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Phase behavior of poly(*N*-isopropylacrylamide) in water–methanol cononsolvent mixtures and its relevance to membrane formation

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Abstract

The phase behavior of poly (*N*-isopropylacrylamide) (PNIPAAm) in solutions composed of water and methanol was studied at 25 °C. The pair of solvents used to dissolve PNIPAAm has been selected for the purpose to perform a cononsolvent system. From the observed phase behavior, PNIPAAm was soluble in either water or methanol individually but liquid–liquid demixing was observed in water/methanol mixtures. Flory–Huggins formalism including three binary interaction parameters and one ternary interaction parameter was used to analyze the phase behavior of the cononsolvent system. The mechanism of cononsolvency and its relation with the ternary interaction parameter were discussed. In addition, the use of two solvents serving as a cononsolvent system, replacing the traditional solvent–nonsolvent pair, for the membrane formation was investigated. Regardless of water or methanol being used as the solvent, it showed a rapidly precipitating system and macrovoid morphology due to liquid–liquid demixing was obtained. Trend expected on the basis of the phase diagram was in reasonable agreement with the observed membrane morphology. Therefore, the principles of membrane formation established for the ternary systems with nonsolvent–solvent–polymer can be extended to a cononsolvent–polymer system.

Keywords: Cononsolvency; Phase behavior; Ternary interaction parameter

1. Introduction

Poly(*N*-isopropylacrylamide) (PNIPAAm) exhibits a well-defined lower critical solution temperature (LCST) in water, and cross-linked PNIPAAm gels undergo analogous collapse transitions in aqueous media. Recently the cononsolvency behavior of PNIPAAm in aqueous media has attracted attention because of its scientific interest and applications [1–3]. Crowther and Vincent showed the swelling degree of PNIPAAm microgel particles decreased to a minimum and then reswelled by the addition of methanol [2]. Hirotsu investigated the phase transition of PNIPAAm gels in water–methanol mixtures [3]. He found the interaction between PNIPAAm and solvent molecules could be changed by using solvent mixtures with various compositions. Schild et al. studied the LCST of PNIPAAm in the cononsolvent mixture of water and methanol by means of cloud-point and microcalorimetric measurements [1]. Flory–Huggins ternary solution theory was used to explain the cononsolvency results only in terms of a change in the water–ethanol interaction parameter in PNIPAAm solutions. They suggested that the perturbation of the binary interaction parameter arose from local contacts between polymer and solvent. However, there has been no investigation in constructing a complete phase diagram of PNIPAAm in water–methanol mixtures as far as we know. It is clearly known that a phase diagram can provide important information in various applications such as the various phase transitions that are responsible for the preparation of membranes by immersion of a polymer solution in a coagulation bath. Therefore, this work provides systematic studies on the complete phase behavior of a cononsolvent system.

Systematic studies of the complete phase behavior of the cononsolvent system are very scarce. In the field of ternary polymer systems the so-called cononsolvency (or cosolvency) is an unusual phenomenon that has not been subjected to extensive investigation [4–8]. It is well known that polymer can be dissolved in an appropriate

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solvent depending on chemical nature of solvent and details of experimental conditions. However, it is difficult to imagine a mechanism by which a polymer can change the mixture of two solvents to be a cononsolvent (or two nonsolvents to be a cosolvent). In our previous publications, the role of ternary interaction parameter, χ_T in the cononsolvent and cosolvent systems has been investigated [6–8]. It can be shown that in the Flory–Huggins theory with inserted χ_T polymer is insoluble in certain mixtures of two solvents. Conversely, two nonsolvents can have the character of a cosolvent for dissolving polymer. In a like manner, the ternary interaction parameter is considered in the water–methanol–PNIPAAm system because only pairwise interactions between components cannot provide a theoretical basis of the formation of ternary complexes. In addition, the use of two solvents serving as a cononsolvent system, replacing the traditional solvent–nonsolvent pair, for the membrane formation was investigated.

2. Experimental section

2.1. Measurement of the cononsolvency of PNIPAAm in the mixtures of water and methanol

The polymer used in this experiment was PNIPAAm synthesized by free-radical polymerization of *N*-isopropylacrylamide (Acros) at 20 °C for 24 h using potassium persulfate (Aldrich) as an initiator and tetramethylethylenediamine (Acros) as a catalyst, as described previously [1]. The cononsolvency of PNIPAAm in the mixture of water (deionized) and methanol (Acros) was obtained according to the following procedure. A specific amount of PNIPAAm polymer was mixed with a suitable amount of single solvent water or methanol in a sealed teflon-lined bottle (20 ml) because of the low boiling point of the solvent. The maximum polymer concentration investigated was 15 wt%. This mixture was mechanically agitated at 25 °C until a clear homogeneous solution was obtained. Subsequently, this solution was blended with a known quantity of another solvent to prepare a series of solutions with different water/methanol proportions. When the concentration of the second solvent was low enough, it did not change the state of the homogeneous solution. With increasing the concentration of the second solvent, solutions became turbid immediately and then turn out to be homogeneous again or liquid–liquid phase separation could be observed after a certain period. The liquid–liquid phase separation included a polymer-poor (very clear) phase coexisting with a polymer-rich (viscous and slightly whitish) phase. The liquid–liquid demixing gap in the ternary phase diagram was determined by all unstable solutions separated into two liquid layers. The binodal points were identified as the composition at which phase separation began to occur in a series of samples, i.e. the boundary of the liquid–liquid demixing gap.

