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Isobaric Vapour-Liquid Equilibrium Data Estimation Of CPME/Methanol System Using NRTL And Modified UNIFAC Dortmund Method

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Abstract - This paper reports experimental data of the isobaric vapor-liquid equilibria (VLE) for the CPME/Methanol at atmospheric pressure, determined using a copper still ebulliometer. The activity coefficients obtained from the experimental data were correlated by using different thermodynamic mathematical models like NRTL and Modified UNIFAC Dortmund Method. All the binary systems show a positive consistency when subjected to the point-to-point test of Van Ness. The prediction of VLE data obtained with the UNIFAC and ASOG methods has been verified with experimental data.

Keywords: VLE isobaric data; Activity coefficient; Methyl ester; Ethanol

I. INTRODUCTION

P. Anastas and J. Warner developed 12 principles of green chemistry in 1991[1]. Green chemistry is a set of principles or instructions that can be utilized in order to reduce or eliminate the use of hazardous substances in various stages of chemical production. Green solvents are the substances which cause less toxicity on the environment, health and safety. The use of green solvents instead of classical solvents can help in reducing the environmental footprint. Unfortunately, most of the solvents used in the chemical process industries are toxic, flammable, and hazardous. Cyclopentylmethylether (CPME) was made commercially available by Zeon Corporation since 2005 and it was approved by the toxic substances control act (TSCA) and the European list of notified chemical substances (ELINCS)[2]. CPME can potentially replace many classical solvents such as dioxane, diethyl ether, tetrahydrofuran, methyl tert-butyl ether and 1,2-dimethoxy ethane. It has several notable properties such as low evaporation energy, low solubility in water, higher boiling point, better stability in the acidic and basic environment, low peroxide formation, narrow explosion area, etc.[3]. These properties make CPME a popular choice as a reaction, extraction and crystallization solvent. CPME can be synthesized by four different alternatives: i) methylation of cyclopentanol by dimethyl sulphate, ii) addition of methanol to cyclopentene, iii) a two-stage process; first, reaction of cyclopentanol with sodium hydroxide to form sodium cyclopentoxide, then reaction of sodium cyclopentoxide with methyl iodide to get CPME, and iv) autocatalytic reaction of primary & secondary alcohols with trimethyl phosphate plus some amount of polyphosphoric acid to give CPME[4].

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:

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

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].

Detailed Procedure of Calculation of Activity Coefficients

Group identification of the compounds CPME and Methanol

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 Qk and Rk are collected from the literature [8] and tabulated in Table 1.

Table 1: Group identification for CPME and Methanol for modified UNIFAC Dortmund method

Compound	Group	Main group No.	Secondary group No.	V_K (I)	R_K	Q_K
CPME (1)	CH_3O	13	24	1	1.1434	1.6022
	c-CH_2	42	78	4	0.7136	0.8635
	c-CH	42	79	1	0.3479	0.1071
Methanol (2)	CH_3OH	6	15	1	0.8585	0.9938

Binary interaction parameters (BIPs) for CPME and Methanol:

The binary interaction parameters amn, bmn, and cmn 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.

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

TABLE 2: BIPS FOR CPME AND METHANOL FOR MODIFIED UNIFAC DORTMUND METHOD

N	M	A_{NM}	B_{NM}	C_{NM}	Ψ_{NM}	MAIN GROUP INTERACTION	SECONDARY GROUP INTERACTION
6	13	-87.48	-0.5522	0	2.250379	$\Psi_{6,13}$	$\Psi_{15,24}$
6	42	68.97	-0.42	0	1.240956	$\Psi_{6,42}$	$\Psi_{15,78}$ $\Psi_{15,79}$
13	42	251.4	-1.021	0	1.319136	$\Psi_{13,42}$	$\Psi_{24,78}$ $\Psi_{24,79}$
13	6	475.2	0.1198	0	0.217368	$\Psi_{13,6}$	$\Psi_{24,15}$
42	6	2540.7	-3.5236	0	0.018396	$\Psi_{42,6}$	$\Psi_{78,15}$ $\Psi_{79,15}$
42	13	-86.6	0.9724	0	0.488652	$\Psi_{42,13}$	$\Psi_{78,24}$ $\Psi_{79,24}$
					1	$\Psi_{6,6}$ $\Psi_{13,13}$ $\Psi_{42,42}$	$\Psi_{15,15}$ $\Psi_{24,24}$ $\Psi_{78,78}$ $\Psi_{79,79}$ $\Psi_{78,79}$ $\Psi_{79,78}$

