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ORIGINAL CONTRIBUTION

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Ion-specific swelling behaviors of partially quaternized poly(4-vinyl pyridine) gel

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Abstract Swelling degrees of partially quaternized poly(4-vinyl pyridine) (p.q.P4VP) were measured as functions of the degree of quaternization (D.Q.: 5, 10, 15, 30, and 50 mol %), salt concentration (0–4 M), and salt species (KF, LiCl, NaCl, KCl, CsCl, $\mathrm{MgCl_2}$, KBr, LiSCN, KSCN, $\mathrm{Na_2SO_4}$, and $\mathrm{MgSO_4}$) to study ion effects on the three kinds of interactions involved with p.q.P4VP in aqueous systems, i.e., electrostatic interaction, hydrogen bonding to the nitrogen of the pyridine ring, and hydrophobic interaction, as well as to estimate the relative contributions of the respective ion effects to gel swelling. Upon addition of salts at the lowest salt concentration studied (0.01 M), p.q.P4VP gels, except for one with D.Q.=10%, significantly deswelled depending on the counterion species; the lowest swelling degree was observed for the thiocyanates and the highest one for KF. In the higher salt concentration region (≧1 M) where electrostatic interactions might well be screened, however, some salt systems (e.g., LiCl, KSCN) showed swelling with increased salt concentration, contrary to the common behavior of usual ionic gels. These ion-specific swelling behaviors were interpreted as being caused by additive ionic effects on the three kinds of interactions.

Keywords Poly(4-vinyl pyridine) · Hofmeister Series · Hydration · Counterion binding · Hydrogel

Introduction

Ion effects on the physico-chemical properties of polymers in aqueous media has long been investigated, and various aspects have been found. Among of them, the most typical and the most famous one may be the Hofmeister Series [1], an order of ions that expresses a relative effectiveness to salt-out some proteins from their aqueous solutions. A typical anionic series is $\mathrm{SO_4^{2-}} < \mathrm{CH_3COO^-} < \mathrm{Cl^-} < \mathrm{Br^-} < \mathrm{SCN^-} < \mathrm{I^-} < \mathrm{ClO_4^-}$, and a typical cationic series is $\mathrm{K^+} < \mathrm{Na^+} \ll \mathrm{Li^+} \sim \mathrm{Ca^{2+}}$. (Going to the right, larger amounts of ions are needed to precipitate a protein.) Similar ionic series or effects have been known for various polymer properties in different systems, and most of them are referred to a kind of Hofmeister Series (H.S.) or lyotropic or caotropic ones. For example, the secondary structures of biopolymers such as DNA, proteins, and polysaccharides in water are significantly stabilized or destabilized upon addition of salts; a collagen fold structure is ion-specifically stabilized as $\mathrm{F^-} > \mathrm{SO_4^{2-}} \gg \mathrm{Cl^-} > \mathrm{Br^-} > \mathrm{NO_3^-} > \mathrm{SCN^-}, \mathrm{I^-}$, and $\mathrm{K^+} > \mathrm{Na^+} > \mathrm{Li^+} > \mathrm{Mg^{2+}} > \mathrm{Ca^{2+}}$ [2]. Also for polymer hydrogels, significant salt effects are often observed; a typical thermo-sensitive polymer gel, poly(N-isopropyl acryl amide) (PNIPA) gel, shows a volume-phase transition with increased temperature, and the transition temperature (or the swelling degree) depends on ionic species added in the system, as $\mathrm{SO_4^{2-}} < \mathrm{F^-} < \mathrm{Cl^-} < \mathrm{Br^-} < \mathrm{I^-}$, and $\mathrm{Ca^{2+}} < \mathrm{Na^+} < \mathrm{Mg^{2+}} < \mathrm{Li^+}$ [3].

For all these examples, some common aspects have been known; one is that anion's effect and cation's one are additive and seem to independently perturb polymer properties [4]. Another is "Cation–Anion Asymmetry"; namely, anion's effects are much more significant than those of cations, and anions' sequences are almost common among many systems, while those for cations are sometimes even inverted. For example, secondary structures of biopolymers are more effectively stabilized by more strongly hydrated anions [4] and the tendency is parallel to the salting-out efficiency or ability to induce collapse for neutral hydrogels [5]. On the other hand, strongly hydrated cations do not always stabilize the relevant secondary structure and sometimes show salting-in effects for polymer solution and gel systems [6]. Indeed, this asymmetry between cations' effects and those of anions' has made it so hard to elucidate the whole mechanism of H.S. In fact, a naive consideration would soon be invalidated because of the cations' irregularities —that strongly hydrated ions should destabilize any hydration structures of polymers in water to induce salting-out effects and/or stabilize intramolecular hydrogen bond of any biopolymers through decrease in water activity. Attempts to invoke differential influences of ions to water structure, i.e., structure maker and breaker concept, for interpretation of H. S. are also only successful for anions. Inomata et al. [7] could find a linear relation between the shift of the transition temperature of PNIPA gel and anions' viscosity B parameter that is often utilized to categorize ions to the so-called "structure maker" or "structure breaker". However, according to other experimental data on the PNIPA gel transition by Suzuki [3], the B coefficients of cations were not correlated with the corresponding temperature shifts. As referred above, for example, the transition temperature increased in order of $Ca^{2+} < Na^{+} < Mg^{2+} < Li^{+}$, while the B coefficients are $Na^{+} < Li^{+} < Ca^{+} < Mg^{2+}$.

