OPTIMIZATION OF GIBBS FREE ENERGY MODEL FOR BINARY MIXTURE

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ABSTRACT
Thermodynamics is mostly concerned with a theory dealing with equilibrium and into one concerned with irreversible processes. The development of an accurate theory for associating fluids has been a challenging field of research in Thermodynamics. Phase Equilibrium study is the key job to be carried out in any equipment design. Experimental phase equilibrium experiments has been carried out for binary system using differential Ebulliometer. In chemical industries during the process design especially for distillation and liquid-liquid separation systems, it is important to evaluate activity coefficients values to carry out phase equilibrium calculations. However, experimental data on activity coefficients from literature survey of various types of liquid solutions are mostly unavailable at desired temperature or composition in which we are interested. In such cases activity coefficient models - which relate $G^E$ to solution composition (at a given T & P) are useful. These models are all characterized by a set of parameters that are temperature dependent. The Vapour liquid equilibrium (VLE) equation is which in which the vapour and liquid phase composition is in equilibrium at desired temperature and pressure. The VLE relation that applies to low pressure systems is that containing an ideal gas phase, but a non-ideal liquid phase. With this purpose and due to the lack of accurate experiment equipment we have taken Vapour liquid equilibrium (VLE) data from others work. Here we present the various forms of activity coefficient models commonly used for VLE calculations. Such models are divided into two groups depending upon their application to various types of solutions:

1. Margules 2-suffix/Margules 3-suffix/Van-Laar.
2. Wilson/NRTL/UNIQUAC.

The experimental data were correlated by $G^E$ based models (Margules 2-suffix, Margules 3-suffix, Van-Laar,Wilson, NRTL, UNIQUAC). In the present work activity coefficient model parameter will be regressed using experimental P-T-X data. Experimental P-T-X data were modelled to find Vapour phase composition using $G^E$ based models with regressed parameters (Binary Interaction parameters) and optimize the best suitable model for binary system.

Keyword: - Gibbs free energy, Activity coefficient, Vapour liquid equilibrium.
1. Introduction

A system is said to be in equilibrium if it shows no tendency to depart from that state either by energy transfer through the mechanism of heat and work or by mass transfer across the phase boundary. Since a change of state is caused by a driving force, we can describe a system at equilibrium as one in which there are no driving forces for energy and mass transfer. That is, for a system in a state of equilibrium, all forces are in exact balance. Phase equilibrium behavior of multi component fluid mixtures is a primary requirement for designing of separation equipment’s to satisfy the demand of chemical production facilities. There are two ways to determine the phase equilibrium data, experimental and model predicted. Equation of state play as important role in chemical engineering Design and they have assumed an expanding role in the estimation of material properties. Advances in statistical mechanics and increase of computer power allowed the development of equation of state based on molecular principles that are accurate for real fluids and mixtures.

The availability of highly accurate thermodynamic and transport properties of fluid mixtures is important for process development. Here for our work we have taken mixture of CPME and Cyclopentanol (CP). Cyclopentyl methyl ether (CPME) is a new green solvent. It is also used in organic synthesis as a process solvent in place of hazardous, halogenated solvent or low boiling ethers. Cyclopentyl methyl ether (CPME), also known as Methoxycyclopentane, is hydrophobic ether solvent. A high boiling point of 106 °C (223 °F) and preferable characteristics such as low formation of peroxides, relative stability under acidic and basic conditions, formation of azeotropes with water coupled with a narrow explosion range render CPME an alternative to other ethereal solvents such as TetraHydroFuran (THF), 2-methyltetrahydrofuran (2-MeTHF), Dióxane (carcinogenic), and 1,2-dimethoxyethane (DME). Cyclopentyl methyl ether is used in organic synthesis, mainly as a solvent. However it is also useful in extraction, polymerization, crystallization and surface coating.Cyclopentyl methyl ether (CPME) has many characteristics, which traditional ether solvents do not have, including a higher hydrophobicity, lower formation of peroxides as well as a better stability under acidic and basic conditions. It contributes to Green Chemistry because of the reduction of total amount of solvents used, waste water, waste solvents and CO2 emissions and its unique properties like high hydrophobicity, a high boiling point and low peroxide formation. Moreover CPME can reduce variable costs due to its high recovery rate and no necessity of extraction and crystallization solvents. Good stability under acidic and basic conditions of CPME contributes to process innovation as well. These unique properties of CPME give innovations such as one-pot synthesis and telescoping.[3]

