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Vapour Liquid Equilibrium Model Testing Based on Activity Coefficient Models Applied to Binary Azeotropic Systems

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Abstract : The isobaric vapour liquid equilibrium data for four azeotropic systems, viz. acetone-chloroform, benzene-cyclohexane, methylacetate-methanol and tetrahydrafuran-water has been determined experimentally using Othmer VLE still. Activity coefficient models namely NRTL, UNIQUAC, UNIFAC and modified forms of Flory-Huggins equation (SRS and TCRS) were tested for theoretical prediction of VLE for the azeotropes. ASOG method of computation for the UNIFAC model and Newton- Raphson's technique for the other four models was adopted for the estimation of VLE. Validation of the simulated VLE data was made using error analysis. The correlation parameters obtained for these four models and the comparison results are reported. RedlichKister method of thermodynamic consistency test was also made and the results are in accordance with the results yielded by the error analysis.

Keywords : Activity coefficient model, Azeotrope, Nonideality, Thermodynamic consistency, Vapour liquid equilibrium.

1. Introduction

The methods of separating solutions and mixtures into their components are among the most important objectives in chemical processing. These separations include distillation, gas absorption, solvent extraction, etc [1]. Certainly distillation is the most widely applied separation technology and will continue as an important process for the foreseeable future because there is simply no industrially viable alternative around [2]. Also, confronted with challenges from other technologies, distillation improves and from time to time, breakthroughs are made which move this technology to a higher level of sophistication [3]. Distillation is a method of separating the components of a solution which depends upon the distribution of the substances between a gas and a liquid phase, applied to cases where all components are present in both phases. It is concerned with the separation of solution where all the components are appreciably volatile. The successful application of distillation methods depends greatly upon an understanding of the equilibria existing between the vapor and liquid phases of the mixture encountered [4]. The primary advantages of distillation are potential for high throughput, any feed concentration, and high purity. Many of the alternatives to distillation carry out only partial separation and cannot produce pure end-products. Thus, several of the other alternative separation methods can be used only in combination with distillation, while distillation itself can be used as a stand-alone operation. Because of these advantages compared with other thermal separation processes, distillation is used in 90% of cases for the separation of binary and multicomponent liquid mixtures. Familiar examples include fractionation of crude oil, in to useful products such as gasoline and heating oil etc. Other example is the distillation process used to distillate water to remove its impurities [5].

Complexities like the formation of azeotropes may introduce an obstacle for the separation by ordinary distillation. Azeotrope is a mixture of two or more liquids (chemicals) in such a ratio that its composition cannot be changed by simple distillation Azeotropy is not a rare phenomenon and is often resulted by the presence of some specific groups, particularly polar groups (oxygen, nitrogen, chlorine and fluorine) [6]. Azeotropes occur at maximum boiling or minimum boiling depending on which, behavior can be exhibited on a constant pressure diagram. A mixture whose total pressure is greater than that computed for ideality show positive deviations from Raoultslaw (minimum boiling azeotropes). When the total pressure of a system at equilibrium is less than the ideal value the system is deviate negatively from Raoults law (maximum boiling azeotropes) [7].

The knowledge of precise vapor-liquid equilibria is a prerequisite to the design of distillation equipment. However, such knowledge is limited, and usually not available when new systems are under consideration, due to the complication to obtain the VLE data experimentally. Predictive methods are therefore essential for process evaluation and design.In the present work fourazeotropic systems namely, acetone-chloroform, benzene-cyclohexane,methyacetate-methanol and tetrahydrafuran-water were taken for study. Experimental VLE of these systems were determined using an Othmer VLE still. Applicability of five activity coefficient models to these systems were tested in the study viz. NRTL, UNIQUAC, UNIFAC and two forms of modified Flory – Huggins equations (SRS and TCRS). Also thermodynamic consistency test for these models was carried out by RedlichKister method.

2. Experimentation

2.1Materials and Methods

All the chemicals (acetone, chloroform, benzene, cyclohexane, methyl acetate, methanol, terahydrafuran) were supplied by the Indian Scientific Chemical Industries Pvt.Ltd., Chennai, India. The purities of all reagents are confirmed to be analyticalgrade by gas chromatographyandwas found to be 0.999 mass fractions formethanol. 0.997 mass fraction for acetone, chloroform and 0.998 mass fractions for methyl acetate, THF, benzene and cyclohexane. The water used in the experiment is deionised water which is prepared in the laboratory.

2.2Experimental Procedure

Figure 1.Othmer VLE Still

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 outfitted 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 × 250μm 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. One 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 electonvolt, a scan time 0.2 seconds and scan interval of 0.1 seconds. The spectra of the components were compared with the database of spectra of known components stored in the GC-MS NIST (2008) library.

