

Superabsorbent Polymeric Materials. IV. Swelling Behavior of Crosslinked Poly[sodium acrylate-*co*-*N,N*-dimethyl(acrylamidopropyl) ammonium propane sulfonate] in Aqueous Salt Solution

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ABSTRACT: A series of xerogels based on sodium acrylate (SA), *N,N*-dimethyl(acrylamidopropyl) ammonium propane sulfonate (DMAAPS), and *N,N'*-methylene bisacrylamide (NMBA) were prepared by inverse suspension polymerization. The water absorbency or swelling behavior for these xerogels in water or various saline solutions was investigated. Results obtained from this study revealed a water absorbency of 721 g H₂O/g sample in deionized water and 83 g H₂O/g sample in 0.9 wt % NaCl solution for a gel containing a 1.50×10^{-2} molar fraction of DMAAPS. The absorbency in the chloride salt solutions decreased with an increase in the ionic strength of the salt. For the same ionic strength of various salt solutions, the swelling amount had the following tendency: $\text{Co}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+}$ for the higher ionic strength of 2.44×10^{-5} – 1.8×10^{-2} M. The Co^{2+} , Ni^{2+} , and Cu^{2+} solutions induce approximately the same degree of swelling at the lower ionic strength of $< 2.44 \times 10^{-5}$ M. The pH effect on the water absorbency for these xerogels was also investigated. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 499–507, 1997

Key words: superabsorbent; sodium acrylate; *N,N*-dimethyl(acrylamidopropyl) ammonium propane sulfonate; water absorbency; xerogel

INTRODUCTION

Superabsorbents can absorb a large amount of water compared with general water absorbing materials in which the absorbed water is hardly removable even under some pressure. Because of their excellent characteristics, superabsorbents are widely used in many applications (such as disposable diapers, feminine napkins, soil for agriculture and horticulture, gel actuators, water-blocking tapes, medicine for the drug delivery system, and absorbent pads) in which water absor-

bency or water retention is important.^{1–8} Modification of these absorbent polymers was carried out by some researchers to enhance their absorbency, gel strength, and absorption rate.^{9–23}

Gross reported that xerogellents are an extension of water-soluble polymer technology. There are five types of hydrophilic polymers: ampholytic, anionic, cationic, nonionic, and zwitterionic. The polyampholytes and zwitterionic polymers have the potential to swell more in salt solutions than in pure water.²⁴ The mechanism of water absorption for hydrophilic polymers was explained in nonionic network or ionic network structure by Flory.²⁵ Ogawa et al. studied the kinetics of the swelling of poly(sodium acrylate) by picture analysis with a microscope-Video-Television-Recorder system, calorimetry, and gravimetry techniques.²⁶

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The swelling behaviors of two series of cross-linked poly(sodium acrylate-*co*-hydroxyethyl methacrylate), poly(SA-HEMA), and poly[sodium *co*-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate], poly(SA-DMAAPS), absorbents were reported in our previous articles.^{27,28} The results for poly(SA-HEMA) showed that the gel exhibited a deswelling behavior in divalent and trivalent chloride salt solutions, and the swelling amount had a tendency as follows: $\text{LiCl} = \text{NaCl} = \text{KCl}$; $\text{CaCl}_2 < \text{SrCl}_2 < \text{BaCl}_2$; and $\text{Fe}^{3+} > \text{Ca}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+}$. But the results for poly(SA-DMAAPS) showed that the water absorbency exhibited values of 1435 g $\text{H}_2\text{O}/\text{g}$ sample and 96 g $\text{H}_2\text{O}/\text{g}$ sample in deionized water and 0.9 wt % NaCl solution, respectively. A gel containing a 1.88×10^{-3} molar ratio of *N,N'*-methylene bisacrylamide (NMBA) was used in the polymerization, and the swelling amount in the presence of various salt solutions had following tendency: $\text{Na}^+ > \text{Fe}^{+3} > \text{Al}^{+3} > \text{Ca}^{+2}$ for the higher ionic strength of 5×10^{-3} – $2 \times 10^{-2} M$ and $\text{Na}^+ > \text{Fe}^{+3} > \text{Ca}^{+2} > \text{Al}^{+3}$ for the lower ionic strength of $< 2 \times 10^{-4} M$. These orders, which are related to the complexing ability of metallic cation and carboxylate group in the polymeric chains, were confirmed.

