Polymer 53 (2012) 4481–4488

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Thermodynamic-based predictions of membrane morphology in water/dimethylsulfoxide/polyethersulfone systems

S.S. Madaeni*, L. Bakhtiari

Membrane Research Center, Chemical Engineering Department, Razi University, Tagh Bostan, Kermanshah 67149, Iran

ARTICLE INFO

Article history:
Received 27 February 2012
Received in revised form
13 June 2012
Accepted 4 July 2012
Available online 24 July 2012

Keywords:
Membrane
Thermodynamic
Cloud point
Ternary system

ABSTRACT

In this paper, ternary phase diagram was used to predict morphology of the membranes prepared via phase inversion process. Theoretical ternary phase diagrams were calculated based on a compressible regular solution (CRS) model for water/dimethylsulfoxide/polyethersulfone membrane forming system. The CRS model is an alternative for the traditional Flory–Huggins theory. The experimental cloud point data were determined using titration method. The constructed theoretical ternary phase diagrams were consistent with the experimental results. The precipitation rate of the polymeric solution in the non-solvent was obtained by light transmission experiments. The membrane morphology was predicted using the theoretical phase diagram and the phase separation kinetics. To verify this prediction, the light scattering experiments were performed.

1. Introduction

The immersion–precipitation technique has recently become a common method to prepare polymeric membranes. This process is described mostly by the equilibrium thermodynamic properties of the ternary polymeric systems. In this way, a cast concentrated solution including polymer and solvent in the form of a thin film is quenched into the coagulation bath containing non-solvent. Then, polymeric solution precipitates due to the exchange of solvent and non-solvent. The non-solvent causes the casting solution to be phase-separated and so the membrane is formed [1–4]. In this case, an initially homogeneous dope solution is separated in two phases (polymer-poor and polymer-rich phases) which are at thermodynamically equilibrium with each other. This phase separation can occur during instantaneous demixing or delayed demixing processes. Finally, the membrane matrix is formed during solidification of the polymer-rich phase. The membrane pores result from the polymer-poor phase growth into the polymer-rich phase. Recently, the ternary phase diagrams were used to study the thermodynamic facets of demixing processes [5]. Various morphologies appear from fabricating membranes using two distinctly different demixing phase separation processes [6]. In an early research, Strathmann et al. reported that delayed demixing and instantaneous demixing processes resulted in producing sponge-like and finger-like membranes, respectively [5].

Membrane morphology possesses a significant effect on its efficiency. Accordingly, the knowledge of membrane morphology and its influence on membrane performance is important. The Flory–Huggins theory is usually used for thermodynamically appraisal of membrane-forming systems [7]. Maghsoud et al. [8] lately used the compressible regular solution (CRS) model to explain these systems. Using the CRS model was relatively well demonstrated to predict the ternary phase diagrams by pure component properties. Beforehand, Ruzette et al. and Gonzalez-Leon et al. explicated the thermodynamic behavior of polymer blends likewise multicomponent polymer mixtures by developing this model. Using the CRS model is more convenient in comparison with the Flory–Huggins model. The use of experiments to measure the interactions between the components is essential in Flory–Huggins model. The latter model depends on these parameters. The variations determine the binodal curve location in the ternary diagram. In the current research, the effect of errors on measuring the interactions between the components was very clear. In the CRS model, the prediction is performed using the properties of pure components as the input parameters. The estimating or measuring the binary interaction parameters is not considered. The comparison of these two models will be reported in details in a forthcoming paper by our group.

The knowledge of membrane morphology and its influence on membrane performance is vital. As a result, prediction of membrane

---

* Corresponding author. Tel.: +98 831 4274530; fax: +98 831 4274542.
E-mail address: smadaeni@yahoo.com (S.S. Madaeni).

0032-3861/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymer.2012.07.005

morphology for manufacturing of membranes is very useful in industry. In the present research, the morphology of polyethersulfone (PES) membranes was predicted by studying the phase behavior of this membrane forming system. Although, non-solvent/solvent/PES systems were widely studied in the literature but the use of theoretical phase diagrams for predicting the morphology of such membranes has not been reported. The objective of this work is predicting morphology on the basis of thermodynamic concepts for PES membrane prepared from a solution including dimethylsulfoxide (DMSO) and water as non-solvent. In this way, the phase diagram of a water/DMSO/PES ternary system has been constructed using the CRS model. The membrane morphology was predicted using the size and location of the miscibility gap, the identification of the binodal and spinodal curves and the critical point.

