Polymer 44 (2003) 1689–1695

polymer

www.elsevier.com/locate/polymer

Phase behavior of poly(ether imide) in mixtures of *N*-methyl-2-pyrrolidinone and methylene chloride

Tai-Horng Young*, Chun-Te Tao, Ping-Shan Lai

Institute of Biomedical Engineering, College of Medicine and College of Engineering, National Taiwan University, Taipei 10016, Taiwan, ROC

Received 8 February 2002; received in revised form 19 November 2002; accepted 30 November 2002

Abstract

The phase behavior of poly(ether imide) (PEI) in solutions composed of *N*-methyl-2-pyrrolidone (NMP) and methylene chloride (MC) was studied at 25 °C. The pair of solvents used to dissolve PEI has been selected for the purpose to perform a cononsolvent system. From the observed phase behavior, PEI was soluble in either NMP or MC individually but liquid–liquid demixing was observed in mixtures of NMP and MC. However, no cononsolvency was found by the theoretical prediction on the basis of Flory–Huggins formalism including three binary interaction parameters. Therefore, attempts were made to correlate the phase behavior of a cononsolvent system with the modified Flory–Huggins theory using a ternary interaction parameter. A good prediction was obtained when a composition-dependent ternary interaction parameter was included into calculations. In addition, the mechanism of cononsolvency and its relation with the ternary interaction parameter in the cononsolvent systems were discussed. Based on the analysis of IR spectroscopy, the ternary interaction parameter correlates well with a more intermolecular complexation of NMP with MC in the presence of PEI. Thus, the driving force for cononsolvency results from the formation of the NMP–MC complexes favoring over NMP–MC–PEI contacts, leading to exclude PEI segments in the vicinity of the NMP–MC complexes.

Keywords: Phase behavior; Cononsolvency; Ternary interaction parameter

1. Introduction

It is interesting to see how the change of the interaction between polymer and solvent when other solvent is added. In a previous study [1], the interaction between poly(ethylene-*co*-vinyl alcohol) (EVAL) and mixtures of water and 2-propanol has been investigated. It was found that EVAL was insoluble in either water or 2-propanol separately but certain mixtures of water and 2-propanol dissolved EVAL. In this work, the polymer studied was poly(ether imide) (PEI). PEI is an amorphous polymer with good chemical and thermal stability. The solvents used were *N*-methyl-2-pyrrolidone (NMP) and methylene chloride (MC). Contrary to the previous so-called ‘cosolvent’ system, PEI is soluble in either NMP or MC separately, whereas liquid–liquid phase separation takes place in certain mixtures of NMP and MC, suggesting the NMP/MC mixture is a so-called cononsolvent for PEI. In ternary polymer systems the cononsolvency is an unusual phenomenon that has not been subjected to extensive investigation [2–4]. It is well known that polymer can be dissolved in an appropriate 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. In addition, there has been no investigation in constructing a complete phase diagram of PEI in NMP–MC mixtures as far as we know. Therefore, this work provides systematic studies on the complete phase behavior of the NMP–MC–PEI cononsolvent system.

There are several theoretical pathways for calculating the free energy of a polymer system. The Flory–Huggins approach [5], a lattice 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 only result in a single-phase mixture over the whole composition range in the NMP–MC–PEI system, i.e. only binary interaction

---

* Corresponding author. Tel.: +886-2-23123456x1455; fax: +886-2-23940049.

E-mail address: thyoung@ha.mc.ntu.edu.tw (T.H. Young).

0032-3861/03/$ - see front matter
PII: S0032-3861(02)00913-8

parameters provided an inadequate description of the phase behavior of PEI in MC/NMP mixtures. Therefore, we used the ternary parameter, χ_T proposed by Pouchly and Zivny [6] to account for the cononsolvency phenomenon. When a ternary interaction parameter was introduced into the Flory–Huggins theory, even though the free energy change was negative over the entire composition range, at some compositions a further decrease in free energy occurred by phase separation of the mixture. Through comparing theoretical calculation and experimentally obtained data, we found an immiscibility gap in the phase diagram and unknown phase boundaries that could not be obtained experimentally could be predicted when a ternary interaction parameter was considered.

