

Superabsorbent Polymeric Materials. I. Swelling Behaviors of Crosslinked Poly(sodium acrylate-co-hydroxyethyl methacrylate) in Aqueous Salt Solution

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SYNOPSIS

A series of crosslinked poly(sodium acrylate-co-hydroxyethyl methacrylate) based on sodium acrylate (SA), 2-hydroxyethyl methacrylate (HEMA), and *N,N*-methylene-bis-acrylamide (NMBA) are prepared by inverse suspension polymerization. The resultant crosslinking polymers are xerogellants. This work investigates not only the absorbency or swelling behavior for these xerogellants composed of different ratios of HEMA/SA in water, but also the effects of various salts and pH values on the swelling properties. Experimental results indicate that the absorbency in deionized water decreases with an increase in the HEMA in copolymeric gel, which is related to the degree of expansion of the network and the strength of the hydrophilic group. The absorbency in the chloride salt solutions decreases with an increase in the salt concentration (swelling is 50 times for the IA group chloride salt solutions, but is less than 5 times for the IIA group salt solution), owing to the osmosis of water and ions between the polymeric gel and the external solution. A decrease in the extent of swelling occurs for divalent and trivalent chloride salt solutions. For the salt solutions of the same ionic strength, the swelling amount has the following tendency: $\text{LiCl(aq)} = \text{NaCl(aq)} = \text{KCl(aq)}, \text{CaCl}_2(\text{aq}) < \text{SrCl}_2(\text{aq}) < \text{BaCl}_2(\text{aq}), \text{and } \text{Fe}^{3+} > \text{Ca}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+}$. These orders are related to the complexing ability between metallic cations and the carboxylate group in the polymeric chains. Finally, the adsorption of ferric ion by these gels is also investigated. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Superabsorbent polymers find extensive product applications such as in disposable diapers, feminine napkins, soil for agriculture and horticulture, gel actuators, water-blocking tapes, medicine, and absorbent pads.¹⁻⁸ In such applications, water absorbency and water retention are essential. Some authors modified these absorbent polymers to enhance their absorbency, gel strength, and absorption rate.⁹⁻²³

Flory thoroughly examined absorption of water in hydrophilic polymers in nonionic network or ionic network structures.²⁴ The kinetics of the swelling of

poly(sodium acrylate) was studied by picture analysis with a VCR system, calorimetry, and gravimetry techniques.²⁵

In addition, several investigators studied the gel transition caused by the interaction between a polar solvent and a polymer.²⁶⁻³² However, the gel deswelling behavior in saline solution has rarely been discussed. In this work, we prepare a series of crosslinked poly(sodium acrylate-co-hydroxyethylmethacrylate) [poly(SA-co-HEMA)] by inverse suspension polymerization. This work aims to investigate not only the swelling behavior of these copolymeric gels composed of the different ratios of HEMA/SA in water, but also the effects of various salt solutions and pH values on the swelling properties. The adsorption of the metal ion Fe^{3+} by these gels is also discussed.

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Table I Compositions of Reactive Species

Sample No.	NaA (g)	HEMA (g)
He 1	20	0
He 2	19	1
He 3	18	2
He 4	17	3
He 5	16	4
He 6	14	6
He 7	Acrylic acid 20 g	

The total weight of water is 60 g. ACVA, 0.1 g; Span60, 0.15 g; NMBA, 0.5 wt %.

EXPERIMENTAL

Materials

The materials used in this study were purchased from Tokyo Kasei Industries Ltd. including acrylic acid (AA), HEMA, sodium hydroxide, and *N,N'*-methylene-bis-acrylamide (NMBA). Sodium hydroxide and NMBA were used directly. AA and HEMA were distilled under reduced pressure before use. 4,4'-Azo-bis(4-cyanovaleric acid) (ACVA) as an initiator and sorbitan monostearate (Span60) as an inverse suspension stabilizer were also purchased from Tokoy Kasei Industries Ltd. Methanol and cyclohexane were of reagent analytical grade.

Preparation of SA Monomer Solution

SA monomer was prepared by gently dropping AA in sodium hydroxide solution under cooling (ice bath). The molar ratio of sodium hydroxide to AA was 1 : 1 to approach complete neutralization.

Inverse Suspension Polymerization

A 300-mL reactor was charged with 0.15 g sorbitan monostearate (HLB 3.4) and 60 mL cyclohexane (bp 85°C). The mixture was stirred until the sorbitan monostearate was dissolved (continuous phase).

The appropriate amount of HEMA and 0.1 g crosslinking agent (NMBA) were introduced into the SA monomer solution, and the mixture was stirred until the NMBA was dissolved completely. The monomer solution and 0.1 g initiator (ACVA, dispersion phase) were added to the reactor. Air was flushed from the reactor by introducing nitrogen until the entire process was completed. The stirrer speed was maintained at 250 rpm. The polymerization reaction was set at 70°C for 4 h. The suspension

solution was then introduced into 800 mL methanol under stirring. The polymer was then precipitated. The precipitate was filtered and washed with methanol several times. The product was dried in a vacuum oven at 120°C for 1 day. The product was weighed and the conversion was about 90%. Table I lists the reactant compositions.

Property Measurements

The samples were dried before any tests were performed. All of the samples were used with a particle size in the range of 60–100 mesh.

Saturated Absorbency

The sample (50 mg) was immersed in the excess of deionized water or 0.9 wt % NaCl(aq) for at least 8 h to reach the swelling equilibrium at room temperature. The residual water was removed by suction filtration with an aspirator (250 mmHg) for 5 min. The gel was weighed and the equilibrium absorbency, Q_{eq} , was calculated by the following equation:

$$Q_{eq} = \frac{\text{wt swollen gel} - \text{wt dried sample}}{\text{wt dried sample}}$$

Kinetics of Swelling

A technique based on the demand wettability (DW) method was adopted.¹⁶ A graduated burette with an air inlet at the bottom was linked by a flexible tube to a plate covered with a metallic grid (250 mesh). After filling with water or saline solution, the burette was closed at the top and air was introduced while the xerogellant absorbed water. Fifty milligrams of absorbent were placed on the grid, and the swelling kinetics were easily measured.

Table II Elemental Analysis of C and H

Sample No.	Theoretical Value (%)		Found Value (%)	
	C	H	C	H
He 1	38.31	3.22	38.02	3.44
He 3	40.02	3.67	39.74	3.92
He 5	41.73	4.12	41.63	4.31
He 6	43.43	4.57	43.16	4.55

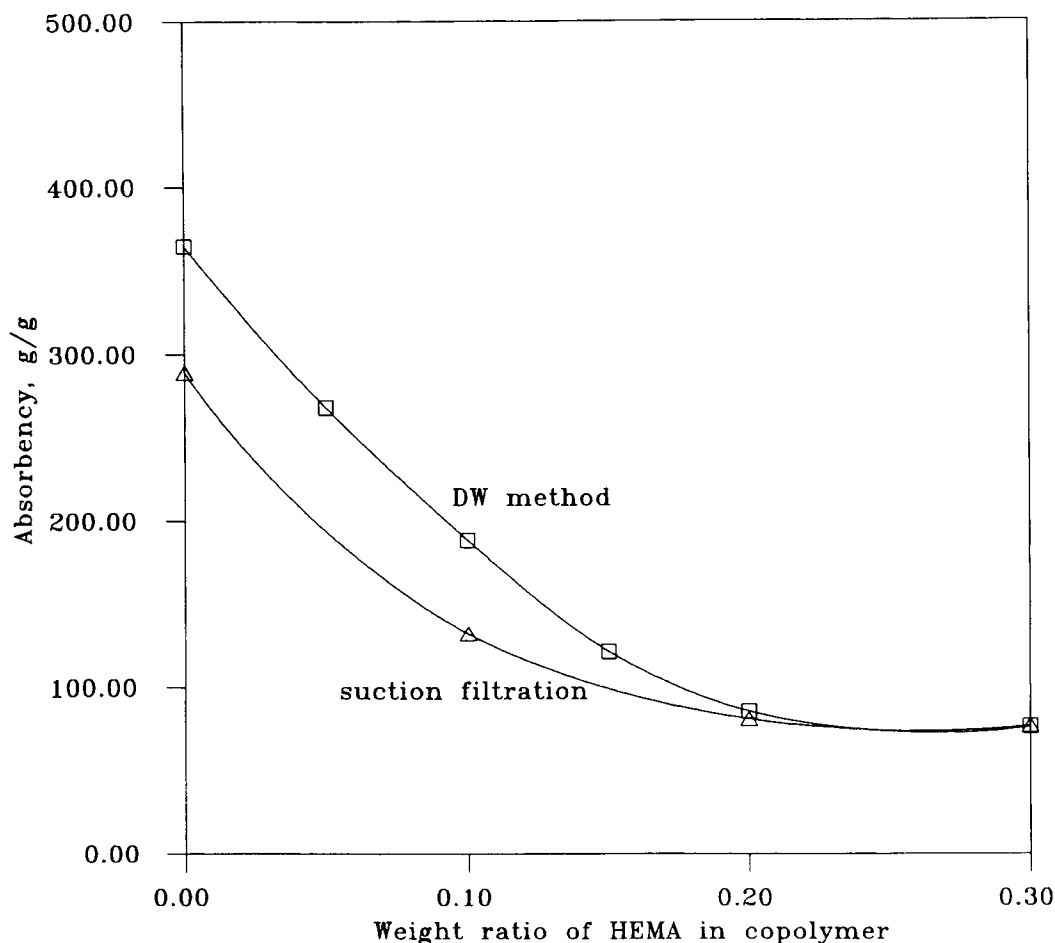


Figure 1 Water absorbency of crosslinked poly(SA-co-HEMA) in deionized water by the DW method and the suction filtration method.

