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PHASE EQUILIBRIUM ESTIMATION OF 2,2,4-TRIMETHYLPENTANE / BENZENE SYSTEM USING GROUP CONTRIBUTION METHOD

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Abstract - *A solvent that creates less hazards to human, animals and environment is called a green solvent. The separation of Benzene/Acetonitrile mixture is carried out using Dimethyl sulphoxide as an entrainer. Dimethyl sulfoxide can be replaced by a greener solvent, 2,2,4-trimethylpentane, also known as iso-Octane. The vapour-liquid phase equilibrium data that are required for the design of separation system for the iso-Octane / Benzene mixture are not available in the literature. The experimental measurement of phase equilibrium data for vapour and liquid is a time-consuming and a costly affair. Instead, group contribution method such as modified UNIFAC Dortmund method can be used to predict the vapour-liquid equilibrium data. These data can be used for the design purpose. However, these data can be used for only preliminary design and for the final design of separation system, experimental data are indispensable.*

Keywords *- Vapour-liquid phase equilibrium, Benzene, iso-octante, 2,2,4-trimethylpentane, modified UNIFAC Dortmund method*

I. INTRODUCTION

Benzene is the simplest and most important member of the aromatic hydrocarbons. It is used as a chemical intermediate for the production of many important industrial compounds such as styrene, aniline, phelol, cyclohexane, alkylbenzenes, chlorobenzenes. These intermediates in turn, supply numerous sectors of the chemical industry producing pharmaceuticals, specialty chemicals, plastics, resins, dyes and pesticides [1]. In the separation of benzene/acetonitrile mixture, iso-octane can be used as a solvent in place of dimethyl sulfoxide (DMSO).

The iso-octane is considered as greener solvent compared to DMSO. The use of iso-octane can reduce the environmental impact to a certain extent which results from the use of solvent in the separation of benzene/iso-octane mixture. The use of iso-octane solvent brings a new mixture of iso-octane/benzene in the system. This mixture can be separated by conventional distillation as there is a considerable difference in vapour pressure of the two components. But the vapour-liquid phase equilibrium data which are required to design the distillation column are not available in the literature [2]. Experimental determination of the phase equilibrium data can often becomes a very difficult task due to limitations such as cost, time, unavailability of experimental apparatus and analytical instruments [3]. In this condition, group contribution methods present a simple and efficient way of estimating the data when little or no experimental data are available [4-6].

II. MODIFIED UNIFAC DORTMUND METHOD

Among the group contribution methods, ASOG, UNIFAC and modified UNIFAC Dortmund methods are well known. In group contribution methods, the characteristic group of a molecule or compound is believed to have the same properties in whichever compounds it exists. The phase equilibrium data prediction and particularly vapour-liquid equilibrium data prediction requires the prediction of activity coefficients since the fugacity coefficient at low or atmospheric pressure is considered as 1. The mathematical equation for the prediction of activity coefficient for both UNIFAC and modified UNIFAC Dortmund methods is as follows:

$$\ln \gamma_i = \ln \gamma_{i(combinatorial)} + \ln \gamma_{i(residual)} \tag{1}$$

The activity coefficient is calculated by the contribution of two parts. Combinatorial part takes into account the differences in shape and size of molecules and the residual part takes into account the differences in intermolecular forces. The detailed equations are not presented in this text; they can be acquired from the literature [7].

III. DETAILED PROCEDURE OF CALCULATION OF ACTIVITY COEFFICIENTS

A. Group identification of the compounds iso-octane and benzene

The functional groups of the compounds of the binary system are identified in the first step. The groups are identified and the parameter values of Q_k and R_k are collected from the literature [8] and tabulated in Table 1.

Table 1: Group identification for iso-octane and benzene for modified UNIFAC Dortmund method

Compound	Group	Main group No.	Secondary group No.	v_k (i)	R_k	Q_k
iso-octane (1)	CH_3	1	1	5	0.6325	1.0608
	CH_2	1	2	1	0.6325	0.7081
	CH	1	3	1	0.6325	0.3554
	C	1	4	1	0.6325	0
Benzene (2)	ACH	3	9	6	0.3763	0.4321

B. Binary interaction parameters (BIPs) for iso-octane and benzene

The binary interaction parameters a_{mn}, b_{mn}, and c_{mn} for modified UNIFAC Dortmund method have been taken from the literature [8-10]. The group-interaction parameter Ψ_{nm} is calculated by the following equation and tabulated in Table 2.

