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Cooperative Hydration, Chain Collapse, and Flat LCST Behavior in Aqueous Poly(*N*-isopropylacrylamide) Solutions

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ABSTRACT: Phase diagrams with very flat LCST phase separation line for aqueous poly(*N*-isopropylacrylamide) (PNIPAM) solutions are theoretically derived on the basis of sequential hydrogen bond formation between polymer chains and water molecules (cooperative hydration) and compared with experimental spinodal curves. The two-phase region systematically changes its shape with the cooperativity parameter σ, and the spinodals turned out to be almost independent of the polymer molecular weight for strongly cooperative hydration (small σ) as observed in PNIPAM solutions. Hydration takes place sharply within a very narrow temperature region. The number of hydrogen-bonded water molecules on a chain is calculated as a function of the temperature and the polymer concentration.

1. Introduction

Phase diagrams of water-soluble polymers often exhibit peculiar phase separation. For instance, aqueous poly(ethylene oxide) (referred to as PEO) solutions show closed-loop phase separation region (miscibility loop) at intermediate temperatures.[1−3] The phase boundary is highly sensitive to the molecular weight of polymers and also to the external pressure. The miscibility loop expands with the polymer molecular weight, and its lower critical solution temperature (LCST) approaches an inverted theta temperature in the limit of infinite molecular weight.[2] The loop also abruptly expands under high pressure at around 4 kbar.[4] These peculiar phase behavior was first theoretically shown to be caused by the hydrogen bonding between ether groups on the polymer chain and water molecules.[5] Later, it was shown by molecular dynamics simulation[6] that a PEO chain takes a loose helical conformation (11/2 helix) in aqueous solution, whose pitch ($\simeq$1.7 nm) just fits the size of a water molecule for adsorption by hydrogen bonds through the two hydrogen atoms on a water molecule. There is a competition in forming polymer−water hydrogen bonds and water−water hydrogen bonds. The hydrogen-bond networks in water are, however, not so strong in the temperature region of loop-shaped phase separation (typically 100−200 °C) that indirect interaction between the neighboring water molecules on a chain via water hydrogen-bond network is expected to be weak. The water molecules are therefore randomly and independently adsorbed into the pockets of the helices. Later, the pressure effect was studied on the basis of the similar picture[7] such that the effective number of hydrogen-bonding sites along a polymer chain is reduced by pressure.

In contrast to PEO, other water-soluble polymers such as poly(*N*-isopropylacrylamide) (referred to as PNIPAM) show very flat LCST behavior whose cloud-point lines and spinodal lines are horizontal up to 20 wt % of polymer concentration and almost independent of the molecular weight.[8,9,12−14] Poly(propylene oxide) oligomers also show similar phase behavior.[1] The phase separation region takes a shape like the bottom part of a square, so that in what follows we refer to it as the miscibility square. Obviously, the miscibility square cannot be explained by random adsorption of water molecules onto a polymer chain. But, if we introduce positive correlation between the neighboring hydrogen bonds along the polymer chain, i.e., if adsorption of a water molecule onto a site next to the already adsorbed one is preferential, phase separation may take place in a narrow temperature region. For PNIPAM, it is in fact the case because the hydrogen-bonding site (amido group) is blocked by a large hydrophobic group (isopropyl group). The random coil parts sharply turn into collapsed globules on approaching the phase separation temperature,[9] so that hydrogen bonding is easier at the boundary between an adsorbed water sequence and a collapsed coil. Such a steric hindrance by hydrophobic isopropyl side groups is the main origin of the strong correlation between the neighboring water molecules. The purpose of this paper is to show theoretically that formation of sequential hydrogen bonds along the polymer chain, or cooperative hydration, in fact leads to miscibility square behavior of aqueous polymer solutions by the so-called domino effect. We calculate the fraction θ of bound water molecules and their average contiguous length $\bar{\zeta}_{\rm w}$ as functions of the temperature and the polymer concentration and derive flat LCST phase diagrams. We compare the results with the recent experimental data on PNIPAM solutions by paying special attention to the molecular weight dependence.

