Optimizing Interaction Parameters Of Various Thermodynamics Models using MATLAB To Estimate Activity Coefficients Of Azeotropic Mixtures

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Abstract: ***The calculation of the liquid-vapor phase equilibrium conditions in multicomponent mixtures is a subject of general interest for engineering. So in this article, interaction parameters of various thermodynamics models are optimized using MATLAB and the vapor-liquid equilibrium conditions are estimated through the application of the modified Raoult's equation. Activity coefficients of azeotropic mixtures are also estimated. The application of conventional models is restricted for those systems that exhibit irregular behavior, that is, they form azeotropic. In these cases, the validity of these models is limited since the experimental data is not satisfactorily explained. The UNIFAC model completely explains the experimental data of non-ideal systems quite well.***

Keywords: UNIFAC model, MATLAB, binary interaction parameters & activity coefficients.

I. INTRODUCTION

Phase equilibrium and specifically vapor/liquid-equilibrium (VLE), plays an important role in distillation and separation process applications. The common method for obtaining VLE data is by direct measurement, i.e. phases are sampled and analyzed. So when these samples are analyzed, the whole composition of components in solution and vapor have been changed, so accordingly the behavior of the systems has been changed with the number of compositions. Further, the analysis of VLE data for infinite dilute solutions is very difficult [1]. Also, the sample analysis of highly volatile components is very difficult. So, therefore, thermodynamics provides the mathematical framework for the systematic correlation, extension, generalization, evaluation, and interpretation of the data [5].

The simplest model available in the literature is Raoult's law [6]. The Raoult's law is valid for low to moderate pressure specifically for the ideal solution, which is represented as:

$$y_i P = x_i P_i^{sat} \quad (i = 1,2, \dots \dots N) \tag{1}$$

Where x_i is a liquid phase mole fraction, y_i is vapor phase mole fraction and P_i^{sat} is the vapor pressure of the pure species i at the temperature of the system. This model is very useful in VLE calculations and also serve as a standard of comparison for more complex systems. This model takes into account the effect of activity coefficient, when the liquid phase in the solution shows deviation for the ideality condition. Hence modified Raoult's law is presented as $y_i P = \gamma_i x_i P_i^{sat} \ (i = 1,2, \dots \dots N)$ The activity coefficients are the function of temperature and liquid phase composition.

Further, this activity coefficients can be used to calculate the excess Gibbs free energy that is the excess energy of the solution that makes it nonideal, which is expressed as:

$$\frac{g^E}{RT} = ln\gamma_i \tag{3}$$

$$ln\gamma_i = \left[\frac{\partial\left(\frac{g^E}{RT}\right)}{\partial n_i}\right]_{T,P,n_i} \tag{4}$$

Perhaps the simplest expression for Gibbs excess function is 1 parameter model known as Margules equation [6].

$$(g^E/RT) = Ax_1x_2 \tag{5}$$

Where A is an adjustable parameter. The activity coefficients γ_1 and γ_2 are given by

$$ln\gamma_1 = \frac{\bar{g}_1{}^E}{RT} = \left[\frac{\partial\{(N_1+N_2)g^E/RT\}}{\partial N_1}\right]_{T,P,N_2} = \left[\frac{\partial}{\partial N_1}\left\{\frac{AN_1N_2}{(N_1+N_2)}\right\}\right]_{N_2,T,P} \tag{6}$$

Or $ln\gamma_1 = \frac{AN_2^2}{(N_1+N_2)^2} = A_1x_2^2$ and $ln\gamma_2 = A_2x_1^2$ (7)

The regular solutions can easily be arranged into van Laar form by writing two adjustable parameters A and B [7].

$$\frac{g^E}{RT} = \frac{Ax_1x_2}{x_1\left(\frac{A}{B}\right)+x_2} \tag{8}$$

$$ln\gamma_1 = Az_2^2 = \frac{A}{\left(1+\frac{Ax_1}{Bx_2}\right)^2} \tag{9}$$

$$ln\gamma_2 = Bz_1^2 = \frac{B}{\left(1+\frac{Bx_2}{Ax_1}\right)^2} \tag{10}$$

The third type of model, which is available in the literature is Wilson equation [7], which is represented as follows:

$$\frac{g^E}{RT} = -x_1ln(x_1+\Lambda_{12}x_2) - x_2ln(x_2+\Lambda_{21}x_1) \tag{11}$$

