Superabsorbent Polymeric Materials. VI. Effect of Sulfobetaine Structure on Swelling Behavior of Crosslinked Poly(sodium acrylate-*co*sulfobetaines) in Aqueous Salt Solutions

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ABSTRACT: A series of xerogels based on sodium acrylate (SA), N,N-dimethyl(acrylamidopropyl) ammonium propane sulfonate (DMAAPS) or dimethyl(methacryloyloxy ethyl) ammonium propane sulfonate (DMAPS), and N,N'-methylene bisacrylamide (NMBA) was prepared by inverse suspension polymerization. The water absorbencies or swelling kinetic behaviors for these xerogels in water or various saline solutions were investigated. The swelling behaviors of these absorbents were related to their chemical structures, their compositions, and the nature of external salt solutions. The water absorbencies of these two copolymeric gel series in deionized water or in various salt solutions would be improved effectively by copolymerizing SA with a small amount of zwitterionic monomer (DMAAPS or DMAPS). The water absorbency of the gel containing DMAPS is larger than that of the gel containing DMAAPS when the amount of zwitterionic monomer in the copolymeric gel is <0.8 mol %, but a contrary result is observed when the zwitterionic monomer content is >0.8 mol %. The tendency of the absorbency for these gels in dilute solution is in the order $Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}$ for CuCl₂, ZnCl₂, CoCl₂, and NiCl₂ aqueous solution, respectively. The absorbency and initial absorption rate for those gels are related with gel compositions and salt concentrations. Finally, the adsorption of cupric ion by these gels is also investigated. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1221-1232, 1999

Key words: superabsorbent; water absorbency; swelling behavior; sodium acrylate; sulfobetaine; xerogel

INTRODUCTION

A superabsorbent 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, these 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, absorbent pads, etc., where water absorbency or water retention is important.^{1–8} The modification of these absorbent polymers was carried out to enhance their absorbency, gel strength, and absorption rate by some researchers.^{9–23}

The mechanism of absorption of the water for hydrophilic polymers was explained in nonionicor ionic-network structure by Flory.²⁴ Ogawa et al. studied the kinetics of the swelling of poly(sodium acrylate) [poly(SA)] by picture analysis with a microscope–VTR system, calorimetry, and

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gravimetry techniques.²⁵ The swelling behaviors of two series of crosslinked poly(SA-co-hydroxyethyl methacrylate) [poly(SA-HEMA)] and poly-[SA-co-dimethyl (methacryloyloxyethyl) ammonium propane sulfonate] [poly(SA-DMAPS)] absorbents were reported in our previous articles.^{26,27} The results for poly(SA-HEMA)²⁶ showed that the gel occurred by a deswelling behavior in divalent and trivalent chloride salt solutions and the degree of swelling had a tendency as follows: LiCl = NaCl = KCl, $CaCl_2 < SrCl_2 < BaCl_2$, and $Fe^{3+} > Ca^{2+} > Zn^{2+} > Cu^{2+}$; but the results for poly(SA-DMAPS)²⁷ showed that the water absorbency exhibited values of 1435 and 96 gH₂O/g sample in deionized water and 0.9 wt % NaCl solution, respectively, when a gel containing 1.53×10^{-3} molar ratio of N, N'-methylene-bis-acrylamide (NMBA) was used in the polymerization. The swelling amount in the presence of various salt solutions had the following tendency: $Na^+ > Fe^{+3} > Al^{+3} > Ca^{+2}$ for the higher ionic strength of $5 imes 10^{-3}$ – $2 imes 10^{-2}$ M and $Na^+ > Fe^{+3} > Ca^{+2} > Al^{+3}$ for the lower ionic strength of $< 2 \times 10^{-4}M$. These orders, related to the complexing ability of metallic cation and carboxvlate groups in the polymeric chains, were confirmed.

The superabsorbent polymers containing zwitterionic monomer or monomer of sulfobetaine are not found in the literature, although some ampholytic monomers and cationic monomers containing absorbent polymers were studied.^{28–31} Hence, a series of crosslinked poly[SA-co-N,N-dimethyl(acrylamidopropyl) ammonium propane sulfonate (DMAAPS)] and poly[SA-co-DMAPS] were prepared by inverse suspension polymerization and the swelling behaviors of these xerogels with various ratios of DMAAPS/SA and DMAPS/SA in aqueous salt solutions were investigated and compared. Because in these gels there occurred a gel transition near the concentration of $2 imes 10^{-3}M$ in the salt solution, the investigation of swelling kinetic behaviors for these gels in CuCl₂, CoCl₂, NiCl₂, and ZnCl₂ aqueous salt solution was the main purpose in this article. The adsorption of cupric ion for SA-DMAPS and SA-DMAAPS copolymeric gels was also investigated in $CuCl_2$ solution.

