

Swelling equilibria of cationic polyelectrolyte gels in aqueous solutions of various electrolytes

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Swelling experiments were carried out with three cationic polyelectrolyte gels of *N*-*n*-butyl-4-vinylpyridinium bromide (BPyBr), *N*-*n*-butyl-*N,N*-dimethyl-4-vinylanilinium bromide (BAnBr) and *N*-*n*-butyl-*N,N*-dimethyl-(*N'*-acryloyl-3-aminopropyl)ammonium bromide (BAPABr). The swelling equilibria of the gels were measured in aqueous solutions of inorganic electrolytes: HBr, NaBr, KBr, NaCl and NaI. The swelling ratios of the gels did not depend on the cationic species of the electrolytes examined but depended strongly on the anionic species. Volume phase transitions were not observed with the BPyBr and BAnBr gels in aqueous solutions of NaCl and NaBr whereas a phase transition was observed in an aqueous solution of NaI. The NaI concentration at which the phase transition occurred was raised with an increase in temperature. On the other hand, no discontinuous change was observed in the swelling equilibria of the BAPABr gel, even in the NaI aqueous solution. Comparison of the present results for the BAPABr gel with previous results for a polyelectrolyte gel verified the importance of hydrophobic interactions, which enhance the occurrence of volume phase transitions.

(Keywords: volume phase transition; cationic polyelectrolyte gel; aqueous electrolyte solution; hydrophobic interaction)

INTRODUCTION

Experimental studies¹⁻⁸ of volume phase transitions of polyelectrolyte gels have usually employed acrylamide derivative gels that introduce charged groups at low concentration levels in their polymer network. However, for a better understanding of the transition, it is useful to obtain experimental data of the swelling of gels that introduce charged groups at high concentration levels.

Most polyelectrolyte gels reported in the literature⁹⁻¹¹ showed phase transition in cosolvents containing water and organic components. However, in general, the use of cosolvents makes it difficult to identify the types of molecular interaction involved, such as electrostatic, dipole, dispersion, hydrogen bonding and hydrophobic interactions. To understand the mechanism of the phase transition of polyelectrolyte gels, it is desirable to obtain experimental data for polyelectrolyte gels that show a phase transition in a single solvent.

Recently the authors¹² prepared *N*-*n*-butyl-*N,N*-dimethyl-4-vinylbenzylammonium bromide (BBABr) gel, which is a cationic polyelectrolyte gel containing a charged group in each monomer. Phase transition of the gel occurred in water by the addition of the electrolyte of NaI. The swelling equilibria of the gel were also measured in aqueous solutions of various electrolytes and the effect of the added electrolytes on the transition was examined. In the present work, we prepared the three cationic polyelectrolyte gels of *N*-*n*-butyl-4-

vinylpyridinium bromide (BPyBr), *N*-*n*-butyl-*N,N*-dimethyl-4-vinylanilinium bromide (BAnBr) and *N*-*n*-butyl-*N,N*-dimethyl-(*N'*-acryloyl-3-aminopropyl)ammonium bromide (BAPABr), and performed swelling experiments in aqueous solutions of various inorganic electrolytes.

EXPERIMENTAL

The gels were synthesized by a free-radical polymerization and successive quaternization reaction. The polymerization was carried out according to the following procedure. A reactant mixture containing a monomer, an initiator, a crosslinker and a solvent, at the compositions listed in Table 1, was prepared in a glass tube (i.d. 1 mm). After the removal of residual oxygen from the reactant mixture, the glass tube was sealed off under a nitrogen atmosphere. The temperature of the reactant mixture was raised to 60°C to initiate the polymerization, and was kept constant for the prescribed time. In the polymerization, the gels of 4-vinylpyridine, *N,N*-dimethyl-4-vinylaniline and *N,N*-dimethylaminopropylacrylamide were synthesized. They were taken out of the glass tube and immersed in an excess amount of *N,N*-dimethylformamide (DMF) to remove the residual monomer and the crosslinker. Subsequently, the gels (about 30 mg polymer content in dry base) were quaternized at 60°C for 40 h in a reaction solvent of DMF/methanol (75/25 vol%, 20 ml) containing a quaternization agent, *n*-butyl bromide (5 ml). The quaternization degrees of the gels were measured by ¹H n.m.r. and elemental analyses. The quaternization degrees

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Table 1 Polymerization conditions for the gels

