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Hydrations and water properties in the super salt-resistive gel probed by FT-IR

Eisuke Okazaki, Mitsuru Satoh*

Department of Chemistry and Materials Science, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8550, Japan

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ABSTRACT

The so-called "Super Salt-Resistive Gel", i.e., poly(4-vinyl phenol) (P4VPh) hydrogel, of different water contents ($H = 95$–40%) was prepared by crosslinking with different amounts of ethylene glycol diglycidyl ether (EGDGE). FT-IR spectroscopy was used to investigate the hydration and hydrogen bond (HB) properties of water in the gel samples. The OH stretching band around 3300 cm^{-1} was deconvoluted into four sub-bands. On the basis of the relative band area and the peak wave number, it was suggested that HB of water in the gel is most stabilized when the acidic proton of the phenol residue is intact, being free from the chemical crosslinking. Difference spectra for the water band obtained in the presence of salts suggested that only sulfate systems specifically affect polymer hydrations in the gel phase. The sulfate systems were also specific in the perturbation on the main chain CH_2 stretching band; namely, with increasing the salt concentration, the peak showed a significant blue shift, which means that the hydrophobic hydration is stabilized by the typical salting-out divalent anion. All the experimental results on the FT-IR spectroscopy for the P4VPh hydrogel seem to be consistent with our previous ^{1}H NMR data on the water T_2 (Sakai Y, Kuroki S, Satoh M. Langmuir 2008; 24:6981-7.) as well as the specific stabilization of water (HB and hydration) in the gel that has been suggested on the basis of the swelling behavior.

1. Introduction

Poly(4-vinyl phenol) is "super salt-resistive" and the hydrogel shows no appreciable deswelling nor swelling even in the presence of typical kosmotropic or chaotropic anions (e.g., SO_4^{2-} and SCN^-, respectively) of their saturation concentrations [1]. The extraordinary property has been ascribed to the stabilization of two kinds of hydrogen bonding hydrations (HBHs); Namely, one is to the acidic proton of the phenolic OH and the other is the π HBH of the benzene ring, which are stabilized by anions and cations, respectively, via their ionic hydrations. These stabilizations were interpreted as caused by enhancement of water EPD (electron pair donicity) and EPA (electron pair acceptance) via anion and cation hydrations, respectively. This mechanism has been supported by ab initio calculations [1–3] and IR measurements [4]. Another remarkable feature of this polymer is that a simple and a slight chemical crosslinking (e.g., 3 mol%) affords a hydrogel of high water content as much as 99% or more, in spite of such an inherent hydrophobicity of the polymer as judged by the sparing solubility in water. A tentative interpretation was that the coexistence of three kinds of hydrations, two HBHs to the acidic proton and the π electron system and the hydrophobic one around the main chain and the benzene CH, may specifically stabilize the water HB structure in the gel phase. In fact, this anticipation has been found to be consistent with our previous NMR study [5], which suggested that the mobility of water in P4VPh hydrogel is more depressed when the water content is higher, and the fraction of water with the lower mobility is also higher for the highly swollen gel. Since the hydrogels of the higher water content were prepared with the lesser degrees of crosslinking between the phenol OH groups, the acidic proton is most preserved in the highly swollen gel. Thus, the HBH to the acidic proton seems to be a major "promoter" for the stable hydration and the resultant high water content of the pertinent gel.

In the present study, we utilized FTIR spectroscopy to probe the water HB and hydrations in the P4VPh hydrogel. Information for the former was obtained by the stretching vibration band of water OH around 3200 cm^{-1} as a function of the water content. Further, effects of added salts on the OH band in gel phase were examined by subtracting the solution spectra from the corresponding gel spectra. If any stabilization of water HB were induced by added ions, components of lower wavelength would be enhanced [6–8]. As for the salt (or ion) effects on the polymer hydrophobic hydration (HPH) around the main chain, the peak

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* Corresponding author. Tel.: +81 3 5734 2133; fax: +81 3 5734 2888.
E-mail address: msatoh@polymer.titech.ac.jp (M. Satoh).

