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Salt effect on volume phase transition of a gel

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The salt effect on the phase transition of *N*-isopropylacrylamide (NIPA) gel was studied for alkali-metal chlorides (NaCl, KCl, and CsCl). Low-frequency Raman scattering experiment was conducted to know the dynamic state of water molecule under the presence of salt and its correlation to macroscopic phase behavior of the gel was investigated together with the thermodynamic activities of water molecule of aqueous alkali-metal chloride solutions. The series of swelling experiment reveal that the change in the gel volume phase transition strongly depends on the salt concentration and is related to the dehydration with respect to hydrophobic hydration. From the analysis of the reduced low-frequency Raman spectra in water and aqueous alkali-metal chlorides solutions by the use of the relaxation mode that takes into account the inertia and the non-white effects, the characteristic values of aqueous salt solutions (i.e., relaxation time and modulation speed) indicate that the addition of alkali-metal chloride to gel fluid affects the disruption of water molecules in the hydration shell around the NIPA gel and the formation of the hydrogen-bonded network structure of water around themselves, as a result of which the gel collapses. The chemical potential and the dynamic nature of water molecule at the transition points are well correlated: the chemical potentials at the transition points are almost constant whereas the structure of bulk water is changed by addition of alkali-metal chlorides or change in temperature. These results strongly suggest that the swelling ratio of *N*-isopropylacrylamide gel is a function of hydration degree, which is regulated by the chemical potential of water.

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I. INTRODUCTION

N-isopropylacrylamide gel (NIPA gel) is known to exhibit a discrete volume phase transition with a change in temperature and/or concentration of added salts [1–3]. NIPA gel is in a swollen phase at lower temperature and is in a collapsed phase at higher temperature. The phase behavior of NIPA gels is opposite to that of liquid-gas system. Such an anomalous phase transition is considered to arise from the hydrophobic interaction between the polymer network and the solvent. In the swollen phase of NIPA gels, water molecules in the vicinity of hydrophobic part of the gel network is considered to form clathrate structure, hydrophobic hydration clusters, to minimize the net free energy of NIPA gel system. In the collapsed phase of NIPA gels, whereas the ordered structure of water molecules around the gel network is broken and the gel network aggregates. Addition of inorganic salts reduces the transition temperature. The effect of salt on the volume phase transition behavior of NIPA gels is considered to reduce the amount of clathrate structure of water around the hydrophobic moieties of the NIPA gels. For example, salt increase the hydrophobic interaction; the effect depends upon the nature of the ions. The Hofmeister series is the order of effectiveness as precipitants of serum globulines. The same series has been observed, in effectiveness, in decreasing the solubility in water (i.e., ‘‘salting out’’) of nonpolar molecules, of affecting the stability of specific conformations of proteins and nucleic acids. It is most likely that these effects on the hydrophobic interaction arise indirectly from effects on the structure of water. The discrete volume reduction in hydrated NIPA gel, therefore, is considered to be induced by the cooperative dehydration of gel chains due to the hydrophobic interaction [4–9]. The hydrophobic interaction is sensitive to the components added to the aqueous solution.

The physicochemical nature of the volume phase transition of NIPA gels has been investigated mainly to clarify the interaction between NIPA gel networks [10]. In the search for the underlying principle of the phase transition of gels,

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driven by hydrophobic interaction such as NIPA gel, it is crucial to understand the roles of the solvent and cosolutes at molecular level.

We have investigated the salt effect on the phase transition of NIPA gel for sodium halides (NaCl, NaBr, and NaI) [7–9]. In order to clarify the interaction between water molecules and salt molecules, the thermodynamic activities of water molecules in aqueous salt solutions and the (coupled) OH stretching Raman spectrum of water was investigated. The activity of water is a measure of the interaction between water and salt. The OH stretching Raman spectra in water and various aqueous solutions in terms of collective proton motions can yield information regarding the structure of the water network in these systems. The good correlation was observed between the chemical potential of water molecules and the volume phase transition of NIPA gel. The swelling behavior of the NIPA gel is well described as a function of chemical potential difference of water molecules in solution from that at the transition. This result strongly suggests that the swelling ratio of NIPA gel is a function of hydration degree, which is regulated by the chemical potential of water molecules. The collective proton motions of water molecules determined by the OH stretching Raman spectra is reduced with the addition of salts and roughly linear dependences are observed upon further addition of salts. The correlation between the chemical potentials and the relative intensity of the band assigned to the in-phase collective motions at the transition points shows that the chemical potentials at the transition points are almost constant whereas the structure of bulk water is changed by addition of salts or change in temperature. These findings indicate that the volume phase transitions due to the different type of perturbation (temperature, salt) are induced by the same mechanism, hydrophobic hydration and dehydration, and therefore can be described in a unified manner in terms of the chemical potential and the collective proton motions of water molecules.

