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An IR study on ion-specific and solvent-specific swelling of poly(*N*-vinyl-2-pyrrolidone) gel

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Abstract

Swelling degrees of poly(*N*-vinyl-2-pyrrolidone) (PVP) gel were measured in aqueous salt solutions and in water/organic solvent mixtures to find marked ion- and solvent-specificities. In order to investigate any correlation of those specificities with hydration or solvation of PVP, IR spectra band of the C=O group was monitored by means of ATR method both for PVP gel and the relevant solution systems. Dependence of the peak frequency on the swelling ratio suggested that hydration of PVP carbonyl group in deswollen gel systems is different from that in the corresponding solution systems. In the solution systems, PVP carbonyl band showed a high-wavenumber shift for deswollen systems, which can be well correlated with changes in water proton charge through ionic hydration and with Gutmann's acceptor number of organic solvents. In the deswollen gel systems, the C=O band showed a low-wavenumber shift, suggesting a strong hydration or doubly hydrated state. This unexpected behavior was interpreted by assuming an intermolecular hydrogen bond of two carbonyl groups intermediated by water molecules. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(*N*-vinyl-2-pyrrolidone) hydrogel; Acceptor number; Intermolecular hydrogen bond

1. Introduction

Polymer gels are known to be very sensitive to surrounding environment, e.g. temperature [1,2], pH [3], composition of solvent mixture [4,5] and co-existing solutes including ions [6,7]. So far we have examined swelling behaviors of several hydrogels of hydrophilic polymers, e.g. poly(*N*-vinyl-2-pyrrolidone) (PVP) [8], poly(vinylalcohol) (PVA) and poly(allylamine) (PAlAm) [9] in aqueous salt solutions. In those studies, we found the following common ion-specificity for the swelling behavior of the gels:

1. Slight swelling in salt solutions containing cations of high charge density, e.g. Li^+ and Mg^{2+}, and marked deswelling in salt solutions containing anions of high charge density, e.g. F^- and SO_4^{2-}.
2. Anion specificity for the gel swelling degrees, $SO_4^{2-} < F^- < Cl^- < SCN^-$, is much more significant than cation-specificity, $Cs^+ < K^+ < Na^+ < Li^+ < Mg^{2+}$, which agree very well with the well-known Hofmeister series [10].

This kind of ion-specificity has also been found for many other polymeric systems [11,12]. However, despite of being a rather ubiquitous phenomenon, the mechanism of such ion-specificity still remain to be fully elucidated. It may be ascribed to a complex fusion of direct and indirect effects of ions to polymer; direct ion binding to polymer substrate and the resultant change in the electrostatic interaction, and indirect interaction of ions with polymer via hydration, in other words, ion effects on the polymer hydration such as, ionic hydration, hydrophobic hydration, and hydrogen-bonding hydration to polar groups.

Recently, we have proposed a mechanism for the ion-specific swelling behavior of hydrophilic polymer gels paying attention to ion-effects on the hydrogen-bonding hydration [8,9]. The model is composed of the following assumptions:

1. Hydrogen-bonding hydration mainly occurs at electronegative atoms on polar groups, e.g. oxygen atom of hydroxyl and carbonyl group and nitrogen atom of amino group.
2. The hydrogen-bonding hydration to the polar groups is stabilized by water with enhanced electron-pair acceptance (EPA) ability and destabilized by water with enhanced electron-pair donation (EPD) ability.

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3. The EPA and EPD of water are enhanced via hydration to cations or anions, respectively.

On the basis of these assumptions, the common features for the ion-specific swelling behavior of hydrogels can be explained. Consider one water molecule, which is making a hydrogen bond with an electronegative atom on a polar group in polymer gel via one of the two water protons. If an anion approaches to the free water proton to form a hydrogen bond, a part of the negative charge on the anion is transferred to the water through the hydrogen-bonding hydration between the pertinent water and anion. This means a reduction of the positive charge on the water proton hydrogen-bonded with the polar group, i.e. decrement of the water's EPA. Then the hydrogen-bonding hydration of the polar group is destabilized and the gel would deswell (salting-out). On the other hand, if a cation approaches the water oxygen, the cation subtracts the negative charge from the water via the ionic hydration. This means an enhancement of the positive charge on the water proton hydrogen-bonded with the polar group, i.e. increment of the water's EPA. Then the hydrogen-bonding hydration of the polar group is stabilized and the gel would swell (salting-in). These changes in EPA (or EPD) of water molecules through ionic hydration and the resultant (de)stabilization of hydrogen-bonding hydration have been confirmed by ab initio molecular orbital calculations on model complexes of organic molecules and hydrated ion clusters [13].

