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SHORT CONTRIBUTION

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Salt resistivity of poly (4-vinyl benzoic acid) gel

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Abstract Salt resistivity of poly (4-vinyl benzoic acid) (P4VBA) gel was investigated to compare with the super salt-resistivity that was found for poly (4-vinyl phenol) (P4VPh) gel containing an acidic proton and π-electron system. Poly (acrylic acid) (PAA) gel was also prepared and used as a reference gel containing only an acidic proton. P4VBA gel showed a moderate salt resistivity, which was less significant than that for P4VPh gel, in many kinds of inorganic salt solutions ($MgCl_2$, LiCl, NaCl, KCl, CsCl, KI, KSCN, Na_2SO_4). On the other hand, PAA gel showed a drastic deswelling in the presence of concentrated $MgCl_2$, LiCl, Na_2SO_4, and $(NH_4)_2SO_4$ solutions, and a significant swelling for KSCN solution. These contrastive behaviors between P4VBA and PAA gels strongly suggest that the combination of acidic proton and π-electron system is essential and necessary for polymer gels to be endowed with the salt resistivity.

Keywords Hydrogel · Hofmeister series · π-Hydrogen-bonding hydration

Introduction

We have been studying interactions of poly (4-vinyl phenol) (P4VPh) with inorganic and organic (or hydrophobic) ions in aqueous systems [1–3]. In a previous study, we first reported that P4VPh gel is super salt-resistive and hardly deswells in many kinds of inorganic salt solutions. This unique property, which seems to be inconsistent with the common Hofmeister series phenomena [4, 5], was interpreted as caused by the stabilization of two kinds of hydrogen-bonding hydrations of P4VPh, hydration to the proton of the phenol OH and π-hydrogen-bonding hydration to the phenol ring, by anions and cations, respectively. The supposed mechanism for the super salt-resistivity of P4VPh gel was partially supported by an ab initio calculation on the stabilization of the hydrogen-bonding hydrations by ions, and by an infrared spectroscopy that also detected the ion effects on the hydrogen-bonding hydrations [1, 2]. However, it may be a most direct proof for the mechanism to find a second example of the salt resistivity for another hydrogel of a polymer with an acidic proton and a π-electron system.

In the present study, on the basis of the above motive, swelling behaviors of a gel having a π-electron system and an acidic proton, i.e., poly (4-vinyl benzoic acid) (P4VBA) gel, are investigated. As a reference gel, poly(acrylic acid) (PAA) gel was also prepared and investigated.

Experimental

Preparation of poly (4-vinyl benzoic acid)

4-Vinylbenzoic acid (4VBA, Aldrich, 97%) was dissolved in 2.0 M NaOH aqueous solution, and the insoluble white precipitate was removed by filtration. The resulting solution was poured into 0.1 M HCl solution to precipitate 4VBA. 4VBA thus obtained was dried under vacuum and dissolved in *N*,*N*-dimethylformamide (DMF), to which AIBN (ca. 1 mol%) was added. The monomer solution was degassed by repeated freeze–thawing under vacuum. The degassed solution was set in a flask with a reduced pressure in an oil bath at 80 °C, and the reaction was continued for 18 h under stirring. After the polymerization, DMF was removed from the solution by heating at 40–50 °C under vacuum. The remaining solution was dissolved in tetrahydrofuran (THF). P4VBA was obtained by reprecipitation in hexane from the THF solution. A small portion of P4VBA was converted into poly(methyl 4-vinylbenzoate) by treating with diazomethane [6]. On the basis of a gel permeation chromatography measurement of methyl ester, which was prepared as described, of P4VBA that was calibrated by polystyrene standards in THF, the average molecular weight (Mw) of P4VBA samples was estimated as ca. 1.0×10^5.

Preparation of poly (4-vinyl benzoic acid) gel

P4VBA gel was prepared by cross-linking the P4VBA with ethylene glycol diglycidyl ether (EGDGE, Aldrich). The cross-linking reaction was carried out for a DMF solution containing ca. 30 wt% P4VBA and a required amount of EGDGE (ca. 24 mol% to P4VBA carboxyl group) at 70 °C for 24 h. Attempts of the gel preparation in aqueous media or at the lower cross-linker concentration proved to be in vain. No gel samples that were strong enough to be utilized for the swelling measurement were obtained. A rod-type gel was prepared in a glass capillary (ϕ=0.69 mm).

For comparison's sake, poly(acrylic acid) (PAA) gel was also prepared.; PAANa (Polysciences; 35% aqueous solution, Mw=6,0000) was diluted to 20 wt% solution, and a desired amount of EGDGE (ca. 21 mol% to the PAA carboxyl group) was added to the solution. Then, the solution was neutralized with 5 M HCl. The cross-linking reaction was performed in room temperature (ca. 25 °C) for 24 h after setting the same type of glass capillaries used for P4VBA into the solution.

