In the ab initio calculation, we employed the cyclic hydration systems as shown in Figs. 2 and 3, namely one organic molecule as a model for polymers and two water molecules. With this structure, one can estimate the relative dominance, if any, between the hydrogen-bond donor site (H) and the acceptor site (O or N) in the total hydration. The calculated geometries, atomic charges, and amounts of electron transfer from lone pair(s) to the O(N)–H antibonding orbital can be seen in the figures. In the case of methanol, methylamine, and aniline, the hydrogen-bond lengths between oxygen or nitrogen of the organic molecule and the water hydrogen (1.988, 2.041, and 2.137 Å for methanol, methylamine, and aniline, respectively) are shorter than those between the polar hydrogen of the organic molecule and the water oxygen. (2.044, 2.282, and 2.253 Å, respectively) Moreover, the amount of electron transfer is larger in the former cases

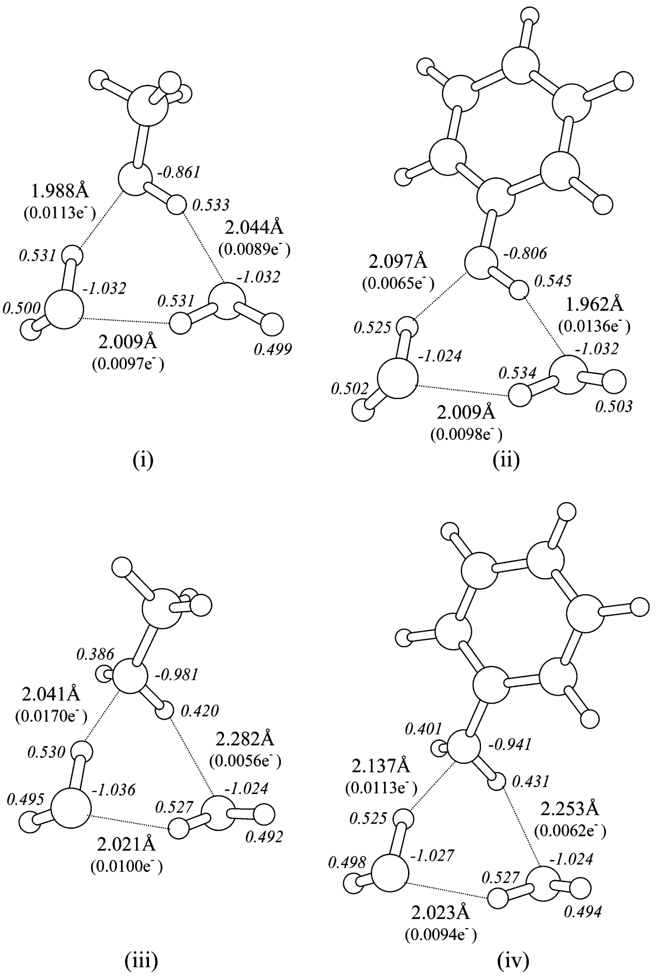

Fig. 2. Geometries, atomic charges, and amounts of electron transfer from lone pair(s) to the O(N)–H antibonding orbital calculated at HF/6-31 + G(d) for cyclic trimers consisting of two water molecules and one organic molecule: **a** methanol, **b** phenol, **c** methylamine, **d** aniline

(0.0113, 0.0170, and $0.0113e^-$ for methanol, methylamine, and aniline, respectively) than in the latter cases. (0.0089, 0.0056, and $0.0062e^-$, respectively). This suggests in the case of PVA and PAlAm gels, which have aliphatic hydroxyl and amino group, respectively, the electronegative oxygen or nitrogen atoms are primary hydration site(s) for HBH. On the basis of the ab initio calculation, one may expect that cations serve as salting-in agents for the relevant hydrogels because they can stabilize HBH on such negative atoms, and anions, which destabilize HBH, show salting-out effects. In fact, this expectation has been experimentally observed as stated in the Introduction; PVA and PAlAm gels show slight swelling in the presence of strongly hydrated cations, for example, Li$^+$, and significant deswelling in the presence of strongly hydrated anions, for example, F$^-$ and SO$_4^{2-}$.