The same situation may also be realized for gels swollen in water/organic solvent mixtures. Namely, water EPA and EPD should be changed through interaction with organic solvent molecules. As a measure of donor–acceptor interaction of organic solvents, the donor number (DN) and the acceptor number (AN) proposed by Gutmann [14] are often utilized. If a solvent having a smaller AN (DN) than that of water is added into water, water's AN (DN) may decrease via interaction with the solvent. Besides this indirect influence, organic solvents can compete with water for polar groups of polymer. Further, organic solvents would solvate favorably non-polar groups of polymer, contributing to the gel swelling. Thus, solvent effects observed for gel swelling in water/organic solvent mixtures should be considered as a sum of above contributions from solvations to polar and non-polar groups. If one examines a correlation between gel swelling and AN and/or DN values of organic solvents added, relative contributions from solvations to polar and non-polar moieties may be estimated. This kind of approach has hardly been employed for investigation of polymer/solvent interaction; in most researches so far Flory's χ parameter and Hildebrand's solubility parameter (δ) have been utilized to estimate an averaged, but not specific, interaction of solvents with polymer.

In the present study, we investigate solvation properties of PVP gel immersed in various aqueous salt solutions and water/organic solvent mixtures by means of the swelling degree measurement and ATR/FT-IR spectroscopy. The aim of the present study is to check our model for ion effects on polymer hydrogels, i.e. (de)stabilization of hydrogen-bonding hydration of polymer through hydration of small ions. As a probe for the hydrogen-bonding hydration, we employ the stretching vibration band of PVP's C=O group. Although the other site as a hydrogen-bond acceptor, i.e. N atom, may also be utilized, hydrogen bond to N atom in amide groups seems to be less significant [15] than that to C=O group because of the resonance structure, $>N^+=C-O^-$ [16]. The peak of C=O band is expected to move toward lower wavenumber upon favorable hydrogen-bonding hydration or solvation at the site. ATR spectroscopy is also performed for the relevant solution systems and the results are utilized to assist elucidation of the swelling and solvation behaviors of the gel. By studying dependencies of the swelling degrees and the C=O band on the ion species and solvent ones, we discuss the effects of water EPA (AN of solvents) on the hydrogen-bonding hydration or solvation to C=O, and its relative contribution to the overall gel swelling.

2. Experimental

2.1. Materials

PVP ($M_w = 630,000$) was purchased from Tokyo Kasei Kogyou Co. Ltd. Salts and organic solvents of analytical grade were purchased from Kanto Chemical Co. Ltd or Nakalai Tesque Co. Ltd Deuterium oxide (99.8%) was purchased from Acros Organics Inc. All materials were used as received. Deionized and then distilled water was used throughout the experiments.

2.2. Preparation of PVP gel

PVP was dissolved in distilled water to make 12 wt% solution. Glass capillaries (ϕ: 0.690 mm) were set in the PVP solution to prepare rod-type gels and the solution in the capillaries was irradiated with γ-rays. PVP gels thus prepared were used for swelling degree measurement. For IR measurement, sheet-type gels were prepared by irradiating PVP solution (12 wt%) set in between two flat glass plates with Teflon sheet (thickness: 1 or 2 mm) as a spacer and sealed with plastic tape. Total dose of 150 kGy was applied to the respective samples.

2.3. Measurement of swelling degree

Rod-type gels were immersed in distilled water for one week to remove uncrosslinked polymer. After establishment of equilibrium swelling, the gels were immersed in 0.01 M aqueous salt solutions ($MgCl_2$, $CaCl_2$, LiCl, NaCl, KCl, CsCl, NaSCN, KSCN, $NaClO_4$, KF, $MgSO_4$, Li_2SO_4 and Na_2SO_4) or 10 vol% mixed solvent of water and organic solvent (methanol (MeOH), ethanol (EtOH), 2-propanol (2PrOH), dimethylsulfoxide (DMSO), acetonitrile (AcN), tetrahydrofuran (THF) and 1,4-dioxane). The salt concentration was increased to 0.1, 1, 2, and 4 mol/l, and the

