

VLE Prediction of Azeotropic Systems using UNIQUAC and UNIFAC Models and Experimental Validation using Othmer VLE Still

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Abstract: Vapour liquid equilibrium data are the basic need in the design of distillation columns. In the present study, VLE prediction of four binary azeotropic systems namely ethanol-water, acetone-water, ethanol-benzene and methanol-water was carried out using UNIQUAC and UNIFAC Models. UNIQUAC parameters of the chosen systems were computed using Newton Raphson's technique. Computations of UNIFAC Model were done using ASOG method. VLE predicted from these models was validated using experimentations carried out in othmer VLE still and thermodynamic consistency test using Redlich Keister method. It was observed that both models are able to fit the experimental VLE data for all the systems. The results show that all the four systems are minimum boiling azeotropes having positive deviation from ideality.

Key words: Activity coefficient, azeotrope, non ideal system, thermodynamic consistency, UNIFAC Model, UNIQUAC Model

INTRODUCTION

Industrial production of chemicals involves purification and recovery of the products by-products and unreacted raw materials. Distillation is a commonly used method for purifying liquids and separating mixtures of liquids into their individual components (McCabe *et al.*, 2004). It is clearly the dominating separation process, accounting for more applications than all the others combined (extraction, adsorption, crystallization, membrane-based technologies and so forth). Familiar examples include fractionation of crude oil into useful products such as gasoline and heating oil, etc., distillation of crude fermentation broths into alcoholic spirits such as gin, vodka and many more (Ognisty, 1995). Distillation columns consume more than 95% of the total energy used in separations in chemical process industries worldwide. Hence, design of distillation columns is a major concern of chemical engineers (Ognisty, 1995). Azeotropic phenomenon is often encountered in distillation operations which complicates the separation process by usual fractionation method. An azeotrope is a mixture of two or more liquids (chemicals) in such a ratio that its composition cannot be changed by simple distillation (Smith *et al.*, 2005). This occurs because when an azeotrope is boiled, the resulting vapor has the same ratio of constituents as the original mixture. As their composition is unchanged by distillation, azeotropes are

also called constant boiling mixtures (Swietoslowski, 1963). The boiling temperature of an azeotrope is either less than the boiling point temperatures of any of its constituents (a positive azeotrope) or greater than the boiling point temperatures of any of its constituents (a negative azeotrope). The defining condition of azeotropic mixtures and physical phenomena leads to non-ideality (Treybal, 1981).

VLE data are essential in the design of distillation columns for industrial applications. VLE computations using theoretical methods rather than experimentations are simpler and cheaper. The objective of the present investigation is to determine the VLE data using UNIQUAC and UNIFAC Models for four azeotropic systems namely ethanol-water, acetone-water, ethanol-benzene and methanol-water. The VLE predicted by these models was validated using experimentation with an Othmer VLE still. Also, thermodynamic consistency test for the UNIQUAC and UNIFAC Models was carried out by Redlich-Kiester method.

MATERIALS AND METHODS

Chemicals: All the chemicals (ethanol, methanol, acetone and benzene) were supplied by the Indian Scientific Chemical Industries, Private Ltd., Chennai, India. The purity of the chemicals was checked by gas chromatography and was found to be 0.999 mass fractions



Fig. 1: Othmer VLE still

for methanol and ethanol and 0.998 mass fractions for acetone and benzene. Deionised water was used in the experiment.

Experimental: Othmer VLE (Fig. 1) still was employed to determine vapour liquid equilibrium data. The capacity of the still is about 100 mL and it is equipped with reflux condenser. Binary liquid mixture of known composition was charged at the top of the VLE still and distilled using electrical heating. The distillate (vapour form) richer in more volatile compound enters the condenser with cold water circulation and is collected at the top. The residual product (liquid) richer in less volatile compound can be collected from the bottom. The still is equipped with a quartz thermometer to measure the azeotropic distillation temperature. After equilibrium was established (indicated by a constant reading in the thermometer), heating was stopped and the contents of the top and bottom products were allowed to cool and analyzed. The samples were analyzed using Clarus 680 GC fused with silica column and packed with Elite-5MS (5% biphenyl 95% dimethylpolysiloxane, 30 m×0.25 mm ID×250 μm df). The components were separated using helium as carrier gas at a constant flow of 1 mL/min. The injector temperature was set at 260°C during the chromatographic run. About 1 μL of extract sample was injected into the instrument and the oven temperature was at 60°C (2 min), followed by 300°C at the rate of 10°C min⁻¹ and 300°C where it was held for 6 min. The mass detector conditions were: transfer line temperature 240°C, ion source temperature 240°C and ionization mode electron impact at 70 eV, a scan time 0.2 sec and scan interval of 0.1 sec. The spectra of the

components were compared with the database of spectra of known components stored in the GC-MS NIST in 2008 library.

