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Analogy between Swelling of Gels and Intrinsic Viscosity of Polymer Solutions for Ion-Complexed Poly(vinyl alcohol) in Aqueous Medium

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ABSTRACT: The swelling/shrinking behavior of chemically cross-linked poly(vinyl alcohol) (PVA) gel complexed with borate ions in aqueous medium and the intrinsic viscosity behavior of the corresponding polymer solutions were compared as a function of the boric acid concentration, b. The equilibrium swelling ratio of the gels, Q/Q_0, and the intrinsic viscosity ratio of the solutions, $[\eta]/[\eta]_0$, were in good accordance when the NaOH concentration, [NaOH], is high enough, where Q_0 and $[\eta]_0$ are the equilibrium swelling volume of the gel and the intrinsic viscosity of the solution without borate ions, respectively. NaOH was added so as to ionize boric acid. However, a significant difference was observed when [NaOH] was lowered. The comparison of Q/Q_0 and $[\eta]/[\eta]_0$ allowed one to elucidate the essential difference in the swelling (or expansion) behavior of polymer chains, which is the presence (in a gel) and absence (in a dilute polymer solution) of the Donnan potential. A free energy function for ion-complexed polymer gels is proposed.

Introduction

Elucidation of inter- and intramolecular interactions of polymer chains in a solvent is of great significance. These interactions rule not only the size and conformation of the chain molecules but also their higher-order structures. Particularly in the case of biopolymers, there exist hydrophobic, hydrogen bonding, and electrostatic interactions, in addition to van der Waals interactions, all of which are responsible for unique configurations and biological functions, such as catalytic reactions and molecular recognition.

Polymer gels in water are relevant models for investigations of molecular interactions because of the following reasons: (1) One can easily bestow any of these interactions to the polymer chains in the gel, and (2) the variation of the molecular interactions due to changes of environmental variables, such as solvent composition,[1,2] temperature,[3] and pH,[4] can be easily monitored as a size change of the gel with high precision.[5] Poly(vinyl alcohol) (PVA) gels in water are capable of ion complexation with borate ions. By adding borate ions, PVA−borate ion complexes are formed and the complexed chains behave as polyelectrolytes.[6−10] The PVA−borate complex also leads to a physical cross-linking of PVA chains, giving rise to gelation as well as precipitation or demixing.[11] Thus, the PVA−borate aqueous solution becomes very sensitive to temperature, borate ion concentration, and pH.

Since the electrostatic force is a long range interaction, it is expected that a theoretical treatment for polymer−ion complexes becomes formidable. However, such a difficulty is circumvented when a large amount of ions is added to the system. This results from the fact that the added ions screen the bare electrostatic interaction among the ions attached to polymer chains. In the previous paper, we showed an analogy of the swelling behavior of chemically cross-linked PVA gels and the intrinsic viscosity of the corresponding PVA aqueous solutions as a function of boric acid concentration.[12] An excellent agreement between the cooperative diffusion constants of the gel network obtained by the dynamics of gel swelling/shrinking and those of the PVA solution measured by dynamic light scattering was also reported. Therefore, by knowing the swelling behavior of the gel, one can deduce a single chain behavior of the corresponding polymer solution without any sophisticated methods, like light scattering or small-angle X-ray scattering, based on an analogy of “the one-to-one correspondence in the size of a single polymer chain in a solvent with that of a subchain in a network”. However, before applying the analogy, which is a hypothesis at this stage, one has to examine the validity of the analogy. This is the objective of this paper.

First, in this paper, we present the results of the viscosity behavior of PVA aqueous solutions and swelling behavior of chemically cross-linked PVA gels in the presence of borate ions. Similarities in boric acid concentration dependence between the intrinsic viscosity of a PVA solution and the swelling ratio of a PVA gel will be shown. Second, a theoretical consideration is made on the basis of the Leibler−Pezron−Pincus (LPP) theory for PVA−borate solutions.[8] Then a modified theory to describe the free energy of ion-complexed polymer gels will be proposed.

