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# Vapor-Liquid Equilibrium Data Prediction by Advanced Group Contribution Methods for a Binary System of Cyclopentyl methyl ether and Acetic acid at Atmospheric Pressure

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# Abstract

The isobaric vapour-liquid equilibrium data predictions for the binary system of cyclopentyl methyl ether and acetic acid have been obtained using UNIFAC method and modified UNIFAC Dortmund method. Group identification is done with Dortmund Data Bank and the same has been confirmed by artist free software. The interaction parameters in the UNIFAC method and modified UNIFAC Dortmund method, for the ether group (-CH<sub>3</sub>O) and acid (-COOH), are used to predict VLE data. Thermodynamic consistency of the predicted VLE data has been checked by the Herington method. The predicted data have been correlated with Van Laar, Wilson and NRTL activity coefficient models. The binary interaction parameters of models had been obtained by regression. The predicted VLE data of UNIFAC method fit much more accurately than that of modified UNIFAC Dortmund method by these activity coefficient models Van Laar, Wilson and NRTL.

**Keywords:** Vapor-liquid equilibrium, cyclopentyl methyl ether, acetic acid, UNIFAC method, modified UNIFAC Dortmund method.

## Introduction

Traditional solvents play a key role in the chemical process industries and hence they are major contributor to the concerns related to their impact on environment, health and safety because most of the solvents are flammable, volatile and toxic. The solvents that have reduced or no toxicity to health and environment compared to the traditional solvents are called green solvents. These green solvents may provide an attractive alternative to the traditional solvents. Cyclopentyl methyl ether (CPME) is considered to be one of the green solvents<sup>1</sup> which has high boiling point (379.15 K) and preferable characteristics such as low peroxide formation, high hydrophobicity, relative stability under acidic and basic conditions, high boiling point and low melting point, low heat of vaporization, narrow explosion area and low solubility of salts. Due to such characteristics CPME is preferred as an alternative to other solvents ethereal such as tetrahydrofuran, 2-methyl tetrahydrofuran, dioxane (carcinogenic), 2and 1, dimethoxyethane, which are hazardous to human health and environment<sup>2</sup>.

The recovery of acetic acid from water has become industrial problem of public concern because this separation process has a major influence on economy of products, resource utilization and important meanings for environmental protection. Hongxun Zhang, Guangyu Liu, Chen Li, et al. measured liquid-liquid equilibria of water + acetic acid + Cyclopentyl methyl ether (CPME) system at different temperatures and concluded that

CPME would be a good substitute for conventional organic solvents to separate acetic acid from water by the method of liquid-liquid extraction followed by heteroazeotropic distillation<sup>3</sup>. After literature survey it is found that vapour-liquid equilibrium data for CPME + Acetic acid system which is essential for the design of distillation column for separating CPME and acetic acid from their mixture does not exist in the literature. So investigation on VLE data of this binary system becomes necessary. The experimental determination of VLE data requires sophisiticated and suitable VLE apparatus and composition measurement instruments such as gas chromatograph, refractometer, spectrophotometer, etc. So this procedure is very costly and time-consuming. Numerical simulations using group contribution methods provide an alternative to experimental measurement of VLE data. The aim of this paper is to predict VLE data for CPME with acetic acid at atmospheric pressure.

Advanced Group Contribution Methods: Reliable values of the properties of materials are necessary for the design of industrial processes. The knowledge of physical properties of fluids is essential in the design of many kinds of products, processes, and industrial equipment<sup>4</sup>. The vapour-liquid equilibrium (VLE) data are essential for the design of chemical and separation processes. When experimental binary data are available, phase equilibrium behaviour is easily modelled with the help of cubic equation of state (using fugacity coefficient data) and local composition g<sup>E</sup> models (using activity coefficient data). When little or no experimental data are available, group