Thus, H.S. is not a very simple phenomenon as to be explained in terms of a single parameter or by considering one kind of mechanism or interaction. This puzzling phenomena should be understood as a complex fusion of direct and indirect effects of ions to polymer; direct ion binding to polymer substrate and indirect interaction of ions with polymer via hydration. As most polymers that can be encountered in aqueous systems consist of three kinds of components, i.e., ionic, polar, and non-polar (or hydrophobic) groups, ions should mainly affect the three kinds of interactions involved with polymer as follows: 1. electrostatic interaction among the polymer-charged groups and that between polymer charges and the counterions (counterion binding), 2. inter- and intramolecular hydrophobic interaction among polymer's nonpolar groups, and 3. hydrogen bonds between polymer's polar groups and that between polymer and water (hydrogen-bonding hydration). If all these ionic effects were qualitatively and quantitatively estimated, summing up of those would take us to a first step to the ultimate elucidation of H.S. In fact, qualitative explanations for the ion effects on the three kinds of interactions and hydrations are already available, as shown below.

1. Ion effects on the electrostatic interaction
   – Ions can affect electrostatic interactions of a poly-ion in two ways. One is the simple screening of electrostatic interaction among the polymer charges, which is determined by the ionic strength and has no ion specificities for ions of the same valence. The other is counterion binding, which can be significantly ion-specific. Such an ion specificity has been interpreted in terms of an empirical rule, "Desnoyer's hydration shell overlapping model" [8], namely, "solutes of a like hydration favorably interact with each other". According to the model, hydration structures between hydrophilic solutes are stabilized, while those between hydrophilic and hydrophobic ones are destabilized, causing a repulsive force between the solutes. If the solutes are both ionic, a cation and an anion, this empirical rule is further extended by utilizing the category on the ionic hydration, i.e., structure maker and structure breaker. In this case, too, "like attracts like" rule applies; a structure maker (breaker) interacts more favorably with another structure maker (breaker) than with structure breakers (makers). As a measure to categorize ions according to the empirical rule, one may use the hydration enthalpy ΔH_{hyd} (kJ/mol) [9]. This can also be applied to polyelectrolyte systems. For example, the counterion binding of alkali metal poly (carboxylate)s [10–13] [e.g., poly(acrylate), poly(l-glutamate), carboxymethylcellulose, etc.] is strong in the order $Cs^{+} < K^{+} < Li^{+} \sim Na^{+}$, and the respective ΔH_{hyd} values [14] are as follows: −274 (Cs^{+}), −324 (K^{+}), −407 (Na^{+}), −522 (Li^{+}), and −423 (CH_3COO^{-} as a monomer analogue for the polymer charged groups). In the case of sulfate or sulfonate polymers [15, 16] [e.g., poly(styrene sulfonate), dextran sulfate, etc.], the counterion specificity is inverted as $Cs^{+}, K^{+} > Na^{+} > Li^{+}$, while ΔH_{hyd} of HSO_4^{-} as a monomer analogue is −289. In the case of polyamines [17–19] [e.g., poly(allyl amine), poly (l-lysine), etc.], the counterion binding is more stable in an order, e.g., F^{-} (−519) < Cl^{-} (−376) < Br^{-} (−345) < NO_3^{-} (−329) < I^{-} (−300) ~SCN^{-} (−307), and ΔH_{hyd} of NH_4^{+} as a monomer analogue is −320. As stronger counterion bindings lead to lesser polymer hydration, small counterions of stronger ionic hydration are to serve as salting-out agents to a polyion having a charged group of a stronger ionic hydration, and vice versa.
2. Ion effects on the hydrophobic interaction
   – As the hydrophobic interaction is caused by the unfavorable hydrophobic hydration, ion effects on the hydrophobic interaction may be understood as ion effects on the pertinent hydration. According to the Desnoyers model, ionic hydration is inconsistent with hydrophobic hydration. In fact, it has been well known that most inorganic ions are repelled from water–hydrocarbon and water–air interface. For example, experiments on water surface tension and potential [20] in the presence of various kinds of inorganic salts, as well as a simulation study [21],

suggest that small anions of high charge density and strong ionic hydration are highly depleted from the water surface compared with large anions, while the cations' specificity is much less significant and generally repelled from the surface. On the other hand, some NMR studies demonstrated that large anions like I^- and SCN^- are even bound to hydrophobic moieties of polymers in water [22]. Thus, a typical anion series for the degree of exclusion from water–hydrocarbon interface is given as $SCN^- < ClO_4^- < I^- < NO_3^- < Br^- < BrO_3^- < Cl^- < OH^- < F^-$, which is very consistent with the Hofmeister Series. Because of this similarity with HS, including the cation–anion asymmetry, in the ion affinity to hydrophobic interface, many researchers interpreted various kinds of HS in terms of this specific interactions of ions with the hydrophobic hydration of the pertinent polymer substrates. However, all cannot be explained only with ion effects to hydrophobic hydration as polymers in aqueous media usually possess polar groups and the hydrogen-bonding hydration. For example, it has been observed [23] that uncharged poly(acrylic acid), which has a hydrogen-bonding hydration as well as hydrophobic hydration in water, is remarkably subject to salting out by small cations such as Li^+ and the degree is comparable to that by typical salting-out anions like SO_4^{2-}. Further, some hydrogels show a slight swelling, instead of the usually observed deswelling, in the presence of small and strongly hydrated cations [6].

