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SHORT COMMUNICATION

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# Ion-specific swelling behavior of poly(vinyl alcohol) gel in aqueous solutions containing some divalent ions

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**Abstract** Swelling behaviors of poly(vinyl alcohol) (PVA) gel were investigated in solutions of salts containing certain divalent ions, namely, alkaline-earth-metal halides and sulfates of alkali-metals, alkaline-earth-metals, and transition metals. The gel deswelled in the solutions of the alkaline-earth-metal chlorides but swelled in those of the bromides. However, the cation specificities of the swelling for both of the halides were roughly the same: the degrees of swelling are $Sr^{2+} < Ca^{2+} < Mg^{2+}$. The gel deswelled for all sulfate solutions with specificities for alkali-metal and alkaline-earth-metal cations: the swelling degrees are $K^+ \cong Na^+ < Mg^{2+} < Li^+$. There was no order for transition metals.

**Keywords** Poly(vinyl alcohol) · Gel · Swelling · Ion specificity

## Introduction

It is well known that polymer gel changes its volume in response to external stimuli. This property of polymer gel has recieved much attention in fundamental research and industrial applications [1, 2, 3]. The effect of salts on the swelling behavior of polymer gel has been extensively studied by many authors [4, 5, 6] and is an important subject for understanding biochemical phenomena [7].

A previous paper [8] investigated the swelling behaviors of uncharged poly(vinyl alcohol) (PVA) gel in the aqueous solutions of sodium halides, alkali-metal nitrates, and alkaline-earth-metal nitrates. It was found that the swelling degrees of the gel were in the following order: $K^+ < Na^+ < Li^+$ and $Sr^{2+} < Ca^{2+} < Mg^{2+}$ for the nitrates and $SO_4^{2-} < Cl^- < Br^- \cong NO_3^- < I^-$ for the sodium salts. Thus, PVA gel swelled in the solutions containing the cation with stronger hydration while the gel deswelled in the solutions containing the anion with stronger hydration. These results were interpreted by assuming certain interactions through the hydration layers of the polymer and ions and by taking into account the hydrogen bonding hydration of PVA. In the present study, we examined the swelling behavior of the same gel in the solutions of some salts containing divalent ions. From the results, the additive effects of the cations and anions on the swelling behavior of the gel were discussed.

## Experimental

### Gel preparation

PVA (Wako Pure Chemical Industries, degree of polymerization = 1000 and degree of saponification = 88 mol%) was washed with methanol by using Soxhlet extractor for 16 h to remove impurities, and dried under reduced pressure at 50 °C for 24 h. The PVA solution was prepared by dissolving 4 wt% PVA in water (deionized and then distilled) under heating with stirring at 90–100 °C for 2 h. Glass capillaries of 0.2 mm inner diameter and 32 mm length were filled with the PVA solution. The gel was prepared by irradiating with $\gamma$-ray of $^{60}Co$. The irradiation dose was 25 kGy.

### Measurement of the degree of swelling

The gels were taken out of the capillaries, cut into specimens of about 5 mm length, and immersed in distilled water to desalt completely and equilibrate. Then the gels were immersed in salt solutions for 24 h. The diameters of PVA gel in distilled water and in salt solutions were measured with a microscope equipped with an eyepiece micrometer, with ±0.1% deviation. The swelling degree of the gels was defined as the ratio, d/dw, of the diameter of the gel in salt solution to that in distilled water. The ratios of change in length of the gel in salt solution were about the same as that in diameter. All the measurements were carried out at 20.0 ± 0.1 °C.

Analytical grade $MgCl_2$, $CaCl_2$, $SrCl_2$, $MgBr_2$, $CaBr_2$, $SrBr_2$, $Li_2SO_4$, $Na_2SO_4$, $K_2SO_4$, $MgSO_4$, $MnSO_4$, $CuSO_4$ and $ZnSO_4$ were employed as the salts.

