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SWELLING OF POLY(VINYL AMINE) GELS: APPLICABILITY OF THE DONNAN THEORY

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ABSTRACT

The volume swelling behaviors of poly(vinyl amine) (PVAm) gels were predicted on the basis of the Donnan theory with the ionic strength of KCl solutions at three different pH (acidic, basic, neutral solution). At neutral (pH 7) and basic (pH 11) conditions, maximum volume swellings were observed in the intermediate concentration of KCl due to the difference in the ionic swelling pressure with the salt concentration. On the contrary, at acidic (pH 3) condition, maximum volume swelling was not found. This was attributed to the full dissociation of the amino groups of PVAm gels even at very low concentration of KCl. In the comparison of the experimental results with the theoretical

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ones, the experimental results agreed fairly well with the simple Donnan theory, verifying a possible application of the Donnan theory to the prediction of the cation-typed gels.

INTRODUCTION

A wide interest in ionic gels has been concentrated on their discontinuous phase transition caused by changing pH of the solvent, by changing salt concentration, and applying an electric field [1-3]. The charged groups in the network have an essential influence on the phase transition behaviors of the gel network. In particular, the phase transition of the ionic gels with the salt concentration was understood in the aspect of the well-known Donnan equilibrium.

The Donnan theory is conventionally used to describe the swelling equilibrium of the ionic gels [3-5]. The Donnan theory is relatively simple because it does take the elastic free energy of the network into account. Ricka *et al*. applied the Donnan theory to predict quantitatively the swelling of polyacryl-amide-acrylic acid copolymer gels as a function of ionic composition of the solvent [3]. They reported that the changes in swelling and swelling extreme occur exactly at predicted ion concentrations in the solutions as long as no multivalent ions are involved.

Previously, we have studied the molecular structures and viscosity behaviors of [6-8]. Polyamines examined were poly(vinyl amine) (PVAm), poly(allyl amine) (PAAm), linear and branched poly(ethylene imines) (LPEI and BPEI, respectively), that provide a full set of primary different molecular structures for amine functional groups. In our previous paper [9], we observed a dramatic viscosity change of PVAm caused by the specific molecular structure of PVAm having the primary amino group linked directly to the main chain. From the viscosity behaviors of PVAm, we developed a new PVAm gels.

In this study, we tried to predict the swelling behavior of PVAm gels having the cationic groups with the concentration of KCl at different pH. The experimental swelling behaviors of PVAm gels in the KCl salt solution at different pH were compared with the theoretical ones. In order to understand the properties of PVAm gel theoretically in KCl solution, the Donnan equilibrium was employed. This concept was established on the basis of the equilibrium distribution of a simple electrolyte between an aqueous polyelectrolyte-electrolyte solution and an aqueous solution of the same simple electrolyte, when a semipermeable membrane separates two phases. Its big advantage followed from its simplicity with the ionic forces depending only on the ionic composition of the solvent and on the concentration of the fixed ionizable groups in the gel.

Theoretical Considerations

Swelling equilibrium between a gel (phase, single prime) and surrounding solution (phase, double prime) must fulfill the criteria,

$$\mu_i^{'} = \mu_i^{''} \tag{1}$$

where, μ is the chemical potential of species i. Equation 1 holds for all components (including ions) that exist both in the gel and in the surrounding solution.

Flory-Huggins equation for the network osmotic pressure (Π^{net}) is given in Equation 2 [13],

$$\Pi_{net} = -\frac{NkT}{v}\left[\phi + \ln(1-\phi) + \frac{1}{2}\frac{\Delta F}{kT}\phi^{2}\right] + \nu kT\left[\frac{1}{2}\frac{\phi}{\phi_0} - \left(\frac{\phi}{\phi_0}\right)^{\frac{1}{3}}\right] \tag{2}$$

where, N is the Avogadro's number, k is the Boltzmann constant, T is the temperature, v is the molar volume of the solvent, ϕ_0 is the volume fraction of the network, ϕ_0 is the volume fraction of the network at the condition that constituent polymer chains have random-walk configurations, ν is the number of constituent chains per unit volume at $\phi_0 = \phi_0$, and ΔF is the free energy decrease associated with the formation of contacts between two polymer segments.