contribution (GC) methods can be employed to predict the phase equilibrium under specified conditions of temperature and composition<sup>5,6</sup>. So prediction of thermodynamic properties is important in chemical process and product design. Various GC methods are available for the prediction of VLE data. Some examples of GC methods which have been developed for the estimation of properties of pure compounds include those published by Joback and Reid<sup>7</sup>, Lydersen<sup>8</sup>, Ambrose<sup>9</sup>, Constantinou and Gani<sup>10</sup> and Marrero and Gani<sup>11,12</sup>. On the other hand, many GC based property models have also been developed to predict properties of mixtures mainly to predict the non-ideality of the liquid phase using activity coefficients which includes ASOG<sup>13,14</sup>, Original UNIFAC<sup>15</sup>, Modified UNIFAC Dortmund<sup>16</sup> and PSRK<sup>17</sup>. In the present work, well known and established group-contribution methods such as UNIFAC method and modified UNIFAC Dortmund method are employed to predict liquid phase activity coefficients for binary mixtures of CPME and acetic acid.

**UNIFAC method and modified UNIFAC Dortmund methods:** The general UNIFAC equation is as follows with the combinatorial and residual contributions:

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

The combinatorial part,

$$\ln \gamma_{i(\text{combinatorial})} = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_j x_j l_j$$
(2)

Where,

$$l_{i} = \frac{z}{2} (r_{i} - q_{i}) - (r_{i} - 1)$$
(3)

$$\theta_{i} = \frac{q_{i} x_{i}}{\sum_{i} q_{j} x_{j}}$$
(4)

$$\Phi_{i} = \frac{r_{i} x_{i}}{\sum_{j} r_{j} x_{j}}$$
(5)

$$\mathbf{r}_{i} = \sum \mathbf{v}_{k}^{(i)} \mathbf{R}_{k} \tag{6}$$

$$q_i = \sum v_k^{(i)} Q_k \tag{7}$$

$$R_{k} = \frac{V_{wk}}{15.17} \tag{8}$$

$$Q_{k} = \frac{A_{wk}}{2.5 \times 10^{9}}$$
(9)

Where:  $V_k^{(i)}$ , always an integer, is the number of groups of type k in molecule i. Group parameters  $R_k$  and  $Q_k$  are obtained from the van der Waals group volume and surface areas  $V_{wk}$  and  $A_{wk}$ , given by Bondi<sup>4</sup>. The value of parameter Z is taken as 10.

And the residual part,

$$\ln \gamma_{i(\text{residual})} = \sum_{k} \nu_{k}^{(i)} \left( \ln \Gamma_{k} - \ln \Gamma_{k}^{(i)} \right)$$
(10)

Where,

$$\ln \Gamma_{k} = Q_{k} \left( 1 - \ln \left( \sum_{m} \theta_{m} \Psi_{mk} \right) - \sum_{m} \frac{\theta_{m} \Psi_{km}}{\sum_{n} \theta_{n} \Psi_{nm}} \right)$$
(11)

Where, the group area fraction  $\theta_m$  and group mole fraction  $X_m$  are given by the following equations:

$$\theta_{m} = \frac{Q_{m}X_{m}}{\sum_{n}Q_{n}X_{n}} \quad (12)$$
$$X_{m} = \frac{\sum_{j}V_{m}^{(j)}x_{j}}{\sum_{j}\sum_{n}V_{n}^{(j)}x_{j}} \quad (13)$$

Where, the group-interaction parameter  $\Psi_{mn}$  is given by the following equation:

$$\Psi_{mn} = \exp\left(-\frac{U_{mn} - U_{nn}}{RT}\right) = \exp\left(-\frac{a_{mn}}{T}\right)$$
(14)

Where:  $U_{mn}$  is a measure of the energy of interaction between group m and n. Note that  $a_{mn}$  has unit of Kelvin and  $a_{mn} \neq a_{nm}$ .

