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SHORT COMMUNICATION

Anti-Hofmeister series properties found for a polymer having a π electron system and acidic protons

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Abstract Anti-Hofmeister series properties have been found for a polymer (PVA-T) having a π electron system and acidic protons, which were prepared by introducing trimellitic anhydride to poly(vinyl alcohol) (PVA). Aqueous dispersion of PVA-T became clear in the presence of 1 M Na_2SO_4, a typical kosmotrope, due to dissolution of the solid polymer sample, while the turbidity in the presence of 1 M KSCN, a typical chaotrope, hardly changed. Being consistent to the salt effects, PVA-T hydrogel, which was prepared by chemical cross-linking, showed marked swelling in sulfate solutions, whereas the swelling degree was only marginal in thiocyanates.

Keywords Hofmeister series · Salt resistivity · Hydrogel · π electron · Acidic proton

Introduction

Although the Hofmeister series (HS) has been extensively investigated for more than one century to elucidate the mechanism, i.e., how ions differently affect the many aspects of polymer properties in aqueous systems, no definite answer has yet been obtained [1]. According to the typical HS, strongly hydrated anions like SO_4^{2-} that are often called "kosmotropic" ions effectively salt out polymers from their aqueous solution and cause significant deswelling of hydrogels in aqueous media. On the contrary, weakly hydrated anions such as SCN^- and I^- show salt-in effects and are called "chaotrope". These ion-specific salting out and salting in behaviors had been partly ascribed to discriminative absorption of ions to hydrophobic moieties of polymer; kosmotropic anions are rejected, and chaotropic ones are specifically absorbed [2]. On the other hand, our previous studies demonstrated that perturbation on water properties caused from ionic hydration essentially affect the hydrogen-bonding hydration (HBHy) of polymer polar groups as another main mechanism for HS [3–6]. Namely, upon hydration to cations, electron pair acceptance (EPA) [7] of water molecule is enhanced, while it declines via hydration to anions. Because of these changes in the water properties, HBHy to negative atoms (e.g., oxygen or nitrogen) of polar groups is to be stabilized or destabilized, respectively. Thus, salting in and salting out behaviors of poly(vinyl alcohol) (PVA) and poly(*N*-vinyl pyrrolidone) hydrogels observed in the presence of strongly hydrated cations (e.g., Li^+, Mg^{2+}) and strongly hydrated anions (e.g., F^-, SO_4^{2-}), respectively, have been successfully ascribed to the (de)stabilization of the HBHy to the hydroxyl oxygen and the carbonyl oxygen.

Our previous ab initio studies [6, 8], on the other hand, suggested that HBHy to acidic proton, which has higher positive partial charge, would be stabilized by water molecules hydrating anions, because the electron-pair donicity (EPD) [7] is enhanced via the ionic hydration. In fact, the prediction proved to be the case, although in a somewhat unexpected way, for poly(4-vinyl phenol) (P4VPh) [9] and poly(4-vinyl benzoic acid) (P4VBA) [10] gels; no deswelling nor swelling was observed in concentrated solutions of kosmotrope (e.g., SO_4^{2-}) and chaotrope (e.g., SCN^-). This

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quite unique swelling behavior has been ascribed to stabilization of two types of HBHy, one to the acidic proton and the other to the π-electron (π-hydrogen-bonding hydration), by anions and cations, respectively.

In the present study, on the basis of the above findings, we investigated effects of introduction of acidic protons together with π-electron system to PVA as a common polymer on the HS behavior. As expected, we have found that SO_4^{2-} may act as a "chaotrope" or a salting-in agent for the modified PVA polymer containing a π electron system and acidic protons, being contrary to the commonsense of colloid chemistry for 120 years.

