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Publication Date
1995-12-01

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December 1995

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MOLECULAR THERMODYNAMICS FOR VOLUME-CHANGE TRANSITIONS IN TEMPERATURE-SENSITIVE POLYMER GELS

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ABSTRACT

A molecular-thermodynamic model is presented to predict volume-change transitions in temperature-sensitive polymer gels. The model uses an extended Flory-Huggins theory as a mixing contribution and a new interpolated affine model suggested by Birshtein as an elastic contribution. The Flory χ parameter is given by the product of a temperature-dependent and a composition-dependent term. Our model also differs from those presented previously because the temperature-dependent term is given by the incompressible lattice-gas model by ten Brinke and Karasz that accounts for specific interactions such as hydrogen bonding. Following conventional practice, the van't Hoff equation is introduced to represent the effect of a small number of ionizable segments in the network chain. Calculated swelling-ratio curves for neutral and weakly ionized aqueous N-isopropylacrylamide gels use molecular parameters obtained from phase-equilibrium data for (non-crosslinked) polymer solutions. In agreement with experiment, the calculated volume-transition temperature of the gel is about 1°C higher than the lower critical solution temperature of the (non-crosslinked) polymer solution.

(Keywords: swelling model; poly(N-isopropylacrylamide); temperature-sensitive gels)

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INTRODUCTION

Numerous experimental and theoretical studies[1-15] have examined polymer gels exhibiting temperature-induced volume-change transition. One of the most extensively studied polymer gels is the poly(N-isopropylacrylamide) (PNIPAAm) gel[3-8] that exhibits volume contraction upon heating. In PNIPAAm gels, volume change can be either continuous or discontinuous depending on the cross-link density and degree of ionization of the network chain[16].

PNIPAAm gels show volume contraction at temperatures where the corresponding PNIPAAm solutions exhibit lower critical solution temperature (LCST) behavior due to hydrogen bonding[7,17,18]. One objective of this work is to elucidate the differences and similarities between cross-linked and non-crosslinked polymer systems containing PNIPAAm.

Although several molecular-thermodynamic models are available for polymer systems, it is a challenging task to represent simultaneously the phase behavior of polymer solutions and that of polymer gels using the same parameters. Currently available models for aqueous polymer gels often require parameters that are different from those for aqueous polymer solutions[4,8] or use too many adjustable parameters[14].

In this paper, we present a simple molecular-thermodynamic model which is applicable to polymer solutions as well as to weakly charged polymer gels that can hydrogen bond with the solvent.

THEORY

Helmholtz Energy of Mixing for Polymer Solutions. Consider first a binary mixture containing solvent (component 1) and linear polymer (component 2) where solvent molecules are represented by spheres and polymer molecules by freely-jointed chains. We use an extended Flory-Huggins lattice theory[19-21] to calculate the Helmholtz energy of mixing ΔA_{mix} :

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$$\frac{\Delta A_{mix}}{k_B T} = n_1 \ln\left(1 - \phi_2\right) + n_2 \ln\phi_2 + n_1 g \phi_2 \qquad (1)$$

where k_B is the Boltzmann constant, T is the absolute temperature, n_i is the number of molecules of component i, ϕ_2 is the volume fraction of polymer, and $g(T,\phi)$ is an empirical function that replaces the customary Flory segmental interaction parameter.

Helmholtz Energy of Mixing for Polymer Gels. We next consider a polymer gel containing solvent (component 1) and a large cross-linked polymer molecule (component 2) having a small number of ionizable segments. The Helmholtz energy of mixing is given by[2,19]

$$\Delta A_{mix} = \Delta A^{\ mix} + \Delta A^{\ elas} + \Delta A^{\ ion} \qquad (2)$$

where the first, second, and third terms represent mixing, elastic, and electrostatic contributions, respectively. For polymer gels, the mixing contribution is given by[19]

$$\frac{\Delta A^{\ mix}}{k_B T} = n_1 \ln\left(1 - \phi_2\right) + n_1 g \phi_2 \ . \qquad (3)$$

In the Flory-Rehner theory[22-27] for cross-link functionality 4, $\Delta A^{\ elas}$ is given by

$$\frac{\Delta A^{\ elas}}{k_B T} = v\left[\frac{3}{2}\left(\alpha^2 - 1\right) - \ln\alpha^3\right] + \frac{1}{2}v\ln\alpha^3 \qquad (4)$$

where α is the expansion factor and v is the number of total chains. In Eq. (4), the terms in the bracket represent the energy change due to affine deformation of an acyclic tree and the last term accounts for the energy change by joining junction points[19,22,26] to

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form a network. Birshtein et al.[28-30] and Grosberg and Kuznetsov[31], however, pointed out that the terms in the bracket in Eq. (4) are applicable only for $\alpha > 1$. For polymer gels that exhibit a volume-change transition, however, α is smaller than unity in the collapsed state.