The superabsorbent polymers containing zwitterionic monomer or sulfobetaine monomer are not found in the literature, though some ampholytic monomers and cationic monomers containing absorbent polymers were studied.^{29–35} A series of sulfobetaine monomers and corresponding cationic monomers, as well as were prepared, and the solution behavior of these polymers in the aqueous salt solutions was investigated in our laboratory.^{36–40} Thus, a series of crosslinked poly[sodium acrylate(SA)-*co*-*N,N'*-dimethyl(acrylamidopropyl) ammonium propane sulfonate (DMAAPS)] xerogels were prepared by inverse suspension polymerization, and the swelling behaviors of these xerogellants at various ratios of DMAAPS/SA in aqueous salt solutions were investigated and are compared in this article with the swelling behaviors of poly(SA-DMAAPS) gels.

EXPERIMENTAL

Materials

The materials used in this study were purchased from Tokyo Kasei Industries, Ltd., including acrylic acid (AA), dimethylaminopropylacrylamide, sodium hydroxide, propane sultone, and *N,N'*-methylene bisacrylamide (NMBA). Sodium

hydroxide, propane sultone, and NMBA were used directly, and the other materials were distilled under reduced pressure before use.

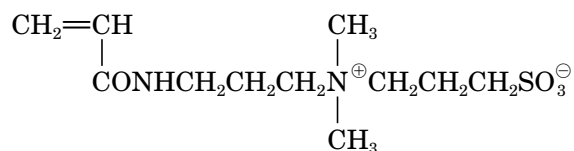
4,4'-Azobis(4-cyanovaleric acid) (ACVA) as an initiator and sorbitan monostearate (Span 60) as an inverse suspension stabilizer were also purchased from Tokyo Kasei Industries, Ltd. Acetone was directly distilled and dried over anhydrous calcium chloride. Methanol and cyclohexane were of the analytical grade. Deionized water was used in the polymerization system.

Preparation of Sodium Acrylate (SA) Monomer Solution

The SA monomer was prepared as previously reported.²⁷

Synthesis of DMAAPS

The monomer DMAAPS was prepared as described previously.³⁸ Its yield was 91.23%, and its melting point was 105°C. The structure of DMAAPS as follows:



Inverse Suspension Polymerization

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

The appropriate amounts of the DMAAPS monomer and the crosslinking agent NMBA (0.07 g, wt % based on total monomer) were introduced into the SA monomer solution, and the mixture was stirred until the NMBA was dissolved completely. The monomer solution and 0.02 g initiator (ACVA, dispersion phase) were introduced into the reactor. Air was flushed from the reactor by adding nitrogen until the entire process was completed. The stirrer speed was maintained at 250 rpm. The polymerization was set at 70°C for 4 h. After the reaction, the suspension solution was cooled and then precipitated by 800 ml cold meth-

anol under stirring. The product was filtered and washed several times by the mixture of water and methanol (1 : 9 in volume). The product was then dried in a vacuum oven at 120°C for 1 day. The white powdered polymer was obtained, and the yield was 94–98%.

Measurement of Water Absorbency

The samples were dried in a vacuum oven at 60°C for 1 day before any tests. All of the samples were used with a particle size in the range of 60–100 mesh. The saturated or equilibrium absorbency, Q_{eq} , measured by the suction filtration method or tea bag method has been described elsewhere.^{27,28}

Swelling Behaviors in Various Salt Solution Concentrations

Fifty milligrams of dried samples were immersed in an excess of various saline solutions with different concentrations ($\text{LiCl}_{(aq)}$, $\text{NaCl}_{(aq)}$, $\text{KCl}_{(aq)}$, $\text{MgCl}_{2(aq)}$, $\text{CaCl}_{2(aq)}$, $\text{SrCl}_{2(aq)}$, $\text{BaCl}_{2(aq)}$, $\text{FeCl}_{3(aq)}$, $\text{CoCl}_{2(aq)}$, $\text{NiCl}_{2(aq)}$, and $\text{CuCl}_{2(aq)}$) and remained there for at least 8 h. The samples were filtered with suction and weighed.

Effect of Various pH Solutions on Water Absorbency

The effect of various pH solutions on water absorbency was determined in the same way the water absorbency was measured in various saline solutions. The pH values of the external solution were adjusted by adding HCl solution or NaOH solution in water.