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shift of the CH_2 stretching vibration band around 2900 cm^{-1}, which is a measure of the stability of the HPH, was utilized. In this case, contrary to the above water HB, the band peak is expected to shift toward higher wavelength upon stabilization of the HPH [9,10]. Thus, effects by chaotropic and kosmotropic ions on the HPH may be deduced in terms of the relevant peak shift, if any.

2. Experimental section

2.1. Materials and gel preparation

Poly(4-vinyl phenol) (P4VPh, Polysciences, Mw:22000) was dissolved in 1 M NaOH aqueous solution to adjust the polymer concentration at 20 wt%. A film gel was prepared on a glass petri dish (φ:5 cm) with 500 µl of the polymer solution containing a desired amount of crosslinker (ethylene glycol diglycidyl ether, EGDGE, Aldrich) by rotating at 4000 rpm for 5 min by a spin coater (SC2005, AIDEN). A plate type gel was prepared on a same petri dish with 3.5 ml of the polymer solution containing EGDGE. Gelation was completed in an overnight crosslinking for the two types of gel. Gel samples thus obtained were immersed in water for three days with daily exchange of the external water to remove some non-reacted polymer and crosslinker. Finally the purified gel samples were immersed in 1.0×10^{-3} M HCl aqueous solution to ensure the uncharged state of the phenol OH group and then immersed in deionized water or a salt solution (Li_2SO_4, Na_2SO_4, LiCl, NaCl, KCl, CsCl, LiSCN, NaSCN, KSCN: 0.5 M, 1.0 M or 4.0 M).

The water content of the plate gel samples thus prepared was determined by drying under vacuum at 60 °C for 48 h. The result is shown on Table 1. These gel samples were used to see effects of water content on the water band (see below). For the other experiments, plate gel and film gel samples, which were prepared by 10% crosslinking (water contents: 90.4% and 84%, respectively), were employed.

As a reference system, poly(vinyl alcohol) (PVA, ACROS, Mw:95000, 95% deacetylated) gel samples were prepared by 20% crosslinking in almost a similar way as those for P4VPh gel, except for the treatment with HCl. Water contents of the plate and the film gels were 92.7 and 85.9%, respectively.

2.2. FT-IR measurements

FT-IR spectroscopy was performed with a Shimazu FT-IR8200PC (resolution:2 cm^{-1}, accumulation:40 times). The ATR method was employed for the plate type gel samples with an ATR-8200H (Shimazu), to observe water bands. The deconvolution of the water band into four sub-bands was automatically carried out with a software of nonlinear regression, which is equipped with the FTIR spectrometer, using Gauss distribution and typical values of the four water sub-bands as the first input data; 3630, 3550, 3400 and 3230 cm^{-1} [11]. As for the film gel, which was utilized to observe polymer bands, the spectra were obtained with the transmission method.

All the measurements were performed at room temperature (25 ± 1.5 °C).

Table 1
Water content of P4VPh gel prepared with various amounts of EGDGE.

Crosslinking degree (mol %)[a]	9	11	13	15	17	20	25	30	50
Water content (wt.%)	94.9	91.3	88.9	85.1	76.1	73.0	60.2	52.3	39.6

[a] Values calculated by 2 × feed mol% of EGDGE to the P4VPh OH group.

