Flory-Huggins Based Model to Determine Thermodynamic Property of Polymeric Membrane Solution

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Abstract. Flory-Huggins (F-H) model has been widely used to analyze the thermodynamic behavior of polymeric membrane solution during the formation of membrane structure in a phase inversion process. The F-H model involves concentration and binary interaction parameter of components in membrane solution. Those parameters are used to calculate the composition of membrane solution at equilibrium which is then plotted on ternary diagram known as a binodal curve. The binodal curve is used to determine the type of demixing of the polymeric membrane solution and to predict the structure of resulted membrane. Several modifications of F-H model have been conducted in relation to composition (ternary or quaternary) and temperature of the membrane solution. In this paper, the development of F-H model used in designing polymeric membrane by phase inversion method, particularly immersion precipitation method, will be reviewed. The structure and performance of membranes that are governed by the thermodynamic property of the membrane solution based on F-H model will be discussed.

Keywords: Flory-Huggins model, immersion precipitation, polymeric membrane, thermodynamic

1. Introduction

Phase inversion method is the most used technique in industrial membrane manufacturing to produce a polymeric asymmetric membrane, both flat-sheet and hollow fiber membrane type [1-6]. This method involves transformation from a homogenous polymeric membrane solution to the final membrane structure (solid) through a phase separation of polymer solution. There are two basic techniques in membrane preparation by phase inversion, i.e. dry and wet techniques [7-11]. In the dry phase inversion technique, solvent is evaporated from the membrane solution to the atmosphere and/or absorbing a vapor phase (non-solvent) from the air moisture. Meanwhile, in the wet technique, membrane structure is formed by immersing the membrane solution into a non-solvent-containing bath. This method is known as immersion precipitation method, which has been widely used in the manufacture of commercial membranes.

The phase separation behavior, also known as liquid-liquid (L-L) demixing, is strongly influenced by thermodynamic and kinetic property of the membrane system. A ternary diagram is commonly used as a tool to analyze the thermodynamic and kinetic behavior of the membrane system (Figure 1). The phase separation of the membrane solution is mentioned as binodal curve (or also called as cloud point curve) in the ternary diagram. When the binodal composition is reached, phase separation (L-L demixing) of the membrane solution begins to occur. Every composition at the boundary conditions
(binodal curve) begins to separate into two liquid phases, i.e. rich polymer (point A) and lean polymer (point B), which differ in compositions but remains in thermodynamic equilibrium with each other [12]. A pair of equilibrium compositions in the phase diagram is connected by a tie line while area within the binodal curve is called as miscibility gap. The thermodynamic properties of membrane solution can be evaluated in terms of degree of shift in binodal curve and miscibility gap area in ternary diagram, which depends on several parameters such as composition of the membrane solution and interaction parameters of each component. Different composition in membrane solution results in different membrane structure and performances. The influence of those parameters on the membrane structure have been explained in some literature [13-15]. The solidification process of the membrane solution is presented by precipitation path (line from point C to D), which describes the composition changes in polymer solution with respect to the solvent–non-solvent exchange rate (or mass transfer) in the membrane solution. During the evaporation of solvent from the polymer solution, the polymer concentration increases and then reaches a very high packing density until all solvent is evaporated (point D). Overall, the resulted membrane morphology is strongly related to the initial composition of membrane solution, binodal curve position, and the precipitation path [16-19]. In this paper, the mathematical model of thermodynamics to predict binodal curve or phase separation behavior of the membrane solution will be discussed.

Figure 1. Ternary diagram of three component membrane system [12]

Several thermodynamic theories have been developed and used to analyze the membrane formation by phase inversion method (Table 1). Among of these theories, Flory-Huggins (F-H) theory has been widely used due to its relative simplicity, low number of input parameters, and provides a good prediction of the phase behavior of polymeric solutions [20]. Although the other models showed better thermodynamic analysis of the membrane solution compared to F-H model, the higher mathematical complexity and less predictive capability become a barrier to the completion of the model [21]. The F-H model is based on the Gibbs free energy ($\Delta G_m$) of the membrane solution, which involves binary interaction parameters ($\chi_{ij}$) and volume fraction ($\phi$) of each component in membrane solution.

