



The gel that memorizes phases

Masahiko Annaka, Masayuki Tokita, Toyoichi Tanaka, Shimei Tanaka, and Takayuki Nakahira

Citation: J. Chem. Phys. **112**, 471 (2000); doi: 10.1063/1.480638 View online: http://dx.doi.org/10.1063/1.480638 View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v112/i1 Published by the AIP Publishing LLC.

Additional information on J. Chem. Phys.

Journal Homepage: http://jcp.aip.org/ Journal Information: http://jcp.aip.org/about/about_the_journal Top downloads: http://jcp.aip.org/features/most_downloaded Information for Authors: http://jcp.aip.org/authors





metals • ceramics • polymers composites • compounds • glasses

Save 5% • Buy online 70,000 products • Fast shipping

The gel that memorizes phases

Masahiko Annaka^{a)} Department of Applied Chemistry, Chiba University, Chiba 263, Japan

Masayuki Tokita

Department of Chemistry for Materials, Mie University, Tsu 514, Japan

Toyoichi Tanaka

Department of Physics and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Shimei Tanaka and Takayuki Nakahira Department of Applied Chemistry, Chiba University, Chiba 263, Japan

(Received 7 July 1998; accepted 28 September 1999)

A poly(4-acrylamidosalicylic acid) gel exhibits multiple phases as characterized by distinct degrees of swelling; the gel can take one of four different swelling values, but none of the intermediate values. The multiple phase behavior appears as a result of the combination of hydrogen bonding and hydrophobic interaction between polymer segments. The gel has remarkable memory: The phase behavior of the gel depends on whether the gel has experienced the most swollen phase or the most collapsed phase in the immediate past. The information is stored and reversibly erased in the form of a macroscopic phase transition behavior. These phenomena are explained by a mean field theory where the number of hydrogen bonds is added to the equation of the state of a gel. \bigcirc 2000 American Institute of Physics. [S0021-9606(99)50848-9]

I. INTRODUCTION

Synthetic polymer gels exist in two phases, swollen and collapsed.^{1,2} Volume transition occurs between the two phases, either continuously or discontinuously. Recently, more than two phases were found in gels consisting of copolymers of randomly distributed positively and negatively charged groups.³ The number of phases depends on the composition of positively and negatively charged monomers, and decreases from a maximum of seven at a particular composition to one at pure cationic or anionic gel composition. Various copolymer gels were found to show the multiple phase behaviors.^{4,5} The criterion for a gel to have the multiple phase behavior is that the polymers interact with each other through randomly distributed repulsive and attractive interactions. The latter should be hydrogen bonding plus one of the hydrophobic or electrostatic interactions. In this study, we will show that such a condition, so far demonstrated only in copolymer gels, can be achieved in homopolymers which are made of a single kind of monomer if they interact with each other through hydrogen bonding and hydrophobic interaction. These phenomena are explained by a mean field theory where the number of hydrogen bonds is added to the equation of state of a gel.

II. EXPERIMENT

4-acrylamidosalicylic acid (Fig. 1) was synthesized from acryloyl chloride and sodium 4-aminosalicylate.⁶ Sodium 4-aminosalicylate (40 g, 0.24 mol) was dissolved in distilled water (250 ml) and was stirred for 1 h. Two separate additions of acryloyl chloride (20 and 10 ml, 0.37 mol) were made, the solution being stirred for 1 h after each addition. Acidification to pH 4.0 with 10 N hydrochloric acid yielded a gray precipitate which was filtered off and washed with distilled water (500 ml) to give 4-acrylamidosalicylic acid (27 g, yield 57%).

The gel was prepared by radical polymerization: 5.0 g of 4-acrylamidosalicylic acid, 0.34 g of N,N'-methylenebisacrylamide (cross-linker), and 0.05 g of azobisisobutyronitrile (initiator) were dissolved in 27 ml of dimethylsulfoxide. The solution was polymerized at 70 °C for 8 h in capillaries of inner diameter 140 μ m (= d_0). After gelation was completed, gels were removed from capillaries, and were cut into small cylinders of length 1 mm. Then gels were immersed in a large amount of dimethylsulfoxide and then in water to wash away residual chemicals. The water was repeatedly changed until the diameter of the gels reached an equilibrium value.

The gel was placed in a glass cell whose temperature was controlled to within 0.1 °C and was continuously flushed with water from a reservoir, the *p*H of which was controlled by addition of HCl solution (to lower *p*H) or water (to increase *p*H) below *p*H 7. NaOH solution was used above *p*H 7. The gel diameter at equilibrium, *d*, was measured under a microscope. To avoid the effect of carbon dioxide in air, all the experiments were carried out under nitrogen gas atmosphere. The temperature was controlled to within ± 0.1 °C by circulating water from LAUDA RC-3 during the measurement.