2. Theory

During the membrane formation, the dilute and the concentrated phases (A and B, respectively) are at the equilibrium condition. The chemical potentials of each component of the equilibrium phases are equal at a specific temperature and pressure [2,9,10].

$$\Delta\mu_i^A = \Delta\mu_i^B \quad (i = 1, 2, 3) \tag{1}$$

Where $\Delta\mu_i$ is the chemical potential difference of component i between the mixture and the pure state, A and B denote the polymer-rich and the polymer-lean phases, respectively and subscripts 1, 2 and 3 refer to nonsolvent, solvent and polymer, respectively.

Ruzette et al. [11] and Gonzalez-Leon et al. [12] have formulated μ_i^A and μ_i^B as a function of volume fraction and pure properties of each component. This formulation was obtained by the derivative of the mixing Gibbs free energy with respect to the number of moles of each component [13]:

$$\frac{\Delta\mu_i}{RT} = \frac{\partial}{\partial n_i}\left(\frac{\Delta G_m}{RT}\right)_{P,T,n_j} \tag{2}$$

Moreover, they computed the Gibbs free energy of mixing per unit volume of a ternary polymer mixture using the CRS model. This energy is defined as Eqs. (3) and (4) for the compressible and incompressible conditions, respectively [8,11,12].

$$\begin{aligned}\Delta G_m = {} & KT\left(\frac{\phi_1\widetilde{\rho_1}}{N_1\nu_1}\ln(\phi_1) + \frac{\phi_2\widetilde{\rho_2}}{N_2\nu_2}\ln(\phi_2) + \frac{\phi_3\widetilde{\rho_3}}{N_3\nu_3}\ln(\phi_3)\right) \\ & + \phi_1\phi_2\left(\widetilde{\rho_1}\delta_{1,0} - \widetilde{\rho_2}\delta_{2,0}\right)^2 + \phi_1\phi_3\left(\widetilde{\rho_1}\delta_{1,0} \right. \\ & \left. - \widetilde{\rho_3}\delta_{3,0}\right)^2 + \phi_2\phi_3\left(\widetilde{\rho_2}\delta_{2,0} - \widetilde{\rho_3}\delta_{3,0}\right)^2\end{aligned} \tag{3}$$

$$\begin{aligned}\Delta G_m = {} & KT\left(\frac{\phi_1\widetilde{\rho_1}}{N_1\nu_1}\ln(\phi_1) + \frac{\phi_2\widetilde{\rho_2}}{N_2\nu_2}\ln(\phi_2) + \frac{\phi_3\widetilde{\rho_3}}{N_3\nu_3}\ln(\phi_3)\right) \\ & + \phi_1\phi_2\widetilde{\rho_1}\widetilde{\rho_2}\left(\delta_{1,0} - \delta_{2,0}\right)^2 + \phi_1\phi_2\left(\widetilde{\rho_1} - \widetilde{\rho_2}\right)\left(\delta_1^2 - \delta_2^2\right) \\ & + \phi_1\phi_3\widetilde{\rho_1}\widetilde{\rho_3}\left(\delta_{1,0} - \delta_{3,0}\right)^2 + \phi_1\phi_3\left(\widetilde{\rho_1} - \widetilde{\rho_3}\right)\left(\delta_1^2 - \delta_3^2\right) \\ & + \phi_2\phi_3\widetilde{\rho_2}\widetilde{\rho_3}\left(\delta_{2,0} - \delta_{3,0}\right)^2 + \phi_2\phi_3\left(\widetilde{\rho_2} - \widetilde{\rho_3}\right)\left(\delta_2^2 - \delta_3^2\right)\end{aligned} \tag{4}$$

Where K is the Boltzmann constant; T is the temperature of the system; ϕ_i and $\widetilde{\rho_i}$ are the volume fraction and the reduced density of component i; N_i is the number of segments in the hard-core volume (ν_i) of component i and $\delta_{i,0}$ is the hard-core solubility parameter at 0 K. The reduced density and the hard-core solubility parameter can be obtained from Eqs. (5) and (6), respectively.

$$\widetilde{\rho_i} = \left(\rho_i/\rho_i^\bullet\right), \quad \widetilde{\rho_i} = \exp(-\alpha_i T) \tag{5}$$

$$\delta_i^2(T) = \delta_i^2(298)\left(\rho_i(T)/\rho_i^\bullet(298)\right) \tag{6}$$

Where α_i and $\rho_i^\bullet$ are the hard-core density and volumetric coefficient of thermal expansion, respectively. $\delta_{i,298}$ is calculated from the group contribution methods.

