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Swelling behaviors of amphoteric gels and the dissociation mechanisms

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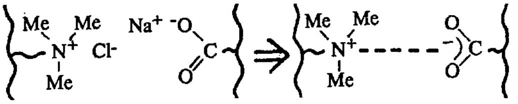
SUMMARY

Various types of amphoteric gels were made with the combinations of anionic monomers (sodium acrylate and sodium styrenesulfonic acid and cationic monomers (dimethylaminopropyl acrylamide and trimethyl-n-acryloly-3-aminopropane ammonium chloride) and the pH-dependent volume behaviors of these amphoteric gels were examined. As a consequence, the specific binding formed in each amphoteric gel could be dissociated into ions in a unique fashion with changes in pH. Four types of dissociation mechanisms could be presumed as follows; 1) ionization of the constituent groups (weak anion and cation groups) in both acidic and alkali solutions, 2) ionization of the constituent group (strong anion groups) in alkali solution, 3) ionization of the constituent group (strong cation groups) in acidic solution, and 4) ionization of the constituent groups (strong anion and cation groups) in both acidic and alkali solutions.

INTRODUCTION

The swelling behavior of amphoteric gels having anionic and cationic groups is one of current topics in polymer science because of its scientific and technological importance. Polymer gels such as anionic gels, cationic gels and nonionic gels are known to undergo reversible, discontinuous volume changes with changes in solvent composition, temperature, salt, and pH.[1-11] These behaviors have been considered as a first order phase transition between a swollen gel and a shrunken gel. Our particular attention is directed toward specific volume behaviors observed for amphoteric gels, because they are essentially different from the volume behaviors observed for mono-ionic polymer gels as previously described. However, no studies of the specific volume behavior observed for amphoteric gels have been conducted, in contrast to a number of fundamental approaches.[12-19] According to our previous study on an amphoteric gel (sodium acrylate / trimethyl-n-acryloyl-3-aminopropane ammonium chloride / acrylamide / N,N′ methylenebisacrylamide copolymer gel),[20,21] the following volume behavior has been clarified. The amphoteric gel having equimolar amounts of anionic and cationic groups did not swell, whereas the gel volume increased with an increase in the anionic or cationic group. Such specific volume behavior could be interpreted by considering a specific bonding between the anionic and cationic groups as shown below and then, the effective, residual ionic density after forming the specific binding could play an important part in determining the equilibrium volume of the amphoteric gel in distilled water and the volume phase transition in acetone-water mixtures. Thus, in the following experiment, pH and ionic strength dependences on the equilibrium volume of the amphoteric gels should be examined. The specific bonding formed between anionic and cationic groups seems to dissociate easily into the constituent ions in response to pH of the solution around the gels. The dissociation mechanism of the specific bonding seems to be correlated with the dissociation constants (pKa and pKb) of constituent monomers incorporated in the gel networks. Thus, the purpose of the present experiment is to clarify the dissociation mechanism of amphoteric gels, prepared with combinations of various types of anionic and cationic monomers, by examining the pH and ionic strength dependences on the equilibrium volumes.



EXPERIMENTAL

Acrylamide (Ac), N,N′-methylenebisacrylamide (Bis), vinylsulfonic acid (VAc) and acrylic acid (Ac) were commercially obtained. All chemicals used were of reagent grade. Styrene sulfonic acid (SSAc) was from Toyo Soutatsu Kogyo Co. Ltd. Dimethylaminopropylacrylamide (DMAPA) and trimethyl-n-acryloyl-3-aminopropane ammonium chloride (TAAPAC)

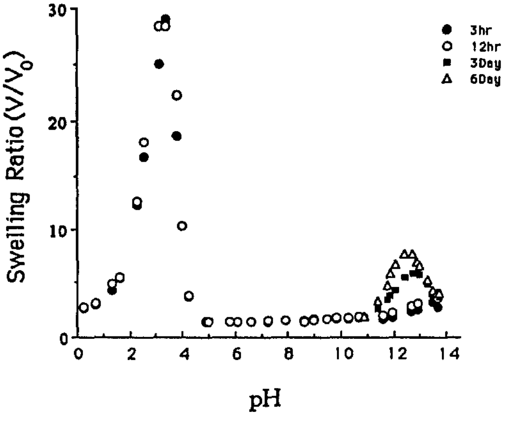


Figure 1 Swelling behavior of an amphoteric gel (SAc / TAAPAC / A / Bis copolymer gel) induced by a change in pH. The time-dependent volume behaviors of the gel are as follows: Δ:60 day, ■:30 day, ○:12 hr, ●:3 hr.

