

Thermoreversible Hydrogels. IX. Swelling Behaviors of Thermosensitive Hydrogels Copolymerized by *N*-Isopropylacrylamide with 1-Vinyl-3-(3-sulfopropyl) Imidazolium Betaine

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ABSTRACT: A series of thermosensitive hydrogels were prepared from the various molar ratios of *N*-isopropylacrylamide, 1-vinyl-3-(3-sulfopropyl) imidazolium betaine (VSIB), and *N,N'*-methylene-bis-acrylamide. The influence of the amount of VSIB in the copolymeric gels on the swelling behaviors in water, in various saline solutions, and at various temperatures was investigated. The results indicated that the higher the VSIB content in the hydrogel system, the higher the swelling ratio and the gel transition temperature. In the saline solution the results showed that when the concentration of salt is higher than the minimum salt concentration (MSC) of poly(VSIB), the deswelling behavior of the copolymeric gel was more effectively suppressed as more VSIB was added to the copolymeric gels. In addition, only the sample containing 12 mol % VSIB (V4) exhibited an antipolyelectrolyte's swelling behavior when the concentration of salt was higher than the MSC of poly(VSIB). This means that the swelling ratio of the hydrogel can be improved with a higher concentration salt solution. In addition, the anion effects were larger than the cation effects in the presence of a common anion (Cl^-) with different cations and a common cation (K^+) with different anions for the hydrogel. Finally, the more VSIB in the hydrogel, the higher the diffusion coefficient in dynamic swelling. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 14–23, 2000

Key words: thermoreversible hydrogel; *N*-isopropylacrylamide; 1-vinyl-3-(3-sulfopropyl) imidazolium betaine; swelling behavior

INTRODUCTION

Hydrogels are crosslinked hydrophilic polymer networks that swell but do not dissolve in water. Hydrogels sometimes undergo a volume change in response to a change in surrounding conditions, such as pH,¹ temperature,^{2,3} ionic strength,⁴ and

electric field.^{5,6} Therefore, they are extensively applied in biochemistry systems.

Poly(*N*-isopropylacrylamide) [poly(NIPAAm)] exhibits a lower critical solution temperature (LCST) at 32°C in aqueous solution; its hydrogel exhibits swelling or deswelling at temperatures below or above the LCST.^{7–9} Poly(NIPAAm) hydrogels have been reported in the field of controlled drug delivery,^{10,11} immobilization of enzymes¹² and cells,¹³ and dewatering of protein solutions.¹⁴ However, only a few of the hydrogels containing a zwitterionic monomer or sulfobetaine's monomer are reported in the literature.^{15–18} For example, Huglin and Rego^{15–17} re-

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ported on copolymeric gels prepared from the copolymerization of 2-hydroxyethyl methacrylate and *N,N*-dimethyl-*N*-methacryloyloxyethyl-*N*-(3-sulfopropyl) ammonium betaine and surveyed their swelling behavior in the presence of potassium thiocyanate (KSCN). In addition, Baker et al.¹⁸ reported on ampholytic hydrogels prepared from the copolymerization of AAm with *N*-(3-sulfopropyl)-*N*-methacrylamido-propyl-*N,N*-dimethylammonium betaine (SB1) (AAm/SB1), *N*-(3-sulfopropyl)-*N*-methacryloyloxyethyl-*N,N*-dimethylammonium betaine (SB2) (AAm/SB2), and [(methacrylamido)propyl] trimethylammonium chloride (MAPTAC) and sodium styrene sulfonate (SSS) (AAm/MAPTAC/SSS). They investigated the swelling behavior of these three xerogels in water and in the various concentrations (10^{-5} – $5M$) of sodium chloride aqueous solution. Their results showed that antipolyelectrolyte behavior was observed for the ampholytic hydrogels. The ampholytic hydrogel reswelled as the concentration of sodium chloride increased to over $0.1M$.

The thermoreversible hydrogels based on NIPAAm and zwitterionic monomer or sulfobetaine's monomer were not found in the literature. A series of sulfobetaine monomers and corresponding cationic monomers were prepared and the aqueous salt behavior of their polymers was investigated in our laboratory.^{19–23} Salamone et al.²⁴ reported on the aqueous salt solution behavior of poly(1-vinyl-3-(3-sulfopropyl) imidazolium betaine) [poly(VSIB)]. In our previous report we investigated the swelling behavior of NIPAAm-*co-N,N'*-dimethyl(acrylamidopropyl) ammonium propane sulfonate (NIPAAm-*co*-DMAAPS) copolymeric hydrogels.²⁵ Hence, a series of crosslinked poly(NIPAAm-*co*-VSIB) were prepared and the swelling behaviors of these xerogellants at various ratios of NIPAAm/VSIB in aqueous salt solutions were investigated.

EXPERIMENTAL

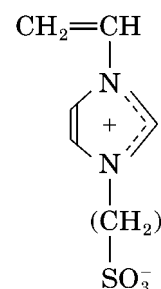
Materials

1-Vinylimidazole (Fluka Chemical Co.) and propane sulfone (TCI Co.) were used as received. The NIPAAm (Fluka Chemical Co.) was recrystallized in *n*-hexane before use to remove an inhibitor. *N,N'*-Methylene-bis-acrylamide (NMBA, Sigma Chemical Co.) as a crosslinker and *N,N,N',N'*-tetramethylethylenediamine (TEMED, Fluka Chemical Co.) as an accelerator were used as received.