Experimental Section

1. Samples. Resaponified poly(vinyl alcohol) (PVA) powder, having the degree of polymerization of 1800, was dissolved in deionized water at 95 °C with stirring. After homogenization, the PVA solution was gradually cooled to room temperature. Thus a homogeneous PVA stock solution was prepared. The solution was mixed and diluted with aqueous solutions of boric acid and sodium hydroxide having predetermined concentrations. Lightly cross-linked PVA gels were prepared in a 5 mm or 10 mm diameter test tube by cross-linking the PVA aqueous solutions with glutaraldehyde under acidic conditions of HCl at 30 °C for 48 h. The sol fraction was removed from the PVA gels with a large amount of water. The details of the sample preparation are given elsewhere.[12]

2. Viscosity Measurement. The viscosity of the solution was measured with a Ubbelohde capillary viscometer at 30.0 °C. The time lag to pass two menisci on the viscometer was recorded and converted to the specific viscosity, η_{sp}, which is

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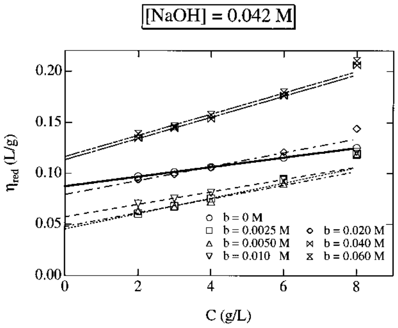

Figure 1. Polymer concentration, *C*, dependence of the reduced viscosity, η_{red}, for PVA aqueous solutions having various boric acid concentrations, *b*.

defined by

$$\eta_{sp} = (\eta - \eta_0)/\eta_0 \tag{1}$$

where η and η_0 are the solution and solvent viscosities, respectively. Note that η_0 is the viscosity for a PVA solution without borate ions. Measurements were repeated at least three times so as to achieve a relative error of less than 0.1%.

3. Swelling Experiment. The swelling or shrinking ratio of the PVA gels was estimated by measuring the diameter, *d*, of cylindrical gels. Either photographic recording or observation under an inverted microscope coupled with an electronic scaler via a video camera was employed to determine *d*. The specific swelling ratio, Q/Q_0, was calculated from

$$Q/Q_0 = d^3/d_0^{\ 3} \tag{2}$$

where d_0 is the diameter of a gel immersed in a solution without borate ions. All measurements were conducted at 25 °C. The temperature dependence of *d* and d_0 was negligible in the temperature range between 20 and 30 °C.

Results

1. Solution Viscosity. Figure 1 shows the variation of the reduced viscosities, $\eta_{red} \equiv \eta_{sp}/C$, for the case of [NaOH] = 0.042 M, as a function of the PVA concentration. The boric acid concentration, *b*, was varied from 0 to 0.06 M. Each set of the data points roughly falls on a straight line, as characterized by the Huggins equation,[13]

$$\eta_{red} \equiv \frac{\eta_{sp}}{C} = [\eta] + k_1[\eta]^2C + ... \tag{3}$$

where $[\eta]$ is the intrinsic viscosity and k_1 is the Huggins constant. $[\eta]$ is a measure of the size of the polymer chain, and k_1 is a parameter indicating the strength of the two-body interaction between neighboring chains. Note that the intercept moves to a lower side and then goes up with increasing *b*. Even the PVA–borate ion complexes are regarded as polyelectrolytes; an upturn in η_{red}, typical for polyelectrolyte solutions, was not observed in this system. This is due to the presence of a strong base, i.e., NaOH, in the system, which screens the electrostatic interaction between the charges on the chain. In the case of PVA–Congo red ion complex, where polymer complexation takes place without a strong base or acid, a steep upturn in η_{red} was observed.[14,15]

Figure 2 shows the variation of $[\eta]$, the intercept of η_{red} in Figure 1, as a function of *b*, which clearly shows an oscillation of $[\eta]$ with respect to *b*. $[\eta]$ decreases first at low *b* and then increases with *b*. This trend is found in all cases having different [NaOH]'s. However, the higher the [NaOH], the lower $[\eta]$ is. A similar phenomenon was reported by Ochiai et al.[6] for PVA–borax aqueous solutions. Leibler et al. interpreted this on the basis of a Flory-type mean field theory.[8] The first reduction of $[\eta]$ is due to a domination of intrachain cross-linking, and the following increase in $[\eta]$ results from an increase of intrachain electrostatic repulsion. Note that no effect of interchain interactions is expected in $[\eta]$ because $[\eta]$ is taken at the limit of zero-polymer concentration. The details of the theory will be discussed later so as to explain the *b* dependence of the specific swelling ratio, Q/Q_0, of gels.

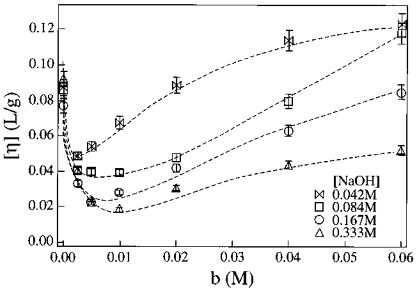

Figure 2. Intrinsic viscosity, $[\eta]$, variations as a function of *b*. It is clearly shown that $[\eta]$ depends on the NaOH concentration, [NaOH], which is added to ionize boric acid. The dashed curves are drawn for the eye.

