



# Phase Diagram Calculations of Water/Tetrahydrofuran/Poly(vinyl chloride) Ternary System Based on a Compressible Regular Solution Model

Zahra Maghsoud<sup>1</sup>, Mohammad Hossein Navid Famili<sup>1\*</sup>,  
and Sayed Siavash Madaeni<sup>2</sup>

(1) Polymer Engineering Group, Faculty of Engineering, Tarbiat Modares University,  
P.O. Box: 14115/143, Tehran, Iran

(2) Membrane Research Center, Chemical Engineering Department,  
Razi University, Kermanshah, Iran

Received 11 October 2009; accepted 29 June 2010

## A B S T R A C T

**M**odified Flory-Huggins theory with concentration dependent binary interaction parameters is often used to predict the phase diagram in a ternary non-solvent/solvent/polymer system. The interaction parameters in this model are usually determined experimentally which limit the model predictive capability. In this paper a compressible regular solution (CRS) model was used to predict the phase diagram of a membrane forming water/tetrahydrofuran/poly(vinyl chloride) system, by pure component properties such as, solubility parameter, coefficient of thermal expansion and hard-core volume. In this respect, the binodal curve, spinodal curve and the critical point were determined by numerical calculations. Properties of components that were needed for these calculations have been taken from available data in the literature. Experimental cloud point data were obtained by the titration method of PVC in THF solutions with concentrations reaching 15 wt%. The good agreement between the theoretical binodal and experimental cloud points indicates that this model is a promising method to calculate the theoretical phase diagram for membrane forming systems, with particular attention to the fact that no adjustable parameters such as binary interaction parameters should be used for theoretical calculations. The result of these calculations revealed that small amounts of water (less than 10%) is needed for liquid-liquid phase separation in water/tetrahydrofuran/poly(vinyl chloride) system.

### Key Words:

CRS model;  
ternary system;  
phase behaviour;  
thermodynamic.

### INTRODUCTION

Membrane separation processes are considered as part of the modern technology. The extensive application of membranes in diverse fields such as water desalination, food processing, gas separation and medical devices [1-4] makes these systems attractive alternatives for conventional separation systems.

Since the invention of asymmetric membranes by Loeb and Surirajan in 1960's, there have been

a large number of research works on different methods of membrane fabrication which among them the immersion precipitation has been the most commonly used [5-7]. In this process a thin film of polymer solution, cast on a support, is immersed in a non-solvent bath. The exchange of solvent and non-solvent during the quench step results in compositional changes which leads to phase separation. Both thermodynamic and kinetic

(\* ) To whom correspondence to be addressed.  
E-mail: [nfamili@modares.ac.ir](mailto:nfamili@modares.ac.ir)

factors control the phase separation phenomenon and thus the resultant membrane morphology. The thermodynamic aspect of membrane formation often involves calculation of a phase diagram using the Flory-Huggins theory, which is usually through calculations of the binodal and spinodal boundaries [8-10].

Up to the present, different researchers have proposed various models for thermodynamic behaviour prediction of polymer mixtures. These models show better descriptions of polymer thermodynamics compared to the Flory-Huggins theory. However, in most cases the increased rigor of these models is accompanied by higher mathematical complexity and less predictive capability [11-13]. This has made F-H theory to be considered as one of the most useful and simplest models, which after about 70 years of introduction continues to be a subject of research interest. However, some modifications are performed on the original form of the F-H theory to increase its accuracy, e.g., use of concentration dependent interaction parameters. Although this approach is the most accepted one among various authors for phase diagram calculation of membrane forming systems, the interaction parameters in the Flory-Huggins model are usually determined experimentally which limit its predictive capability, especially for the systems that have not been studied experimentally. In addition, the precise determination of these parameters is of great importance since they have considerable effects on the size and location of the miscibility gap in a ternary phase diagram [8,14].

Recently, Ruzette et al. [15] and Gonzalez-Leon et al. [16] have developed a compressible regular solution (CRS) model to explain the phase behaviour of polymer blends as well as multicomponent polymer mixtures. This model is in fact an extension of the classical regular solution model to account for compressibility. Thus, in derivation of the expression for free energy of mixing, the free volumes of the constituting components are taken into account. The main feature of the CRS model is its ability to predict the phase behaviour of various polymer mixtures in relatively good agreement with experimental data. According to our knowledge, so far the CRS model has not been used in the calculation of the thermodynamic behaviour of non-solvent/solvent/polymer

membrane forming systems.