The initiator ammonium peroxydisulfate (APS, Wako Pure Chemical Co. Ltd) was further purified by recrystallization.

Synthesis of Monomer

The monomer VSIB was prepared according to the procedure of Salamone et al.²⁴ The yield was 94.3%, and the mp was $190^{\circ}C$.



Preparation of Hydrogels

NIPAAm and VSIB with various ratios and 4 mol % NMBA were dissolved in 10 mL of deionized water. To this solution we added 0.2 wt % of APS and 1 wt % of TEMED as redox initiators, and the mixture was immediately injected into the space between two glass plates. The gel membrane thickness was adjusted with a silicone spacer between the two glass plates. Polymerization was carried out at room temperature for 1 day. After the gelation was completed, the gel membrane was cut into 10-mm diameter disks and immersed in an excess of deionized water for 7 days to remove the residual unreacted monomer. Swollen polymer gels were dried at room temperature for 1 day, and these samples were further dried in a vacuum oven for 2 days at $60^{\circ}C$.

Measurement of Swelling Ratio

The dried gels were immersed in an excess of deionized water or various saline solutions with different concentrations at $25^{\circ}C$ until swelling equilibrium was attained. The weight of the wet sample (W_w) was determined after removing the surface water by blotting it with filter paper. The dry weight (W_d) was determined after drying the gel in a vacuum oven for 2 days. The swelling ratio (Q) based on W_w and W_d was then calculated using the following relationship:

$$Q = \frac{W_w - W_d}{W_d} \quad (1)$$

Table I Characterization of NIPAAm/VSIB Copolymeric Gels

| Sample No. | Feed Composition (mol %) | | Actual Composition (mol %) | | Cloud Point Effect | Gel Transition Temperature | Swelling Ratio (g H ₂ O/g Dry Sample) |
|------------|--------------------------|------|----------------------------|-------|--------------------|----------------------------|--|
| | NIPAAm | VSIB | NIPAAm | VSIB | | | |
| V0 | 100 | 0 | 100 | 0 | st | 30–35 | 14.07 |
| V1 | 97 | 3 | 98.30 | 1.70 | st | 35–40 | 15.59 |
| V2 | 94 | 6 | 94.31 | 5.69 | w | 40–45 | 17.72 |
| V3 | 91 | 9 | 92.35 | 7.65 | w | 50–55 | 18.43 |
| V4 | 88 | 12 | 88.71 | 11.29 | vw | >60 | 20.83 |

st, strong; w, weak; vw, very weak.

Dynamic Swelling

The dried gels were immersed in an excess of deionized water at different temperatures. The swelling ratio was obtained from weighing the initial and swollen samples at various time intervals. The amount of water sorbed, M_t , was reported as a function of time, and the equilibrium sorption at an infinitely long time was designated as M_∞ . Equation (2) can be used to calculate the diffusion coefficient D for $M_t/M_\infty \leq 0.8$.²⁶

$$\frac{M_t}{M_\infty} = \left(\frac{4}{\sqrt{\pi}} \right) \left(\frac{D \times t}{L^2} \right)^{1/2} \quad (2)$$

where t is the time and L is the initial thickness of the dried sample.

RESULTS AND DISCUSSION

Although the swelling behaviors of NIPAAm hydrogels have been widely studied by many researchers,^{7–9} the series of NIPAAm/VSIB copolymeric hydrogels were found to be lacking in the literature. The effect of VSIB on the swelling behavior of the NIPAAm/VSIB copolymeric gels is described here.

Characterization of NIPAAm/VSIB Copolymeric Gels

Some characteristics shown in Table I for the NIPAAm/VSIB copolymeric gels with various feed compositions indicate that the cloud point effect of the copolymeric gels is gradually weakened with increasing VSIB content. The gel transition temperatures are increased with an increase of

the content of VSIB in the copolymeric composition. The equilibrium swelling ratios of the copolymeric gels are also increased with increasing VSIB content (see Fig. 1). The actual compositions obtained by elemental analysis almost approach the feed compositions.

Effect of VSIB Content on Swelling Ratio

The swelling ratios as a function of time for NIPAAm/VSIB copolymeric hydrogels in deionized water shown in Figure 1 indicate that the swelling ratios increase with increasing VSIB

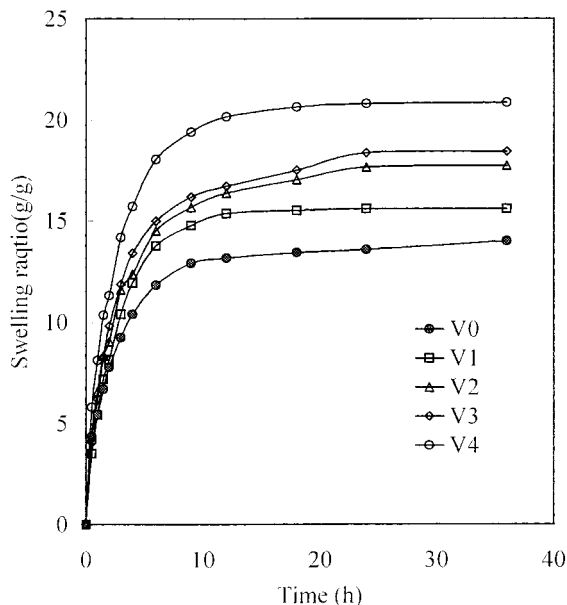


Figure 1 The swelling ratio as a function of time for NIPAAm/VSIB copolymeric hydrogels at 25°C.

