특별강연 I -2

사성분계 시스템의 액액상분리에 관한 연구 (폴리술폰/폴리에테르술폰/NMP/물)

백 기전, 김 제영*, 이 환광**, 김 성철*
대림산업대덕연구소연구관리실, 한국과학기술원화공과*,
충남산업대학교공업화학과**

Liquid-Liquid Phase Separation in a Quaternary System of Polysulfone/Polyethersulfone/N-Methyl-2-pyrrolidone/water

Ki-jun Baik, Je Young Kim*, Hwan Kwang Lee**, and Sung Chul Kim*
Planning Dept., Daelim Industrial Co. Ltd., Dept. of Chem. Eng., KAIST*,
Dept. of Ind. Chemistry, Chungnam Sanup University**

1. INTRODUCTION

The phase inversion method is widely used to prepare a variety of polymeric membranes ranging from micro-filtration to gas separation[1]. The final morphology obtained by immersion precipitation strongly reflects the thermodynamics and kinetics of the system involved. The equilibrium thermodynamics of the ternary system of polymer/solvent/ nonsolvent is still very important to understand and predict membrane structure[2].

Polysulfone (PSf) and polyethersulfone (PES) are important polymers as membrane materials due to the chemical resistance, mechanical strength, thermal stability and transport properies[3,4]. There are several reports on the experimental phase diagrams in ternary mixtures of PSf/solvent/nonsolvent[5-7], and PES/solvent/nonsolvent[6]. It would be interesting to investigate the solution thermodynamics containing these two polymers since PES is slightly less hydrophobic than PSf[4,6].

2. EXPERIMENTAL

Cloud points were determined by the titration of polymer solutions with water at various temperatures (20 °C, 30 °C, 45 °C, and 60 °C). Quantities of materials were determined by weight.

The water was added to the clear polymer solution by a microsyringe until turbidity was observed. After turbidity was observed, the temperature of the bath that contains the sample flask was raised by 30 °C above the titration temperature. If turbidity disappears within several hours, the bath temperature

was lowered to the titration temperature and more water was added.

The thermodynamic interaction parameter between PSf and PES, g_{34}, can be expressed as follows[8],

$$g_{34} = \{\ln \phi_1 + (1-\phi_1)(g_{13}\phi_3 + g_{14}\phi_4)(1-\phi_1)\} / \phi_3\phi_4$$

where ϕ_i's are the volume fraction of each component and can be obtained by the sorption experiment.

Films of PSf and PES were prepared by solution casting on glass plate. Samples (about 50 mm x 50 mm with a thickness of 80-100 mm) were weighed and were immersed into distilled water at 20 °C. They weighed until no weight change was observed and the volume fractions of each component at equilibrium were calculated.

3. RESULTS AND DISCUSSION

Cloud points for the quaternary system of PSf/PES/NMP/water were determined by a titration method at 20 °C, 30 °C, 45 °C, and 60 °C. The cloud point curves of the blend of PSf and PES do not fall in between the cloud point curves of pure PSf and pure PES and the miscible region is narrowed when PES is added to PSf. This is probably caused by the immiscibility between PSf and PES.

The immiscibility induces polymer/polymer separation and results in the narrow miscible region. Because of this, the quaternary system shows two distinct types of phase separation; polymer-rich and polymer-lean phase separation (polymer/liquid separation) and PSf-rich and PES-rich phase separation (polymer/polymer separation).

The calculated binodal curves based on the Flory-Huggins theory fit the experimental cloud points well and the model describes the phase separation behavior of the solution containing the PSf/PES blend appropriately.

LCST behavior was observed in some region. When the polymer concentration is higher than 15 wt-%, the amount of water for initiating the phase separation of the polymer solution decreases with increasing temperature.

4. REFERENCES

1. M. H. V. Mulder, *Basic Principles of Membrane Technology*, Elsevier: Amsterdam, 1991.
2. F. W. Altena and C. A. Smolders, *Macromolecules*, **15**, 1491 (1982).
3. E. Staude and L. Breitbach, *J. Appl. Polym. Sci.*, **43**, 559(1991).
4. T. A. Tweddle, O. Kutowy, W. L. Thayer, and S. Sourirajan, *Ind. Eng.*

Chem. Prod. Res. Dev., **22**, 320(1983).
5. J. G. Wijmans, J. Kant, M. H. V. Mulder, and C. A. Smolders, *Polymer*, **26**, 1539 (1985).
6. B. T. Swinyard and J. A. Barrie, *Br. Polym. J.*, **20**, 317 (1988).
7. W. W. Y. Lau, M. D. Guiver, and T. Matsuura, *J. Membr. Sci.*, **59**, 219 (1991).
8. R. L. Scott, *J. Chem. Phys.*, **17**, 279(1949)

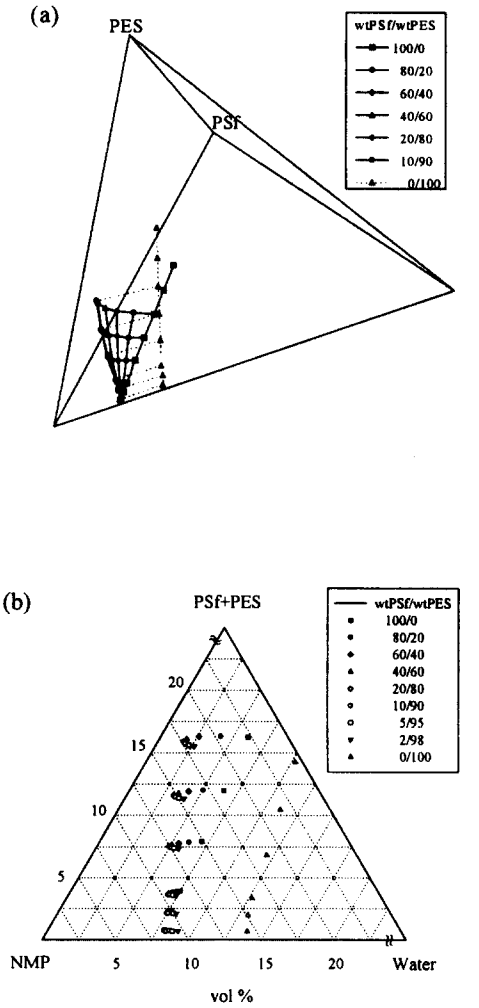

Fig. 1. Experimental cloud points for the quaternary system of PSf/PES/NMP/water at 20 °C: (a) Quaternary phase diagram in tetrahedron; (b) Cross-sections through quaternary phase diagram at a constant weight ratio between the concentrations of PSf and PES (concentrations were converted into vol%).