In general, $\Delta G_m$ in a ternary membrane system is formulated by the following equation based on theory developed by Tompa [22]:

$$\frac{\Delta G}{RT} = \left( \sum \frac{\phi_i}{m_i} \ln \phi_i + \sum \chi_{ij} \phi_i \phi_j \right) \sum m_i n_j$$

(1)

where $m_i$ are molar volume ratio reflecting size different of components ($m = V/V_i$), $n_i$ is mole fraction, $\phi_i$ is volume fraction, and $\chi_{ij}$ is binary interaction parameters of each component in membrane solution. R and T are the gas constant and temperature. In F-H theory, the binary interaction parameter ($\chi_{ij}$) is an excess free energy parameter involving all non-ideality in the membrane system, which contains an
enthalpic as well as an entropic contribution [14]. In the original F-H theory, the \( \chi_0 \) is assumed to be concentration independent, which means that the value does not depend on the number of components in the system. However, some experimental studies have shown that the said assumptions cannot be used in certain cases.

Table 1. Thermodynamic models to analyze the membrane formation by phase inversion method

| Year | Researchers               | Model                        | Computation Method          | Ref. |
|------|---------------------------|------------------------------|------------------------------|------|
| 1982 | Altena F.W. dan Smolders C. A. | Flory-Huggins                | Least square procedure       | [23] |
| 1987 | Shuguang L., et al.       | Flory-Huggins                | Least square procedure       | [24] |
| 1995 | Termonia Y.               | Difiusi Monte Carlo          | -                            | [25] |
| 1997 | J. Young K., et al.       | Flory-Huggins                | Newton Raphson               | [26] |
| 2005 | Akthakul A., et al.       | Kisi Boltzmann (BK)          | -                            | [27] |
| 2006 | Yong M. W., et al.        | Flory-Huggins                | -                            | [28] |
| 2007 | Barzin J., et al.         | Flory-Huggins                | Newton Raphson               | [29] |

When two components are mixed, the free enthalpy of mixing is determined by chemical potential (\( \mu \)) of both components. The chemical potential of a component is defined by the following equation:

\[
\Delta \mu_{ni} = \left( \frac{\partial \Delta G_n}{\partial n_i} \right)_{P,T,n_j,n_k,...}
\]

where \( \mu_i \) is the chemical potential of component containing \( n_i \) moles, while the pressure (P), temperature (T), and the number of moles of other components \( (n_j, n_k, \text{and so on}) \) are held constant. The conditions in liquid-liquid equilibrium (or composition on the binodal curve) are:

\[
\Delta \mu_{Ai} = \Delta \mu_{Bi} \quad i = 1, 2, 3
\]

Subscripts \( A \) and \( B \) refer to the rich-polymer and lean-polymer. The following sections will discuss the development of F-H models for ternary and quaternary systems, along with the determination of binary interactions in membrane systems.

2. Flory Huggins Theory for Ternary Membrane System

Thermodynamic analysis of ternary membrane systems, consisting of polymer (P)/solvent (S)/non-solvent (NS), have been studied with some restrictive assumption to reduce the complexity of phase diagram calculations [22]. In ternary membrane system, there are three interaction parameters, i.e \( \chi_{13} \) (non-solvent/polymer), \( \chi_{23} \) (solvent/polymer), and \( \chi_{12} \) (solvent/non-solvent), which in the early application the F-H model are considered constant (concentration independent). Suh et al. [30] assumed that the polymer concentration in lean phase polymer is near zero or negligible. This assumption is used only if the equilibrium exists between a mixed solvent and a polymer or if the polymer confined to one phase. In other literature, interaction parameter of non-solvent and polymer is assumed as concentration independent (constant).

