

Synthesis and Characterization of pH- and Salt-Responsive Hydrogels Based on Etherificated Sodium Alginate

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ABSTRACT: Hydrogels composed of etherificated sodium alginate (ESA), sodium acrylic acid (NaAA), and poly (vinyl alcohol) (PVA) were synthesized by aqueous solution polymerization. The effects of reaction variables such as terminal pH, ions, and ionic strength on hydrogel swelling ratio (SR) were determined and compared. SR was influenced strongly by pH and ionic strength. SR increased with increasing pH but tended to decrease with PVA content. At a given ionic strength, SR of ESA/NaAA/PVA hydrogel was dependent on the valence of

anion; SR was higher in multivalent anion salt solution than in monovalent anion salt solution, i.e., $SR_{K_2SO_4} > SR_{KCl}$ and $SR_{Na_2SO_4} > SR_{NaCl}$. The swelling kinetic of the hydrogels showed Fickian kinetic diffusion in acidic media and non-Fickian behavior in alkaline media. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3161–3167, 2010

Key words: etherificated sodium alginate; super water absorbent resin; pH-sensitive; salt-sensitive; swelling behavior

INTRODUCTION

Hydrogels are three-dimensional hydrophilic polymer networks capable of imbibing large amount of water or biological fluids. It is of great interest to use hydrogels as food additives, water super-absorbents, chemical traps, drug carriers, artificial organs, or as agents to immobilize enzymes.^{1–4} Hydrogels resemble natural living tissues due to their high water absorbing capacity and soft texture, which are important in tissue engineering. In addition, swelling in response to external environmental stimuli is an important character of hydrogels. These stimuli-sensitive hydrogels exhibit changes in their swelling behavior by adjusting network structure, permeability or mechanical strength in response to changes in the environment pH, ionic strength, temperature, electromagnetic radiation, etc.^{5–9} Hydrogels from various synthetic polymers have been widely investigated. At present, biodegradable materials are of important focus of research in this field because of the increased awareness and concern of environmental protection issues.¹⁰

Sodium alginate (SA) is a water soluble linear polysaccharide and is composed of alternating blocks of 1-4 linked -L-guluronic (G-block) and -D-mannuronic (M-block) acid residues. It has the

following physicochemical properties^{11–16}: (1) relatively inert environment within the matrix, (2) mild room temperature encapsulation porosity, which allows for high diffusion rate of macromolecules, dissolution and biodegradation of the system under normal physiological conditions, (3) strong revegetating and biodegrading ability, and (4) capacity to form ionic gel which has the ability to respond rapidly to changes in pH and salt content of the surrounding media. However, SA hydrogels suffer from low water absorbency and poor mechanical properties. In this work, poly (vinyl alcohol) (PVA) and sodium acrylic acid (NaAA) were used because PVA has better mechanical tenacity¹⁷ and NaAA is a widely accepted monomer used for the synthesis of crosslinked absorbing polymers.

Our objectives were to (1) chemically modify SA by etherification in order to meliorate its compatible performance and chemical stability, (2) prepare NaAA/Etherificated SA/PVA hydrogels using cross-linking agents, (3) determine pH-and salt responsiveness of the hydrogels in various pH buffer solutions and salt solutions of different ionic strength, and (4) study the gel-solvent interaction mechanism.

EXPERIMENTAL

Materials

Acrylic acid (AA), PVA (17-99), SA (M/G = 1.62) were purchased from commercial sources. Analytical

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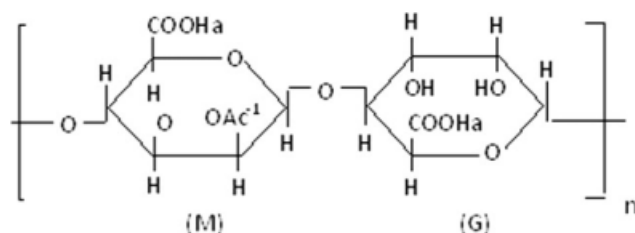


Figure 1 Molecular structures of ESA.