VLE prediction: Gibbs laid the foundation for a systematic study of thermodynamic equilibrium. He proposed the maximum entropy principle as the criterion for stable equilibrium for isolated systems (Lin and Sandler, 2002). Raoult's law is applied for phase equilibrium calculation to ideal solution. Raoult's law is simple to use when both vapour and liquid phases are ideal which is given in Eq. 1 (Skogested, 2009):

$$y_i P = X_i P_i^{sat} \quad (1)$$

Where:

y_i = Mole fraction in vapour phase

x_i = Mole fraction in liquid phase

P_i^{sat} = Vapour Pressure

P = Operating Pressure

Raoult's law can be adapted to non-ideal solutions by incorporating two factors namely fugacity coefficient (ϕ) and activity coefficient (γ) that will account for the non ideality owing to the interaction between the molecules of different substances. Modified Raoult's law that gives the accurate result for non-ideal solution is given as (Rao, 1997):

$$\phi_i y_i P = \gamma_i X_i P_i^{sat} \quad (2)$$

Fugacity coefficient: At low to moderate pressure (0-10 atm), fugacity coefficient can be calculated by the following Eq. 3-6 (Rao, 1997):

$$\ln \phi_i = (B^0 + \omega B^1) P_r / T_r \quad (3)$$

$$f_i = \phi_i P \quad (4)$$

$$B_0 = 0.083 - 0.422 / T_r^{1.6} \quad (5)$$

$$B^1 = 0.139 - 0.172 / T_r^{4.2} \quad (6)$$

Where:

ϕ_i = Fugacity coefficient

B^0 and B^1 = Virial coefficients

ω = Accentric factor

P_r = Reduced Pressure

T_r = Reduced Temperature

Activity coefficients: The prediction of activity coefficients for non-ideal solutions is accomplished using Analytical Solution of Group contribution method

(AGOS). The functional groups are structural units such as CH₃, OH and others which when added form constituent molecules (Wilson and Deal, 1962). In the group contribution methods, a solution of components is treated as a solution of functional groups. The activity coefficients of the components are then determined by the properties of the functional groups rather than by those of the molecules. The group contribution methods are necessarily approximate because the contribution of a given functional group may not be identical in different molecules (Alessi *et al.*, 1982). The assumption involved in the functional contribution methods is that the contribution of one functional group in a molecule is independent of that made by the other functional groups (Fredenslund *et al.*, 1975).

Universal quasi-chemical equation: The UNiVersal QUAsi Chemical UNIQUAC Model was developed by Abrams and Praunitz to express the excess Gibbs free energy of a binary mixture. The UNIQUAC equation for (g^E/RT) contains two parts, a combinatorial part and residual part (Anderson and Prausnitz, 1978). The combinatorial part takes into account the composition, size and shape of the constitution molecules and contains pure component properties only. The residual part takes into account the intermolecular forces containing two adjustable parameters (Fredenslund *et al.*, 1977). The UNIQUAC equation is given by:

$$\frac{g^E}{RT} = \frac{g^E}{RT}(\text{combinatorial}) + \frac{g^E}{RT}(\text{residual}) \quad (7)$$

$$\frac{g^E}{RT}(\text{combinatorial}) = x_1 \ln \frac{\phi_1}{x_1} + x_2 \ln \frac{\phi_2}{x_2} + \frac{z}{2} (q_1 x_1 \ln \frac{\theta_1}{\phi_1} + q_2 x_2 \ln \frac{\theta_2}{\phi_2}) \quad (8)$$

$$\frac{g^E}{RT}(\text{residual}) = -q_1 x_1 \ln(\theta_1 + \theta_2 \tau_{21}) - q_2 x_2 \ln(\theta_2 + \theta_1 \tau_{12}) \quad (9)$$

Where:

ϕ_i = Segment or volume fraction of component $i = (x_i r_i / \sum_j x_j r_j)$

θ_i = Area fraction of component $i = (x_i r_i / \sum_j x_j q_j)$

R_i = Volume parameter of component i

Q_i = Surface area parameter of component i

$\tau_{ij} = \exp \{-(u_{ij}-u_i / RT)\} = \exp \{-a / T_{ij}\} = \text{adjustable parameter}$

u_{ij} = Average interaction energy for the interaction of molecules of components i with the molecules of component j ,

Z = Coordination number usually taken 10

The activity coefficient can obtain as:

$$\ln \gamma_i = \ln \gamma_i^C(\text{combinatorial}) + \ln \gamma_i^R(\text{residual}) \quad (10)$$

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j \quad (11)$$

$$\ln \gamma_i^R = q_i [1 - \ln(\sum_j \theta_j \tau_{ji}) - \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}}] \quad (12)$$

Where:

$$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1) \quad (13)$$

The structural parameters r_i and q_i are calculated as the sum of the group volume and group area parameters R_k and Q_k :

$$r_i = \sum_k v_k^i R_k \quad (14)$$

$$q_i = \sum_k v_k^i Q_k \quad (15)$$

where, v_k^i is the number of two groups of type k in a molecule of component i . The UNIQUAC equation contains only two adjustable parameters τ_{12} and τ_{21} .