Further development of F-H model for ternary membrane system is proposed by Altena and Smolder [23]. Two membrane forming systems are used, i.e cellulose acetate/solvent/water and polysulfone/solvent/water. They suggested that the change of solvent and non-solvent concentration in membrane solution gave a major effect on the formation of membrane structure, thus the interaction parameter between the two components is concentration dependent (denoted as \( g_{12} \)). Meanwhile, the other two interactions are considered constant over the concentration changes. They found that the use of the dependent concentration \( g_{12} \) showed a better agreement between experimental cloud point curves and theoretical binodals. Based on Eq. (1), the Gibbs energy of ternary membrane system is given by the following relation:
\[
\frac{\Delta G_m}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + g_{12}(u_2)n_1\phi_1 + \chi_{12}n_1\phi_2 + \chi_{23}n_2\phi_3
\]

The chemical potential equations derived from the above equation are:

\[
\Delta \mu_1 = RT \left[ \ln \phi_1 + 1 - \phi_1 - s\phi_2 - r\phi_3 + (g_{12}\phi_2 + \chi_{12}\phi_3)(\phi_2 + \phi_3) - s\chi_{23}\phi_3\phi_3 - \phi_2u_1u_2 \frac{dg_{12}}{du_2} \right]
\] (5)

\[
\Delta \mu_2 = RT \left[ s \ln \phi_2 + s - \phi_1 - s\phi_2 - r\phi_3 + (g_{12}\phi_1 + s\chi_{23}\phi_3)(\phi_1 + \phi_3) - \chi_{12}\phi_3\phi_2 - \phi_1u_1u_2 \frac{dg_{12}}{du_2} \right]
\] (6)

\[
\Delta \mu_3 = RT \left[ r \ln \phi_3 + r - \phi_1 - s\phi_2 - r\phi_3 + (\chi_{13}\phi_1 + s\chi_{23}\phi_2)(\phi_1 + \phi_2) - \chi_{12}\phi_3\phi_2 \right]
\] (7)

where \( r \) and \( s \) are molar volume ratio \( V_1/V_2 \) and \( V_1/V_3 \), while \( u_1 = \phi_i/(\phi_i + \phi_j) \) and \( u_2 = \phi_j/(\phi_i + \phi_j) \). The subscripts (1, 2, and 3) refer to non-solvent (1), solvent (2), and polymer (3).

To determine the composition of each component in the equilibrium condition, 6 (six) parameters (\( \phi_{1,A}, \phi_{2,A}, \phi_{3,A}, \phi_{1,B}, \phi_{2,B}, \) and \( \phi_{3,B} \)) should be known. Therefore, some assumptions are proposed to simplify the completion of the F-H equation. Two mass balance equations (\( \sum \phi_i = 1 \)) is used for the rich and lean phase of membrane solution. By choosing one (1) variable, the mass balance equations can be substituted into equations (5) to (7). The procedure can also be simplified by assuming that the polymer concentration in lean-phase (\( \phi_{3,B} \)) is near to zero (10^{-30} up to 10^{-90}) or negligible [23, 24, 31]. The binodal curve is calculated numerically by minimizing the following functions:

\[
F = \sum_{i=1}^{4} \left[ \frac{\Delta \mu_{i,B}}{RT} - \frac{\Delta \mu_{i,A}}{RT} \right]^2
\] (8)

The calculated binodal curves using the above calculation method compared to the cloud point measurement are shown in Figure 2 [23].

![Figure 2](image)

(A) Calculated binodal (full curve) compared to cloud point measurements (dashed line) [23]

Yilmaz et al. [31] studied the effect of variants of interaction parameters on phase diagram characteristics as well as their relevance to membrane formation. They found that F-H theory can be empirically extended using concentration-dependent interaction parameters (\( g_{ij} \)), particularly for \( g_{12} \) and \( g_{23} \). The \( \Delta G_m \) of mixing becomes:
The following penalty function is used to compute the binodal composition, which is similar to the Eq. (8).

$$F_r = \frac{\left(\Delta \mu_{i,d} - \Delta \mu_{i,b}\right)}{\left(\phi_{i,d} - \phi_{i,b}\right) RT}$$

with $r = 1$ or 2. The $\phi_{3,b}$ is assumed as $10^{-90}$ and selected as the independent variable.