2. Free Energy of the Model Solutions

We consider a model solution in which the number N_1 of polymer chains with degree of polymerization (referred to as DP) n are mixed with the number N_0 of water molecules. We are based on the lattice-theoretical picture of polymer solutions and divide the system volume V into cells of size a, each of which can accommodate either a water molecule or a statistical repeat unit of the polymer. We assume incompressibility of the solution, so that we have $\Omega = N_0 + nN_1$, where $\Omega \equiv V/a^3$ is the total number of cells. To describe adsorption of water, let $\mathbf{j} \equiv \{j_1, j_2, ...\}$ be the index specifying the polymer chain carrying the number j_ζ of sequences that consist of a run of hydrogen-bonded ζ consecutive water molecules, and let $N(\mathbf{j})$ be the number

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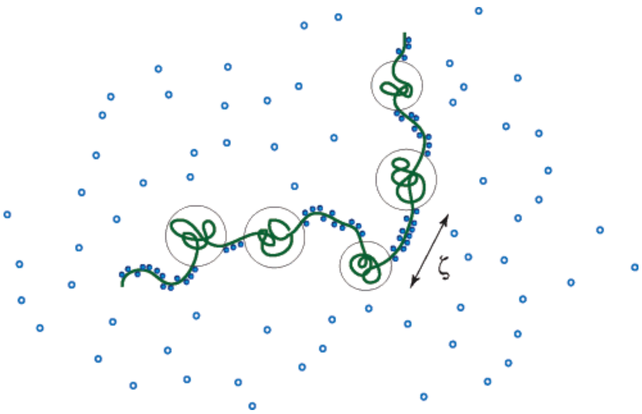

Figure 1. Sequential hydrogen bonds formed along the polymer chain due to the cooperative interaction between the nearest-neghboring bound water molecules. The type of polymer−water associated complex is specified by the index $\mathbf{j} \equiv (j_1, j_2, ...)$, where j_ζ is the number of sequences that consist of a run of hydrogen-bonded ζ consecutive water molecules. The average length of sequences sharply reduces as temeprature approaches LCST from below. The random-coil parts (thin circles) are collapsed near LCST.

of such polymer−water complexes whose type is specified by $\mathbf{j}$ (see Figure 1). The total number of water molecules on a chain specified by $\mathbf{j}$ is given by $\sum \zeta j_\zeta$, and the DP of a complex is given by $n(\mathbf{j}) \equiv n[1 + \theta(\mathbf{j})]$, where

$$\theta(\mathbf{j}) \equiv \sum \zeta j_\zeta / n \tag{2.1}$$

is the fraction of the bound water molecules counted relative to the DP of a polymer.

Then, the free energy of mixing is given by

$$\beta \Delta F = N_{\mathrm{fw}} \ln \phi_{\mathrm{fw}} + \sum_{\mathbf{j}} N(\mathbf{j}) \ln \phi(\mathbf{j}) + \beta \sum_{\mathbf{j}} \Delta A(\mathbf{j})\, N(\mathbf{j}) + \chi \phi (1 - \phi) \Omega \tag{2.2}$$

where $\phi(\mathbf{j}) \equiv n(\mathbf{j}) N(\mathbf{j})/\Omega$ is the volume fraction of the complex $\mathbf{j}$, N_{fw} is the number of free water molecules in the solution, and $\phi_{\mathrm{fw}} \equiv N_{\mathrm{fw}}/\Omega$ is their volume fraction; $\Delta A(\mathbf{j})$ is the conformational free energy to form a complex of the type $\mathbf{j}$ measured relative to the reference conformation $\mathbf{j_0} \equiv \{0, 0, ...\}$ where no water molecule is adsorbed. The total volume of the solution is now written as $\Omega = \sum_{\mathbf{j}} n(\mathbf{j}) N(\mathbf{j}) + N_{\mathrm{fw}}$. The number density of the complexes specified by $\mathbf{j}$ is given by $\nu(\mathbf{j}) = N(\mathbf{j})/\Omega$.

We next derive the chemical potential for the free water and for the associated complex by differentiating the free energy. We find

$$\beta \Delta \mu_{\mathrm{fw}} = \left(\frac{\partial \beta \Delta F}{\partial N_{\mathrm{fw}}} \right)_{T, N(\mathbf{j})} = 1 + \ln \phi_{\mathrm{fw}} - \nu^{\mathrm{S}} + \chi \phi^2 \tag{2.3}$$

for the free water and

$$\beta \Delta \mu(\mathbf{j}) = \left(\frac{\partial \beta \Delta F}{\partial N(\mathbf{j})} \right)_{T, N_{\mathrm{fw}}} = 1 + \beta \Delta A(\mathbf{j}) + \ln \phi(\mathbf{j}) - n(\mathbf{j}) \nu^{\mathrm{S}} + \chi [n(1 - \phi) + n\theta(\mathbf{j})\phi - n(\mathbf{j})\phi(1 - \phi)] \tag{2.4}$$

for the associated complex of the type $\mathbf{j}$, where

$$\nu^{\mathrm{S}} \equiv \nu_{\mathrm{fw}} + \sum_{\mathbf{j}} \nu(\mathbf{j}) \tag{2.5}$$

is the total number of molecules that possess translational degree of freedom.