3. Ion effects on hydrogen bonds

   – Except for cases where direct ion bindings to polymer's polar groups take place, ion effects on polymer's hydrogen bonds may be understood by considering (de)stabilization of hydrogen-bonding hydration of the polymer via ionic hydration. A model for such ionic effects on the hydrophilic hydration has been proposed [6, 24], which is able to give a reasonable explanation in terms of changes in the electron pair donicity (EPD) and acceptability (EPA) [25] of water molecules through ionic hydration. Water's EPD is enhanced and the EPA is reduced upon hydration to an anion as the partial negative charge on the oxygen increases and the positive charge on the protons decreases. On the contrary, water's EPA is enhanced with hydration to a cation as the proton charge increases. These changes in water's EPD and EPA are more significant for smaller ions of higher charge densities. Thus, hydrogen-bonding hydration to a negative atom of a polar group, e.g., oxygen or nitrogen, is to be destabilized in the presence of small anions that reduce the water EPA, and stabilized by small cations that enhance the water EPA. These changes in water EPD and EPA through ionic hydrations and the resultant (de) stabilization of hydrogen-bonding hydrations of some kinds of polar groups, in fact, have been confirmed by ab initio molecular orbital calculations [26–28]. According to this model, a remarkable deswelling in the presence of strongly hydrated anions and a slight swelling for strongly hydrated cations, which have often been observed for hydrogels, e.g., poly(vinyl pyrrolidone) [24, 29] and poly (vinyl alcohol) [6], can be ascribed to the (de) stabilization of the hydrogen-bonding hydration to the respective oxygens.

As shown above, qualitative explanations for those three kinds of ion effects are now available. However, how much differently the respective effects contribute to the actually observed HS phenomena has never been elucidated. Therefore, in the present study, we attempt to estimate the relative effectiveness of the three kinds of ion effects on the polymer interactions. As a measure of the effectiveness, the swelling degree of a hydrogel was employed. How much a typical ion for one of the three ion effects can induce deswelling or swelling of a pertinent gel, being compared with typical (de) swellings by the other two effects, would reflect the relative effectiveness of the pertinent ion effect to an HS for the relevant aqueous polymer system. For this purpose, we employed partially quaternized poly(4-vinyl pyridine) (p.q. P4VP) gels where the three kinds of interactions are involved, namely, the electrostatic and hydrophobic interactions and the hydrogen-bonding hydration at the nitrogen of the unquaternized pyridine rings. By changing the degree of quaternization (D.Q.), the relative dominance of the three kinds of interactions may be altered.

Experimental

Quaternization of P4VP

P4VP (Mw: 2.3×10^5, Koei Chemicals) was purified by reprecipitation in diethyl ether. A P4VP sample thus purified was dissolved in nitro methane and quaternized by reacting with ethyl bromide, the amount of which was adjusted to 5, 10, 15, 30, or 50 mol% to the P4VPh on a basemol basis, at 46°C for 5 days. Actual D.Q. values of P4VPh samples thus quaternized were estimated by ^1H NMR as 3.9, 8.6, 15.4, 30.4, and 51.9%, respectively [30]. Although some deviations from the expected stoichiometry were observed, we employ D.Q. = 5, 10, 15, 30, and 50% to distinguish the respective polymer samples. The quaternized polymers were recollected by filtration as precipitates in the case of D.Q.≧30%, while those with D.Q.≦15% were precipitated in dioxane and then filtered.

Purification and counterion exchange from Br^- to Cl^- of the quaternized P4VP samples were carried out by ultrafiltration through an ultrafilter UK-10 (fractionation Mw: 20000, Advantec Toyo Co). Two different procedures were employed for the filtration depending on the D.Q. values of the polymer samples; namely, p.q.P4VP samples with D.Q.≧30% were dissolved in water, and the ultrafiltration was repeated eight times, and in each filtration the solution volume was reduced to 1/7. NaCl with counterions 20 times equivalent to Br^- was added into the polymer solution at the first and the third filtrations, which enabled an effective counterion exchange, the amount of Br^- that remained is simply estimated as being less than 0.3 mol% to Cl^- counterion. The polymer samples were recollected by freeze-drying the ultrafiltrated polymer solutions. For polymer samples with D.Q.≦15%, 0.1 N HCl was used, instead of water, for eight filtrations because the samples were insoluble in water. The polymer samples in this case were recollected by precipitation in an excess amount of 0.05 N NaOH and filtration. The precipitate was repeatedly washed by water and then dried in vacuo.

