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Volume Phase Transition Behavior of *N*-Isopropylacrylamide Gels as a Function of the Chemical Potential of Water Molecules

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The physicochemical nature of the volume phase transition of hydrogels has been clarified to some extent thanks to intensive investigations during the past two decades.[1] However, a unified understanding of the phenomena is still vague. We have found a good correlation between the chemical potential of water molecules and the phase transition of *N*-isopropylacrylamide gel by analyzing the results of the effect of NaCl,[2] KCl,[3] and sucrose and glucose additives[4] on the volume phase transition behavior of *N*-isopropylacrylamide polymer gel. The results indicate that the chemical potential of water molecules in solution at the transition is kept nearly constant in spite of different transition temperatures, induced by different perturbations. It was also found that the deswelling behavior of the gel was well described as a function of the chemical potential difference of the water molecules in solution from that at the transition. These facts strongly indicate that the order parameter to induce the volume phase transition is well characterized by a thermodynamic variable of the chemical potential of the water molecule.

The swelling behavior of polymer gels has attracted much attention since the discovery of the discontinuous volume reduction of poly(*N*-isopropylacrylamide) gel (GNIPA) with increase in temperature,[5] which is regarded as the volume phase transition. The volume phase transition of NIPA gels has been intensively investigated from various points of view for the past two decades. The ^{1}H spin−spin relaxation time, T_2, of water molecules in the poly(*N*-isopropylacrylamide) (PNIPA) solution showed a sharp change with the temperature around the transition temperature.[6] The endothermic transition heat[7] accompanying the volume phase transition of NIPA gels is similar to that for the PNIPA solution. These findings suggest that the deswelling of NIPA gels is accompanied by the desorption of water molecules (dehydration) from the gel chain. The dehydration can cause an affinity reduction of the chain segment to the solvent and induces chain shrinkage or chain collapse.

At swelling equilibrium of the gel with aqueous phase containing an additive (species *i*) at a concentration of C_i, the following relation should hold:

$$N_h\mu_{H_2O}(T,C_i) = \mu_h(V,T) - \mu_d(V,T) \qquad (1)$$

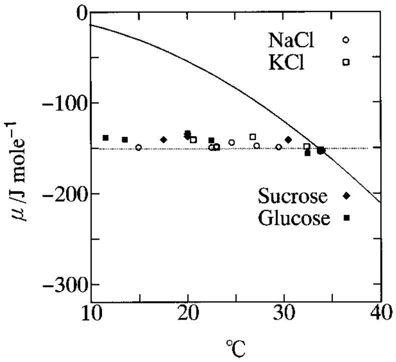

Figure 1. Relation between the volume phase transition temperature of NIPA gel and the chemical potential of water molecules in the solution. The chemical potential at temperature 0 °C is taken as 0. Solid and dotted lines respectively denote the temperature dependence of the chemical potential of pure water and the chemical potential of water at the transition temperature of NIPA gel in water. Four symbols denote the chemical potential of water at the transition temperatures in the presence of the additives.

where $\mu_{H_2O}(T,C_i)$, $\mu_h(V,T)$, and $\mu_d(V,T)$ respectively are the chemical potentials of water molecules, of the chain segment in the hydrated state with N_h bound water molecules, and of the chain segment in the dehydrated state. Here, *V* and *T* respectively are the gel volume and temperature. At the volume phase transition point, eq 1 can be rewritten as

$$N_h\mu_{H_2O}(T,C_i) = \mu_h(V^c,T) - \mu_d(V^c,T) = \mu_h(V^s,T) - \mu_d(V^s,T) \qquad (2)$$

Superscript c and s respectively refer to the collapsed and swollen states, which are in thermodynamic equilibrium with each other. Equation 1 or 2 simply describes the equivalence of the chemical potential of water molecules in the hydration layer and in the bulk solution. The chemical potential of water molecules in solution, $\mu_{H_2O}(T,C_i)$, is given by

$$\mu_{H_2O}(T,C_i) = \mu^0{}_{H_2O}(T) + RT \ln a_W(C_i) \qquad (3)$$

where $\mu^0{}_{H_2O}(T)$ and $a_W(C_i)$ respectively are the chemical potential of pure water at *T* and the activity of water in the presence of an additive C_i.

$\mu_{H_2O}(T,C_i)$ values at the transition temperatures in the presence of NaCl[2] or KCl[3] or glucose or sucrose[4] were evaluated on the basis of the literature values of $\mu^0{}_{H_2O}(T)$[8] and $a_W(C_i)$.[9] The result is shown in Figure 1. The observed chemical potentials of water at different transition temperatures were nearly the same in the four cases examined. This indicates that the free energy of the bound water molecules on the gel at the transition (right-hand side of eq 2) is invariant with respect to temperature.

In Figure 2a,b, the gel volume transition behavior[2,4] is represented in terms of the chemical potential of water molecules instead of temperature. The chemical

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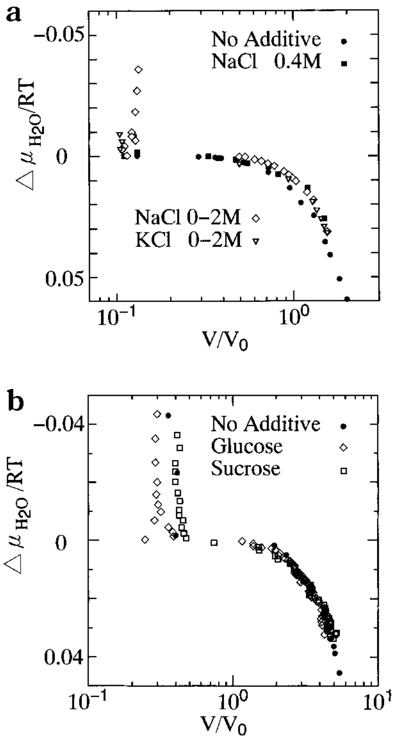

Figure 2. Chemical potential of water molecules as functions of the swelling/collapsing volumes of NIPA gel in solutions of salts (a) and saccharides (b). The closed and open symbols respectively denote the data evaluated from the temperature-induced transition and the isothermal transition induced by changing the concentration of the additives. Chemical potential is given as the difference from that at the transition temperature. The abscissa is a ratio of the gel volume to that at the synthesis.

potential difference of water molecules from that at the transition, $\Delta\mu_{H_2O}$, is shown as the ordinate variable in Figure 2a,b. When $\Delta\mu_{H_2O}$ is positive, water molecules prefer to bind to polymer chain; that is, the hydrated state is well stabilized. The larger the difference, the more water molecules bind to the gel chain. The gel volumes in the swollen state are monotonously increasing functions of the chemical potential difference of the water molecules. This strongly suggests that the degree of swelling of a NIPA gel is a function of the hydration degree, which is regulated by the chemical potential of water molecules. It is remarkable that the volume phase transitions due to different types of perturbation can be described in a unified manner in terms of the chemical potential of water molecules. The volume phase transition of the gel can be theoretically described by using the chemical potential of water molecules as an order parameter.[10]

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