III. RESULTS AND DISCUSSION

Four phases were found in the gel, each of which was denoted by its diameter normalized by the original diameter: $d/d_0 = 0.81$, 1.3, 3.4, and 4.9. When *p*H or temperature was

^{a)}Author to whom correspondence should be addressed; electronic mail: annaka@planet.tc.chiba-u.ac.jp



FIG. 1. Chemical structure of 4-acrylamidosalicylic acid polymers. They can interact with each other through hydrogen bonding, hydrophobic stacking between benzene rings, or ionic repulsive interaction. Temperature influences both hydrogen bonding and hydrophobic interaction, whereas the pH affects the degree of ionization and thus the electrostatic interaction. The monomer undergoes the ionization process twice, once for the carboxyl group and the other time for the hydroxy group.

varied, the gel changed its volume discontinuously. The hysteresis indicates that the transition is of the first order.

In Fig. 2(a), the gel diameter is plotted as a function of pH at 25 °C. At low pH the gel was in a shrunken state (phase 1.3). It swelled discontinuously at pH 9.9 to phase 4.9. As the pH was lowered it shrank back to the lower phase. This process was reproducible.

The temperature was raised starting from phase 1.3 at pH 6.0 and 25 °C [Fig. 2(b)]. The gel shrank to phase 0.81 at 55 °C. When the temperature was lowered to 25 °C, the phase remained unchanged. In Fig. 2(c), the pH dependence was observed where the gel undergoes phase transition between two new phases, 0.81 and 3.4. The cycle was reproducible.

When the *p*H was increased to 12 and decreased, thereafter the gel went back to its original swollen phase (phase 4.9) and after that the phase transition loop remained in the upper loop shown in Fig. 2(a) [Fig. 2(d)]

The gel has remarkable memory: The phase behavior of the gel depends on whether the gel has experienced the most swollen phase (phase 4.9) or the most collapsed phase (phase 0.81) in the immediate past. The gel remained in the hysteresis loop shown in Fig. 2(a) when the pH was changed from phase 1.3. On the other hand, once the gel experienced phase 0.81, the phase transition loop remained in that which was shown in Fig. 2(c). Therefore, the information is stored and reversibly erased in the form of macroscopic phase transition behavior.

These results strongly suggest that a new contracting force is present after the gel experiences the most collapsed phase that is promoted by increasing temperature. The multiple phase behavior is considered to appear as a result of a combination of hydrogen bonding and hydrophobic interaction between polymer segments. 4-acrylamido-salicylic acid molecules can interact with each other through hydrogen bonding, hydrophobic interaction between benzene rings, or



FIG. 2. Diameter of 4-acrylamidosalicylic acid gel as a function of pH and temperature. Measurements were carried out on a single gel under a microscope. The time course was carefully monitored after each pH or temperature change to ensure that equilibrium was reached at each measurement. The sequence of measurements is in alphabetical order [(a)–(d)]. The starting point of each diagram is the last point of the previous diagram. Detailed description of the paths is given in the text.

ionic repulsive interaction (Fig. 1). Temperature influences both hydrogen bonding and hydrophobic interaction, whereas pH affects the degree of ionization and thus the electrostatic interaction. The monomer undergoes the ionization process twice, once for carboxyl groups and the other time for hydroxyl groups.

Recent studies have shown that the incorporation of a hydrophobic moiety into polyelectrolytes leads to a decrease in acidity or basicity.^{7–9} One plausible explanation for this decrease in acidity or basicity is related to the dielectric constant surrounding ionizable groups. In the case of 4-acrylamidosalicylic gel, since benzene rings are less polar than water, the dielectric constant surrounding the charges of carboxyl groups and hydroxyl groups is considered to be lowered with increase in temperature. This will lower the pK_a and is expected to lead to the formation of hydrogen bonds.

Theoretically, multiple phases may be understood as a result of competition among various factors. The mean field free energy consists of terms for rubber elasticity, osmotic pressure by counter ions, net charge repulsion, and virial interactions.^{2,10,11} These few terms with different powers of polymer density can create free energy minima at two distinct densities. It is therefore necessary to introduce new order parameters in addition to the polymer density to predict more than three phases.

