

# Superabsorbent Polymeric Materials. III. Effect of Initial Total Monomer Concentration on the Swelling Behavior of Crosslinked Poly(sodium acrylate) in Aqueous Salt Solution

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**ABSTRACT:** A series of xerogels based on sodium acrylate (SA) and *N,N'*-methylene-bisacrylamide (NMBA) were prepared by inverse suspension polymerization. The water absorbency or swelling behaviors for these hydrogels in water or various saline solutions was investigated. Experimental results indicate that the absorbency of poly(SA) in deionized water increases with decrease in the initial total monomer concentration. Results obtained from this study show that the water absorbency, respectively, exhibited a value of 992 g H<sub>2</sub>O/g sample and 106 g H<sub>2</sub>O/g sample in deionized water and a 0.9 wt % NaCl solution at an initial total monomer concentration of 3.03M. The absorbency in the chloride salt solutions decreases with increase in the ionic strength of the salt. For the same ionic strength of various salt solutions, the swelling amount has the following tendency: Co<sup>2+</sup> > Ni<sup>2+</sup> > Cu<sup>2+</sup> for the higher ionic strength of 6.25 × 10<sup>-4</sup> to 2.0 × 10<sup>-3</sup>M, and Co<sup>2+</sup>, Ni<sup>2+</sup>, and Cu<sup>2+</sup> approximately have the same swelling amount for the lower ionic strength of < 6.25 × 10<sup>-4</sup>M. The influence of monovalent, divalent, and trivalent anions with a common cationic ion (Na<sup>+</sup>) on the water absorbency shows the tendency of monovalent < divalent < trivalent anions for the same ionic strength. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 2371–2380, 1997

## INTRODUCTION

Superabsorbent polymers are found in many applications such as in disposable diapers, feminine napkins, soil for agriculture and horticulture, gel actuators, water-blocking tapes, medicine, and absorbent pads.<sup>1–8</sup> In such applications, water absorbency and water retention are essential. Some authors modified their absorbent polymers to enhance their absorbency, gel strength, and absorption rate.<sup>9–23</sup>

Flory thoroughly examined the absorption of water in hydrophilic polymers with nonionic-network or ionic-network structures.<sup>24</sup> The kinetics

of the swelling of poly(sodium acrylate) was studied by picture analysis with a microscope–VTR system, calorimetry, and gravimetry techniques.<sup>25</sup>

In addition, several investigators studied the gel transition caused by the interaction between polar solvent and polymer.<sup>26–32</sup> However, the effect of the initial total monomer concentration on the swelling and deswelling behavior of the gel in a saline solution has rarely been discussed. In this work, we prepared a series of crosslinked poly(sodium acrylate) [poly(SA)] with various initial total monomer concentrations by inverse suspension polymerization. This work aimed not only to investigate the swelling behavior of these polymeric gels in water, but also to investigate the effects of various salt solutions on the swelling properties.

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## EXPERIMENTAL

### Materials

The materials used in this study were purchased from Tokyo Kasei Industries Ltd. including acrylic acid (AA), sodium hydroxide, and *N,N'*-methylene-bisacrylamide (NMBA). Sodium hydroxide and NMBA were used directly. AA was distilled under reduced pressure before use. 4,4'-Azo-bis(4-cyanovaleric acid) (ACVA) as an initiator and sorbitan monostearate (Span 60) as an inverse suspension stabilizer were also purchased from Tokoy Kasei Industries Ltd. Methanol and cyclohexane were of reagent analytical grade.

### Preparation of Sodium Acrylate (SA)

#### Monomer Solution

The SA monomer was prepared as previously reported.<sup>33</sup>

#### 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 crosslinking agent, NMBA (0.07 g), was introduced into the SA monomer solution and the mixture was stirred until the NMBA was dissolved completely. The monomer solution and 0.02 g of the 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 feed compositions.

### Property Measurements

The samples were dried before any tests were performed. All the samples were used had 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<sub>(aq)</sub> 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:

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

### Tea Bag Method

The tea bag was made of a 250 mesh nylon screen. The tea bag containing the sample (50 mg) was immersed entirely in deionized water or the saline solution and kept there until equilibrium was reached, then was hung up for 15 min to drain the excess solution and weighed (the weight of the tea bag would be deducted). The absorbency was calculated according to eq. (1).

### Kinetics of Swelling

A technique based on the demand wettability (DW) method was adopted.<sup>16</sup> 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 the 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 was easily measured.

### Absorbency in Various Saline Solutions

Fifty milligrams of the dried samples were immersed in the excess of various saline solutions with different concentrations [LiCl<sub>(aq)</sub>, NaCl<sub>(aq)</sub>, KCl<sub>(aq)</sub>; MgCl<sub>2(aq)</sub>, CaCl<sub>2(aq)</sub>, SrCl<sub>2(aq)</sub>, BaCl<sub>2(aq)</sub>; FeCl<sub>3(aq)</sub>; CoCl<sub>2(aq)</sub>, NiCl<sub>2(aq)</sub>, and CuCl<sub>2(aq)</sub>] and remained there for at least 8 h. The sample was filtered by suction and weighed. The effects of saline solutions on the water absorbency could also be obtained.