1.1 Different Activity Models

The activity model which we are going to use in our work is listed in table-1

<table>
<thead>
<tr>
<th>Model</th>
<th>Gibbs free energy</th>
<th>ln ( Y_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Margules 2- suffix</td>
<td>( \frac{G^E}{RT} = Ax_1 x_2 )</td>
<td>( \ln Y_1 = Ax_1^2 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \ln Y_1 = Ax_1^2 )</td>
</tr>
<tr>
<td>Margules 3- suffix</td>
<td>( \frac{G^E}{RT} = (A_{21}x_1 + A_{12}x_2 ) x_1 x_2 )</td>
<td>( \ln Y_1 = x_1^2 [A_{12} + 2(A_{21} - A_{12})x_1 ] )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \ln Y_2 = x_2^2 [A_{12} + 2(A_{12} - A_{21})x_2 ] )</td>
</tr>
<tr>
<td>Model</td>
<td>Equation</td>
<td>In Word</td>
</tr>
<tr>
<td>------------</td>
<td>---------------------------------------------------------------------------------------------</td>
<td>------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Van Laar</td>
<td>( G^E \frac{RT}{RT} = \frac{Ax_1 x_2}{(x_1 \left(\frac{A}{B}\right) + x_2)} )</td>
<td>( \ln Y_1 = \frac{A}{\left(1 + \left(\frac{B}{A}\right)x_1/x_2\right)^2} )</td>
</tr>
<tr>
<td></td>
<td>( \ln Y_2 = \frac{B}{\left(1 + \left(\frac{A}{B}\right)x_2/x_1\right)^2} )</td>
<td></td>
</tr>
<tr>
<td>Wilson</td>
<td>( G^E \frac{RT}{RT} = -x_1 \ln(x_1 + a_{12}x_1) - x_2 \ln(x_2 + a_{21}x_1) )</td>
<td>( \ln Y_1 = -\ln(x_1 + a_{12}x_2) + a_{12}\frac{x_1 + a_{12}x_2}{x_1 + a_{21}x_1 + x_2} )</td>
</tr>
<tr>
<td></td>
<td>( a_{12} = \frac{V_2}{V_1} \exp\left[\frac{\lambda_{12} - \lambda_{11}}{RT}\right] )</td>
<td>( \ln Y_2 = -\ln(x_2 + a_{21}x_1) + a_{21}\frac{x_1 + a_{12}x_2}{a_{21}x_1 + x_2} )</td>
</tr>
<tr>
<td></td>
<td>( a_{21} = \frac{V_1}{V_2} \exp\left[\frac{\lambda_{21} - \lambda_{22}}{RT}\right] )</td>
<td></td>
</tr>
<tr>
<td>NRTL</td>
<td>( G^E \frac{RT}{RT} = x_1 x_2 \left[\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} - \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}}\right] )</td>
<td>( \ln Y_1 = x_2^2 \left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2 G_{21}}\right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2}\right] )</td>
</tr>
<tr>
<td></td>
<td>( \ln Y_2 = x_1^2 \left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1 G_{12}}\right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_3 G_{21})^2}\right] )</td>
<td></td>
</tr>
<tr>
<td>UNIQUAC</td>
<td>( G^E \frac{RT}{RT} = \frac{G^E}{RT} (\text{Combinatorial}) + \frac{G^E}{RT} (\text{Residual}) )</td>
<td>( \ln Y_i = \ln Y_i^C (\text{Combinatorial}) + \ln Y_i^R (\text{Residual}) )</td>
</tr>
<tr>
<td></td>
<td>( \frac{G^E}{RT} (\text{Combinatorial}) = x_1 \ln \phi_1 + x_1 \ln \phi_2 + x_2 \frac{Z \left(q_i x_1 \ln \frac{v_1}{\phi_1} + q_2 x_2 \ln \frac{v_2}{\phi_2}\right)}{Z} + \frac{Z}{2} (q_1 x_1 \ln \frac{v_1}{\phi_1} + q_2 x_2 \ln \frac{v_2}{\phi_2}) )</td>
<td>( \ln Y_i^C (\text{Combinatorial}) = \ln \phi_i + \frac{Z}{2} q_i \ln \frac{v_i}{\phi_i} + l_i - \frac{\phi_i}{\phi_i} \sum x_j l_j )</td>
</tr>
<tr>
<td></td>
<td>( \frac{G^E}{RT} (\text{Residual}) = -q_1 x_1 \ln (v_1 + v_2 \tau_{21}) - q_2 x_2 \ln (v_2 + v_1 \tau_{12}) )</td>
<td>( \ln Y_i^R (\text{Residual}) = q_i [1 - \ln (\Sigma \phi_j \tau_{ij}) - \Sigma \frac{\theta_j \tau_{ij}}{\Sigma_k, \theta_k \tau_{kj}}] )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Where, ( l_i = \frac{Z}{2} (r_i - q_i) - (r_i - 1) ) ( \theta_j = \left(\frac{x_i q_i}{\sum x_i q_i}\right), \phi_i = \left(\frac{x_i r_i}{\sum x_i r_i}\right) )</td>
</tr>
</tbody>
</table>

