Phase Separation Behavior of Poly(ether imide)/N,N-Dimethyl Acetamide/Nonsolvent Systems

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ABSTRACT: The phase separation behavior of a poly-(ether imide) (PEI)/N,N-dimethyl acetamide (DMAc)/nonsolvent system was investigated. Three kinds of nonsolvents were used in the study: H_2O, ethanol, and acetic acid (AA). It was found that the three systems (PEI/DMAc/H_2O, PEI/DMAc/ethanol, and PEI/DMAc/AA) agree with the linearized cloud point (LCP) relation. The binodal lines of the three systems were calculated according to the LCP relation. The binodal line of the PEI/DMAc/(H_2O + DMAc) system was also calculated according to the LCP relation of the PEI/DMAc/H_2O system. The phase separation of the PEI/DMAc/(H_2O + AA) system was studied, and the results agree with the LCP relation. These results can offer useful information for the establishment of dope and coagulation media using for the fabrication of a PEI membrane. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 875–881, 2003

Key words: phase separation; poly(ether imide); membranes

INTRODUCTION

Poly(ether imide) (PEI) is a versatile high-performance polymer that has good thermal and chemical stability. Moreover, it has advantageous gas separation properties for some gas pairs, for example, the selectivities of PEI dense membranes for He/N_2, CO_2/N_2, and O_2/N_2 gas pairs are 264, 37.4, and 7.6, respectively, at 35°C.[1] Therefore, research on its application in gas separation has been reported and various kinds of membrane-forming systems have been investigated.[2–5] It is also reported that PEI can be used in the vapor permeation of water/1-propanol and the ultrafiltration of an oil–water system.[6,7]

PEI asymmetric membranes are usually prepared through the phase inversion technique. To attain the desired membrane morphology and performance, it is well known that the phase inversion process must be carefully controlled. An important factor determining the phase inversion path of the membrane-forming system is the composition of the membrane-forming system and the coagulation media.

There are many works that deal with the phase inversion processes of different membrane-forming systems.[8–11] An important method for a phase inversion process study is the cloud point measurement and phase diagram. Cloud point curves, which are approximate binodal lines, are determined or calculated in the phase diagram. Through the binodal lines, one can compare the thermodynamic differences of different membrane-forming systems and the coagulation power of different nonsolvents.

It is difficult to calculate the binodal and spinodal lines of a membrane-forming system based on Flory–Huggins theory, because the determination of the concentration dependent interaction parameters between different components is a process of trial and error based on the experimental data of cloud point measurements.[9,10] In this problem, the calculated binodal line can be used to predict useful information about the construction of the dope composition.

In a ternary system consisting of one polymer, one solvent, and one nonsolvent, Boom suggested an empirical linearized cloud point (LCP) correlation function.[12] That is,

$$\ln \frac{\phi_1}{\phi_3} = b \ln \frac{\phi_2}{\phi_3} + a \tag{1}$$

where ϕ is the weight fraction of the component; the subscripts 1, 2, and 3 refer to the nonsolvent, solvent, and polymer, respectively; a is the intercept; and b is the slope. When only liquid–liquid demixing occurs, this function is in good agreement with the experimental cloud point. In this relation, only two parameters have to be determined, a and b. Therefore, it is possible to complete the cloud point curve with this relation after a few cloud point measurements are made that can be used in the determination of a and b. Thus, it may be a relatively good and simple solution to establish the dope and coagulant compositions by combining the LCP correlation with the cloud point measurement.
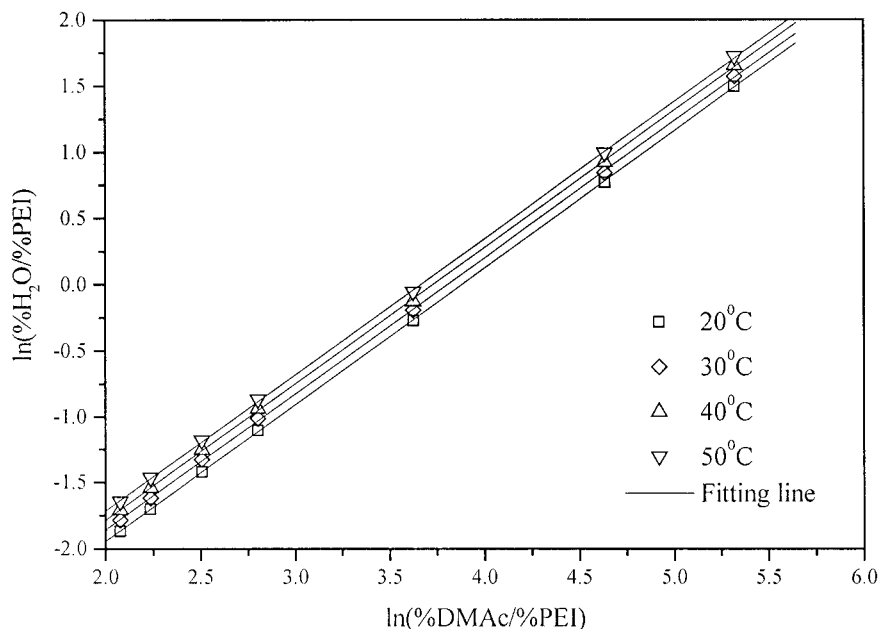
Figure 1 The LCP relation of the PEI/DMAc/H$_2$O system at different temperatures.