3. Results and discussion

3.1. Water band – dependence on the water content

In order to see how the HB of water is perturbed in P4VPh gel, the stretching vibration band of water OH around 3300 cm^{-1} was analyzed by a deconvolution into four sub-bands, the respective peak wave numbers are located around at 3625 cm^{-1} (ν_1), 3550 cm^{-1} (ν_2), 3400 cm^{-1} (ν_3), and 3200 cm^{-1} (ν_4) [11]. In these bands, contributions from OH group of the phenol and those from the EGDGE are also contained. However, they may be safely neglected because the molar ratio to the water OH group is less than 0.1 even for the gel sample of the lowest water content (39.6%). As shown in Fig. 1, the band shape and the four sub-bands of the gel samples with various water contents are almost similar to those of pure water except for the lowest water content sample; small ν_1 and ν_2 bands (ca. 2% and 5% in the total area) and comparable ν_3 and ν_4 bands (ca. 40% and 50%, respectively). Apart from the apparent similarity of the gel spectra to those for bulk water, the respective peak wave numbers, especially those of ν_3 and ν_4, showed appreciable dependency on the water content. Fig. 2 shows results on the wave number and the relative peak area only for the shorter wave number bands because those of the longer ones, which are assigned to water with lesser or weaker HB, varied only slightly and in a non-systematic way. As seen from the figure, the relative area of ν_4 sub-band slightly increased with decreasing the water content and showed a significant increase at the lowest water content, while ν_3 sub-band concomitantly decreased with a significant decrease at the lowest water content. The increasing tendency of ν_4 population with decreasing the water content suggests that HB of water molecules that directly interact with or hydrate the polymer substrate is reflected in this sub-band. Accordingly, water molecules that indirectly interact with and are to some extent influenced by the polymer substrate may be mainly included in the second stable HB band, ν_3. If this rough assignment of water on the basis of the interaction with polymer was once accepted, the behavior of the wave numbers of the two sub-bands may be interpreted in terms of the direct and the indirect interactions of water with polymer. The wave number of theν_4 sub-band in the higher water content region ($\geqq$70%) is almost the same as that of pure water and then significantly increases with decreasing the water content. This result suggests that hydration to the polymer substrate becomes less stable with decreasing water content although it is contrastive to the behavior of common hydrophilic polymers; for example, hydration of PVA and poly(vinyl pyrrolidone) is more stabilized with decreasing the water content because the fraction of water directly interacting with polymer is naturally enhanced [5,7,12]. The somewhat extraordinary behavior of P4VPh polymer hydration that was suggested by the present IR data is in fact consistent with a picture of water and hydration in the same hydrogel system that was derived from NMR T_2 data for water proton [5]. Namely, according to our previous NMR study, as stated in Introduction, hydration and water HB become less stable in the lower water content region ($\leqq$70%). A similar behavior was also observed for theν_3 sub-band except that the wave number in the higher water content region is appreciably lower than that of pure water. This latter behavior suggests that HB of water, which is indirectly interacting with polymer, is also stabilized in P4VPh hydrogel, probably via HB hydration to the acidic proton of phenol OH. This speculation is also supported by the NMR result because water molecules with the shorter T_2 value, which may be assigned to water molecules with a more stable HB structure, are overwhelming (ca.70%) even at the highest water content (97%). Namely, the HB stabilization for the major fraction of water at such high water content must be