Preparation of p.q.P4VP gel samples

Gel preparation was performed by γ-ray irradiation (400 kGy) to 10 wt% p.q.P4VP solutions in 40 vol.% aqueous ethanol containing 1 N HCl, each of which was set in a test tube (φ: 10 mm) containing glass capillaries (φ: 0.69 mm). Degrees of gelation were estimated as ca. 93~97% by Soxhlet extraction with ethanol using the bulk gel samples prepared in the test tube. The rod-type gel samples prepared in glass capillaries were immersed in ion-exchanged and distilled water for ca. 1 week to establish the respective swelling equilibria and then used for measurement of swelling degrees.

Measurement of gel-swelling degree in various kinds of aq. salt solutions

Gel diameters (d) of the capillary type p.q.P4VP gels were measured in 11 kinds of aqueous salt solutions ($MgSO_4$, Na_2SO_4, KF, $MgCl_2$, LiCl, NaCl, KCl, CsCl, KBr, LiSCN, and KSCN) as a function of the salt concentrations (0, 0.01 M, 0.1 M, 1 M, 2 M, 3 M, and 4 M) using an optical microscope (Diaphoto 200, Nikon Co.). The swelling degrees were measured in terms of d or d/d_0, where d_0 is the equilibrium gel diameter in water. Adequate or convenient, one of them would be used in the Discussion section, depending on the relevant purpose. Each gel sample reached the equilibrium swelling a few days after immersion in a salt solution, and then the outer solution was exchanged to the next concentrated one. All the measurements were performed at a room temperature (~25°C) because no essential temperature effects on the gel swelling were observed between 10–40°C.

Results and discussion

Effects of the charge density (D.Q.) on the swelling degree (d)

Polyelectrolytes generally assume an extended conformation in water because of the electrostatic repulsion among the charged groups. Similarly, polyelectrolyte gels swell in water, and the degree is enhanced with increased charge density. However, when a charged group is introduced in a hydrophobic atmosphere, just like in the case of the present p.q.P4VP, an increase in polymer charge density does not always result in gel swelling; gel collapse may occur. Figure 1 shows an example; up to D.Q.=30%, the p.q.P4VP gel swelled in water (counterion: Cl^-) and significantly deswelled at 50%. In fact, another p.q.P4VPh gel sample prepared in our previous study [30] showed a significant collapse with the increase in charge density (D.Q.). A similar collapse has been found for different polyelectrolytes, e.g., poly(diallyldimethylammonium iodide) gel [31], poly(methacrylic acid) gel [32], and sodium poly(acrylate) in methanol [33]. This collapse, induced by ionization, has been theoretically explained by Khokhlov et al. [34] as being caused by ion-pair formation between polymer charges and counterions and the resultant ionomer-type multiplet or ion cluster formation. In fact, it has been known that the gel collapse and the so-called coil–globule transition of a polyelectrolyte is more favorable for counterions which are strongly bound with the relevant polymer charged group [35]. In the present case of alkylammonium cation, anions of weaker hydration

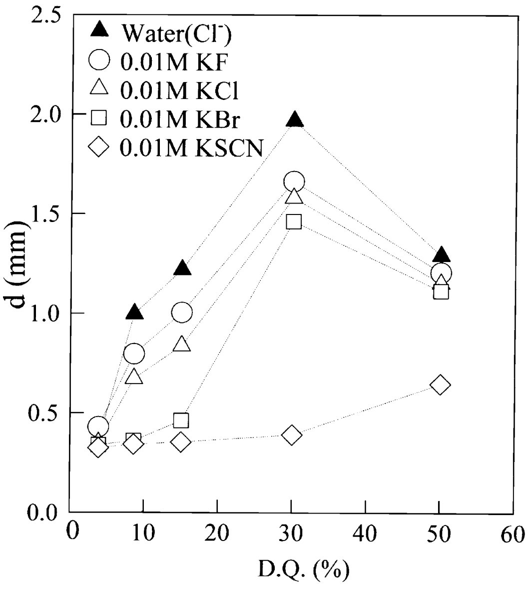

Fig. 1 Dependence on the charge density (D.Q.) of the swelling degree (d) of the p.q.P4VP gels in water and 0.01 M salt systems

are more favorable; for the monovalent anions studied in this paper, $F^- < Cl^- < Br^- < SCN^-$. Figure 1 also contains results where 0.01 M potassium salts were present, showing such a counterion effect. Comparing among the 0.01-M systems, one can see that the relative effect of the counterions to the gel collapse is consistent with the above anion series. Especially, in the case of Br^- and SCN^- counterions, the gel collapse occurred even for D.Q.=10% gel, demonstrating that the relevant anions are able to form rather stable ion pairs with the alkyl ammonium group.

