

Variation of Immiscibility Gap in Polymer Solution Containing Alkane and Effects on Providing the Membrane

M. Rezaeinejad, S. A. Hashemifard*, A. A. Izadpanah

Sustainable Membrane Technology Research Group (SMTRG), Faculty of Petroleum, Gas and Petrochemical Engineering (FPGPE), Persian Gulf University (PGU), P.O. Box 75169-13798, Bushehr, Iran

ARTICLE INFO

Article history:

Received: November 14, 2018

Accepted: December 24, 2018

Keywords:

Additive

Membrane solution

modeling

quaternary system

Alkane

* Corresponding author:

E-mail: salhashemifard@pgu.ac.ir

Tel.: +987733442601

Fax: +987733441495

ABSTRACT

In order to reduce costs and save time for the membrane manufacturing process, it is necessary to improve the quality of membranes by modeling usage. In this study, Flory Huggins model was used to predict quaternary-system containing polyether sulfone, N-Methyl-2-pyrrolidone, water and used alkanes as an additive. Due to the solubility parameters and molar alkane volumes, the interaction parameters changed which influenced the membrane morphology. In the meantime, modeling showed that hexane had no effect on the immiscibility gap, and the decane had a greater effect compared to hexane. But the tetradecane, due to the increased interactions, could greatly increase the immiscibility gap and increase the thermodynamic instability. Hence, those instabilities can become subjected to faster membrane entelechy, construct a pores skin layer, and change the membrane morphology. Whatever the immiscibility gap rise, the proportion of pores in the skin layer will increase and vice versa.

1. Introduction

Many chemical engineering processes deal with the problem of concentration changes in solutions and mixtures, which are not necessarily due to the chemical reactions. The importance of mass-separation processes for all chemical engineers is clear, and it's rarely possible to find a chemical process that does not require the initial purification of the raw material or the final separation of the products from the lateral products obtained from the process. Often, most of the costs associated with the process of producing a product are spent on the separation. In the recent decades, there has also been a growing need for these processes to control pollution and protect the environment [1]. The rapid introduction of membranes into the industry is the development of membrane materials, the invention of a new way to produce membrane, and the development of production component [2]. The unique work of Loeb and Surreyjan researchers in polymer membranes was followed by the use of phase inversion method in industrial and laboratory environments as well as in many commercial membrane manufacturing centers [3-5]. Phase inverse methods are the most important and the most widely used methods for the production of polymer membranes. Because of the time and cost of determining the laboratory charts, the models are used as a powerful and valuable tool for predicting the behavior of multiple systems in educational and industrial centers [6]. To achieve the theoretical knowledge in the membrane construction, and also to properly understand the relationships between the components of the system and to consider the interactions of the components on each other it is necessary to improve the design, control and planning of the membrane construction. Flory and Huggins in 1941 separately proposed a two-dimensional network model. Their model was based on an empirical argument [7, 8]. Other models have been developed to obtain binodal and spinodal points that require more simple calculations, but these models are limited to specific materials or specific conditions. In addition, there are models that require input parameters and many mathematical calculations; therefore, these models can not be used easily [9-13]. Simplicity and easy useage of this model is the reason for the superiority of the Flory Huggins theory compared to the other models. Of course, modifications have also been made to the main form of this theory, including the use of concentration-dependent interaction parameters [14].

Regarding the previous work on obtaining equilibrium curves in the presence of alkanes [15], this study was an attempt to investigate the relations between the four-dimensional systems, the solution of relations, and the equations between the components. Also using the theory of Flory Huggins in addition to the binodal curves the spinodal curves would provide a good prediction of the membrane morphology.

2. Research Method

2.1. Numerical calculation:

In the Flory Huggins model, the free energy of Gibbs is written in the quadratic system in the form of equation (1). By differentiating Gibbs free energy (ΔG_m), chemical potential ($\Delta\mu_i$) can be obtained at constant pressure and temperature.

$$\frac{\Delta G_m}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + n_4 \ln \phi_4 + g_{12} n_1 \phi_1 + g_{13} n_1 \phi_3 + g_{14} n_1 \phi_4 + g_{23} n_2 \phi_3 \quad (1)$$

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

$$\begin{aligned} \frac{\Delta \mu_1}{RT} = & \ln \phi_1 + 1 - \phi_1 - \frac{V_1}{V_2} \phi_2 - \frac{V_1}{V_3} \phi_3 - \frac{V_1}{V_4} \phi_4 + (g_{12} \phi_2 + g_{13} \phi_3 + g_{14} \phi_4)(\phi_2 + \phi_3 + \phi_4) \\ & - \frac{V_1}{V_2} g_{23} \phi_2 \phi_3 - \frac{V_1}{V_3} g_{34} \phi_3 \phi_4 - \frac{V_1}{V_2} g_{24} \phi_4 \phi_2 - u_1 u_2 \phi_2 \left(\frac{dg_{12}}{du_2} \right) \end{aligned} \quad (3)$$

$$\begin{aligned} \frac{\Delta \mu_2}{RT} = & \ln \phi_2 + 1 - \phi_2 - \frac{V_2}{V_1} \phi_1 - \frac{V_2}{V_3} \phi_3 - \frac{V_2}{V_4} \phi_4 + \left(\frac{V_2}{V_1} g_{12} \phi_1 + g_{23} \phi_3 + g_{24} \phi_4 \right) (\phi_1 + \phi_3 + \phi_4) \\ & - \frac{V_2}{V_1} g_{13} \phi_1 \phi_3 - \frac{V_2}{V_4} g_{34} \phi_4 \phi_3 - \frac{V_2}{V_1} g_{14} \phi_4 \phi_1 + u_1 u_2 \phi_1 \frac{V_2}{V_1} \left(\frac{dg_{12}}{du_2} \right) \end{aligned} \quad (4)$$

$$\begin{aligned} \frac{\Delta \mu_3}{RT} = & \ln \phi_3 + 1 - \phi_3 - \frac{V_3}{V_2} \phi_2 - \frac{V_3}{V_1} \phi_1 - \frac{V_3}{V_4} \phi_4 + \left(\frac{V_3}{V_2} g_{23} \phi_2 + \frac{V_3}{V_1} g_{13} \phi_1 + g_{34} \phi_4 \right) (\phi_2 + \phi_1 + \phi_4) \\ & - \frac{V_3}{V_1} g_{21} \phi_2 \phi_1 - \frac{V_3}{V_1} g_{14} \phi_1 \phi_4 - \frac{V_3}{V_2} g_{24} \phi_4 \phi_2 \end{aligned} \quad (5)$$

$$\begin{aligned} \frac{\Delta \mu_4}{RT} = & n \phi_4 + 1 - \phi_4 - \frac{V_4}{V_2} \phi_2 - \frac{V_4}{V_3} \phi_3 - \frac{V_4}{V_1} \phi_1 + \left(\frac{V_4}{V_2} g_{24} \phi_2 + \frac{V_4}{V_3} g_{34} \phi_3 + \frac{V_4}{V_2} g_{14} \phi_1 \right) (\phi_2 + \phi_3 + \phi_1) \\ & - \frac{V_4}{V_2} g_{23} \phi_2 \phi_3 - \frac{V_4}{V_1} g_{13} \phi_3 \phi_1 - \frac{V_4}{V_1} \phi_1 \phi_2 g_{12} \end{aligned} \quad (6)$$

The most important point to consider when using the Flory Huggins model is to calculate the dual interaction parameters [16]. g_{12} is the Flory Huggins interaction between the two components i and j . It is also assumed in most cases that only the solvent-nonsolvent interactions are dependent on the concentration, and the interaction between the solvent-polymer and the nonsolvent-polymer is considered due to the negligible dependence on the concentration of frequently fixed substances [17]. The solvent-non-solvent interaction parameter is calculated by the Gibbs free energy [18-20]. In addition, equations (3) and (4): $u_2 = \frac{\phi_2}{\phi_1 + \phi_2}$ and $u_1 = \frac{\phi_1}{\phi_1 + \phi_2}$ and ϕ_1 is a non-solvent volume fraction and ϕ_2 is a volumetric fraction of a solvent

$$g_{12} = \frac{1}{n_1 \phi_2} \left[n_1 \ln \frac{n_1}{\phi_1} - n_1 \ln (n_1 + \wedge_{12} n_2) + n_2 \ln \frac{n_2}{\phi_2} - n_2 \ln (n_2 + \wedge_{21} n_1) \right] \quad (7)$$

\wedge_{12} and \wedge_{21} are parameters of the Wilson equation (adjustable parameters), which we need to calculate for the specific energy difference values $(\lambda_{21} - \lambda_{22})$ and $(\lambda_{12} - \lambda_{11})$ and the specific volume V_i .

$$\wedge_{12} = \frac{V_2}{V_1} e^{-\frac{(\lambda_{12} - \lambda_{11})}{RT}} \quad (8)$$

$$\wedge_{21} = \frac{V_1}{V_2} e^{-\frac{(\lambda_{21} - \lambda_{22})}{RT}} \quad (9)$$

According to Table 1, calculating the interaction of the PES / NMP / Water system in various articles in numerical order may be slightly different from each other. This is due to different methods of calculating these parameters. Sometimes some values are very close to the clouds, and others are very far away. In this research, the parameters used in the articles were applied.