3. Binary Interaction Parameter in Flory-Huggins Model

Binary interaction ($\chi_{ij}$) parameters play an important role in the F-H theory, which indicates the solubility of each component in the membrane solution and affects the binodal curve position in the ternary diagram (Figure 2) [32]. It shows that an increase in $\chi_{13}$, which indicates a low interaction between non-solvent and polymer, will shift the binodal curve to the left corner of the ternary diagram. It means that the less non-solvent concentration required for the phase separation of the membrane system. The same tendency is obtained when the parameter interaction value of $\chi_{23}$ is enhanced.

Membrane structures that are formed tend to be finger-like. Conversely, the increase of $\chi_{12}$ value will move the binodal curve to the right side of the ternary diagram, which tends to form sponge-like membrane structure. Therefore, the calculation and evaluation of the correct $\chi_{ij}$ parameters are necessary to study the thermodynamic property of membrane solution to predict the resulted membrane structure. In F-H model, the binary interaction parameter can be calculated from activity data or vapor-liquid equilibrium data in some literature. The challenges in determining $\chi_{ij}$ are the limited data of the components used in membrane solution.

Besides the type of components in the membrane system, the value of interaction parameters depends on temperature, concentration, and molecular weight of the components, especially the molecular weight of polymer. Altena et al. [23] found that the demixing behavior of the water/dimethyl formamide (DMF)/polysulfone (PSf)/system is highly affected by interaction parameter value of non-solvent/polymer ($\chi_{13}$) and non-solvent/solvent ($\chi_{12}$). Meanwhile, interaction parameter of solvent/polymer ($\chi_{23}$) gave a small effect to the demixing behavior. The $X_{ij}$ values of different membrane systems have been reported in the literature [20, 33-36].

Figure 3. The effect of interaction parameter value to the position of binodal curve in a ternary diagram: (A) $\chi_{13}$ / $\chi_{23}$ and (B) $\chi_{12}$ [31, 37]
3.1. Interaction parameter non-solvent-polymer ($\chi_{ij}$)

Interaction parameter $\chi_{ij}$ can be measured using equilibrium swelling experiment at different temperature and high concentration of polymer [38]. When a non-solvent is contacted with a polymer, the non-solvent will diffuse into the polymer matrix until the equilibrium is reached. Simultaneously, the polymer matrix will be swelled. When the interaction between polymer and penetrant is relatively low, the $\chi_{ij}$ can be calculated by Eq.(11).

$$\chi = -\frac{\ln(1 - \phi_i) + \phi_i}{\phi_i^2} \quad (11)$$

where $\phi_i$ is volume fraction of polymer.

Li et al [39] calculated the $\chi_{ij}$ of three membrane forming systems based on $g_{13}$ and intrinsic viscosity of polymer in membrane solution, as shown in Table 1 (No. 2). They found that the intrinsic viscosity measurement can be applied in various solvent systems without limitation of the refractive index of the solvents. The calculated $\chi_{ij}$ was nearly the same as that obtained from the light scattering measurements. The proposed models to calculate $\chi_{ij}$ are shown in Table 2.