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Where Λ_{12} and Λ_{21} are two adjustable parameters which are related to pure component molar volumes and characteristic energy differences. Λ_{12} and Λ_{21} are given by

$$\Lambda_{12} = \frac{v_2}{v_1} \exp\left[-\frac{\lambda_{12}-\lambda_{11}}{RT}\right] \quad (12)$$

$$\Lambda_{21} = \frac{v_1}{v_2} \exp\left[-\frac{\lambda_{12}-\lambda_{22}}{RT}\right] \quad (13)$$

Where vi =molar volume of pure component i and λij = energy of interaction between a molecule of component I and a molecule of component j. The activity coefficients are given as

$$ln\gamma_1 = -ln(x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1+\Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1+x_2}\right] \quad (14)$$

$$ln\gamma_2 = -ln(x_2 + \Lambda_{21}x_1) + x_1\left[\frac{\Lambda_{12}}{x_1+\Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1+x_2}\right] \quad (15)$$

The assumption of the Wilson equation is that the local concentration around a molecule is different from the bulk concentration. This difference is due to a difference between the interaction energy of the central molecule with the molecules of its own kind Uii and that with the molecules of the other kind Uij. The energy difference also introduces a non-randomness at the local molecular level. The NRTL model belongs to the so-called local-composition models [7]. The NRTL equation for the excess Gibbs free energy is given by

$$\frac{g^E}{RT} = x_1x_2\left[\frac{\tau_{21}G_{21}}{x_1+x_2G_{21}} + \frac{\tau_{12}G_{12}}{x_2+x_1G_{12}}\right] \quad (16)$$

Where $\tau_{12} = \frac{g_{12}-g_{22}}{RT}$ &$\tau_{21} = \frac{g_{21}-g_{11}}{RT}$ (17)

$$G_{12} = exp\,(-\alpha_{12}\tau_{12}) \quad (18)$$

$$G_{21} = exp\,(-\alpha_{12}\tau_{21}) \quad (19)$$

$$ln\gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1+x_2G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2+x_1G_{12})^2}\right] \quad 20)$$

$$ln\gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2+x_1G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1+x_2G_{21})^2}\right] \quad (21)$$

The UNIFAC MODEL is currently the most convenient standardized method for evaluating activity coefficients in liquid mixtures and the estimated activity coefficients can further be used to predict Vapor-Liquid Equilibrium for non-ideal systems [6-7]. The equation to estimate the deviation of ideality in the equilibrium proposed by the UNIFAC model is the following:

$$\frac{G^E}{RT} = G^{comb} + G^{resid} \quad (22)$$

Where G^{comb} corresponds to the Combinatorial Energy due to the molecular shape and size &G^{resid} corresponds to the Residual Energy caused by molecular interactions. Both energies, combinatorial and residual, are evaluated through the use of specific parameters for each present species defined by UNIFAC through a relative molecular volume r_j; a relative molecular surface area q_j and an interaction parameter $\alpha_{i,j}$ evaluated in binary form between the species. These parameters are obtained by defining the functional units or sub groups that make up a molecule and interact with each other, confirming the characteristics of each chemical species. Each functional unit is associated with a relative volume (R_r) and a relative surface area (Q_k), which are the properties of the subgroups and is also considered the energy effect of association between them. This leads us to the definition of the activity coefficients evaluated by UNIFAC for the expression:

$$ln\gamma_i = (ln\gamma_i)^{comb} + (ln\gamma_i)^{resid} \quad (23)$$

$$(ln\gamma_i)^{comb} = ln\frac{\Phi_i}{x_i} + \frac{z}{2}q_i ln\frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i}\sum_j x_i x_j \quad (24)$$

and $(ln\gamma_i)^{resid} = \sum_j v_i{}^k(ln\Gamma_k - ln\Gamma_k{}^i)$ (25)