Water contents of P4VBA and PAA gels were estimated by weighing the samples before and after drying in a vacuum oven at 120 °C for 48 h. The preparation conditions and properties of the P4VBA and PAA gels are listed in Table 1. As seen from the table, the water contents of the two gel samples were significantly different. This may be ascribed to the differences in the cross-linking degrees and/or in the hydrophobic/hydrophilic properties of the polymeric substrates. Even though the PAA gel has such a significantly higher water content, it may be employed as a reference gel because the aim of the present study is to compare qualitatively, not quantitatively, the ion-specific swelling behavior of P4VBA gel with PAA gel that contains no π-electron system.

Table 1 Preparation conditions and water content of P4VBA and PAA gels

Gel	Polymer concentration (wt%)	Solvent	Cross-linker concentration (mol%)	Water content (wt%)
P4VBA	32.3	DMF	23.7	55.3
PAA	20.0	H_2O	20.8	99.7 (ca. 97%)[a]

[a] Water content in 0.01 M HCl

Measurements of swelling degrees

Swelling behavior of P4VBA and PAA gel in $MgCl_2$, LiCl, NaCl, CsCl, KSCN, and Na_2SO_4 was investigated. The rod-type P4VBA gel samples were first immersed in 0.01 M NaOH until the equilibrium state was attained, and then immersed to 0.001 M HCl and water in sequence until the respective equilibria were established. Swelling measurements were performed for the gel samples thus pretreated and the immersing solutions were changed to a more concentrated one after the respective equilibria were attained. The salt solutions for PAA gel contained 0.01 M HCl to keep the polymer at an uncharged state. Thus, the degree of swelling of the PAA samples was defined by d/d_0' instead of d/d_0 for P4VBA gel, where d, d_0, and d_0' correspond to the gel diameter in the salt solutions, water, and 0.01 M HCl, respectively.

Results and discussion

Swelling behaviors of P4VBA and PAA gels

The swelling degrees of P4VBA and PAA gels in various inorganic salt solutions are shown in Figs. 1 and 2, respectively. As seen from the figures, the P4VBA gel only slightly deswelled with increasing the salt concentration, while the swelling degrees of the PAA gel were significantly ion- (salt-) specific. This ion-specific swelling of the PAA gel, i.e., significant swelling in the presence of weakly hydrated anions (e.g., I^-, SCN^-) and drastic deswelling in the presence of strongly hydrated cations (e.g., Mg^{2+}, Li^+) and anions (SO_4^{2-}, F^-), was found for a PAA gel that was prepared by γ-ray irradiation [7]. According to Muta et al., the swelling tendency observed for the large anion systems is to be ascribed to a specific binding of the relevant anions to hydrophobic moieties of the polymer [8, 9]. The remarkable deswelling for the small anion systems is explained by a specific rejection from such a hydrophobic surface [10] or a salting-out effect by small anions to hydrophobic hydration. On the other hand, the deswelling for the small cation systems was explained by the authors as caused, not only by the salting-out effect by cations to hydrophobic hydration, but also, by unfavorable hydrogen-bonding hydration to the acidic proton in the presence of concentrated cations [7]. In

