Swelling Equilibria of Hydrogels with Sulfonate Groups in Water and in Aqueous Salt Solutions

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ABSTRACT: Swelling equilibria for five sulfonate gels were carried out in water and in aqueous solutions of NaCl, KCl, $CaCl_2$, Na_2SO_4, K_2SO_4, and $CaSO_4$ with concentrations ranging from 10^{-6} to 1 M at 25 °C. These samples were the same DS series of gels used in our previous paper, which were copolymerized using the ionizable monomer 2-(acrylamido)-2-methylpropanesulfonic acid (AMPS), the comonomer *N,N*-dimethylacrylamide (DMMA), and the cross-linker *N,N'*-methylenebis(acrylamide) (BIS). The mole fraction f of AMPS in the gel network ranged from 0.0899 to 0.6076. Before swelling the proton in the gel was exchanged by neutralization to the same cation as that in the salt solution to be equilibrated. The swelling capacity increases with increased charge density in the gels and with decreasing salt concentration. NaCl or KCl solutions more concentrated than 1 M were needed to screen the charge interaction in the DS50 ($f = 0.4318$) and DS70 ($f = 0.6076$) samples. The swelling ratios of DS50 and DS70 gels swollen in pure water and in the salt solutions were found to depend on the counterion species in the increasing sequence as Ca^{2+}, Na^+, and K^+, which cannot be interpreted with the concept of ionic strength. These phenomena seem to be the results of counterion condensation.

Introduction

In recent years, study of the swelling properties of hydrogels has been expanded rapidly and numerous applications have emerged, including controlled drug release,[1] a chemomechanical actuator,[2] an immobilized-enzyme reactor,[3] a solute recovery reagent,[4] and an environment-sensitive membrane.[5] All of these functions are based on the characteristics that a hydrogel will undergo a large volume change, especially the discontinuous volume phase transition,[6] in response to infinitesimal variations in the surrounding medium. The macroscopic volume change reflects the conformation transition in the network chains of the gel from an expanded state to a collapsed one, which can be induced by changing the solution composition,[7] pH value,[8] and temperature,[9] by applying an electric field[10] or mechanical force,[11] and by introducing charged or uncharged linear polymers into the gel system.[12,13] Charged groups attached to the network play an essential role in this transition.[6] Only by changing the electrostatic interactions in the gels can the above factors lead to the volume phase transition, except for the temperature-sensitive gels of N-substituted acrylamide.[14]

As being briefly reviewed in our previous paper,[15] theoretical and experimental efforts have been devoted to investigating the swelling of ionized gels in the last 4 decades. Unfortunately, these works are limited to the relatively lower charge density or the weak electrolyte in the gels. Therefore, we synthesized highly charged copolymer gels of 2-(acrylamido)-2-methylpropanesulfonic acid (AMPS) and *N,N*-dimethylacrylamide (DMAA) with the content of AMPS up to ca. 60 mol % and found some interesting behavior different from that of the weakly ionized gels. For example, the equilibrium shear modulus of these gels depends on the charge density in the rubberlike elastic region,[16] and the volume phase transition occurs in these gels provided the acetone content in water/acetone mixtures goes beyond a certain value regardless of the charge density.[15]

In strong polyelectrolyte gels, numerous charges on the polymer chains create a higher electrostatic potential around them. Consequently, not only is the repulsive force between the chains having the same sign of charge greatly enhanced but a fraction of the counterion will be bound to the polyion as well. The examination of thermodynamic equilibrium properties in aqueous salt solutions for the gels containing strongly dissociative electrolytes to a higher level will reveal the counterion–polyion interactions, which is the most essential factor governing practical functions of hydrogels. For this purpose, we have observed the swelling behavior of our sulfonate gels in aqueous salt solutions of NaCl, KCl, $CaCl_2$, Na_2SO_4, K_2SO_4, and $CaSO_4$. Here, we report the effects of salt concentration, the valence of the counterion and co-ion, and the charge density of the sample.