$$\Psi_{nm} = \exp\left(-\frac{a_{nm} + b_{nm}T + c_{nm}T^2}{T}\right) \tag{2}$$

Table 2: BIPs for iso-octane and benzene for modified UNIFAC Dortmund method

n	m	a_{nm}	b_{nm}	c_{nm}	Ψ_{nm}	Main group interaction	Secondary group interaction
1	3	114.2	0.0933	0	0.668299	$\Psi_{1,3}$	$\Psi_{1,9}$ $\Psi_{2,9}$ $\Psi_{3,9}$ $\Psi_{4,9}$
3	1	16.07	-0.2998	0	1.292033	$\Psi_{3,1}$	$\Psi_{9,1}$ $\Psi_{9,2}$ $\Psi_{9,3}$ $\Psi_{9,4}$
		All other same species BIPs			1	$\Psi_{1,1}$ $\Psi_{3,3}$	$\Psi_{1,1}$ $\Psi_{2,2}$ $\Psi_{3,3}$ $\Psi_{4,4}$ $\Psi_{9,9}$ $\Psi_{1,2}$ $\Psi_{1,3}$ $\Psi_{1,4}$ $\Psi_{2,1}$ $\Psi_{2,3}$ $\Psi_{2,4}$ $\Psi_{3,1}$ $\Psi_{3,2}$ $\Psi_{3,4}$ $\Psi_{4,1}$ $\Psi_{4,2}$ $\Psi_{4,3}$

C. Calculation of VLE data for modified UNIFAC Dortmund method using spreadsheet

In the calculation of activity coefficients using modified UNIFAC Dortmund method, temperature T and liquid phase composition x_1 are given as input and γ_1 and γ_2 are calculated. Using Antoine Eq. (3), p_1^{sat} and p_2^{sat} are calculated, then total pressure P is calculated, and then correct temperature T is found out by regression using Eq. (4). The Antoine equation,

$$\ln p_i^{sat} = A_i - \frac{B_i}{T + C_i} \tag{3}$$

where, pressure is in kPa and temperature is in Kelvin. The constants A, B, and C of Antoine equations of iso-octane and benzene are listed in Table 3.

$$\%AAD \sum(\delta P) = \frac{100}{n}\sum_{i=1}^{n}\frac{\left|P_{i,pre.} - P_{i,cal.}\right|}{P_{i,pre.}} \tag{4}$$

Table 3: Antoine constants [11] for iso-octane and benzene

Compounds	A	B	C
iso-octane	13.6703	2896.31	-52.383
Benzene	13.7819	2726.81	-55.578

The table 4 presents calculated data by modified UNIFAC Dortmund method and Figure 1, 2, and 3 represent the predicted data in graphical form.

Table 4: Predicted VLE Data for iso-Octane/Benzene system using Modified UNIFAC Dortmund method

T (K)	x_1	p_1^{sat} (kPa)	p_2^{sat} (kPa)	γ_1	γ_2
353.1408	0	56.841	101.300	1.574	1.000
353.380	0.05	57.278	102.049	1.453	1.002
353.703	0.1	57.871	103.065	1.359	1.007
354.094	0.15	58.598	104.309	1.286	1.015
354.548	0.2	59.448	105.765	1.227	1.025
355.062	0.25	60.424	107.434	1.180	1.036
355.638	0.3	61.532	109.327	1.142	1.048
356.277	0.35	62.780	111.459	1.111	1.061
356.983	0.4	64.183	113.853	1.087	1.075
357.760	0.45	65.755	116.533	1.067	1.088
358.6128	0.5	67.514	119.529	1.051	1.102
359.545	0.55	69.481	122.875	1.038	1.115
360.562	0.6	71.677	126.606	1.027	1.128
361.669	0.65	74.129	130.766	1.019	1.140
362.871	0.7	76.864	135.401	1.013	1.152
364.172	0.75	79.915	140.562	1.008	1.163
365.577	0.8	83.317	146.308	1.005	1.173
367.092	0.85	87.109	152.703	1.003	1.182
368.721	0.9	91.338	159.818	1.001	1.190
370.469	0.95	96.050	167.731	1.000	1.196
372.339	1	101.300	176.529	1.000	1.212