Recently Head-Gordon *et al.* studied the hydration structure near hydrophobic and hydrophilic amino acids by neutron scattering and molecular dynamics simulation [11–13]. Their results indicated that the structure of water within the hydration shell of hydrophobic amino acid side chains had following features in comparison with pure water. (i) Tetrahedral structure of water is an essential feature around the hydrophobic side chain of amino acid such as leucine. (ii) This clathratelike structure is perturbed, and is distorted to be more planar than that of the tetrahedral structure observed in crystal ice and pure water. (iii) The hydration structure is not rigid, but is continuously formed and destroyed. The correlation time of water molecules consisting of hydration shell around the side chain of leucine is in the same order of bulk water. Our analysis of the OH stretching Raman spectra in terms of collective proton motions, and the studies by Head-Gordon and co-workers suggest that the hydration structure is not rigid, but breaks up and reforms continuously accompanied with the rapid exchange of water molecules in the same order of correlation time as bulk water. The strong electrostatic interaction due to the presence of ions makes water molecules in the hydrophobic hydration shell oriented around the ions. Therefore, the presence of salts tends to disrupt the hydration structures of water molecules in the vicinity of the NIPA side chain, as a result of which the gel collapses. Therefore, it is important to know the dynamic state of water molecule under the presence of salt and its correlation to macroscopic nature of the NIPA gel.

Low-frequency Raman scattering, which occurs in the spectral region below 300 cm^{-1}, has proven to be an effective method for investigating molecular dynamics in the liquid state of water [14–17]. Band assignment has been done for two Raman bands in the low-frequency region, a O-H-O stretching mode (190 cm^{-1}) and a O-O-O bending mode (60 cm^{-1}), within a system of five water molecules [18–20]. The imaginary part of dynamic susceptibility is given by reduced Raman spectra. In the liquid state, three types of modes contribute to the dynamic susceptibility: intramolecular vibrations, intermolecular vibrations, and collective relaxational motions. In the low-frequency region, intermolecular vibrations and collective relaxational motions are observed. Due to the large background in the reduced Raman spectra of water and aqueous electrolyte solution, Amo and Tominaga proposed the use of the relaxation mode that takes into account the inertia and the non-white effects in the reduced Raman spectra of aqueous electrolyte solutions [21–25].

In this paper, the salt effect on the phase transition of NIPA gel was studied for alkali-metal chloride (NaCl, KCl, and CsCl) in terms of dynamical state of water molecule. In order to clarify the salt effect on water molecules microscopically, we have conducted the low-frequency Raman scattering of NaCl, KCl, and CsCl aqueous solutions. We will discuss the correlation between the phase behaviors of NIPA gels in aqueous salt solutions and the dynamic state of water molecules in aqueous alkali-metal chloride solutions together with the thermodynamic activities of water molecules.

II. EXPERIMENT

A. Materials

NaCl, KCl, and CsCl (Wako Pure Chem. Ind. Ltd., Osaka) were used as supplied. *N*-isopropylacrylamide (Kohjin Co., Tokyo) was recrystalized from toluene/hexane mixture three times before use. N,N'-methylenebisacrylamide and N,N,N',N'-tetraethylmethylenediamine and ammoniumpersulfate (Wako Pure Chem. Ind. Ltd., Osaka) were used without further purification.

B. Sample preparation

NIPA gel was prepared by radical polymerization: 7.92 g of *N*-isopropylacrylamide (700 mM), 0.133 g of N,N'-methylenebisacrylamide (cross linker, 8.7 mM), and 22.8 mg of ammoniumpersulfate (initiator) were dissolved in 100 ml of distilled deionized water. 0.24 ml of N,N,N',N'-tetraethylmethylenediamine was further added to initiate the polymerization. The pregel solution was polymerized at 10 °C for 24 h in a capillary of inner diameter 140 $\mu\mathrm{m}\,(=d_0)$. After completion of gelation, the cylindrical gel was removed from the capillary mold and was washed with distilled water. Water was repeatedly changed until the diameter of the gel reached equilibrium.

C. Determination of phase diagram

1. Temperature dependence

The gel was cut into a small cylinder of length 1 mm and placed in a glass capillary. The temperature of the samples was controlled within 0.1 °C by circulating temperature-controlled water around the capillary. Equilibrium gel diameter d was measured under a microscope.

