Vapor-Liquid Equilibrium Data Prediction by Advanced Group Contribution Methods for a Binary System of Cyclopentyl methyl ether and Acetic acid at Atmospheric Pressure

Parsana V.M. 1,2,* and Parikh S.P. 2
1 School of Engineering, RK University, Rajkot, INDIA
2 Chemical Engineering Department, V.V.P. Engineering College, Gujarat Technological University, Ahmedabad, INDIA

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Abstract

The isobaric vapour-liquid equilibrium data predictions for the binary system of cyclopentyl methyl ether and acetic acid have been obtained using UNIFAC method and modified UNIFAC Dortmund method. Group identification is done with Dortmund Data Bank and the same has been confirmed by artist free software. The interaction parameters in the UNIFAC method and modified UNIFAC Dortmund method, for the ether group (-CH\textsubscript{3}O) and acid (-COOH), are used to predict VLE data. Thermodynamic consistency of the predicted VLE data has been checked by the Herington method. The predicted data have been correlated with Van Laar, Wilson and NRTL activity coefficient models. The binary interaction parameters of models had been obtained by regression. The predicted VLE data of UNIFAC method fit much more accurately than that of modified UNIFAC Dortmund method by these activity coefficient models Van Laar, Wilson and NRTL.

Keywords: Vapor-liquid equilibrium, cyclopentyl methyl ether, acetic acid, UNIFAC method, modified UNIFAC Dortmund method.

Introduction

Traditional solvents play a key role in the chemical process industries and hence they are major contributor to the concerns related to their impact on environment, health and safety because most of the solvents are flammable, volatile and toxic. The solvents that have reduced or no toxicity to health and environment compared to the traditional solvents are called green solvents. These green solvents may provide an attractive alternative to the traditional solvents. Cyclopentyl methyl ether (CPME) is considered to be one of the green solvents which has high boiling point (379.15 K) and preferable characteristics such as low peroxide formation, high hydrophobicity, relative stability under acidic and basic conditions, high boiling point and low melting point, low heat of vaporization, narrow explosion area and low solubility of salts. Due to such characteristics CPME is preferred as an alternative to other ethereal solvents such as tetrahydrofuran, 2-methyl tetrahydrofuran, dioxane (carcinogenic), and 1, 2-dimethoxyethane, which are hazardous to human health and environment.

The recovery of acetic acid from water has become industrial problem of public concern because this separation process has a major influence on economy of products, resource utilization and important meanings for environmental protection. Hongxun Zhang, Guangyu Liu, Chen Li, et al. measured liquid-liquid equilibria of water + acetic acid + Cyclopentyl methyl ether (CPME) system at different temperatures and concluded that CPME would be a good substitute for conventional organic solvents to separate acetic acid from water by the method of liquid–liquid extraction followed by heteroazeotropic distillation. After literature survey it is found that vapour-liquid equilibrium data for CPME + Acetic acid system which is essential for the design of distillation column for separating CPME and acetic acid from their mixture does not exist in the literature. So investigation on VLE data of this binary system becomes necessary. The experimental determination of VLE data requires sophisticated and suitable VLE apparatus and composition measurement instruments such as gas chromatograph, refractometer, spectrophotometer, etc. So this procedure is very costly and time-consuming. Numerical simulations using group contribution methods provide an alternative to experimental measurement of VLE data. The aim of this paper is to predict VLE data for CPME with acetic acid at atmospheric pressure.

Advanced Group Contribution Methods: Reliable values of the properties of materials are necessary for the design of industrial processes. The knowledge of physical properties of fluids is essential in the design of many kinds of products, processes, and industrial equipment. The vapour-liquid equilibrium (VLE) data are essential for the design of chemical and separation processes. When experimental binary data are available, phase equilibrium behaviour is easily modelled with the help of cubic equation of state (using fugacity coefficient data) and local composition models (using activity coefficient data). When little or no experimental data are available, group
contribution (GC) methods can be employed to predict the phase equilibrium under specified conditions of temperature and composition\(^{5,6}\). So prediction of thermodynamic properties is important in chemical process and product design. Various GC methods are available for the prediction of VLE data. Some examples of GC methods which have been developed for the estimation of properties of pure compounds include those published by Joback and Reid\(^{7}\), Lydersen\(^{8}\), Ambrose\(^{9}\), Constantinou and Gani\(^{10}\) and Marrero and Gani\(^{11,12}\). On the other hand, many GC based property models have also been developed to predict properties of mixtures mainly to predict the non-ideality of the liquid phase using activity coefficients which includes ASOG\(^{13,14}\), Original UNIFAC\(^{15}\), Modified UNIFAC Dortmund\(^{16}\) and PSRK\(^{17}\). In the present work, well known and established group-contribution methods such as UNIFAC method and modified UNIFAC Dortmund method are employed to predict liquid phase activity coefficients for binary mixtures of CPME and acetic acid.