Absorbency in Various Saline Solutions

Fifty milligrams of dried samples were immersed in the excess of various saline solutions with different concentrations [IA: LiCl(aq), NaCl(aq), KCl(aq); IIA: CaCl₂(aq), SrCl₂(aq), BaCl₂(aq); IIIA: FeCl₃(aq), ZnCl₂(aq), CuCl₂(aq)] and remained there for at least 8 h. The sample was filtered with suction and weighed. The effects of saline solutions on the water absorbency could also be obtained.

Effect of Various pH Values on Water Absorbency

The method was the same as the water absorbency in various saline solutions. The pH values of the external solution were adjusted by adding HCl or NaOH in water.

Thermal Effect on Water Retention

Fifteen grams of saturated swollen gels were placed in an oven at 50°C, 70°C under forcing convection.

The gel was weighed at each time interval and the weight loss of water was calculated.

Adsorption of Metallic Ion

A 50-mg portion of a dried sample was put into various FeCl₃(aq) solutions. After reaching equilibrium, the sample was filtered with suction and the volume of residual water was recorded. The concentration was determined by a Jasco UVIDE-5 spectrophotometer. The adsorbed amount of ferric ion was calculated from the relationship

$$AD = \frac{C_i \times V_i - C_r \times V_r}{W} \quad (1)$$

where AD is the adsorbed moles of Fe³⁺/g sample, C_i is the initial concentration of FeCl₃(aq), V_i is the initial volume of FeCl₃(aq), C_r is the residual concentration of FeCl₃(aq), V_r is the residual volume of FeCl₃(aq), and W is the dried sample's weight.

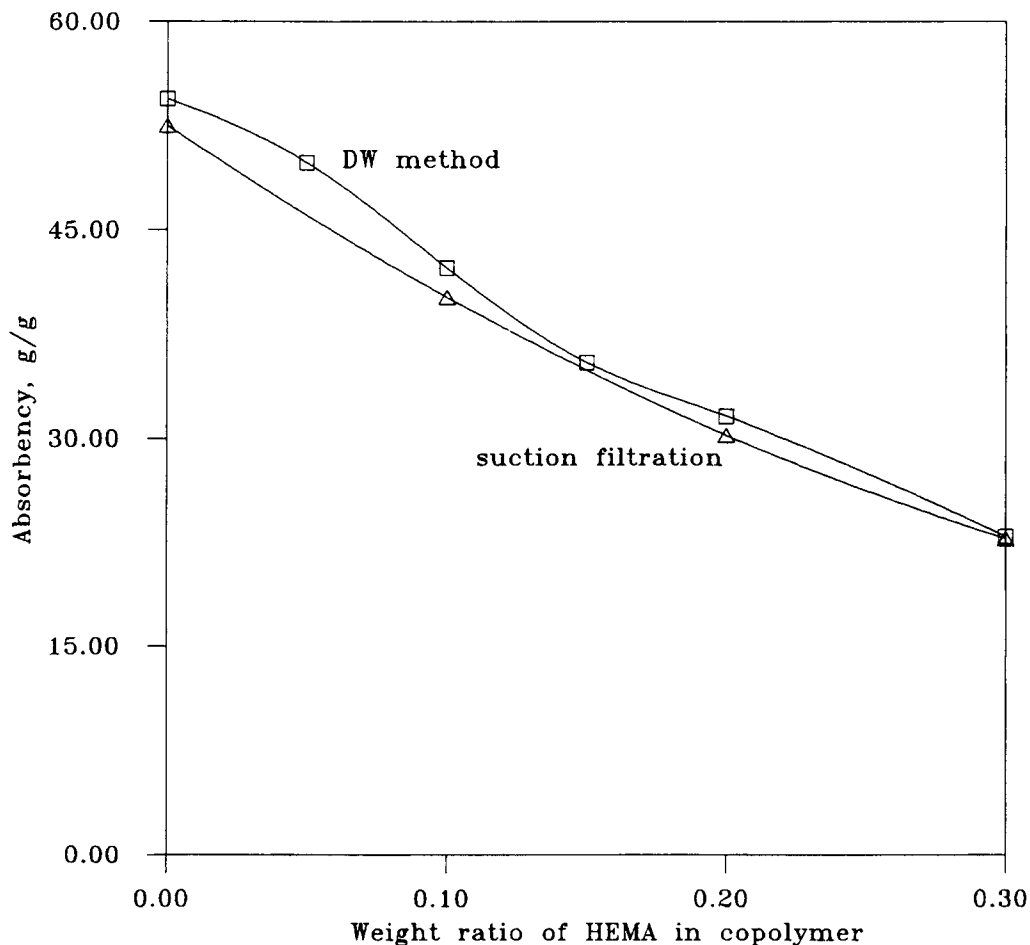


Figure 2 Water absorbency of crosslinked poly(SA-co-HEMA) in 0.9 wt % NaCl_(aq) by the DW method and the suction filtration method.

Elemental Analysis

Elemental analysis was performed with a Perkin-Elmer 2400 to analyze carbon and hydrogen for determining the ratio of HEMA to SA.

RESULTS AND DISCUSSION

The swelling behavior of the absorbents depends on the nature of the polymer and the characteristics of the external solution, and can be accounted for by Flory's theory.²⁴ The polymer's nature involves factors such as the density of crosslinkage, strength of the hydrophilic group, and elasticity of the polymer network. Among the controlling characteristics of the external salt solution are the charge number and the ionic strength.

Characterization of Crosslinked Copolymers

The elemental analysis was performed to determine the content of carbon and hydrogen in the copolymeric gel composition. Table II lists the theoretical values and the observed values of C and H. The proportion of each component is calculated by the weight ratio of C and H elements. This table reveals that the copolymer composition conforms to the initial charge composition. The amount of the crosslinking agent (NMBA) is negligible.

Effect of HEMA on Saturated Absorbency

Figure 1 shows the water absorbency measured by the DW method and suction filtration as a function of the ratio of HEMA in the copolymeric gel (deionized water). This figure indicates that the water absorbency in deionized water is decreased from 360 to 80 and from 280 to 80 g water/g dry sample for