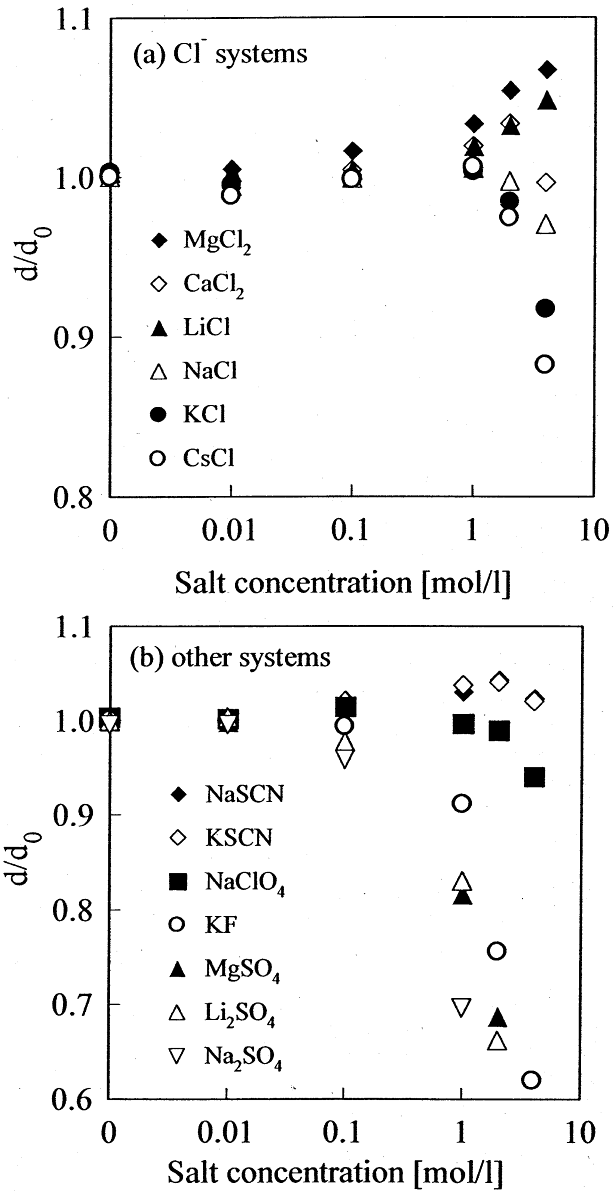

Fig. 1. Swelling behaviors of PVP gels in aqueous salt solutions.

content of organic solvent was increased to 100 vol% by 10 vol%, after the respective equilibrium swellings.

Swelling degree was defined by d/d_0, where d is the gel diameter in salt solutions or in solvents, and d_0 is that in distilled water. d and d_0 were measured by microscope observation (DIAPHOT 200, Nikon Co. Ltd).

2.4. ATR/FT-IR measurement

Sheet-type gels pretreated in the same way as the rod-type ones were used for ATR/FT-IR measurement. In addition to gels, PVP solutions of the same salt concentration or solvent compositions as the corresponding gel systems were also investigated. The polymer concentration in the solution samples was set to 12 wt%, the same as the pre-irradiation solution for gel preparation, because the polymer concentration in water-swollen gel was hardly changed by the irradiation (150 kGy). In some poor solvent systems, 2 wt% solutions were also employed. For 60–90 vol% acetonitrile, 90% THF and 60–100% dioxane, no measurements were made because even 2 wt% PVP solutions could not be made in those solvents. ATR/FT-IR measurement was carried out with Shimadzu FT-IR-8200PC with ATR-8200H attachment. Resolution of spectra was 4 cm^{-1} and scans were repeated 40 times. ATR/FT-IR proved to give fine spectra with higher reproducibility than normal FT-IR, especially for gel samples. Carbonyl stretching band of PVP gels was obtained by subtracting the solvent spectrum from the swollen gel spectrum. In all ATR/FT-IR measurements, deuterium oxide was used instead of distilled water.

3. Results and discussion

3.1. Swelling behavior of PVP gels in aqueous salt solutions and mixed solvents

Fig. 1 shows the swelling behavior of PVP gels in aqueous salt solutions. PVP gels swelled in the presence of cations with higher charge densities, e.g. Mg^{2+}, Ca^{2+} and Li^+, and deswelled in the presence of anions of higher charge densities, e.g. F^- and SO_4^{2-}. These results are consistent with a previous report by Takano et al. [8] and can be explained by changes in water EPA through ionic hydration. For Mg^{2+}, Ca^{2+} and Li^+ systems, the water EPA is greatly enhanced through ionic hydration of these cations and this stabilizes the hydrogen bond between PVP and water. On the other hand, for F^- and SO_4^{2-} systems, the water EPA is greatly reduced through ionic hydration of these anions to destabilize the hydrogen bond. This interpretation has been partially supported by our previous IR and DSC study for water in the PVP gel [8]. Namely, hydrogen bond of water in the gel was found to be strengthened in the presence of strongly hydrated cations and weakened in the presence of strongly hydrated anions, compared with that of salt-free system. Furthermore, the amount of non-freezable water in the gel estimated by DSC was enhanced for swollen gel systems, which suggested that water molecules with stronger hydrogen bonds in the presence of strongly hydrated cations serve as non-freezable water.

