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Simple theory for volume phase transition of hydrated gels

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A simple theory to describe the volume phase transition of hydrated gels is presented. The theory takes a coupling of the volume change and the dehydration of the gel chain into consideration. The change of the excluded volume of chain segments with the dehydration is taken into account in evaluating the free energy of the chain conformation. The mixing free energy of the hydrated and dehydrated chain segments is evaluated by the quasichemical partition function method. The volume change is described as a function of the chemical potential of water molecules. The theory reproduces well the temperature and NaCl salt additive induced volume phase transition behavior of *N*-propylacrylamide gel observed. [S1063-651X(96)05709-1]

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I. INTRODUCTION

The swelling behavior of a polymer gel has attracted much attention after finding the discontinuous volume reduction of poly-*N*-isopropylacrylamide gel (GNIPA) with an increase in temperature [1], which is regarded as the volume phase transition. Before this finding, Dušek and Patterson [2] theoretically investigated what condition of a gel induces such a transition. They considered it on the basis of the Flory-Huggins theory [3] and concluded that the volume phase transition against the variation of a interaction parameter, the χ parameter, occurs for the gel having an unreasonably high cross link concentration and absorbing a huge amount of solvent molecules in the swelling state. The theory predicted that the transition of a gel can occur under strong tension, but not in the free-swelling case [2]. After finding the GNIPA volume phase transition, the volume-dependent χ parameter has been introduced into the theory [4] to explain the transition. In the theory, the χ parameter has been determined as a function of the volume fraction of the gel chain by fitting the theoretical curve to the data [4]. Prange, Hooper, and Prausnitz [5] have applied a quasichemical partition function to elucidate the χ-parameter term. In their theory, the hydrogen bonding force and the dispersion force of van der Waals type acting among chain segments and water molecules were taken into account. The volume transition of GNIPA was qualitatively reproduced by the theoretical calculation with using the interaction parameters fitted to the experimental data on phase separation of the poly(*N*-isopropylacrylamide) (PNIPA) solution [5].

The volume phase transition of GNIPA has been intensively investigated from various points of view for the past decade. The following two experiments suggest that the deswelling of GNIPA is accompanied with the dehydration of the gel chain. The application of the thermal analysis with a differential scanning calorimeter to the GNIPA [6] has revealed that the endothermic transition heat accompanied with the volume phase transition of the gel is a value similar to the heat of a coil-globule-like transition of PNIPA. The ^{1}H spin-spin relaxation time T_2 of water molecules in the PNIPA solution has exhibited a sharp change with temperature around the transition temperature [7]. These findings indicate that the volume phase transition is somehow related to the dehydration and hydration of the gel chain. The dehydration of the gel chain causes the affinity reduction of the chain segment to water molecules, which leads to the volume reduction. The hydration (dehydration) state can be regarded as the water binding (unbinding) state. The gel volume should be a function of the binding degree of water molecules, which is generally described in terms of a thermodynamic variable of the chemical potential of water molecules in the aqueous phase. We have reported elsewhere that both the additive concentration-dependent and the temperature-dependent deswelling behaviors of GNIPA [8] can be described in a unified manner in terms of the chemical potential difference of water molecules from that at the transition [9]. To describe the volume change behavior of a hydrophobic gel such as GNIPA it is essential to take the effects of binding and unbinding of water molecules into consideration.

II. THEORY

The chain segments take two states: the water binding state (*h* state) and the water unbinding state (*d* state). The affinity of the segment in the *h* state to water molecules is greater than the affinity of the segment in the *h* state. A large affinity leads to a small χ parameter. An excluded volume of the segment is proportional to $1-2\chi$ according to the theory of de Gennes [10]. A large excluded volume enlarges an average end-to-end distance of one chain between the cross-link points R, which leads to a large gel volume (since the volume is $\sim R^3$). Therefore, the gel volume increases with an increase in the binding degree of water molecules of the chain segment. At the binding equilibrium of water molecules, the chemical potential difference between the segments in the *h* and *d* states equals the chemical potential of water molecules in the bulk solution. The chemical potentials of *d* and *h* states are strongly coupled to the conformational free energy of the gel chain. The coupling of the binding degree of the water molecule to the chain conformation is taken into consideration in the present theory.