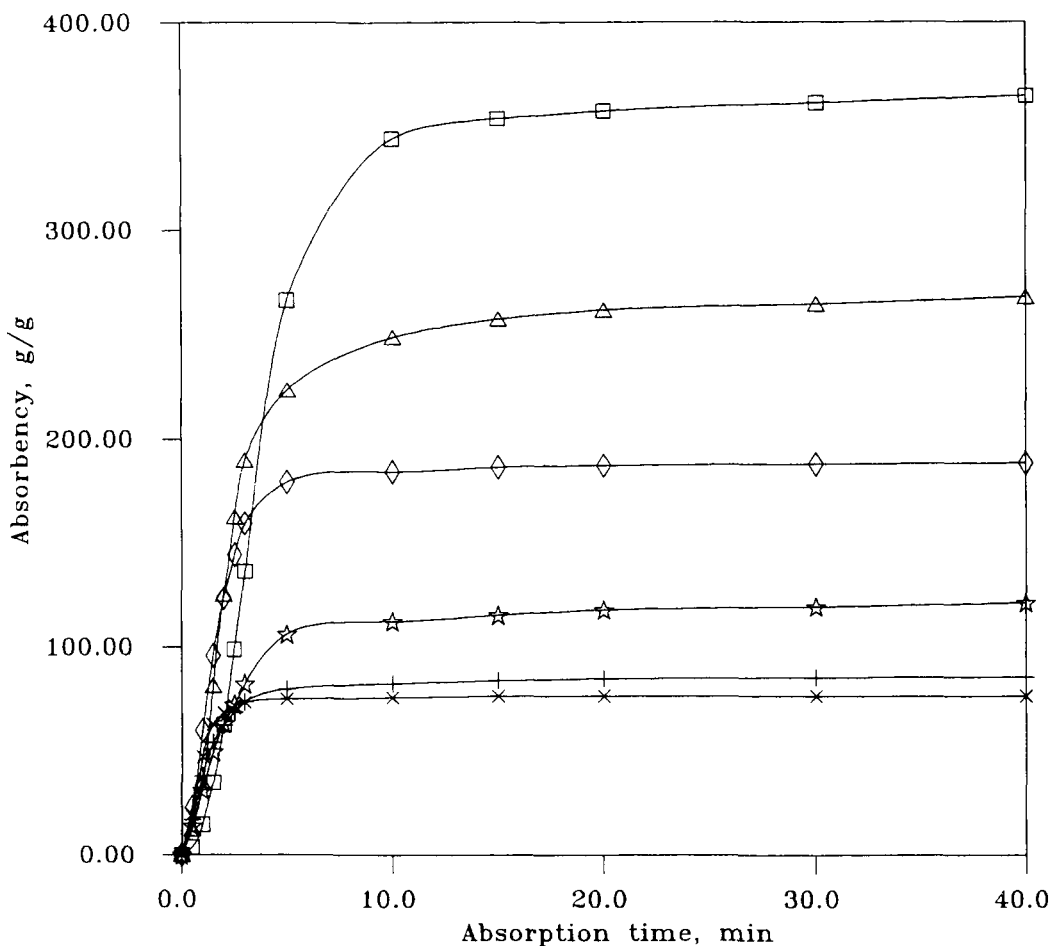


Figure 3 Absorption rate in deionized water by the DW method: (□) He 1, (△) He 2, (◇) He 3, (☆) He 4, (+) He 5, (×) He 6.

the DW method and suction method, respectively, with an increase in HEMA content. The water absorbency measured by the DW method is larger than that measured by the suction method. Because the water absorbency is attributed primarily to the water absorbed by the gels and the free water residing between the gel particles, the smaller absorbency by suction is due primarily to the scarcity of the free water between the gel particles.

According to the Flory ionic swelling theory,²⁴ the hydroxy group of HEMA does not dissociate. The amount of dissociated ions inside the polymeric gel decreases. This occurrence causes the decrease of the osmotic pressure difference between the polymeric gel and the external solution. In addition, the hydroxy group is a weakly hydrophilic group and may subsequently produce a hydrogen bond between two neighboring chains that ultimately causes the network to shrink.

The absorbency in 0.9 wt % NaCl(aq) (Fig. 2) is smaller (about 20–55 times) than that in deionized

water. This result is primarily due to the decrease in the osmotic pressure (ionic pressure) difference between the polymeric gel and the external solution.

Swelling Kinetics

The water or 0.9 wt % NaCl solution absorption rate by the DW method is significantly influenced by the polymer's contact area with water and the ratio of HEMA in the copolymer. Figures 3 and 4 show the absorption rates for a series of absorbent polymers in water or saline solution, respectively. The initial absorption rate in water for poly(SA) absorbent (Table III, He 1) at the initial period (in 30 s) is extremely slow. This phenomenon reveals that the initial swelling process is due primarily to the water penetrating into the polymeric particles through capillarity and diffusion. The penetrated water is adsorbed by hydrogen bonding with the hydrophilic group until the sodium carboxylate group in the polymer begins to be dissociated by the water.

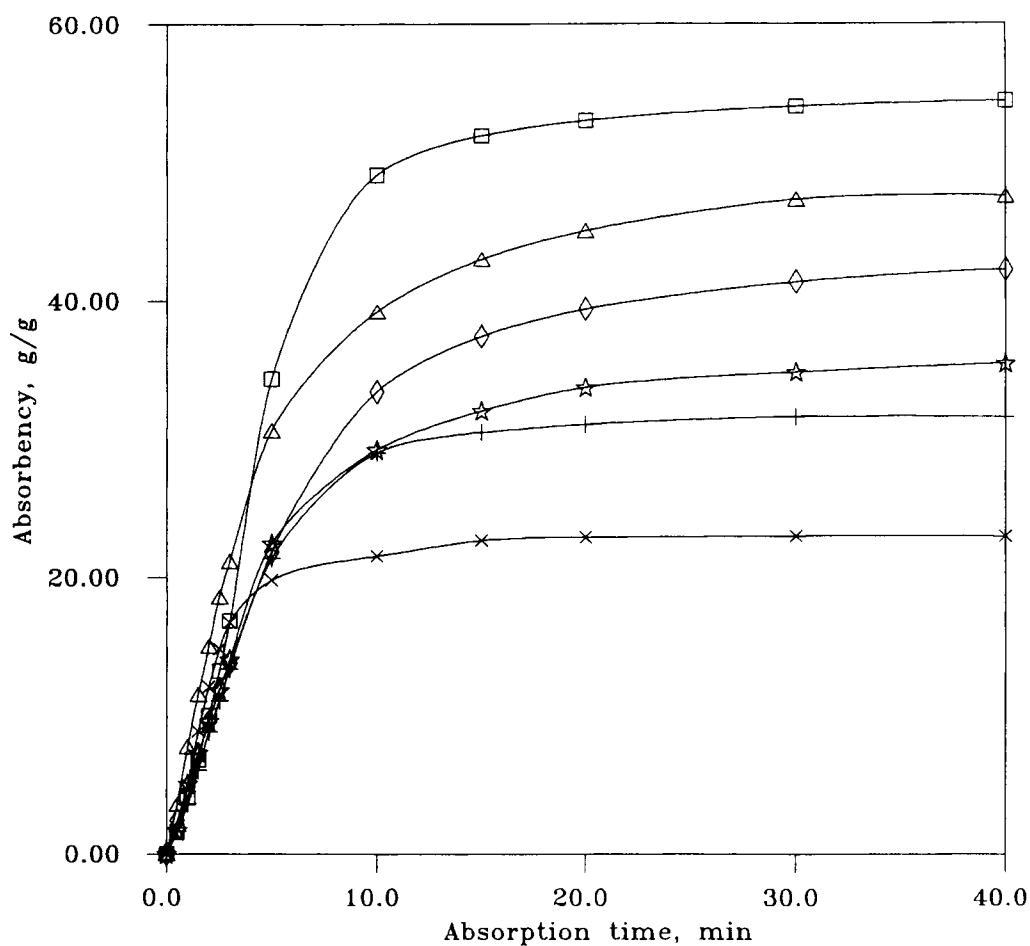


Figure 4 Absorption rate in 0.9 wt % NaCl_(aq) by the DW method: (□) He 1, (△) He 2, (◇) He 3, (☆) He 4, (+) He 5, (×) He 6.

Table III Absorption Characteristics for SA-HEMA Copolymeric Gel Systems

Sample No.	H ₂ O				0.9 wt % NaCl			
	Initial Absorption Rate (g/min)		t_{req} (min)	Q_{eq} (g H ₂ O/g)	Initial Absorption Rate (g/min)		t_{req} (min)	Q_{eq} (g H ₂ O/g)
	30 s	1-3 min			30 s	1-3 min		
He 1	7.0	62.9	17.5	365	3.2	6.4	30	54
He 2	24.6	77.5	14.7	268	7.2	6.7	30	56
He 3	46.0	49.7	6.3	188	4.8	5.7	30	42
He 4	28	25.4	6.0	121	3.4	4.5	20	36
He 5	34.1	17.7	4.9	86	3.4	4.9	10	32
He 6	38.7	13.2	2.8	76	3.6	5.9	5	23

t_{req} , time required to approach equilibrium.