The binodal curve is defined at the condition that the chemical potential of all components is equal in the both liquid phases. The chemical potential of components of the mixture was derived from Gibbs free energy equations reported by Ruzette et al. [11] and Gonzalez-Leon et al. [12].

$$\begin{aligned}\frac{\Delta\mu_1}{RT} = {} & \ln\phi_1 + 1 - \phi_1 - \left(\frac{(N_1\nu_1)\widetilde{\rho_2}}{(N_2\nu_2)\widetilde{\rho_1}}\right)\phi_1 - \left(\frac{(N_1\nu_1)\widetilde{\rho_3}}{(N_3\nu_3)\widetilde{\rho_1}}\right)\phi_3 \\ & + \left(\frac{\left(\widetilde{\rho_1}\delta_{1,0} - \widetilde{\rho_2}\delta_{2,0}\right)^2}{RT}\phi_2 + \frac{\left(\widetilde{\rho_1}\delta_{1,0} - \widetilde{\rho_3}\delta_{3,0}\right)^2}{RT}\right) \\ & \times(\phi_2 + \phi_3)V_1 - \left(\frac{(N_1\nu_1)\widetilde{\rho_1}}{(N_2\nu_2)\widetilde{\rho_2}}\right)\left(\frac{\left(\widetilde{\rho_2}\delta_{2,0} - \widetilde{\rho_3}\delta_{3,0}\right)^2}{RT}\right)V_2\phi_2\phi_3\end{aligned} \tag{7}$$

$$\begin{aligned}\frac{\Delta\mu_2}{RT} = {} & \ln\phi_2 + 1 - \phi_2 - \left(\frac{(N_2\nu_2)\widetilde{\rho_2}}{(N_1\nu_1)\widetilde{\rho_2}}\right)\phi_1 - \left(\frac{(N_2\nu_2)\widetilde{\rho_3}}{(N_3\nu_3)\widetilde{\rho_2}}\right)\phi_3 \\ & + \left(\left(\frac{(N_2\nu_2)\widetilde{\rho_1}}{(N_1\nu_1)\widetilde{\rho_2}}\right)\frac{\left(\widetilde{\rho_1}\delta_{1,0} - \widetilde{\rho_2}\delta_{2,0}\right)^2}{RT}V_1\phi_1 \right. \\ & \left. + \frac{\left(\widetilde{\rho_2}\delta_{2,0} - \widetilde{\rho_3}\delta_{3,0}\right)^2}{RT}V_2\phi_3\right) \times (\phi_1 + \phi_3) \\ & - \left(\frac{(N_2\nu_2)\widetilde{\rho_1}}{(N_1\nu_1)\widetilde{\rho_2}}\right)\left(\frac{\left(\widetilde{\rho_1}\delta_{1,0} - \widetilde{\rho_3}\delta_{3,0}\right)^2}{RT}\right)V_1\phi_1\phi_3\end{aligned} \tag{8}$$

$$\begin{aligned}\frac{\Delta\mu_3}{RT} = {} & \ln\phi_3 + 1 - \phi_3 - \left(\frac{(N_3\nu_3)\widetilde{\rho_1}}{(N_1\nu_1)\widetilde{\rho_3}}\right)\phi_1 - \left(\frac{(N_3\nu_3)\widetilde{\rho_3}}{(N_2\nu_2)\widetilde{\rho_3}}\right)\phi_2 \\ & + \left(\left(\frac{(N_3\nu_3)\widetilde{\rho_1}}{(N_1\nu_1)\widetilde{\rho_3}}\right)\frac{\left(\widetilde{\rho_1}\delta_{1,0} - \widetilde{\rho_3}\delta_{3,0}\right)^2}{RT}V_1\phi_1 \right. \\ & \left. + \left(\frac{(N_3\nu_3)\widetilde{\rho_2}}{(N_2\nu_2)\widetilde{\rho_3}}\right)\frac{\left(\widetilde{\rho_2}\delta_{2,0} - \widetilde{\rho_3}\delta_{3,0}\right)^2}{RT}V_2\phi_2\right) \times (\phi_1 + \phi_2) \\ & - \left(\frac{(N_3\nu_3)\widetilde{\rho_1}}{(N_1\nu_1)\widetilde{\rho_3}}\right)\left(\frac{\left(\widetilde{\rho_1}\delta_{1,0} - \widetilde{\rho_2}\delta_{2,0}\right)^2}{RT}\right)V_1\phi_1\phi_2\end{aligned} \tag{9}$$

The material balance equations of volume fractions of the polymer-rich and the polymer-lean phases are the followings, respectively: