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Effects of specific anions on the relationship between the ionadsorption properties of sulfobetaine gel and its swelling behavior



polyme



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ABSTRACT

The adsorption of cations and anions from four different halide solutions, i.e., KF, KCl, KBr, and KI solutions, onto N,N-dimethyl(acrylamidopropyl)ammonium propane sulfonate (DMAAPS) gels prepared using various cross-linker concentrations was investigated at a variety of temperatures; the swelling degrees of the gel in these solutions were also examined. The amount of K⁺ adsorbed coincided with the adsorption of the anions (i.e., I⁻, Br⁻, Cl⁻, or F⁻) because of simultaneous adsorption of the cations and anions onto DMAAPS gel. The order of anions, which gave larger amount of K⁺ adsorbed onto the gel, was opposite that of the Hofmeister series, i.e., $I^- > Br^- > Cl^- > F^-$. Furthermore, the relationship between the degree of swelling of the gel and amount of K⁺ adsorbed onto the gel was elucidated. The data points laid on the same line for the same halide solution even at different cross-linker concentrations or temperatures. At smaller degrees of swelling, the amount of K^+ adsorbed remained unchanged and then decreased gradually as the degree of swelling increased. In solutions containing anions with lower hydration ability, such as KI, the amount of K⁺ adsorbed decreased at larger degrees of swelling. In contrast, in solutions containing anions with higher hydration abilities, such as KCl, the adsorbed amount of K⁺ decreased at smaller degrees of swelling. Additionally, it was found that, in mixtures of these halide solutions, competitive adsorption of anions occurred. Anions with lower hydration abilities adsorbed more readily in the mixtures than in the single-anion solution. In contrast, anions with higher hydration abilities adsorbed less readily in the mixtures than in the single-anion solution.

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1. Introduction

Various zwitterionic betaine gels, such as phosphobetaine [1–3], sulfobetaine [4–6], carboxybetaine [7,8], semiinterpenetrating network (IPN) gel composed of amphiphilic gel and zwitterionic betaine polymers [9,10], and chemical—physical cross-linked double network (DN) gel, which was obtained by introducing ductile physical networks into the network of chemically cross-linked polysulfobetaine gels [11], have shown excellent chemical stability [12], good biocompatibility [13], ultralow fouling [14,15], and excellent mechanical properties [14,16]. Studies on the properties of polymers or gels based on betaine have received significant attention in the scientific community.

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A zwitterionic betaine polymer that contains both anionic and cationic active groups in the same polymeric repeat unit with an alkylene spacer group is neutral overall. It also offers potential improvement of the ion selectivity toward adsorption because the cations and anions in the solution can bond via both the negative and positive charges located in the same repeating unit [17–19]. Betaine polymers are generally thermosensitive in aqueous solutions [9,16,20]. The transition temperature, which is also referred to as the upper critical solution temperature (UCST), of sulfobetaine polymers varies over a wide range by altering the surrounding conditions and polymer characteristics, such as length of the alkylene spacer groups [16,20]. Interaction of the charged groups of betaine and ions in aqueous solution strongly determines the properties of the betaine polymer [21]. One of the unique properties of betaine is the ability of the fragments to form cyclic conformations of the cationic and anionic groups of neighboring monomer residues (intra-group), form contacts between the cationic and anionic groups of neighboring macromolecules (inter-





chain), and undergo head-to-tail stacking within single macromolecules (intra-chain); these interactions result in betaine being insoluble in pure water [21,22]. The solubility of betaine in solutions depends on the nature of the anions and cations and the charge/ radius ratio of the ions, which is described by the Hofmeister series and Pearson theory [21,23,24].

Recently, numerous studies on the properties related to the transition behaviors of both betaine polymers and gels and on the adsorption behavior of ions onto betaine gels in various aqueous solutions have been reported. A series of copolymeric gels containing sulfobetaine was investigated by Lee et al. [25-28]. The swelling behavior of these copolymer gels was strongly related to their composition, chemical structure, and nature of ions in the solutions. Neagu et al. [17] investigated the retention capacities of divalent and trivalent heavy metals in zwitterionic ion exchangers with carboxybetaine moieties based on 4-vinylpyridine: Divinylbenzene copolymers with two morphological structures, i.e., porous- and non-porous-type gels. Both types of gels synthesized for their study retained metal ions and anions from aqueous solution; however, they did not adsorb alkaline earth metals. The effect of the synthetic conditions of poly(DMAAPS) on polymer yield, intrinsic viscosity, molecular weight, and gel fraction was investigated by J. Ning et al. by varying the monomer concentration [20]. However, there are relatively few studies on the adsorption capacity of betaine gels and the correlation with its swelling ability in solvents with various compositions, temperatures, and ion strengths.