## RESULTS AND DISCUSSION

The swelling behavior of the absorbents depends on the nature of the polymer and the characteris-

**Table I** Characterization of SA Polymeric Hydrogels<sup>a</sup>

Sample No.	Feed Composition			Absorbency (g H <sub>2</sub> O/g Sample)		Percentage of Water Solubles (%)
	SA (g)	H <sub>2</sub> O (mL)	Concentration (M)	Suction Filtration	Tea Bag	
A1	19.911	33	6.44	76	140	2
A2	19.911	40	5.31	132	190	4
A3	19.911	50	4.25	154	210	4
A4	19.911	60	3.54	235	386	4
A5	19.911	70	3.04	993	1162	13

<sup>a</sup> The amount of monomer was 0.213 mol.

tics of the external solution and can be explained by Flory's theory.<sup>24</sup> The polymer's nature involves factors such as the amount of the crosslink agent, 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.

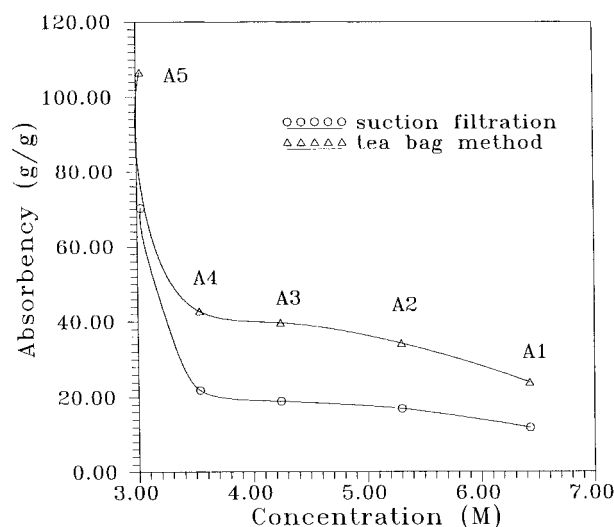
#### Effect of Initial Total Monomer Concentration on the Saturated Absorbency

Table I shows the water absorbency measured by suction filtration and the tea bag method as a function of the initial total monomer concentration in the polymeric gel (deionized water). These data indicate that the water absorbency in deionized water is increased from 140 to 1162 and from 76 to 993 g water/g dry sample for the tea bag method and the suction method, respectively, with a decrease in the initial total monomer concentration. The water absorbency measured by the tea bag 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.

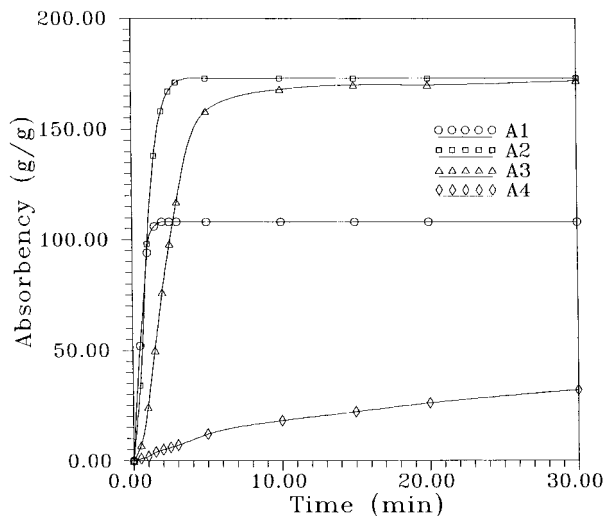
Buchholz<sup>1</sup> reported that the concentration of monomer in the reaction solution affects the properties of the resulting polymer. In addition, chain transfer to the polymer increases with monomer concentration especially at a high extent of conversion. Chain transfer to the polymer increases the amount of branching and self-crosslinking reactions that affect product properties. Baker et al.<sup>34</sup> used the phantom model and the affine model to predict the swelling ratio for cationic acryl-

amide-based hydrogel. They also claimed that the effective crosslink density is probably less than the nominal crosslink density at a low total monomer concentration. Their results showed that the swelling ratio increases with a decrease of the initial monomer concentration. The result for SA hydrogel conforms to the resulting cationic acrylamide-based hydrogels.

Figure 1 shows the water absorbency in 0.9 wt % NaCl<sub>(aq)</sub> as a function of initial total monomer concentration for the preparation of polymeric gels. Their results are similar to those in deionized water. This figure indicates that the water absorbency in 0.9 wt % NaCl<sub>(aq)</sub> is increased from 24 to 106 and from 12 to 70 g water/g dry sample for the tea bag method and the suction filtration method, respectively, with a decrease in initial



**Figure 1** Absorbency in 0.9 wt % NaCl<sub>(aq)</sub> for poly-(SA) hydrogels prepared with various initial total monomer concentrations.



**Figure 2** Absorptive rate in deionized water by DW method.

total monomer concentration. This result is attributed mainly to the decrease in the osmotic pressure difference between the polymeric gel and the external solution and the lower crosslink density at lower monomer concentration.<sup>24,34</sup>

### Swelling Kinetics

The swelling kinetics of spherical polyacrylamide absorbents described in the model by Tanaka and Fillmore<sup>35</sup> was generalized by Candau et al.<sup>36</sup> 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.