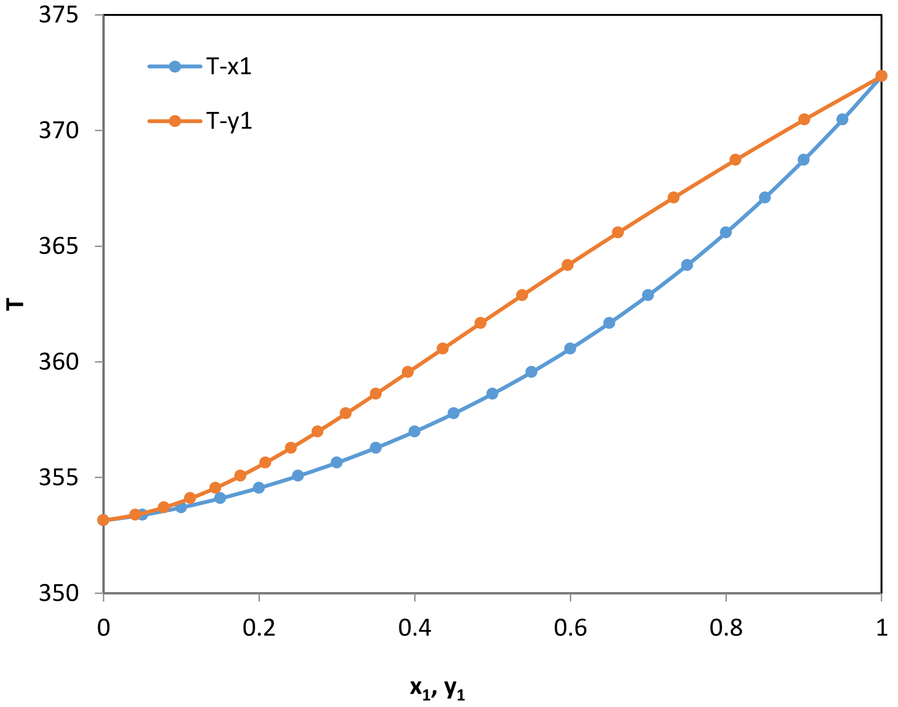

Figure 1: T-x-y diagram for iso-octane/benzene system

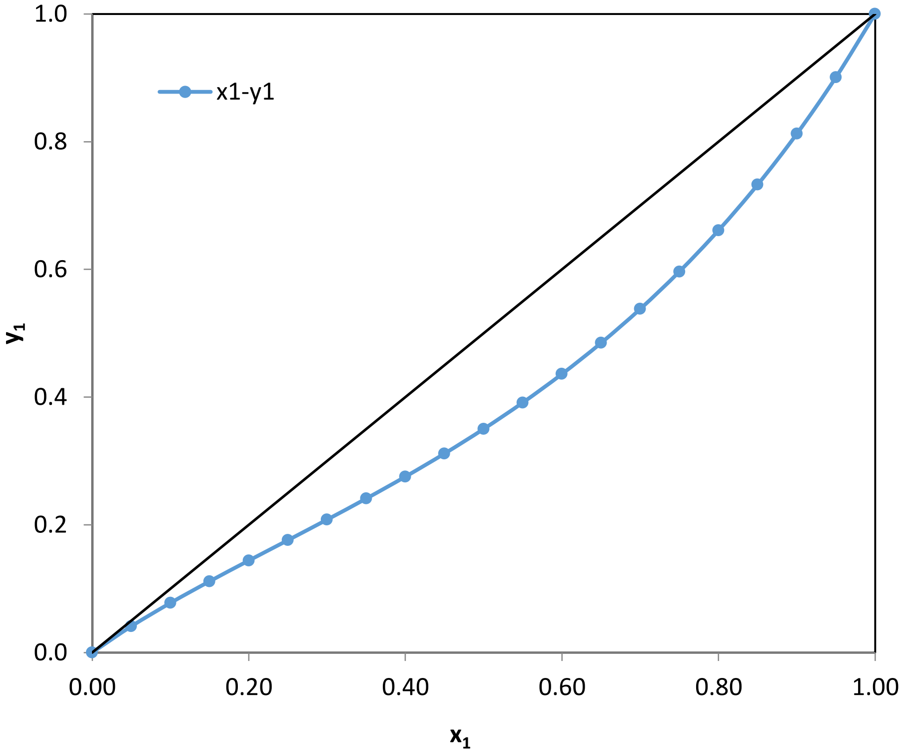

Figure 2: x-y diagram for iso-octane/benzene system

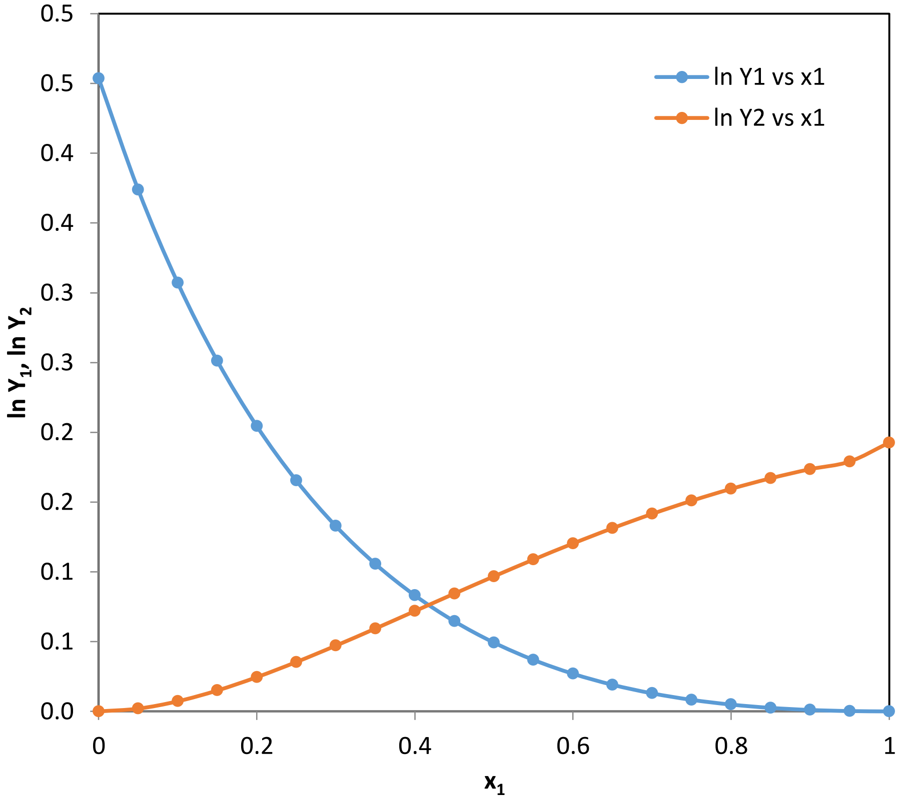

Figure 3: ln γ_i vs x_1 diagram for iso-octane/benzene system

IV. THERMODYNAMIC CONSISTENCY TEST OF THE PREDICTED VLE DATA

The thermodynamic consistency of the predicted vapour liquid equilibrium data is checked by semi-empirical Herington test [12]. In this method, the values for D and J are found out by Eq. (5) and Eq. (6) 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 $\lvert D - J \rvert$ for the binary system are listed in Table 5.

$$D = 100 \frac{\displaystyle\int_{x_1=0}^{x_1=1} \ln \frac{\gamma_1}{\gamma_2} dx_1}{\displaystyle\int_{x_1=0}^{x_1=1} \ln \left| \frac{\gamma_1}{\gamma_2} \right| dx_1} \qquad (5)$$

$$J = 150 \frac{T_{max} - T_{min}}{T_{min}} \qquad (6)$$

where T_{max} and T_{min} are maximum and mimimum boiling points in the system

Table 5: Thermodynamic consistency check for predicted data

D	J	$\lvert D\text{-}J \rvert$	Method	Result
6.7688	8.1546	13859	modified UNIFAC Dortmund	Pass

V. DATA REGRESSION BY EXCESS GIBBS ENERGY MODELS

The predicted VLE data are correlated with various models such as Van Laar, Wilson [13], NRTL [14] and UNIQUAC [15]. The calculated binary interaction parameters of all these models have been tabulated as under.

