Accepted Manuscript

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PII: S0167-7322(18)31674-X
DOI: doi:10.1016/j.molliq.2018.05.015
Reference: MOLLIQ 9070
To appear in: Journal of Molecular Liquids
Received date: 29 March 2018
Revised date: 1 May 2018
Accepted date: 4 May 2018

Please cite this article as: Arash Sadeghi, Hadi Nazem, Mashallah Rezakazemi, Saeed Shirazian, Predictive construction of phase diagram of ternary solutions containing polymer/solvent/nonsolvent using modified Flory-Huggins model. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Molliq(2017), doi:10.1016/j.molliq.2018.05.015

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Predictive construction of phase diagram of ternary solutions containing polymer/solvent/nonsolvent using modified Flory-Huggins model

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Abstract

The Flory-Huggins (FH) model has been one of the most used models in theoretical calculations which has been proved to be sensitive to values assigned as interaction parameters. In this work, a predictive equation is implemented to implicitly couple the concept of compressible regular solution theory of Ruzette and Mayes into the original FH model to obtain a new concentration-dependent interaction parameter equation. Then, the modified model (m-FH) is applied for construction of phase diagram of ternary solutions containing polymer/solvent/nonsolvent where experimental data for ternary systems were collected from the literature. In order to compare and analyze the model performance, the
individual absolute relative deviation (IARD (%)) was used. The m-FH model revealed acceptable accuracy in calculations without prior need for correlation to experimental data.

**Keywords:** Flory-Huggins model; Interaction parameter; Compressible regular solutions; Polymeric solutions; Membranes

1. Introduction

Membrane separation has attracted much attention due to its superior characteristics compared to other separation processes [1-8]. For researchers dealing with membranes, the phase behavior of polymer solutions is of much interest in fabrication of polymeric membranes at dope solution preparation stage [9] where theoretical analysis of thermodynamic models comes to attention [10-13]. It would help reduce associated experimental costs [14], which itself results in development of models in the form of equations of state [15-17], empirical equations [18, 19], activity coefficient models [20-23] and etc. There are various models for the thermodynamic study of binary and multicomponent systems among which the Flory-Huggins (FH) model [24-32] is of great interest due to its unique properties. In this model, some interaction parameters are defined that need to be correlated to experimental data so that behavior of non-ideal mixtures and thermodynamic and equilibrium properties can be reliably determined [33-35]. How consistence this correlation is, the model will perform that much well in accuracy [30-32, 36-39].

Literature review shows that there have been investigations conducted for evaluation of phase behavior of polymeric solutions used in polymeric membranes [30]. Ejraei et al. [23] investigated the phase behavior of 169 binary solutions for modeling of lower and upper
critical solution temperatures. For some weakly interacting polymer blends, Ruzette and Mayes [40, 41] studied the phase behavior of polymeric blends. The construction of phase diagram of various ternary polymeric solutions containing nonsolvent/solvent/polymer has been addressed by various researchers both theoretically and experimentally [23, 41-43]. Arslan [44] studied thermodynamic and kinetic data of membrane forming systems including polysulfone (PSf) / 1-methyl-2-pyrrolidinone (NMP) / water, PSf / tetrahydrofuran (THF) / water, PSf / NMP / ethanol, PSf / THF / ethanol, polymethyl methacrylate (PMMA) / acetone / water, PMMA / THF / water, PMMA / acetone / formamide and PMMA / THF / formamide systems. Keshavarz et al. [45] investigated phase diagram construction of ternary polymeric solutions including polyethersulfone (PES) / NMP / water and cellulose acetate (CA) / acetone (AC) / water. Aroon et al. [46] studied effects of non-solvent additives, polymeric additives, polymer concentration and volatile solvent on the performance and morphology of polysulfone flat sheet gas separation membranes. Kools [47] investigated the binodal curves of systems consisting of two nonsolvents, a solvent and a polymer, and also systems composed of two solvents, one nonsolvent and a polymer. Boom et al. [48, 49] investigated a quaternary membrane-forming system consisting of a nonsolvent, a solvent, a membrane forming polymer and a polymeric additive. Burra [50] investigated the effect of interaction parameter of Flory-Huggins model for a number of ternary systems systematically and found the strong dependency of model performance on its interaction parameter correlations. The same observation was reported in the work of other researchers [51-53] pointing out that the accuracy of Flory-Huggins model depends on the robustness and reliability of employed interaction parameter (χ) [38, 40], which can be measured experimentally or calculated by some phase equilibria calculations as found elsewhere [30, 37-39, 42, 52]. The aim of present work is, therefore, to modify the Flory-Huggins model so that a final pure predictive version
can be obtained which is then examined for the applicability in practical phase calculations of ternary polymeric solutions.