content. According to Flory's swelling theory,²⁷ the following equation is given:

$$Q^{5/3} = [(i/2V_\mu S^{1/2})^{1/2} + (1/2 - \chi_1)/v_1]/(v_e/V_0) \quad (3)$$

where i/V_μ is the concentration of the fixed charge referred to as the unswollen network, S is the ionic concentration in the external solution, $(1/2 - \chi_1)/v_1$ is the affinity of the hydrogel with water, and v_e/V_0 is the crosslinked density of the hydrogel. Hence, the swelling ratio is related to the ionic concentration of the solution, the crosslinked density, and the affinity of the hydrogel with water. The total fixed charge was zero and the crosslinked density was fixed in the present copolymeric hydrogels, so the variable affecting the swelling ratio of the hydrogel was only the affinity of the gel for water. Because VSIB is a hydrophilic zwitterionic monomer, the higher the VSIB content the larger the affinity of the gels with water and the higher the swelling ratio of the hydrogel. In addition, the equilibrium absorption time (about 12 h for these copolymeric gels) was not significantly affected by the addition of VSIB in the NIPAAm gel. This swelling behavior is similar to the NIPAAm/DMAAPS systems.²⁵

Effect of Temperature on Swelling Ratio for NIPAAm/VSIB Copolymeric Gels

The effect of temperature on the swelling ratio for the present copolymeric gels is shown in Figure 2. The results in Figure 2 indicate that the higher the temperature, the lower the swelling ratio and the more the VSIB content, the higher the gel transition temperature. For the NIPAAm gel (V0), because of the hydrophilic group (amide) in the polymer, its structure would form an intermolecular hydrogen bond with surrounding water at low temperature (below the gel transition temperature) and then turn into an intramolecular hydrogen bond at higher temperature. This transformation makes the hydrophobicity of the NIPAAm gel increase. This phenomenon makes the swelling ratio of the gel rapidly decrease at the gel transition temperature. However, the results in Figure 2 also indicate that the higher the VSIB content, the higher the swelling ratio for the present copolymeric gels. This is because the VSIB is a hydrophilic monomer. The larger the hydrophilicity of the gel, the stronger the affinity of the hydrogel with water. Therefore, the curves of the swelling ratio versus the temperature be-

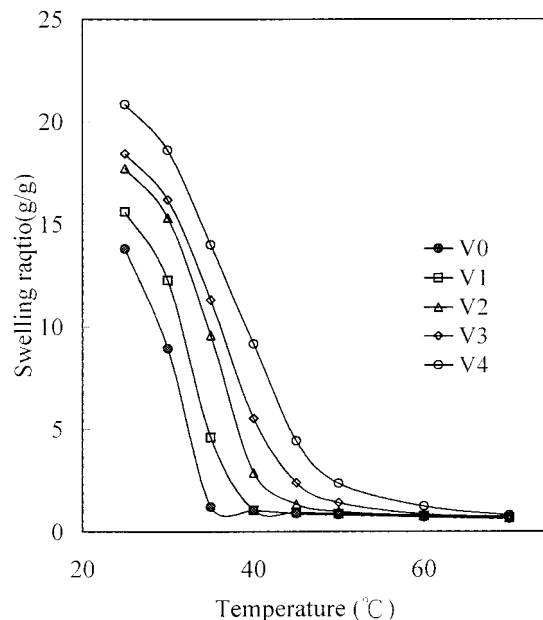


Figure 2 The swelling ratio as a function of temperature for NIPAAm/VSIB copolymeric hydrogels.

come flatter as the VSIB content is increased. This evidence indicates that the gel does not shrink easily as the temperature increases. These results are consistent with our previous studies for *N*-ethoxypropylacrylamide/acrylamide (NIPAAm/DMAAPS)²⁵ and *N*-tetrahydrofurfurylacrylamide/acrylamide (NEPAAm/AAm or NTHFAAm/AAm) hydrogels.²⁸

Investigation of Water Diffusion in Xerogels

The effect of temperature on the swelling ratio for sample V4 shown in Figure 3 indicates that the swelling ratio decreases with an increase in temperature. To elucidate the transport mechanism, the initial swelling data were fitted to the exponential heuristic equation^{29,30}

$$\frac{M_t}{M_\infty} = K t^n \quad (4)$$

where K is a characteristic constant of the gel and n is a characteristic exponent of the mode transport of the penetrant. The n and K were calculated from the slope and intercept of the plot of $\log(M_t/M_\infty)$ against $\log(t)$ at various temperatures. In addition, eq. (2) was used to calculate the diffusion coefficient D from the slope $4\sqrt{D}/\sqrt{\pi}$ of the plot of (M_t/M_∞) against $(t/L^2)^{1/2}$

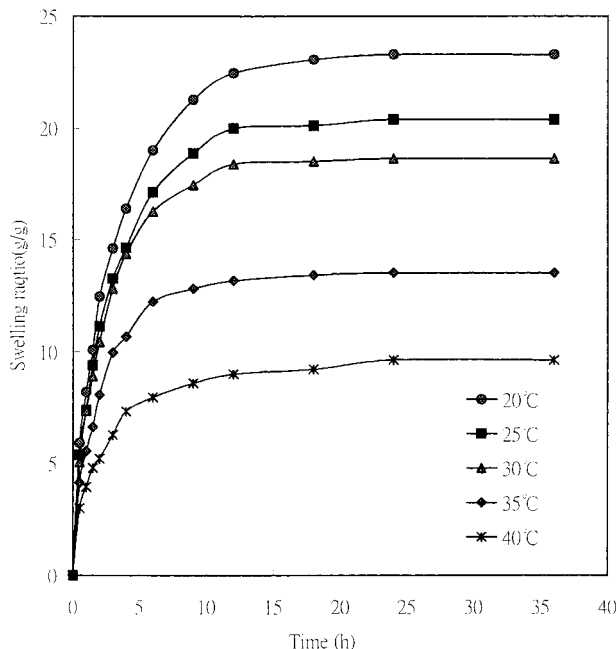


Figure 3 The swelling ratio as a function of time for sample V4 at various temperatures.