Table 6: Binary Interaction Parameters for iso-octane/benzene System

Model	Binary Parameters		AAD (δT)	AAD (δy)
Van Laar	A_{12} 0.4428	A_{21} 0.2130	0.0536	0.0013
Wilson	Λ_{12} -488.0942	Λ_{21} 2045.531	0.0326	0.0007
NRTL	$g_{12} - g_{22}$ 100.214	$g_{21} - g_{11}$ 797.51	0.2632	0.0049
UNIQUAC	$u_{12} - u_{22}$ 2130.747	$u_{21} - u_{11}$ -467.599	0.0096	0.0004

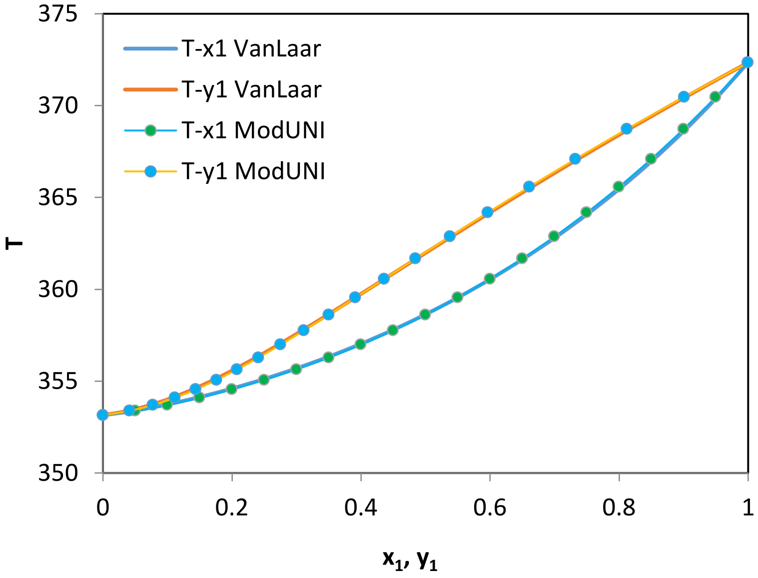

Figure 4: T-x_1-y_1 diagram calculated by Van Laar and predicted by Modified UNIFAC Dortmund method

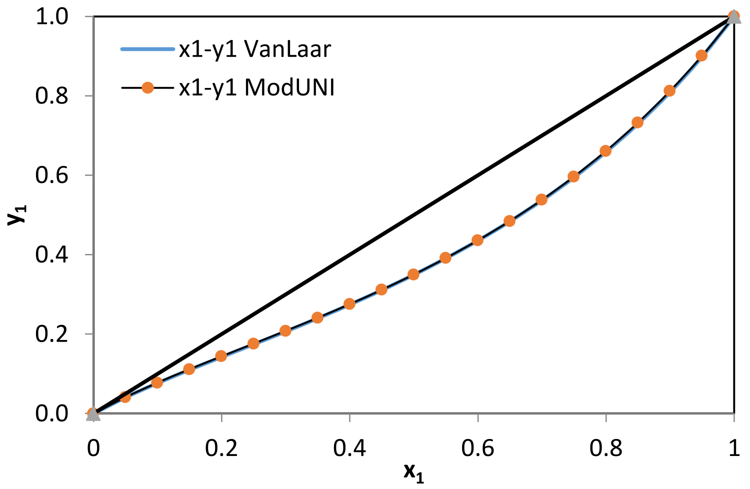

Figure 5: x_1-y_1 diagram calculated by Van Laar and predicted by Modified UNIFAC Dortmund method

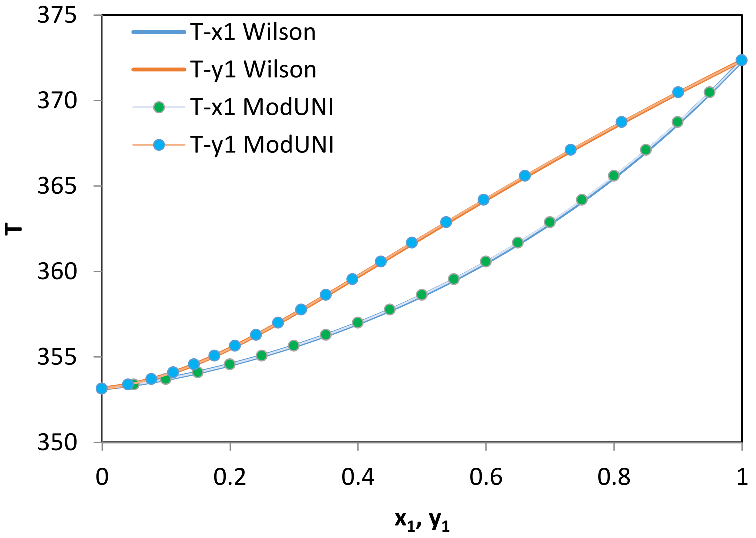

Figure 6: T-x_1-y_1 diagram calculated by Wilson and predicted by Modified UNIFAC Dortmund method