2. Salt concentration dependence

The gels are immersed in salt solutions of different concentrations in succession at 25 °C, starting with a deionized and distilled water and going stepwise to higher concentrated salt solutions. Reversibility and hysteresis were checked with all gels by bringing them back into deionized and distilled water.

D. Activities of water molecules in the salt solutions

Water activities in the salt solutions were evaluated from the osmolarity of the solution at 37 °C, measured with a vapor pressure osmometer (VPO 5500, WESCOR). The relation between the osmolarity Ω and water activity a_w, is given by

$$a_w=\exp(-\overline{V}\Omega), \tag{1}$$

where $\overline{V}$ is the partial molar volume of water.

E. Raman spectroscopy

A silica flow cell (T-45FLUV10, Nippon Silica Glass Inc.) was used for measurements to avoid the optical deadjustment associated with the replacement of the sample. Depolarized Raman spectra were obtained by using a double grating spectrometer (Ramanor U1000, Jovin-Yvon). The exciting light source was an argon-ion laser operating at 488 nm with 400-mW power. The right-angle scattering geometry was adopted with (VH) configuration. The depolarized Raman spectrum was recorded in the frequency range from—50 cm^{-1} to 250 cm^{-1}. The spectral resolution was 0.2 cm^{-1}. All spectra were recorded at 25 °C.

Temperature of the sample was controlled with accuracy within ±0.02 °C. The temperatures were monitored using chromel-constantan thermocouples provided by the chemical thermodynamics laboratory, Osaka University.

III. ANALYSIS OF RAMAN SPECTRA

The dynamical susceptibility is given by

$$\chi''(\nu)=K(\nu_i-\nu)^{-3}[n(\nu)+1]^{-1}I(\nu), \tag{2}$$

where $I(\nu)$ is the Raman spectral intensity obtained by photon counting method, $n(\nu)=[\exp(hc\nu/kT)-1]^{-1}$ is a Bose-Einstein factor, $\nu(=f/c)$ and $\nu_i(=f_i/c)$ are Raman frequency shift and the incident laser light frequency, respectively. The frequencies ν and ν_i are given in cm^{-1}, f and f_i are given in Hz, and c is light velocity. The K is the instrumental constant.

The imaginary part of the susceptibility of the damped harmonic oscillator is represented by

$$\chi''_\nu(\omega_j,\gamma;\omega)=\frac{\omega_j^2\gamma_j\omega}{(\omega_j^2-\omega^2)^2+(\omega\gamma_j)^2}, \tag{3}$$

where $\omega_j=2\pi c\nu_j$ $(j=1,2)$ and $\gamma_j=2\pi c g_j$ $(j=1,2)$ are characteristic angular frequencies and damping constants, respectively. The γ_j and g_j are characteristic frequencies and damping constants, respectively, given in cm^{-1}.

In the present paper, we applied the multiple-random-telegraph (MRT) model to analyze the relaxation component, which takes into account inertia and memory effect according to Amo and Tominaga [21–25]. In the MRT model [26], the complex susceptibility is written in the form

$$\chi^*(\omega)=1-i\omega v[s], \tag{4}$$

where $s=i\omega$. In the asymmetric case, $v[s]$ is given by continued function,

$$v[s]=\cfrac{1}{s+\cfrac{N\tilde{\Delta}_0^2}{s+\tilde{\gamma}+\cfrac{2(N-1)\tilde{\Delta}_0^2}{s+2\tilde{\gamma}+\cfrac{3(N-2)\tilde{\Delta}_0^2}{s+3\tilde{\gamma}+\cdots}}}}, \qquad \cfrac{}{s+(N-1)\tilde{\gamma}+\cfrac{N\tilde{\Delta}_0^2}{s+N\tilde{\gamma}}} \tag{5}$$

where $\tilde{\Delta}_0^2=\Delta_0^2(1-\sigma^2)$ and $\tilde{\gamma}=\gamma-2i\sigma\Delta_0$. The multiple-random-telegraph process is composed of N-independent random-telegraph processes, each of which takes the value $\pm\Delta_0$. The γ is the inverse of the characteristic time of the random-telegraph process. A nonzero value of σ means that each probability of the random-telegraph process was asymmetric. This model contains two specific cases: Gaussian–Markovian limit $(N\rightarrow\infty)$ and narrowing limit $(\alpha_0 \ll 1)$. The narrowing limit corresponds to a Debye-type relaxation. Δ_0, $\alpha_0(=\Delta_0/\gamma)$, σ, N, and relaxation strength A_{MRT} are used as fitting parameters to analyze the low-frequency depolarized Raman spectra. In this model, N must be a positive integer. The simplest case in the present analysis is supposed to be $N=1$. In the case of the MRT model, the fitting function is given by

$$\begin{aligned}\chi''(\nu)=&A_{MRT}\chi''_{MRT}(\Delta_0,\alpha_0,\sigma,N;\nu)+A_1\chi''_\nu(\nu_1,g_1;\nu)\\&+A_2\chi''_\nu(\nu_2,g_2;\nu).\end{aligned} \tag{6}$$