In our previous study, the effects of the temperature and preparation conditions of the gels, such as the cross-linker and monomer concentrations, on the adsorption of cations and anions onto DMAAPS gel were investigated using Al(NO₃)₃, Zn(NO₃)₂, and NaNO₃ solutions with various concentrations [29]. The simultaneous adsorption of cations (Al^{3+} , Zn^{2+} , or Na^+) and anions (NO_3^-) was confirmed. Furthermore, it was found that the amount of cation (Zn^{2+}) adsorbed onto the DMAAPS gel remained unchanged for the gel prepared with a higher cross-linker or monomer concentration even at higher temperatures. In contrast, the amount adsorbed decreased significantly with increasing temperature for the gel prepared at a lower cross-linker or monomer concentration. Based on these results, an interesting correlation between the degree of swelling of DMAAPS gel and amount of cation (Zn²⁺) adsorbed onto the gel was observed using Zn(NO₃)₂ solutions of various concentrations. The data points laid on the same line even at different cross-linker concentrations or temperatures. For the gel with a small degree of swelling, i.e., when the polymer concentration in the gel was higher than ~180 g/L, the amount of Zn^{2+} adsorbed remained unchanged. The adsorption amount is the maximum adsorption amount of Zn^{2+} or NO_3^- onto the DMAAPS gel. For the gel with a large degree of swelling, i.e., when the polymer concentration in the gel was lower than ~180 g/L. the amount of Zn²⁺ adsorbed decreased as the swelling degree increased. Furthermore, at the same swelling degree, the amount of Zn^{2+} adsorbed increased as the concentration of $Zn(NO_3)_2$ increased.

Based on the unique characteristic of DMAAPS mentioned above, the effect of the anion species on the amount of ions adsorbed onto DMAAPS gel and the relationship with its swelling degree or polymer concentration in the gel was examined in this study using solutions of halides, i.e., KF, KCl, KBr, and KI solutions. These halide solutions were chosen because the halide anions in these solutions have different hydration abilities and sizes that may affect their interaction with the charged groups of DMAAPS. These halide anions have been ordered in the Hofmeister series. The purpose of the present study is to evaluate the influence of these anion species on the adsorption behavior onto DMAAPS gel and the swelling behavior of DMAAPS gel in these halide solutions and their relationship. In addition, to elucidate competitive adsorption, the adsorption behavior of ions onto the DMAAPS gel was studied in mixtures of these halide solutions.

2. Experimental section

2.1. Synthesis of DMAAPS

DMAAPS was synthesized using the same method reported in our previous study [29], which was proposed by Lee and Tsai [30]; this reaction involved the ring-opening of *N*,*N*-dimethylaminopropylacrylamide (DMAPAA; KJ Chemicals Co., Ltd., Japan) and 1,3propanesultone (PS; Tokyo Chemical Industry Co., Ltd., Japan). A mixture of PS (75 g) and acetonitrile (75 g) was added dropwise with continuous stirring at 30 °C for 90 min into a mixture of DMAPAA (100 g) and acetonitrile (200 g). Stirring was continued for 16 h and then the solution was allowed to stand for 2 d. Precipitated white crystals of DMAAPS were collected by filtration, washed with 500 mL of acetone, and finally dried under reduced pressure for at least 24 h. The structure of DMAAPS is shown in Fig. 1.

2.2. Preparation of DMAAPS polymer and gel

DMAAPS polymer and gel were prepared by free-radical polymerization. Poly(DMAAPS) was used to evaluate the transition behavior in response to temperature changes. The preparation procedures were the same as those described in our previous study [29]. *N,N,N',N'*-Tetramethylethylenediamine (TEMED; Sigma-Aldrich Co., USA) and ammonium peroxodisulfate (APS; Sigma-Aldrich Co., USA) were used as a polymerization accelerator and initiator, respectively. Furthermore, *N,N'*-methylenebisacrylamide (MBAA; Sigma-Aldrich Co., USA) was used as a cross-linker.

In the preparation of poly(DMAAPS), the concentrations of DMAAPS, TEMED, and APS were 500, 2, and 2 mmol/L, respectively. Initially DMAAPS and TEMED were dissolved in deionized water and the solution volume was increased to 100 mL using deionized water. This monomer solution was charged into a separable flask. The solution was purged with nitrogen gas in order to remove any dissolved oxygen and then 20 mL of APS solution that had also been purged with nitrogen gas was added. Polymerization was carried out under a nitrogen atmosphere for 6 h at 50 °C. The resulting polymer was purified over a period of one week by dialysis using a membrane with a molecular weight cut-off of 12,000-14,000 (Cellu Step T3, Membrane Filtration Products, Inc.). Additionally, the average molecular weight of the produced poly(DMAAPS) was estimated from the intrinsic viscosity $[\eta]$, which was measured in a 0.1 M NaCl solution at 30 °C using a Ubbelohde viscometer, to be 1.13×10^6 g/mol [29].

DMAAPS gels were prepared using the same procedures as those described above for poly(DMAAPS) except that MBAA was used as the cross-linker. A cylindrical gel was prepared to examine the swelling properties. The synthesis was performed in a separable flask containing glass tubes that were 2 mm in diameter and 30 mm long. The gels were cut into pieces that were 2 mm long and rinsed several times with deionized water. The gels were then slowly dried over several days on a Teflon sheet that was spread on a Petri dish.

$$CH_{2} = CH CONH - (CH_{2})_{3} - N^{+} - (CH_{2})_{3} - SO_{3}^{-}$$

Fig. 1. Chemical structure of DMAAPS.

