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ORIGINAL CONTRIBUTION

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Ion-specific swelling behavior of poly(ethylene oxide) gel and the correlation to the intrinsic viscosity of the polymer in salt solutions

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Abstract The swelling behavior of a poly(ethylene oxide) (PEO) gel in solutions of various salts was investigated for the 0–2 mol dm^{-3} region. The gel deswelled in solutions of sodium salts, but the ion specificity for anions was not clearly observed. The gel swelled in solutions containing strongly hydrated cations and the degree of swelling of the gel at 2 mol dm^{-3} was in the following orders: CsCl ≤ KCl < NaCl < LiCl and $BaCl_2 < SrCl_2 < CaCl_2 < MgCl_2$. These results were interpreted in terms of interactions between the polymer and the ions through the hydration layers of the cations. The dimensions of PEO estimated from the results of the intrinsic viscosity of PEO in salt solutions were in accordance with this interpretation. Comparison of the swelling behavior of the PEO gel and that of a poly(vinyl alcohol) gel revealed the large difference in the effect of anions.

Keywords Poly(ethylene oxide) · Gel · Swelling · Ion specificity · Intrinsic viscosity

Introduction

Polymer gels have been extensively investigated and utilized in various fields. One of the well-known properties of polymer gels is to change the volumes in response to external stimuli [1, 2, 3]. Changes in salt species and concentration in the swelling solution can be one of the driving forces to change the volume of a hydrogel. This is caused through various interactions between the polymer moieties of the gel and the salt-constituting ions in the aqueous phase. The interactions are also very important for the use of polymer gels as biocompatible materials. It is pointed out here that in many biological systems, such interactions play an important role for the stability and function of proteins [4].

The properties of polymer gels basically depend on the chemical characters of polymer-constituting groups, of which the most important one is the hydrophilicity. Water-soluble polymers such as poly(vinyl alcohol) (PVA) and poly(ethylene oxide) (PEO) have been studied and used in medical and pharmaceutical fields for their biocompatibility. For example, applications such as drug-release systems [5] or medical devices [6] have been reported in recent years. Elucidation of the interactions between such hydrophilic polymers and salts in gel systems can help the understanding of complicated biochemical phenomena.

In a previous article [7], we reported that PVA gel prepared by γ-ray irradiation exhibits ion-specific swelling behavior in aqueous salt solutions. The gel deswelled in solutions that contained strongly hydrated anions and swelled in solutions that contained strongly hydrated cations. These results were interpreted in terms of interactions between the OH groups of the polymer and ions, presumably through the water molecules hydrating the ions. In the present study, PEO is selected as the gel material. It is known that owing to the change in the state of interaction between PEO and water with an increase in temperature, PEO shows upper and lower critical solution temperatures [8]. Owing to the repetition of ether oxygens in PEO, it is known that PEO forms complexes with various salts containing metal cations in organic solvents

[9]. Although complex formation between PEO and such metal cations in water has not been reported, it is expected that the PEO gel will show unique swelling behavior in aqueous salt systems. As noted earlier, since the chemical nature and the placement of the oxygen in PEO are different from those for PVA, the interaction with metal cations may result in different swelling behavior of PEO. Some reports are available for the preparation and structural analysis of the PEO gel [10], and for the effects of salts on the PEO chain conformation in aqueous and organic solvent systems [11, 12] and in the solid state [13]. However, information for the interaction between the PEO gel and salts in aqueous systems is scarce. In this article, we report the swelling behavior in aqueous salt solutions of PEO gel prepared by γ-ray irradiation. In addition, viscometric measurements were done for aqueous solutions of monodisperse PEO with salts. From data on the swelling of the gel and the viscometric measurement, the change in the dimensions of linear PEO in the solutions was interpreted in terms of interactions between PEO and the cations of the salts.

Experimental

Gel preparation

PEO ($M_w = 5\times10^5$) was purchased from Wako Pure Chemical Industries and was used without further purification. PEO of 8 wt% was dissolved under heating in deionized and afterward distilled water with stirring for 24 h, being followed by degassing to remove air bubbles in the solution.