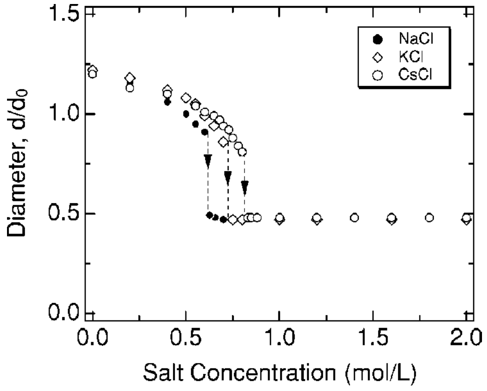

FIG. 1. Diameter d/d_0 of NIPA gel as a function of the alkali-metal chloride concentration at 25 °C.

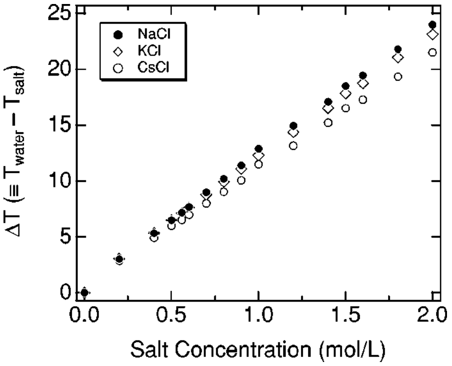

FIG. 2. Change in the transition temperature of NIPA gels due to the addition of salt $\Delta T(\equiv T_{water}-T_{salt})$ as a function of the salt concentration.

In Eq. (5), the relaxation time is not a fitting parameter. To calculate the relaxation time, we define $v(t)$ in the time domain as the inverse Laplace transform of $v[s]$ given by

$$v(t)=\{\cosh(\tilde{\gamma}t/2\tilde{a})+\tilde{a}\sinh(\tilde{\gamma}t/2\tilde{a})\}^N e-N\tilde{\gamma}t/2, \tag{7}$$

where

$$\tilde{a}=[1-4(\tilde{\Delta}_0/\tilde{\gamma})^2]^{-1/2}, \tag{8}$$

and $v(0)=1$. Then we obtain the relaxation time from the following equation:

$$|v(t)|-\frac{1}{2}=0. \tag{9}$$

IV. RESULTS AND DISCUSSION

A. The effect of cations on the phase transition of NIPA gels

Figure 1 shows the salt concentration dependence of the swelling ratios d/d_0 of NIPA gels in aqueous NaCl, KCl, and CsCl solutions at 25 °C. The gel volume gradually decreases with increasing salt concentration, and changes discontinuously at 0.68 mol/l in aqueous NaCl solution, at 0.70 mol/l in aqueous KCl solution, and at 0.83 mol/l in aqueous CsCl solution.

The swelling experiments suggest that the change in the NIPA gel volume phase transition strongly depends on the salt concentration, and the effect of the salt increases in the following order: CsCl<KCl<NaCl. When salt was added to NIPA gel fluid, the thermal behavior of the NIPA was changed. The transition temperature T_{salt} became lower than that in water, T_{water}. As salt concentration increased, the difference between T_{water} and T_{salt} became larger, and the transition width further increased. The decrement of the transition temperature due to the addition of the salts $\Delta T(\equiv T_{water}-T_{salt})$ is shown as a function of the salt concentration in Fig. 2. The ΔT depends on the type of salt and is largest for NaCl. The change in the behavior of the volume phase transition by the addition of salt molecules was induced by the change in the interaction between solvent and network. The observed phase behavior suggests that the clathrate structure in water around the hydrophobic moiety of NIPA gel is broken by the addition of salts to the NIPA gel fluid, and that the net entropy of the water must be affected [29]. No volume change was observed in acrylamide gel in aqueous NaCl solution up to 2 mol/l. This clearly indicates that the hydrophobic hydration around the isopropyl group of NIPA gel plays an essential role in determining the volume. Swelling behaviors were caused by the increase in entropy of the water by the addition of salts. These results indicate that NaCl molecule induced the largest change in the entropy of water.

