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SHORT COMMUNICATION

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Ion-specific swelling behavior of poly(vinyl alcohol) gel prepared by γ-ray irradiation

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Abstract Poly(vinyl alcohol) gel was prepared by γ-ray irradiation of an aqueous solution of the polymer and its swelling behavior in solutions of the alkali-metal and alkaline-earth-metal salts was investigated. The gel deswelled in solutions containing strongly hydrated anions and swelled in solutions containing strongly hydrated cations. The degree of swelling of the gel was in the following order: $SO_4^{2-} < Cl^- < Br^- \cong NO_3^- < I^-$ for the anions and $K^+ < Na^+ < Li^+$ and $Sr^{2+} < Ca^{2+} < Mg^{2+}$ for the cations. These results were interpreted in terms of interactions between the polymer and the ions through the hydration layers.

Key words Poly(vinyl alcohol) · Gel · Swelling · Ion specificity

Introduction

Hydrogel has the special property that it changes its volume in response to a change in the surroundings. Particularly, the study of the swelling behavior of hydrogels in aqueous salt solutions is important in terms of biomedical applications. The significant swelling of the charged gel in water was explained by Flory and Rehner [1] over 50 years ago with a theory taking account of osmotic pressure caused by the mobile counterions in the gel. Ricka and Tanaka [2] explained without free parameters the dependence of the swelling of acrylamide–acrylic acid copolymer on the ionic composition of the solvent by using the Donnan theory. On the other hand, the swelling behavior of uncharged gels is not understood yet because the swelling equilibrium is attained depending on a subtle balance among the gel and solvent components. For the elucidation of factors affecting the swelling behavior of the uncharged gel, the understanding of the effect of ions on the hydration of the polymer is probably most important. Some authors have investigated and analyzed the swelling behavior to interpret the interaction between uncharged hydrogel and ions. Inomata et al. [3] reported the effect of inorganic and tetraalkylammonium salts on the change of the phase transition temperature of poly(*N*-isopropylacrylamide) gel and explained it by the water-structure-making or breaking character of the ions. Takano et al. [4] found ion specificities for the degree of swelling of poly(*N*-vinyl-2-pyrrolidone) gel at higher salt concentration than 1 mol dm^{-3}: the degree of swelling is in the order, $SO_4^{2-} < F^- < Cl^- < SCN^- \leq I^-$ for the potassium salts and $Cs^+ < K^+ \leq Na^+ < Li^+ \leq Ca^{2+} \leq Mg^{2+}$ for the chlorides, respectively. Such specificities of the gel swelling were interpreted in terms of the enhanced electron donation ability of water molecules hydrating highly charged anions and the enhanced electron acceptance ability of water molecules hydrating highly charged cations. In the present work, the swelling behavior of uncharged poly(vinyl alcohol) (PVA) gel in aqueous alkali-metal and alkaline-earth-metal salt solutions was investigated. The gel was prepared by γ-ray irradiation to avoid any chemical contamination of the gel by a cross-linker [5]. Gel preparation by such a method has the advantage that a gel with a similar hydration property for the solution of the polymer can be obtained. The PVA gel deswelled in the solutions that contained strongly hydrated anions and swelled in the solutions that contained strongly hydrated cations. The results were interpreted by assuming certain interactions through the hydration layers of the polymer and ions, the hydrogen-bonding hydration of PVA being taking into account.

Experimental

Gel preparation

The PVA used in this study was purchased from Wako Pure Chemical Industries. The mean degree of polymerization of PVA was 1,000 and the degree of saponification was 88 mol%. To remove impurities, namely acetic acid and sodium acetate, PVA was washed with methanol by using a Soxhlet extractor for 16 h. The PVA solution was prepared by dissolving 4 wt% PVA in deionized and afterward distilled water under heating with stirring at 90–100 °C for 2 h.

The gel was prepared by irradiating the PVA solution with γ-rays of ^{60}Co. The PVA solution was filled in glass capillaries of 0.2-mm inner diameter and length 32 mm. The irradiation dose was 25 kGy. Transparent cylindrical gels were obtained without coloring.