In this work, we use an interpolation expression[28,31] for the energy change associated with affine deformation of an acyclic tree. In that event, ΔA^{elas} is given by[28-31]

$$\frac{\Delta A^{elas}}{k_B T} = \frac{3}{2}v\left[\alpha^2 + \frac{1}{\alpha^2} - 2\right] + \frac{1}{2}v\ln\alpha^3 \ . \tag{5}$$

The expansion factor is given by[22-26]

$$\alpha = \left(\frac{\phi_0}{\phi_2}\right)^{1/3} \tag{6}$$

where ϕ_0 is the volume fraction of polymer in the reference state where the conformation of network chains is closest to that of unperturbed Gaussian chains[27]; ϕ_0 is usually approximated by the volume fraction of polymer at preparation.

Finally, for a small charge density, we express the electrostatic effect using the van't Hoff equation:[11,32]

$$\frac{\Delta A^{ion}}{k_B T} = -mv\ln(n_1 + vN) \tag{7}$$

where m is the number of charged segments per network chain and N is the number of segments per network chain.

Phase Equilibria. To perform phase-equilibrium calculations, we first define the Flory χ parameter by[20,21]

$$\chi \equiv g - \left(\frac{\partial g}{\partial \phi_2}\right)_T = D(T)B(\phi) \tag{8}$$

where $B(\phi)$ is a function of composition and $D(T)$ is a function of temperature. Equation (8) assumes that the Flory χ parameter is given by the product of a composition-dependent term and a temperature-dependent term.

We also define the reduced temperature $\widetilde{T}$ and the interchange energy ε by

$$\widetilde{T} \equiv \frac{k_{\mathrm{B}}T}{\varepsilon} \tag{9}$$

$$\varepsilon \equiv 2\varepsilon_{12} - \varepsilon_{11} - \varepsilon_{22} \tag{10}$$

where ε_{ij} $(i,j=1,2)$ is the segmental interaction energy for non-specific interactions between components i and j.

For $B(\phi)$, we use an expression from Bae et al[21]. For $D(T)$, we use an expression based on the work of ten Brinke and Karasz[33-35]; this expression is able to predict LCST behavior due to specific interactions such as hydrogen bonding:

$$D(T) = \frac{z}{2}\left[\left(1 + 2\delta\varepsilon_{12}/\varepsilon\right)\left(\frac{1}{\widetilde{T}}\right) + 2\ln\left(\frac{1 + s_{12}}{1 + s_{12}\exp\left(\frac{\delta\varepsilon_{12}}{\varepsilon\widetilde{T}}\right)}\right)\right] \tag{11}$$

$$B(\phi) = \frac{1}{1 - b\phi_2} \tag{12}$$

where z is the lattice coordination number ($z=6$ in this work), $\delta\varepsilon_{12}$ is the difference between the segmental interaction energy for specific interactions and that for non-specific interactions, s_{12} is the ratio of degeneracy of non-specific interactions to that of specific interactions, and b is an empirical parameter obtained from polymer-solution data. Equation (11) accounts for specific interactions between unlike molecules[33-35].

References 20 and 21 give equations necessary for phase equilibrium calculations in polymer solutions. For polymer gels, the equilibrium volume fraction of polymer ϕ_e is determined from the equilibrium condition given by

$$\Delta\mu_1\left(\phi_e\right) = \left(\frac{\partial\Delta A_{mix}}{\partial n_1}\right)_{T,V,n_2=1}$$

$$= \ln\left(1 - \phi_e\right) + \phi_e + \chi\phi_e^2 + \frac{\phi_0}{N}\left[\left(\frac{\phi_e}{\phi_0}\right)^{1/3} - \left(\frac{\phi_e}{\phi_0}\right)^{5/3} - \left(m - \frac{1}{2}\right)\left(\frac{\phi_e}{\phi_0}\right)\right] = 0 \qquad (13)$$

where $\Delta\mu_1$ is the change in chemical potential of solvent upon mixing, V is the volume of the gel, and N is the number of segments between junction points. For the elastic term in Eq. (13), we use the interpolated affine model given by Eq. (5). For the mixing term, we use the extended Flory-Huggins theory presented above.