Fig. 2 shows the swelling behavior of PVP gels in water/organic solvent mixtures. As the solvent concentration increases, PVP gels slightly swelled in aqueous alcohols and deswelled in aqueous DMSO. On the other hand, PVP gels largely deswelled in aqueous AcN, THF and dioxane in their higher concentration region. These swelling behaviors may be simply explained by AN of the organic solvents. Since alcohols are protic solvents with relatively high AN's, (41.3 for MeOH, 37.1 for EtOH and 33.5 for 2PrOH) they can interact strongly, but of course more weakly than water (AN = 54.8), with the lone pair of

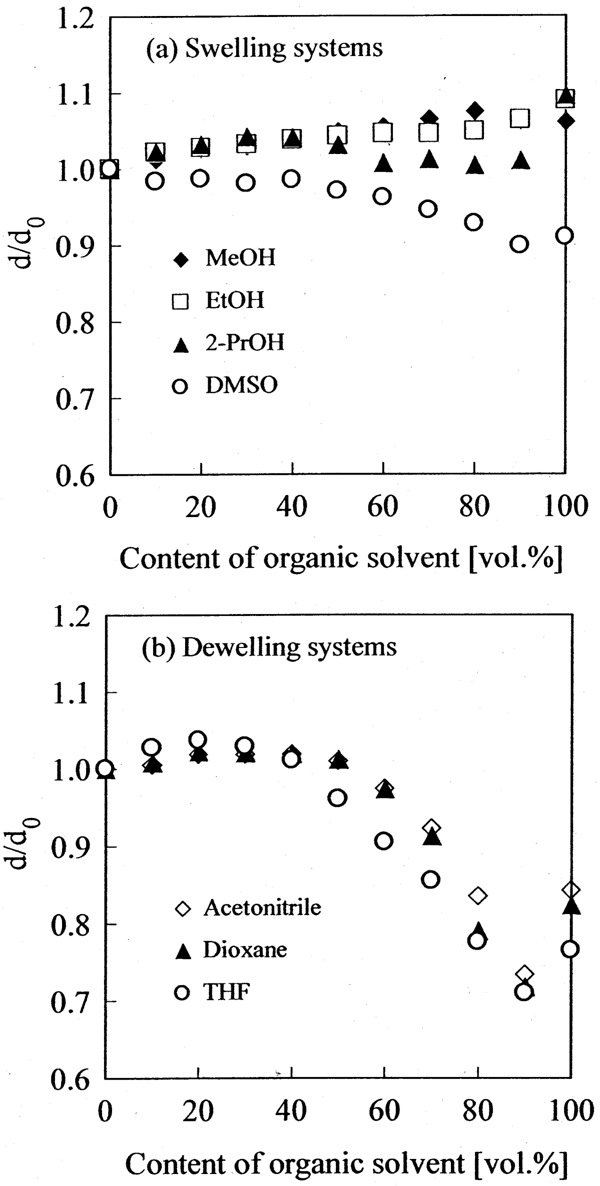

Fig. 2. Swelling behaviors of PVP gels in water/organic solvent mixtures.

oxygen atom of PVP carbonyl. On the other hand, AcN, THF and dioxane are aprotic and have lower AN's, (19.3 for AcN, 8.0 for THF and 10.8 for dioxane), the solvation of the carbonyl group would be unfavorable. Although DMSO is also aprotic and the AN is the same as AcN, the deswelling in the former is not so marked as that in the latter. This suggests that AN is not a sole determining factor for the swelling of PVP gel. Because of the high dielectric constant ($D = 49$), DMSO may be a relatively good solvent for PVP carbonyl group, which has a large dipole moment. This point will be discussed below.

3.2. ATR/FT-IR spectroscopy: relationship with swelling degree of gels

Table 1 shows peak wavenumbers of the stretching band of PVP carbonyl in aqueous salt solutions. In the case of PVP solutions, the wavenumbers in Mg^{2+} and Ca^{2+} systems are lower than or equal to that in pure water (D_2O) while higher in F^- and SO_4^{2-} systems. This can be explained by the (de)stabilization of hydrogen-bonding hydration between PVP carbonyl and water through ionic hydration. On the other hand, in the case of PVP gels, the wavenumbers in F^- and SO_4^{2-} systems are lower than in other systems. This can be clearly seen in Fig. 3, which shows dependence of the peak wavenumber on the swelling degree. In the case of PVP solutions, the wavenumber increases as the swelling degree of the corresponding gels decreases, while in the case of PVP gels the wavenumber decreases. This discrepancy in the gel and the solution systems suggests that the carbonyl group is differently hydrated in these two systems. As one possible cause for the discrepancy may be formation of an intermolecular hydrogen bond intermediated by water molecules in the deswelled gel. A similar postulation has been made to interpret aggregation behavior of PVP in aqueous solution [17,18]. Here we assume a model for cross-links of carbonyls in the deswelled PVP gel, as illustrated in Fig. 4. In PVP solutions, this type of hydrogen bond may be much less dominant than in gel, because it is inevitably accompanied by a large entropy loss due to restriction on polymer chains. Here it should be noted that in Fig. 4, not all the water molecules that participate the carbonyl hydration are illustrated. According to Shinyashiki et al. [19], about five water molecules are involved with the hydration per pyrrolidone unit. Thus, beside the two water molecules directly hydrating the carbonyl group, there may be several water molecules between and/or around them.