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A. Free energy

The free energy per one chain of the system is written in the form

$$G=G_{cf}+G_m+G_W, \tag{1}$$

where

$$\frac{G_{cf}}{T}=\frac{V_{hh}n_h^2+2V_{hd}n_hn_d+V_{dd}n_d^2}{R^3}+\frac{R^2}{n_0b^2}, \tag{2}$$

$$\frac{G_m}{T}=n_h\ln\frac{\xi+2\alpha_h-1}{\xi+1}+n_d\ln\frac{\xi+2\alpha_d-1}{\xi+1}+n_h\ln q_h+n_d\ln q_d, \tag{3}$$

$$\alpha_h=\frac{n_h}{n_0},\quad \alpha_d=\frac{n_d}{n_0},\quad n_0=n_h+n_d, \tag{3a}$$

$$\xi^2=1+4\alpha_h\alpha_d(\zeta^2-1),\quad \zeta=\frac{1}{2}\exp\left(\frac{2\epsilon_{hd}^n-\epsilon_{hh}^n-\epsilon_{dd}^n}{2T}\right), \tag{3b}$$

$$q_h=\exp\left(\frac{\epsilon_h+\epsilon_{hh}^n}{T}\right),\quad q_d=\exp\left(\frac{\epsilon_d+\epsilon_{dd}^n}{T}\right), \tag{3c}$$

$$G_W=\left(\frac{N_W^0}{N_c}-n_hk_h\right)\mu_W. \tag{4}$$

In Eq. (1), G_{cf}, G_m, and G_W, respectively, are the free energy of the chain conformation, the mixing free energy of the hydrated and dehydrated segments in the chain, and the free energy of the water molecules. It should be mentioned that Eq. (2) is a formula of the de Gennes approximation [10] for the conformational free energy of the polymer. The cooperative binding of water molecules is taken into account in Eq. (3). The free energy for mixing the segments of the h and d states in a chain is derived in Eq. (3) by using the quasichemical method [11]. In Eq. (2), V_{ab}, b, n_0, n_h, and n_d, respectively, are the volume mutually excluded by the segments in the a and b states, the unit segment length, the number segments in one chain, the number of segments in the h state, and the number of segments in the d state. In Eqs. (3b) and (3c) ϵ_a and ϵ_{bc}^n, respectively, are the intrinsic energy of the segment in the a state and the interaction energy between the segments in the b and c states, which are neighboring each other along the chain. The cooperativity parameter is denoted by ζ in Eq. (3b). In Eq. (4), N_W^0, N_c, k_h, and μ_W, respectively, are the total number of water molecules in the whole system, the number of chains in the gel, the number of water molecules that are unbound from one segment, which changes from the h state to the d state and the chemical potential of water molecules. The Landau temperature is denoted by T.

We write the excluded volume as

$$\begin{aligned}V_{hh}&=h^3b^3(1-2\chi_{hh}),\\ V_{dd}&=h^3b^3(1-2\chi_{dd}),\\ V_{hd}&\equiv h^3b^3(1-2\chi_{hd}),\end{aligned} \tag{5}$$

$$\begin{aligned}2\chi_{hh}&=\frac{2\epsilon_{hs}-(\epsilon_{hh}+\epsilon_{ss})}{T},\\ 2\chi_{dd}&=\frac{2\epsilon_{ds}-(\epsilon_{dd}+\epsilon_{ss})}{T},\\ 2\chi_{hd}&=\frac{(\epsilon_{hs}+\epsilon_{ds})-(\epsilon_{hd}+\epsilon_{ss})}{T}.\end{aligned} \tag{5a}$$

In Eq. (5a), ϵ_{xy}, ϵ_{xs}, and ϵ_{ss}, respectively, are the interaction energy between the segments in the x and y states, which are not neighboring along the chain, the interaction energy between the segment in the x state and the solvent molecules, and the interaction energy between the solvent molecules. It is assumed that the interaction energy is due to the dispersion force and that the relation $\epsilon_{xy}=-\sqrt{|\epsilon_{xx}||\epsilon_{yy}|}$ holds [11]. Then Eq. (5a) can be rewritten as

$$\begin{aligned}2\chi_{hh}&=\frac{(\sqrt{|\epsilon_{hh}|}-\sqrt{|\epsilon_{ss}|})^2}{T},\\ 2\chi_{dd}&=\frac{(\sqrt{|\epsilon_{dd}|}-\sqrt{|\epsilon_{ss}|})^2}{T},\\ 2\chi_{hd}&=2\sqrt{\chi_{hh}\chi_{dd}}.\end{aligned} \tag{5b}$$