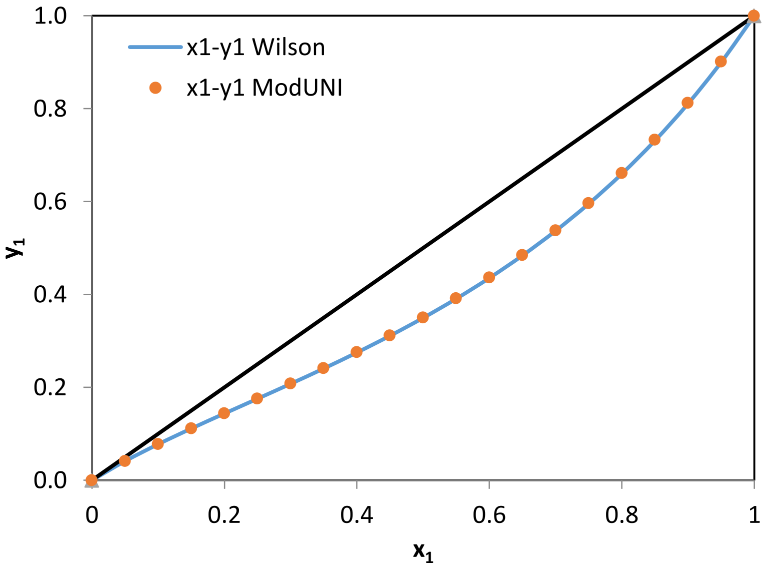

Figure 7: x_1-y_1 diagram calculated by Wilson and predicted by Modified UNIFAC Dortmund method

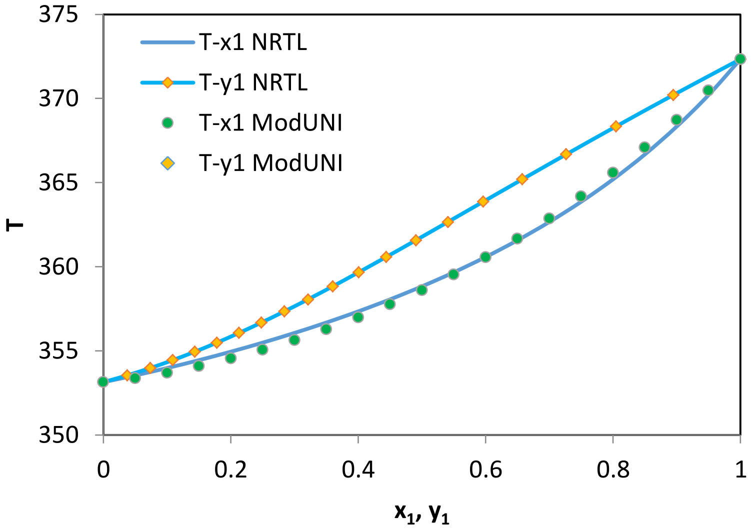

Figure 8: T-x_1-y_1 diagram calculated by NRTL and predicted by Modified UNIFAC Dortmund method

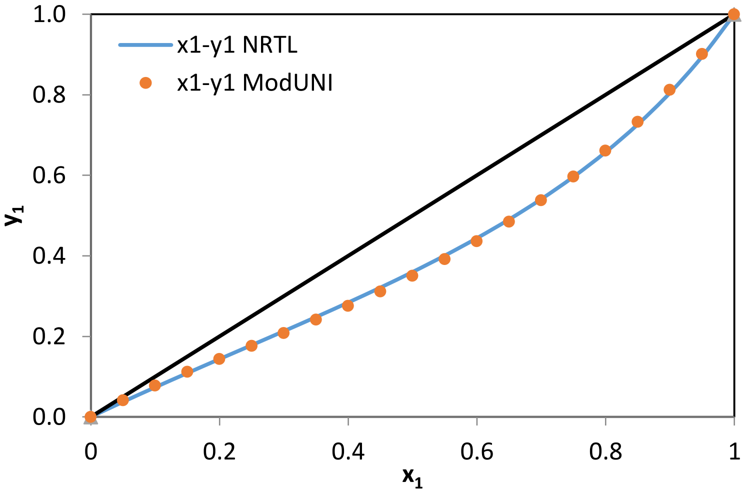

Figure 9: x_1-y_1 diagram calculated by NRTL and predicted by Modified UNIFAC Dortmund method