Experimental Section

The gel samples used in this research were the same as those in the preceding study,[15] so we only give a brief description here. Monomers 2-(acrylamido)-2-methylpropanesulfonic acid (AMPS; Wako Chemicals Co., Japan) and *N,N*-dimethylacrylamide (DMAA; Kohjin Co., Japan) were dissolved in water to make a pregel solution with the cross-linker *N,N'*-methylenebis(acrylamide) (BIS; Wako Chemicals Co.). The water used in synthesis and swelling was distilled and deionized until the resistivity was higher than 10^6 Ω cm. Polymerization of the pregel solution was conducted in glass capillaries of about 2.8 mm i.d. The gel removed from the capillary was sliced into disks and soaked in excess water for purification.

The total molar concentration C_t of all monomers, including BIS in the pregel solution, and the mole fraction C of BIS in all monomers were kept at 0.75 mol/L and 0.013, respectively, for all of the five samples. The nominal mole fraction F_{AMPS} of AMPS monomer in all monomers was varied from 0.10 to 0.70 for these five samples, which were referred to as the DS series, with the code figures corresponding their F_{AMPS} values. The real mole fraction f of AMPS in dried gels was determined by elemental analysis, which stood for the charge density in the gel samples. The F_{AMPS} and f values are presented in Table 1.

Swelling experiments were carried out at 25 °C in pure water and in six salt solutions of NaCl, KCl, $CaCl_2$, Na_2SO_4,

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Table 1. Swelling Ratios in Water for Sulfonic Acid Gels in Acid Type and in Salt Type

			H^+		K^+		Na^+		Ca^{2+}	
sample	F_{AMPS}	f	V/V_0	C_i/mM	V/V_0	C_i/mM	V/V_0	C_i/mM	V/V_0	C_i/mM
DS10	0.10	0.0899			21.01	2.906	14.08	4.336	13.16	2.320
DS20	0.20	0.1819	27.09	5.718	34.08	4.545	25.77	6.011	19.04	4.068
DS30	0.30	0.2674	39.06	5.768	40.18	5.608	33.31	6.764	24.12	4.671
DS50	0.50	0.4318	96.04	3.807	90.04	4.061	76.70	4.767	46.17	3.960
DS70	0.70	0.6076	594.53	0.828	282.19	1.745	250.18	1.969		

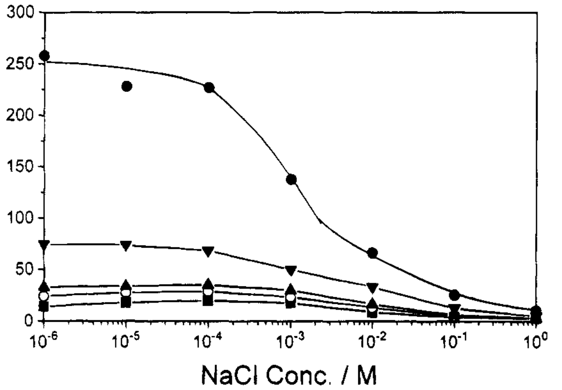

Figure 1. Equilibrated swelling ratios in aqueous NaCl solutions of the gel samples indicated by the symbols as those in Figure 6.

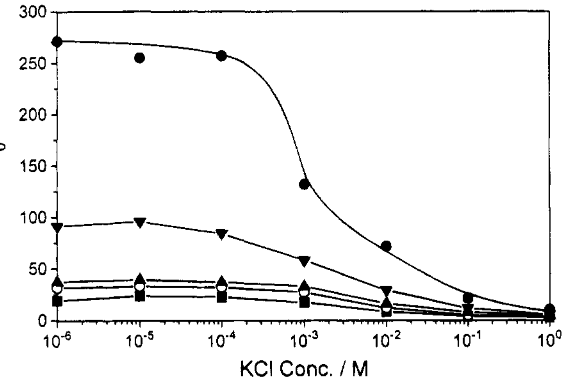

Figure 2. Equilibrated swelling ratios in aqueous KCl solutions of the gel samples indicated by the symbols as those in Figure 6.