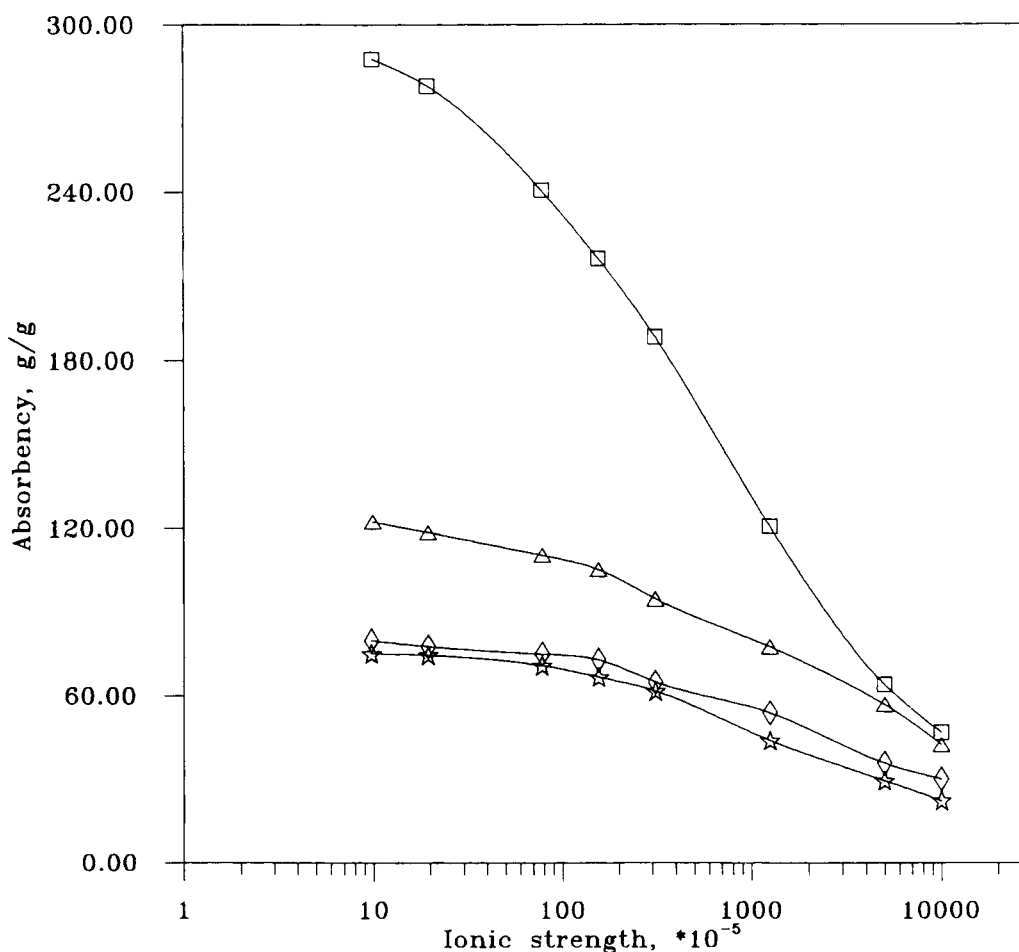
Table IV Influence of HEMA Content on Swelling Characteristic Times (T), Swelling Kinetic Constants (K), and Swelling (Q) of HEMA-SA Absorbent in Water and Saline Solution

Sample No.	T (s)		K (s^{-1})		Q (g H ₂ O/g)	
	H ₂ O	0.9 wt % NaCl	H ₂ O	0.9 wt % NaCl	H ₂ O	0.9 wt % NaCl
He 1	12.3	9.8	0.16	0.12	231	34
He 2	33.7	14.9	0.43	0.19	169	32
He 3	50.5	10.5	0.64	0.13	119	27
He 4	30.4	13.4	0.39	0.17	76	23
He 5	52.9	14.8	0.67	0.19	54	20
He 6	89.8	35.7	1.14	0.45	48	15

$$Q = 0.632 Q_{eq}$$

Before the sodium carboxylate is completely dissociated, the driving force of swelling is small because of a weak network repulsion and a low osmotic pressure difference between the polymeric gel and the external solution caused by low ionic strength in the

polymeric gel. After this period, the absorption rate is rapidly increased with an increase in the absorption time until the swelling of the polymeric gel reaches equilibrium state (saturated absorption) (Table III).


Figure 5 Water absorbency of crosslinked poly(SA-co-HEMA) in various NaCl concentrations: (□) He 1, (△) He 3, (◇) He 5, (☆) He 6.

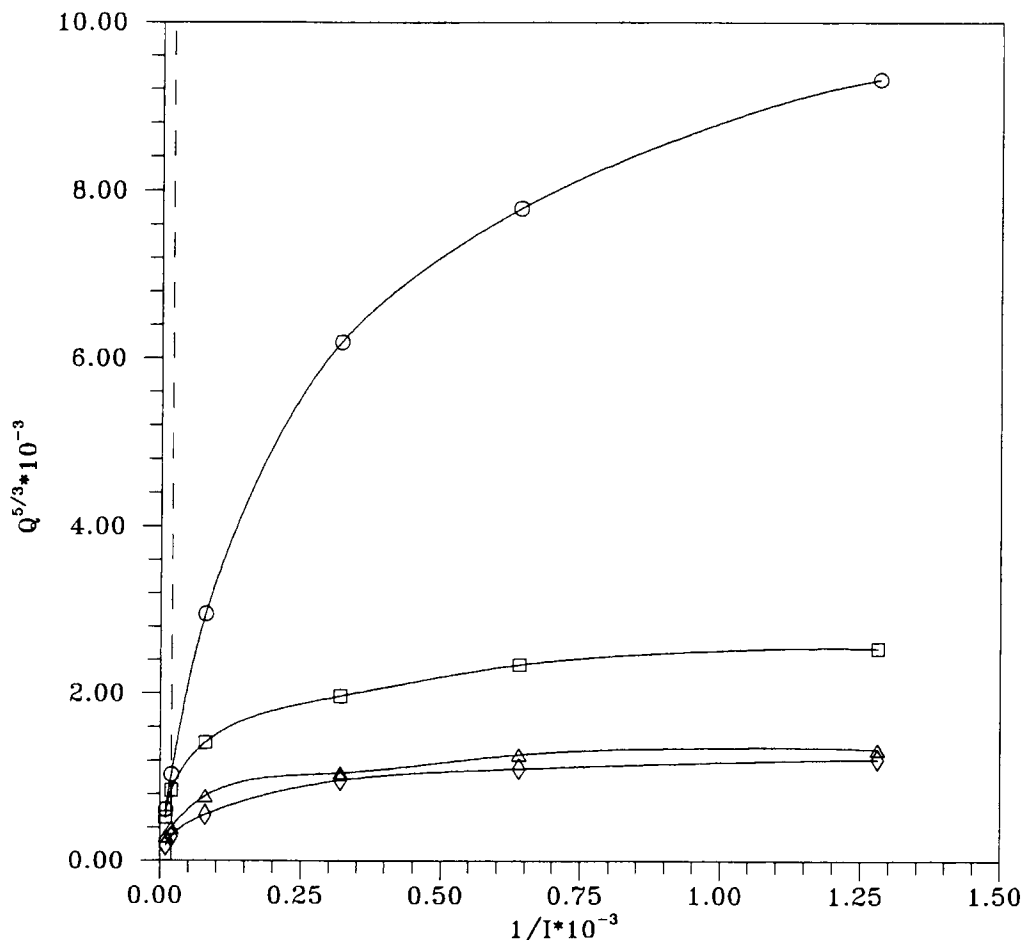


Figure 6 Absorbency plots against the ionic strength (I): (\square) He 1, (\triangle) He 3, (\diamond) He 5, (\star) He 6.

The initial absorption rate is profoundly increased in pure water when the HEMA monomer is added to the SA-HEMA systems. This phenomenon occurs because the hydroxy group on the HEMA monomer increases the affinity to water. However, the absorption rates at the 1-3 min stage decreases with an increase in the HEMA contents. This is due to the decrease of SA content in the copolymeric gel. This leads to not only a decrease in the repulsion force of the carboxylate groups, but also a decrease in the network repulsion volume. This result corresponds to Flory's theory.²⁴ Additionally, from the perspective of the time required to equilibrium absorption (t_{req}), t_{req} decreases with an increase in the HEMA contents. The t_{req} value only requires 2.8 min as the HEMA content reaches 30 wt % in the SA-HEMA system (He 6, Table I). On the other hand, the initial absorption rate of the SA-HEMA polymeric gel in saline solution is significantly smaller than that in pure water; the initial absorption rate in saline solution has the same tendency

(as in pure water) as the HEMA was increased in the copolymeric gel systems. That is, the absorption rate decreases with increasing HEMA content in the SA-HEMA system. The absorption rate in saline solution is more rapid in the 1-3 min stage than in the initial 30 s. The t_{req} , although decreasing with an increase in the HEMA, is still higher than that in pure water. From above results, we can infer that the osmotic pressure difference between the gel and the external solution is the most important parameter in the gel absorption process.