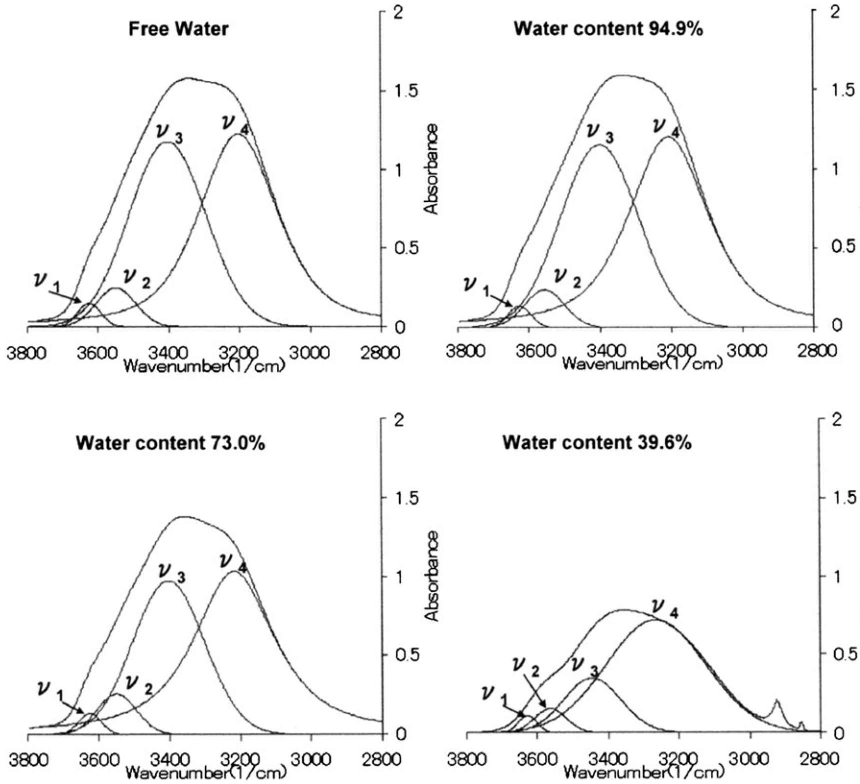

Fig. 1. Examples of deconvolution of the water band to four sub-bands for water and P4VPh gel with different water contents.

attained only when the indirectly interacting water is also stabilized as well as those directly interact with polymer. (At water content = 97%, 215 mol of water is contained per one 4-vinyl phenol monomer residue).

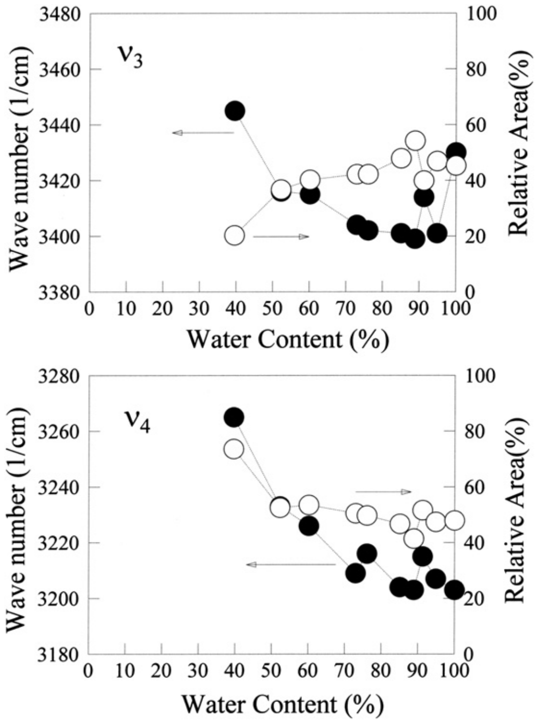

Fig. 2. Dependence of the wave number and the relative peak area of ν_3 and ν_4 sub-bands on the water content of P4VPh gel samples.

3.2. *Salt effect on the OH band*

The super salt-resistivity of P4VPh hydrogel suggested that kosmotropic ions such as SO_4^{2-} and F^- stabilize the HBH to the acidic proton of the phenol OH. In fact, our previous study [4] found that the stretching vibration band peak of C—O bond of the phenol —OH shifts in a rather complex way in the presence of concentrated salts because the stabilization of HBH to the proton and the oxygen of the phenol —OH group occurs at the same time via ionic hydration of the kosmotropic anion and the counter cation.