2.2. Osmotic pressure measurements

Osmosis is the passage of a pure solvent into a solution, which is separated by a semi-permeable membrane. The dilute PNIPAAm solution was injected into an osmometer (Knauer Co., A0330) to determine the osmotic pressure at 25 °C. By making measurements at several concentrations, extrapolating to zero concentration, the binary interaction parameter between the solvent and polymer was established [9].

2.3. Membrane preparation and characterization

Membranes were prepared using the direct immersion–precipitation method. An appropriate amount of PNIPAAm was dissolved in water or methanol to form a 20% polymer solution. This solution was dispersed uniformly on a teflon plate and then immersed into the coagulation bath containing 50% water and 50% methanol to form membranes. Freeze-dried samples of the membranes were examined using a scanning electron microscope (SEM) to obtain the membrane structures.

2.4. Theoretical phase diagram

There are several theoretical pathways for calculating the free energy of a polymer system. The Flory–Huggins approach [9], a lattice of theory, makes valuable predictions concerning the phase behavior of a polymer system based on a consideration of the binary interaction parameter. However, the Flory–Huggins theory could not appropriately predict the phase behavior of a cononsolvent system. Therefore, a ternary interaction parameter, χ_T was introduced into the Flory–Huggins theory to account for the immiscibility gap in solvent–solvent–polymer system and unknown phase boundaries in the phase diagram that could not be obtained experimentally could be predicted.

The Gibbs free energy of mixing (ΔG_m), based on Flory–Huggins theory [9] including a ternary interaction parameter, χ_T [6–8,10], for the polymer solution is

$$\Delta G_m = RT(n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + \chi_{12} n_1 \phi_2 + \chi_{13} n_1 \phi_3 + \chi_{23} n_2 \phi_3 + \chi_T n_1 \phi_2 \phi_3) \quad (1)$$

where n_i and ϕ_i are numbers of moles and volume fraction of component i ($i=1$, water; $i=2$, methanol; $i=3$, PNIPAAm). χ_{ij} is a binary interaction parameter between component i and component j. The first three terms in the parenthesis represent the entropic contribution and the fourth to the sixth terms represent the enthalpic contribution. The role of χ_T in the last term is related to the interaction among water, methanol and PNIPAAm. Differentiating Eq. (1) with respect to n_i, the chemical potential, $\Delta\mu_i(\mu_i - \mu_i^0)$ of the three components is given:

$$\begin{aligned}\frac{\Delta\mu_1}{RT} &= \ln\phi_1 + 1 - \phi_1 - \frac{V_1}{V_2}\phi_2 - \frac{V_1}{V_3}\phi_3 \\ &\quad + (\phi_2\chi_{12} + \phi_3\chi_{13})(\phi_2 + \phi_3) - \frac{V_1}{V_2}\phi_2\phi_3\chi_{23} \\ &\quad - h_1h_2\phi_2\frac{\mathrm{d}\chi_{12}}{\mathrm{d}h_2} - \phi_1\phi_2\phi_3\frac{\partial\chi_{13}}{\partial\phi_2} - \phi_1\phi_3^2\frac{\partial\chi_{13}}{\partial\phi_2} \\ &\quad - \phi_1\phi_3^2\frac{\partial\chi_{13}}{\partial\phi_3} - \frac{V_1}{V_2}\phi_2^2\phi_3\frac{\partial\chi_{23}}{\partial\phi_2} - \frac{V_1}{V_2}\phi_2\phi_3^2\frac{\partial\chi_{23}}{\partial\phi_3} \\ &\quad - \phi_1\phi_2^2\phi_3\frac{\partial\chi_T}{\partial\phi_2} - \phi_1\phi_2\phi_3^2\frac{\partial\chi_T}{\partial\phi_3} + \chi_T\phi_2\phi_3(1 - 2\phi_1) \qquad (2)\end{aligned}$$

$$\begin{aligned}\frac{\Delta\mu_2}{RT} &= \ln\phi_2 + 1 - \phi_2 - \frac{V_2}{V_1}\phi_1 - \frac{V_2}{V_3}\phi_3 \\ &\quad + \left(\frac{V_2}{V_1}\phi_1\chi_{12} + \phi_3\chi_{23}\right)(\phi_1 + \phi_3) \\ &\quad - \frac{V_2}{V_1}\phi_1\phi_3\chi_{13} + \frac{V_2}{V_1}h_1h_2\phi_1\frac{\mathrm{d}\chi_{12}}{\mathrm{d}h_2} \\ &\quad + \frac{V_2}{V_1}\phi_1\phi_3(\phi_1 + \phi_3)\frac{\partial\chi_{13}}{\partial\phi_2} - \frac{V_2}{V_1}\phi_1\phi_3^2\frac{\partial\chi_{13}}{\partial\phi_3} \\ &\quad + \phi_2\phi_3(\phi_1 + \phi_3)\frac{\partial\chi_{23}}{\partial\phi_2} - \phi_2\phi_3^2\frac{\partial\chi_{23}}{\partial\phi_3} \\ &\quad + \frac{V_2}{V_1}\phi_1\phi_2\phi_3(\phi_1 + \phi_3)\frac{\partial\chi_T}{\partial\phi_2} - \frac{V_2}{V_1}\phi_1\phi_2\phi_3^2\frac{\partial\chi_T}{\partial\phi_3} \\ &\quad + \frac{V_2}{V_1}\chi_T\phi_1\phi_3(1 - 2\phi_2) \qquad (3)\end{aligned}$$