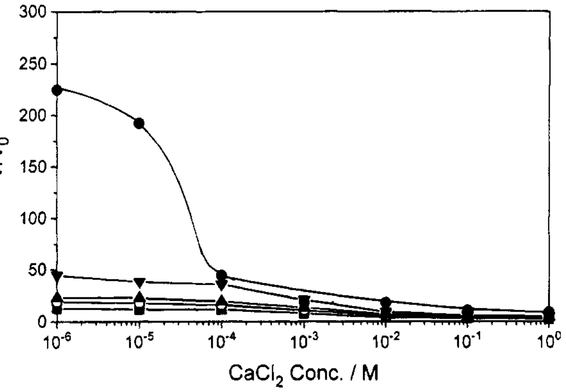

Figure 3. Equilibrated swelling ratios in aqueous $CaCl_2$ solutions of the gel samples indicated by the symbols as those in Figure 6.

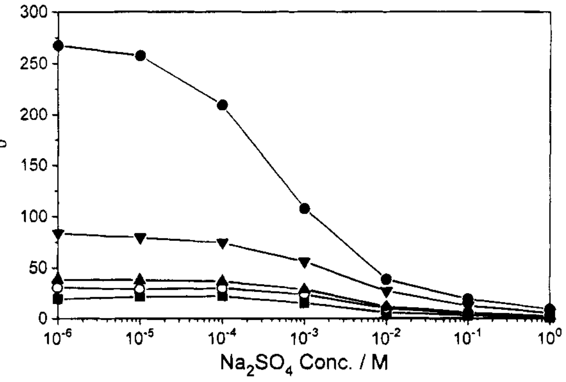

Figure 4. Equilibrated swelling ratios in aqueous Na_2SO_4 solutions of the gel samples indicated by the symbols as those in Figure 6.

K_2SO_4, and $CaSO_4$ with concentrations C_s from 10^{-6} to 1 M. All salts used here were the analytically pure reagents and were used without further purification. To avoid the cation-exchange effect during the swelling process, the gel sample was first neutralized with an excess amount of the dilute alkali solution (0.015–0.02 M) having the same cation as that in the salt solution to be equilibrated, and then the surplus alkali was washed out from samples with water. The samples were allowed to swell in the most concentrated salt solution and then transferred into the next dilute one when the equilibrium was reached, finally into pure water. Each equilibrium process took 10–14 days, during which the salt solution was refreshed once to keep the concentration as feeded. Usually, for 3–4 pieces of sample disks whose volume was ca. 2.5×10^{-3} cm^3 when just polymerized, a total amount of 400 mL of salt solution was used for the swelling equilibrium, so that the concentration change in the surrounding solution caused by the additional solution squeezed from the gel could become negligible.

Swelling capacity is expressed in terms of the swelling ratio V/V_0, which is defined as the gel volume V at the swelling equilibrium related to its original volume V_0 at polymerization and practically evaluated by $V/V_0 = (d/d_0)^3$, where d and d_0 denote the corresponding diameters of the gel disks. The diameter was measured with a slide caliper.

Results and Discussion

Swelling in Salt Solution. Figures 1–6 show the swelling ratios of five sulfonate gels DS10, DS20, DS30, DS50, and DS70 in salt solutions of NaCl, KCl, $CaCl_2$, Na_2SO_4, K_2SO_4, and $CaSO_4$, respectively. We can see from these figures that, in the medium range of salt concentration, the swelling ratio increases with the increased charge density following the sequence from DS10 to DS70 and decreases with increasing salt concentration. When salt solution is diluted beyond a certain value (10^{-4}–10^{-5} M), the swelling curve for a sample holds horizontally, while in concentrated salt solution, the swelling curves converge together. These phenomena can be attributed to the electrostatic repulsion between charged groups on the network chains and to the concentration difference of mobile ions inside the hydrogel and the external solution governed by the Donnan potential. As salt concentration rises, the electrostatic force will be shielded to a lower strength and the mobile ion concentration in the external solution will approach that inside the gel. These two factors make the swelling force fall down. However, the former effect was usually neglected in considerable studies.