It is well known that the swelling kinetics for the absorbent is significantly influenced by factors such as particle size, surface area, and composition of copolymers. The swelling kinetics of SA absorbents is investigated in this section.

The water or the 0.9 wt % NaCl solution absorption rate by the DW method is significantly influenced by the polymer's contact area with water. Figures 2 and 3 show the absorption rates for a series of absorbent polymers in water or the saline solution, respectively. The results show that the poly(SA) gel prepared from a higher initial total monomer concentration exhibits a higher initial absorption rate, a lower saturated absorbency, and a shorter time required to reach absorption equilibrium ( $t_{\text{req}}$ ) (see Table II). The initial absorption rate in water for the A1, A2, and A3 absorbent at the initial period (in 30 s) is

extremely fast, but A4 is very slow. Sample A1 shows excellent properties such as initial absorption rate (208 g H<sub>2</sub>O/min) and  $t_{\text{req}}$  (1 min). It is known that the swelling kinetics in this period is controlled by the diffusion process of the water penetrated into the inside of gels. From above results, we can infer that the initial absorption rate increases with increase of the initial total monomer concentration.

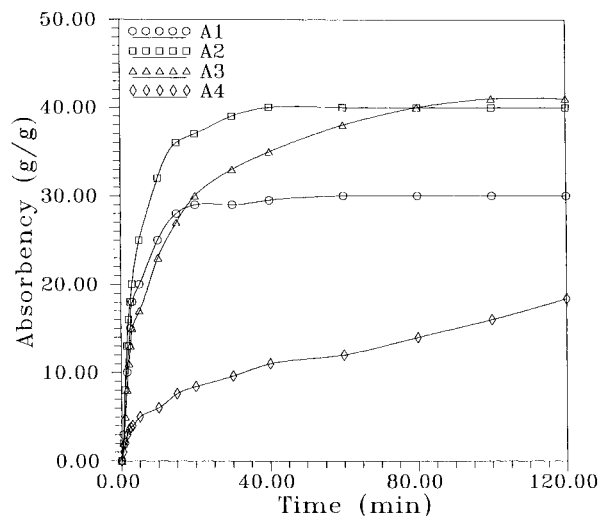
The swelling rate can be described by the following equation<sup>37</sup>:

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

where  $Q_{\text{eq}}$  is the equilibrium absorbency;  $Q$ , the characteristic absorbency;  $K$ , the swelling kinetic constant; and  $T$ , the characteristic swelling time. From eq. (2), a characteristic swelling time is defined at  $Q = 0.632Q_{\text{eq}}$ . Table III presents the influence of the initial total monomer concentration on the characteristic swelling time ( $T$ ), on the swelling kinetic constant ( $K$ ), and on the characteristic absorbency ( $Q$ ) of the SA absorbent in water and in the saline solution. Table III reveals that both  $T$  and  $Q$  increase with decrease in the initial total monomer concentration in the SA gel system in pure water and in the saline solution. The swelling kinetic constants ( $K$ ) for various composition gels in water are larger than those in the saline solution.

### Effect of Salt Solution on the Water Absorbency

The swelling behavior of SA absorbents could be significantly affected by various factors of the ex-



**Figure 3** Absorptive rate in 0.9 wt % NaCl<sub>(aq)</sub> by DW method.

**Table II Absorption Characteristics for SA Polymeric Gel Systems**

Sample No.	H <sub>2</sub> O				0.9 Wt % NaCl			
	Initial Absorption Rate (g/min)		$t_{\text{req}}^{\text{a}}$ (min)	$Q_{\text{eq}}$ (g H <sub>2</sub> O/g)	Initial Absorption Rate (g/min)		$t_{\text{req}}^{\text{a}}$ (min)	$Q_{\text{eq}}$ (g H <sub>2</sub> O/g)
	30 s	1–3 min			30 s	1–3 min		
A1	104	7	1	108	6	3	13	30
A2	68	36.5	1.5	174	6	6.5	18	40
A3	14	46.5	4.2	176	4	5	67	41
A4	2	2.5	315	205	2	2	285	23

<sup>a</sup>  $t_{\text{req}}$ : time required to approach equilibrium.

ternal solution such as its valencies and salt concentrations. SA–HEMA copolymeric gels were reported in a previous article,<sup>33</sup> which showed 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 the osmotic pressure difference between the gel network and the external solution decreases with an increase in the ionic strength of the salt solution.<sup>33</sup>

The effect of the salt solution with various concentrations on the water absorbency for a series of SA polymeric gels was investigated here. Figures 4–6 show the typical absorbency of a series of SA copolymeric absorbents as a function of the ionic strength for NaCl, CaCl<sub>2</sub>, and FeCl<sub>3</sub> salt solutions, respectively. These figures show that the water absorbency in various salt solutions decreases with increase of the ionic strength of the salt solutions. These figures also show that the curves of water absorbency for the monovalent cationic salt solution (Fig. 4) are far flatter than are those in the divalent (Fig. 5) and trivalent (Fig. 6) cationic salt solutions. These results are