$$\begin{aligned}\frac{\Delta\mu_3}{RT} &= \ln\phi_3 + 1 - \phi_3 - \frac{V_3}{V_1}\phi_1 - \frac{V_3}{V_2}\phi_2 \\ &\quad + \left(\frac{V_3}{V_1}\phi_1\chi_{13} + \frac{V_3}{V_2}\phi_2\chi_{23}\right)(\phi_1 + \phi_2) \\ &\quad - \frac{V_3}{V_1}\phi_1\phi_2\chi_{12} - \frac{V_3}{V_1}\phi_1\phi_2\phi_3\frac{\partial\chi_{13}}{\partial\phi_2} \\ &\quad - \frac{V_3}{V_2}\phi_2^2\phi_3\frac{\partial\chi_{23}}{\partial\phi_2} + \phi_3(\phi_1 + \phi_2) \\ &\quad \times\left[\frac{V_3}{V_1}\phi_1\frac{\partial\chi_{13}}{\partial\phi_3} + \frac{V_3}{V_2}\phi_2\frac{\partial\chi_{23}}{\partial\phi_3}\right] - \frac{V_3}{V_1}\phi_1\phi_2^2\phi_3\frac{\partial\chi_T}{\partial\phi_2} \\ &\quad + \frac{V_3}{V_1}\phi_1\phi_2\phi_3(\phi_1 + \phi_2)\frac{\partial\chi_T}{\partial\phi_3} + \frac{V_3}{V_1}\chi_T\phi_1\phi_2(1 - 2\phi_3) \qquad (4)\end{aligned}$$

where μ_i^0 is the chemical potential at standard state, V_i is the molar volume, $h_1 = \phi_1/(\phi_1 + \phi_2)$ and $h_2 = \phi_2/(\phi_1 + \phi_2)$.

At liquid–liquid phase equilibrium at a specified temperature and pressure, the chemical potential of each component between two phases (α and β) is equal:

$$\mu_i^\alpha = \mu_i^\beta \quad (i = 1,\ 2,\ 3) \qquad (5)$$

where μ_i^α and μ_i^β are the chemical potentials of component i in phases α and β. Because the volume fraction of each component adds up to unit in each phase, Eqs. (2)–(5) by using interaction parameters can be calculated to give the binodals of PNIPAAm in water/methanol mixtures.

2.5. Interaction parameters

The concentration dependent interaction parameter for water/methanol binary pair, χ_{12}, was obtained using vapor liquid equilibrium data [11]. Binary interaction parameters between pure liquid and polymer, χ_{13} and χ_{23}, were determined by measuring the osmotic pressure of PNIPAAm in pure liquid [9]. Experimental data for the ternary interaction parameter, χ_T, is not available in literature, so we treated χ_T as an empirical correction parameter. For the details of the computational scheme, one can refer to Ref. [6].

3. Results and discussion

3.1. Experimental phase behavior

In Fig. 1, liquid–liquid demixing boundaries, denoted by filled triangles, from cloud point measurements for PNIPAAm in the mixtures of water and methanol at 25 °C is shown. The weight fractions have been converted to volume fractions using the following values for the density: water: 0.99 g/cm^3; methanol: 0.79 g/cm^3 and PNIPAAm: 1.07 g/cm^3, respectively [1]. A complete phase diagram could not be obtained experimentally because the polymer was gelled in the solvent when the polymer content was too

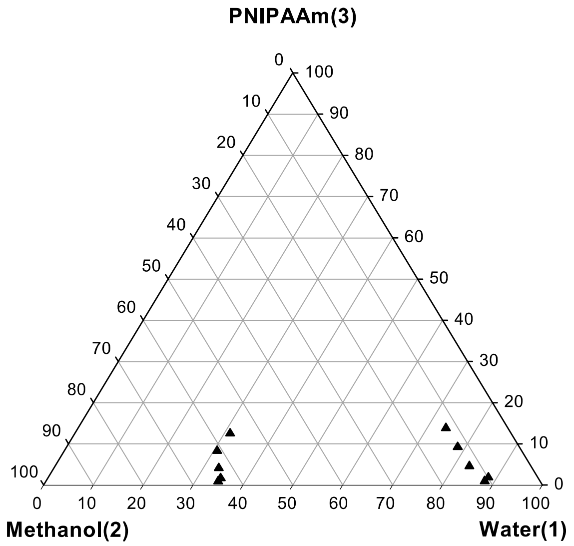

Fig. 1. Phase diagram of water–methanol–PNIPAAm at 25 °C. The data points, denoted by filled triangles, represent the composition of the binodal boundary data points.