grade reagents sodium monochloroacetate ($\text{ClCH}_2\text{COONa}$) ammonium persulfate [$(\text{NH}_4)_2\text{S}_2\text{O}_8$], sodium bisulfite (NaHSO_3), sodium hydroxide (NaOH), sodium chloride (NaCl), potassium chloride (KCl), calcium chloride (CaCl_2), potassium sulfate (K_2SO_4), sodium sulfate (Na_2SO_4), boric acid (H_3BO_3), citric acid ($\text{C}_6\text{H}_8\text{O}_7$), and sodium phosphate (Na_3PO_4) were also purchased. Two kinds of buffers were prepared at room temperature: buffer 1 was made by dissolving 12.37 g boric acid and 10.51 g citric acid in deionized water to make 1000 mL; buffer 2 was prepared by dissolving 38.01 g sodium phosphate in deionized water to make 1000 mL. Buffers of different pHs (2 to 11) were made by mixing buffers 1 and 2 in different ratios.

Preparation of etherificated sodium alginate

To make etherificated sodium alginate (ESA), 20 g of SA and 1 g of NaOH were dissolved in 100 mL of 1 : 1(v/v) isopropyl alcohol-water mixture at room temperature. To this solution 25 mL of sodium monochloroacetate was added and stored at room temperature for 1 h followed by heating at 80°C for 1 to 3 h in a water bath. ESA with different degrees of substitution (DS), depending on the heating time, was obtained and purified by adding excess ethanol and dried at room temperature.¹⁸ Molecular structure of ESA is depicted in Fig. 1.

Synthesis of ESA/NaAA/PVA hydrogel

The pH of AA was adjusted to 6.0 to 6.5 with NaOH to obtain poly (NaAA). NaAA was vortexed and purged with nitrogen for 30 min. ESA (DS = 0.32, 7 wt %) and PVA (16 wt %) were dissolved separately in distilled water under stirring at 25°C and 80°C , respectively. For hydrogel formation, the above solutions were mixed into NaAA solution, $(\text{NH}_4)_2\text{S}_2\text{O}_8 - \text{NaHSO}_3$ (0.1%, 1 : 1, w/w), an initiator, and *N, N'*-methylenebisacrylamide (0.2%, w/w), a crosslinking agent. Three groups of samples, denoted as A_1 , A_2 , A_3 were prepared by using following ESA : NaAA : PVA ratios (wt %): 20 : 75 : 5, 20 : 70 : 10, and 20 : 65 : 15, respectively. The mixture was stirred for

about 20 min and allowed to cure overnight at room temperature. The cured gels were immersed in deionized water until they reached swelling equilibrium. The gels were further purified by several washings with deionized water to remove excess unreacted monomer, $(\text{NH}_4)_2\text{S}_2\text{O}_8 - \text{NaHSO}_3$ and *N, N'*-methylenebisacrylamide. The beads were dried in an oven at 50°C for 16 h. After complete drying the gels were ground to particle size less than 1.0 mm. Poly (NaAA) Hydrogel was also prepared in the same manner and used as controls.

FTIR analysis

The dry poly (NaAA) and ESA/NaAA/PVA were analyzed using a Avatar 300 FTIR spectrophotometer (Thermo Scientific, Waltham, MA). First, products were dried overnight under vacuum until constant weight. The dried samples were ground into fine powder and mixed with dry KBr powder. The mixed samples were compressed into disks. The scanning wave numbers ranged from 4000 cm^{-1} to 550 cm^{-1} .

Determining hydrogel swelling

The swelling behavior of the hydrogels prepared was determined in distilled water, buffer solutions, and salt solutions. Buffer solutions of pH 2 to 11 (at constant ionic strength of 0.15 mol L^{-1}) were used to study the pH-responsiveness of the hydrogels. NaCl , KCl , Na_2SO_4 , K_2SO_4 , MgCl_2 , and CaCl_2 solutions of different ionic strengths between 0.01 and 1.0 mol L^{-1} were used to determine ionic strength responsiveness of the hydrogels. The measurements were conducted at 25°C by tea-bag method. The tea bags, made of 300-mesh nylon net, were 40 cm in diameter. The dry hydrogel (0.5 g) and nylon bag were weighed and recorded as W_0 and W_n , respectively. The hydrogel samples were placed in the tea bags and fully submerged in the immersing solutions. After immersing for 24 h, the tea bags were removed and their surfaces were carefully wiped off with a soft tissue paper to remove the excess surface water.