The gel was prepared by irradiating the PEO solution with γ-rays from ^{60}Co. The PEO solution was filled in glass capillaries of 0.2-mm inner diameter and 32-mm length. The irradiation dose was 100 kGy. Transparent, colorless cylindrical gels were obtained.

Measurement of elastic modulus of PEO gel

The shear modulus of the water-swollen PEO gel was measured by means of an apparatus for measuring dynamic viscoelasticity (Rheolograph Gel, Toyoseiki) with 2 Hz at 25 °C.

The concentration of the effective network, ν_E/V_0, was obtained according to the theory of rubber elasticity from the storage modulus, E_G, of the gel [14]:

$$E_G = RT(\nu_E/V_0)v_2^{1/3}, \tag{1}$$

where ν_E is the number of elastically effective chains, V_0 is the volume of dry networks, vv_2 is the volume fraction of network in the swollen state and RT has the usual meaning. The relation between ν_E and the mean molecular weight, M_c, of the chain between cross-links is given by [14]

$$\nu_E/V_0 = (\rho/M_c)(1 - 2M_c/M), \tag{2}$$

where ρ is the density of the polymer and M is the molecular weight of the initial polymer.

Measurement of the degree of swelling

The gels were taken out of the capillaries, cut into specimens about 5–10-mm long, and immersed in distilled water completely to desalt and then immersed in respective salt solutions for 48 h to make sure that the gels attained the swelling equilibrium. The diameter, d, of the gels was measured microscopically in the solutions with 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. All the measurements were carried out at 20.0 ± 0.1 °C.

Measurement of the viscosity of PEO in salt solutions

For the measurement of the viscosity of aqueous PEO/salt solutions, monodisperse PEO ($M_n = 2.04\times10^4$, $M_w/M_n = 1.06$) was purchased from Scientific Polymer Products and was used without further purification. The measurements were made with a Ubbelohde capillary viscometer using water and aqueous salt solutions (1 mol dm^{-3}) as solvents. The average flow time of water was 411 s. The measurements were carried out at 25.0 °C.

The intrinsic viscosity, $[\eta]$, and the Huggins constant, k', were estimated from the intercept at $c_p = 0$ and slope of the following equation:

$$\eta_{red} = \eta_{sp}/c_p = [\eta] + k'[\eta]^2 c_p, \tag{3}$$

where η_{red}, η_{sp}, and c_p are the reduced viscosity, the specific viscosity, and the polymer concentration, respectively.

As salts, analytical grade NaCl, NaBr, NaI, LiCl, KCl, CsCl, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$, Li_2SO_4, Na_2SO_4, K_2SO_4, $MgSO_4$, $CuSO_4$, $ZnSO_4$, and $MnSO_4$ were employed.

Results and discussion

Evaluation of the concentration of the effective networks

The shear-storage modulus of the water-swollen PEO gel was 1.12 kPa. The concentration of the elastically effective chains, ν_E/V_0, evaluated from the measured modulus by using Eq. (1) is about 1.3 mmol dm^{-3}, and the calculated value of the molecular weight, M_c, of chains between cross-links is about 2×10^5. Although the theoretical expectation based on the affine model does not show a satisfactory fit with the behavior of real PEO networks [15], the large value of M_c reveals that the gel has a loose network structure.

Swelling behavior of PEO gel

Figure 1 shows d/d_w of the PEO gel against the salt concentration, c_s, of the immersing solutions for sodium salts with different anions, namely, NaCl, NaBr, NaI, and Na_2SO_4. In NaCl, NaBr, and NaI solutions, the PEO gel deswells slightly with the increase in the salt concentration and the d/d_w values of the gel for each salt were about 0.96 at 2 mol dm^{-3} salt. Generally for polymer gel systems, it is empirically known that the strength of the hydration of ions affects the swelling behavior of the gel. In many studies of interactions between ions and polymers, experimental data following the lyotropic series have been observed, and, particularly, remarkable effects of anions and the lesser effects