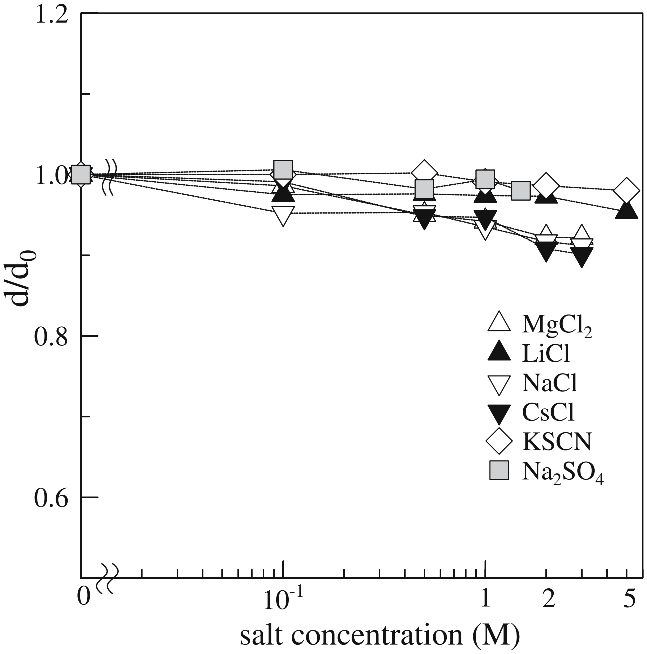

Fig. 1 Swelling behavior of P4VBA gel as a function of salt concentration

principle, these salting-out and salting-in effects by anions and cations should also exist in the present P4VBA gel system, for which, however, no significant salt effects were observed. Furthermore, it should be noted here that the swelling degrees for Na_2SO_4 are slightly but definitely higher than for the NaCl system. This order for the salting-out effect between sulfate and chloride is just opposite to the typical Hofmeister series. These contrastive swelling behaviors may be ascribed to differences in the chemical structures of the monomer residue of these polymers; the main chain and the carboxyl group are common for the polymers and only one difference is the benzene ring as the side chain of 4VBA. Because of the hydrophobicity of the benzene ring, P4VBA is scarcely soluble in water, while PAA is water-soluble to some extent. This apparent hydrophobicity of P4VBA might be a cause for the rather low water content of the gel prepared, ca.55 %. In fact, one may consider that such a low water content of the P4VBA gel is the main reason for the insensitivity of the swelling degrees to salt concentration. As a matter of fact, if the water content were so low that further deswelling hardly occurs, no significant salting-out effects would be observed. However, water content of as much as 50% means that ca. eight molecules of water reside around one monomer residue, which should still allow an appreciable deswelling. Furthermore, one may suppose that the apparent salt resistivity should be ascribed to the bound water that is to be a main component in a hydrogel with water content as low as 50%. The bound water, which strongly interacts with the polymer substrate, may retard any deswelling. However, even this was the case, the inversion of the swelling degrees between Na_2SO_4 and NaCl would not be explained by invoking the strong interaction of the bound water with the polymer substrate. Therefore, the observed moderate insensitivity of the P4VBA gel to salt concentration means that this polymer gel is also salt resistive, although the performance is less significant than P4VPh gel. Then, the existence of the benzene ring must be responsible for the salt resistivity of P4VBA gel. As described in the "Introduction," Muta et al. proposed that a coexistence of an acidic proton and a π-electron system is essential for the super salt resistivity of P4VPh gel. According to this mechanism, the differential swelling behaviors of P4VBA and PAA gels are interpreted in the following explanation.

The benzene ring, being different from common hydrophobic groups like alkyl chains, may be hydrated via π-hydrogen bonding hydration, which can be stabilized by cations via their ionic hydrations. This means that cations are accessible to this "hydrophobic moiety," thus leading to the disappearance of salting-out effects by cations for the P4VBA gel. On the other hand, anions stabilize the hydrogen-bonding hydration of the acidic proton. This stabilization scheme may be illustrated as Fig. 3, which corresponds to Fig. 4 of [1] that was obtained for phenol model systems on the basis of ab initio calculations. In short, both of cations and anions are accessible to the polymer, reducing the common salting-out effects, which always exist as a background due to substantial decrease in the water activity in concentrated salt solutions.

