

Superabsorbent Polymeric Material. V. Synthesis and Swelling Behavior of Sodium Acrylate and Sodium 2-Acrylamido-2-methylpropanesulfonate Copolymeric Gels

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ABSTRACT: A series of xerogels based on sodium acrylate (SA), sodium 2-acrylamido-2-methyl propanesulfonate (NaAMPS), and *N,N*-methylene-bis-acrylamide (NMBA) are prepared by inverse suspension polymerization. The water absorbency and swelling behavior for these high absorbent polymers in deionized water and transition salt solutions are investigated. Experimental results indicated that the absorbency in deionized water increases with an increase of the NaAMPS content in the copolymeric gels, which is related to the degree of charge density of the network and the strength of hydrophilic group. The extent of crosslinking agent also influenced the swelling capacity because of elastic chain force of the polymer chain. The absorbency in chloride salt solutions decreases with an increase in the ionic strength of salt. But the decrease of absorbency is different in monovalent and multivalent salt solution. This behavior can be accounted for in terms of counterion condensation or screening effect for monovalent cations, as well as complexation for multivalent cations. The swelling rates in various salt solutions for these xerogels are also investigated. At last, SA-NaAMPS copolymeric gels were used for ion adsorption. But the result showed that the adsorptive amount of transition metal ions for SA-NaAMPS copolymeric gels was lower than that for pure poly(SA) gel. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 229–237, 1998

Key words: superabsorbent polymeric material; swelling behavior; sodium acrylate; sodium 2-acrylamido-2-methylpropanesulfonate copolymeric gels

INTRODUCTION

Superabsorbents can absorb a large amount of water, and the absorbed water is hardly removable even under some pressure. Superabsorbent materials are valuable in various products such as disposable diapers, feminine napkins, soil for agriculture, and horticulture, gel actuators, wa-

ter-blocking tapes, drug delivery systems, and absorbent pads etc.^{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}

The mechanism of absorption of water by hydrophilic polymers was explained in a nonionic network or ionic network structure by Flory.²⁴ Ogawa et al. studied the kinetics of the swelling of poly(sodium acrylate) with VTR system, calorimeter, and gravimetry techniques.²⁵

The swelling behavior for a series of various

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superabsorbent materials in water or saline solutions have been reported in previous studies, such as poly(sodium acrylate-hydroxyethyl methacrylate), poly(SA-HEMA)²⁶, poly[SA-3,3-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate], poly(SA-DMAPS)²⁷, poly(SA)²⁸, and poly[SA-3,3-dimethyl(acrylamidopropyl) ammonium propane sulfonate], poly(SA-DMAAPS).²⁹ The results, for example, for SA-HEMA xerogels showed that the water absorbency was reduced by introducing nonionic monomer HEMA content, and also showed that gel deswelling behavior occurred for divalent and trivalent chloride salt solutions.

Liu et al. studied the swelling equilibria of hydrogels with ionizable monomer 2-acrylamido-2-methylpropane sulfonic acid (AMPS) and dimethylacrylamide in water and in aqueous salt solutions.³⁰ Their results showed that the swelling capacity increases with increased charge density inside the gel and decreases with increasing salt concentration. Fanta et al. studied the graft copolymerization of AMPS onto starch to enhance the water absorbency.³¹

A series of crosslinked poly(SA-sodium 2-acrylamido-2-methyl propanesulfonate), poly(SA-NaAMPS), is prepared by inverse suspension polymerization in this article. The swelling behaviors for these xerogels in water and saline solution are also investigated.

EXPERIMENTAL

Materials

The materials used were purchased from Tokyo Kasei Industries Ltd. including acrylic acid (AA), 2-acrylamido-2-methyl propanesulfonic acid (AMPS), sodium hydroxide and *N,N'*-methylene-bis-acrylamide (NMBA). Sodium hydroxide, AMPS, and NMBA were used directly, and AA was distilled under reduced pressure before used. 4,4-Azo-bis(4-cyanovaleric acid) (ACVA) as an initiator and sorbitan monostearate (Span60) as an inverse suspension stabilizer were also purchased from Tokyo Kasei Industries Ltd. Methanol and cyclohexane were of reagent analytical grade.

Preparation of SA Monomer Solution

SA monomer was prepared as previously reported.²⁶

Neutralization of AMPS Monomer Solution (NaAMPS)

NaAMPS monomer solution was prepared by adding AMPS powder into sodium hydroxide solution. The molar ratio of sodium hydroxide to AMPS was 1:1 to approach complete neutralization.