RESULTS AND DISCUSSION

Characterization of SA–DMAAPS Copolymeric Gels

The elemental analysis was performed to determine the content of sulfur in the SA–DMAAPS copolymeric gels. The data shown in Table I imply that the actual compositions conform to the feed compositions. Table I also shows that the percentages of water solubles of the said copolymeric gel range from 4 to 7 and that the saturated absorbencies increase with additions to the sulfur content in the copolymeric gels.

Effect of DMAAPS Content on Saturated Absorbency

The swelling behavior of the absorbents depends on the nature of the polymer and the characteristics of the external solution. The polymer's nature involves several parameters such as the charge, ionic content, and crosslinking density. The characteristics of the external salt solution include the charge number and the ionic strength.

Buchanan et al.⁴¹ have plotted the water retention of polyacrylate networks as a function of the degree of neutralization, and a swelling maximum was also observed. It was suggested that the chain expanded to such an extent that the distance between neighboring charges increased owing to repulsion effects between the charges.

The effect of the DMAAPS content in the copolymeric gel on the water absorbency measured by the suction and tea bag methods is shown in Figure 1. The results show that the water absorbency increases with the molar fraction of DMAAPS. The maximum value appears at the molar fraction of 1.50×10^{-2} , and the water absorbency of the copolymeric gel is larger than poly(SA) (sample DM0) in the experimental ranges. This occurrence implies that the water absorbency is efficiently improved, thereby copolymerizing SA with some amount of zwitterionic monomer (DMAAPS). Similar behavior was also observed in SA-co-DMAPS copolymeric gel systems,²⁸ but the maximum water absorbency for poly(SA-DMAPS) gel appeared at a 1.88×10^{-3} molar ratio of DMAPS in the copolymeric gel. This molar ratio of DMAPS in the copolymeric gel is lower than that of DMAAPS in the presented copolymeric (SA-DMAAPS) gel. This occurrence obviously indicates that the DMAPS component effects a more pronounced improvement in the water absorbency for this series of gels. The water absorbency shown in Figure 1 exhibits a maximum value at 1.5×10^{-2} molar fraction of DMAAPS for the said copolymeric gel series. The reason for this phenomenon was explained in our previous report.²⁸

A comparison of the suction filtration and tea-bag methods reveals an extreme difference in their absorbencies (Fig. 1). This occurs because the absorbed water tends to accumulate in the interstices of particles when the tea bag method is adopted, but water is lost when suction filtration (corresponding to gel bearing force) is used.²⁷

Figure 2 shows the water absorbency in 0.9 wt % $\text{NaCl}_{(aq)}$ as a function of DMAAPS content for

Table I Characterization of SA-DMAAPS Copolymer Gels

Sample No.	Feed Composition			Elemental Analysis of Sulfur		Absorbency (g H ₂ O/g sample)	Water Solubles (%)
	SA (g)	NMBA (g)	DMAAPS (g)	Calculation (%)	Found (%)	Tea Bag Method	
DM0	19.911	0.07	0	—	—	386	4
DM1	19.874	0.07	0.111 ($1.88 \times 10^{-3} M$)	0.06	0.01	460	5
DM2	19.836	0.07	0.221 ($3.75 \times 10^{-3} M$)	0.12	0.12	523	7
DM3	19.761	0.07	0.444 ($7.51 \times 10^{-3} M$)	0.25	0.20	580	5
DM4	19.612	0.07	0.886 ($15.0 \times 10^{-3} M$)	0.49	0.45	721	7
DM5	19.462	0.07	1.329 ($22.5 \times 10^{-3} M$)	0.73	0.72	650	7

Quantity of water = 60 g; amount of monomer = 0.213 mol.

the copolymeric gels. The results are similar to those in deionized water. The water absorbency in 0.9 wt % NaCl solution increases from 22 g H₂O/g sample for poly(SA) gels to 51 g H₂O/g sample as measured by the suction filtration method and from 45 g H₂O/g sample to 83 g H₂O/g sample when measured by the tea bag method at a 1.50×10^{-2} molar fraction of DMAAPS for the copolymeric gels. These results conform to our expectation that the zwitterionic (sulfobetaine) monomer could improve the water absorbency in salt solution. This finding is mainly attributable to the increase in the osmotic pressure difference between the polymeric gel and the external solution with high ionic strength. In other words, the difference in osmotic pressure in the same salt concentration for poly(SA) gel is smaller than that for SA-DMAAPS copolymeric gel because the

dissociated sodium ion can bind to the sulfonate group on the DMAAPS chain and reduce the concentration gradient of the free sodium ion.^{37,39}