In this article our primary aim is to investigate the probability of applying a linearized correlation in the PEI/*N*,*N*-dimethyl acetamide (DMAc)/nonsolvent system. Several kinds of nonsolvents were used in this study. Binodal lines at different temperatures were measured and calculated.

EXPERIMENTAL

Materials

PEI (Ultem® 1000) was purchased from GE Plastics. It was dried at 150°C for 4 h before being used. The DMAc, acetic acid (AA), and ethanol were analytical reagents and were used without further purification. Deionized water was also used as a nonsolvent.

Cloud point measurement

The cloud point was determined by the sudden change in turbidity of the polymer solution. A PEI solution containing 50 mL of DMAc and a certain amount of PEI was placed in a glass bottle with a water thermostat. The solution temperature was stabilized at 20, 30, 40, and 50°C through the thermostat and the cloud points of the system at these temperatures were determined. The nonsolvents were added to the polymer solution with a microsyringe. The addition of nonsolvent was stopped when the solution became visually turbid. Then the solution temperature was elevated and the solution became transparent. If the solution became turbid again when the polymer solution was changed to the original temperature, the cloud point was fixed and the required nonsolvent

amount was obtained. Then, based on the starting composition of the PEI solution and the amount of nonsolvent added until solution demixing, the weight percentage of each component of the system at the cloud point was calculated.

RESULTS AND DISCUSSION

LCP relation of PEI/DMAc/nonsolvent systems

Figure 1 shows the LCP relation of the PEI/DMAc/water ternary system at different temperatures. It was found that the experimental points are in good agreement with the relation. The fitting results of the data are shown in Table I.

The high correlation indices in Table I indicate the good correlation of the experimental data. In addition, Boom suggested that the slope *b* is a function of the molar volumes of the component, that is,