The dish was covered with a thin plastic film containing small holes to decrease the drying speed because the gels tended to break if dried too quickly. Other gels were cut into small pieces, washed, and then dried in an oven. Finally, the dried gels were ground into a powder and sieved to greater than 180 mesh size for the adsorption experiments. The synthetic conditions for the DMAAPS gels are listed in Table 1.

2.3. Measurement of the amount of cation and anion adsorbed onto DMAAPS gel from the halide solutions

Ion-adsorption experiments were performed using the same procedure described previously [29], as follows: Ground DMAAPS gel (1 g) was added to 20 mL of the halide solutions, i.e., KF, KCl, KBr, and KI solutions, or mixtures of the solutions in a glass bottle. The concentrations of these halide solutions were fixed at 10 mmol/L. The bottle containing the solution and gels was placed in a water bath at the desired temperature and stirred gently for 12 h to allow the gels to swell and reach adsorption equilibrium [29]. After adsorption, the gels were removed from the solution using a centrifuge at 3500 rpm and syringe filter (0.45 µm, Toyo Roshi Kaisha, Ltd.) in order to measure the residual ion concentration in the solution. The cation (K⁺) and anion (F⁻, Cl⁻, Br⁻, and I⁻) concentrations were then measured using ion chromatography. The measurements were performed using a SUS TSKgel Super IC-A/C (Tosoh Corp.) column (6.0 mm I.D \times 150 mm) with a solution containing 6.0 mmol/L 18-crown-6 ether, 0.45 mmol/L 5-sulfosalicylic acid, 5.0 mmol/L L-tartaric acid, and 5% acetonitrile as the mobile phase. The adsorbed amounts of cation and anion were calculated from their concentrations in the solution before and after adsorption using the following equation:

$$Q = \frac{(C_0 - C)V}{m},\tag{1}$$

where Q is the amount of cation or anion adsorbed, C_0 and C are the concentrations of cation or anion in the initial solution and aqueous solution after adsorption for a certain period, respectively, V is the volume of the aqueous phase, and m is the weight of the dry sample gels.

2.4. Measurement of the swelling degree of DMAAPS gel in the halide solutions

The swelling degree of the DMAAPS gel was measured using a reported procedure [29]. Initially, the diameter of the cylindrical dry gel was measured using a cathetometer. The gel was then immersed in water, one of the four halide solutions, i.e., KF, KCl, KBr, and KF solutions, or mixtures of these solutions at 70 °C. The gel was allowed to swell for 24 h, which was sufficient for the gel to reach its equilibrium swollen state [29]. The diameter of the swollen cylindrical gel was then measured using a cathetometer. The temperature was reduced in increments, and the swollen gel diameter was measured again. This procedure was repeated until

Table 1

Synthesis condition of DMAAPS gel.

		Concentration [mmol/L]
Monomer	: <i>N,N</i> -dimethyl(acrylamidopropyl)ammonium propane sulfonate (DMAAPS)	1000
Linker	: N,N'-methylenebisacrylamide (MBAA)	5, 10, 30
Accelerator	: <i>N</i> , <i>N</i> , <i>N</i> ', <i>N</i> '-tetramethylethylenediamine (TEMED)	10
Initiator	: Ammonium peroxodisulfate (APS)	0.5

the temperature reached 10 $^{\circ}$ C. The swelling degree was calculated from the following equation:

$$SD = \frac{d_{swell}^3}{d_{dry}^3},\tag{2}$$

where d_{swell} and d_{dry} indicate the diameters of the swollen and dry gels, respectively.

2.5. Measurement of the phase transition of poly(DMAAPS) in the halide solutions

The phase transition of poly(DMAAPS) in response to temperature changes was also measured using a reported procedure [29] to elucidate the effect of the halide-solution concentration on the transition temperature of poly(DMAAPS). The transition temperature was evaluated from the temperature dependence of the transmittance at 600 nm of the poly(DMAAPS) solution using a spectrophotometer equipped with a temperature control system (V-530, Japan Spectroscopy Co., Ltd.). Poly(DMAAPS) is transparent above the transition temperature because the polymer solution is soluble in water and aqueous halide solutions. In contrast, the polymer solution became opaque or milky white below the transition temperature because poly(DMAAPS) is insoluble in water and aqueous halide solutions. The transition temperature was defined as the value at 50% transmittance.

3. Results and discussion

3.1. Adsorption behavior of ions on DMAAPS gel in halide solutions

In this section, the effect of the anion species in halide solutions, i.e., KF, KCl, KBr, and KI solutions, on the amount of cation (K⁺) and anions (F⁻, Cl⁻, Br⁻, and I⁻) adsorbed onto DMAAPS gel was examined. The gels were prepared using three different cross-linker concentrations, i.e., 5, 10, and 30 mmol/L Fig. 2(a)–(d) show the amount of K⁺ adsorbed onto DMAAPS gel from these halide solutions as a function of temperature. In our previous work, it was confirmed that the DMAAPS gel simultaneously adsorbed cations and anions from salt solutions [29]; thus, the amount of cation (K⁺) adsorbed in this study coincided with the amount of anion (F⁻, Cl⁻, Br⁻, or I⁻) absorbed. Furthermore, the amount of K⁺ adsorbed depended strongly on the interactions between the anion in the halide solution and N⁺ of DMAAPS.