III. 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 x1 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 CPME and Methanol 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 FOR CPME AND METHANOL

COMPOUNDS	A	B	C
CPME	15.0255	3798.52	-14.16
METHANOL	16.5785	3638.27	-33.424

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

TABLE 4: PREDICTED VLE DATA FOR CPME/METHANOL SYSTEM USING MODIFIED UNIFAC DORTMUND METHOD

T (K)	X_1	P_1^{SAT} (KPA)	P_2^{SAT} (KPA)	Γ_1	Γ_2
337.617	0	26.628	101.300	3.226	1.000
337.893	0.05	26.896	102.405	2.627	1.005
338.273	0.1	27.270	103.944	2.273	1.017
338.721	0.15	27.714	105.780	2.035	1.033
339.224	0.2	28.221	107.873	1.860	1.052
339.776	0.25	28.785	110.210	1.722	1.076
340.375	0.3	29.408	112.793	1.609	1.103
341.021	0.35	30.093	115.637	1.513	1.136
341.719	0.4	30.847	118.775	1.430	1.174
342.476	0.45	31.684	122.260	1.357	1.219
343.306	0.5	32.621	126.176	1.294	1.271
344.228	0.55	33.690	130.648	1.237	1.333
345.273	0.6	34.936	135.875	1.188	1.406
346.486	0.65	36.431	142.160	1.144	1.491
347.939	0.7	38.288	149.996	1.106	1.592