**UNIFAC method and modified UNIFAC Dortmund methods**: The general UNIFAC equation is as follows with the combinatorial and residual contributions:

\[
\ln \gamma_i = \ln \gamma_i^{(\text{combinatorial})} + \ln \gamma_i^{(\text{residual})} \tag{1}
\]

The combinatorial part,

\[
\ln \gamma_i^{(\text{combinatorial})} = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_j x_j l_j
\tag{2}
\]

Where,

\[
l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1)
\tag{3}
\]

\[
\theta_i = \frac{q_i x_i}{\sum_j q_j x_j}
\tag{4}
\]

\[
\Phi_i = \frac{r_i x_i}{\sum_j r_j x_j}
\tag{5}
\]

\[
r_i = \sum_v v^{(i)} R_k
\tag{6}
\]

\[
q_i = \sum_v v^{(i)} Q_k
\tag{7}
\]

\[
R_k = \frac{V_{wk}}{15.17}
\tag{8}
\]

\[
Q_k = \frac{A_{wk}}{2.5 \times 10^9}
\tag{9}
\]

Where:\(V^{(i)}\), always an integer, is the number of groups of type \(k\) in molecule \(i\). Group parameters \(R_k\) and \(Q_k\) are obtained from the van der Waals group volume and surface areas \(V_{wk}\) and \(A_{wk}\), given by Bondi\(^{18}\). The value of parameter \(Z\) is taken as 10.

And the residual part,

\[
\ln \gamma_i^{(\text{residual})} = \sum_k \gamma^{(i)} \left( \ln \Gamma_k - \ln \Gamma^{(i)}_k \right)
\tag{10}
\]

Where,

\[
\ln \Gamma_k = Q_k \left( 1 - \ln \left( \sum_m \theta_m \Psi_{mn} \right) - \sum_m \sum_n \theta_m \Psi_{nm} \right)
\tag{11}
\]

Where, the group area fraction \(\theta_m\) and group mole fraction \(X_m\) are given by the following equations:

\[
\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n}
\tag{12}
\]

\[
X_m = \frac{\sum_j \gamma^{(j)} X_j}{\sum_j \sum_n \gamma^{(j)} X_j}
\tag{13}
\]

Where, the group-interaction parameter \(\Psi_{mn}\) is given by the following equation:

\[
\Psi_{mn} = \exp \left( -\frac{U_{mn} - U_{nm}}{RT} \right) = \exp \left( -\frac{a_{mn}}{T} \right)
\tag{14}
\]

Where: \(U_{mn}\) is a measure of the energy of interaction between group \(m\) and \(n\). Note that \(a_{mn}\) has unit of Kelvin and \(a_{mn} \neq a_{nm}\).

In the Original UNIFAC model, the interaction parameters are considered to be independent of temperature. Therefore, quantitative predictions of excess enthalpies, \(H^E\) could not be obtained. In order to improve this and other things, the modified UNIFAC Dortmund method was developed. The usage of modified UNIFAC Dortmund method leads to much better results. This means that the introduction of temperature-dependent parameters allows a more reliable temperature extrapolation and the extension of the range of applicability\(^{18,19}\). In both UNIFAC method and modified UNIFAC Dortmund method, there is a difference in both combinatorial and residual part. These differences are given in the following equations.

In modified UNIFAC Dortmund method, equation-2 and equation-14 of UNIFAC method are replaced by equation-15
and equation-19 as described below.

\[
\ln \gamma_{(\text{combinatorial})} = 1 - V_i + \ln V_i - 5q_i \left(1 - \frac{V_i}{R_i} + \ln \frac{V_i}{R_i}\right)
\]  

(15)

Where,

\[
V_i = \frac{r_i}{\sum_j x_i R_j}
\]

(16)

\[
F_i = \frac{q_i}{\sum_j x_i Q_j}
\]

(17)

\[
V' = \frac{r_i^{3/4}}{\sum_j x_i r_j^{3/4}}
\]

(18)

and

\[
\Psi_{mn} = \exp \left(-\frac{a_{mn} + b_{mn} T + c_{mn} T^2}{T}\right)
\]

(19)

In addition to that, in the residual part, temperature dependent interaction parameters are used where they have a logarithmic and quadratic dependency towards temperature. Due to this temperature dependency, the predictions of VLE, H and γ have improved since it is based on more experimental data. The modified UNIFAC Dortmund method can also extrapolate reliably the predictions of VLE at higher temperatures compared to the Original UNIFAC\textsuperscript{19}.

