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ORIGINAL CONTRIBUTION

Swelling behavior of ionically cross-linked polyampholytic hydrogels in varied salt solutions

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Abstract Ionically cross-linked polyampholytic hydrogels were synthesized by redox copolymerization of acrylamide and an ionic complex of (*N*,*N*-diethylamino)ethyl methacrylate and acrylic acid (designated as PADA hydrogel). The swelling behavior of the hydrogels in water indicated that a minimal equilibrium swelling ratio is found when the molar ratio of anionic/cationic monomers was 1.55. In NaCl solution, the hydrogels exhibited the typical swelling behavior of conventional polyampholytic gels. Their equilibrium swelling ratios increased with an increase in the NaCl concentration. In solutions of multivalent ions ($CaCl_2$ and trisodium citrate solutions), the equilibrium swelling ratios of the hydrogels increased first and were then followed by a decrease with an increase in salt concentration. Interestingly, an unexpected abrupt swelling phenomenon was observed when the fully swollen hydrogels in salt solution were transmitted to pure water. The unique swelling behavior of PADA hydrogels depends not only on the molar ratio of the anionic/cationic monomers but also on the valency of the ions.

Keywords Polyampholytic hydrogels · Ionical cross-linking · Swelling behavior

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Introduction

In general, conventional polyampholytic hydrogels are chemically cross-linked polymeric 3D networks containing both positively and negatively charged groups. Similar to some biomacromolecules, the long-range Coulombic interactions in polyampholytic hydrogels result in a complicated dynamic swelling behavior [1–3]. For example, polyampholytic gels shrink at the isoelectric point (pI, defined as the pH at which the gel has a minimal equilibrium swelling ratio (SR_e) and shows an antipolyelectrolyte effect [4–7].

The swelling behavior of chemically cross-linked polyampholytic hydrogels has been much discussed elsewhere. Their swelling behavior depends on the ambient conditions such as solvent [8, 9], pH [5, 7], temperature [1, 10, 11], ionic strength [2], electric fields [3], etc. Long-range Coulombic interactions are a main factor that governs the swelling behavior of the polyampholytic gels [12, 13]. The classical Donnan theory cannot interpret the swelling behavior of polyampholytic gels because electrostatic interactions between ions are not considered [12, 14]. Satoh and coworkers reported ion-specific swelling behavior of poly(vinyl alcohol) gels containing sulphonate and quaternary ammonium groups in solutions of strongly hydrated anions, such as F^-, SO_4^{2-}, HPO_4^{2-} and citrate anion [15]. They suggested that the ion-specific swelling behavior could be explained by the compatibility of ionic hydration of the polymer hydroxyl groups through the electron pair donation and acceptance abilities of the water molecules. However, less attention has been paid to the swelling behavior of ionically cross-linked polyampholytic hydrogels, particularly in various salt solutions.

Unlike conventional chemically cross-linked polyampholytic hydrogels or ionically cross-linked polyampholytic hydrogels with strongly basic and acidic groups, in the

Table 1 Feed composition for the preparation of PADA gels

Ingredients	PADA-a	PADA-b	PADA-c	PADA-d
AAc (mmol)	19.6	24.3	28.8	34
DEAEM (mmol)	20.4	15.7	11.2	6
AAm (mmol)	11.3	11.3	11.3	11.3
H_2SO_4 (98%, ml)	1.44	–	–	–
H_2O (ml)	4	4	4	4
APS (8%, ml)	0.5	0.5	0.5	0.5
PBS (4%, ml)	0.25	0.25	0.25	0.25
A/C[a]	0.96	1.55	2.57	5.67

[a] The molar ratios of anionic/cationic monomers

present work, an ionic complex monomer was obtained when weak basic (*N*,*N*-diethylamino)ethylmethacrylate (DEAEM) was protonated with weak acidic acrylic acid (AAc). Through free radical copolymerization of the ionic complex with acrylamide (AAm), the ionically cross-linked polyampholytic hydrogel poly(AAc-DEAEM-AAm) (designated as PADA) was prepared. Ambient ions can be attracted to their opposite-charged groups on polymeric chains and weakened or destroyed ionic cross-linkages in PADA hydrogel. To understand the influence of the valent status, concentration, and feature of ambient ions on the ionic cross-linkage in PADA hydrogels, the swelling behavior of PADA gels with varied molar ratios of anionic/cationic monomers (A/C) were investigated in aqueous sodium chloride, calcium chloride, and trisodium citrate solutions.