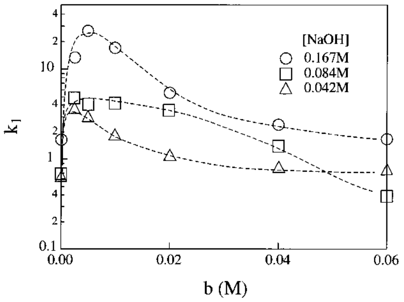

Figure 3. *b* dependence of the Huggins constant, k_1. The dashed curves are drawn for the eye.

Since k_1 is a measure of the strength of the two-body (interchain) interaction, it is worthy to examine the variation of k_1 with *b*. Figure 3 shows the *b* dependence of k_1, which is estimated from Figure 1 and eq 3. Interestingly, k_1 increases dramatically by addition of a small amount of borate ions, i.e., $b = 0.0025$ M, and then gradually decreases with *b*. The first upturn indicates that a strong electrostatic repulsive interaction is switched on between charged chains although the individual polymer chains are contracted due to an intrachain cross-linking (see Figure 2). The following gradual decrease of k_1 is ascribed to the fact that an increase of free ions screens the bare electrostatic interaction between polymer chains.

2. Swelling Ratio of Gels. The specific swelling ratio of gels, Q/Q_0, is a function of time since it takes a finite time for a piece of gel to attain a swelling equilibrium. The time course of Q/Q_0 is characterized by the collective diffusion constant, *D*, which is of the order of 10^{-7} cm^2/s.[12] Figure 4 shows the time course of Q/Q_0 for the cases of (a) [NaOH] = 0.085 M and (b) [NaOH] = 0.042 M. Note that some gels swell and the others shrink, depending on *b*. A swelling/shrinking equilibrium seems to be attained at $t \geq 1200$ h in both cases (10 mm diameter gel). The specific swelling ratio of gels, Q/Q_0, was obtained at this equilibrium. The kinetics of the swelling/shrinking was already discussed elsewhere.[12] Recently, we found an interesting phe-

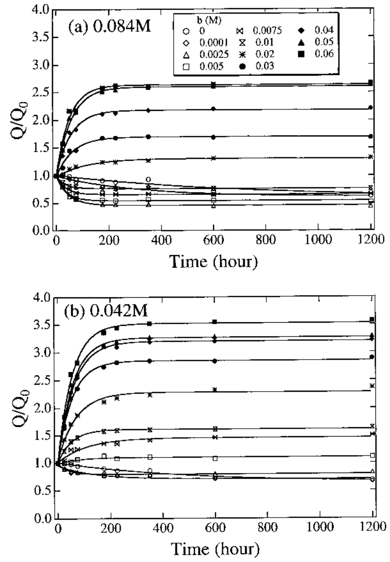

Figure 4. Time evolution of the swelling ratio, Q/Q_0, for PVA gels immersed in aqueous solutions of boric acid, *b*, and NaOH: (a) [NaOH] = 0.084 M; (b) [NaOH] = 0.042 M.

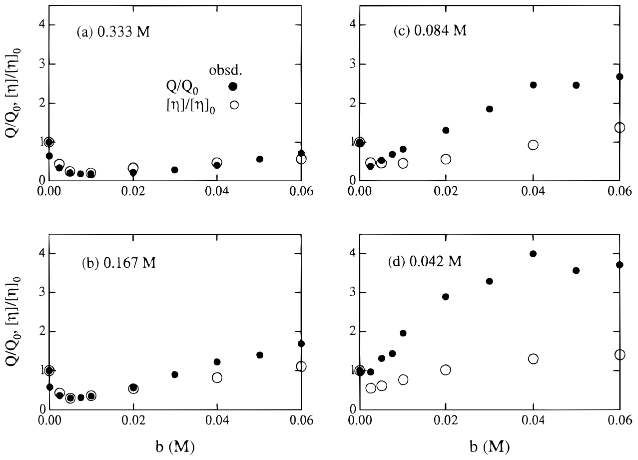

Figure 5. Comparison of the *b* dependencies of Q/Q_0 for gels and $[\eta]/[\eta]_0$ for the corresponding PVA solutions. The NaOH concentrations are (a) 0.333, (b) 0.167, (c) 0.084, and (d) 0.042 M.

nomenon in two-step swelling/shrinking kinetics, which will be reported in the forthcoming paper.[16]