Where $\Phi_i \equiv \frac{x_i r_i}{\sum_j x_j r_j}$ and $\theta_i \equiv \frac{x_i q_i}{\sum_j x_j q_j}$

Subscript i identifies species and j is a dummy index, x_i is mole fraction $ln\Gamma_k$ is group residual activity coefficient and

$$ln\Gamma_k = Q_k[1 - ln(\sum_m \theta_m\psi_{mk}) - \sum\frac{\theta_m\psi_{mk}}{\sum_n \theta_n\psi_{nm}}] \quad (26)$$

where $\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n}$ and $\psi_{mk} = exp\left(\frac{-a_{mn}}{T}\right)X_m$ is mole fraction of group m in the mixture a_{mn} is group interaction parameter.

II. METHODOLOGY

Five different types of binary systems (1-5), the data for which has already been reported in the literature were chosen for the comparative analysis of different models i.e. Margules, van Laar, Wilson, and NRTL. The vapor pressure of the components of the binary systems chosen was estimated using Antoine equation [8], which is of the following form:

$\log(P) = A - \frac{B}{T+C}$ (27)where P is Vapour pressure of the component, mmHg and T is the temperature in °C.

Boiling points and Antoine equation constants of these components are reported in table 1[8].

The binary interaction parameters of Margules, van Laar, Wilson, and NRTL were calculated using MATLAB. Whereas for the UNIFAC model, the literature values of interaction parameters were used. A nonlinear regression analysis was carried out considering a minimization of the following objective function (OF):

$$OF = \sum_1^n(\gamma_1{}^{exp} - \gamma_1{}^{calc})^2 + \sum_1^n(\gamma_2{}^{exp} - \gamma_2{}^{calc})^2 \quad (28)$$

Then interaction parameters of the respective models were used for the prediction of activity coefficients. The activity coefficients thus obtained were used to calculate the vapor phase composition by using the modified Raoult's law.

Table 1: Boiling point and Antoine equation constants for various components [8]

System 1 (Acetic acid + p – Xylene)[1]		
Component	***Boiling point (°C) at 1 atm***	***Antoine Equation***
Acetic acid	114.7	A = 7.2996, B = 1479.02, C = 216.082
p – Xylene	132.2	A = 6.992, B = 1145.43, C = 215.307
System 2 (Pentane + Acetone) [2]		
Component	***Boiling point (°C) at 1 atm***	***Antoine Equation***
Pentane	36.5	A = 6.876, B = 1075.78, C = 233.205
Acetone	56.15	A = 7.2316, B = 1277.03, C = 237.23
System 3 (Methanol + Benzene) [3]		
Component	***Boiling point (°C) at 1 atm***	***Antoine Equation***
Methanol	64.7	A = 8.6324, B = 1574.99, C = 238.205
Benzene	80.1	A = 6.992, B = 1145.43, C = 215.307
System 4 (Methyl Acetate + Methanol) [4]		
Component	***Boiling point (°C) at 1 atm***	***Antoine Equation***
Methyl Acetate	56.8	A =4.264, B =1194.58, C =233.66
Methanol	64.7	A = 8.6324, B = 1574.99, C = 238.205
System 5 (Chloroform + Methanol) [4]		
Component	***Boiling point (°C) at 1 atm***	***Antoine Equation***
Chloroform	61.2	A = 6.9371, B = 1171.2, C = 227.05
Methanol	64.7	A = 8.6324, B = 1574.99, C = 238.205

III. RESULTS & DISCUSSION

The binary interaction parameters of all the different models were calculated and are summarized in Table 2.

Table 2: Binary interaction parameters for various models.