In the KF solution, negligible amounts of K⁺ adsorbed onto the gels prepared at three different MBAA concentrations (i.e., 5, 10, and 30 mmol/L) at temperatures in the experimental range of 10–70 °C (Fig. 2(a)). In other halide solutions, the amounts of K⁺ adsorbed onto the gels prepared at three different MBAA concentrations at 10 °C were almost the same, regardless of the anion species (Fig. 2(b)–(d)). At a lower cross-linker concentration (5 mmol/L), the amount of K⁺ adsorbed decreased significantly with increasing temperature, especially at 50 and 70 °C. In contrast, at 10 mmol/L MBAA, there was a slight decline in the amount of K⁺ adsorbed, and, at 30 mmol/L, it remained unchanged with increasing temperature.

The phenomenon above can be explained as follows. At low temperature and in the gels synthesized with higher cross-linker concentration, the electroneutrality of the charge groups results from the intra-group ionic pairs formation [31]. An increase of the cross-linker concentration increases the polymer concentration in the gel and the network density in the gel. In this condition, the expansion of the polymer network of DMAAPS gel is restricted and the sulfonate groups become close to each other. In the halide



Fig. 2. Amount of K⁺ adsorbed onto DMAAPS gel from 10 mmol/L (a) KF, (b) KCl, (c) KBr, and (d) KI solutions at various temperatures. The gels were prepared at three different cross-linker concentrations

solutions, only a part of the charged groups in the DMAAPS gel interacts with K+ and anions (F⁻, Cl⁻, Br⁻, I⁻) because the interaction between the SO_3^- and N^+ groups of the DMAAPS gel that forms an intra-group ionic pairing is quite strong; in other words the amount of ions adsorbed onto the DMAAPS gel is limited and it reached a constant value. This adsorption amount is regarded as maximum adsorption amount of ions onto the gel. In contrary, at high temperature and in the gels synthesized with lower crosslinker concentration, the polymer network of DMAAPS gel swells largely. Furthermore, the thermal motion weakens the interaction between the N^+ and SO_3^- groups of DMAAPS. The breakages of associations caused by temperature increase are consistent with what was observed for sulfobetaine gel [32] and sulfobetaine polymer solids [33]. The thermal motion simultaneously weakens the ionic pairings force between the charged groups in the DMAAPS gel and the K⁺ and/or anions (F⁻, Cl⁻, Br⁻, I⁻) from the halide solutions. These conditions reduce the adsorption of ions from the halide solutions onto the DMAAPS gel, thereby decreasing the amount of K⁺ adsorbed on the gel.

The order of increasing adsorption from the halide solutions was KI > KBr > KCI > KF, and the order of anion in these halide solutions, i.e., $I^- > Br^- > CI^- > F^-$, was opposite that in the Hofmeister series. The typical order of the anion series is:

The Hofmeister series is related to the anions' ability to directly interact with the positively charged groups of DMAAPS, N⁺, and their adjacent hydration shells [34-36]. The species at the left of the Hofmeister series are referred to as kosmotropes or "waterstructure makers". These anions are small and strongly hydrated [36]. In contrast, the species at the right of the Hofmeister series are referred to as chaotropes; these species are large and less hydrated and are known as "water-structure breakers" [34,35]. The Cl⁻, Br⁻, and I⁻ ions used in this study are chaotropes and exhibit a weaker resistance to dehydration [37] in the following order: $Cl^- > Br^- > l^-$. Therefore, when DMAAPS gel was immersed in a KI solution, the Iions strongly interacted with the N⁺ groups of DMAAPS, which resulted in greater adsorption. In contrast, F⁻ ions are kosmotropes [37]; therefore, this strongly hydrated species exhibits stronger interactions with water molecules than the cohesive forces of water molecules. Therefore, F⁻ remained hydrated [38] resulting in less interaction of the F^- ions with the N^+ of DMAAPS, which led to smaller adsorption.

3.2. Swelling behavior of DMAAPS gel in halide solutions

Fig. 3(a)–(d) shows the temperature dependence of the swelling degree of DMAAPS gels prepared at three different MBAA concen-



Fig. 3. Swelling degrees of DMAAPS gel measured in 10 mmol/L (a) KF, (b) KCl, (c) KBr, and (d) KI solutions at various temperatures. The gels were prepared at three different cross-linker concentrations.

trations in 10 mmol/L KF, KCl, KBr, and KI solutions. In each solution, the swelling degree increased with increasing temperature and was only significant for the gel prepared at a low MBAA concentration (5 mmol/L). The addition of these halides into the poly(DMAAPS) solution led to dissociation of N⁺ and SO₃⁻ because of the new ionic interactions between the ions in the halide solution and the charged groups of poly(DMAAPS), i.e., SO₃⁻ and N⁺. For the DMAAPS gel synthesized with lower cross-linker concentration, at equilibrium swelling the polymer network of the gel expands largely. However, the degree of swelling of the gel prepared with a higher cross-linker concentration (30 mmol/L) increased only slightly with increasing temperature. Interesting phenomenon was found that although the swelling degree increased at a higher cross-linker concentration (30 mmol/L), the amount of K⁺ adsorbed onto the gel prepared at the same cross-linker concentration remained unchanged as seen in Fig. 2. This result is thought to be due to the fact that the increasing of the swelling degree is also influenced by the enhancement of the thermal motion.