Monomer	Amount of monomer (g)	Initiator, AIBN (g)	Solvent, DMF (ml)	Crosslinker ^a	Amount of crosslinker (g)	Temperature (°C)	Time (h)
4-vinyl pyridine	0.98	0.01	1.0	DVB	0.023	60	1
<i>N,N</i> -dimethyl-4-vinylaniline	0.95	0.01	1.0	DVB	0.020	60	24
<i>N,N</i> -dimethylamino-propylacrylamide	0.90	0.01	1.0	EDA	0.030	60	3

^a DVB, divinylbenzene; EDA, ethylenediacrylate

of the BPyBr and BANBr gels, determined by ¹H n.m.r. from the ratio of intensities between the heterocyclic or aromatic rings and the butyl group, were found to be 100%. The quaternization degree of the BAPABr gel could not be determined by n.m.r. analysis because of the overlap of the peak intensities. In the elemental analyses the quaternization degrees of the BPyBr, BANBr and BAPABr gels were determined from the molar ratio of nitrogen and carbon, and were 91.8, 86.3 and 102.2%, respectively.

To measure the swelling equilibria, the cylindrical gel was immersed in aqueous solutions (50 ml) of various inorganic electrolytes for 3 days at a desired temperature. The diameter of the gel was measured to determine the swelling ratio of the gel defined as $V/V_0 (=d^3/d_0^3)$, where V and d are equilibrium volume and diameter of the gel, and V_0 and d_0 are the volume and diameter of the gel at synthesis, respectively.

RESULTS AND DISCUSSION

Figure 1 shows the swelling ratios of the BPyBr gel in aqueous electrolyte solutions at 30°C. In the solutions that commonly contained Br⁻ ion as an ionic species, the swelling ratios decrease continuously with an increase in the electrolyte concentration and indicate no strong dependence on the cationic species. A similar tendency was observed with the gels of BANBr and BAPABr. However, in aqueous solutions of electrolytes containing different anionic species, a continuous change in the gel volume was observed in the NaCl and NaBr aqueous solutions, and a discontinuous change in the NaI aqueous solutions. The order of effectiveness of the electrolytes that brought about the shrinkage of the gel was given as $I^- > Br^- > Cl^-$. This order coincides with that of the association constants of anionic species for ammonium ion in protonic solvent¹³. Similar results were obtained in our previous swelling experiments with the BBABr gel¹². These results suggest the importance of the ionic association in transition behaviour.

Figure 2 shows the results of the BANBr gel in aqueous electrolyte solutions containing different anionic species at 30°C. The swelling behaviour of the BANBr gel is similar to that of the BPyBr gel in Figure 1, except that the phase transition of the BANBr gel occurs at a higher concentration of NaI. As can be seen in Figure 3, a phase transition is not observed with the BAPABr gel even in the aqueous solution of NaI.

Generally, the volume phase transition of a polyelectrolyte gel depends on the association state of ionic groups and the affinity of the constituent of the gel to solvent. Previously, the authors^{14,15} pointed

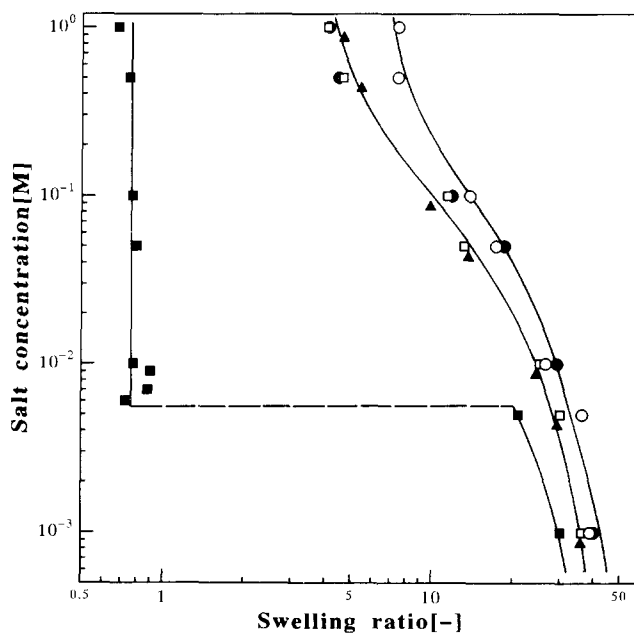


Figure 1 Swelling ratio of the BPyBr gel in the aqueous solutions of various electrolytes: ▲, HBr; ●, NaBr; □, KBr; ○, NaCl; ■, NaI

