

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), Dioxane (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

Model	Gibbs free energy	ln Y _i
Margules 2-suffix	$\frac{G^E}{RT} = Ax_1 x_2$	ln Y ₁ = Ax ₂ ² ln Y ₂ = Ax ₁ ²
Margules 3-suffix	$\frac{G^E}{RT} = (A_{21}x_1 + A_{12}x_2) x_1 x_2$	ln Y ₁ = x ₂ ² [A ₁₂ + 2(A ₂₁ - A ₁₂)x ₁] ln Y ₂ = x ₁ ² [A ₁₂ + 2(A ₁₂ - A ₂₁)x ₂]

<p>Van Laar</p>	$\frac{G^E}{RT} = \frac{Ax_1 x_2}{(x_1 \left(\frac{A}{B}\right) + x_2)}$	$\ln Y_1 = \left(\frac{A}{(1+\frac{A}{B})x_1/x_2}\right)^2$ $\ln Y_2 = \left(\frac{B}{(1+\frac{B}{A})x_2/x_1}\right)^2$
<p>Wilson</p>	$\frac{G^E}{RT} = -x_1 \ln(x_1 + a_{12}x_2) - x_2 \ln(x_2 + a_{21}x_1)$ $a_{12} = \frac{V_2}{V_1} \exp\left[-\frac{\lambda_{12} - \lambda_{11}}{RT}\right]$ $a_{21} = \frac{V_1}{V_2} \exp\left[-\frac{\lambda_{21} - \lambda_{22}}{RT}\right]$	$\ln Y_1 = -\ln(x_1 + a_{12}x_2) + x_2 \left[\frac{a_{12}}{x_1 + a_{12}x_2} - \frac{a_{21}}{a_{21}x_1 + x_2}\right]$ $\ln Y_2 = -\ln(x_2 + a_{21}x_1) + x_1 \left[\frac{a_{12}}{x_1 + a_{12}x_2} - \frac{a_{21}}{a_{21}x_1 + x_2}\right]$
<p>NRTL</p>	$\frac{G^E}{RT} = x_1 x_2 \left[\frac{\tau_{21}G_{21}}{x_1 + x_2G_{21}} - \frac{\tau_{12}G_{12}}{x_2 + x_1G_{12}}\right]$ <p>Where, $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$ Where, $i=1, j=2$ or $i=2, j=1$</p>	$\ln Y_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + x_1G_{12})^2}\right]$ $\ln Y_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1 + x_2G_{21})^2}\right]$
<p>UNIQUAC</p>	$\frac{G^E}{RT} = \frac{G^E}{RT} (\text{Combinatorial}) + \frac{G^E}{RT} (\text{Residual})$ $\frac{G^E}{RT} (\text{Combinatorial}) = x_1 \ln \frac{\phi_1}{x_1} + x_2 \ln \frac{\phi_2}{x_2} + \frac{Z}{2} (q_1 x_1 \ln \frac{v_1}{\phi_1} + q_2 x_2 \ln \frac{v_2}{\phi_2})$ $\frac{G^E}{RT} (\text{Residual}) = -q_1 x_1 \ln(v_1 + v_2 \tau_{21}) - q_2 x_2 \ln(v_2 + v_1 \tau_{12})$	$\ln Y_i = \ln Y_i^C (\text{Combinatorial}) + \ln Y_i^R (\text{Residual})$ $\ln Y_i^C (\text{Combinatorial}) = \ln \frac{\phi_i}{x_i} + \frac{Z}{2} q_i \ln \frac{v_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum x_j l_j$ $\ln Y_i^R (\text{Residual}) = q_i [1 - \ln(\sum_j \phi_j \tau_{ji}) - \sum_j \frac{\theta_j \tau_{ij}}{(\sum_k \theta_k \tau_{kj})}]$ <p>Where, $l_i = \frac{Z}{2}(r_i - q_i) - (r_i - 1)$</p> $\theta_j = \left(\frac{x_j q_j}{\sum x_i q_i}\right), \phi_i = \left(\frac{x_i r_i}{\sum x_i r_i}\right)$