UNIquas Functional group Activity Coefficient (UNIFAC)

method: UNIFAC is based on UNIQUAC Model has a combinatorial term that depends on the volume and surface area of each molecule and a residual term that is the result of the energies of interaction between the molecules (Gmehling, 1995). In the UNIFAC Model, both combinatorial and residual terms are obtained from group contribution methods. When using the UNIFAC Model, one first identifies the functional subgroups present in each molecule. Next the activity coefficient for each species is written as (Kikic *et al.*, 1980):

$$\ln \gamma_i = \ln \gamma_i(\text{combinatorial}) + \ln \gamma_i(\text{residual}) \quad (16)$$

The combinatorial term is evaluated using Eq. 11. However, the residual term is also evaluated by a group contribution method, so that, the mixture is envisioned as a mixture of functional groups, rather than of molecules. The residual contribution to the logarithm of the activity coefficient of group k in the mixture, $\ln \Gamma_k$ is computed from the group contribution analog of Eq. 12 which can be written as (Gmehling *et al.*, 1998):

$$\ln \Gamma_K = Q_k \left[1 - \ln \left(\sum_m \phi_m \Psi_{mk} \right) - \sum_m \frac{\phi_m - \Psi_{km}}{S_n \phi_n \Psi_{nm}} \right] \quad (17)$$

ϕ_m = Surface area fraction of group m:

$$= \frac{x_m Q_m}{\sum_n x_n Q_n} \quad (18)$$

X_m = Mole fraction of group m in mixture:

$$\Psi_{mn} = \exp \left[\frac{u_{mn} - u_{nn}}{KT} \right] \quad (19)$$

$$= \exp \frac{-a_{mn}}{T} \quad (20)$$

where, u_{mn} is measure of the interaction energy between groups m and n and the sums are over all groups in the mixture. The residual part of the activity coefficient of species i is computed from:

$$\ln \gamma_i \text{ (residual)} = \sum_k v_k^i [\ln \Gamma_k - \ln \Gamma_k^i] \quad (21)$$

Where:

v_k^i = The number of k groups present in species i

Γ_k^i = The residual contribution to the activity coefficient of group k in a pure fluid of species i molecule

The volume (R_k) and surface (Q_k) parameters are a_{nm} and a_{nn} for each pair of functional groups (Papadopoulos and Derr, 1959). Continuing with the group contribution idea, it is next assumed that any pair of functional groups m and n will interact in the same manner that have the same value of a_{nm} and a_{nn} independent of the mixtures in which these two groups occur. Consequently by a regression analysis of great quantities of activity coefficient data, the binary parameters a_{nm} and a_{nn} for many group-group interactions can be determined (Voutsas and Tassios, 1996). These parameters can then be used to predict the activity coefficient in mixtures for which no experimental data are available. The advantage of this group contribution approach is that with a relatively small number of functional groups (Redlich *et al.*, 1959) the properties of the millions up on millions of different molecules can be obtained. The parameters used in this model were taken from Table 1-8.

Table 1: The group identification and the parameters R_k , Q_k of UNIFAC Model for ethanol-water system

Molecule names	Main No.	Section No.	V_k^i	R_k	Q_k
Ethanol					
CH ₃	1	1	1	0.9011	0.848
CH ₂	1	2	1	0.6744	0.540
OH	5	14	1	1.0000	1.200
Water					
H ₂ O	7	16	1	0.9200	1.400

Table 2: Group interaction parameters of UNIFAC equation for ethanol-water system

Main groups 1	Main groups 2	Interaction parameter 1-2	Interaction parameter 2-1
1:CH ₂	5:OH	986.500	156.400
1:CH ₂	7:H ₂ O	1318.000	300.000
5:H ₂ O	7:H ₂ O	353.500	-229.100

Table 3: The group identification and the parameters R_k , Q_k of UNIFAC Model for acetone-water system

Molecule names	Main No.	Section No.	V_k^i	R_k	Q_k
Acetone					
CH ₃	1	1	1	0.9011	0.848
CHCO	9	18	1	1.6724	1.488
CH ₂	1	1	1	0.9011	0.848
Water					
H ₂ O	7	16	1	0.9200	1.400

Table 4: Group interaction parameters of UNIFAC equation for acetone-water system

Main groups 1	Main groups 2	Interaction parameter 1-2	Interaction parameter 2-1
1:CH ₂	7:H ₂ O	1318.000	300.000
1:CH ₂	9:CH ₂ CO	476.400	26.760
7:H ₂ O	9:CH ₂ CO	-195.400	472.500

Table 5: The group identification and the parameters R_k , Q_k of UNIFAC Model for ethanol-benzene system

Molecule names	Main No.	Section No.	V_k^i	R_k	Q_k
Ethanol					
CH ₃	1	1	1	0.9011	0.848
CH ₂	1	2	1	0.6744	0.540
OH	5	14	1	1.0080	1.200
Benzene					
ACH	3	9	6	0.5313	0.400

Table 6: Group interaction parameters of UNIFAC equation for ethanol-benzene system