Under specific conditions, however, two gel phases can coexist at one temperature. At these conditions, a polymer gel exhibits a discontinuous volume change. The conditions for coexistence of two phases are[24]

$$\Delta\mu_1\left(\phi_e'\right) = \Delta\mu_1\left(\phi_e''\right) = 0 \qquad (14)$$

$$\int_{\phi_e'}^{\phi_e''} \Delta\mu_1 \phi_2^{-2}\, d\phi_2 = 0 \qquad (15)$$

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where superscripts $'$ and $''$ denote coexisting phases. Equation 15 is derived by the Gibbs-Duhem equation for component 2.

RESULTS AND DISCUSSION

PNIPAAm Solutions. We apply our model to PNIPAAm gels in water. Parameters for the mixing term are obtained from phase-equilibrium data for aqueous PNIPAAm solutions. Aqueous PNIPAAm solutions, exhibit LCST behavior at about 32 °C with an enthalpy of phase transition near 1.5 kcal/mol of repeating units[7,17,18]. In these systems, the temperature-composition diagram is very flat near the LCST[7,17,18]. In addition, the LCST is insensitive to the molecular weight of polymer when the molecular weight is sufficiently high.

In our lattice model, the interchange energy is the energy required to form a pair of contacts between components 1 and 2 by breaking a contact between segments of component 1 and a contact between segments of component 2. Therefore, the enthalpy of phase transition per repeating unit of polymer may be approximated as the negative one half of the interchange energy at LCST when a repeating unit is represented by a single segment. In the present model, the interchange energy including specific interactions is ω given by[34,35]

$$\omega = \varepsilon + f_{12}(2\delta\varepsilon_{12}) \tag{16}$$

where ε is given by Eq. (10) and f_{12} is the fraction of 1-2 contacts that is specific; f_{12} is given by

$$f_{12} = \frac{1}{1 + s_{12}\exp\left(\dfrac{\delta\varepsilon_{12}}{\varepsilon\widetilde{T}}\right)} . \tag{17}$$

The mixing term requires three adjustable parameters: ε, the ratio of $\delta\varepsilon_{12}$ to ε, and s_{12}. We preset s_{12} to 5000 as discussed in Reference 34. From phase-equilibrium data for the non-crosslinked aqueous polymer solution, we then obtain ε=0.698 kcal/mol and the ratio of $\delta\varepsilon_{12}$ to ε of −7 such that the interchange energy given by Eq. (16) is approximately equal to the enthalpy of phase separation ~1.5 kcal/mol per repeating unit at 32 °C.

Neutral PNIPAAm Gels. We next apply the model to neutral PNIPAAm gels in water using the parameters obtained from aqueous PNIPAAm solutions. PNIPAAm gels show abrupt volume contraction at about 33 to 34 °C. Figure 1a shows theoretical swelling-ratio curves from the interpolated affine model with an extended Flory-Huggins theory (m=0) for various values of parameter b. For each curve, parameter N in Eq. (13) was adjusted such that the swelling ratio is 2.5 at 20 °C with ϕ_0=0.07, which roughly corresponds to the PNIPAAm gels studied by Hirotsu et al.[4] The volume transition becomes steeper as parameter b rises, i.e., polymer gels exhibit a steeper volume-change transition if the corresponding solution shows a flatter coexistence curve near the LCST.

In the present model for polymer solutions, calculated critical temperatures are insensitive to parameter b in Eq. (12). The role of parameter b is to make the coexistence curve flatter near the critical solution temperatures. To fit the coexistence curves for polymer solutions, typical values for b used by Bae et al.[21] are 0.5 to 0.6. Using the same set of parameters for the mixing term obtained here, our model with b=0.65 represents the phase diagram for non-crosslinked PNIPAAm solutions as well as that for PNIPAAm gels.

Figure 1b compares theoretical curves based on the interpolated affine model with those based on the original affine model (Eq. (4) for ΔA^{elas}). Both models use the same extended Flory-Huggins theory for the mixing contribution. The transition temperature predicted by the interpolated affine model is about 1 °C higher than that by the original

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affine model which predicts the transition temperature at about 32 °C, essentially the same temperature as the LCST for PNIPAAm solutions. Experimental data show that the volume-change transition temperature in PNIPAAm gels is about 1 to 2 °C higher than the LCST for PNIPAAm solutions[7].