high. A composition outside data points was a homogeneous and transparent solution. However, the water–methanol mixture reduced the solvation character of PNIPAAm and acted as a cononsolvent between these two boundaries. An originally homogeneous solution became separated into a polymer-rich phase in equilibrium with a polymer-poor solution. On the other hand, the lowest binodal points near the water/methanol axis were very dilute, which were close to the critical point. Consequently, the liquid–liquid miscibility gap almost overlapped the water/methanol axis. Such a phenomenon is ordinarily observed in ternary polymer systems [12].

As shown in Fig. 1, both water and methanol are solvents for PNIPAAm individually, yet the phase diagram shows that certain proportions result in immiscibility with respect to liquid–liquid demixing. This suggests the mixtures of water and methanol can play the roles of solvent or nonsolvent for PNIPAAm, depending on their composition. In other words, the pairwise interaction between two components will be changed in the presence of the third component, which argues against treatments based on the Flory–Huggins theory [9]. Therefore, if a ternary system increases the interaction between two solvents or decrease the interaction between polymer and solvent in certain mixtures of two solvents, then the polymer chains will be rejected to be drawn into solution by the mixed solvent.

3.2. Calculated phase behavior

Since the experimental phase equilibrium data could not be measured as the polymer content was too high, calculations of phase equilibrium were performed to investigate a complete phase diagram of a cononsolvent system. In Fig. 2, calculated binodals with a constant ternary interaction parameter, χ_T determined by solving Eqs. (2)–(5) and the experimental liquid–liquid demixing data points are shown. The physical constants for water, methanol and PNIPAAm employed in computations are given in Table 1. The concentration-dependent interaction parameter χ_{12} (water–methanol) was calculated from the vapor–liquid equilibrium data [8] and the results are given in Table 2. The values of χ_{13} and χ_{23}, measured from osmotic pressure experiments at 25 °C, were found to be 0.502 and 0.450, respectively. As expected, these two values are consistent with both water and methanol being solvents for PNIPAAm.

The value of χ_T was zero for the first analysis, i.e. the ternary interaction parameter was neglected. Unfortunately, almost no liquid–liquid demixing region was predicted, that is, the calculation predicted a soluble situation over the whole composition range. This completely disagreed with the experimental data; suggesting only binary interaction parameters could not be used to describe the characteristic of cononsolvency for a polymer with two solvents. Obviously, there ought to exist some repulsive forces among the three components to demix PNIPAAm solution in the mixture of water and methanol. Since χ_{13} and χ_{23} values are close to the θ solvent and do not account for the effect of cononsolvency, it was further attempted to see if it would be possible to fit the experimental data by considering the ternary interaction parameter [6–8].

Table 1
Physical properties of water, methanol and PNIPAAm at 25 °C

Component	Molecular weight	Density (g/cm^3)	Molar volume (cm^3/mol)
Water	18.05	0.99	18.10
Methanol	32.04	0.79	40.51
PNIPAAM	150,000	1.07	140,000

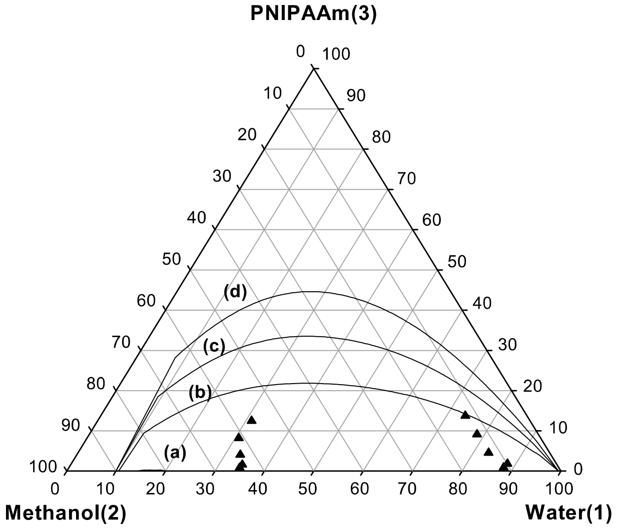

Fig. 2. Comparison between experimentally determined binodal boundary data points (denoted by filled triangles) and theoretically calculated binodals with a constant ternary interaction parameter, χ_T. (a) $\chi_T=0$, (b) $\chi_T=0.5$ (c) $\chi_T=0.7$ and (d) $\chi_T=1.0$.