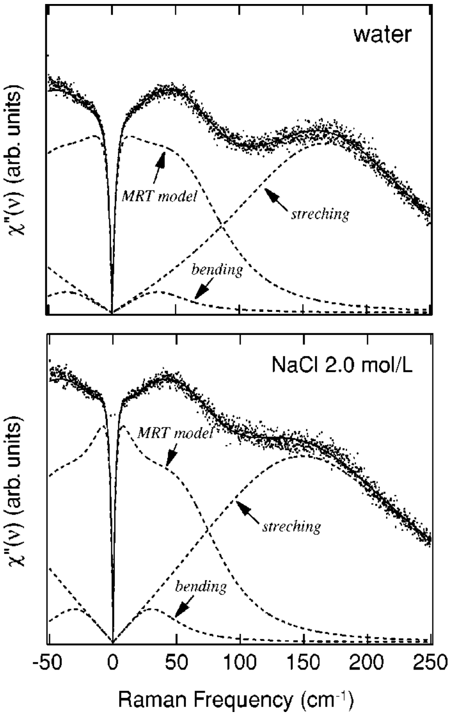

FIG. 3. Reduced low-frequency Raman spectra of (a) pure water and (b) 2.0 mol/l aqueous NaCl solution at 25 °C. The fitting function contains the MRT model and two damped harmonic oscillations.

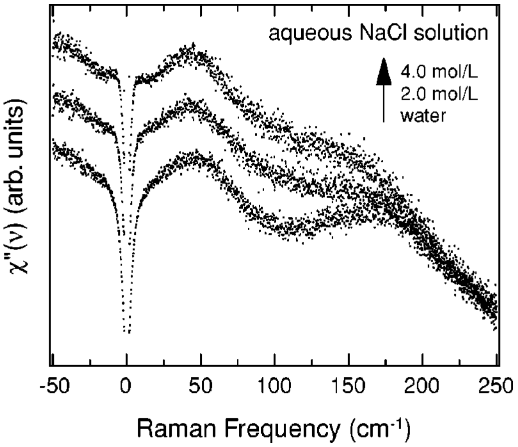

FIG. 4. Concentration dependence of the reduced low-frequency Raman spectra of aqueous NaCl solutions at 25 °C.

B. Low-frequency Raman scattering

Figure 3 shows the reduced low-frequency Raman spectra of pure water and 2.0 mol/l aqueous NaCl solution at 25 °C and the best-fitted curves. Figure 4 shows the concentration dependence of spectral shape of aqueous NaCl solutions. The central mode changed with increasing concentration.

Figures 5(a)–5(d) indicate the concentration dependence of fitting parameters. The relaxation time increases with increasing concentration. The order of the relaxation time is $Cs^+ < K^+ < Na^+$. The α_0, which is a measure of the modulation speed of angular frequency of the MRT model, increases with NaCl concentration, while it decreases in aqueous KCl and CsCl solutions. Figures 5(c) and 5(d) indicate the concentration dependence of the parameters of the two damped harmonic oscillators coupled with the MRT model. ν_{60}, and g_{60} are the parameters of band 60 cm^{-1}, and ν_{190}, and g_{190} are the parameters of band 190 cm^{-1}. The characteristic frequencies of the 60-cm^{-1} and 190-cm^{-1} modes slightly decrease with increasing concentration. The damping constant of the 190-cm^{-1} mode increase at lower concentration and then become almost constant at higher concentration. The damping constant of the 60-cm^{-1} mode is almost constant in the concentration range in this study.

The intensities of the relaxation mode and the two damped oscillator modes increased with salt concentration. For liquid water, the correlation time observed in low-frequency Raman scattering has been suggested to correspond to the duration time of creation and annihilation process of the hydrogen bond network among water molecules [30–32]. The broad band around 190 cm^{-1} is attributed to the stretchinglike vibrations of hydrogen bonds among five water molecules. The broad band around 60 cm^{-1} corresponds to the bendinglike vibrations of hydrogen bond among at least three water molecules. In aqueous salt solutions, the dynamical structure of water molecules is distorted because of the formation of the hydration shell around ions. This distortion may be one of the origins to increase the intensity of each mode.