Hydrogen bonding may be a natural choice for a new



FIG. 3. Diameter of 4-acrylamidosalicylic acid gel as a function of concentration of aqueous urea solution. Open squares indicate the process increasing the concentration of urea. Solid squares indicate the process decreasing the concentration of urea. (a) Equilibrium swelling degree d/d_0 of the 4-acrylamidosalicylic acid gel in water as a function of *p*H at 25 °C. (b) The starting point of the diagram is the last point of (a). The temperature was fixed at 25 °C and was controlled to within ± 0.1 °C by circulating water from LAUDA RC-3 during the measurement.

contracting force.^{3–5} The formation of hydrogen bonds is energetically favorable, but entropically undesirable since it restricts the freedom of chain configurations. This competition can create two free energy minima for a fixed polymer density ρ . Since hydrogen bonding density, $\rho_{\rm HB}$, and ρ are coupled, the free energy $F(\rho, \rho_{\rm HB})$ can have four minima in the $\rho - \rho_{\rm HB}$ plane.

The swelling behavior of the most collapsed gel (phase 0.81) was examined as a function of urea concentration at 25 °C to confirm the formation of hydrogen bonds. As shown in Fig. 3(a), the gel swelled discontinuously at the urea concentration of 0.75 mol/ ℓ to phase 2.5. As the urea concentration was reduced from 6 mol/ ℓ to pure water (0 mol/ ℓ), the gel shrank gradually and finally went back to the original shrunken phase (phase 1.3). After that, the phase transition loop remained in the loop shown in Fig. 2(a)[Fig. 3(b)]. Urea is protein denaturant and is considered to break protein hydrogen bonds. From these facts, it is most likely that the multiple phase behavior and the memory effect will appear when hydrogen-bonding effects are significant.

These phenomena may be explained by the mean field theory in which the effect of the formation of hydrogen bonds is considered. A simple theoretical calculation will be given in Sec. IV.

IV. THEORETICAL CONSIDERATION

It is well established that swelling behaviors of the gels are uniquely determined by the osmotic pressure of the gel. The osmotic pressure of the gel is usually written within the framework of the mean field theory:^{1,2,10,11}

$$\Pi = -\frac{N_A kT}{\nu} \left[\phi + \ln(1-\phi) + \frac{\Delta F}{2kT} \phi^2 \right] + \nu_0 kT \left[\frac{\phi}{2\phi_0} + \left(\frac{\phi}{\phi_0} \right)^{1/3} \right] + f \nu_0 kT \left(\frac{\phi}{\phi_0} \right), \quad (1)$$

where N_A is Avogadro's number, k the Boltzmann constant, T the temperature, ν the molar volume of the solvent, ϕ the volume fraction of the polymer network, ϕ_0 the volume fraction of polymer network at the reference state, ΔF the excess free energy for the association between polymer segment and solvent, ν_0 the number of elastically active chains per unit volume at ϕ_0 , and f the number of dissociated counter ions per effective chain. The osmotic pressure difference between the inside and outside of the gel should be zero at equilibrium. Therefore, the following equation is obtained under such condition:

$$\tau \equiv 1 - \frac{\Delta F}{kT} = \frac{2\nu v_0}{N_A \phi_0^2} \left[\left(\frac{\phi}{\phi_0}\right)^{-5/3} - \left(f + \frac{1}{2}\right) \left(\frac{\phi}{\phi_0}\right)^{-1} \right] + 1 + \frac{2}{\phi} + \frac{2\ln(1-\phi)}{\phi^2}, \quad (2)$$

where τ is the reduced temperature. The equation of the state of a gel (2) uniquely determines the equilibrium swelling degree of the gel, $V/V_0 = \phi_0/\phi$ at a given value of the reduced temperature. Three values of ϕ , which correspond to two minima and one maximum value of the free energy, satisfy Eq. (2) for a certain value of τ .

Equations (1) and (2), however, do not predict well the experimental results shown in Figs. 2 and 3 because these equations apply to only the nonhydrogen-bonding network. These results suggest that a new, attractive and short-range interaction arises in the polymer network of 4-acrylamidosalicylic acid gel after the gel experiences the most collapsed phase. In the case of 4-acrylamidosalicylic acid gel, carboxylic acid groups can lead to the formation of both ionic and hydrogen bonds. When a hydrogen bond is formed, it influences the equation of state: it adds a new cross-linking between polymers and effectively shortens the polymer chain length, and the energy is lowered due to hydrogen bonding.

We will construct the equation of the state of a gel by considering hydrogen bonds to form a new cross linking. In the present model, we consider only hydrogels prepared in the presence of a large amount of diluent. The following three assumptions are made.^{12,13}

(1) Hydrogen bonding gives rise to physical crosslinking points in the chains, which comprise the gel. The formation of these cross-linking points divides a chain into short connected chains of equal length. The number of elastically active chains per unit volume at ϕ_0 changes to $(h + 1)v_0$ due to the formation of *h* cross-linking points.