The total mass of the tea bag together with the swollen hydrogel was measured and recorded as W_t . The swelling ratio (SR) of the hydrogel was calculated as follows:

$$\text{SR (g/g)} = (W_t - W_0 - W_n)/W_0 \quad (1)$$

Kinetic experiments

In order to further investigate the diffusion mechanism of ESA/NaAA/PVA hydrogel, buffer solutions

of pH 3 and pH 10 were selected. The mass of hydrogels was recorded during the course of swelling at one hour interval until equilibrium. The kinetic of gels diffusion was analyzed using the following semi-empirical equation.^{19,20}

$$M_t/M_\infty = K t^n \quad (2)$$

where, M_t is the mass of water absorbed at time t , M_∞ is the value of M_t when $t \rightarrow \infty$, K is a characteristic constant of the gel microsphere, and n is a characteristic exponent related to the mode of transport of the penetrant.

RESULTS AND DISCUSSION

FTIR analysis

Figure 2 shows the infrared spectra of the hydrogels of poly(NaAA) and ESA/NaAA/PVA. The carbonyl group of carboxylic acid group on the poly(NaAA) chain exhibits a peak at approximate 1750 cm^{-1} from the literature.²¹ When the carbonyl group forms intermolecular bond, there is a negative shift in the FTIR spectrum. We observed a peak at 1629 cm^{-1} for the carbonyl group for the poly(NaAA)

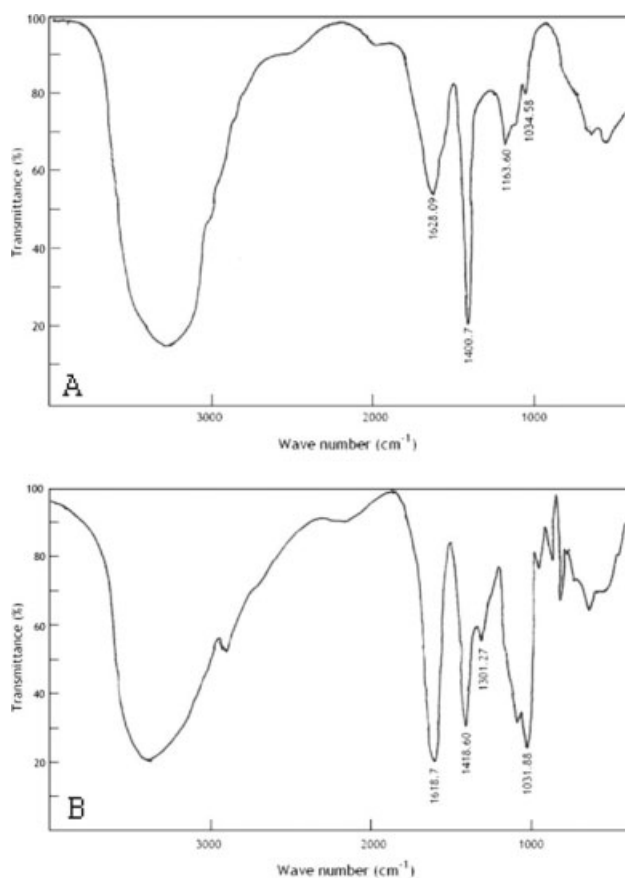


Figure 2 FTIR spectroscopy of A) poly(NaAA) and B) ESA/NaAA/PVA.

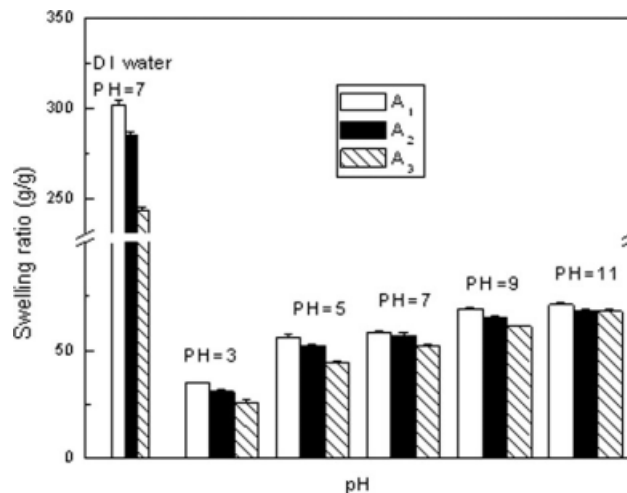


Figure 3 Swelling ratio of ESA/NaAA/PVA hydrogels in DI water and in buffer with ionic strength adjusted to 0.15 mol L^{-1} . ESA/NaAA/PVA composition (wt %) of different hydrogels: A₁, 20/75/5; A₂, 20/70/10; A₃, 20/65/15.