Inverse Suspension Polymerization

A 300-mL four-neck separable flask equipped with reflux condenser, stirring rod, and thermometer was charged with 60 mL of cyclohexane and a 0.15 g sorbitan monostearate. The mixture was stirred until the sorbitan monostearate was dissolved (continuous phase).

The crosslinking agent, NMBA, and NaAMPS monomer solution were introduced into SA monomer solution and the mixture was stirred until the NMBA was dissolved completely. The monomer solution and a 0.15 g initiator, ACVA, (dispersion phase) were added to the reactor. Air was flashed from the reactor by introducing nitrogen until the entire process was completed. The stirrer speed was 250 rpm. The polymerization was carried out at 70°C for 4 h. After the reaction, the suspension solution was cooled and then precipitated by 800 mL of cold methanol. The product was filtered and washed several times with a mixture of water and methanol (1 : 9, by volume). The product was then dried in a vacuum oven at 120°C for 1 day. A white powdered polymer was obtained, and the yield was > 95%. The compositions of materials used are listed in Table I.

Measurement of Water Absorbency

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

Saturated Absorbency

The sample (50 mg) was immersed in an excess of deionized water or 0.9 wt % NaCl(aq) for at least 8 h to reach 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:

Table I Feed Compositions of SA-NaAMPS Xerogels

Sample No.	SA (g)	NaAMPS (g)	NMBA (g)	Yield (%)	Water Soluble (%)
AP1	20	0	0.07 (2.14×10^{-3})	95.7	5
AP2	19.95	0.11 (2.5×10^{-3})	0.07 (2.14×10^{-3})	97.2	3
AP3	19.85	0.331 (7.51×10^{-3})	0.07 (2.14×10^{-3})	98.1	4
AP4	19.7	0.661 (1.5×10^{-2})	0.07 (2.14×10^{-3})	99.2	3
AP5	19.55	0.992 (2.25×10^{-2})	0.07 (2.14×10^{-3})	97.6	7
AP6	19.4	1.324 (3.01×10^{-2})	0.07 (2.14×10^{-3})	99.4	5
AP7	19.4	1.324 (3.01×10^{-2})	0.05 (1.53×10^{-3})	98.3	4
AP8	19.4	1.324 (3.01×10^{-2})	0.10 (3.06×10^{-3})	99.3	3
AP9	19.4	1.324 (3.01×10^{-2})	0.14 (4.29×10^{-3})	96.8	4
AP10	19.4	1.324 (3.01×10^{-2})	0.21 (6.43×10^{-3})	98.7	2

Parentheses denote the molar ratio of each monomer to total monomer. The total weight of water is 60 g. ACVA, 0.1 g; Span60, 0.15 g.

$$Q_{eq} = \frac{\text{wt of swollen gel} - \text{wt of dried sample}}{\text{wt of dried sample}} \quad (1)$$

Kinetics of Swelling (Absorption Rate)

A technique based on DW (Demand Wettability) method was adopted. The technique was described in our previous report.²⁶

Absorbency in Various Saline Solutions

Fifty milligrams of dried samples were immersed in an excess of various saline solutions with different concentrations [NaCl(aq), CaCl₂(aq), FeCl₃(aq), CuCl₂(aq), CoCl₂(aq), NiCl₂(aq)] and remained there for at least 8 h. The sample was filtered with suction and weighed.

Adsorption of Transition Ions

A dried sample (50, 100, 200 mg) was put in a beaker, and CuCl₂, CoCl₂, and NiCl₂ solutions of various concentrations were introduced. After the equilibrium was reached, the sample was filtered with suction and the volume of residue water was recorded. The concentration of metal ions was determined by Jasco UVIDE-5 spectrophotometer. The adsorption amount was calculated from the relationship.

$$AD = \frac{C_i V_i - C_R V_R}{D}$$

where AD is the adsorptive moles of transition ions per gram sample, C_i is the initial concentra-

tion of transition ions, V_i is the initial volume of solution containing transition ions, C_R is the residue concentration of transition ions, V_R is the residue volume of the solution containing transition ions, and D is the weight of the dried sample.

