CATION- AND ANION-ADSORPTION PROPERTIES OF SULFOBETAINE TYPE GELS AND THEIR RELATIONSHIP WITH SWELLING OR TRANSITION BEHAVIORS IN AQUEOUS SALT SOLUTIONS

（種々の塩水溶液中でのスルフォベタイン型ゲルへのカチオンおよびアニオンの吸着特性と膨潤あるいは転移挙動との相関）

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Abstract

Studies on the properties of polymers or gels based on zwitterionic betaine have received much attention in the scientific and engineering communities. Various type of zwitterionic betaine polymers or gels, such as phosphobetaine, sulfobetaine, and carbobetaine have shown excellent chemical stability, good biocompatibility, ultralow fouling, and excellent mechanical properties. Zwitterionic betaine type polymer or gels containing both anionic and cationic active groups in the same side chain of the polymeric repeat unit with a spacer composed of methylene groups between them bears an overall neutral charged. 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, and they regarded as one of the effective method in the separation process such as in the application of column chromatography. Furthermore, it is well known that zwitterionic betaine polymers are generally thermosensitive in aqueous solutions as shown by their upper critical solution temperature (UCST). However, there are relatively few studies on the adsorption of cations and anions onto sulfobetaine polymers and gels, although the adsorption behavior is recognized to affect the swelling and transition behaviors. Therefore, the objectives of the present study are the investigation on the ion-adsorption properties, swelling behavior, and transition behavior of sulfobetaine gels and/or polymers in various salt solutions, and their relationships. In the present study, two types sulfobetaine, i.e., *N,N*-dimethyl(acrylamidopropyl)ammonium propane sulfonate (DMAAPS) and *N,N*-dimethyl(acrylamidopropyl)ammonium butane sulfonate (DMAABS) were used.

This thesis is organized in the following way. The background, previous research, and main objectives of the thesis are included in **Chapter 1**.

In **Chapter 2**, the simultaneous adsorption of cations and anions onto DMAAPS gel was confirmed using $NaNO_3$, $Zn(NO_3)_2$, and $Al(NO_3)_3$ solutions. Furthermore, the effect of the preparation conditions such as cross-linker and monomer concentrations on the adsorption and

swelling behaviors of the gel in $Zn(NO_3)_2$ solution was investigated under various temperatures and nitrate concentrations. In addition, an interesting correlation between the degree of swelling of the gel and the amount of Zn^{2+} adsorbed onto the gel was found; the data points laid on the same line even at different cross-linker and/or monomer concentrations or temperatures when the $Zn(NO_3)_2$ concentration was the same. As the swelling degree decreased, the adsorption amount increased to eventually achieve a constant value, which can be recognized as the maximum amount of ion adsorbed onto the gel. It was shown to be proportional to the equilibrium concentration of $Zn(NO_3)_2$ in the solution in the experimental range.

In **Chapter 3**, the adsorption of cations and anions in four kinds of halide solutions, i.e., KF, KCl, KBr and KI solutions, onto the DMAAPS gels prepared with various cross-linker concentrations was investigated at various temperatures. The swelling degree of the gel in these solutions was also examined. It was found that the order of the amount of K^+ adsorbed onto the gel in these solutions was opposite that of anion species in the Hofmeister series, i.e., $I^- > Br^- > Cl^- > F^-$. Furthermore, the similar relationship between the swelling degree of the gel and the amount of K^+ adsorbed onto the gel observed in Chap. 2 was confirmed. Additionally, it was found that in the mixture of these halide solutions, the competitive adsorption of anions occurred. In the mixture, the adsorbed amount of the anion on the more right side of the Hofmeister series became larger than that in the single-components solutions, while those on the more left side of the Hofmeister series became smaller than in the single-components solutions.

In **Chapter 4**, introduces a study on the transition temperature of the poly(DMAAPS) in various aqueous salt solutions. The transition temperature of poly(DMAAPS) was strongly influenced by the salt solution concentration and anion or cation species in the solutions. It was found that the transition temperature of poly(DMAAPS) initially increased with increasing the salt concentration in the solution, and then decreased as the concentration of salt increased further. Furthermore, an interesting relationship between the transition temperature of poly(DMAAPS) and the maximum amount of ion adsorbed onto the DMAAPS gel in various solutions was obtained. The transition temperature of poly(DMAAPS) initially increased and then decreased as the maximum amount of ion adsorbed increased, which depend on the ion species and ion concentration. In other words, the data points laid on the same line even at different ion species when the ion concentration was the same. This result suggests that the maximum amount of ion adsorbed can be simply estimated by measuring the transition temperature of poly(DMAAPS), which can be obtained easily by measuring the temperature dependence of transmittance through the salt solution containing poly(DMAAPS).

In **Chapter 5**, the effect of methylene groups spacer between the charged functional groups of sulfobetaine on the adsorption, swelling, and transition behaviors using the DMAAPS and DMAABS polymers and/or gels was investigated in the $NaNO_3$, $Zn(NO_3)_2$ solutions. The amount of ion adsorbed onto the DMAAPS gel and its swelling degree depended strongly on the temperature and cross-linker concentration in the preparation of the gel. In contrast, the amount of ion adsorbed onto the DMAABS gel was independent of the cross-linker concentration used in the preparation of the gel. Furthermore, the swelling degree of the DMAABS gel was also independent of the cross-linker concentration and temperature. In addition, the transition temperature of poly(DMAABS) slightly increased with that of poly(DMAAPS). These results suggest that the interaction between positive and negative charged groups in the DMAABS is stronger than that in the DMAAPS.

In **Chapter 6** contains the conclusions obtained in Chapter 2 to 5.

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Chapter 1

Introduction

1.1. Background

In the last five decades, polymers incorporating zwitterionic species have been recognized as promising candidates for responsive systems geared towards various potential applications such as biosensors, catalysts, drug delivery systems, and separation media [1,2]. The specific, sensitive, and instantaneous responsiveness demonstrated by polyzwitterions has been the focus of considerable scientific research, and study of these materials has continued to gain momentum in recent decades. The zwitterionic betaine polymer containing both anionic and cationic active groups in the same side chain of the polymeric repeat unit with an alkylene group between them bears an overall neutral charge. Zwitterionic polymers such as sulfobetaine [3–6], phosphobetaine [7,8], and carboxybetaine [9–11] respectively contain sulfonate, phosphate, and carboxylate species as the cationic active group with the quaternary ammonium ion as the anionic active group. Zwitterionic betaine polymers differ considerably from ionic polymers, where the latter contain only negatively or positively charged functional groups. Zwitterionic betaine polymers also exhibit ion selectivity because the ions can bond via both the negative and positive charges located in the same repeat unit [12–14].

One of the unique characteristics of zwitterionic betaine is the ability of the fragments forming a cyclic conformation of the cationic and anionic groups of neighboring monomer residues (intra-group), or cationic and anionic groups contact between neighboring macromolecules (inter-chain), and head-to-tail stacking within single macromolecules (intra-chain) which results in the insolubility of zwitterionic betaine in pure water [15,16]. These interactions depend on the flexibility of spacer between opposite charges and length. This dependency determines the solubility, phase, volume, ionization ability and conformational state of polymeric betaine in aqueous solutions.

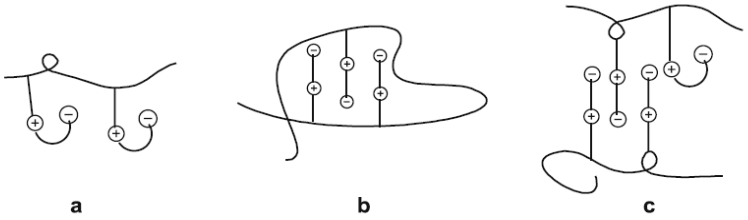


Fig. 1–1 Intra-group (**a**), intra-chain (**b**), and inter-chain (**c**) salt bonds in polybetaine.

Furthermore, zwitterionic betaine polymers are generally thermosensitive in aqueous solutions; that is, they are insoluble in water below the transition temperature and soluble above the transition temperature. The transition temperature is referred to as the upper critical solution temperature (UCST). At temperatures below the UCST, the zwitterionic polymer is in a collapsed-coil state due to the intra- and/or inter-chain interactions. However, at temperatures above the UCST, the polymer adopts an extended conformation because the thermal motion of the polymer molecules overcomes the intra- and/or inter-chain interactions [17]. Moreover, the UCST of zwitterionic polymers increases with increasing polymer concentration, which is attributed to an increase in the intra- and/or inter-chain pairings. Consequently, more thermal energy is required to overcome these interactions [18]. The interaction of the charge groups of zwitterionic betaine and aqueous salt solution also strongly determines the zwitterionic betaine properties [15]. The solubility of zwiterionic betaine in salt solutions depends on the nature of the anions and cations and is well described by the charge/radius ratio, Hofmeister series and Pearson theory [15,19,20].

1.1.1. Properties of zwitterionic betaine gels

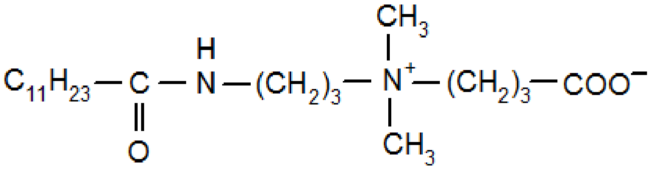
Polymeric betaine gel or usually known as polyzwitterions constitutes a special class of polyampholytes containing identical number of positively or negatively charged species on the same monomer units [15]. Polymeric betaines are soluble in pure water, but they are soluble in salt solutions. In contrast, polymeric carboxybetaine, sulfobetaine, and phosphobetaine have a very small disturbing effect on the structure of the hydrogen-bonding network of water molecules in dilute solutions, because of the intra- and inter-tether proximity between the oppositely charged groups [5]. Low molecular weight zwitterions are able to fold intra-molecularly into a loop conformation in according to molecular modeling calculations and NMR spectra. The positive charge of zwitterions on one end of the molecule interacts with the negative charge on the other end, in dependence on the length and flexibility of the spacer. This folding pattern is useful for the design of supramolecular polymers or gels by varying the linker flexibility and length [21].

Numerous studies of zwitterionic sulfobetaine type polymers and gels have been reported in recent years, most of which have placed emphasis on the synthesis and solution properties of the polymers, such as the thermosensitive properties mentioned above, or the swelling degree of the gels, which varies with the monomer concentration [22], cross-linker concentration [23–25], salt concentration [18,26,27], ionic strength [28,29], etc. In contrast, there are relatively few studies on the adsorption of cations and anions on such polymers and gels, although the adsorption behavior is recognized to affect the swelling and transition behaviors. Moreover, there is very little information on the effects of the conditions utilized in the preparation of the gels, such as the cross-linker and monomer concentrations, on the amount of ions adsorbed onto the gel. The adsorption behavior of zwitterionic sulfobetaine type polymers and gels is primarily determined by the interaction between the charged groups in the sulfobetaine (SO_3^- and N^+) group and the ions (cation and anion) in the solutions.

1.1.2. Type of betaine gels

1.1.2.1. Polycarbobetaine gels

Polycarbobetaine contain carboxylate species as the cationic active group with the quaternary ammonium ion as the anionic active group. Polycarbobetaine can be synthesized via a number of reaction pathways by functionalization of suitable monomers or polymers. The chemical structure of most polycarbobetaine is divided into three groups: polyzwitterions derived from polymeric heterocyclic or aromatic vinyl compounds, quaternary esters or amides of methacrylic acid, in which the quaternary nitrogen is substituted by an alkoxy group of different chain length, and quaternary polypyrrolidinium compounds containing linear and branched alkylcarboxy groups [15]. The polymerization kinetics of carbobetaine monomers is strongly pH dependent due to the possible protonation of the carboxylate moiety in aqueous acidic solution. In some cases, the ionic strength of the solvent was increased by inorganic salts [30,31], obviously to increase the solubility of the polymers. Polycarbobetaine are better soluble in water than polysulfobetaine. One of the examples of polycarbobetaine is lauroyl amino propyl dimethyl carbobetaine, with chemical structure shown in Fig. 1–2.

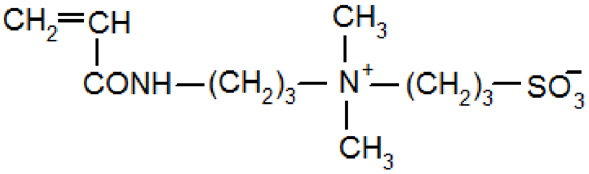


$$C_{11}H_{23}-\underset{\underset{O}{\|}}{C}-\overset{H}{N}-(CH_2)_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}}-(CH_2)_3-COO^-$$

Fig. 1–2 Structure of lauroyl amino propyl dimethyl carbobetaine.

1.1.2.2. Polysulfobetaine gels

Polysulfobetaine contain sulfonate species as the cationic active group with the quaternary ammonium ion as the anionic active group. Sulfobetaine are prepared by alkylsulfonation of a monomeric or polymeric tertiary amine with strained sultones, usually 1,3-propanesultone or 1,4-butanesultone as shown in Fig. 1–4. Most of early investigations on polymeric betaines relate to the sulfo derivatives. Chemical structure of polysulfobetaine can also be divided in several groups: quaternary esters or amides of methacrylic acid, quaternary polypyrrolidinium compounds, ionenes, and polyvinylpyridinium or polyvinylimidazolium compound [15]. Example of the sulfobetaine-type polymer or gel is *N,N*-dimethyl(acrylamidopropil)-ammonium propane sulfonate (DMAAPS) represented by Fig. 1–3.

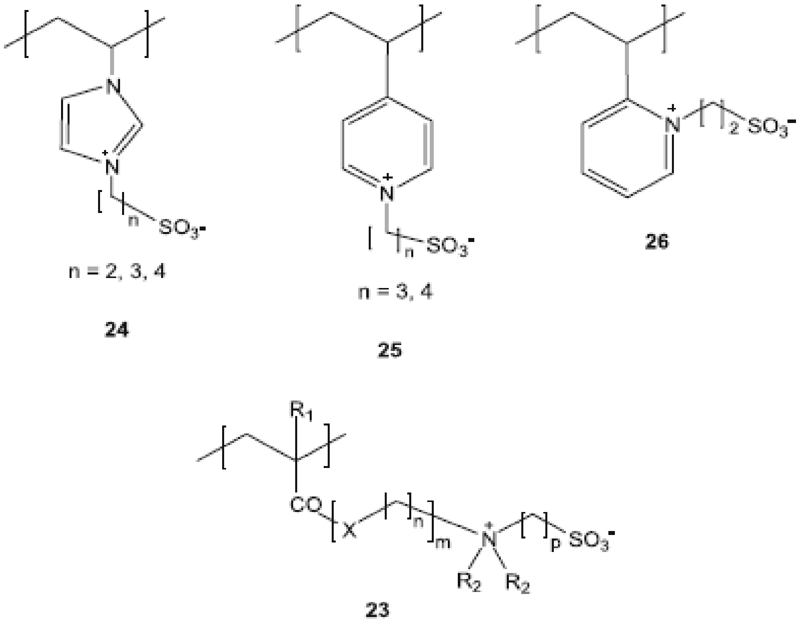


$CH_2{=}CH{-}CONH{-}(CH_2)_3{-}N^+(CH_3)_2{-}(CH_2)_3{-}SO_3^-$

Fig. 1–3 Structure of *N,N*-dimethyl(acrylamidopropil)ammonium propane sulfonate (DMAAPS).

The main difference between polycarboxybetaine and polysulfobetaine is the basicity, the carboxylate group in polycarboxybetaine is stronger base than the sulfonate group of polysulfobetaine [31,32]. By lowering pH in aqueous solution, carboxylate group can be rendered nonionic, whereas sulfonate group remains anionic even at low pH due to the low pKa. This leads the reduced viscosity of polycarboxybetaine passes through a minimum undergoing a polyanion ↔ polyzwitterion ↔ polycation transition. In contrast, at low pH polysulfobetaine does not exhibit an enhanced viscosity due to the weak basicity of the sulfonate group [15]. A combination of static and dynamic laser light scattering was employed to study the effects of temperature, pH, and ionic strength on inter-and intra-chain interactions in poly(*N,N*-dimethylmethacrylamidopropyl)ammonium propiolactone [33]. The equilibrium shifts from associates toward individual chains by increasing the temperature to 50 ^{o}C. The addition of NaOH results in the ionization of carboxylic groups, which suppresses inter-chain aggregates. Moreover, the addition of a small amount of NaCl at pH 12 at first enhances the dissociation of interchain associates, because both the hydrodynamic radius and molar mass decrease. The further addition of salt leads in chain extension as the intra-chain association is broken up. Thus, at sufficiently high salt concentration intra-group, intra-chain, and inter-chain ion contacts are disrupted.

In this thesis, sulfobetaine type polymers and gels was employed to study the adsorption, swelling, and transition behaviors of the polymers and gel, because of their facile synthesis, stable in adsorption, less influenced by pH, and generally showed a thermosensitive properties in aqueous solutions.

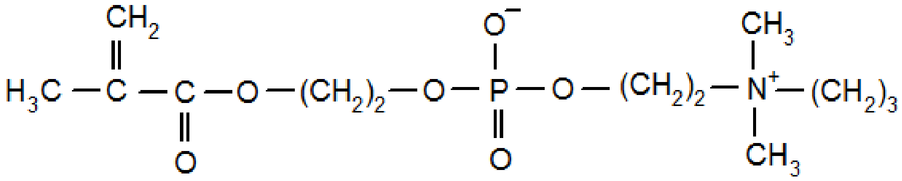


23	R_1	X	n	m	R_2	p
a	H	NH	3	1	$-CH_3$	3
b	$-CH_3$	O	2	1	$-CH_3$	3
c	H	O	2	1	$-CH_3$	3
d	$-CH_3$	O	2	2,3,4	$-CH_3$, $-C_2H_5$	4
e	$-CH_3$	NH	3	1	$-CH_3$	3

Fig. 1–4 Polysulfobetaine compiled in several reviews.

1.1.2.3. Polyphosphobetaine gels

Polyphosphobetaine contain phosphate species as the cationic active group with the quaternary ammonium ion as the anionic active group. Polymerization of polyphosphobetaine gel is mostly achieved by redox-initiated, thermally or photochemically induced free radical polymerization of the zwitterionic monomers. Example of the phosphobetaine-type polymer or gel is 2-methacryloyloxyethyl phosphorylcholine (MPC) represented by Fig. 1–5.



$H_3C-C(=CH_2)-C(=O)-O-(CH_2)_2-O-P(O^-)(=O)-O-(CH_2)_2-N^+(CH_3)_2-(CH_2)_3$

Fig. 1–5 Structure of 2-methacryloyloxyethyl phosphorylcholine (MPC).

Occasionally, in order to achieve stepwise polymerization and cross-linking of self-organized structures, the different polymerizable groups were cumulated in such reactive lipids [34,35]. A major difficulty in the synthesis of polyphospobetaine is the incorporation of the phosphatidylcholine moiety into the polymerizable lecithins. Nowadays, the main and highly versatile pathway to phosphobetaine vinyl monomers is the reaction of an OH group containing methacrylate or methacrylamide with 2-chloro-2-oxo-1,3,2-dioxaphospholane, with subsequent ring opening by trimethylamine leading to phosphorylcholine-containing compounds [36]. Polymers based on MPC are excellent bio and blood compatibilities. Phosphobetaines MPC copolymers with methacrylic acid prepared by radical polymerization in water show spontaneous gelation [37]. To improve the gel properties a new dimethacrylate cross-linker with a phosphorylcholine-like linkage was used in the copolymerization of MPC and 2-hydroxyethyl methacrylate [38]. It was found by Wang et al. that cross-linking of the acrylamide derivative with *N*,*N*-methylenebisacrylamide leads to a decrease in swelling degree of the gel with increasing temperature [39].

The interaction of the charge groups of zwitterionic betaine gel and aqueous salt solution also strongly determines the zwitterionic betaine gel properties [15]. The solubility of zwiterionic betaine polymer and swelling degree of the gel in salt solutions depends on the nature of the anions and cations and is well described by the charge/radius ratio, Hofmeister series and Pearson theory [15,19,20]. For salts with a common anion (Cl^-) and monovalent cations, the solubility decreases as $K^+ > Na^+ > NH_4^+ > Li^+$, while for divalent cations the solubility decreases in the order $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+.}$ Furthermore, the solubility decreases in the order ClO_4^- > I^- > Br^- > Cl^- > F^- in the presence of salts with a common cation (K^+) but different anions species. Polybetaine have a strong binding capacity with respect to low molecular weight salts due to the high density in dipolar units and dipole moment, and used broadly as solid electrolytes for high-energy batteries. Such behavior was demonstrated for a number of polybetaine blended with $LiClO_4$, NaClO4, $NaNO_3$, NaBr, or NaI [33,40–42].

1.2. Review of previous work

1.2.1. Phase transition of betaine polymer

Zwitterionic moieties form associations through the interactions between the cationic and anionic groups that determine many properties of zwitterionic materials. For instance, Azzaroni et al. [43] showed that associations among sulfobetaine moieties might lead zwitterionic sulfobetaine polymer brushes to be hydrophobic. The antipolyelectrolyte effect of zwitterionic polymers is also attributed to the influences of salts on the associations of zwitterionic moieties [44]. Several reports on the factors affecting the UCST have been presented. For example, the UCST shifted to higher temperature with increasing molecular weight and concentration of the sulfobetaine polymer [45–48] whereas the UCST shifted to lower temperature when salt was added to the solution or when the pH changed from 7 [18,46,49]. Schultz et al. [47] showed that adding salts could decrease the upper critical solution temperature of sulfobetaine polymers. They also observed an inverted lower critical solution temperature for sulfobetaine polymers. They proposed that such behaviors are due to the variation of the associations among sulfobetaine moieties. Takahashi et al. [18] investigated that in water as the zwitterionic polymer concentration was increased; there was an increase in the UCST. On the other hand, when the polymer concentration was low, the change in the transmittance was broad. This behavior is due to when the polymer concentration increase, the intra-chain and/or inter-chain parings also increase, and more thermal energy is required to overcome the intra-chain and/or inter-chain interactions. However, the inter-chain and/or intra-chain parings decreased and are distributed inhomogeneously when the polymer concentration was low.

It has also been reported that the phase transition and associated UCST vary with the synthetic procedure and resulting molecular structure, such as interpenetrating [50] or semiinterpenetrating networks [18], block copolymers [51,52] and fullerene (C60)-end-capped polymers [53]. The effects of molecular weight, chemical cross-link density and copolymerization on the UCST of poly(DMAAPS) have been reported by Ning et al. [22]. It was found that the UCST was maximal at a critical polymer concentration as a result of the combined effects of the inter-chain association of zwitterionic groups and the restricted motion of the polymer chains in the condensed state. The physically cross-linked poly(DMAAPS) gels could be dissolved by immersion in aqueous NaCl solution at room temperature, or by immersion in hot water (>UCST), through a combination of dissociation of ionic interactions and overall dilution. In the case of the poly(DMAAPS) gel with a chemically cross-linked network, the UCST shifted to lower temperatures with increasing cross-linking density, and at a very high degree of chemical cross-linking, the phase transition almost disappeared.

1.2.2. Swelling behavior of betaine gel

Polybetaine gels are similar to polyelectrolyte gels i.e., sensitive to the external stimuli such as pH, temperature, ionic strength, solvent nature, and DC electric field [6,54]. Polyelectrolyte gels also can swell, shrink, or bend when an external electric current is applied [55,56]. The electric-stimuli property of the polybetaine gels depends on the pH of the outer solution, the ionic strength, the direction of the electric field with respect to the gel specimen, and the applied voltage [57]. The swelling of sulfobetaine polymers gel vary as a function of salt concentration and temperature, indicating the importance of associations among zwitterionic moieties in performance of zwitterionic materials [6,58]. The swelling and mechanical properties of a gel based on the zwitterionic monomer *N,N*-dimethylmethacryloyloxyethyl-N-(3-sulphopropyl)ammonium betaine cross-linked with ethylene glycol dimethacrylate have been determined as a function of temperature by Huglin et al. [24]. The volumetric swelling has been found to decrease slightly with temperature. On the other hand, the Young's moduli as well as the experimental cross-link density increases with temperature. 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) was reported. The swelling behaviors were related to their chemical structures, their compositions, and the nature of external salt solutions [6]. Swelling behavior of various copolymer gel based on sulfobetaine have also been reported. Lee at al. [59] investigated the swelling properties of zwitterionic gels in various salt solutions. The zwitterionic gels were prepared from N-isopropylacrylamide (NIPAAm), trimethyl acrylamidopropyl ammonium iodide (TMAAI), and 3-dimethyl (methacryloxyethyl) ammonium propane sulfonate (DMAPS) in various salt solutions. It was found that in saline solution, the swelling ratio of pure NIPAAm gel did not significantly change with an increase in the salt concentration until the salt concentration was larger than 0.5 M. In addition, the copolymer gels exhibited polyelectrolytic behavior under lower salt concentration (10^{-5}–10^{-1} M), exhibited a nonionic gel (like NIPAAm) behavior at the salt concentration from 0.1 to 0.5 M, and showed an antipolyelectrolytic behavior or polyzwitterionic effect at a concentration of salt over 0.5 M.

1.2.3. Adsorption properties of ions onto betaine gel

The absorption capacity of polybetaine is more pronounced which is the subject of the present study. Recent development on zwitterionic ion-exchangers showed that these ionexhangers exhibited unique separation selectivity and the possibility of simultaneous separations of cations and anions on a single column. Furthermore, the presence of oppositely charged groups on the surface of the stationary phase can provide separation of zwitterionic analytes due to simultaneous interactions of the analytes with both functional groups of the stationary phase [14]. Neagu et al. [12] 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.

Adsorption in a series of zwitterionic hybrid polymers prepared from the ring-opening polymerization of pyromellitic acid dianhydride (PMDA) and phenylaminomethyl trimethoxysilane (PAMTMS), and a subsequent sol–gel process was investigated by Liu et al. [1]. It was found that the zwitterionic hybrid polymers have larger affinity for Pb^{2+}. The desorption efficiency of Cu^{2+} and Pb^{2+} reached up to 96 and 89%, respectively; indicating that they can be regenerated and recycled in industry. Their findings suggest that these polymers are promising adsorbents for the selective removal of Pb^{2+} from $Pb^{2+/}Cu^{2+}$ mixed aqueous solution, and can be applied to separate and recover the heavy metal ions from contaminated water and waste chemicals. In addition, Tsukamoto et al. [4] has synthesized novel sulfobetaine-type adsorbents and characteristics of their adsorption of polar solutes in hydrophilic SPE. The results indicate that all ionic reference solutes such as nucleobases (uracil, adenine and cytosine), acids (acephate and levulinic acid) and zwitterions (tetracyclines) were entrapped and released by the adsorbent. However, it showed almost no adsorption of non-ionic polar solutes such as saccharides, which are highly soluble in water.