In the present study, we attempted to trace the supposed stabilization of the HBH to the acidic proton by SO_4^{2-} through the polymer OH stretching band. Since this band includes contributions from water OH band that may be perturbed via hydration to the polymer, this is also an indirect approach. However, the attempt proved to be fruitful as shown in Fig. 3a, which compares difference spectra around the OH band (4000–2800 cm^{-1}) that were obtained by subtracting the salt solution spectra (1.0 M Na_2SO_4, NaCl, NaSCN) from those of the corresponding gel samples. Only for Na_2SO_4 system a double peak appeared at around 3550 cm^{-1} and 3100 cm^{-1}, while NaCl and NaSCN showed only one peak around 3500 cm^{-1} and 3400 cm^{-1}, respectively. Almost the same double band was also found for Li_2SO_4 system (data not shown). Since the difference spectra should reflect how ions affect the phenol OH and the water OH involved with polymer hydration, the extra band observed only for the sulfate systems at the lower wave number region suggests that the anion stabilized the polymer hydration, especially the HBH to the acidic proton. However it should be noted that the peak at the higher wave number (ca. 3550 cm^{-1}) is significantly blue-shifted compared with those in NaCl and NaSCN

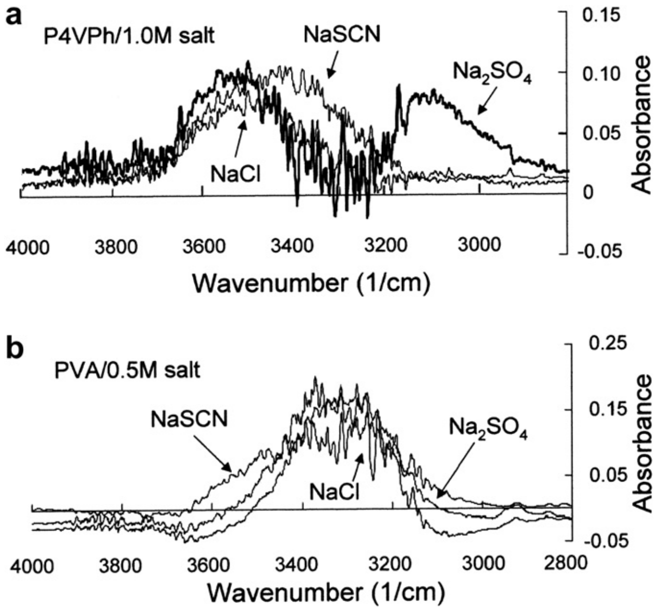

Fig. 3. Water bands obtained as difference spectra of P4VPh (a) and PVA (b) gels with the respective immersing salt solutions. The negative region in the difference spectra, especially in (b), may be ascribed to a population shift of OH vibration due to the hydration in gel phase.

systems (3500 and 3450 cm^{-1}, respectively). This means that SO_4^{2-} also has a destabilization effect on the OH hydration and/or water HB in the gel phase. Although the real origin of the destabilization may not be definitely assigned to any polymer hydration at the present stage, the counterbalancing effect might be a main reason why the stabilization of HBH to the acidic proton does not lead to a gel swelling in the sulfate solution systems.

The unique behavior of sulfate anion seems to be specific for P4VPh gel since no double peak was observed for PVA hydrogel as shown in Fig. 3b. Here the salt concentration was set at 0.5 M instead of 1.0 M to avoid a complete collapse of PVA gel in such a concentrated Na_2SO_4 solution. In the case of PVA gel, the single band peak appeared around 3300 cm^{-1} irrespective of the anion species present, which is significantly red shifted compared with those observed for P4VPh/NaCl and NaSCN systems. Since the peak wave numbers of the phenol OH and the alcohol OH in dried P4VPh and PVA films were both found around 3400 cm^{-1}, the red shift of PVA OH band in the hydrogel means that the OH hydration is more stabilized than in the P4VPh gel/NaCl, NaSCN systems. However, such a significant red shift was observed only when compared for systems that swelled in concentrated salt solutions. In fact, as shown in Fig. 4, the OH stretching band of P4VPh gel swollen in 0.1 M Na_2SO_4 was observed as a single band and had a peak around 3300 cm^{-1}. A similar trend was also found for NaCl and NaSCN systems; the OH band peak was observed around 3300 cm^{-1} (data not shown). These results suggest that the phenol OH hydration is destabilized in the hydrogel swollen with concentrated NaCl or NaSCN solution. The same may be said for P4VPh/sulfate system; the relative peak area of the higher wave number band is higher for 1.0 M Na2SO4 than in 0.5 M. This also suggests that destabilization of the phenol OH hydration is enhanced in the presence of more concentrated SO_4^{2-}. P4VPh hydrogel is, however, super salt-resistive and hardly deswollen even in saturated Na_2SO_4 solution. Then, how is the swollen state attained in such a concentrated, typically salting-out condition? The answer will be given in the next section on the hydrophobic hydration of the main chain.