Table-1 Different Activity Models
2. Methods

Here we have shown the method of obtaining the deviation from ideality using excel.

2.1 Obtaining Binary Interaction Parameter (BIP) through BUBL P calculation

1. Set T, x and assume BIP.
2. Calculate \( P_{sat} \) using Antoine equation.
3. Calculate activity coefficient \( \Gamma_i \) using assumed BIP.
4. Calculate the pressure \( P_{cal} \) using equation

\[
P_{cal} = \sum x_i \Gamma_i P_{sat}^i
\]

The BIPS were obtained by minimizing \( %AAD \) given by following equation,

\[
%AAD = \frac{100}{N} \sum_{i=1}^{n} \frac{P_{exp}-P_{cal}}{P_{exp}}
\]

Above Procedure was implemented in Microsoft excel solver tool.

5. Objective function = \( \sum %AAD \) (minimum)
6. Variables = Binary interaction parameters
7. Solve to get values.

Various models requires different BIPs. A general list is provided in Table-2.

<table>
<thead>
<tr>
<th>Model</th>
<th>Binary Interaction Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Margules 2-suffix</td>
<td>A</td>
</tr>
<tr>
<td>Margules 3-suffix</td>
<td>( A_{12}, A_{21} )</td>
</tr>
<tr>
<td>Van laar</td>
<td>( A, B )</td>
</tr>
<tr>
<td>Wilson</td>
<td>( \lambda_{12}, \lambda_{21} )</td>
</tr>
<tr>
<td>NRTL</td>
<td>( b_{12}, b_{21} )</td>
</tr>
<tr>
<td>UNIQUAC</td>
<td>( a_{12}, a_{21} )</td>
</tr>
</tbody>
</table>

Table-2 Models BIP

Regressed parameter for Margules 3-suffix model is listed in Table-3 for different pressure. Table: Margules 3-suffix BIPs average

<table>
<thead>
<tr>
<th>Margules 3 Suffix</th>
</tr>
</thead>
<tbody>
<tr>
<td>P (mm Hg)</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>400</td>
</tr>
<tr>
<td>480</td>
</tr>
</tbody>
</table>
Since we have obtained PTx data at six various pressures. The values of BIPs are also coming out to be different for various pressures as can be observed from Table 4.9. However, for modelling the system we require one set of values of BIP. To obtain the best value we have followed the following procedure.

1. List out all the binary interaction parameter (BIP) for each model at various pressures.
2. Take average of BIPs for each models at various pressure as shown in Table.
3. Now make single column of various pressure for each models individual.
4. Again follow the 2.1 procedure but take initial guess of BIP as the average value as per step no. 2.
5. Now run the solver and get the new regressed value of BIP which are shown in Table-4

### Table-3 Margules 3-suffix parameter

<table>
<thead>
<tr>
<th>Pressures (kPa)</th>
<th>0.6437</th>
<th>0.7102</th>
</tr>
</thead>
<tbody>
<tr>
<td>540</td>
<td>0.6437</td>
<td>0.7102</td>
</tr>
<tr>
<td>600</td>
<td>0.4174</td>
<td>0.6596</td>
</tr>
<tr>
<td>680</td>
<td>0.4126</td>
<td>0.6449</td>
</tr>
<tr>
<td>760</td>
<td>0.0714</td>
<td>0.7508</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td>0.6198</td>
<td>0.7677</td>
</tr>
</tbody>
</table>

