



Molecular thermodynamic analysis for reentrant and reentrant-convex type swelling behaviors of thermo-sensitive hydrogels in mixed solvents

Suk Yung Oh, Young Chan Bae*

Division of Chemical Engineering and Molecular Thermodynamics Laboratory, Hanyang University, Seoul 133-791, Republic of Korea

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ABSTRACT

The relationship between co-nonsolvency of poly(*N*-isopropylacrylamide) (PNIPA) and the reentrant swelling transition of PNIPA gels in solvent mixtures was studied using a molecular thermodynamic framework based on the modified double lattice (MDL) theory of mixing and the Flory-Rehner (FR) chain model for elasticity. A secondary lattice concept of specific interactions was employed to correlate binary water/PNIPA solutions, and composition dependence of the energy parameter was adopted to describe the co-nonsolvency of the ternary solutions. The swelling equilibrium of crosslinked PNIPA gels was calculated using molecular interaction parameters obtained from lower critical solution temperature (LCST) transition behaviors of non-crosslinked PNIPA solutions. We applied the proposed method to PNIPA solutions containing methanol, acetone, dioxane (DO), tetrahydrofuran (THF), and poly(ethylene glycol) (PEG). Our results agreed with experimental reentrant and reentrant-convex type swelling data based on few adjustable parameters. In addition, the partitioning of solvent mixtures inside and outside the PNIPA gels as successfully predicted, which is significant for the application of hydrogels. The method presented here provides a theoretical basis for understanding the equilibrium behaviors of polymers and polymer gels in solvent mixtures.

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1. Introduction

Hydrogels are three-dimensional hydrophilic networks that are able to absorb large quantities of solvent, and are influenced by external stimuli, such as temperature [1,2], solvent composition [3–5], salt concentration [6,7], UV or visible light [8–10], pH [11], and type of surfactants [12,13]. Hydrogels have widespread applications in tissue engineering [14], superabsorbers [15], drug delivery systems [16], microactuators [17], and cell culture substrata [18]. To promote the development of hydrogels in all these applications, it is vital to understand and predict their swelling behaviors.

Swelling behaviors of crosslinked poly(*N*-isopropylacrylamide) (PNIPA) gels have proven interesting both experimentally and theoretically because they and their derivatives have extensive potential technological uses [18–21]. PNIPA is a thermo-sensitive polymer that is well-known for having a lower critical solution temperature (LCST) around 32–34 °C in water [22–24]. Similarly, PNIPA gels undergo an abrupt volume phase transition near this LCST [23–26]. PNIPA has a simple structure, possessing both

hydrophilic amide groups and hydrophobic isopropyl groups. This amphiphilic nature is a driving force of LCST transition of PNIPA in water. At low temperatures (below the LCST), the mixture could form a homogenous phase because strong hydrogen bonds form between the amide group of PNIPA and water. At high temperatures (above the LCST), neither the favorable hydrogen bonds nor the favorable mixing entropy dominate, inducing a heterogenous phase. PNIPA conformation changes from a random coil to a compact globule as temperature increases [24,27,28]. According to the same thermodynamic mechanisms, crosslinked PNIPA gels remain swollen state below the LCST, and collapse above the LCST.

The LCST phase transition of aqueous PNIPA solutions can be perturbed by adding additives such as salts, surfactants, organic solutes, or solvents [29]. In particular, adding organic solvents induces a drastic change in the LCST according to its composition. For example, PNIPA is insoluble in a proper mixture of water and methanol, even though both water and methanol are good solvents for PNIPA at low temperatures. This insolubility might result from the formation of water/methanol clusters [30] due to the entropic advantages of small solvent molecules compared with large PNIPA molecules. The reentrant coil to globule to coil transition of PNIPA takes place in a water/methanol solution with increasing methanol concentrations at room temperature. This co-nonsolvency of mixed solvents for linear PNIPA chain manifests as reentrant swelling

* Corresponding author.

