

## Preparation of Polyvinylchloride Membranes from Solvent Mixture by Immersion Precipitation

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**ABSTRACT:** In this study, polyvinylchloride (PVC) membranes were prepared through the immersion precipitation method using a mixture of two solvents (tetrahydrofuran (THF) and dimethyl formamide (DMF)), which had different affinities with the nonsolvent (water). Membranes prepared from PVC/THF/water system showed a sponge-like structure with isolated pores, which were impermeable to water even at a feed pressure of 20 bars, whereas those prepared from PVC/DMF/water exhibited a porous macrovoid containing morphology with a high water flux. The precipitation time and polymer concentration profiles were calculated by using a simple mathematical model and were in good agreement with the experimental findings on PVC/THF/water and PVC/DMF/water systems. By using a mixture of DMF and THF as solvent and changing the mixed solvent composition, membranes with different morphologies from sponge-like to macrovoid containing were obtained. The membranes showed no water flux below a DMF concentration of 50 wt % and then became increasingly permeable with increasing DMF content in the casting solution. Measurement of the system cloud points showed a linear change of system thermodynamics with variation of the mixed solvent composition. The obtained results showed that although the system thermodynamics could explain the overall behavior of the system, but the local changes such as change of membrane performance from impermeable to permeable at a certain mixed solvent composition could not be explained by the thermodynamics alone. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40206.

**KEYWORDS:** membranes; polyvinylchloride; phase behavior; kinetics

Received 1 July 2013; accepted 18 November 2013

DOI: 10.1002/app.40206

### INTRODUCTION

Membrane preparation by immersion precipitation is possibly the most studied membrane formation method since the introduction of membrane technology.<sup>1–4</sup> In this technique, the polymer solution is cast as a thin film on a proper substrate and then immersed into a coagulation bath containing a nonsolvent. The exchange of solvent and nonsolvent causes unstable thermodynamic condition in the cast film and final precipitation of the polymer occurs. The ultimate structure of the membrane is affected by a number of different variables, which enable one to adjust the membrane performance through proper selection of these variables. A key factor affecting membrane morphology is the choice of solvent/nonsolvent system. Low mutual affinity between solvent and nonsolvent results in a relative dense structure, whereas high mutual affinity favors the formation of a more porous structure.<sup>5</sup> Therefore, it is possible to tailor the membrane structure by use of appropriate solvent/nonsolvent pairs. It is also possible to prepare membranes with a wide range of porosities by using a mixture of two solvents with

different affinities toward the nonsolvent.<sup>6–11</sup> In this case, the membrane structure is directly affected by the composition of the solvent mixture.

Kools<sup>6</sup> have reported that in Polysulfone/*N*-methylpyrrolidone (NMP)-tetrahydrofuran (THF)/water system, with increasing the amount of THF in the solvent mixture (NMP-THF), macrovoids become smaller and broader and their number decreases. They have concluded that different morphologies could be obtained by changing the ratio of the NMP-THF in the solvent mixture. Shieh and Chung<sup>7</sup> used cellulose acetate (CA)/NMP-THF/water system to prepare hollow fiber membranes and reported similar results. Li et al.<sup>8</sup> have used NMP/gamma-butyrolactone (GBL) mixture as solvent to prepare CA membranes. They have shown that there exists a critical ratio between the two solvents (NMP(25):GBL(75)) where the morphology changes from finger-like to sponge-like structure. They ascribed these results to the poorer solubility of CA in GBL and lower interaction of GBL with water in comparison to NMP. Yoo et al.<sup>9</sup> have studied the polyimide/NMP-GBL/water system and

observed that increasing the amount of GBL in the solvent mixture gives rise to sponge-like structure with a dense top layer. This was due to the poor miscibility of water and GBL, because the mixing is endothermic whereas that of NMP/water is an exothermic one. Peinemann et al.<sup>10</sup> used polyetherimide/GBL-THF/water system and showed that higher gas permeation and thinner membrane skins could be observed by increasing GBL in the GBL/THF mixture. It has been reported that by changing the ratio of the solvent to the co-solvent, membranes with controllable molecular weight cut off (MWCO) can be obtained. In this way, See-Toh et al.<sup>11</sup> succeeded to produce polyimide membranes with controllable performance without the need to make composite membrane to achieve proper performance. It is promising because it allows preparation of membranes with different structures and separation performance from one polymer by changing the ratio of the two solvents in the solvent mixture. This method seems likely to give the desired structure in any membrane forming system provided that the solvent pair is chosen appropriately.

In this article, we have studied membrane formation from polyvinylchloride (PVC)/dimethyl formamide (DMF)-THF/water system with changing THF to DMF ratio. PVC is a low cost polymer with good chemical and mechanical properties, which make it a suitable material for fabrication of membranes.<sup>12–16</sup>

Knowledge of the thermodynamics and kinetic aspects of membrane formation is an essential part of membrane formation studies.<sup>5</sup> In this study, the thermodynamics was studied through cloud point measurement. Because of the rapid changes in the casting solution during solvent–nonsolvent exchange, a mathematical model is often used to investigate the kinetic aspects of membrane formation. Different models based on the original work by Cohen et al.<sup>17</sup> modified by Reuvers et al.<sup>18–20</sup> have been proposed so far to model the diffusion process during membrane formation. Most of these models are somewhat complicated and need some input parameters, which are difficult to obtain. In this study, we have applied a simple diffusion model proposed by Fernandes et al.,<sup>21</sup> which uses a Fickian diffusion equation to calculate the local compositions in the cast film as a function of time and position. This model requires a limited number of input parameters and will be discussed further in the following.