Measurement of the degree of swelling

The gels were taken out of the capillaries, cut into specimens about 5-mm long, and immersed in distilled water completely to desalt and equilibrate. Then, the gels were immersed in respective salt solutions for 24 h. The diameter, *d*, of the gels was measured in the solution with $\pm 0.1\%$ deviation. The degree of swelling of the gels was defined as the ratio, d/d_w, of the diameter in salt solution to that in distilled water. The ratios of the change in the length of the gel in salt solution were about the same as that of the diameter. All the measurements were carried out at 20.0 ± 0.1 °C.

As salts, analytical grade NaCl, NaBr, NaI, Na_2SO_4, $LiNO_3$, $NaNO_3$, KNO_3, $CsNO_3$, $Mg(NO_3)_2$, $Ca(NO_3)_2$ and $Sr(NO_3)_2$ were employed.

Results and discussion

Plots of the d/d_w values of PVA gel against the salt concentration, c_s, of the immersing solution for NaCl, NaBr, NaI, $NaNO_3$ and Na_2SO_4 are shown in Fig. 1. The d/d_w values contain the experimental errors for the diameter measurement and are plotted with error bars in the figure. At $c_s = 2$ mol dm^{-3}, the order of the d/d_w values is $SO_4^{2-} < Cl^- < Br^- \cong NO_3^- < I^-$. This order corresponds exactly to the well-known lyotropic series. The interpretation of this series has been established as the order of the strength of the hydration of the ions [6]. In NaCl and Na_2SO_4 solutions, the gels deswelled and the d/d_w values decreased with the increase in the salt concentration. Particularly, for Na_2SO_4 significant deswelling was observed. The deswelling of PVA gel in these salt solutions can be thought to be primarily the result of the decreased hydration of PVA, because the order corresponds to the strength of the hydration of the anions, which depends on the crystallographic radius of the anions. For Na_2SO_4 solution, owing to the strong hydrating character of the anion, the resulting increase in the number of the hydrogen bonds between the hydroxyl groups of PVA chains results in significant deswelling. For NaBr and $NaNO_3$ solutions, PVA gel deswelled slightly in the higher-concentration region. Generally, ions with crystallographic radius larger than about 0.15 nm and low surface charge density attract water molecules weakly, which breaks the hydrogen bonds between the water molecules around the ions. The interaction of Br^- and NO_3^- with water molecules is weak as a whole, so it seems that the hydration of PVA molecules is not affected significantly. In NaI solution, PVA gel swelled with the increase in the salt concentration and was red. For NaI solution, the activity of water in PVA gel is reduced to the same extent as in the case of other salt solutions, and deswelling of the gel is expected. However, it is well known that PVA forms a complex with iodine [7, 8]. Similar interaction should take place in the PVA gel. The binding of I^- to the PVA gel enhances the interim hydrophilicity of the PVA chain, giving rise to the swelling of the PVA gel. It is presumed that swelling behavior of PVA gel in NaI solution is determined by the balance of the swelling factors, i.e., the increased hydrophilicity of the PVA gel owing to the binding of I^-, and the deswelling factor, the decrease in the activity of water in the gel.

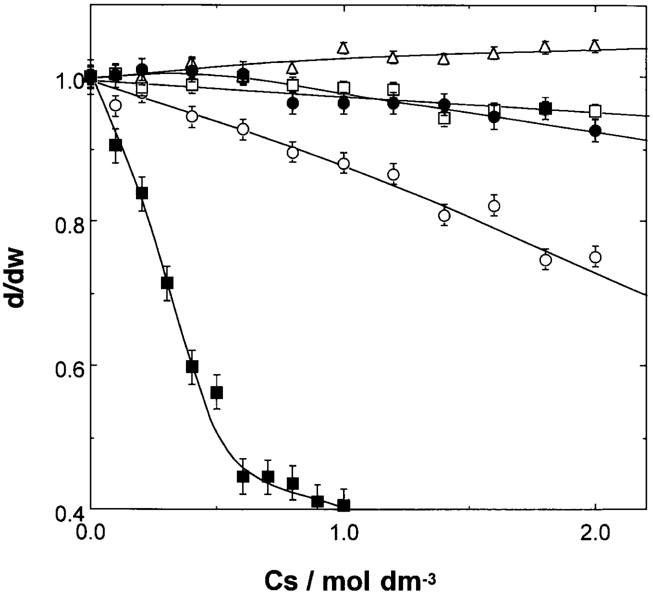

Fig. 1 Plots of the degree of swelling for poly(vinyl alcohol) (*PVA*) gel versus salt concentration: NaCl(○);NaBr(□);NaI(△);$NaNO_3$ (●);Na_2SO_4 (■)