Materials and methods

Materials

All chemicals were commercially available. (*N*,*N*-diethylamino) ethyl methacrylate (DEAEM, Aldrich) and acrylic acid (AAc, Aldrich) were distilled before use. Acrylamide (AAm, Aldrich) was recrystallized from anhydrous alcohol before use. Aqueous ammonium persulfate (APS) solutions and aqueous potassium bisulfite (PBS) solutions were prepared for polymerization in concentrations of 8 and 4 wt%, respectively. Sodium chloride (NaCl), calcium chloride ($CaCl_2$), and trisodium citrate (TSC) were used as received.

Preparation of PADA Gels

The feed composition for preparation of the PADA gels is listed in Table 1. The detailed procedure of preparation has been described previously [16].

The four kinds of ionically cross-linked polyampholytic hydrogels are designated as PADA-a, PADA-b, PADA-c, and PADA-d, respectively (Table 1). The molecular structures of PADA hydrogels are shown in Scheme 1.

Swelling studies

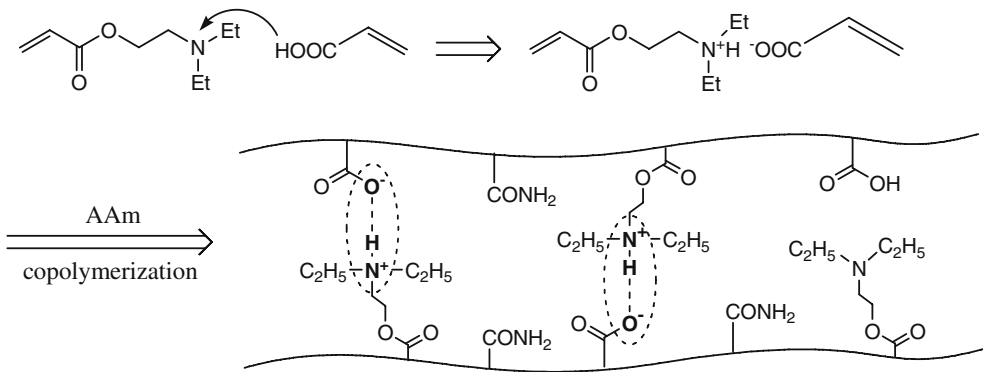
The swelling of PADA gels in pure water was carried out as follows. Pieces of xerogel (ca 10–20 mg) were immersed in 100 ml distilled water at 25 °C. The samples of swollen PADA gel were weighed after removal of surface water using filter paper at designed time intervals. Subsequently, the samples were put into 100 ml of freshly distilled water to maintain a constant pH and ionic concentration in distilled water.

The swelling of PADA gels in salt solutions was performed similarly. Pieces of xerogel (ca 10–20 mg) were immersed in 100 ml of various salt solutions at 25 °C. The samples of swollen PADA gels were weighed after removal of surface water using filter paper. All samples were monitored in this way until the swelling equilibrium was reached.

The swelling ratio of PADA gels was calculated from:

$$\mathrm{SR} = W_t/W_0 \tag{1}$$

Herein, SR is the swelling ratio of PADA gels. W_t is the weight of gels swollen at time t. W_0 is the weight of the xerogels.