1.3. Objective and outline of this thesis

To describe clearly this study, the thesis is broken down into six chapters. These chapters are brief outlined as follows.

Chapter 1 is "Introduction". The background, previous research, and main objectives of the thesis are discussed.

Chapter 2 is "Effects of preparation condition of DMAAPS gel on ion-adsorption properties and swelling behavior". In the second chapter, the adsorption of cations and anions on the sulfobetaine type *N,N*-dimethyl(acrylamidopropyl)ammonium propanesulfonate (DMAAPS) gels in $NaNO_3$, $Zn(NO_3)_2$, and $Al(NO_3)_3$ solutions was investigated. Furthermore, the effect of the preparation conditions such as cross-linker and monomer concentrations on the adsorption and swelling behaviors of the gel in $Zn(NO_3)_2$ solution was investigated under various temperatures and nitrate concentrations. The adsorption behavior of cations and anions on the DMAAPS gel is discussed herein by considering the degree of swelling of the gel as well as the polymer concentration in the gel. An interesting correlation between the degree of swelling of the gel and the amount of Zn^{2+} adsorbed onto the gel was found; the data points laid on the same line even at different cross-linker and/or monomer concentrations or temperatures when the $Zn(NO_3)_2$ concentration was the same. In addition, to elucidate the role of the ionic interactions in the adsorption behavior of the DMAAPS gel relative to the copolymer gel, the gel comprising a negatively charged sodium 2-(acrylamido)-2-methylpropanesulfonate (NaAMPS) and a positively charged *N,N*-dimethylaminopropyl-acrylamide methyl chloride quaternary (DMAPAA-Q) unit was also prepared. The DMAPAA-Q-*co*-NaAMPS gel network also consists of N^+ and SO_3^- groups. However, these ions have Cl^- and Na^+ as counter ions, respectively.

Chapter 3 is "Cation- and anion-adsorption properties of DMAAPS gel and its relationship with swelling behavior in aqueous salt solutions". In this chapter, the influences of cation and anion species on the adsorption and swelling behaviors of DMAAPS gel and their relationship were evaluated using halides and aqueous salt solutions. It was observed that the order of the amount of ion adsorbed onto the gel in the aqueous salt solutions was opposite that of ion species in the Hofmeister series. In addition, to elucidate competitive adsorption, the adsorption behavior of ions onto the DMAAPS gel was studied in mixtures of the halide solutions.

Chapter 4 is "Phase transition of poly(DMAAPS) and its relationship with cation- and anion-adsorption properties of DMAAPS gel in aqueous salt solutions". The phase transition of poly(DMAAPS) was investigated in aqueous salt solutions. Furthermore, the relationship between the transition behavior of poly(DMAAPS) and the maximum amount of ion adsorbed onto the gel in various solutions were also studied. It was found that the transition temperature of poly(DMAAPS) initially increased with increasing the salt concentration in the solution, and then decreased as the concentration of salt increased further. Furthermore, the transition temperature of poly(DMAAPS) initially increased and then decreased as the maximum amount of ion adsorbed onto the DMAAPS gel increased, which depend on the ion species and ion concentration.

Chapter 5 is "Comparison between DMAAPS and DMAABS polymers and gels on ion-adsorption, swelling, and transition behaviors". In this chapter, the influences of number of methylene spacer between the charged groups of betaine on the adsorption and swelling behaviors of DMAAPS and DMAABS gels were investigated using $Zn(NO_3)_2$ and $NaNO_3$ solutions. In addition, the effects of the contact time, the heating rate, the salt solution concentration and anion and cation species in the solutions on the transition temperature of poly(DMAAPS) and poly(DMAABS) were also elucidated. From the comparison of the adsorption properties, swelling behavior, and transition behavior between DMAAPS and DMAABS gels and/or polymers, the results suggest that the interaction of positive and negative charged groups in the DMAABS is stronger than that in the DMAAPS.

Chapter 6 is "Conclusions". The conclusions in this study are given and some insights provided by this study are presented.

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Chapter 2

Effects of preparation condition of DMAAPS gel on ion-adsorption properties and swelling behavior

2.1. Introduction

In this Chapter, the adsorption of cations and anions on the sulfobetaine type *N,N*-dimethyl(acrylamidopropyl)ammonium propanesulfonate (DMAAPS) gels in nitrate solutions was investigated. The adsorption behavior is recognized to affect the behaviors of swelling and transition by temperature change. Moreover, there is very little information on the effects of the conditions utilized in the preparation of the gels, such as the cross-linker and monomer concentrations, on the amount of ions adsorbed onto the gel. Therefore, the effects of the temperature and the conditions employed in the preparation of the DMAAPS gel on the adsorption were evaluated. The adsorption behavior is discussed herein in relation to the degree of swelling of the DMAAPS gel as well as the polymer concentration in the gel. $NaNO_3$, $Zn(NO_3)_2$, and $Al(NO_3)_3$ were selected as the target solutions.

In addition, to elucidate the role of the ionic interactions between the charged network in the DMAAPS gel and ions in the solution in the adsorption behavior, the copolymer gel comprising a negatively charged sodium 2-(acrylamido)-2-methylpropanesulfonate (NaAMPS) and a positively charged *N,N*-dimethylaminopropylacrylamide methyl chloride quaternary (DMAPAA-Q) was also prepared. The DMAPAA-Q-*co*-NaAMPS gel network also consists of N^+ and SO_3^- groups. However, these ions have Cl^- and Na^+ as counter ions, respectively. The adsorption behavior of the cations and anions by the DMAPAA-Q-*co*-NaAMPS gel was compared with that by the DMAAPS gel.

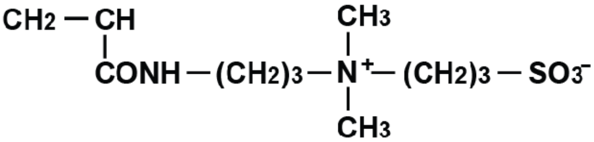
2.2. Experimental Section

2.2.1. Materials

1,3-Propanesultone (PS) and 2-(acrylamido)-2-methylpropanesulfonate (AMPS) were purchased from Tokyo Chemical Industry Co., Ltd. and used as received. *N,N*-Dimethyl-aminopropylacrylamide (DMAPAA) and DMAPAA-Q were kindly supplied by KJ Chemicals corp. DMAPAA was purified by vacuum distillation and DMAPAA-Q was used as received. *N,N′*-Methylenebisacrylamide (MBAA), *N,N,N′,N′*-tetramethylethylene-diamine (TEMED), and ammonium peroxodisulfate (APS) were purchased from Sigma-Aldrich Co. (USA) and used without further purification. Acetonitrile and acetone were purchased from Kanto Chemical Co., Inc. and Nacalai Tesque, Inc., respectively.

2.2.2. Synthesis of DMAAPS

DMAAPS was synthesized by the ring-opening reaction of DMAPAA and PS [1]. A mixture of PS (75 g) and acetonitrile (75 g) was added dropwise to a mixture of DMAPAA (100 g) and acetonitrile (200 g) with continuous stirring at 30 °C for 90 min. Stirring was then continued for 16 h, and the solution was allowed to stand for 2 d. The precipitated white crystals of DMAAPS were collected by filtration and washed with 500 mL of acetone. Finally, the obtained DMAAPS crystals were dried under reduced pressure for 24 h. The structure of DMAAPS is shown in Fig. 2–1.



$$CH_2{-}CH(CONH{-}(CH_2)_3{-}N^{+}(CH_3)_2{-}(CH_2)_3{-}SO_3^{-})$$

Fig. 2–1 Chemical structure of *N,N*-dimethyl(acrylamidopropyl)ammonium propane sulfonate (DMAAPS).

2.2.3. Preparation of the DMAAPS gel

The DMAAPS gel was prepared by free radical polymerization using TEMED, APS, and MBAA as the polymerization accelerator, initiator, and cross-linker, respectively. In the preparation of the DMAAPS gel, the concentrations of TEMED and APS were fixed and those of DMAAPS and MBAA were varied. DMAAPS, MBAA, and TEMED were dissolved in 100 mL of deionized water and charged into a separable flask. The dissolved oxygen in the solution was removed by purging with nitrogen. A 20 mL aliquot of APS solution, from which the dissolved oxygen had already been removed, was then added to the mixture. Polymerization was carried out for 6 h at 50 °C under a nitrogen atmosphere. The synthesis of the DMAAPS gels was carried out in a separable flask containing glass tubes (2 mm in diameter and 30 mm in length) to prepare the cylindrical gels. The gels prepared in the glass tubes were cut into pieces of 2 mm in length and rinsed with deionized water. The gels were then slowly dried over several days. During the drying process, the gels were placed on a Teflon sheet that was spread on a Petri dish. Because the gels break if they are dried quickly, the dish was covered with a thin plastic film with small holes to decrease the drying speed. These gels were used to measure the degree of swelling. Other gels were cut into small pieces, washed, and then dried in an oven. The dried small gels were then ground into powder and sieved to over 180 mesh size. These ground gels were used for the adsorption experiments. The compositions employed in the synthesis of the DMAAPS gels are summarized in Table 2–1.

Table 2–1 Synthesis composition of DMAAPS gel.

		concentration [mol/m^3]
Monomer	: *N,N*-dimethyl(acrylamidopropyl)ammonium propane sulfonate (DMAAPS)	500, 750, 1000
Linker	: *N,N'*-methylenebisacrylamide (MBAA)	5, 10, 30
Accelerator	: *N,N,N',N'*-tetramethylethylenediamine (TEMED)	10
Initiator	: Ammonium peroxodisulfate (APS)	0.5

2.2.4. Preparation of the copolymer gel of NaAMPS and DMAPAA-Q

The chemical structures of DMAPAA-Q and NaAMPS are shown in Fig. 2–2. NaAMPS was prepared by neutralization of its acid form, AMPS, with an equimolar amount of sodium hydroxide (NaOH) in methanol in the same manner as outlined by Teramoto et al. [2]. In the preparation of the copolymer gel, the concentrations of DMAPAA-Q, NaAMPS, MBAA, TEMED, and APS were 500, 500, 30, 10, and 0.5 mmol/L, respectively. The method used for preparation of the gel is similar to that used for the DMAAPS gel.

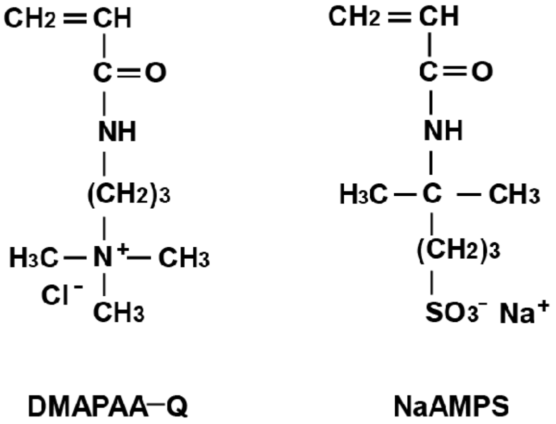


Fig. 2–2 Chemical structures of *N,N*-dimethylaminopropylacrylamide methyl chloride quaternary (DMAPAA-Q) and sodium 2-(acrylamido)-2-methylpropane-sulfonate (NaAMPS).

2.2.5. Measurement of the amount of cation and anion adsorbed on the gel

The adsorption experiments were performed using nitrate solutions, i.e., $NaNO_3$, $Zn(NO_3)_2$, and $Al(NO_3)_3$ solutions. One gram of the ground gel was placed in a glass bottle containing 20 mL of the selected nitrate solution of the desired concentration. The bottle was placed in a water bath at the desired temperature, and the solution containing the gels was gently agitated for a desired period using a magnetic stirrer to allow the gels to swell and attain the equilibrium adsorption state. In order to measure the concentration of the cation

(Na^+, Zn^{2+}, or Al^{3+}) or anion (NO_3^-) in the solution after adsorption, the gels were removed from the solution by centrifugation at 3500 rpm for 10 min and subsequently filtered using a syringe filter (0.45 μm, Toyo Roshi Kaisha, Ltd.). The amount of cation or anion adsorbed onto the gel was calculated from the concentration difference of cation or anion between in the initial solution and in the solution after adsorption by using the following equation:

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

where Q is the amount of cation or anion adsorbed, C_0 is the concentration of cation or anion in the initial solution, C is the concentration of cation or anion in the solution after adsorption for a certain period, V is the volume of the solution, and m is the weight of the dry ground gels.

The concentrations of Na^+, Zn^{2+}, and NO_3^- were measured using ion chromatography. The Na^+ and Zn^{2+} assay was carried out using a 4.6 mm (ID) × 100 mm (L) TSKgel IC-Cation 1/2 HR column (Tosoh Corp.) with 2 mmol/L HNO_3 as the mobile phase. The NO_3^- concentration was determined using a 4.6 mm (ID) × 100 mm (L) Shim-pac IC-A1column (Shimadzu Corp.) with 2.5 mmol/L phthalic acid as the mobile phase, and the Al^{3+} concentration was determined by using inductively coupled plasma (ICP) atomic emission spectrometry (Seiko Instruments Inc. SPS. 3000).

2.2.6. Measurement of the degree of swelling of the DMAAPS gel

The degree of swelling was determined according to the following procedures. The cylindrical dry gel, the diameter of which was predetermined using a cathetometer, was immersed in water or nitrate solution at 70 °C, and the gel was allowed to swell for 24 h; this time was sufficient for the gel to reach its equilibrium swollen state. The diameter of the swollen gel was then measured with a cathetometer. The temperature was reduced stepwise and the diameter of the swollen gel was measured again. This procedure was repeated until the temperature was reduced to 10 °C. The degree of swelling, *SD*, was defined by the following equation:

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

where d_{swell} and d_{dry} respectively indicate the diameter of swollen gel and dry gel.

2.3. Results and discussion

2.3.1. Time dependence of adsorption of ion onto the DMAAPS gel

Fig. 2–3 shows the time course of the amount of Zn^{2+} adsorbed onto the DMAAPS gel at 50 °C, which was measured in the $Zn(NO_3)_2$ solution at the initial concentration of 5 mmol/L. The adsorbed amount increased proportional to the time within the first 6 h followed by a much slower rate, and the adsorption ultimately achieved equilibrium at about 8 h. This result leads to the conclusion that 12 h of contact time is enough to reach the equilibrium adsorption and was further used in investigating the amount of ions adsorbed onto the DMAAPS gel.

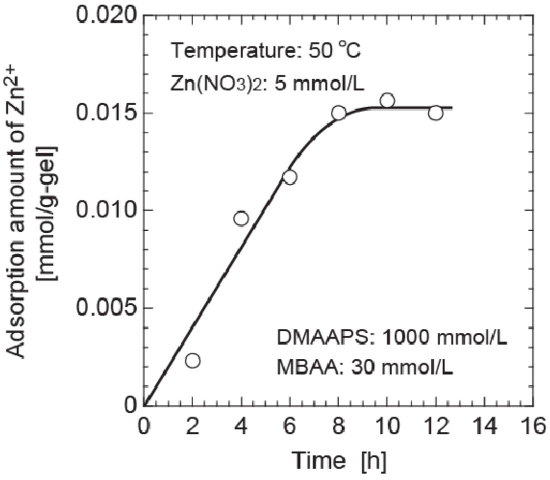


Fig. 2–3 Time dependence of the amount of Zn^{2+} adsorbed onto the DMAAPS gel at 50 °C in 5 mmol/L $Zn(NO_3)_2$ solution.

2.3.2. Simultaneous adsorption of cation and anion onto the DMAAPS gel

To gain insight into the process of simultaneous adsorption of the cation and anion onto the DMAAPS gel, adsorption experiments were conducted using $NaNO_3$, $Zn(NO_3)_2$, and $Al(NO_3)_3$ solutions. The amounts of cation (Na^+, Zn^{2+}, and Al^{3+}) and anion (NO_3^-) adsorbed onto the DMAAPS gel in these nitrate solutions of various concentrations at 50 °C are shown in Figs. 2–4(a), (b), and (c), respectively. The cation and anion were both adsorbed onto the DMAAPS gel, and the amount of each ion adsorbed increased as the concentration of ion in the solution increased. In the case of the $NaNO_3$ solution (Fig. 2–4(a)), the amounts of Na^+ and NO_3^- adsorbed, expressed in units of [mmol/g-dry gel], were almost the same. In the case of the $Zn(NO_3)_2$ solution (Fig. 2–4(b)), the amount of NO_3^- adsorbed was larger than that of Zn^{2+}. Furthermore, in the case of the $Al(NO_3)_3$ solution, the amount of NO_3^- adsorbed was markedly higher than that of Al^{3+} (Fig. 2–4(c)). The observed order of adsorption amount was as follow: $NaNO_3 < Zn(NO_3)_2 < Al(NO_3)_3$. This order can be explained by the fact that the fixed ionic groups of the DMAAPS gel interact more strongly with ions having higher valence [3].

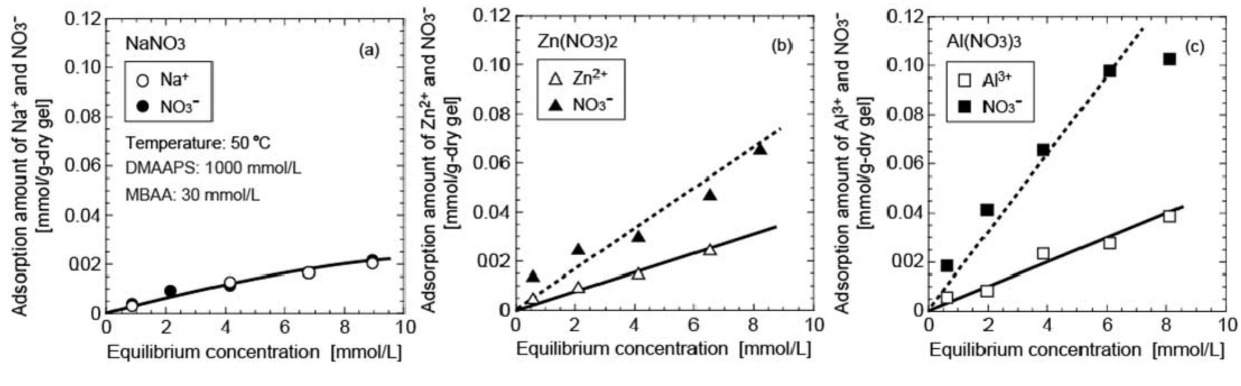


Fig. 2–4 Amounts of the cation and anion adsorbed onto the DMAAPS gel in (a) $NaNO_3$ solution, (b) $Zn(NO_3)_2$ solution, and (c) $Al(NO_3)_3$ of various concentrations.

Fig. 2–5 shows the relationship between the amount of cation and anion adsorbed. The amount of cation adsorbed is proportional to that of anion adsorbed for each nitrate solution, and the slopes of the plots are inversely proportional to the valence of the cation. This result implies that the cation and anion are simultaneously adsorbed onto the DMAAPS gel. Therefore, the amount of anion adsorbed can be simply determined by that of cation adsorbed, or vice-versa.

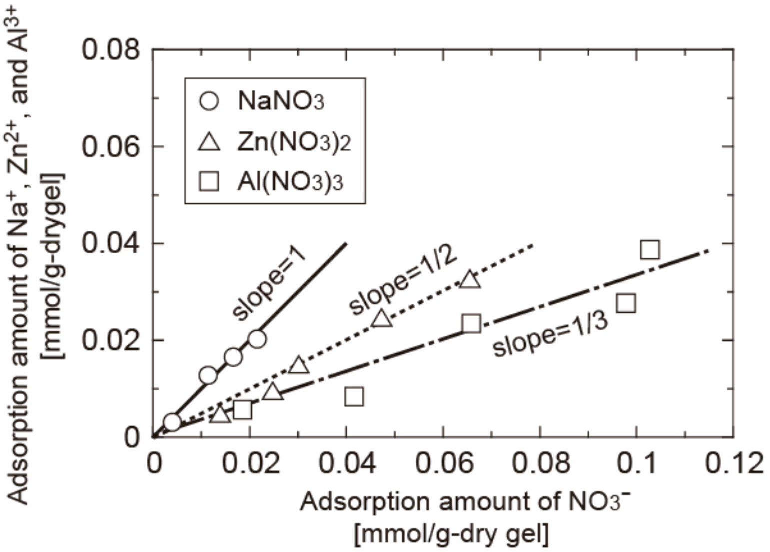


Fig. 2–5 Relationship between the amounts of the cations (Na^+, Zn^{2+}, and Al^{3+}) and anion (NO_3^-) adsorbed onto the DMAAPS gel in $NaNO_3$, $Zn(NO_3)_2$, and $Al(NO_3)_3$ solutions of various concentrations.

2.3.3. Ion exchange adsorption of anion and cation onto the copolymer gel of NaAMPS and DMAPAA-Q

The adsorption behavior of the DMAAPS gel in the $Zn(NO_3)_2$ solution was compared with that of the DMAPAA-Q-*co*-NaAMPS gel in $Zn(NO_3)_2$ and $Al(NO_3)_3$ solutions. Fig. 2–6(a) shows the amount of Zn^{2+} and NO_3^- adsorbed as a function of the $Zn(NO_3)_2$ equilibrium concentrations and Fig. 2–6(b) shows the amount of Al^{3+} and NO_3^- adsorbed as a function of the $Al(NO_3)_3$ equilibrium concentrations. The amount of Zn^{2+} and Al^{3+} adsorbed increased significantly, as the concentration of $Zn(NO_3)$ or $Al(NO_3)_3$ increased, and reached a constant value at higher concentration. On the other hand, the adsorption of NO_3^- was insignificant. These results imply that the adsorption of Zn^{2+} and Al^{3+} on the copolymer gel occurs by ion exchange with Na^+, which is the counter ion of SO_3^- in the NaAMPS groups in the copolymer gel. However, ion exchange between NO_3^- and Cl^-, which is the counter ion of N^+ in the DMAPAA-Q groups in the copolymer gel, hardly occurs. Thus, the amount of Na^+ released due to ion exchange was also measured, and the results are presented in Fig. 2–6 along with the amount of NO_3^- and Zn^{2+} or Al^{3+} adsorbed. The amount of Na^+ released was almost twice or three times higher than that of Zn^{2+} or Al^{3+} adsorbed, respectively. Figs. 2–4(b-c) and 6(a-b) illustrate that the amount of Zn^{2+} or Al^{3+} adsorbed onto the copolymer gel was larger than that adsorbed onto the DMAAPS gel at the same equilibrium concentration. These results are attributed to the fact that the adsorption of Zn^{2+} and Al^{3+} onto the copolymer gel occurs via ion-exchange with Na^+, whereas that on the DMAAPS gel is controlled not only by the affinity between Zn^{2+} or Al^{3+} and SO_3^- but also the affinity between NO_3^- and N^+ in the DMAAPS gel due to the simultaneous adsorption of Zn^+ or Al^{3+} and NO_3^-.

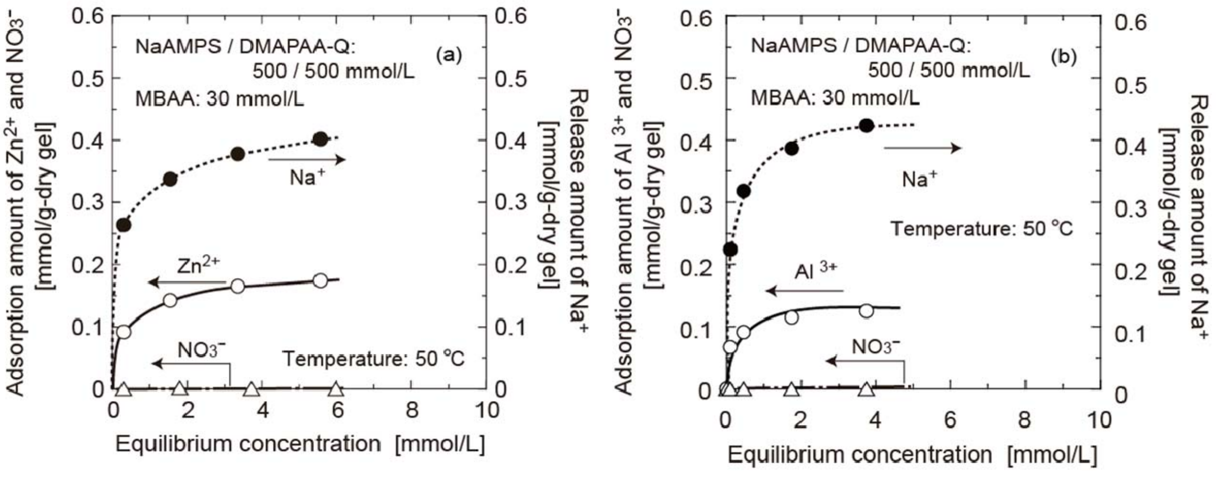


Fig. 2–6 Adsorbed amount of Zn^{2+}, Al^{3+} and NO_3^- onto the DMAPAA-Q-*co*-NaAMPS gel and released amount of Na^+ from the DMAPAA-Q-*co*-NaAMPS gel in (a) $Zn(NO_3)_2$ solution and (b) $Al(NO_3)_3$ solution of various concentrations.

2.3.4. Adsorption and swelling behaviors of the DMAAPS gel prepared by various cross-linker concentrations

Fig. 2–7(a) shows the effect of the concentration of cross-linker used in the preparation of the DMAAPS gel on the amount of Zn^{2+} adsorbed onto the DMAAPS gel in $Zn(NO_3)_2$ solutions of various concentrations at 50 °C. The gels were prepared at three different cross-linker concentrations, i.e., 5, 10, and 30 mmol/L. The amount of Zn^{2+} adsorbed increased significantly as the concentration of $Zn(NO_3)_2$ increased, and the use of a higher cross-linker concentration also led to increase the amount of Zn^{2+} adsorbed.