The main goal of the present work is to propose a quick and reliable method for phase diagram prediction of membrane forming systems. In this respect, the phase behaviour of a water/tetrahydrofuran/poly(vinyl chloride) ternary system has been determined using CRS model for multicomponent systems developed by Gonzalez-Leon et al. [16]. This model uses only pure component properties which makes it a unique thermodynamic tool for the prediction of polymer mixture phase behaviour. For the ternary system studied here the phase diagrams including binodal curve, spinodal curve and critical point were calculated. In order to evaluate the phase behaviour experimentally, cloud point measurement was carried out, as well. The used PVC was suspension grade which contained minor amounts of additives affecting the experimental phase diagram.

According to our knowledge there are two works [17,18] regarding experimental phase diagram of PVC containing membrane-forming systems. In the first work, the H<sub>2</sub>O/THF/PVC system and in the second one H<sub>2</sub>O/DMF/PVC system have been investigated. None of these works have dealt with theoretical calculation of the phase diagram. In addition, the PVC used by Kawai et al. [17] has molecular weight of over  $7 \times 10^5$  which is much higher than that used in the present work.

## EXPERIMENTAL

### Materials

PVC with a K value of 70 was obtained from Bandar Imam Petrochemicals Co., Iran, without any additives. The PVC molecular weight was  $\overline{M}_n = 91000$  g/mol with a polydispersity of 2.45 which were determined by gel permeation chromatography (GPC) (Agilent 110, USA). THF was purchased from Merck and distilled water was used as the non-solvent.

### Determination of the Cloud Point Curve

The cloud point curve was determined by the titration method [19,20]. For this purpose, samples of PVC in THF solutions with concentrations of 3, 5, 8, 9, 11, 13 and 15 wt% were prepared by mixing desired amount

of PVC powder in THF in sealed glass bottles. These mixtures were stirred for at least 24 h with magnetic stirrer. During the titration process water was slowly added to the polymer solution under agitation by an adjustable volume micropipette (Biohit, Finland). The introduction of water into the bottle was done dropwise through a rubber septum stopper. At the first sight of turbidity, the addition of H<sub>2</sub>O was stopped and the cloudy solution was agitated for 10-30 min. More H<sub>2</sub>O was added only when the solution was homogeneous again, otherwise the cloudy solution was considered as the onset of the final cloud point. The composition of the cloud point was determined by measurement of the amounts of H<sub>2</sub>O, THF and PVC presented in the bottle. Cloud points were obtained at 18°C.

## RESULTS AND DISCUSSION

### Cloud Point Data

The cloud point curve for the H<sub>2</sub>O/THF/PVC system is shown in Figure 1. It should be noted that by increasing polymer concentration, it is difficult to obtain the cloud point curve because of non-homogenities due to inefficient mixing caused by high viscosity of the solution. Thus, the experimental cloud point for this system has been limited to 15 wt% concentration. It is usual to obtain the whole phase

diagram through theoretical calculation of the binodal curve [8-10,14,19,20]. It is reported that polydispersity of polymer could be the cause of anomaly between theoretical binodal and experimental cloud point [21].

### Binodal Curve

According to the CRS model, the Gibbs free energy of mixing per unit volume ( $\Delta g_{mix}$ ) of a ternary polymer mixture is defined as eqn (1) [16] which is shown in Scheme I.

The eqn (1) can be separated into compressible and incompressible terms as given in eqn (2) in Scheme I, where  $\phi_i$  is the volume fraction of *i*th component with  $N_i$  segments of hard-core (0 K, zero pressure) volume  $v_i$ .  $K$  is the Boltzmann constant and  $T$  is the temperature. The reduced density  $\tilde{\rho}_i = (\rho_i/\rho_i^0)$  is given by  $\tilde{\rho}_i = \exp(-\alpha_i T)$  and  $\rho_i^0$  and  $\alpha_i$  are the hard-core density and volumetric coefficient of thermal expansion, respectively. The hard-core solubility parameter,  $\delta_{i,0}$ , can be obtained from  $\delta_i^2(T) = \delta_i^2(298) (\rho_i(T)/\rho_i(298))$  at  $T=0$  K.  $\delta_i(298)$  is the component solubility parameter at 298 K which can be calculated from group contribution methods.