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_i^{sat} using Antoine equation.
3. Calculate activity coefficient γ_i using assumed BIP.
4. Calculate the pressure P_{cal} using equation

$$P_{\text{cal}} = \sum x_i \gamma_i P_i^{\text{sat}}$$

The BIPs were obtained by minimizing %AAD P given by following equation,

$$\% \text{AAD} = \frac{100}{n} \sum_{i=1}^n \frac{(P_{\text{exp}} - P_{\text{cal}})}{P_{\text{exp}}}$$

Above Procedure was implemented in **Microsoft excel solver tool**.

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

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

Model	Binary Interaction Parameter
Margules 2-suffix	A
Margules 3-suffix	A_{12}, A_{21}
Van laar	A, B
Wilson	$\lambda_{12}, \lambda_{21}$
NRTL	b_{12}, b_{21}
UNIQUAC	a_{12}, a_{21}

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

Margules 3 Suffix		
P (mm Hg)	A_{12}	A_{21}
400	1.2554	1.0638
480	0.9186	0.7772

540	0.6437	0.7102
600	0.4174	0.6596
680	0.4126	0.6449
760	0.0714	0.7508
Average	0.6198	0.7677

Table-3 Margules 3-suffix parameter

2.2 Procedure for obtaining best value of BIP

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

Model	Binary Interaction parameter	Best value	%AAD
Margules 2-suffix	A	0.6860	4.26
Margules 3-Suffix	A ₁₂	0.5431	4.00
	A ₂₁	0.7844	
Van laar	A	0.5527	4.00
	B	0.7975	
NRTL	b ₁₂	1851335.9	3.98
	b ₂₁	721870.7	
Wilson	λ_{12}	103906.3	4.20
	λ_{21}	2313163.4	

Table-4 BIP value for different Model

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}^T , P_{sat}^i , x_i , y_i , $\sum y_i$, BIP, γ_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_{sat}^i, γ_i for corresponding model, will be $P_{cal}^T, \sum y_i$ 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) $P_{cal}^T = P_{exp}^T$

2) $\sum y_i$ (column) = 1.0

Now solve to get T, y_i at given P^T, x_i .

We have also calculated RMSD T given by following equation,

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

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

Component	CPME	CP
A	8.298431886	6.02228055
B	499.0687765	84.05204659
C	-242.9250126	-352.1528743

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 vapour. The volume change accompanying vaporization $\Delta V = V_G - V_L$ is therefore approximately equal to V_G , the molar volume of vapour.

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

From Clausius/Clapeyron equation, relates the latent heat of vaporization directly to the vapor-pressure curve. We can observed that ΔH_v is proportional to the slope of $\ln P_{sat}$ vs. $(1/T)$. Plot of $\ln P_{sat}$ vs. $(1/T)$ for CPME and CP is shown in Fig-1 and Fig-2