The d/d_w values of the PVA gel in $LiNO_3$, $NaNO_3$, KNO_3 and $CsNO_3$ solutions are shown in Fig. 2. The swelling measurement for $CsNO_3$ was carried out only up to 1 mol dm^{-3} for insolubility of the salt at higher concentration. In $LiNO_3$ solution, the gel swelled slightly at the higher concentration. For $NaNO_3$ and KNO_3, d/d_w was about unity at 0–0.5 mol dm^{-3} and deswelled at 1–2 mol dm^{-3}. For $CsNO_3$ solution, d/d_w of the gel remained about unity over the whole range of the salt concentration, i.e., neither swelling nor deswelling of the gel took place. For alkali-metal salt solutions, d/d_w

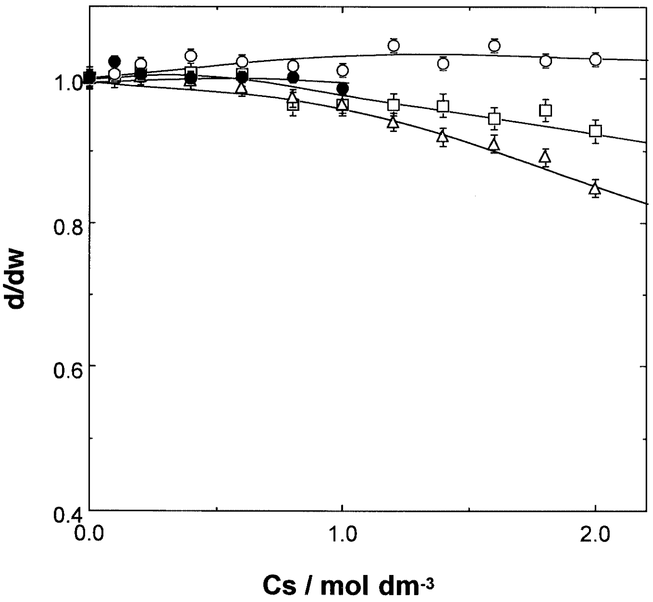

Fig. 2 Plots of the degree of swelling for PVA gel versus salt concentration: $LiNO_3$ (○);$NaNO_3$ (□);KNO_3 (△); $CsNO_3$ (●)

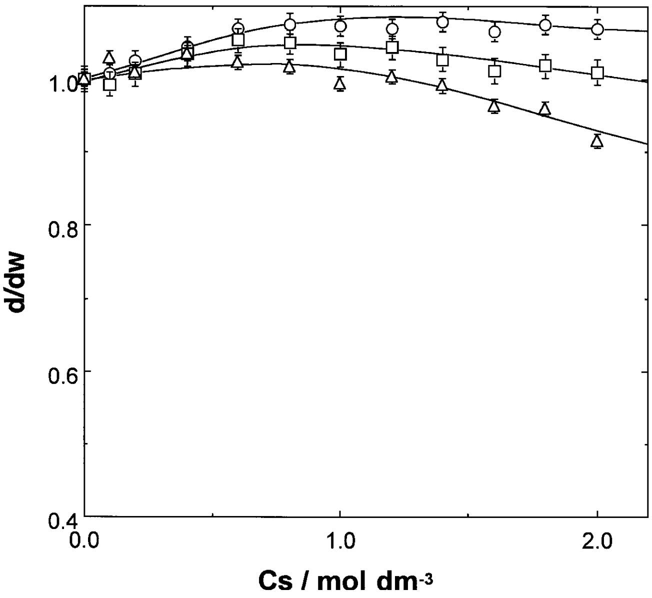

Fig. 3 Plots of the degree of swelling for PVA gel versus salt concentration: $Mg(NO_3)_2$ (○);$Ca(NO_3)_2$ (□);$Sr(NO_3)_2$ (△)