Table 1. Interaction between solvent-non-solvent and polymer-non-solvent in PES / NMP / Water system

reference	g_{12}	X_{13}
[21]	$0.3497 + \frac{0.1981}{(1 - 0.7797u_2)}$	1.58
[21]	$0.5483 - 0.092u_2 + 2.0522u_2^2 - 3.9428u_2^3 + 2.6792u_2^4$	1.58
[22]	$0.37594 + \frac{0.18089}{(1 - 0.79295u_2)}$	1.54
[21]	$0.58 - 0.45u_2 + 3.07u_2^2 - 5.06u_2^3 + 3.1u_2^4$	1.58
[23]	$0.3164 + \frac{0.4683}{(1 - 0.4993u_2)}$	2.5
[24]	$0.486 + 0.8029u_2$	2.55
[25]	$0.718 + 0.669u_2$	2.8
[26]	$0.785 + 0.665u_2$	2.81

In this study, all the equations in Table 1 were used and it was found that the equation in reference [23] had the best match.

2.1.1 Calculation of the binodal curve

The solution in this case consists of two completely separate liquid phases that are in equilibrium at a constant temperature and pressure, and the chemical potential of each component in the two phases (α and β) will be the same.

$$\Delta\mu_i^\alpha = \Delta\mu_i^\beta \quad (10)$$

The composition of the components in the two thermodynamic liquid phases is placed on the binodal curve. To determine the combinations of the two tie lines, it is necessary to calculate the eight unknowns, which are the same as $\phi_i \rightarrow i = 1 \dots 8$. To calculate these unknowns, you can use the six equations that exist between them. Four unknowns from the placement of the chemical potential equations of the components (3) to (6) were obtained in the equation of chemical potential equation in the two equilibrium phases (10).

From the equilibrium relationship between the two poor and rich phases of the polymer, two other equations can be achieved:

$$\sum_{i=1}^n \phi_i^\alpha = 1 \quad n = 1,2,3,4 \quad (11)$$

$$\sum_{i=1}^n \phi_i^\beta = 1 \quad n = 1,2,3,4 \quad (12)$$

Two other unknowns can be used to solve one of the unknowns, using two methods (A) and (B). The use of any of these two methods is optional and depends on the ease of doing the calculations:

Method (A): The amount of the fourth component in both the polymer-rich and polymer-poor phases is always constant. In such a way that the total

mass fraction of the two phases is used in the density of the fourth component equal to the constant value of the mass [27].

$$(\phi_4^\alpha + \phi_4^\beta)\rho_4 = m_4 \quad (13)$$

Method (B): In another way, since the ratio of the amount of the third component to the fourth one (in the case of both polymers) is constant, therefore, it can be stated that:

$$\phi_3^\alpha + \lambda\phi_4^\alpha = 0 \quad (14)$$

In this equation, λ is the ratio of the value of the third component to the fourth one [28]. The algorithm of the binodal methodology is accessible in appendix 5. A.

2.1.2 Calculate the spinodal curve:

The boundary between the unstable and unstable region is known in the triangular diagram with the spinodal curve, so that equation (15) holds true.

$$\frac{\partial^2 \Delta G_m}{\partial \phi^2} = 0 \quad (15)$$

In order to obtain the equations for calculating the spinodal curve, the Hessian matrix determinant of ΔG_m was used. H is the Hessian matrix:

$$H = \begin{pmatrix} G_{22} & G_{23} & G_{24} \\ G_{32} & G_{33} & G_{34} \\ G_{42} & G_{43} & G_{44} \end{pmatrix}$$

After simplifying the spinodal equations, the final equation was presented as below.

$$G_{22}(G_{33}G_{44} - G_{34}^2) - G_{23}(G_{23}G_{44} - G_{34}G_{24}) + G_{24}(G_{23}G_{34} - G_{33}G_{24}) = 0 \quad (16)$$

As $G_{ij} = \frac{\partial^2 \left(\frac{\Delta G_m}{RT} \right)}{\partial \phi_i \partial \phi_j} V_{ref}$ [29, 30]. Here, Part 1 was selected as a reference

component. In order to draw the spinodal curve, there is no need for any phase equilibrium, and only the numerical value of the volume fraction of polymer, solvent, non-solvent and, if necessary, the amount of additive is required. For the unknown and unknown numbers to be the same, given that only the existing equations is Equation (16) and the total equation of the fraction of volumes are:

$$\sum_{i=1}^4 \phi_i = 1 \quad i = 1, 2, 3, 4 \quad (17)$$

And the ratio of the values of ϕ_3 and ϕ_4 is constant. Also, the ratio of the values of ϕ_3 and ϕ_4 is constant, so you can select the independent variable ($\phi_3 + \phi_4$). The corresponding modalities can be solved by solving nonlinear equations using "MATLAB" software. The algorithm of the spinodal methodology is accessible in appendix 5. B.

3. Results and Analysis

In the dope solution of alkane, the membrane's formation and exchange of the material in the membrane was: at first there was one kind of alkane in a solution of a dope with solvents and polymers. After adding water, the first phase separation was created. This phase exchange was not the result of the

displacement of the polymer or even of the solvent, rather the result of the exchange and the displacement of the alkanes in the solution. Therefore, two phases were formed, one of which consisted of all polymers, a small amount of alkanes, a large amount of solvent and a small amount of water, and the second phase contained a very high amount of alkanes, a small amount of water and a small amount of solvent. By proceeding and adding water to the solution, the second phase separation process took place. The reason for these different phase separations can be found in the solubility of the materials in each other.

In Table 2, the molar volumes of the components and the solubility parameters (δ_i) for different materials are presented. It shows that their solubility parameter consists of three dispersion sections (δ_d), polarity (δ_p) and hydrogen bond (δ_h). According to equation 26, it was computed [31].

$$\delta_i^2 = \delta_p^2 + \delta_h^2 + \delta_d^2 \quad (18)$$

Polymer and the solvent are solved well in each other if their solubility parameters are equal or close to each other. Table 2. illustrates the solubility parameters of the materials studied. As shown in Figure 1, we can consider the three dimensional space of solubility parameters, each of which has its own solubility parameters. Solubility is most affected by the polarity and the hydrogen bonding. It can then be reduced from the three-dimensional space to two-dimensional space and define the new parameter δ_v such that $\delta_v^2 = \delta_d^2 + \delta_p^2$ [32]. By this greates approximation, the solubility parameter could be compared with each other easily. If one assumes that a sphere with a radius of 5 units of the solvability parameter is closer to each other, one can conclude that the material is better solved in each other. In Figure 1, if the center of the cores becomes closer to the solvent core, they can be well solved together.

Table 2. Solubility parameters and volume of solvent, non-solvent and polymer systems

name	V_i (ml)	$\delta_{i,d}$ (MPa ^{0.5})	$\delta_{i,p}$ (MPa ^{0.5})	$\delta_{i,h}$ (MPa ^{0.5})	$\delta_{i,v}$ (MPa ^{0.5})	δ_i (MPa ^{0.5})
PES	25000	18.6	10.4	7.8	21.8	21.9
NMP	96.5	18	12.3	7.2	20.44	23
Tetradecane	261.3	16.2	0	0	16.2	16.2
Decane	142.28	15.7	0	0	15.7	15.7
Hexane	86.178	14.9	0	0	14.9	14.9
Water	18	15.5	16	42.3	22.27	47.8

The effect of solubility parameters on thermodynamics and the sequence of the two phases of polymeric solution in the Alkane / NMP / Water triplet system are as follows: Tetradecane> Decane> Hexane.