## EXPERIMENTAL

### Materials

PVC (K70) with molecular weight of  $M_n = 91,000$  g/mol and PDI = 2.45 was obtained from Bandar Imam Petrochemicals, Iran, without any additive. DMF and THF were purchased from Merck and used as received. Distilled water was used as the nonsolvent.

### Membrane Preparation

For membrane preparation, 10 wt % PVC in DMF/THF solutions were prepared by mixing PVC powder and solvents in sealed glass bottles for 24 h at ambient temperature. Membranes were cast on a glass substrate using an adjustable knife with a thickness of 200 micron. The cast film was immediately immersed in a coagulation bath containing distilled water. Then

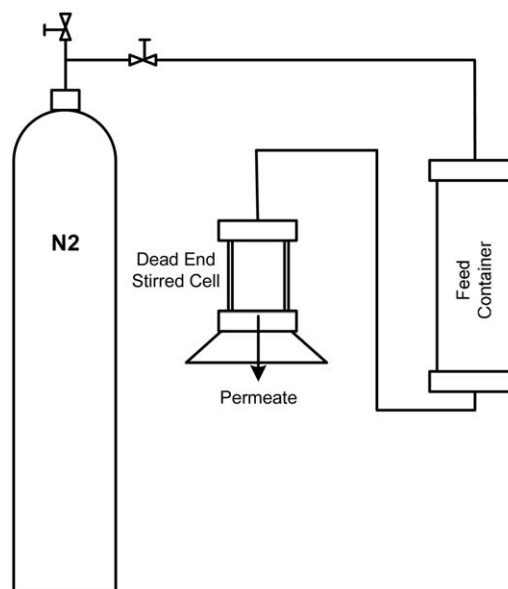


Figure 1. Dead end type membrane test cell.

the membranes were kept in fresh water for 24–48 h to remove residual solvent.

### Membrane Performance

A home-made dead end type membrane test cell was used for water flux measurement, which is shown in Figure 1. The water flux ( $J_w$ ) was calculated from the following equation:

$$J_w \left( \frac{L}{m^2 hr} \right) = \frac{Q}{A \times t} \quad (1)$$

Where  $Q$  is the permeate volume passed through the area  $A$  of membrane at time  $t$ . Pure water flux was determined at a pressure range of 2–8 bars.

### Ternary Phase Diagrams

Cloud point curve was determined by the titration method. For this purpose, PVC in DMF/THF solutions with concentrations of 3, 5, and 8 wt % were prepared by mixing desired amount of PVC powder and known ratio of DMF/THF in sealed glass bottles. The detail of titration procedure is described in an earlier article.<sup>22</sup>

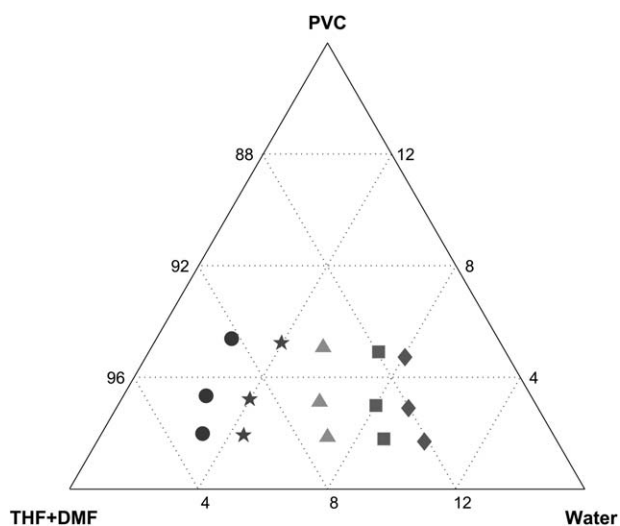
### Scanning Electron Microscopy Study

Membrane cross section morphology was studied with a scanning electron microscopy (SEM), (Philips XL 30). For this purpose membranes were fractured in liquid nitrogen and then coated with gold.

## RESULTS AND DISCUSSION

### Thermodynamics

Figure 2 shows the cloud point curve of PVC/DMF-THF/water system with different ratios of DMF to THF. As it can be seen, PVC/THF/water shows delayed demixing whereas PVC/DMF/water system has instantaneous demixing characteristics. In the case of PVC/DMF solution, phase separation occurs immediately after immersion in water. When a mixture of DMF-THF is used, cloud point position changes toward PVC-water axis with increasing THF in the solvent mixture. In other words, more



**Figure 2.** The cloud point curve of PVC/THF:DMF/water system with change in THF:DMF ratio;  $\blacklozenge$  (100:0),  $\blacksquare$  (75:25),  $\blacktriangle$  (50:50),  $\star$  (25:75),  $\bullet$  (0:100).

water is needed to cause phase separation with increasing THF in PVC/DMF-THF/water system.