$$b = \frac{v_1 - v_3}{v_2 - v_3} \qquad (2)$$

TABLE I
LCP Fitting Results for Cloud Points of PEI/DMAc/H$_2$O System

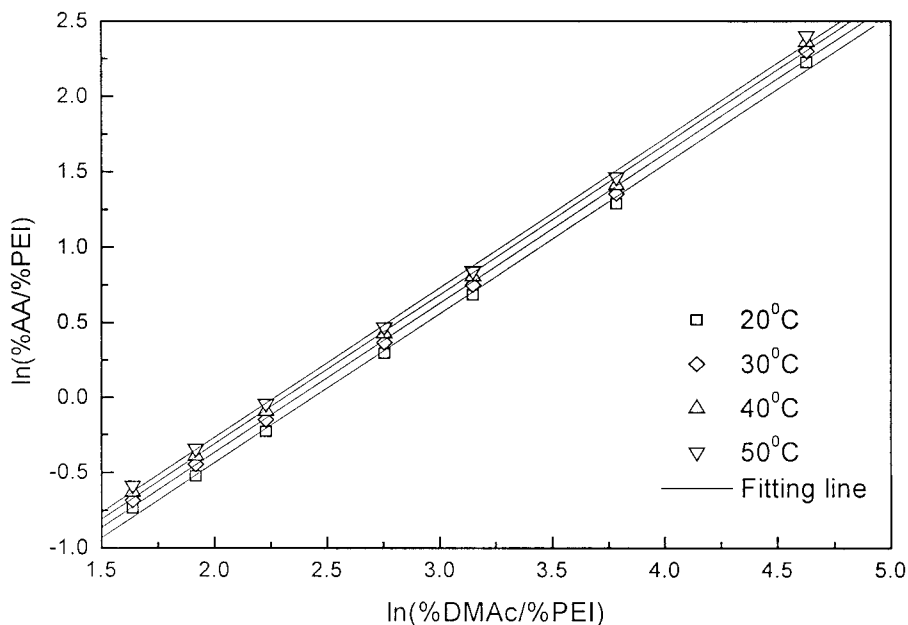| Temperature	Intercept *a*	Slope *b*	Correlation Index *R*
20°C	−4.009 ± 0.010	1.033 ± 0.003	0.99998
30°C	−3.912 ± 0.014	1.029 ± 0.004	0.99996
40°C	−3.844 ± 0.017	1.031 ± 0.005	0.99994
50°C	−3.773 ± 0.017	1.030 ± 0.005	0.99995

Figure 2 The LCP relation of the PEI/DMAc/AA system at different temperatures.

Thus, the slope only contains entropic parameters and will be larger than a value of one.[12] The data in Table I confirm this conclusion.

The LCP relations of the PEI/DMAc/AA and PEI/DMAc/ethanol systems are shown in Figures 2 and 3, respectively. The fitting results are summarized in Tables II and III. In Table II the slopes are somewhat smaller than one. However, considering the experi-

mental errors, it may be reasonable to say that the PEI/DMAc/AA system is in agreement with the LCP correlation. From Figure 3 and Table III it can be concluded that the PEI/DMAc/ethanol system is also in agreement with the LCP correlation.

Because the above-mentioned systems conform to the LCP correlation, it is possible to extrapolate the binodal lines of the systems with LCP correlation to a more wide
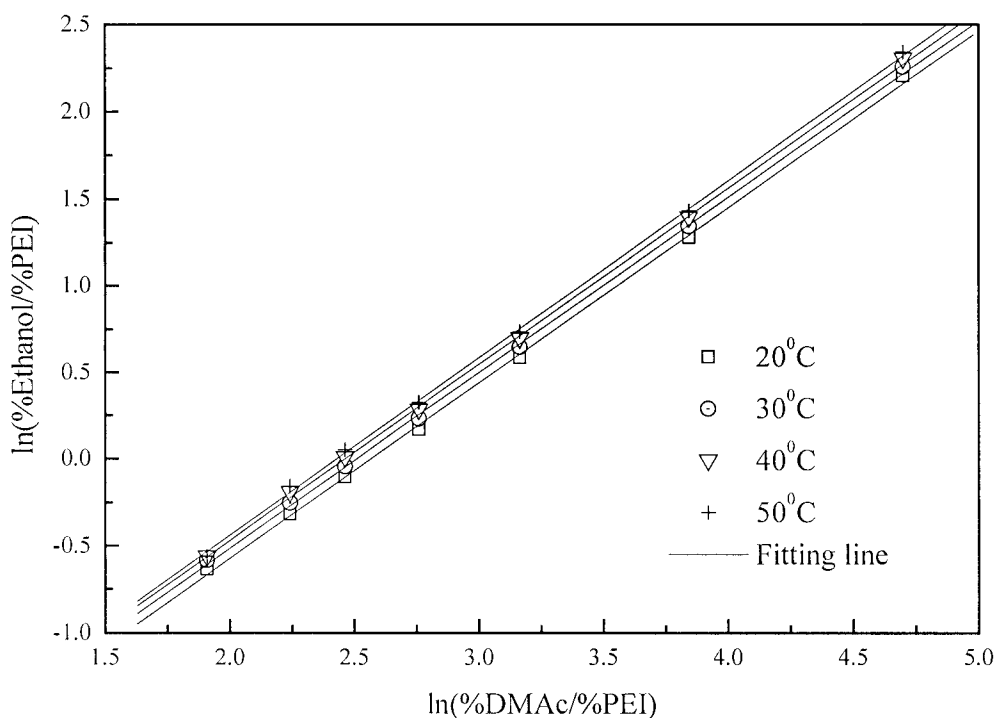

Figure 3 The LCP relation of the PEI/DMAc/ethanol system at different temperatures.