The solubility of these alkanes with non-solvent can be observed only by using the despersion solubility parameter. This parameter in tetradecane is the most distinct compared with other alkanes. Therefore, a smaller amount of water is needed to make the two-phase system when it has tetradecane. Another reason that is very influential is the size of the alkane. As the tetradecane volume is higher than the other two alkanes, the interaction parameter increases.

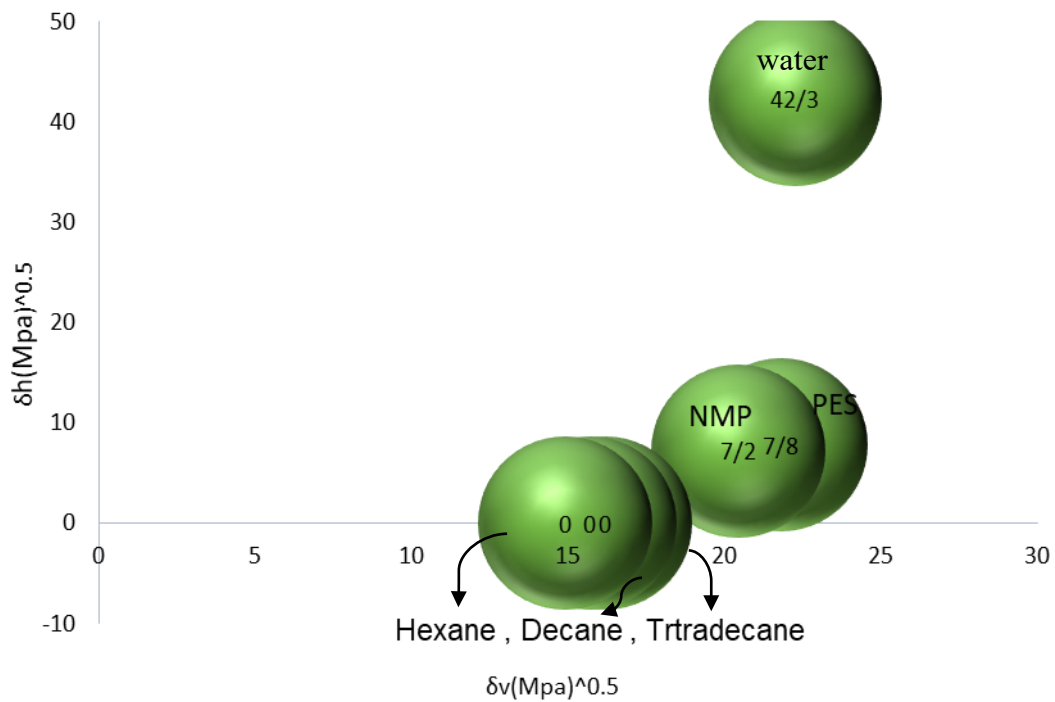


Figure 1: Solubility of materials using solubility parameters

By adding water to the system, the tetradecane additive begins the separation faster than other additives, and then the decane starts separation and eventually hexane exits from the system, which is consistent with the molecular weight of each additive.

All the interaction values used in this study were optimized parameters which were obtained by fitting the equilibrium curves and the experimental data. Table 3 illustrates the calculated values of the equilibrium curve interaction parameters of the PES / NMP + Hexane / Water system for the various concentrations.

Since hexane is adjacent to the solvent, it can be seen that the interaction between the polymer and the solvent (X_{23}), also solvent and non-solvent (g_{12}) were changed.

Table 3. Interaction value in PES / NMP / Water and Alkane / NMP / Water systems

System	g_{12}	X_{13}	X_{23}
PES/NMP/Water	$(0.3164 + \frac{0.4683}{(1 - 0.4993u_2)})$	2.21	0.003
PES/NMP+0.2% Hexane /Water	$1.012(0.3164 + \frac{0.4683}{(1 - 0.4993u_2)})$	2.21	0.003
PES/NMP+0.4% Hexane /Water	$1.026(0.3164 + \frac{0.4683}{(1 - 0.4993u_2)})$	2.21	0.0035
PES/NMP+0.6% Hexane /Water	$1.034(0.3164 + \frac{0.4683}{(1 - 0.4993u_2)})$	2.21	0.004

Figure 2 (A) demonstrates the changes in the interaction between the solvent and the polymer and (B) demonstrates the changes in the interaction between the non-solvent and the solvent in relation to the increase in the concentration of hexane additive in the PES / NMP / Water system. However, these changes are not so tangible and the slope of these changes is low. The reason for this can be found in the low molecular volume and thus the reduced interaction.

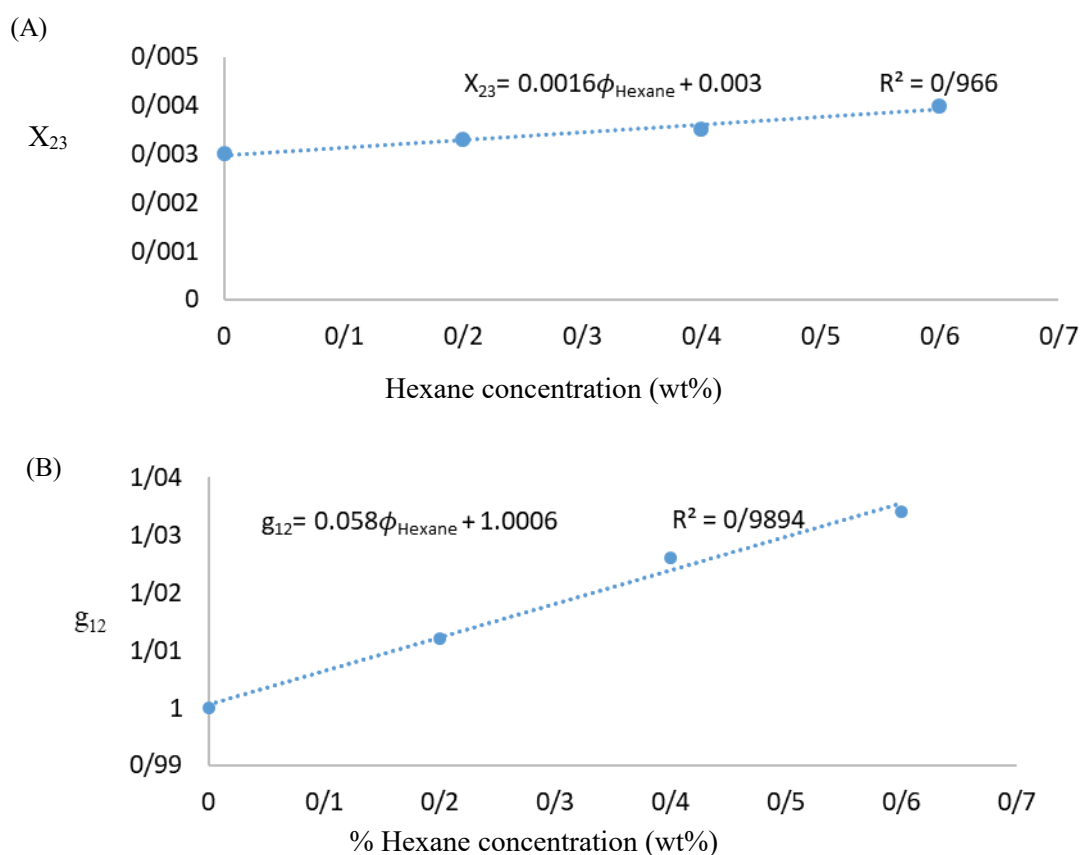


Figure 2 Changing the interaction between a) polymer and solvent (X_{23}); b) solvent and non-solvent (g_{12}) relative to the increase of hexane additive in PES / NMP + Hexane / Water system

On the other hand, by comparing the binodal and spinodal curves, it is observed that these two curves are almost in each other in the concentrations that were used. Figure 3 illustrates the effects of different hexane concentrations on the thermodynamic behavior of the system. As shown in this Figure, all cloudy points of solutions containing additive are completely coincided with cloudy points of the solution without any additive, and no difference between pure state behavior and other solutions containing hexane can be observed. According to the optimum parameters listed in Table 4, the observed Binodal and spinodal curves had a good fit with the cloudy points.