RESULTS AND DISCUSSION

Effect of NaAMPS Content on Saturated Absorbency

The effect of NaAMPS content in the copolymeric gel on the water absorbency in deionized water or 0.9 wt % NaCl solution measured by the suction method is shown in Figure 1. This figure indicates

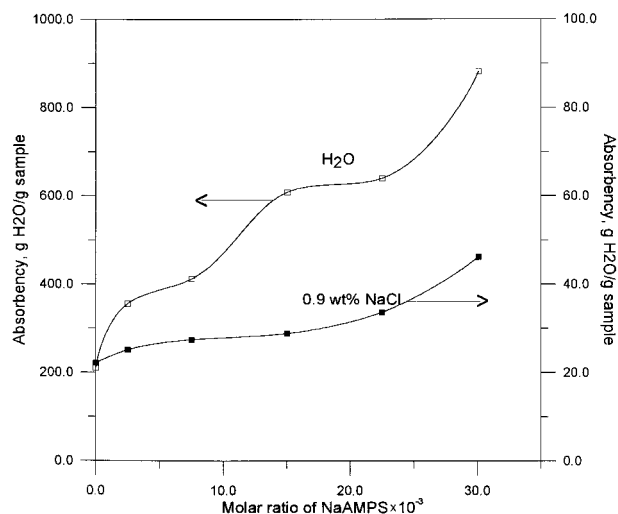


Figure 1 Effect of NaAMPS content on absorbency in deionized water and 0.9 wt % NaCl solution.

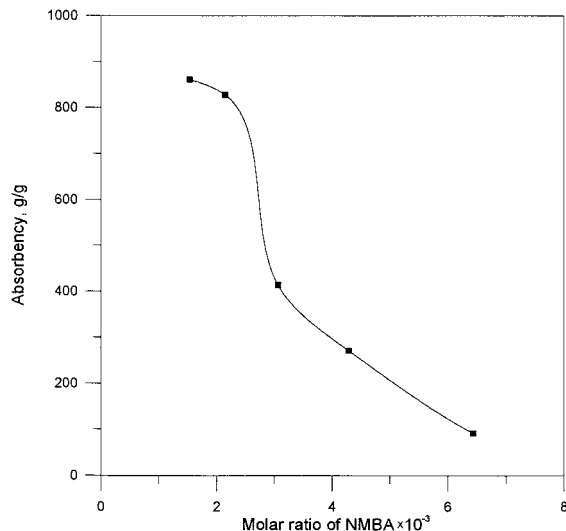


Figure 2 Effect of the extent of crosslinking agent on absorbency in deionized water.

that the water absorbency in deionized water is increased from 200 to 880 g water/g dry sample as the molar ratio of NaAMPS in the system is increased from 0 to 30×10^{-3} . The result shows that the water absorbency is increased with increasing NaAMPS content, and that the water absorbency of the copolymeric gel is much larger than that of poly(SA) in the experimental ranges. Water absorbency is improved by copolymerizing SA with only a small amount anionic monomer (NaAMPS). This describes that the sulfonate group in the copolymeric gel is more hydrophilic than the carboxyl group in the polymeric gel. The absorbency in 0.9 wt % NaCl(aq) is smaller than that in deionized water (also see Fig. 1). This result is primarily due to the decrease in the osmotic pressure (ionic pressure) difference between copolymeric gel and external solution at high ionic strength. This behavior is different from the swelling behavior of crosslinked poly(SA-sulfobetaine)s reported in our previous articles.^{27,29}

Considering the effect of the extent of crosslinking agent on the water absorbency (AP6–AP10), the gel absorbency conforms to the expected result, that is, the higher the extent of the crosslinking agent, the lower the water absorbency (Fig. 2). The copolymeric gel containing 2.73×10^{-2} molar ratio of NaAMPS exhibits an absorbency of 880 g water/g sample when the NMBA molar ratio is 1.53×10^{-3} (AP7), but the water absorbency decreases to 95 g water/g sample when the NMBA

molar ratio increases to 6.43×10^{-3} (AP10). This result obeys the Flory theory, which indicated that the elastic chain force of the gel network is only negative effect on water absorbency.²⁴ Hence, the more the extent of NMBA, the higher the crosslinking density of the gel, and the higher the elastic chain force and the lower the water absorbency.

Swelling Kinetics

The swelling kinetics of spherical polyacrylamide absorbents described in the model by Tanaka and Fillmore³² was generalized by Candau et al.,³³ who considered a single isolated gel sphere partly swollen and put in an excess of solvent. There is an osmotic pressure difference, and the gel swells to reach a new equilibrium volume. The swelling behavior of the absorbent was explained by water penetrating into the polymeric network. According to Buchholz, swelling kinetics for the absorbent is significantly influenced by factors such as swelling capacity, size distribution of powder particles, specific surface area, and apparent density of the polymer.¹⁰ Figure 3 shows the swelling kinetics for AP10 in water and in various saline solutions and shows that equilibrium water capacity for AP10 in various salt solutions increases in the order $\text{H}_2\text{O} > \text{NaCl} > \text{MgCl}_2 > \text{CuCl}_2 > \text{CaCl}_2 > \text{SrCl}_2$. The result obeys Flory's swelling theory for polymeric gels in salt solutions and conforms to our previous results.^{26–29} Hence, the equilibrium