### Table-4 BIP value for different Model

<table>
<thead>
<tr>
<th>Model</th>
<th>Binary Interaction parameter</th>
<th>Best value</th>
<th>%AAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Margules 2-suffix</td>
<td>A</td>
<td>0.6860</td>
<td>4.26</td>
</tr>
<tr>
<td>Margules 3-Suffix</td>
<td>A_{12}</td>
<td>0.5431</td>
<td>4.00</td>
</tr>
<tr>
<td></td>
<td>A_{21}</td>
<td>0.7844</td>
<td></td>
</tr>
<tr>
<td>Van laar</td>
<td>A</td>
<td>0.5527</td>
<td>4.00</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.7975</td>
<td></td>
</tr>
<tr>
<td>NRTL</td>
<td>b_{12}</td>
<td>1851335.9</td>
<td>3.98</td>
</tr>
<tr>
<td></td>
<td>b_{21}</td>
<td>721870.7</td>
<td></td>
</tr>
<tr>
<td>Wilson</td>
<td>λ_{12}</td>
<td>103906.3</td>
<td>4.20</td>
</tr>
<tr>
<td></td>
<td>λ_{21}</td>
<td>2313163.4</td>
<td></td>
</tr>
</tbody>
</table>

### 2.3 Bubble T calculation to find vapor phase composition

1. Tubulate all the terms with corresponding equations in MS excel sheet - T, p_{cal}, p_{sat,i}, x_i, y_i, Σ y_i, BIP, y_i
2. First input P_{exp}, composition, BIP data that calculated as mentioned in 3.5 calculation.
3. Guess initial \( T \) for all the points in a \( T \) column in expected range.

4. Other data \( P_{\text{sat}}, y_i \) for corresponding model, will be \( P_{\text{cal}}^T, y_i \), calculated from input data.

Above Procedure was implemented in Microsoft excel solver tool.

Objective function \( -\sum y_i \) (first point only) = 1.0

- Variables - \( T \) column
- Constrains -
  1) \( P_{\text{cal}}^T = P_{\text{exp}}^T \)
  2) \( \sum y_i \) (column) = 1.0

Now solve to get \( T, y_i \) at given \( P, T \).

We have also calculated RMSD \( T \) given by following equation,

\[
\text{RMSD} = \sqrt{\frac{\sum (T_{\text{exp}} - T_{\text{cal}})^2}{n}}
\]

3. Result

3.1 Antoine constant

As per Antoine equation
\[
\ln P = A - \frac{B}{T + C},
\]
Where \( P \) in mm Hg and \( T \) in K

Antoine parameters were fitted using least square method implement in Microsoft Excel. Values of each Antoine constant for CPME and CycloPentanol are listed in Table-5

<table>
<thead>
<tr>
<th>Component</th>
<th>CPME</th>
<th>CP</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>8.298431886</td>
<td>6.02228055</td>
</tr>
<tr>
<td>B</td>
<td>499.0687765</td>
<td>84.05204659</td>
</tr>
<tr>
<td>C</td>
<td>-242.9250126</td>
<td>-352.1528743</td>
</tr>
</tbody>
</table>

Table-5 Antoine constant for CPME and CP

3.2 Heat of vaporization

If the temperature is not too near the critical point, the volume of the liquid is small in comparison with the volume of vapor. The volume change accompanying vaporization \( \Delta V = V_G - V_L \) is therefore approximately equal to \( V_G \), the molar volume of vapor.

\[
\frac{d\ln P^S}{dT} = \frac{\Delta H}{RT^2}
\]

From Clausius/Clapeyron equation, relates the latent heat of vaporization directly to the vapor-pressure curve. We can observed that \( \Delta H_v \) is proportional to the slope of \( \ln \text{Psat} \) vs. \( (1/T) \). Plot of \( \ln \text{Psat} \) vs. \( (1/T) \) for CPME and CP is shown in Fig-1 and Fig-2
3.3 Vapour-Liquid Equilibria data