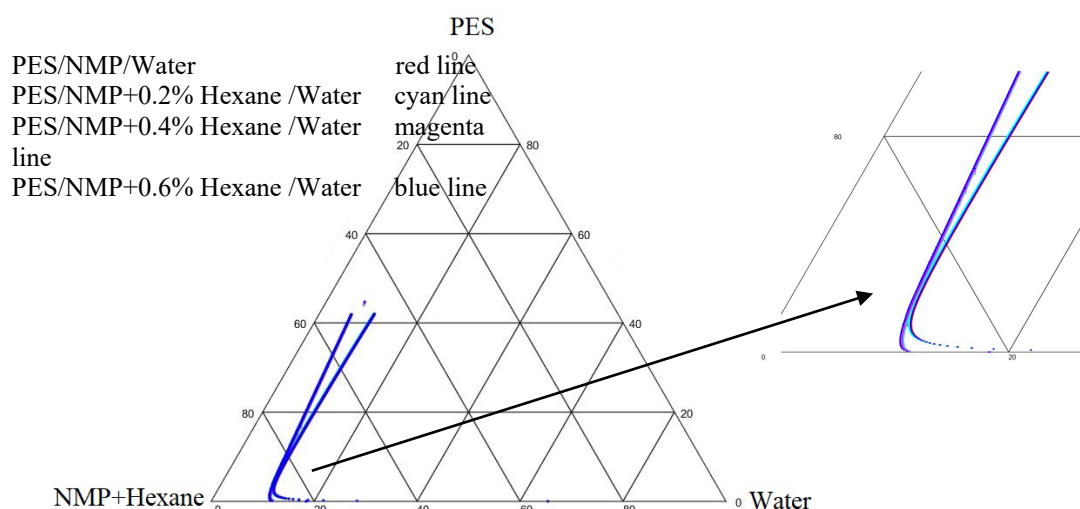


Figure 3. Binodal and spinodal curves in the PES / NMP / Water ternary system of PES / NMP + 0.2% Hexane / Water, PES / NMP + 0.4 Hexane / Water and PES / NMP + 0.6% Hexane / Water

By changing the type of alkane from hexane to the decane, its interaction parameters also changed. Table 5 illustrates the proportion of these parameters. Also, Figure 4 (A) demonstrates changes in the interaction between the solvent and the polymer and (B) demonstrates changes in the interaction between the solvent and the non-solvent in relation to increasing the concentration of the additive in the PES / NMP / Water system according to the parameters in Table 4.

Table 4. Parameters of intermolecular interaction in the PES / NMP + Decane / Water system

System	g_{12}	x_{13}	x_{23}
PES/NMP/Water	$(0.3164 + \frac{0.4683}{(1 - 0.4993u_2)})$	2.21	0.003
PES/NMP+0.2% Decane/Water	$1.032(0.3164 + \frac{0.4683}{(1 - 0.4993u_2)})$	2.21	0.0055
PES/NMP+0.4% Decane/Water	$1.064(0.3164 + \frac{0.4683}{(1 - 0.4993u_2)})$	2.21	0.007
PES/NMP+0.6% Decane /Water	$1.096(0.3164 + \frac{0.4683}{(1 - 0.4993u_2)})$	2.21	0.0085

Since the molecular volume of the component is higher than hexane, it can be seen that the effect of this alkane on the interaction in comparison with hexane is higher. The change in the interaction between the solvent and the polymer is proportional to the increase in the percentage of the additive in the system in Figure 4 (A) and the changes in the interaction between the solvent and the nonsolvent in Figure 4 (B) are illustrated.

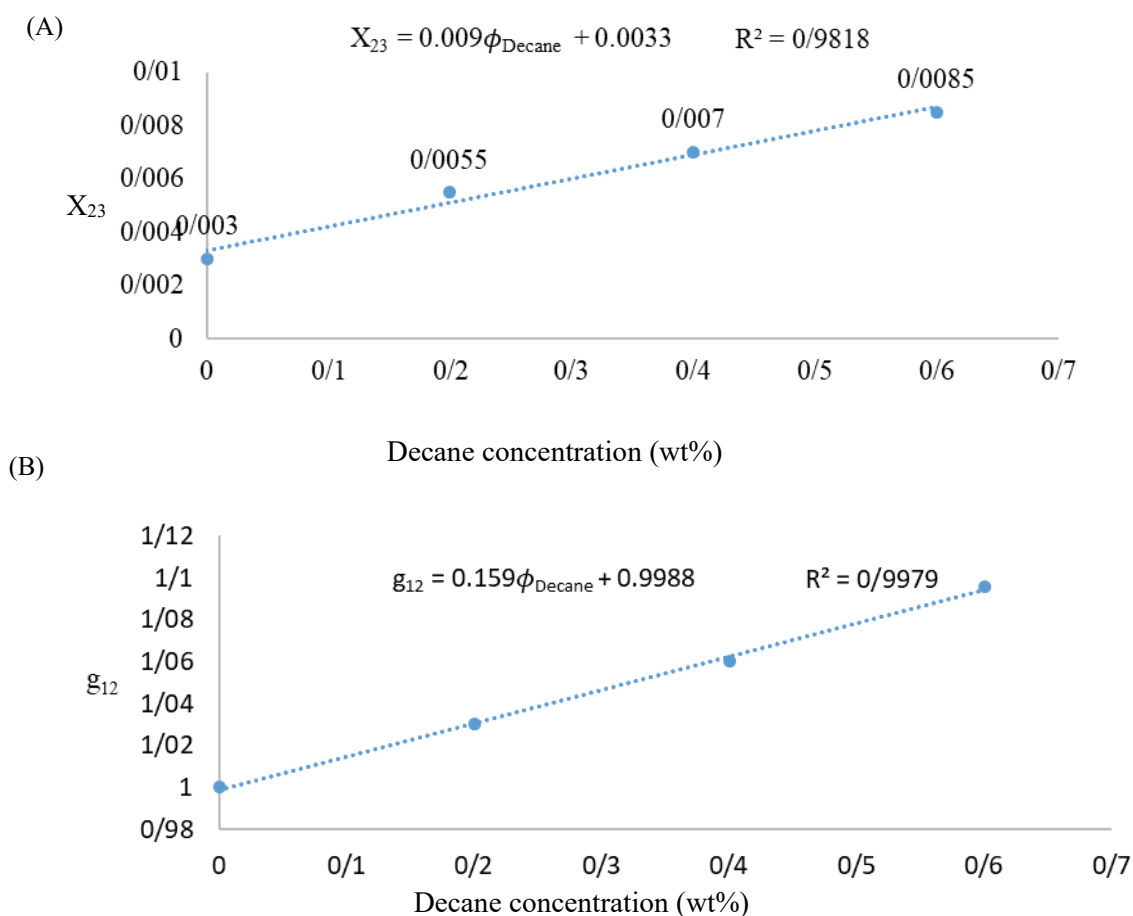


Figure 4: Changing the interaction between a) polymer and solvent (X_{23}); b) solvent and non-solvent (g_{12}) as compared to increasing the percentage of the additive in the PES / NMP + Decane / Water system

Figure 5 illustrates the effect of various concentrations (0.2, 0.4 and 0.6) of the decane additive on the thermodynamic equilibrium of the PES / NMP + Decane / Water system. In this system, similar to the previous system, although there is a slight difference between the curves at different concentrations, the curves are still very close to each other. In Figure 5, the binodal curve along with the spinodal is drawn according to the optimal parameters listed in Table 4, which fits well with the cloudy points.