### Table 2. Some equations to calculate interaction parameter of non-solvent/polymer ($\chi_{ij}$)

| No | Equations | Remarks | Reference |
|----|-----------|---------|-----------|
| 1 | $\chi = -\frac{\ln(1 - \phi_i) + \phi_i}{\phi_i^2}$ | $\phi_i$ is volume fraction of polymer | [14] |
| 2 | $Y = -\chi_{ij} + (1 - 2a_x)g_{12}\phi_2$ | $\chi_{ij}$ is determined as intercept of $Y$ against $g_{12}\phi_2$. ($1 - 2a_x$) is a constant related to intrinsic viscosity of polymer and interaction parameter $g_{12}$. | [39] |
| 3 | $\ln a_{1g} = \ln(\phi_i) + \left(1 - \frac{v_i}{V_o}\right)\phi_1 + \chi_{ij}\phi_i^2$ | Using F-H equation in Eq. (4), by specifying $n_2$, $\phi_2 = 0$, $\ln a_{1g}$ is vapor phase activity of the non-solvent. | [34] |
| 4 | $\chi = \frac{\Delta H}{RTV^2} \left[\ln(1 - v) + v\left(1 - V^o/V^o\right)\right]$ | $T$ is temperature, $V^o/V^o$ is the ratio molar volumes for liquid and polymer, while $v$ is volume fraction. | [40] |
| 5 | $g_{13}(\phi_i) = a + b\phi_i$ | System H$_2$O/PES 49w (T=32°C): $a = 2.00$ and $b = 0.10$, System H$_2$O/PSf 39w (T=32°C): $a = 2.30$ and $b = 0$, $\phi_i$ is volume fraction of polymer | [41] |

Note: PES = polyethersulfone; PSf = polysulfone

3.2. Interaction parameter non-solvent-sovent ($\chi_{ij}$)

The concentration dependent interaction parameter between non-solvent and solvent, which noted as $g_{12}$, is generally determined from excess Gibbs free energy data, as shown in the following equation [14]:

$$g_{12} = \frac{1}{x_1\phi_2} \left[ x_1 \ln \frac{x_1}{\phi_1} + x_2 \ln \frac{x_2}{\phi_2} + \frac{G^E}{RT} \right] \quad (12)$$

$G^E$ can be determined from activity coefficient data or experimental data, which are available in the literature. Meanwhile, several researchers suggested the following polynomial equation to calculate $g_{12}$ based on the equilibrium data of non-solvent/solvent:
\[ g_{12} = a_0 + a_1 \phi_2 + a_2 \phi_2^2 + \ldots . \]  

Different \( g_{12} \) values have been reported with different values of \( a \) in the literature [23, 24, 29]. The differences resulted from different sources of equilibrium data. A change in solvent and non-solvent type will change the \( g_{12} \) value. Meanwhile, [41] calculated \( g_{12} \) by the following equation, based on experimental data obtained by means of Headspace-Gas Chromatography (HSGC):

\[ g_{12}(\phi_2) = \alpha + \frac{\beta}{1 - \gamma \phi_2^2} \]  

For binary system \( \text{H}_2\text{O}/\text{DMF} \) at 32°C, the value of \( \alpha \) is 0.3223, while \( \beta \) and \( \gamma \) are 0.0751 and 0.9604, respectively.

### 3.3 Interaction parameter solvent-polymer (\( \chi_{23} \))

Experimentally, the \( \chi_{23} \) value can be measured by light scattering, vapor pressure depression, and membrane osmometry [14, 35]. In membrane osmometry technique, the dilute solvent in polymer solution moves to the concentrated phase (pure solvent) through a tight membrane. Osmotic pressure (\( \pi \)) of the pure solvent will increase, and then used to calculate \( \chi_{23} \) by the following equation:

\[ \pi = \frac{RT}{V_2} \phi_2 + \frac{RT}{V_1}(0.5 - \chi)\phi_2^2 \]  

Other method is proposed by Karimi et al. [42]. They measured \( \chi_{23} \) of various polymer solutions based on solvent activity that measured by vapor pressure osmometry (VPO) data.

\[ \frac{\ln(a_2/\phi_3) - \phi_3}{\phi_3} = \chi_{23} \]  

\( a_2 \) is measured solvent activity from VPO data. The interaction parameter \( \chi_{23} \) is obtained as slope of a fitted straight line if \( \ln(a_2/\phi_3) - \phi_3 \) data are plotted versus \( \phi_3 \). Besides of VPO method, the activity values of the solvents can be determined by other methods that have been reported in the literature [43, 44].