Figures 1 and 2 indicate that NaCl or KCl solution of concentration higher than 1 M is required in order to

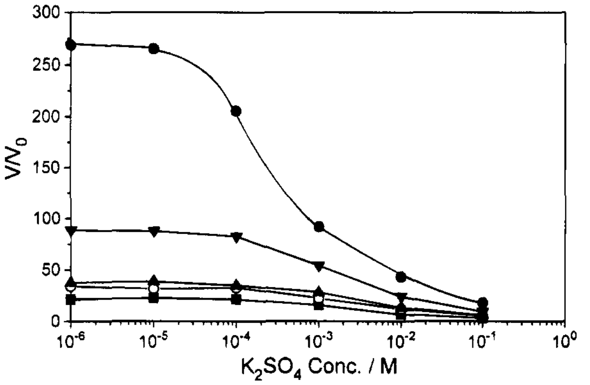

Figure 5. Equilibrated swelling ratios in aqueous K_2SO_4 solutions of the gel samples indicated by the symbols as those in Figure 6.

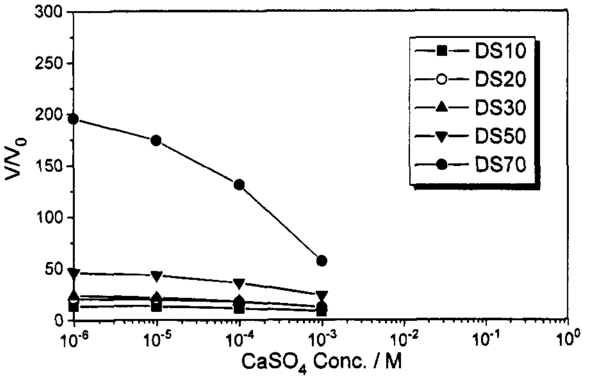

Figure 6. Equilibrated swelling ratios in aqueous $CaSO_4$ solutions of the gel samples as indicated by the symbols in this figure.

have DS70 and DS50 gels behave like an uncharged hydrogel. Gooda and Huglin[17] also reported that a concentrated NaCl solution of 4.5 M was used to screen the charge repulsion for the linear polymer of AMPS. These facts suggest that the electrostatic force would be much stronger in the strong polyelectrolytes than in the weak electrolytes. Therefore, the strength of the charge potential may be another different respect to distinguish strong and weak electrolytes besides the dissociation degree. Unfortunately, this concept has not been accepted in the present models.

Swelling in Pure Water. The swelling data in pure water at 25 °C are listed in Table 1 for our DS gels in their acid and salt types with three counterions K^+, Na^+, and Ca^{2+}, respectively. As expected from the completely dissociating nature of strong electrolytes, the gel with higher charge density swells to a higher extent no matter which type it is. When comparing the swelling ratios for one gel with different counterions, one can find its decrease with counterion change in the order of K^+, Na^+, and Ca^{2+}. The potassium sulfonate gels exhibit a swelling capacity similar to that of the original sulfonic acid gels, while the sodium sulfonate gels can only swell to a lower level, though both alkali metal ions are identically univalent. This tendency becomes obvious for the samples DS50 and DS70 with higher charge density.