3. Comparison of the Intrinsic Viscosity and Swelling Behavior. Solid circles in Figure 5 show the variations of Q/Q_0 with *b* for (a) [NaOH] = 0.333, (b) [NaOH] = 0.167, (c) [NaOH] = 0.084, and (d) [NaOH] = 0.042 M. The viscosity ratios, $[\eta]/[\eta]_0$, for the corresponding polymer solutions are also shown in the figure with open circles. In Figure 5a, an excellent agreement between Q/Q_0 and $[\eta]/[\eta]_0$ is obtained. This eloquently shows that gels are macroscopic manifestations of the size change of individual polymer chains in a solvent. By decreasing [NaOH], however, a deviation of Q/Q_0 from $[\eta]/[\eta]_0$ becomes clear. Gels swell more than the expansion of the corresponding polymer chains at a lower [NaOH] and at a higher *b*. In the next section, we try to elucidate the origin of the deviation of Q/Q_0 behavior from that of $[\eta]/[\eta]_0$ and discuss the limitation of the hypothesis on the similarity of gels and solutions.

Discussion

1. Mean Field Theory for Weakly Charged Polymer Solutions (LPP Theory). The oscillation of $[\eta]/[\eta]_0$ with *b*, which was first observed by Ochiai et al.,[6] results from several kinds of contributions, such as the excluded volume effect, the electrostatic interaction, and chemical equilibria on complexation. The importance of these contributions was pointed out by Leibler, Pezron, and Pincus (LPP).[8] The free energy of a chain, *F*, of which the fraction *f* ($0 < f < 1$) is complexed with ions is given by

$$\frac{F}{kT} = \frac{3R^2}{2Na^2} + v\frac{N^2(1-f)^2}{R^3} + v'\frac{f^2N^2}{R^3} - uK_2\frac{f(1-f)N^2}{R^3} \qquad (4)$$

where kT is the Boltzmann energy, R is the end-to-end distance of the chain having the degree of polymerization N and the monomeric length a. v is the excluded volume, v' is the additional excluded volume due to the electrostatic interaction, and uK_2 is the energy gain in units of kT for one cross-link formation. The equilibrium size of the chain is given by $dF/dR = 0$. The intrinsic viscosity is obtained by using the relation $[\eta] \equiv R^3/N$, and $R_0 \equiv v^{1/5}N^{3/5}a^{2/5}$ as follows:

$$\frac{[\eta]}{[\eta]_0} = \frac{R^3}{R_0^{\,3}} = \left[(1-f)^2 + \frac{v'}{v}f^2 - \frac{uK_2}{v}f(1-f)\right]^{3/5} \qquad (5)$$

where R_0 is the end-to-end distance of the chain in the absence of borate ions. The additional excluded volume, v', is given by

$$v' = 1/2N_A I \qquad (6)$$

where N_A and I are the Avogadro number and the ionic strength, respectively. The fraction of charged segments on a PVA chain, *f*, is given by

$$f = \frac{\tilde{K}_1 C_M}{1 + \tilde{K}_1 C_M} \cong \frac{\tilde{K}_1 b}{1 + \tilde{K}_1 b} \qquad \text{for } b < [\mathrm{NaOH}] \qquad (7)$$

where $\tilde{K}_1$ is the effective monocomplexation constant and C_M is the free borate ion concentration. $\tilde{K}_1$ is dependent on the ionic strength and is given by

$$\tilde{K}_1 = K_1 \exp\left[-\frac{\alpha l_B}{L}\exp(-\kappa L)\right] \qquad (8)$$

where K_1 is the monocomplexation constant in the absence of electrostatic effect, α is a numerical factor, l_B is the Bjerrum length, and κ^{-1} is the Debye screening length. L is the average spatial distance between two neighboring charges on a chain and is given by

$$L = n^{1/2}a \qquad (9)$$

where n is the number of segments between the charges. n is related to f in the following form

$$n = \frac{1}{f + N_c^{\,-1}} \qquad (10)$$

where N_c is the number of segments between neighboring chemical cross-links. In eq 10, we consider the contribution of the chemical cross-link. Therefore, n becomes N_c for $f = 0$ and 1 for $f = 1$. In the original LPP theory, the term N_c^{-1} was not considered, which is the case of a linear polymer chain without cross-links. The ionic strength, I, is given by the sum of the concentrations of Na^+, OH^-, and borate ions, $[B(OH)_4^-]$

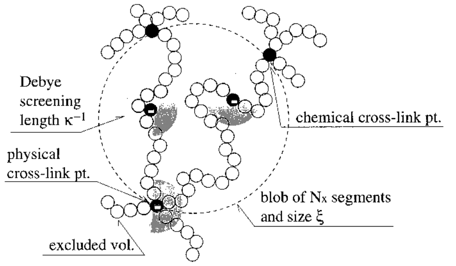

Figure 6. Blob model for the swelling equilibrium on weakly charged chemically cross-linked gels.