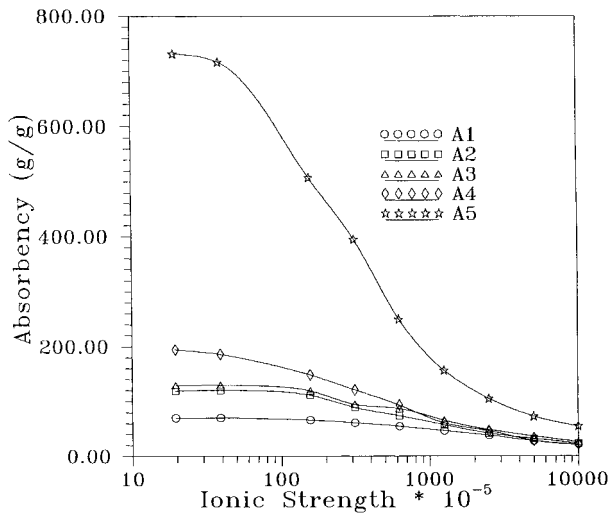
due to the fact that the osmotic pressure difference between the polymeric gel and the external solution is reduced with increase in the external solution concentration. Comparing Figure 4 with Figures 5 and 6 reveals that the absorbency curves are much steeper for multivalent salt solutions than those for a monovalent salt solution. Moreover, the absorbency is converged to zero in a high ionic strength for divalent and trivalent salt solutions, but not for the monovalent salt solution. Restated, for a given high ionic strength, the water absorbency in monovalent cation solutions is higher than that in multivalent cation solutions.

Figure 7 also shows the deswelling behavior of sample A4. The gel deswelling is apparently found to be in the range of the ionic strength of  $1 \times 10^{-4}$  to  $0.02M$  for the multivalent salt solution. The phenomenon observed from our experiments reveals that the absorbents swelled first and then deswelled while the hydrogels were immersed into the high concentration multivalent cationic salt solution. This event can be explained by the fact that the swelling step corresponded to the

**Table III Influence of Initial Total Monomer Concentration on the Swelling Characteristic Times ( $T$ ), on the Swelling Kinetic Constants ( $K$ ), and on the Swelling ( $Q$ ) of SA Absorbent in Water and Saline Solution**

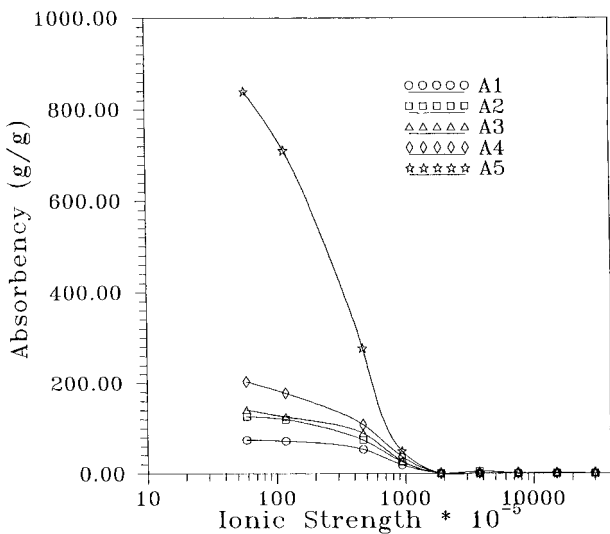
Sample No.	$T$ (min)		$K$ (min <sup>-1</sup> )		$Q^{\text{a}}$ (g H <sub>2</sub> O/g)	
	H <sub>2</sub> O	0.9 Wt % NaCl	H <sub>2</sub> O	0.9 Wt % NaCl	H <sub>2</sub> O	0.9 Wt % NaCl
A1	0.37	5.88	2.67	0.17	68	19
A2	0.71	7.69	1.41	0.13	110	25
A3	2.13	12.50	0.47	0.08	111	26
A4	100.0	97.0	0.01	0.01	130	15

<sup>a</sup>  $Q = 0.632 Q_{\text{eq}}$ .

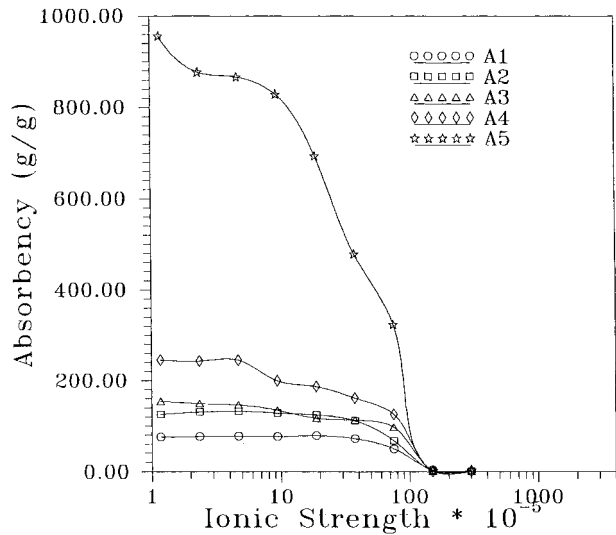


**Figure 4** Water absorbency of poly(SA) gel in the NaCl aqueous solutions with various ionic strengths.

water entering the network quickly by the osmotic pressure difference and that the deswelling step was related to the exchange of cations. The deswelling degree varied with the exchange capacities of multivalent cations. In addition, the dried gel sample which had once been immersed in the high concentration multivalent cation solution will never be reswelled in water again. This occurrence can be attributed to the increase in the crosslinking density arising from the complexation of the multivalent cations with the carboxylate groups. This behavior agrees with the consequence reported by Gugliemelli et al.<sup>38</sup> on the vis-



**Figure 5** Water absorbency of poly(SA) gel in the CaCl<sub>2</sub> aqueous solutions with various ionic strengths.



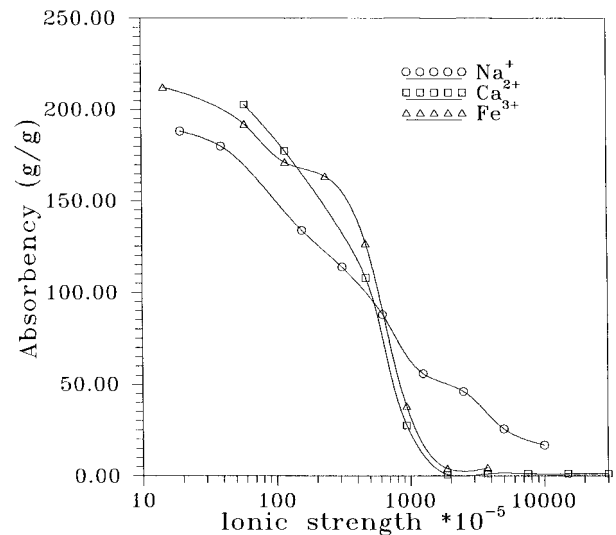
**Figure 6** Water absorbency of poly(SA) gel in the FeCl<sub>3</sub> aqueous solutions with various ionic strengths.

cosity of hydrolyzed starch graft polyacrylonitrile dispersions in various salt solutions.

The effect of the ionic strength on the water absorbency was determined using the relation suggested by Hermans<sup>39</sup>:

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

where  $Q_{eq}$  is the water absorbency at equilibrium;  $i$ , the concentration of the charges bound to the gel;  $I$ , the ionic strength of the external solution;



**Figure 7** Water absorbency of sample A4 in the NaCl, CaCl<sub>2</sub>, and FeCl<sub>3</sub> aqueous solutions with various ionic strengths.

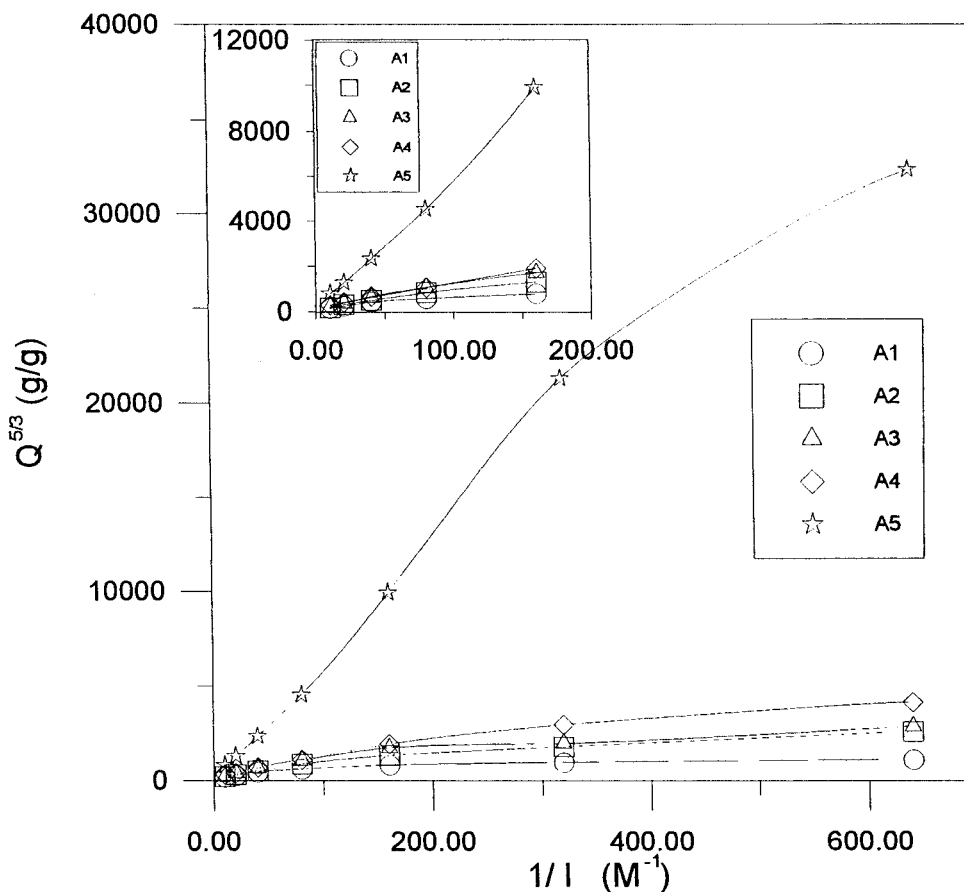


Figure 8 Absorbency plots against the ionic strength in the NaCl aqueous solution.

and  $A$  and  $B$ , the empirical parameters. A good linear relationship shown in Figures 8 and 9 is achieved for a high ionic strength at the range of  $1/I$  at 20–160 and at 50–210  $M^{-1}$  for NaCl and  $CaCl_2$  solutions, respectively. However, a discrepancy is observed from the range of low  $I$  values. These events are because the swelling force is counteracted by the chain's elastic forces. These phenomena are also observed in a series of gels SA-HEMA<sup>33</sup> and a hydrolyzed polyacrylonitrile starch graft copolymer.<sup>16</sup>

Buchanan et al.<sup>40</sup> reported that all univalent cationic species of the same concentration have a similar effect on the water absorbency of the poly(SA) gel, i.e., 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.<sup>16</sup> also reported that the calcium ion ( $Ca^{2+}$ ) can decrease drastically the swelling values for a hydrolyzed starch graft polyacrylonitrile, due to the

complexing ability of the carboxylate groups inducing intramolecular and intermolecular complex formation. The influence of different cations with a common anion ( $Cl^{-1}$ ) on the water absorbency of SA hydrogels is shown in Figures 10 and 11. Results obtained from the SA polymeric 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  $LiCl_{(aq)} > NaCl_{(aq)} > KCl_{(aq)}$  (see Fig. 10) and  $MgCl_{2(aq)} > CaCl_{2(aq)} > BaCl_{2(aq)}$  (see Fig. 11). Those results correspond to previous investigations.<sup>16,40</sup> This result is due to their cationic radius or their hydration force. The hydration radius grows as a result of the small cation surrounded with a large amount of water. In other words, the cationic charge density is low and the binding ability to the carboxylate group is weak. The cation with a large radius therefore tends to enter the network and bind easily to the carboxylate groups.

To confirm the complexation of multivalent cations with a carboxylate group in the polymeric gel, the water absorbencies of the gel sample (A4)

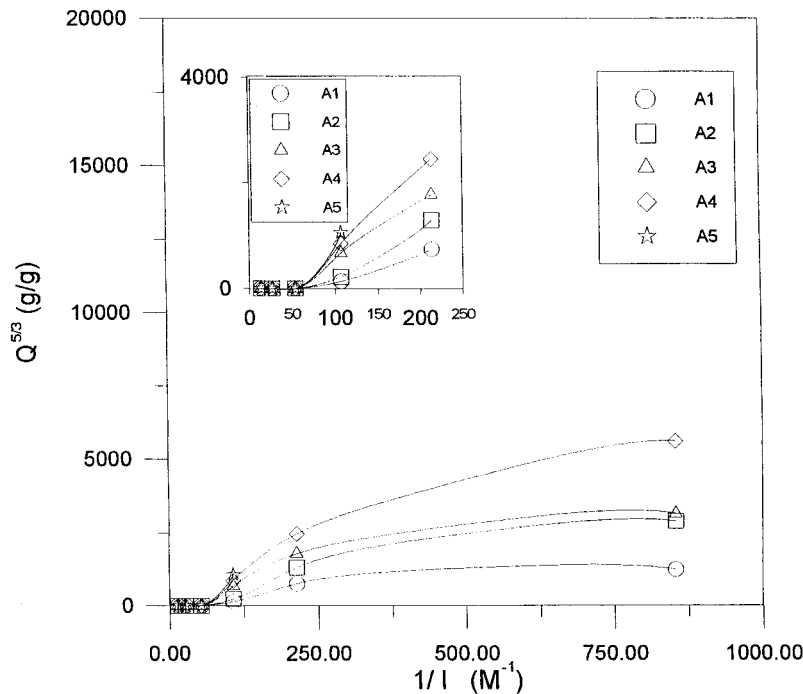


Figure 9 Absorbency plots against the ionic strength in the  $\text{CaCl}_2$  aqueous solution.

immersed in various multivalent salt solutions, i.e.,  $\text{NiCl}_2$ ,  $\text{CoCl}_2$ , and  $\text{CuCl}_2$ , with various ionic strengths are shown in Figure 12. The result shows that the water absorbencies for sample A4 show the following tendencies at different ranges of ionic strengths, i.e.,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cu}^{2+}$  approximately have the same swelling amount in the ionic strength of  $< 6.25 \times 10^{-4} M$  and  $\text{Co}^{2+}$

$> \text{Ni}^{2+} > \text{Cu}^{2+}$  in the ionic strength of  $6.25 \times 10^{-4}$  to  $2.0 \times 10^{-2} M$ . The results also reveal that these three cations have the same effect on the water absorbency which converges to zero is observed from higher ionic strength ( $> 6.25 \times 10^{-4} M$ ). Similar results are also observed from our previous report and conform to the formation constant of complexation.<sup>33,38</sup>

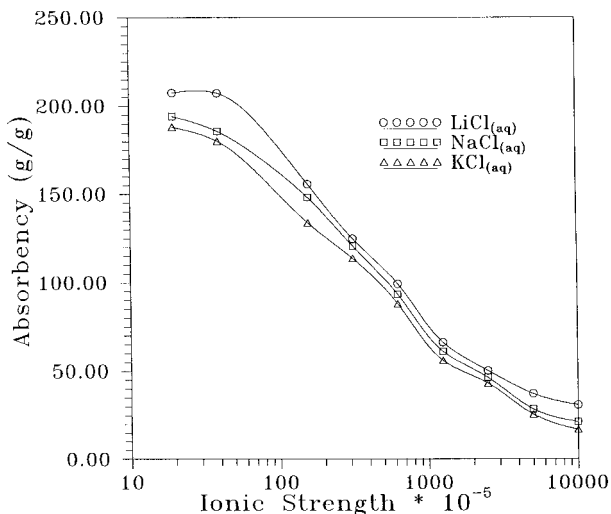


Figure 10 Water absorbency of sample A4 in the  $\text{LiCl}$ ,  $\text{NaCl}$ , and  $\text{KCl}$  aqueous solutions with various ionic strengths.

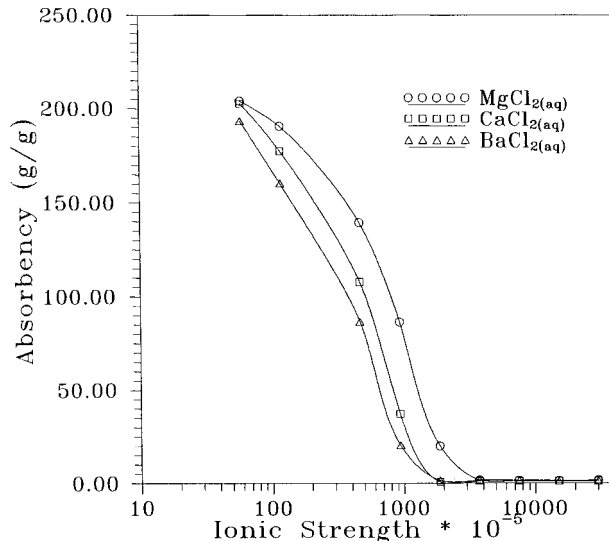


Figure 11 Water absorbency of sample A4 in the  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ , and  $\text{BaCl}_2$  aqueous solutions with various ionic strengths.

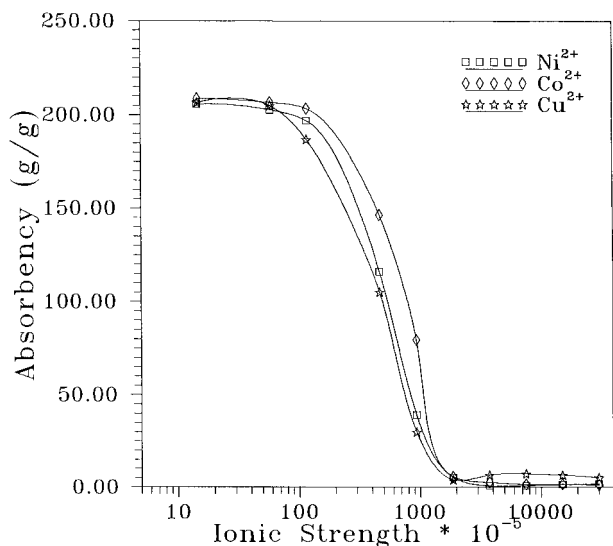


The order at a higher ionic strength for sample A4 gel having carboxylate groups can be interpreted by the formation constants of complexation. The logarithm of formation constants of the ethylenediaminetetraacetic acid (EDTA) with multivalent cations at 0.1M are 16.31, 18.62, and 18.80 for  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cu}^{2+}$ , respectively.<sup>41</sup> 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.<sup>33</sup>