hydrogel but at 1616 cm^{-1} for the ESA/NaAA/PVA hydrogel. The absorption of the carboxylate—OH stretching band appears over a wide range of $3500\text{--}2500 \text{ cm}^{-1}$. The stretching vibration of C—O on ESA shifts from 1163 cm^{-1} to 1301 cm^{-1} . These shifts signify that intermolecular hydrogen bond occurred during the formation of ESA/NaAA/PVA hydrogel.

pH-dependence of swelling ratio in water

The SR of the hydrogels, evaluated in distilled water and in various of pH solutions showed a significant pH-dependence (Fig. 3). It was evident that the SR increased with the increasing medium pH. ESA/NaAA/PVA is a kind of polyelectrolyte and there are many carboxylic groups in its molecular chain. The degree of protonation of carboxylic groups is closely related to the swelling medium pH, which gives the hydrogel its pH-responsiveness. When the medium pH increases, most of the carboxylic groups are negatively charged and the negatively charged ionic backbone of the ESA and poly (NaAA) are more expanded and therefore, at later stages, this expanded form makes for easy diffusion of water molecules into the hydrogel network. On the contrary, at low pH, the hydroxyl groups are mostly in the protonated form, and show less polar character and therefore, result in a polymer with lower affinity to water. Thus, hydrogels are less expanded at pH 3.0. PVA concentration also influenced the swelling capacity of the hydrogel. It is also evident in Figure 3 that SR trended downward with the increase the PVA content in the medium at different surrounding pHs. The situation can be attributed to osmotic pressure change in the hydrogel network due to the

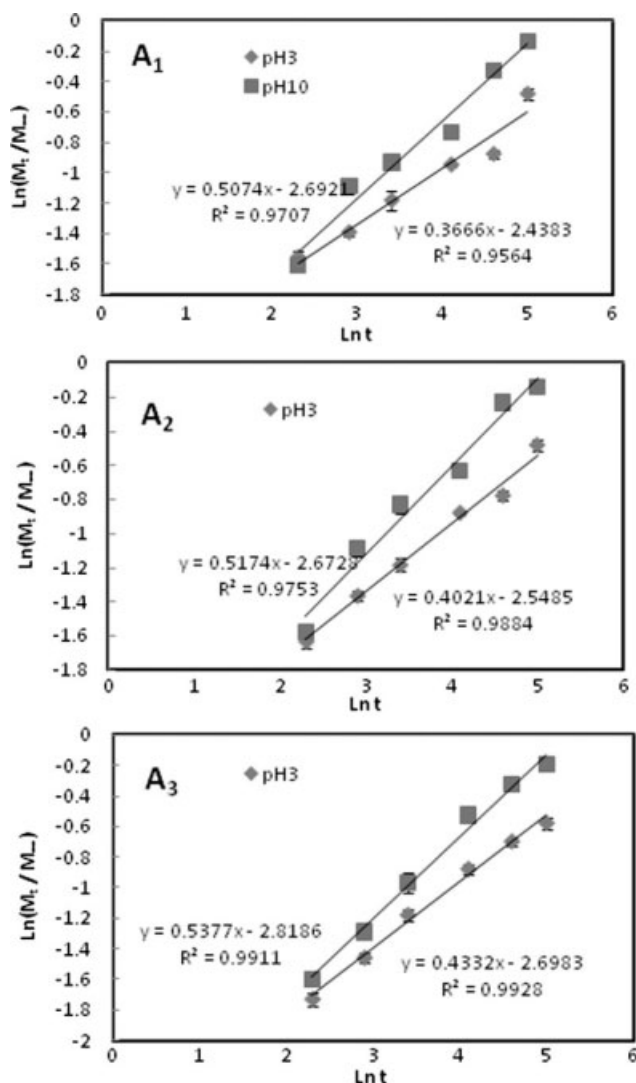


Figure 4 pH effects on ESA/NaAA/PVA hydrogels swelling kinetics with ionic strength adjusted to 0.15 mol L⁻¹. ESA/NaAA/PVA composition (wt %) of different hydrogels: A₁, 20/75/5; A₂, 20/70/10; A₃, 20/65/15.

change in charge density and network structure from etherificated alginate and unneutralized AA with changing pH. According to the DLVO theory, electrostatic repulsion between the carboxylic acid in the polymer chains, the ions present in the buffer solution and the ionic osmotic pressure generated from mobile counterions to charged ions in the network may also be responsible for the increase in SR. Because PVA is not ionic and thus dilutes the charge density of the hydrogel, the effect of protonated carboxylic acid and electrostatic repulsion is weakened, which lowers the SR.