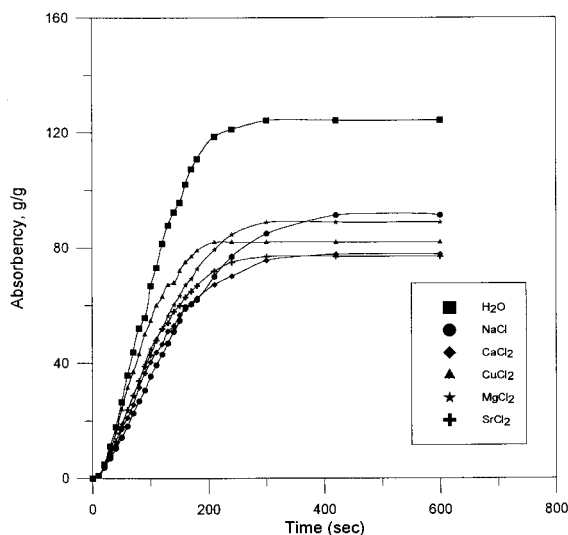


Figure 3 Absorptive rate in deionized water by DW method.

Table II Absorption Characteristics for SA-NaAMPS (AP10) Copolymeric Gel in Water and Various Salt Solutions

Solution	Initial Absorption Rate (g/min)		treq* (min)	Qeq (gH ₂ O/g)
	30 (s)	1–3 (min)		
H ₂ O	22.4	38	4.0	124.3
NaCl	13.8	22	7.0	91.3
CaCl ₂	17.2	21	7.0	77.7
CuCl ₂	19.4	24	3.5	81.9
MgCl ₂	18	25	5.0	88.8
SrCl ₂	16	22	4.0	77

*treq, time required to approach equilibrium.
The ionic strength of the salt solution is 0.0025 M.

swelling tendency for this gel is not affected by the content of NaAMPS incorporated into the poly(SA) gel in these salt solutions. The initial absorption rate for this gel in water at the 30-s period is faster than in salt solutions (see Table II). This phenomenon reveals that the initial swelling process is primarily due to the water penetrating into the polymeric gel through capillarity and diffusion. At this 30-s period, the absorption rate for the gel in NaCl solution is lower than that in divalent cationic salt solutions. This may be attributed to the common ion effect (Na⁺) between the polymeric gel and external salt solution. However, the absorption rate at the period of 1–3 min is faster in water than that in various salt solutions. This result indicates that the swelling process in this period is due to the reduction of osmotic pressure difference between polymeric gel and external solution, ion exchange, and complexity (for divalent cationic salt solutions). The time required for equilibrium absorption (*t_{req}*) is only 3.5 min in CuCl₂ solution, but 4 min in water. The *t_{req}* value, thus, depends not only on swelling absorption rate but also on the equilibrium swelling capacity.

According to Yao and Zhou,³⁴ the swelling rate can be described by the following equation:

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

where *Q_{eq}* is equilibrium absorbency, *Q* is the characteristic absorbency, *K* is the swelling kinetic constant, and *T* is the characteristic swelling time. From eq. (2), the characteristic swelling

time is defined at $Q = 0.632 Q_{eq}$. Table III presents the influence of sample AP10 in various saline solutions on the characteristic swelling time (*T*), on the swelling kinetic constant (*K*), and on the swelling capacity (*Q*). The table reveals *T* was decreased with the increasing of the *K* value, and the swelling kinetic constant (*K*) is largest in CuCl₂ salt solution.

Effect of Salt Solution on Water Absorbency

The swelling behavior of absorbents is significantly affected by the factors of external solution, such as their charge valences and salt concentrations. The effect of salt solutions of various concentrations on the water absorbency for a series of SA–NaAMPS copolymeric gels is investigated in this section. Figures 4, 5, and 6 show the absor-

Table III Influence of AP10 in Water and Various Salt Solutions on Swelling Characteristic Time (*T*), Swelling Kinetic Constants (*K*), and Swelling (*Q*)

Solution	AP10		
	<i>T</i> (min)	<i>K</i> (min ⁻¹)	<i>Q</i> * (gH ₂ O/g)
H ₂ O	4.32	0.886	78.6
NaCl	7.79	0.451	57.7
CaCl ₂	5.53	0.606	49.1
CuCl ₂	3.23	1.053	51.8
MgCl ₂	5.05	0.690	56.1
SrCl ₂	4.00	0.836	48.7

* $Q = 0.632 Q_{eq}$.