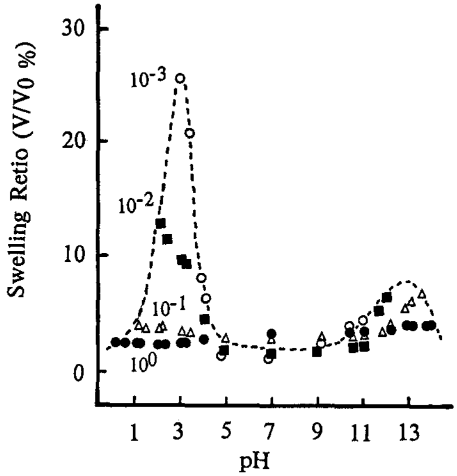


Figure 2 Ionic strength-dependent volume behavior of an amphoteric gel (SAc / TAAPAC / A / Bis copolymer gel) immersed in various pH solutions. The ionic strength for each pH solution is;
○:0.001, ■:0.01, △:0.1, ●:1

were obtained from Kojin Co. Ltd. All reagents obtained were of adequate purity of more than 99% (w/w). Sodium salts (SVAc, SAc and SSSAc) were prepared by reacting VAc, Ac and SSAc with sodium carbonate and served as materials for the syntheses of various types of amphoteric gels. The prepared sodium salts were used after several recrystallizations. To clarify the dissociation mechanisms of the amphoteric gels immersed in various pH solutions, the following four amphoteric gel samples were prepared. The first sample was a SAc / DMAPA / A / Bis copolymer gel, where SAc is a sodium salt of a weak organic acid (Ac) and DMAPA, a weak organic base. SAc (258.3 mg), DMAPA (336.6 mg), A (1 g) and Bis (26.7 mg) were dissolved in distilled water to a final volume of 20 ml, and then the mixture contained equimolar amounts of SAc and DMAPA. The gel sample was prepared by solution copolymerization at 50 C for 1 hr, after the addition of ammonium persulfate (40 mg). The second sample was a SAc / TAAPAC / A / Bis copolymer gel, where TAAPAC was an ammonium salt of a weak organic base. SAc (296.9 mg), TAAPAC (720.4 mg), A (1 g) and Bis (26.6 mg) were dissolved in distilled water to a final volume of 20 ml, whereupon the solution contained equimolar amounts of SAc and TAAPAC. The gel sample was prepared by solution polymerization at 50 C for 1 hr, after the addition of ammonium persulfate (40 mg). The third sample was a SSSAc / DMAPA / A / Bis copolymer gel, where SSSAc was a sodium salt of a strong organic acid. SSSAc (519.1 mg), DMAPA (514.5 mg), A (1.0 g) and Bis (26.7 mg) were dissolved in distilled water to a final volume of 20 ml, and then the solution contained equimolar amounts of SSSAc and DMAPA. The gel sample was prepared by solution polymerization at 50 C for 1 hr, after addition of ammonium persulfate (40 mg). The final sample was a SSSAc / TAAPAC / A / Bis copolymer gel. SSSAc (529.4 mg), TAAPAC (543.8 mg), A (1.0 g) and Bis (26.7 mg) were dissolved in distilled water to a final volume of 20 ml, whereupon the solution contained equimolar amounts of SSSAc and TAAPAC. The gel sample was also prepared by solution polymerization under the same experimental conditions as already described. The sample preparation procedures were all the same as in the

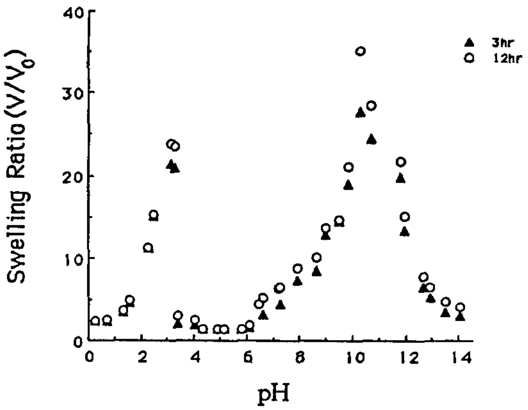


Figure 3 pH-dependent volume behavior of an amphoteric gel (SAc / DMAPA / A / Bis copolymer gel). The time-dependent volume behaviors of the gel are; ○:12 hr, ▲:3 hr

previous work.[20] The gel samples were washed in distilled water for a week to eliminate impurities and immersed into solutions of desired pH and ionic strength. After equilibrium was reached, diameters of the cylindrical gel samples were measured and then the gel volumes were estimated by cubing the diameters.