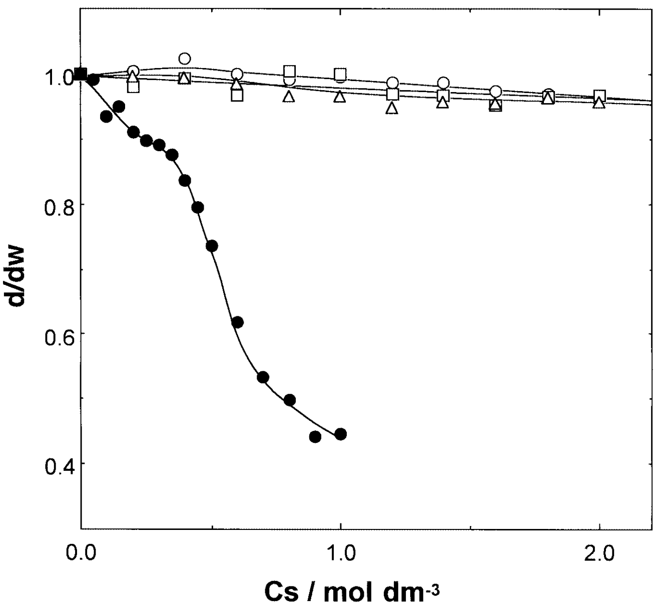

Fig. 1. Plots of the degree of swelling for poly(ethylene oxide) (*PEO*) gel against the external salt concentration: NaCl (*open circles*); NaBr (*squares*); NaI (*triangles*); Na_2SO_4 (*filled circles*)

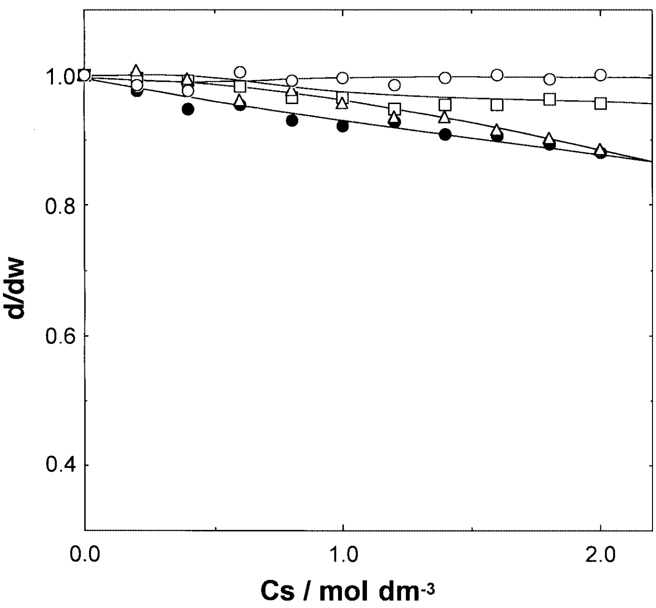

Fig. 2. Plots of the degree of swelling for PEO gel against the external salt concentration: LiCl (*open circles*); NaCl (*squares*); KCl (*triangles*); CsCl (*filled circles*)

of cations have been reported [16, 17]. Furthermore, binding of Cl^- to PEO has been reported [18]; however, in this system, ion specificity for the anions or any sign of interaction of Cl^- and PEO was not clearly observed. It appears that the effects of these anions on the swelling behavior of the PEO gel are the same. This point will be discussed later, by making a comparison with the PVA case. On the other hand, in Na_2SO_4 solution, the PEO gel deswells significantly and the d/d_w value of the gel becomes 0.44 at 1 mol dm^{-3}. It seems that the effect caused by the hydrated SO_4^{2-} ion is much stronger compared with the other anions. The strong hydration of SO_4^{2-} deprives the hydrating water of the polymer chain, resulting in the remarkable deswelling of the gel.