at different temperatures. Table II shows the values D , n , and K for the present copolymeric gels at various temperatures. The results indicate that the swelling exponents n for the copolymeric hydrogels at various temperatures are between 0.5 and 1.0. This result indicates that the swelling transport mechanism belongs to non-Fickian transport. The data in Table II also indicate that the swelling exponent increases as the temperature is increased. These results indicate that the swelling transport mechanism of the gels is affected by temperature.

The data shown in Table II also indicate that the D for the NIPAAm/VSIB copolymeric gels increases with an increase in temperature. According to the Arrhenius equation,

$$D = D_0 \cdot \exp(-E_a/RT) \quad (5)$$

The activation energies (E_a) of water that diffused into the glassy polymer for these copolymeric gels are calculated from the plot of the logarithm of D against the reciprocal of temperature. The results indicate that the activation energies for various copolymeric gels are in the order $V0 > V1 > V2 > V3 > V4$. In other words, the higher the VSIB content, the smaller the activation energy of diffusion of water into the xerogel (i.e., the water is easily diffused into the hydrogel). This result leads to a

higher water uptake rate and a shorter equilibrium swelling time. On the other hand, the E_a values for the present hydrogels are higher than those for the NIPAAm/DMAAPS copolymeric gels.²⁵ This result implies that the hydrophilicity of DMAAPS is larger than VSIB.

Effect of Salt Solution on Swelling Ratio

Influence on Swelling Ratio of Different Monovalent Cations with Common Anion (Cl⁻)

Figure 4 shows the swelling ratios of the present copolymeric gels (V0, V1, V2, V3, and V4) in salt solutions of LiCl, NaCl, and KCl. The results in Figure 4(a) indicate that the swelling ratios for the present copolymeric hydrogels keep almost constant values until the salt concentration of $1.56 \times 10^{-2}M$ and then rapidly decrease when the concentration of salt is higher than $0.1M$. This result indicates that the higher concentration of the salt solution is a “poor solvent” for the present hydrogel. This phenomenon is also called the salt screen effect. This behavior and explanation were described in our previous report.²⁵

The results shown in Figure 4(b) indicate that the rapidly decreased swelling ratio is suppressed by the addition of VSIB monomer into NIPAAm gels at the salt concentration range from 1.56×10^{-2} to $1.0M$. This phenomenon can be accounted for by the nature of poly(VSIB). Salamone et al.³¹ reported that the poly(VSIB) was insoluble in deionized water, because the collective positive charges on the polyampholyte attracted the collective negative charges to form an inner ionically crosslinked network. When the concentration of salt was higher than the minimum salt concentration (MSC) of the poly(VSIB), the poly(VSIB) could be dissolved in the aqueous solution. For this reason, when the salt concentration is increased, a part of the positive and negative charges of the salt would site bind on the sulfonate group (SO_3^-) and quaternary ammonium group (R_4N^+) on the VSIB. The charges will be neutralized by the counterion in the aqueous solution. This occurrence will reduce the degree of ionically crosslinked networks of VSIB and remove the entanglement of molecular chains and expand the molecular chains. According to the aforesaid reason, the MSC of poly(VSIB) in LiCl aqueous solution is $0.50M$. Hence, when the salt concentration is less than $0.50M$, the inner ionic ring of VSIB cannot be ruptured and the net charge of the discussed copolymeric gel is still

Table II Initial Diffusion Coefficient (D), Characteristic Exponent (n), Characteristic Constant (K), and Activation Energy (E_a) of Water Penetrated Through NIPAAm/VSIB Copolymeric Gels at Various Temperatures

| Sample No. | T (°C) | n | K | $D \times 10^7$ (cm ² /s) | Equilibrium Swelling Time (h) | E_a (kJ/mol) |
|------------|----------|------|------|--------------------------------------|-------------------------------|----------------|
| V0 | 20 | 0.52 | 0.24 | 0.59 | 24 | 34.79 |
| | 25 | 0.53 | 0.32 | 0.61 | 18 | |
| | 30 | 0.58 | 0.34 | 1.18 | 18 | |
| | 35 | 0.59 | 0.41 | 1.27 | 4 | |
| | 40 | 0.60 | 0.41 | 1.27 | 3 | |
| V1 | 20 | 0.53 | 0.29 | 0.59 | 24 | 32.02 |
| | 25 | 0.54 | 0.33 | 0.74 | 18 | |
| | 30 | 0.57 | 0.36 | 0.92 | 12 | |
| | 35 | 0.59 | 0.39 | 1.09 | 12 | |
| | 40 | 0.62 | 0.41 | 1.21 | 4 | |
| V2 | 20 | 0.54 | 0.34 | 0.61 | 24 | 27.32 |
| | 25 | 0.56 | 0.39 | 0.79 | 18 | |
| | 30 | 0.59 | 0.40 | 0.94 | 12 | |
| | 35 | 0.62 | 0.40 | 1.04 | 9 | |
| | 40 | 0.63 | 0.41 | 1.19 | 9 | |
| V3 | 20 | 0.56 | 0.35 | 0.63 | 24 | 23.47 |
| | 25 | 0.58 | 0.40 | 0.82 | 18 | |
| | 30 | 0.61 | 0.41 | 0.98 | 12 | |
| | 35 | 0.63 | 0.42 | 1.06 | 12 | |
| | 40 | 0.65 | 0.44 | 1.24 | 9 | |
| V4 | 20 | 0.59 | 0.36 | 0.67 | 24 | 23.26 |
| | 25 | 0.61 | 0.42 | 0.91 | 18 | |
| | 30 | 0.63 | 0.43 | 1.01 | 12 | |
| | 35 | 0.66 | 0.44 | 1.09 | 12 | |
| | 40 | 0.67 | 0.47 | 1.26 | 9 | |