Main groups 1	Main groups 2	Interaction parameter 1-2	Interaction parameter 2-1
1:CH ₂	3:ACH	61.130	-11.120
1:CH ₂	5:OH	986.500	156.400
3:ACH	5:OH	636.100	89.600

Table 7: The group identification and the parameters R_k , Q_k of UNIFAC Model for methanol-water system

Molecule names	Main No.	Section No.	V_k^i	R_k	Q_k
Methanol					
CH ₃	1	1	1	0.9011	0.848
OH	5	14	1	1.0000	1.200
Water					
H ₂ O	7	16	1	0.9200	1.400

Error analysis: The relative error percentages of the models are calculated using equation:

Table 8: Group interaction parameters of UNIFAC equation for methanol-water system

Main groups 1	Main groups 2	Interaction parameter 1-2	Interaction parameter 2-1
1:CH ₂	5:OH	986.500	156.400
5:H ₂ O	7:H ₂ O	353.500	-229.100

$$REy_1 = \frac{|y_1 \text{ experimental} - y_1 \text{ calculated}|}{y_1 \text{ experimental}} \times 100 \quad (22)$$

Consistency of VLE: The thermodynamic consistency of measured (vapour+liquid) equilibrium data is validated using Redlich-Kiester method. According to this method only pure components are involved at the two end state and no mixing effect occurs, $\Delta G^E = 0$ (Redlich and Kister, 1948) at these points:

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx_1 = 0 \quad (23)$$

where in γ_1/γ_2 calculated from two models is evaluated and plotted against x_1 . The area above the x-axis will be equal to area below it for thermodynamically consistent data.

RESULTS AND DISCUSSION

The experimental VLE data of the four binary azeotropes namely ethanol-water, acetone-water, ethanol-benzene and methanol-water are shown in Fig. 2-4 and Table 9-11, respectively. The experimental values are compared with literature and found to be reasonably accurate.

The calculated fugacity coefficients for four azeotropes were found to be closer to unity, hence, it is reasonable to assume that vapour phase is ideal. The activity coefficient (γ_1) calculated from the experimental values using Eq. 2 for the four binary systems is also included in Table 9-11. It is evident from the values of the activity coefficients (greater than unity) from experimental VLE that the liquid phase non-ideality is too high. This is due to the fact that the molecules of the compounds present in each of the azeotropes are not chemically similar. While water is ionised and strongly polar, ethanol, methanol and acetone are more organic in character (Luben and Wenzel, 1988). The experimental T_{xy} diagram of four binary azeotropes are given in Fig. 2-5. For all the four azeotropes the mixture has higher vapour pressure than Raoult's law, yielding positive deviation from ideality (minimum boiling azeotrope). The molecules present in the four azeotropes repel each other but do not attract. This results in higher concentration of molecules in vapour phase than in the liquid phase with higher activity coefficient. Eventually, minimum temperature was reached at the azeotropic composition for all the systems representing minimum boiling homogenous azeotropism.

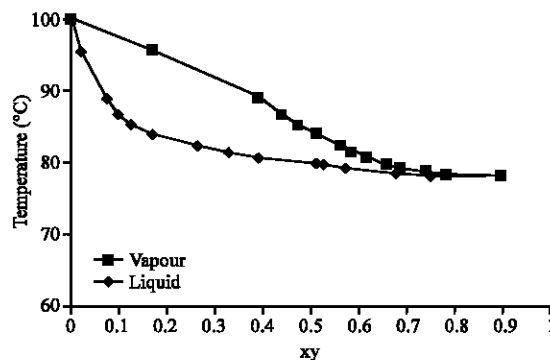


Fig. 2: Experimental T_{xy} diagram of ethanol-water system at 101.325 kPa

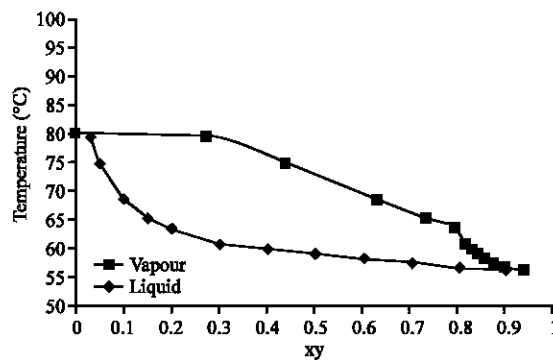


Fig. 3: Experimental T_{xy} diagram of acetone-water system at 101.325 kPa

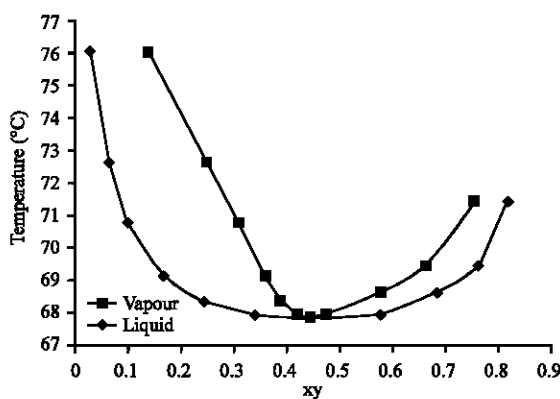


Fig. 4: Experimental T_{xy} diagram of ethanol-benzene system at 101.325 kPa

Modelling: VLE computation with UNIQUAC Model was made using Newton Raphson technique. This was accomplished using computer programming with Java 1.6 version. The model parameters of the systems estimated from the program are presented in Table 12-14.