Figure 2 shows d/d_w of the PEO gel in solutions of chlorides with different cations, namely, LiCl, NaCl, KCl, and CsCl. In LiCl solution, the PEO gel deswells slightly and d/dw was 0.99 at 2 mol dm^{-3} salt. The difference in the two values of d/d_w at 2 mol dm^{-3} for the two different salts can be regarded as significant since the standard deviations of d were about 1% for repeated measurements of the different gel specimens. In NaCl solution, the PEO gel deswells slightly more than in LiCl solution, d/d_w was 0.96 at 2 mol dm^{-3}, and in KCl and CsCl solutions, d/d_w was 0.93 at 2 mol dm^{-3}. The degree of swelling of the PEO gel at 2 mol dm^{-3} is in the order CsCl $\leq$ KCl $<$ NaCl $<$ LiCl for the alkali-metal salt solutions. A similar tendency for cations has been reported by Bailey and Callard [19] for the salting-out effectiveness of ions on an ionic strength basis for PEO aqueous solution. On the other hand, Ono et al. [20] reported the interactions between PEO and alkali-metal cations in methanol by measuring the conductance. According to their results, the order of apparent binding constants to the polymer for the alkali-metal cations is Li $<$ Na $<$ K $<$ Cs $<$ Rb, which is exactly opposite to the order observed in this study. They interpreted this order as a result of direct interactions between the alkali-metal cations and the solvent or the polymer chain. Alkali-metal cations would bind favorably to either the solvent or the polymer chain for their own stability in methanol; thus, the larger size of the bare cations favors the interaction with PEO. In the aqueous system, the effect of hydration of ions and polymer seems to become important for the interaction between ions and oxygen atoms on the polymer chain. From the viewpoint of the increase and decrease of water activity in the electrolyte solution, the gel deswells more in the salt solution containing strongly hydrated ions owing to the reduction of the activity of water in the gel. However, the result shown in Fig. 2 seems to have the reverse order of the strength of the hydration of alkali-metal cations. Contrary to the result for the effect of the anions shown in Fig. 1, this result shows the tendency that the more strongly the hydrated cation is contained in the solution, the larger the value of d/d_w of the PEO gel is. According to the studies for aqueous PEO/salt solution, for example, Boucher and Hines [21] reported sequences of the decreasing effect of cations on the theta temperature of PEO as follows: Li $<$ Na $<$ K; Mg $<$ Ca $<$ Sr for the chlorides, Li $<$ M$\approx$K$\approx$Na for the sulfates. Ataman [22] reported that for the effect of salts on the cloud points and the theta temperatures of aqueous PEO/electrolyte solution, the order of the salting-out power of alkali cations for PEO aqueous solution was $Li^+ < Cs^+ \approx Na^+ \approx Rb^+ \approx K^+$. Ataman interpreted the results as the cation with stronger structure-breaking ability being more effective in the salting out of the polymer. With the present gel system, it seems remarkable that there are interactions between hydrated cations and PEO, rather than the formation of a bare cation–polymer complex in direct contact. The consideration based on the contribution of water-structure breaking or making properties of ions seems dubious because the correlation between the polymer–medium affinity and the water structure is obscure. PEO seems to interact with the hydrated cation to different degrees on the ether oxygen of the main chain and behaves like a pseudo-polycation, consequently leading to the swelling of the gel owing to the electrostatic repulsion of the temporary charged polymer chain. This interpretation is in line with the PVA case, where the interaction of hydrated alkali cations with the oxygen atom on the side chain was taken into account [7].

Figure 3 shows d/d_w of the PEO gel in the chlorides of alkaline-earth cations, namely, $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$ solutions. The swelling measurement for $BaCl_2$ was carried out only up to 1 mol dm^{-3} because of the insolubility of the salt at higher concentration. In $MgCl_2$ solution, the PEO gel swells with the increase in the salt concentration and d/d_w is 1.05 at 2 mol dm^{-3}. In $CaCl_2$ and $SrCl_2$ solutions, the PEO gel deswells slightly and d/d_w at 2 mol dm^{-3} is 0.98 and 0.95, respectively. In $BaCl_2$ solution, the PEO gel deswells with d/d_w 0.94 at 1 mol dm^{-3}. The degree of swelling of the PEO gel is in the order $BaCl_2 < SrCl_2 < CaCl_2 < MgCl_2$. Similarly to the case of the alkali-metal salt solutions shown in Fig. 2, the dependence of the swelling behavior of the PEO gel on the alkaline-earth cation species is in the same order in the sense that the smaller the cation, the more the gel swells. Moreover, in comparing Figs. 2 and 3, d/d_w of the gel is larger in solutions containing divalent cations than in solutions containing univalent cations. This is quite reasonable considering the higher charge of the former cations.