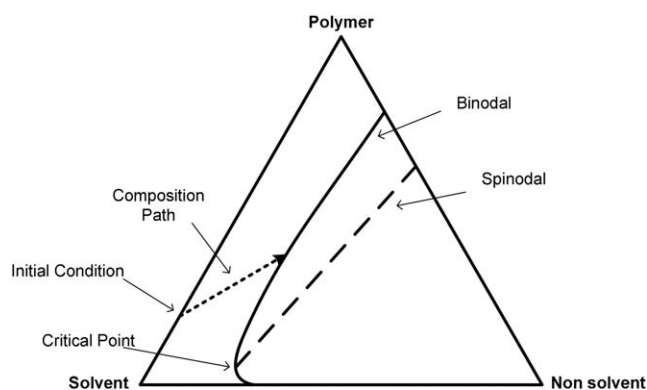
Among different solvents used for membrane preparation, THF and DMF have different characteristics in view of miscibility with water. DMF has a high tendency to mix with water (high mutual affinity), whereas THF/water mixtures have low mutual affinity. The change of cloud point position is almost proportional to the amount of each solvent present in the mixture. That is, it seems that the solvent mixture acts as a solvent whose affinity with water is a function of the composition of the solvent mixture.

### Kinetics of Membrane Formation

As said before, in the immersion precipitation process a film of polymer solution (Phase 1) is immersed in a nonsolvent bath (Phase 2). The exchange of solvent and nonsolvent leads to unstable thermodynamic conditions in the film and finally phase separation occurs. To describe the involved mass transfer, Fernandes et al.<sup>21</sup> have proposed a simple diffusion equation. The indices 1, 2, and 3 represent solvent, nonsolvent and polymer, respectively:

$$\frac{\partial C_{(i,j)}}{\partial t} = D_{(i,j)} \cdot \frac{\partial^2 C_{(i,j)}}{\partial x^2} \begin{cases} i=1,2 & \text{for } j=1 \\ i=1 & \text{for } j=2 \end{cases} \quad (2)$$

$C_{(i,j)}$  is the molar concentration of component  $i$  in phase  $j$  ( $\text{mol}/\text{m}^3$ ),  $D_{(i,j)}$  is the diffusion coefficient of component  $i$  in phase  $j$  ( $\text{m}^2/\text{s}$ ), and  $x$  is the mass transfer direction (m). It is assumed that there is no mass transfer in the borders of the system and continuity of mass applies at the interface. There is also a thermodynamic equilibrium condition at the interface, which is described through partition coefficients and will be discussed next. It is also possible to account for the moving boundary by means of this model.<sup>21</sup> The finite difference method is used to solve the diffusion equations. In this way, the composition of all points located inside the casting solution and also in the coagulation bath could be obtained with time. Once



**Figure 3.** Calculation of the precipitation time.

the composition path in the ternary phase diagram reaches the binodal curve, it is assumed that precipitation occurs and the calculated time is reported as the precipitation time. This is shown in Figure 3.

The input parameters of the model are molecular weight, density, partition coefficient, and diffusion coefficient of the components. The physical properties of the PVC, THF, DMF, and water are listed in Table I.

### Partition Coefficients

Among the boundary conditions used by Fernandes et al.<sup>21</sup> there is a thermodynamic equilibrium constraint described as below

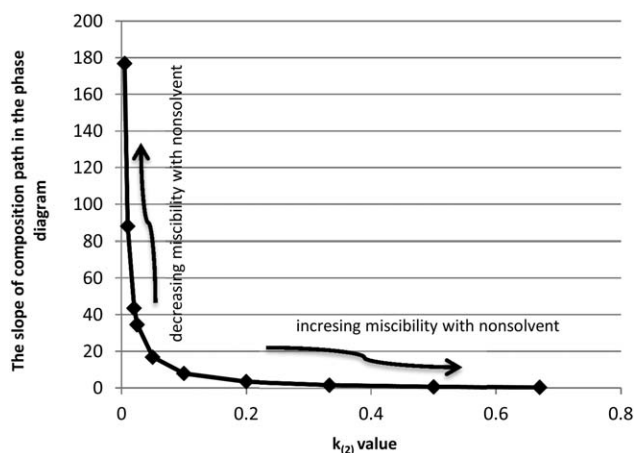
$$C_{(i,1)}|_L = k_{(i)} \cdot C_{(i,2)}|_L \quad i=1,2 \quad (3)$$

Where  $L$  is the casting film thickness and  $k_{(i)}$  is the partition coefficient of component  $i$ . Fernandes et al.<sup>21</sup> have used a typical  $k_{(i)}$  value of 1 and 0.5 for solvent and nonsolvent, respectively, as there is not a measured value reported in the literature. They gave no more explanation on this assumption. Our calculations showed that  $k_{(i)}$  should change between 0 and 1. If both  $k_{(1)}$  (solvent partition coefficient) and  $k_{(2)}$  (non solvent partition coefficient) are 1, no exchange occurs. Reasonable results are obtained when  $k_{(1)}$  is 1 and  $k_{(2)}$  changes between 0 and 1.