The major characteristics of the CRS theory is its capacity to account for free volumes of pure components and the mixture defined as the difference between the total and hard-core volumes. This feature gives it some superiority over the classical Flory-

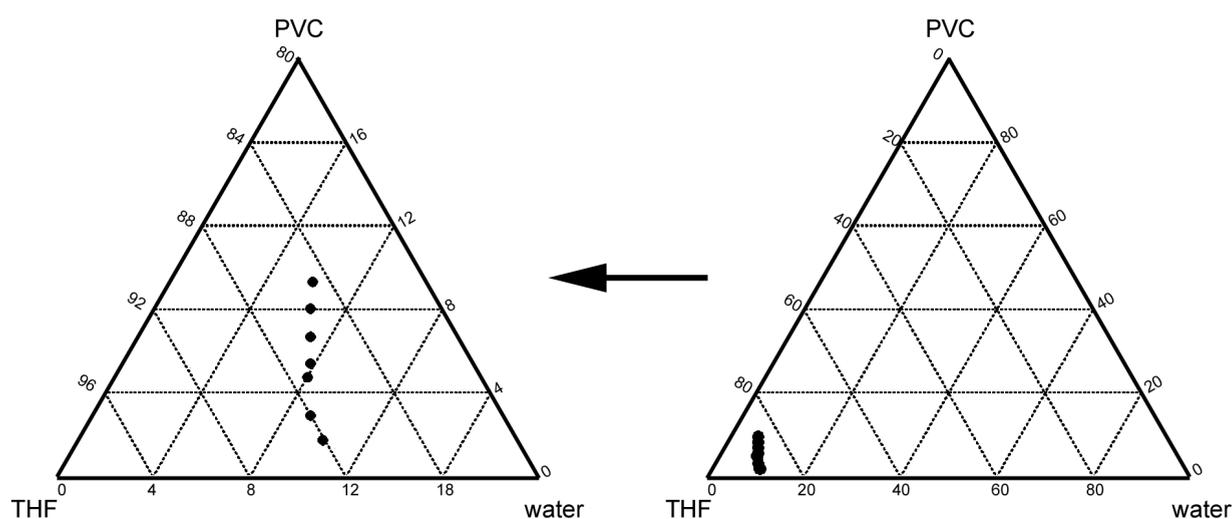


Figure 1. The experimental cloud point data for the H<sub>2</sub>O/THF/PVC system at T= 291 K.

$$\Delta g_{mix} = KT \left( \frac{\varphi_1 \tilde{\rho}_1}{N_1 v_1} \ln(\varphi_1) + \frac{\varphi_2 \tilde{\rho}_2}{N_2 v_2} \ln(\varphi_2) + \frac{\varphi_3 \tilde{\rho}_3}{N_3 v_3} \ln(\varphi_3) \right) + \varphi_1 \varphi_2 (\tilde{\rho}_1 \delta_{1,0} - \tilde{\rho}_2 \delta_{2,0})^2 + \varphi_1 \varphi_3 (\tilde{\rho}_1 \delta_{1,0} - \tilde{\rho}_3 \delta_{3,0})^2 + \varphi_2 \varphi_3 (\tilde{\rho}_2 \delta_{2,0} - \tilde{\rho}_3 \delta_{3,0})^2 \quad (1)$$

$$\Delta g_{mix} = KT \left( \frac{\varphi_1 \tilde{\rho}_1}{N_1 v_1} \ln(\varphi_1) + \frac{\varphi_2 \tilde{\rho}_2}{N_2 v_2} \ln(\varphi_2) + \frac{\varphi_3 \tilde{\rho}_3}{N_3 v_3} \ln(\varphi_3) \right) + \varphi_1 \varphi_2 \tilde{\rho}_1 \tilde{\rho}_2 (\delta_{1,0} - \delta_{2,0})^2 + \varphi_1 \varphi_2 (\tilde{\rho}_1 - \tilde{\rho}_2) (\delta_1^2 - \delta_2^2) + \varphi_1 \varphi_3 \tilde{\rho}_1 \tilde{\rho}_3 (\delta_{1,0} - \delta_{3,0})^2 + \varphi_1 \varphi_3 (\tilde{\rho}_1 - \tilde{\rho}_3) (\delta_1^2 - \delta_3^2) + \varphi_2 \varphi_3 \tilde{\rho}_2 \tilde{\rho}_3 (\delta_{2,0} - \delta_{3,0})^2 + \varphi_2 \varphi_3 (\tilde{\rho}_2 - \tilde{\rho}_3) (\delta_2^2 - \delta_3^2) \quad (2)$$

## Scheme I

Huggins theory, e.g., the possibility of capturing the lower critical solution temperature (LCST) behaviour which F-H model is not able to describe. Another advantage of CRS model is its predictive capability that needs only pure component properties as input variables but it does not estimate or measure any binary or ternary parameters.