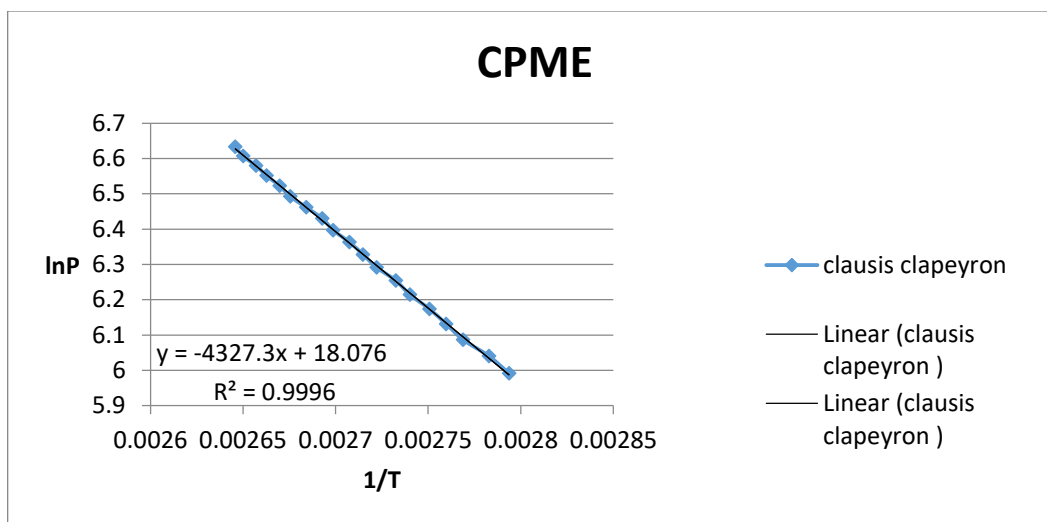


Fig-1:- Plot for CPME

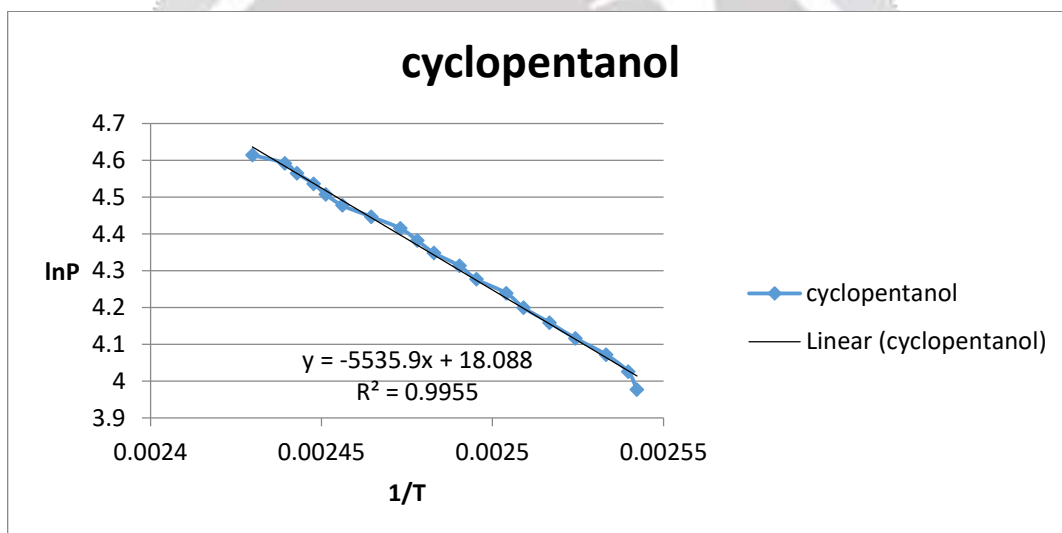


Fig-2:- Plot for CP

	CPME	CP
Heat of vaporization (KJ/Kmol)	35977.39	46025.29585

Table-6:- ΔH_v for CPME and CP

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.

400 mmHg		480 mmHg		540 mmHg		600 mmHg		680 mmHg		760 mmHg	
x_1	T (°C)	x_1	T (°C)	x_1	T (°C)	x_1	T (°C)	x_1	T (°C)	x_1	T (°C)
1	84.8	1	90.4	1	94.2	1	97.4	1	101.4	1	104.8
0.9358	86	0.9358	92.6	0.9261	96.4	0.9375	99.6	0.9281	103.4	0.9281	106.4
0.8488	88	0.8488	93.6	0.8283	97.6	0.8587	101.2	0.8394	104.4	0.8394	107.8
0.7514	91.2	0.7514	96.6	0.7221	100.4	0.7839	103.4	0.7572	107	0.7572	110.4
0.6415	93.2	0.6415	98.8	0.6060	102.4	0.6427	105.2	0.6073	109.2	0.6073	112.4
0.5585	95.4	0.5585	101.4	0.5210	105	0.5534	107.8	0.5159	111.4	0.5159	114.8
0.4295	98.4	0.4295	104	0.3929	107.6	0.4203	110.2	0.9840	113.2	0.3840	118
0.3174	99.8	0.3174	106.8	0.2856	110.4	0.3067	115.8	0.2755	119.6	0.2755	123.8
0.1871	106.2	0.1871	111	0.1651	115.4	0.1849	119.6	0.1632	123.2	0.1632	128.8
0.0835	110.4	0.0835	115.6	0.073	121.2	0.0925	123.4	0.08054	127.2	0.0805	131.4
0	120.2	0	124.2	0	127.8	0	130.4	0	134.8	0	138.4

Table-7:- VLE data

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 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.