The swelling properties of the gels in $Zn(NO_3)_2$ solutions of various concentrations were also examined. Fig. 2–7(b) shows the degree of swelling of the DMAAPS gel measured at 50 °C. The degree of swelling of the gel prepared at a cross-linker concentration of 30 mmol/L increased gradually as the $Zn(NO_3)_2$ concentration increased, although this increase was not significant. Reducing the cross-linker concentration to 5 mmol/L increased the degree of swelling significantly. For polyzwitterionic betaine gel synthesized at higher cross-linker concentration, the electroneutrality of the charge groups results from the intra-group ionic pairs formation [4]. Furthermore, an increase of the cross-linker concentration increases the polymer concentration in the gel, in other words, increases the network density in the gel. As the swelling degree of DMAAPS gel is small enough, the polymer network of DMAAPS gel become close to each other and the distance between sulfonate groups decreases. This condition promotes the formation of cation bridges between two neighboring sulfonate groups; thereby increasing adsorption of Zn^{2+} ions from the $Zn(NO_3)_2$ solution on the DMAAPS gel. In contrast, decreasing the cross-linker concentration reduces the polymer concentration in the gel. In addition, at equilibrium swelling the polymer network of DMAAPS gel expands largely and eventually increases the distance between the sulfonate groups. The reduction in the amount of Zn^{2+} adsorbed onto the DMAAPS gel indicates the weakening of the interaction between SO_3^- groups of the DMAAPS gel and the Zn^{2+} from the

$Zn(NO_3)_2$ solution due to the expansion of the gel network.

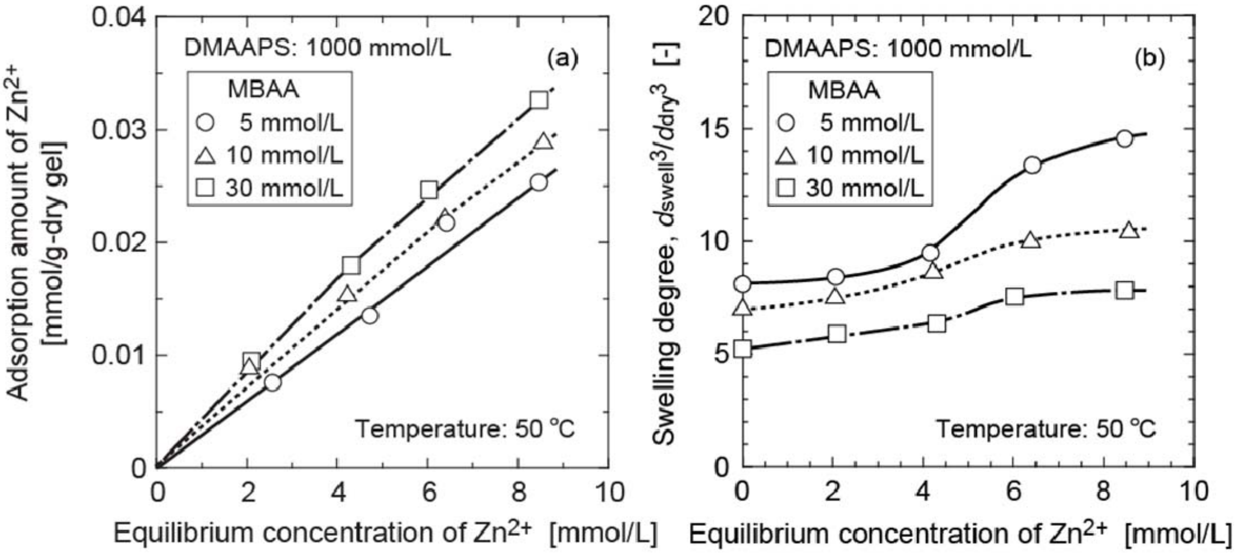


Fig. 2–7 (a) Amount of Zn^{2+} adsorbed onto the DMAAPS gel and (b) the degree of swelling of the DMAAPS gel in $Zn(NO_3)_2$ solutions of various concentrations at 50 °C. The gels were prepared at three different cross-linker concentrations.

It is well known that the DMAAPS gel exhibits thermosensitive properties [5,6]. Thus, the ability of DMAAPS gel to adsorb Zn^{2+} in 10 mmol/L $Zn(NO_3)_2$ solution was studied by conducting different sets of experiments at various temperatures. Fig. 2–8(a) shows the effect of varying the temperature on the amount of Zn^{2+} adsorbed onto the DMAAPS gel prepared at three different cross-linker concentrations, i.e., 5, 10, and 30 mmol/L. At 10 °C, the amount of Zn^{2+} adsorbed onto these gels was almost the same. At a low cross-linker concentration of 5 mmol/L, the amount of Zn^{2+} adsorbed onto the gel decreased significantly as the temperature increased from 10 to 70 °C. In contrast, at 10 mmol/L of cross-linker concentration, the amount of Zn^{2+} adsorbed decreased gradually. Furthermore, at a higher cross-linker concentration of 30 mmol/L, there was no significant change in the amount of Zn^{2+} adsorbed at temperatures in the range of 10−70 °C. This phenomenon can be explained as follows. For the DMAAPS gel synthesized at lower cross-linker concentration, at equilibrium swelling the polymer network of the gel expanded largely. This implies that the distance between the neighboring sulfonate groups of DMAAPS is far enough. Moreover, the thermal motion weakens the interaction between the charged groups in the DMAAPS gel and the Zn^{2+} and NO_3^- ions from the $Zn(NO_3)_2$ solution. As a result, the adsorbed amount of Zn^{2+} decreased with increasing temperature, particularly for the gel synthesized at lower cross-linker concentrations.

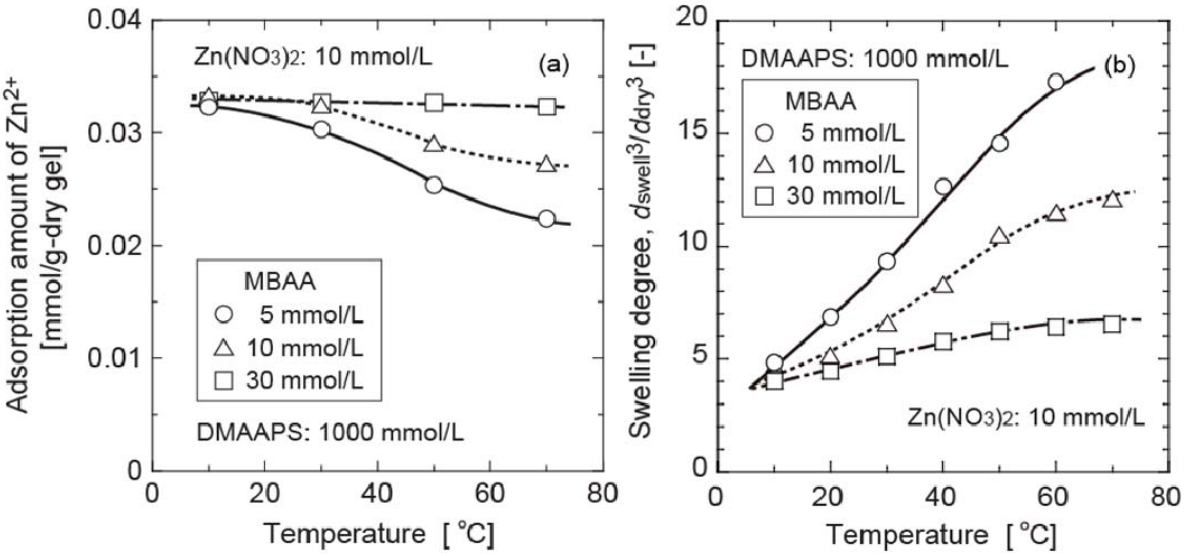


Fig. 2–8 (a) Amount of Zn^{2+} adsorbed onto the DMAAPS gel and (b) degree of swelling of the DMAAPS gel in 10 mmol/L $Zn(NO_3)_2$ solution at various temperatures. The gels were prepared at three different cross-linker concentrations.

The effect of temperature on the swelling properties of the gels in 10 mmol/L $Zn(NO_3)_2$ solution was also examined and shown in Fig. 2–8(b). The gel prepared at a lower cross-linker concentration (5 mmol/L) swelled significantly with increasing temperature. However, the degree of swelling of the gel prepared at a higher cross-linker concentration (30 mmol/L) increased only slightly with increasing temperature.

2.3.5. Adsorption and swelling behaviors of the DMAAPS gel prepared by various monomer concentrations

Fig. 2–9(a) shows the effect of the concentration of the DMAAPS monomer used in the preparation of the gel on the amount of Zn^{2+} adsorbed in $Zn(NO_3)_2$ solutions of various concentrations. The gels were prepared at three different monomer concentrations, i.e., 500, 750, and 1000 mmol/L, at a fixed cross-linker concentration of 30 mmol/L. The amount of Zn^{2+} adsorbed increased with increasing $Zn(NO_3)_2$ concentration. Furthermore, the amount of Zn^{2+} adsorbed onto the DMAAPS gel prepared at a higher monomer concentration was larger than that prepared at a lower monomer concentration. The swelling behavior of these gels is shown in Fig. 2–9(b). The gel prepared at a lower monomer concentration can swell to a greater extent than that prepared at a higher monomer concentration.

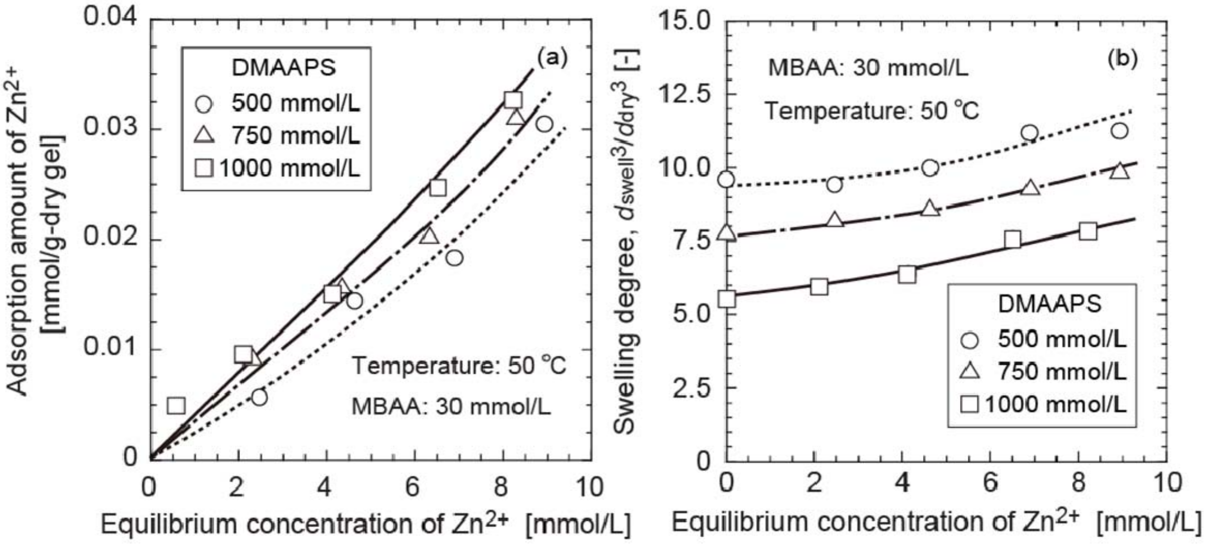


Fig. 2–9 (a) Amount of Zn^{2+} adsorbed onto the DMAAPS gel and (b) degree of swelling of the DMAAPS gel in $Zn(NO_3)_2$ solutions of various concentrations at 50 °C. The gels were prepared at three different monomer concentrations.

Fig. 2–10(a) shows the effect of temperature on the gels at a $Zn(NO_3)_2$ concentration of 10 mmol/L. At 10 °C, the amount of Zn^{2+} adsorbed onto the gels was almost the same. The amount of Zn^{2+} adsorbed decreased slightly as the temperature increased from 10 to 70 °C when the gels that were prepared at monomer concentrations of 500 and 750 mmol/L were immersed in the $Zn(NO_3)_2$ solution. Moreover, the amount of Zn^{2+} adsorbed remained unchanged in the case of the gel prepared at a higher monomer concentration of 1000 mmol/L, as shown previously in Fig. 2–8(a). In addition, the degree of swelling of these gels increased with increasing temperature and was significant for the gel prepared at a lower monomer concentration, i.e., 500 mmol/L, as shown in Fig 2–10(b).

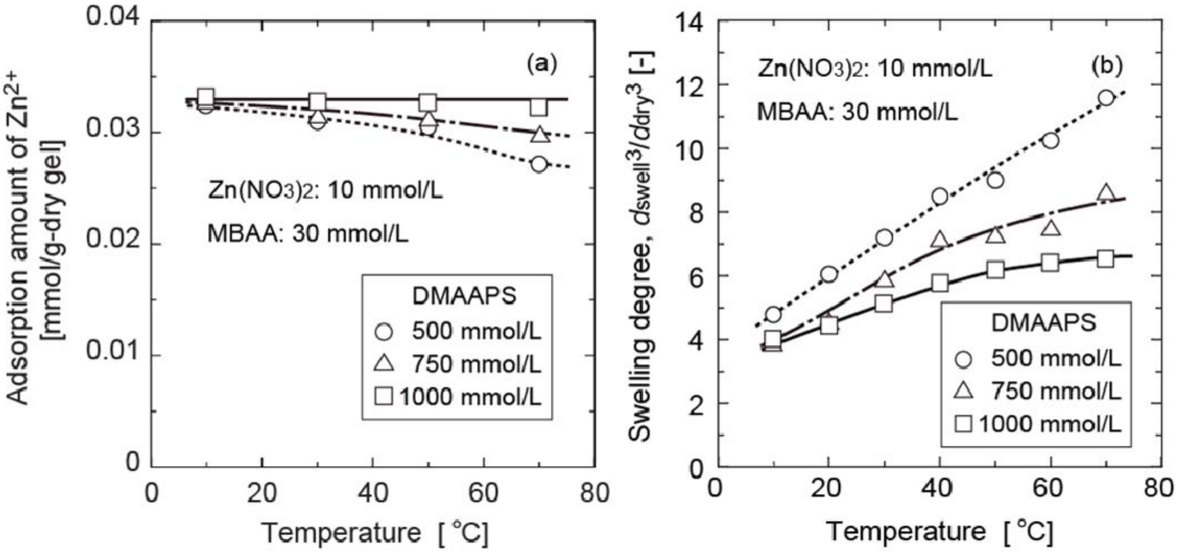


Fig. 2–10 (a) Amount of Zn^{2+} adsorbed onto the DMAAPS gel and (b) degree of swelling of the DMAAPS gel in 10 mmol/L $Zn(NO_3)_2$ solution at various temperatures. The gels were prepared at three different monomer concentrations.

2.3.6. The relationship between the adsorption and swelling behaviours

The relationship between the amount of Zn^{2+} adsorbed and the degree of swelling of the DMAAPS gels prepared at three different cross-linker concentrations, i.e., 5, 10, and 30 mmol/L, measured at various temperatures, i.e., 10, 30, 50, and 70 ºC, and in various concentrations of $Zn(NO_3)_2$ solutions, i.e., 2.5, 5, 7.5, and 10 mmol/L, is summarized in Fig. 2–11(a). The data reveal an interesting correlation; the data points laid on the same line even at different cross-linker concentrations or temperatures when the $Zn(NO_3)_2$ concentration was the same. Furthermore, when the degree of swelling was lower, the amount of Zn^{2+} adsorbed remained unchanged and decreased gradually at a higher degree of swelling. The line depended on the $Zn(NO_3)_2$ concentration, and at the same degree of swelling, the amount of Zn^{2+} adsorbed increased as the concentration of $Zn(NO_3)_2$ increased.

In addition, the relationship between the amount of Zn^{2+} absorbed and the degree of swelling was considered by converting the degree of swelling to the polymer concentration in the gel, which could be calculated using the following equation:

$$C_p = \frac{W_0}{V_0} \times \frac{1}{SD} \tag{3}$$

where C_p is the concentration of the polymer in the gel, W_0 is the weight of the dry sample gels, and V_0 is the volume of the dry sample gels.

Fig. 2–11(b) shows the relationship between the amount of Zn^{2+} adsorbed onto the DMAAPS gel and the concentration of polymer in the gel. When the concentration of polymer in the gel was lower, i.e., at a higher degree of swelling, the amount of Zn^{2+} adsorbed increased with increasing polymer concentration. In contrast, when the concentration of polymer in the gel was higher than about 180 g/L, the amount of Zn^{2+} adsorbed remained unchanged with increasing polymer concentration. This implies that the number of charged groups in the DMAAPS gel that are available to interact with the ions in the $Zn(NO_3)_2$ solution does not increase. A similar trend was also observed for each solution irrespective of the concentration.

This behavior can be explained as follows. At higher polymer concentration in the gel, which is observed at lower temperature and higher cross-linker concentration, the interaction is dominated by intra-group ionic pairs [4]. Because the interaction between the SO_3^- and N^+ groups of the DMAAPS gel that forms an intra-group ionic pairing is quite strong, only a part of the charged groups in the DMAAPS gel interacts with Zn^{2+} and NO_3^- in the $Zn(NO_3)_2$ solution; in other words, the amount of ions adsorbed by the DMAAPS gel is limited. In contrast, at lower polymer concentration in the gel, which is observed at higher temperature and lower cross-linker concentration, the thermal motion weakens the interaction between the N^+ and SO_3^- groups of DMAAPS. The breakages of associations caused by temperature increase is already observed for sulfobetaine hydrogel [7] and sulfobetaine polymer solids [8]. Simultaneously, the thermal motion also weakens the ionic pairings force between the charged groups in the DMAAPS gel and the Zn^{2+} and NO_3^- ions from the $Zn(NO_3)_2$ solution. These phenomena reduce the adsorption of ions from the $Zn(NO_3)_2$ solution onto the DMAAPS gel, thereby decreasing the amount of Zn^{2+} adsorbed onto the gel.

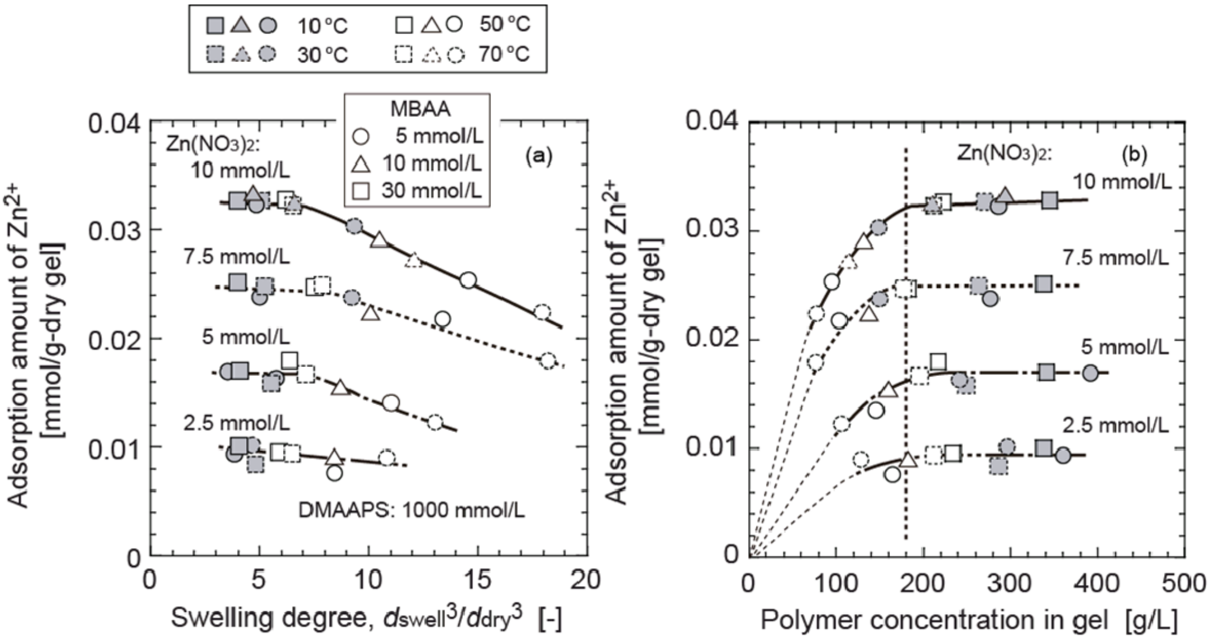


Fig. 2–11 Relationship between the amount of Zn^{2+} adsorbed onto the DMAAPS gel and (a) the degree of swelling of the DMAAPS gel and (b) the polymer concentration in the gel. The gels were prepared at three different cross-linker concentrations; the amount of Zn^{2+} adsorbed and the degree of swelling were measured in the $Zn(NO_3)_2$ solutions of various concentrations (2.5, 5, 7.5, and 10 mmol/L) and at various temperatures (10, 30, 50, and 70 ºC).

The constant amount of Zn^{2+} adsorbed onto the DMAAPS gel was regarded as the maximum adsorption amount of Zn^{2+}. In the case of adsorption behavior of the DMAAPS gel in $Zn(NO_3)_2$, maximum amount of Zn^{2+} ion adsorbed was reached when the concentration of polymer in the gel was higher than about 180 g/L despite variation of the $Zn(NO_3)_2$ and cross-linker concentration. Fig. 2–12 shows the relationship between the maximum amount of Zn^{2+} adsorbed onto the DMAAPS gel and $Zn(NO_3)_2$ equilibrium concentrations. It is seen that the maximum adsorption amount increased linearly with equilibrium concentration of Zn^{2+} in the experimental range. The value of maximum adsorption amount can be obtained by the following equation:

$$Q_{max} = 0.0039\, C_e \qquad (4)$$

where Q_{max} is maximum amount of Zn^{2+} adsorbed onto the DMAAPS gel and C_e is the equilibrium concentration of Zn^{2+}.

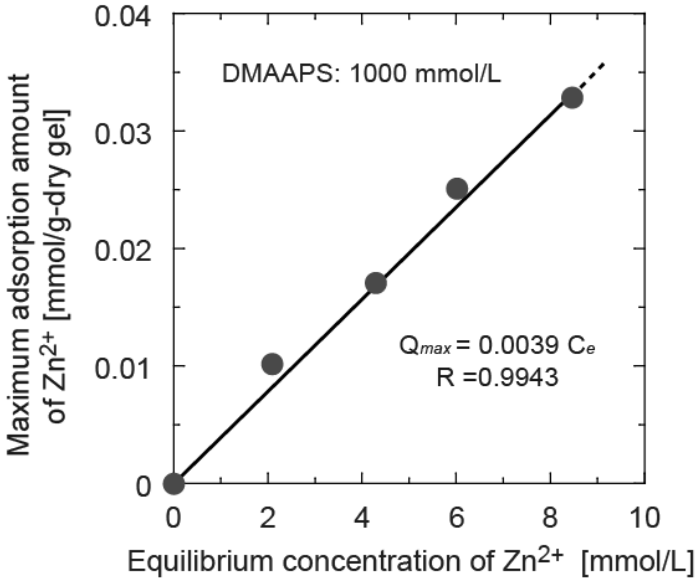


Fig. 2–12 Relationship between the maximum amount of Zn^{2+} adsorbed onto the DMAAPS gel and $Zn(NO_3)_2$ equilibrium concentrations.

The relationship between the degree of swelling and the amount of Zn^{2+} adsorbed onto the gels prepared at three different monomer concentrations was also examined (Fig. 2–13(a)); the $Zn(NO_3)_2$ concentration was 10 mmol/L. A similar correlation was found despite variation of the monomer concentration used in the preparation of the gel. The correlation between the polymer concentration and the amount of Zn^{2+} adsorbed is shown in Fig. 2–13(b). These results were similar to those described in Fig. 2–11, regardless of the monomer concentration. The amount of Zn^{2+} adsorbed increased with increasing polymer concentration when the polymer concentration in the gel was lower. Furthermore, at a polymer concentration higher than about 180 g/L, the amount of Zn^{2+} adsorbed remained unchanged with increasing polymer concentration.

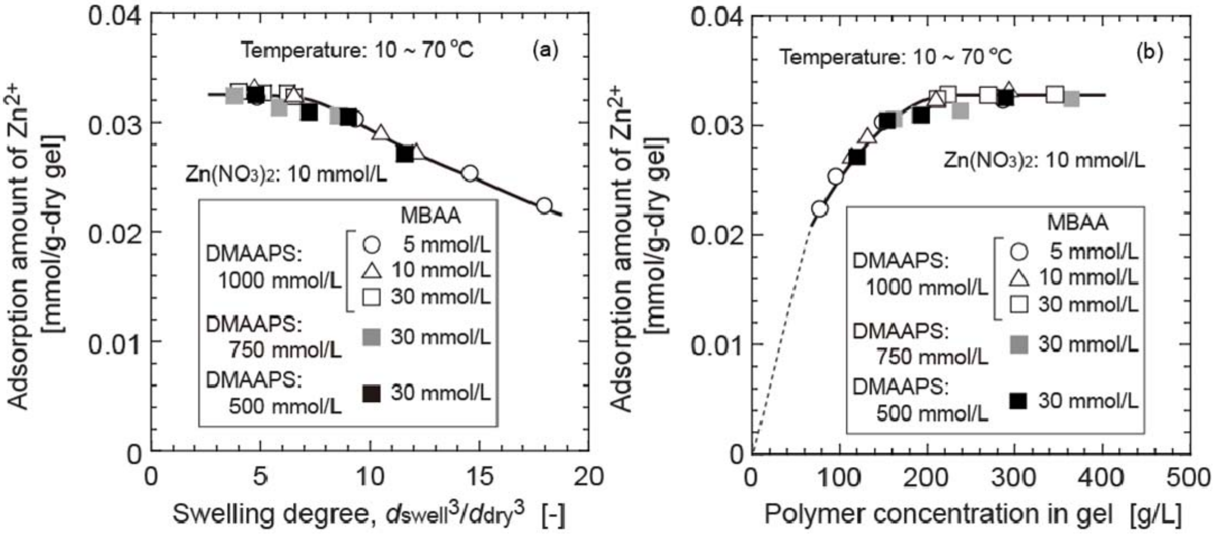


Fig. 2–13 Relationship between the amount of Zn^{2+} adsorbed onto the DMAAPS gel and (a) the degree of swelling, and (b) the polymer concentration in the gel. The gels were prepared at three different monomer concentrations; the amount of Zn^{2+} adsorbed and the degree of swelling were measured in $Zn(NO_3)_2$ solutions of various concentrations and at various temperatures.