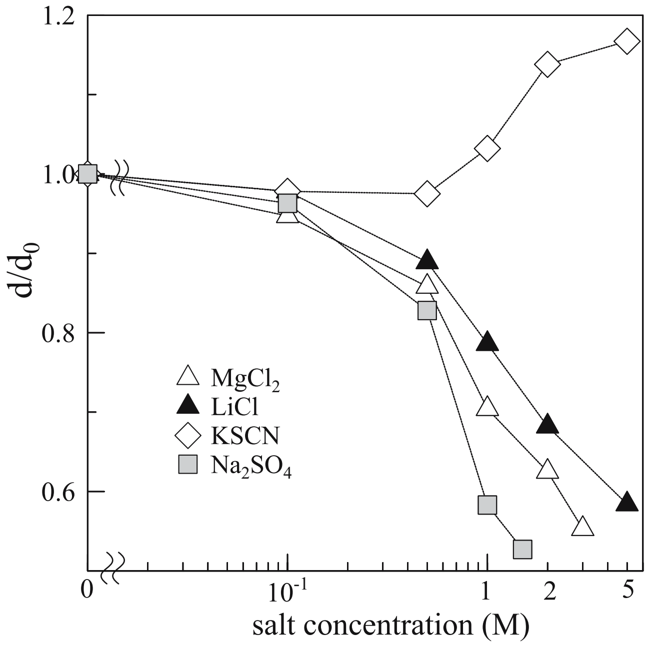

Fig. 2 Swelling behavior of PAA gel as a function of salt concentration

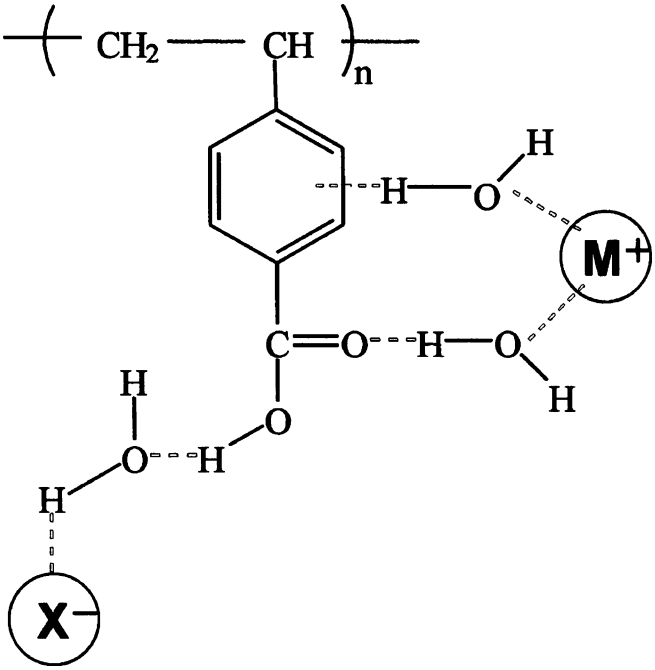

Fig. 3 Scheme of salt resistivity caused by stabilization of hydrogen-bonding hydrations of P4VBA through ionic hydrations

One should note here another uncommon behavior of the P4VBA gel: it did not show any significant swelling as well as deswelling. As previously stated, large and weakly hydrated anions were apt to be bound to common hydrophobic polymers. Thus, in systems of such anions, significant gel swelling must be observed. In the P4VPh gel systems, even a slight deswelling was observed in the presence of SCN^- [1]. Therefore, these results for P4VPh and P4VBA gels strongly suggest that the "hydrophobic hydration" of the polymers is essentially different from the common one. Although the mechanism for the specific anion binding to and rejection from hydrophobic interface is still under debate [11], the present results may cause a stir in this problem.

Conclusion and some complementary comments

In the present study, we have found that P4VBA shows a salt resistivity, which is less significant than that of P4VPh but highly distinct compared with common hydrophilic and hydrophobic polymers, both in gel and dispersion systems. This experimental fact strongly suggests that the combination of an acidic proton and π-electron system is essential for polymers to be endowed with salt resistivity, as proposed in the previous studies.

As a matter of fact, one may find an example in nature or biological systems that may be correlated with the present finding, i.e., the acidic proton–π-system combination seems to impart some specific properties to polymers, e.g., salt resistivity and hydrophilicity, which is unexpectedly higher than judged by hydrophobicity of the constituting groups. The example is the extraordinarily high hydrophilicity of tyrosine, which is measured with the so-called hydropathy index by Engleman et al. [12]. The index values for tyrosine, phenylalanine, serine, and alanine were tabulated in Table 2. The index has been accepted as an effective measure of hydrophobicity or hydrophilicity of amino acids. Since this index was estimated on the basis of the free energies of transfer of side chain parts of amino acids between water and a nonpolar medium of dielectric constant 2, one can relatively judge the hydrophobicity (hydrophilicity) of the relevant side chains, which is free from influence of ionic hydrations around the carboxyl anion and the ammonium cation. As shown in the table, tyrosine is the most hydrophilic among the listed amino acids, while phenylalanine is most hydrophobic. Thus, the hydrophilicity of tyrosine is attributed to the addition of the hydroxyl group to phenylalanine. On the other hand, the hydrophobicity of serine is not so weakened by the addition of the hydroxyl group to alanine. This means that the combination of an acidic proton and π-electron system specifically enhances the hydrophilicity of the pertinent molecules. One should note here that the relative hydrophilicities between the side chains of tyrosine and serine are not consistent with the water solubility of phenol and methanol. This apparent contradiction may be interpreted by noting that the hydrophilicity of the phenol residue measured by this index is valid for an isolated or fully hydrated residue. Even if a solid or liquid material is insoluble in water, it may become hydrophilic when it is molecularly dispersed in water and fully hydrated. This is in fact consistent with an unfavorable property of P4VPh gel; it loses an ability to swell in water once it was dried. Although the hydropathy index suggests only that the true hydrophilicity of phenol residue is much higher than that expected by the water solubility, one may conclude that the combination of an acidic proton and π-electron system endows molecules with some specific properties in aqueous media.

We have found a favorable property for the present P4VBA gel through the present study; it can swell in water even after fully dried. (A dried sample gel absorbed water

Table 2 Comparison of the hydropathy index values for some amino acids

Amino acid	Hydropathy index
Phenylalanine	+3.7
Alanine	+1.6
Serine	+0.6
Tyrosine	−0.7

up to ca. 82%, which was much higher than the original value of 55%.) This may be ascribed to the partial dissociation of the carboxyl group upon contact with water. By developing this property, one may manufacture a polymeric material, which can absorb concentrated saline water containing sulfate anions, which is so far impossible with common hydrogels.

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