E-mail address: ycbae@hanyang.ac.kr (Y.C. Bae).

behavior of crosslinked PNIPA gels [4,5,30–33]. This phenomena observed in PNIPA has been reported in other aqueous systems containing alcohols [32], dimethyl sulfoxide (DMSO) [25,34,35], *N,N*-dimethylformamide (DMF) [36,37], acetone [38], acetonitrile [34], DO [34], THF [5,34,39–41], PEG [42–45], and other solvents.

Thermodynamically, both the free energy of mixing and the free energy of elasticity govern the swelling equilibrium of gel systems. Many research groups [23,46–51] have developed thermodynamic models to quantitatively describe the swelling behaviors of PNIPA gels, since the pioneering work of Tanaka and his coworkers [3]. Tanaka et al. [11,33] also provided the first the swelling equilibrium model for the reentrant swelling behaviors of PNIPA gels in mixed solvents using a simple Flory-Huggins (FH) formula for osmotic pressure that treated binary solvents as pseudo-pure components. Okay et al. [52,53] developed a ternary swelling model by combining the FH mixing contribution with the Flory affine elastic contribution [54]. The Gibbs excess energy model based on the UNIQUAC equation with a free volume contribution was employed by Maurer et al. [38,45] to describe their experimental reentrant swelling data. Recently, Zhi et al. [55] developed a thermodynamic model by integrating a modified multiple lattice model [56] as the mixing term and Flory's Gaussian chain model [54] as the elastic term.

Although various molecular thermodynamic models are available to describe the swelling behaviors of polymer gels, they either require parameters that are different from those for polymer solutions or use many adjustable parameters. In the binary PNIPA/water system, several models simultaneously described the phase behaviors of polymer solutions and polymer gels using the same model parameters [37,49,50]. However, such modeling studies have not yet reported the reentrant swelling behaviors of ternary gel systems.

In our previous works [57–59], we developed a multi-component model based on our modified double lattice (MDL) theory, and successfully described the liquid–liquid equilibrium (LLE) of ternary polymer systems. The cosolvency and co-nonsolvency effects were analyzed based on energy behavior.

Here, we present a new method to describe the reentrant swelling behaviors of PNIPA gels in mixed solvent systems. We adopted the MDL theory [57–59] for the mixing contribution and the Flory-Rehner (FR) theory [2] for the elastic contribution. We first correlated the LCST transition behaviors of ternary PNIPA solutions, and subsequently calculated the reentrant swelling behaviors of PNIPA gels in corresponding solutions using molecular interaction parameters from PNIPA solutions. This approach minimizes the fitting parameters so that various swelling properties can be predicted. A secondary lattice concept [60] as used to consider specific interactions in the LCST behavior of binary water/PNIPA solution, and a composition dependence of energy parameter was employed for ternary water/solvent/PNIPA solutions. We verified the reliability of our modeling technique by applying it to various PNIPA gel systems.

2. Model development

2.1. Phase behavior of polymer solutions

Consider a fluid mixture composed of N_i molecules of the i th component, where each molecule occupies r_i sites on a lattice. At temperature T , the framework of the lattice model starts with a simple cubic lattice (coordination number $z = 6$) containing $N_r (= \sum_{i=1}^K N_i r_i)$ sites composed of K components. In the MDL multi-component model [57–59], the Gibbs energy change of mixing ΔG_{mix} is expressed as

$$\frac{\Delta G_{\text{mix}}}{N_r kT} = \sum_{i=1}^K \frac{\phi_i}{r_i} \ln \phi_i + \frac{C_\beta}{2} \sum_{i=1}^K \sum_{j=1}^K \phi_i \phi_j \left(\frac{1}{r_i} - \frac{1}{r_j} \right)^2 + \sum_{i=1}^K \times \sum_{j=1}^K a_{ij} \phi_i \phi_j - \left(\sum_{i=1}^K \sum_{j=1}^K a_{ij}^* \phi_i \phi_j \right)^2 \quad (1)$$