EXPERIMENTAL

Materials

The materials used in this study were purchased from Tokyo Kasei Industries, Ltd (Tokyo, Japan), including acrylic acid (AA), dimethylaminopropylacrylamide, dimethylaminoethyl methacrylate, sodium hydroxide, propane sultone, and N,N'methylene-bis-acrylamide (NMBA). Sodium hydroxide, propane sultone, and NMBA were used directly, and the others 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 SA Monomer Solution

SA monomer was prepared as previously reported.^{26,27,32,33}

Synthesis of DMAAPS Monomer

The monomer DMAAPS was prepared as described previously.³⁴

Yield: 91.23%, melting point (mp): 105°C

The structure is given below.

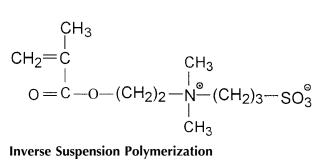
$$\begin{array}{ccc} \mathsf{CH}_2 & & \mathsf{CH}_3 \\ | & & |_{\mathfrak{S}} \\ & \mathsf{CONHCH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{N} \ \mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{SO}_3 \\ & | \\ & & \mathsf{CH}_3 \end{array}$$

Synthesis of DMAPS Monomer

The monomer DMAPS was prepared as described previously.^{34–36}

Yield: 92%, mp: 95°C.

The structure is given below.



A 300-mL four-neck separable flask equipped with a reflux condenser, a stirring rod, and a thermometer was charged into 60 mL cyclohex-

Sample No.	SA (g)	DMAAPS (g)	DMAPS (g)
A1	20.0		_
DM1	19.874	0.111 (0.2)	
DM2	19.836	0.221(0.4)	
DM3	19.761	0.444 (0.8)	
DM4	19.612	0.886 (1.6)	
DM5	19.4622	1.329(2.0)	—
DS1	19.975		0.112 (0.2)
DS2	19.950	_	0.223 (0.4)
DS3	19.700	_	0.891 (1.6)
DS4	19.550		1.337 (2.0)

Table ICompositions of the SA/DMAAPSand SA/DMAPS Xerogels

 $\rm H_2O~(60~g)$ used for each solution. 0.07 g NMBA added as crosslinking agent; 0.02 g ACVA added as initiator in the dispersion phase. Values within parentheses represent molar percent of sulfobetaine monomer based on total monomer.

ane and 0.15 g sorbitan monostearate. The mixture was stirred until the sorbitan monostearate was dissolved (continuous phase).

The appropriate amounts of the DMAAPS (or DMAPS) monomer and the crosslinking agent NMBA (0.07 g; wt % based on total monomer), were introduced into 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 introducing 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 methanol under stirring. The product was filtered and washed several times by the mixture of water and methanol (1:9 vol). The product was then dried in a vacuum oven at 120°C for 1 day. A white powdered polymer was obtained. The compositions of samples are listed in Table I.

Measurement of Water Absorbency in Salt Solutions

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 $Q_{\rm eq}$ measured by suction filtration method was described elsewhere.^{27,32,33}

Kinetics of Swelling

A technique based on the demand wettability (DW) method was adopted.^{16,33} A graduated bu-

rette 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 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 were easily measured. The absorbency at every time interval was calculated by the following equation:

$$Q = (V_s \times d_{\rm H_2O})/W_d \tag{1}$$

where Q is the characteristic absorbency, V_s is sorbed volume, $d_{\rm H_2O}$ is the density of water, and W_d is the weight of dry sample.

Measurement of Adsorption in Salt Solutions

Fifty milligrams of dried samples were immersed in 50 mL various concentrations (C_0) of $\operatorname{CuCl}_{2(aq)}$ solution to adsorb and to remain there until equilibrium (about 1 day). The sample was filtered and surplus volume (V_1) was measured. Then, a UV spectrophotometer at wavelength $\lambda = 815$ nm was used to analyze the surplus Cu^{2+} concentration (C_1) in solution. The adsorption amount was calculated by the following formula:

Adsorption amount (ppm) = $0.05 \times C_0 - V_1 \times C_1$

RESULTS AND DISCUSSION

Effect of Sulfobetaine Content on Saturated Water Absorbency

The Flory ionic swelling theory²⁴ indicates that the swelling force of a gel is dependent on the rubbery elasticity, ionic osmotic pressure, and affinity of gel toward water. According to this theory, it is well known that the equilibrium water absorbency of a hydrogel increases with an increase in the number of hydrophilic groups in the gel. The results, shown in Table II, demonstrate that the saturated (equilibrium) water absorbencies by the suction $(Q_{\rm eq})$ or the DW method (Q'_{eq}) for these two series gels are increased with an increase in the content of sulfobetaine in the copolymeric gels. The results, shown in Figure 1, also show that the water absorbencies are increased with increasing sulfobetaine content in the gels. It is apparent that the $Q_{\rm eq}$ values for DMAPS (DS) gels are larger than for DMAAPS (DM) gels. However, the $Q'_{\rm eq}$ values for DS gels are higher than for DM gels when the content of sulfobetaine in the gel composition is lower (i.e., DM1,

Conditions	A1	DS1	DS2	DS3	DS4	DM1	DM2	DM3	DM4	DM5
Initial absorption rate (g/min)										
(30 s)	4.0	3.9	3.9	11.8	19.5	3.9	4.0	4.0	4.0	7.8
(1–3 min)	3.1	2.5	5.0	14.8	83.3	1.9	3.9	3.7	4.1	15.4
$t_{ m req}~({ m min})$	300	150	100	50	8	300	300	300	120	30
$Q'_{\rm eq}$ (g H ₂ O/g)	120	106	118	144	305	84	99	112	215	464
$Q_{\rm eq} ({\rm g} {\rm H_2O/g})$	235	331	400	560	780	269	410	434	541	599

Table IIAbsorptive Characteristics for SA, SA/DMAPS, and SA/DMAAPSCopolymeric Gels in Pure Water

 $t_{\rm req}$, time required to approach equilibrium; $Q_{\rm eq}$, equilibrium water absorbency by suction method; $Q'_{\rm eq}$, equilibrium water absorbency by DW method (i.e., $Q_{\rm max}$).

DM2, DM3, DS1, and DS2). However, a contrary result for the higher content of sulfobetaine in the gel composition is obtained (i.e., the $Q'_{\rm eq}$ values for DM gels are larger than those for DS gels). From the above results, it is implied that the equilibrium water absorbency of a gel is also dependent on the gel's nature (i.e., its chemical structure and composition), except for the test methods.

In further investigation of the characteristic absorption data of these two series gels, the results shown in Table II indicate that the initial absorption rates for the DS series are faster than those for DM series. In addition, the initial absorption rates for these gels increase with an increase in the sulfobetaine content. At the same time, the results also show the time required to approach equilibrium $(t_{\rm req})$ decreases with an increase in the sulfobetaine content in the gel composition.

Effect of Salt Concentration on the Swelling Behavior of Gels (Before Gel Transition Concentration)

The phenomenon of gel transition in the salt concentration of $2 \times 10^{-3}M$ for the SA/DMAPS and SA/DMAAPS copolymeric gels was observed in

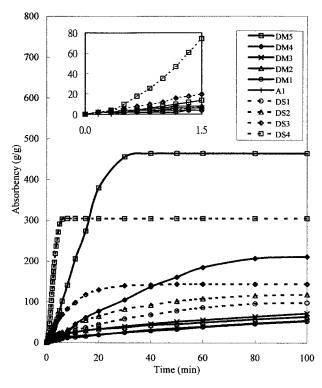


Figure 1 Swelling behavior of various xerogels in deionized water by DW method.

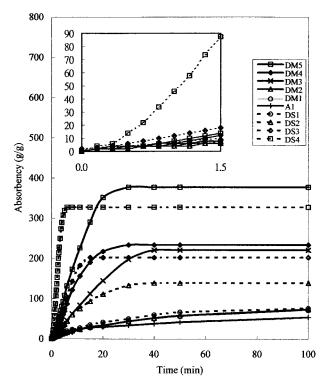


Figure 2 Swelling behavior of various xerogels in 2 $\times 10^{-4}M$ CuCl_{2(aq)} by DW method.

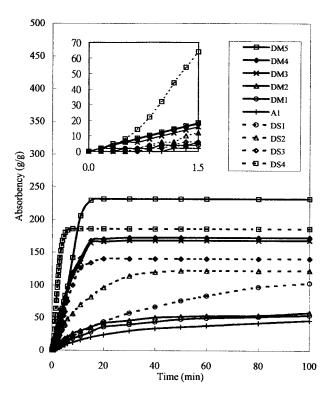


Figure 3 Swelling behavior of various xerogels in 2 $\times 10^{-4}M$ CoCl_{2(aq)} by DW method.

the previous reports.^{27,32} Hence, the swelling behaviors for these two series of gels, near the gel transition concentration (GTC) in transition metal salt solutions, are of much interest and are investigated in this section. The typical swelling kinetic curves for two series xerogels under the four transition metal salt solutions in the concentration of $2 \times 10^{-4}M$ (before GTC) are shown in Figures 2–5 for CuCl_{2(aq)}, CoCl_{2(aq)}, NiCl_{2(aq)}, and ZnCl_{2(aq)} solutions, respectively.

Figure 2 shows the water absorbency in 2 \times 10⁻⁴*M* CuCl_{2(aq)} as a function of sulfobetaine content in the copolymeric gels. Their results are similar to those in deionized water. The water absorbency obtained by DW method in $2 imes 10^{-4} M$ $CuCl_{2(aq)}$ solution increases from 68 gH₂O/g sample for poly(SA) (A1) gels to 327 and 377 $gH_2O\!/g$ sample at 2.0 \times 10⁻² molar fraction of sulfobetaine for the copolymeric gels DS4 and DM5, respectively. These results conform to our expectation that the zwitterionic (sulfobetaine) monomer could improve the water absorbency in salt solution. This result is mainly attributed to the increase in the osmotic pressure difference between the polymeric gel and the external salt solution with high ionic strength. In other words, the difference of osmotic pressure in the same salt concentration for A1 gel is smaller than that for

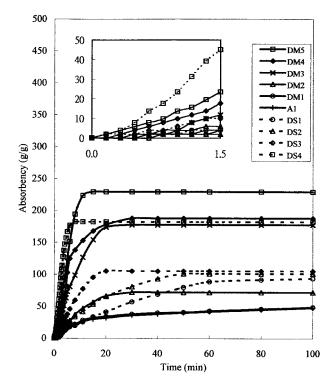


Figure 4 Swelling behavior of various xerogels in 2 $\times 10^{-4}M$ NiCl_{2(aq)} by DW method.

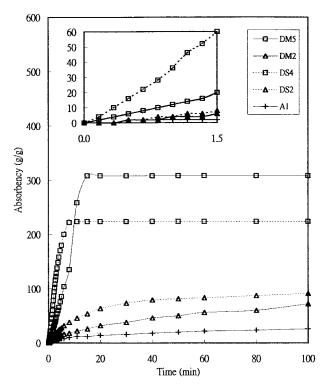


Figure 5 Swelling behavior of various xerogels in 2 $\times 10^{-4}M$ ZnCl_{2(aq)} by DW method.

Conditions	DM1	DM2	DM3	DM4	DM5
	2 imes	$10^{-4}M$ CuCl ₂			
Initial absorption rate (g/min)		2			
(30 s)	7.9	4.0	3.8	8.1	7.9
(1–3 min)	2.7	2.8	7.7	14.7	22.6
$t_{ m req} ({ m min})^{ m a}$	400	400	40	30	30
$Q'_{\rm eq}$ (gH ₂ O/g)	117	132	221	234	377
	2 imes	$10^{-4}M$ CoCl ₂			
Initial absorption rate (g/min)					
(30 s)	4.0	4.0	11.9	11.9	8.0
(1–3 min)	2.9	3.1	15.5	16.5	17.5
$t_{\rm req}~({\rm min})$	300	300	30	30	15
$Q'_{\rm eq}$ (gH ₂ O/g)	74	80	168	173	232
	2 imes	$10^{-4}M$ NiCl ₂			
Initial absorption rate (g/min)					
(30 s)	0	0	0	8.0	11.8
(1–3 min)	4.4	4.4	19.5	17.6	26.1
$t_{\rm req} ({\rm min})$	100	30	30	30	15
$Q'_{ m eq}~(m gH_2O/ m g)$	46	72	178	188	229
	2 imes	$10^{-4}M$ ZnCl ₂			
Initial absorption rate (g/min)		2			
(30 s)	_	4.0	_	_	11.9
(1–3 min)	_	3.4	_	_	17.9
$t_{\rm req} ({\rm min})$	_	300	_	_	15
$Q_{\rm eq}^{\prime}$ (gH ₂ O/g)	_	110	_	_	308

Table III	Absorption Characteristics for SA/DMAAPS Copolymeric
Gel Syster	ns Before Gel Transition Concentration

SA–sulfobetaine copolymeric gels. This is because the dissociated sodium ions could bind to the sulfonate group on the DMAAPS or DMAPS chain and reduce the concentration gradient of the free sodium ion.³²