It seems that  $k_{(i)}$  values as the limiting mass transfer condition have a marked influence on the modeling results. In Figure 4 the effect of  $k_{(2)}$  value on the slope of composition path (shown in Figure 3) is shown. Decreasing the solvent–nonsolvent affinity (decreasing  $k_{(2)}$ ) results in increase of the slope of the composition path. This means that with decreasing the miscibility of solvent and nonsolvent, it takes a longer time to enter the

**Table I.** Physical Properties of Membrane Forming System Components

Molecular weight (g/gmol)	Density ( $\text{g}/\text{cm}^3$ )	Component
91000	1.41	PVC
72.11	0.889	THF
73.09	0.944	DMF
18	0.997	Water



**Figure 4.** Effect of  $k_{(2)}$  value (partition coefficient of nonsolvent) on the slope of the composition path.

two phase region (cross the binodal) and as a result precipitation occurs with delay. At finite  $k_{(2)}$  values it is also possible that the composition path does not cross the binodal and direct solidification of polymer occurs, which results in a dense structure.<sup>23</sup> According to these results, change of the  $k_{(2)}$  value results in the change of the membrane structure.

In this study, we have used DMF and THF as solvents where increasing the DMF concentration in the casting solution causes a shift of the binodal curve toward the polymer–solvent axis in the phase diagram. As was discussed in the previous section, this is attributed to higher tendency of DMF to mix with water in comparison to THF. In chemistry,  $\text{Log } K_{ow}$  is the octanol/water partition coefficient used to represent how hydrophilic or hydrophobic a chemical substance is. In Table II,  $\text{Log } K_{ow}$  of some common solvents used for membrane preparation is shown.<sup>24</sup> According to these data,  $K_{ow}$  of THF ( $\text{log } K_{ow} = -0.46$ ) is about 30 times larger than that of DMF ( $\text{log } K_{ow} = -1.01$ ). So it is clear that using the same  $k_{(i)}$  values for both DMF and THF to model the phase inversion process might not be correct. It seems reasonable to use  $K_{ow}$ 's to estimate the  $k_{(i)}$  values.

$$\frac{k_{\text{THF}}}{k_{\text{DMF}}} \approx \frac{k_{ow \text{ DMF}}}{k_{ow \text{ THF}}} \approx \frac{1}{30} \quad (4)$$

We used the same 0.5 value for  $k_{\text{DMF}}$  which gives a value of about 0.02 for  $k_{\text{THF}}$ . However, if another value except 0.5 were used for  $k_{\text{DMF}}$  that of THF would lessen about 1/30 and there was no problem in comparing the results.

### Diffusion Coefficients

For estimating the solvent–nonsolvent diffusion coefficient, the Wilke–Chang equation<sup>25</sup> is used:

$$D_{AB} = \frac{7.4 \times 10^{-8} (\phi M_B)^{1/2} T}{\mu_B V_A^{0.6}} \quad (5)$$

Where  $D_{AB}$  is the mutual diffusion coefficient of solute  $A$  at low concentrations in solvent  $B$  ( $\text{cm}^2/\text{s}$ ),  $M_B$  is the molecular weight of solvent  $B$  ( $\text{g/mol}$ ),  $V_A$  is the molar volume of solute  $A$  at its normal boiling temperature ( $\text{cm}^3/\text{mol}$ ),  $\Phi$  is the association factor of solvent  $B$  (dimensionless),  $T$  and  $\mu_B$  are temperature ( $K$ )

**Table II.**  $\text{Log } K_{ow}$  for Some Common Solvents Used for Membrane Preparation

$(k_{ow})$	$\text{log}(k_{ow})$	Solvent
0.0977	-1.01	Dimethylformamide
0.1698	-0.77	Dimethylacetamide
0.2884	-0.54	<i>N</i> -methylpyrrolidone
0.537	-0.27	Dioxane
0.5754	-0.24	Acetone
2.884	-0.46	Tetrahydrofuran

and viscosity of the solvent  $B$  ( $\text{cP}$ ), respectively. If the solvent is water,  $\Phi$  would be 2.6.  $V_A$  is determined via group contribution methods.

Calculation of diffusion coefficient for DMF/water and THF/water systems shows that the diffusion coefficients are the same and equal to  $1.039 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ . This value is close to what assumed by Fernandes et al.<sup>21</sup> for solvent and nonsolvent diffusion coefficient in the coagulation bath. The solvent and nonsolvent diffusion coefficients in the polymer solution were assumed to be the same as those of Fernandes et al.<sup>21</sup>

### Calculation of the Precipitation Time

The calculated precipitation time for PVC/DMF/water and PVC/THF/water is shown in Table III.<sup>24</sup> It takes a much longer time in PVC/THF/water system for demixing to occur, which is in fair agreement with the experimental observations. Using these calculated times; it is possible to obtain the polymer volume fraction at precipitation, which is shown in Figure 5. The resulting predicted membrane structure is not the same for PVC/THF/water and PVC/DMF/water systems. The skin layer in PVC/THF/water is a dense one. The concentration of polymer at the interface is much lower in PVC/DMF/water system, which is due to the occurrence of instantaneous demixing in this system.