In general, it can be concluded that the addition of hexane and decane to the dope solution did not have much effect on the thermodynamic of the systems. On the other hand, in Figure 6, by adding tetradecane to the dope solution, the binodal curves were transmitted to the left of the chart. It is observed that by increasing the additive concentration, the displacement of the binodal curve increased and the system stability (between the polymer-solvent axis and the binodal curve) decreased. Since this region illustrates the thermodynamic stability of the system, so solutions containing the tetradecane additive are less stable than the non-additive solutions. Due to the higher molar volume, tetradecane has been able to influence the interaction parameters more than any other additive. As shown in Table 5, the induced instability can be increased by increasing the interaction parameters and increasing this additive concentration.

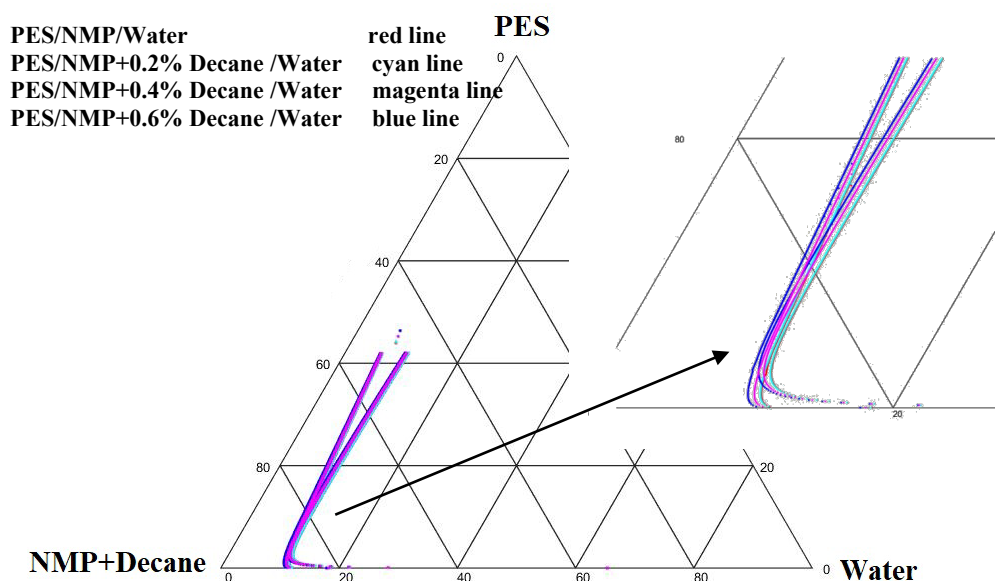


Figure 5. Binodal and spinodal curves in the PES / NMP / Water triplet system, PES / NMP + 0.2% Decane / Water, PES / NMP + 0.4% Decane / Water as well as PES / NMP + 0.6% Decane / Water

Table 5. Parameters of Intermolecular Interaction in the PES / NMP + Tetradecane / Water System

System	g_{12}	x_{13}	x_{23}
PES/NMP/Water	$0.3164 + \frac{0.4683}{(1 - 0.4993u_2)}$	2.21	0.004
PES/NMP+0.2% Tetradecane /Water	$1.34(0.3164 + \frac{0.4683}{(1 - 0.4993u_2)})$	2.21	0.065
PES/NMP+0.4% Tetradecane /Water	$1.62(0.3164 + \frac{0.4683}{(1 - 0.4993u_2)})$	2.21	0.105
PES/NMP+0.6% Tetradecane /Water	$2.07(0.3164 + \frac{0.4683}{(1 - 0.4993u_2)})$	2.21	0.145

As shown in Figure 6 (A), changes in the interaction between the solvent and the polymer and (B) changes in the interaction between the solvent and the solvent in relation to the increase of the concentration of additive tetradecane in the PES / NMP / Water system are plotted according to the parameters in Table 6.

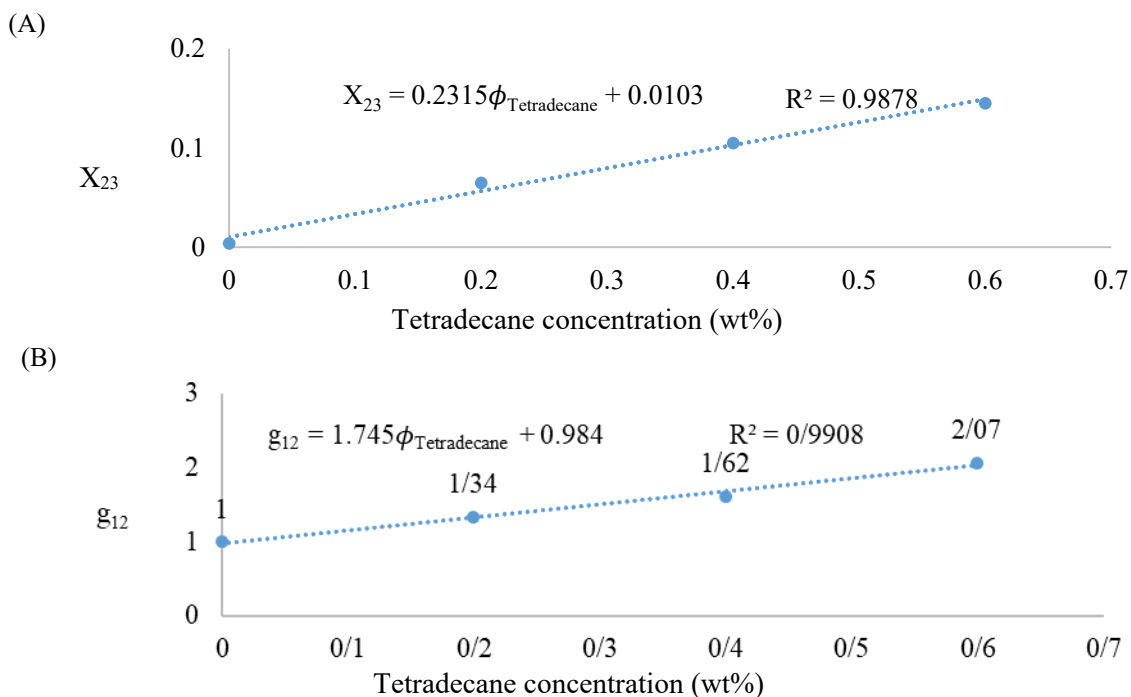


Figure 6. Changing parameter of the interaction between a) polymer and solvent (X_{23}); b) solvent and non-solvent (g_{12}) relative to the increase in the percentage of additive tetradecane in the PES / NMP + Tetradecane / Water system

In Figure 7, the binodal curve with spinodal is drawn according to the optimal parameters given in Table 5, which is well suited to the cloud computing.

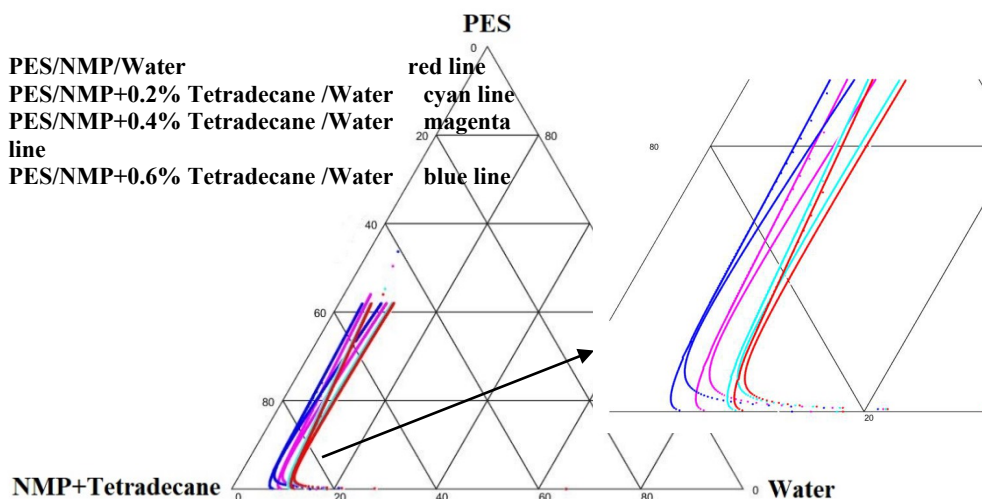


Figure 7. Binodal and spinodal curves in the PES / NMP / Water triple system , PES / NMP + 0.2% Tetradecane / Water PES / NMP + 0.4% Tetradecane / Water as well as PES / NMP triple system + 0.6% Tetradecane / Water

Figure 8 illustrates the separation of each additive and PES separately in a graph. It is seen that the separation start point for the hexane additive occurs after the PES phase separation. This means that the separation of PES is faster

than the separation of the hexane additive. But in the system containing the Decane additive, the polymer and additive separation occurs almost simultaneously, which means that the presence of the decane additive has a slight effect on the thermodynamic equilibrium. Since the startup point for tetradecane occurs much earlier than the PES separation, it has a great influence on the thermodynamic equilibrium of the system. Similar to the previous sections, the interaction parameters of this system are calculated in Table 6. These parameters are obtained by fitting the curve and the experimental data.