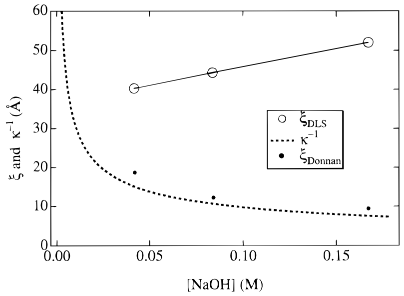

Figure 7. [NaOH] dependencies of the correlation length, ξ_{DLS}, estimated by dynamic light scattering, and the Debye screening length, κ^{-1}. Dots represent ξ_{Donnan}, which are discussed in conjunction with Figure 9.

$\approx$ b. However, since the same amount of NaOH is consumed to ionize boric acid, I is the same as [Na$^+$],

$$I = \frac{1}{2}\{[\mathrm{Na}^+] + b + ([\mathrm{OH}^-] - b)\} = [\mathrm{Na}^+] \quad (11)$$

Thus, wherever [NaOH] > b, the concentration of ionized borate ions [B(OH)$_4^-$] $\approx b$. On the other hand, for [NaOH] $\leq b$, [B(OH)$_4^-$] = [NaOH] = I. This is why a level off in Q/Q_0 and in $[\eta]/[\eta]_0$ is observed for $b \geq 0.042$ M in Figure 5 d.

2. Blob Model for Ion-Complexed Polymer Network. Figure 6 schematically shows a blob in a polymer network. Open and filled circles denote monomeric units and cross-link points, respectively. Several monomer units are charged by ion complexation, as illustrated by a minus sign, some of which participate in cross-linking (physical cross-links). In a swelling equilibrium, a blob is determined by these chemical and physical cross-link points and is characterized by size ξ. When a polymer chain is charged, electrostatic interaction is generated. Since this is a long range interaction, the blob concept, i.e., elimination of long range interactions larger than ξ, becomes invalid, in principle. However, if the free charge concentration is high enough, the Debye screening effect, characterized by the Debye screening length, κ^{-1}, becomes significantly small compared with ξ, i.e., $\kappa^{-1} \ll \xi$. This is when the blob model recovers. In this case, the LPP theory can be applied to a blob because both a polymer chain in a dilute regime (LPP) and a subchain in a blob can be treated as a single chain problem.

Figure 7 shows the [NaOH] dependence of the correlation length, ξ_{DLS}, measured by dynamic light scattering (DLS)[16] and that of the Debye length, κ^{-1}. ξ_{DLS} is estimated by

$$\xi_{DLS} = \frac{kT}{6\pi\eta_s D_{coop}} \quad (12)$$

where η_s is the solvent viscosity and D_{coop} is the average cooperative diffusion constant obtained by DLS in the concentration range $0.02 \leq b \leq 0.06$ M. By assuming $\xi \cong \xi_{DLS}$, the criterion of the blob model, $\kappa^{-1} \ll \xi$ seems to be satisfied in this study since ξ is a few times larger than κ^{-1}. The dots in the figure indicate ξ_{Donnan} which will be discussed later.

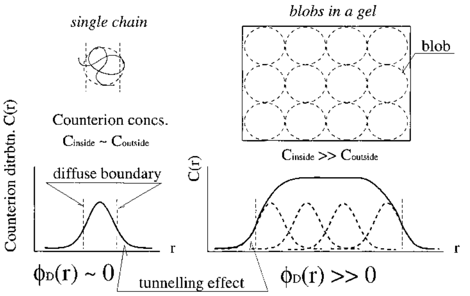

Figure 8. Comparison of the Donnan potential, $\phi_D(r)$, for a charged single chain and a charged gel.

3. Donnan Potential. If the blob model for the ion-complexed network is relevant, we expect a similar behavior between Q/Q_0 and $[\eta]/[\eta]_0$. The experimental evidence, however, does not support this prediction, particularly for low [NaOH]'s. This contradiction can be answered by realizing the absence of the Donnan potential term in the LPP theory. The Donnan potential is very important for ionized gels, which leads to a dramatic swelling power. Though many researchers describe the Donnan potential with their own manner, the essential part is the same and the potential is given by the free energy of the counterions in a gel.[17-25]

The Donnan potential term, however, does not need to be taken into account in the original LPP theory since there is no "Donnan membrane" for a dilute polymer solution. Figure 8 shows the difference of the significance of the Donnan potential between the single polymer chain in a dilute solution and a gel in a solvent. In the case of a single chain, the counterion distribution, $C_{ion}(r)$, has a diffuse boundary around the envelope of the chain. However, $C_{ion}(r)$'s for blob chains in a gel are heavily overlapped with each other and is highly accumulated in the gel because of the close packing of individual blobs. Though a diffuse distribution of $C_{ion}(r)$ may be seen at the gel boundary as a "tunneling effect", the difference of the Donnan membrane effect between the two systems is clear.