On the other hand, Fig. 1 also shows a simple ionic strength effect on the gel swelling. The lower swelling degrees (*d* values) for 0.01 M KCl, compared with those in water, must be caused solely by the increase in the ionic strength because in this case no counterion exchange occurred. In this case, one may note that the deswelling degrees in 0.01 M KCl for D.Q.=5 and 50% samples are only marginal, ca. 5 and 10%, respectively. The former case may be ascribed to the low water content, ca. 40%. This sample already collapsed and any further deswelling seems to be unfavorable. In the case of the D.Q.=50% sample, the ion clusters were partially formed in the gel, and the swelling degree was already somewhat reduced. Thus, the deswelling due to the increase in the ionic strength seems to be less apparent.

Effects of the salt concentration on the relative swelling degree (*d/d0*)

Figure 2 a–e shows the relative swelling degrees (d/d_0) of p.q.P4VP gel samples with different D.Q. values (5–50%) as a function of the salt concentration. With these plots, one can see how added ions (counterions and coions) affect the gel swelling through the non-specific electrostatic interaction (reduction of the long-range repulsion among the charged groups) and specific ones (e.g., ion-pair formation of a counterion with the charged group and (de)stabilization of the polymer's hydrophobic hydration and hydrogen-bonding one). A common tendency, except for D.Q.=5%, can be seen; a significant deswelling up to 1 M and a slight swelling or deswelling in the higher salt concentration region (1–4 M). The deswelling in the lower concentration region may be ascribed to the electrostatic interactions including counterion binding, and the changes in the swelling degree in the higher concentration region may reflect ion effects on the hydrophobic and hydrogen-bonding hydrations of the polymer because the electrostatic effects should be well saturated in such a high-salt-concentration region. In the case of D.Q.=5%, however, only a slight change in the swelling degree was observed in the whole salt concentration region. This may be ascribed to the low water content (ca. 40%, much lower than 97–99% of the other samples).

These swelling behaviors of the p.q.P4VP gels as a function of salt concentration are, in fact, comparable with those of other polyelectrolyte gels, although few studies are available that are concerned with such a high-salt-concentration region as 1–4 M. For example, Liu et al. [36] reported swelling behaviors of a copolymer gel consisting of 2-(acrylamido)-2-methyl propanesulfonic acid (AMPS) and *N*,*N*-dimethylacrylamide in a wide range of salt concentration, i.e., from 10^{-6} to 1 M and discussed on salt effects in terms of the counterion condensation [37], while no experiments were performed in the higher salt concentration region (>1 M). Thus, to the present authors' knowledge, this is the first report on ion-specific swelling behaviors of a polyelectrolyte gel in the higher salt concentration region, where one may have considered that no appreciable changes in the swelling degree would be observed because of the almost completely screened electrostatic interaction. As a matter of fact, as demonstrated in Fig. 2, significant ionic specificities can be seen. For example, increasing the salt concentration from 1 to 4 M significantly decreased the d/d_0 value of the D.Q=50% sample in aqueous KF from 0.80 to 0.47, while that of the aqueous LiSCN increased from 0.48 to 0.66. These substantial swelling changes must be caused by ion effects on the hydrophobic hydration and the hydrogen-bonding hydration of the polymer, as discussed in a later section.

Effects of ions on the relative swelling degree (*d/d0*) in the lower salt-concentration region

As described in the above sections, there exist marked ion specificities in the swelling degree of the p.q.P4VP gel samples. To see the cation and anion specificities in the lower salt concentration region, d/d_0 values in 0.01 M systems, as typical ones, were plotted against D.Q. values for chlorides and potassium salts, respectively, in Fig. 3 a,b. As the gel swelling in the lower salt concentration region is dominated by the electrostatic interactions (counterion binding and non-specific charge screening), the stronger interaction of a counterion with the charged group and/or favorable distribution of the salt into the gel phase (namely, the higher ionic strength in gel) would cause a more significant gel deswelling. Thus, by comparing the d/d_0 values among different cation or anion systems at a D.Q. value, one can see which ion favorably interacts with the gel substrate. In Fig. 3a, the deswelling degrees of $MgCl_2$ and CsCl are significant, compared with the other chlorides. For the former salt, however, the deswelling may be only apparent, because the ionic strength of a 1:2 salt is three times as high as that of 1:1 salts at the same molarity. On the other hand, the similar deswelling degrees of the CsCl system suggest that partition of Cs^+ into the gel phase is more favorable than the other monovalent cations. One possible reason may be that the weak ionic hydration of the large cation is relatively

