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Thermodynamic Study of a Water-Tetrahydrofuran-Polyvinylchloride Ternary System

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Abstract
A compressible regular solution model was used to predict the spinodal curve of a membrane forming water-tetrahydrofuran-polyvinylchloride system, employing only pure component properties. Experimental cloud point data were obtained by cloud point measurement. The relative good agreement between theoretical calculations and experimental cloud points indicates that this is a promising method to calculate theoretical phase diagram for membrane forming systems.

Keywords: Membrane- Ternary System- Phase behavior- Thermodynamic

Introduction
The phase inversion process is one of the main methods to obtain most commercially available polymer membranes. In general a ternary nonsolvent/solvent/polymer system is used to prepare asymmetric membranes by the immersion precipitation. Both thermodynamic and kinetic factors determine the ultimate structure of the membrane. The thermodynamic behavior of membrane forming water/solvent/polymer systems has been studied extensively, [1] both experimentally and theoretically. It is common to use the classical Flory–Huggins theory for polymer solutions extended to ternary systems for theoretical determination of thermodynamic behavior. [2] In this theory the Gibbs free energy of mixing is expressed as:

$$\Delta G_m / RT = n_1 \ln \varphi_1 + n_2 \ln \varphi_2 + n_3 \ln \varphi_3 + g_{12}(u_2) n_1 \varphi_2 + g_{13} n_1 \varphi_3 + g_{23} n_2 \varphi_3 \quad (1)$$

where subscripts 1, 2 and 3 refer to nonsolvent, solvent and polymer, respectively, $n1$ and φ1 are the amount and volume fraction of component i (nonsolvent, solvent and polymer); R and T are the gas constant and temperature, and gij are binary interaction parameters between the components i and j. The interaction parameters in the Flory–Huggins model are usually determined experimentally which limits its predictive capability, especially for the systems that have not been studied experimentally. In this paper the phase behavior of a Water-Tetrahydrofuran-Polyvinylchloride ternary system has been determined using compressible regular solution (CRS) model developed by Mayes et al. [3] for multicomponent systems. This model uses only pure component properties which makes it a unique thermodynamic tool for the prediction of polymer mixture phase behavior. For the ternary system studied here only the spinodal curve was calculated which seems sufficient for qualitative prediction of the phase behavior. In order to evaluate the phase behavior experimentally, cloud point measurement was carried out.

Experimental
PVC with a Kvalue of 70 was obtained from Abadan Petrochemicals, Iran, without any additive. THF was purchased from Merck and distilled water was used as the nonsolvent.

Determination of the cloud point curve
The cloud point curve was determined by the titration method. For this purpose, PVC in THF solutions with concentrations of 3, 5, 8, 9, 11 and 15 wt% were prepared by mixing desired amount of PVC powder and THF in sealed glass bottles. These mixtures were stirred for 24 h with a magnetic stirrer. During the titration process water was slowly added to the polymer solution under agitation by an adjustable volume micropipette (Biohit, Finland). At the first sight of turbidity, the addition of H_2O was stopped and the cloudy solution was agitated for 10 to 30 min. More H_2O was added only when the solution turned to homogeneous again, otherwise

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