Effect of Salt Solution on the Water Absorbency

The swelling behavior of sodium acrylate absorbents can be significantly affected by various factors in the external salt solution such as its valency and concentration. SA-HEMA copolymeric gels have been discussed in a previous article²⁷ that demonstrated that the expansion of the gel network decreases because the repulsive counterion (carboxylate group) on the polymeric chain is shielded by the bound ionic charge (cation) and that the osmotic pressure difference between the gel network and the external solution decreases

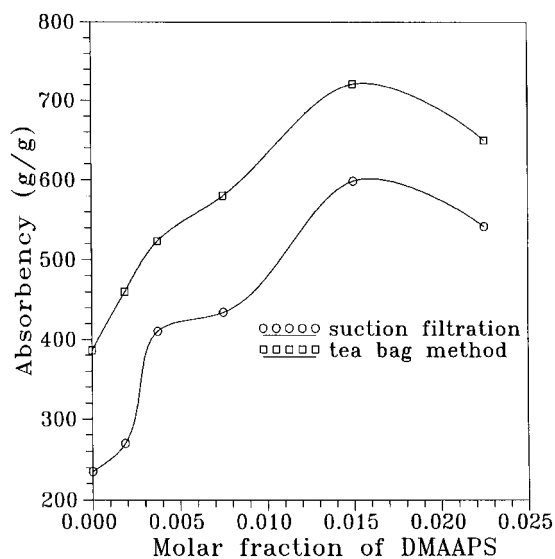


Figure 1 Effect of DMAAPS content on absorbency in deionized water.

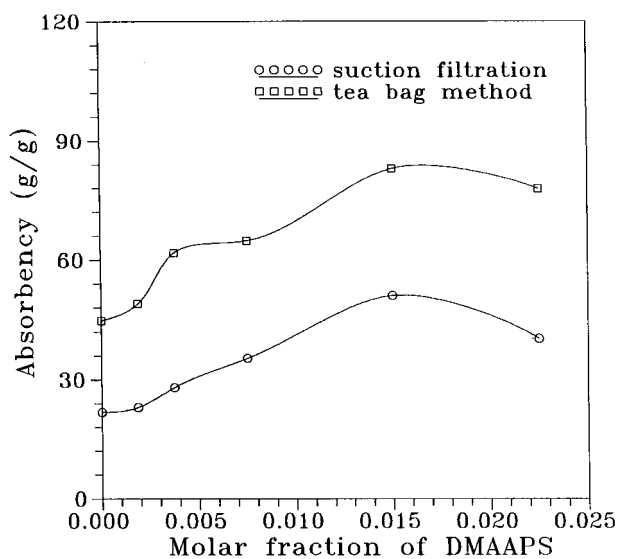


Figure 2 Effect of DMAAPS content on absorbency in 0.9 wt % NaCl_(aq).

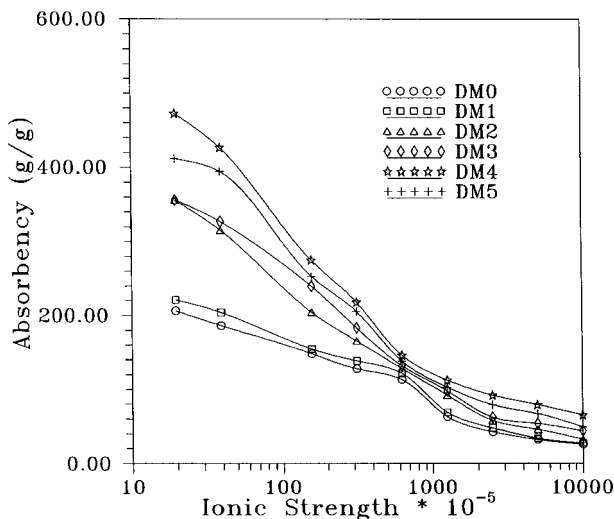


Figure 3 Water absorbency of crosslinked poly(SA-co-DMAAPS) gel in NaCl aqueous solutions of various ionic strengths.