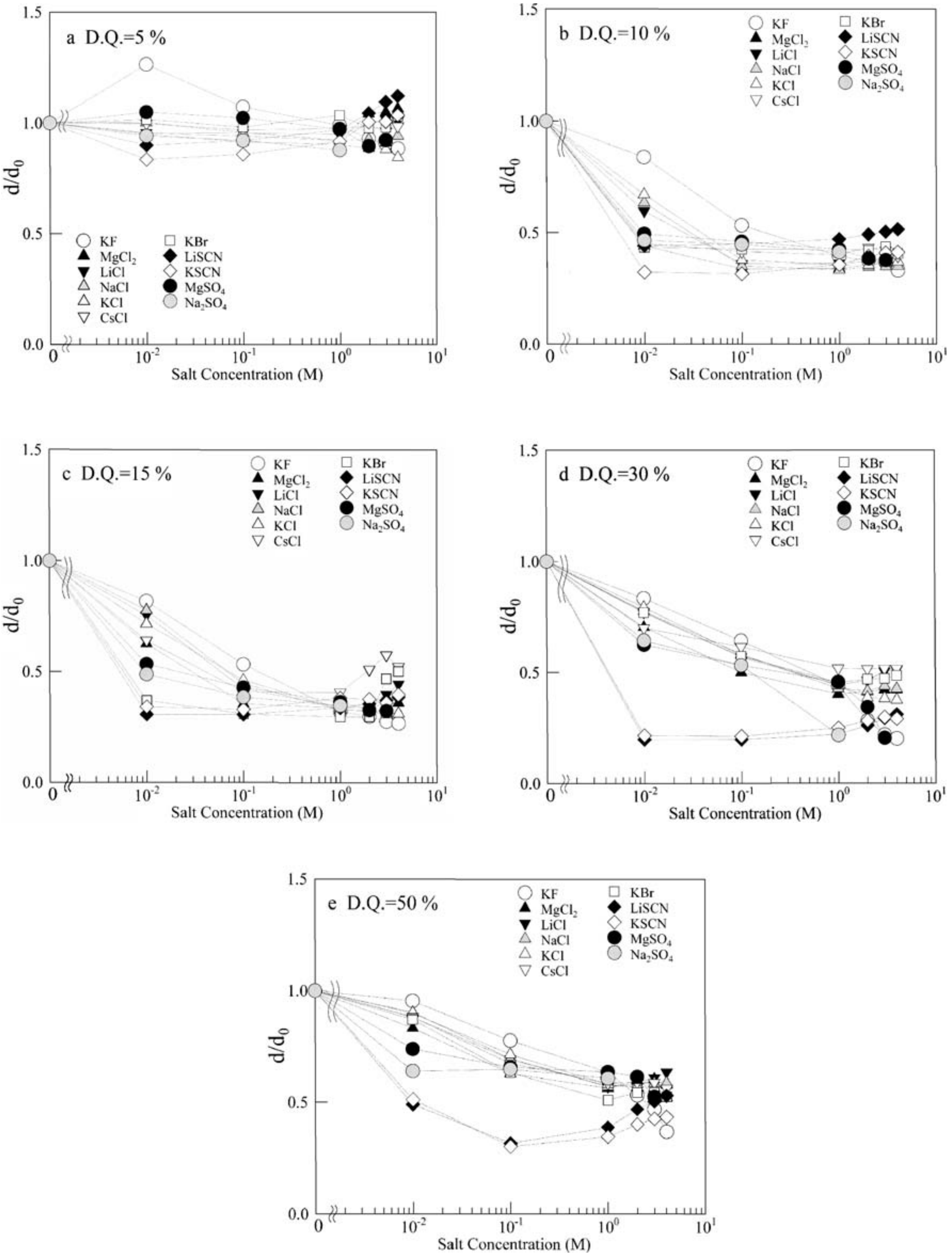

Fig. 2 Swelling behaviors of the p.q.P4VP gels as a function of salt concentration. **a** D.Q.=5%, **b** 10 %, **c** 15%, **d** 30%, **e** 50%

consistent with the hydrophobic hydration around the free pyridine residues. In fact, the deswelling degree of CsCl is more significant for the lower D.Q. samples except for the D.Q.=5% sample which already collapsed in water. For the other cation species, no appreciable specificities were observed. This is rather natural because cations, as coions to the polymer in this case, are to be rejected by the fixed

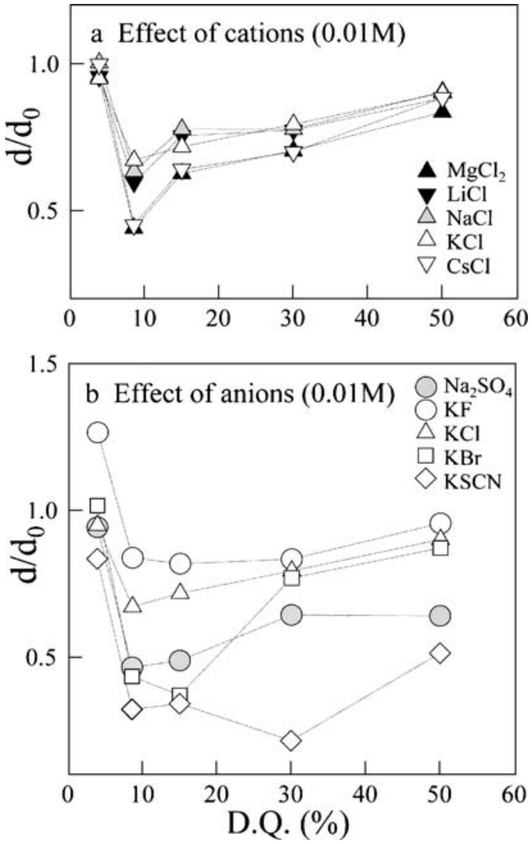

Fig. 3 Cation (**a**) and anion (**b**) specificities for the p.q.P4VP gel swelling in the lower-salt-concentration region (0.01 M)

charge that should mainly determine the swelling degree in the lower-salt-concentration region.