<table>
<tr><th colspan="4">TABLE II
LCP Fitting Results for Cloud Points of PEI/DMAc/AA
System</th></tr>
<tr><th>Temperature</th><th>Intercept a</th><th>Slope b</th><th>Correlation
Index R</th></tr>
<tr><td>20°C</td><td>−2.416 ± 0.051</td><td>0.991 ± 0.017</td><td>0.99929</td></tr>
<tr><td>30°C</td><td>−2.351 ± 0.048</td><td>0.992 ± 0.016</td><td>0.99935</td></tr>
<tr><td>40°C</td><td>−2.298 ± 0.048</td><td>0.994 ± 0.016</td><td>0.99937</td></tr>
<tr><td>50°C</td><td>−2.252 ± 0.047</td><td>0.994 ± 0.015</td><td>0.99939</td></tr>
</table>

TABLE II
LCP Fitting Results for Cloud Points of PEI/DMAc/AA System

Temperature	Intercept a	Slope b	Correlation Index R
20°C	−2.416 ± 0.051	0.991 ± 0.017	0.99929
30°C	−2.351 ± 0.048	0.992 ± 0.016	0.99935
40°C	−2.298 ± 0.048	0.994 ± 0.016	0.99937
50°C	−2.252 ± 0.047	0.994 ± 0.015	0.99939

TABLE III
LCP Fitting Results for Cloud Points of PEI/DMAc/Ethanol System

Temperature	Intercept a	Slope b	Correlation Index R
20°C	−2.596 ± 0.030	1.012 ± 0.010	0.99959
30°C	−2.538 ± 0.024	1.012 ± 0.008	0.99973
40°C	−2.498 ± 0.023	1.015 ± 0.007	0.99977
50°C	−2.482 ± 0.025	1.022 ± 0.008	0.99972

concentration range. Figure 4 illustrates the extrapolation results. It can be seen that the coagulation power of the three kinds of nonsolvents decreases in the order of water > ethanol > AA. This result will be useful information for the use of nonsolvents in forming the dope composition.

In order to obtain the desired membrane morphology, one usually adds some amount of nonsolvent to the polymer solution. With the help of the extrapolated binodal lines, one can determine how much nonsolvent can be added to the polymer solution at a certain polymer concentration when phase separation occurs. This is quite useful for the control of membrane morphology.

Phase separation of PEI/DMAc/(DMAc + H₂O)

In the fabrication of asymmetric membranes, the solvents for the polymer are often added to the coagulant in order to change the coagulation process. However, the details of the addition of the solvents have been infrequently mentioned in the literature.

In our work the binodal lines of the PEI/DMAc/(DMAc + H₂O) system were calculated with the assistance of the LCP relation of the PEI/DMAc/H₂O system.