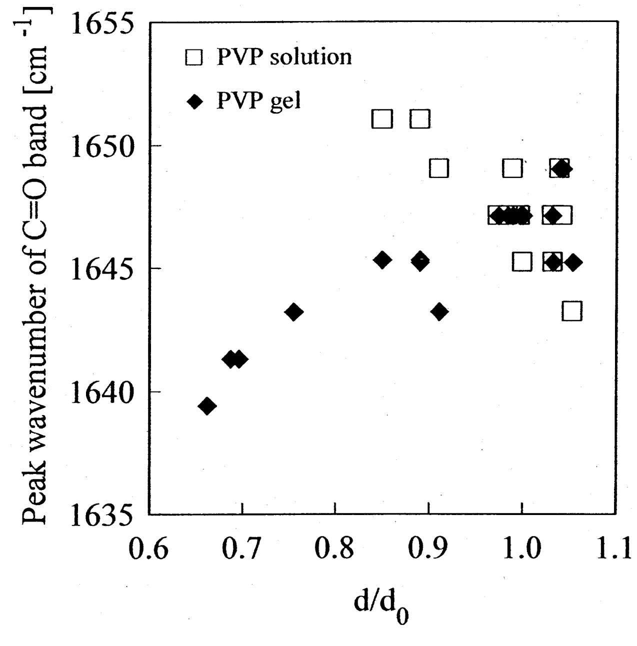

Fig. 3. Relationship between peak wavenumber of C=O band and the swelling degree of PVP gel in aqueous salt solutions.

Table 1
Peak wavenumbers of PVP C=O band in solutions and gels, and swelling ratio of PVP gels in aqueous salt solutions

Salt	Concentration (M)	Solution C=O (cm^{-1})	Gel C=O (cm^{-1})	d/d_0
D_2O	–	1645.2	1647.1	1.000
$MgCl_2$	2	1643.2	1645.2	1.054
$CaCl_2$	2	1645.2	1645.2	1.033
LiCl	2	1647.1	1647.1	1.032
NaCl	2	1647.1	1647.1	0.997
KCl	2	1647.1	1647.1	0.984
CsCl	2	1647.1	1647.1	0.974
NaSCN	2	1647.1	1649.0	1.043
KSCN	2	1649.0	1649.0	1.040
$NaClO_4$	2	1649.0	1647.1	0.989
KF	1	1649.0[a]	1643.2	0.911
	2	–	1643.2	0.755
$MgSO_4$	0.5	1651.0[a]	1645.3	0.890
	2	–	1641.3	0.687
Li_2SO_4	0.5	1651.0[a]	1645.2	0.890
	2	–	1639.4	0.662
Na_2SO_4	0.5	1651.0[a]	1645.3	0.850
	1	–	1641.3	0.696

[a] PVP concentration: 2 wt%; the others: 12 wt%.

Fig. 5 shows dependence of the peak wavenumber of PVP carbonyl band in the gel and the solution systems on the swelling degree in water/organic solvent mixtures. In the case of alcohols and DMSO, the wavenumbers in the gel and the corresponding solution systems increase with the content of the organic solvents. This means that the solvation to PVP carbonyl becomes unfavorable with the organic solvent composition. However, PVP gels in these solvents do not show any marked deswelling. These results also suggest that the swelling degree of PVP gels is not only determined by solvation of the carbonyl group, but also by solvation to the hydrophobic moiety of PVP.

In the case of mixed solvents of water and acetonitrile, THF or dioxane, the wavenumber increases with the solvent composition for the solution systems, while in the case of PVP gels the behavior is rather complex; the wavenumber first increases and then decreases with the solvent composition, and finally increases again in pure solvents. One should note that the last increase in the wavenumber in the respective 90–100 vol% regions are just corresponding to their swelling behavior as shown in Fig. 2. This coincidence strongly suggests that the gel swelling in these mixed solvents is mainly determined by the solvation at the carbonyl group.

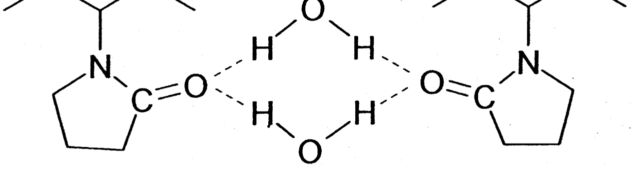

Fig. 4. Intermolecular hydrogen bond of PVP intermediated by water molecules.

The monotonous increasing trend of the wavenumber in the solution systems is contrastive to the decreasing tendency in the gel systems at the solvent-rich region aside from the re-increase in the wavenumber. This situation is similar to the deswelled systems in aqueous salt solutions containing F^- and SO_4^{2-}. Therefore, the contrastive behavior observed for the mixed solvent systems may also be ascribed to the intermolecular hydrogen bond. In fact, one can give a reasonable explanation for the re-increase in the wavenumber and the swelling degree with this 'intermolecular hydrogen bond' model. Namely, by immersing a PVP gel that has been immersed in a 90 vol% mixed solvent into the pure solvent, most of water molecules hydrogen-bonded to PVP carbonyl groups would be removed by large excess amount of organic solvent. Thus, the resultant unfavorable solvation of the carbonyl group and decrement of effective crosslinkage by the intermolecular hydrogen bond seem to be responsible for the characteristic re-increase in the wavenumber and the swelling degree.