Group identification of the compounds: Group contribution methods predict properties of pure compounds or mixtures based on the groups existing in the compounds so correct identification of groups is very essential. Group identification for UNIFAC method is done using the data given in the literature\textsuperscript{4} and for modified UNIFAC Dortmund method it is done using the data given in the literature\textsuperscript{18}. The identified groups are presented in table-1 and table-2 respectively. The identified groups have been verified with Dortmund data bank by using artist free software.

Binary interaction parameters (BIPs): Binary interaction parameters (a_{mn}) for UNIFAC method have been taken from the literature\textsuperscript{4} and (a_{mn}, b_{mn}, and c_{mn}) for modified UNIFAC Dortmund method have been taken from the literature\textsuperscript{18,19,20} which are presented in table-3 and table-4 respectively.

Calculation of VLE data using group contribution methods: The VLE data for binary system CPME and acetic acid are calculated through a spread sheet in which temperature T and x_j are given as input and γ_1 and γ_2 are calculated using group contribution methods as described in the previous sections. Using Antoine equation-20, p_1^{sat} and p_2^{sat} are calculated, then total pressure P is calculated and correct temperature T is found out by regression using equation-23. The calculated data are presented in table-5 and table-6 for UNIFAC method and modified UNIFAC Dortmund method respectively.

### Table-1

<table>
<thead>
<tr>
<th>Molecule (i)</th>
<th>Name</th>
<th>Group no.</th>
<th>v_k (°)</th>
<th>R_k</th>
<th>Q_k</th>
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<tr>
<td></td>
<td></td>
<td>M</td>
<td>S</td>
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<td></td>
</tr>
<tr>
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<td>CH\textsubscript{2}</td>
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<td>2</td>
<td>4</td>
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<td>24</td>
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<td>1.1450</td>
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</table>

M=Main Group no., S=Secondary Group no.

### Table-2

<table>
<thead>
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<th>v_k (°)</th>
<th>R_k</th>
<th>Q_k</th>
</tr>
</thead>
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<td>M</td>
<td>S</td>
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<td></td>
</tr>
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M=Main Group no., S=Secondary Group no.

### Table-3

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<th>CH\textsubscript{3}O</th>
<th>COOH</th>
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<td>315.3</td>
<td>315.3</td>
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</table>

The Antoine equation,

\[
\ln p_i^{sat} = A_i - \frac{B_i}{T + C_i}
\]

(20)

Where pressure is in kPa and temperature is in Kelvin\textsuperscript{21}. The constants A, B, and C of Antoine equations of CPME and acetic acid are listed in table-7.

Thermodynamic Consistency Test: The thermodynamic consistency of the predicted VLE data for the binary system is checked by semi-empirical Herington method. In this method, the values for D and J are found out by equation-21 and equation-22 respectively. If the value of D – J is not larger than 10 then the predicted VLE data are said to be thermodynamically consistent. The values of D – J for the
binary systems are listed in Table-8.

\[
D = 100 \frac{\int_{x_1=0}^{x_1=1} \ln \frac{y_1}{y_2} \, dx_1}{\int_{x_1=0}^{x_1=1} \ln \frac{y_1}{y_2} \, dx_1}
\]

\[J = 150 \frac{T_{\text{max}} - T_{\text{min}}}{T_{\text{min}}}
\]

Data Reduction Using g^K Models: The predicted VLE data are correlated by various models such as Van Laar, Wilson and NRTL\textsuperscript{24,25}. The vapor pressures of pure components are calculated by equation-20. By the minimization of the objective function \(\%\text{AAD} \Sigma (\delta P)\), the binary interaction parameters are obtained for these models which are used to minimize error by the regression procedure. (\%\text{AAD} = \text{absolute average deviation and n represents no. of predicted data points}) Similarly AAD \(\Sigma (\delta T)\) and AAD \(\Sigma (\delta y)\) are calculated by equation-24 and equation-25 respectively. The “pre” and “cal” subscripts represent the predicted and calculated values respectively.