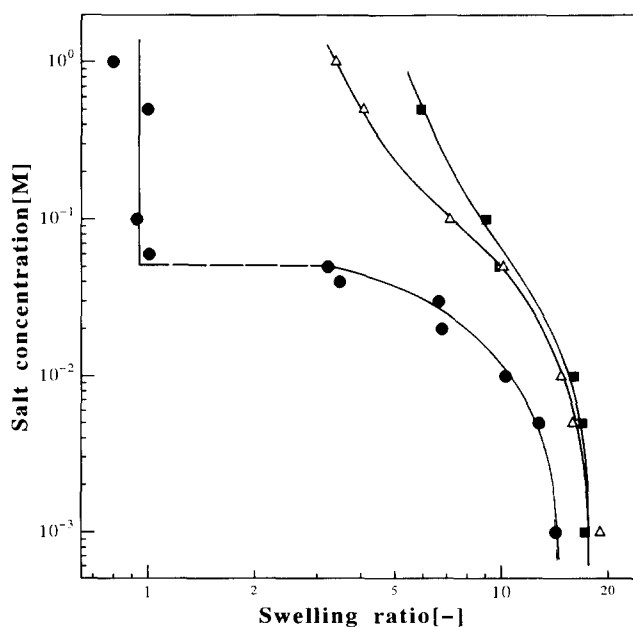


Figure 2 Swelling ratio of the BANBr gel in the aqueous solutions of various electrolytes containing a different anion: ■, NaCl; △, NaBr; ●, NaI

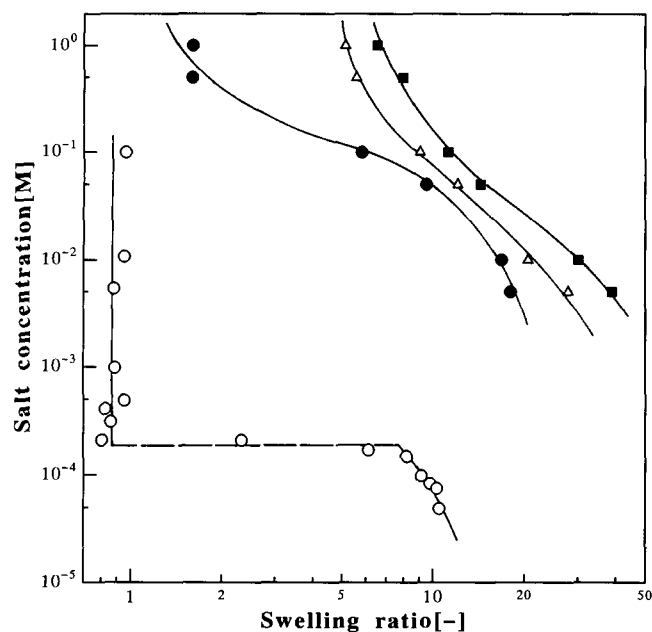


Figure 3 Swelling ratio of the BAPABr gel in the aqueous solutions of various electrolytes containing a different anion: ■, NaCl; △, NaBr; ●, NaI. ○, Swelling ratio of the BBABr gel in NaI aqueous solutions

out the importance of hydrophobic interactions as a controlling factor for the phase transition. Recently, Siegel and Firestone¹⁶ reported experimental results which suggested that the introduction of hydrophobic groups to a polyelectrolyte gel enhances the occurrence of volume phase transitions.

In this report, we present clear evidence for the importance of hydrophobic interactions. The previous result for the BBABr gel in the NaI aqueous solution is compared to the result for BAPABr gel in the same solution, as shown in Figure 3. The gels of BBABr and BAPABr have the same ionic group of $-\text{CH}_2-\text{N}-n\text{-butyl}(\text{CH}_3)_2\text{Br}$. The dissociation ability of this ionic group is considered to be similar for both the gels. However, it should be noted that the molecular structure of the BAPABr gel is less hydrophobic in comparison with the BBABr gel*. As seen from Figure 3, the BBABr gel, which has higher hydrophobicity, reveals a discontinuous change in swelling behaviour, while the BAPABr gel shows a continuous change. If a gel is hydrophilic, a repulsive force acts between the segments of the gel. In contrast, hydrophobic interaction acts as an attractive force between the segments. Qualitatively, the phase transition of the gel can be enhanced by raising attractive forces such as the phenomenon of condensation of molecules.

Two important factors for the phase transition of a polyelectrolyte gel are the hydrophobic interaction and the association of ionic groups. When the temperature of a system is changed, the two factors are expected to act in opposite ways. Namely, an increase in temperature strengthens the hydrophobic interaction, bringing about a reduction in the ionic concentration resulting in collapse of the gel. On the other hand, an increase in temperature lowers the association constant, eventually leading to an increase in the ionic concentration for the collapse.