Fig. 6 shows relationships between AN of organic solvents and peak wavenumber of carbonyl band of PVP in the gel swollen in the respective pure solvents and in the corresponding solution systems. In the solution systems, the wavenumber increases as AN of the organic solvents decreases. This tendency of wavenumber shift means that the solvation of the carbonyl group is mainly determined by the donor–acceptor interaction. On the other hand, in the gel system, the points for organic solvents with lower AN's, i.e. acetonitrile, THF and dioxane, significantly deviate downward from the linear relation. This may be ascribed to the hydration of carbonyl group by water. Namely, since the gel samples swollen in those pure solvents were prepared by transferring the samples from the respective 90 vol% mixed

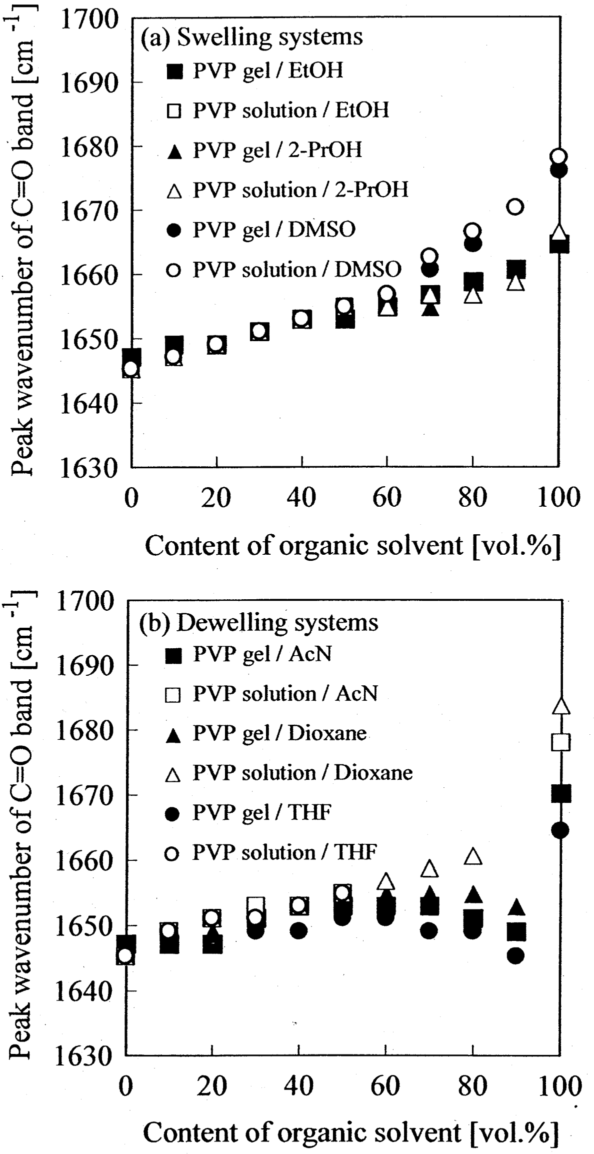

Fig. 5. Relationship between peak wavenumber of C=O band and the swelling degree in water/organic solvent mixtures.

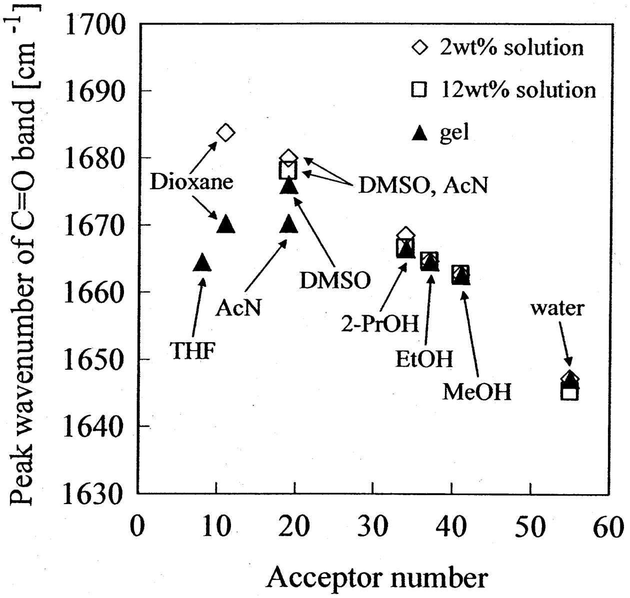

Fig. 6. Relationship between AN of organic solvents and peak wavenumber of C=O band of PVP.

solvents into the pure ones, water still remained in the 'pure' solvents to some extent.