According to Yao and Zhou,³³ the swelling rate can be described by the following equation:

$$-\log(Q_{\text{eq}} - Q) = K/2.303T \quad (2)$$

where Q_{eq} is the equilibrium absorbency, Q is the characteristic absorbency, K is the swelling kinetic constant, and T is the characteristic swelling time. From eq. (2) a characteristic swelling time is defined at $Q = 0.632Q_{\text{eq}}$. Table IV presents the influence of

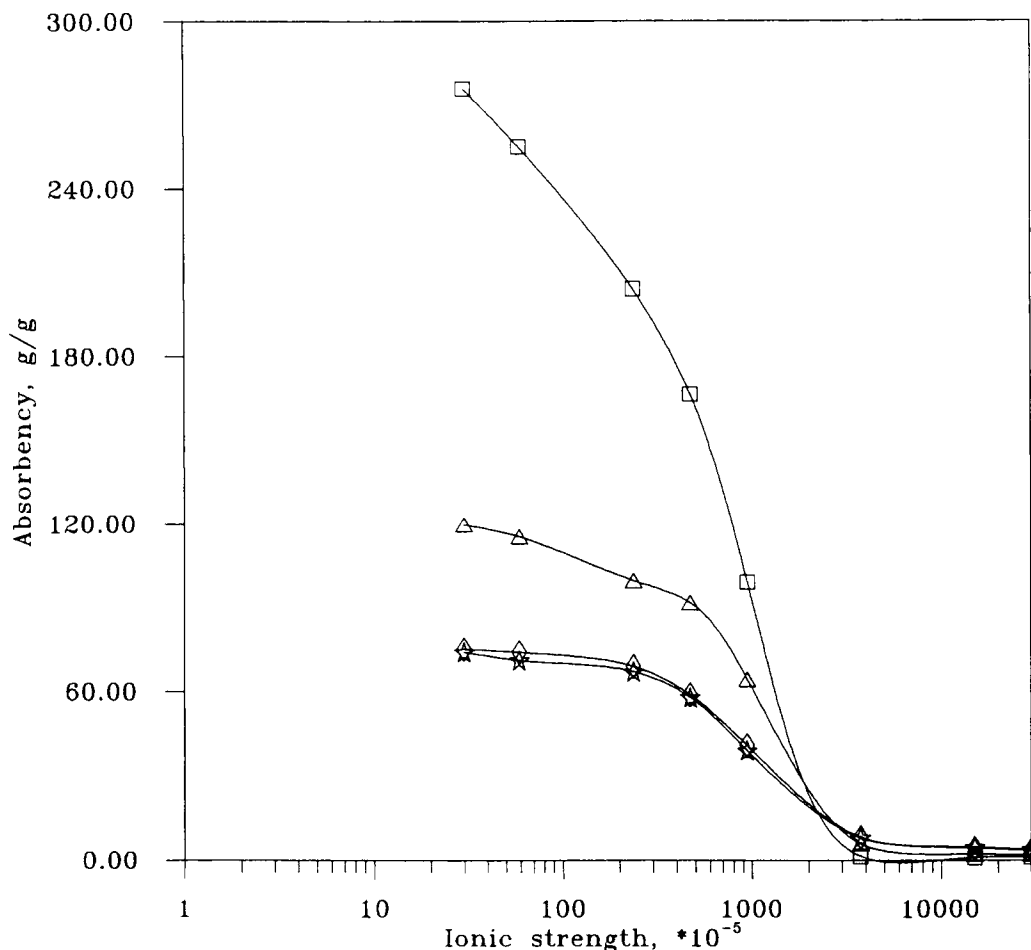


Figure 7 Water absorbency of crosslinked poly(SA-co-HEMA) in various CaCl_2 concentrations: (□) He 1, (△) He 3, (◇) He 5, (☆) He 6.

the HEMA contents on the characteristic swelling time (T), on the swelling kinetic constant (K), and on the swelling (Q) of the HEMA-SA absorbent in water and saline solution. This table reveals that T increases and Q decreases with an increase in the HEMA contents in the SA-HEMA gel system in pure water and saline solution. The swelling kinetic constants (K) for various composition gels in water are larger than that in saline solution; however, no correlation is made between the HEMA contents and the K in these gel systems.

Effect of Salt Solution on Water Absorbency

A change in this external parameter also significantly affects the absorbent's water absorbency. The SA-HEMA copolymeric gel belongs to an anionic type absorbent, thereby making it worthwhile to investigate the effect of counterion (cation) on the anionic group (carboxylate group). The absorbent's

swelling behavior is also significantly affected by the salt solution's ionic strength. Figure 5 shows the typical swelling of a series of SA-HEMA copolymeric absorbents as a function of ionic strength. The decrease of the expansion of the network is due not only to the screening of the ionic charges bound to the network, but also to the decrease of the osmotic pressure difference between the gel and the external solution when the ionic strength increases. The effect of the ionic strength on swelling was determined using the relation suggested by Hermans³⁴:

$$Q_{\text{eq}}^{5/3} = A + Bi^2/I \quad (3)$$

where Q_{eq} is the water absorbency at equilibrium, i is the concentration of the charges bound to the gel, I is the ionic strength of the external solution, and A and B are empirical parameters. Good linear relationships are achieved for a high ionic strength; however, a discrepancy is observed for low I values.

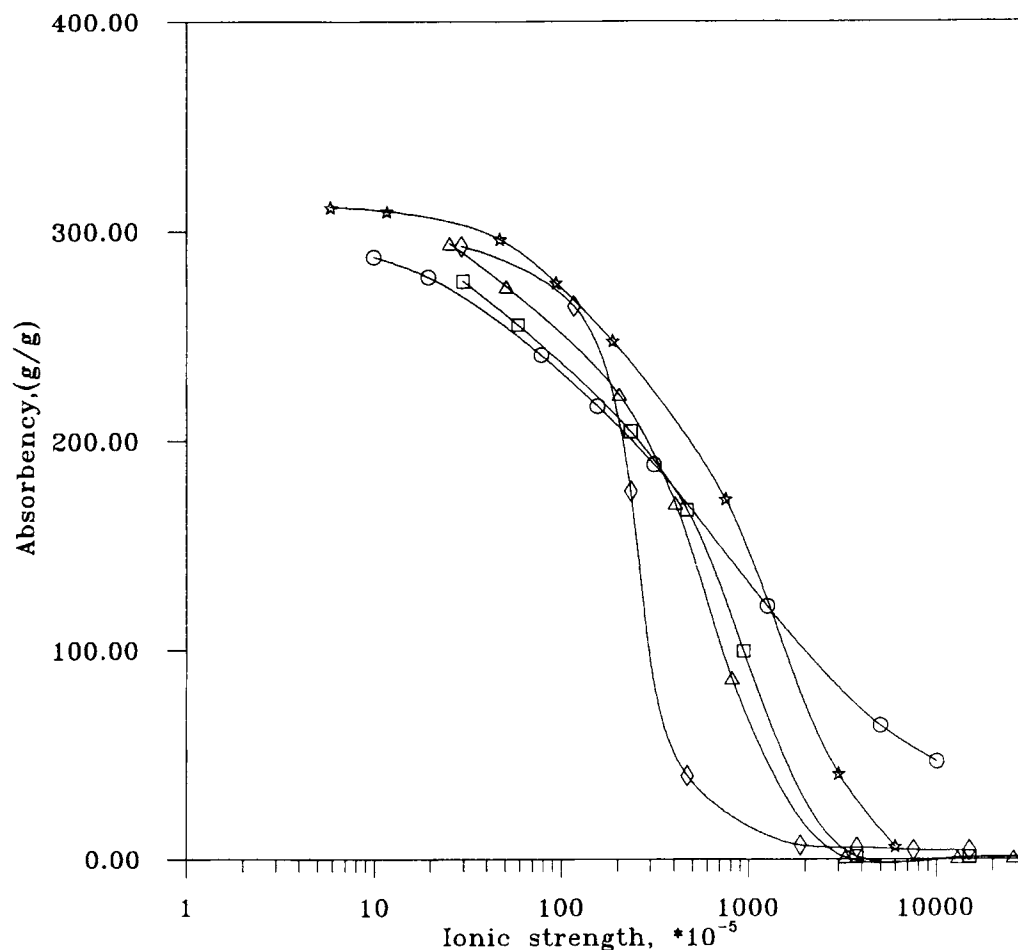


Figure 8 Water absorbency of crosslinked poly(SA) (He 1) in various ionic concentrations: (O) Na⁺, (□) Ca²⁺, (Δ) Zn²⁺, (◇) Cu²⁺, (★) Fe³⁺.

This event is due to the fact that the swelling force is counteracted by the crosslinked chain's elastic forces (Fig. 6). Castel et al. also observed this fact when investigating the influence of NaCl concentration on the absorbency of a hydrolyzed polyacrylonitrile starch graft copolymer.¹⁶

The influence of different cations with a common anion (Cl⁻) on water absorbency of SA-HEMA copolymeric gel is investigated in the following section. Figures 5 and present the behavior of the water absorbency vs. the ionic strength. Experimental data (partially shown) demonstrate that the absorbency apparently decreases with an increase of the ionic strength in various salt solutions. These results are due to the fact that the osmotic pressure difference between the polymeric gel and the external solution is reduced with an increase in external solution concentration. Comparing Figure 5 with Figure 7 reveals that the absorbency curves are steeper for multivalent salt solutions than those for a monovalent

salt solution. Moreover, the absorbency is reduced to zero in a high ionic strength for divalent salt solution, but not for monovalent salt solution. Re-stated, for a given high ionic strength, the water absorbency in monovalent cation solutions is higher than that in multivalent cation solutions.