Analytical Solution of Group contribution method (ASOG) was adopted in VLE calculation using UNIFAC

Table 9: Experimental and model prediction of VLE ethanol-water system at 101.325 kPa

T/C	Experimentals			UNIQUAC			UNIFAC		
	x_1	y_1	γ_1	$\hat{\gamma}_1$	y_1	y_1 error (%)	$\hat{\gamma}_1$	y_1	y_1 error (%)
92.5	0.0170	0.1589	5.4644	5.7189	0.1663	2.6391	5.6446	0.1641	3.2973
90.5	0.0621	0.3789	3.8360	3.8925	0.3844	1.4636	3.9483	0.3900	2.9275
88.5	0.0856	0.4375	3.4586	3.4478	0.4361	0.3094	3.4355	0.4345	0.6693
86	0.1238	0.4805	2.8834	2.8135	0.4688	2.4224	2.8580	0.4762	0.8822
84.5	0.1561	0.5219	2.6287	2.4903	0.4944	5.2550	2.6499	0.5260	0.8028
84.5	0.2508	0.5580	1.7493	1.6873	0.5382	3.5461	1.8225	0.5813	4.1810
82.5	0.3075	0.5826	1.6081	1.5386	0.5574	4.3185	1.6647	0.6031	3.5246
80.5	0.4065	0.6223	1.4040	1.3047	0.5782	7.0710	1.4180	0.6284	0.9939
79.5	0.4979	0.6564	1.2573	1.1344	0.5922	9.7705	1.2473	0.6511	0.7999
79	0.5198	0.6629	1.2404	1.1207	0.5989	9.6533	1.2255	0.6549	1.2057
78	0.5923	0.6921	1.1823	1.0644	0.6230	9.9709	1.1513	0.6739	2.6282
77	0.6963	0.7495	1.1333	1.0515	0.6953	7.2241	1.0977	0.7259	3.1480
75.5	0.7572	0.7965	1.1762	1.1121	0.7530	5.4546	1.1367	0.7697	3.3619
74.5	0.9143	0.9243	1.1770	1.1300	0.8873	3.9943	1.1319	0.8888	3.8383
Overall error percentage						5.2209			2.3043

Table 10: Experimental and model prediction of VLE acetone-water system at 101.325 kPa

T/C	Experimentals			UNIQUAC			UNIFAC		
	x_1	y_1	γ_1	$\hat{\gamma}_1$	y_1	y_1 error (%)	$\hat{\gamma}_1$	y_1	y_1 error (%)
74.8	0.0615	0.5981	5.3416	4.9006	0.5487	8.2529	5.0863	0.5695	5.0170
68.53	0.1253	0.7401	3.9329	4.1109	0.7735	4.5153	3.9143	0.7365	0.4882
65.26	0.1492	0.7616	3.7698	3.9432	0.7966	4.6009	3.7134	0.7501	1.5217
63.59	0.2124	0.7912	2.9033	3.0613	0.8342	5.4456	2.9388	0.8008	1.2028
60.75	0.3214	0.8204	2.1833	2.2066	0.8291	1.0631	2.1688	0.8149	0.6739
59.95	0.4201	0.8369	1.7497	1.7003	0.8132	2.8268	1.7034	0.8147	2.7218
59.12	0.4961	0.8387	1.5265	1.4761	0.8109	3.3113	1.4738	0.8097	3.5767
58.29	0.6126	0.8592	1.3021	1.2345	0.8145	5.1958	1.2317	0.8127	5.7173
57.49	0.6971	0.8712	1.1920	1.1337	0.8285	4.9006	1.1341	0.8288	5.1074
56.68	0.7838	0.8895	1.1125	1.0729	0.8577	3.5690	1.0741	0.8587	3.5760
56.3	0.8923	0.9233	1.0276	1.0202	0.9166	0.7298	1.0208	0.9171	0.6734
Overall error percentage						4.0374			2.7524

Table 11: Experimental and model prediction of VLE ethanol-benzene system at 101.325 kPa