## Results and discussion

The plots of d/dw values of PVA gel against the salt concentration, Cs, of the immersing solution for $MgCl_2$, $CaCl_2$ and $SrCl_2$ are shown in Fig. 1. The d/dw values contain the experimental errors for the diameter measurement, and are plotted with error bars in the figure. The gel deswelled slightly in $MgCl_2$ and $CaCl_2$ solutions and moderately in $SrCl_2$ solution with d/dw of 0.83 at 2 mol $dm^{-3}$. The order of d/dw values at 2 mol $dm^{-3}$ of the salts is $Sr^{2+} < Ca^{2+} \cong Mg^{2+}$. In the previous study [8], we found that PVA gel swells in the solutions that contain strongly hydrated cations among alkali-metal and alkaline-earth-metal nitrates. We inferred that cations with relatively small crystallographic radius (hence high charge density) interact with hydroxyl groups of PVA chain through hydration water. For $MgCl_2$ and $CaCl_2$ solutions in the present study, interim charge and hydrophilicity is given to the gel by the interaction between cations and the hydroxyl group on PVA chain. This results in the small deswelling tendencies of the gel. For $SrCl_2$, the deswelling effect of the hydration of the anion may exceed the weaker swelling effect of the larger strontium cation. Plots of the d/dw of the PVA gel in $MgBr_2$, $CaBr_2$, and $SrBr_2$ solutions are shown in Fig. 2. The measurements for these salts were carried out only up to the limits of solubility of the salts at higher concentrations. Swelling tendency, i.e., d/dw > 1, was observed for all the salts. The order of the value of d/dw is $Sr^{2+} < Ca^{2+} < Mg^{2+}$, which appears similar to the case of chlorides shown in Fig. 1. The effect of anions is considered here from the results of Figs. 1 and 2. PVA gel deswells in the chloride solutions while the gel swells in the bromide solutions. It was shown in our previous study that PVA gel deswells in the solution containing

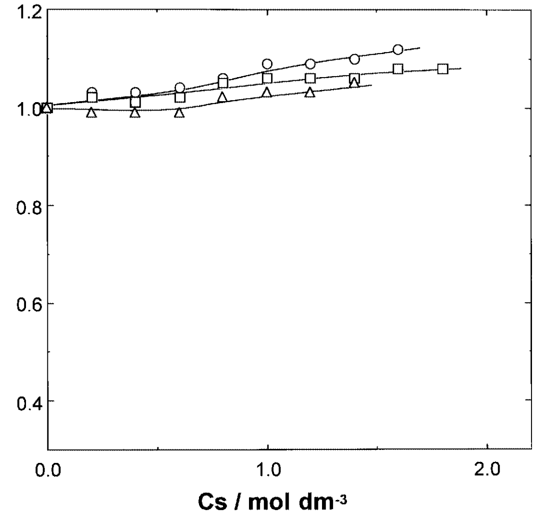

**Fig. 2.** Degree of swelling for PVA gel vs. salt concentration: (○) $MgBr_2$; (□) $CaBr_2$; (△) $SrBr_2$

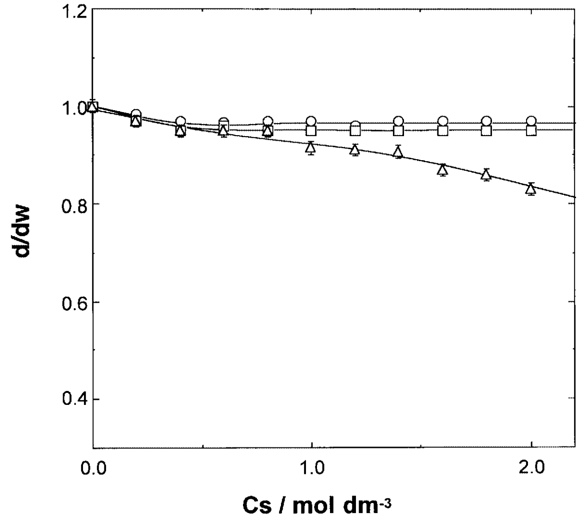

**Fig. 1.** Degree of swelling for PVA gel vs. salt concentration: (○) $MgCl_2$; (□) $CaCl_2$; (△) $SrCl_2$

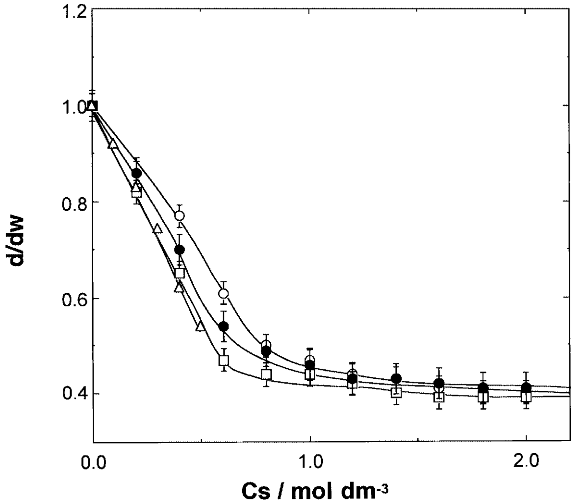

**Fig. 3.** Degree of swelling for PVA gel vs. salt concentration: (○) $Li_2SO_4$; (□) $Na_2SO_4$; (△) $K_2SO_4$; (●) $MgSO_4$