This problem can be clearly recognized by comparing the LPP theory with the Flory–Rehner (FR) theory for gel swelling.[17,18] A term-to-term comparison of both equations, as described in the Appendix, discloses the following facts: Though the elastic and the excluded-volume terms are the same between LPP and FR equations, the LPP does not have the Donnan potential term and the FR does not have the electrostatic interaction term. Thus, when one applies the LPP theory, the Donnan potential term has to be added to the LPP equation. In the previous paper,[12] we simply applied this LPP theory for a single polymer chain to a blob in a gel without any extensive discussion, and we got the following equation,

$$\frac{F}{kT} = \frac{3\xi^2}{2\xi_{00}{}^2} + v\frac{N_x{}^2(1-f)^2}{\xi^3} + v'\frac{N_x{}^2 f^2}{\xi^3} - uK_2\frac{f(1-f)N_x{}^2}{\xi^3} + \ln\left(\frac{\xi_{00}{}^3}{\xi^3}\right)^{\gamma} \quad (13)$$

where ξ and ξ_{00} are the size of the blob having polymerization index N_x with borate ions and that of the blob in the unperturbed state, respectively. The unperturbed dimension of the blob is given by

$$\xi_{00} = N_x^{1/2} a \tag{14}$$

The parameter γ is the excess number of counterions per blob in the gel, which is given by

$$\gamma = \xi^3(\rho_i - \rho_o) \equiv \xi^3 \Delta\rho \tag{15}$$

where ρ_i and ρ_o are the counterion (=H^+ and/or Na^+) concentrations inside (i) and outside (o) the gel, respectively. We discuss here the validity of this treatment. Equation 13 can be rewritten to

$$\frac{F}{kT} = \frac{3\xi^2}{2\xi_{00}^2} + \frac{A}{\xi^3} + \gamma \ln\left(\frac{\xi_{00}^3}{\xi^3}\right) \tag{16}$$

where

$$A = [v(1-f)^2 + v'f^2 - uK_2 f(1-f)]N_x^2 \tag{17}$$

By differentiating F with respect to ξ, one gets the following equation:

$$z^5 - \gamma\left(\frac{\xi_{00}}{\xi_0}\right)^2 z^3 - \frac{\xi_{00}^2}{\xi_0^5} A = 0 \tag{18}$$

where $z = \xi/\xi_0$ and

$$\xi_0 = v^{1/5} N_x^{3/5} a^{2/5} \tag{19}$$

which is the blob size in the absence of borate ions. If there is no Donnan potential contribution, the second term of eq 16 is zero, i.e., $\gamma = 0$. Thus we simply solve eq 16 and the solution is

$$z_0 \equiv \left(\frac{[\eta]}{[\eta]_0}\right)^{1/3} = \left(\frac{\xi_{00}^2}{\xi_0^5} A\right)^{1/5} = \left[\frac{v(1-f)^2 + v'f^2 - uK_2 f(1-f)}{v}\right]^{1/5} \tag{20}$$

which is the case of the polymer solution. Note that there is no N_x dependence in z_0. On the other hand, for $\gamma \neq 0$, eq 18 has to be solved numerically for given values of A and γ. The parameter γ is the excess number of counterions per blob having a volume ξ^3. In the case of monovalent polyelectrolyte in the presence of monovalent salt, the Donnan membrane equilibrium gives the following concentration difference between inside and outside the membrane (gel):[22,26]

$$\Delta C = \sqrt{(z_p C_p)^2 + 4I^2} - 2I \tag{21}$$

where z_p and C_p are the number of noncondensed charges per monomer residue and the polymer concentration in monomeric unit, respectively. We assumed here an equivalence of the activity coefficients inside and outside the membrane. Since ΔC has the units mol/L, one has to convert this to ions/Å^3 so as to obtain $\Delta\rho$ in eq 15. γ is finally obtained as