2.3 VLE Prediction for Non ideal Mixture

The simplest case is an ideal liquid mixture and ideal gas where Raoult's law states that for any component i, the partial pressure $p_i=y_i p$equals the vapor pressure ofthe pure component i multiplied by its mole fraction x_i in the liquid phase[8] that is

$$y_i p = x_i p_i^{Sat} \tag{1}$$

y_i is mole fraction in vapour phase; x_i is mole fraction in liquid phase; p_i^{sat} is vapour pressure and p is operating pressure.

The solution of liquids which do not obey Raoult's laws is called non ideal solution. The non ideal solution shows deviation from Raoult's law[9]. The deviation from ideal behavior can be accounted for by the use of activity coefficient (liquid phase) and fugacity coefficient (vapour phase).The equation for describing non ideal solution is modified Raoult's law it is given by

$$\phi_i y_i p = \gamma_i x_i p_i^{Sat} \tag{2}$$

ϕ isfugacity coefficient; γ isactivity coefficient. The above equation accounts for only liquid phase non ideality while maintaining the ideality of the vapour phase.

2.4 Fugacity Coefficient

The fugacity coefficient can be evaluated from the compressibility factor (Z) and can be evaluated in two ways either from PVT data or obtained analytically from equations of state .The two term virial equation of state is applicable to pressures up to 5 bars. There are various methods to calculate the second virial coefficients including the Pitzer and Curlcorrelation, correlation of Tsonopolous, Hayden and O'Connell method. The method described in this work is the Pitzer-type correlation. At low to moderate pressure compressibility factor z is given by [10]

$$Z = \frac{P\upsilon}{RT} = 1 + \frac{BP}{RT} = 1 + \left(\frac{BP_c}{RT_c}\right)\frac{P_r}{T_r} \tag{3}$$

$$\ln \phi_i = (B^0 + \omega B^1)P_r/T_r \tag{4}$$

$$f_i = \phi_i P \tag{5}$$

$$B^0 = 0.083 - 0.422/T_r^{1.6} \tag{6}$$

$$B^1 = 0.139 - 0.172/T_r^{4.2} \tag{7}$$

Where T_c is critical temperature; P_r is reduced pressure; T_r is reduced temperature; and B is virial coefficient

2.5Activity Coefficient Models

2.5.1 NRTL (Non-Random Two Liquid) Model

The non random two liquid (NRTL) equation proposed by Renon [11] is applicable to partially miscible as well as completely miscible systems. The equations for the activity coefficients are

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \qquad (8)$$

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] \qquad (9)$$

where G_{12} and G_{21} energy interaction between the molecules.

2.5.2 UNIQUAC (UNIversal Quasi-Chemical) model

The UNIQUAC equation was developed by Abrams and Prausnitz [12] who incorporated the two-liquid model and the theory of local composition. The UNIQUAC equation consists of two parts a combinatorial part that takes into accounts the differences in sizes and shapes of the molecules and the residual part that is due to the intermolecular forces between the molecules. In the form of an equation, this is represented as

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \Sigma_j \, x_j l_j \qquad (10)$$

$$\ln \gamma_i^R = q_i \, [1 - \ln (\Sigma_j \theta_j \tau_{ji}) - \Sigma_j \frac{\theta_j \tau_{ij}}{\Sigma_k \theta_k \tau_{kj}} \qquad (11)$$

$$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1) \qquad (12)$$

$$r_i = \Sigma_k v_k^i R_k \qquad (13)$$

$$q_i = \Sigma_k v_k^i Q_k \qquad (14)$$

where ϕ_i = segment or volume fraction of the component

θi = area fraction of the component

r_i = volume parameter of the component

q_i = surface area parameter of the component

The UNIQUAC equation contains only two adjustable parameters τ_{12} and τ_{12}.

2.5.3 UNIquac 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 [13].The combinatorial term is evaluated using equation (14).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 [14]

$$\ln \gamma_i = \ln \gamma_i \text{ (combinatorial)} + \ln \gamma_i \text{ (residual)} \qquad (15)$$

$$\ln \gamma_i \text{ (residual)} = \Sigma_k \, v_k^i \, [\ln \Gamma_k - \ln \Gamma_k^i] \qquad (16)$$

$$\ln\Gamma_K = Q_k[1-\ln(\Sigma_m \phi_m \Psi_{mk}) - \Sigma_m \frac{\phi_m - \psi_{km}}{\Sigma_n \phi_n \Psi_{nm}}] \tag{17}$$

$$\Psi_{mn} = \exp - \left[\frac{u_{mn} - u_{nn}}{RT}\right] = \exp\frac{-a_{mn}}{T} \tag{18}$$

where Γ_k^i is residual activity coefficient; a_{mn} is interaction parameter; $u_{mn}$is interaction energy between group m and n.