In a further comparison of the swelling behaviors of these two series gels, it is found that the $Q'_{\rm eq}$ values for the DM series are higher than those for the DS series with the sulfobetaine content in the copolymeric gel over 8.0×10^{-3} molar ratio, but the initial absorption rates for DS gels are faster than those for DM gels. However, when the content of sulfobetaine in these gels is < 8.0 $imes 10^{-3}$ molar ratio, the $Q'_{
m eq}$ and the initial absorption rate for DS gels are larger than those for DM gels. These results explicitly show that the swelling behaviors of these gels would be affected by the internal structure and the content of the sulfobetaine in the copolymeric gels. In addition, the copolymeric gel with DMAPS component has a higher water absorbency and initial absorption rate in the presence of $2 \times 10^{-4} M \text{ CuCl}_{2(aq)}$ solution. Hence, the effect of a carboxylate group in DMAPS on the swelling behavior of the copolymeric gel is more obvious than that of an amido group in DMAAPS when a small amount of sulfobetaine is added to the gel system. A similar result is also obtained from Figures 3–5 for the two series of gels in the presence of $CoCl_{2(aq)}$, $NiCl_{2(aq)}$, and $ZnCl_{2(aq)}$ aqueous solutions.

More absorption characteristic data for DM and DS series gels in four metal salt solutions before the gel transition concentration (2 $\times 10^{-4}M$) are shown in Tables 3 and 4, respectively. Comparing the initial absorption rates for the stages of the first 30 s and from $\sim 1-3$ min in Tables III and IV, nearly the same initial absorption rates for the gels with a lower content of sulfobetaine can be observed. The initial absorption rates increase with increasing sulfobetaine content in the gels. The absorption rate for DS4 sharply increases, and the $t_{\rm req}$ is shorter (only 6 min). The trend of the water absorbencies is in the order CuCl_{2(aq)} > ZnCl_{2(aq)} > CoCl_{2(aq)} > NiCl_{2(aq)}

Conditions	A1	DS1	DS2	DS3	DS4
	2 imes	$10^{-4}M$ CuCl ₂			
Initial absorption rate (g/min)		2			
(30 s)	8.0	7.8	8.0	11.9	27.8
(1–3 min)	3.1	3.9	7.5	13.7	93.4
$t_{ m req} \ ({ m min})^{ m a}$	200	500	40	15	6
$Q'_{\rm eq}$ (gH ₂ O/g)	68	175	139	203	327
	2 imes	$10^{-4}M$ CoCl ₂			
Initial absorption rate (g/min)					
(30 s)	0	3.8	0	0	16.0
(1–3 min)	1.8	3.4	10.5	13.0	55.5
$t_{\rm req}~({\rm min})$	200	300	50	20	8
$Q_{\rm eq}^{\prime}({\rm gH_2O\!/g})$	52	118	122	140	186
	2 imes	$10^{-4}M$ NiCl ₂			
Initial absorption rate (g/min)					
(30 s)	0	3.9	4.0	4.0	15.7
$(1-3 \min)$	3.8	3.9	6.5	8.6	46.0
$t_{\rm req}~({\rm min})$	150	150	50	20	8
$Q'_{\rm eq}~({\rm gH_2O/g})$	52	116	101	106	182
	2 imes	$10^{-4}M$ ZnCl ₂			
Initial absorption rate (g/min)		_			
(30 s)	4.0	—	4.0	—	32.0
(1–3 min)	2.0	—	6.6	—	46.5
$t_{\rm req}$ (min)	300	—	300	—	11
$Q'_{\rm eq}$ (gH ₂ O/g)	83.3	_	127.0	_	224.0

Table IV	Absorption Characteristics for SA/DMAPS Copolymeric
Gel Syste	ms Before Gel Transition Concentration

for the two gel systems under these four salt solutions. This trend is different from that obtained by the suction method $(CoCl_{2(aq)} > CuCl_{2(aq)}) > NiCl_{2(aq)})$.³² The orders of initial absorption rate during the 1–3 min stage in the latter salt solutions are $NiCl_{2(aq)} > CuCl_{2(aq)} > ZnCl_{2(aq)} > CoCl_{2(aq)}$ and $CuCl_{2(aq)} > CoCl_{2(aq)} > ZnCl_{2(aq)} > NiCl_{2(aq)}$ for DM5 and DS4, respectively.

Effect of Salt Concentration on the Water Absorbency

The typical swelling kinetics for DM5 and DS4 gels in three concentrations $(2 \times 10^{-4}, 2 \times 10^{-3}, and 2 \times 10^{-2}M)$ of $CuCl_{2(aq)}$, $CoCl_{2(aq)}$, $NiCl_{2(aq)}$, and $ZnCl_{2(aq)}$ solutions are, respectively, shown in Figures 6–9. The results from these figures show that the Q'_{eq} values decrease with an increase in salt concentration. On the other hand, the Q'_{eq} values for DM5 are higher than for DS4 in these salt solutions. This result implicitly indicates that the complexing ability of these salts with DS4 is

larger than that with DM5. Obviously, the internal structure of sulfobetaine significantly affects the complexing ability of the gels with salts; in other words, the carboxylate group (—COO—) in DMAPS has a larger complexity ability in these four salt solutions.