The \( \chi_{23} \) value can also be determined based on solubility data of each component in membrane solution. Shuguang et al. [24] combined Hildebrand-Scatchard theory with F-H theory to calculate the \( \chi_{23} \) of water/dimethylacetamide (DMAc)/polysulfone (PSF) system, as the following equation:

\[ \chi_{23} = (\delta_2 - \delta_3)^2 V_1 / RT \]  

where \( V_1 \) is molar volume of the solvent, while \( \delta_1 \) and \( \delta_2 \) are the solubility parameters of solvent and polymer (cal^{1/2}.cm^3). The calculated \( \chi_{23} \) by the above equation had a different value with those obtained from gas-liquid chromatography measurement. Therefore, they suggested that the \( \chi_{13} \) and \( \chi_{23} \) should be concentration dependent. Table 3 shows several models to calculate the \( \chi_{13} \).

### 4. Development of Flory-Huggins Theory for Quaternary Membrane Solution

The F-H model for a quaternary system has been developed by Boom et al [45]. They modified F-H model, as shown in Eq. (1), for a membrane system consisting of non-solvent (1), solvent (2), membrane forming polymer (3), and second polymer or additive (4). The modified F-H model gave the Gibbs energy of mixing as a function of concentration-dependent interaction parameters and then used to calculate the binodal composition, as follows:

\[ \Delta G / RT = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + n_4 \ln \phi_4 + n_1 \phi_1 g_{12}(u_2) + n_2 \phi_2 g_{23}(u_3) + n_3 \phi_3 g_{34}(u_4) \]

\[ + n_2 \phi_3 g_{23}(v_2) + n_2 \phi_4 g_{24}(w_2) + n_3 \phi_3 g_{34}(v_3) \]  

(18)
where \( n_i \) and \( \phi_i \) are mol and volume fraction, respectively. \( \chi_{ij} \) is considered as independent-concentration interaction parameter due to low affinity between the weak affinity between the two binary components. Meanwhile, the other interaction parameters are dependent on the following variables:

- \( g_{ij} \) is dependent on \( u_i \), where \( u_i = \phi_i/(\phi_i + \phi_j) \).
- \( g_{ij} \) is dependent on \( v_i \), where \( v_i = \phi_i/(\phi_i + \phi_j) \).
- \( g_{ij} \) is dependent on \( u_i \), where \( u_i = \phi_i/(\phi_i + \phi_j) \).
- \( g_{ij} \) is dependent on \( w_i \), where \( w_i = \phi_i/(\phi_i + \phi_j) \).

### Table 3. Equations to calculate interaction parameter of non-solvent/polymer (\( \chi_{ij} \))

| No | Equations | Remarks | References |
|----|-----------|---------|------------|
| 1  | \( \frac{\ln(a_i/\phi_i) - \phi_i}{\phi_i} = \chi_{23}\phi_3 \) | \( a_i \) = solvent activity, \( \phi_i \) = volume fraction of solvent, \( \phi_3 \) = volume fraction of polymer | [29] |
| 2  | \( \chi_{23} = (\delta_1^2 - \delta_2^2)\frac{V_i}{RT} \) | \( V_i \) is molar volume of the solvent, while \( \delta_1 \) and \( \delta_2 \) are solubility parameters of solvent and polymer | [24] |
| 3  | \( A_2 = \frac{1}{2} - \chi_{23} \) | \( \rho_2 \) = density of polymer (g/cm\(^3\)), \( V_i \) = molar volume of solvent (cm\(^3\)/mol). \( A_2 \) is a second virial coefficient, which is a function of intrinsic viscosity and molecular weight of polymer. | [40] |
| 3  | \( \chi_{23} = \chi_1 + \chi_2v + \chi_3v^2 + ... \) | Coefficient \( \chi_1, \chi_2, \ldots \), are function of molecular characteristics and temperature. \( v \) is polymer volume fraction at equilibrium (maximum) degree of swelling | [46, 47] |
| 4  | \( g_{23}(\phi_3) = a - 3b - 5c - b(2\phi_i - 1) + c(2\phi_i - 1)^2 \) | Membran system (T=32°C): - H\(_2\)/DMF/PES 49w | [41] |