Furthermore, the attractive and repulsive interactions between the polymer and the mixed solvent, and the connection between the ternary and binary interaction parameters in the cononsolvent system were studied. Since Infrared (IR) absorption spectroscopy is sensitive to the molecular environment of the oscillation dipole, it was used to analyze the potential interacting centers that are involved in interactions and so lead to a free energy change for the process of cononsolvency. Based on the analysis of IR spectroscopy, it was found an appreciable amount of interaction between NMP and MC and such interaction became more strongly when PEI was added. We suggested that PEI can support the NMP–MC complexes and such complexes exclude PEI segments in the vicinity of the complexes. Therefore, the system is described at which polymer is insoluble in mixtures of two solvent, whereas is soluble in either liquid separately, suggesting that binary interaction parameters are not the controlling parameter in this system.

2. Theory

In this study, the Flory–Huggins theory including a ternary interaction parameter, χ_T [1,6,7], was used to describe the Gibbs free energy of mixing (ΔG_m) for ternary polymer solutions

$$\begin{aligned}\Delta G_\mathrm{m} = {} & RT(n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + \chi_{12} n_1 \phi_2 \\ & + \chi_{13} n_1 \phi_3 + \chi_{23} n_2 \phi_3 + \chi_T n_1 \phi_2 \phi_3), \end{aligned} \tag{1}$$

where n_i and ϕ_i are numbers of moles and volume fraction of component i ($i = 1$: NMP; $i = 2$: MC; $i = 3$: PEI). 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 NMP, MC and PEI. It has been shown previously that polymer solubility in a mixed solvent is favored by a negative interaction parameter χ_T [1]. 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

$$\begin{aligned}\frac{\Delta\mu_1}{RT} = {} & \ln \phi_1 + 1 - \phi_1 - \frac{V_1}{V_2}\phi_2 - \frac{V_1}{V_3}\phi_3 + (\phi_2\chi_{12} \\ & + \phi_3\chi_{13})(\phi_2 + \phi_3) - \frac{V_1}{V_2}\phi_2\phi_3\chi_{23} \\ & - h_1 h_2 \phi_2 \frac{\mathrm{d}\chi_{12}}{\mathrm{d}h_2} - \phi_1\phi_2\phi_3 \frac{\partial\chi_{13}}{\partial\phi_2} - \phi_1\phi_3^2 \frac{\partial\chi_{13}}{\partial\phi_2} \\ & - \phi_1\phi_3^2 \frac{\partial\chi_{13}}{\partial\phi_3} - \frac{V_1}{V_2}\phi_2^2\phi_3 \frac{\partial\chi_{23}}{\partial\phi_2} - \frac{V_1}{V_2} \\ & \times \phi_2\phi_3^2 \frac{\partial\chi_{23}}{\partial\phi_3} - \phi_1\phi_2^2\phi_3 \frac{\partial\chi_T}{\partial\phi_2} - \phi_1\phi_2\phi_3^2 \frac{\partial\chi_T}{\partial\phi_3} \\ & + \chi_T\phi_2\phi_3(1 - 2\phi_1) \end{aligned} \tag{2}$$

$$\begin{aligned}\frac{\Delta\mu_2}{RT} = {} & \ln \phi_2 + 1 - \phi_2 - \frac{V_2}{V_1}\phi_1 - \frac{V_2}{V_3}\phi_3 \\ & + \left(\frac{V_2}{V_1}\phi_1\chi_{12} + \phi_3\chi_{23}\right)(\phi_1 + \phi_3) - \frac{V_2}{V_1} \\ & \times \phi_1\phi_3\chi_{13} + \frac{V_2}{V_1} h_1 h_2 \phi_1 \frac{\mathrm{d}\chi_{12}}{\mathrm{d}h_2} + \frac{V_2}{V_1}\phi_1\phi_3(\phi_1 \\ & + \phi_3)\frac{\partial\chi_{13}}{\partial\phi_2} - \frac{V_2}{V_1}\phi_1\phi_3^2 \frac{\partial\chi_{13}}{\partial\phi_3} + \phi_2\phi_3(\phi_1 \\ & + \phi_3)\frac{\partial\chi_{23}}{\partial\phi_2} - \phi_2\phi_3^2 \frac{\partial\chi_{23}}{\partial\phi_3} + \frac{V_2}{V_1}\phi_1\phi_2\phi_3(\phi_1 \\ & + \phi_3)\frac{\partial\chi_T}{\partial\phi_2} - \frac{V_2}{V_1}\phi_1\phi_2\phi_3^2 \frac{\partial\chi_T}{\partial\phi_3} + \frac{V_2}{V_1}\chi_T\phi_1\phi_3(1 \\ & - 2\phi_2) \end{aligned} \tag{3}$$

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

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

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

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 binodal of PEI in NMP/MC mixtures.