2.4. Summary

The adsorption of cations and anions on DMAAPS gel was investigated using $NaNO_3$, $Zn(NO_3)_2$, and $Al(NO_3)_3$ solutions. Cations and anions were simultaneously adsorbed from the nitrate solutions by the DMAAPS gel. The adsorbed amount of cation (Na^+, Zn^{2+}, or Al^{3+})

was proportional to that of anion (NO_3^-) and the slope was inversely proportional to the valence of the cation. Furthermore, the adsorbed amount increased with increasing valence of the cations. The amount of Zn^{2+} adsorbed onto the DMAAPS gel was compared with that on the copolymer gel of DMAPAA-Q-*co*-NaAMPS that also possesses SO_3^- and N^+ groups. The amount of Zn^{2+} adsorbed onto the copolymer gel by the ion exchange was larger than that adsorbed onto the DMAAPS gel.

The amount of Zn^{2+} adsorbed onto the DMAAPS gel increased as the concentration of cross-linker and monomer used in the preparation of the gel increased. Furthermore, for the gel prepared at a higher cross-linker or monomer concentration, increasing the temperature did not cause any significant change in the amount of Zn^{2+} adsorbed onto the DMAAPS gel. In contrast, the amount of Zn^{2+} adsorbed decreased significantly with elevation of the temperature for the gel prepared at a lower cross-linker or monomer concentration.

In addition, an interesting correlation between the degree of swelling of the DMAAPS gel and the amount of Zn^{2+} adsorbed onto the gel was observed. The data points laid on the same line even at different cross-linker concentrations or temperatures when the $Zn(NO_3)_2$ concentration was the same. Furthermore, for the gel with a low degree of swelling, i.e., when the polymer concentration in the gel was higher than about 180 g/L, the amount of Zn^{2+} adsorbed remained unchanged. In contrast, when the gel exhibited a high degree of swelling, i.e., when there was a lower polymer concentration in the gel, the amount of Zn^{2+} adsorbed decreased as the swelling degree increased. At the same swelling degree, the amount of Zn^{2+} adsorbed increased as the concentration of $Zn(NO_3)_2$ increased. Moreover, the adsorbed amount of Zn^{2+} observed at above 180 g/L of polymer concentration was regarded as the maximum amount of Zn^{2+} adsorbed onto the DMAAPS gel, and the value can be evaluated by the Eq. (4) as the equilibrium concentration of Zn^{2+} in the $Zn(NO_3)_2$ solution.

2.5. References

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Chapter 3

Cation- and anion-adsorption properties of DMAAPS gel and its relationship with swelling behavior in aqueous salt solutions

3.1. Introduction

In the present chapter the effect of the anion and cation species on the amount of ions adsorbed onto DMAAPS gel was studied. Furthermore, the relationship with its swelling degree or polymer concentration in the gel was also examined using solutions of halides, i.e., KF, KCl, KBr, KI and $ZnCl_2$, $ZnSO_4$ 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. Moreover the effect of the cation 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 using $Zn(NO_3)_2$, $Mg(NO_3)_2$, and $Ca(NO_3)_2$ solutions.

The purpose of the present study is to evaluate the influence of these anion and cation species on the adsorption behavior onto DMAAPS gel and the swelling behavior of DMAAPS gel in these 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.

3.2. Experimental Section

The preparation DMAAPS gel was the same as those described previously in Chapter 2. The concentrations of DMAAPS, TEMED, and APS were 1000, 10, and 0.5 mmol/L, respectively. The swelling degree of the DMAAPS gel was measured using a reported procedure [1]. Ion-adsorption experiments were also performed using the same procedure described in the previous Chapter 2, except that the cation (K^+) and anion (F^-, Cl^-, Br^-, and I^-) concentrations were measured using ion chromatography using a SUS TSKgel Super IC-A/C (Tosoh Corp.) column (6.0 mm I.D × 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 Zn^{2+}, Mg^{2+}, and Ca^{2+} assay was carried out using a 4.6 mm (ID) × 100 mm (L) TSKgel IC-Cation 1/2 HR column (Tosoh Corp.) with 2 mmol/L HNO_3 as the mobile phase.

3. 3. Results and discussion

3.3.1. The adsorption and swelling behaviors of the DMAAPS gel in various halide solutions

3.3.1.1. The amount of cations adsorbed onto the DMAAPS gel prepared by various cross-linker concentrations

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. Figs. 3–1(a)–(d) show the amount of K^+ adsorbed onto DMAAPS gel from these halide solutions as a function of temperature. In the previous Chapter 2, it was confirmed that the DMAAPS gel simultaneously adsorbed cations and anions from salt solutions [1]; 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 3–1(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 (Figs. 3–1(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 [2]. 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 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 cross-linker 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 is consistent with what was observed for sulfobetaine gel [3] and sulfobetaine polymer solids [4]. 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 > KCl > KF, and the order of anion in these halide solutions, i.e., $I^- > Br^- > Cl^- > F^-$, was opposite that in the Hofmeister series. The typical order of the anion series is:

$$CO_3^{2-} > SO_4^{2-} > S_2O_3^{2-} > H_2PO_4^- > F^- > Cl^- > Br^- \approx NO_3^- > I^- > ClO_4^- > SCN^- \qquad (1)$$

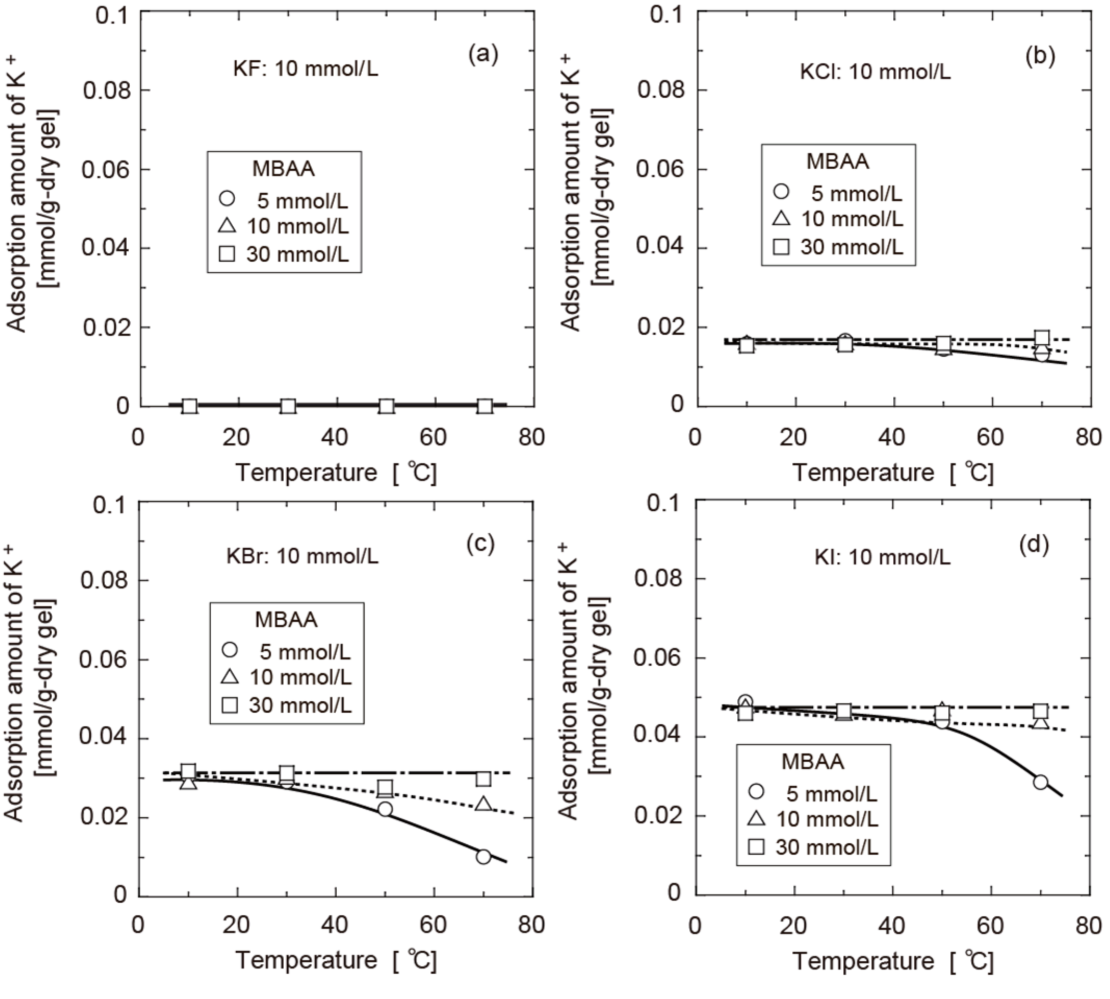

Fig. 3–1 Amount of K^+ adsorbed onto DMAAPS gel from 10 mmol/L (a) KF, (b)

KCl, (c) KBr, and (d) KI solutions at various temperatures. The gels were prepared at three different cross-linker concentrations.

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 [5–7]. The species at the left of the Hofmeister series are referred to as kosmotropes or "water-structure makers". These anions are small and strongly hydrated [7]. 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" [5,6]. The ion sizes of F, Cl, Br, and I are 119, 167, 182, and 206 pm, respectively. Furthermore, the hydration energy of F^-, Cl^-, Br^-, and I^- are -457, -381, -351, -307 kJ/mol. F^- with the highest charge and smallest sizes, has the highest hydration energy. Therefore, F^- attracts water molecules very strongly and an aqueous solution of F^- is formed with relative ease. The hydration energy gets progressively less exothermic along the series of F^-, Cl^-, Br^-, I^- because the ionic size gets progressively larger along series.

The Cl^-, Br^-, and I^- ions used in this study are chaotropes and exhibit a weaker resistance to dehydration [8] in the following order: $Cl^- > Br^- > I^-$. Therefore, when DMAAPS gel was immersed in a KI solution, the I^- ions strongly interacted with the N^+ groups of DMAAPS, which resulted in greater adsorption. In contrast, F^- ions are kosmotropes [8]; therefore, this strongly hydrated species exhibits stronger interactions with water molecules than the cohesive forces of water molecules. Therefore, F^- remained hydrated [9] resulting in less interaction of the F^- ions with the N^+ of DMAAPS, which led to smaller adsorption.

3.3.1.2. The swelling degree of the DMAAPS gel prepared by various cross-linker concentrations

Figs. 3–2(a)–(d) show the temperature dependence of the swelling degree of DMAAPS gels prepared at three different MBAA concentrations 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 SO_3^- because of the new ionic interactions between the ions in the halide solution and the charged groups of poly(DMAAPS), i.e., SO_3^- 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. 3–2. 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 $F^- > Cl^- > Br^- > I^-$, while the swelling degree of DMAAPS gel decreased in the following order: KI > KBr > KCl > KF as seen in Fig. 3–2. 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 (Figs. 3–2(a) and (b)); however, in the KBr and KI solutions (Figs. 3–2(c) and (d)), the swelling degrees of these three gels varied significantly at all temperatures.

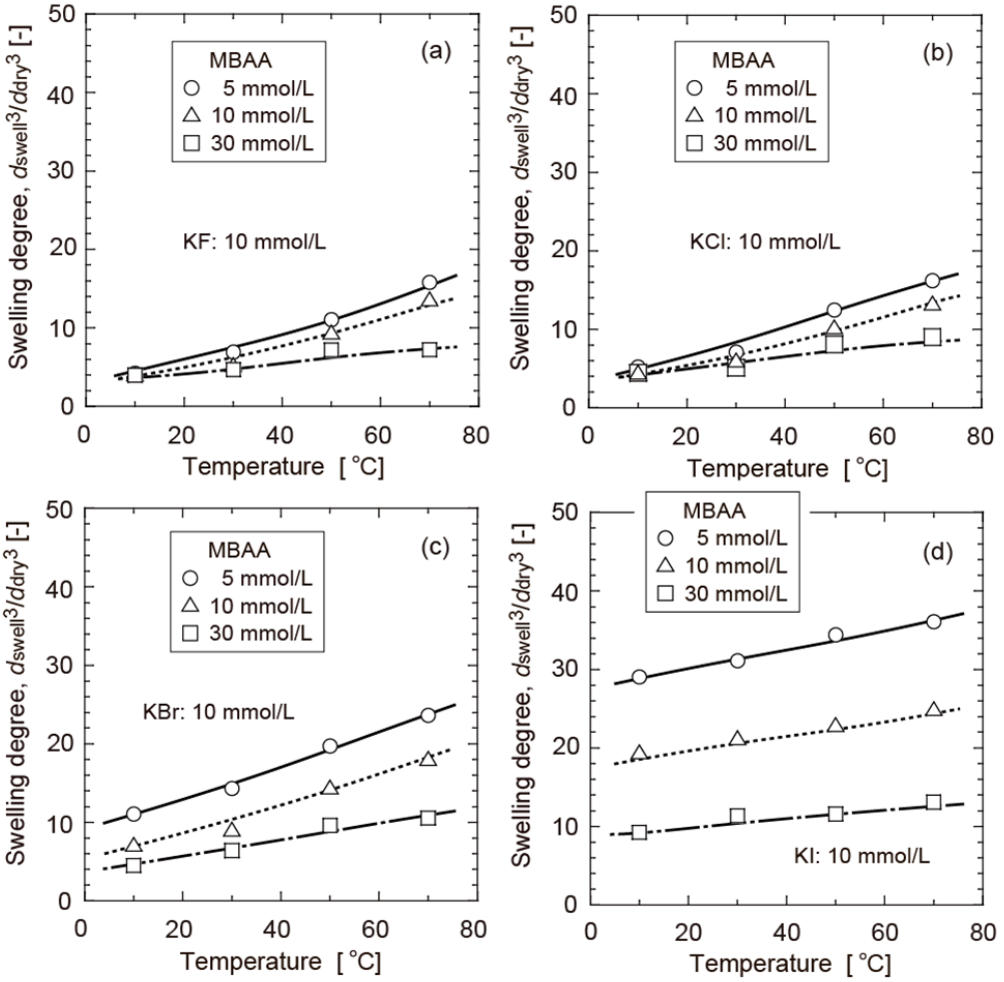

Fig. 3–2 Swelling degrees of DMAAPS gel measured in 10 mmol/L (a) KF, (b) KCl, (c) KBr, and (d) KI solutions at various temperatures. The gels were prepared at three different cross-linker concentrations.

The swelling degrees of DMAAPS gels prepared at three different MBAA concentrations in the halide solutions and water were compared, as shown in Figs. 3–3(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. 3–3(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 SO$_3^-$and N$^+$ of DMAAPS gel, respectively, as shown by the amount of K$^+$ adsorbed (Fig. 3–2).

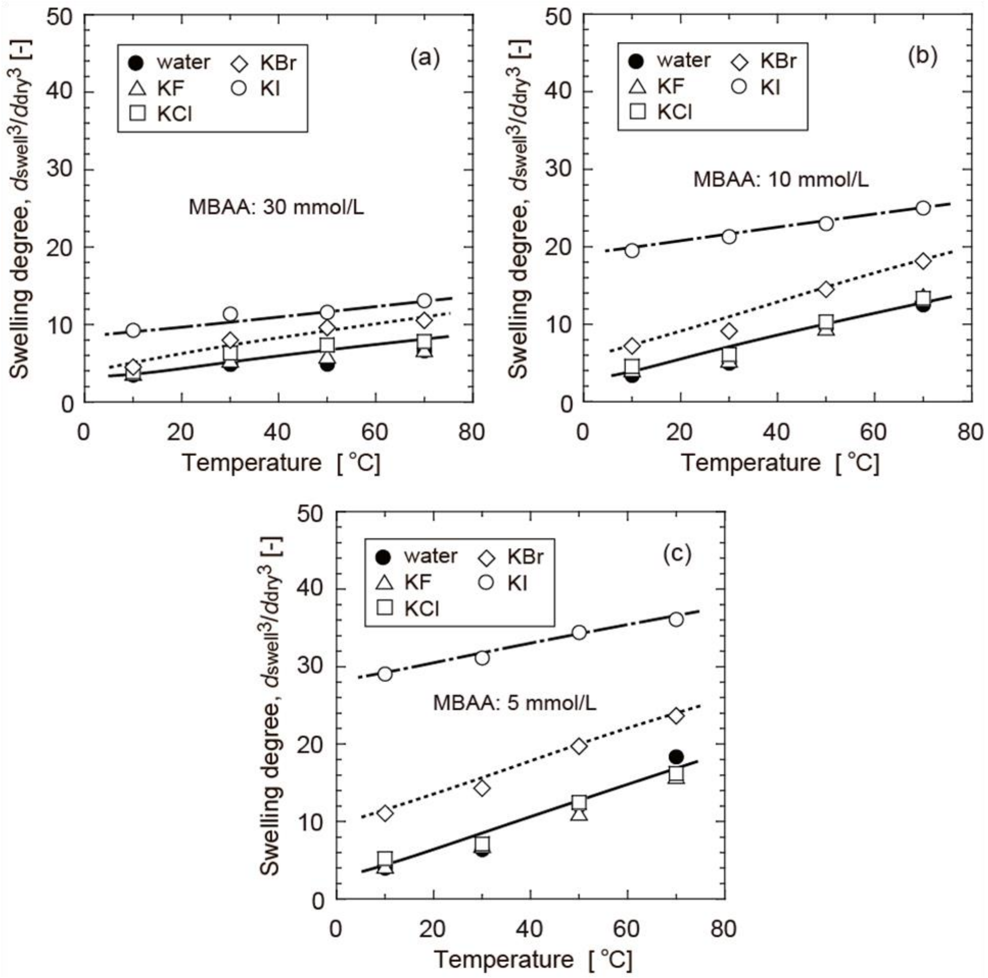

Fig. 3–3 Swelling degrees of DMAAPS gel prepared using (a) 30, (b) 10, and (c) 5 mmol/L of cross-linker measured in water and 10 mmol/L KF, KCl, KBr, and KI solutions at various temperatures.

3.3.1.3. Competitive adsorption of ions onto the 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. 3–4. 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 the previous Chapter 2 [1].

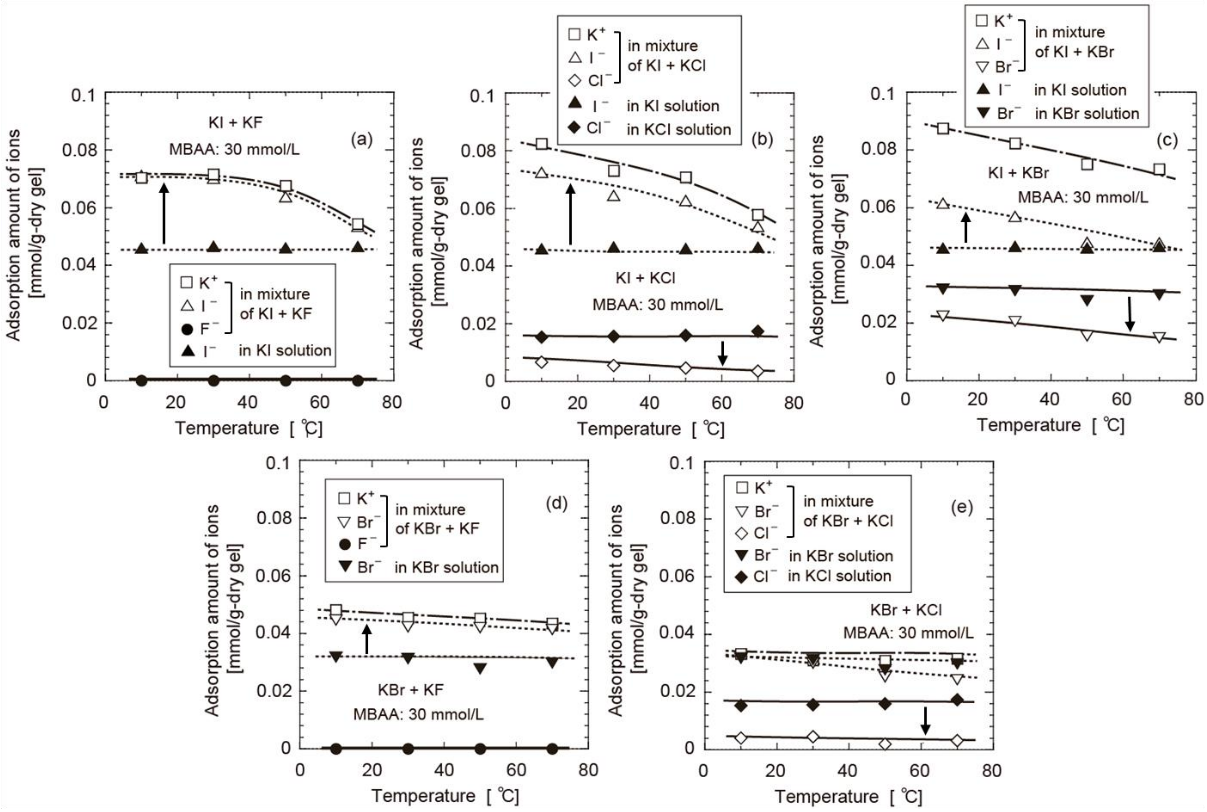

Fig. 3–4 Amounts of ions adsorbed onto DMAAPS gel in (a) KI + KF, (b) KI + KCl, (c) KI + KBr, (d) KBr + KF, and (e) KBr + KCl mixtures at various temperatures. The concentration of each halide solution was 10 mmol/L. The DMAAPS gels were prepared at a 30 mmol/L cross-linker concentration.

In all the mixed-halide solutions, i.e., KI + KF, KI + KCl, KI + KBr, KBr + KF, and KBr + KCl, 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 $I^{-} > Br^{-} > Cl^{-} > F^{-}$, 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. (1). 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 (Figs. 3–4(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 (Figs. 3–4(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. (1) tended to adsorb in larger amounts. To compensate for this increase, the anions on the left side of the Hofmeister series shown in Eq. (1) 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, Figs. 3–4(a)–(c) show the effect of temperature on the amounts of ions adsorbed from mixtures containing KI. As shown in Fig. 3–1, in single-component solution and for gels prepared at a cross-linker concentration of 30 mmol/L, increasing the 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 (Figs. 3–4(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. 3–4(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. 3–4(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. 3–4(a).

3.3.1.4. The swelling degree of the DMAAPS gel by competitive adsorption

The swelling degrees of DMAAPS gel in KI + KF, KI + KCl, KI + KBr, KBr + KF, and KBr + KCl mixtures are shown in Figs. 3–5(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. 3–5(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 decreasing swelling degrees in the mixtures was KI + KBr > KI + KCl > KI + KF > KBr + KCl > KBr + KF, as shown in Fig. 3–5(b).

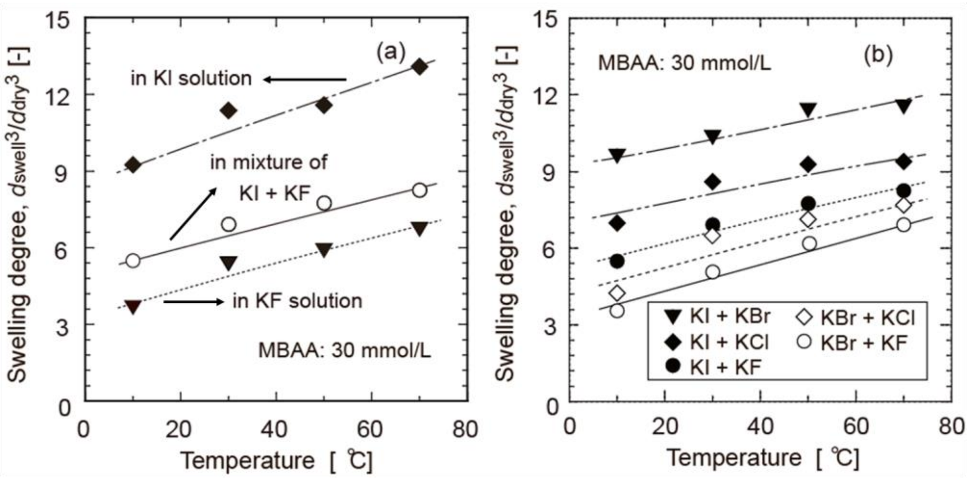

Fig. 3–5 Swelling degrees of DMAAPS gels measured in (a) a KI + KF mixture and (b) KI + KF, KI + KCl, KI + KBr, KBr + KF, and KBr + KCl mixtures at various temperatures. The concentration of each halide solution was 10 mmol/L. The DMAAPS gels were prepared at 30 mmol/L cross-linker concentration.

3.3.1.5. The relationship between the adsorption and swelling behaviors of the DMAAPS gel

To elucidate the adsorption and swelling behaviors, similar to in the previous Chapter 2 [1], 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. 3–6(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 the previous Chapter 2 [1]. At smaller swelling degrees, the amount of K^+ adsorbed remained unchanged and decreased gradually as the swelling degree increased. Although the trends 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 the previous Chapter 2 [1], 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:

$$C_p = \frac{W_0}{V_0} \times \frac{1}{SD} \tag{2}$$

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.

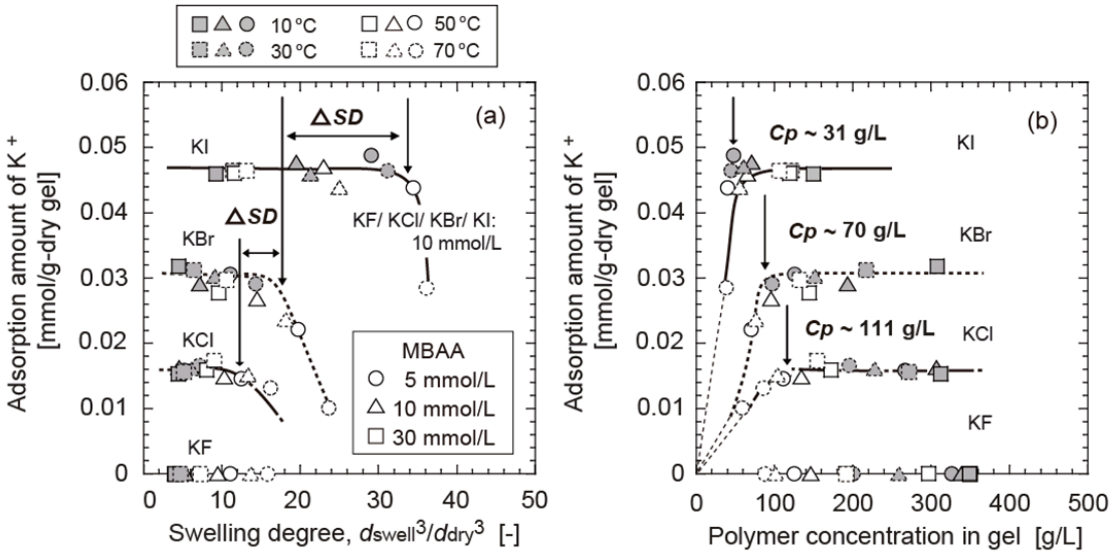

Fig. 3–6 Relationship between the amount of K$^+$ adsorbed onto DMAAPS gel and (a) the swelling degree of the DMAAPS gel and (b) the polymer concentration in the gel. The gels were prepared at three different cross-linker concentrations, and the amounts of K$^+$ adsorbed and swelling degrees were measured in KF, KCl, KBr, and KI solutions at various temperatures.

The relationship between the amount of K$^+$ adsorbed and polymer concentration in the gel is shown in Fig. 3–6(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 the previous Chapter 2 [1]. 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 the previous Chapter 2 [1]: Gels with high polymer concentrations feature gel networks that are dominated by intra-group ionic pairing interactions [2]. 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 [1]. 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 $I^- > Br^- > Cl^- > F^-$, 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 $I^- > Br^- > Cl^- > F^-$, as obtained from the Hofmeister series shown in Eq. (1).

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. 3–7. 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.

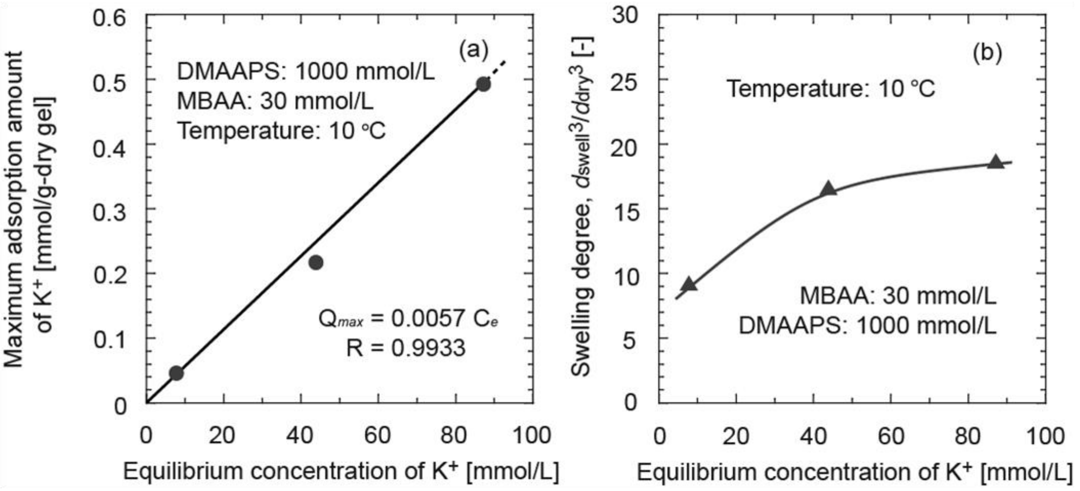

Fig. 3–7 Relationship between KI equilibrium concentrations and (a) maximum adsorption amount of K^+ onto DMAAPS gel for K^+ and (b) degree of swelling of the DMAAPS gel in diluted concentrations of KI solutions at 10 °C. The DMAAPS gels were prepared at a 30 mmol/L cross-linker concentration.

Fig. 3–7(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:

$$Q_{max} = 0.0057\, C_e \tag{3}$$

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. 3–7(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 SO_3^- 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 concentrations in our experimental range. In addition, the swelling degree of the DMAAPS gel in concentrated solutions of KI is shown in Fig. 3–7(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 SO_3^- 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.

3.3.2. Adsorption and swelling behaviors of the DMAAPS gel in various solutions

3.3.2.1. The relationship between the adsorption and swelling behaviors of the DMAAPS gel in various solutions containing monovalent cations

In addition to the type of anion, the effect the type of monovalent cation with a common anion of NO_3^- on the correlation between the swelling degree and amount of cation adsorbed has been investigated to understand deeply on the adsorption and swelling behaviors of DMAAPS gel. Fig. 3–8 shows the relationship between the amount of cation adsorbed on the DMAAPS gel and the swelling degree of the DMAAPS gel or the polymer concentration in the gel in KNO_3, $LiNO_3$ solutions. The gels were also prepared at different cross-linker concentrations, and the adsorption amount of Zn^{2+} and swelling degree were measured in various temperatures. The amount of cation adsorbed remained unchanged at low swelling degree and decreased as the swelling degree increased. In contrast, it increased with increasing polymer concentration until it reached a constant maximum amount. This trend was the same as those described in the halide solution above. As it seen that although KNO_3, $LiNO_3$ have the same valence of cation, however the maximum adsorption amount of cations in these solutions were quite different. As explained by Grooth et al. [10] that the order of swelling in various cation depends on the ion concentration, however at concentration below 0.8 M, the order is:

$$Li^{+} < Na^{+} < K^{+} \qquad (4)$$

Since the ion concentration in this research is below 0.8 M, above order can be followed in explaining both adsorption and swelling behavior. This order also follows the Hofmeister series ordering; that the cation having bigger size tends to become water structure breaker. In addition, the maximum adsorption amount of cations in the KNO_3 and $LiNO_3$ solutions was reached at polymer concentration in the gel were 180 and 210 g/L, respectively.

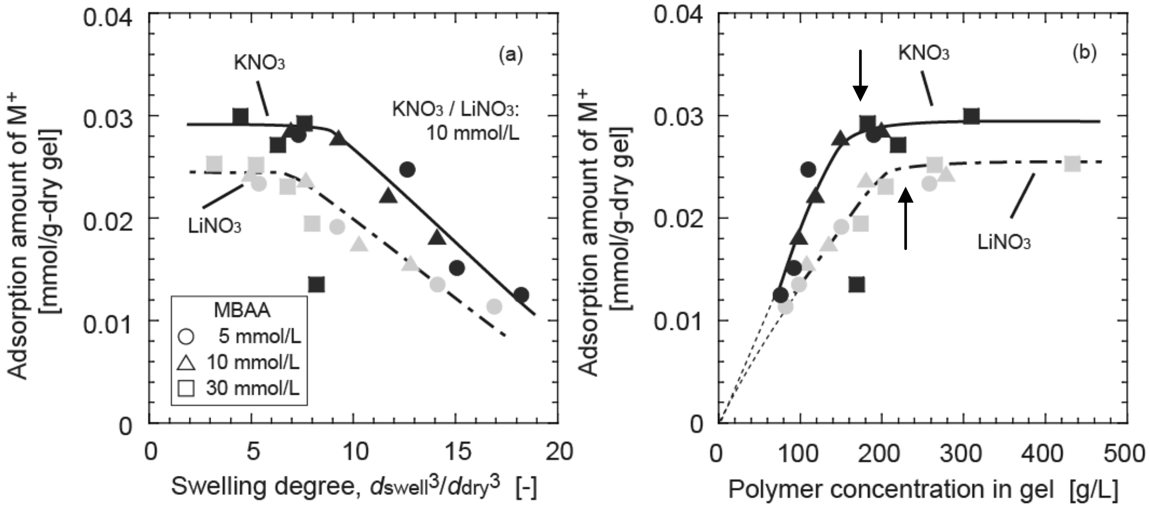

Fig. 3–8 The relationship between the amount of cation adsorbed on the DMAAPS gel and (a) the swelling degree of the DMAAPS gel and (b) the polymer concentration in the gel. The gels were prepared at different cross-linker concentrations, and the adsorption amount of Zn^{2+} and swelling degree were measured in the KNO_3, $LiNO_3$ solutions of various temperatures.

3.3.2.2. The relationship between the adsorption and swelling behaviors of the DMAAPS gel in various solutions containing divalent cations

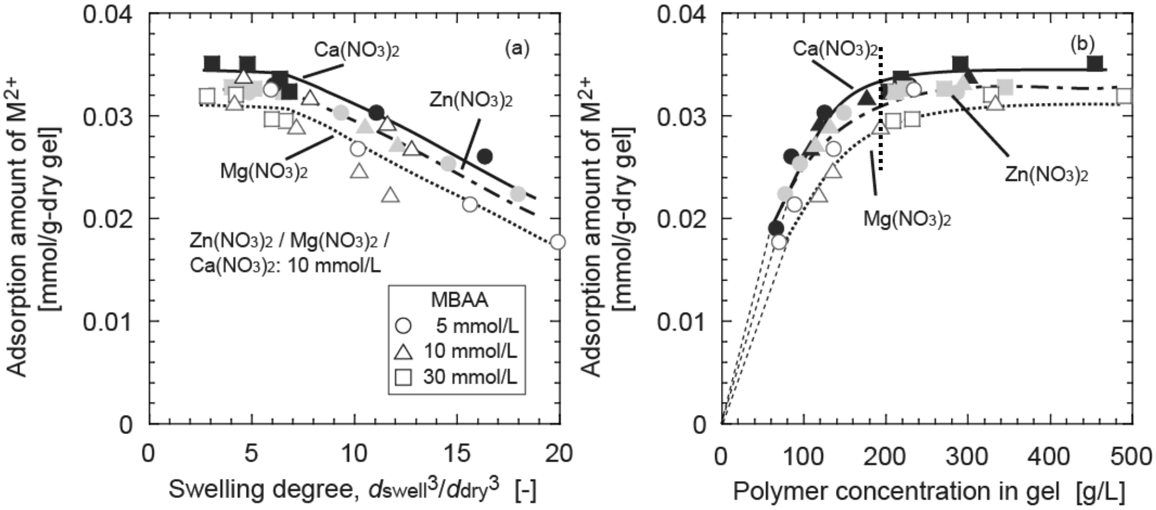

Fig. 3–9 The relationship between the amount of Zn^{2+} adsorbed on the DMAAPS gel and (a) the swelling degree of the DMAAPS gel and (b) the polymer concentration in the gel. The gels were prepared at different cross-linker concentrations, and the adsorption amount of Zn^{2+} and swelling degree were measured in the $Ca(NO_3)_2$, $Zn(NO_3)_2$, and $Mg(NO_3)_2$ solutions of various temperatures.

In this section, the effect of divalent cation species in nitrate solutions on the relationship between the amount of cation adsorbed onto the gel and its swelling degree was examined in the $Ca(NO_3)_2$, $Zn(NO_3)_2$, and $Mg(NO_3)_2$ solutions. As shown in Fig. 3–9 the data points also laid on the same line for the same solution even at different cross-linker concentrations and temperatures. Furthermore, the amount of Zn^{2+} adsorbed increased with increasing polymer concentration until it reached a constant maximum amount.; this result was similar to that was obtained in the halide solutions above. Although it is seen that the adsorption amount of cation from $Ca(NO_3)_2$ solutions was higher compared with other solutions, the effect of cation species especially for divalent in nitrate solution was less pronounced compared with that monovalent cation. This can be observed by the polymer concentration in the gel at which the maximum adsorbed amount of cation was obtained was quite similar in these solution i.e., 180 g/L.

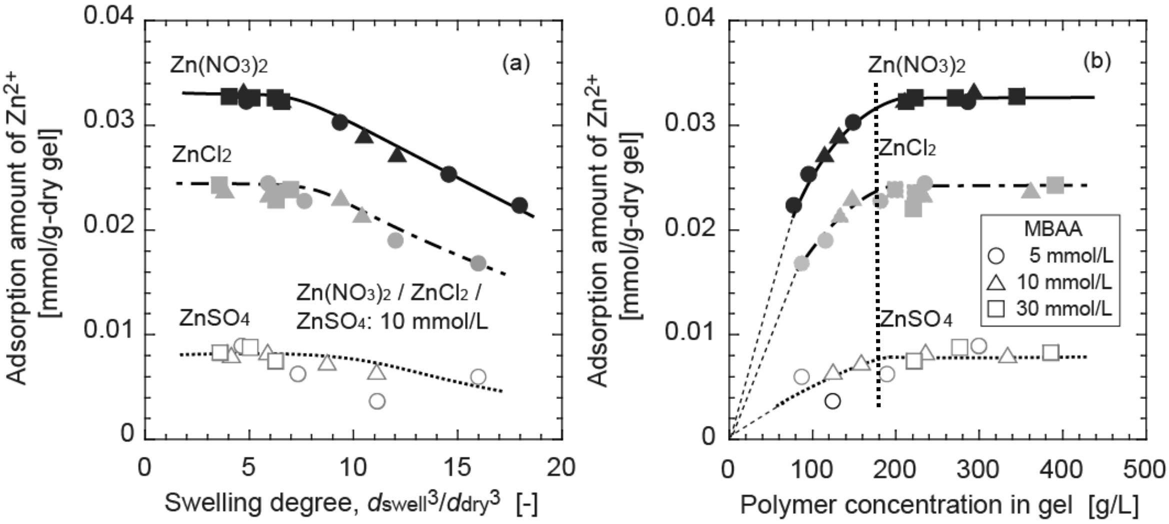

Fig. 3–10 The relationship between the amount of Zn^{2+} adsorbed on the DMAAPS gel and (a) the swelling degree of the DMAAPS gel and (b) the polymer concentration in the gel. The gels were prepared at different cross-linker concentrations, and the adsorption amount of Zn^{2+} and swelling degree were measured in the $Zn(NO_3)_2$, $ZnCl_2$, and $ZnSO_4$ solutions of various temperatures.

Since in nitrate solution the effect of divalent cation species less clear, the cation species was the fixed to be Zn^{2+} and the anion species was varied i.e., NO_3^-, Cl^-, SO_4^- to investigate the adsorption and swelling behavior of DMAAPS gel and its relationship as shown in Fig. 3–10. As seen that the amount of cation adsorbed on the DMAAPS gel was not only dependent on the temperature, cross-linker concentration, and the cation species but also affected by the kind of anion species. The order of anion which gives the higher amount of cation adsorbed was $NO_3^- > Cl^- > SO_4^-$. This behavior is an agreement with the result in various halide solutions as previously explained (See Fig. 3–1) i.e., the order of adsorption tends to follow the Hofmeister series. When the DMAAPS gel was immersed in the solution containing chaotropes anion, they exhibit weaker interactions with water molecules and then facilitates higher amount of anion interact with the ammonium groups of DMAAPS or in other words the adsorption ability of DMAAPS toward anion increased. The amount of cation adsorbed on DMAAPS gel also shows the ion selectivity of the tested cations toward the N^+ groups of DMAAPS.

From above phenomena, we can conclude that in the solution containing monovalent or divalent cation, the maximum adsorption amount of cation onto the DMAAPS gel was influenced especially by the anion species that always follow the Hofmeister series. However, the polymer concentration in the gel at which the adsorption of ion remained constant, was found to be similar in the solution containing divalent cation despite variation of the anion species. In contrast, the influence of anion species in the solution containing monovalent cation is more significant to the polymer concentration in the gel at which the adsorption of ion remained constant. This can be considered due to the divalent cation tend to be more breaker than monovalent and are known to have increased interaction with organic ions [11].

3.4. Summary

The effect of the anion and cation species in the solutions, i.e., KF, KCl, KBr, KI, KNO_3, $LiNO_3$, $Zn(NO_3)_2$, $Mg(NO_3)_2$, $Ca(NO_3)_2$, $ZnCl_2$, and $ZnSO_4$ on the amount of cation or anions adsorbed onto DMAAPS gel was investigated. In the halide solutions, 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 the previous Chapter 2. 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. In addition, it was found that in the mixture of these halide solutions, the competitive adsorption of anions occurred. In the mixture, the adsorbed amount of the anion on the more right side of the Hofmeister series became larger than that in the single-components solutions, while those on the more left side of the Hofmeister series became smaller than in the single-components solutions.

Additionally, the relationship between the amount of cation adsorbed and swelling degree of DMAAPS in KNO_3, $LiNO_3$, $Zn(NO_3)_2$, $Mg(NO_3)_2$, $Ca(NO_3)_2$, $ZnCl_2$, and ZnSO4 solutions was also observed to comprehend the behaviour of DMAAPS in various ions species. It was found that the influence of anion is usually more significant as compared to that of cation on the maximum adsorption amount and the polymer concentration in the gel at which the adsorption of ion remained constant primarily in the solution containing divalent cation.

3.5. References

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Chapter 4

Phase transition of poly(DMAAPS) and its relationship with cation- and anion-adsorption properties of DMAAPS gel in aqueous salt solutions

4.1. Introduction

Considering the sensitive nature of polysulfobetaine on the ions as observed in previous Chapters by the swelling and adsorption behaviors of DMAAPS gel toward ions from salt solutions, in this Chapter we made a detailed study of transition behavior of poly(DMAAPS). It has reported by previous researcher that poly(DMAAPS) is insoluble in water at lower temperature and is soluble at high temperature; in other word the poly(DMAAPS) has an upper critical solution temperature (UCST). Furthermore, the zwiterionic polymer is considered to be a collapse-coil state in water below the UCST due to the intra-chain and /or inter-chain interaction; however, above the UCST the polymer adopts an extended conformation because the thermal motion of the polymer molecule overcome the intra-chain and/or inter-chain interaction. In addition, the inter-chain and/or intra-chain interaction are disrupted by the addition of salts, and the resulting expansion of the polymer chain leads to a decrease in UCST [1,2]. In other words, the solubility of the polymer is enhanced by the addition of salts.

The main purpose of this Chapter is to confirm the phase transition change of polysulfobetaine, i.e., poly(DMAAPS) in aqueous salt solutions, i.e., $NaNO_3$, $Zn(NO_3)_2$, $Al(NO_3)_3$, KF, KCl, KBr, KI, $ZnCl_2$, $ZnSO_4$, $Mg(NO_3)_2$, and $Ca(NO_3)_2$. The effect of salt solution concentration, cation and anion species on the phase transition behavior of these polysulfobetaine was investigated. Furthermore, the relationship between the phase transition behavior of poly(DMAAPS) in aqueous salt solutions and the amount of ions adsorbed onto this gel as shown previously in Chapters 2 and 3was also elucidated.

4.2. Experiment Section

4.2.1. Preparation of the poly(DMAAPS)

The DMAAPS polymer was prepared by free radical polymerization, and was used to evaluate the transition behavior in response to the temperature change. The preparation procedures were the same as those described in our paper [3]. *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 an initiator, respectively. In the preparation of the poly(DMAAPS), the concentrations of TEMED and APS were fixed. The synthesis conditions of the poly(DMAAPS) are listed in Table 4–1.

Initially the DMAAPS and TEMED were dissolved in deionized water and the solution volume was made up to 100 mL with deionized water. This monomer solution was charged into a separable flask. The solution was purged with nitrogen gas in order to remove dissolved oxygen and then 20 mL of APS solution, from which the dissolved oxygen had also been removed by purging with nitrogen gas, was added. Under a nitrogen atmosphere, polymerization was carried out for 6 h at 50 °C. Finally, the resulting polymer was purified over a period of one week by dialysis using a membrane with a molecular weight cut off of 12000−14000 (Cellu Step T3, Membrane Filtration Product, Inc.).

Table 4–1 Synthesis composition of DMAAPS polymer.

		concentration [mmol/L]
Monomer	: *N,N*-dimethyl(acrylamidopropyl)ammonium propane sulfonate (DMAAPS)	500
Accelerator	: *N,N,N',N'*-tetramethylethylenediamine (TEMED)	2
Initiator	: Ammonium peroxodisulfate (APS)	2

4.2.2. Measurement of the phase transition of the poly(DMAAPS)

The phase transition of poly(DMAAPS) in response to the temperature change was also measured using a reported procedure [3] to elucidate the effects of contact time, $Zn(NO_3)_2$ solution concentration, polymer concentration, and molecular weight of the polymer on the transition temperature of poly(DMAAPS). The transition temperature was evaluated from the temperature dependence of the transmittance at 600 nm through the polymer solution using a spectrophotometer equipped with a temperature control system (V-630, Japan Spectroscopy Co., Ltd.). The transition temperature was defined as the value at 50% of the transmittance.

4.3. Results and Discussion

4.3.1. The phase transition of the poly(DMAAPS) in $Zn(NO_3)_2$ solution of various concentrations

The transition temperature of poly(DMAAPS) was also measured to verify the effect of the concentration of $Zn(NO_3)_2$ on the amount of Zn^{2+} adsorbed as shown in Figs. 2−11(a) and (b). Fig. 4−1 shows the temperature dependence of the transmittance through the 100 g/L poly(DMAAPS) solution with C_m of 500 mmol/L in $Zn(NO_3)_2$ solutions of various concentrations. Increasing the $Zn(NO_3)_2$ concentration resulted in a gradual decrease of the transition temperature of poly(DMAAPS) from 47 to 38 °C. This phenomenon is attributed to dissociation of the N^+ and SO_3^- pairings resulting from the new ionic interactions of the ions in the $Zn(NO_3)_2$ solution, i.e., Zn^{2+} and NO_3^-, with the charged groups of poly(DMAAPS), i.e., SO_3^- and N^+ [4]. Increasing the solution concentration enhances the dissociation of the chain pairings because the amount of ions (Zn^{2+} and NO_3^-) adsorbed on poly(DMAAPS) also increases. At higher dissociation of the chain pairings of poly(DMAAPS), the transition temperature shifted to lower value. This result is congruent with the dependence of the adsorption amount on the solution concentration observed in Figs. 2−11(a) and (b).

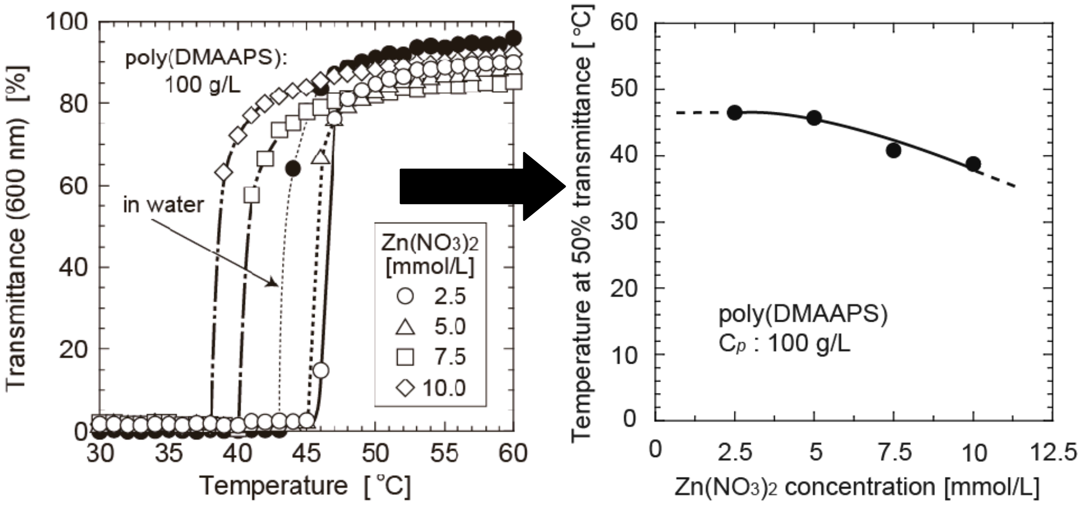

Fig. 4−1 Transition behavior of poly(DMAAPS) (100 g/L) in $Zn(NO_3)_2$ solutions of various concentrations.

4.3.2. The phase transition of the poly(DMAAPS) in halide solutions containing different anion species

The transition behaviors of poly(DMAAPS) in halide solutions with various concentrations are shown in Figs. 4−2(a)–(d). C_p and C_m of poly(DMAAPS) were 20 g/L and 500 mmol/L, respectively. 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. 4−2(d)); this increase might have been due to partial dissociation of N^+ and SO_3^- pairing resulting from the new ionic interactions with I^- and K^+, respectively. At these low KI concentrations, the amounts of ions (K^+ and I^-) available to disrupt the interactions of the N^+ and SO_3^- 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 [5] 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 SO_3^- and N^+, which occurred easier in highly concentrated KI solutions because a significant number of ions (K^+ and I^-) were available for disruption [4].

In addition, it is seen in Fig. 4−2 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 Figs. 4−2(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 [3]. 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. 3−1. 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 SO_3^- pairings causing a shift in the transition temperature to a lower value. In contrast, dissociation of N^+ and SO_3^- pairing was limited in solutions containing anions with higher hydration abilities, such as F^-; accordingly, the transition temperature of poly(DMAAPS) was higher in these solutions.

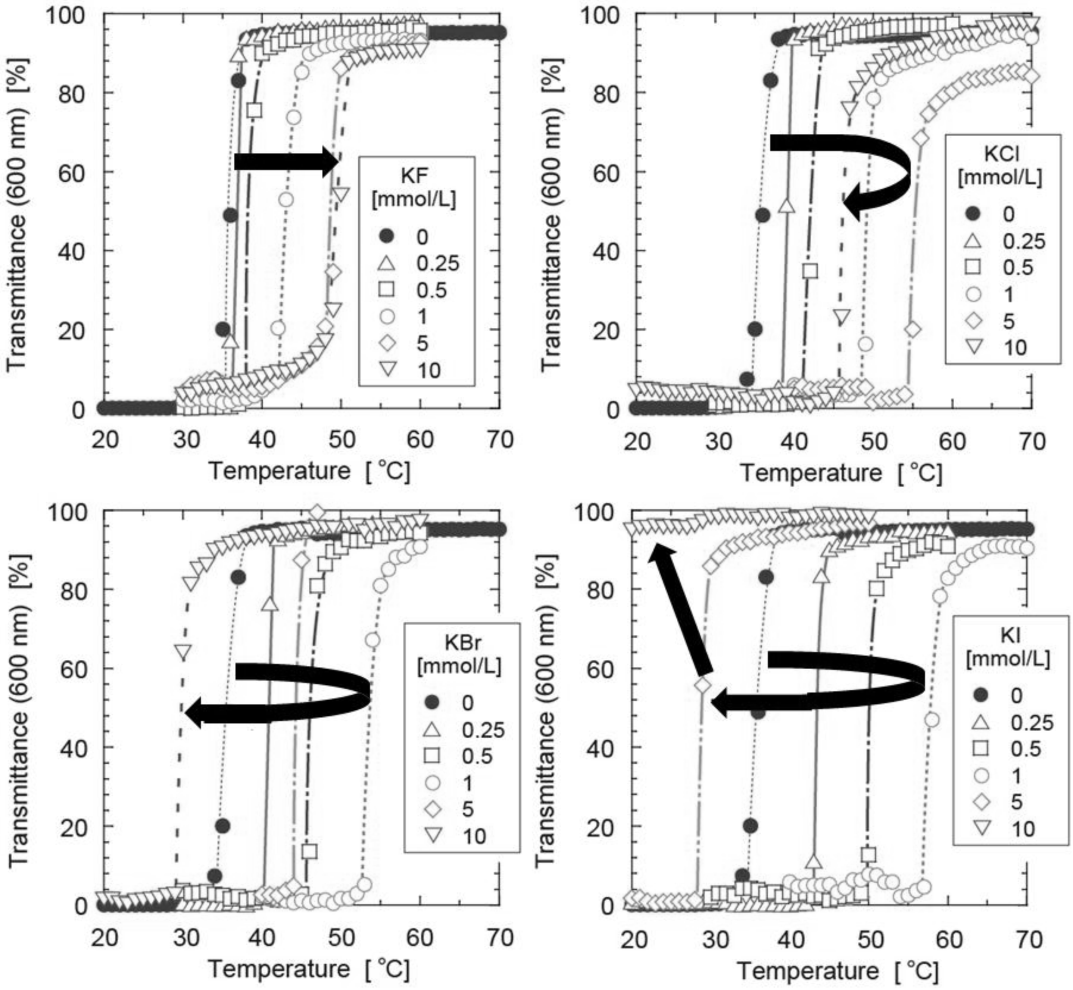

Fig. 4−2 Transition behavior of poly(DMAAPS) (20 g/L) in (a) KF, (b) KCl, (c) KBr, and (d) KI solutions of various concentrations.

4.3.3. The phase transition of the poly(DMAAPS) in various solutions containing different cation and anion species

Fig. 4−3 shows the effect of anion species in various salt solutions (nitrate, chloride, sulphate) on the transition temperature of poly(DMAAPS) in 10 mmol/L solutions. C_p and C_m of poly(DMAAPS) were 20 g/L and 500 mmol/L, respectively. The transition temperature of poly(DMAAPS) in $Zn(NO_3)_2$ as shown in Fig. 4−3 (a) was less than that in water. However, when poly(DMAAPS) was dissolved in $ZnSO_4$ and $ZnCl_2$ solutions, the transition temperature was found larger than that in water. The order of the transition temperature of the poly(DMAAPS) in these solutions was $NO_3^- < Cl^- < SO_4^-$. This phenomenon can be understood by considering the Hofmesiter series that explained the anions' ability to directly interact with the positively charged groups of DMAAPS, N^+, and their adjacent hydration shells [6–8]. The typical order of the anion series is:

$$CO_3^{2-} > SO_4^{2-} > S_2O_3^{2-} > H_2PO_4^- > F^- > Cl^- > Br^- \approx NO_3^- > I^- > ClO_4^- > SCN^- \qquad (1)$$

Very similar transition behavior was observed when the poly(DMAAPS) was dissolved in various salt solutions (nitrate, chloride, sulphate) with a common cation of Ni^{2+}. These results are slightly different from those in the solutions containing monovalent cation Na^+ and K^+ as shown in Fig. 4−3(c−d). Although, the transition temperature in nitrate solution was the lowest compared with that chloride and sulphate solutions, the transition temperature in chloride solution was higher than that in sulphate solution. These results attributed to the fact that, in the solutions containing monovalent cations, the amount of ions adsorbed onto the gel is smaller compared with that in the solutions containing divalent cations as shown in Chapter 2 (see Fig. 3−10). It was found that the maximum adsorption amount of K^+ in the K_2SO_4 and KCl were almost zero and 0.016 mmol/g-dry gel, respectively. This means that the entanglement due to partial dissociation by the addition of low concentration of solutions is very small and can be neglected. Since the amount of K^+ adsorbed onto the gel in KCl solution was quite high, the partial dissociation might induced chain mobility, which led to the enhancement of the inter-chain interactions [5] and the aggregation of the polymer that inevitably increased the transition temperature. This reason can also be used for explaining the phenomenon of the transition behavior in solutions with a common cation of Na^+ as shown in Fig. 4−3(c).

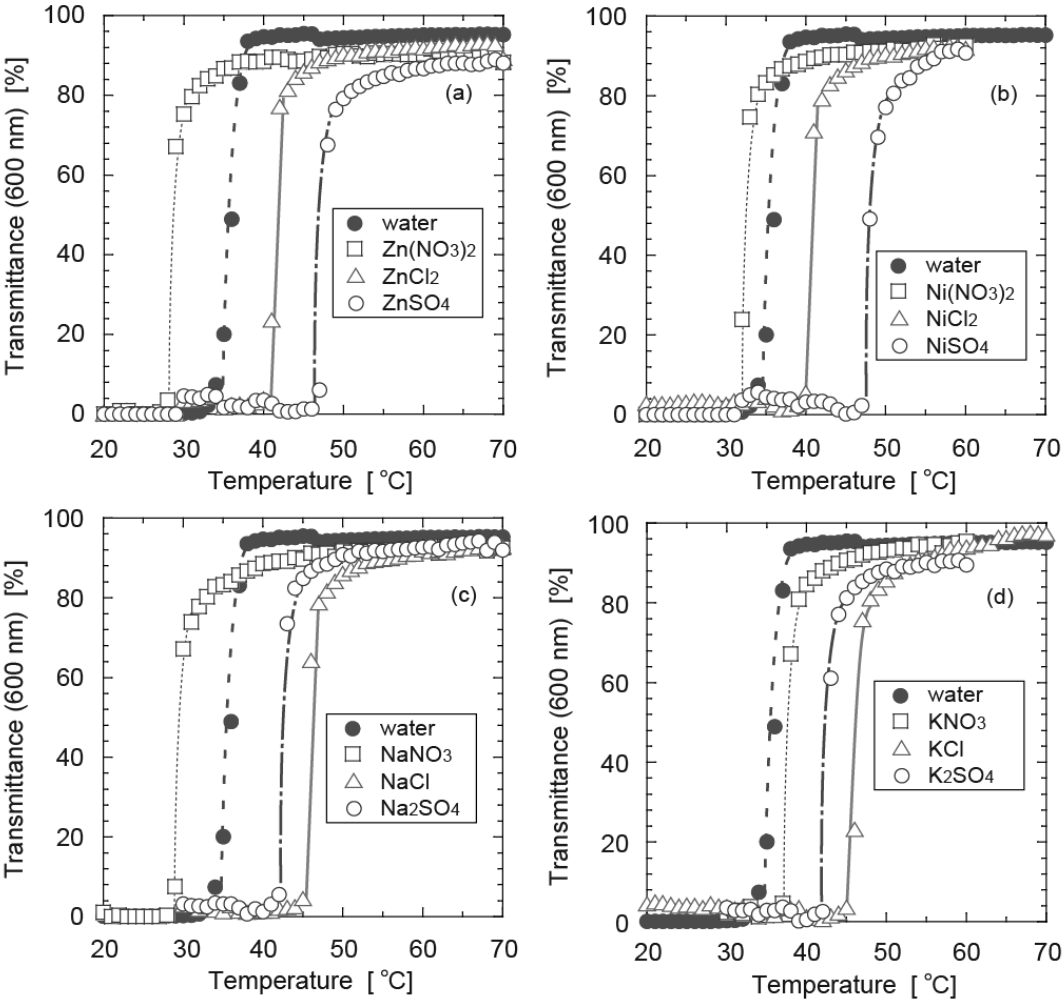

Fig. 4−3 Transition behavior of poly(DMAAPS) in 10 mmol/L nitrate, sulphate and chloride solutions with a common cation of (a) Zn^{2+} (b) Ni^{+} (c) Na^{+} (d) K^{+}.

The effect of cation species in various salt solutions (nitrate, chloride, sulphate) on the transition behavior of poly(DMAAPS) is shown in Fig. 4−4. C_p and C_m of poly(DMAAPS) were 20 g/L and 500 mmol/L, respectively. The solutions concentration was 10 mmol/L. It is well known that a decrease in the transition temperature of poly DMAAPS is related to the dissociation of N^{+} and SO_3^{-} pairings resulting from the new ionic interactions between the ions in the salt solution and the charged groups of poly(DMAAPS), i.e., SO_3^{-} and N^{+} as seen in Fig. 4−4(a). In nitrate solution containing divalent cations, i.e., Zn^{2+} and Ni^{2+} ions, the transition temperatures of poly(DMAAPS) were observed at around 28 °C and 32 °C, respectively. In the case of monovalent cations, the transition temperatures were 29 °C, and

37 °C for Na^+ and K^+, respectively.

In comparison of four kinds of solutions, the transition temperature of poly(DMAAPS) in $Zn(NO_3)_2$, $Ni(NO_3)_2$, and $NaNO_3$ solutions were shift to a lower temperature compared with that in water. In contrast, the transition temperature of poly(DMAAPS) in KNO_3 solution was higher than that in water. The effect of divalent cation, i.e., Ni^{2+} ion to the transition temperature was less than monovelant cation, i.e., Na^+. This behavior can be explained by the fact that the dissociation of DMAAPS pairing was not only dependent on the amount of cation adsorbed but also by the valence of the cation and anion species. The divalent interacted more strongly with the DMAAPS gel network than the monovalent cation, which was indicated by the amount of cation adsorbed as explained previously in Chapter 2 in Fig. 2−4. Furthermore, in the solutions containing divalent cations, cation bridges are formed between the negatively charged, i.e., SO_3^- groups in the DMAAPS chains, by intra- and/or inter-bridging. But since this cation bridging leads to the formation of new cross-linking points between DMAAPS chains, and the dissociation is hindered by this interaction. Therefore, the ionic pairings of betaine are more effectively to be dissociated by Na^+ or K^+ than that by Zn^{2+} or Ni^{2+}. However, in the case of Zn^{2+}, since the amount of cation adsorbed by the DMAAPS gel was higher, the dissociation was also improved.

The transition behavior of poly(DMAAPS) in chloride and sulphate solutions containing different cation species is shown in Fig. 4−4(b) and (c), respectively. The effect of cation species in chloride solution was lower than in nitrate solution. These phenomena are attributed to the fact that the interaction between charge groups of DMAAPS with anion and cations from solution was insufficient to make the DMAAPS chain dissociate, instead of promoted the entanglement of chains and the aggregation of the polymer, as a result the transition temperature increased. This phenomenon was similar to that reported by Lee et al. [9], when the NaCl concentration is high enough, the salt makes the polymeric chain bend and diminishes the intrinsic viscosity.

In addition, the transition temperature of poly(DMAAPS) in sulphate solution containing divalent cation was higher than the transition temperature in water. The transition temperature increased because of the partial dissociation of ionic pairings of DMAAPS. The partial dissociation might occur due to the amount of cation adsorbed was low and the characteristic of SO_4^{2-}. SO_4^{2-} is referred as kosmotropes anion that can increase the aggregation of the polymeric chain. The entanglement of DMAAPS chain was suppressed when poly(DMAAPS) was diluted in sulphate solution containing monovalent cation.

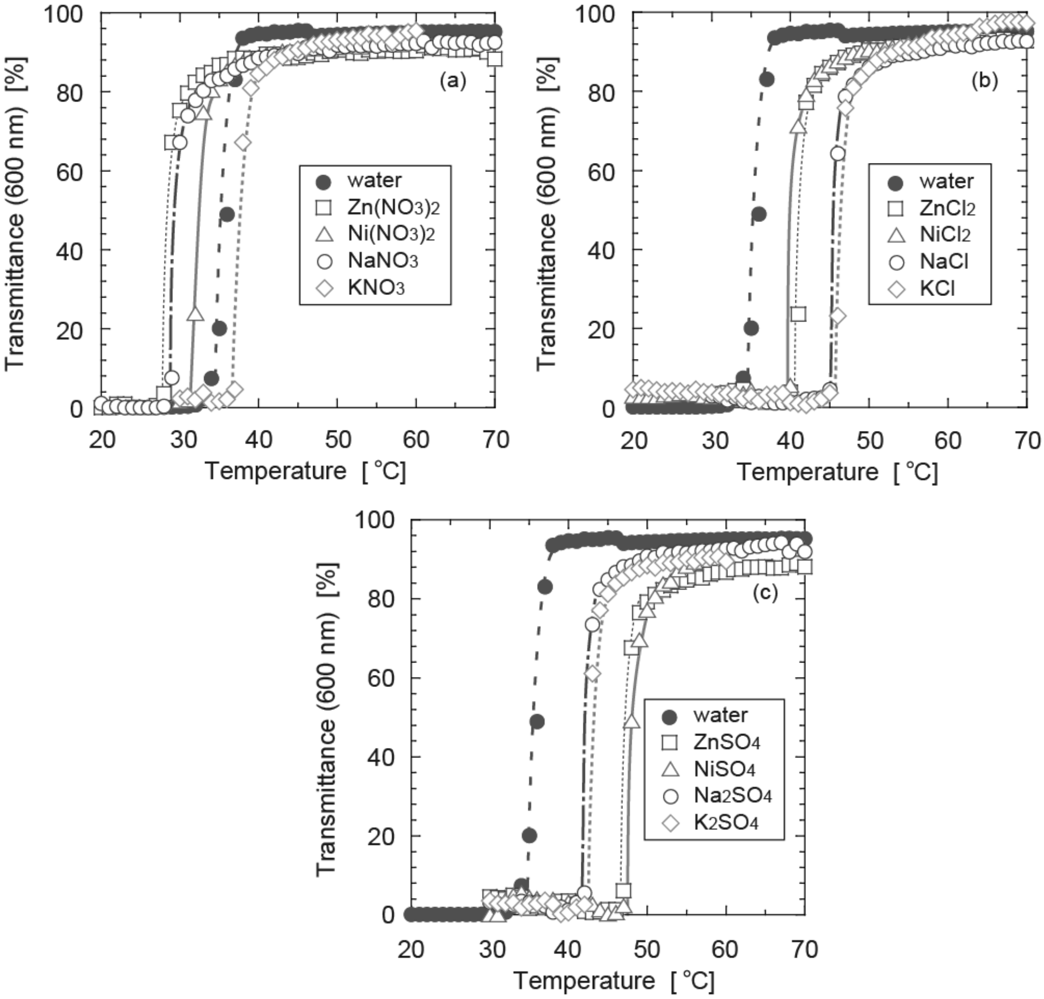

Fig. 4−4 Transition behavior of poly(DMAAPS) in 10 mmol/L (a) nitrate (b) chloride and (c) sulphate solutions containing different cation species.

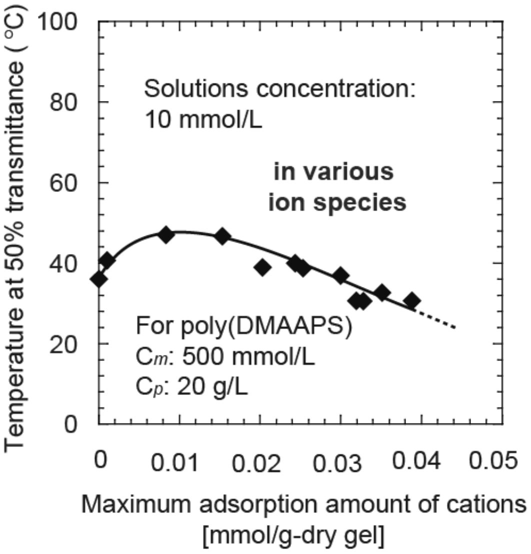

Fig. 4−5 Relationship between the transition behavior of poly(DMAAPS) and the maximum adsorption amount of cations in various solutions with concentration of 10 mmol/L.

From Fig. 4−(1−4), we have elucidated the transition behavior of poly(DMAAPS) in various salt solutions. An interesting phenomenon was found especially for poly(DMAAPS); the transition temperature can be observed over a wide range of monomer concentration in the solutions. Furthermore, interaction of charged groups with ions from salt solutions may lead to the dissociation or entanglement of polymeric chains of DMAAPS. On the other hand, it was difficult to identify when the polymeric chains of DMAAPS will dissociate or entangle. Based on this consideration, the relationship between the transition behavior of poly(DMAAPS) and the maximum adsorption amount of cations onto the gel in various solutions such as water, $Zn(NO_3)_2$, ZnCl, ZnSO4, KNO_3, KCl, K_2SO_4, $Ca(NO_3)_2$, $Mg(NO_3)_2$, $LiNO_3$, $Al(NO_3)_3$, and $NaNO_3$ was investigated as shown in Fig. 4−5. The solutions concentration was fixed at 10 mmol/L. The transition temperature of poly(DMAAPS) initially increased and then decreased as the maximum amount of ion adsorbed onto the DMAAPS gel increased, which depend on the ion species and ion concentration. An increase in the transition temperature of poly(DMAAPS) at lower amount of cation adsorbed (0–0.015 mmol/g-gel) means that the entanglement of the polymer chain occurred. Whereas, a decrease in the transition temperature at relatively higher amount of cation adsorbed (0.015–0.039 mmol/g-gel) is attributed to the dissociation of the polymer chain. This result suggests that the maximum amount of ion adsorbed can be simply estimated by measuring the transition temperature of poly(DMAAPS), which can be obtained easily by measuring the temperature dependence of transmittance through the salt solution containing poly(DMAAPS).

4.4. Summary

The transition temperature of the poly(DMAAPS) was examined in various salt solution containing different anion and cation species. The transition temperature of poly(DMAAPS) was strongly influenced by the salt solution concentration and anion and cation species in the solutions. Interaction of charged groups with ions from salt solutions may lead to the dissociation or entanglement of polymeric chains of DMAAPS. When the poly(DMAAPS) was immersed in the solutions containing anion or cation species at the left of the Hofmeister series, the transition temperature of poly(DMAAPS) shifted to a higher value due to the entanglement of polymer chain as a result from the partial dissociation of the charge groups by the ions from solutions. In contrast, the transition temperature of poly(DMAAPS) shifted to a lower value when the poly(DMAAPS) was immersed in the solutions containing anion or cation species at the right of the Hofmeister series due to the dissociation of the chain pairings of poly(DMAAPS) increased significantly as a result from higher amount of ions adsorbed by the poly(DMAAPS). Additionally, the relationship between the transition temperature of poly(DMAAPS) and the maximum amount of ion adsorbed by the DMAAPS gel in various solutions was elucidated. The transition temperature of poly(DMAAPS) initially increased and then decreased as the maximum amount of ion adsorbed onto the DMAAPS gel increased, which depend on the ion species and ion concentration. This result suggests that the maximum amount of ion adsorbed can be easily determined by investigating the transition temperature of poly(DMAAPS) even if anion and cation species in the solutions are different.

4.5. References

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Chapter 5

Comparison between DMAAPS and DMAABS polymers and gels on ion-adsorption, swelling, and transition behaviors

5.1. Introduction

Based on the previous researcher findings [1–4], it seemed apparent that the chain length of the charged functional groups of sulfobetaine would affect the polymer hydrophobicity and the interaction between each positive and negative charges i.e., inter-chain, intra-chain, and intra-group association of sulfobetaine that eventually influenced the adsorption properties of zwitterionic polymers toward external ion. However, it was reported by previous researcher only within a very limited range of polymer concentration, molecular weight, and salt concentration. Therefore, in this Chapter the effect of the number of methylene groups spacer of sulfobetaine on the adsorption, swelling, and transition behaviors using the DMAAPS and *N,N*-dimethyl(acrylamidopropyl)ammonium butane sulfonate (DMAABS) polymers and/or gels was investigated in the $NaNO_3$, $Zn(NO_3)_2$ solutions. The effects of the contact time, the heating rate, the salt solution concentration and anion and cation species in the solutions on the transition temperature of poly(DMAAPS) and poly(DMAABS) were elucidated. Furthermore, the relationship between the degree of swelling of DMAAPS gels and the amount of cation or anion adsorbed onto these gels was also observed.

5.2. Experimental Section

5.2.1. Materials

1,4-butane sultone (BS) was used to prepare DMAABS monomer, which was purchased from Tokyo Chemical Industry Co., Ltd. and used as received. Other materials were the same with what is used in preparing DMAAPS as mentioned previously in Chapter 2.

5.2.2. Synthesis of DMAABS

DMAABS was synthesized using the same synthetic method by the ring-opening reaction of *N,N*-dimethylaminopropylacrylamide (DMAPAA; KJ Chemicals Co., Ltd., Japan) and 1,4-butane sultone (BS) [5] as explained previously in Chapter 2. A mixture of BS (79 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 synthesis reaction of DMAABS is shown in Fig. 5–1.

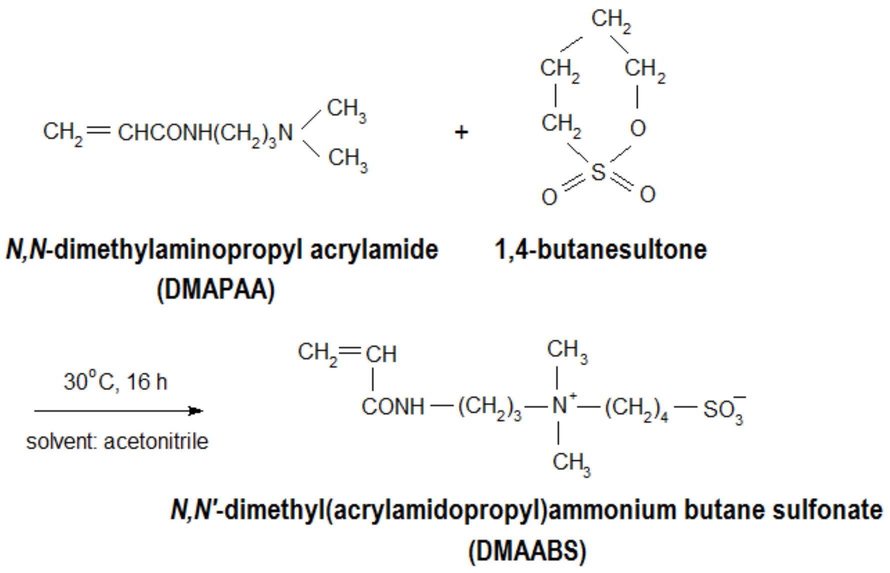

Fig. 5–1 Synthesis reaction and chemical structure of *N,N*-dimethyl(acrylamidopropyl)ammonium butane sulfonate (DMAABS).

5.2.3. Preparation of the DMAABS gel

500 mmol/L of monomer concentration was chosen for study the adsorption and swelling behaviors because the DMAABS monomer was difficult to dissolve at high concentration. Moreover, the DMAAPS gels were also prepared with 500 mmol/L of monomer concentration as a comparison purpose. The DMAAPS and DMAABS gels were prepared by free radical polymerization and the preparation procedures were the same as those described in previous chapter and the synthesis conditions of the gels are listed in Table 5–1.

Table 5–1 Synthesis composition of DMAAPS and DMAABS gel.

		concentration [mmol/L]
Monomer	: *N,N*-dimethyl(acrylamidopropyl)ammonium propane sulfonate (DMAAPS) *N,N*-dimethyl(acrylamidopropyl)ammonium butane sulfonate (DMAABS)	500
Linker	: *N,N'*-methylenebisacrylamide (MBAA)	5, 10, 30
Accelerator	: *N,N,N',N'*-tetramethylethylenediamine (TEMED)	10
Initiator	: Ammonium peroxodisulfate (APS)	0.5

The intrinsic viscosity of the product poly(DMAAPS) was varied by altering the monomer concentration in the preparation of the polymer. The intrinsic viscosity of the poly(DMAAPS) [η] was measured in 0.1 M NaCl solution at 30 °C using a Ubbelohde viscometer (SU-7Z40, SIBATA, Japan) [4]:

$$[\eta] = \lim_{c \to 0} \eta_{sp} / Cp \qquad (1)$$

Here, specific viscosity, η_{sp} was calculated by $\eta_{sp} = \eta_{rel} - 1$, and relative viscosity, η_{rel} was calculated by η_{rel} = time for solution with C_p/ time for solvent, where C_p is the polymer concentration. The intrinsic viscosity [η] of the synthesized poly(DMAAPS) varies from 0.11, 0.12, 0.25 dL/g. The synthesis conditions of the poly(DMAAPS) and poly(DMAABS) are listed in Table 5–2.

Table 5–2 Synthesis composition of DMAAPS and DMAABS polymer.

		concentration [mmol/L]
Monomer	: *N,N*-dimethyl(acrylamidopropyl)ammonium propane sulfonate (DMAAPS)	20, 40, 100
	N,N-dimethyl(acrylamidopropyl)ammonium butane sulfonate (DMAABS)	20, 40, 100
Accelerator	: *N,N,N',N'*-tetramethylethylenediamine (TEMED)	2
Initiator	: Ammonium peroxodisulfate (APS)	2

5. 3. Results and discussion

5.3.1. Time dependence of adsorption onto the DMAABS gel

The effect of contact time on Zn^{2+} adsorption onto DMAABS gel was investigated to study the rate of adsorbed amount of Zn^{2+}. Fig. 5–2 shows the amount of Zn^{2+} adsorbed on the DMAABS gel in $Zn(NO_3)_2$ solution at 50 °C as a function of adsorption time. The concentration of $Zn(NO_3)_2$ was fixed 10 mmol/L. This result showed that the amount of Zn^{2+} adsorbed onto the DMAABS gel increased significantly within the first 1 h and with further prolongation of the adsorption time, the amount of Zn^{2+} adsorbed onto the DMAABS gel did not increase and finally the adsorption ultimately achieved equilibrium. The equilibrium adsorption of Zn^{2+} onto the DMAABS gel was reached very fast (less than 3 h) compared with that onto the DMAAPS gel as seen in Fig. 5–2. As shown in Chapter 2, in the case of DMAAPS gel, the equilibrium adsorption was achieved at about 8 h (See Fig. 2–3). This phenomenon is due to the effective formation of the inter-chain pairing of the charged groups of the DMAABS gel. Since the pairings are strong, the DMAABS gel becomes very dense; or in other words the swelling ability of the gel network is limited. In this condition, the penetration of ion into the network of DMAABS gel is also restricted. Therefore, the equilibrium adsorption of Zn^{2+} onto the DMAABS gel can be reached rapidly.

From above adsorption behaviors, 12 h contact time was used in investigating the amount of ions adsorbed onto the DMAAPS and DMAABS gels in various preparation conditions. This contact time is same as the time used for the DMAAPS gel as obtained in our previous study [6].

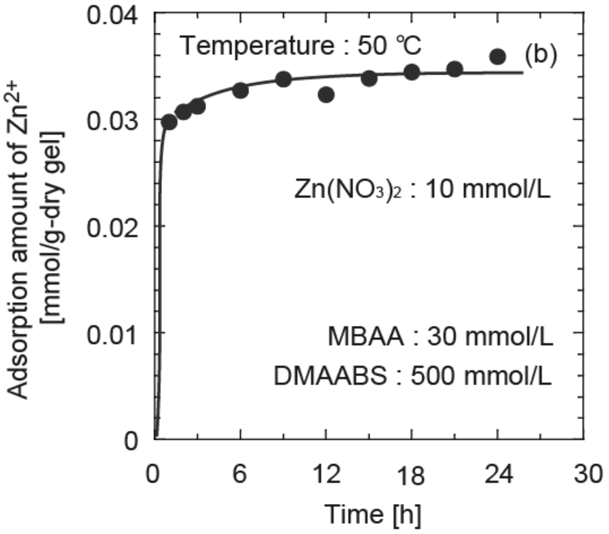

Fig. 5–2 Time dependence of the amount of Zn^{2+} adsorbed onto the DMAABS gel at 50 °C in 10 mmol/L $Zn(NO_3)_2$ solution.

5.3.2. A comparison of the adsorption behaviors of ions onto the DMAAPS and DMAABS gels in $Zn(NO_3)_2$ and $NaNO_3$ solutions

As explained previously that there are at least three possible conformation structures for pairwise interaction of zwitterionic betaine, i.e.,intra-group, or intra-chain, and inter-chain interaction [7,8]. In this section, the adsorption behavior of ions onto DMAAPS gel was compared with that of DMAABS gel in order to clearly explain the effect of chain length of the charged groups to the charged group conformation and their interaction toward ions from salt solution. Adsorption behavior of cation onto the DMAAPS and DMAABS gels was examined by using gels prepared with three different cross-linker concentrations, i.e., 5, 10, and 30 mmol/L as similar as our previous study [6].

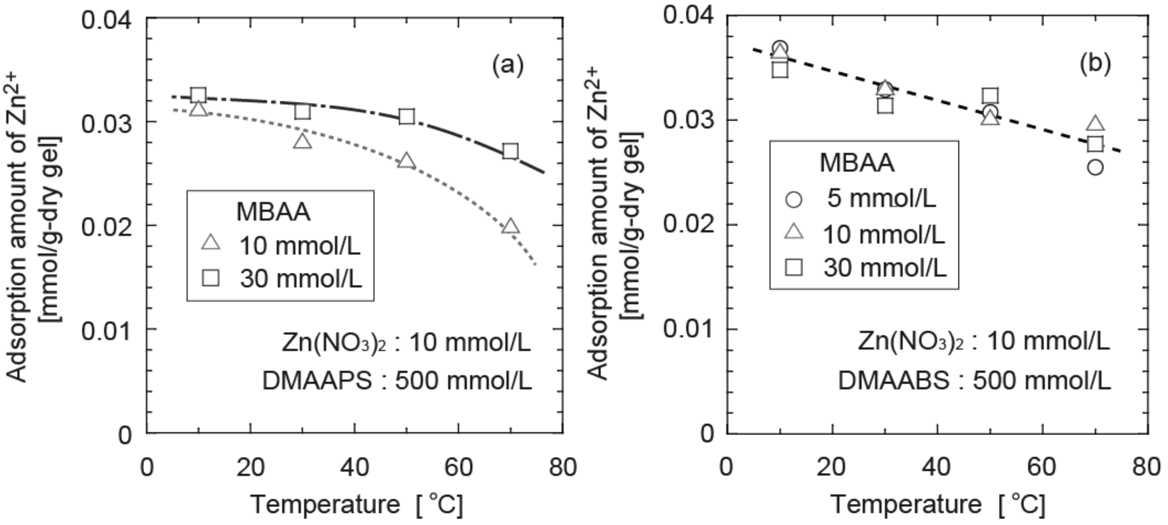

Fig. 5–3 Amount of Zn^{2+} adsorbed onto the (a) DMAAPS and (b) DMAABS gels in 10 mmol/L $Zn(NO_3)_2$ solution at various temperatures. The gels were prepared with three different cross-linker concentrations.

The amounts of ion adsorbed onto DMAAPS and DMAABS gels from $Zn(NO_3)_2$ solution as a function of temperature are shown in Figs. 5–3(a)–(b). From Fig. 5–3(a), it is seen that the amount of Zn^{2+} adsorbed onto the DMAAPS gel prepared with different MBAA concentrations (10 and 30 mmol/L) was almost the same at 10 ºC. This phenomenon showed satisfactory agreement with our previous study [6]. With the use of a higher cross-linker concentration of 30 mmol/L, there was no significant change in the amount of Zn^{2+} adsorbed was almost constant at temperatures in the range of 10−50 °C and only decreased at temperature 70 °C. At a lower cross-linker concentration of 10 mmol/L, the amount of Zn^{2+} adsorbed decreased significantly as the temperature increased from 50 to 70 °C. Then the adsorption behavior of ions onto DMAAPS is compared with that onto DMAABS as shown in Fig. 5–3(b). The amount of Zn^{2+} adsorbed onto DMAABS gel prepared with a higher cross-linker concentration of 30 mmol/L only decreased gradually with increasing temperature.

Furthermore, this similar tendency and value of the amount of Zn^{2+} adsorbed onto DMAABS was also observed in the gels prepared with lower cross-linker concentrations of 10 and 5 mmol/L. As our expectation that with increasing chain length of the charged functional groups may increase the intra-chain separation [3] that results in higher adsorption ability of the charged groups toward ions from salt solution. However, from both figures it can be seen that at lower temperature and higher cross-linker concentration, the amount of Zn^{2+} adsorbed onto the DMAABS gel is only slightly higher than that onto the DMAAPS gel. This phenomenon is attributed to the fact that in the case of polymer, DMAABS molecules become more hydrophobic [4] than that DMAAPS. Weers et al. [3] found that there was no spectroscopic evidence for charged groups wrapping around to form ion-pair, i.e., intra-groups ionic pairing formation in longer chain with increasing the flexibility of the charge groups. Additionally, Jiang et al. [9] reported that the two charged groups of carboxybetaine molecule with a short carbon spacer length (CSL) (carbon < 3) are less charged due to the strong interplay between them, whereas the charged groups exhibits nearly identical and the interplay between them decreases sharply for molecule with a long spacer (carbon ≥ 3). By considering the similarity between sulfobetaine and carboxybetaine, it is estimated that sulfobetaine with 4 methylene groups spacer (DMAABS) are highly charged that promoted the effective formation of inter-chain pairing of the charged groups of sulfobetaine, as a result the intra-chain pairings between the adjacent charged groups are suppressed. Since these inter-chain pairing are quite strong, an increase of the cross-linker concentration had no remarkable influence on the adsorbed amount of ions. In contrast, it depends on the adsorption temperature; as temperature increase, the thermal motions weaken the interaction between ions in the $Zn(NO_3)_2$ solution and the charged groups of poly(DMAAPS), i.e., SO_3^- and N^+ [6,10]

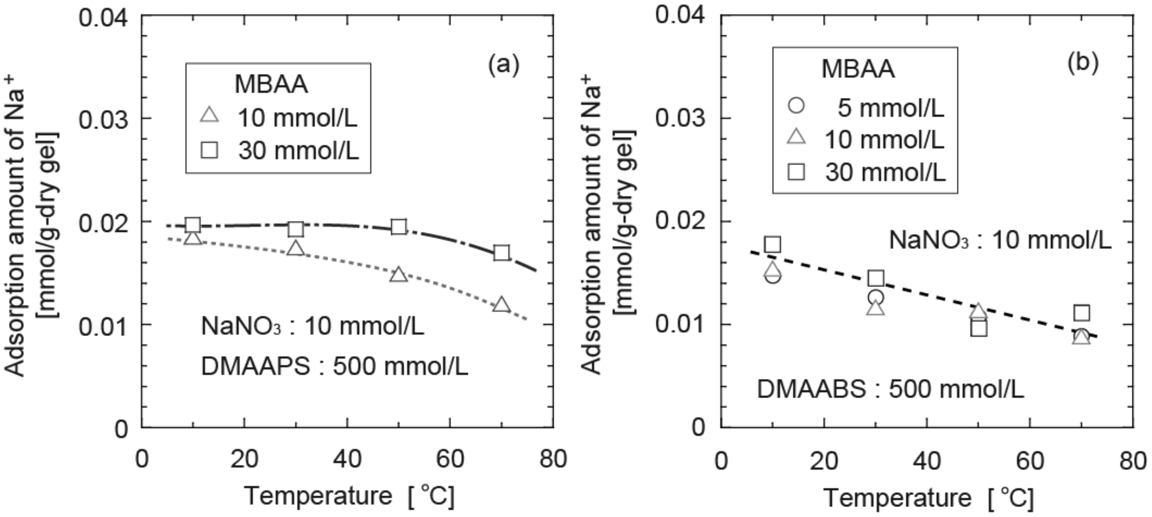

Fig. 5–4 Amount of Na^+ adsorbed onto the (a) DMAAPS and (b) DMAABS gels in 10 mmol/L $NaNO_3$ solution at various temperatures. The gels were prepared with three different cross-linker concentrations.

To assure that the adsorption data of DMAAPS and DMAABS gels above are reliable, the the adsorption experiment was also studied in $NaNO_3$ solution. Figs. 5–4(a)–(b) show the amounts of Na^+ adsorbed onto DMAAPS and DMAABS gels from $NaNO_3$ solution. Interestingly, the adsorption behavior of Na^+ has the similar trend with Zn^{2+}. The amount of Na^+ adsorbed onto DMAAPS gel varied depends on the cross-linker concentration. Furthermore, it decreased with increasing cross-linker concentration. However, the amounts of Na^+ adsorbed onto DMAABS gel remained unchanged with increasing cross-linker concentration as shown in Fig. 5–4(b).

5.3.3. A comparison of the swelling behaviors of DMAAPS and DMAABS gels in $Zn(NO_3)_2$ and $NaNO_3$ solutions

The swelling behaviors of the DMAAPS and DMAABS gels in $Zn(NO_3)_2$ solutions of various temperatures were also examined. Fig. 5–5(a) shows the degree of swelling of the DMAAPS gel measured in 10 mmol/L $Zn(NO_3)_2$. The degree of swelling of the DMAAPS gel prepared using a cross-linker concentration of 30 mmol/L increased gradually as the $Zn(NO_3)_2$ concentration increased, although this increase was not significant. Reducing the cross-linker concentration to 10 mmol/L increased the degree of swelling significantly. However, it was difficult to examine the swelling degree of the DMAAPS gel prepared at 5 mmol/L, since this gel was too fragile to form cylinder-shaped gel. The swelling behavior of DMAABS gel in $Zn(NO_3)_2$ is shown in Fig. 5–5(b). The network of the DMAABS gel did not expand with increasing temperature and cross-linker concentration used in preparation of the gel causing the swelling degree of the DMAABS gel in $Zn(NO_3)_2$ solution remained constant.

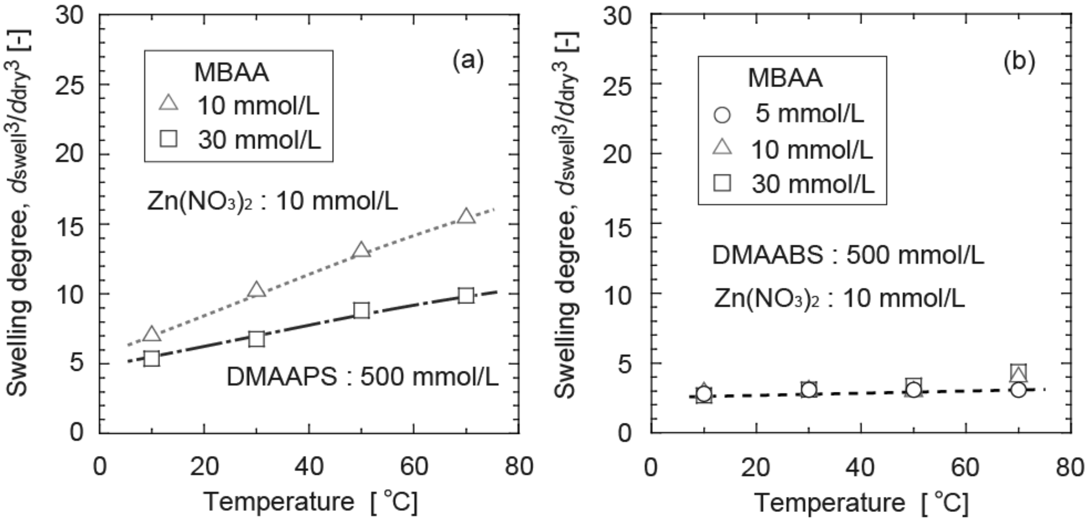

Fig. 5–5 Degree of swelling of the (a) DMAAPS and (b) DMAABS gels in 10 mmol/L $Zn(NO_3)_2$ solution at various temperatures. The gels were prepared using different cross-linker concentrations.

The similar tendency of swelling of the DMAAPS and DMAABS gels was also observed in $NaNO_3$ solution as shown in Fig. 5–6. In the case of the DMAAPS gel, this phenomenon explained that difference between the maximum amount of cation adsorbed by the gel in $NaNO_3$ and $Zn(NO_3)_2$ which was about 0.012 mmol/L, did not change largely on the swelling degree of the gel. Furthermore, the swelling degree of DMAABS in $NaNO_3$ also remained unchanged despite variation of the temperature and cross-linker concentration. Although a detail understanding of the mechanism behind the effect of chain length of the charged functional groups has not obtained yet, except due to increasing of the hydrophobicity. It also might be due to the effective formation of inter-chain pairing which is resulted from their isolated charged [4], leading to the dramatically increase of the chain entanglement of the DMAABS. In this condition, the swelling ability of the DMAABS gel is limited because the pairings are strong. Although the swelling ability of these DMAABS gel is limited, the gel is still available to adsorb the ions from $Zn(NO_3)_2$ and $NaNO_3$, as shown by Fig. 5–3 and Fig. 5–4. This phenomenon is due to the fact that the the possibility of inter-chain pairing to interact with the ions from salt solution is still higher than that of intra-chain pairing. However, since a large number of inter-chain pairings are formed and the DMAABS gel becomes dense, the penetration of the ions into the gel network is hindered as a result the amount of ions adsorbed is suppressed.

The polymer concentration in the gel needs to be considered for the better understanding of the anomalous swelling and adsorption observed in DMAABS gel as shown in Figs. 5–3 to 5–6.

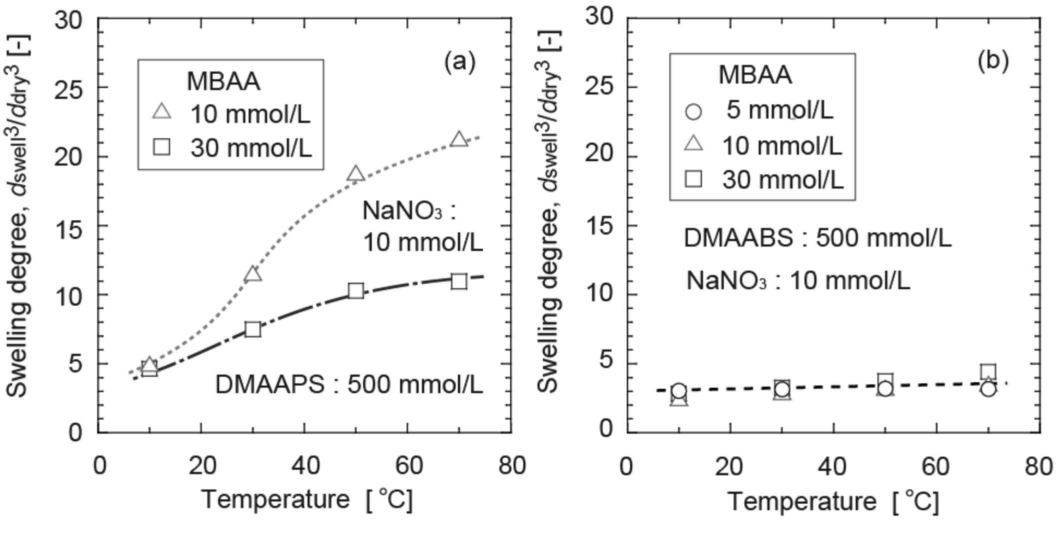

Fig. 5–6 Degree of swelling of the (a) DMAAPS and (b) DMAABS gels in 10 mmol/L $NaNO_3$ solution at various temperatures. The gels were prepared using different cross-linker concentrations.

5.3.4. A comparison of the relationship between the adsorption and swelling behaviors of DMAAPS and DMAABS gels

The relationship between the swelling degree of the gel and amount of Zn^{2+} adsorbed onto the DMAAPS and DMAABS gels prepared at three different cross-linker concentrations, i.e., 10 and 30 mmol/L, at various temperatures, i.e., 10, 30, 50, 70 °C, are summarized in Figs. 5–7(a)–(b). As seen in Fig. 5–7(a), the data points laid on the same line for $Zn(NO_3)_2$ solution even at different cross-linker concentrations and temperatures; these results associated with that of our previous study [6]. In this work, the swelling and adsorption behaviors were investigated in the DMAAPS gel prepared with 500 mmol/L, which was only half monomer concentration than that used in previous study. As explained previously, the relationship between the degree of swelling and the amount of Zn^{2+} adsorbed on the DMAAPS gels exhibits similar correlation despite variation of the monomer concentration used in the preparation of the gel.

Fig. 5–7(b) shows the amount of Zn^{2+} adsorbed onto the DMAABS gel. The amount of Zn^{2+} adsorbed onto the DMAABS gel remained unchanged with increasing the swelling degree. In the case of DMAABS gel, the correlation between the swelling degree and amount of ions adsorbed in this gel is difficult to examine due to the fact that cross-linker concentration and temperature have only little influence on the swelling and adsorption behaviors of the DMAABS gel. The effective formation of the inter-chain pairing of the charged groups of sulfobetaine gel with 4 methylene groups spacer (DMAABS) resulted from their isolated charged caused a consequence; limits the ability of the gel to swell and makes the DMAABS gel dense. This condition hinders the penetration of the ions into the gel network as a result the amount of ions adsorbed is suppressed.

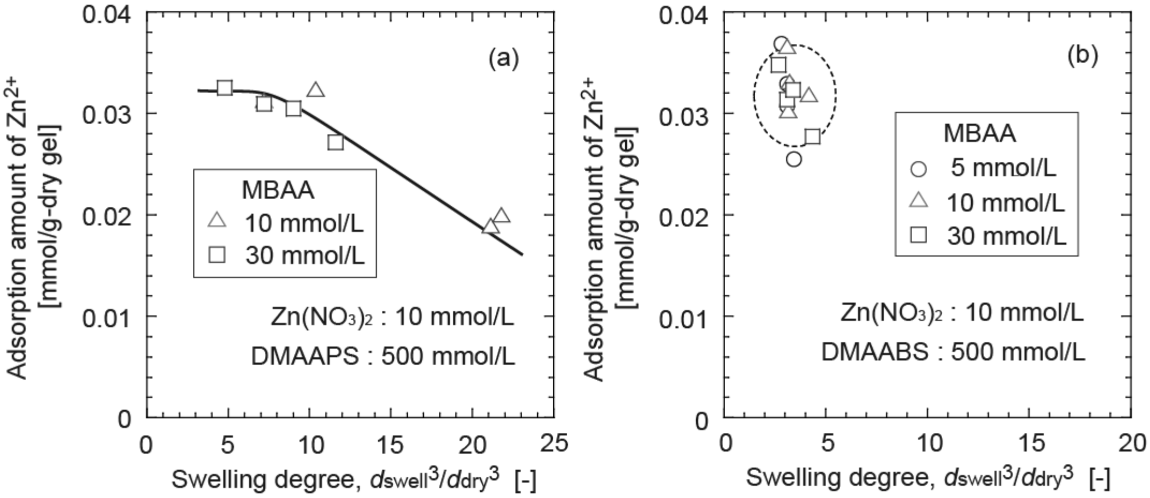

Fig. 5–7 Relationship between the amount of Zn^{2+} adsorbed onto the (a) DMAAPS and (b) DMAABS gels and the degree of swelling of the gels. The gels were prepared using different cross-linker concentrations; the amount of Zn^{2+} adsorbed and the degree of swelling were measured in the $Zn(NO_3)_2$ solutions of 10 mmol/L and at various temperatures (10, 30, 50, and 70 ºC).

Therefore, an increase in the cross-linker concentration or temperature had no remarkable influence on the adsorbed amount of ions or swelling degree of the gel.

By converting the degree of swelling to the polymer concentration in the gel, by the following equation:

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

where C_p is the concentration of the polymer in the gel, W_0 is the weight of the dry sample gels, and V_0 is the volume of the dry sample gels, we found that the polymer concentration of the DMAABS gel were in range 318-516 g/L. At these polymer concentrations in the gel, the DMAABS gel has the same amount of Zn^{2+} adsorbed. In contrast, the tendency of the relationship between the amount of Zn^{2+} adsorbed and the swelling degree of the DMAAPS gel with a monomer concentration of 500 mmol/L in the preparation of the gel was exactly the same to that of 1000 mmol/L, as described previously in Chapter 2 (Fig. 2–13).

Fig. 5–8 show the relationship between the swelling degree of the gel and amount of Na^+

adsorbed onto the DMAAPS and DMAABS gels in $NaNO_3$ solution. Comparing this relationship to that in $Zn(NO_3)_2$ solution, same trend was observed although maximum adsorption capacity of DMAAPS gel in $NaNO_3$ was lower than in $Zn(NO_3)_2$.. These phenomenon can be explained by the strong interaction between the fixed ionic groups of the DMAAPS gel with ions having higher valence [11]. Furthermore, for the DMAABS gel in $NaNO_3$ solution, the amount of Na^+ adsorbed also remained unchanged with increasing the swelling degree or polymer concentration in the gel, similar to that of in $Zn(NO_3)_2$ as shown by Fig. 5–8. This result can be explained due to the dramatic increase of the formation of inter-chain pairing. Since the inter-chain pairing in the gel is strong enough, the swelling ability of the gel is restricted and the gel network is difficult to expand. As a result the swelling degree of the DMAABS gel remained small and was not influenced by the variation of the temperature and cross-linker concentration. The smaller swelling degree means the higher polymer concentration in the gel and the amount of cation adsorbed onto the gel [6] as also explained in Chapter 2.

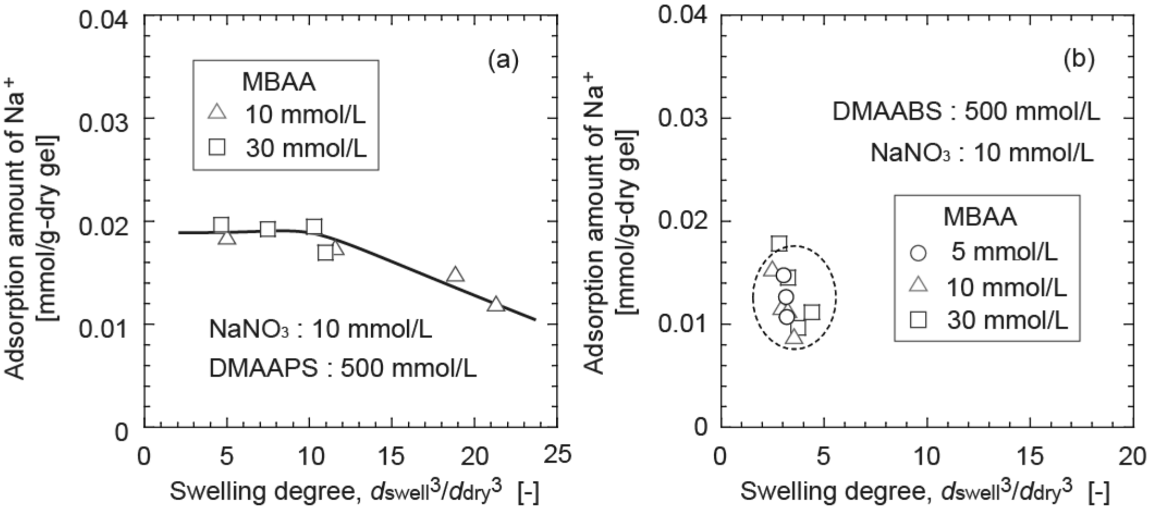

Fig. 5–8 Relationship between the amount of Na^+ adsorbed onto the (a) DMAAPS and (b) DMAABS gels and the degree of swelling of the gels. The gels were prepared using different cross-linker concentrations; the amount of Na^+ adsorbed and the degree of swelling were measured in the $NaNO_3$ solutions of 10 mmol/L and at various temperatures (10, 30, 50, and 70 ºC).

5.3.5. Time dependence of the phase transition of the poly(DMAAPS) and poly(DMAABS) in water and $Zn(NO_3)_2$ solution

As reported in our previous study [3] that the adsorption behavior of such anions and cations from salt solution onto the gels are well explained by the transition temperature of polysulfobetaine. The interaction between the charged groups of the sulfobetaine (SO_3^- and N^+) and the ions (cation and anion) from the salt solutions have a direct impact on the transition temperature of polysulfobetaine. In this section, the transition behaviors of poly(DMAAPS) and poly(DMAABS) in $Zn(NO_3)_2$ solutions under various heating rate, solution concentrations, polymer concentrations, and molecular weight of polymer were examined to understand the effect of the number of methylene groups spacer on the interaction between the charged groups of sulfobetaine and ions from salt solution and its correlation with the adsorption behavior.

Temperature dependence of the transmittance of poly(DMAAPS) and poly(DMAABS) solutions in water and in 1 mmol/L $Zn(NO_3)_2$ were plotted against time at 20 °C is shown in Fig. 5−9. The monomer concentration used in the preparation of the polymers was 20 mmol/L. The polymer concentration of poly(DMAAPS) and poly(DMAABS) in the solution was 1 g/L. Firstly, temperature of polymer solution was controlled at 50 °C in order to reach stable conformation of polymer chains and dissociation of charged groups by ions from salt solutions. After constant transmittance was obtained, the temperature was then changed eventually to 20 °C, and the measurement of the transmittance was started. As seen in Fig. 5−9, initially the transmittance of poly(DMAABS) in water and 1 mmol/L $Zn(NO_3)_2$ was low, and the polymer solution was turbid. The initial turbidity slowly disappeared and the transmittance of poly(DMAABS) in water increased step by step with contact time. This transmittance continued to increase until 5 h of contact time. It was obtained that the transmittance of the poly(DMAABS) in 1 mmol/L $Zn(NO_3)_2$ increased rapidly compared with that in water. In addition, the transmittance reached a constant value after 3 h of contact time.

In contrast, in the case of poly(DMAAPS) in water or in 1 mmol/L Zn(NO_3)$_2$, the polymer solutions were completely transparent even at early contact time. The transmittance of the poly(DMAAPS) reached almost 100% despite increasing the contact time.