where $\phi_i (= N_i r_i / N_r)$ is the volume fraction of the i th component, and both a_{ij} and a_{ij}^* are generalized functions of $\tilde{\varepsilon}_{ij}$, Chain lengths r_i and r_j , given by

$$a_{ij} = \frac{\tilde{\varepsilon}_{ij}}{2} \left(2 - \left(\frac{\phi_i}{r_i} + \frac{\phi_j}{r_j} \right) + \left(\frac{1}{r_i} + \frac{1}{r_j} \right) \right) \quad (2)$$

$$a_{ij}^* = \tilde{\varepsilon}_{ij} \sqrt{C_\gamma / 4} \quad (3)$$

The reduced interchange energy between i th and j th components, $\tilde{\varepsilon}_{ij}$, is defined by

$$\tilde{\varepsilon}_{ij} = \varepsilon_{ij} / kT = (\epsilon_{ii} + \epsilon_{jj} - 2\epsilon) / kT \quad (4)$$

where ε_{ij} is the interchange energy, and ϵ_{ij} is the interaction energy between components i and j . The remaining coefficients, C_β and C_γ , are universal constants, which are 0.1415 and 1.7986, respectively [60].

To consider the specific interactions between the segments of molecules, the secondary lattice concept was used by Oh and Bae [60]. The expression is given by

$$\frac{\Delta G_{\text{sec},ij}}{N_{ij} kT} = \frac{2}{z} \left[\eta \ln \eta + (1 - \eta) \ln(1 - \eta) + \frac{z C_\alpha \delta \tilde{\varepsilon}_{ij} (1 - \eta) \eta}{1 + C_\alpha \delta \tilde{\varepsilon}_{ij} (1 - \eta) \eta} \right] \quad (5)$$

where $\Delta G_{\text{sec},ij}$ is the Gibbs energy change of mixing of the secondary lattice for an i – j segment–segment pair, N_{ij} is the number of i – j pairs, $\delta \tilde{\varepsilon}_{ij} (\delta \varepsilon_{ij} / kT)$ is the reduced energy parameter contributed by the oriented interactions and η is the surface fraction permitting oriented interactions ($\eta = 0.3$). C_α is a universal constant: 0.4881. This method was used to deal with specific interactions in the binary LCST curves. If oriented interaction occurs in the i – j segment–segment pairs, $\tilde{\varepsilon}_{ij}$ is replaced by $(\varepsilon_{ij} / kT) + 2(\Delta G_{\text{sec},ij} / N_{ij} kT)$ in Eq (4).

For phase equilibrium calculations, the chemical potentials of each component are required, and they can be determined using the following equation

$$\frac{\Delta \mu_i}{kT} = \left[\frac{\partial (\Delta G_{\text{mix}} / kT)}{\partial N_i} \right]_{T, V, N_{j \neq i}} \quad (6)$$

A coexistence curve can be calculated using the following conditions,

$$\Delta \mu_i^\alpha = \Delta \mu_i^\beta \quad (i = 1, 2, \dots, K) \quad (7)$$

where $\Delta \mu_i$ is the change in chemical potential upon isothermally transferring component i from the pure state to the mixture. The superscripts α and β denote two phases at equilibrium. The critical conditions required to calculate the LLE are given by

$$|\Delta G'| \equiv \begin{vmatrix} \overline{\Delta G'_{11}} & \overline{\Delta G'_{12}} & \cdots & \overline{\Delta G'_{1K}} \\ \overline{\Delta G'_{21}} & \overline{\Delta G'_{22}} & \cdots & \overline{\Delta G'_{2K}} \\ \vdots & \vdots & \ddots & \vdots \\ \overline{\Delta G'_{K1}} & \overline{\Delta G'_{K2}} & \cdots & \overline{\Delta G'_{KK}} \end{vmatrix} = 0 \quad (8)$$

and

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