The order of decreasing the hydration of ability of the anions was $F^- > CI^- > Br^- > I^-$, while the swelling degree of DMAAPS gel decreased in the following order: KI > KBr > KCl > KF as seen in Fig. 3. Furthermore, we observed that, at 10 °C, the swelling degrees of the gels prepared at three different MBAA concentrations were almost the same in the KF and KCl solutions (Fig. 3(a) and (b)); however, in the KBr and KI solutions (Fig. 3(c) and (d)), the swelling degrees of these three gels varied significantly at all temperatures.

The swelling degrees of DMAAPS gels prepared at three different MBAA concentrations in the halide solutions and water were

compared, as shown in Fig. 4(a)–(c). In water, the swelling degree of the gel prepared at a higher MBAA concentration (i.e., 30 mmol/L) increased gradually with increasing temperature; this increase was not significant and increased from 3.5 at 10 °C to only 6.6 at 70 °C (Fig. 4(a)). Comparison of this swelling degree in water with those in the halide solutions revealed that the swelling degrees in the KF and KCl solutions were almost the same as that in water. This similarity was observed at all three MBAA concentrations (i.e., 5, 10, and 30 mmol/L). However, in the KBr solution, the swelling degree was larger than that in water at the three different MBAA concentrations. Furthermore, the swelling degree in the KI solution was much larger than those in water and the KF, KCl, and KBr solutions. These results indicated that K⁺ and I⁻ ions interacted strongly with the SO₃ and N⁺ of DMAAPS gel, respectively, as shown by the amount of K⁺ adsorbed (Fig. 3).

3.3. Transition behavior of poly(DMAAPS) in halide solutions

The transition behaviors of poly(DMAAPS) in halide solutions with various concentrations are shown in Fig. 5(a)-(d). The concentration of poly(DMAAPS) was fixed at 20 g/L. The results showed that increasing halide concentration resulted in an initial increase in the transition temperature at a specific halide concentration followed by a decrease above that concentration.

At lower KI concentration of 0-1 mmol/L, the transition temperature gradually increased from 36 to around 58 °C (Fig. 5(d)); this increase might have been due to partial dissociation of N⁺ and SO₃⁻ pairing resulting from the new ionic interactions with I⁻ and



Fig. 4. Swelling degrees of DMAAPS gel prepared using (a) 30, (b) 10, and (c) 5 mmol/L of cross-linker measured in water and 10 mmol/L KF, KCl, KBr, and KI solutions at various temperatures.

K⁺, respectively. At these low KI concentrations, the amounts of ions (K⁺ and I⁻) available to disrupt the interactions of the N⁺ and SO₃ groups in poly(DMAAPS) were restricted; thus, dissociation of the ionic interactions occurred locally (i.e., partial dissociation). Partial dissociation induced chain mobility, which led to enhanced inter-chain interactions [39] leading to aggregation of the polymer that inevitably increased the transition temperature. Upon further increasing the KI concentration to 10 mmol/L, the transition temperature decreased significantly to less than 20 °C, which is out of the experimental range; this can be explained by dissociation of the ionic pairing of SO₃ and N⁺, which occurred easier in highly concentrated KI solutions because a significant number of ions (K⁺ and I⁻) were available for disruption [20].

In addition, it is seen in Fig. 5 that the transition temperature of poly(DMAAPS) in KF and KCl of 0.25 mmol/L is lower than that in KBr and KI at the same concentration. Furthermore, the difference between the transition temperature of poly(DMAAPS) in water and in 0.25 mmol/L halide solutions increased with decreasing the hydration ability of the anions in the following order: KI > KBr > KCl > KF. This order can be explained by the fact that in solutions of lower concentration, ions from solution leads to the partial dissociation of the ionic pairings as a result from the ionic interaction with K⁺ and anions (F⁻, Cl⁻, Br⁻, I⁻) from halide solutions. But since the ability of the chaotropes ions (Cl⁻, Br⁻, I⁻) to disrupt these pairing is greater than that the kosmotropes ions (F⁻), the chain mobility of polymer in the solution containing chaotropes ions is greatly enhanced especially for the ions having lower hydration ability. As explained above, the chain mobility leads to

aggregation of the polymer that eventually increased the transition temperature. As a consequence, the transition temperature of poly(DMAAPS) in KI and KBr solutions of 0.25 mmol/L is higher than that in KCl and KF solutions at the same concentration.