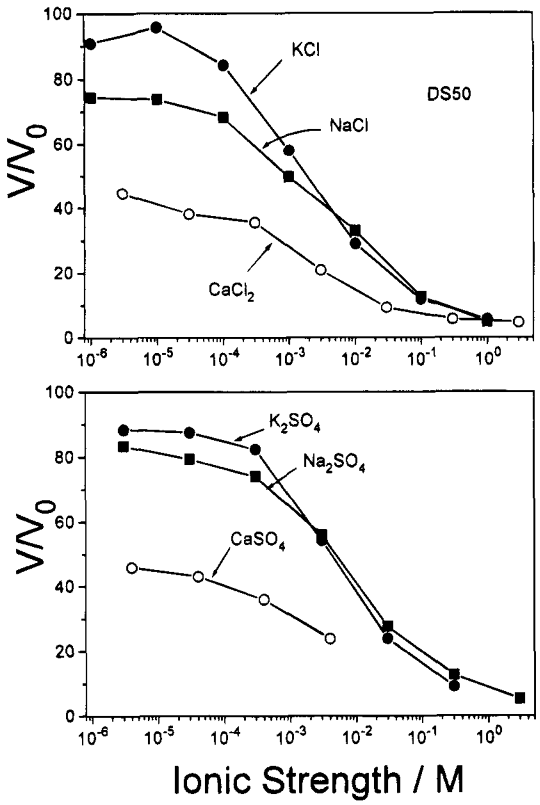

Figure 7. Swelling curves of the DS50 gel in the six types of salt solutions, showing the dependence on the counterion species.

From the composition of the gel just polymerized and the equilibrium swelling ratio, we can evaluate the concentration C_i of mobile ions within each gel sample (here is the counterion only). These mobile ions must remain inside the gel for the maintenance of electroneutrality. As seen also in Table 1, C_i for one kind of counterion varies with the charge density in the samples, reaching a maximum value for the case of the DS30 gel, in contrast to the monotonical increase in the V/V_0 value with the charge density for the same counterion. This result means that the electrostatic interaction will be an important swelling driving force other than the colligative property caused by the mobile ions inside the gel,[18] since the other network parameters are identical for all the samples. We cannot estimate a universal curve correlating C_i with V/V_0 as that done by Ricka and Tanaka,[19] and our data of C_i and V/V_0 locate beyond their scope.

Ionic Species Dependence. Swelling ratios for the DS50 gel in the six salt solutions are summarized in Figure 7, taking the ionic strength as a common concentration variable. The co-ions in the salts are identical in each panel; i.e., Cl^- is in the upper panel and SO_4^{2-} in the lower, and three counterions are concerned in each panel. It is obvious that these data cannot be fit with a single curve, especially for those in Ca^{2+} solutions. This fact suggests the dependence of swelling capacity for the strong polyelectrolyte gel on the chemical nature of counterions even at low and moderate salt concentrations. The swelling ratio at the same ionic strength decreases with the change in counterion species as the sequence of K^+, Na^+, and Ca^{2+}, the same as in pure water, irrespective of the co-ion.

The Debye–Hückel theory is ordinarily applied to calculating the electrostatic free energy for polyelectrolyte in ionized salt solutions, in which the Debye radius κ^{-1} is a measure of shielding power for the medium solution.[20] However, this theory contains only a quantity of the ionic strength to express the concentration and valence of the salt. The above results seems to suggest that the swelling behavior of strong polyelectrolyte gels could hardly be described by the Debye–Hückel theory. We have reported in a previous paper

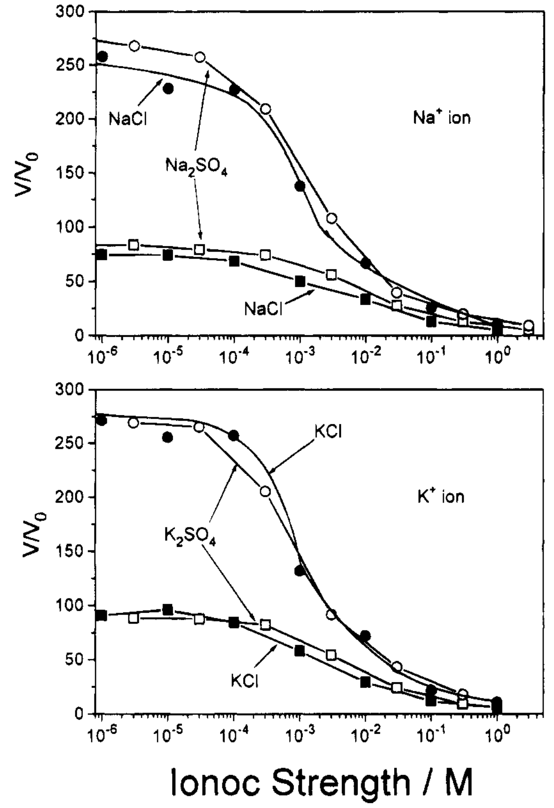

Figure 8. Swelling curves of DS50 (□, ■) and DS70 (○,●) gels in salt solutions with the same cation Na^+ (upper panel) and K^+ (lower panel) and different anions.