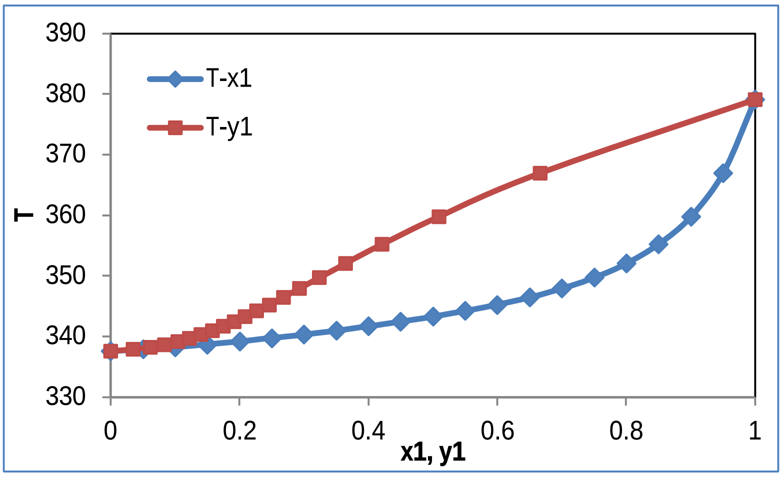

FIGURE 1: T-X-Y DIAGRAM FOR CPME/METHANOL SYSTEM

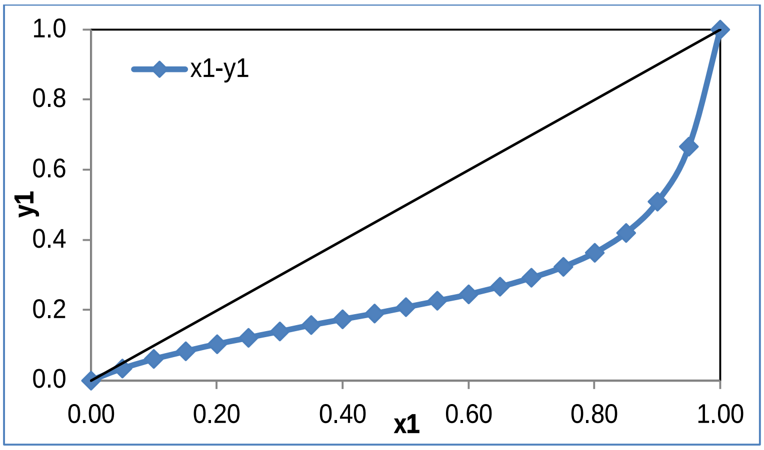

FIGURE 2: X-Y DIAGRAM FOR CPME/METHANOL SYSTEM

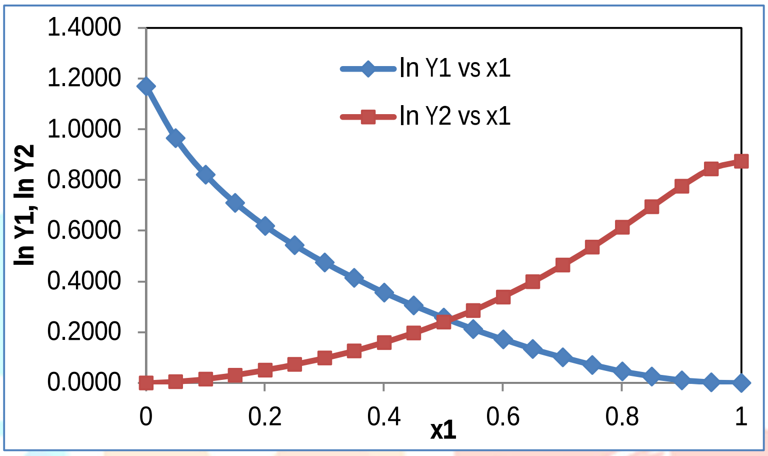

FIGURE 3: LN Γ_I VS X_1 DIAGRAM FOR CPME/METHANOL SYSTEM

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 [11]. 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 $|D - J|$ for the binary system are listed in Table 5.

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

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

Table 5: Thermodynamic consistency check for predicted data

D	J	│D-J│	Method	Result
5.6586	18.4494	12.7908	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 [12], NRTL [13] and UNIQUAC [14]. The calculated binary interaction parameters of all these models have been tabulated as under.

Table 6: Binary Interaction Parameters for CPME/Methanol System

Model	Binary Parameters		AAD (ΔT)	AAD (ΔY)
Van Laar	A_{12}	A_{21}	0.1076	0.0028
	1.000192	0.947433		
Wilson	$\Lambda_{12}-\Lambda_{11}$	$\Lambda_{21}-\Lambda_{22}$	0.0950	0.0014
	-1534.944	4805.7954		
NRTL	$G_{12}-G_{22}$	$G_{21}-G_{11}$	0.1014	0.0021
	1583.311	1486.08		
UNIQUAC	$U_{12}-U_{22}$	$U_{21}-U_{11}$	0.1343	0.0021
	3582.682	-861.969		