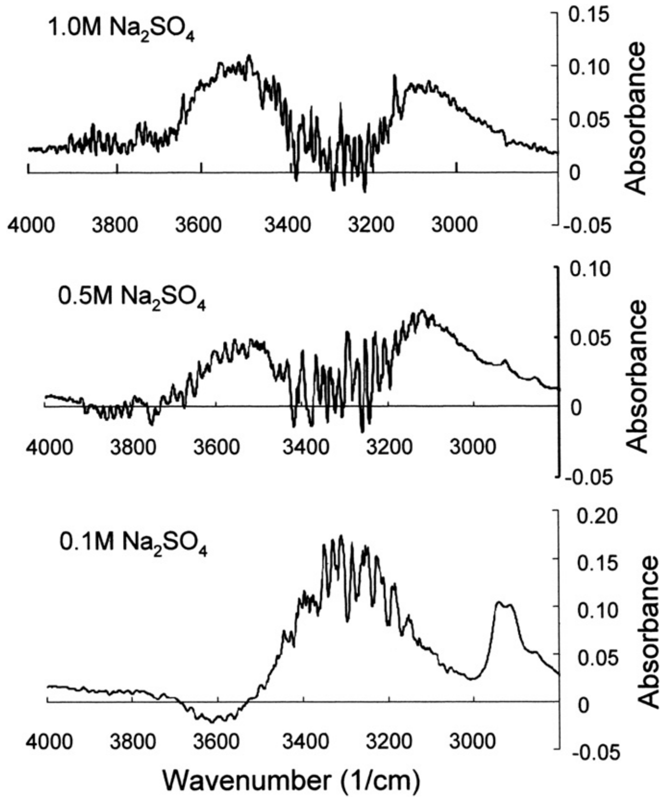

Fig. 4. Water bands obtained as difference spectra of P4VPh gel samples with Na_2SO_4 solutions of different concentrations. The significant peak around 2900 cm^{-1} seen only for 0.1 M system is CH_2 stretching vibration band, which is masked in 0.5 M and 1.0 M systems by the tail of the OH band stabilized by SO_4^{2-}.

3.3. Salt effects on the hydrophobic hydration of polymer main chain

In the present study the CH_2 stretching vibration band was examined to see salt effects on the hydrophobic hydration of the main chain. It has been known that the hydrophobic hydration absorbs large anions such as SCN^- and rejects cations and small anions [13]. The latter means that the hydrophobic hydration would be destabilized to induce the hydrophobic interaction accompanied by desolvation. Thus, in addition to sulfates and thiocyanates, the expected cation effect was also investigated by using alkali chlorides (LiCl, NaCl, KCl and CsCl). A typical IR spectrum was shown in Fig. 5 for the case of 1.0 M KCl system. Peak d and peak e are assigned to the stretching vibration of C═C of the

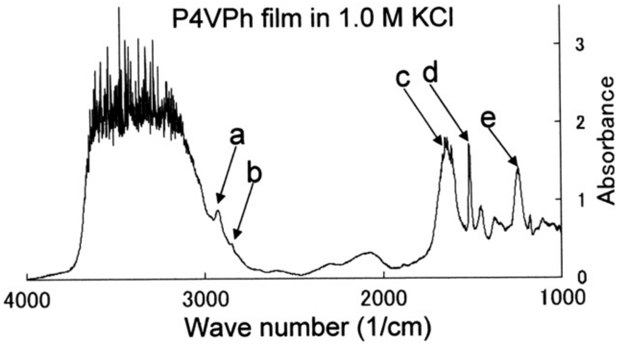

Fig. 5. Typical FTIR spectrum for P4VPh gel film swollen in 1.0 M KCl aqueous solution. See text for assignments of peaks a–e.