The conditions for liquid-liquid equilibrium in a membrane forming system consisting of non-solvent (1), solvent (2) and polymer (3) are as follows:

$$\Delta \mu'_i = \Delta \mu''_i \quad i = 1, 2, \text{ and } 3 \quad (3)$$

where, *i* represents different components, prime and double prime indices denote polymer-lean and polymer-rich phases, respectively. The expressions of chemical potentials of the components in the mixture derived from eqn (1) are shown in Scheme II.

In eqns (4)-(6)  $V_i$  represents the pure molar volume of *ith* component and  $R$  is the gas constant. with accessible  $\tilde{\rho}_i$  (reduced density),  $\delta_{i,0}$  (hard-core solubility parameter) and  $v_i$  (hard-core molar volume) chemical potential of each component at specified composition can be calculated readily from the above equations.

$$\frac{\Delta \mu_1}{RT} = \ln \varphi_1 + 1 - \varphi_1 - \left( \frac{(N_1 v_1) \tilde{\rho}_2}{(N_2 v_2) \tilde{\rho}_1} \right) \varphi_2 - \left( \frac{(N_1 v_1) \tilde{\rho}_3}{(N_3 v_3) \tilde{\rho}_1} \right) \varphi_3 + \left( \frac{(\tilde{\rho}_1 \delta_{1,0} - \tilde{\rho}_2 \delta_{2,0})^2}{RT} \varphi_2 + \frac{(\tilde{\rho}_1 \delta_{1,0} - \tilde{\rho}_3 \delta_{3,0})^2}{RT} \varphi_3 \right) (\varphi_2 + \varphi_3) V_1 - \left( \frac{(N_1 v_1) \tilde{\rho}_2}{(N_2 v_2) \tilde{\rho}_1} \right) \left( \frac{(\tilde{\rho}_2 \delta_{2,0} - \tilde{\rho}_3 \delta_{3,0})^2}{RT} \right) V_2 \varphi_2 \varphi_3 \quad (4)$$

$$\frac{\Delta \mu_2}{RT} = \ln \varphi_2 + 1 - \varphi_2 - \left( \frac{(N_2 v_2) \tilde{\rho}_1}{(N_1 v_1) \tilde{\rho}_2} \right) \varphi_1 - \left( \frac{(N_2 v_2) \tilde{\rho}_3}{(N_3 v_3) \tilde{\rho}_2} \right) \varphi_3 + \left( \left( \frac{(N_2 v_2) \tilde{\rho}_1}{(N_1 v_1) \tilde{\rho}_2} \right) \frac{(\tilde{\rho}_1 \delta_{1,0} - \tilde{\rho}_2 \delta_{2,0})^2}{RT} V_1 \varphi_1 + \frac{(\tilde{\rho}_2 \delta_{2,0} - \tilde{\rho}_3 \delta_{3,0})^2}{RT} V_2 \varphi_3 \right) (\varphi_1 + \varphi_3) - \left( \frac{(N_2 v_2) \tilde{\rho}_1}{(N_1 v_1) \tilde{\rho}_2} \right) \left( \frac{(\tilde{\rho}_1 \delta_{1,0} - \tilde{\rho}_3 \delta_{3,0})^2}{RT} \right) V_1 \varphi_1 \varphi_3 \quad (5)$$

$$\frac{\Delta \mu_3}{RT} = \ln \varphi_3 + 1 - \varphi_3 - \left( \frac{(N_3 v_3) \tilde{\rho}_1}{(N_1 v_1) \tilde{\rho}_3} \right) \varphi_1 - \left( \frac{(N_3 v_3) \tilde{\rho}_2}{(N_2 v_2) \tilde{\rho}_3} \right) \varphi_2 + \left( \left( \frac{(N_3 v_3) \tilde{\rho}_1}{(N_1 v_1) \tilde{\rho}_3} \right) \frac{(\tilde{\rho}_1 \delta_{1,0} - \tilde{\rho}_3 \delta_{3,0})^2}{RT} V_1 \varphi_1 + \left( \frac{(N_3 v_3) \tilde{\rho}_2}{(N_2 v_2) \tilde{\rho}_3} \right) \frac{(\tilde{\rho}_2 \delta_{2,0} - \tilde{\rho}_3 \delta_{3,0})^2}{RT} V_2 \varphi_2 \right) (\varphi_1 + \varphi_2) - \left( \frac{(N_3 v_3) \tilde{\rho}_1}{(N_1 v_1) \tilde{\rho}_3} \right) \left( \frac{(\tilde{\rho}_1 \delta_{1,0} - \tilde{\rho}_2 \delta_{2,0})^2}{RT} \right) V_1 \varphi_1 \varphi_2 \quad (6)$$