T/C	Experimentals			UNIQUAC			UNIFAC		
	x_1	y_1	γ_1	$\hat{\gamma}_1$	y_1	y_1 error (%)	$\hat{\gamma}_1$	y_1	y_1 error (%)
78	0.0187	0.1297	7.0951	8.0323	0.1468	13.25360	6.9394	0.1268	2.1665
74	0.0523	0.2394	5.5072	5.8102	0.2525	5.48030	6.0404	0.2625	9.6574
73	0.0993	0.3067	3.8719	4.2007	0.3398	10.80860	4.1638	0.3298	7.5480
68.5	0.1567	0.3596	3.4788	3.7332	0.3858	7.29421	3.4421	0.3558	1.0483
66.5	0.2345	0.3989	2.8115	2.9613	0.4201	5.33460	2.7496	0.3901	2.1860
66	0.3241	0.4322	2.2527	2.3351	0.4479	3.64410	2.1784	0.4179	3.2970
65.5	0.4500	0.4567	1.7524	1.7658	0.4601	0.76410	1.7274	0.4501	1.4254
64.5	0.5228	0.4780	1.6498	1.5683	0.4543	4.94140	1.6356	0.4738	0.8786
63	0.7101	0.5228	1.4202	1.3337	0.4909	6.09790	1.5057	0.5542	6.0061
62	0.7866	0.5760	1.4775	1.3705	0.5342	7.24300	1.5449	0.6022	4.5625
60.5	0.8743	0.6834	1.6882	1.6098	0.6516	4.64290	1.7828	0.7216	5.5999
60	0.9230	0.7734	1.8516	1.8717	0.7817	1.07830	1.8774	0.7841	1.3930
Overall error percentage						5.88190			3.8141

Model. Comparison of the VLE predicted from the two models with the experimental data is presented in Table 5-8 for ethanol-water, acetone-water, ethanol-benzene and methanol-water respectively.

Figure 6-9 portray the comparison of experimental VLE with the UNIQUAC and UNIFAC Models. The overall error percentages of the VLE for ethanol-water

system using UNIQUAC and UNIFAC Models are 5.2209 and 2.3043, respectively. Similarly for acetone-water system, the calculated overall error percentages from UNIQUAC and UNIFAC Models are 4.0374 and 2.7524. In the case of ethanol-benzene system, the error percentage was 5.8819 for UNIQUAC Model and 3.8141 for UNIFAC Model. Percentage errors for methanol-water system

Table 12: Experimental and model prediction of VLE methanol-water system at 101.325 kPa

T/C	Experimentals			UNIQUAC			UNIFAC		
	x_1	y_1	γ_1	\hat{y}_1	\hat{y}_1	y_1 error (%)	\hat{y}_1	\hat{y}_1	y_1 error (%)
96.4	0.0189	0.1234	1.8695	2.0014	0.1321	7.1202	2.0132	0.1328	7.6899
93.5	0.0389	0.2230	1.8432	1.8238	0.2206	1.0380	1.6667	0.2016	9.5590
91.2	0.0588	0.3104	1.8652	1.9152	0.3187	2.6750	1.8575	0.3091	0.4027
89.3	0.0827	0.3665	1.6888	1.8075	0.3922	7.0394	1.7138	0.3719	1.4887
87.7	0.1032	0.4228	1.6643	1.8326	0.4655	10.1006	1.6704	0.4243	0.3548
84.4	0.1485	0.5117	1.4777	1.6324	0.5652	10.4740	1.5058	0.5214	1.8995
81.7	0.1897	0.5729	1.4504	1.5652	0.6182	7.9244	1.4837	0.5860	2.3003
78.0	0.3016	0.6765	1.1839	1.2295	0.7025	3.8465	1.1872	0.6783	0.2758
75.3	0.3982	0.7311	1.1058	1.1272	0.7452	1.9325	1.1239	0.7430	1.6324
72.1	0.5120	0.7819	1.0148	1.0313	0.7945	1.6209	1.0315	0.7947	1.6422
67.2	0.6015	0.8305	1.0331	1.0435	0.8388	1.0111	1.0459	0.8407	1.2372
66.3	0.7127	0.8689	1.0993	1.1081	0.8758	0.7965	1.1112	0.8782	1.0753
64.5	0.8257	0.9211	1.0416	1.0312	0.9118	1.0135	1.0332	0.9136	0.8132
Overall error percentage						4.3533			2.3362

Table 13: Estimated UNIQUAC parameters of four binary systems

Systems	UNIQUAC parameters J/mol K	
	$u_{12}-u_{22}$	$u_{21}-u_{11}$
Ethanol-water	200.5876	1350.3425
Acetone-water	716.1895	1950.1587
Ethanol-benzene	350.2287	1000.5827
Methanol-water	858.3737	1034.8543

Table 14: VLE consistency test for four azeotropes

Systems	Area	
	UNIQUAC	UNIFAC
Ethanol-water	0.0700	0.0050
Acetone-water	0.0502	0.0055
Ethanol-benzene	0.0182	0.0038
Methanol-water	0.0241	0.0027

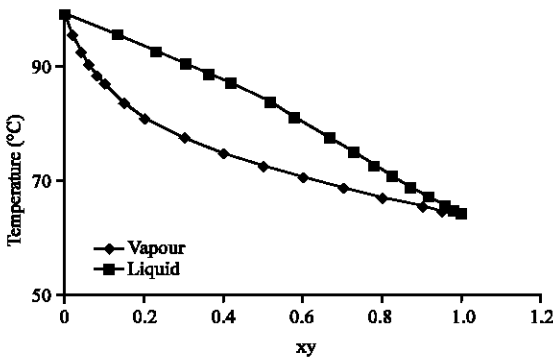


Fig. 5: Experimental T_{xy} diagram of methanol-water system at 101.325 kPa

using UNIQUAC and UNIFAC Model were found to be 4.3522 and 2.3362. Though both models are able to give better results in VLE prediction for the systems, UNIFAC Model has relatively lesser error percentage (Table 13 and 14).