B. Basic equations at equilibrium

The minimization condition of the free energy at equilibrium gives

$$\frac{\partial G}{\partial R}=0, \tag{6}$$

$$\frac{\partial G}{\partial n_d}=0. \tag{7}$$

The binding reaction of water molecules is described by

$$k_h\ \mathrm{H_2O}+d\ \text{state}\rightleftharpoons h\ \text{state}, \tag{8a}$$

$$dn_d=-dn_h=\frac{1}{k_h}\,dN_W. \tag{8b}$$

Equation (6) gives the relation

$$-3(\alpha_h^2V_{hh}+2\alpha_h\alpha_dV_{hd}+\alpha_d^2V_{dd})\,\frac{n_0^2}{R^4}+2\,\frac{R}{n_0b^2}=0. \tag{9}$$

Equation (9) leads to

$$R^5=\frac{3n_0^3b^2}{2}\,(\alpha_h^2V_{hh}+2\alpha_h\alpha_dV_{hd}+\alpha_d^2V_{dd}) \tag{10}$$

and

$$V_r^* \equiv \frac{R^3(\alpha_d=1)}{R^3(\alpha_h=1)} \equiv \frac{\mathcal{V}(\alpha_d=1)}{\mathcal{V}(\alpha_h=1)} = \left(\frac{V_{dd}}{V_{hh}}\right)^{3/5} = \left(\frac{1-2\chi_{dd}}{1-2\chi_{hh}}\right)^{3/5}, \tag{11}$$

where $\mathcal{V}$ is the volume. Using this relation, we can compare the value of $(1-2\chi_{dd})/(1-2\chi_{hh})$ from the ratio (V_r^*) of the gel volume in the completely deswollen state $(\alpha_d=1)$ to that in the completely swollen state $(\alpha_h=1)$. Equation (7) gives the relation

$$[-\alpha_h V_{hh}+(\alpha_h-\alpha_d)V_{hd}+\alpha_d V_{dd}]\,\frac{2n_0}{R^3}+\ln\frac{\xi+2\alpha_d-1}{\xi+2\alpha_h-1}$$

$$=-\,\frac{k_h\mu_W^0+\mu_d-\mu_h}{T}\quad(\equiv k_h S), \tag{12}$$

where

$$\mu_d=T\,\ln q_d,\qquad \mu_h=T\,\ln q_h\,.$$

When $V_{hh}=V_{hd}=V_{dd}$, the first term in Eq. (12) vanishes and S is a monotonically increasing function of α_d.

Substituting Eq. (10) into Eq. (12), we can obtain the relation

$$S=S_0+\Gamma, \tag{13}$$

$$S_0=\frac{1}{k_h}\ln\frac{\xi+2\alpha_d-1}{\xi+2\alpha_h-1}, \tag{13a}$$

$$\Gamma=\frac{1}{k_h}\left(\frac{2}{3}\right)^{3/5} n_0^{-4/5}h^{2/5}(1$$

$$-2\chi_{hh})^{2/5}\,\frac{-2\alpha_h+2(\alpha_h-\alpha_d)\,\dfrac{V_{hd}}{V_{hh}}+2\alpha_d\,\dfrac{V_{dd}}{V_{hh}}}{\left(\alpha_h^2+2\alpha_h\alpha_d\,\dfrac{V_{hd}}{V_{hh}}+\alpha_d^2\,\dfrac{V_{dd}}{V_{hh}}\right)^{3/5}}. \tag{13b}$$

Equation (10) gives the following relation to describe the volume change behavior:

$$V_r \equiv \frac{R^3}{[R(\alpha_d=0)]^3} = \left(\alpha_h^2+2\alpha_h\alpha_d\,\frac{V_{hd}}{V_{hh}}+\alpha_d^2\,\frac{V_{dd}}{V_{hh}}\right)^{3/5}. \tag{14}$$

