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	作成者: Tanaka, Shimon, Takushi, Eisei, Yonekura, Nobuaki, Miyagi, Yusei, 米蔵, 誠哲, 宮城, 雄清
	メールアドレス:
	所属:
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The Volume Phase Transitions of Chemically Cross-Linked DNA Gels Induced by Salts : Na$^+$ and Mg^{2+} Ions II

Shimon TANAKA*[†], Eisei TAKUSHI*, Nobuaki YONEKURA** and Yusei MIYAGI**

*Department of Physics and **Department of Chemistry, Faculty of Science,
University of the Ryukyus, Okinawa 903-0129, Japan

Abstract

A chemically cross-linked DNA gel in acetone-water mixtures involving salt is demonstrated to bring about the volume phase transition with varying the salt concentration. The salt concentration at the discrete volume change depends strongly on the valency of the positive salt ion in the solution. The transition salt comcentration for NaCl is several hundred times larger than the transition MgCl$_2$ concentration. For NaCl, the first order phase transition is observed at the NaCl concentration of 4×10^{-2} mol/l for the 60% acetone-water mixtures. For MgCl$_2$, the discrete volume change are observed at 8×10^{5} mol/l of MgCl$_2$ concentration for 50% acetone-ware mixtures, 7×10^{5} mol/l for 60%, respectively.

Introduction

An ionized polymer gel undergoes a discrete and reversible volume phase transition with change in temperature, pH and solvent composition [1], [2]. The phase transition is brought about by shrinking of molecules due to tension added to gel, this phenomenon is theoretically predicted by Dusek and Patterson[3] based on Flory-Huggins theory in 1968. The theory of the first order phase transition induced by collapse of single strand DNA under the condition of random coil was reported in 1979 by Post and Zimm[4]. Recently, a chemically cross-linked DNA gel is found to bring about a volume phase transition upon varying solvent composition[5], [6]. Amiya and Tanaka clearly demonstrated the existence of a first order volume phase transition of natural polymer gels such as DNA, gelatin and agarose gels in acetone-water mixtures [5]. In 1982, Ohmine and Tanaka found to undergo a discrete phase transition in equilibrium volume upon varying the salt concentration in the solution [7]. The transition salt concentration depends strongly on the valency of the positive salt ion added to the solution. The gels that have been found to exhibit salt effects on the phase transition of ionic gels so far are all synthetic polymers. The question remains whether discrete phase transition upon varying the salt concentration in the solution is universal for cross-linked polymer gels. In the present study, the salt concentration dependence in the acetone-water solution on the volume phase transition of chemically cross-linked DNA gel is discussed with ionic osmotic pressure. It is observed that, for the first time, the volume phase transition of chemically cross-linked DNA gel induced by salts. The transition salt concentration for NaCl is several hundred larger than that of MgCl$_2$.

Results and Discussion

The samples were prepared by standard method [4]. DNA (SIGMA, Type III sodium salt from salmon testes, DNA fiber include 5.6% of Na and 12.9% of H_2O) in water (20%) is cross-linked by using ethylene glycol diglycidyl ether (50% of DNA) at pH 11, 55℃, for 3h. The quantity V_1/V_0 represent the ratio of the final volume to initial volume. The ratio is given by (d_1/d_0), where d_0 and d_1 are the initial and final equilibrium diameters of the gel, respectively. All the experiments were carried out at room temperature(25C°).
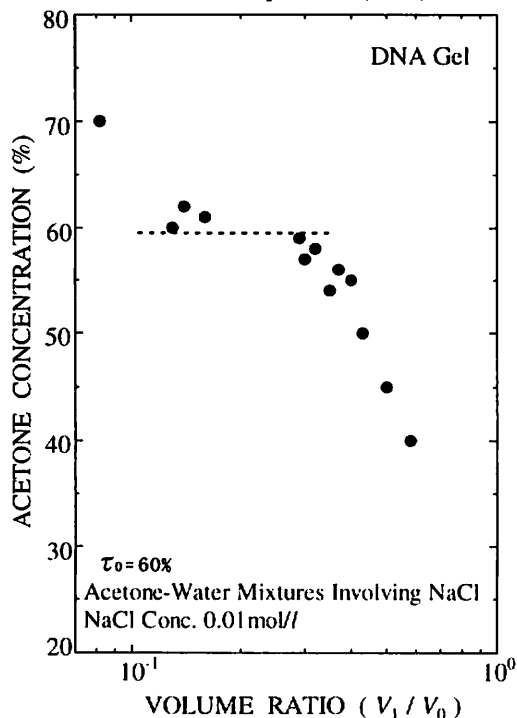