When $\chi_T<0$ was considered, the calculated liquid–liquid demixing region still completely disappeared in the phase diagram. Similar to the binary interaction parameter, the parameter χ_T with a negative value stands for a strong interaction among three components, i.e. PNIPAAm should be dissolved in any composition of the water/methanol mixture. Thus, the positive χ_T value was attempted. Fig. 2 shows an immiscible region was obtained for taking a series of positive χ_T values, which is consistent with the phase behavior of a cononsolvent system. Furthermore, the immiscible region below the binodal boundary was enlarged to move toward the polymer apex with increasing the χ_T value. Compared to experimental data, overestimation of demixing region was found when the parameter χ_T was 0.7,

Table 2
Summary of interaction-parameter data at 25 °C

Binary systems	Interaction parameter, χ_{ij}
Water (1)/methanol (2)	$-0.7908+1.2624/(1.0-0.1441\phi_2)$
Water (1)/PNIPAAM (3)	0.502
Methanol (2)/PNIPAAM (3)	0.450

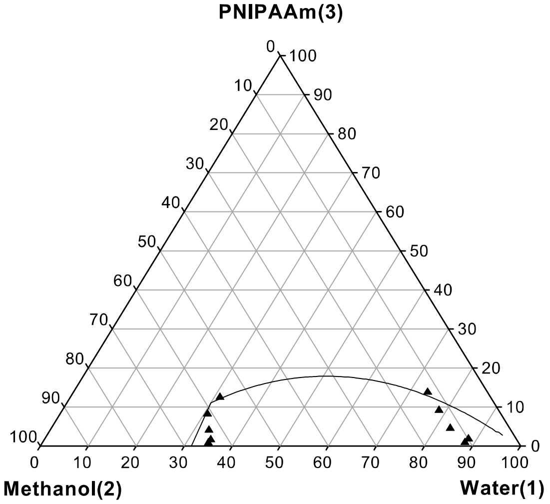

Fig. 3. Comparison between theoretically calculated phase behavior (—) using $\chi_T = 0.53 - 0.05\phi_2 + 0.25\phi_3$ and experimentally determined binodal boundary data points (▲).

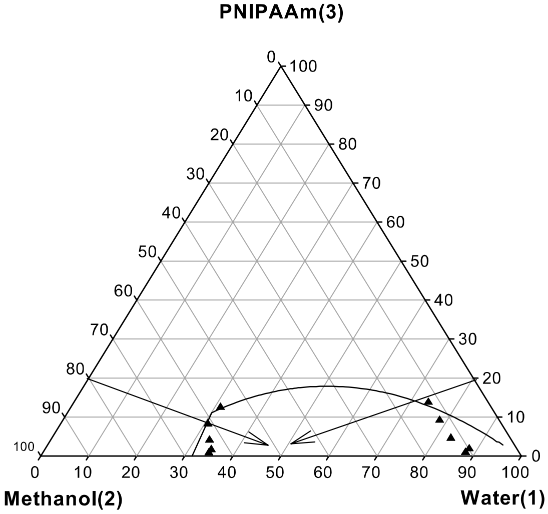

Fig. 4. The diffusion route of immersing 20% polymer solution into the coagulation bath containing 50% water and 50% methanol.

whereas a slight wider demixing region was obtained by using $\chi_T = 0.5$.

Subsequently, concentration-dependent χ_T was used to fit the experimental data. A three-parameter rational form of χ_T was followed [6–8].

$$\chi_T = a + b\phi_2 + c\phi_3 \tag{6}$$

The best fitting value of χ_T was $0.53 - 0.05\phi_2 + 0.25\phi_3$, determined by a try-and-error procedure. The calculated binodal is shown in Fig. 3. Although Fig. 3 shows that the computed binodal matches appropriately the experimental data points in the phase diagram, it still departs a little from the experimental data. This can be attributed to the errors involved in the linear form of χ_T and the measurement of the solution composition due to the low boiling point of methanol. However, it is still a reliable calculation with a ternary interaction parameter when binary parameters provide an inadequate description of cononsolvency.

3.3. The relationship between cononsolvency and membrane formation

In this paragraph, the membrane formation from a cononsolvent–polymer system is discussed by taking into account the thermodynamic interactions of the cononsolvency property. Although water and methanol are energetically favorable to dissolve PNIPAAm separately, they are the cononsolvent for PNIPAAm when these two solvents are mixed together. Phase separation will occur when a sufficient number of water–methanol contacts exist in the vicinity of a polymer chain to form the maximum number of energetically unfavorable water–methanol–PNIPAAm contacts. Fig. 4 shows the diffusion routes of immersing 20% polymer solution into the coagulation bath containing 50% water and 50% methanol, from which it can be observed that mass exchange brings the membrane solution into a metastable state with respect to liquid–liquid demixing. Following the diffusion route by using methanol as the solvent, an asymmetrical structure consisting of a dense skin layer and very large macrovoids in the cross section was observed, as indicated in Fig. 5. The kinetics of membrane formation is a typical instantaneous demixing process. It is reasonable to attribute the instantaneous demixing process to the interaction between two solvents is much stronger than that of solvent–polymer, so the polymer chains are rejected to be drawn into solution by the mixed solvent rapidly. When water was used to dissolve PNIPAAm, the membrane structure was identical to that using methanol to prepare polymer solution (not shown here). It is believed that the macrovoid structure is a consequence of liquid–liquid demixing process. Although, the liquid–liquid demixing region is smaller than that of the traditional nonsolvent–solvent–polymer system, PNIPAAm membranes with macrovoids still could be prepared by using this small demixing region. Hence, trends expected on the basis of the phase diagram was in reasonable agreement with the observed membrane morphology. In other words, the principles of membrane formation established for the ternary systems with nonsolvent–solvent–polymer can be extended to a cononsolvent–polymer system.