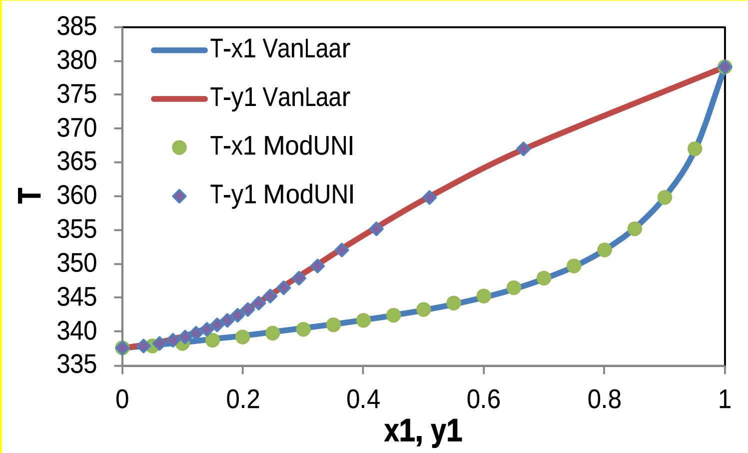

FIGURE 4: T-x_1-y_1 DIAGRAM CALCULATED BY VAN LAAR AND PREDICTED BY MODIFIED UNIFAC DORTMUND METHOD

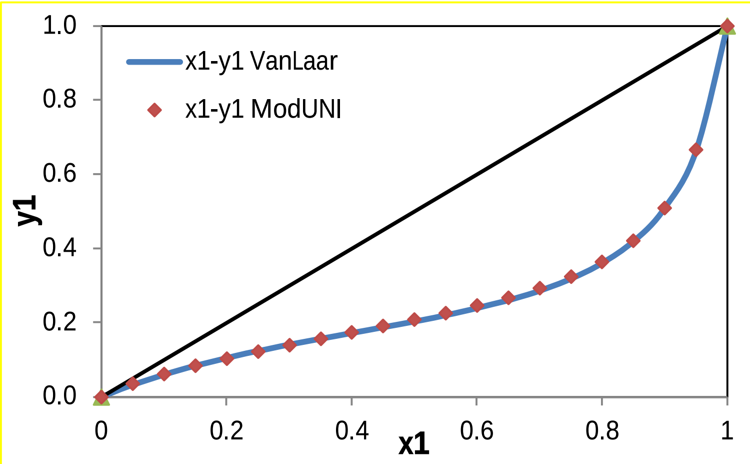

FIGURE 5: x_1-y_1 DIAGRAM CALCULATED BY VAN LAAR AND PREDICTED BY MODIFIED UNIFAC DORTMUND METHOD

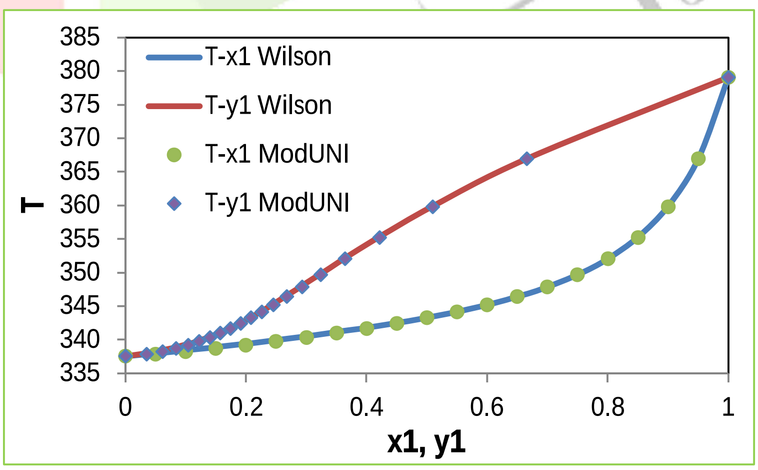

FIGURE 6: T-x_1-y_1 DIAGRAM CALCULATED BY WILSON AND PREDICTED BY MODIFIED UNIFAC DORTMUND METHOD

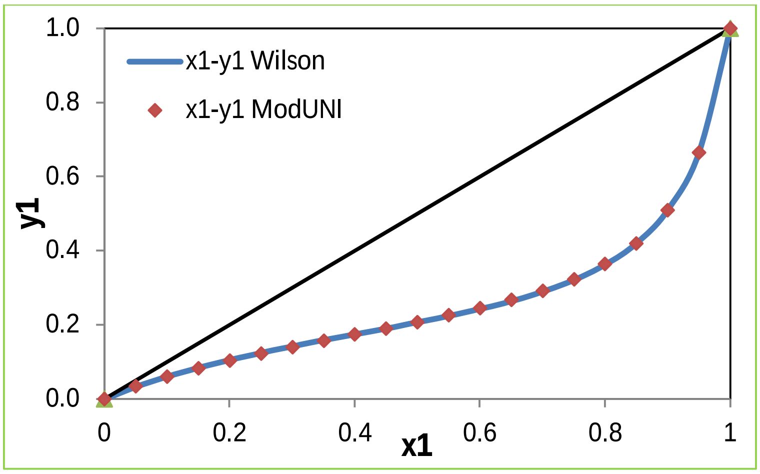

FIGURE 7: X_1-Y_1 DIAGRAM CALCULATED BY WILSON AND PREDICTED BY MODIFIED UNIFAC DORTMUND METHOD

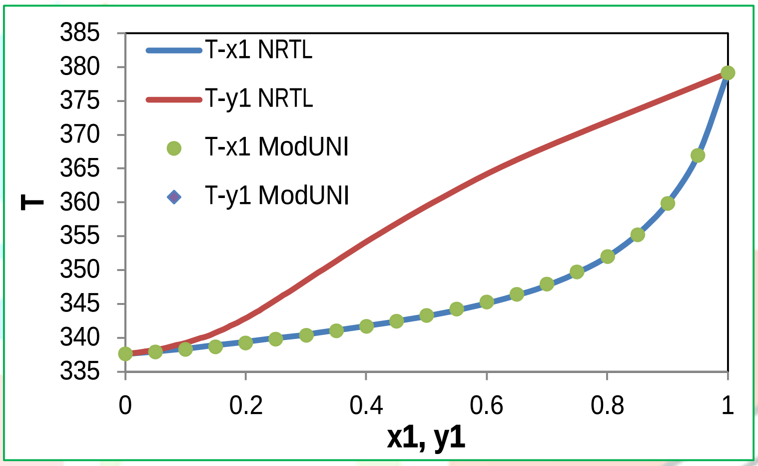

FIGURE 8: T-X_1-Y_1 DIAGRAM CALCULATED BY NRTL AND PREDICTED BY MODIFIED UNIFAC DORTMUND METHOD

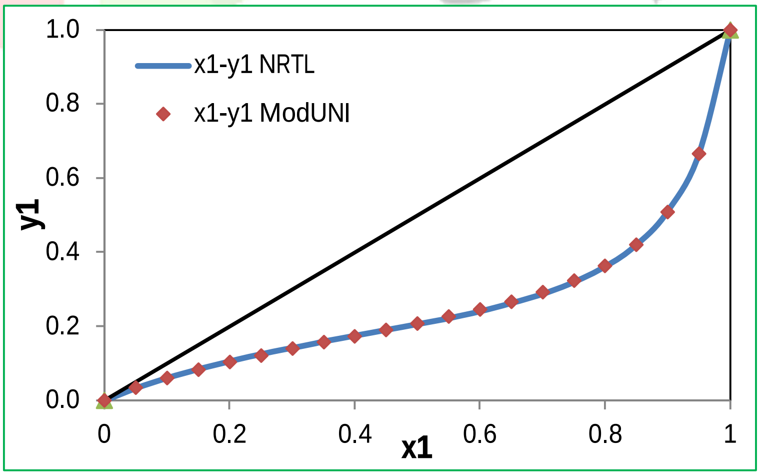

FIGURE 9: X_1-Y_1 DIAGRAM CALCULATED BY NRTL AND PREDICTED BY MODIFIED UNIFAC DORTMUND METHOD

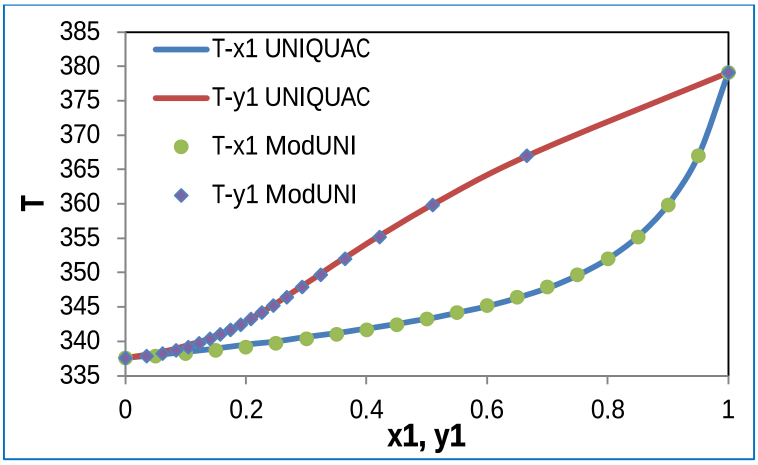

FIGURE 10: T-X_1-Y_1 DIAGRAM CALCULATED BY UNIQUAC AND PREDICTED BY MODIFIED UNIFAC DORTMUND METHOD

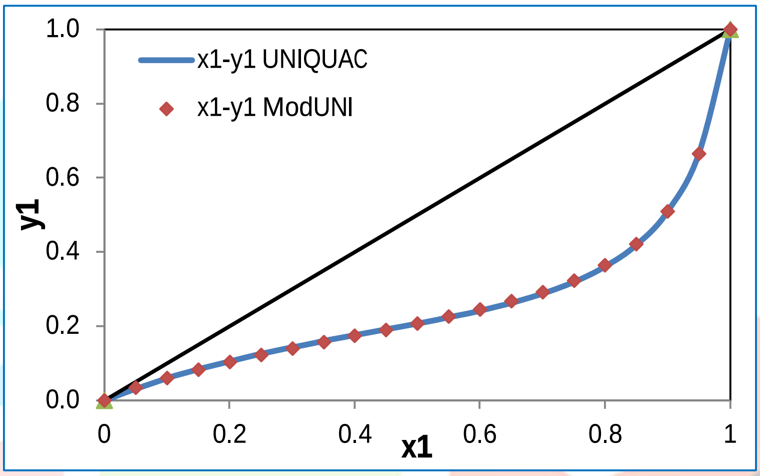

FIGURE 11: X_1-Y_1 DIAGRAM CALCULATED BY UNIQUAC AND PREDICTED BY MODIFIED UNIFAC DORTMUND METHOD

VI. RESULTS AND DISCUSSION

Table 6 shows the binary interaction parameters, correlated from predicted VLE data by modified UNIFAC Dortmund method. 