2.1. Interaction parameters

The concentration-dependent interaction parameter for NMP/MC binary pair, χ_{12}, was obtained using vapor liquid equilibrium data generated by a computer code based on the UNIFAC method [8]. Binary interaction parameters between pure liquid and polymer, χ_{13} and χ_{23}, were determined by measuring the osmotic pressure of PEI in pure liquid [5]. 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. [1].

3. Experimental section

3.1. Materials

The polymer, PEI purchased from Aldrich Co. with average molecular weight of 12000 was used after vacuum drying at 150 °C for 8 h [9]. The solvents were NMP (Tedia Co.) and MC (Acros Co.), which were used without further purification.

3.2. Liquid–liquid demixing

The phase diagram of the NMP–MC–PEI system was obtained according to the following procedure. A specific amount of dried PEI polymer was mixed with a suitable amount of single solvent NMP or MC in a sealed Teflon-lined bottle (20 ml) because of the low boiling point of MC. The maximum polymer concentration investigated was 250 g/l. 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 NMP/MC proportions. The location of the liquid–liquid miscibility gap in the ternary phase diagram was determined by observing unstable solutions separated into two clear liquid layers. The binodal points were identified as the composition at which phase separation began to occur in a series of samples. Furthermore, the weight of two liquid phases was determined by aspirating the lighter phase, taking care not to remove the layer of the denser phase. The composition of the dilute phase, which contained essentially only NMP and MC, was determined by a refractometer (Bellingham Stanley Ltd, 60/ED). Knowing the overall composition, the tie line compositions were calculated.

3.3. Osmotic pressure measurements

The dilute PEI 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 [5].

3.4. Infrared absorption spectroscopy

The samples of solution were analyzed by infrared absorption spectroscopy employing a Bio-Rad FTS-3000 spectrophotometer provided with a liquid cell (International crystal Lab., SL-2) at 25 °C. All spectra were taken by 64 scans at a nominal resolution of 4 cm^{-1}. The changes of IR spectra were taken as evidence of interactions among NMP, MC and PEI.

4. Results and discussion

4.1. Experimental phase behavior

The measured phase diagram for PEI in the mixtures of NMP and MC at 25 °C is shown in Fig. 1. The data points, denoted by filled triangles, represent the compositions of the binodal boundaries. An originally homogeneous solution becomes separated into a polymer-rich phase in equilibrium

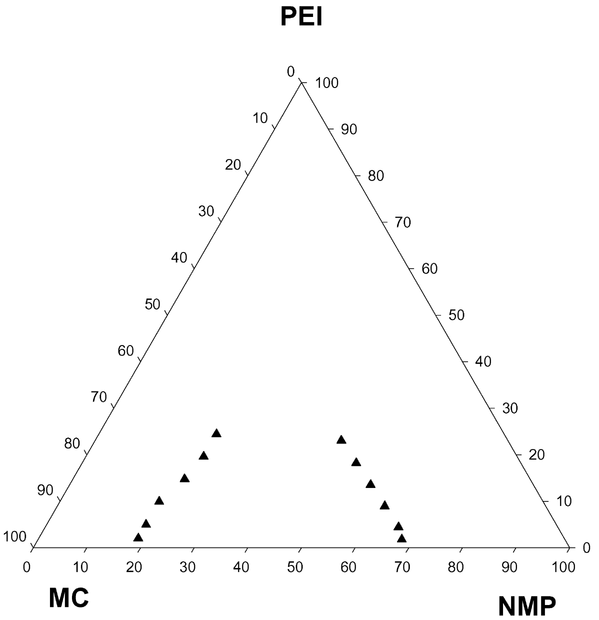

Fig. 1. Phase diagram of NMP–MC–PEI at 25 °C. The data points, denoted by filled triangles, represent the composition of the binodal boundary.

with a polymer-poor solution between these two boundaries. Outside these two boundaries is one phase region. However, as the polymer content exceeded about 25%, the sample became so gelled that a homogeneous solution became mechanically impractical. On the other hand, the lowest binodal points near the NMP/MC axis are very dilute, which are close to the critical point. Therefore, the liquid–liquid miscibility gap almost overlaps the NMP/MC axis. Such a phenomenon is ordinarily observed in ternary polymer systems [10].