For NaCl, KCl, and CsCl aqueous solutions, the characteristic frequencies of the stretchinglike mode shift to the lower side with increasing salt concentration as shown in Fig. 5(c). The characteristic frequencies of bendinglike modes slightly decrease. The distributions of characteristic frequencies in both stretchinglike and bendinglike modes slightly increase with increasing salt concentration as shown in Fig. 5(d). If the intermolecular interactions produce both vibration modes, the behaviors of these two modes against salt concentration should be the same. Therefore, the salt concentration dependence of the characteristic times of both

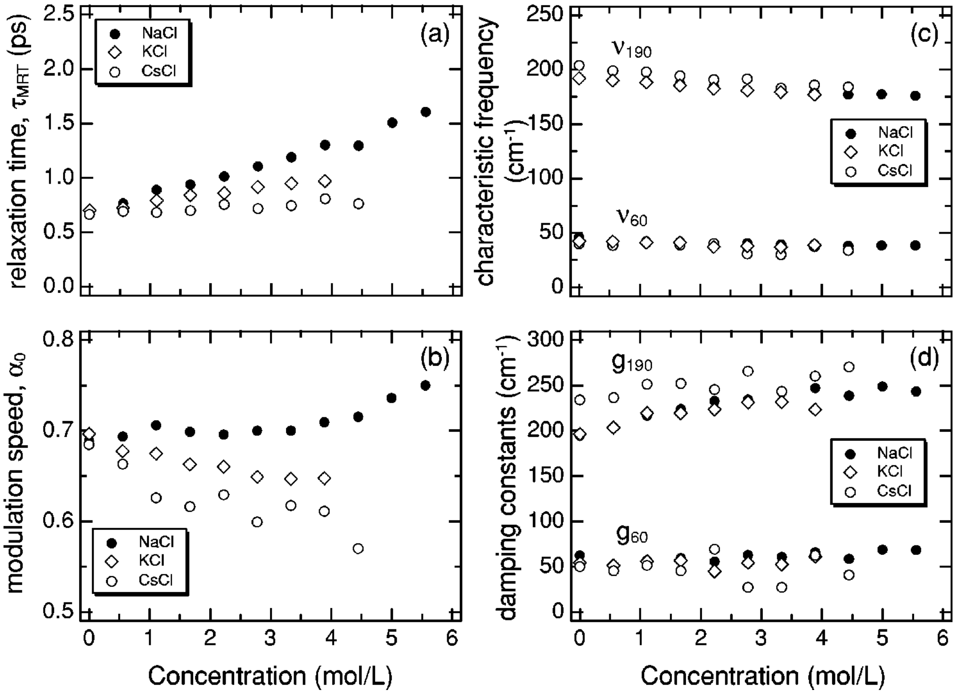

FIG. 5. Fitting results with one MRT model and two damped harmonic oscillations for aqueous alkali-metal chloride solutions at 25 °C. (a) The relaxation time calculated from the MRT model as a function of concentration. (b) The modulation speed as a function of concentration. (c) The characteristic frequencies ν_{190} and ν_{60} as a function of concentration. (d) The damping constants g_{190} and g_{60} as a function of concentration.

stretchinglike and bendinglike modes appear in Fig. 5(c) are considered to be reasonable.

Na^+ ion is considered to be structure-making ion, while K^+ and Cs^+ be structure-breaking ions. Relaxation rate of proton of water molecule in aqueous NaCl solution is larger than that of pure water, while the proton relaxation rates of water molecule in aqueous KCl and CsCl solutions are smaller than that in pure water [33]. The self-diffusion constant of water in aqueous NaCl solution is smaller than that in pure water, while those in aqueous KCl and CsCl solutions are larger than that in pure water [34]. As shown in Fig. 5(b), α_0 varies consistently with the proton relaxation rate and the self-diffusion constant. The α_0 refers to the correlation rate of the heat bath originating from thermal fluctuation of water molecules. Larger α_0 indicates the existence of stronger correlation in fluctuating motion of water molecules. The relaxation rates of aqueous salt solutions within the concentration range studied here are slower than that of pure water. The Debye-type relaxation in water by the dielectric relaxation measurement has been reported and the obtained relaxation times are 8.32 and 1.02 ps [35]. The relaxation time of water molecules obtained in present paper is shorter than the dielectric relaxation time. Therefore, we consider that the relaxation process observed by low-frequency Raman scattering in aqueous solutions does not correspond to the collective rotational motion of water molecules. Amo and Tominaga interpreted that the relaxation time of MRT model as the averaging lifetime of the vibrating unit [22,24,25]. Salt concentration dependences of α_0 indicate that the relaxation mode observed in low-frequency Raman scattering should contain the information of the reorientational motion in the hydration shell.

Parameter α_0, the correlation strength of the heat bath, is considered to be an indicator of structure-breaking and structure-making nature of each salt.