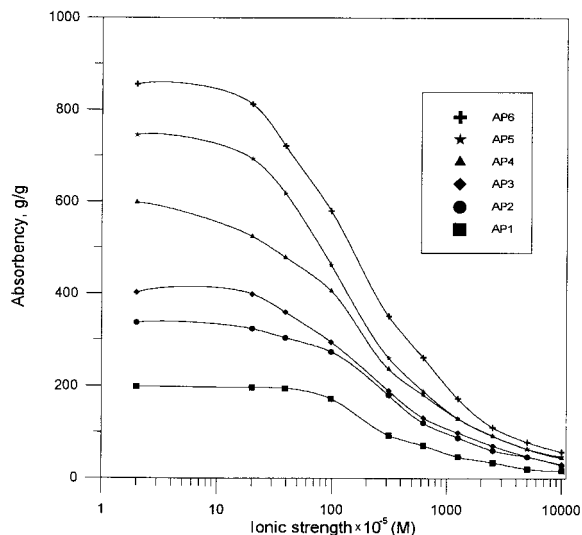


Figure 4 Water absorbency of poly(SA-NaAMPS) gels in NaCl aqueous solutions with various ionic strengths.

bency of a series of SA-NaAMPS copolymeric absorbents as a function of ionic strength in NaCl, CaCl₂, and FeCl₃ solution, respectively. These figures show that absorbency in various salt solutions decreases with increasing ionic strength of salt solution for copolymeric gels (AP1-AP6). Figures 5 and 6 show water absorbency vs. ionic strength of multivalent cation salt solution. Absorbency for these gels does not change signifi-

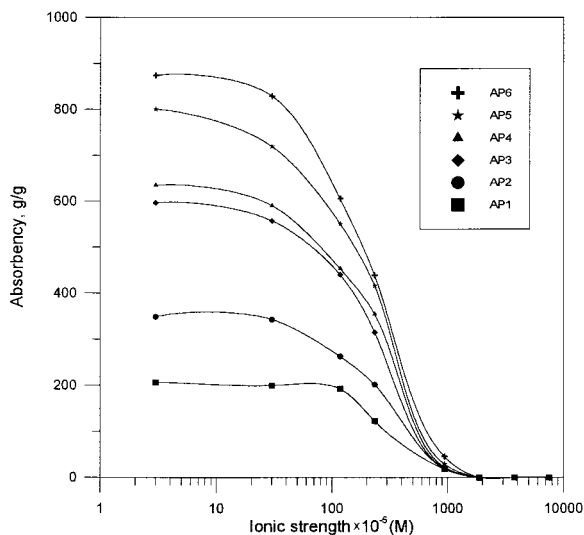


Figure 5 Water absorbency of poly(SA-NaAMPS) gels in CaCl₂ aqueous solutions with various ionic strengths.

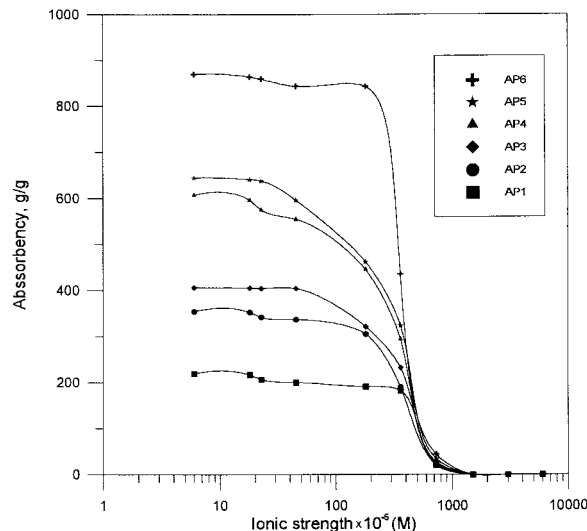


Figure 6 Water absorbency of poly(SA-NaAMPS) gels in FeCl₃ aqueous solutions with various ionic strengths.

cantly when polymers were immersed into dilute salt solution ($<10^{-4}M$). However, the absorbencies converge to zero when those gels were immersed into concentrated salt solution ($0.01M$). The Figures also show that the curve for decreasing water absorbency for monovalent cation salt solution (Fig. 4) is flatter than curves for divalent (Fig. 5) and trivalent (Fig. 6) cation salt solutions. For monovalent cation salt solution, the decrease in absorbency could be explained by the osmotic pressure difference between the polymeric network and external solution. But for multivalent cations, it can be described by complexation.²⁷⁻²⁹