The PVAm gels used in this study are neutralized by the mobile counterion, Cl^-. Cl^- ions in the gel create an excess osmotic pressure. Therefore, the osmotic pressure difference due to the ions (Π_{ion}) is defined in Equation 3,

$$\Pi_{ion} = (n_{gel} - n_0)NkT \tag{3}$$

where, n_{gel} and n_o denote the total molar number of mobile ions per unit volume in the gel and solvent, respectively.

The equilibrium conditions for the ionized gel in salt solution can generally be expressed in Equations 4-7,

$$\frac{c_n^{'}}{c_n^{''}} = 1 \tag{4}$$

$$\frac{c_i}{c_i'} = K^{z_i} \tag{5}$$

$$-\Pi_{net} = \Pi_{ion} = RT\sum\left(c_i - c_i'\right) \tag{6}$$

$$K_a = c_h\left(\frac{\alpha}{1-\alpha}\right) \tag{7}$$

Equation 4 states that the concentration of the neutral solute of type n is the same in the gel (c_n') and in the outer solution (c_n''). Equation 5 describes the distribution of mobile ions of type i between the gel and the solution, here we introduce the Donann ratio K. z_i is the valency of ions of type i in the gel. Equation 6 represents that, in equilibrium, Π_{net} is balanced by Π_{ion}. Equation 7 gives the dissociation constant K_a, α is the degree of dissociation and c_h is the molar concentration of hydrogen ions in the gel.

Inserting Equations 5 and 7 into the charge balance equation in the gel, we can obtain an equation for the Donnan ratio K, (Equation 8),

$$\sum_i z_i K^{z_i} c_i' + \frac{n}{1+\dfrac{c_h' K}{K_a}} = 0 \tag{8}$$

where, n is the concentration of the fixed ions in the gel and c_h' is the molar concentration of hydrogen ions in the outer solution. Therefore, Equation 6 can be rewritten in terms of the Donnan ratio (Equation 9).

$$-\Pi_{net} = \Pi_{ion} = RT\sum_i c_i'\left(K^{z_i} - 1\right) \tag{9}$$

EXPERIMENTAL

Materials

PVAmHCl (poly(vinyl amine)) prepared by radical polymerization of N-vinylforamide followed by acidic hydrolysis [9] was supplied from Mitsubishi Kasei Co., Tokyo. The ^{1}H-NMR spectrum of PVAmHCl showed no signal due to formyl proton (δ 8.1); the amount of N-formyl group in PVAmHCl was less than 1%, if any. The average molecular weight of PVAm was 8.0x10^5 g mol^{-1}

[10]. A bis-epoxide, nonaethylene glycol diglycidyl ether (EX830) used as a crosslinking agent was gifted from Nagase Kasei Co. [11]. Buffer solutions used in the measurement of pH dependency of the PVAm gel volume swelling Q were purchased from Shinyo Pure Chemicals Co.

Preparation of Poly(vinyl amine) Gel

The gels were prepared by using 3.5 g of PVAm and 1.0 g of a bis-epoxide. The 3.5 ml of 2.11 mol l^{-1} PVAm solution was carefully mixed with the 0.7 ml of the bis-epoxide (0.164 mol^{-1}), and then transferred to a glass mold, which was allowed to stand for 4 hours at room temperature to give a transparent gel. The diameter and the thickness of the gel are 10.0 mm and 2.0 mm, respectively. The plate thus prepared was immersed in the distilled water at room temperature for several days before use.

Determination of Degree of Volume Swelling Q

In order to discuss how to measure and calculate the volume change of PVAm gels at various concentrations of KCl solutions, the degree of volume swelling Q of the gels is defined in Equation 10.

$$Q = \left(\frac{V}{V_0} - 1\right) \times 100(\%) \tag{10}$$

where, V_0 and V are the volume of the gel before and after swelling, respectively. Assuming that the gel swells isotropically, Equation 11 can be achieved.

$$\frac{V}{V_0} = \left(\frac{D}{D_0}\right)^3 \tag{11}$$

where, D_0 and D represent the corresponding gel diameters. Knowing the swelling capacity of the gels in the solution, we determined their swelling capacity for a given volume (diameter) change. The swelling was carried out with varying the KCl concentration in the ionic strength-controlled buffer solutions (pH 3, 7, and 11) at 25°C. All measurements were performed under CO_2-free conditions.