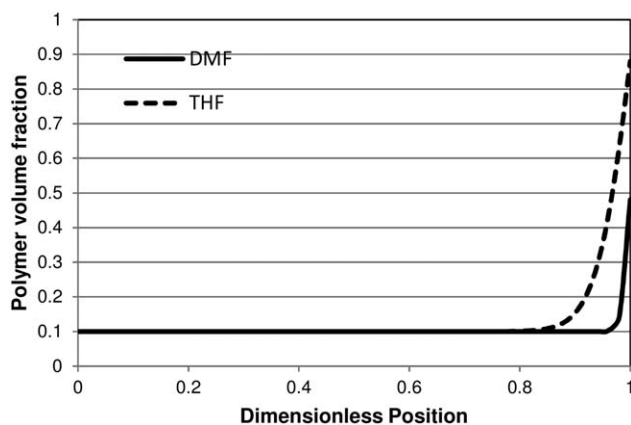
### Membrane Structure and Performance

The pure water flux of membranes prepared from PVC/DMF/water and PVC/THF/water systems is shown in Figure 6. For the PVC/DMF casting solution, the resulting membrane permeation is typical of ultrafiltration membranes, with a pure water flux of about  $500 \text{ L/m}^2 \text{ h}$  at a pressure of 4 bars. The water flux increases rapidly as the feed pressure increases. It is interesting to see that PVC/THF casting solution results in a membrane with no permeation. These membranes were impermeable to water even at a pressure of as high as 20 bars. The initial polymer concentration in both PVC/THF and PVC/DMF solutions were 10%, which was approximately the least castable concentration under laboratory conditions. Both membranes were

**Table III.** Calculated Precipitation Times for PVC/THF/Water and PVC/DMF/Water Systems

Precipitation time (sec)	Membrane forming system
30	PVC/THF/water
0.2	PVC/DMF/water

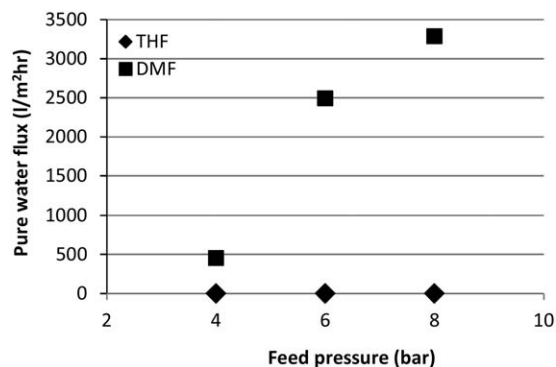




**Figure 5.** Polymer volume fraction at precipitation for membranes cast from PVC/THF/water (precipitation time = 30 s) and PVC/DMF/water (precipitation time = 0.2 s).

prepared under the same conditions. Therefore, the notable difference in membrane permeation is related to considerable difference in membrane structures and different demixing mechanism of membrane formation predicted by the theoretical modeling.

Figure 7 shows cross sectional morphology of membranes obtained from PVC/DMF/water and PVC/THF/water systems. Using THF as the solvent, a thick dense layer could be observed in both sides of the membrane, which acts as a barrier for water permeation and as a result, membranes were impermeable to water. Some isolated pores beneath the skin layer could also be observed, which essentially confirms the sponge-like structure as a result of delayed demixing. Using DMF as the solvent, the resultant membrane contains broad macrovoids, which is the typical cross sectional morphology of instantaneous demixing mechanism. The results obtained from permeation measure-