Table 6: Interaction calculation in PES / NMP / Water, Alkane / NMP / Water systems

System	g_{12}	x_{13}	x_{23}
PES/NMP/Water	$0.3164 + \frac{0.4683}{(1 - 0.4993u_2)}$	2.21	0.003
Hexane /NMP/Water	$0.3164 + \frac{0.4683}{(1 - 0.4993u_2)}$	4.55	1.11
Decane /NMP/Water	$0.3164 + \frac{0.4683}{(1 - 0.4993u_2)}$	4.59	1.15
Tetradecane /NMP/Water	$0.3164 + \frac{0.4683}{(1 - 0.4993u_2)}$	4.8	1.2

The process of increasing the interaction between alkanes with solvent and alkanes with non-solvents are indicated in Figures 8 (A) and (B), respectively.

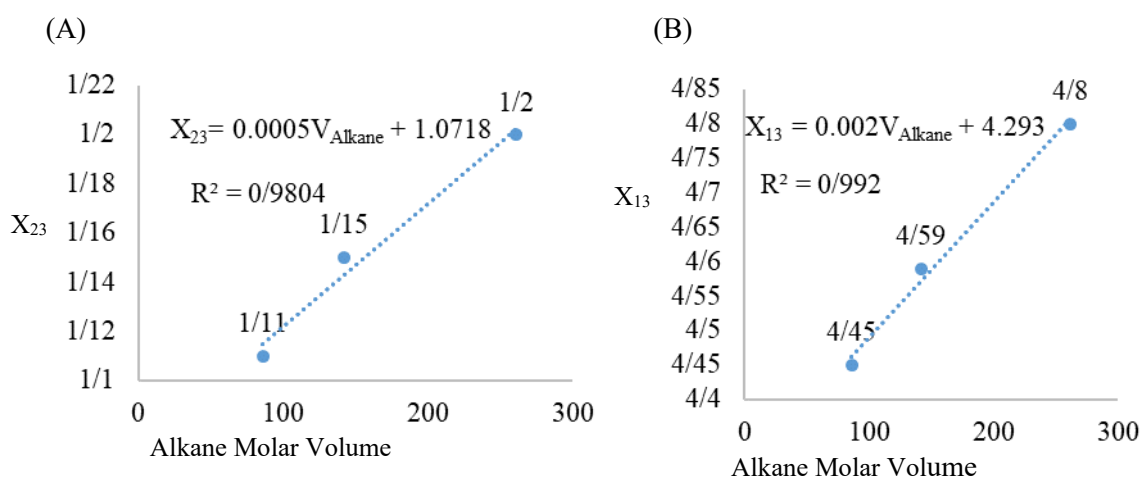


Figure 8. Effect of interaction between alkanes with solvent and non-solvent A) Increasing alkane and solvent interaction by increasing molar alkane volume b) Increasing alkaline and non-solvent interaction by increasing molar alkane volume

Figure 9 is drawn from the binodal curves along with the spinodal. Observed with respect to the interaction parameters in Table 6, this curve is well positioned on the cloudy points.

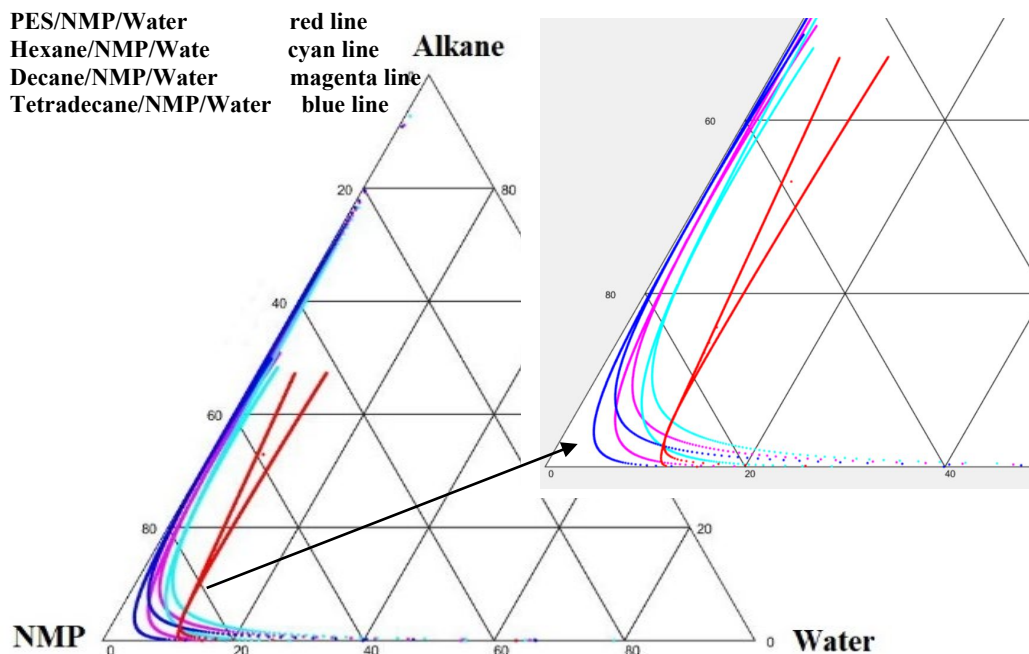


Figure 9. Binodal and spinodal curves in the PES / NMP / Water system, Hexane / NMP / Water, Decane / NMP / Water and the Tetradecane / NMP / Water triple system

4. Conclusion

In this study, it was observed that polymer phase inversion and alkane phase inversion can occur simultaneously or at two different times, and this can be derived from the interaction parameters of the materials which depend on the molar volume and the solubility parameters. Also, the phase separation associated with hexane occurred after the polymeric phase separation. Therefore, this alkane can not affect the instability of the system because before the polymerization, the polymeric phase inversion had occurred and the system was unstable. Regarding the phase decomposition of the decane, it was observed that this separation occurred with polymer phase inversion almost simultaneously, so it can be seen that these additives had a slight effect on the instability of the system. In the tetradecane phase separation of this phase inversion, it can also be seen that the first phase inversion of the tetradecane has occurred, and then the polymer phase inversion occurred. Hence, the additive tetradecane can affect the instability of the system and affect the bimodal and spinodal curves which will change the morphology of membranes.

Acknowledgements

The authors would like to acknowledge Persian Gulf University for financially supporting the paper.

5. Appendices

The algorithm of the bimodal and spinodal methodology is shown in Figure (1) and (2) respectively which can calculate all curves in “MATLAB” software.