RESULTS AND DISCUSSION

A basic assumption for the present theory is that the swelling of the charged gels depend only on the valency and concentration of the ions in the solution but not on their size and chemical properties. Ricka *et al*. nicely verified this assumption by testing the swelling in neutral solutions of various salts [3]. They also justified the assumption of no interaction between the neutral network and the ionic solute by measuring the swelling of the charge-free acryamide gels. In this study, we used these basic assumptions without further verification.

Figure 1 shows the dependency of volume swelling Q on pH for PVAm gel. The respective Q value was determined after the gel volume reached constant in a pH buffer solution. The PVAm gel took the most swollen state at around pH 3. In the regions of pH<3 and pH>3, however, the gel came to contract. The degree of dissociation is 100 percent around pH 3, i.e., all the amino groups attached to the polymer chain are protonated [8]. Thus, the polymer chains take the most stretched structure in this pH region because of the electrostatic repulsion among neighboring ammonium groups. On the other hand, in regions of pH<3 and pH>3, the Q value decreased dramatically since the repulsion is relaxed and the flexibility of chain is enhanced [8, 9].

Firstly, the swelling behaviors of PVAm gels in a solution of a univalent salt of KCl were observed at pH 7. Figure 2 shows the volume swelling Q change of PVAm gels with the concentration of KCl at pH 7. The maximum swelling was

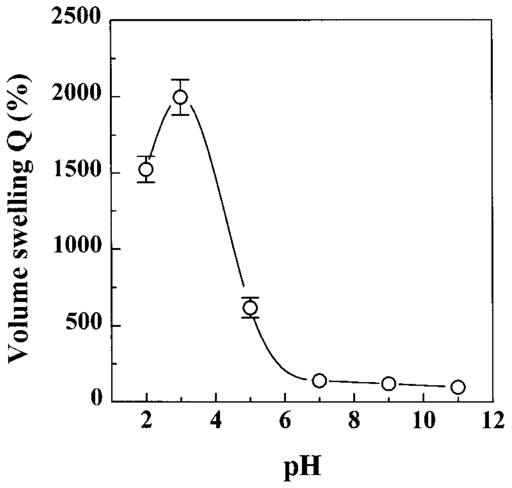

Figure 1. The dependency of the volume swelling Q on pH for PVAm gel.

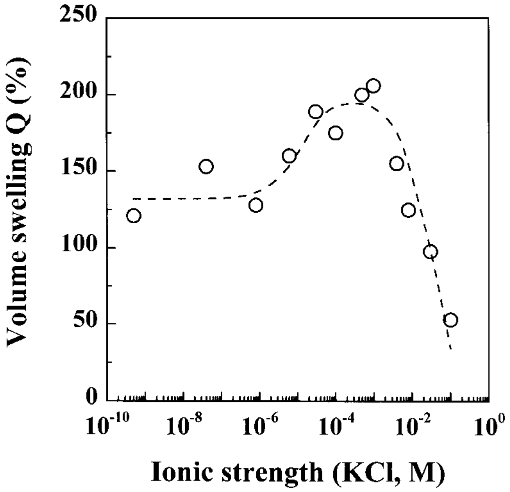

Figure 2. The volume swelling Q change of PVAm gels with the concentration of KCl at pH 7. The dashed line is the calculated curve from Donnan theory.

observed at the intermediate concentration of KCl. This can be explained by considering that as the concentration of KCl increased from zero, the ion swelling pressure increased because of the increasing production of free counterions by dissociation of amino groups in PVAm gels. Continuously, after the completion of the dissociation of amines, any further increase in KCl concentration reduced the ion swelling pressure. So the swelling degree was decreased. Above results were in good agreement with the work of Ricka *et al*. [3], except that the ions in the gels were exchanged for the anion salts. In this observation, however, it was important that the cation-typed PVAm gels were also possibly applicable to the prediction of the swelling behaviors by using the Donnan theory.