\( a = 0.3719; b = 0.0793; c = -0.0236 \)

\( H_2O/DMF/PSf 39w \)

\( a = 0.4685; b = 0.1472; c = -0.0728 \)

\( \phi_3 \) is volume fraction of polymer

Note: DMF = dimethyl formamide

The chemical potentials of the quaternary system (\( \Delta \mu_i \)) are obtained by deriving the Gibbs energy in Eq. (18) with respect to the number of moles of each component:

\[
\frac{\Delta \mu_i}{RT} = \ln \phi_i - s\phi_i - r\phi_i - t\phi_i + (1 + g_{12}\phi_2 + \chi_{13}\phi_3 + g_{14}\phi_4)(1 - \phi_i) - s g_{23}\phi_2\phi_3 - r g_{34}\phi_3\phi_4
\]

\[\frac{\Delta \mu_j}{RT} = s\ln \phi_i - \phi_i - r\phi_i - t\phi_i + (s + g_{12}\phi_2 + s g_{23}\phi_3 + s g_{24}\phi_4)(1 - \phi_i) - \chi_{13}\phi_3\phi_3 - g_{14}\phi_4
\]

\[
- r g_{24}\phi_4 - \phi_i u_2 (1 - u_2) \left( \frac{dg_{12}}{du_2} \right) - s \phi_3 v_2 \left( \frac{dg_{23}}{dv_2} \right) - s \phi_4 v_2 (1 - w_2) \left( \frac{dg_{24}}{dv_2} \right)
\]

(19)
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\[
\frac{\Delta \mu_i}{RT} = r \ln \phi_i - \phi_i - s \phi_2 - t \phi_4 + (r + \chi_{13} \phi_i + s \chi_{34} \phi_2 + rg_{34} \phi_4)(1 - \phi_i) - g_{13} \phi_2 \phi_4 - g_{14} \phi_2 \phi_4
\]

\[
- s g_{23} \phi_2 \phi_4 - s \phi_2 v_2 (1 - v_2) \left( \frac{dg_{23}}{dv_2} \right) - r \phi_4 \phi_2 (1 - v_3) \left( \frac{dg_{34}}{v_3} \right)
\]

\[
\frac{t \Delta \mu_4}{RT} = t \ln \phi_4 - \phi_4 - s \phi_3 - r \phi_3 + (t + g_{14} \phi_4 + s g_{23} \phi_4 + rg_{34} \phi_4)(1 - \phi_4) - g_{13} \phi_2 \phi_4 - \chi_{34} \phi_3
\]

\[
- s g_{23} \phi_3 \phi_4 + \phi_4 u_4 (1 - u_4) \left( \frac{dg_{34}}{u_4} \right) - s \phi_2 w_2 (1 - w_2) \left( \frac{dg_{24}}{w_2} \right) - r \phi_4 v_2 (1 - v_3) \left( \frac{dg_{34}}{v_3} \right)
\]

The Eq. (19) to (22) is solved using an objective function as described in Eq. (8) through Newton-type algorithm.

Thermodynamic properties of a quaternary system, consisting of water/N-Methylpyrrolidone (NMP)/ polyethersulfone (PES)/Poly(vinylpyrrolidinone) (PVP), has been studied by Boom et al. [48]. They studied the role of polymeric additive on the binodal curve position in pseudo-ternary diagram, as shown in Figure 4. They found that the presence of additive decreased the size of demixing gap, which means that the solution more compatible with the non-solvent and led to delay demixing. At high concentration of additive with no movement between the two polymers, the non-solvent concentration can reach 50% by volume to disturb the equilibrium of membrane solution. In this condition, smaller membrane pore size is formed.