benzene ring and the phenol C—O, respectively. Salt effects on those bands were already investigated in our previous study [2]. Peaks a and b are C—H stretching vibration bands of CH_2 of the main chain. It has been known that a blue shift of these bands is caused by stable hydration (hydrophobic hydration) as CH…O (O of water) [9,10]. Since peak b is rather weak and sometimes not observed, we employed peak a to see ion effects on the hydrophobic hydration of the polymer main chain. Fig. 6a and b show the peak wave numbers, which were obtained from corresponding difference spectra with solution systems, as a function of ion species. The cation dependency is distinct as seen from Fig. 6a; the wave number increases with increasing the cation size irrespective of the anion species. This means that larger cations are favorable for stabilization of hydrophobic hydration of the main chain and may be ascribed to their weaker ionic hydration because strong ionic hydration is incompatible with hydrophobic hydration. Namely, the observed cation effect seems to be parallel to the common trend often observed for ion effects on the hydrophobic hydration as Hofmeister Series.

As for the anion effect, however, a completely opposite trend was found; when compared at a same concentration (1 M), the peak wave number decreased with decreasing the "strength" of the ionic hydration of the three anions. Nevertheless to say, SO_4^{2-} is a typical kosmotropic anion and SCN^- is a representative chaotropic one. Hence, the observed tendency is contrastive to the "expectation" on the basis of the Hofmeister Series. Further, it should be noted here that the peak wave number increased with increasing the salt concentration, and all the peak wave numbers obtained for salt solution systems are blue-shifted compared with that of the pure water system. The latter is in fact opposite to an observation with PVA gel film where a slight red shift was found; 2.9 cm^{-1} for 1 M Na_2SO_4 and 2.0 cm^{-1} for 1 M NaCl and NaSCN compared with the peak wave number of the PVA gel (2949.9 cm^{-1}) swollen in pure water. All these results and comparison strongly suggest that the hydrophobic hydration of the main chain of P4VPh is specifically stabilized in the presence of concentrated salts, especially strongly hydrated anions and weakly hydrated cations. Thus, the salt-resistivity of P4VPh hydrogel seems to come not only from stabilization of two kinds of HBHs (one to —OH and the other to the benzene ring) by ions but also from the unexpected stabilization of HPH of the main chain.

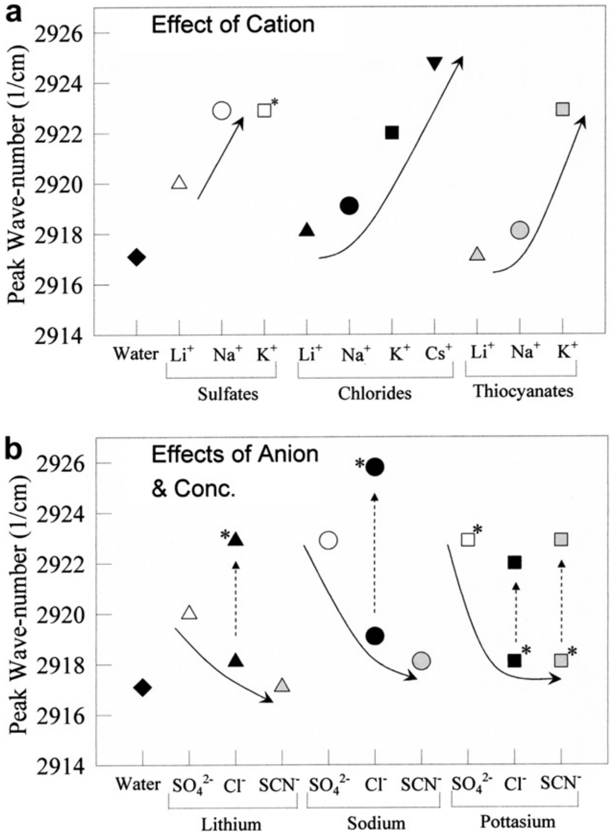

Fig. 6. The wave number of CH_2 stretching vibration band in water and salt solutions. a. Dependency on the cation species, b. Dependency on the anion species and the concentration effect. Symbols without *: 1 M, * at the upper right: 0.5 M * at the upper left: 4 M.