Overall, any alteration in the composition of PNIPAAm solution, which either decreases water–PNIPAAm and methanol–PNIPAAm contacts or increases water–methanol contacts, will increase the net free energy of the system. When the system is no longer possible to maintain sufficient water–PNIPAAm and methanol–PNIPAAm contacts, the polymers associate to a greater extent with other polymer molecules and the solution demises to form membranes. However, the mechanical property of PNIPAAm membrane is very weak due to the presence of macrovoids. Actually,

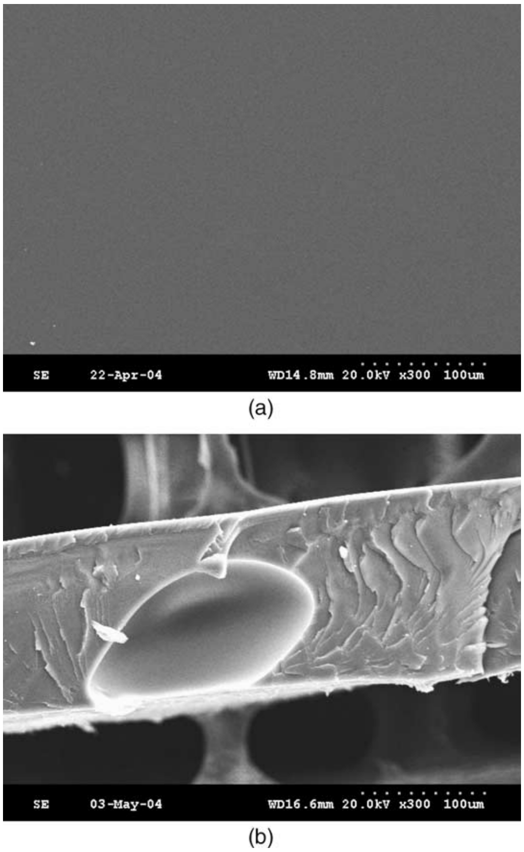

Fig. 5. SEM pictures of PNIPAAm membranes prepared by immersing 20% polymer solution dissolved in methanol into the coagulation bath containing 50% water and 50% methanol. (a) Top view; (b) cross-section view.

only few studies on the separation of solutes through PNIPAAm membranes were performed [13,14].

3.4. The mechanism of cononsolvency

Fig. 6(a) is a typical phase diagram of nonsolvent–solvent–polymer system. Fig. 6(b) is the alternative representation of a ternary phase diagram, which exchanges the apexes of solvent and nonsolvent. In these two diagrams, any composition in the regions I, I′ and II, II′ will be homogeneous and metastable with respect to liquid–liquid demixing, respectively. Fig. 6(c) is the overlapping of these two diagrams, which divides the phase diagram into four parts: $\mathrm{I}+\mathrm{I}'$, $\mathrm{I}+\mathrm{II}'$, $\mathrm{I}'+\mathrm{II}$, and $\mathrm{II}+\mathrm{II}'$. It is noted that the region $\mathrm{II}+\mathrm{II}'$ is similar to the cononsolvency range of water–methanol–PNIPAAM ternary system, as shown in Fig. 3. Since the region II and II′ are originally within the binodal phase envelope in Fig. 6(a) and (b), it is reasonable that the so-called cononsolvency phenomenon occurs in the region $\mathrm{II}+\mathrm{II}'$ (low polymer concentration region) of a solvent–solvent–polymer system when two solvents play the roles of solvent and nonsolvent simultaneously, i.e. the solvent power of the mixed solvent is less than that of either solvent independently. Conversely, for the case of a nonsolvent–nonsolvent–polymer system, if the solvent power of the mixed nonsolvent is higher than that of either nonsolvent independently, a cosolvency phenomenon will occur in the region $\mathrm{I}+\mathrm{I}'$ (high polymer concentration region). In fact, such a cosolvency behavior has been investigated by Young et al. for poly (ethylene-*co*-vinyl alcohol) in water/2-propanol mixtures by using different ternary interaction parameters [6]. When the χ_T value decreases, the cosolvency region will enlarge from near the polymer apex toward the composition at lower polymer concentration and even change from the region above two binodals to that between two binodals; see Fig. 7. Conversely, when the χ_T value increases, the cononsolvency region will be from the composition at lower polymer concentration extending toward the higher polymer concentration; see Fig. 8.