Experimental

Polymer preparation

Poly(vinyl alcohol) (PVA) (Acros Organics, 99–100% hydrolyzed, Mw=86,000) (1.33 g; OH group, 30 mmol) was dissolved in 25 ml of dimethyl sulfoxide. To this solution, triethylamine (3.0 g, 21 mmol), 4-(*N*,*N*′-dimethylamino) pyridine (0.0758 g, 0.6 mmol), and trimellitic anhydride (Tokyo Kasei, 11.55 g, 60 mmol) were added and dissolved. After stirring at 25 °C for 24 h, the polymer solution was poured into 1% HCl aq. to precipitate the trimellitic acid-modified PVA. (PVA-T). The precipitate was washed with water and dissolved in acetone–methanol (1:1) mixed solvent after drying in air. The solution was poured into 1 M HCl to reprecipitate the polymer, which was then dissolved in water by adding 3 M NaOH. This PVA-T solution was repeatedly ultrafiltrated (Advantec ultrafilter Q2000, fraction Mw= 200,000) to remove extra alkali and low molecular weight substances. PVA-T thus purified was recollected by precipitation in 0.1 M HCl aq. and dried in vacuo. The reaction scheme for the esterification is shown in Fig. 1. Reaction of the free carboxyl group (–COOH) other than the anhydride group is negligible under the mild condition used in the present study. The introduction of trimellitic acid to PVA was confirmed by Fourier transform infrared spectroscopy (Shimadzu FTIR-8200PC) and the esterification degree was estimated to be 73% by conductometric titration (Horiba ES-51) with NaOH. Introduction of phthalic anhydride to PVA was also made with a similar procedure as above. The esterification degree of the phthalic acid-modified PVA (PVA-P) was estimated to be 75% by conductometry.

Turbidity measurement

Dispersion samples of PVA-P, PVA-T, P4VPh, and P4VBA were prepared as follows: 0.0300 g of the respective polymer samples (0.0238 g for P4VPh) was dissolved in 1.6 ml (1.2 ml for P4VPh) of 0.1 M NaOH and then diluted by 16 ml (16.8 ml for P4VPh) of water. The resultant aqueous polymer solutions (1.6 or 1.2 ml for P4VPh) were added into 2.4 ml (2.0 ml for P4VPh) of 0.1 M HCl under vigorous stirring. Stock dispersions thus prepared were further diluted by water and/or salt solutions (LiCl, Na_2SO_4, or KSCN). Appropriate dilution degrees were determined so as to adjust the absorbance at 600 nm in the absence of salts at around 0.2–0.3. Turbidity in the presence of the salts was measured as an absorbance at 600 nm with a spectrophotometer (V-570, JASCO). Each dispersion sample was sonicated for 5 min with a US cleaner (55 W, US-1A, ASONE) before the turbidity measurements. The salt concentration was varied from 0.1 to 4.0 M except for Na_2SO_4 because of the low saturation concentration (ca. 1.5 M).

Gel preparation and swelling degree measurement

Rod-like gel samples of PVA-T were prepared by cross-linking with ethylene glycol diglycidyl ether (Aldrich); dimethylformamide (DMF) solution of PVA-T (20 wt%) was vigorously mixed with EGDGE (9 mol% to the polymer carboxyl group). Glass capillaries (Drummond Sci.; inner diameter, 0.69 mm) were put into the solution, the temperature of which was kept at 70 °C for 24 h. The resultant capillary gels were immersed in DMF to allow the samples to reach the equilibrium swelling. The immersing solvent was gradually changed to water by repeating addition of small amount of distilled water with the equilibrium swelling state kept. The