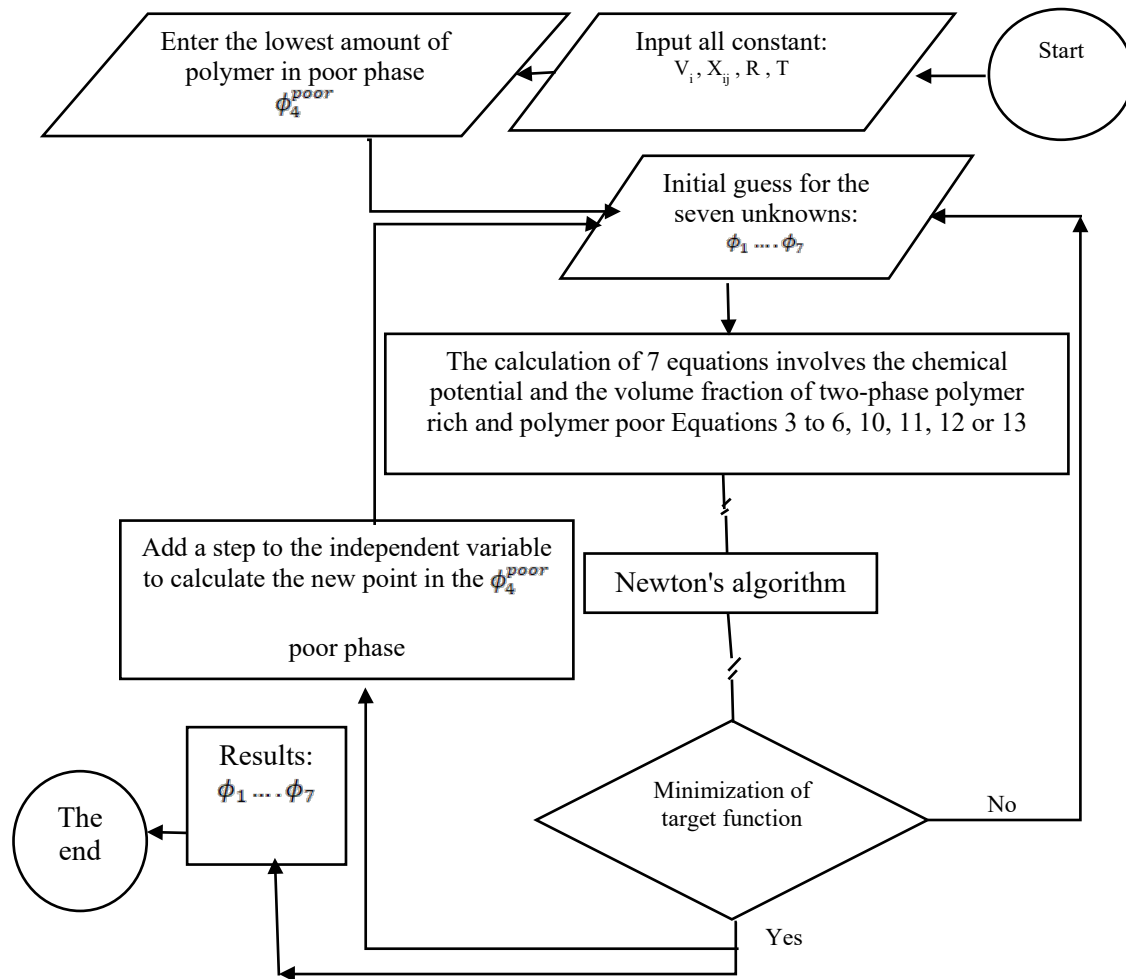


Figure 1. numerical computing algorithm to obtain the binodal curve

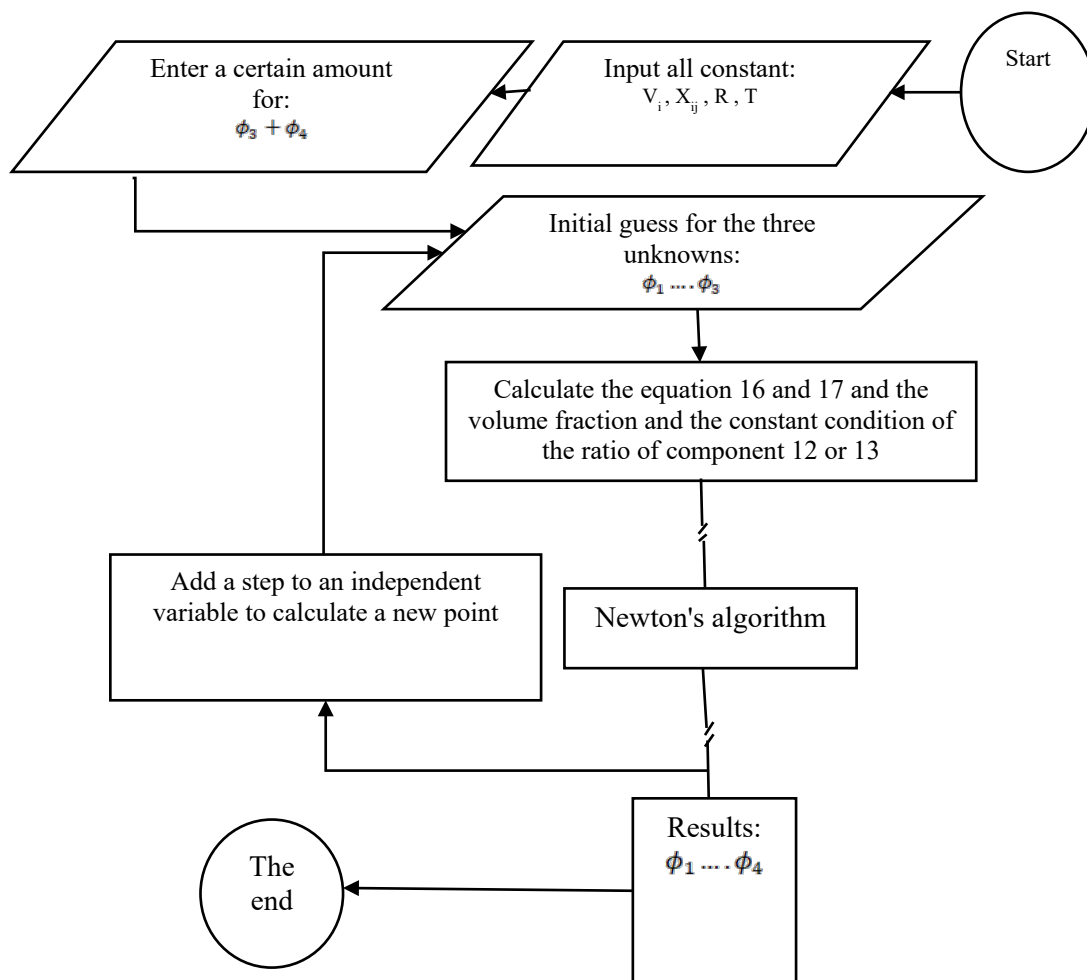


Figure 2. numerical computing algorithm to obtain the spinodal curve

Nomenclature

$i = 1$	Non-solvent
$i = 2$	Solvent
$i = 3$	Polymer
$i = 4$	Additive
ΔG_m	Gibbs free energy of mixing
μ	chemical potential
n	Number of molecules
ϕ	Volume fraction of component
g_{ij}	Flory Huggins interaction between two components i and j
R	Universal gas constant
T	Temperature
V	Specific volume
Λ_{ij}	Parameters of the Wilson equation
α	Poor phase of polymer
β	Rich phase of polymer
m	molar masses
ρ	Density
λ	ratio of the ϕ of the third component to ϕ fourth one

H	Hessian matrix
δ	Solubility parameters
δ_d	Dispersion section
δ_p	Polarity section
δ_h	Hydrogen bond section

References

- [1] M. Mulder. *Basic principles of membrane technology*. seconde ed., Netherlands, CA: Kluwer Academic Publishers, 1996, pp. 1-20.
- [2] H. Strathmann, L. Giorno, and E. Drioli, *Introduction to membrane science and technology*. John Wiley & Sons, Vol. 544. 2011, pp. 17-53.
- [3] Zeman, L.J. and A.L. Zydney, *Microfiltration and ultrafiltration: principles and applications*. Italy, Marcel Dekker 1996. pp. 10-42.
- [4] Mulder, M., *Transport in membranes*, in *Basic Principles of Membrane Technology*. Springer. 1996, pp. 210-279.
- [5] M. Mulder. *Encyclopedia of membrane science Membrane Preparation / phase inversion membranes*, 2000, pp. 3331-3346
- [6] J.A. Gonzalez-Leon and A.M. Mayes. "Phase behavior prediction of ternary polymer mixtures." *Macromolecules*, vol. 36, pp. 2508-2515, 2003.
- [7] M.L. Huggins. "Solutions of long chain compounds." *The Journal of Chemical Physics*, vol. 9, pp. 440-440, 1941.
- [8] P.J. Flory. "Thermodynamics of high polymer solutions." *The Journal of Chemical Physics*, vol. 10, pp. 51-61, 1942.
- [9] Z. Maghsoud, M. Navid Famili, and S.S. Madaeni i. "Phase diagram calculations of water/tetrahydrofuran/poly (vinyl chloride) ternary system based on a compressible regular solution model." *Iranian Polymer Journal*, vol. 19, pp. 581-588, 2010.
- [10] I. Sanchez and C. Panayiotou. "Equations of state thermodynamics of polymer and related solutions." *chemical industries-New York-Marcel Dekker*, pp. 187-187, 1993.
- [11] I.G. Economou. "Statistical associating fluid theory: a successful model for the calculation of thermodynamic and phase equilibrium properties of complex fluid mixtures." *Industrial & engineering chemistry research*, vol. 41, pp. 953-962, 2002.
- [12] A. Horta. "Statistical thermodynamics of preferential sorption." *Macromolecules*, vol. 12, pp. 785-789, 1979.
- [13] A. Horta. "Statistical thermodynamics of preferential sorption. 2." *Macromolecules*, vol. 18, pp. 2498-2504, 1985.
- [14] A.Sadeghi, H Nazem, M Rezakazemi and S. Shirazian. "Predictive construction of phase diagram of ternary solutions containing polymer/solvent/nonsolvent using modified Flory-Huggins model." *Journal of Molecular Liquids*, vol. 263: pp. 282-287, 2018.
- [15] M. Teimoori, S.A. Hashemifard, A.F. Ismail and M. Abbasi. "The impact of nonpolar coagulation bath-immiscible liquid additives on the