zero. Therefore, the swelling ratios for the present gels do not change very much when the salt concentration, $\text{LiCl}_{(\text{aq})}$, is changed. On the other hand, the inner ring of VSIB would be opened because the salt concentration is higher than $0.50M$, and the molecular side chain of VSIB will be expanded and the polymer–solvent interaction parameter χ_1 reduced. This behavior implies that the tendency for a rapidly decreased swelling ratio in concentrated salt solution would be effectively suppressed as the VSIB was introduced. Figure 4(b) shows the swelling ratios of samples V4 and V0 as a function of the salt concentrations for LiCl, NaCl, and KCl solutions. The results indicate that the effect of different cations with a common anion (Cl^-) on the swelling ratio for samples V4 and V0 is evidently not observed.

Influence on Swelling Ratio of Different Divalent Cations with Common Anion (Cl^-)

Figure 5(a) shows the swelling behavior for five NIPAAm/VSIB xerogels in CaCl_2 solutions. The

swelling ratios for these copolymeric gels have tendencies similar to these gels in LiCl, NaCl, and KCl solutions. When the salt concentration is higher than the MSC of poly(VSIB), the rapidly decreased swelling ratio for these gels at the higher salt concentration will be more effectively suppressed as more VSIB is added to the copolymeric gels.

Figure 5(b) shows the swelling ratio of samples V4 and V0 as a function of the salt concentration for MgCl_2 , CaCl_2 , and BaCl_2 solutions. The results show that the influence of different divalent cations with a common anion (Cl^-) on the swelling ratio of samples V4 and V0 is relatively small, but there is a significant difference for samples V0 and V4 at a high concentration. We found that the swelling ratio for samples V0 and V4 is higher in MgCl_2 solution than that in CaCl_2 and BaCl_2 solutions when the concentration of salt is higher than $0.1M$. This result is due to their hydration radius of cations. The hydration radius grows as a result of the smaller cation surrounded with a

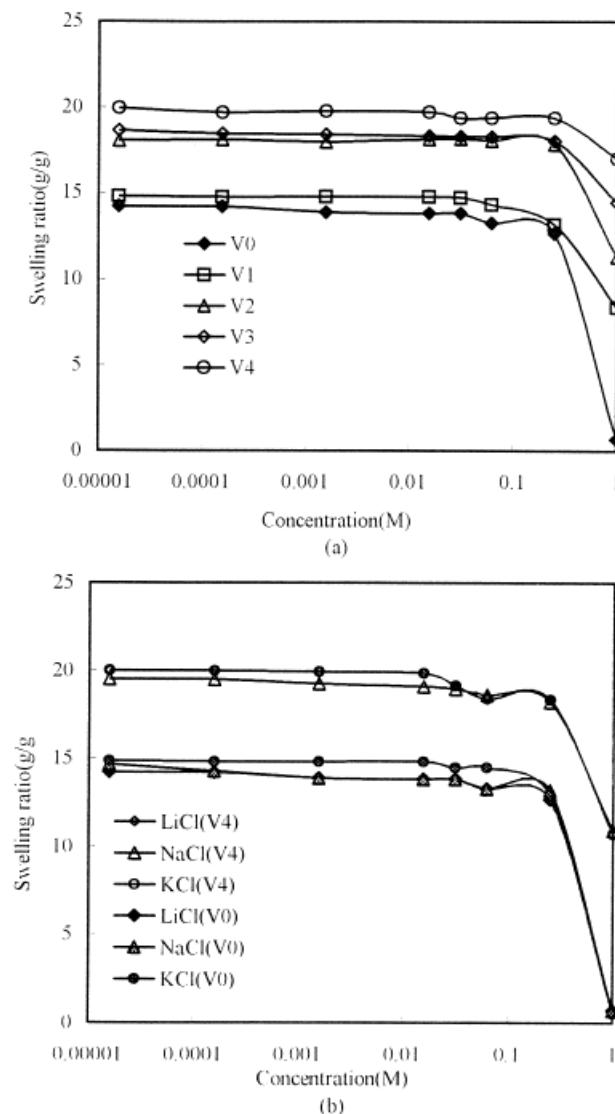


Figure 4 The swelling ratio as a function of the aqueous salt solution for NIPAAm/VSIB copolymeric hydrogels at 25°C: (a) $\text{LiCl}_{(\text{aq})}$ and (b) V0 and V4.

large amount of water. Therefore, the swelling ratio for samples V0 and V4 is higher in MgCl_2 solution than that in CaCl_2 and BaCl_2 solutions.