In the Original UNIFAC model, the interaction parameters are considered to be independent of temperature. Therefore, quantitative predictions of excess enthalpies, H<sup>E</sup> could not be obtained. In order to improve this and other things, the modified UNIFAC Dortmund method was developed. The usage of modified UNIFAC Dortmund method leads to much better results. This means that the introduction of temperature-dependent parameters allows a more reliable temperature extrapolation and the extension of the range of applicability<sup>18,19</sup>. In both UNIFAC method and modified UNIFAC Dortmund method, there is a difference in both combinatorial and residual part. These differences are given in the following equations.

In modified UNIFAC Dortmund method, equation-2 and equation-14 of UNIFAC method are replaced by equation-15

and equation-19 as described below.

$$\ln \gamma_{i(\text{combinatorial})} = 1 - V_i' + \ln V_i' - 5q_i \left( 1 - \frac{V_i}{F_i} + \ln \left( \frac{V_i}{F_i} \right) \right)$$
(15)

Where,

$$\mathbf{V}_{i} = \frac{\mathbf{r}_{i}}{\sum_{i} \mathbf{x}_{j} \mathbf{r}_{j}} \tag{16}$$

$$F_{i} = \frac{q_{i}}{\sum_{j} x_{j} q_{j}}$$
(17)

$$\mathbf{V}_{i}^{'} = \frac{r_{i}^{\frac{3}{4}}}{\sum_{j} x_{j} r_{j}^{\frac{3}{4}}}$$
(18)

and

$$\Psi_{mn} = \exp\left(-\frac{a_{mn} + b_{mn}T + c_{mn}T^2}{T}\right)$$
(19)

In addition to that, in the residual part, temperature dependent interaction parameters are used where they have a logarithmic and quadratic dependency towards temperature. Due to this temperature dependency, the predictions of VLE,  $H^E$  and  $\gamma_i^{\infty}$  have improved since it is based on more experimental data. The modified UNIFAC Dortmund method can also extrapolate reliable the predictions of VLE at higher temperatures compared

reliably the predictions of VLE at higher temperatures compared to the Original UNIFAC<sup>19</sup>.

**Group identification of the compounds:** Group contribution methods predict properties of pure compounds or mixtures based on the groups existing in the compounds so correct identification of groups is very essential. Group identification for UNIFAC method is done using the data given in the literature<sup>4</sup> and for modified UNIFAC Dortmund method it is done using the data given in the literature<sup>18</sup>. The identified groups are presented in table-1 and table-2 respectively. The identified groups have been verified with Dortmund data bank by using artist free software.

**Binary interaction parameters (BIPs):** Binary interaction parameters  $(a_{mn})$  for UNIFAC method have been taken from the literature<sup>4</sup> and  $(a_{mn}, b_{mn}, and c_{mn})$  for modified UNIFAC Dortmund method have been taken from the literature<sup>18,19,20</sup> which are presented in table-3 and table-4 respectively.

**Calculation of VLE data using group contribution methods:** The VLE data for binary system CPME and acetic acid are calculated through a spread sheet in which temperature T and  $x_1$ are given as input and  $\gamma_1$  and  $\gamma_2$  are calculated using group contribution methods as described in the precious sections. Using Antoine equation-20,  $p_1^{sat}$  and  $p_2^{sat}$  are calculated, then total pressure P is calculated and correct temperature T is found out by regression using equation-23. The calculated data are presented in table-5 and table-6 for UNIFAC method and modified UNIFAC Dortmund method respectively.