C. Volume phase transition

If V_{hh} is larger than both V_{hd} and V_{dd} it is possible that S is a decreasing function of α_d in a certain region of α_d. To confirm this, numerical calculations of Eqs. (13) and (14) were carried out for the case that $n_0=100$, $\zeta=4.1$, $\chi_{hh}=0.15$, $k_h=13$, and $h=6$. The k_h value used here is the reported number of water molecules released from a dehydrating monomeric unit of the GNIPA chain [12]. The α_d dependence of S, S_0, Γ, and V_r is shown in Fig. 1(a) for the cases of $V_r^*=0.5$ and 0.05. The gel volumes in both cases are monotonically decreasing functions of α_d. The curve of S for $V_r^*=0.05$ exhibits a valley at the vicinity of $\alpha_d=0.99$. The S value decreases with an increase in α_d at α_d between about 0.96 and 0.99. Three α_d values coexist for one S value (S is threefold degenerate with respect to α_d) between about $\alpha_d=0.92$ and 0.995, as shown in Fig. 1(a). The largest and smallest α_d are stable binodal points and the intermediate α_d is a metastable point. In the polymer solution, a phase separation occurs when S is degenerate. The separated phases in one gel are very unstable because the stress yielded at the phase boundary in the gel increases the free energy of the system. When S increases to be degenerate, a smaller value of binodal α_d hardly jumps to a larger value of binodal α_d, unless the energy to overcome the stress energy was provided. The stress energy can be regarded as an activation energy for jumping into the other phase. Thus the α_d value continuously changes in the range of smaller binodal values with an increase in S unless S exceeds the largest degenerate S value. When S exceeds it, the α_d value jumps from α_d value at the peak S [$\alpha_d\sim0.96$ in Fig. 1(a)] into the largest binodal α_d value (~0.995). In the jumping of α_d, the activation energy can be provided with the difference of the free energy of bulk water molecules from that of hydrating water molecules to the gel whose α_d value is that at the peak S. When S decreases, the jumping of α_d occurs in a similar manner from a larger binodal α_d value [~0.99 in Fig. 1(a)]

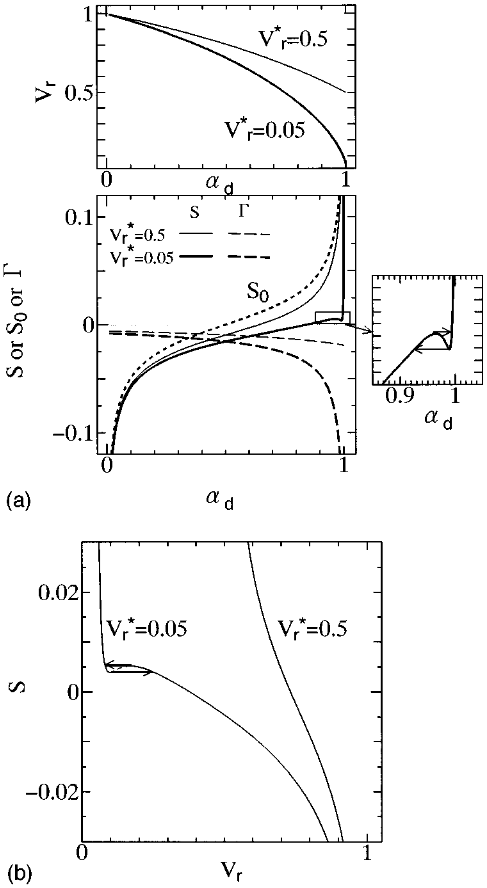

FIG. 1. Numerically calculated results of Eqs. (13) and (14). (a) Dependence of S, S_0, Γ, and V_r on α_d and (b) relation between S and V_r are shown. The transitions are indicated by arrows. The broken lines in (b) show the metastable state. The ordinates of S, S_0, and Γ are expressed in T units and the V_r is the volume ratio of the gel to that in the fully swollen state. The abscissa of α_d is the degree of dehydration defined by Eq. (3a). The parameter values used are $n_0=100$, $\zeta=4.1$, $\chi_{hh}=0.15$, $k_h=13$, and $h=6$.