RESULTS AND DISCUSSION

Figure 1 shows the plots of the swelling ratio (V/V$_0$) of an amphoteric gel (SAc / TAAPAC / A / Bis copolymer gel) as a function of pH. The amphoteric gel immersed in aqueous solutions of pH 5 or above was observed to maintain nearly the initial volume (V/V$_0$ 1). However, a small increase in volume was observed in the region above pH 11, whereupon the gel underwent a time-dependent volume change. Thus, the gel volume increased gradually with the passage of time and finally reached an equilibrium swelling ratio in 60 days. As a consequence, a small peak appeared at pH 12.5.

As the pH decreased in the region below pH 5, the gel volume increased rapidly and then decreased via a maximum at pH 3.2. The volume behavior below pH 5 can be explained by considering a dissociation mechanism of a specific bonding formed in the amphoteric gel. In such a pH region, the specific bonding can dissociate into a quaternary ammonium group and a carboxyl group, whereupon the quaternary ammonium group can be immediately ionized but the carboxyl group can be not ionized. The ionization of the quaternary ammonium group depends upon not only the dissociation constant (pK) of the constituent TAAPAC but also the pH of the gel. The ionization increases with a decrease in pH and reaches a maximum at pH 3.2. This is one reason why the largest equilibrium volume was observed at pH 3.2. On the other hand, the abrupt volume decrease in the region below pH 3.2 can be explained by considering an ionic strength of acidic solution around the gel, because the ionic strength should generally influence the equilibrium volume of polymer gels to a greater degree than

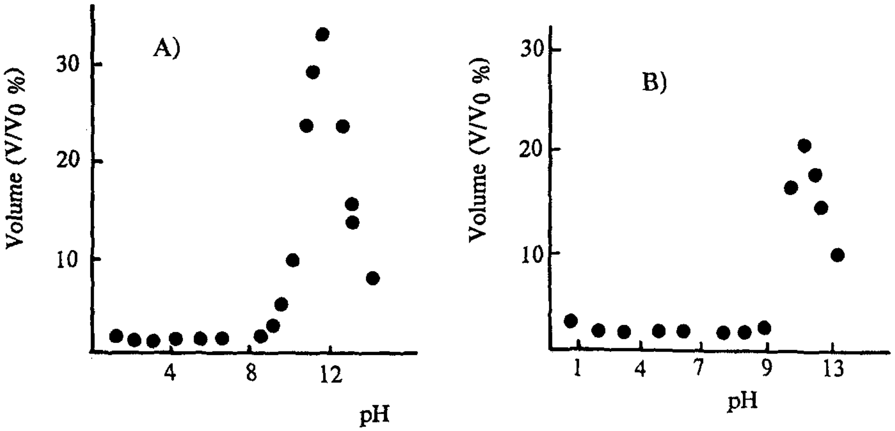


Figure 4. A) pH-dependent volume behavior of an amphoteric gel (SSSAc / DMAPA / A /Bis copolymer gel). B) pH-dependent volume behavior of an amphoteric gel (SSSAc / TAAPAC / A / Bis copolymer gel).

does the ionized group in the gel. This is one reason for the abrupt volume decrease below pH 3.2.

Figure 2 shows the plots of the swelling ratio (V / V_0) of an amphoteric gel (SAc / TAAPAC / A / Bis copolymer gel) immersed in pH solutions as a function of ionic strength. When the ionic strength was kept at a high level of 1, the swelling ratio of the amphoteric gel remained nearly 1 over the entire pH range. This is consistent with the fact that ionic gels generally collapse when they are immersed in concentrated electrolyte solutions. As the ionic strength decreased, the swelling ratio increased gradually in both acidic and alkali regions. An envelope of the equilibrium volumes observed at each pH (a dotted line in the Figure) gave two peak tops at pH 3.2 and 12.5. This was in fair accord with the dissociation curve as shown in Figure 1.