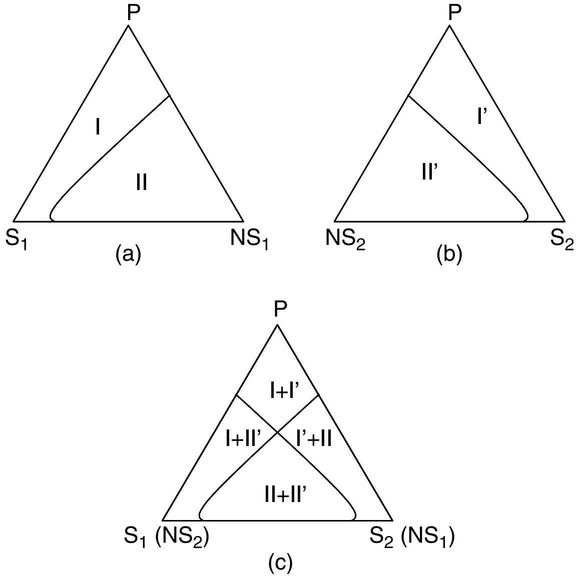

Fig. 6. (a) and (b) are typical phase diagrams of nonsolvent–solvent–polymer system, which exchanges the apexes of solvent and nonsolvent. Any composition in the regions I, I′ and II, II′ will be homogeneous and metastable with respect to liquid–liquid demixing, respectively; (c) is the overlapping of these two diagrams, which divides the phase diagram into four parts: $\mathrm{I}+\mathrm{I}'$, $\mathrm{I}+\mathrm{II}'$, $\mathrm{I}'+\mathrm{II}$, and $\mathrm{II}+\mathrm{II}'$.

The phase behavior of a similar system, PNIPAAm gels in the same mixtures, had been studied by Amiya et al. [15] They found that a strong interaction between water and methanol in the presence of PNIPAAm gel, but the concentration dependent interaction parameter for water/methanol in the binary solution is $-0.7908+1.2624/(1-0.1441\phi_2)$, whose value is in the range between 0.48 and 0.7, i.e. they are not particularly favored energetically. Therefore, the attractive interaction for methanol and water is enhanced by the PNIPAAm in the ternary system. In other words, another possible trial for the cononsolvency can be tested by regulating χ_{12} values rather than incorporating additional ternary interaction parameter to fit the experimental data. Fig. 9 is the fitted result with $\chi_{12}=0$ and different χ_{13} and χ_{23} values ranging from 0.52 to 0.75.

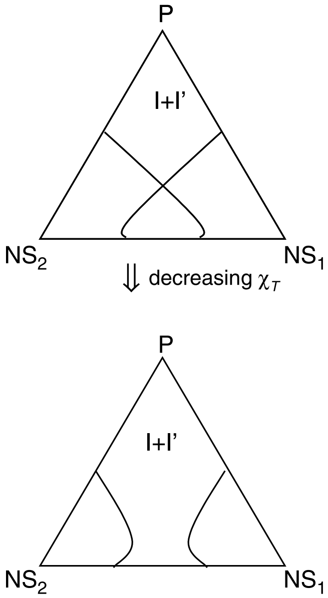

Fig. 7. When χ_T value decreases, the cosolvency region will enlarge from near the polymer apex toward the composition at lower polymer concentration and even change from the region above two binodals to that between two binodals.

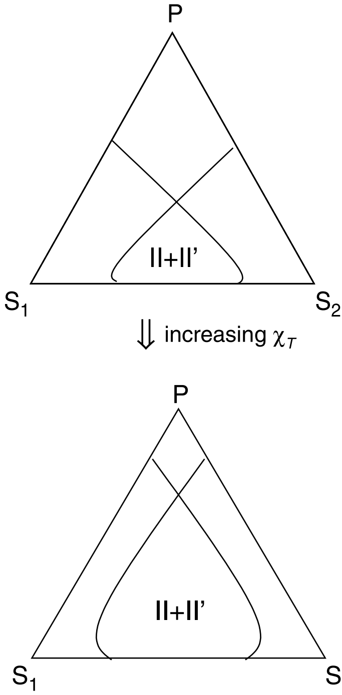

Fig. 8. When χ_T value increases, the cononsolvency region will enlarge from the composition at lower polymer concentration toward the composition at higher polymer concentration.

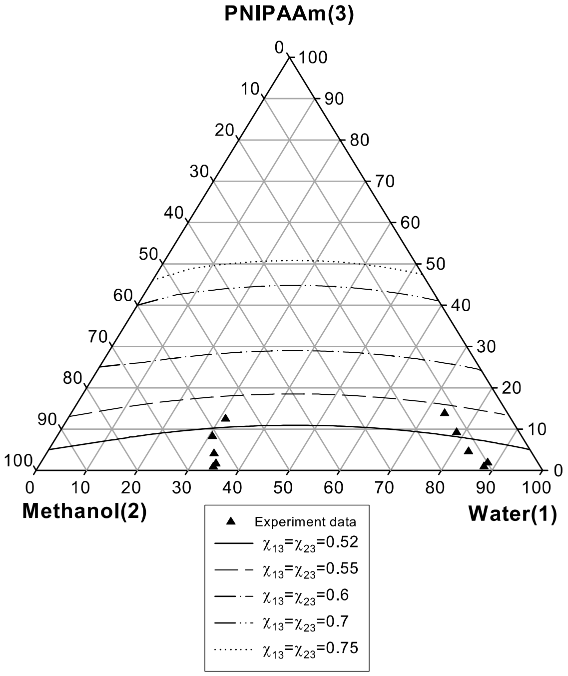

Fig. 9. Comparison between experimentally determined binodal boundary data points (denoted by filled triangles) and theoretically calculated binodals using $\chi_T=0$, $\chi_{12}=0$ and different χ_{13} and χ_{23} values.