Influence on Swelling Ratio of Different Halide Ions with Common Cation (K^+)

The influence of different halide ions with a common cation (K^+) on the swelling ratio for the present copolymeric hydrogels was investigated. The results are shown in Figure 6. The swelling ratios of these hydrogels in the KF solutions exhibit a decrease with the increase in the salt concentration [Fig. 6(a)]. This is because poly-

(VSIB) is insoluble in KF solution²¹; KF is a poor solvent for poly(NIPAAm-co-VSIB) hydrogels and makes the polymer-solvent interaction parameter χ_1 increase. Therefore, the swelling ratios of hydrogels decrease with an increase of the salt concentration. This phenomenon is not observed in Figure 6(b,c).

Figure 6(b,c) shows the swelling ratios of the present hydrogels in salt solutions of KBr and KI , respectively. Salamone et al.³¹ reported that the MSCs of poly(VSIB) in KBr and KI aqueous solutions are 0.13 and 0.05 M, respectively. For the above-mentioned reason, the swelling ratios for these copolymeric gels have the same tendency: when the salt concentration is higher than the MSC of poly(VSIB), the higher the VSIB content

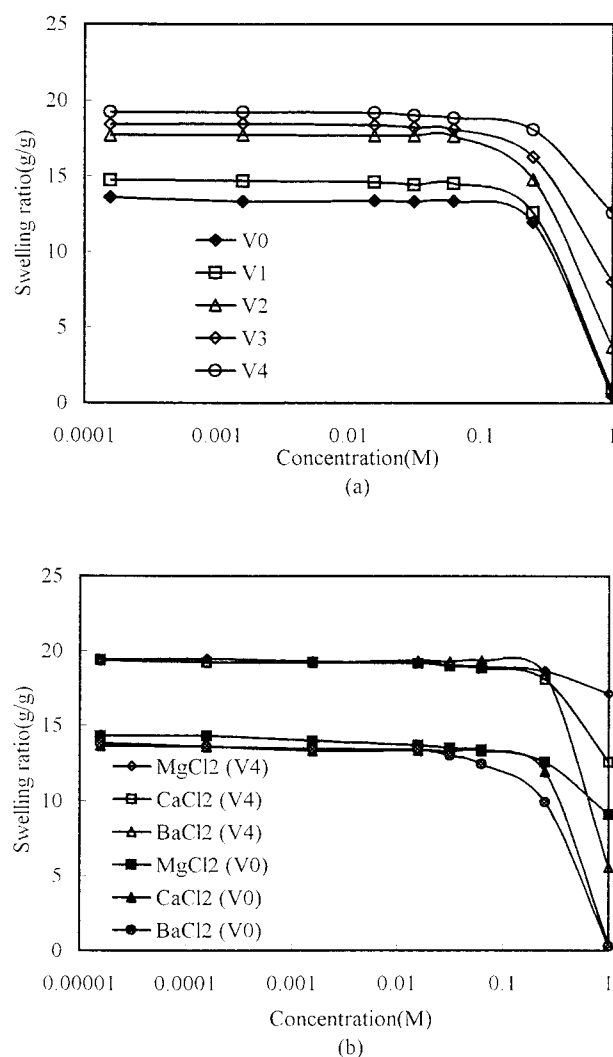


Figure 5 The swelling ratio as a function of the aqueous salt solution for NIPAAm/VSIB copolymeric hydrogels at 25°C: (a) $\text{CaCl}_{2(\text{aq})}$ and (b) V0 and V4.