with the increase in the ionic strength of the salt solution.²⁷

We investigated the effect of varying the salt solution concentration on water absorbency for a series of SA-DMAAPS copolymeric gels. Figures 3, 4, and 5 show the typical absorbency of a series of SA-DMAAPS copolymeric absorbents as a function of the ionic strength for a series of salt solutions. The figures reveal that the water absorbency in various salt solutions decreases with an increase of the ionic strength of the salt solutions

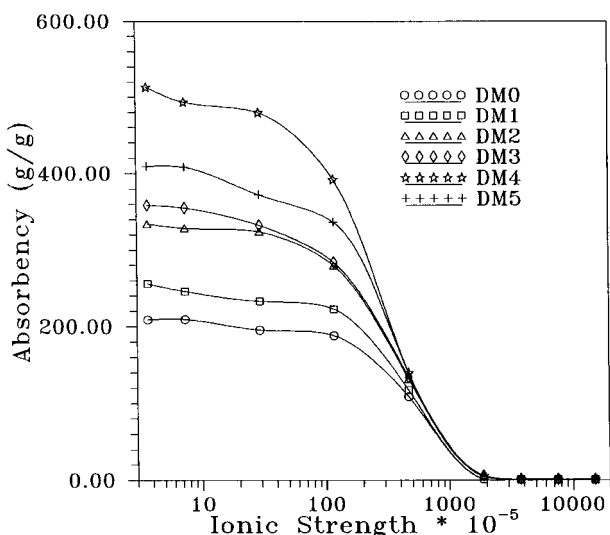


Figure 4 Water absorbency of crosslinked poly(SA-co-DMAAPS) gel in CaCl₂ aqueous solutions of various ionic strengths.

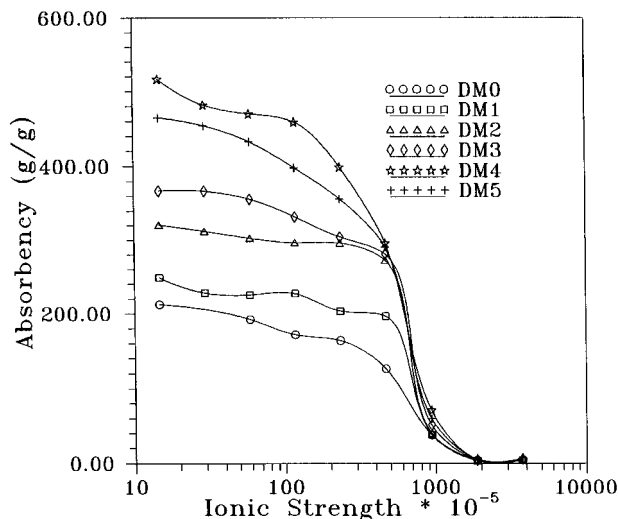


Figure 5 Water absorbency of crosslinked poly(SA-co-DMAAPS) gel in FeCl₃ aqueous solutions of various ionic strengths.

and that the water absorbency in various solutions for a series of SA-DMAAPS copolymeric gels is enhanced by the addition of the zwitterionic (sulfobetaine) monomer to the copolymeric compositions. Figures 3, 4, and 5 show the typical absorbency of a series of SA-DMAAPS copolymeric absorbents as a function of ionic strength for NaCl, CaCl₂, and FeCl₃ solutions, respectively. Note that the curves of water absorbency for the monovalent cationic salt solution (Fig. 3) are far flatter than those for divalent (Fig. 4) and trivalent (Fig. 5) cationic salt solutions. These results are due to the reduction in the osmotic pressure difference between the polymeric gel and the external solution with the increase in external solution concentration. Comparing Figure 3 with Figures 4 and 5 reveals that the absorbency curves are steeper for multivalent salt solutions than those for a monovalent salt solution. Moreover, the absorbency converges to zero in the presence of high ionic strength for divalent and trivalent salt solutions, but not for monovalent salt solutions. Restated, for a given high ionic strength, the water absorbency in monovalent cation solutions is higher than that in multivalent cation solutions.