Scheme 1 Molecular structure of PADA hydrogels; the 3D network is formed by the electrostatic attraction between positively charged amide groups and negatively charged carboxyl groups as illustrated in the *dashed ellipse*

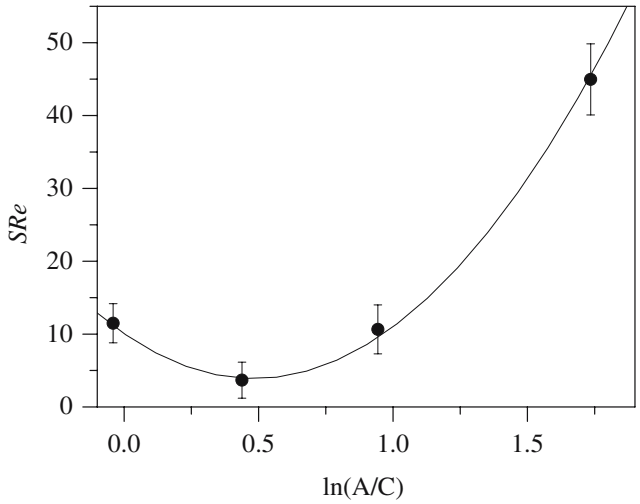


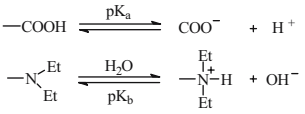
Fig. 1 Influence of the logarithm of A/C ratios on the equilibrium swelling ratio (SR_e) of PADA gels in water

Results and discussion

The equilibrium swelling of PADA gels in water

Figure 1 shows the SR_e of PADA gels in water as a function of the values of ln(A/C). In general, polyampholytic gels have a minimal SR_e when the value of A/C is 1 [17, 18]. We find a minimal SR_e (ca 3.8) of PADA gels when the value of A/C is 1.55.

Scheme 2 Ionic equilibrium of the monomers of AAc and DEAEM in water



As strongly acidic/basic groups can be completely ionized in water, the ion equilibrium in polyampholytic hydrogel with strong acid and basic groups is only determined by the molar ratio of the A/C. When the value of A/C is 1, the net charge of polyampholytic hydrogel should be 0. In this case, the electrostatic attraction in the polymer network should be at a maximum, and the polymer gel has a minimal SR_e. However, the ion equilibrium is not only determined by the A/C ratio but also by the dissociation constants of the ionizing groups in PADA gels containing weakly acidic and basic groups. As shown in Scheme 2, the ionic equilibrium in the monomer mixture resulted in a difference of pK_a and pK_b. In this case, zero net charge for PADA gels was found when A/C was 1.55 in stead of 1. Thereby the SR_e was influenced not only by the molar ratio of anionic and cationic monomer but also by the pK_a (ca 5.0) of AAc and pK_b (ca 7.9) of DEAEM [19]. As a