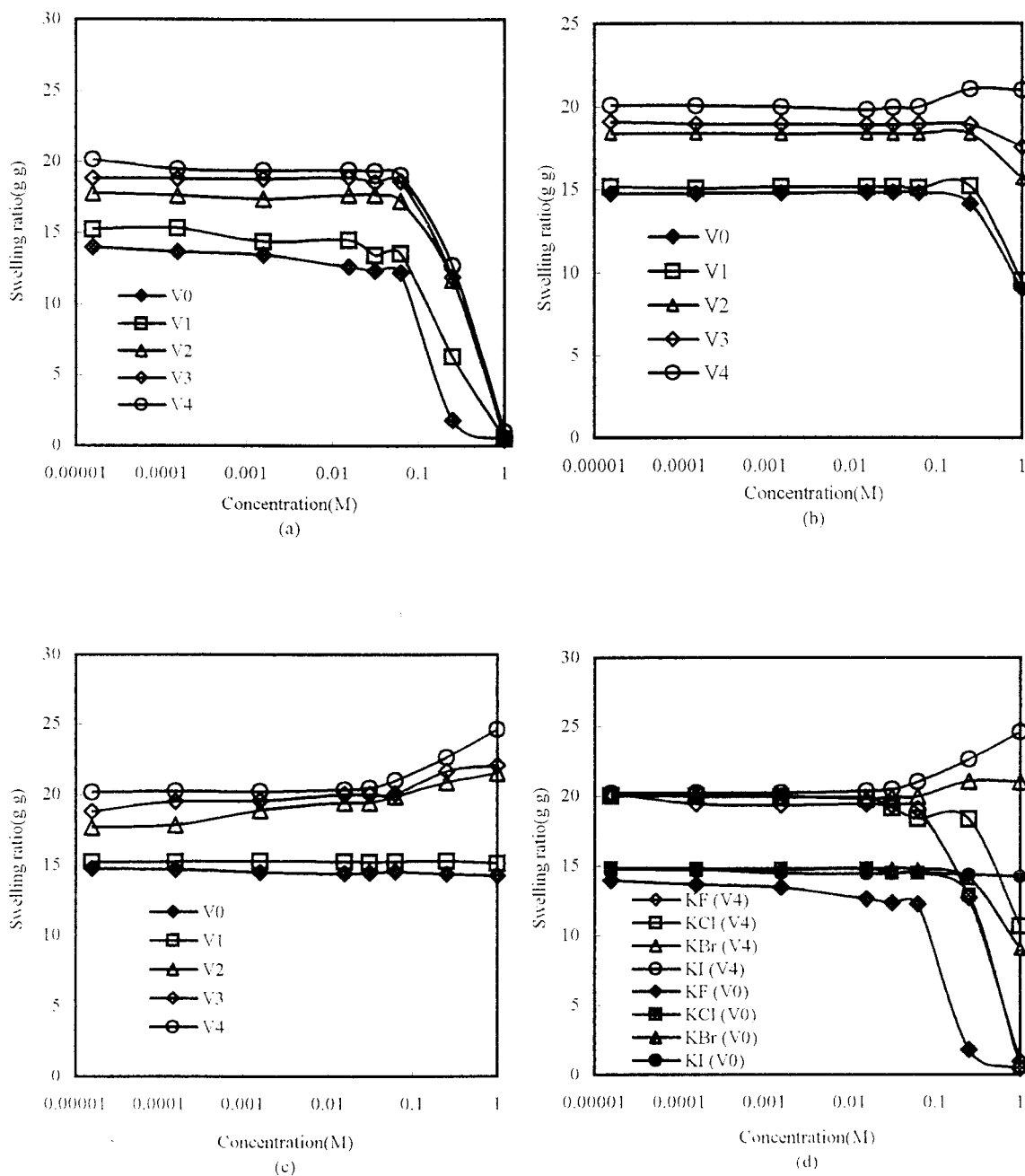


Figure 6 The swelling ratio as a function of the aqueous salt solution for NIPAAm/VSIB copolymeric hydrogels at 25°C: (a) KF_(aq), (b) KBr_(aq), (c) KI_(aq), and (d) V0 and V4.

in the copolymeric gels, the more the effectiveness in suppressing the rapidly decreased swelling ratio for these gels at the higher salt concentration. But the swelling ratios for these copolymeric gels only have a small change at the salt concentration below the MSC. In addition, hydrogel V4 also shows an antipolyelectrolyte's swelling behavior during the salt concentration range from 6.25×10^{-2} to $1.0M$. This phenomenon was also ob-

served by Baker et al.¹⁸ This antipolyelectrolyte behavior is more significant for the respective gels in the KI solution [Fig. 6(c)].

Figure 6(d) shows the swelling ratios of samples V4 and V0 in salt solutions of KF, KCl, KBr, and KI. The results indicate that there is a large difference in the swelling ratio curves for these four salt solutions. For the potassium salts Figure 6(d) indicates an increase in the swelling ratio of

hydrogels in the order $F^- < Cl^- < Br^- < I^-$ for KF, KCl, KBr, and KI, respectively. An anion with a small charge/radius ratio was easily bound on the quaternary ammonium group (R_4N^+) of VSIB. This is because the ion with the smaller charge density can be easily polarized during the ionization of salt near to and bound on the quaternary ammonium group (R_4N^+) of VSIB. Therefore, the larger anion can easily infiltrate into the ionically crosslinked network and expand the molecular chain. Hence, as the anion size of the external salt solution is increased, the antipolyelectrolyte's swelling behavior of hydrogels is more obvious.

From the above results we found the anion effect is larger than the cation effect in the presence of a common anion (Cl^-) with different cations [Figs. 4(b), 5(b)] and a common cation (K^+) with different anions [Fig. 6(d)] for the hydrogels. These results are similar to our previous report on the NIPAAm/DMAAPS gel system²⁵ and consistent with the Pearson principle.³⁰

Influence on Swelling Ratio of Different Acidic Ions with Common Cation (Na^+)

The influence of different acidic ions (ClO_4^- , NO_3^- , NO_2^- , and CH_3COO^-) with a common cation (Na^+) on the swelling ratio for the present hydrogels was investigated. The results shown are similar to the swelling behavior of the hydrogels in monovalent and divalent chloride salt solutions.

Figure 7 shows the swelling ratio of samples V4 and V0 in the $NaClO_4$, $NaNO_3$, $NaNO_2$, and CH_3COONa solutions. The results indicate that the swelling behaviors of the hydrogels are similar to Figure 6(d). The tendency can be observed from the different acidic groups in Figure 7 and is in the order $CH_3COO^- < NO_2^- < NO_3^- \approx ClO_4^-$ for CH_3COONa , $NaNO_2$, $NaNO_3$, and $NaClO_4$. The acetate ion (CH_3COO^-) is a weak acid group and easily associates to form acetic acid in aqueous solution, so the ionic intensity is very small. Therefore, the swelling ratio of the hydrogels is the lowest among other anions. This tendency is consistent with the previous NIPAAm/DMAAPS gel systems.²⁵

Figure 8 shows the swelling ratios of V4 and V0 hydrogels in salt solutions of Na_2SO_4 , Na_2SO_3 , and $Na_2S_2O_3$. The results indicate that the swelling ratio decreases with an increase of the salt concentration (even in a higher concentration of salt). This result is different from the gel in other salt solutions mentioned above. This is because