Figure 6 shows the deswelling behavior of the sample DM4. The gel deswelling is apparently found in the range of the ionic strength of 2×10^{-4} – $0.01M$ for the multivalent salt solutions. Our experiments (not shown) revealed that the absorbents first swelled and then deswelled while the xerogels were immersed in the high-concen-

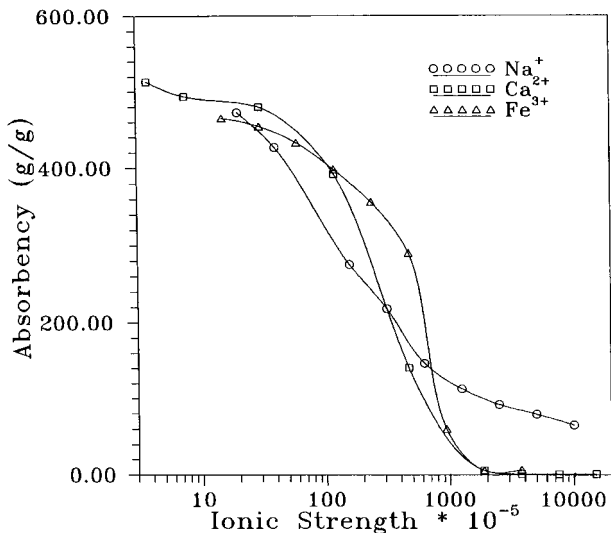


Figure 6 Water absorbency of sample DM4 in NaCl, CaCl₂, and FeCl₃ aqueous solutions of various ionic strengths.

tration multivalent cationic salt solution. This phenomenon occurred because the swelling step corresponded to the water entering the network rapidly by osmotic pressure difference, and the deswelling step was related to the exchange of cations. The degree of deswelling varied with exchange capacities of the multivalent cations. In addition, these dried gel samples, which had once been immersed in a higher-concentration multivalent cation solution, will never be reswelled in water again. This occurrence can be attributed to the increase in crosslinking density arising from the complexation of the multivalent cations with the carboxylate groups. This behavior agrees with the results reported by Gugliemelli et al.⁴² on the viscosity of hydrolyzed starch graft polyacrylonitrile dispersions in various salt solutions.

Influence of Different Cations with a Common Anion (Cl⁻) on the Water Absorbency

Buchanan et al.⁴¹ reported that all univalent cationic species of the same concentration had a similar effect on the water absorbency of the poly(SA) gel (i.e., the effect 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. D. Castel et al.¹⁶ also reported that calcium ion (Ca²⁺) can drastically decrease the swelling values for a hy-

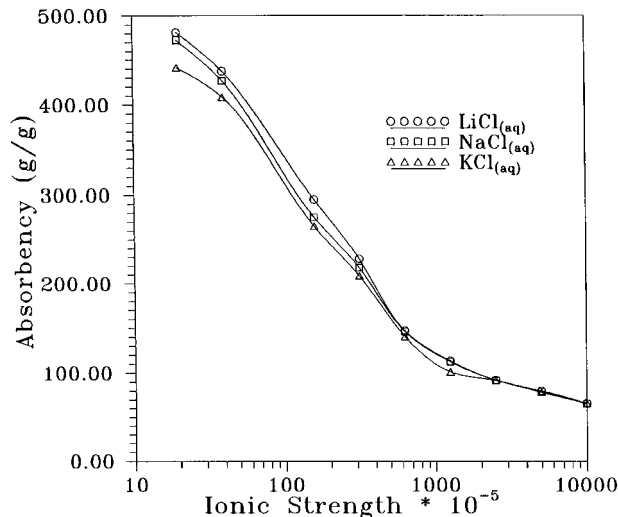


Figure 7 Water absorbency of sample DM4 in the LiCl, NaCl, and KCl aqueous solutions of various ionic strengths.

drolyzed starch graft polyacrylonitrile owing to the complexing ability of the carboxylate groups to induce intramolecular and intermolecular complex formation. The influence of different cations with a common anion (Cl⁻) on the water absorbency of SA-DMAAPS xerogels is shown in Figures 7 and 8. Results obtained from the said copolymeric gel systems demonstrate that the water absorbency tendency for the said gel in the salt solutions is in the order LiCl_(aq) > NaCl_(aq) > KCl_(aq)