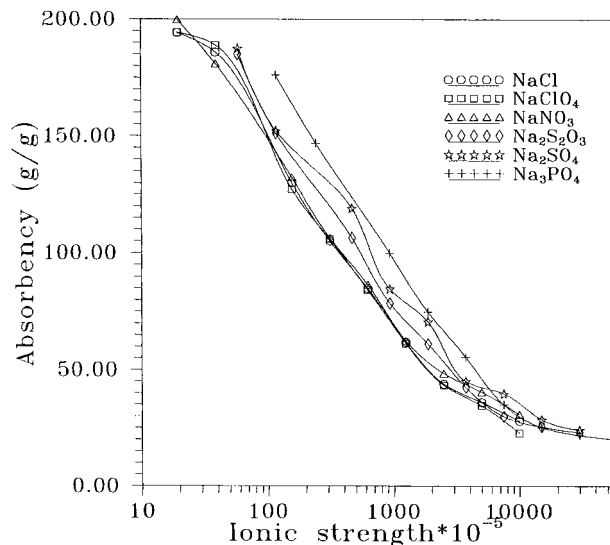
Figure 13 shows the water absorbency of sample A4 as a function of the ionic strength for NaCl,  $\text{NaClO}_4$ ,  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_3$ ,  $\text{Na}_2\text{S}_2\text{O}_3$ , and  $\text{Na}_3\text{PO}_4$  solutions, respectively. The results exhibit that the influence of monovalent, divalent, and trivalent anions with a common cation ( $\text{Na}^+$ ) on the water absorbency of sample A4 has the following tendencies: i.e., monovalent < divalent < trivalent anions for the same ionic strength. The effect of the radius of anions with same charge number on the water absorbent is not significant (i.e.,  $\text{Cl}^- = \text{ClO}_4^- = \text{NO}_3^- < \text{S}_2\text{O}_3^{2-} = \text{SO}_4^{2-} < \text{PO}_4^{3-}$ ).

## CONCLUSIONS

The swelling behavior of the crosslinked poly(SA) is related to the initial total monomer concentration and the nature of the external solution. The



**Figure 12** Water absorbency of sample A4 in the  $\text{CuCl}_2$ ,  $\text{CoCl}_2$ , and  $\text{NiCl}_2$  aqueous solutions with various ionic strengths.



**Figure 13** Water absorbency of sample A4 in the  $\text{NaCl}$ ,  $\text{NaClO}_4$ ,  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{S}_2\text{O}_3$ , and  $\text{Na}_3\text{PO}_4$  aqueous solutions with various ionic strengths.

water absorbency decreases with increase of the initial total monomer concentration used in the preparation of the polymeric gel. For a given ionic strength, the absorbency of the SA gels in a multivalent saline solution decreases strongly in comparison with that in the monovalent saline solution. This behavior can be accounted for in terms of the counterion condensation or the screening effect for monovalent cations, as well as the complexation for multivalent cations.

## REFERENCES

1. F. L. Buchholz, *CHEMTECH*, **Sept.**, 38 (1994).  
F. L. Buchholz and N. A. Peppas, Eds., *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.* 40,087 (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, 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, *Func. Mater.*, **6**, 76 (1986).
18. K. Isomi, *Jpn. Kokai, Tokyo Koho JP* 56,707 (1989).
19. K. Nagasuna, N. Suminaga, K. Kimura, and T. Shimomura, *Jpn. Kokai, Tokyo Koho JP* 126,314 (1989).
20. H. Imada and M. Fujikawa, *Jpn. Kokai, Tokyo Koho JP* 141,938 (1989).
21. A. Fujio, T. Komae, and Y. Yutaka, *Jpn. Kokai, Tokyo Koho JP* 210,463 (1989).
22. S. Yada, T. Shibano, and K. Ito, *Jpn. Kokai, Tokyo Koho JP* 215,801 (1990).
23. M. Sano, H. Mikamo, T. Suehiro, and N. Wakabayashi, *Jpn. Kokai, Tokyo Koho JP* 258,839 (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. T. Tanaka, *Polymer*, **20**, 1404 (1979).
27. S. Katayama, Y. Hirokawa, and T. Tanaka, *Macromolecules*, **17**, 2641 (1984).
28. M. Ilavsky, J. Hrouz, J. Stejskal, and K. Bouchal, *Macromolecules*, **17**, 2868 (1984).
29. J. Ricka and T. Tanaka, *Macromolecules*, **17**, 2916 (1984).
30. S. Katayama and A. Ohata, *Macromolecules*, **18**, 2782 (1985).
31. Y. Hirose, T. Amiya, Y. Hirokawa, and T. Tanaka, *Macromolecules*, **20**, 1342 (1987).
32. N. Wada, Y. Yagi, H. Inomata, and S. Saito, *Macromolecules*, **25**, 7220 (1992).
33. W. F. Lee and R. J. Wu, *J. Appl. Polym. Sci.*, to appear.
34. J. P. Baker, L. H. Hong, H. W. Blanch, and J. M. Pransnitz, *Macromolecules*, **27**, 1446 (1992).
35. T. Tanaka and D. J. Fillmore, *J. Chem. Phys.*, **70**, 1214 (1979).
36. S. J. Candau, J. Bastide, and M. Delsanti, *Adv. Polym. Sci.*, **41**, 27 (1982).
37. K. J. Yao and W. J. Zhou, *J. Appl. Polym. Sci.*, **53**, 1533 (1994).
38. L. A. Gugliemelli, M. O. Weaver, C. R. Russell, and C. E. Rist, *J. Appl. Polym. Sci.*, **13**, 2007 (1969).
39. J. J. Hermans, *Flow Properties of Disperse Systems*, Wiley-Interscience, New York, 1953, p. 61.
40. K. J. Buchanan, B. Hird, and T. M. Letcher, *Polym. Bull.*, **15**, 325 (1986).
41. R. A. Day, Jr. and A. L. Underwood, *Quantitative Analysis*, 6th ed., Prentice-Hall, Englewood Cliffs, NJ, 1994, p. 664.