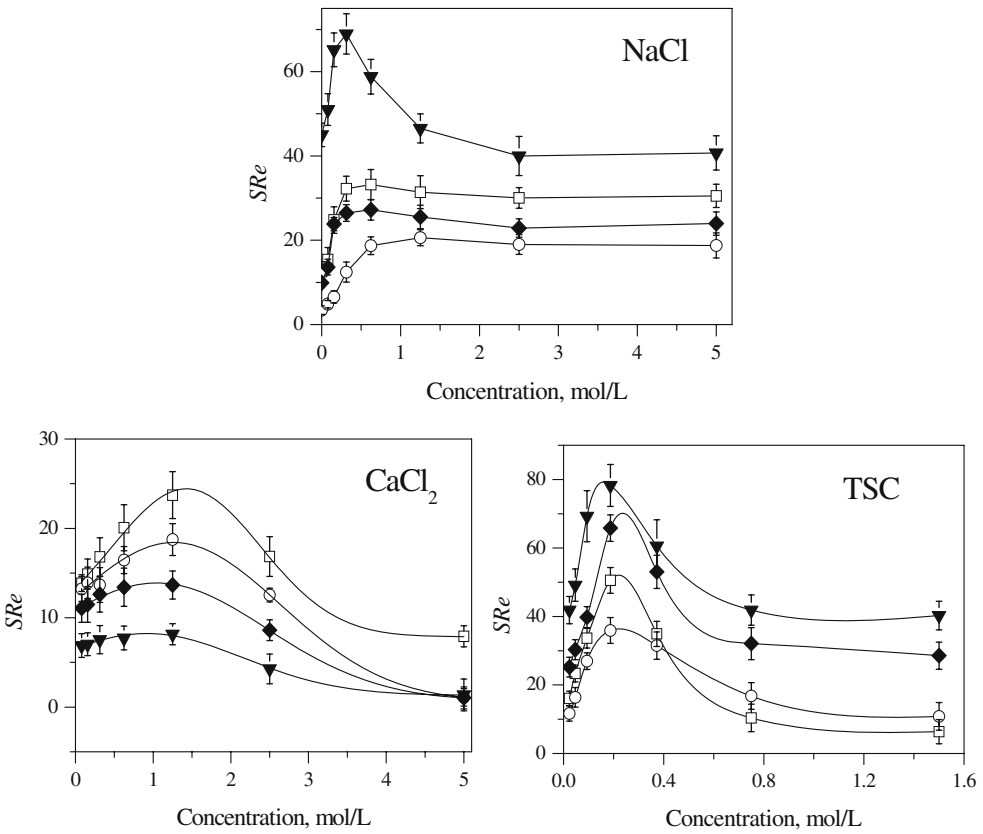
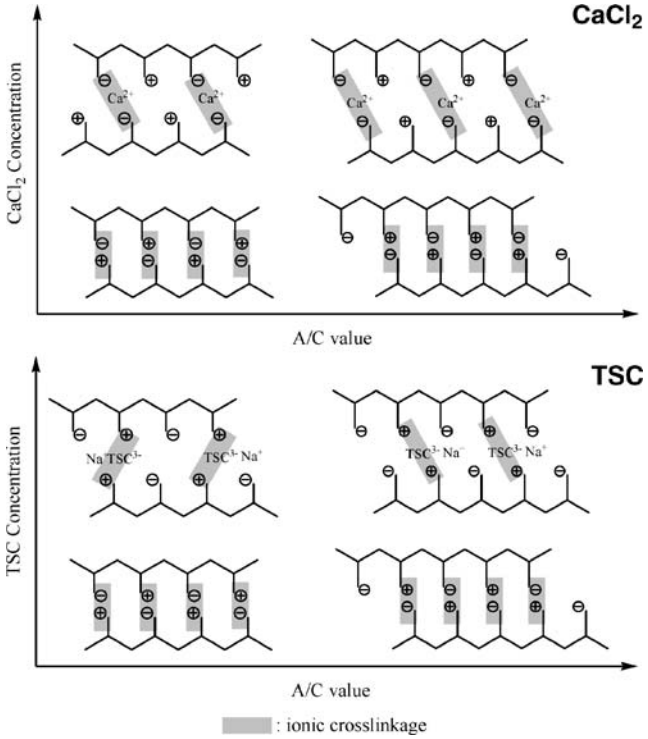


Fig. 2 SR_e of PADA gels as a function of the NaCl, $CaCl_2$, and TSC concentration. PADA-a (*open squares*), PADA-b (*open circles*), PADA-c (*filled diamonds*), and PADA-d (*filled triangles*)



Scheme 3 Schematic representation for the influence of the A/C values on the SR_e of PADA hydrogel in $CaCl_2$ and TSC solutions

result, the minimal SR_e of PADA gels was observed when PADA gels had zero net charge, which implies a maximal cross-linking density.

Dependence of the SR_e of PADA gels on the concentration of salt solutions

Figure 2 shows the SR_e of PADA gels in NaCl, $CaCl_2$, and TSC solutions. PADA gels exhibit a typical antipolyelectrolyte effect of polyampholytic gels when the A/C value is in the range of 0.96−2.57 in NaCl solutions. However, more complicated swelling behavior was found in multivalent ion solutions containing $CaCl_2$ or TSC. The swelling behavior of PADA gels in a low concentration range of multivalent ions is similar to that in NaCl solutions. In the high concentration range, PADA gels deswelled with an increase in concentration of multivalent ions. The trend of deswelling for the case of $CaCl_2$ is more obviously than that for the case of TSC.