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-x1-y1 data by Van Laar, Wilson, NRTL and UNIQUAC models for the binary system CPME/Methanol 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 CPME and Methanol 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 CPME and Methanol 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.

References

1. Kirk-Othmer Encyclopedia of Chemical Technology. 4th ed. Vol. 4. New York: John & Wiley Sons Inc.; 1998: 73-103.

2. V.M. Parsana and S.P. Parikh, Need for Vapour-Liquid Equilibrium Data Generation of Systems Involving Green Solvents, Int. J. Eng. Res. App. 5, 6(3), pp. 56–62 (2015)

3. J.D. Raal and A.L. Muhlbauer, Phase equilibria measurement & computation, first ed., Taylor & Francis, USA, 1998.

4. P.M. Gadhiya, V.M. Parsana, S.P. Parikh and M.H. Joshipura, Vapor-Liquid Equilibrium Data Prediction by Advanced Group Contribution Methods for a Binary System of Cyclopentyl Methyl Ether and Cyclopentanol at Atmospheric Pressure, International Journal of Advance Engineering and Research Development, 2(2), pp. 260-269 (2015)

5. V. M. Parsana and S. P. Parikh, Vapor-Liquid Equilibrium Data Prediction by Advanced Group Contribution Methods for a Binary System of Cyclopentyl methyl ether and Acetic acid at Atmospheric Pressure, Res. J. of Chem. Sci. 5, pp. 64-72 (2015).