(2) Physical cross-linking points are randomly distributed in the network, and no cooperative interactions are considered.

(3) Solvent molecules and monomers composing the gel system have the same molar volume.

Under these assumptions, we propose a model to clarify the effects of hydrogen bonding on volume phase transition.

A. Rubber elasticity

The Flory calculation for the free energy of rubber elasticity of the gel treated the gel as a group of ν_0 polymers consisting of N freely jointed segments of persistence length

b.^{1,2,10} The number of ionized monomer units on an active chain is represented by f. The number of hydrogen bonds that are formed in an active chain is given by h. The active chain divided into h+1 chains by the formation of h hydrogen bonds. Therefore, the number of monomer units in an active chain decreases by a factor of 1/(h+1) when h hydrogen bonds are formed. The radius of this chain, which has a random-walk configuration, is given by⁸

$$R_0(h) = \left(\frac{N}{h+1}\right)^{1/2} b = N^{1/2} b(h+1)^{-1/2} = R_0(h+1)^{-1/2}, \quad (3)$$

where R_0 denotes the radius of the intact active chain that has the random-walk configuration. Taking into account that there are $(h+1)\nu_0$ such active chains in a unit volume of the gel, the pressure that arises from the rubber elasticity of the polymer network is expressed as

$$\frac{\pi_{\rm el}(h)}{kT} = (h+1)\nu_0 \\ \times \left\{ \frac{1}{2} \left(\frac{\phi}{\phi_0} \right) (h+1)^{-3/2} - \left(\frac{\phi}{\phi_0} \right)^{1/3} (h+1)^{-1/2} \right\}.$$
(4)

Here, ϕ is the volume fraction of the polymer network of the gel, and ϕ_0 corresponds to the volume fraction of the polymer network under the conditions that the active chains have the random-walk configurations. ν_0 is the number of the elastically active chains per unit volume at ϕ_0 in the nonhydrogen-bonded network.

B. Polymer-solvent interactions

The pressure of the polymer network of the gel due to the free energy decrease associated with the formation of a contact point between polymer segments can be written as follows:

$$\frac{\pi_{\rm ps}}{kT} = -\frac{\Delta F}{kT} \left(\frac{\phi^2}{2\,v_0}\right),\tag{5}$$

where v_0 is the volume of the solvent. The formation of *h* hydrogen bonds in an active chain further decreases the free energy of the system. The probability of the formation of the hydrogen bond is assumed to be proportional to the square of the polymer density ϕ . Since there are v_0 active chains in a unit volume of the gel, the total decrease in the free energy for a unit volume of the gel can be written as follows:

$$\frac{\pi_{\rm HB}}{kT} = -\frac{\Delta F_{\rm HB}}{kT} \nu_0 \frac{h}{2} \phi^2. \tag{6}$$

Thus, the osmotic pressure given by the total interaction energy can be written as follows:

$$\frac{\pi_{\text{interaction}}(h)}{kT} = -\frac{\Delta F}{kT} \left(\frac{\phi^2}{2v_0}\right) - \frac{\Delta F_{\text{HB}}}{kT} v_0 \frac{h}{2} \phi^2.$$
(7)

C. Counter ion

The number of the counter ion in the gel is either maintained or altered by the hydrogen bonding that depends on the chemical structure of the hydrogen bonding units. Since there are $f v_0$ counter ions in a unit volume of the intact gel,



FIG. 4. Examples of numerical factor Z, and types of hydrogen bonds.

the osmotic pressure of the gel due to the counter ion for the hydrogen-bonded state of the gel is generally given as follows:

$$\frac{\pi_{\rm ion}(h)}{kT} = (f - Zh)\nu_0(h+1)^{-3/2} \left(\frac{\phi}{\phi_0}\right). \tag{8}$$

Here, Z is a numerical constant that depends on the chemical structure of the hydrogen-bonded units. Some examples of the numerical factor, Z, are shown in Fig. 4. In the case of (a), both ionizable parts of carboxylic acids are consumed to form hydrogen bond, Z equals to 1. In the case that one of the two ionizable parts of carboxylic acids contributes to form hydrogen bond as shown in (b), Z equals to 0.5.