Weakly-Charged PNIPAAm Gels. It is well known that PNIPAAm gels copolymerized with ionizable monomers swell more than neutral PNIPAAm gels[15] and exhibit more abrupt volume contraction[4,36]. Figure 2 shows calculated swelling-ratio curves for aqueous PNIPAAm gels with b=0.65 at various m, the number of ionizable segments per network chain. In Figure 2, the number of segments per network chain is 89. Consistent with experimental data reported by Hirotsu et al.[4], theory predicts an enhanced discontinuous volume change as m rises[4].

Using the Donnan theory for weakly charged ionic gels[32], the present model is readily extended to the system where the surrounding water is a dilute electrolyte solution.

CONCLUSIONS

A semi-empirical model is presented for predicting the volume-change transition in polymer gels. The model accounts for the effect of specific interactions such as hydrogen bonding using the incompressible lattice-gas model by ten Brinke and Karasz. The present model uses an interpolated affine model by Birshtein for the elastic contribution. The van't Hoff equation is used to represent the effect of a small number of ionizable segments in the network chain. Because of the interpolated affine model by Birshtein, the calculated volume-transition temperature of the gel is about 1°C higher than the lower critical solution temperature of the (non-crosslinked) polymer solution. The model given here represents the swelling properties of neutral and weakly charged

aqueous PNIPAAm gels using molecular parameters obtained from phase-equilibrium data for (non-crosslinked) polymer solutions.

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FIGURE CAPTIONS

Figure 1.   Calculated swelling-ratio curves for neutral PNIPAAm gels in water[4] using an extended Flory-Huggins theory: $\varepsilon=0.698$ kcal/mol, $\delta\varepsilon_{12}/\varepsilon=-7$, $s_{12}=5000$, $\phi_0=0.07$. For each curve, N in Eq. (13) is adjusted such that the swelling ratio is 2.5 at 20 °C. (a) Curves from the interpolated affine model at various b. (b) Comparison of curves from the interpolated affine model with those from the original affine model.

Figure 2.   Calculated swelling-ratio curves from the interpolated affine model with an extended Flory-Huggins theory for charged PNIPAAm gels in water[4]: $\varepsilon=0.698$ kcal/mol, $\delta\varepsilon_{12}/\varepsilon=-7$, $s_{12}=5000$, $\phi_0=0.07$, $b=0.65$, $N=89$.