Figure 3 shows the volume swelling Q change of PVAm gels with the concentration of KCl at pH 11. At high pH, the maximum swelling was also observed at the intermediate concentration of KCl. However, the overall swelling degree was rather reduced and the maximum swelling was displayed at higher concentration of KCl, compared with that in Figure 2. This was believed that at high pH, the dissociation of the amino groups of PVAm gels restricted by the rich OH^- ions, resulting in somewhat lower degree of volume swelling. Therefore, higher concentration of KCl seemed to be required for better dissociation of the amino groups in the gels.

When the pH of salt solutions lowered, all amino groups in the gel are completely dissociated, even at very low salt concentration. In order to confirm

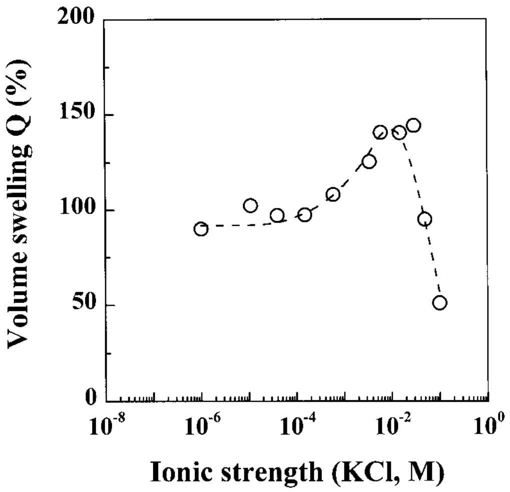

Figure 3. The volume swelling Q change of PVAm gels with the concentration of KCl at pH 11. The dashed line is the calculated curve from Donnan theory.

this, the volume swelling Q change of PVAm gels was observed with the concentration of KCl at pH 3, and shown in Figure 4. The maximum in the swelling curve could not found. The swelling showed a plateau at low salt concentration. Then, as the salt concentration increased, a deswelling was observed. Lastly, the

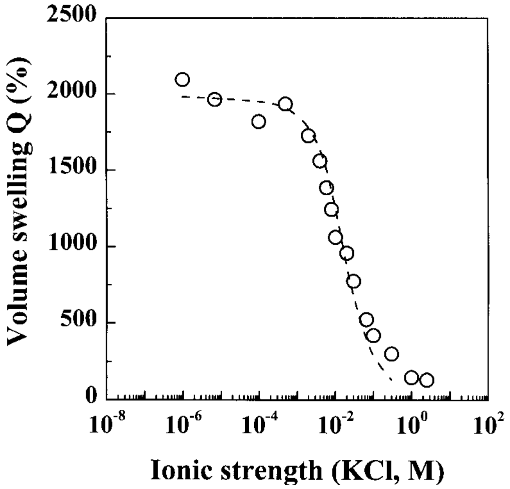

Figure 4. The volume swelling Q change of PVAm gels with the concentration of KCl at pH 3. The dashed line is the calculated curve from Donnan theory.

leveling off was followed at high salt concentration. This was because after the full dissociation of the amino groups of PVAm gels at low salt concentration, the further increase of the salt concentration resulted in the reduced swelling pressure, just like the cases of pH 7 and 11.

We compared the experimental data with the theoretical curves for the swelling ratio Q as a function of KCl concentration, as shown in Figures 2-4 (the dashed lines are the calculated curves). In all three cases (pH 3, 7, and 11), the theory agreed fairly well with the experimental ones. In the prediction of the swelling behaviors of ionic gels, it is common to consider the interactions between the ionized fixed charges and the salt ions by using a correction, such as the Debye-Hückel correction. So the prediction can be improved. However, just as Ricka *et al*. said in their paper [3], for a univalent salt solution, it was possible to represent the theory without using a further correction. In our study, it could be also observed that the theoretical curves were well matched with the experimental results without using any other correction.

CONCLUSION

The volume swelling behaviors of PVAm gels with the concentration of KCl at different pH were predicted successfully by using a simple theory, based on Donnan equilibrium. This suggests that the cation-typed gels also be possibly applicable to the prediction of the swelling behaviors by using the Donnan theory. One big advantage in the application of this theory was its simplicity with the ionic forces depending only on the ionic composition of the solvent and on the concentration of the fixed ionizable amino groups in the PVAm gels. Moreover, the theoretical results were fairly well matched with the experimental ones, which means that the interactions between the localized fixed charges and the salt ions could be neglected.

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