* The BAPABr gel has a hydrophilic group together with a small hydrophobic group in each monomer, while the BBABr gel has a bulky hydrophobic group

Figure 4 shows experimental results in which the temperature effect on swelling was examined with the BPyBr gel in NaI aqueous solution. The equilibrium curves indicate that the increase in temperature raises the ionic concentration for the collapse. A similar result was obtained with the BAnBr gel. These results suggest that the effect of the ionic association is reflected in the variation of swelling with temperature.

Previously the authors¹² reported the swelling behaviour of *N*-*n*-butyl-*N,N*-dimethyl-4-vinylbenzylammonium iodide (BBAI) gel, which had a molecular structure like that of the BBABr gel but with iodine substituted for bromine, and was in a shrunken state in pure water. On the other hand, the gels of *N*-*n*-butyl-*N,N*-dimethyl-4-vinylpyridinium iodide (BPyI) and *N*-*n*-butyl-*N,N*-dimethyl-4-vinylanilinium iodide (BAnI), which were newly synthesized in the present work, were in a swollen state in water. The synthetic procedure of the BPyI and BAnI gels was the same as that described in the Experimental section, except for the use of a quaternization agent, *n*-butyl iodide. The quaternization degree of the gels was 100%, as determined by ¹H n.m.r. and elemental analyses. Figures 5 and 6 show the swelling equilibria of the gels in aqueous solutions of NaI and NaBr. The gels in NaBr solution show a continuous change while in NaI solution a discontinuous change is observed. This fact reconfirms the strong relation between the phase transition and the association degree of ionizable groups.

Our previous study¹² showed that the phase transition of the BBABr gel in NaI aqueous solution occurred at an I^- ion concentration less than the concentration of the ionic group in the gel. Based on the results shown in Figures 5 and 6, in addition to those in Figures 1 and 2 obtained for the BPyBr and BAnBr gels, we can conclude that the phase transitions of these gels in NaI aqueous solution occur at I^- concentrations higher than the concentration of the ionic group in the gels. This was confirmed by measurements of the I^- concentration with an ion-selective electrode.

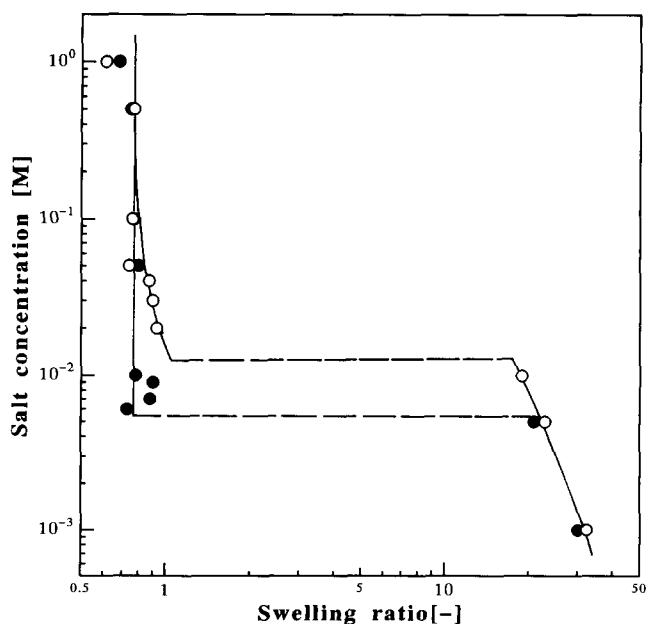


Figure 4 Swelling ratio of the BPyBr gel in NaI aqueous solutions at different temperatures: ●, 30°C; ○, 45°C

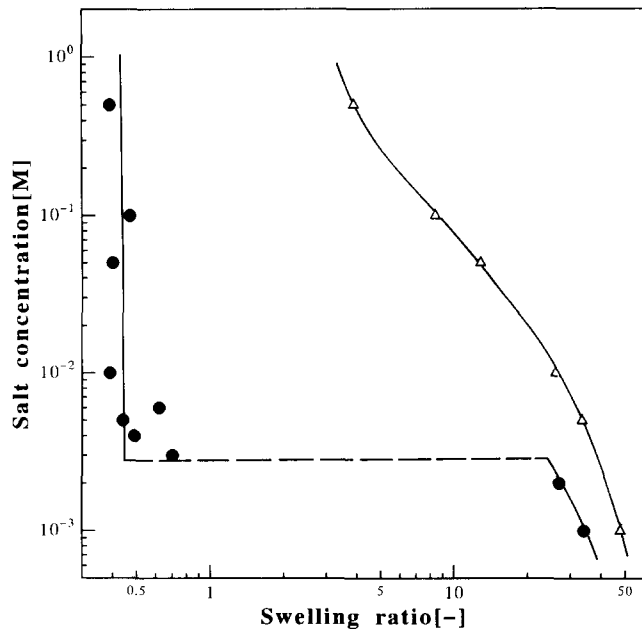


Figure 5 Swelling ratio of the BPyI gel in aqueous solutions of NaBr (Δ) and NaI (\bullet)