## Scheme II

For calculation of the binodal curve, six unknown variables should be determined that represent the compositions of the two coexisting phases, the polymer-lean ( $\varphi_1', \varphi_2', \varphi_3'$ ) and polymer-rich phases ( $\varphi_1'', \varphi_2'', \varphi_3''$ ) which are connected through the tie lines. Three relations between these unknown variables are given by eqns (4) - (6). Another two relations are found from the material balance equation  $\sum \varphi_i = 1$  for the dilute and concentrated phases, respectively. Taking one composition as independent, five non-linear equations are solved simultaneously to determine the unknown variables. The objective function is as follows:

$$F_i = (\Delta\mu_i' - \Delta\mu_i'') / RT \quad i = 1, 2, \text{ and } 3 \quad (7)$$

The chemical potentials are given through eqns (4) - (6). The numerical procedure is the same as that of Yilmaz et al. [9]. They have stated that for large portions of the dilute part of the binodal curve, polymer concentrations are very small and close to zero. Thus, the calculation procedure can be simplified by assuming that the dilute phase contains zero polymer at the neighbourhood of the critical point. For preceding the calculation, the last calculated tie line (based on zero polymer assumption in the dilute phase) is used as the initial hypothesis. In this way, the whole binodal curve can be obtained.

### Spinodal Curve

The equation for the spinodal is given in eqn (8) [8]:

$$\Delta G_{22} \Delta G_{33} - \Delta G_{23}^2 = 0 \quad (8)$$

From eqn (1) further deductions may be as eqns (9)-(11) which are shown in Scheme III.

In fact the CRS model can be regarded as a special case of the modified Flory-Huggins model (concentration dependent interaction parameters) in which the interaction parameters are assumed to be constant but the effect of compressibility has been considered through the reduced density parameter.

In the case of spinodal, one variable is chosen as independent and substitution in the material balance eliminates the other variables. This would give one equation with one unknown variable to be solved. The numerical procedure is the same as that of binodal case.

### Critical Point

The equation for obtaining the critical point is as follows [9]:

$$1 - \frac{V_1}{V_2} \left( \frac{\varphi_1^c}{\varphi_2^c} \right)^2 - 3 \frac{G_{22}}{G_{23}} \left( 1 - \frac{G_{22}}{G_{23}} \right) - \left( 1 - \frac{V_1}{V_3} \right) \left( \frac{\varphi_1^c}{\varphi_3^c} \right)^2 \left( \frac{G_{22}}{G_{23}} \right)^3 = 0 \quad (12)$$

For the critical point, two eqns (8) and (12) which are in conjunction with material balance should be solved simultaneously to calculate the compositions  $\varphi_1$ ,  $\varphi_2$  and  $\varphi_3$ .

We used Matlab 7.0 to determine the phase diagram of the H<sub>2</sub>O/THF/PVC system. The values of the component parameters used for calculation of

$$G_{22} = \frac{1}{\varphi_1} + \left( \frac{1}{\varphi_2} \right) \left( \frac{(N_1 v_1) \tilde{\rho}_2}{(N_2 v_2) \tilde{\rho}_1} \right) - 2 \frac{(\tilde{\rho}_1 \delta_{1,0} - \tilde{\rho}_2 \delta_{2,0})^2}{RT} V_1 \quad (9)$$

$$G_{23} = \frac{1}{\varphi_1} - \left( \frac{(\tilde{\rho}_1 \delta_{1,0} - \tilde{\rho}_2 \delta_{2,0})^2}{RT} + \frac{(\tilde{\rho}_1 \delta_{1,0} - \tilde{\rho}_3 \delta_{3,0})^2}{RT} \right) V_1 + \left( \frac{(N_1 v_1) \tilde{\rho}_2}{(N_2 v_2) \tilde{\rho}_1} \right) \frac{(\tilde{\rho}_2 \delta_{2,0} - \tilde{\rho}_3 \delta_{3,0})^2}{RT} V_2 \quad (10)$$

$$G_{33} = \frac{1}{\varphi_1} + \left( \frac{1}{\varphi_3} \right) \left( \frac{(N_1 v_1) \tilde{\rho}_3}{(N_3 v_3) \tilde{\rho}_1} \right) - 2 \frac{(\tilde{\rho}_1 \delta_{1,0} - \tilde{\rho}_3 \delta_{3,0})^2}{RT} V_1 \quad (11)$$