\[
\%\text{AAD} \Sigma (\delta P) = \frac{100}{n} \sum_{i=1}^{n} \frac{|P_{\text{pre},i} - P_{\text{cal},i}|}{P_{\text{pre},i}}
\]

\[
\text{AAD} \Sigma (\delta T) = \frac{1}{n} \sum_{i=1}^{n} |T_{\text{pre},i} - T_{\text{cal},i}|
\]

\[
\text{AAD} \Sigma (\delta y) = \frac{1}{n} \sum_{i=1}^{n} |y_{\text{pre},i} - y_{\text{cal},i}|
\]

### Table-4

<table>
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<tr>
<th>Group</th>
<th>m</th>
<th>n</th>
<th>(a_{mn})</th>
<th>(b_{mn})</th>
<th>(c_{mn})</th>
<th>(a_{nm})</th>
<th>(b_{nm})</th>
<th>(c_{nm})</th>
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### Table-5

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### Table-6

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<th>(y_2)</th>
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The binary interaction parameters, correlated from predicted VLE data by UNIFAC method and modified UNIFAC Dortmund method, are shown in table-9 and table-10 respectively. α which is a characteristic constant of the non-randomness for the binary system is recommended as 0.3 for this binary system because it belongs to type I system according to the definition given in the literature. The comparison of predicted data by UNIFAC method and modified UNIFAC Dortmund method with calculated T-x1-y1 data by Van Laar, Wilson, and NRTL models for the binary system CPME (1) + acetic acid (2) at atmospheric pressure is given through figure-1 to figure-6.
Figure-2
T-x₁-y₁ diagram calculated by Wilson and predicted by UNIFAC method

Figure-3
T-x₁-y₁ diagram calculated by NRTL and predicted by UNIFAC method
Figure 4

T-x<sub>1</sub>-y<sub>1</sub> diagram calculated by Van Laar and predicted by modified UNIFAC Dortmund method.

Figure 5

T-x<sub>1</sub>-y<sub>1</sub> diagram calculated by Wilson and predicted by modified UNIFAC Dortmund method.
From figure-1 to figure-6, it can be seen that isobaric VLE data predicted by UNIFAC method and modified UNIFAC Dortmund method are very well represented by Van Laar, Wilson and NRTL models.

**Conclusion**

The VLE data for the binary system CPME with acetic acid have been predicted at atmospheric pressure using UNIFAC method and modified UNIFAC Dortmund method. The activity coefficient models Van Laar, Wilson and NRTL have been found capable of accurately fitting the predicted VLE data by UNIFAC method and modified UNIFAC Dortmund method. However, they fail the consistency test by Herington. Azeotrope formation is found for this system.

**Nomenclature**

- $P$ - Absolute pressure, kPa
- $T$ - Absolute temperature, K
- $\theta_i$ - Surface area fraction of compound i
- $\Phi_i$ - Volume fraction of compound i
- $r_i$ - Relative Van der Waals volume of compound i
- $q_i$ - Relative Van der Waals surface area of compound i
- $Q_k$ - Relative Van der Waals surface area of subgroup k
- $R_k$ - Relative Van der Waals volume of subgroup k
- $\Gamma^*$ - Temperature dependent integration constant
- $\theta_m$ - Surface area fraction of subgroup m

- $X_m$ - Mole fraction of subgroup m
- $\Psi$ - Group-interaction parameter
- $V_i$ - Volume/mole fraction of compound i in the mixture
- $F_i$ - Surface area fraction of compound i in the mixture
- $V'_i$ - Modified volume/mole fraction of compound i in the mixture (modified UNIFAC Dortmund method)
- $\ln$ - Natural logarithm (base e)
- $\log$ - Logarithm (base 10)
- $x_i$ - Liquid phase mole fraction of $i^{th}$ species
- $y_i$ - Vapor phase mole fraction of $i^{th}$ species
- $\gamma_i$ - Activity coefficient of $i^{th}$ species
- $H^E$ - Excess enthalpy
- $A_{ij}$ - Adjustable parameter (Van Laar Model)
- $\lambda_{ij}$ - Interaction parameter (Wilson Model)
- $\Lambda_{ij}$ - Adjustable parameter (Wilson Model)
- $\alpha_i$ - The non-randomness of the fluid empirical parameter
- $\tau_i$ - Adjustable parameter (NRTL Model)
- $A, B, C$ - Antoine equation constants

**Superscripts**

- $E$ - Excess property
- $\text{sat}$ - Saturated property value
- $\infty$ - Property at infinite dilution concentration

**Subscripts**

- 1 - Component 1
References


6. 3rd International Conference on Medical Sciences and Chemical Engineering (ICMSCE'2013), Bangkok (Thailand), Dec. 25-26, (2013)


