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共不溶現象對高分子造膜系統之影響(2/3)

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行政院國家科學委員會專題研究計畫成果報告

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中文摘要

本文主要研究高分子共非溶劑 NMP-MC-PEI 系統的熱力學行為，除了利用三成份作用力參數研究系統的行為外，並利用了紅外線光譜儀來檢測本系統共非溶現象的成因，而從兩者可得到合理的解釋。因此，在共非溶系統中，是不能不考慮三成份作用力參數，而僅考慮兩兩成份間的作用力參數的。

關鍵字：共非溶劑，三成份作用力參數。

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: cononsolvency; ternary interaction parameter.

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). 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 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.

Theory

In this study, the Flory-Huggins theory including a ternary interaction parameter, t_T ,¹ was used to describe the Gibbs free energy of mixing (ΔG_m) for ternary polymer solutions:

$$\Delta G_m = RT(n_1 \ln w_1 + n_2 \ln w_2 + n_3 \ln w_3 + t_{12} n_1 w_2 + t_{13} n_1 w_3 + t_{23} n_2 w_3 + t_T n_1 w_2 w_3) \quad (1)$$

where n_i and w_i are numbers of moles and volume fraction of component i ($i = 1$: NMP; $i = 2$: MC; $i = 3$: PEI). t_{ij} is a binary interaction parameter between component i and component j . Differentiating eqn. (1) with respect to n_i , the chemical potential, $\Delta \mu_i$ ($\mu_i - \mu_i^0$) of the three components can be obtained.

At liquid-liquid phase equilibrium at a specified temperature and pressure, the chemical potential of each component between two phases (\mathcal{L} and \mathcal{S}) is equal:

$$\tilde{\mu}_i^{\mathcal{L}} = \tilde{\mu}_i^{\mathcal{S}} \quad (i=1, 2, 3) \quad (2)$$

where $\tilde{\mu}_i^{\mathcal{L}}$ and $\tilde{\mu}_i^{\mathcal{S}}$ are the chemical potentials of component i in phases \mathcal{L} and \mathcal{S} .

Experimental Section

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. 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.

Results

Experimental phase behavior.

As shown in Figure 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.

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 Figure 2, calculated binodals with a constant t_T and the experimental binodal boundary data points are shown. The concentration-dependent interaction parameter t_{BC} (NMP-MC) was calculated from the excess Gibbs energy data using the group contribution method of UNIFAC. The values of t_{13} and t_{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.

The value of t_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 (Figure 2). When $t_T < 0$ was considered, the calculated liquid-liquid demixing region still completely disappeared in the phase diagram. Thus, PEI should be dissolved in any composition of the NMP/MC mixture and the positive t_T was further attempted to see if it would be possible to fit the experimental data. Figure 2 shows an immiscible region was obtained for taking a positive t_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 t_T value. Compared to experimental data, a lower but wider demixing region was obtained by using $t_T = 0.2$, whereas overestimation of demixing region was found when the parameter t_T was 0.5. Therefore, the experimentally found trends were appropriately predicted between $t_T = 0.2$ and 0.5, suggesting it would be possible to fit the experimental data by using a concentration-dependent t_T . The best fit was obtained by using $t_T = 0.25 + 0.25w_2 + 0.7w_3$, determined by a try-and-error procedure. The calculated binodal and tie lines are shown in Figure 3.

Discussion

IR absorption spectroscopy is a very sensitive tool for studying molecular interactions. The FTIR spectra of NMP and the NMP/MC mixture in this range are shown in Figure 4. The peak at 1689 cm^{-1} (curve a) in IR spectrum of NMP can be assigned to the carbonyl absorption peak. As the MC was added, the carbonyl stretching band of NMP was shifted to the lower frequency 1685.25 cm^{-1} (Figure 4, curve b). The frequency decrease of carbonyl absorption induced by mixing MC with NMP reveals MC would interact with NMP via carbonyl group. Therefore, NMP and MC may associate with each other to further increase the single-bond character of the carbonyl group of NMP. The IR spectrum of PEI in a mixture of NMP and MC was also studied. The carbonyl absorption peak at 1722 cm^{-1} (Figure , 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 shows the more remarkable carbonyl absorption frequency decrease upon mixing of MC with NMP in the presence of PEI.

Based on the analysis of IR spectroscopy, the t_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.

REFERENCES

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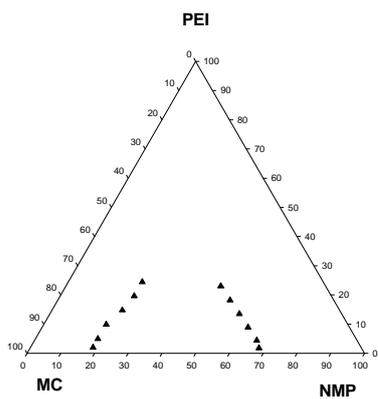


Figure 1. Phase diagram of NMP-MC-PEI at 25°C. The data points, denoted by filled triangles, represent the composition of the binodal boundary.

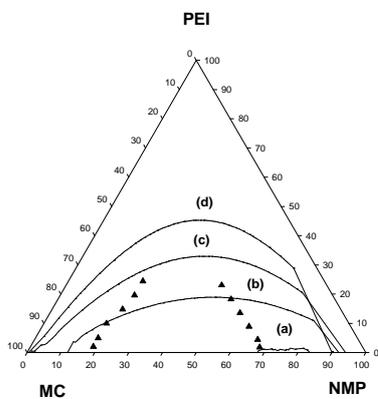


Figure 2. Comparison between experimentally determined binodal boundary data points (denoted by filled triangles) and theoretically calculated binodals with a constant ternary interaction parameter. (a) $t_T = 0$, (b) $t_T = 0.2$, (c) $t_T = 0.5$ and (d) $t_T = 1.0$.

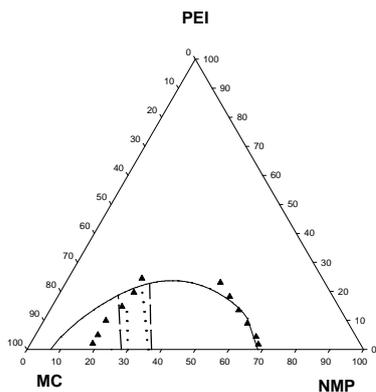


Figure 3. Comparison between theoretically calculated phase behavior using $t_T = 0.25 + 0.25w_2 + 0.7w_3$ and experimentally determined phase behavior. (—: calculated binodal; \blacktriangle : measured binodal boundary data points; \cdots : measured tie lines; - - -: calculated tie lines).

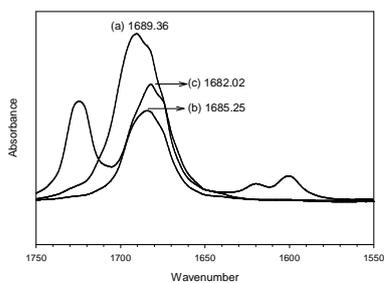


Figure 4. The carbonyl stretch absorption of NMP at 25°C. (a) pure NMP: 1689.36 cm^{-1} ; (b) 70 wt.% NMP / 30 wt.% MC: 1685.25 cm^{-1} ; (c) 65 wt.% NMP / 25 wt.% MC / 10 wt.% PEI: 1682.02 cm^{-1} .