It can be seen from Figure 5 that the binodal line of the system shifts to the mixture–polymer axis with the addition of DMAc to the coagulation mixture. Moreover, in the beginning of the addition of solvent to the mixture, the shift of the binodal line is smaller. However, when the amount of the solvent added to the mixture exceeds 50 wt %, the change is more marked. These results will be profitable in establishing the composition of coagulation media for PEI membrane fabrication.
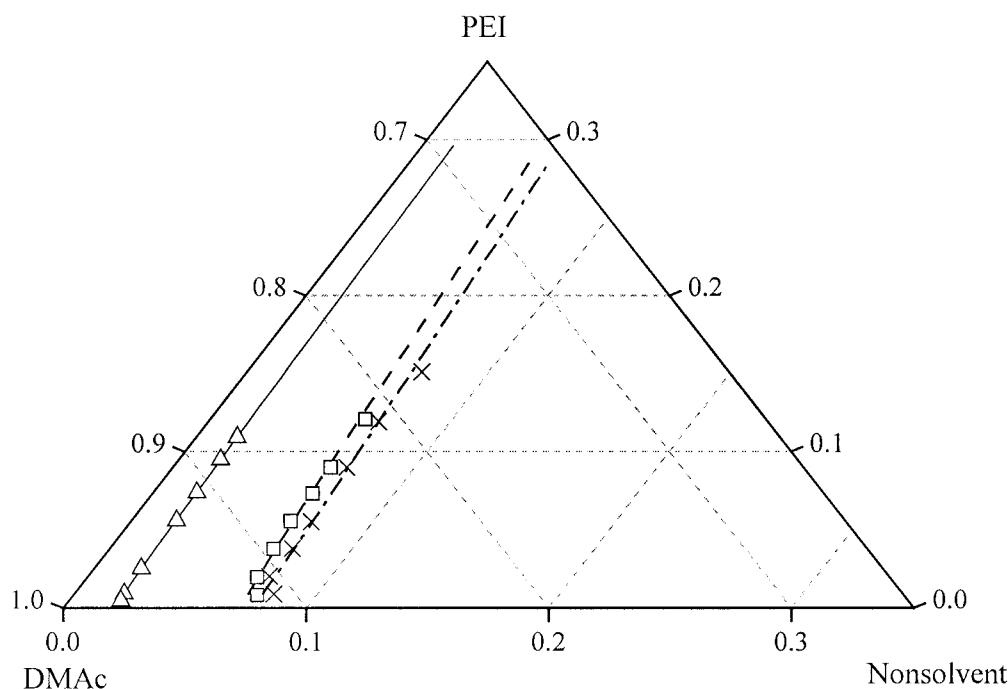

Figure 4 The calculated binodal lines of PEI/DMAc/nonsolvent systems at 20°C: (—) calculated for water, (△) the cloud point for water, (– – –) calculated for ethanol, (□) the cloud point for ethanol, (- · -) calculated for AA, and (×) the cloud point for AA.
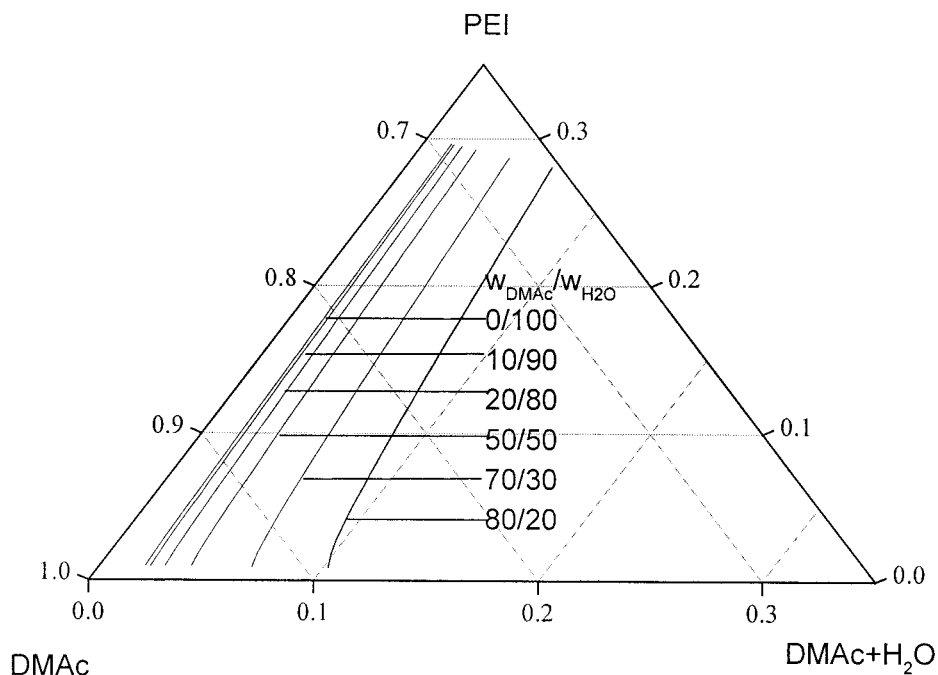
Figure 5 The calculated binodal lines of PEI/DMAc/(DMAc + H$_2$O) systems with different DMAc/H$_2$O weight ratios (W_{DMAc}/W_{H2O}) at 20°C.