Buchanan et al.³⁵ reported that all univalent cationic species of the same concentration have a similar effect on the water absorbency of the poly(SA) gel, that is, independent of the radius of the cation or the nature of the anion. Similarly, all multivalent cations of the same charge concentration influenced the swelling of the gel to the same extent. They thought that this was due to ionic crosslinking by polyvalent species. Castel et al.¹⁶ also reported that a calcium ion (Ca²⁺) can drastically decrease the swelling values for a hydrolyzed polyacrylonitrile starch graft, due to the complexing ability of the carboxylate groups inducing intramolecular and intermolecular complex formation. Results obtained

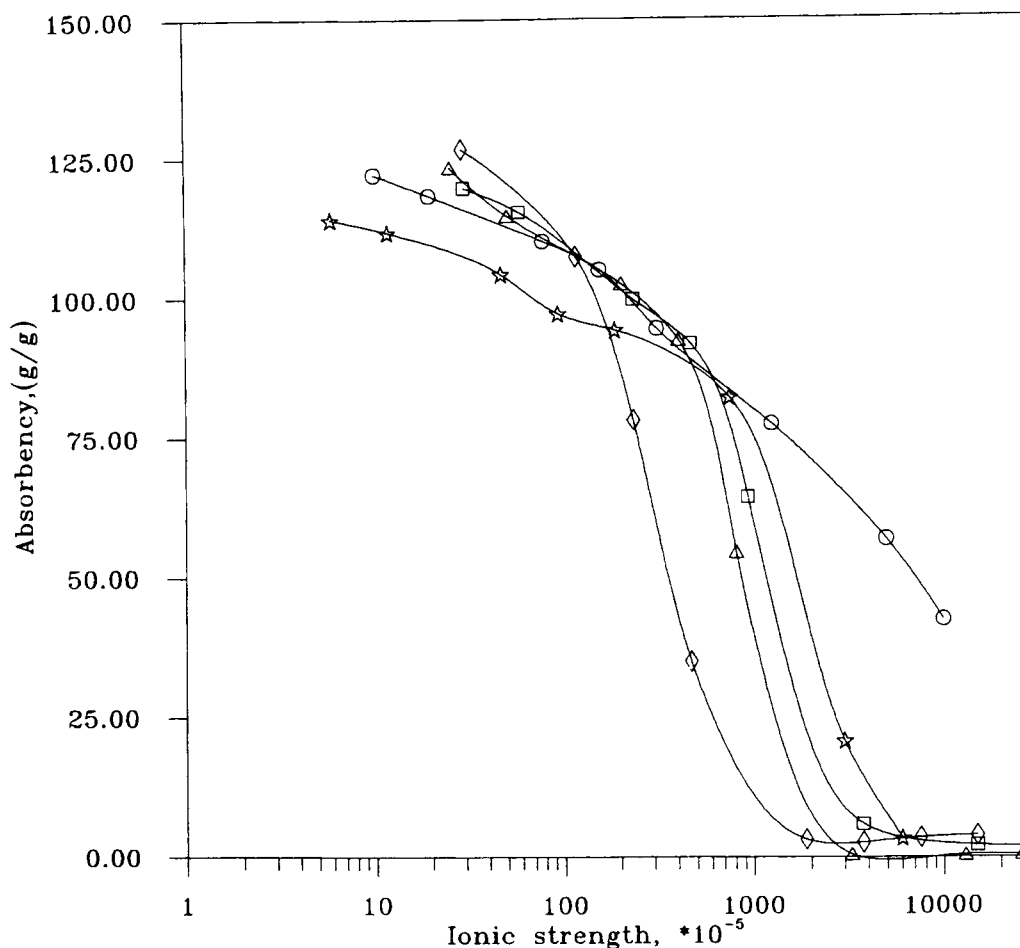


Figure 9 Water absorbency of crosslinked poly(SA-co-HEMA) (He 3) in various ionic concentrations: (○) Na^+ , (□) Ca^{2+} , (△) Zn^{2+} , (◇) Cu^{2+} , (★) Fe^{3+} .

from the SA-HEMA copolymeric gel systems demonstrate that the tendency of the water absorbency for the said gel in the IA and IIA group salt solution is in the order $\text{LiCl}_{(\text{aq})} = \text{NaCl}_{(\text{aq})} = \text{KCl}_{(\text{aq})}$, $\text{CaCl}_{2(\text{aq})} < \text{SrCl}_{2(\text{aq})} < \text{BaCl}_{2(\text{aq})}$. Those results correspond to previous investigations.^{16,35}

To prove the complexation of multivalent cations with a carboxylate group in polymeric gel, the gel was immersed in various multivalent salt solutions with various ionic strengths: CaCl_2 , ZnCl_2 , CuCl_2 , FeCl_3 . Figures 8 and 9 summarize the results for SA gel (He 1) and SA-HEMA copolymeric gel (He 3), respectively. Those results demonstrate the tendency to be in the order $\text{Fe}^{3+} > \text{Ca}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+}$ at a higher ionic strength, and $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ca}^{2+}$ at a lower ionic strength ($< 2 \times 10^{-3} M$) for SA gel. Moreover, the tendency is in the order $\text{Fe}^{3+} > \text{Ca}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+}$ at higher ionic strength, but $\text{Fe}^{3+} < \text{Ca}^{2+} = \text{Zn}^{2+} < \text{Cu}^{2+}$ at lower ionic strength ($< 1 \times 10^{-3} M$) for SA-HEMA copolymeric gel (He 3).

The order at a higher ionic strength for the two gels having carboxylate groups can be interpreted by the formation constants of complexation. The logarithm of formation constants of the ethylenediaminetetraacetic acid (EDTA) with multivalent cations at 0.1M are 7.76, 8.63, 10.70, 16.5, 18.80, and 25.1 for Ba^{2+} , Sr^{2+} , Ca^{2+} , Zn^{2+} , Cu^{2+} , and Fe^{3+} , respectively.³⁶ Hence, the greater the formation constant, the stronger the complexation, and the weaker the water absorbency. Such an inference conforms to the result obtained from SA or SA-HEMA gels at a higher ionic strength solution.

Figures 8 and 9 also show the deswelling behavior of the polymeric gels (He 1 and He 3). The gel deswelling is found to be in the range of the ionic strength of 0.001–0.01M for the multivalent salt solution (typically, Figs. 5, 7–9). This gel deswelling is more evident when the larger proportion of SA is contained in the copolymeric gel (Fig. 5). This corresponds to the fact that the carboxylate groups