System	Van Laar equation		Margules equation		Wilson equation		NRTL equation (α = 0.3)	
	A	***B***	***A1***	***A2***	Λ_{12}	Λ_{21}	τ_{12}	τ_{21}
System 1 (Acetic acid + p – Xylene)	2.78	1.68	2.42	1.24	1.18	1.84	1.93	0.18
System 2 (Pentane + Acetone)	2.19	1.64	2.14	1.55	0.37	-0.05	0.64	1.61
System 3 (Methanol + Benzene)	2.12	1.79	2.11	1.79	0.22	0.31	0.89	1.45
System 4 (Methyl Acetate + Methanol)	1.07	1.08	1.06	1.07	0.54	0.52	0.61	0.57
System 5 (Chloroform + Methanol)	0.93	2.05	0.74	1.96	0.87	0.13	2.23	-0.24

The MRQE values for different models have been reported in Table 3. Based on the statistical analysis reported in Table 3, it has been observed that the UNIFAC model offered the least value of MRQE in comparison to all other conventional models, for all the studied systems. The above binary interaction parameters were used in Eqns. [7, 9, 10, 14, 15 20, 21] to calculate the activity coefficients for Margules, van Laar, Wilson, and NRTL models respectively. Whereas group interaction parameters were used in Eqn.[23] to calculate the activity coefficients for the UNIFAC model. The activity coefficients were used in the calculation of vapor phase composition by using the modified Raoult's law. The calculated values of the vapor phase composition using different models were compared with the experimental values reported in the literature. The deviation of the calculated values from the experimental values was estimated and reported in terms of MRQE. MRQE is defined as

$$\text{M.R.Q.E. (Mean Relative Quadratic Error)} = \sqrt{\frac{\sum\left(\frac{\text{experimental value} - \text{theroetical value}}{\text{theroetical vlaue}}\right)^2}{N-1}} \quad (29)$$

Where N is the no. of data points.

Table 3: Statistical comparison of various models

ystem	Van Laar equation	Margules equation	Wilson equation	NRTL equation	UNIFAC model
System 1 (Acetic acid + p – Xylene)	8.45%	8.54%	14.70%	10.30%	5.23%
System 2 (Pentane + Acetone)	36.80%	37.50%	57.40%	36.40%	15.20%
System 3 (Methanol + Benzene)	5.15%	5.65%	3.54%	4.50%	1.60%
System 4 (Methyl Acetate + Methanol)	7.40%	7.40%	6.90%	7.30%	5.50%
System 5 (Chloroform + Methanol)	6.01%	6.30%	6.24%	6.36%	2.20%

The T-x1-y1 diagrams for all the 5 binary systems at atmospheric pressure are shown in Figs. 1 (a) to (e). Graphs show a comparison of the experimental vapor phase and liquid phase component values available in literature with the values predicted using different models. It can be observed from the graphs that the deviation between the predicted and experimental values is minimum using UNIFAC model for all types of binary systems. Similarly, activity coefficients are also plotted and shown in Figs 2(a) to 2(e).Figure 3 (a – e), i.e. the parity plots of all the system shows that UNIFAC model gives a good fit to the experimental data and show acceptable mean deviations for the prediction of the vapor phase composition. The model gives a good fit to the experimental data and shows

acceptable mean deviations for the prediction of the vapor phase composition.