that the swelling curve of the DS gels in pure water cannot be quantitatively interpreted by the HID theory,[15] in which the electrostatic interaction is formulated with the Debye–Hückel equation for the free energy.[21]

This dependence on counterion species appears to relate to the counterion condensation because the linear charge density β roughly estimated for our gels will be larger than the Bjerrum length Q when $f > 0.365$ for univalent counterions, resulting in the criterion value ξ of the Manning theory[22,23] larger than unit. The binding of counterions on network chains of the polyion will reduce the repulsion force between the charged groups, leading to the decrease in swelling capacity of the gels.

On the other hand, if we compare the swelling curves for DS50 and DS70 gels in salt solutions having the same cation and different co-ions as shown in Figure 8, the effect induced by the co-ion species cannot be recognized. This may be another evidence of counterion condensation in highly swollen gels.

Figure 9 presents the results of the DS30 gel swollen in the six salt solutions. The swelling curves with four kinds of salts having univalent cations Na^+ and K^+ merge into one, apparently opposite to the above investigation on DS50 and DS70 gels. A reasonable explanation for this is that the charge density in the DS30 gel ($f = 0.2674$) is lower than that in DS50 gels ($f = 0.4318$). In order to observe the counterion effect in polyelectrolyte hydrogels, one should use a sample with quite high charge density to meet the critical condition deduced by Manning.[23] Ricka and Tanaka found that the swelling of a weak polyelectrolyte gel in salt solution was independent of the chemical species of salt ions,[19] but the nominal content of acrylic acid (the ionizable component) was only about 5 mol % in their copolymer gels, much lower than ours. The situation is different for the DS30 gel in Ca^{2+} solutions. The counterion condensation may occur already on the DS30 gel since the criterion for divalent counterions is $f > 0.183$.

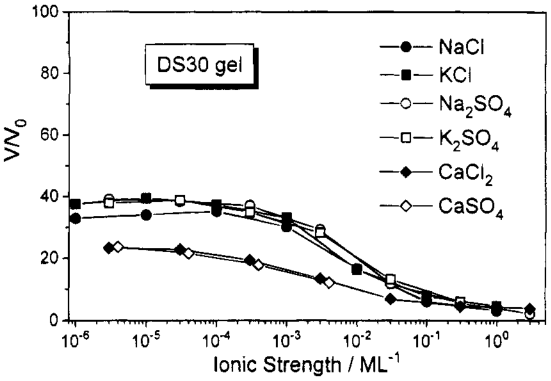

Figure 9. Swelling ratios V/V_0 of the DS30 gel ($f = 0.2674$) plotted against the ionic strength in the six salt solutions as indicated.

Concluding Remarks

The swelling properties of sulfonate gels were studied in water and in six aqueous solutions of NaCl, KCl, $CaCl_2$, Na_2SO_4, K_2SO_4, and $CaSO_4$. Quite concentrated (> 1 M) salt solutions of uni–uni salts would be required to make these gels behave like an uncharged one because the sulfonate group was a very strong electrolyte. In addition, the dependence of swelling capacity on the counterion species was found in water and in salt solutions, especially for the DS50 and DS70 samples of higher charge density. The extent of equilibrated volume increases with the counterion in the following sequence of Ca^{2+}, Na^+, and K^+ at the same ionic strength.

Some abnormal phenomena, such as charge density dependence of the equilibrium modulus and counterion dependence of the swelling ratio, have been found for the strong polyelectrolyte gels, differing from the behavior of weakly charged ionic gels. There may be an essential distinction in the performance between these two sorts of polyelectrolytes. Most of the present theories, however, make no difference in dealing with the characteristics of these two polyelectrolytes except for the dissociation degree and fail in predicting the above observations. The difference in the activity coefficients of counterions is considered with the Manning theory, but it is a limiting law for the infinitely dilute solutions. Therefore, further progress of theory and experiments in this field is being looked at for future studies.

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