These results revealed that extra ionic cross-linkages may be formed between multivalent salt ions and opposite charged groups of PADA at higher concentration, which resulted in a collapse of the PADA gels. The cationic and anionic ions of the salt can bind with the oppositely charged groups (COO^- and $\equiv N^+H$) of PADA. Thereby the electrostatic attraction between those charged groups will be screened, and the ionic cross-linking structures of the polymer will be broken. On the other hand, when the A/C value is higher, as for the PADA-d gel (A/C=5.67), PADA gels behave more as polyanion gels than as a polyampholytic gel. Polyelectrolyte hydrogels usually collapse with an increase in salt concentration owing to the osmotic pressure of the counter-ions [20, 21].

Interestingly, Fig. 2 shows some regularity in the swelling behavior: with an increase in the A/C ratios, i.e., more negatively charged groups and less positively charged groups in the PADA gels, the SR_e increases in the following order in $CaCl_2$ solutions, and decreased in the same order in TSC solutions:

$$\text{PADA} - \text{a} > \text{PADA} - \text{b} > \text{PADA} - \text{c} > \text{PADA} - \text{d}$$

This might be attributed to the different charge sign of the multivalent ions. With an increase in the A/C values (from PADA-a to PADA-d), the increased number of carboxyl groups could form more ionic cross-linkages with Ca^{2+}, leading to the decreasing SR_e of PADA hydrogels in $CaCl_2$ solutions. However, in the TSC solutions, the increased number of carboxyl groups does not influence the amount of ionic cross-linkages between quaternary

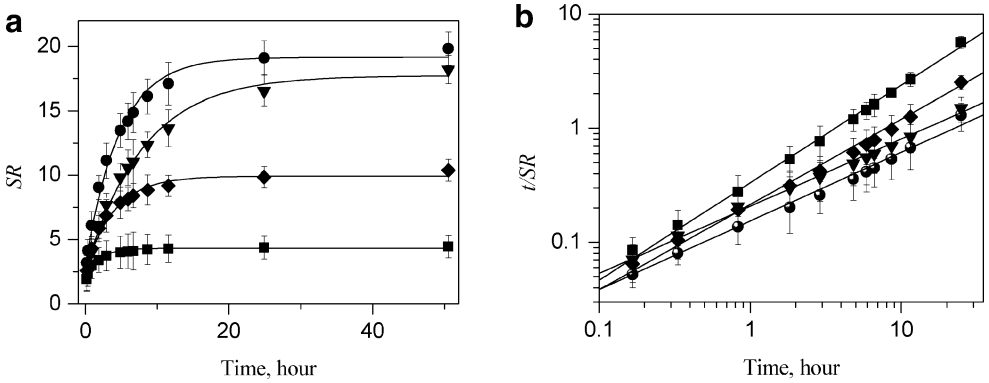


Fig. 3 The SR (**a**) and *t*/SR (**b**) of PADA-b gels versus the swelling time in NaCl solutions at different concentrations: 0.08 mol/l (*filled squares*), 0.3 mol/l (*filled diamonds*), 1.3 mol/l (*filled circles*), and 5 mol/l (*filled triangles*)