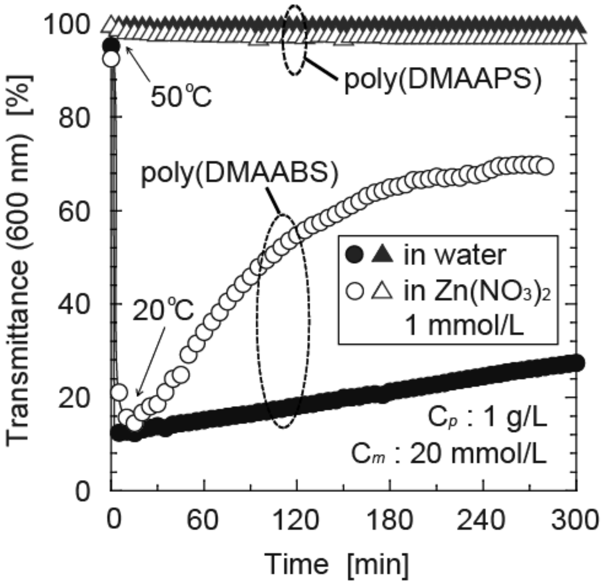

Fig. 5−9 Transition behavior of poly(DMAAPS) and poly (DMAABS) in water and 1 mmol/L Zn(NO_3)$_2$ solutions of various contact time at 20 °C.

5.3.6. The phase transition of the poly(DMAAPS) and poly(DMAABS) in water and Zn(NO_3)$_2$ solution in various heating rates

Effect of heating rate on the transition behavior of poly(DMAABS) in water and 5 mmol/L Zn(NO_3)$_2$ solution is shown in Fig. 5−10. The transition temperature of poly(DMAABS) was observed at 50% transmittance for comparison purpose, since the transition temperature of poly(DMAABS) was broad. Heating rate was varied from 0.1–10 °C/min and the polymer concentration was 1 g/L. From Fig. 5−10(a), we could not observed the transition temperature of poly(DMAAPS) in both water and Zn(NO_3)$_2$ solution, since in all value of heating rate the transition temperatures were out of temperatures in the experimental range of 10–70 °C. In contrast, a slower heating rate of the thermosensitive poly(DMAABS) solution, i.e., 0.1 °C/min produced lower transition temperature. The value of transition temperature was obtained close to each other at slower heating rate from 0.1–1 °C/min at about 39 °C. With increasing heating rate from 1–10 °C/min, the transition temperature was enhanced and increased from 39–43 °C. A faster heating rate induced instability of the polymer conformation at a certain temperature as shown by some discontinuity of temperature dependence of the transmittance. In contrast, at lower heating rate the instability conformation of the poly(DMAABS) did not occur. This phenomenon can be observed clearly in Fig. 5−10(b), that at lower heating rate the difference in the transition temperature can be neglected. This result attribute to the fact that at lower heating rate, longer time is required for each 1°C temperature increment. From this result heating rate of 1 °C/min was chosen to investigate the transition temperature of poly(DMAABS) under various conditions.

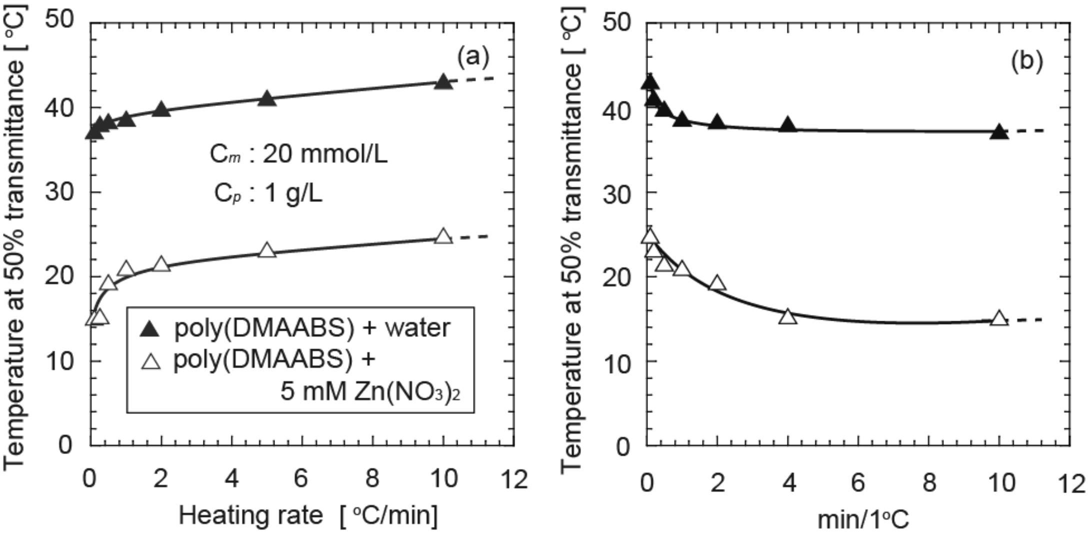

Fig. 5−10 Transition behavior of poly(DMAABS) (1 g/L) in water and 5 mmol/L $Zn(NO_3)_2$ solutions of various heating rate.

5.3.7. The phase transition of the poly(DMAAPS) and poly(DMAABS) of various intrinsic viscosities in water and $Zn(NO_3)_2$ solution

It is well known that viscosity of a betaine polymer affects the UCST of the polymer solution as reported by previous researcher [12]. Ning et al. [12] has been reported a change in the UCST of poly(DMAAPS) by simultaneously varying the molecular weight of polymer at different C_m of 2.5–361 g/L. The UCST found increased at low to intermediate C_m (2.5–100 g/L), and exhibited a gradual decrease with increasing C_m (~100 g/L). Another study [4] has only reported the UCST of poly(DMAABS) in very limited range of C_m, i.e., 292 g/L which was higher than 100 °C.

Therefore, in this section, the effect of intrinsic viscosity on the transition behavior of poly(DMAAPS) and poly(DMAABS) solutions was investigated and compared simultaneously by varying the monomer concentration from the C_m (20–100 mmol/L). The polymer concentration in the solution was made only in 1 g/L to clearly observe the transition temperature in poly(DMAABS) solution. The temperature dependence of the transmittance of poly(DMAABS) and poly(DMAAPS) is shown in Fig. 5−11. From Fig. 5−11, it is seen that the transition temperature of poly(DMAABS) at C_m of 20 mmol/L was 39 °C. At a higher C_m of 40 mmol/L, the transition temperature of poly(DMAABS) increased to 65 °C. With further increasing the C_m to 100 mmol/L, the transition temperature of poly(DMAABS) increased to higher than the maximum temperature in the experimental range of 70 °C. Above result gives an explanation that a small increase in the molecular weight of poly(DMAABS) significantly increase the formation of inter-chain pairing between the charged groups of sulfobetaine as also explained previously in the adsorption behavior of ions onto this DMAABS gel. However, the transition temperatures of poly(DMAAPS) in water at C_m of 20, 40, 100 mmol/L are lower than 20, 14, and 16 °C, respectively, and that in $Zn(NO_3)_2$ solution was out of experimental temperature range 10–70 °C. As reported by previous researcher that the transition temperature of poly(DMAAPS) in water [12] and in various $Zn(NO_3)_2$

concentrations [6] can be observed even at high monomer concentration.

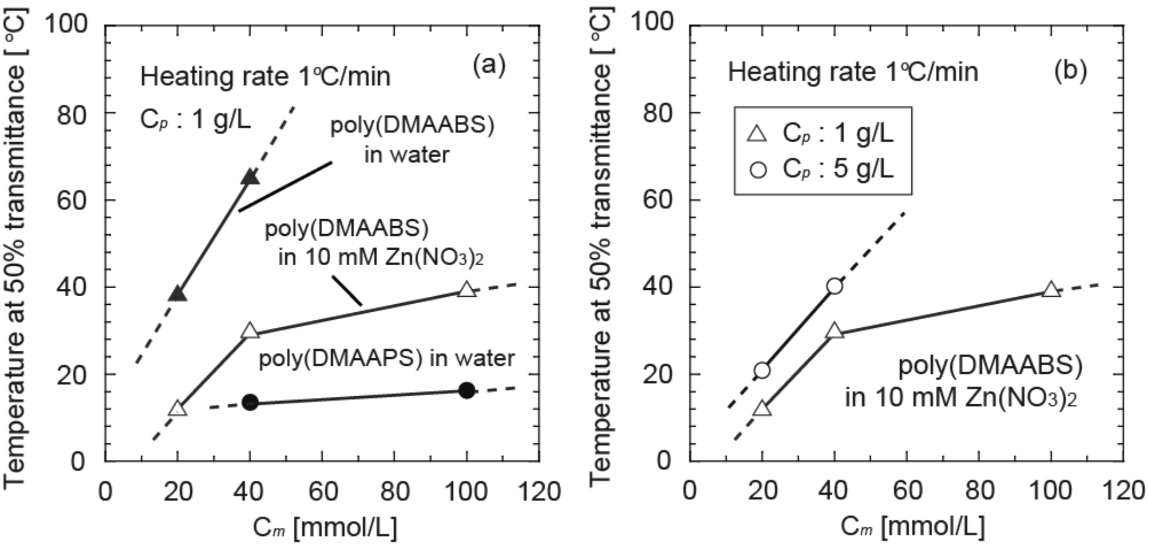

Fig. 5−11 Transition behavior of poly(DMAAPS) and poly(DMAABS) in water of various viscosity of the polymer.

Furthermore, an interesting result was found in the transition temperature poly(DMAABS) in 10 mmol/L of $Zn(NO_3)_2$ solution as shown in Fig. 5−11(a) and (b). At higher monomer concentration, the transition temperature difference of poly(DMAABS) was small and almost constant. As seen in Fig. 5−11(a), the transition temperature of poly(DMAABS) at C_p of 1 g/L and C_m of 20, 40, and 100 mmol/L were 12, 30, and 39 °C, respectively. With further increasing the C_p to 5 g/L as shown in Fig. 5−11(b) the transition temperature of poly(DMAABS) at C_m of 20, 40, and 100 mmol/L were 21, 36, and higher than 100 °C, which is out of the experimental range, respectively. An increase in the transition temperature of poly(DMAABS) at higher monomer and polymer concentrations can be explained due to the fact that the ability of ions to dissociate the pairing is restricted. This restriction occurred because of the effective formation of isolated charged of the poly(DMAABS) [4]. This phenomenon is also in agreement with the swelling and adsorption behaviors of the DMAABS gel (see Fig. 5−(3−6)); the amount of ion adsorbed onto the DMAABS gel almost remained unchanged despite variation of the temperature and cross-linker concentration at (C_p > 300 g/L).

5.3.8. The phase transition of the poly(DMAAPS) and poly(DMAABS) of various polymer concentration in water and $Zn(NO_3)_2$ solution

The temperature dependence of the transmittance through an aqueous solution of poly(DMAAPS) and poly(DMAABS) at different polymer concentrations is shown in Fig. 5−12. For poly(DMAABS) in water, as the polymer concentration increased (0.5−5 g/L), the transition temperature of the polymer increased from 28 to 48 °C. Similar tendency of the transition temperature was observed for the poly(DMAABS) in $Zn(NO_3)_2$, although the difference of the transition temperature was quite large about 25 °C. In contrast, the transition temperature of poly(DMAAPS) can only be observed at C_p of 5 and 10 g/L; which only slightly increased from 13 to 17 °C. The transition temperatures of poly(DMAAPS) solution of lower polymer concentration (0.5−2 g/L) were lower than 10 °C.

This phenomenon is in agreement with the results of previous researchers for poly(DMAAPS) [7,13]. An increase in the polymer concentration leads to an increase in the intra-chain and/or inter-chain interaction. Therefore, more thermal energy is required to overcome this interaction as a result the transition temperature of poly(DMAAPS) increased with increasing polymer concentration. Additionally, the polymer is soluble in water above the UCST; the hydrated polymer chains form an expanded structure due to the fact that the thermal motion of the polymer chains can overcome the interaction between the side chains of the polymer, that is, the inter- and/or intra-chain interactions of the N^+ and SO_3^- groups in poly(DMAABS). However, below the UCST, they form aggregates because the intra- and/or inter-chain interactions are stronger than the force of molecular motion [14]. Such a high transition temperature shown by poly(DMAABS) is due to a high probability of the ion pair formation, and high stability against heating as a result from their high hydrophobicity [3,4].

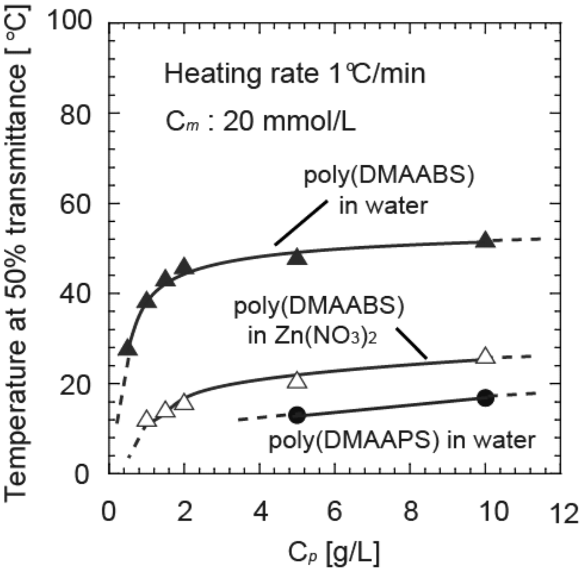

Fig. 5−12 Transition behavior of poly(DMAAPS) and poly (DMAABS) (1 g/L) in water of various polymer concentrations.

5.3.9. The phase transition of poly(DMAAPS) and poly(DMAABS) in $Zn(NO_3)_2$ solution of various concentration

The transition behavior of poly(DMAABS) in $Zn(NO_3)_2$ solution is shown in Fig. 5−13. The poly(DMAAPS) concentration was 1 g/L. As the $Zn(NO_3)_2$ concentration increased, the transition temperature of poly(DMAABS) decreased. When poly(DMAABS) was dissolved in the $Zn(NO_3)_2$ solutions with concentrations from 0 to 5 mmol/L, the transition temperature decreased from 39 to ~ 21 °C. A decrease in the transition temperature indicated that the ionic pairing between N^+ and SO_3^- was dissociated by Zn^{2+} and NO_3^-. With further increasing the $Zn(NO_3)_2$ concentration to 10 mmol/L, the transition temperature decreased significantly to less than 10 °C which is out of the experimental range and induced a change in the transparency of the solution. In the case of highly concentrated $Zn(NO_3)_2$ solution, the dissociation of the ionic pairing of SO_3^- and N^+ occurred easier because a significant number of ions (Zn^{2+} and NO_3^-) were available for disruption of the inter- and/or intra-chain association [12]. Because of such dissociation of ionic pairing, soluble polymer chains and transparent solution were obtained. A similar phenomenon, in which the UCST of the solution decreases because of the dissociation of ionic pairing, was previously reported by Ning et al. [12]. In contrast, when the poly(DMAAPS) was dissolved in $Zn(NO_3)_2$ solution, no transition can be observed despite the variation of the $Zn(NO_3)_2$ concentration.

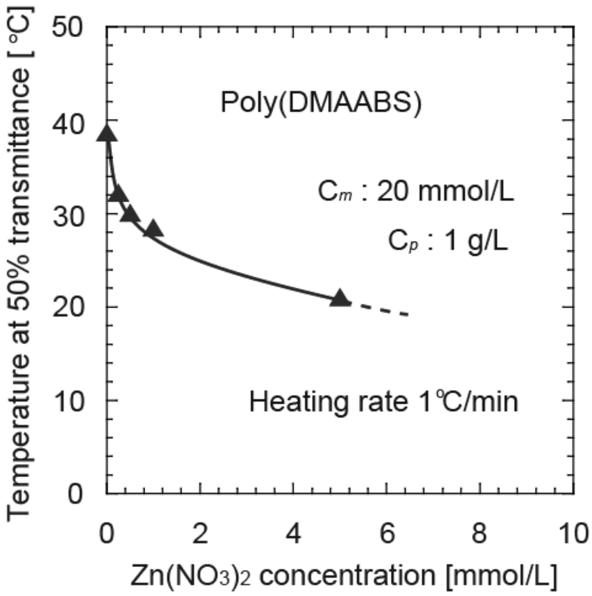

Fig. 5−13 Transition behavior of poly(DMAABS) (1 g/L) in $Zn(NO_3)_2$ solutions of various concentrations.

5.4. Summary

The effect of methylene groups spacer between the charged functional groups of sulfobetaine on the adsorption, swelling, and transition behaviors of the DMAAPS and DMAABS polymers or gels was investigated using $NaNO_3$, $Zn(NO_3)_2$ solutions. The amount of ion adsorbed onto the DMAAPS gel and its swelling degree depended strongly on the temperature and cross-linker concentration in the preparation of the gel. In contrast, the amount of ion adsorbed onto the DMAABS gel was independent of the cross-linker concentration used in the preparation of the gel. Furthermore, the swelling degree of the DMAABS gel was also independent of the cross-linker concentration and temperature. In addition, the correlation between the degree of swelling of the DMAAPS gel and the amount of Zn^{2+} adsorbed on the gel was compared with that of the DMAABS gel. In the case of the DMAAPS gel, the data points fell on the same line correlation despite variation of the cross-linker concentration or temperature, similar as our previous study. On the other hand, the correlation between the swelling degree and amount of Zn^{2+} adsorbed onto the DMAABS gel was difficult to examine since the amount of Zn^{2+} adsorbed on the DMAABS gel remained unchanged with increasing the swelling degree because of the effective formation of the inter-chain pairing of the charged groups of the DMAABS gel.

The transition temperature of poly(DMAAPS) and poly(DMAABS) was strongly influenced by the contact time, the heating rate, the salt solution concentration and anion and cation species in the solutions. It was found that the transition temperature of poly(DMAAPS) could be observed over a wide range of polymer and monomer concentration in the preparation of the polymer. However, the transition temperature of poly(DMABS) especially in water was observable only for a small range of monomer concentration in the preparation of the polymer i.e., 20-40 mmol/L. Additionally, the transition temperature of poly(DMAABS) slightly increased with that of poly(DMAAPS). These results suggest that the interaction between positive and negative charged groups in the DMAABS is stronger than that in the DMAAPS.

5.5. References

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Chapter 6

Conclusion

The overall goal of this work was to study the ion-adsorption properties, swelling behavior, and transition behavior of zwitterionic sulfobetaine type, *N,N*-dimethyl-(acrylamidopropyl)ammonium propane sulfonate (DMAAPS) and *N,N*-dimethyl-(acrylamidopropyl)ammonium butane sulfonate (DMAABS), polymers and gels and their relationship. The major conclusions obtained in this thesis are as follows,

1. Various effects of the temperature and the conditions employed in the preparation of the gel, i.e., cross-linker and monomer concentrations, on the adsorption of cations and anions onto the sulfobetaine type DMAAPS gels were investigated in various nitrate solutions. The simultaneous adsorption of cations and anions was observed. Furthermore, an interesting correlation between the degree of swelling of the DMAAPS gel and the amount of ion adsorbed onto the gel was found; the data points laid on the same line, even at different cross-linker and monomer concentrations in the preparation of the gel or temperatures, when the ion concentration was the same. From this correlation the maximum amount of ion adsorbed onto the gel for the specific ion species could be estimated, and it was found to be proportional to the equilibrium concentration of ion in the solution.

2. It was observed that anion and cation species in aqueous salt solutions, i.e., KF, KCl, KBr, KI, KNO_3, $LiNO_3$, $Zn(NO_3)_2$, $Mg(NO_3)_2$, $Ca(NO_3)_2$, $ZnCl_2$, and $ZnSO_4$ influenced the adsorption and swelling behaviors of the DMAAPS gel as well as their relationship. In the halide solutions, the order of the amount of ion adsorbed onto the gel was opposite that of

ion species in the Hofmeister series. Additionally, it was found that in the mixture of these halide solutions, the competitive adsorption of anions occurred. In the mixture, the adsorbed amount of the anion on the more right side of the Hofmeister series became larger than that in the single-components solutions, while those on the more left side of the Hofmeister series became smaller than in the single-components solutions. It was also found in other aqueous salt solutions that the influence of anion is usually more significant as compared to that of cation on the maximum adsorption capacity and the polymer concentration in the gel at which the adsorption of ion remained constant primarily in the solution containing divalent cations.

3. In order to understand the role of ionic interaction between the charged groups of sulfobetaine and ions from salt solutions, the transition behavior of the poly(DMAAPS) was investigated in various salt solutions containing different anion and cation species. The transition temperature of poly(DMAAPS) was strongly influenced by the salt solution concentration and anion and cation species in the solutions. Interaction of charged groups with ions from salt solutions may lead to the dissociation or entanglement of polymeric chains of DMAAPS. Additionally, the relationship between the transition temperature of poly(DMAAPS) and the maximum amount of ion adsorbed by the DMAAPS gel in various solutions was elucidated. The transition temperature of poly(DMAAPS) initially increased with increasing the salt concentration in the solution, and then decreased as the concentration of salt increased further. Furthermore, the transition temperature of poly(DMAAPS) initially increased and then decreased as the maximum amount of ion adsorbed onto the DMAAPS gel increased, which depend on the ion species and ion concentration. This result suggests that the maximum amount of ion adsorbed can be simply estimated by measuring the transition temperature.

4. The effect of methylene groups spacer between the charged functional groups of sulfobetaine on the adsorption, swelling, and transition behaviors using the DMAAPS and DMAABS polymers and/or gels was investigated in the $NaNO_3$, $Zn(NO_3)_2$ solutions. The amount of ion adsorbed onto the DMAAPS gel and its swelling degree depended strongly on the temperature and cross-linker concentration in the preparation of the gel. In contrast, the amount of ion adsorbed onto the DMAABS gel was independent of the cross-linker concentration used in the preparation of the gel. Furthermore, the swelling degree of the DMAABS gel was also independent of the cross-linker concentration and temperature. In addition, the transition temperature of poly(DMAABS) slightly increased with that of poly(DMAAPS). These results suggest that the interaction between positive and negative charged groups in the DMAABS is stronger than that in the DMAAPS.

APPENDIX

Nomenclature

Q	amount of cation or anion adsorbed	[mmol/g-dry gel]
C_0	concentration of cation or anion in the initial solution	[mmol/L]
C	concentration of cation or anion in the solution after adsorption	[mmol/L]
V	volume of the solution	[L]
m	weight of the dry ground gels	[g]
d_{swell}	diameter of swollen gel	[mm]
d_{dry}	diameter of dry gel	[mm]
C_p	concentration of polymer in the gel or in the solution	[g/L]
C_m	concentration of monomer in the preparation of the polymer	[mmol/L]
W_0	weight of dry sample gels	[g]
V_0	volume of dry sample gels	[L]
Q_{max}	maximum amount of cation adsorbed onto gel	[mmol/g-dry gel]
C_e	equilibrium concentration of cation	[mmol/L]
η_{sp}	specific viscosity	–
η_{rel}	relative viscosity	–
$[\eta]$	intrinsic viscosity	[dL/g]

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Chapter 1.

Chapter 2.

Fig. 2–7 (a) Amount of Zn^{2+} adsorbed onto the DMAAPS gel and (b) the degree of swelling of the DMAAPS gel in $Zn(NO_3)_2$ solutions of various concentrations at 50 °C. The gels were prepared at three different cross-linker concentrations.

Fig. 2–8 (a) Amount of Zn^{2+} adsorbed onto the DMAAPS gel and (b) degree of swelling of the DMAAPS gel in 10 mmol/L $Zn(NO_3)_2$ solution at various temperatures. The gels were prepared at three different cross-linker concentrations.

Fig. 2–9 (a) Amount of Zn^{2+} adsorbed onto the DMAAPS gel and (b) degree of swelling of the DMAAPS gel in $Zn(NO_3)_2$ solutions of various concentrations at 50 °C. The gels were prepared at three different monomer concentrations.

Fig. 2–10 (a) Amount of Zn^{2+} adsorbed onto the DMAAPS gel and (b) degree of swelling of the DMAAPS gel in 10 mmol/L $Zn(NO_3)_2$ solution at various temperatures. The gels were prepared at three different monomer concentrations.

Fig. 2–11 Relationship between the amount of Zn^{2+} adsorbed onto the DMAAPS gel and (a) the degree of swelling of the DMAAPS gel and (b) the polymer concentration in the gel. The gels were prepared at three different cross-linker concentrations; the amount of Zn^{2+} adsorbed and the degree of swelling were measured in the $Zn(NO_3)_2$ solutions of various concentrations (2.5, 5, 7.5, and 10 mmol/L) and at various temperatures (10, 30, 50, and 70 ºC).

Fig. 2–12 Relationship between the maximum adsorption capacity of DMAAPS gel for Zn^{2+} and $Zn(NO_3)_2$ equilibrium concentrations.

Fig. 2–13 Relationship between the amount of Zn^{2+} adsorbed onto the DMAAPS gel and (a) the degree of swelling, and (b) the polymer concentration in the gel. The gels were prepared at three different monomer concentrations; the amount of Zn^{2+} adsorbed and the degree of swelling were measured in $Zn(NO_3)_2$ solutions of various concentrations and at various temperatures.

Chapter 3.

Fig. 3–1 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.

Fig. 3–2 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.

Fig. 3–3 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.

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Fig. 3–5 Swelling degrees of DMAAPS gels measured in (a) a KI + KF mixture and (b) KI + KF, KI + KCl, 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.

Fig. 3–6 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.

Fig. 3–7 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.

Chapter 4.

Chapter 5.

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Fig. 5–6 Degree of swelling of the (a) DMAAPS and (b) DMAABS gels in 10 mmol/L $NaNO_3$ solution at various temperatures. The gels were prepared using different cross-linker concentrations.

Fig. 5–7 Relationship between the amount of Zn^{2+} adsorbed onto the (a) DMAAPS and (b) DMAABS gels and the degree of swelling of the gels. The gels were prepared using different cross-linker concentrations; the amount of Zn^{2+} adsorbed and the degree of swelling were measured in the $Zn(NO_3)_2$ solutions of 10 mmol/L and at various temperatures (10, 30, 50, and 70 ºC).

Fig. 5–8 Relationship between the amount of Na^+ adsorbed onto the (a) DMAAPS and (b) DMAABS gels and the degree of swelling of the gels. The gels were prepared using different cross-linker concentrations; the amount of Na^+ adsorbed and the degree of swelling were measured in the $NaNO_3$ solutions of 10 mmol/L and at various temperatures (10, 30, 50, and 70 ºC).

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