Very similar transition behavior was observed when poly(-DMAAPS) was dissolved in KF, KCl, and KBr solutions, as shown in Fig. 5(a)–(c). Comparison of the transition temperatures of poly(-DMAAPS) in KCl, KBr, KI, and KF solutions revealed that the gap between the maximum and minimum transition temperatures within the experimental halide concentration range decreased in the following order: KI > KBr > KCl > KF. Furthermore, the transition temperatures of poly(DMAAPS) in KF, KCl, KBr, and KI solutions (10 mmol/L) were 50, 47, 31, and <20 °C, respectively. The transition behaviors of poly(DMAAPS) in halide solutions were strongly related to the adsorption behavior of ions onto poly(DMAAPS), as explained in our previous study [29]. Based on the adsorption and transition behaviors, the transition temperatures of poly(DMAAPS) in 10 mmol/L halide solutions decreased in the following order of halides: KF > KCl > KBr > KI; in contrast, the amounts of K^+ adsorbed showed the opposite trend. For the KF, KCl, KBr, and KI solutions, the amounts of K⁺ adsorbed onto DMAAPS gel in these solutions were almost zero, 0.015, 0.03, and 0.047 mmol/g-dry gel, respectively, as shown in Fig. 2. In addition, at a fixed halide concentration of 10 mmol/L, the anions with lower hydration ability, such as I⁻, promoted dissociation of the N⁺ and SO₃ pairings causing a shift in the transition temperature to a lower value. In contrast, dissociation of N⁺ and SO₃ pairing was limited in solutions containing anions with higher hydration abilities, such as F⁻;



Fig. 5. Transition behavior of poly(DMAAPS) (20 g/L) in (a) KF, (b) KCI, (c) KBr, and (d) KI solutions of various concentrations.

accordingly, the transition temperature of poly(DMAAPS) was higher in these solutions.

3.4. The relationship between the amount of ions adsorbed and degree of swelling of DMAAPS gel in halide solutions

To elucidate the adsorption and swelling behaviors, similar to in our previous study [29], we examined the relationship between the swelling degree of the gel and amount of K^+ adsorbed onto the DMAAPS gels prepared at three different cross-linker concentrations, i.e., 5, 10, and 30 mmol/L, at various temperatures, i.e., 10, 30, 50, 70 °C, in 10 mmol/L KF, KCl, KBr, and KI solutions. The relationships are summarized in Fig. 6(a). The data points laid on the same line for the same halide solution even at different cross-linker concentrations and temperatures; this result was similar to that obtained in our previous study [29]. At smaller swelling degrees, the amount of K⁺ adsorbed remained unchanged and decreased gradually as the swelling degree increased. Although the trends



Fig. 6. Relationship between the amount of K⁺ adsorbed onto DMAAPS gel and (a) the swelling degree of the DMAAPS gel and (b) the polymer concentration in the gel. The gels were prepared at three different cross-linker concentrations, and the amounts of K⁺ adsorbed and swelling degrees were measured in KF, KCl, KBr, and KI solutions at various temperatures.

remained the same, the adsorbed amount of K⁺ decreased at larger degrees of swelling in solutions containing anions with lower hydration abilities, such as KI. However, in solutions containing anions with higher hydration abilities, such as KCl, the amount of K⁺ adsorbed decreased at smaller degrees of swelling. The amount of K⁺ adsorbed from the KI, KBr, and KCl solutions decreased when the swelling degree reached about 35, 23, and 16, respectively; however, it was difficult to determine the swelling degree at which the adsorption amount decreased in the KF solution because almost no K⁺ was adsorbed from the KF solution.

To clearly elucidate the relationship between the amount of ions adsorbed and degree of swelling, similar to in our previous study [29], the concentration of polymer in the gel (C_p) at the equilibrium swollen state was determined from the swelling degree of the DMAAPS gels, as follows:

$$C_p = \frac{W_0}{V_0} \times \frac{1}{SD},\tag{4}$$

where W_0 is the weight of the dry sample gel, V_0 is the volume of the dry sample gel, and *SD* is the swelling degree of the gel, which is defined by (swollen gel diameter)³/(dry gel diameter)³.

The relationship between the amount of K^+ adsorbed and polymer concentration in the gel is shown in Fig. 6(b). The amount of K^+ adsorbed increased with increasing polymer concentration until it reached a constant maximum amount. This trend was the same as those described in our previous study [29]. The constant maximum value was regarded as the maximum adsorption amount of K^+ onto the DMAAPS gel in the specific halide solution.

This phenomenon was explained as follows in our previous study [29]: Gels with high polymer concentrations feature gel networks that are dominated by intra-group ionic pairing interactions [31]. Since the interaction between the SO_3^- and N⁺ groups of the DMAAPS gel that formed intra-group ionic pairings was quite strong, the amount of ions adsorbed by DMAAPS gel was limited [29]. However, at low polymer concentrations, thermal motion weakened the interactions between ions in the halide solution and the charged groups of poly(DMAAPS), i.e., SO_3^- and N⁺.