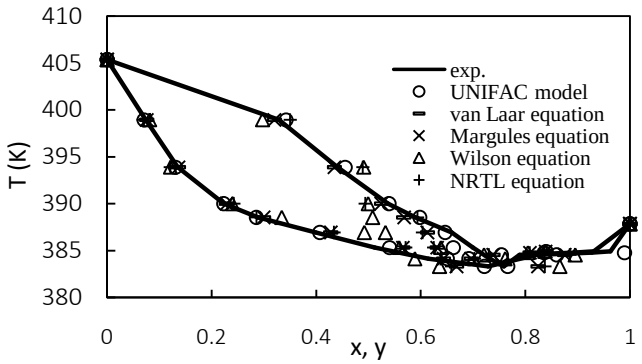

Figure 1(a) T – x – y plot of Acetic acid + p – Xylene

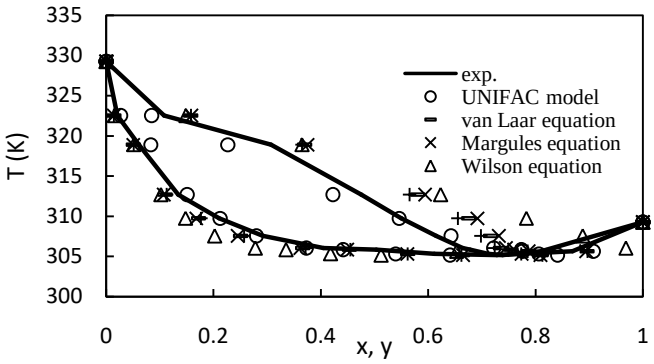

Figure 1(b) T – x – y plot of Pentane + Acetone

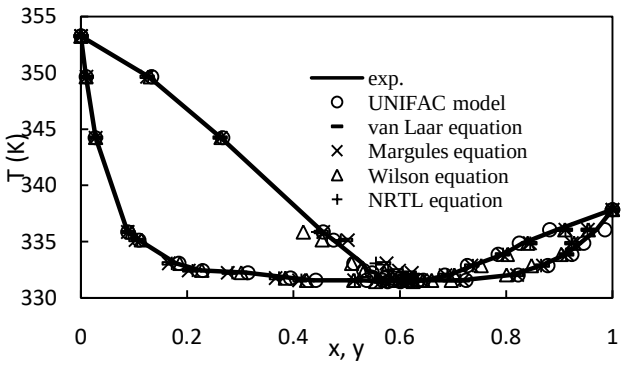

Figure 1(c) T – x – y plot of Methanol + Benzene

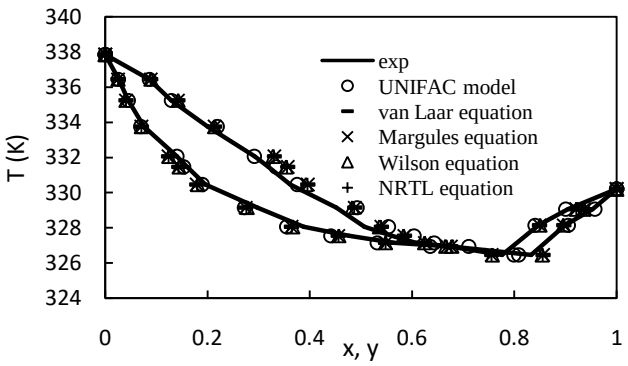

Figure 1(d) T – x – y plot of Methyl Acetate + Methanol

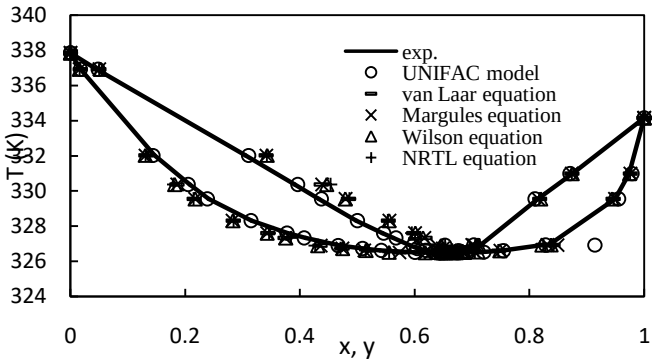

Figure 1(e) T – x – y plot of Chloroform + Methanol

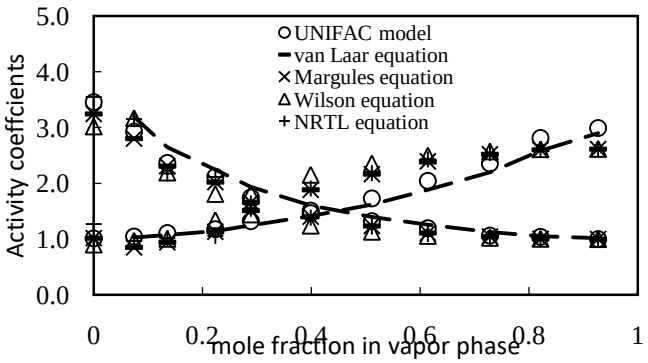

Figure 2(a) Activity coefficients vs. vapor phase mole fraction plot of Acetic acid + p – Xylene