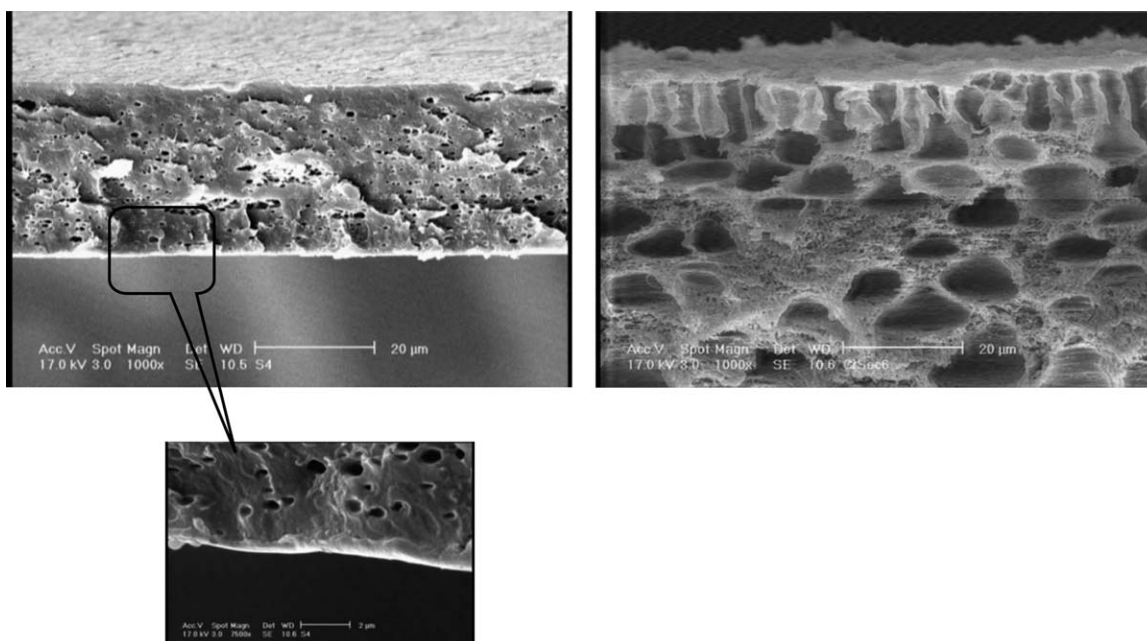


**Figure 6.** Pure water flux of membranes prepared from PVC/THF/water and PVC/DMF/water systems.

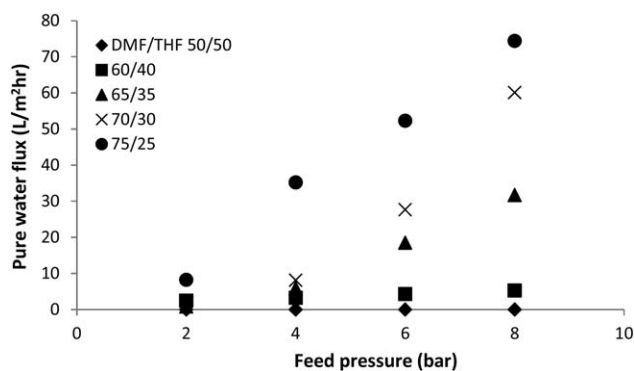
ment and morphological observations are in fair agreement with modeling results on prediction of membrane structure specially the membrane skin.

#### Preparation of Membranes from Solvent Mixture

Considering the fact that different membrane structures are obtainable from PVC/THF and PVC/DMF casting solutions immersed in water as the coagulation media, it seems that using a solvent mixture based on DMF/THF mixture could help to manipulate membrane structure with changing the solvents ratio. The cloud point curve indicates that the system thermodynamics changes in accordance to solvent composition in the casting solution. If the partition coefficient (the governing factor in diffusion calculations) of the mixture is assumed to be a linear function of the solvents ratio, then it is expected that the structure and performance of these membranes would also be a linear function of the solvent ratio in the casting solution. To further study the influence of solvent composition on the membrane structure and performance, membranes from different



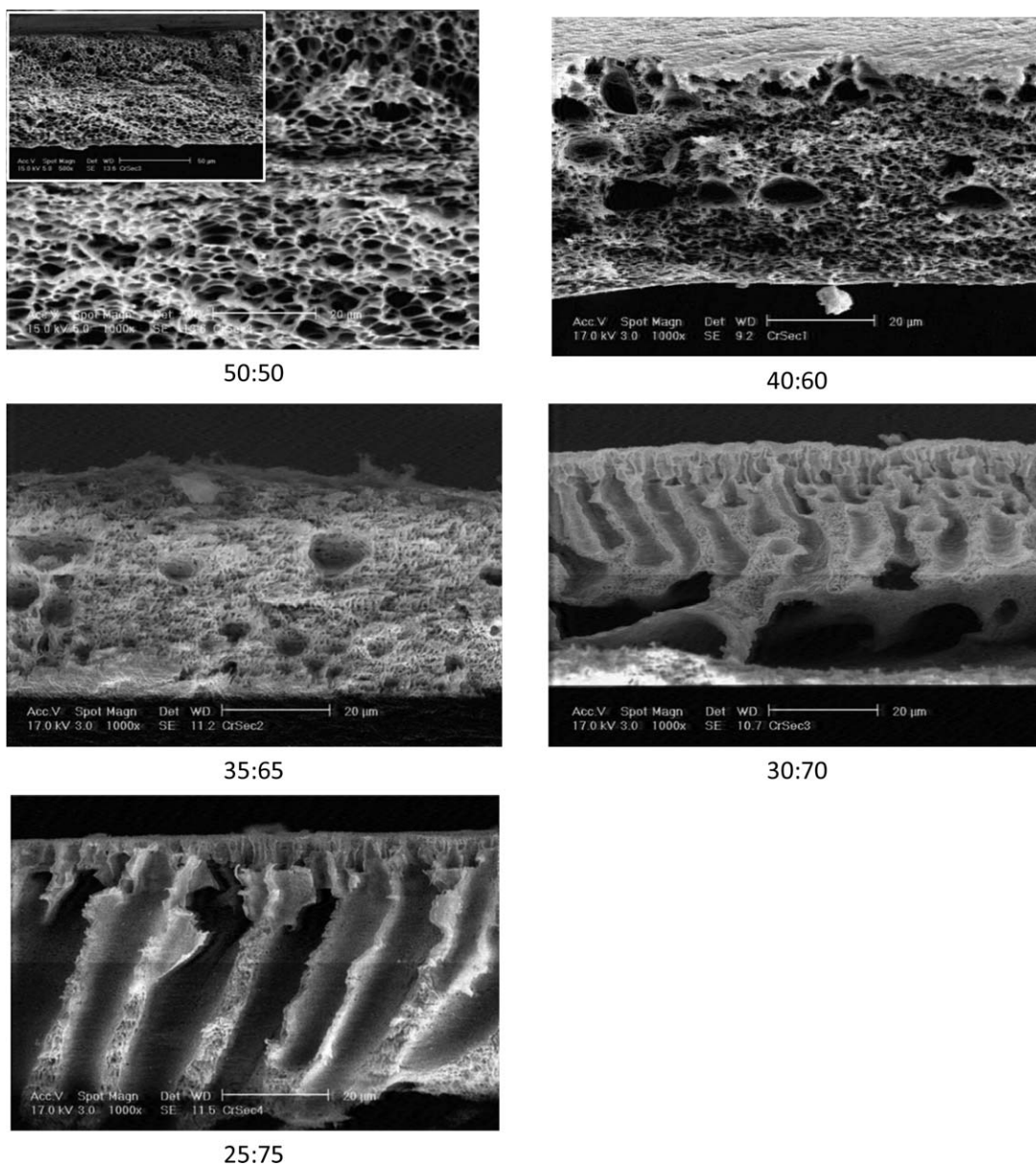
**Figure 7.** Cross sectional morphology of membranes obtained from PVC/THF (Left) and PVC/DMF (Right) casting solutions coagulated in water bath.