In addition, for the halide solutions containing chaotropic anions with higher hydration abilities, such as the KCl solution, the amount of K^+ adsorbed reached a constant maximum amount at higher polymer concentrations in the gel. However, for halide solutions containing chaotropic anions with lower hydration abilities, such as the KI solution, the maximum adsorbed amount of K^+ occurred at a lower polymer concentration in the gel. The polymer concentrations in the gel at which the maximum adsorbed amount of K⁺ were obtained were about 31, 70, and 111 g/L for KI, KBr, and KCl solutions, respectively. Furthermore, the maximum adsorption amount of K⁺ depended strongly on the anion species. These results were attributed to the anion size, which decreases in the order of $I^- > Br^- > CI^- > F^-$, and that penetration of into the side chain of DMAAPS was more difficult for larger anions than smaller anions. Furthermore, the order of decreasing interaction with N⁺ in DMAAPS of the anions was $I^- > Br^- > CI^- > F^-$, as obtained from the Hofmeister series shown in Eq. (3).

In order to clarify the behavior of the gel over a wide concentration range, the adsorption and swelling behaviors of DMAAPS gel were further investigated in concentrated solutions of KI i.e., 50 mmol/L (8.3 g/L) and 100 mmol/L (16.6 g/L) as shown in Fig. 7. KI solution was chosen to represent the adsorption and swelling behaviors in the concentrated solutions because the maximum adsorption amount of K⁺ onto the gel in this solution was the highest among four kinds of halide solutions. Furthermore, the DMAAPS gel was prepared at a 30 mmol/L cross-linker concentration and was measured at 10 °C to obtain the maximum adsorption amount of K⁺ onto the gel.

Fig. 7(a) shows the maximum adsorption amount of K^+ at a certain KI equilibrium concentrations. It is seen that the maximum adsorption amount of K^+ increased linearly with equilibrium concentration of K^+ over a wide range of experimental concentrations. The value of adsorption amount can be obtained by the following equation:

$$Q_{\rm max} = 0.0057 \, Ce$$
 (5)

where Q_{max} is the maximum adsorption amount of K⁺ by DMAAPS gel and C_e is the equilibrium concentration of K⁺. This result leads to the conclusion that the maximum adsorption amount of K⁺ is proportional to the concentration of KI solution in the experimental range. In addition, as seen in Fig. 7(a) the maximum adsorption amount of K⁺ onto the gel in 100 mmol/L of KI solution of 0.49 mmol/g-gel was estimated to be ~13.7% of the sulfonate content in the gel. This means that the sulfonate content in the gel to be used to interact with K⁺ from halide solution was still low even if the KI concentration was relatively high. This can be explained by the fact that the ionic pairings between SO₃⁻ and N⁺ groups of the DMAAPS gel is quite strong. From this result, we can conclude that the selectivity of the ions from halide solutions (KF, KCl, KBr, and KI) toward the charge groups of DMAAPS; or in other words the order of the adsorption was unchanged with increasing the solutions



Fig. 7. Relationship between KI equilibrium concentrations and (a) maximum adsorption amount of K⁺ onto DMAAPS gel for K⁺ and (b) degree of swelling of the DMAAPS gel in diluted concentrations of KI solutions at 10 °C. The DMAAPS gels were prepared at a 30 mmol/L cross-linker concentration.

concentrations in our experimental range. In addition, the swelling degree of the DMAAPS gel in concentrated solutions of KI is shown in Fig. 7(b). The degree of swelling of the gel increased with increasing KI equilibrium concentrations and was significant for KI concentration, i.e., 100 mmol/L. The addition of relatively high concentration of KI solution into the gel promoted more dissociation of N⁺ and SO₃⁻ because of the new ionic interactions between the ions in the halide solution and the charged groups of as a result polymer network of the gel expanded and swelling degree increased.

3.5. Competitive adsorption of anions onto DMAAPS gel

Competitive adsorption of anions onto the DMAAPS gel from these halides was investigated using KI + KF, KI + KCl, KI + KBr, KBr + KF, and KBr + KCl mixtures; the results are summarized in Fig. 8. The concentration of each halide was 10 mmol/L. The gels were prepared at 30 mmol/L MBAA, and the amounts of K⁺ and anions (I⁻, Br⁻, Cl⁻, and F⁻) adsorbed onto the gels were measured at various temperatures, i.e., 10, 30, 50, and 70 °C. The amount of K⁺ adsorbed was equal to the total amount of both anions adsorbed onto the DMAAPS gel because of the simultaneous adsorption of anions and cations onto DMAAPS gel, as was shown in our previous study [29].