$$\gamma = \sqrt{(fN_x)^2 + 4(KI)^2} - 2KI \tag{22}$$

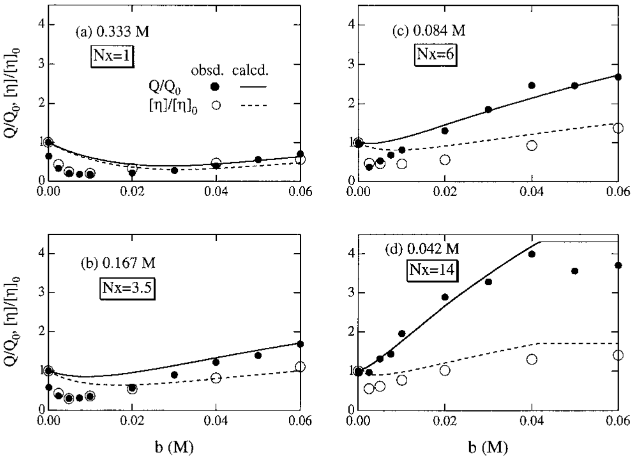

Figure 9. Comparison of the observed and calculated values of Q/Q_0 for gels and $[\eta]/[\eta]_0$ for the corresponding PVA solutions.

where K is a conversion factor given by

$$K = 10^{-27} \xi^3 N_A$$

In the following calculation, we further assume $\xi \approx \xi_0 \approx \xi_{00}$ to simplify the analysis. Thus we obtain the following equation

$$z^5 - \gamma z^3 - z_0^5 = 0 \tag{23}$$

4. Numerical Calculation of the Swelling Ratios. Figure 9 shows the comparison of the observed and theoretical values of Q/Q_0 and $[\eta]/[\eta]_0$ for (a) [NaOH] = 0.333, (b) 0.167, (c) 0.084, and (d) 0.042 M. The open and closed symbols represent the observed $[\eta]/[\eta]_0$ and Q/Q_0, respectively. The calculated curves were obtained with eq 5 and by solving eq 23, respectively, for $[\eta]/[\eta]_0$ and Q/Q_0. The following values, $K_1 = 11$ L/mol, $uK_2N_A = 0.7$ L/mol, $a = 5$ Å, $v = (7\ \text{Å})^3/2$, and $\alpha = 4$, were chosen to calculate $[\eta]/[\eta]_0$. Although all the values except for uK_2 were the same as those employed by Leibler et al.,[8] a smaller value of uK_2 was chosen. The literature value of uK_2 leads to a negative value of the parentheses of eq 5, indicating a phase separation. However, in reality, the polymer solution at [NaOH] = 0.333 M was homogeneous and no phase separation was observed. Therefore we reduced the value of uK_2.

For Q/Q_0, the same set of parameters were employed. The deviation of Q/Q_0 from $[\eta]/[\eta]_0$ is reproduced by varying N_x. As can be seen in Figure 9, a relatively good agreement between the observed and theoretical values is attained for both Q/Q_0 and $[\eta]/[\eta]_0$ irrespective of the NaOH concentration. Disagreement between the observed and calculated values at low b may be due to an underestimation of the ionic strength dependence of the complexation constant. The level off of the calculated functions of Q/Q_0 and $[\eta]/[\eta]_0$ observed in the case of [NaOH] = 0.042 M is also well recovered, which is due to the lack of NaOH to ionize boric acid because of $b >$ [NaOH]. This is proved by Figure 10, where pH for the case of [NaOH] = 0.042 M suddenly drops around $b = 0.04$ M.

The fitting parameter, N_x (the polymerization index for a blob chain), seems to be considerably smaller than it should be. Note that N_x is expected to be about 60–100 ($\approx(\xi_{00}/a)^2$) from the DLS data in Figure 7. When one uses a larger number for N_x, the calculated Q/Q_0 becomes remarkably large and it does not fit with the

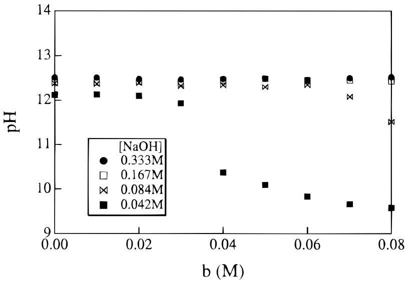

Figure 10. *b* dependence of pH for aqueous solutions having different concentrations of NaOH.

observed one at all. This problem is accounted for as follows: Since the salt concentration, C_s (=[NaOH]), is considerably high, a strong ionic screening effect has to be taken into account. As a matter of fact, the fitted N_x gives a different value in ξ (=ξ_{Donnan}) which is rather closer to κ^{-1}, as shown in Figure 7. This may indicate that the "ionic" correlation length ($\xi \approx \kappa^{-1}$) is not the same as the "spatial" correlation (ξ_{DLS}). In other words, the Donnan potential is strongly suppressed by the counterion atmosphere when C_s (=[NaOH]) is high, as employed in this work. This may be the reason why a small (even unrealistic) number of N_x has to be employed to simulate Q/Q_0.