6. V.M. Parsana, and S.P. Parikh, Isobaric Vapour-Liquid Equilibrium Data Prediction for a Binary System of 2-Methyltetrahydrofuran and Acetic acid using Group Contribution Methods, Proceedings of the 1st International Conference on Research & Entrepreneurship, RK University, Rajkot, India, 5-6, pp. 1750–1764 (Jan 2016) ISBN: 978-93-5254-061-7

7. B.E. Poling, J.M. Prausnitz, and J.P. O'Connell, The properties of gases and liquids, fifth ed., The McGraw-Hill Company limited, New York, pp. 8–23 (2012)

8. J. Gmehling, J. Li, M. Schiller, A modified UNIFAC model. 2. Present Parameter Matrix and Results for Different Thermodynamic Properties, Ind Eng Chem Res., 32(1), 178-93 (1993)

9. J. Lohmann, R. Joh, et al., From UNIFAC to Modified UNIFAC (Dortmund), Ind. Eng. Chem. Res. 40, pp. 957-964 (2001)

10. E.F.G. Herington, Tests for the consistency of experimental isobaric vapor-liquid equilibrium data, J. Inst. Pet. 37, pp. 457–470 (1951)

11. G.M. Wilson, Vapor-Liquid Equilibrium. XI. A New Expression for the Excess Free Energy of Mixing, J. Am. Chem. Soc. 86, pp. 127–130 (1964) doi:10.1021/ja01056a002

12. H. Renon and J.M. Prausnitz, Local compositions in thermodynamics excess functions for liquids mixtures, AIChE J. 14, pp. 135–144 (1968) doi: 10.1002/aic.690140124

13. H.C. VanNess, S.M. Byer and R.E. Gibbs, Vapor-Liquid Equilibrium: Part 1. An Appraisal of Data Reduction Methods, AlChE J. 19, pp. 238–244 (1973) doi: 10.1002/aic.690190206