Similar ionic specificity is found in Fig. 4, which shows d/d_w of the PEO gel in sulfate salt solutions. In all the solutions, the PEO gel deswells to a compact state at 2 mol dm^{-3} (at 1 mol dm^{-3} for Na_2SO_4). However, differences in the swelling curves are observed in the 0.5–1 mol dm^{-3} region. The degree of swelling decreased most steeply in Na_2SO_4 and K_2SO_4 solutions, and the less steeply in $MgSO_4$ and Li_2SO_4 solutions. In other words, cations such as Mg^{2+} and Li^+ show abilities toward swelling to respective extents even in the presence of a strongly hydrated anion like SO_4^{2-}.

d/d_w of the PEO gel in $CuSO_4$, $ZnSO_4$, and $MnSO_4$ solutions is shown in Fig. 5. The PEO gel deswells in all the solutions to approximately the same degree and d/d_w is 0.5 at 1 mol dm^{-3}. In contrast to the results for alkali-metal and alkaline-earth-metal salts mentioned earlier, any specificity of the swelling behavior was not observed with these transition-metal salts. The crystallographic ionic radii of these transition-metal cations are about the

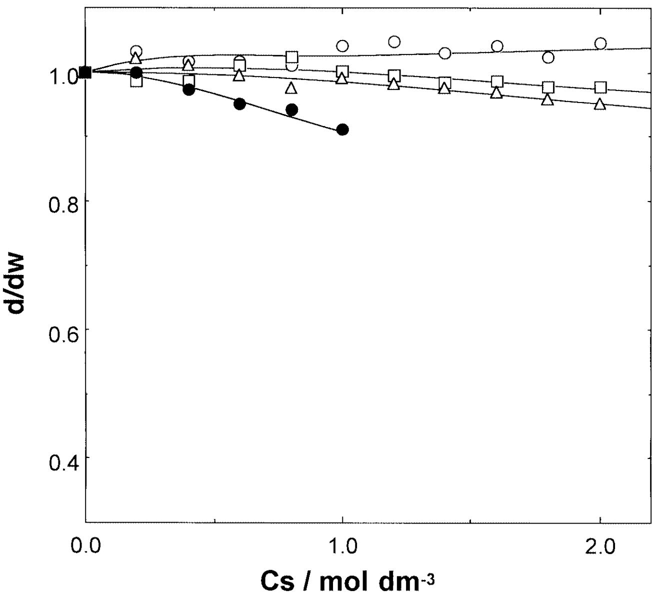

Fig. 3. Plots of the degree of swelling for PEO gel against the external salt concentration: $MgCl_2$ (*open circles*); $CaCl_2$ (*squares*); $SrCl_2$ (*triangles*); $BaCl_2$ (*filled circles*)