Phase separation of PEI/DMAc/(H$_2$O + AA)

In order to change the coagulation path of the polymer solution and to attain ideal membrane morphology, nonsolvent additives are often added to the polymer solution. If the coagulation media is a nonsolvent different than the added one, then the system becomes a quaternary system. Predicting the phase separation behavior of these kinds of systems is interesting and useful work. When treating the two nonsolvents as one, if the LCP relation holds true in the pseudoternary system, it will be more beneficial in the membrane-forming process. In this study various amounts of AA were added to the polymer solution and water was used as the coagulation media.
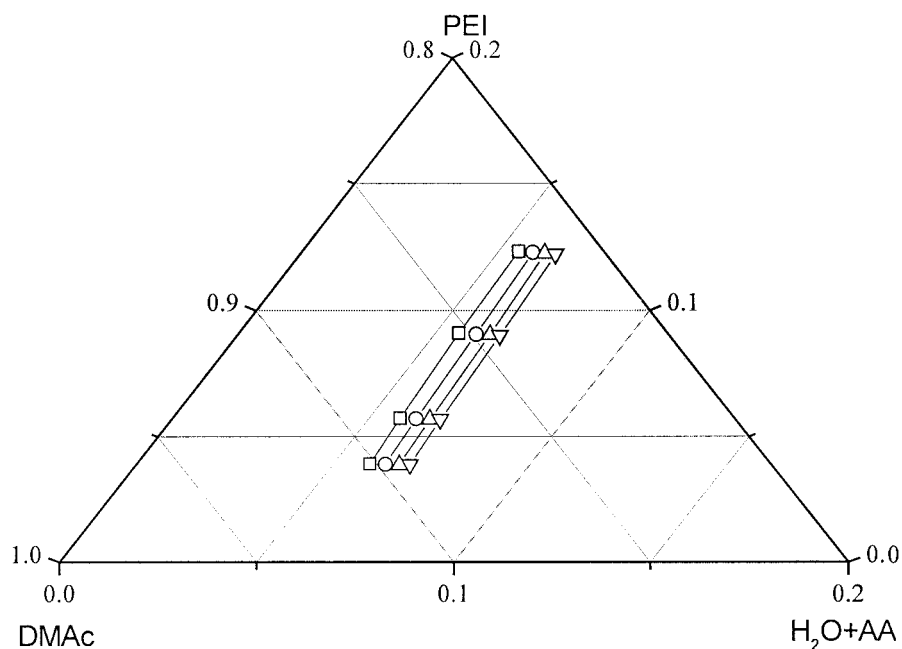

Figure 6 Phase diagrams of the PEI/DMAc/(AA + H$_2$O) system with $\alpha_{AA} = 0.7$ at ($\square$) 20°C, ($\bigcirc$) 30°C, ($\triangle$) 40°C, and ($\triangledown$) 50°C.
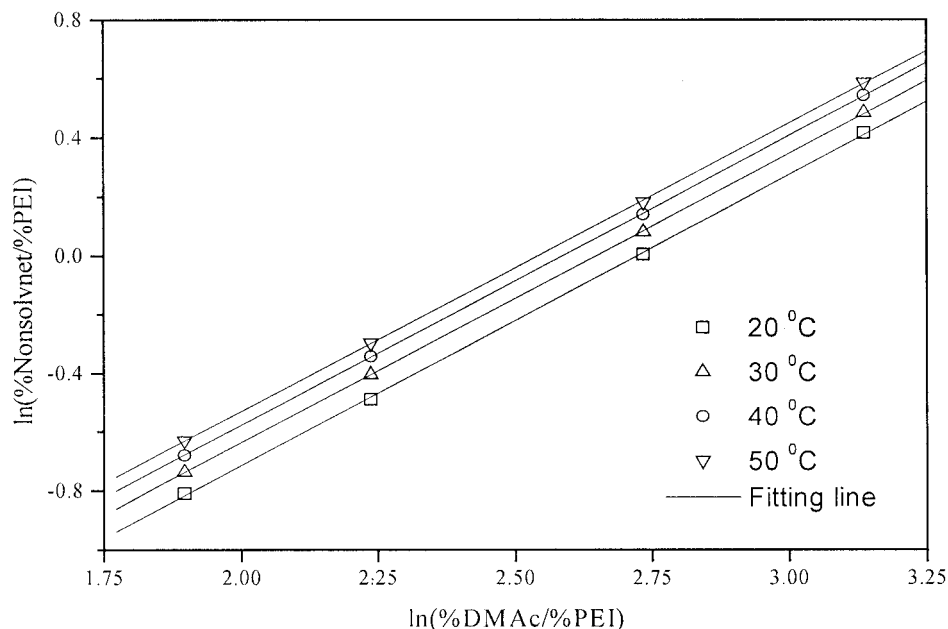
Figure 7 The LCP relation of the PEI/DMAc/(AA + H_2O) system with α_{AA} = 0.7 at different temperatures.