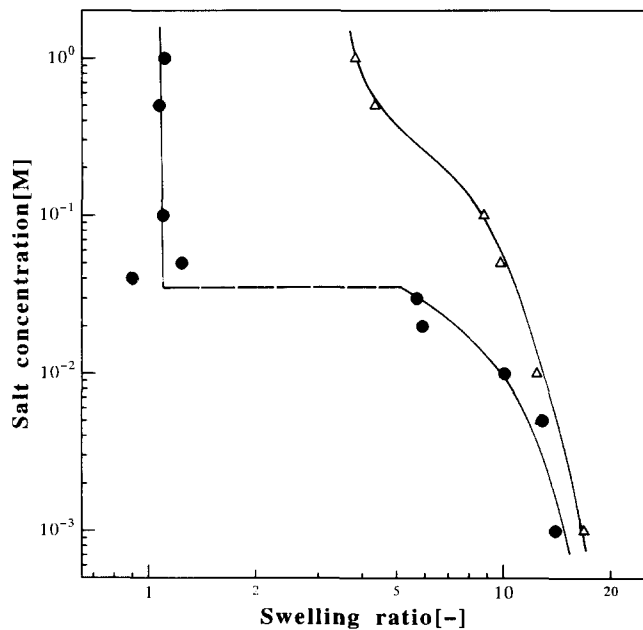


Figure 6 Swelling ratio of the BAnI gel in aqueous solutions of NaBr (Δ) and NaI (\bullet)

CONCLUSION

The swelling ratios of the BPyBr, BAnBr and BAPABr gels do not depend on the cationic species in the aqueous electrolyte solutions examined but depend strongly on the anionic species. The BPyBr and BAnBr gels underwent volume phase transition in NaI aqueous solutions. The NaI concentration at which the phase transition occurs increases with an increase in temperature. This result suggests the importance of the ionic association for the transition. On the other hand, the BAPABr gel did not undergo phase transition in any of the aqueous electrolyte solutions. Comparison of the swelling behaviour of the BAPABr gel with the BBABr gel verifies the importance of hydrophobic interaction, which enhances the occurrence of the transition.

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REFERENCES

- 1 Tanaka, T. *Phys. Rev. Lett.* 1978, **40**, 820
- 2 Ilavsky, M. *Macromolecules* 1982, **15**, 782
- 3 Katayama, S., Hirokawa, Y. and Tanaka, T. *Macromolecules* 1984, **17**, 2641
- 4 Ilavsky, M., Hroutz, J. and Havlicek, I. *Polymer* 1985, **26**, 1514
- 5 Ricka, J. and Tanaka, T. *Macromolecules* 1985, **18**, 83
- 6 Katayama, S. and Ohta, A. *Macromolecules* 1985, **18**, 2781
- 7 Hirokawa, Y., Tanaka, T. and Sato, E. *Macromolecules* 1985, **18**, 2782
- 8 Hirotsu, S., Hirokawa, Y. and Tanaka, T. *J. Chem. Phys.* 1987, **87**, 1392
- 9 Tanaka, T., Fillmore, D. J., Sun, S. T., Swislow, G. and Shah, A. *Phys. Rev. Lett.* 1980, **40**, 1636
- 10 Ohmine, I. and Tanaka, T. *J. Chem. Phys.* 1982, **77**, 5725
- 11 Ricka, J. and Tanaka, T. *Macromolecules* 1984, **17**, 2916
- 12 Kudo, S., Kosaka, N., Konno, M. and Saito, S. *Polymer* 1992, **33**, 5040
- 13 Thomas, J. and Evans, D. F. *J. Phys. Chem.* 1970, **74**, 3812
- 14 Otake, K., Inomata, H., Konno, M. and Saito, S. *J. Chem. Phys.* 1989, **91**, 1345
- 15 Otake, K., Inomata, H., Konno, M. and Saito, S. *Macromolecules* 1990, **23**, 1838
- 16 Siegel, R. A. and Firestone, B. A. *Macromolecules* 1988, **21**, 3254