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Investigation of ion adsorption properties of sulfobetaine gel and relationship with its swelling behavior

Eva Oktavia Ningrum [a, b], Yukiko Murakami [a], Yasuhiro Ohfuka [a], Takehiko Gotoh [a], Shuji Sakohara [a, *]

[a] *Department of Chemical Engineering, Graduate School of Engineering, Hiroshima University, Kagamiyama 1-4-1, Higashi-Hiroshima 739-8527, Japan*
[b] *Department of Chemical Engineering, Faculty of Industrial Technology, Sepuluh Nopember Institute of Technology, Kampus ITS Sukolilo, Surabaya 60111, Indonesia*

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ABSTRACT

The adsorption of cations and anions in nitrate solutions on *N*,*N*-dimethyl(acrylamidopropyl)ammonium propane sulfonate (DMAAPS) gels prepared using various cross-linker and monomer concentrations was investigated. The influence of the temperature and nitrate concentration on the adsorption properties of the gel was evaluated, demonstrating simultaneous adsorption of cations and anions. The amount of Zn^{2+} adsorbed on the gel in $Zn(NO_3)_2$ solution increased as the cross-linker and monomer concentrations used in the gel preparation increased. For the gel prepared using a higher cross-linker or monomer concentration, elevation of the temperature did not induce any significant change in the amount of Zn^{2+} adsorbed on the gel. Furthermore, for the gel prepared using a lower cross-linker or monomer concentration, the amount of Zn^{2+} adsorbed on the gel decreased significantly as the temperature increased. In addition, an interesting correlation between the degree of swelling of the gel and the amount of Zn^{2+} adsorbed on the gel was found. As the degree of swelling decreased, the adsorption amount increased to eventually achieve a constant value.

1. Introduction

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. 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,

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* Corresponding author.
E-mail address: sakohara@hiroshima-u.ac.jp (S. Sakohara).

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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 zwitterionic 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].

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 [21], cross-linker concentration [22–24], salt concentration [18,25,26], ionic strength [27,28], 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 on 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.

To address this paucity of information, the adsorption of cations and anions on the sulfobetaine type *N*,*N*-dimethyl(acrylamidopropyl)ammonium propane sulfonate (DMAAPS) gels in various nitrate solutions was investigated in this study. The effects of the temperature and the conditions employed in the preparation of the gel, i.e., cross-linker and monomer concentrations, on the extent of adsorption of cations and anions on the DMAAPS gel were evaluated. 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. $NaNO_3$, $Zn(NO_3)_2$, and $Al(NO_3)_3$ were selected as the target solutions.

In addition, to elucidate the role of the ionic interactions 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*-dimethylaminopropylacrylamide 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.

2. Experimental section

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*-Dimethylaminopropylacrylamide (DMAPAA) and DMAPAA-Q were kindly supplied by Kohjin Film & Chemicals Co., Ltd. DMAPAA was purified by vacuum distillation and DMAPAA-Q was used as received. *N*,*N*′-Methylenebisacrylamide (MBAA), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (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. Synthesis of DMAAPS

DMAAPS was synthesized by the ring–opening reaction of DMAPAA and PS [29]. 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. 1.

2.3. Preparation of the DMAAPS polymer and gel

The DMAAPS polymer and gel were prepared by free radical polymerization using TEMED and APS as the polymerization accelerator and initiator, respectively. In the preparation of the DMAAPS polymer [poly(DMAAPS)], the concentrations of DMAAPS, TEMED, and APS were 500, 2, and 2 mmol/L, respectively. DMAAPS 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 resulting polymer was purified by dialysis using a membrane with a molecular weight cut off of 12,000–14,000 (Cellu Step T3, Membrane Filtration Product, Inc.) over a period of one week.

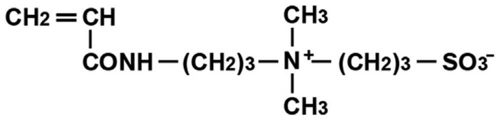
The average molecular weight of the synthesized poly(DMAAPS) was 1.13×10^6 g/mol, as estimated from the intrinsic viscosity [η] that was measured in 0.1 M NaCl solution at 30 °C using a Ubbelohde viscometer. The weight-average molecular weight $[\overline{Mw}]$ was calculated using the following equation, which has previously been proposed by Ning et al. [21]:

$$[\eta] = 2.3 \times 10^{-5}\overline{Mw}^{0.78} \tag{1}$$

The DMAAPS gels were prepared using the method presented for the synthesis of poly(DMAAPS), with the exception that MBAA was used as a cross-linker. 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 conditions employed in the synthesis of the DMAAPS gels are summarized in Table 1.

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. NaAMPS was prepared by neutralization of the monomer



$$\begin{array}{l} CH_2{=}CH \\ \;\;| \\ \;\;CONH-(CH_2)_3-\overset{CH_3}{\underset{CH_3}{N^+}}-(CH_2)_3-SO_3^- \end{array}$$

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