Figure 7 shows the result of immersing xerogel (AP4) in various salt solutions, i.e., NaCl, CaCl₂, and FeCl₃, with various ionic strengths. The results demonstrate the tendency to be in various orders in different ranges of varying ionic strengths. The result shown in Figure 7 demonstrate that the water absorbency for AP4 has the tendency at various ranges of ionic strength, i.e., $Fe^{3+} > Ca^{2+} > Na^+$, and $Na^+ > Ca^{2+} > Fe^{3+}$ in the ionic strength of $3 \times 10^{-3}M$, and $3 \times 10^{-3}M$ to $1M$, respectively. Similar results were also observed from our previous report²⁶ and conformed to the formation constant of complexation. The results also show that the absorbencies of the polymeric gels sharply decrease in the range of the ionic strength from 5×10^{-4} to $0.01M$ for the multivalent salt solution. We also found the

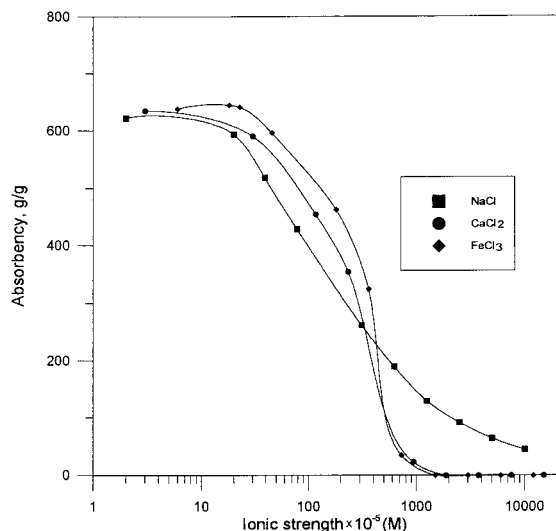


Figure 7 Water absorbency of sample AP4 in NaCl, CaCl₂, and FeCl₃ aqueous solutions with various ionic strengths.

phenomenon that the absorbent swelled firstly and then deswelled during the xerogels were immersed into high concentration multivalent cation salt solution. This phenomenon corresponds to the fact that the swelling step is the water penetrating into the network first by osmotic pressure difference, and the deswelling step is related to the exchange of cations. The dried sample that had once been immersed in high-concentration

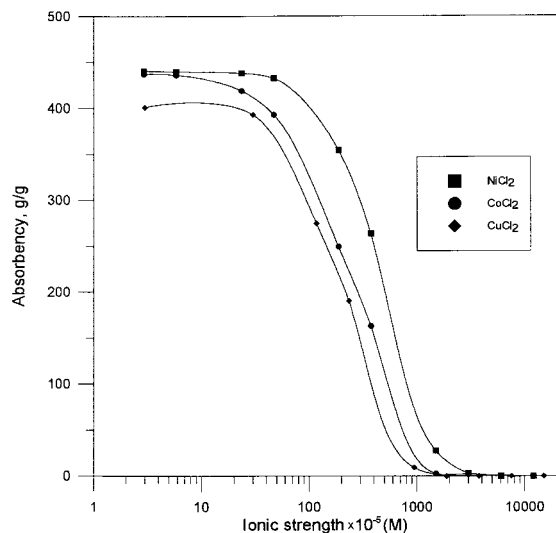


Figure 8 Water absorbency of sample AP5 in CuCl₂, CoCl₂, and NiCl₂ aqueous solutions with various ionic strengths.

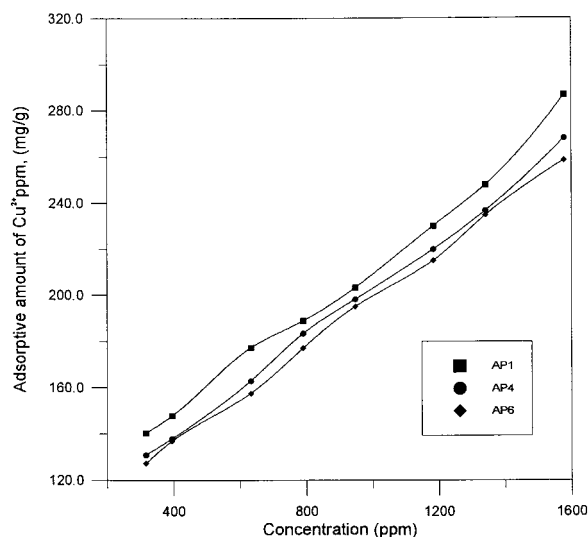


Figure 9 Adsorptive amount of Cu²⁺ ion in various CuCl₂ concentrations.

multivalent cation solutions will be never re-swelled in water again. This occurrence can be attributed to the increase of crosslinking density arising from the complexation of the multivalent cations with carboxylate groups. The above behavior was also observed in our previous reports (SA-HEMA system).²⁶⁻²⁸