On the other hand, in the case of phenol, the hydrogen-bond lengths between the oxygen of phenol and the water hydrogen (2.097 Å) are longer than those between the polar hydrogen of phenol and the water oxygen (1.962 Å). Moreover, the amount of electron transfer is smaller in the former case ($0.0065e^-$) than in the latter case. ($0.00136e^-$) This situation is the same in the case of acetic acid. Obviously, hydrogen bonds between the acidic hydrogen and the water oxygen (the lengths are 1.907, 1.828, and 1.949Å in Fig. 3a, b, and c, respectively) are all shorter than the others between the acetic acid oxygen and the water proton. Moreover, the amounts of electron transfer (0.0179, 0.0250, and $0.0151e^-$, respectively) are also larger between the acidic hydrogen and water. These differences in the hydration properties of phenol and acetic acid from those of methanol, methylamine, and aniline can be attributed to the difference in the charge balance of polar groups. The atomic charges on polar groups of isolated, i.e., non-hydrogen-bonded organic molecules, and those in the case of corresponding cyclic trimers are shown in Table 1. It can be clearly seen that the positive charges on the polar hydrogen of phenol and acetic acid are larger than those of methanol, methylamine, and aniline. On the other hand, the negative charges on the oxygen(s) of phenol and acetic acid are smaller than those of methanol, methylamine, and aniline. This suggests that the charge balance of the polar group plays an essential role in the hydration properties of the polar group, and hence on the swelling behavior of hydrogels. Thus, in phenol and acetic acid systems the acidic proton can be the primary hydration site; the (de)stabilization of the HBH would essentially influence the swelling behavior of the corresponding hydrogels. In fact, the stabilization of HBH on the acidic proton by strongly hydrated anions has been found for P4VPh gel as the super salt-resistivity. On the other hand, in the present PAA system, the most striking swelling behavior was observed as the significant salting-out ability of small cations. This may also be explained in terms of HBH on the acidic proton, because HBH of the water oxygen to the acidic polar hydrogen of PAA competes with the cation's hydration that also occurs at the water oxygen. Namely, strongly hydrated cations effectively remove water from acidic polar hydrogens, leading to larger deswelling. This type of salting-out is similar to the conventional one that has been ascribed to the reduced water activity in concentrated salt solutions. However, in the present case, it seems to be the decrement in the "activity" or availability of water "oxygen" rather than the water activity itself that essentially affects the polymer hydration. Thus, discrimination of the primarily important site for hydration, on the negative atom (O, N) or on the acidic proton, seems to be essential to understand the ion-specific swelling behavior of polymer hydrogels and further physicochemical properties of polymers in aqueous systems.

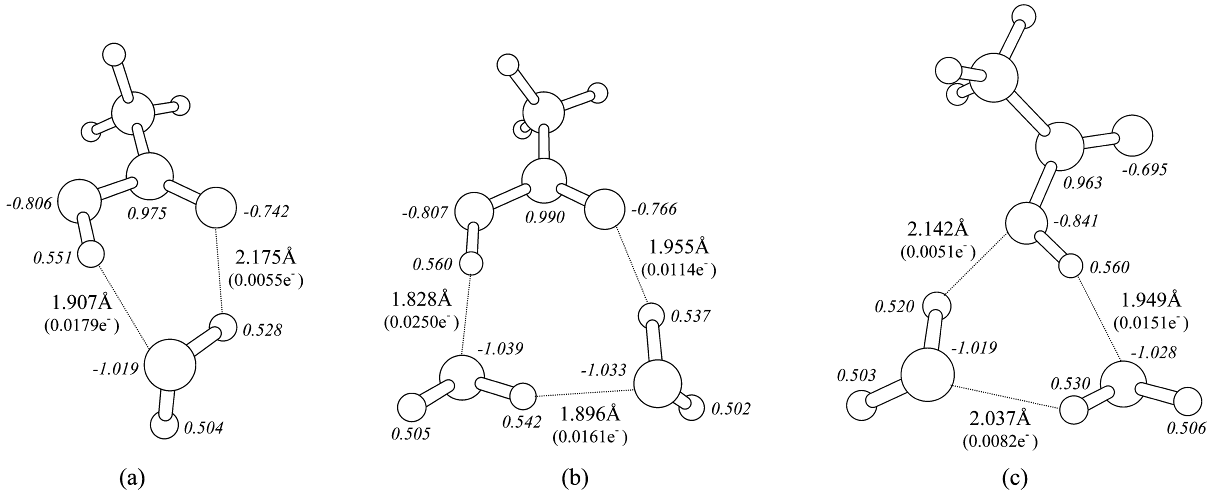

Fig. 3. Geometries, atomic charges, and amounts of electron transfer from lone pair(s) to the O–H antibonding orbital calculated at HF/6-31+G(d) for **a** a cyclic dimer and **b**, **c** trimers consisting of one or two water molecules and one acetic acid molecule

Table 1. Atomic charges on polar groups of isolated organic molecules and those in cyclic trimers

Molecules	q_{Hiso}	q_{Oiso} (q_{Niso})	q_{Hcycl}	q_{Ocycl} (q_{Ncycl})
Methylamine	0.382	−0.941	0.420	−0.981
Aniline	0.402	−0.895	0.431	−0.941
Methanol	0.491	−0.813	0.533	−0.861
Phenol	0.504	−0.757	0.545	−0.806
Acetic acid	0.520	−0.792 (O–H) −0.700 (C=O)	0.560 [a]	−0.841 (O–H) [a]
Water	0.486	−0.971	–	–

[a]Geometry in Fig. 3c

Another remarkable point in Fig. 1 is the degree of swelling for the CsCl system, which remains constant on increasing the salt concentration even up to 4 M. This suggests that the Cl^- ion is exerting a certain stabilization effect on HBH to the acidic proton; otherwise the polymer gel would show at least an appreciable deswelling owing to the nonspecific salting-out effect in such a concentrated salt solution even if the cation's hydration is rather weak. This point will be discussed later.