D. Mixing entropy

The entropy of mixing to the first approximation is unchanged. Therefore the osmotic pressure of the gel due to the mixing entropy is given as follows:

$$\frac{\pi_{\text{mixing}}}{kT} = -\frac{1}{\nu_0} [\ln(1-\phi) + \phi].$$
(9)

The combination of Eqs. (4), (7), (8), and (9) yields the total osmotic pressure of the gel in the hydrogen-bonded state, $\Pi_{gel}(h)$,

$$\Pi_{\text{gel}}(h) = (h+1)\nu_{0} \\ \times \left\{ \frac{1}{2} \left(\frac{\phi}{\phi_{0}} \right) (h+1)^{-3/2} - \left(\frac{\phi}{\phi_{0}} \right)^{1/3} (h+1)^{-1/2} \right\} \\ - \frac{\Delta F}{kT} \left(\frac{\phi^{2}}{2\nu_{0}} \right) - \frac{\Delta F_{\text{HB}}}{kT} \nu_{0} \frac{h}{2} \phi^{2} + (f-Zh) \\ \times \nu_{0}(h+1)^{-3/2} \left(\frac{\phi}{\phi_{0}} \right) - \frac{1}{\nu_{0}} [\ln(1-\phi) + \phi].$$
(10)

The osmotic pressure of the gel should be zero at an equilibrium state. We, therefore, obtain the following relationship between the reduced temperature and the swelling ratio of the gel, ϕ/ϕ_0 , in which *h* hydrogen bonds are formed:

$$\begin{aligned} \tau &= 1 - \frac{\Delta F}{kT} \\ &= \frac{2 \, v \nu_0}{N_0 \phi^2} \bigg[(h+1)^{1/2} \bigg(\frac{\phi}{\phi_0} \bigg)^{1/3} - (h+1)^{-3/2} \\ &\quad \times \bigg\{ \frac{(1-Zh/f)}{h+1} f + \frac{1}{2} \bigg\} \bigg(\frac{\phi}{\phi_0} \bigg)^{-1} \bigg] + \frac{2 \, v \nu_0}{N_0} \frac{h}{2} \frac{\Delta F_{\rm HB}}{kT} \\ &\quad + 1 + \frac{2}{\phi} + \frac{2 \ln(1-\phi)}{\phi^2} \end{aligned} \tag{11}$$

Here, *v* represents the molar volume of the solvent and τ the reduced temperature.

It is worth noting that Eq. (11) coincides with the equation of state for a nonhydrogen-bonding network (2) when h=0.

In its original form, Eq. (8) does not take into account the effect of the Donnan equilibrium and makes use only of the theory for osmotic pressure under ideal conditions. This is equivalent to regarding the mobile ions inside the gel as the molecules of an ideal gas exerting a "swelling pressure" on the gel. The number of mobile ions inside the gel is assumed to be equal to the number of fixed charges on the polymer, irrespective of the ionic strength of the solution. The theory of Donnan equilibrium states that the higher the ionic concentration outside a semipermiable membrane with a polyelectrolyte inside, the lower is the difference in concentration of mobile ions between the two sides of the membrane. Because the gel chains are interlinked, the gel acts as if it provides its own semipermiable membrane. Equation (8) thus may not be suitable for predicting the swelling behavior of ionic gels as a function of pH unless the parameter f is calculated as a function of internal gel pH and internal polymer concentration.

To allow for changes in swelling caused by altering pH outside the gel, it is necessary to treat the ionic term, π_{ion} , as the effective difference in chemical potential of the solvent due to mobile ions inside the gel. A gel with the negatively charged group COO⁻ is neutralized by mobile counter ions H⁺ or Na⁺. The osmotic pressure generated by Donnan potential is then give by

$$\pi_{\rm ion} = -\frac{\Delta\mu}{\nu} \approx (n-n')N_A kT, \qquad (12)$$

where ν denotes the molar volume of the solvent, *n* and *n'* the concentrations of mobile ions inside the gel and outside the gel, respectively. The total mobile ion concentrations are

$$n = n_{\rm H^+} + n_{\rm OH^-} + n_{\rm Na^+}$$
 (inside the gel), (13)

$$n' = n'_{H^+} + n'_{OH^-} + n'_{Na^+}$$
 (outside the gel), (14)

Since the charges are fixed on the polymer network, a Donnan potential is set up across the gel–solvent boundary, which leads to an unequal distribution of ions inside and outside the gel:

$$\frac{n_{\rm H^+}}{n_{\rm H^+}'} = \frac{n_{\rm OH^-}}{n_{\rm OH^-}} = \frac{n_{\rm Na^+}}{n_{\rm Na^+}'}.$$
(15)