As discussed above, the variations of $[\eta]/[\eta]_0$ and Q/Q_0 with *b* are reconstructed on the basis of the LPP theory and its modification. The main reason for the deviation of Q/Q_0 is ascribed to the presence of Donnan potential in a gel. The calculated Q/Q_0 curves well account for the experimental findings. However, since the systems studied here are in the regime of a semidilute polymer solution (not a dilute) and the salt concentration is high, which is far from the case of typical polyelectrolyte solutions, many assumptions employed in the derivation have to be re-examined so as to improve the theory by taking account of the Debye limiting law, equality of the activity coefficient, and so on.

Concluding Remarks

The comparison of the swelling ratio, Q/Q_0, of chemically cross-linked PVA gels in a borate solution with the intrinsic viscosity ratio, $[\eta]/[\eta]_0$, of the corresponding PVA solution discloses the following facts: (1) Weakly cross-linked chemical gels have a local environment similar to that of the corresponding polymer solution. This is explained with the analogy between a single chain in a dilute solution and a blob in a network when the electrostatic screening effect is dominant. (2) The swelling ratio, Q/Q_0, is larger than the intrinsic viscosity ratio, $[\eta]/[\eta]_0$, due to the presence of Donnan potential in the gel. (3) By taking account of Donnan potential in the Leibler−Pezron−Pincus theory, the variation of Q/Q_0 with *b* is semiquantitatively interpreted.

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Appendix

Let us compare the LPP theory for an isolated charged polymer chain with the Flory−Rehner (FR) theory for gel swelling. The LPP free energy (eq 4) is defined for a single polymer chain and consists of the elastic free energy, $F^{\text{LPP}}{}_{\text{el}}$, the mixing free energy, $F^{\text{LPP}}{}_{\text{mix}}$, the ionic potential terms, $F^{\text{LPP}}{}_{\text{ion}}$, and the energy gain term by dicomplexation, $F^{\text{LPP}}{}_{\text{dicomplex}}$, as given by

$$F^{\text{LPP}} \equiv F|_{\text{chain}} = F^{\text{LPP}}{}_{\text{el}} + F^{\text{LPP}}{}_{\text{mix}} + F^{\text{LPP}}{}_{\text{ion}} + F^{\text{LPP}}{}_{\text{dicomplex}} \qquad \text{(A1)}$$

Each term of the right-hand side of eq A1 corresponds to the one in eq 4 in the same order. The Flory−Rehner (FR) free energy for gel swelling is defined for a unit volume and is given by

$$F^{\text{FR}} \equiv F|_{\text{cm}^3} = F^{\text{FR}}{}_{\text{el}} + F^{\text{FR}}{}_{\text{mix}} + F^{\text{FR}}{}_{\text{D}} \qquad \text{(A2)}$$

where $F^{\text{FR}}{}_{\text{D}}$ is the Donnan potential term. The elastic term is given by

$$F^{\text{FR}}{}_{\text{el}} = \frac{3}{2}\nu kT\left[\left(\frac{R}{R_{00}}\right)^2 - 1 - \ln\left(\frac{R}{R_{00}}\right)\right] \approx \frac{3}{2}\nu kT\left(\frac{R}{R_{00}}\right)^2 \quad \text{(swelling)} \qquad \text{(A3)}$$

where R and R_{00} are the chain dimensions in the swollen and in the unperturbed states, respectively, and ν is the number of cross-links in a unit volume. The mixing term can be written as

$$F^{\text{FR}}{}_{\text{mix}} \cong \frac{nkT}{2}\phi^2(1 - 2\chi) \qquad \text{(A4)}$$

where n, ϕ, and χ are the number of monomer units in a unit volume, the volume fraction of the polymer chains, and the interaction parameter, respectively. Equation A4 can be rewritten as

$$F^{\text{FR}}{}_{\text{mix}} \cong nkT\,\frac{v}{2a^3}\phi^2 \qquad \text{(A5)}$$

where v is the excluded volume given by

$$v = a^3(1 - 2\chi) \qquad \text{(A6)}$$

Knowing

$$\phi = \frac{N(1-f)}{R^3} \quad \text{and} \quad n = \frac{R^3}{a^3} \qquad \text{(A7)}$$

one can reduce eq A4 to $F^{\text{LPP}}{}_{\text{mix}}$ by multiplying by a^2R^3/n. Similarly, eq A3 is reduced to $F^{\text{LPP}}{}_{\text{el}}$ by dividing it by ν. This comparison indicates that the corresponding terms of LPP and of FR theories are equivalent to each other. However, the LPP theory does not have the Donnan term, and the FR does not take into account the terms of the electrostatic interaction and energy gain by cross-link formation.

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