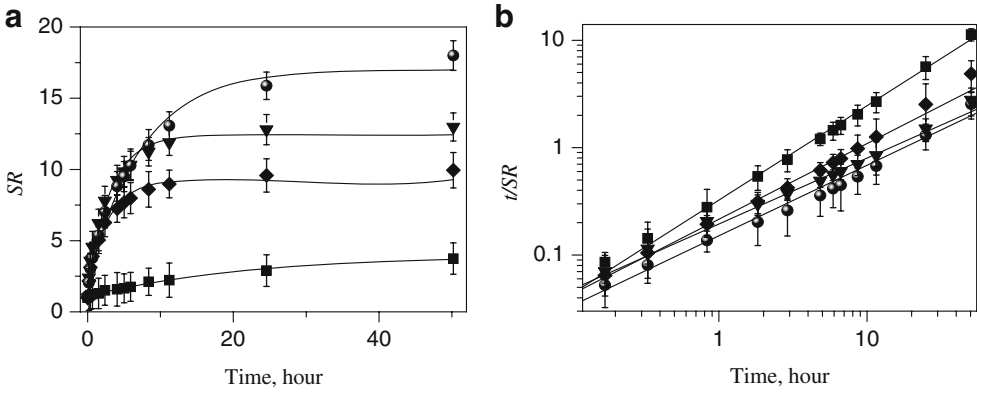


Fig. 4 The SR (**a**) and *t*/SR (**b**) of PADA-b gels versus the swelling time in $CaCl_2$ solutions at different concentrations: 0.08 mol/L(*filled squares*), 0.3 mol/l (*filled diamonds*), 1.3 mol/l (*filled circles*), and 5 mol/l (*filled triangles*)

ammonium groups and citrate ions. Therefore, an increase in electrostatic repulsion among carboxyl groups leads to the increase in SR_e of PADA hydrogels in TSC solutions (Scheme 3).

The swelling kinetics of PADA gel in NaCl, $CaCl_2$ and TSC solutions

The swelling kinetics of PADA gels in three kinds of salt solutions are shown in Figs. 3a, 4a and 5a. The swelling kinetics could be divided into two stages: the fast swelling occurring before 24 h and the equilibrium swelling occurring after 24 h. The characteristics and concentration of salt seem to have less influence on the swelling kinetics. The second-order swelling kinetic theory proposes that the swelling rate of a hydrogel is controlled by both the diffusion of solvent molecules and the relaxation of macromolecule chains [14], i. e., the swelling rate is directly proportional to the square of the remaining swelling capacity $(SR_e–SR)^2$. Thus:

$$\frac{d\mathrm{SR}}{dt} = K[\mathrm{SR_e} - \mathrm{SR}]^2 \tag{2}$$

Equation (2) is integrated between the limits SR=0, when t=0 and SR for t and rearranged. The well-known Schott's equation is obtained:

$$\frac{t}{\mathrm{SR}} = \frac{t}{\mathrm{SR}_e} + \frac{1}{k \cdot \mathrm{SR_e^2}} \tag{3}$$

Herein, SR is the swelling ratio of the gel at time t, and SR_e is the equilibrium swelling ratio of the gel. k is the rate constant.

Figures 3b, 4b and 5b show the plots of t/SR as a function of time t in three kinds of salt solutions. The swelling kinetics of PADA gels are in good agreement with the second-order kinetic equation (3).

Unique swelling behavior of PADA gels in water after full swelling in salt solutions

The covalently cross-linked polyampholytic hydrogels usually swell in salt solutions and deswell in water [15, 22, 23]. As shown in Fig. 6, an unexpected abrupt reswelling phenomenon for PADA-b gels was observed when the fully swollen gels in salt solutions, particularly in

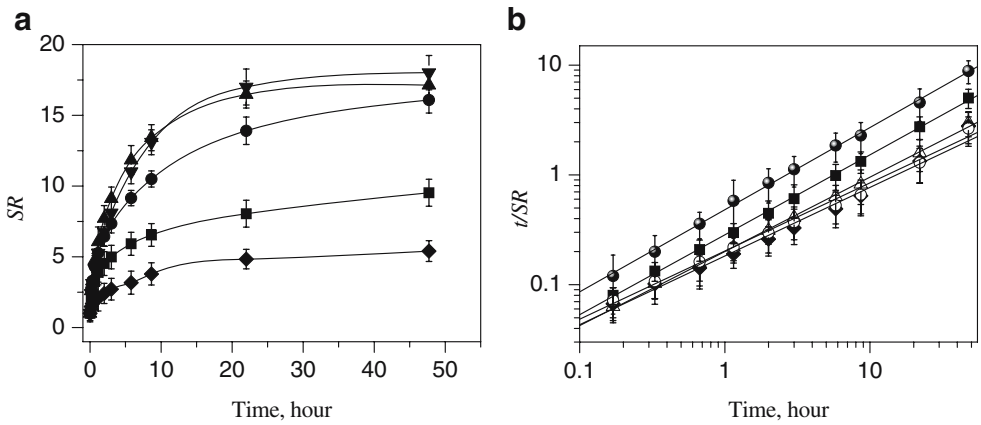


Fig. 5 The SR (**a**) and *t*/SR (**b**) of PADA-b gels versus the swelling time in TSC solutions at different concentrations: 0.09 mol/l (*filled squares*), 0.2 mol/l (*filled triangles*), 0.4 mol/l (*filled diamonds*), 0.8 mol/l (*filled circles*), and 1.5 mol/l (*filled circles*)