2.6 Modified form of Flory – Huggins equation

2.6.1 Simplified Ruckenstein and Shulgin model (SRS)

Ruckenstein and Shulgin modified the local composition and Flory-Huggins equations (F-H) for non electrolyte solutions. Their equations for ln γ_i are [15],

$$\ln\gamma_1 = -\ln(x_1 + x_2 L_{12}) - x_2[A_{12} - A_{21}] - (\ln L_{12} + \ln L_{21})\left[\varphi_1\varphi_2 + x_2\varphi_2\frac{\partial\varphi_1}{\partial x_1} + x_2\varphi_1\frac{\partial\varphi_2}{\partial x_1}\right] \tag{19}$$

$$\ln\gamma_2 = -\ln(x_2 + x_1 L_{21}) - x_1[A_{12} - A_{21}] - (\ln L_{12} + \ln L_{21})\left[\varphi_1\varphi_2 + x_1\varphi_2\frac{\partial\varphi_1}{\partial x_1} + x_1\varphi_1\frac{\partial\varphi_2}{\partial x_1}\right] \tag{20}$$

Where $A_{ij} = \left[\frac{L_{ij}}{x_1 + x_2 L_{ij}}\right]$ (21)

$$L_{ij} = \frac{V_j}{V_i}\exp\left[-\frac{\lambda_{ij-}\lambda_{ii}}{RT}\right] \tag{22}$$

$$\varphi_i = \frac{x_1}{x_1 + x_2 L_{ji}} \tag{23}$$

$$\varphi_j = \frac{x_2}{x_2 + x_1 L_{ji}} \tag{24}$$

where x_1 and x_2 are mole fraction in liquid phase. A_{12} and A_{21} are two adjustable parameters

related to pure component molar volume and characteristic energy difference.φ_1 and φ_2 are segment fraction of the components and χ is an energy interaction between molecules of components.

2.6.2 Theoretically Consistent Ruckenstein and Shulgin model (TCRS)

Like NRTL equation the new equation (TCRS) is also three parameter models. Their expression for ln γ_i's are[15]

$$\ln\gamma_1 = -\ln(x_1 + x_2 L_{12}\exp(x_1\delta_{12})) + x_2[A_{ij} - A_{ji}] - x_1 x_2^2 \delta_{12}(A_{ij} - A_{ji}) - (\ln L_{12} + \ln L_{21} + \delta_{12}(x_1 - x_2))$$
$$\left[\varphi_1\varphi_2 + x_2\varphi_2\frac{\partial\varphi_1}{\partial x_1} + x_2\varphi\frac{\partial\varphi_2}{\partial x_1}\right] - 2x_2\varphi_1\varphi_2\delta_{12} \tag{25}$$

$$\ln\gamma_2 = -\ln(x_2 + x_1 L_{21}\exp(-x_2\delta_{12})) - x_1[A_{12} - A_{21}] - x_1^{\,2} x_2\delta_{12}(A_{12} - A_{21}) - (\ln L_{12} + \ln L_{21} + \delta_{12}(x_1 - x_2))$$

$$\left[\varphi_1\varphi_2 - x_1\varphi_2\frac{\partial\varphi_1}{\partial x_1} + x_1\varphi_1 - x_1\varphi_1\frac{\partial\varphi_2}{\partial x_1}\right] + 2x_1\varphi_1\varphi_2\delta_{12} \qquad (26)$$

$$\text{where}\quad \mathrm{Lij} = \frac{V_j}{V_i}\exp\left[\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right] \qquad (27)$$

$$\delta_{12} = \left[\frac{\lambda_{12} - \lambda_{21}}{RT}\right] \qquad (28)$$

$$A_{ij} = \left[\frac{L_{ij}\exp(x_1\delta_{12})}{x_1 + x_2 L_{ij}\exp(x_1\delta_{12})}\right] \qquad (29)$$

$$\varphi_i = \frac{x_1}{x_1 + x_2 L_{ij}\exp[x_1\delta_{12}]} \qquad (30)$$

$$\varphi_j = \frac{x_2}{x_2 + x_1 L_{ji}\exp[-x_2\delta_{12}]} \qquad (31)$$

2.7Error Analysis

The relative error percentages of the activity coefficient models are calculated using equation

$$\mathrm{REy}_1 = \frac{|y_1\ \mathrm{Experimental} - y_1\ \mathrm{Calculated}\ |}{y_1\ \mathrm{Experimental}}\,x\,100 \qquad (32)$$