Table-1 Group identification for CPME and acetic acid for UNIFAC

methou								
Name	Group no.*		Group no.*		V <sub>k</sub> (i)	R <sub>k</sub>	$\mathbf{Q}_{\mathbf{k}}$	
	Μ	S						
$CH_2$	1	2	4	0.6744	0.540			
CH	1	3	1	0.4469	0.228			
CH <sub>3</sub> O	13	24	1	1.1450	1.088			
CH <sub>3</sub>	1	1	1	0.9011	0.848			
COOH	20	42	1	1.3013	1.224			
	Name           CH2           CH           CH3O           CH3           COOH	Gr           Name         Gr           M         M           CH2         1           CH         1           CH3O         13           CH3         1           COOH         20	Name         Grownow           M         S           CH2         1         2           CH         1         3           CH3O         13         24           CH3         1         1           COOH         20         42	Internota           Name $Group no.*$ $V_k$ (i)           M         S $S$ CH <sub>2</sub> 1         2         4           CH         1         3         1           CH <sub>3</sub> O         13         24         1           CH <sub>3</sub> 1         1         1           COOH         20         42         1	Method           Name         Group no.* $V_k$ (i) $R_k$ M         S         V         V         R			

M=Main Group no., S=Secondary Group no.

Table-2 Group identification for CPME and acetic acid for modified UNIFAC Dortmund method

Molecu	Name	Group no. <sup>*</sup>		V <sub>k</sub> (i)	R <sub>k</sub>	Q <sub>k</sub>
le (1)		Μ	S			
CDME	c-CH <sub>2</sub>	42	78	4	0.7136	0.8635
(1)	c-CH	42	79	1	0.3479	0.1071
	CH <sub>3</sub> O	13	24	1	1.1434	1.6022
Acetic	CH <sub>3</sub>	1	1	1	0.6325	1.0608
acid (2)	COOH	20	42	1	0.8000	0.9215

<sup>\*</sup>M=Main Group no., S=Secondary Group no.

Table-3
BIPs for CPME and acetic acid for UNIFAC method

Diff of the und accele acta for erth fre method									
Group	CH <sub>3</sub>	CH <sub>2</sub>	СН	CH <sub>3</sub> O	СООН				
CH <sub>3</sub>	0.0	0.0	0.0	251.5	663.5				
$CH_2$	0.0	0.0	0.0	251.5	663.5				
CH	0.0	0.0	0.0	251.5	663.5				
CH <sub>3</sub> O	83.36	83.36	83.36	0.0	664.6				
COOH	315.3	315.3	315.3	-338.5	0.0				

The Antoine equation,

$$\ln p_i^{\text{sat}} = A_i - \frac{B_i}{T + C_i}$$
(20)

Where pressure is in kPa and temperature is in Kelvin<sup>21</sup>. The constants A, B, and C of Antoine equations of CPME and acetic acid are listed in table- $7^{22}$ .

**Thermodynamic Consistency Test:** The thermodynamic consistency of the predicted VLE data for the binary system is checked by semi-empirical Herington method. In this method, the values for D and J are found out by equation-21 and equation-22 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

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binary system are listed in table-8.

$$D = 100 \frac{\int_{x_1=0}^{x_1=1} \ln \frac{\gamma_1}{\gamma_2} dx_1}{\int_{x_1=0}^{x_1=1} \ln \left| \frac{\gamma_1}{\gamma_2} \right| dx_1}$$
(21)

$$J = 150 \frac{T_{max} - T_{min}}{T_{min}}$$
(22)

**Data Reduction Using g<sup>E</sup> Models:** The predicted VLE data are correlated by various models such as Van Laar, Wilson and NRTL<sup>24,25</sup>. The vapor pressures of pure components are calculated by equation-20. By the minimization of the objective function %AAD  $\sum(\delta P)$ , the binry interaction parameters are

obtained for these models which are used to minimize error by the regression procedure. (%AAD = absolute average deviation and n represents no. of predicted data points). Similarly AAD  $\sum(\delta T)$  and AAD  $\sum(\delta y)$  are calculated by equation-24 and equation-25 respectively. The "pre" and "cal" subscripts represent the predicted and calculated values respectively.