Kinetic of diffusion in the hydrogels

According to the literature,²² *n* values from eq. (2) are given as follows: $n < 0.45$ for Fickian diffusion

(Case I), $0.45 < n < 0.89$ for non-Fickian diffusion (or anomalous), $n = 0.89$ for zero order (Case II), and $n > 0.89$ for super Case II type of penetrating mechanism. The anomalous case is considered by the summation of Fickian diffusion (Case I) and non-Fickian diffusion (Case II).¹⁹

The values of parameter *n*, calculated from Figure 4 are presented in Table I. As seen clearly, the *n* values of A₁, A₂, A₃ hydrogels were less than 0.45 at pH 3.0 and higher than 0.45 at pH 10.0. Thus, the water absorption mechanism of the hydrogels is governed by Fickian diffusion at pH 3.0. Increase in the pH of the surrounding liquid to 10.0, the water uptake profile becomes more dependent on the polymer diffusion and governed by non-Fickian diffusion ($n > 0.45$). This effect is attributed to the protonation of carboxylic group at low pH, which can promote hydrogen bond formation with hydroxyl group and pull the polymer chains closely to form a tight network, thus reducing SR. However, as pH increases, AA forms carboxylate ions, which cause repulsion between the molecular chains, resulting in rapid increase in SR. Apparently, when pH increases to 10.0, the hydrophobic groups may already be exposed and may remain so; dispersion and unfolding of carboxylate ions are enhanced.

Salt-responsive properties

Considering the hydrogels as a polyelectrolyte suggests that their porosity should decrease as ionic strength increases. As shown in Figure 4, the swelling of ESA/NaAA/PVA gels in various chloride and sulfate salt solutions appreciably reduced compared to that measured in deionized water. This results from a charge-screening effect of the additional cations causing an anion-anion electrostatic repulsion, which leads to decreased osmotic pressure difference between the polymer network and the external solution. At a given ionic strength, Mg²⁺ and Ca²⁺ contribute more charges than monovalent cations Na⁺ and K⁺ and induce a bigger drop in intermolecular repulsion and increased

TABLE I
Values of Parameters *n* in eq. (2) for ESA/NaAA/PVA Hydrogels (ESA/NaAA/PVA Composition (wt %) of Different Hydrogels: A₁, 20/75/5; A₂, 20/70/10; A₃, 20/65/15) Swollen in Buffer Solution at pH 3.0 and 10.0 with Ionic Strength Adjusted to 0.15 mol L⁻¹

Hydrogels	<i>n</i>		R^2	
	pH = 3	pH = 10	pH = 3	pH = 10
A1	0.367	0.507	0.956	0.971
A2	0.402	0.517	0.988	0.975
A3	0.433	0.538	0.933	0.991

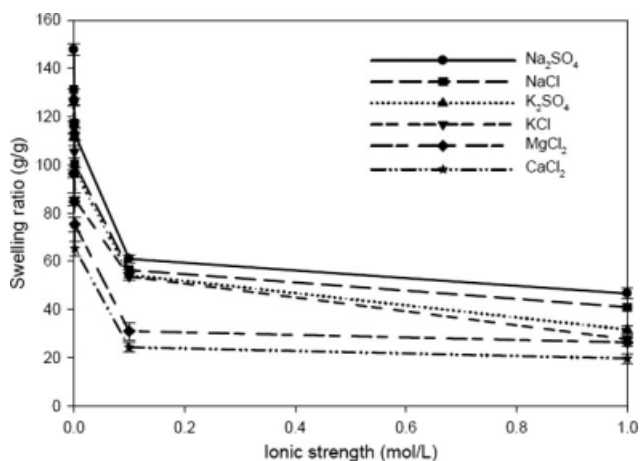


Figure 5 Effect of ionic strength on swelling properties of ESA/NaAA/PVA hydrogels in terms of different salt solutions.