As shown in Fig. 1, both NMP and MC are solvents for PEI individually, yet the phase diagram shows that certain proportions result in immiscibility with respect to liquid–liquid demixing. This suggests NMP and MC play the roles of solvent and nonsolvent simultaneously for PEI, depending on the composition of the solution.

4.2. Calculated phase behavior

Since the experimental phase equilibrium data could not be measured as the polymer content exceeded about 25%, calculations of phase equilibrium were performed to predict a complete phase diagram of a cononsolvent system. In Fig. 2, calculated binodals with a constant χ_T and the experimental binodal boundary data points are shown. The physical constants for NMP, MC and PEI employed in computations are given in Table 1. The concentration-dependent interaction parameter χ (NMP–MC) was calculated from the excess Gibbs energy data using the group contribution method of UNIFAC [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 0.507 and 0.483, respectively. As expected, these two values are consistent with both NMP and MC being solvents for PEI.

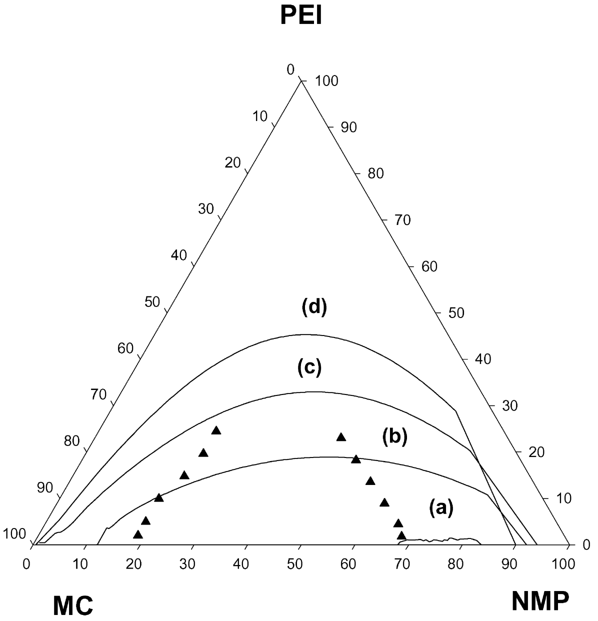

Fig. 2. Comparison between experimentally determined binodal boundary data points (denoted by filled triangles) and theoretically calculated binodals with a constant ternary interaction parameter. (a) $\chi_T = 0$, (b) $\chi_T = 0.2$, (c) $\chi_T = 0.5$ and (d) $\chi_T = 1.0$.

Table 1
Physical properties of NMP, MC and PEI at 25 °C

Component	Molecular weight	Density (g/cm^3)	Molar volume (cm^3/mol)
NMP	99.1	1.024	96.81
MC	84.9	1.317	64.49
PEI	12,000	1.24	9677

The value of χ_T was zero for the first analysis, i.e. the ternary interaction parameter was neglected. Compared to the experimental data, unfortunately, almost no liquid–liquid demixing region was predicted (Fig. 2), that is, the calculation predicted a soluble situation over the whole composition range. This totally disagreed with the experimental data; suggesting only binary interaction parameters could not be used to properly describe the characteristic of cononsolvency. Obviously, there ought to exist some repulsive forces among the three components to demix PEI solution in mixtures of NMP and MC. Since χ_{13} and χ_{23} values are close to the θ solvent and do not account for the effect of cononsolvency, we proposed the use of χ_T as a whole to account for the effect of the solvent pair on a polymer solubility.