- polyethersulfone membranes structure and performance." *Journal of Applied Polymer Science*, vol. 13, pp. 134-146, 2017.
- [16] S.Madaeni, L. Bakhtiari, and E. Salehi. "Influence of binary interactions on phase behavior of water/dimethylsulfoxide/polyethersulfone casting solution: Thermodynamic modeling." *Polymers for Advanced Technologies*, vol. 24, pp. 1011-1017, 2013.
- [17] F.W. Altena and C. Smolders, "Calculation of liquid-liquid phase separation in a ternary system of a polymer in a mixture of a solvent and a nonsolvent." *Macromolecules*, vol. 15, pp. 1491-1497, 1982.
- [18] J. Zhang, Y. Zhang, and J. Zhao. "Thermodynamic study of non-solvent/dimethyl sulfoxide/polyacrylonitrile ternary systems: effects of the non-solvent species." *Polymer bulletin*, vol. 67, pp. 1073-1089, 2011.
- [19] A. Fredenslund, R.L. Jones, and J.M. Prausnitz. "Group-contribution estimation of activity coefficients in nonideal liquid mixtures." *AIChE Journal*, vol. 21, p. 1086-1099, 1975.
- [20] R. Koningsveld and L. Kleintjens, "Liquid-liquid phase separation in multicomponent polymer systems. X. Concentration dependence of the pair-interaction parameter in the system cyclohexane-polystyrene." *Macromolecules*, vol. 4, pp. 637-641, 1971.
- [21] Y.M. Wei, Z.L. Xu, X.T. Yang and H.L. Liu. "Mathematical calculation of binodal curves of a polymer/solvent/nonsolvent system in the phase inversion process." *Desalination*, vol. 192, pp. 91-104, 2006.
- [22] Z. Li and C. Jiang. "Determination of the nonsolvent-polymer interaction parameter χ_{13} in the casting solutions." *Journal of Membrane Science*, vol. 174, pp. 87-96, 2000.
- [23] M. Karimi, W. Albrecht, M. Heuchel, M.H. Kish, J. frahn, T. Weigel and A. Lendlein. "Determination of water/polymer interaction parameter for membrane-forming systems by sorption measurement and a fitting technique." *Journal of membrane science*, vol. 265, pp. 1-12, 2005.
- [24] J. Barzin, S. Madaeni, and S. Pourmoghadas. "Hemodialysis membranes prepared from poly (vinyl alcohol): Effects of the preparation conditions on the morphology and performance." *Journal of Applied Polymer Science*, vol. 104, pp. 2490-2497, 2007.
- [25] M.J. Han and D. Bhattacharyya. "Morphology and transport study of phase inversion polysulfone membranes." *Chemical Engineering Communications*, vol. 128, pp. 197-209, 1994.
- [26] J.Y. Kim, H.K. Lee, K.J. Baik and S.C. Kim. "Liquid-liquid phase separation in polysulfone/solvent/water systems." *Journal of applied polymer science*, vol. 65, pp. 2643-2653, 1997.
- [27] S. Mohsenpour, F. Esmailzadeh, A. Safkordi, M. Tavakolmoghadam, F. Rekabdar and H. Hemmati. "The role of thermodynamic parameter on membrane morphology based on phase diagram." *Journal of Molecular Liquids*, vol. 224, pp. 776-785, 2016.
- [28] K.V. Kurada and S. De. "Modeling of solution thermodynamics: A method for tuning the properties of blend polymeric membranes." *Journal of Membrane Science*, vol. 540, pp. 485-495, 2017.

-
- [29] L. Yilmaz and A. McHugh. "Analysis of nonsolvent–solvent–polymer phase diagrams and their relevance to membrane formation modeling." *Journal of applied polymer science*, vol. 31, pp. 997-1018, 1986.
- [30] K.V. Kurada and S. De. "Role of thermodynamic and kinetic interaction of poly (vinylidene fluoride) with various solvents for tuning phase inversion membranes." *Polymer Engineering & Science*, vol. 58, pp. 1062-1073, 2018.
- [31] S. Hashemifard, A. Ismail, and T. Matsuura. "Co-casting technique for fabricating dual-layer flat sheet membranes for gas separation." *Journal of membrane science*, vol. 375, pp. 258-267, 2011.
- [32] E. Bagley, T. Nelson, and J. Scigliano, "Three-dimensional solubility parameters and their relationship to internal pressure measurements in polar and hydrogen bonding solvents." *Journal of paint technology*, vol. 43, pp. 35-42, 1971.

تغییر شکاف امتزاج پذیری محلول پلیمری حاوی آلکان و تاثیرات آن بر روی ساخت غشا

محمد رضایی نژاد، سید عبدالطیف هاشمی فرد*، امیر عباس ایزدپناه

ایران، بوشهر، دانشگاه خلیج فارس، دانشکده مهندسی نفت، گاز و پتروشیمی، گروه تحقیقاتی تکنولوژی غشاء

شخصیات مقاله

تاریخچه مقاله:

دریافت: ۲۳ آبان ۱۳۹۷

پذیرش نهایی: ۳ دی ۱۳۹۷

کلمات کلیدی:

افزودنی

ساخت غشا

مدل سازی

سیستم چهارتایی

آلکان

* عهده دار مکاتبات؛

رایانامه:

salhashemifard@pgu.ac.ir

تلفن: +۹۸ ۷۷ ۳۳۴۴۲۶۰۱

دورنگار: +۹۸ ۷۷ ۳۳۴۴۱۴۹۵

چکیده

به منظور کاهش هزینه ها و زمان در فرایند ساخت غشاها، لازم است که کیفیت غشاها را با انجام مدل سازی بهبود ببخشیم. در این پژوهش از تئوری فلوری هاگینز در پیش بینی سیستم چهارتایی شامل پلی اتر سولفون، ان متیل ۲-پیرولیدون، آب و آلکانها به عنوان افزودنی، استفاده شده است. پارامترهای حلالیت و حجم مولی منجر به تغییر در پارامترهای برهمکنش اجزای سیستم می شوند که این تغییرات موجب تاثیر بر ساختار نهایی غشا خواهد شد. این در حالی است که با مدل سازی می توان مشاهده کرد که هگزان هیچ تاثیری بر روی ناحیه امتزاج پذیری نداشته و همچنین دکان توانسته تاثیر ناچیزی بر این ناحیه بگذارد. اما تترادکان با توجه به افزایش برهمکنش ها توانسته تاثیر چشم گیری بر روی ناحیه امتزاج پذیری و پایداری ترمودینامیکی سیستم بگذارد. بنابراین این ناپایداری ها توانسته منجر به تشکیل سریع تر غشا و ایجاد ساختار لایه سطحی متخلخل و نهایتاً تغییر در ریخت شناسی غشا شود. هرچه ناحیه ناپایداری افزایش یابد، میزان حفرات لایه سطحی افزایش پیدا خواهد کرد و برعکس.