The neutrality condition for the gel is written as

$$n_{\rm H^+} + n_{\rm Na^+} = n_{\rm OH^-} + n_{\rm COO^-},$$
 (16)

where n_{COO^-} is the concentration of COO⁻ groups. For π_{ion} , it is necessary to estimate the polyion concentration n_{COO^-} , which is given by

$$n_{\text{COO}^{-}} \equiv [\text{COO}^{-}] = \alpha C_p \tag{17}$$

where C_p , [COO⁻], and α are the concentration of polymer in the gel, the concentration and degree of ionization of carboxylic groups, respectively. The degree of ionization of carboxylic groups, α , is related to internal gel *p*H, $pH_{in} (\equiv -\log n_{H^+})$, by Henderson–Hasselbach equation,^{14,15}

$$pH_{\rm in} = pK_a - n_0 \, \log \frac{1 - \alpha}{\alpha},\tag{18}$$

where pK_a is the apparent dissociation constant, n_0 is the numerical factor. $n_0=1$ is employed for simplicity. From Eq. (12), one obtains

$$\alpha = \frac{1}{10^{(pK_a - pH_{\rm in})} + 1}.$$
(19)

 pH_{in} was controlled by adding HCl solution (to lower pH_{in}) or water (to increase pH_{in}) below pH_{in} 7. NaOH solution was used above pH_{in} 7. According to Eqs. (13) and (14), the following relations are given,¹²

$$n_{\rm COO^-} + n_{\rm OH^-} + n_{\rm CI^-} = n_{\rm Na^+} + n_{\rm H^+} \quad \text{(inside the gel)},$$

$$n_{\rm OH^-}' + n_{\rm CI^-}' = n_{\rm Na^+}' + n_{\rm H^+}' \quad \text{(outside the gel)}. \tag{20}$$

The osmotic balance leads to

$$n_{\rm H^+} n_{\rm Cl^-} = n'_{\rm H^+} n'_{\rm Cl^-} \equiv I^2 \quad (\text{for } p_{\rm H_{in}} < 7),$$

$$n_{\rm OH^-} n_{\rm Na^+} = n'_{\rm OH^-} n'_{\rm Na^+} \equiv I^2 \quad (\text{for } 7 < p_{\rm H_{in}}) \qquad (21)$$

where I is the ionic strength of the system, and the contribution of activity coefficients are ignored. By solving Eqs. (20) and (21), the following relation is obtained:

$$\Delta n_{\text{mobile}} \equiv n - n' \approx \sqrt{[\text{COO}^-]^2 + 4I^2} - 2I, \qquad (22)$$

$$[\text{COO}^{-}] = \alpha C_p = \frac{C_p}{10^{(pK_a - pH_{\text{in}})} + 1}.$$
 (23)

I is given by as follows:

$$I = \frac{1}{2}(n_{\mathrm{H}^{+}} + n_{\mathrm{OH}^{-}} + n_{\mathrm{Na}^{+}}) \cong n_{\mathrm{H}^{+}} \quad (\text{for } p_{\mathrm{Hin}} < 7),$$

$$I = \frac{1}{2}(n_{\mathrm{H}^{+}} + n_{\mathrm{OH}^{-}} + n_{\mathrm{Na}^{+}}) \cong n_{\mathrm{OH}^{-}} \quad (\text{for } 7 < p_{\mathrm{Hin}}).$$
(24)

Here Eq. (8) can be modified by considering the osmotic pressure due to the ions. In the case of 4-acrylamidosalicylic acid gel, all the monomers have ionized groups. Therefore the following equation represents the osmotic pressure generated due to the Donnan potential per unit volume of the gel:

$$\frac{\pi_{\rm ion}(h)}{kT} = \sqrt{\left[\frac{f_0}{10^{(pK_a - pH_{\rm in})} + 1}\right]^2 + 4I^2} - 2I,$$
(25)

where f_0 is the *f* value at 100% ionization. When the *p*H is increased by the addition of NaOH, the concentration of Na⁺ in the outer solution will also increase. These cations will be



FIG. 5. Swelling curves of the non hydrogen-bonding network for various values of $f(=\alpha f_0)$ with $2 v \nu_0 / N = 0.25$, $\phi_0 = 0.1$, and $\Delta F_{\text{HB}} / kT = 10$.

attracted into the gel and will replace mobile H^+ ions. New H^+ ions will be supplied by the yet undissociated carboxylic acid groups. The concentration of mobile ions in the gel will thus increase more rapidly than that in the outer solution, and the ion swelling pressure will increase.