interaction between molecules, which, in turn, cause to a large extent the hydrogel collapse. In addition, Mg^{2+} and Ca^{2+} can chelate carboxylic group, leading to a compact network and causing further shrinking of the hydrogel. On the other hand, we also find from Figure 5 that the smaller the radius of atom of the same valent monatomic cation, the more the water absorption capacity was. The order of the water absorption capacity of different cations was $Na^+ > K^+ > Mg^{2+} > Ca^{2+}$. Experiments indicate that the equilibrium swelling properties of hydrogel was also dependent on the valence of anion. SR in multivalent anion salt solution was higher than in monovalent anionic salt solutions, i.e., $SR_{K_2SO_4} >$

SR_{KCl} and $SR_{Na_2SO_4} > SR_{NaCl}$. This finding is consistent with that of an earlier study.²³

Gel-solvent interaction

The swelling properties of hydrogel can be examined by investigating the inherent gel-solvent interactions, in which hydrogen bonding plays the most important role (Figure 6). The stability of hydrogen bonding within the hydrogel network is significantly affected by the ionic strength of the system. Table II shows the equilibrium swelling ratios of hydrogels when the ionic strength in buffer and salt solution is very similar. The SR was observed lower in buffer solutions than in monovalent salt solutions (NaCl, KCl) but significantly ($p > 0.05$) higher in buffer solutions than in divalent salt solutions ($MgCl_2$, $CaCl_2$). This can be attributed to different kinds of ions in buffer and salt solutions which influence the hydrogen bonding of the hydrogel with different strength. This effect can be elucidated by employing hydrogen-bond hydration model of polymer side chains, depicted by Hajime et al.²⁴ According to the model, the ion-specific swelling behavior is caused by stabilization or destabilization of the hydrogen-bonding hydration through ionic hydration. In the case of hydration to anions, positive charge on the water oxygen decreases and negative charge on the water oxygen increases. These changes in the charges on the water hydrogen and oxygen due to hydration to ions correspond to a decrease in the ability of electron-pair acceptance (Type A) and an increase in the ability of electron-pair donation (Type B) of water, respectively. In our ESA/NaAA/PVA hydrogel

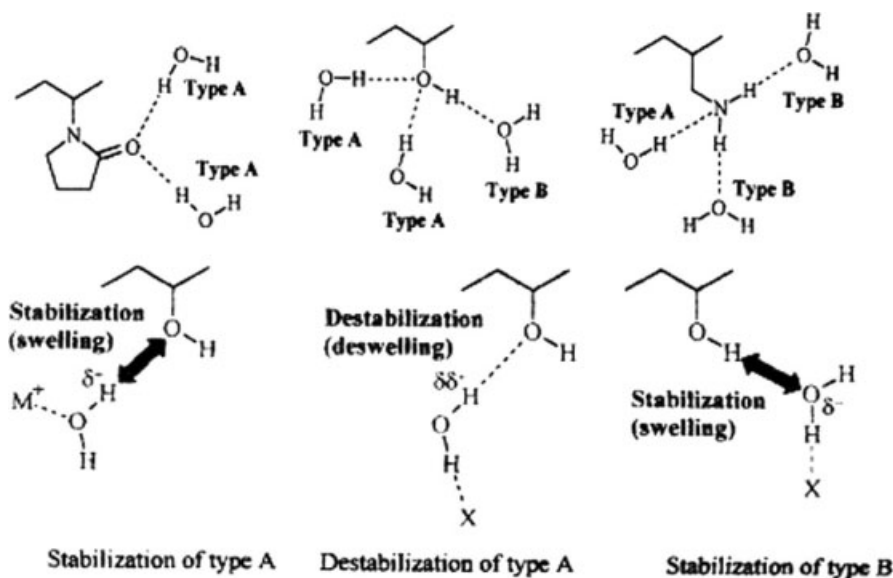


Figure 6 Hydrogen bonding hydration model of polymer side chains used to explain the effect of ionic strength to ESA/NaAA/PVA hydrogel swelling properties (Muta et al., 2001).