**Figure 4.** The influence of additive concentration on binodal curve position in pseudo-ternary diagram: (a) \( \phi_3/\phi_4 = 0 \), (b) \( \phi_3/\phi_4 = 0.1 \), (c) \( \phi_3/\phi_4 = 0.5 \), (d) \( \phi_3/\phi_4 = 1.0 \). Composition: (1) Water, (2) NMP, (3) PES, and (4) PVP [49]

It has been reported that the binodal curve is not affected by the molecular weight of polymer as long as the polymer is a macromolecule in nature. The polymer-solvent interactions, \( g_{34} \) and \( g_{35} \), are not important as long as the miscibility of both polymers occurs [45]. When using two (2) polymers in the membrane systems, polymer-polymer interaction \( (\chi_{34}) \) can be calculated using Eq. (17). Emerson et al. [33] determined \( \chi_{34} \) for poly(3-hexylthiophene) (P,HT) and polystyrene (PS). A correction factor based on solvent vapor swelling data is used, thus the Eq. (17) becomes:

\[
\chi_{34} = \frac{V_3}{RT} (\delta_3 - \delta_4)^2 + 0.34
\]

Ariono et al. [12] and Aryanti et al. [50] found a different result. They added PEG400 instead of PVP as an additive into membrane solution (water/DMAC/PSf/PEG400) and then studied the thermodynamic behavior of the membrane system. The \( \chi_{34} \) of the components is calculated based on the cloud point test data. They found that the increase of PEG400 concentration shifted binodal composition to the left corner of the ternary diagram. Instantaneously demixing is occurred, which form a longer finger-like pore in the final membrane structure (Figure 5). It means that the binodal curve is not only influenced...
by the concentration of the additive but also affected by the type of additive. It suggested that PVP has higher molecular weight than PEG400, which inhibited the membrane pore growth \cite{51,52}. Therefore, smaller pore size is produced in the final structure. During the thermodynamic analysis, an interaction between additive-solvent and additive-non-solvent should also be considered.

Up to this time, the development of F-H equation and model or method to calculate interaction parameters are continued to minimize poor agreement between theoretical and experimental result. Further development is needed, in which the current membrane modification already involves more than four compositions. Several factors should be considered before analyzing the thermodynamic property of membrane solutions, such as molecular weight and type of each component in membrane solution, temperature, concentration, and binary interaction between the components. Those parameters are used to evaluate the theoretical result, which may produce different characteristics of the membrane with the experimental results.

![Figure 5. The influence of PEG400 concentration in polysulfone membrane solution to binodal composition](image)

**5. Conclusions**

In this paper, the development of F-H model used in designing polymeric membrane by phase inversion method, particularly immersion precipitation method, has been reviewed. The F-H model is based on the Gibbs free energy of the membrane solution to determine the thermodynamic equilibrium of the membrane solution. This model involves binary interaction parameters ($Z_{ij}$) and volume fraction of each component in membrane solution. Those parameters are used to calculate the composition of membrane solution at equilibrium which is then plotted on ternary diagram known as a binodal curve. The binodal curve is used to determine the type of demixing of the polymeric membrane solution and to predict the structure of resulted membrane, whether finger-like or sponge-like.

Up to this time, several modifications of F-H model have been conducted in relation to composition (ternary or quaternary) and temperature of the membrane solution to minimize the poor agreement between theoretical and experimental data. Several parameters should be considered before analyzing the thermodynamic property of membrane solutions, such as molecular weight and type of each component in membrane solution, intrinsic viscosity of the solution, temperature, concentration, and binary interaction between the components. It is suggested that dependent-concentration interaction parameters result in better agreement with the experimental data.
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