$$\% \text{AAD} \Sigma(\delta P) = \frac{100}{n} \sum_{i=l}^{n} \frac{\left| P_{i,\text{pre.}} - P_{i,\text{cal.}} \right|}{P_{i,\text{pre.}}}$$
(23)

$$AAD \sum (\delta T) = \frac{1}{n} \sum_{i=1}^{n} \left| T_{i, \text{pre.}} - T_{i, \text{cal.}} \right|$$
(24)

$$AAD \sum (\delta y) = \frac{1}{n} \sum_{i=1}^{n} \left| y_{i, \text{pre.}} - y_{i, \text{cal.}} \right|$$
(25)

Table-4
BIPs for CPME and acetic acid for modified UNIFAC Dortmund method

	Group	m	n	a <sub>mn</sub>	b <sub>mn</sub>	c <sub>mn</sub>	a <sub>nm</sub>	<b>b</b> <sub>nm</sub>	c <sub>nm</sub>
CH <sub>3</sub>	CH <sub>3</sub> O	1	13	-9.654	-0.03242	233.1	-0.3155	0	0
CH <sub>3</sub>	СООН	1	20	2017.7	-9.0933	1182.2	-3.2647	0.009198	0.01024
CH <sub>3</sub>	c-CH <sub>2</sub> , c-CH	1	42	1020.8	-6.0746	-680.95	4.0194	-0.006878	0.01015
CH <sub>3</sub> O	c-CH	13	20	-310.82	0	521.48	0	0	0
CH <sub>3</sub> O	c-CH <sub>2</sub> , c-CH	13	42	-86.6	0.9724	251.4	-1.021	0	0
COOH	c-CH <sub>2</sub> , c-CH	20	42	582.81	1.4976	1169.3	-3.0737	0	0

#### Table-5 VLE data for CPME and acetic acid binary system at atmospheric pressure by UNIFAC method

T/K	x <sub>1</sub>	<b>y</b> <sub>1</sub>	$\gamma_1$	$\gamma_2$
379.15	1.0000	1.0000	1.0000	
378.57	0.9500	0.9367	1.0025	1.8825
378.24	0.9000	0.8850	1.0094	1.7298
378.07	0.8500	0.8406	1.0200	1.6074
378.03	0.8000	0.8009	1.0339	1.5079
378.08	0.7500	0.7643	1.0508	1.4258
378.21	0.7000	0.7296	1.0706	1.3571
378.42	0.6500	0.6960	1.0934	1.2990
378.69	0.6000	0.6628	1.1192	1.2494
379.03	0.5500	0.6295	1.1484	1.2067
379.44	0.5000	0.5956	1.1813	1.1697
379.92	0.4500	0.5605	1.2185	1.1375
380.49	0.4000	0.5238	1.2606	1.1094
381.14	0.3500	0.4847	1.3087	1.0848
381.90	0.3000	0.4424	1.3640	1.0635
382.80	0.2500	0.3958	1.4282	1.0453
383.85	0.2000	0.3432	1.5036	1.0299
385.11	0.1500	0.2824	1.5930	1.0175
386.66	0.1000	0.2097	1.7007	1.0081
388.60	0.0500	0.1191	1.8324	1.0021
391.12	0.0000	0.0000		1.0000

Table-6 VLE data for CPME and acetic acid binary system at atmospheric pressure by modified UNIFAC Dortmund