Same trend of results is observed with the Redlich Kister method of thermodynamics consistency test Eq. 23. This can be seen from Fig. 10-13 for the four

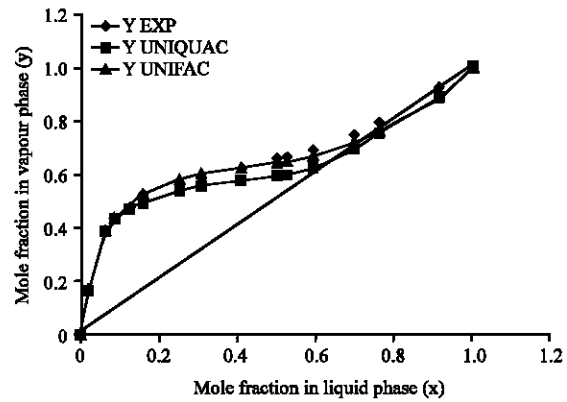


Fig. 6: Experimental and correlated xy diagram of ethanol-water system at 101.325 kPa

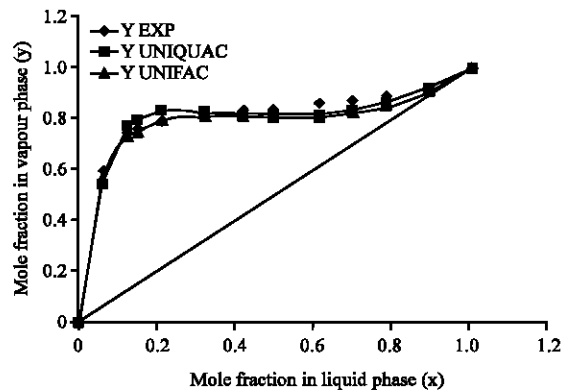


Fig. 7: Experimental and correlated xy diagram of acetone-water system at 101.325 kPa

binary systems. These plots are made using the activity coefficients calculated from UNIQUAC and UNIFAC Models (Table 13). Area under the curve computed from UNIQUAC and UNIFAC Models for all systems is shown in Table 14. It can be observed

that the computed values are closer to zero for the UNIQUAC Model and almost zero for the UNIFAC Model.

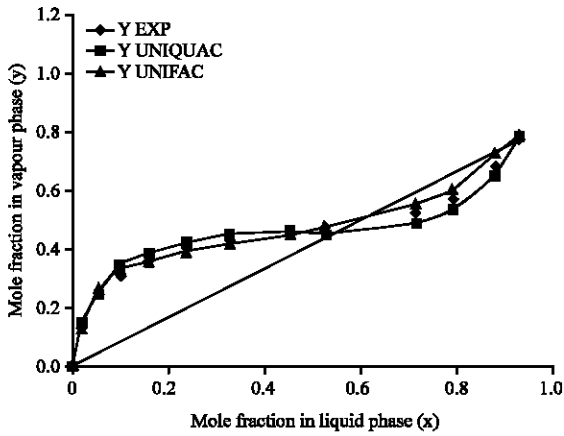


Fig. 8: Experimental and correlated xy diagram of ethanol-benzene system at 101.325 kPa

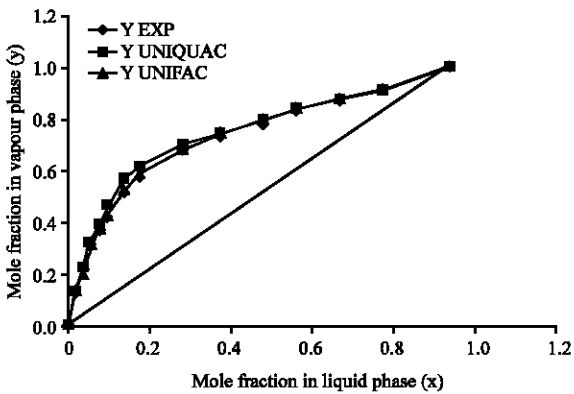


Fig. 9: Experimental and correlated xy diagram of methanol-water system at 101.325 kPa