**Figure 8.** Pure water flux of PVC membranes prepared from PVC/DMF-THF solution immersed in water with different THF:DMF ratios in the casting solution.

DMF/THF ratios in the casting solution were prepared, and the pure water fluxes were measured.

Interestingly no flux was observed up to 50 wt % THF in the casting solution (DMF50/THF50). As shown in Figure 8, with decreasing THF content in the casting solution from 50 wt %, membranes become permeable and pure water flux increases with further decrease of THF. In the case of 25:75 DMF/THF casting solution, the obtained membranes show a relative high pure water flux; but the flux is far below that of pure DMF prepared membranes. This is opposite to what expected from thermodynamic behavior of the system; the change of membrane performance is not proportional to the solvent content in the casting solution. It seems that at 50:50 DMF/THF, a significant change in membrane structure occurs. In Figure 9, cross



**Figure 9.** Cross sectional morphology of PVC membranes prepared from PVC/DMF-THF solution immersed in water with different (THF:DMF) ratios in the casting solution.

sections of membranes prepared from DMF/THF solutions with compositions according to those of Figure 8, are shown.

For 50:50 DMF/THF casting solution, a typical sponge-like structure can be seen. As compared to membranes cast from pure THF, the number of cells has been increased significantly and the skin thickness decreased substantially; but the membrane is still impermeable to water.

As THF content in the solvent mixture falls below 50 wt %, large tear-like macrovoids appear among cells. Further decrease of THF content results in large finger like macrovoids extending through membrane cross section with a considerable decrease of sponge-like portion.

Although the observed structural change has been reported by several other authors<sup>6,8,11</sup> and ascribed to the change of demixing mechanism from instantaneous to delayed (or vice versa), the fact that considerable change of structure occurs at a specific ratio of the two solvents should be given more attention. Different solvents have different interaction with the polymer. Therefore, one of the solvents would be a better solvent for the polymer than the other. As a result, the viscosity of the polymer solution varies with change of mixed solvent composition in the casting solution and causes instantaneous or delayed demixing. For example Li et al.<sup>8</sup> have reported that in the system CA/NMP-GBL/water, a main change of membrane structure from macrovoid to sponge-like occurs at a ratio of 20:80 (NMP/GBL) in the casting solution. They have measured the viscosity of the CA/NMP-GBL solution. According to these results the viscosity changes almost linearly and no significant change in viscosity could be observed in the region of main morphological transition.

By decreasing the mutual affinity between the solvent pair and the nonsolvent (increasing the interaction parameter), the system thermodynamic changes. As was shown previously the cloud point curve shifts toward the polymer–nonsolvent axis. This shift is almost linear; i.e., proportional to the amount of each solvent present in the solvent mixture.

According to the kinetic modeling, by decreasing the mutual affinity between solvent(s) and the nonsolvent (decreasing  $k_{(2)}$ ), the slope of composition path increases. As said before,  $k_{(2)}$  has a thermodynamic nature. The model can predict a linear change of polymer volume fraction in membrane skin with the change of mixed solvents composition, but the main structural change from sponge-like to macrovoid is not predictable by this simple diffusion model. It is opposite to what expected from system thermodynamics. Because if the thermodynamics were the structure controlling parameter of membrane formation, the 50:50 DMF/THF casting solution should have shown some water flux. Albrecht et al.<sup>26</sup> have shown that in the system polyetherimide/DMF-NMP/water, the apparent diffusion coefficient changes with variation of the mixed solvent composition in a complex way. The apparent diffusion coefficient first increases up to a DMF concentration of 25 wt %, then decreases until about 80 wt % DMF and then again increases. Although the general demixing behavior is instantaneous and the change of diffusion coefficient is not within an order of magnitude, but could deeply affect the membrane structure. The calculated

cloud point of the system shows a linear decrease with increasing DMF in the DMF-NMP mixture up to about 85 wt % DMF and then becomes constant. According to Albrecht et al.,<sup>26</sup> with changing the mixed solvent composition, the membrane formation process may be thermodynamic or kinetic dominant. So in the system PVC/DMF-THF/water, measurement of the concentration dependence of diffusion coefficient can help us to decouple the thermodynamics from kinetics of the system and to determine their contribution in membrane formation, which is the subject of further studies.