In all the mixed-halide solutions, i.e., KI + KF, KI + KCI, KI + KBr, KBr + KF, and KBr + KCI, the anion of the halide on the left side adsorbed better than on the right side; accordingly, the observed order of decreased adsorption ability of the anions was $I^- > Br^- > CI^- > F^-$, although the amount of F^- adsorbed was almost zero. This order is opposite that of the anion species in the

Hofmeister series shown in Eq. (3). Furthermore, the amount of I⁻ adsorbed in the KI + KF, KI + KCl, and KI + KBr mixtures was larger than that in the solution of KI (Fig. 8(a)-(c)), and the amounts of Cl⁻ or Br⁻ adsorbed were smaller than that in the single solution of KCl or KBr, although the amount of F⁻ adsorbed was too small to be compared with that in the solution of KF. In addition, the amounts of Br⁻ adsorbed from the KBr + KF and KBr + KCl solutions were also larger than that from the KBr solution (Fig. 8(c) and (d)), and the amount of Cl⁻ adsorbed was smaller than that from the KCl solution of KCl; the amount of F⁻ adsorbed was too small to be compared with that from the KF solution. These results were attributed to the fact that the concentrations of K⁺ cations in the mixtures were double that in the single-halide solutions. The higher concentration of K⁺ promoted adsorption of K⁺, which promoted adsorption of the anions because of simultaneous adsorption of cations and anions. However, adsorption of anions from the mixtures was competitive: The anions on the right side of the Hofmeister series shown in Eq. (3) tended to adsorb in larger amounts. To compensate for this increase, the anions on the left side of the Hofmeister series shown in Eq. (3) adsorbed less. Therefore, the amounts of anions on the right side of the Hofmeister series, such as I⁻, adsorbed from the mixtures were higher than that from the single-halide solutions, as shown above; accordingly, the amounts of anions on the left side of the Hofmeister series adsorbed from the mixtures were lower than that from the single-halide solutions.

In addition, Fig. 8(a)-(c) shows the effect of temperature on the amounts of ions adsorbed from mixtures containing KI. As shown in Fig. 2, in single-component solution and for gels prepared at a cross-linker concentration of 30 mmol/L, increasing the



Fig. 8. Amounts of ions adsorbed onto DMAAPS gel in (a) KI + KF, (b) KI + KCl, (c) KI + KBr, (d) KBr + KF, and (e) KBr + KCl mixtures at various temperatures. The concentration of each halide solution was 10 mmol/L. The DMAAPS gels were prepared at a 30 mmol/L cross-linker concentration.



Fig. 9. Swelling degrees of DMAAPS gels measured in (a) a KI + KF mixture and (b) KI + KF, KI + KCI, KI + KBr, KBr + KF, and KBr + KCl mixtures at various temperatures. The concentration of each halide solution was 10 mmol/L. The DMAAPS gels were prepared at 30 mmol/L cross-linker concentration.

temperature did not induce any significant change in the amount of K⁺ adsorbed onto the gel. However, in the mixture, the amount of K⁺ adsorbed decreased gradually as the temperature increased from 10 to 70 °C (Fig. 8(a)–(c)). In the presence of competitive adsorption between two less-hydrated anions in a mixture, such as the KI + KBr solution, the amount of K⁺ adsorbed decreased significantly with increasing temperature, as shown in Fig. 8(c). In contrast, in mixtures containing more strongly hydrated anions, such as the KI + KCl solution, the amount of K^+ adsorbed only decreased gradually with increasing temperature, as shown in Fig. 8(b). Additionally, in the mixture composed of KI and KF, the amount of K⁺ adsorbed was almost constant and only decreased at 70 °C, as shown in Fig. 8(a).

3.6. Effect of competitive adsorption on the swelling degree

The swelling degrees of DMAAPS gel in KI + KF. KI + KCl. KI + KBr, KBr + KF, and KBr + KCl mixtures are shown in Fig. 9(a) and (b). The gels were prepared at 30 mmol/L MBAA, and the swelling degrees of the gels were measured at various temperatures, i.e., 10, 30, 50, and 70 °C. Comparison of the swelling degree in the KI + KF mixture with those in the single-component solutions of KI and KF (Fig. 9(a)) revealed that the swelling degree of the gel in the mixture is intermediate those in each single-halide solution that comprised the mixtures. The observed order of swelling degrees decreasing in the mixtures was KI + KBr > KI + KCl > KI + KF > KBr + KCl > KBr + KF, as shown in Fig. 9(b).

4. Conclusion

The effect of the anion species in the halides, i.e., KF, KCl, KBr, and KI, on the amount of cation (K⁺) or anions (F⁻, Cl⁻, Br⁻, or I⁻) adsorbed onto DMAAPS gel was investigated. The order of increased adsorption of the anion onto DMAAPS gel was opposite that in the Hofmeister series, although almost no K⁺ and F⁻ were adsorbed from the KF solution. Furthermore, the relationship between the degree of swelling of the gel and amount of K⁺ adsorbed onto the gel was elucidated. The data points laid on the same line for the same halide solution even at different cross-linker concentrations and temperatures; these results correlated with those of our previous study. The effect of the polymer concentration in the gel on the degree of swelling was also investigated. As the polymer concentration in the gel increased, the swelling degree decreased, and the amount of K⁺ adsorbed increased to a constant maximum adsorption amount, i.e., the maximum adsorption amount, above polymer concentrations of 31, 70, and 111 g/L in KI. KBr. and KCl solutions, respectively, Additionally, adsorption of anions was competitive in mixtures of these halide solutions. In the mixtures, the anions on the right side of the Hofmeister series adsorbed in larger quantities than in the single-components solutions, while those on the left side of the Hofmeister series adsorbed in smaller quantities than in the single-component solutions.

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