method									
T/K	x <sub>1</sub>	<b>y</b> <sub>1</sub>	$\gamma_1$	$\gamma_2$					
379.15	1.0000	1.0000	1.0000	1.6644					
378.97	0.9500	0.9465	1.0015	1.5714					
378.90	0.9000	0.8987	1.0058	1.4910					
378.92	0.8500	0.8551	1.0126	1.4216					
379.01	0.8000	0.8143	1.0219	1.3613					
379.18	0.7500	0.7757	1.0334	1.3090					
379.40	0.7000	0.7383	1.0471	1.2634					
379.68	0.6500	0.7015	1.0630	1.2236					
380.02	0.6000	0.6649	1.0810	1.1888					
380.42	0.5500	0.6279	1.1012	1.1583					
380.88	0.5000	0.5901	1.1237	1.1314					
381.40	0.4500	0.5510	1.1488	1.1078					
381.99	0.4000	0.5102	1.1769	1.0870					
382.66	0.3500	0.4670	1.2085	1.0686					
383.41	0.3000	0.4209	1.2442	1.0524					
384.26	0.2500	0.3710	1.2854	1.0383					
385.23	0.2000	0.3163	1.3336	1.0261					
386.35	0.1500	0.2552	1.3912	1.0158					
387.65	0.1000	0.1852	1.4619	1.0077					
389.20	0.0500	0.1025	1.5510	1.0021					
391.12	0.0000	0.0000	1.6667	1.0000					

Table-7 Antoine equation constants

Compound	Anto	temperature		
Compound	Α	В	С	range/K
CPME	15.0255	3798.52	-14.2	357 to 395
AA	15.0694	3580.79	-48.5	375 to 395

Table-8 Thermodynamic consistency check

D	)	J	D-J	Method
22.	01	4.74	17.27	UNIFAC
26.	46	4.74	21.72	modified UNIFAC Dortmund

The binary interaction parameters, correlated from predicted VLE data by UNIFAC method and modified UNIFAC Dortmund method, are shown in table-9 and table-10 respectively.  $\alpha$  which is a characteristic constant of the non-randomness for the binary system is recommended as 0.3 for this binary system because it belongs to type I system according to the definition given in the literature<sup>25</sup>. The comparison of predicted data by UNIFAC method and modified UNIFAC Dortmund method with calculated T-x<sub>1</sub>-y<sub>1</sub> data by Van Laar, Wilson, and NRTL models for the binary system CPME (1) + acetic acid (2) at atmospheric pressure is given through figure-1 to figure-6.

Table-9 Correlated model BIPs from predicted data by UNIFAC method

inctriou									
Model	Binary	Parameter	AAD (ΔT)	AAD (Δy)					
Van	A <sub>12</sub>	A <sub>21</sub>	0.0601	0.0022					
Laar	0.6358	0.6760	0.0001	0.0025					
Wilson	a <sub>12</sub>	a <sub>21</sub>	0.0564	0.0020					
w iisoii	-1253.267	3534.491275	0.0304	0.0020					
NRTL	b <sub>12</sub>	b <sub>21</sub>	0.0649	0.0022					
	1311.714	883.945	0.0048	0.0025					

Table-10 Correlated model BIPs from predicted data by modified UNIFAC Dortmund method

Model	Binary I	Parameter	AAD (ΔT)	AAD (Δy)
Van	A <sub>12</sub> A <sub>21</sub>		0.0200	0.0021
Laar	0.4714	0.4819	0.0399	0.0021
Wilson	a <sub>12</sub>	a <sub>21</sub>	0.0363	0.0018
w iison	-1428.309	3044.001492	0.0303	0.0018
NDTI	b <sub>12</sub>	b <sub>21</sub>	0.0204	0.0010
INKIL	778.801	795.580	0.0394	0.0019



T-x<sub>1</sub>-y<sub>1</sub> diagram calculated by Van Laar and predicted by UNIFAC method



T- $x_1$ - $y_1$  diagram calculated by Wilson and predicted by UNIFAC method



T- $x_1$ - $y_1$  diagram calculated by NRTL and predicted by UNIFAC method



T-x1-y1 diagram calculated by Van Laar and predicted by modified UNIFAC Dortmund method



T-x<sub>1</sub>-y<sub>1</sub> diagram calculated by Wilson and predicted by modified UNIFAC Dortmund method



T-x<sub>1</sub>-y<sub>1</sub> diagram calculated by NRTL and predicted by modified UNIFAC Dortmund method

From figure-1 to figure-6, it can be seen that isobaric VLE data predicted by UNIFAC method and modified UNIFAC Dortmund method are very well represented by Van Laar, Wilson and NRTL models.