3.3. Analysis of PVP carbonyl band by peak deconvolution

Fig. 7 shows examples of the detailed shape of PVP carbonyl band. The band seems to consist of several peaks. According to Karaputadze et al. [20], Kobianov et al. [21] and Kirsh et al. [22], free carbonyl group has a peak at 1680 cm^{-1}, and when singly and doubly hydrated by D_2O, the peak shifts to 1660 and 1641.3 cm^{-1}, respectively. Therefore, we attempted peak deconvolution of PVP carbonyl band by assuming that PVP carbonyl band in aqueous salt solution systems consists of two peaks for singly and doubly hydrated C=O groups, and the band in the mixed solvent systems also contains free one. For the actual deconvolution, we fixed the wavenumber of one peak at 1641.3 cm^{-1}, which is the experimental wavenumber of PVP carbonyl band hydrated by two water (D_2O) molecules. By this method, PVP carbonyl bands were resolved into two or three peaks. In the systems of aqueous salt solutions, most of the second peak for singly hydrated C=O was deconvoluted around at 1660 ± 2 cm^{-1}. In the systems of mixed organic solvents, the second peak appeared around at 1660 ± 2 cm^{-1}, while the third one for free C=O at 1687 ± 2 cm^{-1}. Although the position of the second peak is reasonable for singly hydrated C=O group, the third peak for the mixed solvent systems is somewhat deviated from the supposed value (1680 cm^{-1}) for free C=O. However, since the latter's contribution to the whole C=O band is rather small (less than 10% for aqueous solvent systems by the peak area estimation), we utilize the results of the deconvolution to discuss the solvation of PVP C=O group. In the following, for the sake of simplicity we confine our discussion to the peak for doubly hydrated C=O group.

Fig. 8 shows dependence of peak fractions of the doubly hydrated C=O in gels swollen in aqueous salt solutions and in the corresponding PVP solutions on the swelling degree. In solution systems, the peak fraction decreases with making the solution poorer for PVP. This is consistent with our model on ion effects on the hydrogen-bonding hydration. On the other hand, for gel systems, the peak fraction first decreases but then increases with the decrement of the swelling ratio. The increase in the doubly hydrated C=O fraction observed for deswelled gels may be interpreted as follows; In general, as solvent becomes poor, polymer would contract to enhance interaction

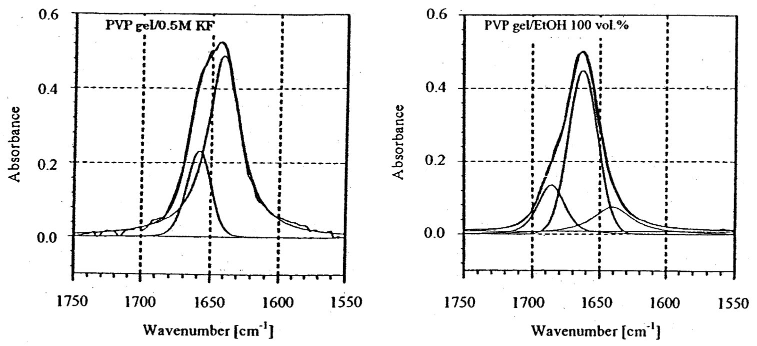

Fig. 7. Examples of PVP carbonyl band and the deconvolution.

among the polymer segments. In mixed solvent systems, increase in the fraction of poor solvent would result in exclusion of the poor component from around the polymer and enhanced interactions between the remained good solvent and polymer and/or among polymer segments during polymer contraction. In the salt solution systems of PVP, water molecules hydrating small anions and small cations would serve as poor and good solvents, respectively. When the effectiveness as the poor solvent of anion-hydrating water overwhelmed that of cation-hydrating water, the salt would be excluded from the polymer [7]. Then, water molecules free from ionic hydration would remain as good solvent around the polymer. The most efficient interaction among the carbonyl groups and the water molecules in such a situation would be realized by a hydration structure, for example, as shown in Fig. 4, because the hydrogen-bonding sites of PVP are effectively occupied by least numbers of water molecules. This structure is enthalpically favorable but entropically not. Thus, in the gel system, in which entropic disadvantage due to chain constraint is prepaid, such hydration structure may be favored, and the more favored with the decrement in the swelling degree or with enhanced contraction of polymer chain.