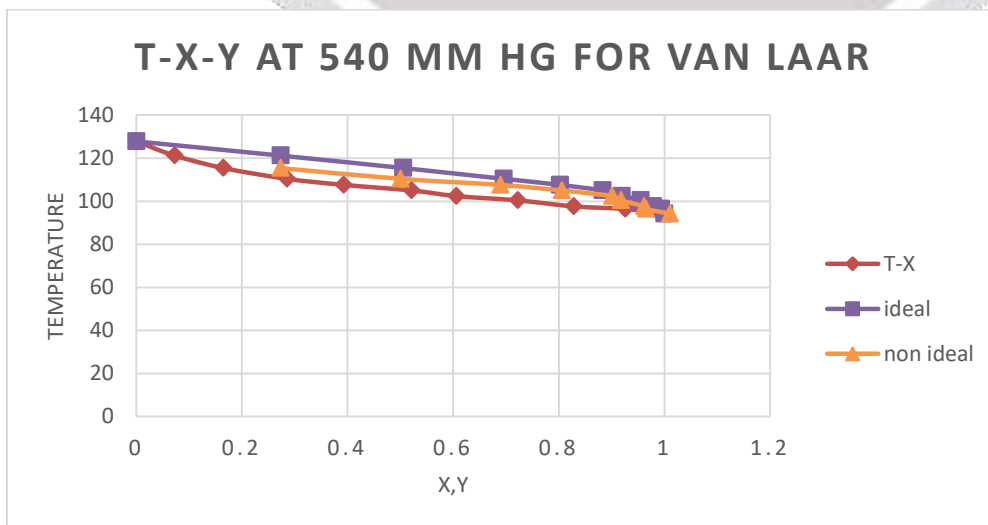
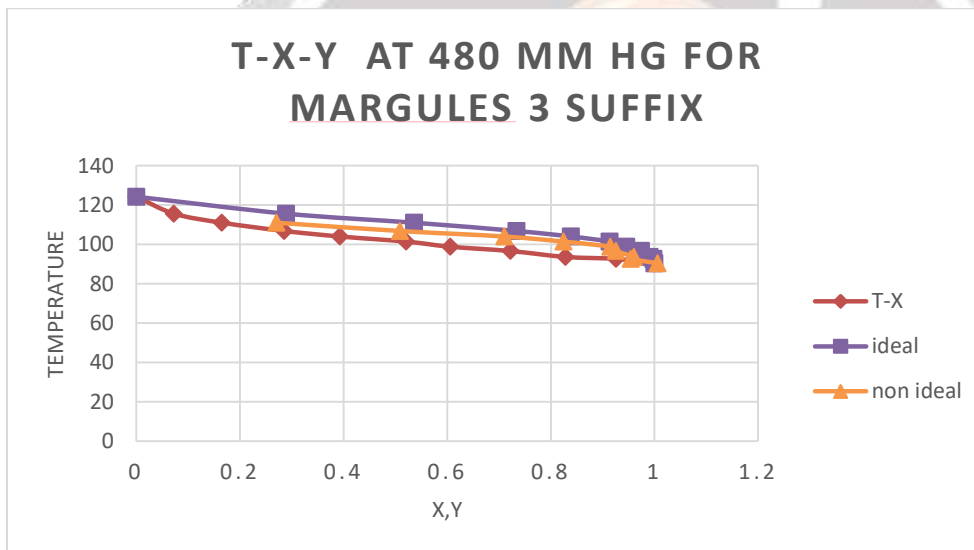
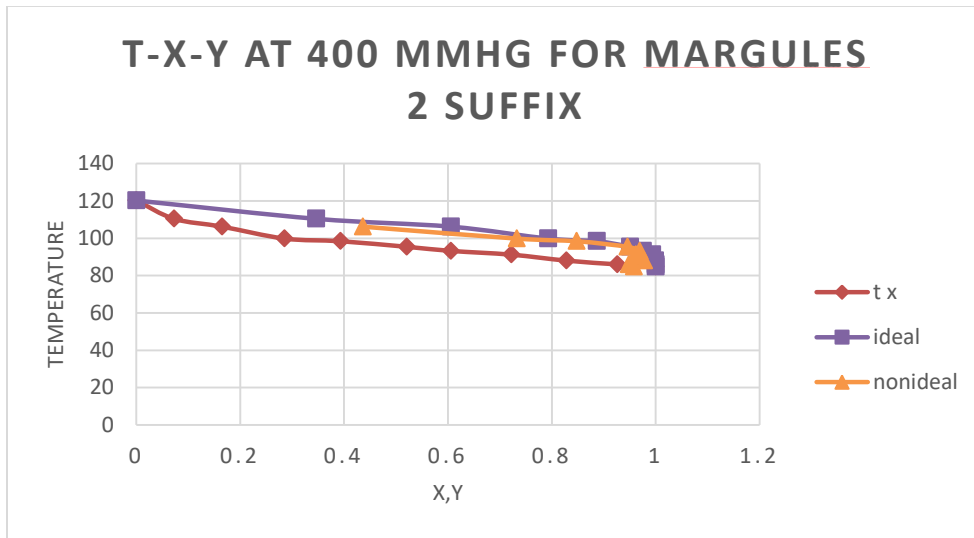
Models	Margules 2 suffix	Margules 3 suffix	Van-laar	Wilson	NRTL	UNIQUAC
P (mmHg)	%AAD T					
400	0.82	0.83	0.77	0.73	0.85	0.79
480	1.05	1.08	1.01	1.01	0.92	0.68
540	0.39	0.33	0.32	0.34	0.46	0.34
600	0.99	0.68	0.58	0.65	0.74	0.88
680	0.79	0.82	0.73	0.74	0.83	0.97
760	1.25	1.35	1.14	1.13	1.28	1.435