Scheme III

**Table 1.** Parameters used for calculations.

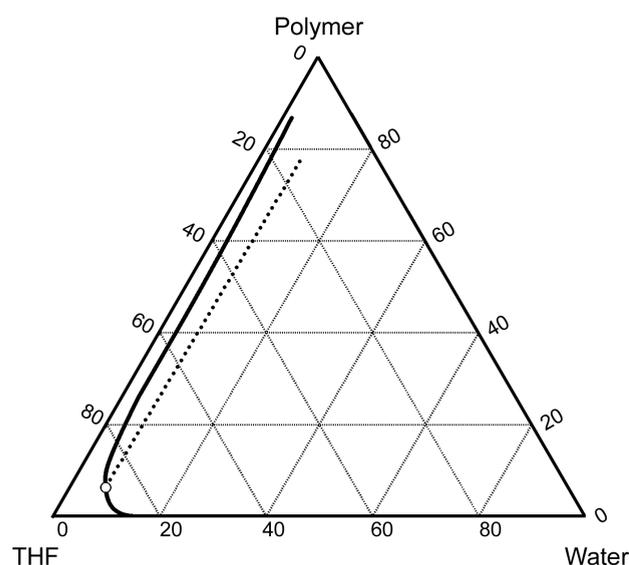
	$\rho^*$ (g/cm <sup>3</sup> )	$\alpha$ $\times 10^{-4}$ (K <sup>-1</sup> )	$\delta(298)$ (J <sup>1/3</sup> /cm <sup>3/2</sup> )	$N_{Av}V$ (cm <sup>3</sup> /mol)
PVC <sup>a</sup>	1.79	2.1	19.20	35.09
THF <sup>b</sup>	1.36	12.6	18.60	52.82
H <sub>2</sub> O <sup>c</sup>	1.07	2.07	47.96	16.82

(a) P-V-T data from ref. 15 and solubility parameter from ref. 22, (b) P-V-T data from ref. 23, and (c) P-V-T properties estimated using ref. 24.

binodal, spinodal and the critical point are listed in Table 1.

### Phase Diagram for the H<sub>2</sub>O/THF/PVC Ternary System

Figure 2 shows the calculated binodal curve, spinodal curve and the critical point for the H<sub>2</sub>O/THF/PVC system at T = 291 K. The system shows a small miscible region and small changes in water volume fraction of the polymer-rich phase. It is clear that small amounts of water (less than 10%) is needed for liquid-liquid phase separation. Thus the membranes are likely to form by instantaneous demixing upon coagulation step and hence it is expected to form a relatively porous top layer that makes it suitable for



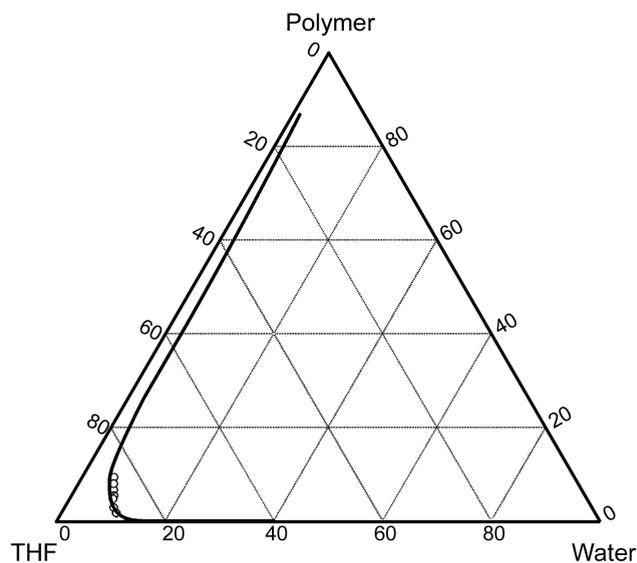
**Figure 2.** Calculated phase diagram for H<sub>2</sub>O/THF/PVC system at T = 291 K, (–) binodal curve, (...) spinodal curve and (o) critical point.

ultrafiltration and microfiltration applications [6,8,25].