# Conclusion

The VLE data for the binary system CPME with acetic acid have been predicted at atmospheric pressure using UNIFAC method and modified UNIFAC Dortmund method. The activity coefficient models Van Laar, Wilson and NRTL have been found capable of accurately fitting the predicted VLE data by UNIFAC method and modified UNIFAC Dortmund method. However, they fail the consistency test by Herington. Azeotrope formation is found for this system.

# Nomenclature

- P Absolute pressure, kPa
- T Absolute temperature, K
- $\theta_i$  Surface area fraction of compound i
- $\Phi_{i}$  Volume fraction of compound i
- r<sub>i</sub> Relative Van der Waals volume of compound i
- q<sub>i</sub> Relative Van der Waals surface area of compound i
- $Q_k$  Relative Van der Waals surface area of subgroup k
- R<sub>k</sub> Relative Van der Waals volume of subgroup k
- $\Gamma$  Temperature dependant integration constant
- $\theta_m$  Surface area fraction of subgroup m

- X<sub>m</sub> Mole fraction of subgroup m
- $\Psi$  Group-interaction parameter
- V<sub>i</sub> Volume/mole fraction of compound i in the mixture
- $F_{i_{1}}$  Surface area fraction of compound i in the mixture
- $\dot{V_i}$  Modified volume/mole fraction of compound i in the mixture (modified UNIFAC Dortmund method)
- ln Natural logarithm (base e)
- log Logarithm (base 10)
- $x_i$  Liquid phase mole fraction of  $i^{th}$  species
- y<sub>i</sub> Vapor phase mole fraction of i<sup>th</sup> species
- $\gamma_i$  Activity coefficient of i<sup>th</sup> species
- $H^E$  Excess enthalpy
- A<sub>ii</sub> Adjustable parameter (Van Laar Model)
- $\lambda_{ii}$  Interaction parameter (Wilson Model)
- $\Lambda_{ii}$  Adjustable parameter (Wilson Model)
- $\alpha_{ii}$  -The non-randomness of the fluid empirical parameter
- $\tau_{ii}$  Adjustable parameter (NRTL Model)
- A, B, C- Antoine equation constants

### Superscripts

- E Excess property
- sat Saturated property value
- $\infty$  Property at infinite dilution concentration

#### Subscripts

1 - Component 1

- 2 - Component 2
- Property of i<sup>th</sup> species
  Property of j<sup>th</sup> species i
- i

# References

- 1. Kiyoshi W., The Toxicological Assessment of Cvclopentvl Methyl Ether (CPME) as a Green Solvent. Molecules, 18(3), 3183-3194 (2013)
- 2. Kiyoshi W., Noriyuki Y. and Yasuhiro T., Cyclopentyl Methyl Ether as a New and Alternative Process Solvent, Organic Process Research and Development, 11(2), 251-258 (2007)
- Zhang H., Liu G., Li C. and Zhang L., Liquid-Liquid 3. Equilibria of Water + Acetic Acid + Cyclopentyl Methyl Ether (CPME) System at Different Temperatures, Journal of Chemical and Engineering Data, 57(11), 2942-2946 (2012)
- Poling B.E., Prausnitz J.M. and O'Connell J.P., The 4. Properties of Gases and Liquids, 5th ed., The McGraw-Hill Company limited, New York, pp-8.23 (2012)
- Gmehling J., From UNIFAC to Modified UNIFAC to 5. PSRK with the Help of DDB, Fluid Phase Equilibria, 107(1), 1-29 (1995)
- 6. 3rd International Conference on Medical Sciences and Chemical Engineering (ICMSCE'2013), Bangkok (Thailand), Dec. 25-26, (2013)
- 7. Joback K.G. and Reid R.C., Estimation of Pure-Component Properties from Group-Contributions, Chem. Eng. Commun., 57(1-6), 233 -243 (1987)
- 8. Lydersen A.L., Estimation of Critical Properties of Organic Compounds, College Engineering University Wisconsin, Engineering Experimental Station Report 3, Madison, WI, April (1955)
- 9. Ambrose D., Correlation and Estimation of Vapor-Liquid Critical Properties. I. Critical Temperatures of Organic Compounds, National Physical Laboratory, Teddington, UK, NPL Report Chem., 92, September (1978)
- 10. Gani R. and Constantinou L., Molecular Structure Based Estimation of Properties for Process Design, Fluid Phase Equilibria, 116(1-2), 75-86 (1996)
- Marrero J. and Gani R., Group-Contribution Based 11. Estimation of Pure Component Properties, Fluid Phase Equilibria, 183-184, 183-208 (2001)
- Hukkerikar A.S., Sarup B., Kate A.T., Abildskov J., Sin 12. G. and Gani R., Group-Contribution+ (GC+) Based Estimation of Properties of Pure Components: Improved Property Estimation and Uncertainty Analysis, Fluid Phase Equilibria, 321, 25-43 (2012)
- Derr E.L. and Deal C.H., Analytical Solutions of Groups: 13. Correlation of Activity Coefficients Through Structural