Anion specificity

Fig. 1 also contains the swelling behavior for the common cation (K^+) systems; the degree of swelling decreased as $KI > KNO_3 > KBr > KCl$. This anion specificity is similar to that found for many other hydrogels, for example, PVA, PVP, PAlAm, and PNIPA, and may be ascribed to the interaction with HPH. However, as suggested by the swelling behavior in the CsCl system, small anions also seem to contribute to the stabilization of HBH of PAA to some extent. Further, a comparison of the degree of swelling of the NaCl and Na_2SO_4 systems suggests that strongly hydrated anions stabilize HBH of PAA. Here we use the ratio of the degree of swelling of the Na_2SO_4 system at 1 M to that of NaCl at 2 M as a measure of the relative effects of SO_4^{2-} compared to those of Cl^-. With this ratio, the effects of Na^+ are cancelled out. Although the effects of one SO_4^{2-} ion are compared with those of two Cl^- ions, this ratio can be utilized for comparison among different polymer systems. The ratio for the present system is around 1.2, which is significantly higher than for other hydrogels, for example, 0.95, 0.93, 0.77, 0.69, and 0.45 for PVA [13], PHEMA [1], PAlAm [13], PVP [6], and PEG [5] gels, respectively. These data suggest that the salting-out ability of the SO_4^{2-} ion relative to the Cl^- ion is lowest for the PAA gel and this can be explained in terms of stabilization of HBH on the acidic proton of

Table 2 Comparison of ion effects on polar and hydrophobic groups for poly(acrylic acid) and some other polymer gels

Polymers	Poly(acrylic acid)			Poly(vinyl pyrrolidone), poly(vinyl alcohol), poly(allyl amine)			Poly(4-vinyl phenol)	
Ions	Small cation		Small anion	Small cation		Small anion	Small cation	Small anion
Polar groups	Salting-out		Salting-in	Salting-in		Salting-out	Salting-out	Salting-in
Hydrophobic groups	Salting-out	$\ll$	Salting-out	Salting-out	$\ll$	Salting-out	Salting-in (π hydrogen bond)	Salting-out
Total effects	Salting-out	$\gg$	Salting-out	Salting-in or neutral		Salting-out	Salt-resistive	Salt-resistive

PAA by strongly hydrated anions. A similar observation has been reported for the PAA solution system in the presence of 0.01 M HCl [28]; the salting-out effects of alkali and alkaline-earth metal sulfates, which are strong salting-out agents for most polymer systems, are comparable to those of the corresponding chlorides. Thus, the anion effects on HBH of PAA seem to be qualitatively similar to those for P4VPh; nevertheless the PAA gel deswelled in the presence of more strongly hydrated anions. This result means that the salting-out effect exerted by anions on the HPH of PAA totally overwhelmed the salting-in effect on HBH to the acidic proton. In fact, it is known that HPH is largely developed around PAA [11]. However, the situation is not so simple; uncharged PAA is soluble in water but P4VPh is insoluble! Therefore it would be no wonder if the salting-out effects by anions on HPH were more significant for the latter than for the former; the reverse has been observed, however. The discrepancy from such a simple expectation may be traced to the difference in the cation's effect on HPH, or the cation's accessibility to the respective hydrophobic groups. In the case of P4VPh, cations are accessible to the benzene ring owing to the stabilization of the π hydrogen bond [14]. In the case of PAA, cations would be repelled from the HPH region. Thus, in the case of P4VPh, cations and anions can help each other in their attractive interactions with the π system and the acidic proton, respectively, because of the local electroneutrality condition. However, in the case of PAA, cations are repelled from the HPH of the polymer and would retard the otherwise favorable interaction of anions with the acidic proton of the carboxyl group.

Ion effects on hydrations on polar and hydrophobic groups for PAA hydrogel are compared in Table 2 with those for other typical polymers. With this table, one may qualitatively understand in which cases marked salting-out effects are observed and why they appear for small cations in some cases and for small anions in other cases.

Conclusion

In order to demonstrate the previously mentioned speculations, detailed spectroscopic studies on HPH for the hydrophobic groups, for example, by IR spectroscopy and NMR would be required, and such an investigation by an IR method is now being undertaken. At the present stage, however, we may conclude that salt-specific swelling behaviors of uncharged polymer hydrogels are to be understood as being caused from a complex fusion of the respective interactions of anions and cations with HPH and HBH of the polymer substrate. As summarized in Table 2, when small cations (or anions) exert salting-in for polar groups and salting-out for hydrophobic ones, the resultant cation or anion effect would be determined by the relative significance of the salting-in and out effects. This versatility seems to be the main cause of the difficulty in the straightforward prediction of a particular ion specificity for a given polymer, which must be a prerequisite for thorough elucidation of the Hofmeister series in general.

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