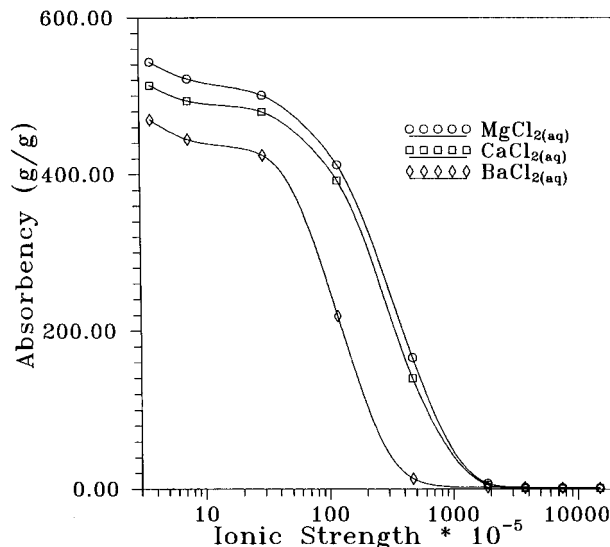


Figure 8 Water absorbency of sample DM4 in various the MgCl₂, CaCl₂, and BaCl₂ aqueous solutions of various ionic strengths.

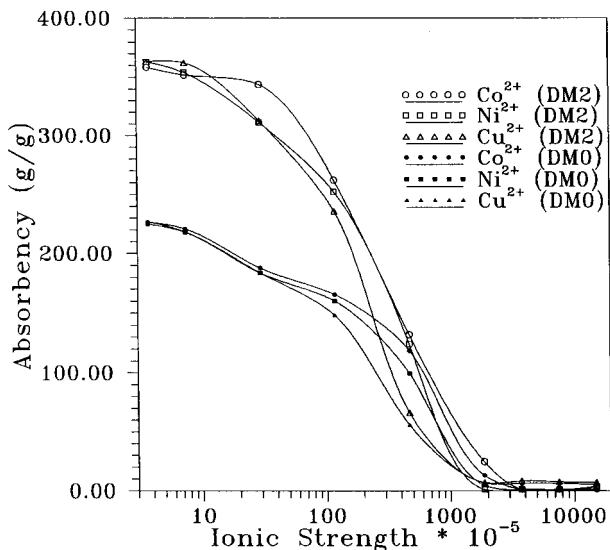


Figure 9 Water absorbency of samples DM0 and DM2 in CuCl_2 , CoCl_2 , and NiCl_2 aqueous solutions of various ionic strengths.

(Fig. 8); $\text{MgCl}_{2(\text{aq})} > \text{CaCl}_{2(\text{aq})} > \text{SrCl}_{2(\text{aq})} > \text{BaCl}_{2(\text{aq})}$ (Fig. 8). These findings correspond to the previous investigations and are due to the cationic radius or hydration force. The hydration radius grows as a result of the small cation being surrounded by a large amount of water. In other words, the lower the cationic charge density, the weaker the binding affinity to the carboxylate group. The cation with a large radius therefore tends to enter the network and easily bind to the carboxylate groups.

Effect of the Transition Metal Ions (Ni^{2+} , Co^{2+} , and Cu^{2+}) on Water Absorbency

To understand the effect of DMAAPS on the complexing ability of the SA-DMAAPS systems, the said gels were immersed in different salt solutions (i.e., NiCl_2 , CoCl_2 , and CuCl_2), with various ionic strengths. Figures 9 and 10 summarize the results for SA gel and SA-DMAAPS copolymeric gels [i.e., (DM0 and DM2) and (DM0 and DM4), respectively]. These results show that the water absorbencies for the samples DM2 and DM4 have the same tendencies at various ranges of ionic strengths (i.e., $\text{Co}^{2+} \approx \text{Ni}^{2+} \approx \text{Cu}^{2+}$ and $\text{Co}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+}$ in the ionic strength of $< 2.44 \times 10^{-5}M$ and $2.44 \times 10^{-5} - 1.8 \times 10^{-2}M$, respectively). But water absorbency for DM0 has the tendency at various ranges of ionic strengths (i.e., $\text{Co}^{2+} \approx \text{Ni}^{2+} \approx \text{Cu}^{2+}$ and $\text{Co}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+}$

in the ionic strength of $< 2.0 \times 10^{-4}M$ and $2.0 \times 10^{-4} - 1.8 \times 10^{-2}M$, respectively). These results also reveal that the same effect of multivalent cation solution on water absorbency as it converges to zero is observed from higher ionic strength ($> 1.8 \times 10^{-2}M$). Similar results were also observed from our previous report and conformed to the formation constant of complexation.^{27,41,43}