2. Modified Flory-Huggins model

For a binary solution, the Flory-Huggins model [30] has been given as in Eq. 1 where \( \phi_i \) indicates volume fraction, \( N_i \) number of segments of volume \( v_i \) for molecules \( i \), \( k \) the Boltzmann constant and \( \chi_{AB} \) Flory-Huggins interaction parameter. The subscript \( A \) and \( B \) indicates components:

\[
\frac{\Delta G_m}{kT} = \phi_A \ln \phi_A + \phi_B \ln \phi_B + \frac{\phi_A \phi_B \chi_{AB}}{N_A v_A N_B v_B} \tag{1}
\]

In literature [38], a model for Flory-Huggins interaction parameter has been introduced by the combination of regular solution model of Flory-Huggins and regular solution model of Ruzette and Mayes [40] as given in Eq. 2:

\[
\chi_{AB} = (\beta_i^A - 1) \frac{\sqrt{v_A v_B}}{N_A v_A} \phi_A \ln \phi_A + (\beta_i^B - 1) \frac{\sqrt{v_A v_B}}{N_B v_B} \phi_B \ln \phi_B + \beta_i^A \beta_i^B \phi_A \phi_B \sqrt{v_A v_B} (\delta_{i,0} - \delta_{i,0})^2 L \\
+ (\beta_i^A - \beta_i^B) (\delta_{A}^2 - \delta_{B}^2) \sqrt{v_A v_B} \tag{2}
\]

where, \( \beta_i \) is the reduced density of component \( i \), \( v_i \) the hardcore volume of the component \( i \), \( \delta_{i,0} \) the hardcore solubility parameter at 0 K. The reduced density (\( \beta_i \)) can be calculated from the Sanchez and Lacombe’s lattice-fluid (LF) equation of state [42]. The hardcore solubility parameters \( \delta_i \) and \( \delta_i^2 (298) \) can be calculated from a group contribution method such as the Hoftyzer and van Krevelen group contribution method [41]. For calculation of \( N_i v_i \), one might use \( N_i v_i = M_w / \rho^* \) equality [31, 41], where \( M_w \) is the molecular weight of components (for the polymer, the repeating unit). \( N_i \), the number of segments in hardcore, itself, can be
obtained as \( N_i = M_w P^*/R^* T^* \rho^* \). \( \rho^* \) is the lattice-fluid (LF) scaling constant of Sanchez and Lacombe [51] calculated using Boudouris et al. [51, 53] modified group contribution method of Constantinou and Gani [51]. For the detailed instruction of the application of covered methods, the interested reader may refer to Ref. [45].

Combining Eq. 2 and Eq. 1, the final model can be pure predictive and expected to be reliable as it implements Compressible regular solution (CRS) theory implicitly in its relationships [54]. Then, the chemical potentials for compound \( A \) and compound \( B \), can be given as in Eqs. 3-4 [51, 55] where \( V_i \) is molar volume:

\[
\frac{\Delta \mu_A}{RT} = \ln \varphi_A - \left[ 1 - \frac{V_A}{V_B} \right] \varphi_B + \chi \varphi_B^2
\]

\[
\frac{\Delta \mu_B}{RT} = \ln \varphi_B - \left[ 1 - \frac{V_B}{V_A} \right] \varphi_A + \chi \varphi_A^2
\]

Similarly, for ternary solutions, for which the Flory-Huggins model expression is given as in Eq. 5 [12, 18, 45] where subscripts \( A-C \) respectively indicates the compounds, the corresponding chemical potential relationships are given as in Eqs. 6-8 [26, 52] where \( \chi_{ij} \) is the Flory-Huggins interaction parameter between compound \( i \) and \( j \) can be inserted from Eq. 2 as given elsewhere in details [47]:

\[
\frac{\Delta G_m}{RT} = n_A \ln \varphi_A + n_B \ln \varphi_B + n_C \ln \varphi_C + \chi_{AB} n_A \varphi_B + \chi_{AC} n_A \varphi_C + \chi_{BC} n_B \varphi_C
\]