Castel et al.¹⁶ reported that calcium ion can decrease the swelling value for a hydrolyzed starch graft polyacrylonitrile, due to the complexing ability of the carboxylated group inducing intermolecular and intramolecular complex formation. In our previous study,²⁶ it was found that water absorbency for poly(SA) in CoCl₂, CuCl₂, and NiCl₂ aqueous solution was in the order Co²⁺ = Ni²⁺ = Cu²⁺ and Co²⁺ > Ni²⁺ > Cu²⁺ in the ionic strength of $6.25 \times 10^{-4} M$ and 6.25×10^{-4} to $2.0 \times 10^{-2} M$, respectively. This result conforms to the formation constant of complexation presented in a previous report.²⁶ To understand whether the NaAMPS component influences the complexing ability of poly(SA) in transition metal solutions, the gel AP5 was respectively immersed into these three salt solutions. The results shown in Figure 8 indicate that the absorbency rapidly decreases from 400, 420, and 440 g H₂O/g sample to 0, 0, and 20 g H₂O/g sample for AP5 gel in CuCl₂, CoCl₂, and NiCl₂ at ionic strengths of 3.0×10^{-4} and 2×10^{-2} , respectively. The results also show that absorbencies are in the order Ni²⁺ > Co²⁺ > Cu²⁺ for NiCl₂, CoCl₂, and NiCl₂, respectively. This result differs from poly(SA) gel

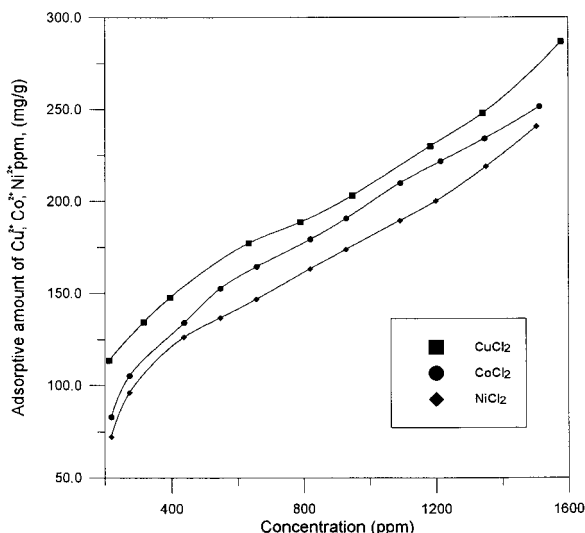


Figure 10 Adsorptive amount of Cu^{2+} , Co^{2+} , and Ni^{2+} ions in various CuCl_2 , CoCl_2 , and NiCl_2 concentrations.

in the order of CoCl_2 and NiCl_2 solution. This difference may result from the sulfonate group introduced into the gel. Hence, the complexing ability of carboxylate group with transition metal ions could be affected by the sulfonate group.

Adsorption of Transition Metal Ions

Figure 9 shows the adsorbed amount of Cu^{2+} ion for pure poly(SA) gel (AP1) and SA-NaAMPS copolymeric gels (AP4 and AP6) in various concentrations of CuCl_2 . It is well known that the adsorption occurs at the carboxylate group for poly(SA); the SA-NaAMPS copolymeric gels can be used to access ion adsorption ability when NaAMPS component was added to SA gel. This figure demonstrates that a larger amount of Cu^{2+} ion can be adsorbed by pure poly(SA) than SA-NaAMPS copolymeric gels (AP4 and AP6). The adsorptive amount of Cu^{2+} ion was increased with the initial concentration of aqueous solution.

The amount of transition metal ions absorbed was compared in various concentrations of CuCl_2 , CoCl_2 , and NiCl_2 solutions, respectively. The results shown in Figure 10 shows that the adsorptive amount of transition metal ions was in the order $\text{Cu}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+}$. The result shown in Figure 10 conforms to that shown in Figure 8.

CONCLUSION

The swelling behavior of these absorbent is related to their structure, their chemical composi-

tion, and the nature of external solutions. The water absorbency of poly(SA) series in deionized water or in 0.9 wt % NaCl solution would be effectively improved by copolymerizing SA with a small amount of anionic monomer NaAMPS. The absorption rate is effectively dependent on the external solutions and the tendency is in the order of $\text{H}_2\text{O} > \text{divalent salt solutions} > \text{monovalent salt solution}$. The absorbency of poly(SA-NaAMPS) in multivalent saline solution strongly decreases in comparison with that in the monovalent saline solution. The deswelling behavior can be attributed to the complexation of multivalent cations with the carboxylate group on the polymeric chain.