TABLE II
Swelling Properties of ESA/NaAA/PVA Hydrogels (ESA/NaAA/PVA Composition (wt %) of Different Hydrogels: A₁, 20/75/5; A₂, 20/70/10; A₃, 20/65/15) in Buffer and Salt Solutions With Different Ionic Strength

Ionic strength (pH)	Swelling ratio (g/g)			Ionic strength (salt)	Swelling ratio (g/g)		
	A ₁	A ₂	A ₃		A ₁	A ₂	A ₃
0.1643 (5)	55.8 ± 1.2 ^a	52.1 ± 0.8 ^a	50.0 ± 1.0 ^a	0.1628 (NaCl)	60.4 ± 0.7 ^a	58.3 ± 1.2 ^a	53.0 ± 1.2 ^a
0.1346 (7)	57.8 ± 1.0 ^a	57.8 ± 0.6 ^a	56.5 ± 1.0 ^a	0.1378 (KCl)	63.1 ± 1.1 ^a	61.0 ± 1.1 ^a	58.4 ± 0.6 ^a
0.0964 (10)	67.1 ± 0.9 ^a	66.0 ± 1.2 ^a	61.3 ± 1.2 ^a	0.0947 (MgCl ₂)	40.3 ± 0.8 ^a	32.5 ± 0.9 ^b	29.7 ± 0.8 ^b
0.0856 (11)	69.6 ± 0.5 ^a	66.2 ± 0.6 ^a	64.6 ± 0.8 ^a	0.0806 (CaCl ₂)	30.6 ± 0.8 ^a	27.0 ± 1.2 ^b	26.1 ± 0.8 ^b

Values are recorded as mean ± standard deviations.

Different letters within the same row of buffer and salt solution indicate significant differences, respectively ($\alpha = 0.05$).

system, the existence of cations in the medium, such as K⁺, Na⁺, and Ca²⁺, enhances the hydrogen bond strength of the hydrogel because more electrical charges are pushed to oxygen molecules between O—H bond in the water molecule, increasing the capacity of hydrogen atom of water to accept the electrical pairs donated by the hydrogel oxygen atom, and thus increase the hydrogen bonding of the hydrogel, which stabilizes the Type A hydrogen bond. Because K⁺ has a smaller hydration radius than Na⁺ and Ca²⁺, it exhibits the strongest ionic hydration effects. At the same time, the existence of anions of Cl⁻ and SO₄²⁻ and PO₄³⁻ make water molecule serving as hydrogenbond acceptor. Hydrogen-bonding hydration of Type B is stabilized through hydration to anion because of enhancement of water electron-pair donation. The deswelling behavior of ESA/NaAA/PVA hydrogel observed in our system can be ascribed to the destabilization of Type A by anions. Type A hydrogen bonding is enhanced with the existence of cations but weakened by the presence of anions such as Cl⁻ and SO₄²⁻ and PO₄³⁻. Because Cl⁻ has higher electronegativity, it shows stronger weakening effect of Type A hydrogen bond than other anions, leading to higher degree of shrinking.

CONCLUSIONS

Swelling ratio of ESA/NaAA/PVA hydrogel is influenced by medium pH and ionic strength. The hydrogel exhibited different swelling properties at different pH environment at a given ionic strength. As pH increases, SR of the hydrogel increases because of the negatively charged ionic backbone of ESA and poly (NaAA) are more expanded. SR tended to decrease with increasing the PVA content at a given surrounding medium pH because PVA dilutes the charge density of the hydrogels. The water absorbency was extremely influenced by the type of ions and ionic strength.

The smaller the hydration radius of the same valent monatomic cation, the more the water absorption capacity was, and SR decreased with high number of atoms of the univalent. Ions with more charges affect swelling-shrinking properties to a greater extent. At a given ionic strength the water absorbent capacity of ESA/NaAA/PVA hydrogel was dependent on the valence of anion. SR in multivalent anion salt solution is higher than in univalent anion salt solutions, i.e., SR_{K₂SO₄} > SR_{KCl} and SR_{Na₂SO₄} > SR_{NaCl}. When the ionic strength in buffer and salt solution is close, the hydrogel has larger SR in salt solution than in buffer, but shows lower SR in divalent metal solutions. In the acidic media, protonation solvent diffusion dominates the hydrogel swelling, showing Fickian kinetic diffusion behavior. In the alkaline environment, however, swelling is dominated by protonation diffusion and shows non-Fickian behavior.

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