How is the HPH stabilized in the presence of concentrated ions? Although the former (two HBHs) stabilization can be rationalized by supposing direct interaction of relevant ions with the HBH water molecules and the resultant modification of water EPD and EPA, the observed stabilization of the HPH may not be ascribed to any direct interaction with ions, because ionic hydration should be inherently incompatible with HPH. Then, we note that some "coexistence" effect must be operating for the polymer hydrations to effect the unexpectedly stable hydration in gel phase, as suggested by our previous NMR study [5]. For example, stabilization of the HBH to the acidic proton may cause the stability of the main chain HPH. Although this speculation is a kind of an "allosteric effect", it may not always be excluded; in fact a long range interaction (∼10 nm) between polar groups on biopolymers via HBH has been suggested [14,15]. Further, the stabilization of the HBH to the phenol OH proton by, e.g., SO_4^{2-} means that the kosmotropic anion exists near the side chain, far from the hydrophobic main chain. This situation is favorable to keep the HPH intact. On the other hand, for the stabilization of π HBH, cation must be in the vicinity of the benzene ring, and hence near the main chain. Then, the weakly hydrated cations (K^+, Cs^+) must be favorable to the main chain hydration.

Finally we should return to the experimental observation that all the peak wave numbers for the C—H vibration were blue-shifted compared with that of the pure water system (Fig. 6) to note that it is consistent with the results on the salt effects on the water band (Fig. 5). Namely, the difference spectra suggested that the water HB in P4VPh gel is destabilized to some extent in the concentrated salt solutions compared with the pure water system. These apparently unfavorable salt effects on the super salt-resistivity of the relevant hydrogel may be compensated by the stabilization of the main chain HPH. For example, in the case of Na_2SO_4, the relative peak area of the higher wave number band of the two bands (Fig. 4) is enhanced at 1.0 M. This destabilization of phenol OH hydration may be, qualitatively at least, compensated by the stabilization tendency of HPH that was found for more concentrated sulfate systems.

4. Conclusion

We previously ascribed the super salt-resistivity of P4VPh hydrogel to the stabilization of HBHs to the phenol acidic proton and the π electron by anions and cations, respectively. However, it had remained to be answered why both the typical kosmotropic anion and the chaotropic one, SO_4^{2-} and SCN^-, induced neither appreciable swelling nor deswelling for the relevant gel. An answer for that has been provided by the present study; Namely, for the sulfate systems that are expected to stabilize the acidic proton HBH, both stabilization and destabilization were suggested for the phenol OH hydration and the latter seemed to overwhelm the former in the concentrated salt systems. It proved, however, that this destabilization effect by SO_4^{2-} onto the OH hydration might be compensated by the stabilization of the HPH of the main chain, which was more enhanced with increasing the salt concentration. On the other hand, the observed cation effect on the HPH is also counterbalancing the π-HBH to the benzene ring; the smaller the cations, the less stable the HPH becomes while the more stable the π-HBH is. Thus, the super salt-resistivity of P4VPh gel is interpreted as being resulted from the canceling-out of those counteracting ionic effects.

A modified interpretation on the mechanism for the super salt-resistivity of P4VPh gel has been thus proposed, while it should be subjected to an independent examination on the validity. Poly (4-vinyl benzoic acid) gel, which also shows the super salt-resistivity [16,17], must be a promising candidate system for such an investigation. And it is now undertaken to report soon.

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