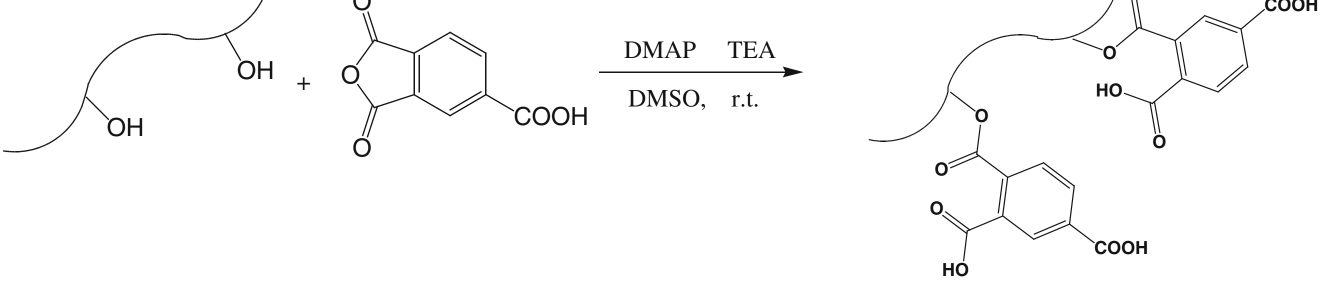

Fig. 1 Reaction scheme for introduction of trimellitic anhydride to PVA

water-swollen gel samples (water content at the equilibrium, 99.6%) were then immersed in 10^{-3} M HCl. In the acidic solution, samples significantly deswelled (water content, 35.3%), but remained transparent. The swelling degree in aqueous salt solutions containing 10^{-3} HCl was determined as d/d_0 (d, the gel diameter in salt solution; d_0, d in water) with an optical microscope (Nikon, Diaphot 200). Salt concentration of the external solution was increased after a d value at equilibrium swelling was obtained, for which several days were necessary. Salts used were Li_2SO_4, Na_2SO_4, LiCl, NaCl, KCl, CsCl, LiSCN, NaSCN, and KSCN (Analytical grade, Nacalai Tesque). Except for the sulfates with lower saturation concentration, the salt concentration was changed up to 5.0 M.

Results and discussion

Turbidity

Firstly, effects of introducing the trimellitic or phthalic acid group to PVA were tested by turbidity (absorbance at 600 nm) measurement. As reference systems, P4VPh and P4VBA dispersions were also used because these polymers have already proved to be super-salt-resistive. The results are shown in Fig. 2a–d. As seen from Fig. 2a and b, even for Na_2SO_4 system, the absorbance of P4VPh and P4VBA dispersions are almost constant or even slightly decreased with an increase in the salt concentration. Thus, this salt tolerance behavior of the polymer dispersions against concentrated salt solutions must be another manifestation of the super-salt-resistivity of the relevant polymers.

On the other hand, in the case of PVA-P system, a similar salt tolerance was observed except for LiCl system. Although the transient aggregation behavior for LiCl system may not be explained at the present stage, the salt tolerance observed for Na_2SO_4 system strongly suggests that introduction of π electron system and acidic proton is effective to endow common polymers with salt resistivity.

For PVA-T, which has two carboxyl groups on one benzene ring, somewhat unexpected behaviors were observed; for Na_2SO_4 system, the dispersed polymer particles were completely dissolved, leading to a clear solution. For LiCl, a similar dissolution occurred only between 0.2 and