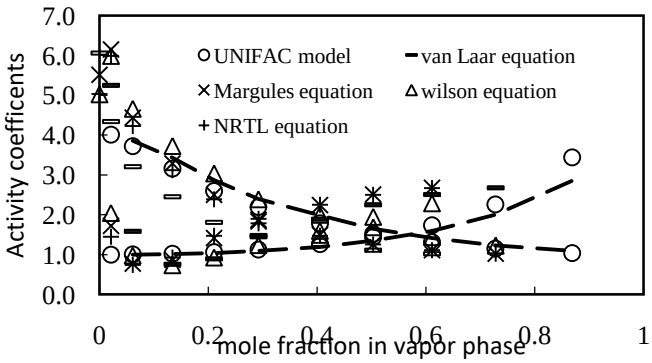

Figure 2(b) Activity coefficients vs. vapor phase mole fraction plot of Pentane + Acetone

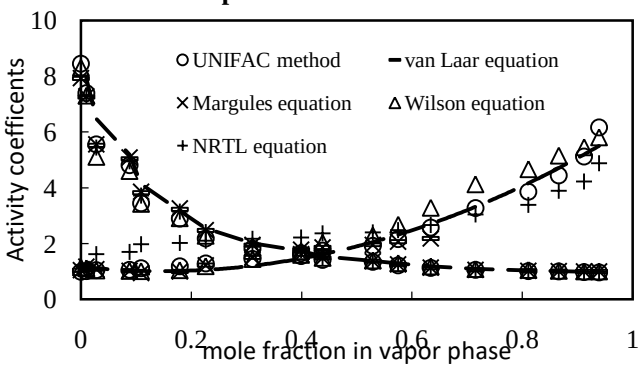

Figure 2(c) Activity coefficients vs. vapor phase mole fraction plot of Methanol + Benzene

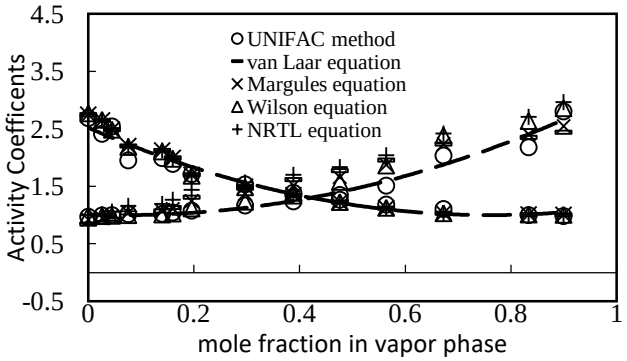

Figure 2(d) Activity coefficients vs. vapor phase mole fraction plot of Methyl Acetate + Methanol

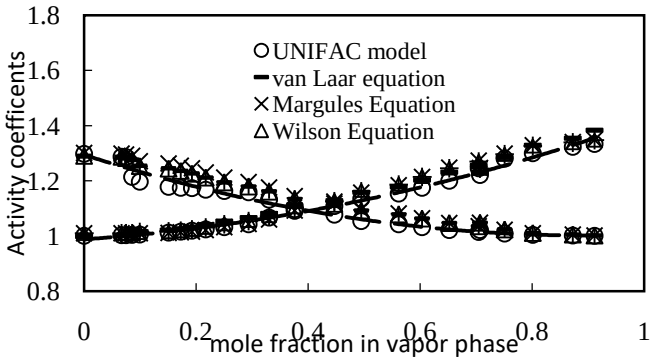

Figure 2(e) Activity coefficients vs. vapor phase mole fraction plot of Chloroform + Methanol