P-T-x data were found out from the literature survey at different pressure has been evaluated in this and this data has been used to fit the activity coefficient such as margules, NRTL, van laar, UNIFAC, UNIQUAC etc.
Table 7: VLE data

<table>
<thead>
<tr>
<th>400 mmHg</th>
<th>480 mmHg</th>
<th>540 mmHg</th>
<th>600 mmHg</th>
<th>680 mmHg</th>
<th>760 mmHg</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_1$</td>
<td>$T^\circ C$</td>
<td>$x_1$</td>
<td>$T^\circ C$</td>
<td>$x_1$</td>
<td>$T^\circ C$</td>
</tr>
<tr>
<td>1</td>
<td>84.8</td>
<td>1</td>
<td>90.4</td>
<td>1</td>
<td>94.2</td>
</tr>
<tr>
<td>0.9358</td>
<td>86</td>
<td>0.9358</td>
<td>92.6</td>
<td>0.9261</td>
<td>96.4</td>
</tr>
<tr>
<td>0.8488</td>
<td>88</td>
<td>0.8488</td>
<td>93.6</td>
<td>0.8283</td>
<td>97.6</td>
</tr>
<tr>
<td>0.7514</td>
<td>91.2</td>
<td>0.7514</td>
<td>96.6</td>
<td>0.7221</td>
<td>100.4</td>
</tr>
<tr>
<td>0.6415</td>
<td>93.2</td>
<td>0.6415</td>
<td>98.8</td>
<td>0.6060</td>
<td>102.4</td>
</tr>
<tr>
<td>0.5585</td>
<td>95.4</td>
<td>0.5585</td>
<td>101.4</td>
<td>0.5210</td>
<td>105</td>
</tr>
<tr>
<td>0.4295</td>
<td>98.4</td>
<td>0.4295</td>
<td>104</td>
<td>0.3929</td>
<td>107.6</td>
</tr>
<tr>
<td>0.3174</td>
<td>99.8</td>
<td>0.3174</td>
<td>106.8</td>
<td>0.2856</td>
<td>110.4</td>
</tr>
<tr>
<td>0.1871</td>
<td>106.2</td>
<td>0.1871</td>
<td>111</td>
<td>0.1651</td>
<td>115.4</td>
</tr>
<tr>
<td>0.0835</td>
<td>110.4</td>
<td>0.0835</td>
<td>115.6</td>
<td>0.073</td>
<td>121.2</td>
</tr>
<tr>
<td>0</td>
<td>120.2</td>
<td>0</td>
<td>124.2</td>
<td>0</td>
<td>127.8</td>
</tr>
</tbody>
</table>

3.4 Experimental $G^E$ based modelling

To obtain vapor phase composition we used BUBL T procedure. Best BIPs values obtained in previous section were used for the same. Binary systems VLE data are generated using activity models. Detailed results of CPME-CP system are reported in this chapter. The above system is modelled using various activity coefficient models. Table 4.9 shows regressed parameters of activity coefficient models. Activity coefficient model parameters of Margules 2-suffix, Margules 3-suffix, Van-laar, NRTL, Wilson parameters are regressed at experimental P-T-x data generated.

BUBL T and experimental data modelling calculations performed by $G^E$ based models are reported in Table and plotted in figure. %AAD T of experimental and model predicted BUBL T is calculated and tabulated in Table where Margules 3-suffix shows minimum %AAD and NRTL-Wilson shows almost same results. All model give reasonable fit to experimental data shown in figure. CPME-CP system experimental binary P-T-x data are modelled using regressed parameters to find vapor composition as shown in Table and figure. All predicted VLE data are nearly same with minimum error between predicted temperature and experimental temperature.
### Table 8: %AAD at Different Pressure for Different Models