Group Parameters. 1, Chem. E. Symp., Ser. No. 32, Instn. Chem. Engrs., London, 3, 88 (1969)

- 14. Ronc M. and Ratcliff G.A., Prediction of Excess Free Energies of Liquid Mixtures by an Analytic Group Solution Model, Can. J. Chem. Eng., 49(6), 825-830 (1971)
- 15. Fredenslund A., Jones R.L. and Prausnitz J.M., Group Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures, AIChE Journal, 21(6), 1086-1099 (1975)
- 16. Weidlich U. and Gmehling J., A Modified UNIFAC Model. 1- Prediction of VLE,  $h^{E}$ , and  $\gamma^{\infty}$ , *Ind. Eng. Chem.* Res., 26(7), 1372-1381 (1987)
- 17. Holderbaum T. and Gmehling J., PSRK: A Group Contribution Equation of State Based on UNIFAC, Fluid Phase Equilibria, 70(2-3), 251-265 (1991)
- Gmehling J., Li J. and Schiller M., A Modified UNIFAC 18. Model. 2. Present Parameter Matrix and Results for Different Thermodynamic Properties, Ind. Eng. Chem. Res., 32(1), 178-193 (1993)
- 19. Lohmann J., Joh R. and Gmehling J., From UNIFAC to Modified UNIFAC (Dortmund), Ind. Eng. Chem. Res., 40(3), 957-964 (2001)
- Jakob A., Grensemann H., Lohmann J. and Gmehling J., 20. Further Development of Modified UNIFAC (Dortmund): Revision and Extension 5, Ind. Eng. Chem. Res., 45(23), 7924-7933 (2006)
- 21. Smith J.M., VanNess H.C. and Abbott M.M., Introduction to chemical engineering thermodynamics, 7th ed., Tata McGraw Hill Education private limited, New Delhi, (2010)
- 22. Modi C.K., M.Tech. Thesis, Determination Of VLE Data For System Containing CPME, Institute of Technology, Nirma University, May (2014)
- 23. Wisniak J.A., The Herington test for thermodynamic consistency, Ind. Eng. Chem. Res., 33(1), 177-180 (1994)
- 24. Wilson G.M., A New Expression for the Excess Free Energy of Mixing, J. Amer. Chem. Soc., 86(2), 127-130 (1964)
- 25. Renon H. and Prausnitz J.M., Local compositions in thermodynamic excess functions for liquid mixtures, AIChE Journal, 14(1), 135-144 (1968)
- 26. Gadhiya P.M., Parsana V.M., Parikh S.P. and Joshipura M.H., 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), 260-269 (2015)