Fig.1 The volume phase transition of the DNA gel in acetone-water mixtures involving NaCl. The transition acetone concentration τ_0 is about 60% under the condition of gel diameter 2.48mm, and 1×10^{-2} mol/l of NaCl concentration.
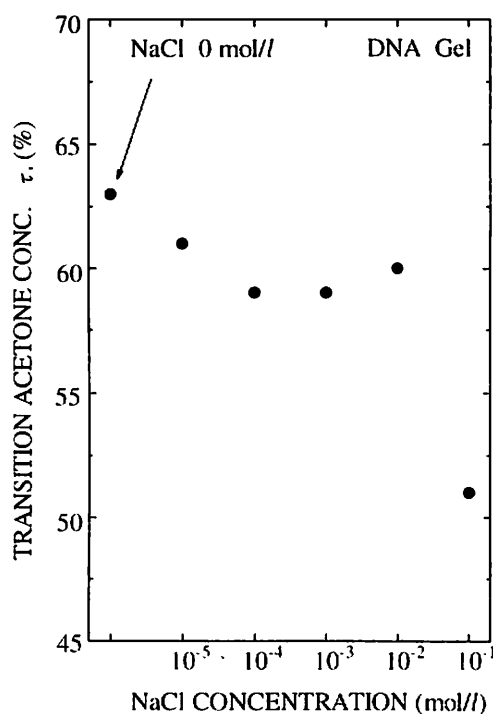
Fig.2 The dependence of NaCl concentration on transition acetone concentration τ_0 in acetone-water mixtures.

At first, the volume phase transition of the DNA gels in acetone-water mixtures involving NaCl is demonstrated. Figure 1 shows a typical volume phase transition of the DNA gel in acetone-water mixtures involving NaCl under the condition of 1×10^{-2}mol/l NaCl concentration. The discontinuous phase transition of the DNA gel occurs at about 60% acetone concentration. The volume change at the first order phase transition is about 2 times.

Figure 2 shows the dependence of the transition acetone concentration (τ_0) on NaCl concentration for the volume phase transition in acetone-water mixtures involving NaCl. The transition acetone concentration is changed gently with NaCl concentration range from 1×10^{-5} mol/l to 1×10^{-2} mol/l; τ_0 is 61% for NaCl concentration of 1×10^{-5} mol/l, 59% for 1×10^{-4} mol/l, 59% for 1×10^{-3} mol/l, 60% for 1×10^{-2} mol/l, respectively. The extremely decreasing of transition acetone concentration occurs at the NaCl concentration of 1×10^{-1} mol/l. We analyzed experimental results of the dependence of the transition acetone concentration τ_0 on the NaCl concentration, and obtained that varying NaCl concentration is brought about the volume phase transition of chemically cross-linked DNA gel in various acetone-water mixtures.
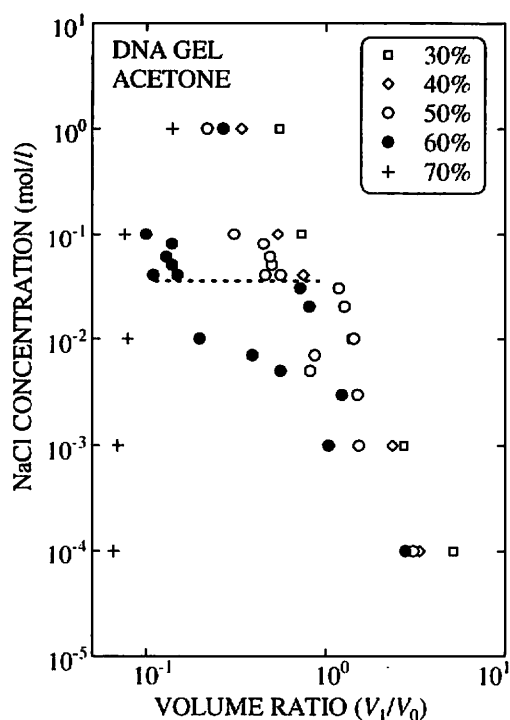
Fig.3 The swelling volume ratio V_1/V_0 depends on the NaCl concentrations in 30%, 40%, 50%, 60% and 70% acetone-water mixtures. The transition NaCl concentration is about 4×10^{-2}mol/l for 60% acetone-water mixtures.
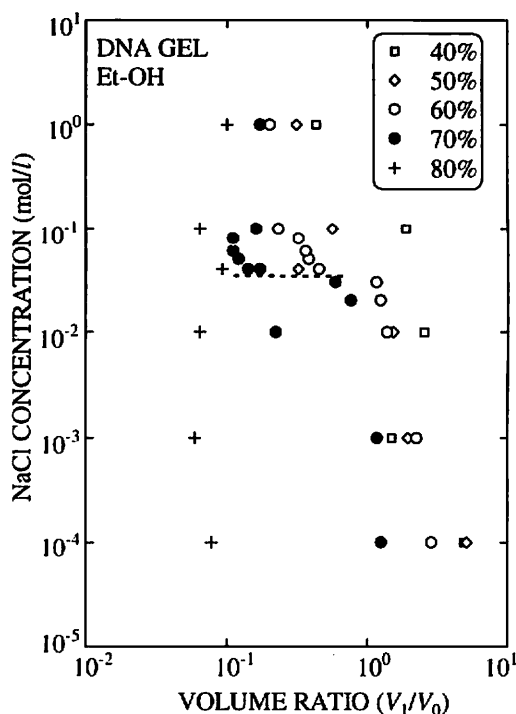
Fig.4 The swelling volume ratio V_1/V_0 depends on the NaCl concentrations in 40%, 50%, 60%, 70% and 80% ethanol-water mixtures. The transition NaCl concentration is about 4×10^{-2}mol/l for 70% ethanol-water mixtures.