3. Association Equilibrium and the Number of Bound Water Molecules

We assume the association equilibrium and give the conditions

$$\Delta \mu(\mathbf{j}) = \Delta \mu(\mathbf{j}_0) + n\theta(\mathbf{j}) \Delta \mu_{\mathrm{fw}} \tag{3.1}$$

to find the equilibrium distribution of associated complexes. Then, we find

$$\nu(\mathbf{j}) = K(\mathbf{j}) \nu(\mathbf{j_0}) {\phi_{\mathrm{fw}}}^{n\theta(\mathbf{j})} \tag{3.2}$$

for the number density of the complexes specified by $\mathbf{j}$, where

$$K(\mathbf{j}) \equiv \exp[n\theta(\mathbf{j}) - \beta \Delta A(\mathbf{j})]/[1 + \theta(\mathbf{j})] \tag{3.3}$$

is the association equilibrium constant. The total polymer volume fraction ϕ is then given by

$$\phi = \phi(\mathbf{j_0})\, g_0(\phi_{\mathrm{fw}}) \tag{3.4}$$

and the total volume fraction of water is given by

$$1 - \phi = \phi_{\mathrm{fw}} + \phi(\mathbf{j_0})\, g_1(\phi_{\mathrm{fw}}) \tag{3.5}$$

Here, new functions $g(y)$ are defined by

$$g_0(y) \equiv \sum_{j} K(\mathbf{j}) y^{n\theta(\mathbf{j})}, \quad g_1(y) \equiv \sum_{\mathbf{j}} \theta(\mathbf{j}) K(\mathbf{j}) y^{n\theta(\mathbf{j})} \tag{3.6}$$

These coupled equations should be solved for $\phi(\mathbf{j_0})$ and ϕ_{fw} to find the cluster distribution function in terms of the polymer volume fraction and the temperature. Upon eliminating $\phi(\mathbf{j_0})$, the second equation is transformed to

$$1 - \phi = \phi_{\mathrm{fw}} + \phi G(\phi_{\mathrm{fw}}) \tag{3.7}$$

where the function G is defined by

$$G(y) = g_1(y)/g_0(y) = \partial \ln g_0(y)/n\, \partial \ln y \tag{3.8}$$

The total number ν^{S} of free water molecules and associated complex is given by

$$\nu^{\mathrm{S}} = \phi_{\mathrm{fw}} + \phi/n \tag{3.9}$$

From the Gibbs−Dühem relation for the free energy of mixing $f \equiv \Delta F/\Omega = \phi_{\mathrm{fw}} \Delta \mu_{\mathrm{fw}} + \sum \nu(\mathbf{j}) \Delta \mu(\mathbf{j})$ with help of the reaction equiliblium conditions, we find

$$f = f_{\mathrm{FH}} + f_{\mathrm{AS}} \tag{3.10}$$

where

$$\beta f_{\mathrm{FH}}(\phi, T) = (1 - \phi) \ln(1 - \phi) + \frac{\phi}{n} \ln \phi + \chi \phi (1 - \phi) \tag{3.11}$$

is the usual Flory−Huggins mixing free energy and

$$\beta f_{\mathrm{AS}}(\phi, T) = \frac{\phi}{n} \ln\left(\frac{\phi(\mathbf{j}_0)}{\phi} \right) + (1 - \phi) \ln\left(\frac{\phi_{\mathrm{fw}}}{1 - \phi} \right) + 1 - \phi - \phi_{\mathrm{fw}} \tag{3.12}$$

is the additional free energy due to hydrogen bonding association. This part can be written in the form

$$\beta f_{\mathrm{AS}}(\phi,T) = -\frac{\phi}{n}\ln g_0(\phi_{\mathrm{fw}}) + (1-\phi)\ln[1-\phi G(\phi)/(1-\phi)] + \phi G(\phi_{\mathrm{fw}}) \quad (3.13)$$

by the substitution of relations 3.4 and 3.5.

The free energy of association can be regarded as the renormalization of the χ parameter. The original χ parameter due to van der Waals type contact interaction is modified to $\chi + \Delta\chi$ by hydrogen-bonding association, where the renormalization part

$$\Delta\chi(\phi,T) \equiv \beta f_{\mathrm{AS}}(\phi,T)/\phi(1-\phi) \quad (3.14)$$

depends on the polymer concentration in a complex way. The appearance of peculiar-shaped phase separation regions on the phase plane originates in this effective interaction term.

An attempt to derive the phase diagram of PNIPAM solution by using effective interaction parameter $\chi_{\mathrm{eff}}(T,\phi)$ was made by Baulin and Halperin.[10] They used, however, an empirical power expansion formula by Afroze et al.[11] with many numerical coefficients, whose molecular origin is completely unknown. Although our above renormalization formula due to hydrogen bonding depends implicitly upon the concentration, we can expand it in power series in the dilute regime and directly compare the result with the experimental measurements on the second virial coefficient of the osmotic pressure. We will discuss this point in the final section of this paper.