Figure 3 shows the plots of the swelling ratio of an amphoteric gel (SAc / DMAPA / A / Bis copolymer gel) as a function of pH. The swelling ratio of the amphoteric gel was maintained at nearly 1 in the pH 4-6. As the pH of the gel increased in the region above pH 6, the gel volume increased gradually and reached a maximum at pH 10.7 and then decreased. As the pH decreased in the region below pH 4, the gel volume increased gradually and reached a maximum at pH 3 and then decreased. This suggests that two entirely ionized structures are present in both pH regions below 4 and above 6. The former is an ionized structure of the tertiary amine group ($-N(CH_3)_2$) and the latter, an ionized structure of the carboxyl group (COOH). The gradual decreases above pH 10.7 and below pH 3 can be also interpreted by the ionic strength of the aqueous solution around the gel.

Figure 4A shows the plots of the swelling ratio of an amphoteric gel (SSSAc / DMAPA / A / Bis copolymer gel) as a function of pH. The amphoteric gel immersed in aqueous solutions below pH 8.5 had a swelling ratio (V/V_0) of ca. 1.

This suggests that neither the sulfonic group ($-SO_3$ Na) nor the tertiary amine group can be fully dissociated in this pH region. As the pH increased in the region above pH 8.5, the gel volume increased and then decreased via a maximum at pH 12. The maximal peak can be explained by the entire dissociation of the sulfonic group and the subsequent decrease above pH 12 can be also explained by the ionic strength of the aqueous solution around the gel.

Figure 4B shows the plots of the swelling ratio of an amphoteric gel (SSSAc / TAAPAC / A / Bis copolymer gel) as a function of pH. No swelling could be detected in the region below pH 9. The maximum volume was observed at pH 12.4. As a consequence, the swelling behavior was similar in pattern to that observed for the above amphoteric gel which consisted of SSSAc and DMAPA. If a dissociation constant of the sulfonic group is comparable to that of the quaternary ammonium group, two maximum peaks can be presumed to appear in both regions of low and high pH. However, the only one maximum peak was actually observed in the high alkali region. This suggests that the dissociation constant of SSSAc may be greater than that of TAAPAC.

From the results of the present experiment, the following dissociation mechanism for the amphoteric gel can be speculated. The dissociation mechanism should be divided into two dissociation processes that occur with changes in pH. The first is a dissociation process of the specific binding of the amphoteric gels and the second is a successive ionization process of the dissociated groups. The former dissociation is influenced by the dissociation constant (pK) of the specific bindings, and the latter ionization is influenced by the pKa or pKb of the constituent monomers. When various types of amphoteric gels are made with combinations of anionic and cationic monomers, they can be classified into four types of dissociation mechanisms. In general, the anionic groups in an alkali solution and the cationic groups in an acidic solution are known to be well ionized, while the anionic groups in an acidic solution and the cationic groups in an alkali solution can be only slightly ionized. Based on the above general idea, the amphoteric gel made with a combination of weak anionic and cationic groups may be ionized separately in both alkali and acidic solutions when the specific bonding formed in an amphoteric gel was dissociated. This is a dissociation mechanism observed for the amphoteric gel consisting of SAc and DMAPA. The amphoteric gel made with a combination of strong anionic and cationic groups may be also ionized independently in both alkali and acidic solutions. Unfortunately, this type of dissociation mechanism has not been observed yet. The amphoteric gel made with a combination of strong anionic group and a weak cationic group can be dissociated into an anionic ion in alkali solution but not dissociated into a cationic ion in acidic solution. If the weak cationic group in alkali solution would be ionized, it should immediately recombine with the strong anionic ion to the specific bonding. This is the dissociation mechanism of the amphoteric gel made with a combination of SSSAc and DMAPA. The amphoteric gel made with a combination of a weak anionic group and a strong cationic group can be dissociated into a cationic ion in acidic solution, but not dissociated into an anionic ion in alkali solution. This is because the weak anionic group in acidic solution can be only slightly ionized, otherwise it could immediately recombine to the specific binding. This is the dissociation mechanism of the amphoteric gel made up of a combination of SAc and TAAPAC. Further detailed observations of pH-dependent volume changes of amphoteric gels are now in progress.

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