A polymer solution system with α_{AA} = 0.7 was investigated, where α is the ratio of the amount of AA added into the system to the amount of AA that induces demixing of the polymer solution. The amount of AA added when the polymer solution demixes is calculated with the assistance of the LCP relation of the PEI/DMAc/AA system in Figure 2. Figure 6 is the phase separation diagram of PEI/DMAc/(H_2O + AA), where AA and H_2O are treated as one nonsolvent. Figure 7 is the fitting results of the PEI/

DMAc/(H_2O + AA) system with the LCP relation. It can be seen that the pseudoternary system agrees with the LCP relation quite well in our study.

It is also very interesting to find the amount of experimental nonsolvent for the demixing of the system to coincide with the calculated result from the LCP relation. That is, at α_{AA} = 0.7, the sum of 70% of the AA amount that induces the demixing of the system and 30% of the water amount that induces demixing of the system will also induce the
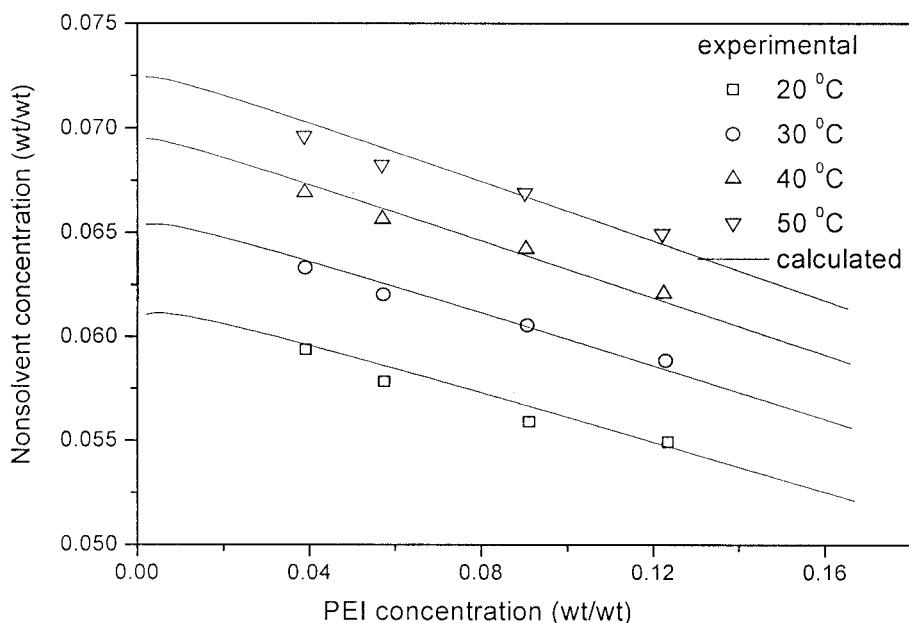