of the gel was in the order $K^+ < Na^+ < Li^+$. Lozinsky et al. [9] observed similar ion-specific swelling of PVA gel made by a freezing–thawing process for alkali-metal chlorides. At 1 mol dm^{-3}, the water activity of alkali nitrate solutions is in the order $LiNO_3 < NaNO_3 < KNO_3 < CsNO_3$ [10]. Generally, with a decrease in the water activity in the solution, the gel deswells more. When hydrogel is immersed in salt solution, the activity of water in the gel is reduced and then competition of hydrations between the ions and the polymer components takes place. If the hydration of the solute ions is stronger than that of the polymer, the amount of the hydrating water of the polymer is reduced and the gel deswells. As mentioned previously, PVA gel deswelled more in a solution containing an anion with smaller crystallographic radius and higher charge. However, it is clear from Fig. 2 that PVA gel swells in a solution that contains a strongly hydrated cation, namely Li^+. It seems that Li^+ interacts with hydroxyl groups of PVA chains via the hydration water, giving interim charge and hydrophilicity to the gel. In the case of Cs^+, similarly to the case of other alkali-metal salts, a decrease in the activity of water in the gel takes place to a lesser extent than Na^+ and K^+; hence, the deswelling of the gel is less.

The degree of swelling of PVA gel in $Mg(NO_3)_2$, $Ca(NO_3)_2$ and $Sr(NO_3)_2$ solutions is shown in Fig. 3. The gel swelled for these all salts at 0–1.5 mol dm^{-3} and d/d_w of the gel was found to be in the order $Sr^{2+} < Ca^{2+} < Mg^{2+}$. The water activity of these salts at 1 mol dm^{-3} is in the order $Mg(NO_3)_2 < Ca(NO_3)_2 < Sr(NO_3)_2$ [10] and the values are lower than those of alkali nitrates. Therefore the effect of these salts on deswelling of PVA gel may be thought to be stronger than alkali nitrates. In contrast to this anticipation, however, for alkaline-earth-metal salt solutions, PVA gel swelled with an increase in salt concentration up to about 1.2 mol dm^{-3}. Alkaline-earth-metal ions seemed to interact with hydroxyl groups of PVA chains via the hydration water similarly to the case of Li^+ mentioned earlier. In the higher-concentration region, d/d_w of the gel decreased slightly in all cases. It seems that in the higher-concentration region, the degree of the association of the cation and anion becomes higher and, therefore, the effect of the ions on swelling of the gel is lowered.

This swelling behavior is different between the cation and the anion series: the cation, with stronger hydration, makes the PVA gel more swollen, while the anion, with stronger hydration, deswells the gel more. Okazaki et al. [11] reported the ion-specific swelling behavior of the ampholytic PVA gels composed of PVAs containing 10% sulfonate and quaternary ammonium groups, respectively. They assumed that the hydration of the polymer network was dominated by the hydration of the hydroxyl groups rather than by that of the ionic groups and/or hydrophobic groups of the polymer, and on the basis of this assumption, they explained the ion specificity of the gel from the change in the electron pair donation and acceptance abilities [12] of water molecules. In the case of such ampholytic gels, however, the hydrations of both the ionic groups should be taken into account, which adds some complications in forming the salt bridge between the groups and hence the swelling behavior. The present study confirms that the swelling behavior of PVA gel is largely affected by the interaction between hydrated ions and hydroxyl groups on PVA chains. The swelling behavior of PVA gel shown in Figs. 2 and 3 can be reasonably understood by assuming that cations with high charge density interact with the hydroxyl groups of PVA chains via hydration to form interim PVA polycations. Thus, the balance of the binding of hydrated ions to PVA chains assumed earlier and the decrease in the activity of water in PVA gel becomes the main factor in controlling the swelling behavior of PVA gel in salt solutions. Undoubtedly, specific interaction between the polymer moieties and ions through the water in the gel is important for designing of ion-selective functional hydrogels.

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