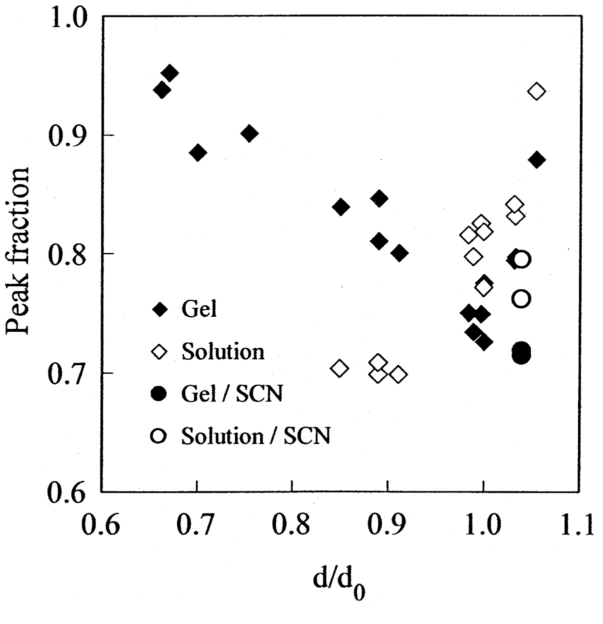

Fig. 8. Peak fractions of the doubly hydrated C=O of PVP gels swollen in aqueous salt solutions and those of the corresponding PVP solutions.

Here, we must comment on the behavior of SCN salts. As marked in Fig. 8, the data points are deviated downward from the increasing trend of the peak fraction with the swelling ratio. Similar deviation has been found in our previous study for strength of water's hydrogen bond and fraction of non-freezable water in the corresponding PVP gel systems. This may be ascribed to the specific binding of the anion to PVP. Namely, SCN^- binds to PVP to increase the swelling ratio, not by stabilization of C=O hydrogen-bonding hydration. Thus, it is rather natural that systems including this ion show different behaviors from the others where gel swelling is primarily determined by the hydrogen-bonding hydration.

Fig. 9 shows peak fractions of the doubly hydrated carbonyl in PVP gels swollen in mixed organic solvents and those in the corresponding PVP solutions. Among the organic solvents studied, methanol and AcN are chosen as a representative of good solvent and poor one, respectively. In the case of methanol system, the fraction of doubly hydrated carbonyl decreases as the concentration of methanol increases in the solution and gel systems. This again suggests that interaction of PVP's hydrophobic moiety with organic solvents significantly contributes to the overall gel swelling. In the case of AcN, the fraction of doubly hydrated carbonyl in the solution system decreases with AcN concentration, while in gel system the fraction increases in the higher concentration region and then sharply decreases at 100 vol%. This again suggests that the intermolecular hydrogen bond for C=O groups exists only in the gel system.

4. Conclusion

In the present study, we investigated solvation properties of PVP in aqueous salt solutions and water/organic solvent mixtures by measuring swelling degrees of PVP gels and by ATR/FT-IR spectroscopy for PVP solutions and gels. We

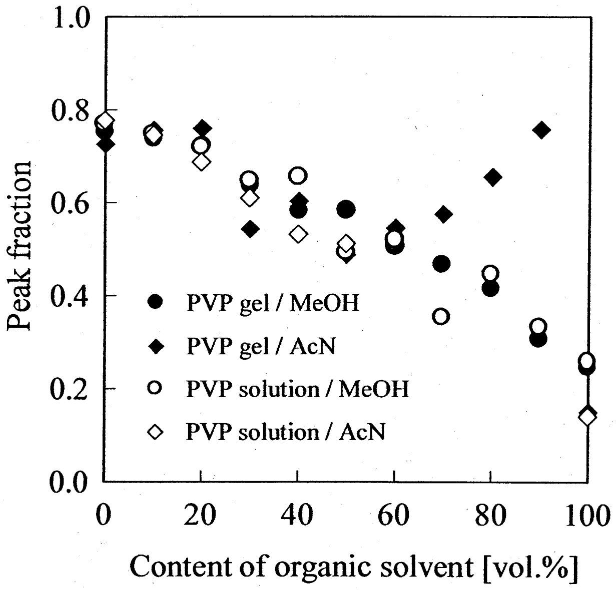

Fig. 9. Peak fractions of the doubly hydrated C=O of PVP gels swollen in water/organic solvent (MeOH and AcN) mixtures and those of the corresponding PVP solutions.

found that the peak wavenumber of PVP carbonyl group as a measure of hydrogen-bonding hydration or solvation has a good correlation with changes in water EPA through ionic hydration and AN of organic solvents. On the other hand, in the gel systems, the swelling behavior was strongly affected by interaction of solvents with hydrophobic moiety of PVP. Moreover, in the case of deswelled PVP gels, intermolecular hydrogen bond intermediated by water molecules seemed to play an important role on the deswelling. These results were also consistent with those from deconvolution of the carbonyl band.

Combining swelling behavior of gels, a macroscopic observation, and ATR/FT-IR measurement of solutions and gels, microscopic information, proved to be effective for investigation on the ion-specific and solvent-specific gel swelling. By applying the present approach to many other polymer gel systems, effects of ions and solvents on gel swelling and the correlation with site-specific solvations would be further clarified.

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