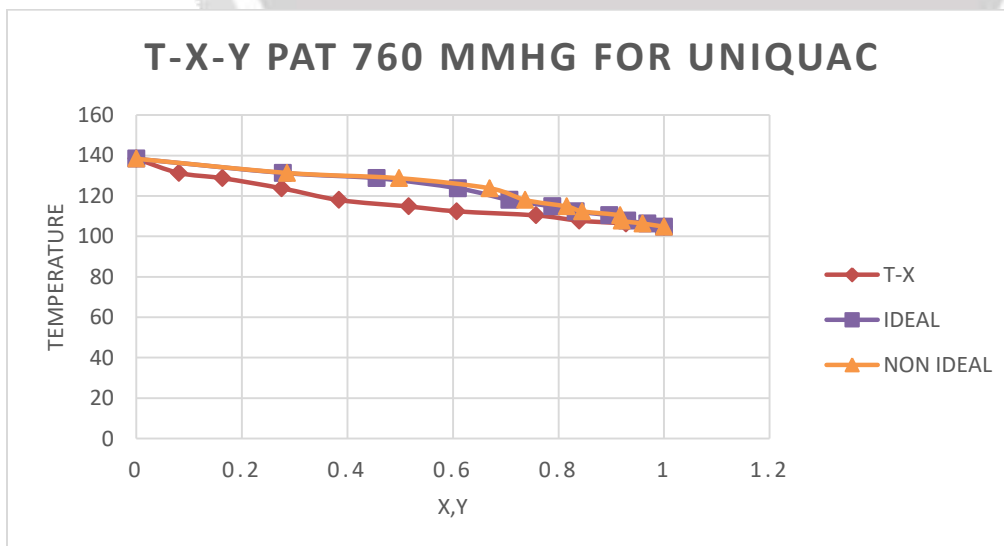
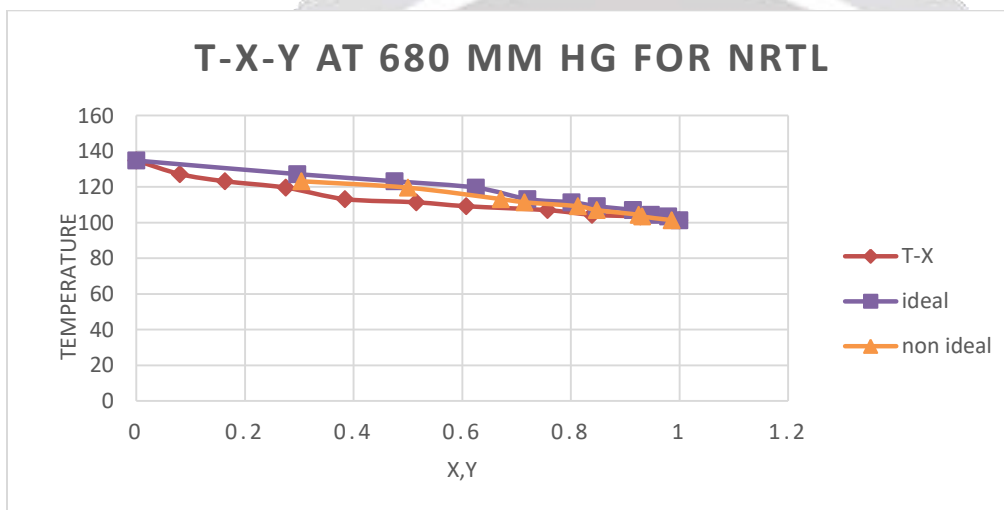
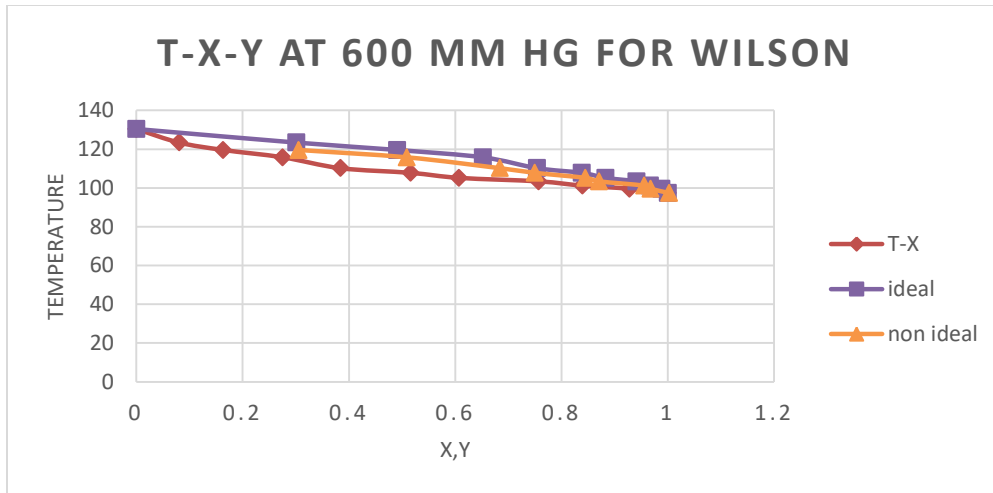
Table-8:- %AAD at Different pressure for Different Models

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

Table-9:- RMSD T at Different pressure for Different Models

3.5 T-xy Diagram





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 $\ln P^S$ vs. $1/T$ values.

	A	B	C	ΔH_v (KJ/Kmol)	Temperature Range (K)
CPME	8.298431886	499.0687765	-242.9250126	35913.35	357.95-377.95
CP	6.02228055	84.05204659	-352.1528743	46025.3	393.15-411.55

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.

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