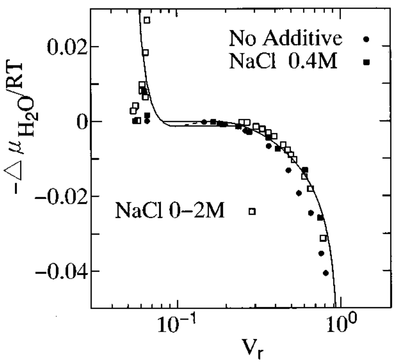

FIG. 2. Comparison of the theoretical calculation with the experiment of GNIPA. The closed and open symbols, respectively, denote the data evaluated from the temperature induced transition and the isothermal transition induced by changing the concentration of NaCl. The theoretically calculated transitions are indicated by arrows. The ordinate is the difference of the T-unit chemical potential of water molecule from that at the transition. The broken line shows the metastable state. The parameter values used are $n_0 = 100$, $\zeta = 4.1$, $\chi_{hh} = 0.15$, $k_h = 13$, $h = 6$, and $V_r^* = 0.05$.

at the bottom S of the valley to a smaller α_d [$\sim$0.92 in Fig. 1(a)] at the bottom S value. The jumping pathways in increasing S and decreasing S are indicated by arrows in Fig. 1(a). The difference of the pathways can be observed as a hysteresis in the experiment. The jumping of α_d leads the volume phase transition as indicated by the arrows in Fig. 1(b), which shows the relation between S and V_r. The transition is not observed in the case $V_r^* = 0.5$. In this case, S monotonically increases with α_d as shown in Fig. 1(a). It should be mentioned that S_0 is a monotonically increasing function of α_d for any large value of cooperativity parameter ζ. Without the sharp decrease in Γ, that is, the large decrease in R, the valley of S never appears.

III. DISCUSSION

It is worthwhile to examine how quantitatively the present theory can explain the experimental results of volume phase transition behavior of GNIPA [8], which is described in terms of the chemical potential difference of water molecules from that at the transition [9]. The transitions induced by the temperature change and the NaCl concentration change [8] were examined in the present study. The chemical potential of water molecules is obtained from the relation

$$\mu_W = \mu^0_{H_2O}(T) + T \ln a_W(C),$$

where $\mu^0_{H_2O}(T)$ and $a_W(C)$, respectively, are the chemical potential of pure water at T and the activity of water. The literature values of temperature-dependent $\mu^0_{H_2O}(T)$ [13] and NaCl-concentration-dependent $a_W(C)$ [14] were used. Figure 2 shows a comparison of the experimental data with the calculated result based on the present theory. In this calculation, the values of $V_r^* = 0.05$, $n_0 = 100$, $\zeta = 4.1$, $\chi_{hh} = 0.15$, $k_h = 13$, and $h = 6$ were used. The values of $V_r^* = 0.05$ and $n_0 = 100$, respectively, are given by the observed volume ratio of V_r^* and the experimental condition [8]. The chemical potential difference of water molecules from that at the transition, $\Delta\mu_{H_2O}$ in the present theory, is given by $S^* - S$, where S^* is the S value at an upper transition pathway. Here $\mu_h - \mu_d$ is assumed a constant. The agreement between them is satisfactory, as shown in Fig. 2. The value of $\zeta = 4.1$ corresponds to $\epsilon^n_{hd} - \epsilon^n_{hh}/2 - \epsilon^n_{dd}/2 = 2.1T$ (5.3 kJ/mol at 30 °C), which is close to the transition heat of GNIPA (3.3–4.5 kJ/mol) [6]. The value of $\chi_{dd} = 0.497$, which indicates a very poor affinity of the dehydrated segment to water molecules, is obtained from the value of $\chi_{hh} = 0.15$. The value of $h = 6$ is considered to correspond to $k_h = 13$ since the excluded volume is proportional to the thickness of the hydration layer, that is, the number of bound water molecules. The hysteresis temperature converted from the hysteresis of $\Delta\mu_{H_2O}/T$ observed in the calculated result is about 0.4 °C as the transition temperature of GNIPA is 34 °C. This value is close to a reported value of 0.2 °C [15]. It should be mentioned here that the theoretical curve can be better fit to the experimental results by adjusting the parameters in detail.

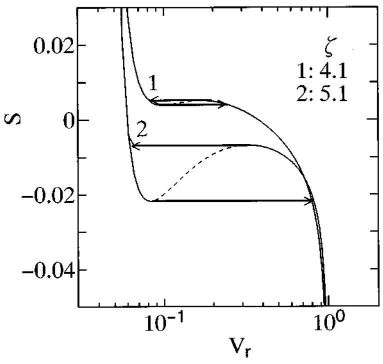

FIG. 3. Dependence of the volume phase transition behavior on the ζ value. The transitions are indicated by arrows. The S is expressed in T units and the V_r is the volume ratio of the gel to that in the fully swollen state. The broken lines show the metastable states. The parameter values used are $n_0 = 100$, $\chi_{hh} = 0.15$, $k_h = 13$, $h = 6$, and $V_r^* = 0.05$.