4. Osmotic Pressure and the Spinodal Condition

The osmotic pressure π can be found by the thermodynamic relation $\pi a^3 = -\Delta\mu_{\mathrm{fw}}$ and is given by

$$\beta\pi a^3 = -\beta\Delta\mu_{\mathrm{fw}} = -1 - \ln[1-\phi-\phi G(\phi_{\mathrm{fw}})] + [1-\phi-\phi G(\phi_{\mathrm{fw}}) + \phi/n] - \chi\phi^2 \quad (4.1)$$

By expanding the function $G(y)$ in powers of the concentration as $G(y) = G_0 + G_1\phi + ...$, we find the second virial coefficient in the form

$$A_2 = \frac{1}{2}(1+G_0)^2 - \chi \quad (4.2)$$

where G_0 is the value of $G(y)$ in the limit of infinite dilution.

The spinodal condition is found by differentiating the osmotic pressure once more by the concentration. We find

$$\frac{1}{n\phi} + \frac{\kappa(\phi)}{1-\phi} - 2\chi = 0 \quad (4.3)$$

where

$$\kappa(\phi) \equiv [1+G(\phi_{\mathrm{fw}})]^2(1-\phi)/[1+\phi G'(\phi_{\mathrm{fw}})]\phi_{\mathrm{fw}} \quad (4.4)$$

gives the effect of hydration. The volume fraction ϕ_{fw} of free water is assumed to be solved as a function of the total polymer volume fraction ϕ and substituted into this function κ. Hence, κ is regarded as a function of ϕ.

5. Cooperative Association

Let us now proceed to the study on the models of association. If water molecules are independently and randomly hydrogen bonded onto the polymer chain, as was studied previously,[5] the index **j** can be replaced by the number m of the bound water molecules, and $K(\mathbf{j})$ is replaced by $K_{\mathrm{m}} = (1 + m/n)_n C_m \lambda^m$, where ${}_nC_m = n!/m!(n-m)!$ is the number of different ways to choose m hydrogen-bonding sites from the number n of the total available sites, and $\lambda(T) \equiv \exp(-\beta\Delta f_0)$ is the association constant (Δf_0 being the free energy of one hydrogen bond). The functions appearing in thermodynamic properties are given by $g_0(y) = (1+y)^n$, $g_1(y) = y(1+y)^{n-1}$, and $G(y) = y/(1+y)$, where $y \equiv \lambda\phi_{\mathrm{fw}}$ is the reduced concentration of the free water. All results reduce to those found in our previous study on phase diagrams of PEO solutions.[5]

Now, let us move onto cooperative hydration. The equilibrium constant is most generally written as

$$K(\mathbf{j}) = \omega(\mathbf{j})\prod_{\zeta=1}^{n}\eta_\zeta^{j_\zeta} \quad (5.1)$$

where

$$\omega(\mathbf{j}) \equiv (n - \sum\zeta j_\zeta)!/\Pi j_\zeta![n - \sum(\zeta+1)j_\zeta]! \quad (5.2)$$

is now the number of different ways to select sequences specified by **j** from a chain, and η_ζ is the statistical weight for a single water sequence of the length ζ formed on a reference coil.[15]

Since summing up all possible types **j** in the above functions is mathematically difficult, we replace the sum by the contribution from the most probable type $\mathbf{j}^*$ (one-mode approximation). The necessary functions are then given by

$$g_0(y) = \omega(\mathbf{j}^*)\prod_{\zeta=1}^{n}(\eta_\zeta y^\zeta)^{j_\zeta} \quad (5.3)$$

and $g_1(y) = \theta(\mathbf{j}^*)g_0(y)$, and $G(y) = \theta(\mathbf{j}^*)$. The function G reduces to the coverage θ of the bound water in the type $\mathbf{j}^*$.

The most probable type, or sequence distribution, can be found by minimizing the free energy f_{AS} by changing **j**, i.e., by the condition $\partial f_{\mathrm{AS}}/\partial j_\zeta = 0$. We find that it is given by

$$j_\zeta/n = (1-\theta)t\eta_\zeta q^\zeta \quad (5.4)$$

where q is defined by the equation

$$q \equiv (1-\phi-\theta\phi)t\exp[R(q,\phi)] \quad (5.5)$$

Here, the function $R(\theta,\phi) \equiv \theta\phi/(1-\phi-\theta\phi)$ gives the ratio of the total number of bound water molecules to that of the free ones. The parameter t is given by $t \equiv 1 - \nu/(1-\theta)$. Substituting this distribution function 5.4 into the definitions of θ and ν, we find

$$\theta(q) = [1-\theta(q)]t(q)\,V_1(q) \quad (5.6)$$

and

$$\nu(q) = [1 - \theta(q)]t(q)\, V_0(q) \tag{5.7}$$

and hence

$$t(q) = 1/[1 + V_0(q)] \tag{5.8}$$

Here new functions V are defined by

$$V_0(q) \equiv \sum \eta_\zeta q^\zeta \quad \text{and} \quad V_1(q) \equiv \sum \zeta \eta_\zeta q^\zeta \tag{5.9}$$

Now, θ and t must be regarded as functions of q, so that eq 5.5 is an equation for the unknown variable q to be solved in terms of the concentration ϕ.