<table>
<thead>
<tr>
<th>Models</th>
<th>Margules 2 suffix</th>
<th>Margules 3 suffix</th>
<th>Van-laar</th>
<th>Wilson</th>
<th>NRTL</th>
<th>UNIQUAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>P (mmHg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>0.82</td>
<td>0.83</td>
<td>0.77</td>
<td>0.73</td>
<td>0.85</td>
<td>0.79</td>
</tr>
<tr>
<td>480</td>
<td>1.05</td>
<td>1.08</td>
<td>1.01</td>
<td>1.01</td>
<td>0.92</td>
<td>0.68</td>
</tr>
<tr>
<td>540</td>
<td>0.39</td>
<td>0.33</td>
<td>0.32</td>
<td>0.34</td>
<td>0.46</td>
<td>0.34</td>
</tr>
<tr>
<td>600</td>
<td>0.99</td>
<td>0.68</td>
<td>0.58</td>
<td>0.65</td>
<td>0.74</td>
<td>0.88</td>
</tr>
<tr>
<td>680</td>
<td>0.79</td>
<td>0.82</td>
<td>0.73</td>
<td>0.74</td>
<td>0.83</td>
<td>0.97</td>
</tr>
<tr>
<td>760</td>
<td>1.25</td>
<td>1.35</td>
<td>1.14</td>
<td>1.13</td>
<td>1.28</td>
<td>1.435</td>
</tr>
</tbody>
</table>

### Table 9: RMSD T at Different Pressure for Different Models

<table>
<thead>
<tr>
<th>Models</th>
<th>Margules 2 suffix</th>
<th>Margules 3 suffix</th>
<th>Van-laar</th>
<th>Wilson</th>
<th>NRTL</th>
<th>UNIQUAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>P (mmHg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>0.82</td>
<td>0.83</td>
<td>0.77</td>
<td>0.79</td>
<td>0.34</td>
<td>0.33</td>
</tr>
<tr>
<td>480</td>
<td>0.41</td>
<td>0.49</td>
<td>0.46</td>
<td>0.40</td>
<td>0.35</td>
<td>0.31</td>
</tr>
<tr>
<td>540</td>
<td>0.16</td>
<td>0.14</td>
<td>0.14</td>
<td>0.14</td>
<td>0.19</td>
<td>0.13</td>
</tr>
<tr>
<td>600</td>
<td>0.37</td>
<td>0.31</td>
<td>0.30</td>
<td>0.34</td>
<td>0.41</td>
<td>0.43</td>
</tr>
<tr>
<td>680</td>
<td>0.44</td>
<td>0.39</td>
<td>0.37</td>
<td>0.40</td>
<td>0.47</td>
<td>0.50</td>
</tr>
<tr>
<td>760</td>
<td>0.71</td>
<td>0.63</td>
<td>0.61</td>
<td>0.65</td>
<td>0.73</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Table 8: %AAD at Different Pressure for Different Models
Table 9: RMSD T at Different Pressure for Different Models
3.5 T-xy Diagram

**T-X-Y AT 400 MMHG FOR MARGULES 2 SUFFIX**

**T-X-Y AT 480 MM HG FOR MARGULES 3 SUFFIX**

**T-X-Y AT 540 MM HG FOR VAN LAAR**
T-X-Y AT 600 MM HG FOR WILSON

T-X-Y AT 680 MM HG FOR NRTL

T-X-Y PAT 760 MMHG FOR UNIQUAC
4. CONCLUSIONS

From this we have learnt that how important is thermodynamics in chemical engineering. What is the importance of Vapour liquid equilibrium in separation process. How phase equilibria affect separation. What is the role of activity coefficient model and how it fit the experimental data with theoretical data. In this work we obtained pure component vapor pressure data and modelled it into Least Square method and got Antoine coefficient of CPME, CP as tabulate in Table and also got Heat of vaporization value by plotted lnP vs. 1/T values.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>$\Delta H_V$ (KJ/Kmol)</th>
<th>Temperature Range (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPME</td>
<td>8.298431886</td>
<td>499.0687765</td>
<td>-242.9250126</td>
<td>35913.35</td>
<td>357.95-377.95</td>
</tr>
<tr>
<td>CP</td>
<td>6.02228055</td>
<td>84.05204659</td>
<td>-352.1528743</td>
<td>46025.3</td>
<td>393.15-411.55</td>
</tr>
</tbody>
</table>

Activity coefficient model gives good prediction for binary system as which has been done in this project. It can also extended to multi component system. Parameter sets of activity coefficient models were regressed for binary system CPME-CP for eight different compositions at six pressure using generated experimental P-T-x data. It is concluded from the results that van laar shows minimum %AAD T and Wilson, Margules shows almost same results. %AAD T, RMSD T are maximum at high pressure and minimum at low pressure in case of all the activity coefficient models.

5. ACKNOWLEDGEMENT

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6. REFERENCES