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. Thus, PEI should be dissolved in any composition of the NMP/MC mixture and the positive χ_T was further attempted to see if it would be possible to fit the experimental data. Fig. 2 shows an immiscible region was obtained for taking a positive χ_T value; this 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, a lower but wider demixing region was obtained by using $\chi_T = 0.2$, whereas overestimation of demixing region was found when the parameter χ_T was 0.5. Therefore, the experimentally found trends were appropriately predicted between $\chi_T = 0.2$ and 0.5, suggesting it would be possible to fit the experimental data by using a concentration-dependent χ_T. The role of concentration-dependent χ_T in the

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

Binary systems	Interaction parameter, χ_{ij}
NMP(1)/MC(2)	$-0.00682 - 0.245/(1.0 - 0.0106\phi_2)$
NMP(1)/PEI(3)	0.507
MC(2)/PEI(3)	0.483

water (nonsolvent)-2-propanol (nonsolvent)-EVAL system at 60 °C has been investigated in a previous publication [1]. It could be shown that in the Flory–Huggins theory with inserted χ_T two nonsolvents has the character of a cosolvent. Conversely, in the present study, concentration-dependent χ_T was used to demonstrate the presence of ‘cononsolvency’ for the system NMP–MC–PEI. A three-parameter rational form of χ_T was followed [1]:

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

In this study, the best fit was obtained by using $\chi_T = 0.25 + 0.25\phi_2 + 0.7\phi_3$, determined by a try-and-error procedure. The calculated binodal and tie lines are shown in Fig. 3.

Although Fig. 3 shows that the calculated binodal matches appropriately the experimental data points in the phase diagram, it still departed a little from the experimental data near the MC corner. 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 MC. However, the agreement on the slopes of tie lines between the calculated and experimental data supports a reliable binodal calculation. Therefore, it is reasonable to introduce a ternary interaction parameter when binary parameters provide an inadequate description of cononsolvency.

4.3. The mechanism of cononsolvency

From the calculated phase behavior (Figs. 2 and 3), it is reasonable to postulate a χ_T to create a liquid–liquid demixing region enclosed in solution region. However, a question about the physical meaning of χ_T remains to be interpreted. What is the mechanism for the existence of cononsolvency in the NMP–MC–PEI system? The optimum χ_T value for the cosolvent system water-2-propanol-EVAL at 60 °C is $-1.7 + 0.5\phi_2 + 1.0\phi_3$ [1]. Such a negative χ_T implies a strong interaction exists among the three components and even overweigh binary repulsive interactions [1]. Conversely, there ought to be some specific repulsive interactions in the cononsolvent system NMP–MC–PEI. Therefore, the positive χ_T among the NMP, MC and PEI was proposed to overweigh binary solvent–polymer interactions to demix PEI solution in mixtures of NMP and MC.

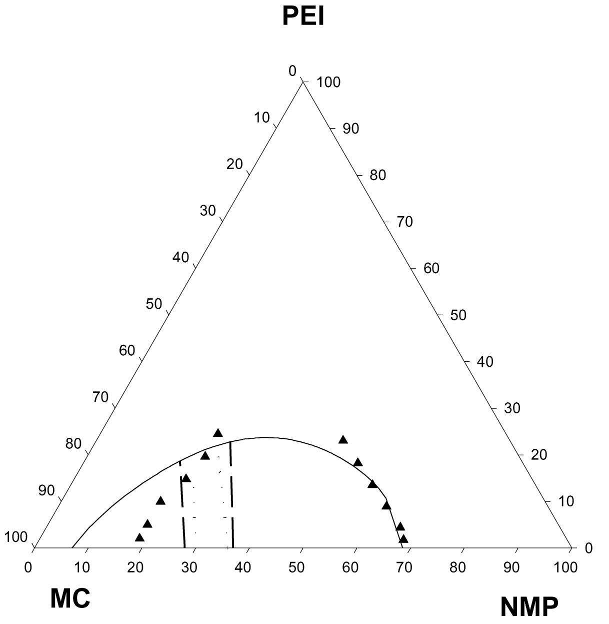

Fig. 3. Comparison between theoretically calculated phase behavior using $\chi_T = 0.25 + 0.25\phi_2 + 0.7\phi_3$ and experimentally determined phase behavior. (—: calculated binodal; ▲: measured binodal boundary data points; ···: measured tie lines; – –: calculated tie lines).