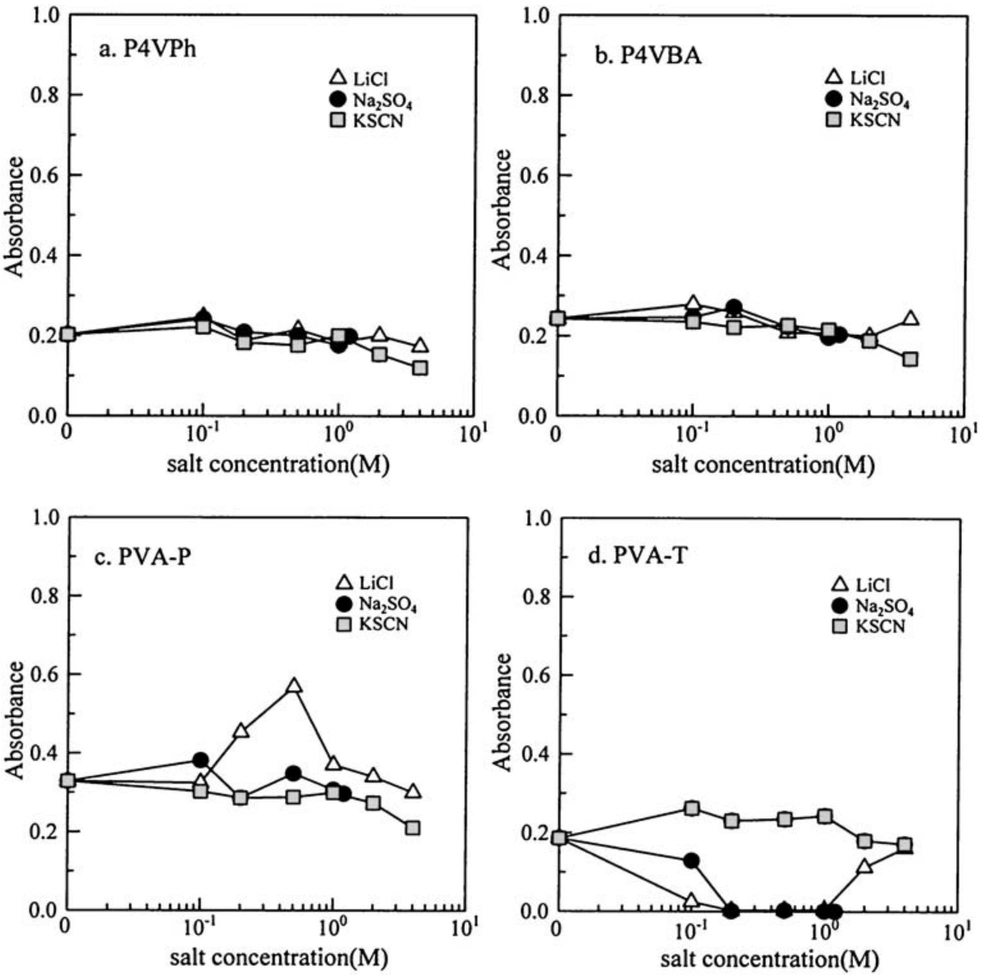

Fig. 2 Turbidity (absorbance at 600 nm) of aqueous polymer dispersions as a function of salt concentration. **a** P4VPh, **b** P4VBA, **c** PVA-P, **d** PVA-T

1.0 M, while the KSCN system showed almost constant turbidity, a similar behavior as those in P4VPh, P4VBA, and PVA-P systems. (It was confirmed that the zero absorbance was not due to precipitation.) Here, we note the contrasted behavior between Na_2SO_4 and KSCN systems, i.e., classically typical salting-out and salting-in agents. Comparing with PVA-P, the significant salting-in ability of Na_2SO_4 for PVA-T suggests that the two acidic protons of the latter compound compared with the only one for the former type must be responsible; the HBHy onto the acidic protons are to be stabilized by SO_4^{2-} via ionic hydration. Therefore, the salting-in behavior found for PVA-T/Na_2SO_4 system strongly suggests the validity of our mechanism for HS as described in the "Introduction" section.

Gel swelling behavior

In order to confirm the salting-in effect observed for Na_2SO_4 on the PVA-T dispersion, swelling of a PVA-T gel immersed in 1.0 M Na_2SO_4 was compared with that in water. As seen from Fig. 3, a significant volume increase (ca. 30 times) was in fact observed (in the deswollen state, the water content of PVA-T gel was 52%, while in 1 M Na_2SO_4 it increased to ca. 98%.), confirming the salting-in ability of the pertinent salt even though it is a complete opposite behavior for common hydrogels such as PVA.

For a further detailed investigation on the salt effects, swelling degrees of PVA-T gel samples were measured in various kinds of salt solutions as a function of the salt concentration. As shown in Fig. 4, the gel significantly swelled only for sulfate systems. Since a slight salting-in effect (swelling) was noted for LiSCN system, but no swelling in LiCl, the anion specificity for inducing gel swelling at 1 M is $Cl^- < SCN^- < SO_4^{2-}$. This order, especially that of SCN^-, a most typical chaotrope, and SO_4^{2-}, a most typical kosmotrope, is just opposing the traditional HS. Thus, the gel swelling behavior also demonstrates that the PVA-T is an anti-Hofmeister series polymer. As for the cations, the specificity at 1 M is $Cs^+, K^+ < Na^+ < Li^+$. These ion specificities suggest that ion effects on the trimellitic acid group and the vinyl alcohol moiety are in additive. Namely, the observed anion and cation specificities are interpreted as follows: in the first place, owing to ionic hydration to anions of higher charge density, e.g., SO_4^{2-}, the hydration water's ability to donate electron pair is enhanced [9], leading to stabilization of the hydrogen-bonding hydration to the acidic proton of the two carboxyl groups. For this reason, $SCN^- < Cl^- < SO_4^{2-}$ is expected for an ion specificity on the salting-in effect. Second, π-hydrogen-bonding hydration to the benzene is also stabilized by cations because the positive charge of the hydration water's protons are enriched via ionic hydration. For this, $Cs^+ < K^+ < Na^+ < Li^+$ is expected for the salting-in ability. In fact, the more marked swelling observed for Li_2SO_4 compared with Na_2SO_4 may be partly ascribed to this effect. Third, the salting-in abilities of ions for PVA gel must be added; it has been known that the order is $SO_4^{2-} < Cl^- < Br^- < I^-$ and $Cs^+ < K^+ < Na^+ < Li^+$ on the basis of gel swelling degrees [4, 11]. The observed slight swelling of PVA gel in the concentrated solutions of NaI and LiCl has been ascribed to specific stabilization of HBHy on the hydroxyl oxygen by Li^+ and specific binding of I^- on the hydrophobic hydration around the main chain, respectively. The latter binding of I^- to hydrophobic groups in polymer is common to weakly hydrated large anions including SCN^-. On the other hand, strongly hydrated small anions, so-called kosmotropic anions like SO_4^{2-}, show a strong salting-out effect because the anions are rejected from the hydrophobic moiety of PVA and destabilize the HBHy to the OH group. In this respect, Cl^- is also categorized to a salting-out agent to PVA. Thus, the observed total ionic specificities in the present gel system may be interpreted as a result of concomitant contributions from the above salting-in (out) effects.