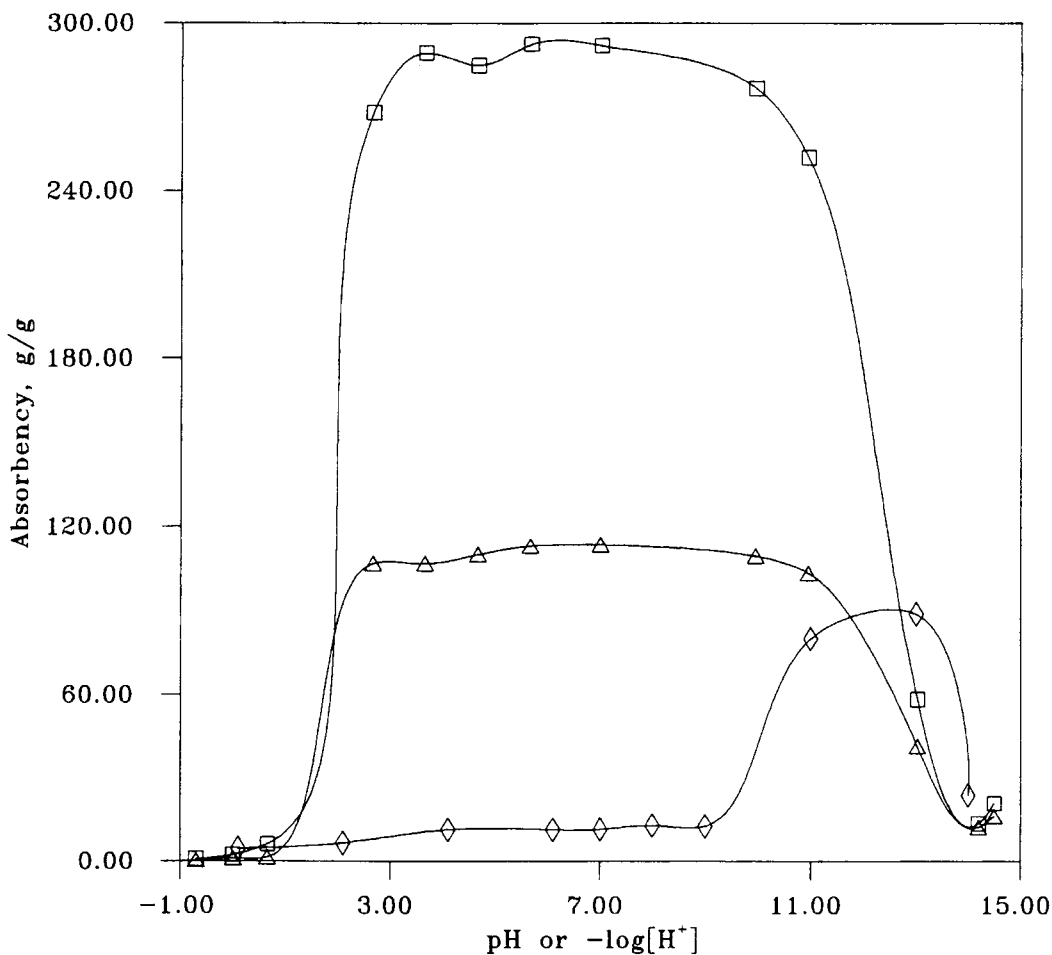
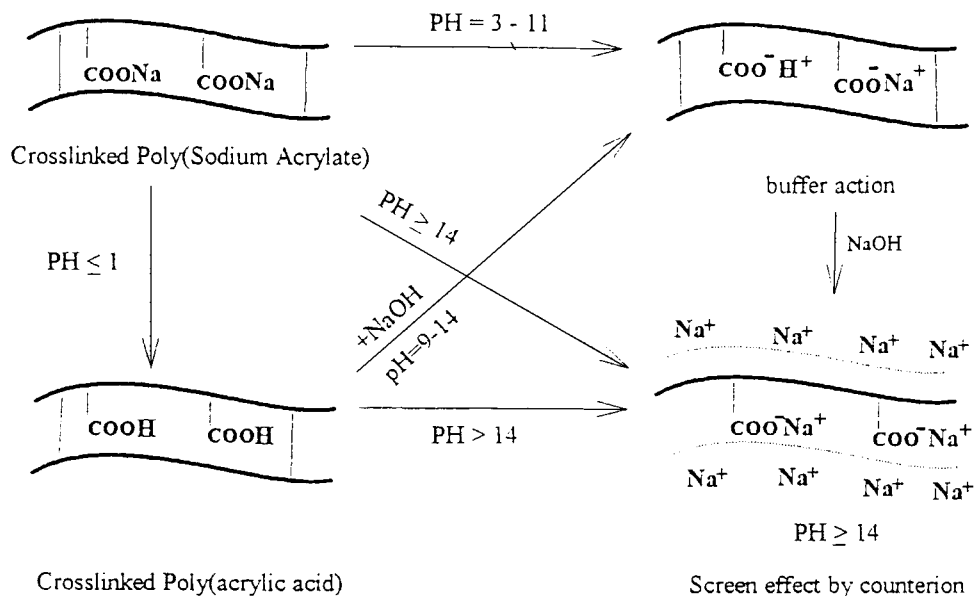


Figure 10 Relation between water absorbency and pH values: (\square) He 1, (\triangle) He 3, (\diamond) He 7.



Scheme 1 Crosslinked poly(SA) transformation at various pH values.

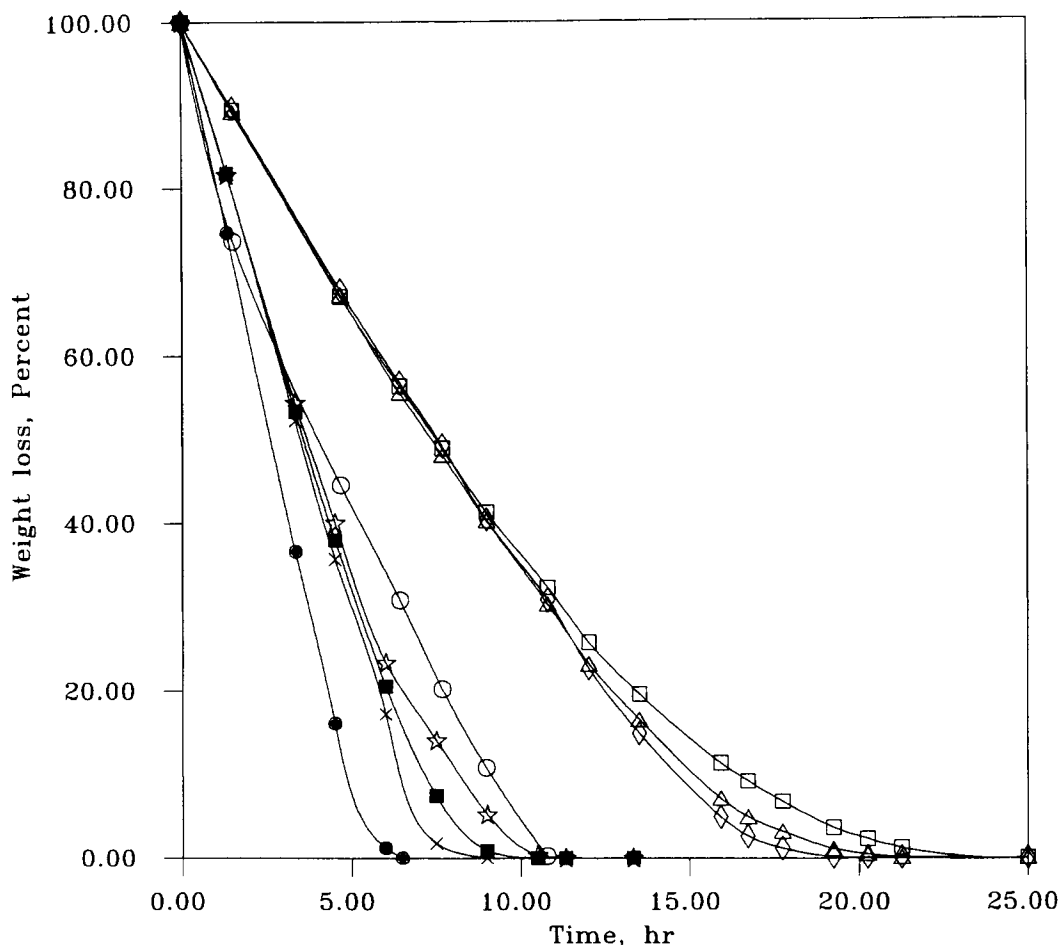


Figure 11 Thermal effect on water retention for (SA-co-HEMA) copolymeric gel: (★) He 1 at 70°C, (■) He 3 at 70°C, (×) He 5 at 70°C, (□) He 1 at 50°C, (△) He 3 at 50°C, (◇) He 5 at 50°C, (●) H₂O at 70°C, (○) H₂O at 50°C.

easily form a complex with a multivalent cation, especially for a cupric ion. For instance, the water absorbency for SA polymeric gel at the salt ionic strength between 0.001 and 0.01M reduces from 280 to 14 g water/g dry sample, 237 to 97 g water/g dry sample, and from 231 to 131 g water/g dry sample for CuCl₂, CaCl₂, and NaCl, respectively. This effect subsequently causes the volume of swelling gel to decrease abruptly as the salt solution reaches a proper concentration. In sum, the stronger the polymeric gel's ionic property, the more evident is the gel deswelling. Similarly, the polymer of a high HEMA content with high absorbency in the high ionic strength (>0.02M) can be explained with the same reason.

Effect of pH on Absorbency

The swelling behavior of the absorbent in various pH value solutions is investigated in this subsection.

The absorbency roughly maintains a constant from pH 3 to 11 (Fig. 10). This behavior can be accounted for by the buffer action of the sodium carboxylate group with an acid or base. The absorbency decreased rapidly from pH 3 to 2 and from pH 11 to 12, implying that the buffer action has disappeared. As excess acid or base exists, the absorbency will be decreased to zero at an extremely low pH value (<1). This occurrence is due to the carboxylate group on the polymeric chain having been reduced to the carboxylic acid group by the strong acid (HCl). However, at a high pH value (>14), the absorbency is decreased to 15 times, then increased as pH value is increased. This phenomena is explained by the increase of the hydration of the sodium ion.