C. Correlation between the phase behaviors of NIPA gels and the characteristics of water molecules in aqueous alkali-metal chloride solutions

As shown in Fig. 2, the shift in transition temperature ΔT of NIPA gel is sensitive to the effect of additives. ΔT is considered to be a measure of the salt effect on the entropy of bulk water. It is important to know the correlation between ΔT and the change in the dynamic nature of the water by addition of salts. Figures 6(a) and 6(b), respectively, indicate the relaxation time and the modulation speed of water molecules in aqueous salt solutions in terms of the shift in transition temperature ΔT of NIPA gel.

The chain segment of the NIPA gel is considered to take two states, the hydrated and dehydrated state. The affinity of segment in hydrated state to water molecules is larger than that in the dehydrated state. A large affinity leads to a large excluded volume of the segment and vice versa. A large excluded volume favors a large average end-to-end distance of an effective chain between the cross links, and therefore a large gel volume. The gel volume increases with an increase in number of the chains in the hydrated state. The dehydration causes an affinity reduction of the chain segment to the solvent and induces the chain collapse [6–8]. The fraction of the chain segment in the hydrated state increase with the increase in the chemical potential of water molecule in the bulk and so does the gel volume. The water molecules dissociate from the chains to the bulk when the chemical potential (free energy) of water is lower than that of the polymer associated water molecule. The presence of salts tends to reduce the chemical potential of water, which cause the desorption of water molecules from the gel network chains, probably the proximity of isopropyl group. The phase transition of NIPA gel is, therefore, induced by a transitionlike decrease in the fraction of the hydrated segment with decrease in the chemical potential of water molecule in the bulk as salt concentration rises.

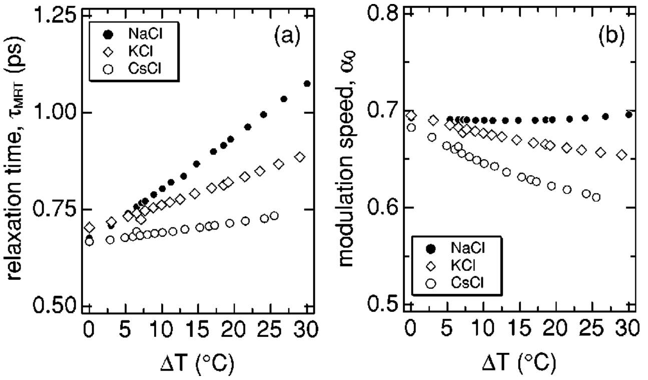

FIG. 6. Relationship (a) between the change in the relaxation time τ_{MRT} with the addition of alkali-metal chloride, and the decrement of transition temperature ΔT; and (b) between the change in the modulation speed α_0 with the addition of alkali-metal chloride, and the decrement of transition temperature ΔT of NIPA gel in the aqueous alkali-metal chloride solutions.

Chemical potential of water decreases with increasing temperature due to the entropy contribution. At a given temperature, the chemical potential of water in the salt solution decreases with increasing the salt concentration due to the free energy mixing. Therefore, increase in salt concentration and increase in temperature has the same effect of decreasing the chemical potential of water. The chemical potential of water in solution containing an additive (species i) at concentration of C_i, $\mu_{H_2O}(T,C_i)$, is given by [12,27]

$$\mu_{H_2O}(T,C_i)=\mu^0_{H_2O}(T)+RT\ln a_w(C_i), \tag{10}$$

where $\mu^0_{H_2O}(T)$ and $a_w(C_i)$ are the chemical potential of pure water at temperature T, and the activity of water in the presence of an additive C_i. Therefore, the decrement of the chemical potential of water caused by the addition of alkali-metal chloride, $\Delta\mu_{H_2O}(=\mu^0_{H_2O}-\mu_{H_2O})$, is given by $-RT\ln a_w$ in terms of activity a_w.

Figure 7 shows the relation between $\Delta\mu_{H_2O}$ and ΔT, the decrement of the transition temperature of NIPA gels due to the alkali-metal chloride. The activities of water in aqueous alkali-metal chloride solutions are assumed to be independent of temperature range of 10–35 °C. This assumption was

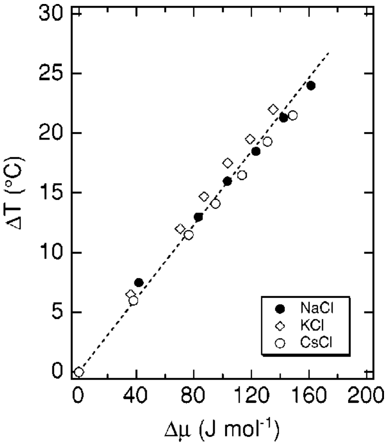

FIG. 7. Relationship between $\Delta\mu_{H_2O}$, the decrement of the chemical potential of water molecules with the addition of alkali-metal chloride, and the decrement of transition temperature ΔT of NIPA gel in the aqueous alkali-metal chloride solutions.

shown to be valid since the activity at 37 °C obtained in the present paper agreed with the values in the literature [28] within the experimental error (3%). As shown in Fig. 6, good linear relations are found between $\Delta\mu_{H_2O}$ and ΔT for all alkali-metal chlorides studied here.