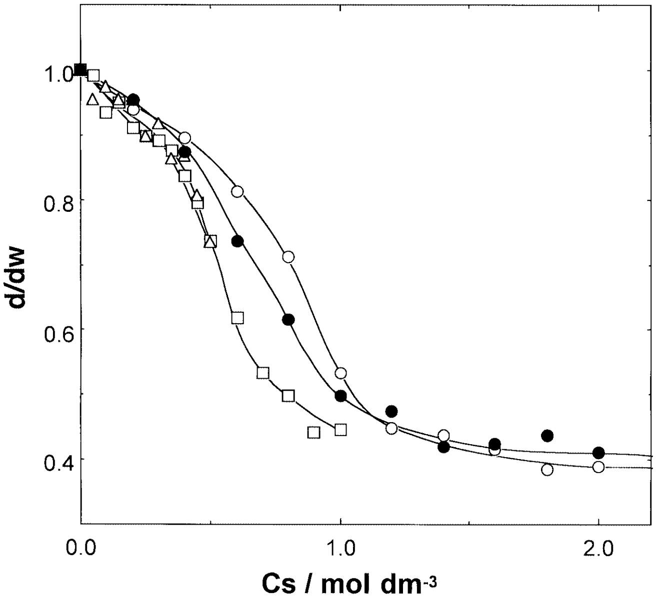

Fig. 4. Plots of the degree of swelling for PEO gel against the external salt concentration: Li_2SO_4 (*open circles*); Na_2SO_4 (*squares*); K_2SO_4 (*triangles*); $MgSO_4$ (*filled circles*)

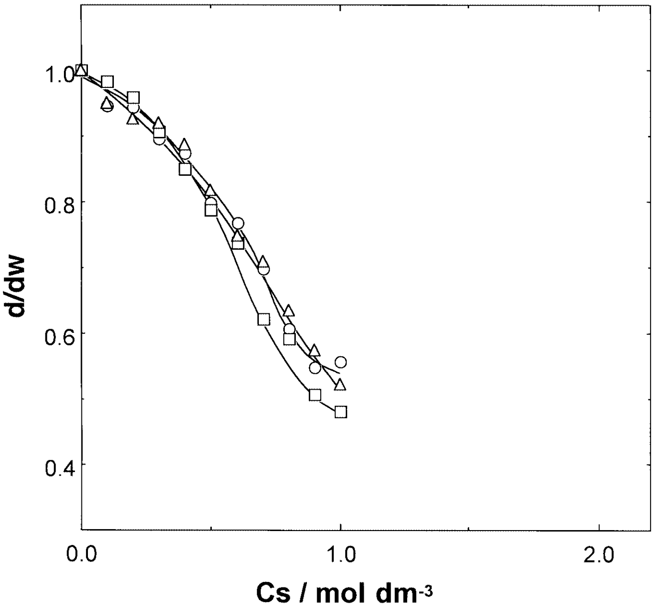

Fig. 5. Plots of the degree of swelling for PEO gel against the external salt concentration: $CuSO_4$ (*open circles*); $ZnSO_4$ (*squares*); $MnSO_4$ (*triangles*)

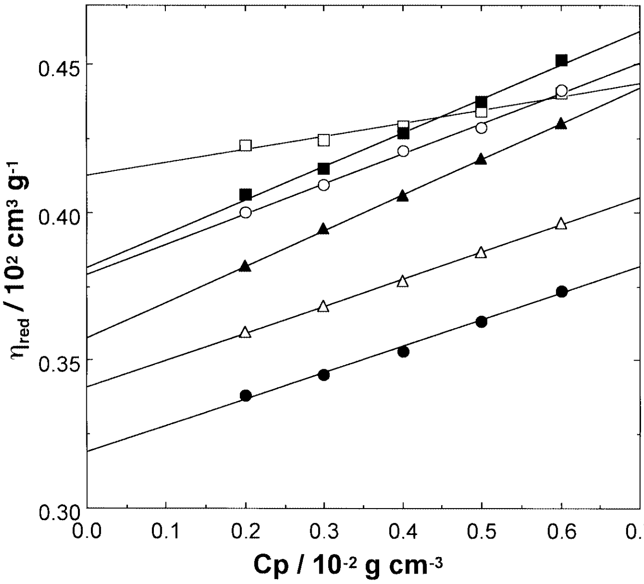

Fig. 6. Plots of the reduced viscosity for PEO/salt solutions against polymer concentration at 25 °C: none (*open circles*); LiCl (*open squares*); NaCl (*open triangles*); KCl (*filled circles*); $MgCl_2$ (*filled squares*); $CaCl_2$ (*filled triangles*). The concentration of each added salt was 1 mol dm^{-3}

Table 1. Viscosity data for poly(ethylene oxide)/salt solutions. 25 °C, salt concentration = 1 mol dm^{-3}

Salt	$[\eta]$ (10^2 cm^3g^{-1})	k'
None	0.379	0.716
LiCl	0.412	0.263
NaCl	0.341	0.786
KCl	0.319	0.878
$MgCl_2$	0.381	0.786
$CaCl_2$	0.358	0.942

same; therefore, the swelling behavior seemed to be caused by the same strength of the hydration of the metal cations.