In Figure 3 the theoretical binodal curve and the experimental cloud points are compared. There is a good agreement between experimental data and the low concentration part of the binodal curve, despite the fact that no experimental measurement of model parameters has been done. With increasing polymer concentration some deviations are observed from theoretically calculated binodal curve which are attributed to the polydispersity of the PVC polymer and the experimental errors.

The use of the CRS model has enabled us to calculate the phase diagram of the H<sub>2</sub>O/THF/PVC membrane forming system directly from pure component properties. As can be seen the general thermodynamic behaviour of the system is relatively well demonstrated. However if we desire to use the F-H model to calculate the phase diagram, we would have to measure or estimate the binary interaction parameters which take more time and possibly accompanied by some errors.

In the F-H model, three interaction parameters should be calculated for each component. For H<sub>2</sub>O/THF/PVC system the  $g_{13}$  (H<sub>2</sub>O/PVC binary interaction parameter) which has a considerable effect on the phase diagram [14] has not been reported in



**Figure 3.** Comparison of the cloud point curve and the theoretical binodal curve: (–) theoretical binodal curve and (o) cloud point curve.

literature, either. It is usual to measure this parameter through swelling measurement. We tried to measure this parameter by this method but water sorption of PVC is so negligible that we could not detect a measurable increase in polymer weight.

Wei et al. [10] have proposed the use of Hansen solubility parameter to obtain the interaction parameters. We employed this method but the results were unacceptable and the binodal curve obtained by the calculated interaction parameters was in poor agreement with experimental data.

It should be noted here that in spite of its advantages, the CRS model fails to predict the phase behaviour of strong specific interactions such as hydrogen bonding and its predictive capability is limited to weak interaction systems [15,16].

The composition of the critical point is  $\phi_1 = 0.066$ ,  $\phi_2 = 0.87$  and  $\phi_3 = 0.063$  which corresponds to an initial polymer concentration of ~11 wt% in solvent. The critical polymer composition determines the mechanism of liquid-liquid phase separation. Above the critical point, nucleation of the polymer-lean phase occurs and the polymer-rich phase will form the continuous phase. Therefore, upon membrane production, the composition of the initial casting solution should be selected over the critical polymer composition to ensure sufficient mechanical stability of the membrane [6].

## CONCLUSION

The cloud point curve for a ternary system of water/THF/PVC was obtained with the titration method. The theoretical phase diagram was calculated employing the CRS model. A good agreement between experimental measurements and theoretical calculations leads to the conclusion that the model can serve as a promising thermodynamic tool to predict phase behaviour of non-solvent/solvent/polymer membrane forming systems.

## SYMBOLS AND ABBREVIATIONS

$(\Delta g_{mix})$  : Gibbs free energy of mixing per unit volume  
 $\alpha_i$  : Volumetric thermal expansion coefficient

$\delta_i$  : Solubility parameter  
 $\delta_{i,0}$  : Hard-core solubility parameter  
 $\mu_i$  : Chemical potential  
 $v_i$  : Hard-core molar volume  
 $\rho_i$  : Density  
 $\tilde{\rho}_i$  : Reduced density  
 $\rho_i^*$  : Hard-core density  
 $\phi_i$  : Volume fraction of *ith* component  
 $K$  : Boltzman constant  
 $N_{Av}$  : Avogadro's number  
 $N_i$  : Number of segments  
 $T$  : Temperature  
 $V_i$  : Molar volume