In addition, the initial absorption rates (initial slope) shown in these figures decrease with an increase of salt concentrations. In contrast to the $Q'_{\rm eq}$ value, the initial absorption rates for DS4 are larger than those for DM5. This result obviously indicates that the hydrophilicity for DS4 gel is higher than that for DM5.

The absorption characteristic for some SA/sulfobetaine copolymeric gels at gel transition concentration $(2.0 \times 10^{-3}M)$ and after gel transition concentration $(2.0 \times 10^{-2}M)$ in the four salt solutions are summarized in Tables V and VI, respectively. From Table V, the Q'_{eq} values are in the orders NiCl₂ > CuCl₂ > ZnCl₂ = CoCl₂, CuCl₂ > NiCl₂ > ZnCl₂ > CoCl₂, CuCl₂ > NiCl₂ = CoCl₂, and

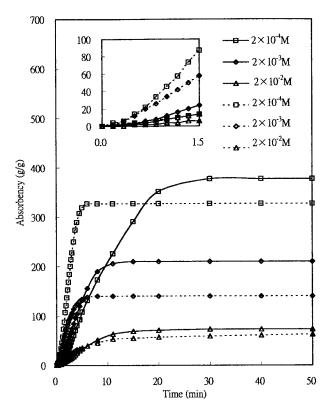


Figure 6 Swelling behaviors for DM5 (\longrightarrow) and DS4 (\cdots) by DW method in three CuCl₂ concentrations.

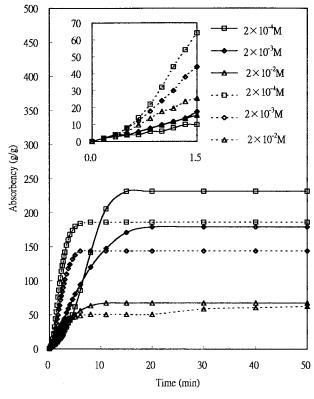


Figure 7 Swelling behaviors for DM5 (-----) and DS4 (\cdots) by DW method in three $CoCl_2$ concentrations.

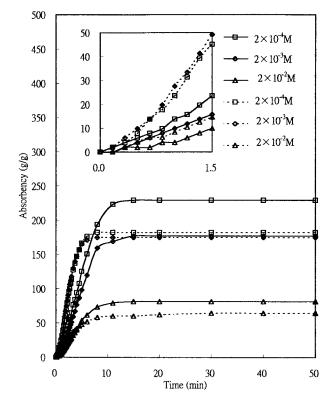


Figure 8 Swelling behaviors for DM5 (\longrightarrow) and DS4 (\cdots) by DW method in three NiCl₂ concentrations.

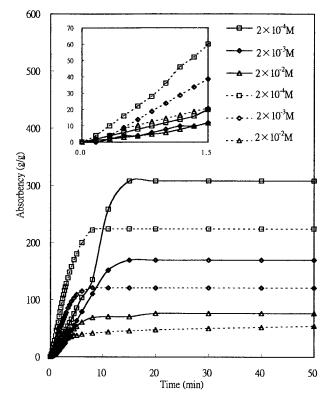


Figure 9 Swelling behaviors for DM5 (----) and DS4 (\cdots) by DW method in three ZnCl₂ concentrations.

Conditions	A1	DM2	DM5	DS2	DS4
	2 imes 1	$10^{-3}M$ CuCl ₂			
Initial absorption rate (g/min)		2			
(30 s)	3.9	4.0	4.0	4.0	24
(1–3 min)	3.7	5.5	31.6	7.6	36.0
$t_{ m req} \ ({ m min})^{ m a}$	300	60	15	60	8
$Q'_{\rm eq}$ (gH ₂ O/g)	59	94	210	97	140
	2 imes 2	$10^{-3}M$ CoCl ₂			
Initial absorption rate (g/min)		_			
(30 s)	0	0	7.9	4.0	16
(1–3 min)	2.5	2.3	18.5	5.2	39.4
$t_{\rm req}~({\rm min})$	270	230	20	140	6
$Q'_{\rm eq}$ (gH ₂ O/g)	53	57	179	71	144
	2 imes 1	$10^{-3}M$ NiCl ₂			
Initial absorption rate (g/min)					
(30 s)	3.9	0	7.9	4.0	19.7
(1–3 min)	4.0	5.3	21.5	9.1	46.9
$t_{\rm req}~({\rm min})$	150	50	15	40	8
$Q'_{\rm eq}~({ m gH_2O/g})$	68	78	177	109	175
	2 imes 1	$10^{-3}M$ ZnCl ₂			
Initial absorption rate (g/min)		-			
(30 s)	0	0	7.9	8.0	17.9
(1–3 min)	2.6	4.3	13.5	7.5	26.8
$t_{\rm req}$ (min)	>300	>300	15	150	8
$Q'_{\rm eq}$ (gH ₂ O/g)	59	69	170	70	121

Table VAbsorption Characteristics for SA/DMAAPS and SA/DMAPSCopolymeric Gel Systems in Gel Transition Concentration

 $\rm NiCl_2 > \rm CuCl_2 = \rm CoCl_2 > \rm ZnCl_2$, for A1, DM2, DM5, DS2, and DS4 xerogels, respectively. These results show that the tendency of complexation of the said cations with carboxylate group in the DS series gel is similar to A1 gel, but the DM series is different from A1 gel under this salt concentration. At the same time, it is found that the complexing ability of gels with $\rm Zn^{2+}$ or $\rm Co^{2+}$ ions is larger than that with $\rm Ni^{2+}$ or $\rm Cu^{2+}$ ions. This result is significantly different from those obtained by the suction method presented in previous reports.^{27,32,33}

The initial absorption rates are somewhat improved by adding more sulfobetaine into copolymeric gels, especially for DM5 and DS4 gels. The $t_{\rm req}$ rapidly decreases as more of the sulfobetaine is copolymerized into the gels.

The swelling behavior by the suction method for DM gels exhibited deswelling behavior and converged to zero at higher salt concentration as reported in our previous article.³² The swelling kinetic behaviors by the DW method for some gels at higher salt concentrations (over the gel transition concentration) are shown in Table VI.

The Q'_{eq} values at $2 \times 10^{-2}M$ concentration are in the orders $\text{ZnCl}_2 > \text{CuCl}_2 = \text{NiCl}_2 > \text{CoCl}_2$, $\text{NiCl}_2 > \text{ZnCl}_2 > \text{CuCl}_2 > \text{CoCl}_2$, $\text{ZnCl}_2 > \text{NiCl}_2$ $= \text{CuCl}_2 > \text{CoCl}_2$, and $\text{ZnCl}_2 > \text{NiCl}_2 = \text{CuCl}_2$ $= \text{CoCl}_2$, for DM2, DM5, DS2, and DS4, respectively. These results show that the complexing ability of the salt cations with the gels (over the gel transition concentration) has the same tendency, except for the DM5 gel. This result also shows that the larger complexing ability of gels is found with CoCl₂. This phenomenon is different from the result obtained by the suction method. The initial absorption rates for the gels are sharply decreased under this condition, especially for DM5 and DS4, and the all t_{reg} 's are increased.

From the above discussion, the complexing ability of a gel with salt cation is strongly dependent on the kind and concentration of salt aqueous solutions during the gel swelling process and

Conditions	DM2	DM5	DS2	DS4
	2 imes 10	^{-2}M CuCl ₂		
Initial absorption rate (g/min)		2		
(30 s)	0	3.9	4.0	7.9
(1–3 min)	1.1	5.9	2.2	8.2
$t_{ m req} \ ({ m min})^{ m a}$	390	30	300	60
$Q'_{\rm eq}$ (gH ₂ O/g)	58	73	59	65
	2 imes 10	^{-2}M CoCl ₂		
Initial absorption rate (g/min)		2		
(30 s)	3.9	7.7	3.9	11.8
(1–3 min)	3.3	11.6	3.9	12.3
$t_{\rm req} ({\rm min})$	230	11	160	50
$Q_{\rm eq}^{\prime} ({\rm gH_2O/g})$	55	68	51	63
	2 imes 10	^{-2}M NiCl ₂		
Initial absorption rate (g/min)				
(30 s)	0	4.0	0	8.3
(1–3 min)	2.3	11.9	3.8	12.5
$t_{\rm req}$ (min)	> 150	15	> 150	30
$Q'_{\rm eq}$ (gH ₂ O/g)	58	82	60	65
	2 imes 10	^{-2}M ZnCl ₂		
Initial absorption rate (g/min)		4		
(30 s)	4.0	6.0	3.8	16.7
(1–3 min)	4.0	12.2	3.1	8.7
$t_{\rm req} ({\rm min})$	>300	20	>300	180
Q'_{eq} (gH ₂ O/g)	72	76	67	75

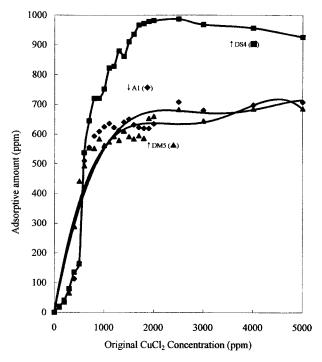
Table VI	Absorption Characteristics for SA/DMAAPS and SA/DMAPS
Copolyme	ric Gel Systems After Gel Transition Concentration

is also dependent on the gel compositions and constituents.

Adsorption of Copper Ion

To access the effect of the sulfobetaine component in the copolymeric gel on adsorption of salt ion (Cu^{2+}) , samples of A1, DS4, and DM5 immersed into various concentrations of copper chloride aqueous solution were selected. Figure 10 shows the adsorbed amount of copper ion (Cu^{2+}) for sample gels A1, DS4, and DM5. The results shown in Figure 10 demonstrate that the adsorbed amount for DS4 gel is higher than that for A1 gel at higher salt concentration (>700 ppm), but they have almost the same adsorbed amount at a lower concentration. This is due to the adsorption of copper ion being attributed mainly to sodium carboxylate group (A1) at a lower salt concentration. However, the influence of sulfobetaine component in DS4 occurs until the SA component reaches saturation under higher salt concentration, but the sulfobetaine component (DMAAPS) in DM5 gel does not show the same influence as the DS4 gel. This evidence explicitly indicates that sulfobetaine structure in the gel affects the adsorption of metal ions in aqueous salt solution. Furthermore, the results shown in Figure 11 indicate that the maximum adsorbed amounts for A1, DM5, and DS4 are 600, 500, and 700 ppm, respectively.

Figure 12 shows the relation of the adsorbed amount of Cu^{2+} with various gel sample amounts in a fixed copper chloride concentration. The results show that, in the same salt concentration, the more gel sample used, the lower the amount adsorbed. This is because more water was adsorbed by gel, per se, when more gel sample was used; that is, the adsorbed copper ion was relatively decreased. In addition, Figure 12 also shows that the optimal amount of gel sample used is 0.05 and 0.1 g for 500 and 1000 ppm salt con-



2000 2000ppm 1800 1500ppm 1000ppm 1600 500ppm 1400 Adsorptive amount (ppm) 1200 1000 800 600 400 200 0 0.05 0.15 0.2 0 0.1 0.25 Sample weight (g)

Figure 10 Adsorptive amount of Cu^{2+} in various $CuCl_2$ concentrations for DS4 (\blacksquare), A1 (\blacklozenge), and DM5 (\blacktriangle).

centration, respectively. Theoretically, the more gel used, the more the copper is adsorbed. However, an optimal adsorbed amount was observed. Hence, to confirm this observation, the experi-

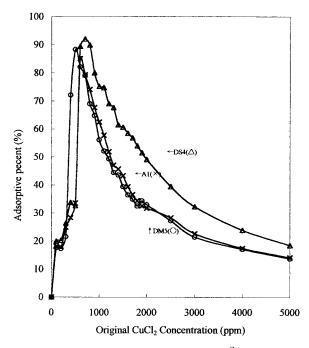


Figure 11 Adsorptive amount of Cu^{2+} in various $CuCl_2$ concentrations for DS4 (\triangle), A1 (\times), and DM5 (\bigcirc).

Figure 12 Adsorptive amount of Cu^{2+} of various sample weights.

ment was further carried out on higher salt concentrations. The results in Figure 12 also show optimal values at 0.15 and 0.20 g for 1500 and 2000 ppm salt concentration, respectively, confirming this observation.

CONCLUSION

The swelling kinetic behaviors of these super absorbents are related to their structures, their chemical compositions, and the nature of external solutions. The water absorbency of the sulfobetaine copolymeric gel series in deionized water or in various salt solutions would be improved effectively by copolymerizing SA with a small amount of a zwitterionic monomer (DMAAPS or DMAPS). The water absorbency of gel with DMAPS is larger than that of a gel with DMAAPS when the amount of zwitterionic monomer added is <0.8mol %. A contrary result is obtained when the amount of zwitterionic monomer added is >0.8 mol %. In aqueous salt solution, the absorbencies and initial absorption rates of these gels are strongly dependent on the kinds and concentrations of salt. In lower copper ion concentration, the adsorptive amount of a gel with DMAAPS (DM5) exhibits the best adsorption, but at higher

copper ion concentration, the optimal adsorption is the gel with DMAPS (DS4).

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