\[
\frac{\Delta \mu_A}{RT} = \ln \varphi_A - \frac{V_A}{V_B} \varphi_2 - \frac{V_A}{V_C} \varphi_C + \left[ (1 + \chi_{AB} \varphi_B + \chi_{AC} \varphi_C) (1 - \varphi_A) \right] - \varphi_B \varphi_C \left( \frac{V_A}{V_B} \chi_{BC} \right) - \frac{\varphi_B \varphi_C}{(\varphi_B + \varphi_C)^2} \left( \frac{d \chi_{AB}}{\varphi_B + \varphi_C} \right)
\]
For quaternary solutions, the Flory-Huggins model expressions can be found elsewhere [27, 52] as given by Eq. 9 where subscripts A-D respectively indicate components:

$$\frac{\Delta G_m}{RT} = n_A \ln \phi_A + n_B \ln \phi_B + n_C \ln \phi_C + n_D \ln \phi_D + \chi_{AB} n_A \phi_B + \chi_{AC} n_A \phi_C + \chi_{AD} n_A \phi_D + \chi_{BC} n_B \phi_C + \chi_{BD} n_B \phi_D + \chi_{CD} n_C \phi_D$$

The corresponding chemical potential relationships are given as in Eqs. 10-13 [31, 47, 56] where \(\chi_{ij}\) is the Flory-Huggins interaction parameter between compound \(i\) and \(j\) can be inserted from Eq. 2.

$$\frac{\Delta \mu_A}{RT} = \ln \phi_A - \frac{V_A}{V_B} \phi_B - \frac{V_A}{V_C} \phi_C - \frac{V_A}{V_D} \phi_D + \left( 1 + \chi_{AB} \phi_B + \chi_{AC} \phi_C + \chi_{AD} \phi_D \right) \left( 1 - \phi_A \right)$$

$$- \phi_A \phi_B \frac{V_A}{V_B} \chi_{BC} - \phi_A \phi_D \frac{V_A}{V_D} \chi_{BD}$$

$$\frac{\Delta \mu_B}{RT} = \ln \phi_B - \frac{V_B}{V_A} \phi_A - \frac{V_B}{V_C} \phi_C - \frac{V_B}{V_D} \phi_D + \left( 1 + \chi_{AB} \frac{V_B}{V_A} \phi_A + \chi_{BC} \phi_C + \chi_{BD} \phi_D \right) \left( 1 - \phi_B \right)$$

$$- \phi_A \phi_B \frac{V_B}{V_A} \chi_{AC} - \phi_A \phi_D \frac{V_B}{V_D} \chi_{AD} - \phi_C \phi_D \frac{V_B}{V_C} \chi_{CD}$$
With regard to the application of thermodynamic models in equilibrium calculations, it is known that when two arbitrary phases of $I$ and $II$ are contacted, the chemical potentials of each compound in two contacting phases must be equal [56] at the operating conditions i.e. temperature ($T$) and pressure ($P$) as given by Eq. 14 [29, 47, 56]:

$$
\frac{\Delta \mu}{RT} = \ln \phi_c - \frac{V_C}{V_A} \phi_A - \frac{V_C}{V_B} \phi_B - \frac{V_C}{V_D} \phi_D + \left( 1 + \chi_{AC} \frac{V_C}{V_A} \phi_A + \chi_{BC} \frac{V_C}{V_B} \phi_B + \chi_{CD} \frac{V_C}{V_D} \phi_D \right) (1-\phi_C)
$$

$$
-\phi_A \phi_B \frac{V_C}{V_A} \chi_{AB} - \phi_A \phi_D \frac{V_C}{V_A} \chi_{AD} - \phi_B \phi_D \frac{V_C}{V_B} \chi_{BD}
$$

$$
\frac{\Delta \mu}{RT} = \ln \phi_d - \frac{V_D}{V_A} \phi_A - \frac{V_D}{V_B} \phi_B - \frac{V_D}{V_C} \phi_C + \left( 1 + \chi_{AD} \frac{V_D}{V_A} \phi_A + \chi_{BD} \frac{V_D}{V_B} \phi_B + \chi_{CD} \frac{V_D}{V_C} \phi_C \right) (1-\phi_D)
$$

$$
-\phi_A \phi_B \frac{V_D}{V_A} \chi_{AB} - \phi_A \phi_C \frac{V_D}{V_A} \chi_{AC} - \phi_B \phi_C \frac{V_D}{V_B} \chi_{BC}
$$