Intrinsic viscosity of PEO and the relationship with the degree of swelling of the PEO gel

To confirm the interaction between alkali and alkaline-earth cations and PEO discussed previously, viscosity measurements were carried out for aqueous PEO solutions with added salts (1 mol dm^{-3}). The reduced viscosities of PEO in water and salt solutions are shown in Fig. 6. Straight lines in the plots against the polymer concentration were obtained for all the solutions. The parameters obtained from the viscosity data for PEO solutions are summarized in Table 1. The intrinsic viscosity of PEO in water was estimated as 0.379 from the intercept of the plot of η_{red} versus c_p. From the following viscosity formula for PEO with $M_w > 6\times10^3$ reported by Kawaguchi et al. [23], the viscosity-average molecular weight was estimated as $M_\eta = 2.15\times10^4$.

$$[\eta] = 4.33 \times 10^{-4} M_\eta^{0.679} 10^2 \mathrm{cm^3 g^{-1}}. \qquad (4)$$

Referring to the authentic data ($M_n = 2.04\times10^4$) of the PEO used for these measurements, this estimation is reasonable. From Fig. 6, the sequence of $[\eta]$ values was in the order $KCl < NaCl < CaCl_2 <$ water $< MgCl_2 < LiCl$. This result indicates that the dimensions of the PEO chain in LiCl or $MgCl_2$ solutions are more expanded than in water at 25 °C. The relationship between the degrees of swelling of the PEO gel at 2 mol dm^{-3} salt concentration and $[\eta]$ of PEO solution is shown in Fig. 7. They seem to be roughly correlated for the group of cations with deswelling tendency, namely $CaCl_2$, NaCl, and KCl. For Li^+ and Mg^{2+} with swelling tendency, the relation of the intrinsic viscosity and the degree of swelling is the reverse of that of the cations with deswelling tendency. A discussion with Huggins constants is added here. According to Yamakawa's theory, the Huggins constant would take a value from 0.2 (good solvent system) to 0.5 (poor solvent system) [24]. On the other hand, higher values, for example, k' is about 0.594–0.801 [18] or 0.69–1.64 [25] under various theta conditions, have been reported for the PEO aqueous system. In this study, it seems that the relatively high values of the Huggins constant for the group of cations with deswelling tendency reflect the shrinkage of the PEO chain due to the addition of salts. It is clear from Table 1 that aqueous LiCl is a good solvent for

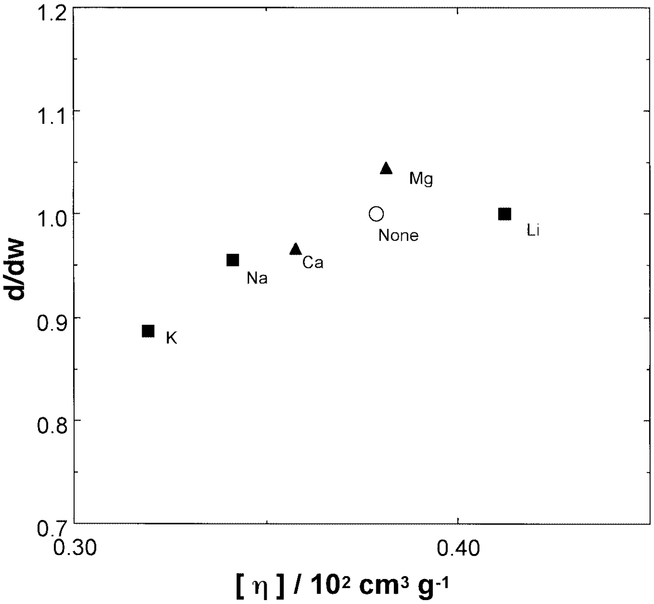

Fig. 7. Correlation of the degree of swelling of PEO gel and the intrinsic viscosity of PEO/salt solutions

PEO at 25 °C compared with the other salts or salt-free solutions. The PEO chain seems to be considerably expanded in LiCl solution. This can be evidence of the interaction between PEO and Li^+.