Figure 8 The relationship between the required amount of nonsolvent (AA + H_2O) for the demixing of the system and the starting polymer concentration (α_{AA} = 0.7).
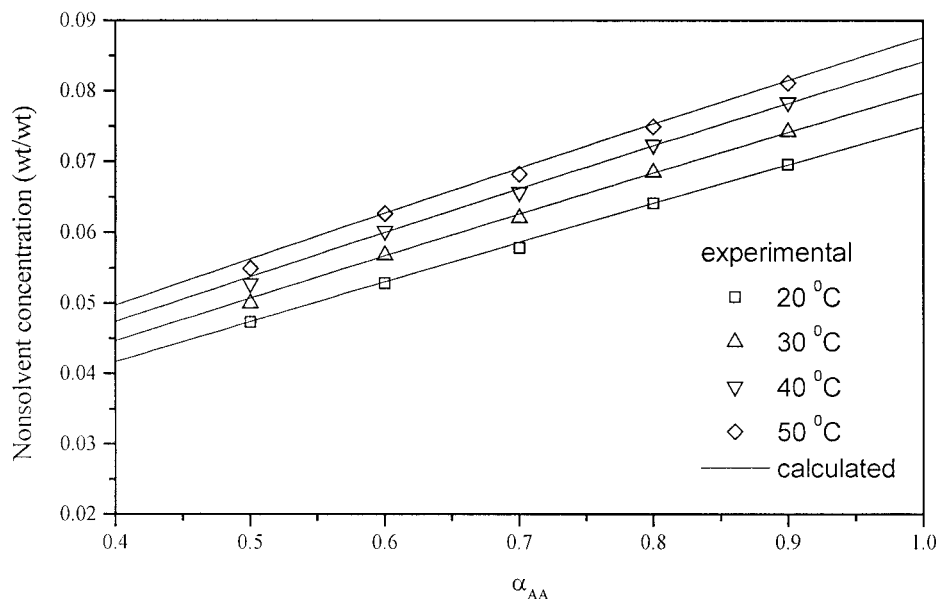
Figure 9 The relationship between the required nonsolvent (AA + H$_2$O) amount for the demixing of the system and α_{AA} (initial polymer concentration = 6.1 wt %).

demixing of the same system. The results are shown in Figure 8.

In order to investigate this phenomenon further, the experimental results and the calculated results from the LCP relation are compared with each other at different α_{AA} values with a fixed initial polymer concentration. The results are shown in Figure 9. It is obvious that the experimental results and the calculated results agree.

CONCLUSIONS

The phase separation behaviors of PEI/DMAc/nonsolvent systems were investigated. Three kinds of nonsolvents (water, ethanol, and AA) were used in the study. It was found that the three systems (PEI/DMAc/H$_2$O, PEI/DMAc/ethanol, and PEI/DMAc/AA) are in good agreement with the LCP relation. The coagulation power is in the following order: water > ethanol > AA.

The binodal lines of the three systems can be calculated in a wider starting polymer concentration range according to the LCP relation. Moreover, the binodal line of the PEI/DMAc/(H$_2$O + DMAc) system was also calculated according to the LCP relation of the PEI/DMAc/H$_2$O system. This is beneficial for the composing the coagulant.

The phase separation behavior of a PEI/DMAc/ (H$_2$O + AA) system was studied. The system also agrees with the LCP relation. It can offer useful information for establishing the dope composition and the composition of coagulation media.

References

1. Barbari, T. A.; Koros, W. J.; Paul, D. R. J Membr Sci 1989, 42, 69.
2. Peinemann, K.-V. U.S. Pat. 4,673,418, 1987.
3. Kneifel, K.; Peinemann, K.-V. J Membr Sci 1992, 65, 295.
4. Wang, D. L.; Li, K.; Teo, W. K. J Membr Sci 1998, 138, 193.
5. Shieh, J. J.; Chung, T. S. Ind Eng Chem Res 1999, 38, 2650.
6. Cranford, R. J.; Darmstadt, H.; Yang, J.; Roy, C. J Membr Sci 1999, 155, 231.
7. Xu, Z. L.; Chung, T. S.; Huang, Y. J Appl Polym Sci 1999, 74, 2220.
8. Wang, D. L.; Li, K.; Teo, W. K. J Appl Polym Sci 1999, 71, 1789.
9. Kim, Y. D.; Kim, J. Y.; Lee, H. K.; Kim, S. C. J Appl Polym Sci 1999, 73, 2377.
10. Baik, K. J.; Kim, J. Y.; Lee, H. K.; Kim, S. C. J Appl Polym Sci 1999, 74, 2113.
11. Shinde, M. H.; Kulkarni, S. S.; Musale, D. A.; Joshi, S. G. J Membr Sci 1999, 162.
12. Boom, R. M.; van den Boomgaard, T.; van den Berg, J. W. A.; Smolders, C. A. Polymer 1993, 34, 2348.