Figure 1

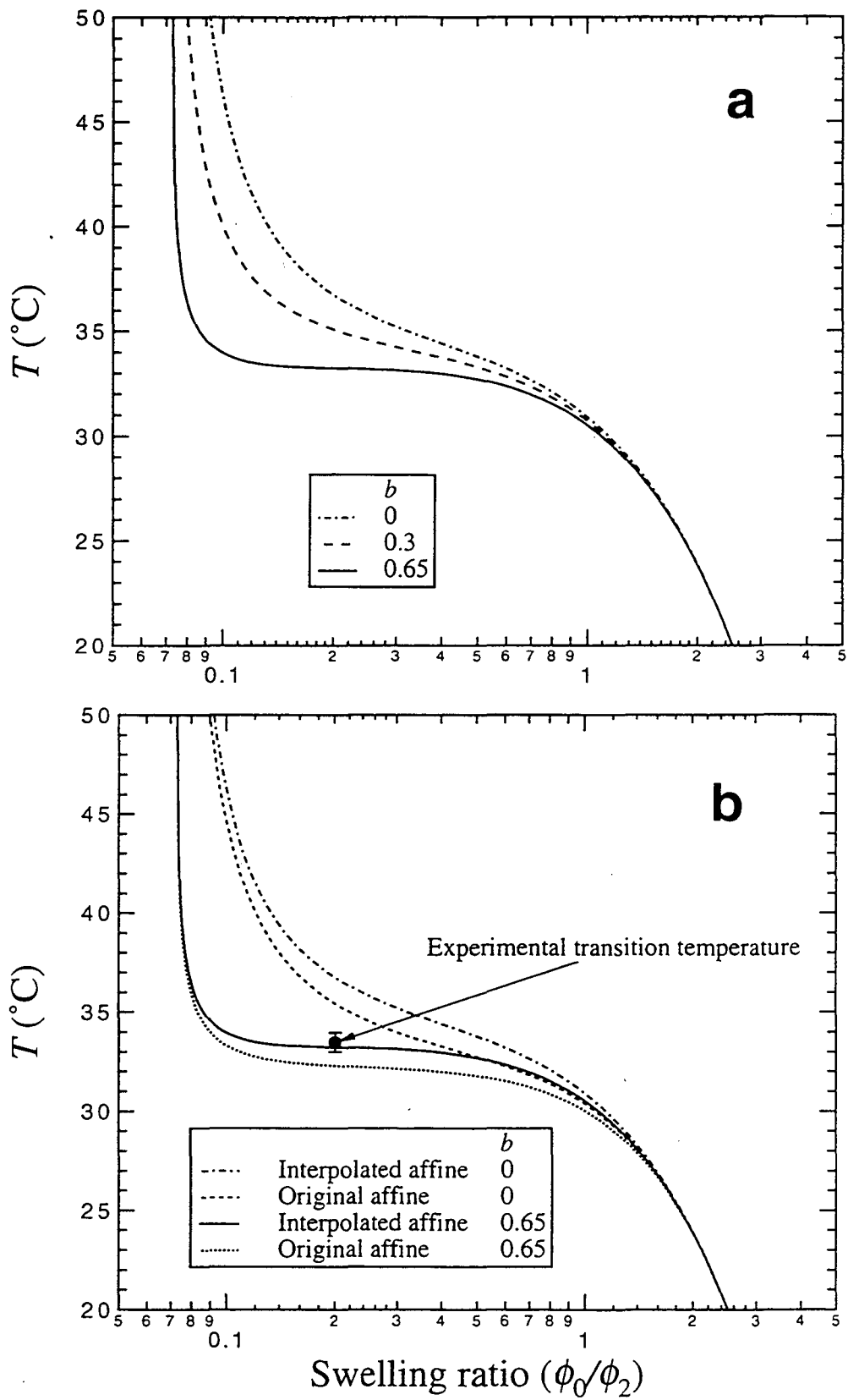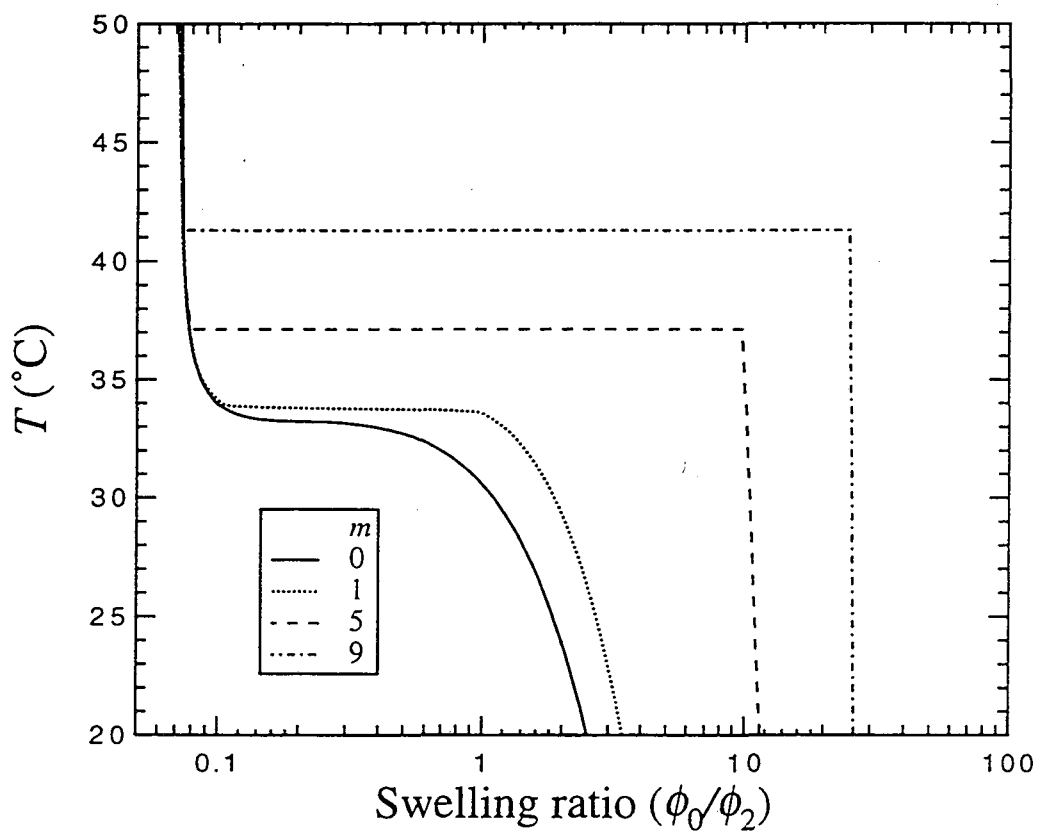Swelling ratio (ϕ_0/ϕ_2)

Figure 2

Swelling ratio (ϕ_0/ϕ_2)

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