It is interesting to examine how the variation of parameter values of ζ, h, and χ_{hh} affects the deswelling and transition behavior. Figure 3 shows the change of the transition behavior with an increase in ζ. The transition S values in both processes of increasing and decreasing S decreases with an increase in the cooperativity parameter ζ. The discrete volume change at the transition and the hysteresis of S increase as ζ is increased. The ζ value given by Eq. (3b) increases as $2\epsilon^n_{hd} - \epsilon^n_{hh} - \epsilon^n_{dd}$ increases. The ζ value increases with the strength of the hydrophobicity of the gel since the stability of the dehydrated state increases, that is, the ϵ^n_{dd} value decreases with an increase in the hydrophobicity strength. It should be noted that the distinction between the phase transition behavior of N-normalpropylacrylamide gel (GNNPA) and that of GNIPA [16] is very similar to the difference due to the ζ value, as shown in Fig. 3. A more hydrophobic normalpropyl group than an isopropyl group gives a larger ζ value to GNNPA than to GNIPA. The changes of the transition behavior with an increase in h and a decrease in χ_{hh}, shown in Figs. 4 and 5, are similar to the behavior change with an increase in ζ. The contribution of the Γ term to S increases with h since Γ is proportional to $h^{2/5}$, as indicated

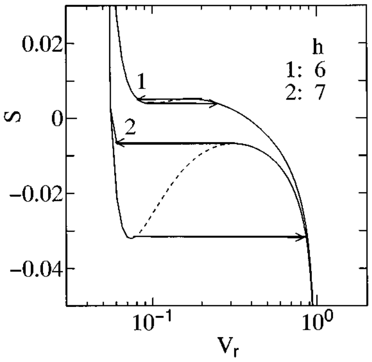

FIG. 4. Dependence of the volume phase transition behavior on the *h* value. The transitions are indicated by arrows. The broken lines show the metastable states. The *S* is expressed in *T* units and the V_r is the volume ratio of the gel to that in the fully swollen state. The parameter values used are $n_0=100$, $\zeta=4.1$, $\chi_{hh}=0.15$, $k_h=13$, and $V_r^*=0.05$.

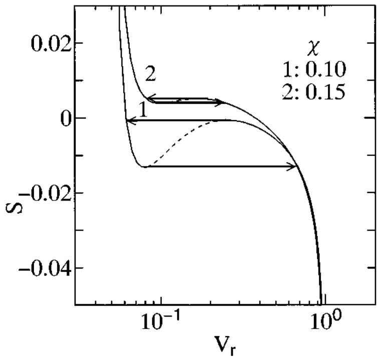

FIG. 5. Dependence of the volume phase transition behavior on the χ_{hh} value. The transitions are indicated by arrows. The broken lines show the metastable states. The *S* is expressed in *T* units and the V_r is the volume ratio of the gel to that in the fully swollen state. The parameter values used are $n_0=100$, $\zeta=4.1$, $k_h=13$, $h=6$, and $V_r^*=0.05$.

by Eq. (13b). The value of V_{hd}/V_{hh} increases with a decrease in χ_{hh} for a constant V_r^* (=0.05), as indicated by Eqs. (5) and (11). The increase of V_{hd}/V_{hh} leads an increase of the Γ term contribution to *S* at high α_d. The increase of the decrement rate of Γ against α_d accompanied by the increases of Γ has nearly the same effect on the transition behavior as the decrease of the increment rate of S_0 against α_d, which is led by the increase in ζ.

It is necessary for the occurrence of the volume phase transition that the decrement rate of Γ against α_d is larger than the increment rate of S_0 in a certain region of α_d. The large decrement rate of Γ is led by the large decrement of *R* as indicated by Eq. (12) or (13b). When the decrement of *R* is reduced by the swelling perturbation on the gel system, it is possible for the discrete change of α_d to become continuous, which leads to the disappearance of the transition. The present theory expects that the phase transition of the gel consisting of partially ionized chain becomes vague or disappears when the Donnan osmotic pressure [17] swells the gel. This has been observed in the experiments of Beltran *et al.* [18] and Kawasaki, Sasaki, and Maeda [19].

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