In Fig. 3, a discrete transition of the gel volume occurs at certain critical concentration of NaCl for a given acetone-water mixtures is shown. The first order transition is observed at the NaCl concentration of 4×10^{-2} mol/l for the 60% acetone-water mixtures. The DNA gel is shrunken state completely in the 70% acetone-water mixtures, regardless of the NaCl concentration, since the DNA gel undergoes a collapse at about 60% acetone concentration without NaCl. The volume of DNA gel shows only continuous change in 30%, 40% and 50% acetone-water mixtures. The ethanol-water mixtures also be used to demonstrate the volume phase transition induced by varying NaCl concentration. The discontinuous volume change is observed at the NaCl concentration of 4×10^{-2}mol/l in the 70% ethanol-water mixtures (Fig.4). The DNA gel shows only continuous volume change for varying NaCl concentration in 40%, 50% and 60% ethanol-water mixtures, and completely collapsed state in 80% ethanol concentration.

For MgCl₂, the DNA gel shows discrete phase transition at salt concentrations much lower than for NaCl. The DNA gel required much longer, about five weeks, to attain equilibrium. The volume of DNA gel in 40% acetone-water mixtures shows continuous change upon varying MgCl₂ concentration. The first order phase transitions are observed at 8×10^{-5} mol/l of MgCl₂ concentration for 50% acetone-water mixtures, 7×10^{-5} mol/l for 60%, respectively (Fig.5). For ethanol-water mixture, the volume phase transitions are observed at 2×10^{-4}mol/l of MgCl₂ concentration for 50% and 60% ethanol-water mixtures, 3×10^{-5}mol/l for 70%, respectively (Fig.6).

The total osmotic pressure of the gel consists of π network and π ion. π network is network osmotic pressure, given by the Flory-Huggins formula. The ion osmotic pressure π ion is defined the sum of the term of counter ion osmotic pressure and the term of the excess decrease of free energy of
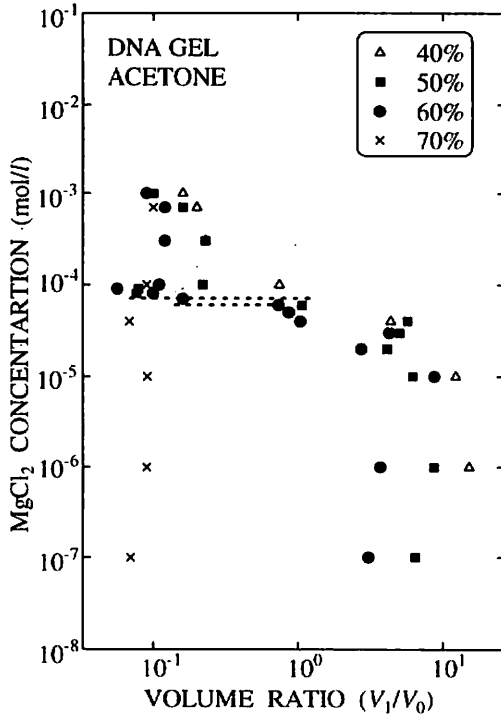
Fig.5 The swelling volume ratio V_1/V_0 depends on the MgCl₂ concentrations in 40%, 50%, 60% and 70% acetone-water mixtures. The transition MgCl₂ concen-tration is about 8×10^5mol/l for 50% acetone-water mixtures, 7×10^5mol/l for 60%, respectively.
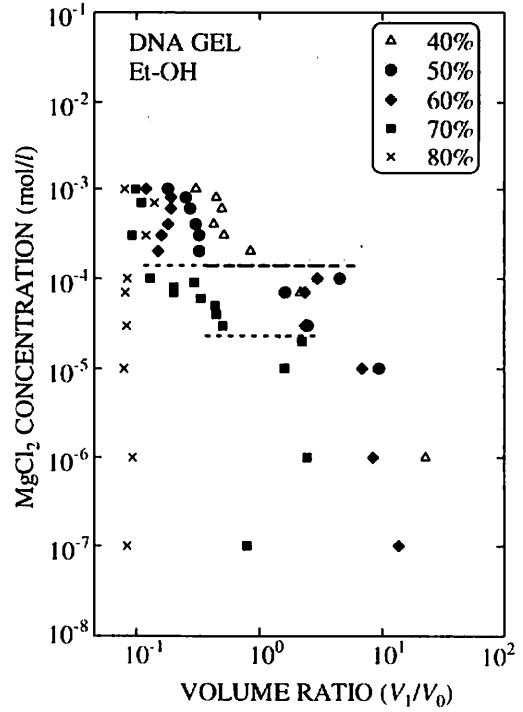
Fig.6 The swelling volume ratio V_1/V_0 depends on the MgCl₂ concentrations in 40%, 50%,60%,70% and 80% ethanol-water mixtures. The transition MgCl₂ concen-tration is about 2×10^4mol/l for 50% and 60% ethanol-water mixtures, 3×10^5mol/l for 70%, spectively.