IR absorption spectroscopy is a very sensitive tool for studying molecular interactions because of its ability to detect the small perturbations of IR absorption that occur when such interactions take place. The chemical structures of NMP and MC are shown in Fig. 4. Since the absorption of the carbonyl stretching vibration is sensitive to environmental factors and there is no absorption of MC in the region of 1700–1620 cm^{-1}, the FTIR spectra of NMP and the NMP/MC mixture in this range are shown in Fig. 5. The peak at 1689 cm^{-1} (curve a) in IR spectrum of NMP can be assigned to the carbonyl absorption peak, which occurs at lower frequency than normal carbonyl absorption. This is attributed to the resonance effect when the nitrogen atom conjugates with the carbonyl group, resulting in increased single-bond character and a lowering of the carbonyl absorption frequency [11].

As the MC was added, the carbonyl stretching band of NMP was shifted to the lower frequency 1685.25 cm^{-1} (Fig. 5, curve b). The frequency decrease of carbonyl absorption induced by mixing MC with NMP reveals MC would interact with NMP via carbonyl group. On the other hand, the C–Cl absorption peak of MC at 740.54 cm^{-1} (Fig. 6, curve a) was also shifted to the lower frequency 736.26 cm^{-1} in the presence of NMP (Fig. 6, curve b). Therefore, NMP and MC may associate with each other to further increase the single-bond character of the carbonyl

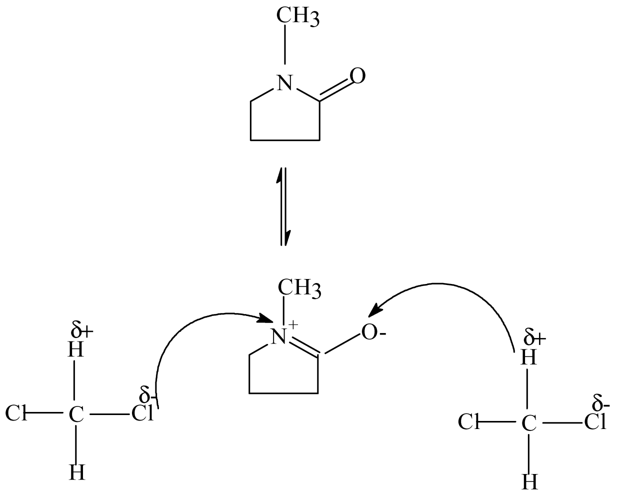

Fig. 4. Schematic presentation of interaction between NMP and MC.

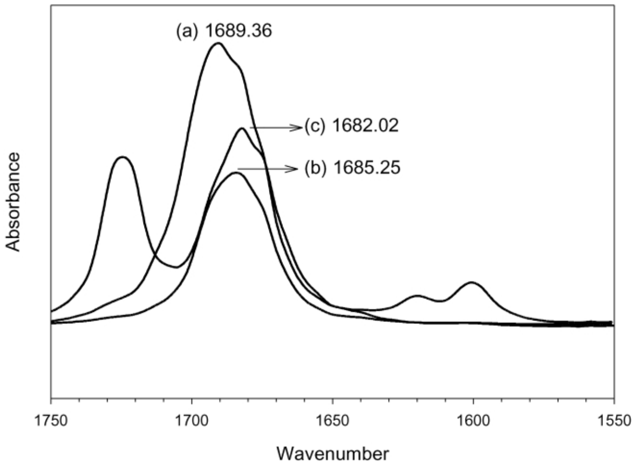

Fig. 5. The carbonyl stretch absorption of NMP at 25 °C. (a) Pure NMP: 1689.36 cm^{-1}; (b) 70 wt% NMP/30 wt% MC: 1685.25 cm^{-1}; (c) 65 wt% NMP/25 wt% MC/10 wt% PEI: 1682.02 cm^{-1}.

group of NMP. As shown in Fig. 4, in the addition of MC to NMP, the nucleophile C–Cl$^{\delta-}$ and the electrophile C–H$^{\delta+}$ will assist in supporting the resonance structure of NMP by interacting with the positive charge of the nitrogen atom and the negative charge of the oxygen atom in NMP, respectively, which reflects strong interaction (negative χ_{12}) between the NMP–MC complex.