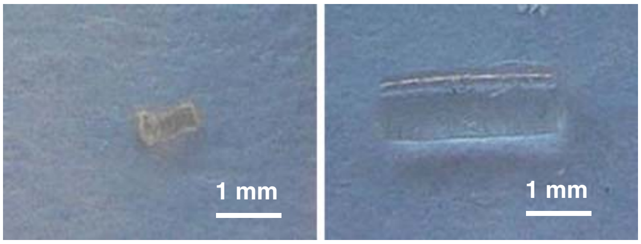

Fig. 3 Optical microscope pictures of deswollen (*left*, in water) and swollen (*right*, in 1 M Na_2SO_4 aq.) PVA-T gel

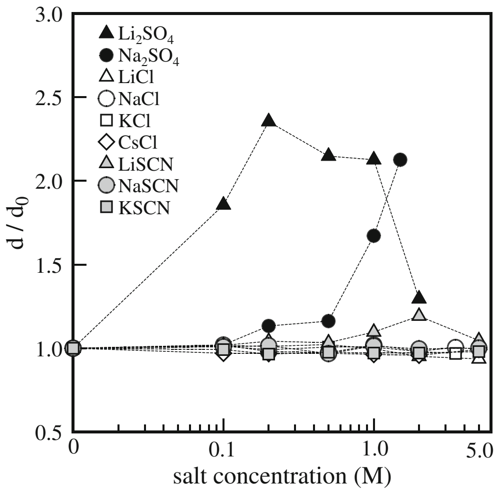

Fig. 4 Swelling degree of PVA-T gel under acidic condition as a function of salt concentration. d (d_0); gel diameter in aqueous salt solutions (water) containing 10^{-3} M HCl

In this context, we should note the opposing effect of SO_4^{2-} to the PVA-T gel swelling; salting in for the acidic protons, whereas salting out for PVA. This subtle balance may explain the significant deswelling observed at 2.0 M Li_2SO_4 solution. Namely, in the lower concentration, both Li^+ and SO_4^{2-} act as salting-in agents to dissociate the intermolecular hydrogen bonds between –COOH and/or –OH groups of PVA-T that was deswollen in the acidic aqueous solution (10^{-3} M HCl), and hence the gel swells. With increasing salt concentration, however, the favorable interaction of SO_4^{2-} with the acidic protons via HBHy would be saturated. In fact, e.g., if the water content is assumed to be 93% at 1.0 M Li_2SO_4 on the basis of the swelling degree, the molar ratio of SO_4^{2-} to trimellitic acid group is ca. 3. Then, the salting-out effect by the divalent anion onto the PVA OH and the hydrophobic main chain may come into operation to overwhelm the preceding salting-in effect.

In conclusion, we have found that PVA-T is an anti-HS polymer and hence the traditional HS for anions is not common or fixed any longer. One cannot refer to SO_4^{2-} as a “typical” kosmotrope. However, as a matter of fact, the PVA-T prepared in the present study is not a genuine anti-HS polymer because the traditional HS behavior still remains; thiocyanates showed a second effective salting-in behavior. Thus, if PVA-T with 100% substitution or related polymers having a trimellitic acid group but not a vinyl main chain were obtained, the ultimate challenge to the traditional HS would be realized. Effects of the substitution degree on the polymer performance are now being undertaken.

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