With regards to the application of thermodynamic models in equilibrium calculations, it is known that when two arbitrary phases of $I$ and $II$ are contacted, the chemical potentials of each compound in two contacting phases must be equal [56] at the operating conditions i.e. temperature ($T$) and pressure ($P$) as given by Eq. 14 [29, 47, 56]:

$$
\mu_i^I = \mu_i^II
$$

One can rewrite Eq. 14 as shown by Eq. 15 where superscript $I$ and $II$ respectively accounts for polymer rich and polymer lean phases which are connected to each other by a tie-line. Subscript $i$ denotes the compound $i$, $\mu$ denotes the chemical potential and $\Delta$ accounts for the change in chemical potential referring to a reference state [26]:

$$
\mu_i^I - \mu_i^0 = \mu_i^II - \mu_i^0 \rightarrow \Delta \mu_i^I = \Delta \mu_i^II
$$

From Eq. 15, chemical potential and the material balances, $\sum \phi_i^I = 1$ and $\sum \phi_i^II = 1$, the equilibrium points can be evaluated and determined [26, 57]. Then, the calculated data can be compared to the experimentally measured data for assessment of model prediction ability.
3. Dataset used

For evaluation of modified Flory-Huggins mode, a number of data were collected from the literature. The data are collected from the most commonly used systems in membrane fabrication. For binary solutions, we have just evaluated the reliability of model equations in Ref. [45] for binary systems THF + poly-vinyl-methyl-ether and THF + polystyrene (data from [26]). So, here, ternary and quaternary systems are concerned. For assessment of modified Flory-Huggins model for ternary systems, here two case studies are used; PES - NMP – distilled Tap water (H2O) at 27 °C and PSf – NMP - H2O at 38 °C, for which the experimental data are retrieved from our previous work [45]. The selection is because model performance can be compared to other models used in the study of Ghasemi et al. [13] also. For quaternary solutions, data of PES / Cellulose Acetate Propionate (CAP) / NMP / Water were retrieved from Ref. [31], data of CO2 / 1-dodecanol / dodecanoic acid / quinoxaline and CO2 / 1-dodecanol / dodecanoic acid / 1,8-octanediol were retrieved from Ref. [58].

In order to compare and analysis models performance, the Individual Absolute Relative Deviation (IARD (%)) was used as defined in Eq. 16:

\[
IARD(\%) = 100 \left( \frac{\left| x_{Exp}^i - x_{Cal}^i \right|}{x_{Exp}^i} \right)
\]

where, \(x_{Exp}^i\) and \(x_{Cal}^i\) shows the experimental and calculated points, respectively.

4. Results and discussion

The modified Flory-Huggins model was used to calculate equilibrium data of binary, ternary and quaternary solutions. The model is already validated for binary systems in a recent work of authors [13]. For ternary systems of PES/NMP/distilled tap water (H2O) at 27 °C and
PSf/NMP/H₂O at 38 °C ternary systems, the model was applied and results are shown in Fig. 1 and Fig. 2 respectively.

Fig. 1. The binodal curve (bold solid line), measured cloud point (solid circles) from Ref. [13] and tie-lines (dotted lines) for ternary system PES/NMP/H₂O.
Fig. 2. The binodal curve (bold solid line), measured cloud point (solid circles) from Ref. [59] and tie-lines (dotted lines) for ternary system PSf/NMP/H\(_2\)O.

Desirable agreement between experimental and calculated data was obtained as can be concluded from Fig. 1 and Fig. 2. The accuracy of predictions by modified Flory-Huggins model is given in Table 1 and Table 2 for PES/NMP/H\(_2\)O at 27 °C and PSf/NMP/H\(_2\)O at 38 °C ternary systems in terms of IARD (%).

Table 1. Comparison of model calculated and experimental data for PES/NMP/H\(_2\)O ternary system (data from Ref. [60]).

<table>
<thead>
<tr>
<th>Polymer Lean Phase</th>
<th>Polymer Rich Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>01</strong></td>
<td><strong>02</strong></td>
</tr>
<tr>
<td>Exp.</td>
<td>IARD (%)</td>
</tr>
<tr>
<td>0.53</td>
<td>0.72</td>
</tr>
<tr>
<td>0.49</td>
<td>0.04</td>
</tr>
<tr>
<td>0.45</td>
<td>0.39</td>
</tr>
<tr>
<td>0.41</td>
<td>0.94</td>
</tr>
</tbody>
</table>
Table 2. Comparison of model calculated and experimental data for PSf/NMP/H₂O ternary system (data from Ref. [31]).