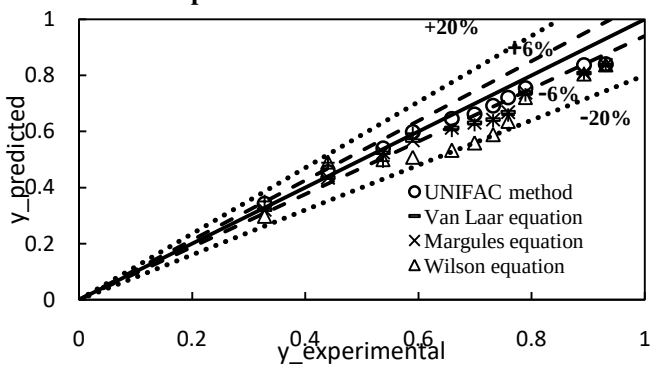

Figure 3(a) Parity plot of Acetic acid + p – Xylene

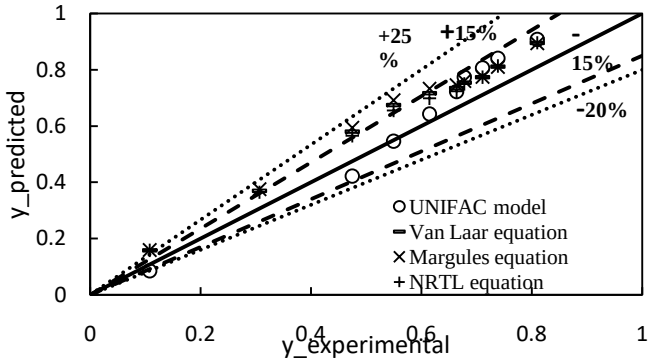

Figure 3(b) Parity plot of Pentane + Acetone

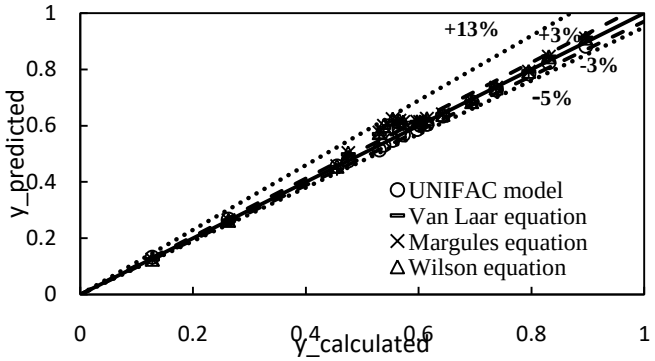

Figure 3(c) Parity plot of Methanol + Benzene

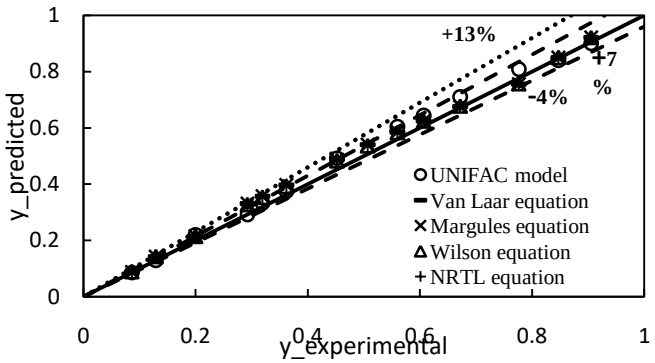

Figure 3(d) Parity plot of Methyl Acetate + Methanol

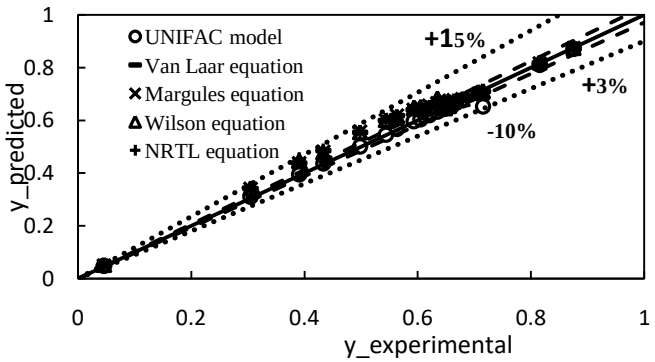

Figure 3(e) Parity plot of Chloroform + Methanol

IV. CONCLUSION

VLE data for 5 different binary systems were analyzed at atmospheric pressure. The activity coefficients and liquid and vapor phase compositions were calculated using traditional models and UNIFAC model. The calculated values from different models were compared with the experimental values cited in the literature and the statistical comparison has been reported in terms of MRQE. It has been observed that the UNIFAC model gave the least value of MRQE. The same contrast has been made graphically as well. It has been observed that the calculated values using UNIFAC model fitted well with the experimental data. Moreover, the model has the advantage of predicting the activity coefficient theoretically or without actually carrying out the experiment.

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