REFERENCES

1. F. L. Buchholz, *CHEMTECH*, **38** (1994, September); F. L. Buchholz and N. A. Peppas, Ed., *Superabsorbent Polymers: Science and Technology*, ACS symposium series 573, American Chemical Society, Washington, DC, 1994.
2. T. Sakiyama, C. H. Chu, T. Fujii, and T. Yano, *J. Appl. Polym. Sci.*, **50**, 2021 (1993).
3. M. Yoshida, M. Asano, and M. Kumakura, *Eur. Polym. J.*, **25**, 1197 (1989).
4. T. Shiga, Y. Hirose, A. Okada, and T. Kurauchi, *J. Appl. Polym. Sci.*, **44**, 249 (1992).
5. T. Shiga, Y. Hirose, A. Okada, and T. Kurauchi, *J. Appl. Polym. Sci.*, **47**, 113 (1993).
6. K. Hogari and F. Ashiya, in *Advances in Superabsorbent Polymers*, American Chemical Society, Washington, DC, 1994.
7. P. H. Ericksen, H. V. Nguyen, B. Oczkowski, and T. A. Olejnik, *Eur. Pat.* 40087 (1981).
8. T. Kobayashi, *Kobunshi*, **36**, 612 (1987).
9. N. W. Taylor, G. F. Fanta, W. M. Doane, and C. R. Russell, *J. Appl. Polym. Sci.*, **22**, 1343 (1978).
10. R. C. Burr, G. F. Fanta, and W. M. Doane, *J. Appl. Polym. Sci.*, **24**, 1384 (1979).
11. G. F. Fanta, R. C. Burr, and W. M. Doane, and C. R. Russell, *J. Appl. Polym. Sci.*, **27**, 2713 (1982).
12. Y. Kejun and W. Benlian, *J. Appl. Polym. Sci.*, **41**, 3079 (1990).
13. G. F. Fanta, R. C. Burr, and W. M. Doane, *J. Appl. Polym. Sci.*, **24**, 2015 (1979).
14. M. Yoshinobu, M. Morita, and I. Sakata, *J. Appl. Polym. Sci.*, **45**, 805 (1992).
15. H. T. Lokhande, P. V. Varadarjan, and V. Iyer, *J. Appl. Polym. Sci.*, **45**, 2031 (1992).
16. D. Castel, A. Ricard, and R. Audebert, *J. Appl. Polym. Sci.*, **39**, 11 (1990).
17. I. Zoda, *Functional Materials*, **6**, 76 (1986).

18. K. Isomi, *Jpn. Kokai, Tokyo Koho JP*, 56707 (1989).
19. K. Nagasuna, N. Suminaga, K. Kimura, and T. Shimomura, *Jpn. Kokai, Tokyo Koho JP*, 126314 (1989).
20. H. Imada and M. Fujikawa, *Jpn. Kokai, Tokyo Koho JP*, 141938 (1989).
21. A. Fujio, T. Komae, and Y. Yutaka, *Jpn. Kokai, Tokyo Koho JP*, 210463 (1989).
22. S. Yada, T. Shibano, and K. Ito, *Jpn. Kokai, Tokyo Koho JP*, 215801 (1990).
23. M. Sano, H. Mikamo, T. Suehiro, and N. Wakabayashi, *Jpn. Kokai, Tokyo Koho JP*, 258839 (1991).
24. P. J. Flory, *Principle of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
25. I. Ogawa, H. Yamano, and K. Miyogawa, *J. Appl. Polym. Sci.*, **47**, 217 (1993).
26. W. F. Lee and R. J. Wu, *J. Appl. Polym. Sci.*, **62**, 1099 (1996).
27. W. F. Lee and R. J. Wu, *J. Appl. Polym. Sci.*, **64**, 1702 (1997).
28. W. F. Lee and P. L. Yeh, *J. Appl. Polym. Sci.*, **64**, 2371 (1997).
29. W. F. Lee and P. L. Yeh, *J. Appl. Polym. Sci.*, to appear.
30. X. Liu, T. Zhen, and H. Ou, *Macromolecules*, **28**, 3813 (1995).
31. G. F. Fanta, *J. Appl. Polym. Sci.*, **24**, 2015 (1979).
32. T. Tanaka and D. J. Fillmore, *J. Chem. Phys.*, **70**, 1214 (1979).
33. S. T. Candau, J. Bastide, and M. Delsanti, *Adv. Polym. Sci.*, **41**, 27 (1982).
34. K. J. Yao and W. J. Zhou, *J. Appl. Polym. Sci.*, **53**, 1533 (1994).