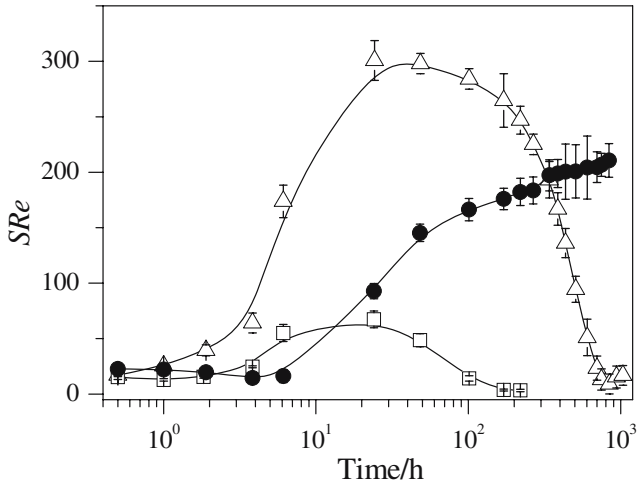


Fig. 6 The plot of the SR of PADA-b gels in water versus the logarithm of time after full swelling in 1.25 mol/l NaCl (*open squares*), 1.25 mol/l $CaCl_2$ (*filled circles*), and 1.5 mol/l TSC (*open triangles*) solutions

multivalent $CaCl_2$ and TSC solutions, were placed in pure water. The maximal SR could reach more than 200. Subsequently, it was followed by deswelling.

In contrast to the antipolyelectrolyte behavior of conventional polyampholyte hydrogels [4–7], the abrupt reswelling phenomenon of polyampholytic gels has scarcely been reported in the literature. It can be attributed to the change of counter-ions in the PADA hydrogels. When the PADA-b gel was immersed in salt solution, the electrostatic interaction among the ionic groups was weakened or screened by the salt ions with an opposite charge. When the gel was transmitted from salt solutions to pure water, the concentration of ions in the gel was initially much higher than that in water. The osmotic pressure difference produced by these counter-ions led to an abrupt swelling of PADA hydrogels.

After abrupt reswelling in pure water, PADA hydrogels were then followed by deswelling with an increase in time. This can be ascribed to easy scission of the bound counter-ions (COO^-Na^+) in pure water. Thus, ionic cross-linkages between ionized carboxyl groups and quaternary amino groups were formed again as shown in Scheme 1, resulting in a collapse of the gels. However, fully swollen PADA hydrogels in $CaCl_2$ solution maintained their swelling states in pure water. This might be ascribed to the difficult dissociation of the bound counter-ions [$(COO^-)_2Ca^{2+}$] in water.

Conclusion

The swelling behavior of PADA gels depends not only on the A/C value, but also on the dissociation constant of the acidic and basic groups. In comparison with conventional polyampholytic gels, the minimum swelling ratio of PADA gels was found when the value of A/C was 1.55 rather than 1. PADA gels showed the typical antipolyelectrolyte effect of polyampholytic gels in NaCl solutions and also at low concentration of $CaCl_2$ and TSC solutions containing multivalent cations. The increase in A/C resulted in a decrease in SR_e in $CaCl_2$ solutions in the following order: PADA-a > PADA-b > PADA-c > PADA-d, whereas SR_e increased in TSC solutions in the same order. The swelling kinetics of PADA gels in three kinds of salt solutions are in good agreement with second-order swelling kinetics. An unexpected abrupt swelling phenomenon was observed for fully swollen PADA gels in salt solutions, especially in $CaCl_2$ and TSC solutions. The change of counterions in the gel might be responsible for this unique swelling property.

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