<table>
<thead>
<tr>
<th>POLYMER LEAN PHASE</th>
<th>POLYMER RICH PHASE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp.</td>
<td>IARD (%)</td>
</tr>
<tr>
<td>0.37</td>
<td>0.23</td>
</tr>
<tr>
<td>0.35</td>
<td>0.73</td>
</tr>
<tr>
<td>0.32</td>
<td>0.86</td>
</tr>
<tr>
<td>0.30</td>
<td>0.31</td>
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<tr>
<td>0.28</td>
<td>0.46</td>
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<tr>
<td>0.27</td>
<td>0.10</td>
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<tr>
<td>0.26</td>
<td>0.71</td>
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<tr>
<td>0.25</td>
<td>0.40</td>
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<tr>
<td>0.23</td>
<td>0.33</td>
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<td>0.22</td>
<td>0.10</td>
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<tr>
<td>0.21</td>
<td>0.37</td>
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<tr>
<td>0.20</td>
<td>0.58</td>
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<tr>
<td>0.19</td>
<td>0.63</td>
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<tr>
<td>0.18</td>
<td>0.99</td>
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<tr>
<td>0.17</td>
<td>0.66</td>
</tr>
<tr>
<td>0.16</td>
<td>0.02</td>
</tr>
<tr>
<td>0.16</td>
<td>0.35</td>
</tr>
</tbody>
</table>
Ghasemi et al. [13] also made a theoretical analysis for these systems and compared different thermodynamic modeling approaches and models. Our modified version of Flory-Huggins model is compared with models considered in their work. The best correlation result reported by Ref. [13] in terms of AARD % (average of IARD % overall data points) is 2.47 while m-FH model results in an AARD % value of 1.85.

For a quaternary system of PES/CAP/NMP/Water (data from Ref. [13]), modified Flory-Huggins model was used for calculations and the results are shown in Fig. 3. Consistency results were obtained for calculation of equilibrium data of the studied system. For quaternary system data of CO₂ / 1-dodecanol / dodecanoic acid/quinoxaline and CO₂/1-dodecanol + dodecanoic acid / 1,8-octanediol (retrieved from Ref. [60]), the modified Flory-Huggins model was used and results are shown in Fig. 4.
Fig. 3. The equilibrium curve (bold solid line), measured cloud point (solid circles) from Ref. [13] for quaternary system PES/CAP/NMP/H$_2$O.

Fig. 4. The accuracy of modified Flory-Huggins for quaternary system data of CO$_2$ / 1-dodecanol / dodecanoic acid / quinoxaline and CO$_2$ / 1-dodecanol + dodecanoic acid / 1,8-octanediol (data from Ref. [60]).

Noting to the results, it can be readily concluded that the modified Flory-Huggins model is highly reliable in calculations. Employing implicitly compressible regular solution theory of Ruzette and Mayes into the original Flory-Huggins model particularly in interaction parameter equation, the final model was pure predictive and computationally feasible. High accuracy and the low deviation between experimental and calculated data showed the reliability of this modification.
5. Conclusions

In this work, attempts were made to modify the Flory-Huggins model by utilization of a predictive equation for interaction parameters. The modified Flory-Huggins model revealed acceptable ability in the calculation of binodal curve without the need of any experimental data for prior estimation and determination of interaction parameters as the modified model uses a predictive expression for evaluation of interaction parameters which is concentration dependent that increases its consistency to system phase behavior. The modification, in a way, implements/couples the predictive ability of compressible regular solution (CRS) into the original Flory-Huggins model implicitly and the CRS model has shown considerable versatility in the description of the phase behavior of various systems. The modification applied to the original Flory-Huggins model provides a simple and easy to use method for wider application of the model. The application of the modified model in equilibrium calculation showed desirable agreement to the experimental data. It can be used for estimation of interaction parameters prior to experimental measurements.

References


[60] A. Kordikowski, G.M. Schneider, Fluid phase equilibrium studies on ternary and quaternary mixtures of carbon dioxide with 1-dodecanol, dodecanoic acid, quinolaxine and
1,8-octanediol at 393.2 K and at pressures up to 40 MPa, Fluid Phase Equilibria, 105 (1995) 129-139.
Research Highlights

- Development of a thermodynamic model for prediction of liquid phase equilibria
- Predicting phase diagram of ternary solutions containing polymer/solvent/nonsolvent
- Modification of the Flory-Huggins (FH) model
- Obtaining a new concentration-dependent interaction parameter for FH model