A crosslinked poly(AA) (He 7) was prepared to confirm this buffer action. The water absorbency for the He 7 was also measured at various pHs (see Fig. 10, He 7). The result shown in Figure 10 for He 7 demonstrates that the water absorbency increases

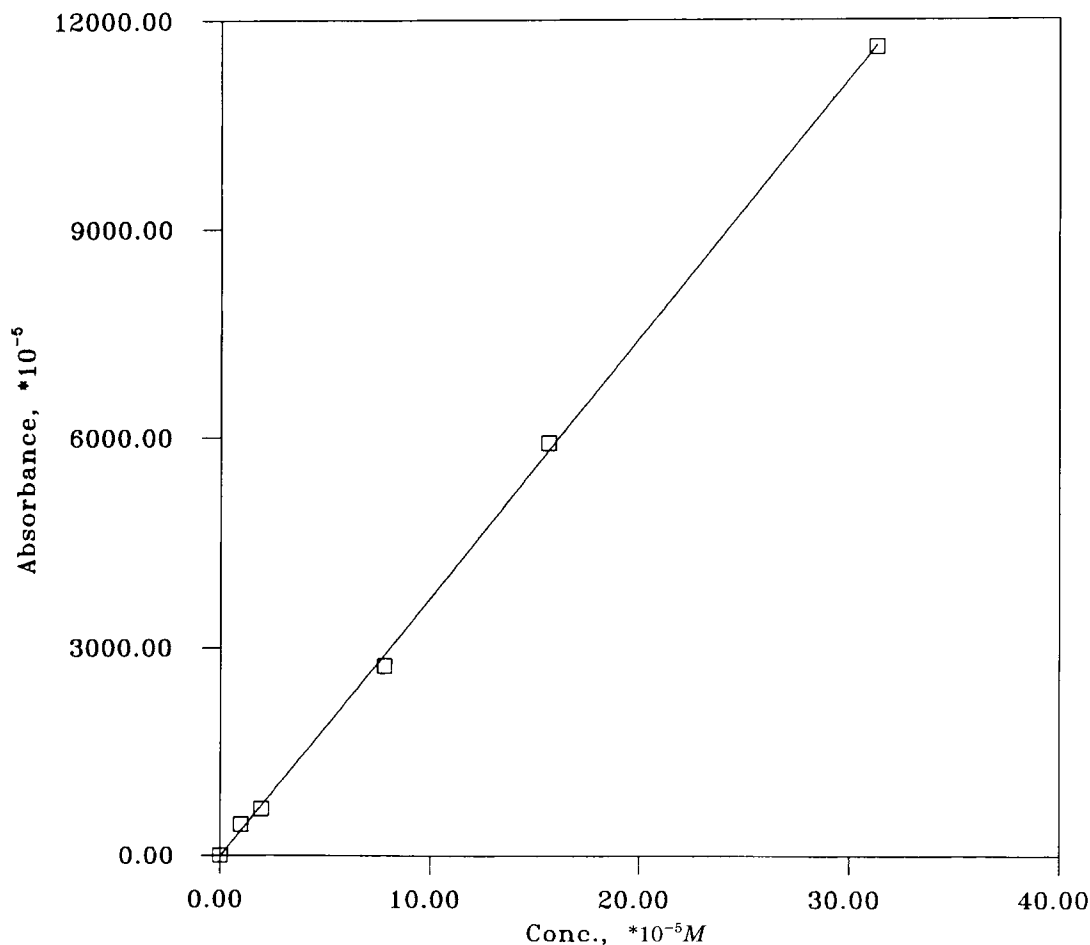


Figure 12 Relationship between FeCl_3 concentration and absorbance.

slowly until pH < 9 and decreased at pH 14. This result implies that the carboxylic acid group (COOH) on the poly(AA) is not completely dissociated at pH < 9 (charge density too low); it is neutralized by sodium hydroxide to produce the carboxylate group (COO^-) from pH 9 to 14 (buffer action region); and the water absorbency decreases rapidly at pH 14. This behavior is mainly due to the screening effect of the counterion on the polyanion chain (see Scheme 1).

Water Retention in High Temperature

Figure 11 shows the water retention capacity for the SA-HEMA copolymers at various temperatures. This figure indicates introducing a HEMA unit into an SA main chain to increase the water retention capacity is unsuccessful. From Figure 11, the difference at various temperatures is not clear at the initial period; however, a significant difference occurs over the long period. This is due to the bonded water

decreasing as the HEMA unit in the copolymer is increased, and the water is removed with difficulty.

Adsorption of Metal Ion

The cellulosic graft materials containing a nitrile or carboxylate group would be expected to remove metal ions from an aqueous solution. The removal of heavy metal ions from solution using cellulosic materials and polyelectrolytes has been reported.^{37,38}

Figure 12 shows the calibration curve of the ferric ion at the concentration of the range $0-30 \times 10^{-5} M$. According to eq. (1), Figure 13 shows the adsorbed amount of ferric ion for the pure poly(SA) gel (He 1) and SA-HEMA copolymeric gel (He 3) in various concentrations of ferric chloride. It is well known that the adsorption occurs at the carboxylate group for poly(SA); the SA-HEMA copolymeric gel can be accessed to use for ion adsorption. This figure demonstrates that a larger amount of ferric ion can be adsorbed by pure SA gel (He 1) than SA-HEMA

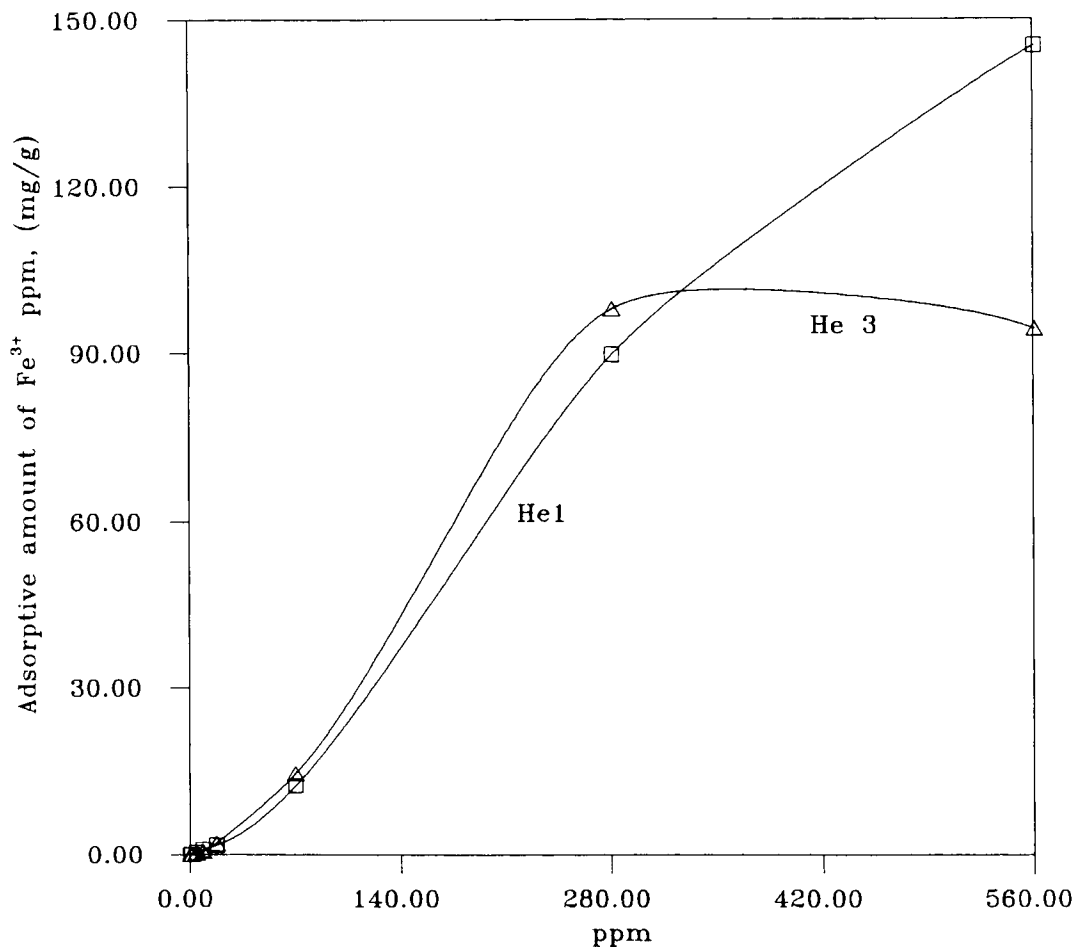


Figure 13 Adsorptive amount of Fe^{3+} in various FeCl_3 concentrations: (\square) He 1, (\triangle) He 3.

copolymeric gel (He 3). Furthermore, the saturated amount (100 ppm) of the ferric ion adsorbed by He 3 is reached as the concentration of ferric chloride reaches $5 \times 10^{-3}M$ (280 ppm).

CONCLUSION

The swelling behavior of the crosslinked poly(SA-co-HEMA) is related to the chemical structure, the chemical composition, and the nature of the external solution. The water absorbency decreases with an increase in the HEMA ratio in the copolymeric gel. The expansion degree of the network volume is lower when the nonionic characteristic of HEMA replaces some SA monomer units. For a given ionic strength, the absorbency of the SA-HEMA in multivalent saline solution decreases strongly in comparison with that in the monovalent saline solution. This behavior can be accounted for in terms of counterion con-

densation or screening effect for monovalent cations, as well as complexation for multivalent cations.

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