Comparison of the swelling behavior of PEO gel with that of PVA gel

In a previous article [7], the ion-specific swelling behavior of PVA gel was discussed. The PVA gel deswelled in solutions containing strongly hydrated anions, and swelled in solutions containing strongly hydrated cations. On the other hand, for the case of the PEO gel in the present work, ion specificity for anions or any interaction with iodide was not observed. For cations, the PEO gel showed similar ion specificity as the PVA gel and the order of the degree of swelling was qualitatively the same as for the PVA gel, and it is in the reverse order of cation specificity for the interaction between PEO and alkali cations in an organic solvent [21]. In the case of the organic system, the characteristic size of the ions seemed to be the factor for the interaction, whereas for the aqueous PEO gel system in this work, similarly to the discussion for the PVA gel previously reported, the interaction between the functional groups of the polymer and the hydrated ions seems to become the main factor. Takano et al. [26] categorized the ion effects on the swelling behavior of poly(*N*-vinyl-2-pyrrolidone) gel into three groups, namely, salting-out (small anions with high charge density), salting-in (small cations with high charge density), and ion-binding (large anions with low charge density) groups. The first and second classifications are basically in line with the results for the PEO and PVA gels. The difference in the effects of anions is caused by the difference in the functional groups of these polymers. PEO consists of ether oxygens in main chain, in other words, PEO has only electron donation ability on the oxygens. On the other hand, PVA contains hydroxyl groups in the side chain, that is, PVA has both electron-donating oxygen and electron-accepting hydrogen on the side chain; thus, PEO has no interaction with anions, while PVA has some interaction with the anions. This difference results in the absence and in the presence of the effects of anions for PEO and PVA gels.

Conclusion

The swelling behavior in aqueous salt solutions of a PEO gel prepared by γ-ray irradiation was investigated. The degree of swelling of the PEO gel was estimated by the ratio, d/d_w, of the diameter of the gel in salt solution to that in distilled water. In NaCl, NaBr, and NaI solutions, the PEO gel deswelled slightly; however, ion specificity for these anions was not clearly observed. In Na_2SO_4, the PEO gel deswelled remarkably. It seems that the strong hydration character of SO_4^{2-} and the resulting dehydration of the gel is the main factor for the deswelling. In alkali-metal salt solutions, the PEO gel deswells in solutions containing cations of larger size and the order of the value of d/d_w is as follows: $CsCl \le KCl < NaCl < LiCl$. In alkaline-earth-metal salt solutions, similar specificity of d/d_w was obtained in following order: $BaCl_2 < SrCl_2 < CaCl_2 < MgCl_2$. For these cation specificities, the interaction of the PEO oxygen with hydrated cations seems to play an important role. Cations would interact with ether oxygens on the PEO main chain through their hydration, consequently making the PEO chain behave as a temporal polycation. The order of the effect of cations on the swelling behavior of the PEO gel follows that of the strength of the hydrations. The order of the $[\eta]$ values for PEO/salt solutions is $KCl < NaCl < CaCl_2 <$ water $< MgCl_2 < LiCl$. The $[\eta]$ values for each salt solution and d/d_w of the PEO gel were roughly correlated. From the Huggins constants, it was shown that LiCl solution was a good solvent for PEO at 25 °C, which is evidence of the expansion of the PEO chain in LiCl solution. These results of viscometry support the consideration of interaction between hydrated cations and PEO presented in this study. This consideration for the swelling mechanism of the PEO gel is similar to that for a PVA gel reported previously, that is, the balance of the binding of hydrated cations to PEO chains assumed here and the decrease in the activity of water in the gel due to added salts becomes the main factor controlling the swelling behavior. It was found that the effect of anions on the swelling behavior is largely different between PEO and PVA gels. The difference was interpreted in terms of the functional groups, ether oxygen and hydroxyl group, the latter of which can be affected by anions at the electron-attracting hydrogen.

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