The supply of H⁺ ions is, however, limited. Eventually, all carboxylic acid groups will be dissociated. Any further increase in *p*H will reduce the Donnan ratio, Eq. (15), and make it approach one rapidly. There will always be an excess of cations and a deficit of anions in the gel but their contributions to π_{ion} will cancel each other out. With increasing *p*H, the ion swelling pressure will begin to decrease again. The total osmotic pressure of the gel $\Pi_{gel}(h)$, therefore, is expressed by the following formula:

$$\Pi_{gel}(h) = (h+1)\nu_0 \left\{ \frac{1}{2} \left(\frac{\phi}{\phi_0} \right) (h+1)^{-3/2} - \left(\frac{\phi}{\phi_0} \right)^{1/3} \\ \times (h+1)^{-1/2} \right\} - \frac{\Delta F}{kT} \left(\frac{\phi^2}{2\nu_0} \right) - \frac{\Delta F_{HB}}{kT} \nu_0 \frac{h}{2} \phi^2 \\ + \left(\sqrt{\left[\frac{f_0}{10^{(pK_a - pH_{in})} + 1} \right]^2 + 4I^2} + 2I \right) \\ - \frac{1}{\nu_0} [\ln(1-\phi) + \phi].$$
(26)

The total gel osmotic pressure $\Pi_{gel}(h)$ varies with internal gel *p*H, *p*H_{in}. The volume fraction, ϕ , at swelling equilibrium was obtained by solving Eq. (26) for $\Pi_{gel}(h) = 0$.

For the nonhydrogen-bonded network (h=0), Eq. (26) determines the equilibrium network concentration as a function of pH_{in} . Figure 5 schematically shows the equilibrium volume fraction of the polymer network as a function of pH_{in} for the different values of ϕ .

When the *p*H is high, the gel is swollen in the solvent. The state of the gel is represented, for example, by a point (state point) on the f=1 curve at the swollen side. According to Eq. (23), lowering the *p*H of the solvent leads to a decrease in the *f* value and finally the *f* value disappears. If the *p*H_{in} value is initially high, the trajectory of the state point does not cross the unstable region, and the gel concentration changes continuously with decreasing *p*H_{in}. How-



FIG. 6. Swelling curves of the gel for various values of *h*, the number of hydrogen bonds on an active chain, calculated using Eq. (9), with $2 v \nu_0 / N = 0.25$, $\phi_0 = 0.1$, $\Delta F_{\rm HB} / kT = 10$, and fN = 10.

ever, if the pH_{in} is initially low (shaded region in Fig. 5), the trajectory of the state point may cross the unstable region, including a discrete jump in the gel concentration.

In the case of hydrogen-bonded networks, Eq. (11) determines the equilibrium volume fraction of the polymer network ϕ as a function of the reduced temperature and the number of hydrogen bonds h. Thus, a set of swelling curves corresponding to different numbers of hydrogen bonds is obtained. The calculated results are shown in Fig. 6. Phase behaviors of the 4-acrylamidosalicylic acid gel shown in Fig. 2(b) is considered to correspond to the hydrogen-bonded network (h = const. case shown in Fig. 5). The equation (26) determines the equilibrium volume fraction of the polymer network ϕ as a function of pH_{in} and the number of hydrogen bonds h. A set of swelling curves with different numbers of hydrogen bonds obtained are considered to correspond to the hydrogen-bonding network (h = const). The discrete volume phase transition temperature of the gel becomes lower as one increases the number of the hydrogen bonds in the gel, then it disappears at a critical value of h, i.e., $h = h_c$. The volume change at the phase transition temperature becomes smaller as one increases the value of h. The swelling curves of the gel are monotonous above the critical value of h. The swelling ratio of the gel in the swollen state becomes smaller as increasing the number of hydrogen bonds in the gel while that of the collapsed state is insensitive to the number of hydrogen bonds. The numerical calculation yields that the critical value of the number of the hydrogen bond h_c is 2.8 under the present conditions. It indicates that formation of only three hydrogen bonds out of ten acrylic acid units in an intact active chain causes a drastic change in the swelling behaviors of the gel. These results imply that the hydrogen bond in the polymer network effectively changes the phase behavior of the gel.

The three-dimensional phase diagrams of the gel can be constructed by expanding these curves along an axis that represents the hydrogen bonding density $\rho_{\rm HB}$. They are schematically shown in Fig. 7.