## CONCLUSION

PVC membranes were prepared from PVC/DMF-THF/water solutions with various DMF/THF ratios. The thermodynamic behavior of PVC/DMF-THF/water system was studied through cloud point measurement for 3, 5, and 8% wt PVC in DMF-THF solutions. The occurrence of liquid–liquid demixing is almost a function of the ratio of the DMF/THF present in the solution, i.e., the cloud point position changes according to the ratio of the solvent mixture. Calculation of the precipitation time and polymer concentration profiles was performed using a simple mathematical model, which was in good agreement with the experimental findings on PVC/THF/water and PVC/DMF/water systems. According to the model, the structure controlling parameter, i.e., the partition coefficient, has a thermodynamic nature. Although it was expected that the membrane structure and performance would be a linear function of DMF/THF ratio in the casting solution, membranes prepared from PVC/DMF-THF/water showed no water flux below a DMF/THF ratio of 50:50 wt %. In addition, the change of membrane morphology from sponge like to finger like, which occurs through change of mixed solvent composition could not be explained based on thermodynamics alone. Although the phase diagram obtained through cloud point measurement could be used to explain the overall behavior of the system by change of DMF/THF ratio, but it fails to explain the real membrane performance and structure and more work should be performed on this subject, especially the concentration dependence of the diffusion coefficient should be checked for this system.

## REFERENCES

1. Guillen, G. R.; Pan, Y.; Li, M.; Hoek, E. M. V. *Ind. Eng. Chem. Res.* **2011**, *50*, 3798.
2. Baker, R. W. *Membrane Technology and Applications*; John Wiley & Sons: Chichester, **2004**, p 191.
3. Strathmann, H.; Drioli, L.; Giorno, E. In *Comprehensive Membrane Science and Engineering. Basic Aspects in Polymeric Membrane Preparation* Giorno, E., Drioli, L., Eds.; Elsevier: Kidlington, **2010**; Vol. 1, p 1.05.
4. Peinemann, P. K. V.; Nunes, S. *Membrane Technology in the Chemical Industry*; Wiley-VCH: Weinheim, **2006**.
5. Mulder, M. *Basic Principles of Membrane Technology*; Springer: Norwell, **1996**.
6. Kools, W. F. C. *Membrane Formation by Phase Inversion in Multicomponent Polymer Systems, Mechanisms and Morphologies*, *PhD Thesis; University of Twente*. **1998**.

7. Shieh, J. J.; Chung, T. S. *J. Membrane Sci.* **1998**, *140*, 67.
8. Li, Z.; Ren, J.; Fane, A. G.; Li, D. F.; Wong, F. S. *J. Membrane Sci.* **2006**, *279*, 601.
9. Yoo, S. H.; Jho, J. Y.; Won, J.; Park, H. C.; Kang, Y. S. *J. Ind. Eng. Chem.* **2000**, *6*, 129.
10. Peinemann, K. V.; Maggioni, J. F.; Nunes, S. P. *Polymer* **1998**, *39*, 3411.
11. See-Toh, Y. H.; Silva, M.; Livingston, A. *J. Membrane Sci.* **2008**, *324*, 220.
12. Bodzek, M.; Konieczny, K. *J. Membrane Sci.* **1991**, *61*, 131.
13. Hiroshi, O.; Kazuhiko, R.; Tadashi, U. *J. Membrane Sci.* **1993**, *83*, 199.
14. Xu, J.; Xu, Z. L. *J. Membrane Sci.* **2002**, *208*, 203.
15. Khayet, M.; García-Payoa, M. C.; Qusay, F. A.; Zubaidy, M. A. *J. Membrane Sci.* **2009**, *330*, 30.
16. Mei, S. H.; Xiao, C. H.; Hu, X. *J. Appl. Polym. Sci.* **2011**, *120*, 557.
17. Cohen, C.; Tanny, G. B.; Prager, S. *J. Polym. Sci. Pol. Phys.* **1979**, *17*, 477.
18. Reuvers, J. A. Membrane Formation, Diffusion Induced Demixing Processes in Ternary Polymeric Systems, PhD Thesis; University of Twente: *Chemical Engineering*, **1984**.
19. Reuvers, A. J.; van den Berg, J. A. W.; Smolders, C. A. *J. Membrane Sci.* **1987**, *34*, 45.
20. Reuvers, A. J.; van den Berg, J. W. A.; Smolders, C. A. *J. Membrane Sci.* **1987**, *34*, 67.
21. Fernandes, G. R.; Pinto, J. C.; Nobrega, R. *J. Appl. Polym. Sci.* **2001**, *82*, 3036.
22. Maghsoud, Z.; Famili, M. H. N.; Madaeni, S. S. *Iran. Polym. J.* **2010**, *19*, 581.
23. Stropnik, Č.; Musil, V.; Brumen, M. *Polymer* **2000**, *41*, 9227.
24. Sangster J. LOGKOW, a databank of evaluated octanol-water partition coefficients (Log P). [Online] Sangster Research Laboratories; **2011**. Available at <http://logkow.cisti.nrc.ca/logkow/>.
25. Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. The Properties of Gases and Liquids; McGraw-Hill: New York, **2001**, p 11.1.
26. Albrecht, W.; Weigel, Th.; Schossig-Tiedemann, M.; Kneifel, K.; Peinemann, K. V.; Paul, D. *J. Membrane Sci.* **2001**, *192*, 217.