The IR spectrum of PEI in a mixture of NMP and MC was also studied. The carbonyl absorption peak at 1722 cm^{-1} (Fig. 5, curve c) is the characteristic peak from PEI, which is irrelevant to the carbonyl absorption peak of NMP. The imide group of the PEI molecule is similar to the N–C=O group of the NMP molecule, thus NMP and PEI can compete to interact with MC via the same mechanism. NMP has a relatively smaller size than PEI, so NMP–MC complexes are preferred to PEI–MC contacts. In comparison to the spectrum of curves b and c (Fig. 5) shows the more remarkable carbonyl absorption frequency decrease upon mixing of MC with NMP in the presence of PEI. Likewise, the C–Cl absorption peak of MC was also shifted to the lower frequency in the presence of PEI (Fig. 6). These suggest a more intermolecular complexation of NMP with MC in the presence of PEI.

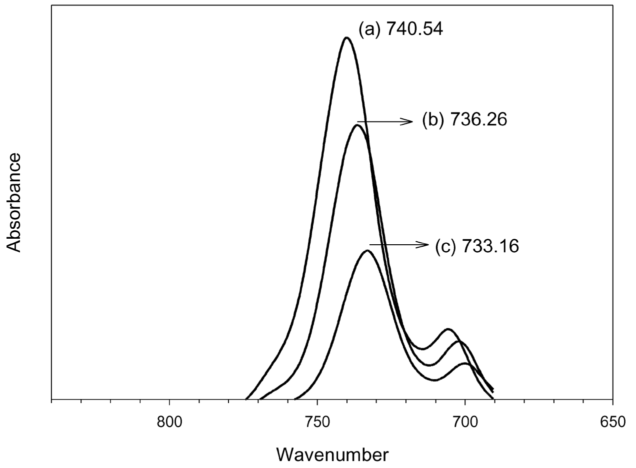

Fig. 6. The C–Cl stretch absorption of MC at 25 °C. (a) Pure MC: 740.54 cm^{-1}; (b) 70 wt% NMP/30 wt% MC: 736.26 cm^{-1}; (c) 60 wt% NMP/30 wt% MC/10 wt% PEI: 733.16 cm^{-1}.

Based on the analysis of IR spectrum, 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, and the (1–2) contacts form the most favorable complexes in the presence of component (3), which implies the unfavorable interaction between component (3) and the (1–2) complex. For a solvent, the solvent–polymer contact is energetically favorable and the polymer can dissolve. In a cononsolvent system, one can postulate addition of another solvent to this solution leads to the formation of less favorable (1–2–3) contacts, which may raise the free energy of the system. Although (1–3) and (2–3) contacts are energetically favorable, if component (1) and component (2) are simultaneously increased in the system, such a change will reduce the (1–3) and (2–3) contacts and there will be more (1–2) contacts (due to the (1–2) contacts form the most favorable complexes) than the polymer can tolerate. Therefore, phase separation will occur when a sufficient number of (1–2) contacts have formed in the vicinity of a polymer chain to reject it to be drawn into solution, i.e. the formation of (1–2–3) contacts is energetically unfavorable. In contrast, when the polymer concentration increases, there will be more (1–3) and (2–3) contacts in the system. This leads to the observed phase behavior that PEI is insoluble at lower polymer concentration and in a range of mixtures of NMP and MC.

Wolf and Williams proposed that cononsolvency occurs when the two solvents are close to demixing ($\chi_{12} \approx +2$) or when they complex between themselves ($\chi_{12} < 0$) [2]. Our calculations supports the latter. Thus, one may suggest that the negative χ_{12} value can be considered the origin of cononsolvency in the NMP–MC–PEI system. However, 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. Thus, the larger experimental binodal might be reasoned by modifying the χ_{12} value to be more negative. In addition, our IR result shows the formation of the MC–NMP complex is induced rather easily. That is to say such a strong NMP–MC complexation might be expected to reduce the strength of originally favorable NMP–PEI or MC–PEI interactions. Therefore, another possible trials were attempted with different χ_{ij} values rather than incorporating additional ternary interaction parameter to fit the experimental data. Fig. 7 is the best-fitted phase diagram with $\chi_T = 0$ and χ_{12}, χ_{13} and χ_{23} being -0.35, 0.55 and 0.53, respectively. Fig. 7 illustrates the calculation were able to yield an immiscible region but to generate a larger immiscibility gap. This result further suggests that PEI increases the strength of NMP–MC contacts. Thus, the driving force for cononsolvency is the preference of MC to complex with NMP rather than with PEI in this ternary system, which can be predicted by the Flory–Huggins