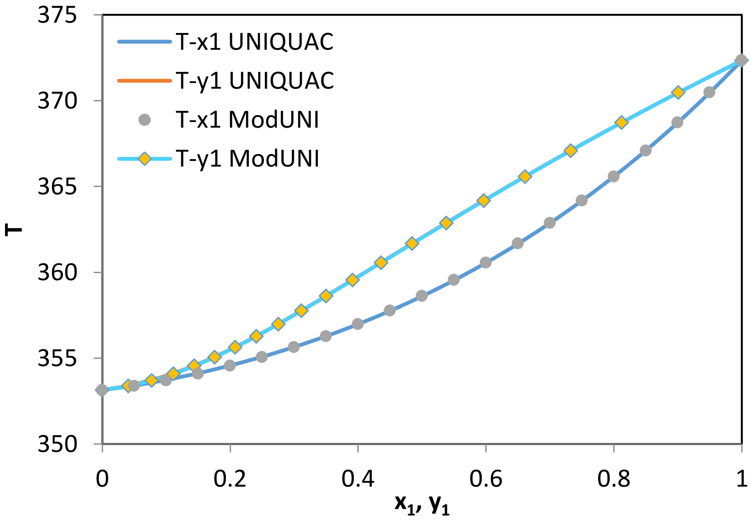

Figure 10: T-x_1-y_1 diagram calculated by UNIQUAC and predicted by Modified UNIFAC Dortmund method

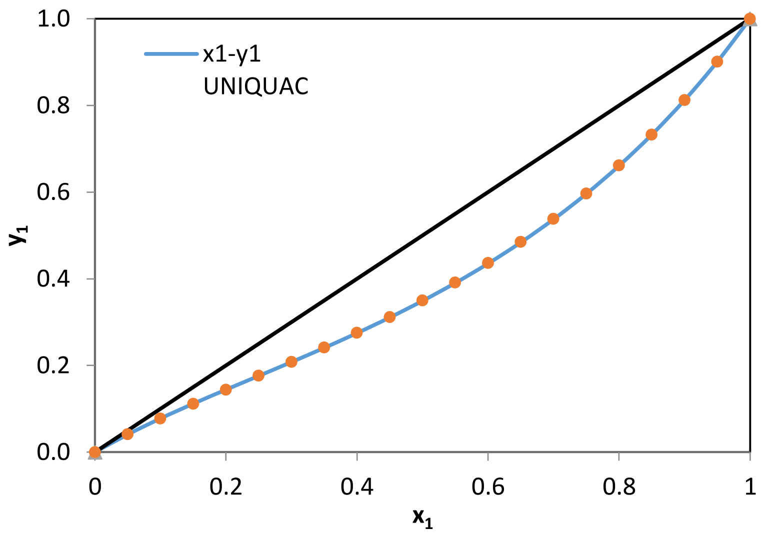

Figure 11: x_1-y_1 diagram calculated by UNIQUAC and predicted by Modified UNIFAC Dortmund method

VI. RESULTS AND DISCUSSION

Table 6 shows the binary interaction parameters, correlated with predicted VLE data by modified UNIFAC Dortmund method by various excess Gibbs energy models. α which is a characteristic constant of the non-randomness for the binary system is taken as 0.3. The comparison of predicted data by modified UNIFAC Dortmund method with calculated T-x_1-y_1 data by Van Laar, Wilson, NRTL and UNIQUAC models for the binary system iso-octane/benzene is given through Fig. 4 to Fig. 11. From the figures, it can be seen that isobaric VLE data predicted by modified UNIFAC Dortmund method for the system iso-octane and benzene are very well represented by Van Laar, Wilson, NRTL and UNIQUAC models.

VII. CONCLUSION

The vapour and liquid phase equilibrium data for the binary system 2,2,4-trimethylpentane and benzene system have been predicted at atmospheric pressure using modified UNIFAC Dortmund method. The activity coefficient models Van Laar, Wilson, NRTL and UNIQUAC have been found capable of accurately fitting the predicted VLE data by modified UNIFAC Dortmund method. The predicted data was found to be thermodynamically consistent. Azeotrope formation is not found for this system.

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