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 16.31, 18.62, and 18.80 for Co^{2+} , Ni^{2+} , and Cu^{2+} , respectively.⁴³ 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.²⁷

Effect of pH on Water Absorbency

The swelling behavior of the absorbent in various pH value solutions reveals that the absorbency is a roughly constant from pH = 3 to pH = 11 and from pH = 4 to pH = 10 for poly(SA) gels and SA-DMAAPS copolymeric gels, respectively (Fig. 11). This behavior was explained by the buffer action of the sodium carboxylate group with acid or base in a previous paper.²⁷ In our previous re-

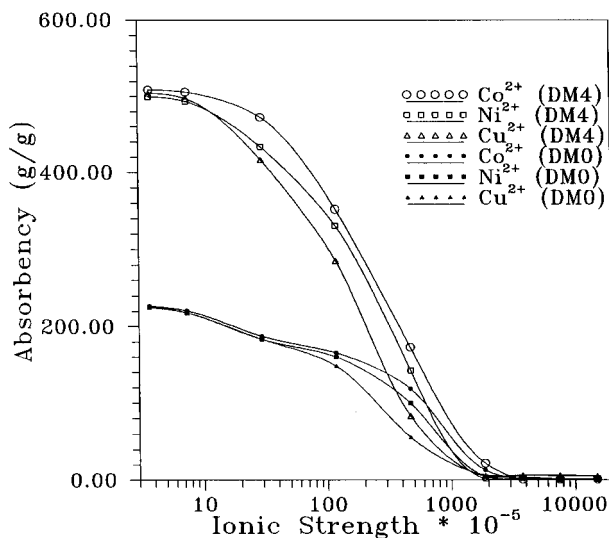


Figure 10 Water absorbency of samples DM0 and DM4 in CuCl_2 , CoCl_2 , and NiCl_2 aqueous solutions of various ionic strengths.

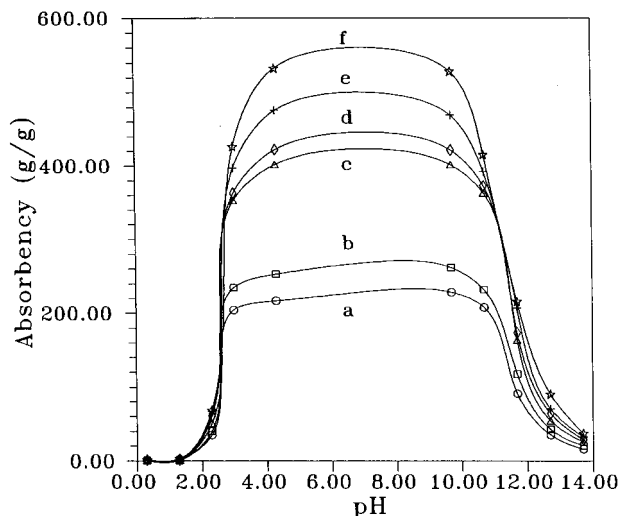


Figure 11 The swelling behavior in various pH value solutions: (a) DM0; (b) DM1; (c) DM2; (d) DM3; (e) DM4; (f) DM5; and (g) poly(AA).

port, the SA-HEMA gel series revealed that the HEMA component (a nonionic monomer) has no effect on the buffer action in various pH solutions. In contrast to the SA-DMAAPS gel series, the DMAAPS component exhibits some influence on the buffer action because the DMAAPS monomer is a zwitterionic monomer. The buffer action disappears at pH values below 4 and above 10 and below 3 and above 11 for the SA-DMAAPS gel series and poly(SA) [i.e., (DM4) and (DM0)], respectively.

CONCLUSIONS

The swelling behavior of these absorbents is related to their structure, their chemical composition, and the nature of external solutions. The water absorbency of the SA-DMAAPS copolymeric gel series in deionized water or in 0.9 wt % NaCl solution can effectively be improved by copolymerizing SA with a small amount of zwitterionic monomer DMAAPS. The deswelling behavior of these gels occurred as the ionic strength of the external salt solution increased, especially for the multivalent salt solutions. This deswelling behavior can be attributed to the complexation of multivalent cations with the carboxylate group on the polymeric chain. The pH effect on water absorbency for this series of gels showed that a narrower range of buffer action resulted from the addition of DMAAPS to the gel.

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