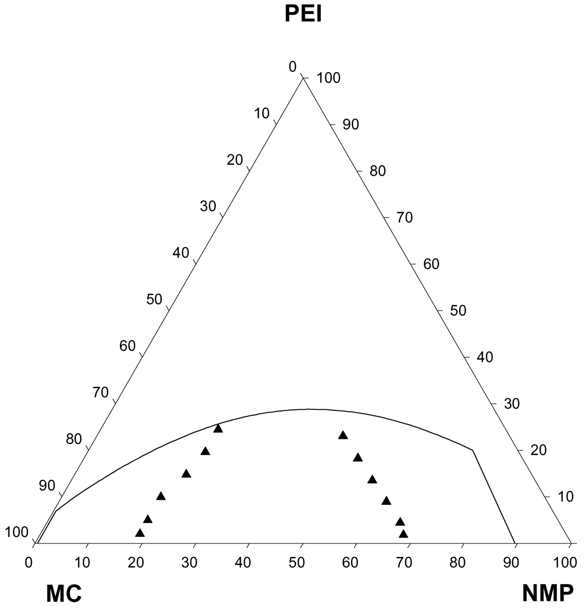

Fig. 7. Comparison between experimentally determined binodal boundary data points (denoted by filled triangles) and theoretically calculated binodals with $\chi_T = 0$ and χ_{12}, χ_{13} and χ_{23} being -0.35, 0.55, and 0.53, respectively.

theory modified with different binary interaction parameters or, more accurately, modified with incorporating a positive ternary interaction parameter.

5. Conclusion

The phase behavior of PEI in NMP–MC mixtures was studied at 25 °C. Basically, this work considered the case of immiscibility of a polymer in an essentially mixed solvent. The outcome is distinct from our experience, where PEI was soluble at some compositions but not at others. In addition, this system clearly indicates that only binary interaction parameters approaching to the problem of cononsolvency was inadequate. On the contrary, the theoretical calculations with a ternary interaction parameter could lead to a complete phase diagram. The optimum value of χ_T was $0.25 + 0.25\phi_2 + 0.7\phi_3$. The positive χ_T suggests no affinity or even rejection is present between the PEI and the NMP–MC mixtures, i.e. this system disfavors the formation of NMP–MC–PEI contacts. Although the χ_T value was only an estimate, the study indicates that χ_T could not be neglected, conversely, dominated the calculated phase behavior to coincide with the experimental data. Furthermore, based on the analysis of IR spectroscopy, the χ_T correlates well with the formation of intermolecular complexes of NMP and MC in the presence of PEI. Thus, the driving force for cononsolvency results from that the NMP–MC complexes are preferred to NMP–MC–PEI contacts.

Acknowledgements

The authors thank the National Science Council of Taiwan, the Republic of China for their financial support of this research.

References

[1] Young TH, Cheng LP, Hsieh CC, Chen LW. Macromolecules 1998;31:1229.
[2] Wolf BA, Willms MM. Makromol Chem 1978;179:2265.
[3] Katayama S, Hirokawa Y, Tanaka T. Macromolecules 1984;17:2641.
[4] Schild HG, Muthukumar MM, Tirrel DA. Macromolecules 1991;24:948.
[5] Flory PJ. Principles of polymer chemistry. Ithaca, NY: Cornell University Press; 1953.
[6] Pouchly J, Zivny A, Solc KJ. Polym Sci Part (C) 1968;23:245.
[7] Chuang WY, Young TH, Wang DM, Luo RL, Sun YM. Polymer 2000;41:8339.
[8] Gmehling J, Onken U, Arlt W. Vapor–liquid equilibrium data collection aqueous organic systems (supplement 1). Dechema Chemistry Data Series, vol. I. NY: Dechema; 1977. Part 1a.
[9] Shieh JJ, Chung TS. Ind Engng Chem Res 1999;38:2650.
[10] Cheng LP, Shaw HY. J Polym Sci, Polym Phys 2000;38:747.
[11] Nyquist RA, Fiedler SL. Vib Spectrosc 1995;8:365.