Cleary, the calculation was able to yield an immiscible region and larger immiscibility gaps existed for increasing χ_{13} and χ_{23}. However, cononsolvency could not be observed for χ_{12} changing from 0.1 to 0.4 with χ_{13} and $\chi_{23}>0.5$. Compared to $\chi_{12}=0$ for the same χ_{13} and χ_{23} values, larger immiscibility gap could be obtained when χ_{12} was keeping at a lower value, -0.1 (not shown here). On the other hand, if χ_{13} and $\chi_{23}<0.5$, no liquid–liquid demixing region could be predicted in Fig. 9, regardless the value of χ_{12} being zero or negative. Therefore, water and methanol are no longer solvent for PNIPAAm in ternary cononsolvent system from the viewpoint of binary interaction parameter, which disagrees the binary behavior of PNIPAAm in water or methanol at 25 °C. Compared to experimental data, the best fitted curve with $\chi_{12}=0$ is $\chi_{13}=\chi_{23}=0.55$.

Based on the above results, the cononsolvency can be reasoned by modifying the χ_{12} value to be more negative and the χ_{13} and χ_{23} values more positive simultaneously. This result suggests if a ternary system increases the strength of solvent–solvent contacts and decrease the interaction between polymer and solvent, then a polymer will not be soluble in certain mixtures of two solvents. Thus, any alteration in the composition of PNIPAAm solution, which either increase the interaction between water and methanol or decreases the strength of water–PNIPAAm and methanol–PNIPAAm contacts, will increase the net free energy of the system to drive phase separation. This indicates the pairwise interaction between two components will be changed in the presence of the third component, which argues against treatments based on the Flory–Huggins theory [9]. In addition, we cannot measure such binary interaction parameters for fitting the cononsolvency in a ternary system from experimental data of independent binary systems. In other words, even though modified binary interaction parameters are correlated to a cononsolvent system, their absolute magnitude does not have much significance in independent binary systems. Therefore, we postulated the existence of a ternary interaction parameter χ_T to rationalize the cononsolvent effect of the solvent pair on a polymer. The original Flory–Huggins relation generalized for three-component systems is a special case of Eq. (1) where χ_T is equal to zero.

In our previous publication, the optimum χ_T value for the cosolvent system water-2-propanol-EVAL at 60 °C is $-1.7+0.5\phi_2+1.0\phi_3$ [6]. Such a negative χ_T value implies a strong interaction exists among the three components and even overweigh binary repulsive interactions [6]. Conversely, for the system under study, it clearly shows the calculated binodal for $\chi_T=0$ was very smaller than the measured data, as shown in Fig. 2. Therefore, there ought to be some specific repulsive interactions, i.e. the positive χ_T value $0.53-0.05\phi_2+0.25\phi_3$ in the water–methanol–PNIPAAm cononsolvent system to overweigh binary solvent–polymer interactions to demix PNIPAAm solution in mixtures of water and methanol.

On the basis of the foregoing discussion, a mechanism for cononsolvency is proposed: This system favors the formation of (1–2), (1–3) and (2–3) contacts than (1–2–3) contacts. However, what is the mechanism for the formation of unfavorable (1–2–3) contacts? The positive χ_T value suggests that (1–2) pairs reject component (3), (1–3) pairs reject component (2) or (2–3) pairs reject component (1) to raise the free energy of the system. Indeed, the phase diagram shows cononsolvency only occurs at lower polymer concentration region, suggesting the (1–2) pairs disliking component (3) as a more likely explanation of the existence of cononsolvency. When the concentration of component (3) is decreased in the system, there will be less formation of (1–3) and (2–3) contacts, which leads to the more (1–2) contacts than the polymer can tolerate, i.e. forming the unfavorable (1–2–3) contacts. Therefore, demixing occurs when a sufficient number of (1–2) contacts have formed in the vicinity of component (3) to reject it to be drawn into solution. In contrast, when the polymer concentration increases, the cononsolvency phenomenon disappears because there will be more energetically favorable (1–3) and (2–3) contacts in the system. This is consistent with the cononsolvency phenomenon occurs at lower polymer concentration region, as shown in Figs. 3 and 6(c). Thus, it is reasonable to prepare PNIPAAm membranes by decreasing (1–3) or (2–3) contacts but increasing (1–2) contacts in the system, i.e., immersing the PNIPAAm solution (dissolved in water or methanol) into the mixture of water and methanol.

In summary, the positive χ_T value is used to illustrate the repulsive ternary interaction between (1–2) pairs and component (3) in this study, that is, the ternary interaction parameters cannot be evaluated from experimental data of independent binary systems. This suggest the ternary interaction parameter can be considered as an adjustable one to experimental data and encompasses all deviations of the real system from the idealized system for which only the binary terms are considered. Thus, only binary interaction parameters provide an inadequate description of the phase behavior of PNIPAAm in methanol/water mixtures.

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