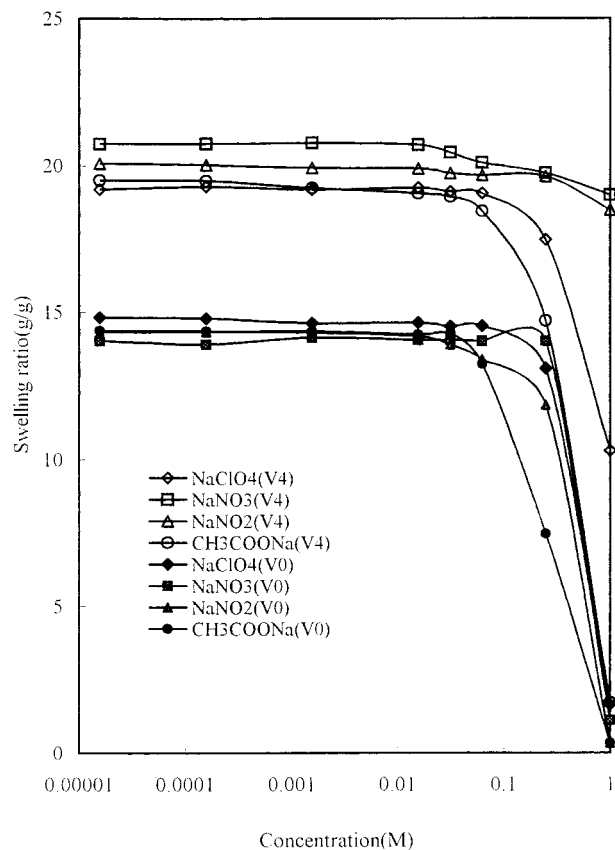


Figure 7 The swelling ratio as a function of $NaClO_{4(aq)}$, $NaNO_{3(aq)}$, $NaNO_{2(aq)}$, and $CH_3COONa_{(aq)}$ for V0 and V4 copolymeric hydrogels at 25°C.

divalent acid groups with a larger charge density and the neighboring quaternary ammonium group (R_4N^+) on the side chain of VSIB were easily attracted in the aqueous solution at the same time. This attraction would result in coagulation of the side chains. This occurrence would reduce the hydrogel network expansion that resulted from destroying the ionically crosslinked network.²² The results show that the influence of different divalent acidic ions with a common cation (Na^+) on the swelling ratio of samples V4 and V0 is not significant.

CONCLUSIONS

The swelling ratios of NIPAAm/VSIB copolymeric gels increase and the equilibrium absorption time of hydrogels becomes faster with an increase of VSIB content in the hydrogels. The higher the VSIB content, the larger the affinity with water.

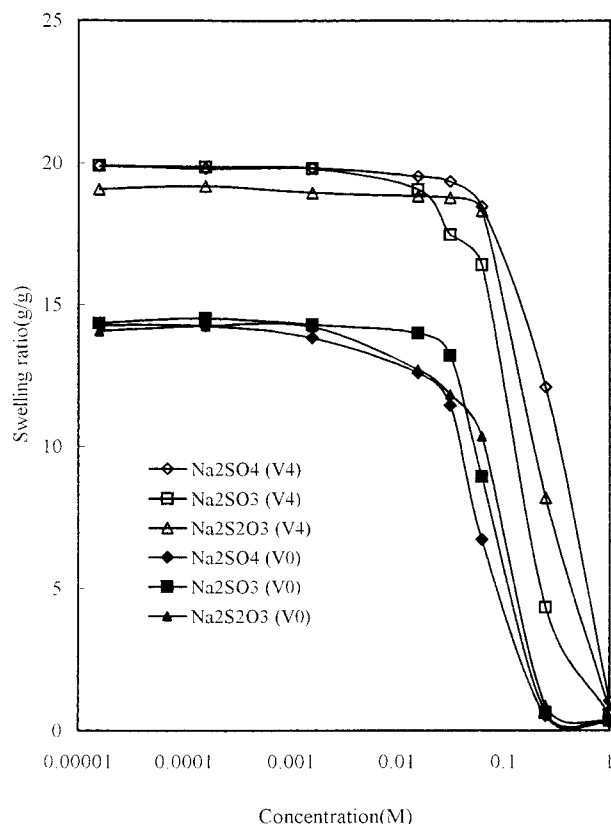


Figure 8 The swelling ratio as a function of $\text{Na}_2\text{SO}_{4(\text{aq})}$, $\text{Na}_2\text{SO}_{3(\text{aq})}$, and $\text{Na}_2\text{S}_2\text{O}_{3(\text{aq})}$ for V0 and V4 copolymeric hydrogels at 25°C.

The gel transition temperatures increase as the VSIB content is increased.

In dynamic swelling the results indicate that the values of the swelling exponent n for all NIPAAm/VSIB copolymeric gels at various temperatures are in the range of 0.52–0.67. This implies that the swelling transport mechanism belongs to non-Fickian transport. The activation energy has the following tendency: $V0 > V1 > V2 > V3 > V4$. This indicates that the water is easily diffused into the hydrogels containing more VSIB.

The effect of salt solution on the swelling ratio for these series gels shows a special behavior. The swelling ratios for these hydrogels can be effectively increased when the salt concentration is higher than the MSC of poly(VSIB). We found that the swelling ratio of the hydrogel in a higher concentration of salt solution can be improved when the zwitterionic monomer is appropriately introduced. The anion effect is larger than the cation effect in the presence of a common anion (Cl^-) with different cations and a common cation (K^+) with different anions for the hydrogels.

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