The α_0 value is considered to measure the entropy of the water molecules: small α_0 value indicate the ordered structure of water molecule, which corresponds to the high free energy of bulk water. When α_0 is smaller, the free energy of bulk water is higher, and hydrated water molecules to NIPA gel network are stable and prefer to bind to the polymer chain. The smaller the α_0 value, the more the water molecules binds to the polymer chain. While α_0 value is larger, the hydrated water molecules to NIPA gel network become unstable and prefers to dissociate from the polymer chain.

Figures 8(a) and 8(b), respectively, show the correlation between the chemical potential and the relaxation time τ_{MRT}, and that between the chemical potential of water molecule and the modulation speed α_0 at the transition points. These indicate that the chemical potentials at the transition points are almost constant, whereas the dynamic structure of bulk water is changed by addition of alkali-metal chlorides or by changing temperature. This indicates that the free energy of the bound water molecules in the NIPA gel at the transition is invariant with respect to dynamic parameters of water.

The observed correlation between the swelling behavior of NIPA gel and the experimentally determined parameters of water in the gel suggests that the volume phase transitions due to the different type of perturbation (temperature, salt) are induced by the same mechanism, hydrophobic hydration and dehydration, and therefore can be described in a unified manner in terms of the chemical potential of water.

V. CONCLUDING REMARKS

The salt effect on the phase transition of NIPA gel was studied for alkali-metal chlorides (NaCl, KCl, and CsCl). The series of swelling experiment reveal that the change in the NIPA gel volume phase transition strongly depends on the salt concentration and is related to the dehydration with respect to hydrophobic hydration. From the analysis of the low-frequency Raman spectra in water and various aqueous solutions, the presence of salts tends to disrupt the hydration structures of water molecules in the vicinity of the NIPA side chain, as a result of which the gel collapses. The swelling behavior of NIPA gels and the characteristic values of aqueous salt solutions (i.e., relaxation time τ_{MRT} and modulation speed α_0) obtained from Raman spectra indicate that the addition of alkali-metal chloride to gel fluid affects the disruption of water molecules in the hydration shell around the NIPA gel and on the formation of the hydrogen-bonded network structure of water around themselves.

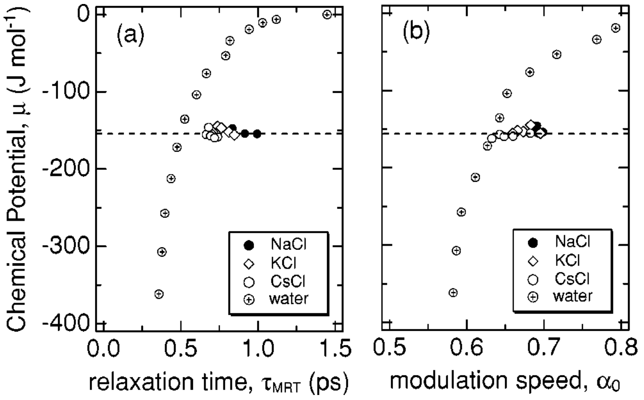

FIG. 8. Correlation (a) between the chemical potential of water molecules and the relaxation time τ_{MRT} at the transition points, and (b) between the chemical potential of water molecules and the modulation speed α_0 at the transition points. The chemical potential at 0 °C is taken as 0. The dotted line denotes the chemical potential of pure water at the transition temperature of NIPA gel in water (=34 °C).

The swelling behavior of the NIPA gel is well described as a function of chemical potential difference of water in solution from that at the transition. The correlation between the chemical potentials and the dynamic nature of water molecules (i.e., relaxation time τ_{MRT} and modulation speed α_0) at the transition points indicates that the chemical potentials at the transition points are almost constant whereas the structure of bulk water is changed by addition of alkali-metal chlorides or change in temperature. These results strongly suggest that the swelling ratio of NIPA gel is a function of hydration degree, which is regulated by the chemical potential of water.

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