The observed swelling behaviors of the 4-acryl amidosalicylic acid gel shown in Figs. 2(b) and 3 are quali-



FIG. 7. Schematics of the three-dimensional phase diagrams of the gel. Numbers in parentheses indicate the corresponding experimental swelling curve of the gel shown in Figs. 2 and 3.

tatively explained by using three-dimensional phase diagrams in which the state of the gel is defined for various combinations of reduced temperature, swelling ratio, and hydrogen bonding density. When the temperature of the gel is raised from the intermediate phase (phase 1.3), the gel follows one of the lines given in Fig. 5. The gel changes its volume discontinuously from the intermediate phase to the collapsed one (phase 0.81) at higher reduced temperatures. The gel does not change its phase with a further increase in the temperature. Generally, the volume phase transition is reversible and the volume of a gel goes back to the original one with hysteresis. The pH dependence of the swelling ratio of the gel corresponds to this case. However, when hydrogen bonds are formed in the collapsed phase at higher temperatures, hydrogen-bonding density becomes higher than that in the initial phase. The gel, therefore, follows a different swelling curve that is identified to have a higher hydrogen bonding density than that in the initial phase when the temperature is lowered. In the case of the 4-acrylamidosalicylic acid gel, all monomers on an active chain are *potentially* hydrogen bondable, and a large number of hydrogen bonds are expected to form. Therefore, the gel remains in the collapsed phase (phase 0.81) even at low temperatures. The projection of these swelling curves onto a plane of swelling ratio and temperature represents the temperature dependence of the swelling ratio of the gel. This swelling behavior predicted from theoretical swelling curves agrees with the experimental result qualitatively [Fig. 2(b).]

Urea is one of the most commonly used protein denaturant. The 4-acrylamidosalicylic acid gel, which is in the most collapsed phase (phase 0.81), swells when the concentration of urea in the solution increases. The swelling of the gel in aqueous urea solution is evidence of the dissociation of hydrogen bonds between polymer chains of the gel. The swelling behavior observed in aqueous urea solution can be explained in a similar way to the case of the temperature dependence. The number of hydrogen bonds formed in the gel decreases when the concentration of urea is increased. This corresponds to a decrease in the hydrogen bonding density, $\rho_{\rm HB}$, at constant temperature. The gel changes its volume when the swelling curve across the unstable region.

V. CONCLUSION

The swelling behaviors of 4-acrylamidosalicylic acid gel are studied. 4-Acrylamidosalicylic acid gel exhibits multiple phases as characterized by distinct degrees of swelling; the gel can take one of four different swelling values, but none of the intermediate values. The gel has remarkable memory: The phase behavior of the gel depends on whether the gel has experienced the most swollen phase or the most collapsed phase in the immediate past. The information is stored and reversibly erased in the form of a macroscopic phase transition behavior. The phase behavior appears to be a result of the combination of hydrogen bonding and hydrophobic interaction between polymer segments. These phenomena are explained by the mean field theory where the effects of the formation of hydrogen bonds are considered. Extensive study is needed, however, to identify the microscopic structure of the gel to clarify the gel phase behavior on the τ $-\rho_{\rm HB}$ plane and to construct a theory which takes into account the cooperativity which is essential feature of hydrogen bonding.

ACKNOWLEDGMENTS

This work has been supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture (No. 11740382 for MA and No. 09440153 for MT). M.A. is grateful to Yazaki Memorial Foundation for Science and Technology Foundation for financial support.

- ¹T. Tanaka, Phys. Rev. Lett. **40**, 820 (1978).
- ²T. Tanaka, D. J. Fillmore, S.-T. Sun, I. Nishio, G. Swislow, and A. Shah, Phys. Rev. Lett. 45, 1636 (1980).
- ³M. Annaka and T. Tanaka, Nature (London) 355, 430 (1992).
- ⁴M. Annaka, D. Berling, J. Robert, and T. Tanaka, Macromolecules 26, 3234 (1993).
- ⁵M. Annaka and T. Tanaka, Phase Transit. **B47**, 143 (1994).
- ⁶J. F. Kennedy, S. A. Baker, J. Epton, and G. R. Kennedy, J. Chem. Soc., Perkin Trans. 1, 488 (1973).
- ⁷R. A. Siegel and B. A. Firestone, Macromolecules 21, 3254 (1988).
- ⁸A. P. Sassi, S. Beltrán, H. H. Hooper, H. W. Blanch, J. Prausnitz, and R. A. Siegel, J. Chem. Phys. **97**, 8767 (1992).
- ⁹H. Kawasaki, S. Sasaki, and H. Maeda, J. Phys. Chem. 101, 5089 (1997).
- ¹⁰P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, 1953).
- ¹¹P. G. de Gennes, *Scaling Concepts in Polymer Physics*, (Cornell University Press, Ithaca, New York, 1979).
- ¹²M. Annaka, Ph.D. thesis, The University of Tokyo, 1994.
- ¹³M. Tokita, Polymer Application 47, 242 (1998) (in Japanese).
- ¹⁴C. Tanford, *Physical Chemistry of Macromolecules* (Wiley, New York, 1961).
- ¹⁵ M. Shibayama, F. Ikkai, S. Inamoto, and S. Nomura, J. Chem. Phys. **105**, 4358 (1996).