

論 文 の 要 旨

題 目 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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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 , $\text{Zn}(\text{NO}_3)_2$, and $\text{Al}(\text{NO}_3)_3$ 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 $\text{Zn}(\text{NO}_3)_2$ 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 $\text{Zn}(\text{NO}_3)_2$ 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 $\text{Zn}(\text{NO}_3)_2$ 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., $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$. 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 , $\text{Zn}(\text{NO}_3)_2$ 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.