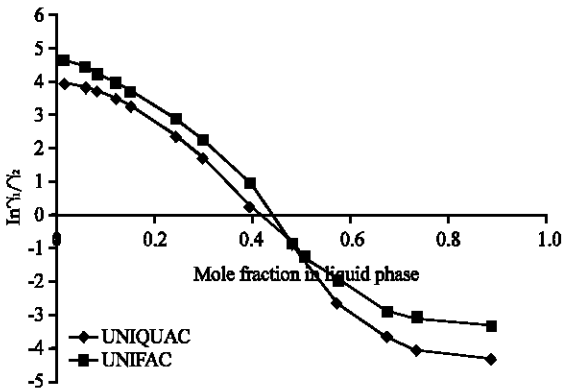


Fig. 10: Thermodynamic consistency test of ethanol-water system using Redlich Kister method for UNIQUAC and UNIFAC Models

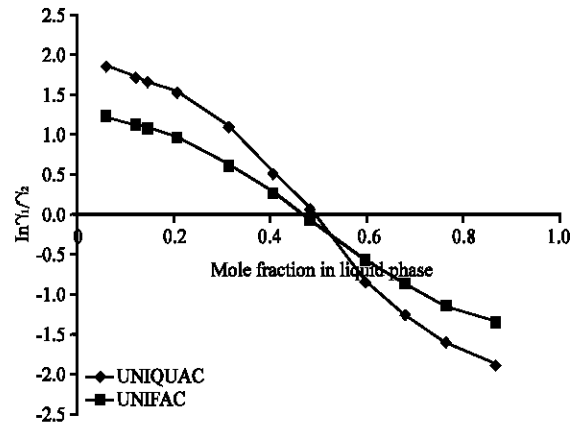


Fig. 11: Thermodynamic consistency test of acetone-water system using Redlich Kister method for UNIQUAC and UNIFAC Models

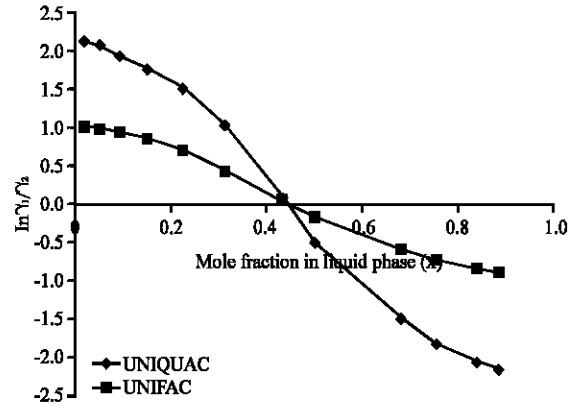


Fig. 12: Thermodynamic consistency test of ethanol-benzene system using Redlich Kister method for UNIQUAC and UNIFAC Models

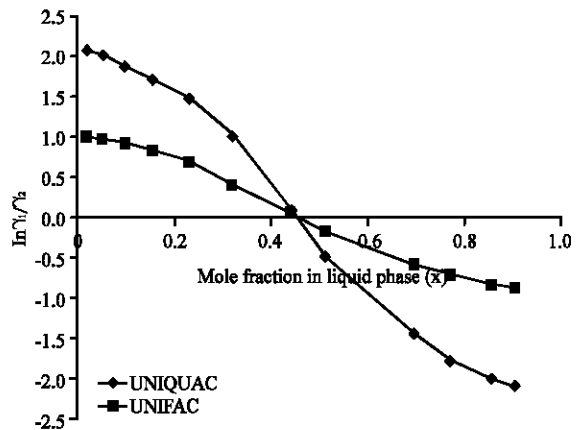


Fig. 13: Thermodynamic consistency test of methanol-water system using Redlich Kister method for UNIQUAC and UNIFAC Models

CONCLUSION

In case of VLE prediction of azeotropes, UNIQUAC and UNIFAC Models were tested for the systems ethanol-water, acetone-water, ethanol-benzene and methanol-water. The experimental VLE findings prove that all the systems are minimum boiling azeotropes. Major finding of the present research is the estimation of UNIQUAC parameters for the four systems. These parameters can be utilized for VLE calculation at any pressure conditions. The error analysis and thermodynamics consistency test studies reveal that both models give good representation of VLE for all the chosen systems.

NOMENCLATURE

B^0 and B^1	= Virial coefficients
f_i	= Fugacity of the component i in standard state
P	= Operating Pressure
P_i^{sat}	= Saturation Pressure of the component i
P_r	= Reduced Pressure
q_i	= Group volume parameter of the component i
Q_i	= Surface area parameter of the component i
r_i	= Group volume parameter of the component i
R_i	= Volume parameter of the component i
R_i and Q_k	= Group area parameters
T_r	= Reduced Temperature
u_{ij}	= Average interaction energy for the interaction of molecules of components i with the molecules of component j
x_i	= Mole fraction in liquid phase of the component i
y_i	= Mole fraction in vapour phase of the component i
z	= Coordination number which is usually taken 10
γ_i	= Activity coefficient of the component i
ϕ_i	= Fugacity coefficient of the components i
ω	= Accentric factor
ϕ_i	= Segment or volume fraction of the component i
θ_i	= Area fraction of the component i
τ_{ji}	= Adjustable parameters of the components i and j
γ_i^C	= Combinatorial term of the component i
γ_i^R	= Residual term of the component i

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