contact between polymer segments.

$$\pi_{\text{network}} = -\frac{NkT}{v}\left[\phi + \ln(1-\phi) + \frac{1}{2}\frac{\Delta F}{kT}\phi^2\right] + \nu kT\left[\frac{1}{2}\frac{\phi}{\phi_0} - \left(\frac{\phi}{\phi_0}\right)^{1/3}\right] \quad (1)$$

$$\pi_{\text{ion}} \equiv f\nu kT\frac{\phi}{\phi_0} + \Delta Fs\frac{N\phi^2}{2v} \quad (2)$$

Where N is Avogadoro's number, k is the Boltzmann constant, T is temperature, v is the molar volume of solvent, ϕ_0 is the volume fraction of the network at the condition the constituent polymer chains have random-walk configurations, ν is the number of constituent chains per unit volume at $\phi = \phi_0$, and Δ F denotes the free energy decrease associated with the formation of contacts between two polymer segments. ΔFs may be regarded as the excess decrease of free energy of contact between polymer segments. In equilibrium, the osmotic pressure on a gel immersed in a large volume of solvent is equal to zero;

$$\pi_{\text{network}} + \pi_{\text{ion}} = 0 \quad (3)$$

Equation (3) is transformed by Eq. (1) and (2) as follows,

$$\tau \equiv 1 - \frac{\Delta F - \Delta F_S}{kT},$$

that is

$$\tau = -\frac{v\,\nu}{N\phi^2} \left[(2f + 1)\,\frac{\phi}{\phi_0} - 2\left(\frac{\phi}{\phi_0}\right)^{1/3} \right] + 1 + \frac{2}{\phi} + -\frac{2\ln(1 - \phi)}{\phi^2}. \qquad (4)$$

The τ is called the reduced temperature, which varies with temperature, solvent composition and salt composition through the parameter Δ Fs. Within the gel and solvent there are four kinds of mobile ions: H^+, OH^-, Cl^- and Na^+ or Mg^{2+}. These mobile counter ions in the gel create an excess osmotic pressure. The free energy of contact between polymer segments is changed by increasing salt concentration. For lower NaCl concentration, network-fixed negative groups is neutralized by mobile counter ions. When NaCl concentration increases and equals to the hydrogen ion concentration, the hydrogen ions in the gel are replaced by the Na^+. This replacement does not bring about changes in ion osmotic pressure for monovalent ions. But this replacement brings about drastic change in ion osmotic pressure for divalent positive ions. When NaCl concentration equals to that of negative charges fixed on the network, the osmotic pressure of the ions in the solvent increases and the net osmotic pressure of ions decreases. This situation denote that the value of f decrease for the varying salt concentration. At the same time, the reduced temperature τ first increase, and cross the unstable region. Thus, the gel bring about volume phase transition at the optimal NaCl concentration.

In the case of divalent salts such as $MgCl_2$, when the hydrogen ions in the gel are replaced by the Mg^{2+}, ion osmotic pressure already drastic change, although not change ion osmotic pressure for the monvoalent ion. At the same time, value of f becomes half value. If the initial reduced temperature is low enough the trajectory may cross the unstable region at this $f \rightarrow f/2$ change.

In conclusion, it is demonstrated, for the first time in chemically cross-linked DNA gel, that the universality of the first order volume phase transition is induced by varying salt concentration in the acetone-water solution.

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