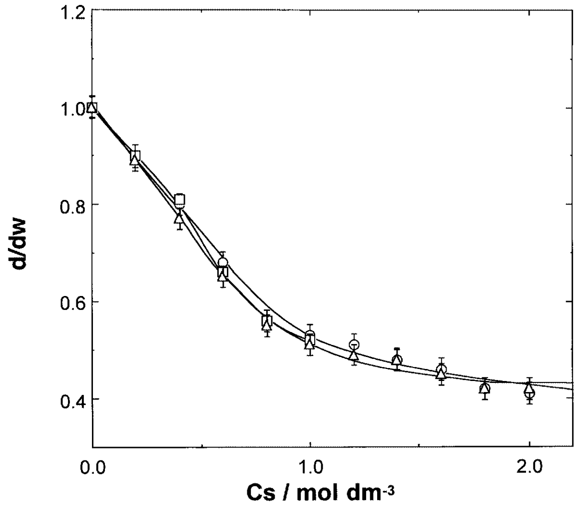

**Fig. 4.** Degree of swelling for PVA gel vs. salt concentration: (○) $MnSO_4$; (□) $CuSO_4$; (△) $ZnSO_4$

strongly hydrated anion. The interaction of $Br^-$ with water molecules is weaker than that of $Cl^-$, and has less effect on hydration of PVA chain. Therefore, the swelling effect of the cations appears in the swelling behaviors in Fig. 2, as $Sr^{2+} < Ca^{2+} < Mg^{2+}$.

The plots of d/dw of PVA gel for $Li_2SO_4$, $Na_2SO_4$, $K_2SO_4$, and $MgSO_4$ solutions are shown in Fig. 3. Due to the strong hydrating character of $SO_4{}^{2-}$, significant deswelling of the gel was observed for all salts and the d/dw value was about 0.4 at 2 mol $dm^{-3}$. However, in the range 0.4–0.6 mol $dm^{-3}$ in which the differences in the swelling curves are observed, the order of d/dw was $K^+ \cong Na^+ < Mg^{2+} < Li^+$. Even in the presence of a strongly hydrated anion like $SO_4{}^{2-}$, cations such as $Mg^{2+}$ and $Li^+$ can make the gel swell.

The plots of d/dw of PVA gel for $MnSO_4$, $CuSO_4$, and $ZnSO_4$ solutions are shown in Fig. 4. Similar to the case shown in Fig. 3, PVA gel significantly deswelled for all the salts. However, any difference in the degrees of swelling was not observed. This is probably because of the small difference in the crystallographic radii of these transition metal ions and the strong effect of hydration of $SO_4{}^{2-}$ ion. Comparing with Fig. 3, the values of d/dw in Fig. 4 are larger in the whole range of the salt concentration; e.g., at 0.6 mol $dm^{-3}$, d/dw value for $Li_2SO_4$ solution is 0.61 while those for transition metal sulfates are about 0.65–0.68. It seems that the deswelling effect of $SO_4{}^{2-}$ may be weakened by the ionic association of the transition metal sulfates in the solution.

In this study, it was found that specificity of the gel-swelling effect of alkaline-earth-metal cations persists in solutions containing anions of deswelling tendency such as chlorides and sulfates. These observations indicate that hydrated cations interact with PVA chains through hydrated water and that therefore the balance and imbalance of the strength of hydrations between anions and cations determined the swelling behavior of PVA gel in such solutions. As in the previous study, hydration of both of PVA and ions pertains to the swelling behaviors of PVA gel.

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## References

1. Kokufuta E, Tanaka T (1991) Macromolecules 24:1605
2. Zhang YQ, Tanaka T, Shibayama M (1992) Nature 360:142
3. Jeon CH, Makhaeva EE, Khokhlov AR (1998) Macromol Chem 199:2665
4. Inomata H, Goto S, Otake K, Saito S (1992) Langmuir 8:687
5. Liu X, Tong Z, Hu O (1995) Macromolecules 28:3813
6. Takano M, Ogata K, Kawauchi S, Satoh M, Komiyama J (1998) Polymer Gels and Networks 6:217
7. Baldwin RL (1996) Biophys J 71:2056
8. Masuda Y, Tanaka T, Nakanishi T (2001) Colloid Polym Sci 279:1241