On the other hand, the anion specificity is much more remarkable, as shown in Fig. 3b; the deswelling degree is significant in the order of $F^- < Cl^- < SO_4^{2-}$, $Br^- < SCN^-$. This sequence is just consistent, except for the position of SO_4^{2-}, with those for the anions' affinities to ammonium cations and to hydrophobic hydration which have been cited in the Introduction. In the case of the divalent anion SO_4^{2-}, the strong ionic hydration must be unfavorable for ion-pair formation with the quaternary ammonium cation having a weak ionic hydration, while the polymer-charge neutralization efficiency by multivalent counterions must be absolutely higher than that by monovalent ones. Thus, the moderate deswelling behavior of Na_2SO_4 system may be interpreted as a result of a counterbalance between those two contrasting effects.

Another point to be noted in this paper is the anion specificity at D.Q.=5%. In spite of the almost collapsed state of the gel sample, the original counterion, Cl^-, was effectively exchanged to the others during immersion into 0.01-M salt solutions, resulting the different deswelling degrees. Especially, the appreciable swelling and deswelling upon exchange to F^- and SCN^-, respectively, demonstrate how the former counterion is ineffective for the ion-pair formation with the quaternary ammonium cation, compared with others, and how the latter is the opposite.

Effects of ions on the swelling degree (*d*) in the higher salt concentration region

To see ion effects on gel swelling in the higher salt concentration region (1–4 M), *d* values were plotted against the salt concentration. Typical ion effects can be seen in Fig. 4. As the electrostatic interaction is well masked in this salt concentration region, the ion effects should manifest through (de)stabilization of the hydrogen-bonding hydration to the pyridine nitrogen and the hydrophobic hydration. Thus, any swelling tendency with increase in salt concentration means that the relevant anion and/or cation are favorably interacting with at least one of those hydrations, and vice versa.

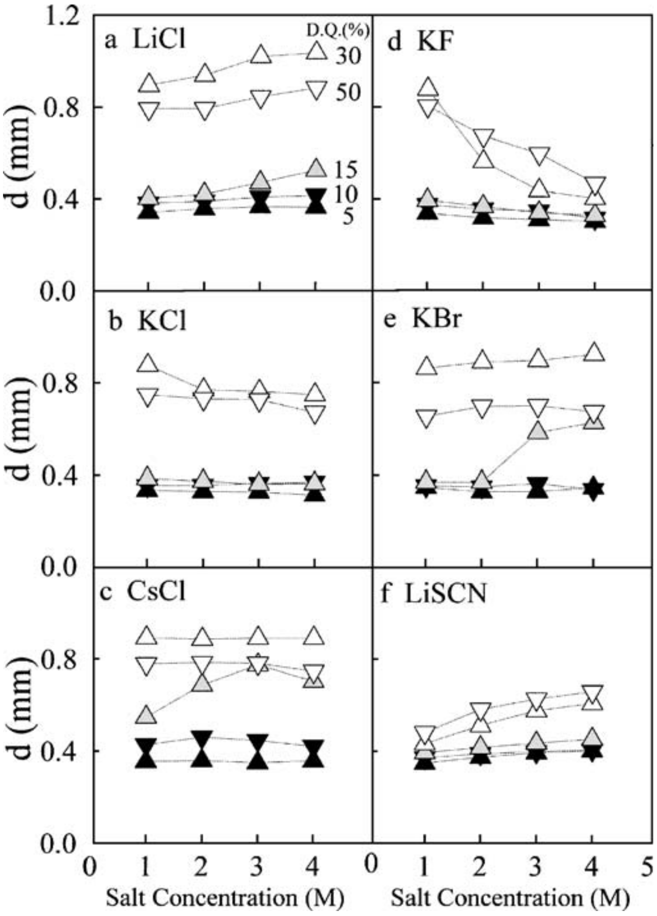

Fig. 4 Ion specificities for the p.q.P4VP gel swelling in the higher-salt-concentration region (1–4 M). **a** LiCl, **b** KCl, **c** CsCl, **d** KF, **e** KBr, **f** LiSCN

For LiCl and LiSCN systems, a slight but definite swelling tendency was observed for higher D.Q. samples (≧15%). This may be ascribed mainly to the stabilization by Li$^+$ of the hydrogen-bonding hydration. Although this stabilization should be more significant for the lower D.Q. samples having more free pyridine residues, the experimental result is the opposite. This may be because in such a collapsed gel, water molecules are mainly distributed around the quaternized pyridine residues and only few molecules are involved with the hydrogen-bonding hydration. The same may be said for LiSCN system; the hydrophobic hydration, which SCN$^-$ ions are to stabilize or to be bound to, would not be formed around the free pyridine residues at the collapsed state.