## REFERENCES

1. Baker RW, *Membrane Technology and Applications*, 2nd ed, Wiley, 191-235, 2004.
2. Catapano G, Vienken J, Biomedical Applications of Membranes. In: *Advanced Membrane Technology and Applications*, Li NN, Fane AG, Winston Ho WS, Matsuura T (Eds), Wiley, New Jersey, Part II, 489-517, 2008.
3. Baker RW, Membrane gas-separation applications. In: *Membrane Operations Innovative Separations and Transformations*, Drioli E, Giorno L (Eds), Wiley-VCH, Weinheim, Ch 8, 167-194, 2009.
4. Cheryan M, Alvarez JR, Food and beverage industry applications. In: *Membrane Separations Technology: Principles and applications*, Noble RD, Stern SA (Eds), Elsevier, Amsterdam, Ch 9, 415-465, 1995.
5. Loeb S, Sourirajan S, Sea water demineralization by means of an osmotic membrane, *Adv Chem Ser*, **38**, 117-132, 1962.
6. Mulder M, *Basic Principles of Membrane Technology*, Kluwer Academic, Dordrecht, 81-156, 1996.
7. Reuvers AJ, van den Berg JWA, Smolders CA, Formation of membranes by means of immersion precipitation. Part I: a model to describe mass transfer during immersion precipitation, *J Membr Sci*, **34**, 45-65, 1987.
8. Altena FW, Smolders CA, Calculation of liquid-liquid phase separation in a ternary system

- of a polymer in a mixture of a solvent and a nonsolvent, *Macromolecules*, **15**, 1491-1497, 1982.
9. Yilmaz L, McHugh AJ, Analysis of nonsolvent-solvent-polymer phase diagrams and their relevance to membrane formation modeling, *J Appl Polym Sci*, **31**, 997-1018, 1986.
  10. Wei Y-M, Xu Z-L, Yang X-T, Liu H-L, Mathematical calculation of binodal curves of a polymer/solvent/nonsolvent system in the phase inversion process, *Desalination*, **192**, 91-104, 2006.
  11. Horta A, Statistical thermodynamics of preferential sorption, *Macromolecules*, **12**, 785-789, 1979.
  12. Sanchez IC, Panayiotou CG, Equations of state thermodynamics of polymer and related solutions. In: *Models for Thermodynamic and Phase Equilibria Calculations*, Sandler SI (Ed), Marcel & Dekker, New York, 187-285, 1994.
  13. Economou IG, Statistical associating fluid theory: a successful model for the calculation of thermodynamic and phase equilibrium properties of complex fluid mixtures, *Ind Eng Cham Res*, **41**, 953-962, 2002.
  14. Karimi M, Albrecht W, Heuchel M, Kish MH, Frahn J, Weigel T, Hofmann D, Modarress H, Lendlein A, Determination of water/polymer interaction parameter for membrane-forming systems by sorption measurement and a fitting technique, *J Membr Sci*, **265**, 1-12, 2005.
  15. Ruzette AVG, Mayes AM, A simple free energy model for weakly interacting polymer blends, *Macromolecules*, **34**, 1894-1907, 2001.
  16. Gonzalez-Leon JA, Mayes AM, Phase behavior prediction of ternary polymer mixtures, *Macromolecules*, **36**, 2508-2515, 2003.
  17. Kawai T, Lee YM, Yamada S, Preparation of asymmetric porous membranes of poly(vinyl chloride), *Polymer*, **38**, 1631-1637, 1997.
  18. Bodzek M, Konieczny K, The influence of molecular mass of poly(vinyl chloride) on the structure and transport characteristics of ultrafiltration membranes, *J Membrane Sci*, **61**, 131-156, 1991.
  19. Barzin J, Sadatnia B, Theoretical phase diagram calculation and membrane morphology, evaluation for water/solvent/polyethersulfone systems, *Polymer*, **48**, 1620-1631, 2007.
  20. Tan L, Pan D, Pan N, Thermodynamic study of a water-dimethylformamide-polyacrylonitrile ternary system, *J Appl Polym Sci*, **110**, 3439-3447, 2008.
  21. Boom RM, van den Boomgaard T, van den Berg JWA, Smolders CA, Linearized cloud point curve correlation for ternary systems consisting of one polymer, one solvent and one non-solvent, *Polymer*, **34**, 2348-2356, 1993.
  22. van Krevelen DW, te Nijenhuis K, *Properties of Polymers: Their Correlation with Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions*, 4th ed, Elsevier Science, Amsterdam, 189-228, 2009.
  23. Flick EW, Ethers. In: *Industrial Solvents Handbook*, Noyes Data Corporation, New Jersey, 487, 1998.
  24. Water Thermal Properties, [http://www.engineeringtoolbox.com/water-thermal-properties-d\\_162.html](http://www.engineeringtoolbox.com/water-thermal-properties-d_162.html), available in 4 October 2009.
  25. Reuvers, AJ, Membrane formation, diffusion induced demixing processes in ternary polymeric systems, PhD Thesis, Membrane Technology Group, Twente University, Dec 1986.