The κ function in our spinodal condition (eq 4.3) now takes the form

$$\kappa(q;\phi) = \frac{1 + (1 - \theta)QR}{1 + (1 - \theta)QR^2}(1 + \theta)^2(1 + R) \tag{5.10}$$

where

$$Q(q) \equiv \theta(q) - [1 - \theta(q)]\overline{\zeta_{\mathrm{w}}}(q) \tag{5.11}$$

and

$$\bar{\zeta}_{\mathrm{w}}(q) \equiv V_1(q)/V_0(q) \tag{5.12}$$

being the weight-average sequence length of the bound water.

Our strategy is therefore as follows. We first solve eq 5.5 for the unknown q for a given concentration ϕ and temperature T and then find θ, ν, and t as functions of them. We then substitute the result into the function $\kappa(q;\phi)$ to find the spinodals.

To carry out complete calculations, we have to specify the statistical weight η_ζ. To do this, we employ the simplest form proposed by Zimm and Bragg[16] for the study of coil-to-helix transition of biopolymers, i.e.

$$\eta_\zeta = \sigma \lambda(T)^\zeta \tag{5.13}$$

The front factor σ gives the statistical weight for a boundary between a helix and a coil (a hydrated sequence and a collapsed random coil in the present context) and is called the cooperativity parameter. In the case of random adsorption where there is no interaction between the adsorbed water molecules, it is given by $\sigma = 1$, and the model reduces to our previous one.[5] Let $\Delta f_0 \equiv \epsilon - T\Delta s$ be the free energy of a hydrogen bond, and let $\Delta\epsilon$ be the interaction energy between the nearest-neighboring bound water molecules. The statistical weight $\lambda(T) = \exp[-\beta(\Delta f_0 + \Delta\epsilon)]$ (called association constant) includes both hydrogen-bonding free energy and the nearest-neighbor interaction energy, and the cooperativity parameter is given by $\sigma \equiv \exp(-\beta|\Delta\epsilon|)$.

Equation 5.5 to decide q now takes the form

$$q = \lambda(T)[1 - \phi - \theta(q)\phi]\mathrm{e}^{R(q,\phi)}/[1 + \sigma q w_0(q)] \tag{5.14}$$

where λq is written as q for simplicity. The coverage θ by bound water molecules is given by

$$\theta(q) = \sigma q w_1(q)/[1 + \sigma q w_{01}(q)] \tag{5.15}$$

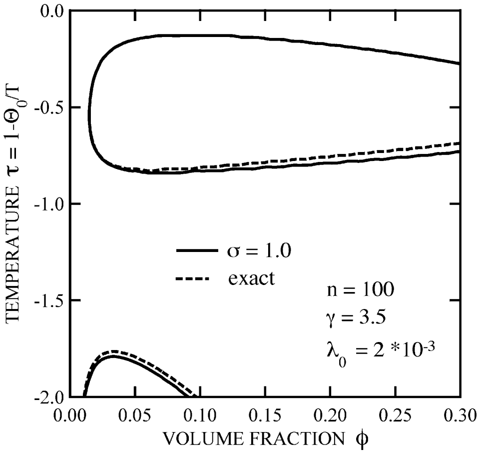

Figure 2. Comparison of the spinodal lines derived by the complete calculation (broken lines) and by one-mode approximation (solid lines).

Here, functions w are defined by

$$w_0(x) \equiv \sum x^{\zeta-1} \quad \text{and} \quad w_1(x) \equiv \sum \zeta x^{\zeta-1} \tag{5.16}$$

and $w_{01}(x) \equiv w_0(x) + w_1(x)$. The average sequence length is given by $\bar{\zeta}_{\mathrm{w}} = w_1(q)/w_0(q)$.

6. Phase Diagrams and the Fraction of Bound Water

For numerical calculation of the phase diagrams, we fix the necessary parameters in the following way. We first assume the conventional Shultz–Flory form $\chi(T) = {}^1\!/_2 - \psi\tau$ for the χ parameter,[17] where $\tau \equiv 1 - \Theta_0/T$ is the reduced temperature deviation measured from the reference theta temperature Θ_0 satisfying $\chi(\Theta_0) = {}^1\!/_2$, and ψ is a material parameter of order unity. At the temperature Θ_0, the second virial coefficient of a hypothetical Flory–Huggins solution without hydrogen-bonding interaction vanishes. The association constant is then expressed as $\lambda(T) = \lambda_0 \exp(|\epsilon + \Delta\epsilon|/k_{\mathrm{B}}T) = \lambda_0 \exp[\gamma(1 - \tau)]$, where λ_0 gives the entropy part of the binding free energy and $\gamma \equiv |\epsilon + \Delta\epsilon|/k_{\mathrm{B}}\Theta_0$ gives the binding energy measured relative to the thermal energy at the reference theta temperature. The reference temperature Θ_0 is not the true theta temperature Θ at which the second virial coefficient of the osmotic pressure vanishes. The latter lies far below Θ_0. Throughout the present numerical calculation, we fix ψ at $\psi = 1.0$ and change the amplitude λ_0, dimensionless binding energy γ, and the cooperative parameter σ. In particular, we are interested in the effect of the cooperativity parameter σ and see how the bottom part of the miscibility square becomes flatter with decrease in σ or increase in cooperativity.

To check the accuracy of one-mode approximation, we first compare new result on the phase diagrams of randomly hydrated polymers $\sigma = 1.0$ with the old calculation.[5] Figure 2 plots the two spinodal lines on top of each other. Solid lines are calculated by one-mode approximation, while the broken lines are calculated by taking into consideration all possible random placement of water molecules discussed in ref 5. We can see that the one-mode approximation is sufficiently accurate for $n = 100$. The larger the values of DP, the better the approximation becomes.

Let us move onto cooperative hydration. Figure 3 draws the spinodal curves for different cooperative

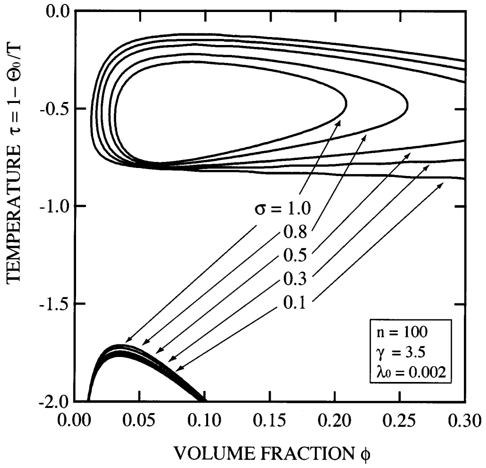

Figure 3. Spinodal lines drawn on the (reduced) temperature and concentration plane for different cooperative parameter σ. Other parameters are fixed at $n = 100$, $\psi = 1.0$, $\lambda_0 = 0.002$, and $\gamma = 3.5$. The bottom part of the miscibility square becomes flatter with decrease in the cooperative factor σ.

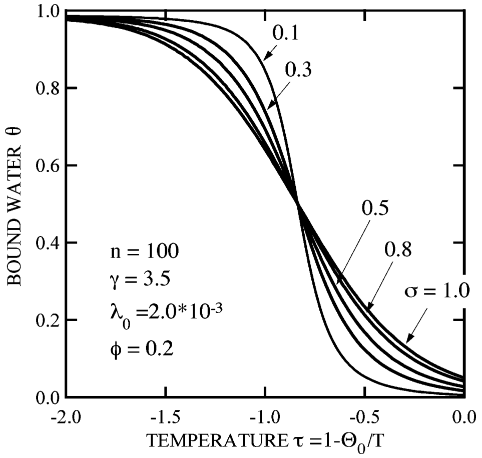

Figure 4. Coverage θ of a polymer chain by hydrogen-bonded water molecules plotted against the temperature. The cooperative parameter σ is changed from curve to curve. Dehydration of bound water becomes sharper with increase in the cooperativity (decrease in σ).

parameter σ with fixed other parameters. It theoretically demonstrates how the bottom part of the miscibility squares become flatter with decrease in σ. In the calculation, usual miscibility domes with UCST appear at low temperature, but these are not observable in the experiments because of the freezing of water. For the polymer concentration higher than $\phi = 0.5$, our theoretical description becomes poor because of the depletion of water molecules; i.e., the number of water molecules becomes insufficient to cover the polymers.

Figure 4 shows the dehydration curves; i.e., the coverage θ of a polymer chain by hydrogen-bonded water molecules is plotted against the temperature. The cooperative parameter σ is changed from curve to curve. Dehydration of bound water takes place near the phase separation temperature and becomes sharper with increase in the cooperativity.

Figure 5 plots the all critical points (UCST and LCST of the miscibility loop and UCST of the miscibility dome) against the polymer molecular weight (more precisely, the reciprocal $1/n$ of the number of statistical units on a chain). For random hydration ($\sigma = 1.0$), the miscibility loop shrinks to a point at about $n = 40$. This point is called the hypercritical point and indicated by HCP in the figure. Also, at a high molecular weight about $n = 1800$, the loop merges with the miscibility dome at low temperatures and turns into an hourglass. This point is called the double critical point and indicated by DCP. For cooperative hydration with $\sigma = 0.3$, however, DCP does not appear. HCP shifts to lower DP and is shaped like an angular square. From this figure, it is evident that cooperative hydration leads to flat LCST with almost no molecular weight dependence.

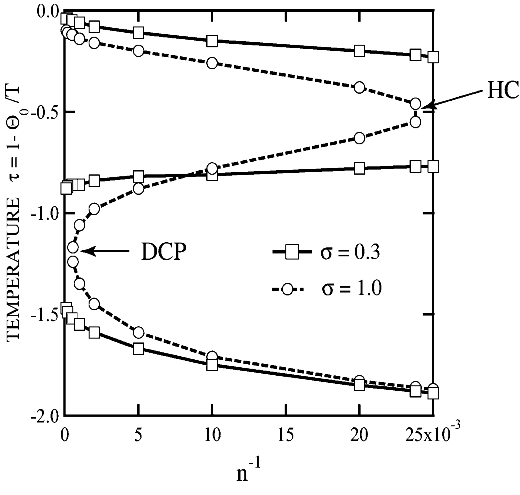

Figure 5. Molecular weight dependence of the LCST. The critical temperatures are plotted against the reciprocal of DP. HCP stands for hypercritical point where the miscibility loop shrinks to a point. DCP stands for a double critical point where LCST of the miscibility loop merges with UCST of the miscibility dome into a single point.

7. Comparison with the Experiments

Figure 6a compares theoretical calculation with experimental data[12] on the spinodal points, and Figure 6b shows the fraction θ of the bound water molecules plotted as functions of the temperature for three different polymer concentrations. In the experiments, the upper part of the miscibility square cannot be observed because temperature is too high. Also, UCST phase separation seen in the theoretical calculation is not observable because of the freezing of water. The polymer molecular weight used in the experiment is $M_w = 615\,500$, so that the nominal number of monomers is roughly given by $n = 5400$. Although polymers used in the experiment are polydisperse with the index $M_w/M_n = 2.04$, we expect that this may not cause any serious problems because the dependence of binodals as well as spinodals on the polymer molecular weight becomes weaker with increase in cooperativity in hydration. Since the statistical unit used in the lattice theory must be regarded as a group of monomers, we have tried to fit the data by $n = 100$ and 1000. (Theoretical calculation does not depend so much upon the number n if it is larger than 500.) We have seen a good agreement by fixing the cooperative parameter at $\sigma = 0.3$. There is, however, a slight discrepancy in the dilute regime; i.e., the theoretical curve predicts a sharper bend. Closer examination on the very dilute regime from both experimental and theoretical viewpoint is therefore necessary.

From the curve θ of the bound water as a function of the temperature, we can find the enthalpy ΔH of dehydration. If the fraction $-\Delta\theta$ is dehydrated by a small temperature rise ΔT, the absorption of heat is

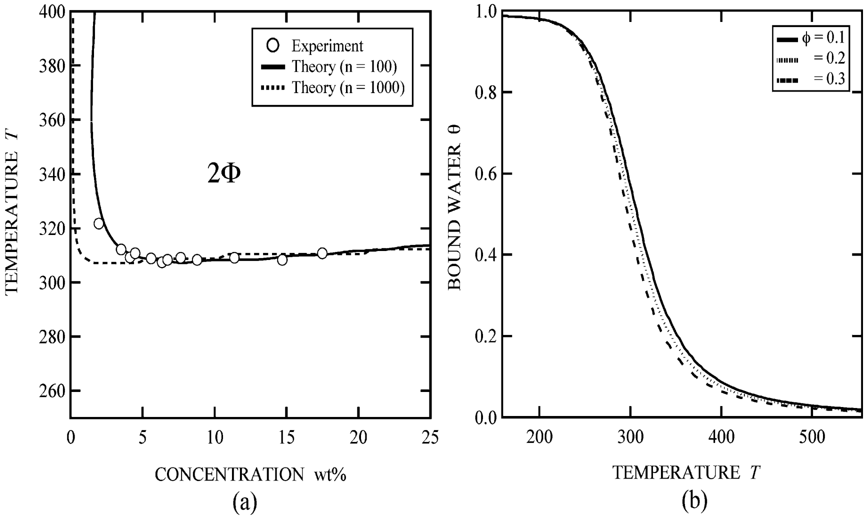

Figure 6. (a) Phase diagrams of aqueous PNIPAM solution. Experimental data (○) of the spinodal curve is compared with theoretical calculation. The DP of the polymer is $n = 100$ (solid line) and $n = 1000$ (broken line). Theoretical parameters used is $\Theta_0 = 555$ and $\lambda_0 = 0.002$ for $n = 100$, and $\Theta_0 = 565$ and $\lambda_0 = 0.003$ for $n = 1000$. Other parameters are fixed at $\gamma = 3.5$, $\sigma = 0.3$. (b) Content θ of the bound water plotted against temperature for three polymer volume fractions for $n = 100$.

given by

$$\Delta H = |\epsilon + \Delta\epsilon|\phi\Delta\theta/M \tag{7.1}$$

It shows a peak at the temperature where θ changes most sharply, i.e., at the phase separation temperature. The polymer chains collapse into compact globules as soon as bound water is dehydrated.

8. Osmotic Pressure and Effective Interaction

Let us now study the effect of cooperative hydration on the second virial coefficient eq 4.2 of the osmotic pressure within one mode approximation. The function $G(y)$ in this approximation is identical to the coverage θ of the bound water. Therefore, the value G_0 in the limit of infinite dilution is given by θ_0, which can be calculated by using the solution q_0 of eq 5.14 at $\phi = 0$, i.e.

$$q_0 = \lambda(T)/[1 + \sigma q_0 w_0(q_0)] \tag{8.1}$$

The coverage is given by

$$\theta_0 = \sigma q_0 w_1(q_0)/[1 + \sigma q_0 w_{01}(q_0)] \tag{8.2}$$

This is essentially equivalent to Zimm–Bragg's equation[18] for the single-chain problem. Figure 7 plots the second virial coefficient A_2 as a function of the temperature. The cooperative parameter σ is varied from curve to curve. There are in principle three theta temperatures where A_2 vanishes. The one lying in the middle temperature is the relevant theta temperature to which LCST approaches in the infinite molecular weight. With increase in cooperativity, dehydration becomes sharper, so that the (negative) slope of A_2 becomes larger.

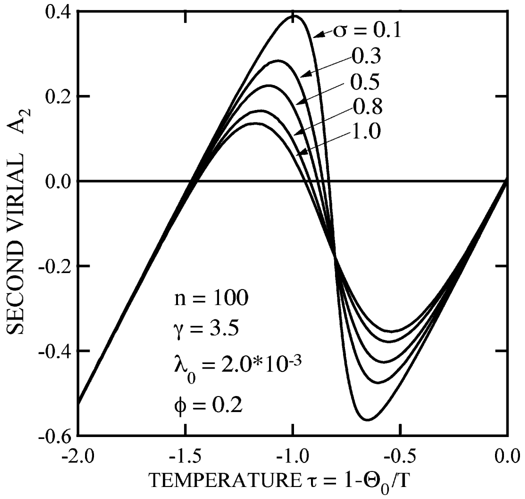

Figure 7. Second virial coefficient A_2 plotted against the temperature. The cooperative parameter σ is varied from curve to curve. There are in principle three theta temperatures where A_2 vanishes. The one lying in the middle temperature is relevant theta temperature to which LCST approaches in the infinite molecular weight.

9. Conclusions and Discussion

We have theoretically studied phase separation in aqueous polymer solutions. By the calculation of phase diagrams, we have confirmed that correlation, or cooperativity, between the neighboring water molecules that are hydrogen-bonded onto the polymer chain leads to flat LCST behavior with only little molecular weight dependence. The phase separation experimentally seen in aqueous PNIPAM solutions falls onto this category and is markedly different from PEO solutions where miscibility loops with UCST and LCST depend sensitively on the polymer molecular weight. From the temperature profile of dehydration curve, the sharpness of the single-chain coil/globule transition is also expected to originate in this cooperativity. The pearl-necklace conformation (Figure 1) driven by the cooperative hydration agrees with the recent measurements of concentration fluctuations in PNIPAM cross-linked gels by the neutron scattering method.[18] They found necklace-like microstructure through the study of the static structure factor profile appearing after a shallow quench into the collapsed state. Comparison between solutions and gels may lead to more profound understanding of the temperature sensitivity of PNIPAM chains.

The present study also suggests that the association behavior of hydrophobically modified PNIPAM in aqueous solutions is also different from that of hydrophobically modified PEO. We are investigating phase behavior and rheological properties of newly synthesized telechelic PNIPAM solutions[19] by paying special attention to the shift of LCST by association of hydrophobic end chains and shear thickening of transient polymer networks. Details will be reported in the forthcoming paper.

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