For the KBr system, a significant swelling was observed for D.Q.=15% gel with increased salt concentration. This may be ascribed to the specific binding of Br$^-$ anion to the hydrophobic moieties/water interface, which overwhelmed the deswelling due to the stable ion-cluster formation. A similar swelling tendency was also observed for CsCl system. As any cations including Cs$^+$ are to have a tendency to be rejected from the hydrophobic surface, the same explanation as for the KBr system cannot be applied. We remind here that Cs$^+$ cations are relatively favorably distributed in the gel phase at the lower salt concentration (0.01 M) probably because of the weak ionic hydration. In the higher salt concentration region (1–4 M), direct electrostatic or dipolar interaction without intervening hydration water of the large cation may be possible with the pyridine nitrogen that has a partial negative charge.

Finally to be noted, the behavior of KF system is most remarkable. The moderately charged gels (D.Q.=30 and 50%) showed a significant deswelling with increased concentration from 1 to 4 M. This is to be ascribed to the definite salting-out effect by F$^-$ onto the hydrophobic hydration and the hydrogen-bonding hydration to the pyridine nitrogen.

Total ion effects on water retention of p.q.P4VP gel

As a summary of the present study, we present a figure showing how water retention (w.r.) of the pertinent gel is affected by ionic species present in the gel phase. In Fig. 5 , plotted are amounts of water molecules in mol/mol of monomer residue of P4VP (D.Q.=30%) as a function of concentration of some selected salts (LiCl, KF, KCl, and KSCN). The most distinct difference of w.r. is seen between KF and KSCN or between F$^-$ and SCN$^-$ of the respective 0.01 M systems (the lowest salt concentration studied); the former w.r. is ~1,000 while the latter is ~10, thus differing by a factor of 100! On the other hand, at the highest salt concentration studied (4 M), another remarkable difference as much as 30 times is seen between LiCl and KF. These results demonstrate that ion effects on the gel swelling through (de)stabilization of hydrogen bonding and hydrophobic hydrations can be substantial, compared with the ion effects via electrostatic interactions.

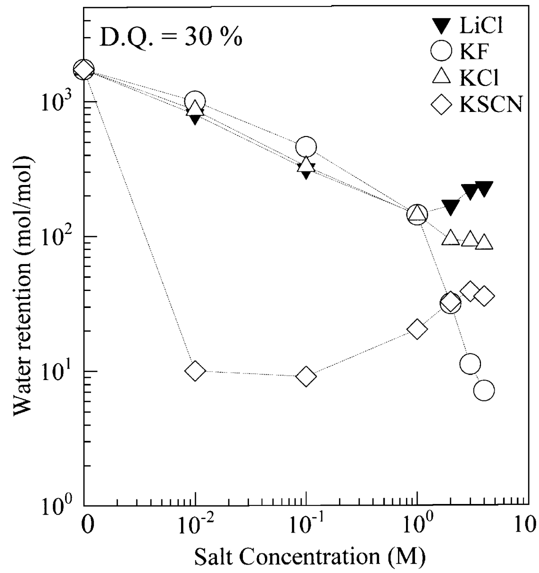

Fig. 5 Water retention of a p.q.P4VP gel (D.Q.=30%) swollen in some typical salt solutions as a function of salt concentration

Finally, we estimate relative contributions of typical ionic effects on the gel swelling in terms of the changes in w.r., as shown in Fig. 5: the contribution from the simple electrostatic interaction may be estimated by a ratio of the w.r. value at 1 M to that at 0 M, while the ion effects on the hydrogen-bonding hydration and the hydrophobic hydration are by a ratio of the w.r. at 4 M to that at 1 M, because above 1 M the electrostatic effects would be negligible. With this criterion, the non-specific electrostatic interaction reduced the w.r. to ca. 1/12, on the basis of the result of KCl system, in the lower salt concentration region (0~1 M), while the specific electrostatic one or the ion-cluster formation was furthermore significant in dehydrating the gel, i.e., ca. 1/100 as shown by the 0.01 M KSCN system.

In the higher salt-concentration region (≧1 M), one can directly compare the effects of LiCl, KCl, and KF as the w.r. values at 1 M are almost the same. In this paper, we assume that K$^+$ ions are inert and affect the polymer hydrations the least. Then, the slight decrease, as much as ca.0.6, in the w.r. for the KCl system in the relevant concentration region, may be taken as being caused only by Cl$^-$. Thus, the salting-in effect by Li$^+$, in turn, may be estimated as much as ca. 2.7. In a similar way, the salting-out effect by F$^-$ is evaluated as ca. 1/20, which is comparable with the non-specific effect (1/12) in the lower-salt-concentration region. The salting-in effect by SCN$^-$ on the hydrophobic hydration, though the w.r. value at 1 M is different from the others, may be estimated as ca. 1.8. This value is never insignificant, because the gel swelling was being attained by opposing the stable ion-cluster formation with the counter anion.

In conclusion, the ion effects on the three kinds of interaction or hydrations of charged polymers can be comparable. Especially, in the higher salt concentration where the Hofmeister Series is concerned, the salting-in and salting-out effects by anions and cations on the hydrogen-bonding hydration are never insignificant, compared with those by anions on the hydrophobic hydration. Thus, by selecting a combination of the cations and anions present in the system, the physicochemical properties of hydrogels can be largely altered through the respective ion effects on the three kinds of interactions or hydrations.

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