2.8 Thermodynamic Consistency

The measurement of temperature, pressure and both liquid and vapour compositions for a binary VLE system, results in an “over-specification” of the system. The vapour compositions usually display the greatest error and thus the thermodynamic consistency tests usually focus on the vapour compositions (y) to determine the thermodynamic consistency of the VLE data [16]. A number of methods have been described in the literature for VLE Consistency namely slope test, area test, point test and direct test[17]. In the present work the thermodynamic consistency of measured (vapour + liquid) equilibrium data is validated using area test proposed by RedlichKister. The area test is relatively simple and provides sufficient information for the evaluation of thermodynamic consistency. Expression for the area test is given by[18],

$$\left(\frac{G^E}{RT}\right)\exp = x_1\ln\gamma_1^{\exp} + x_2\ln\gamma_2^{\exp} \qquad (33)$$

$$\int_0^1\left(\ln\frac{\gamma_1^{\exp}}{\gamma_2^{\exp}}\right)dx_1 = 0 \qquad (34)$$

The bracketed term is plotted against the mole fraction of the component such that a graph creating an area both above and below the x axis exists. The area test requires that the area above the x axis be similar to area below the xaxis for thermodynamically consistent data.

3. Results and Discussion

VLE data for the five binary systems namely Acetone-chloroform, Benzene-cyclohexane, Methyl acetate-methanol, and THF-water were determined and the results are represented in table 1-4. Comparison of experimental data indicates no systematic difference from literature value. To characterize the vapour phase ideality, fugacity coefficients for four azeotropic systems were calculated using Virial coefficient correlation using equation 4-7 from the computations it was found that the fugacity coefficients are in the range of unity. Therefore it can be inferred that the vapour phase is ideal.The activity coefficients(γ_1)were calculated from the experimental values using modified Raoult's law (Equ.2) for the four azeotropic systems and presented in tables 1-4. The results show that values of the activity coefficients outsize from unity and hence the liquid phase attributes strong nonideality. This is due to the fact that the liquid phase molecules are much closely spaced than in vapor phase due to which attraction/ repulsion among the molecules are high. Out of the four azeotropic systems four azeotropes namely benzene-cyclohexane, methyl acetate-methanol, and tetrahydrafuran-water exhibit positive deviation from ideality (minimum boiling azeotropes). Molecules that are dissimilar enough from each other will exert repulsive forces. The repulsive forces result in activity coefficient (γ) greater than unity, since the molecules tend to leave the liquid phase. When dissimilar molecules are mixed together, a greater partial pressure is exerted, resulting in a positive deviation from ideality. The azeotropic system acetone-chloroform yields negative deviation from ideality (maximum boiling azeotropes). This is due to the fact that the molecule of the components present in the azeotrope acetone-chloroform attracts each other, the activity coefficients will be less than unity, since the molecules will exert lower partial pressure than if they are pure.

3.1 Modeling

In perspective of estimation of activity coefficients theoretically five models detailed earlier are tested. The models NRTL, UNIQUAC, SRS and TCRS for the azeotropic systems were estimated using Newton Raphson technique. This was accomplished using computer programming with Java software of 1.6 version.The parameters estimated are presented in table 5. Binary interaction parameters for UNIFAC method have been taken from theliterature [9].The comprehensive comparison of VLE predicted from the five models with the experimental data is presented in tables 1-4. The correlated and experimental xy diagrams of four azeotropic systems using five activity models are given in figures 2-5.The overall error percentages of the VLE for acetone-chloroform system using five activity coefficient models (NRTL, UNIQUAC, UNIFAC, SRS and TCRS) are 14.0058, 6.8721, 10.8571,12.5217and 4.4082 respectively as indicated in table 1. It is observed that UNIQUAC and SRS model have lesser error percentages than the other three models. Benzene-cyclohexane system shows appreciable validity for the UNIQUAC model with the least error percentage of 4.8256 whereas the other models have more than 5 % table 2. Error occurred in NRTL model 4.6794 % provide good representation of VLE for methylacetate-methanol system when compared to other models table 3. The NRTL and UNIQUAC model gave better results for tetrahydrafuran-water system yielding an error percentage of 4.0974 and 2.937 table 4. These implications are further justified using the Redlich-Kister method of thermodynamics consistency test (Eqn.34). This is depicted in figures 6-9 for the four azeotropic systems respectively.These plots are made using the activity coefficients calculated from five models listed in tables 1-4. Areas calculated from these models are given in table 6. From the table it can be observed that the computed value for TCRS model is closest to zero for Acetone-chloroform system when compared to remaining models. In a similar fashion the Benzene-cyclohexane system shows best thermodynamic consistency for the UNIQUAC activity coefficient model whereas the methyl acetate - methanol systems possess good agreement with NRTL model respectively. For the tetrahydrafuran – water azeotrope the area value of UNIQUAC model is closer to zero.

Table1.Experimental and model prediction of VLE acetone-chloroform system at 101.325 kpa

T	X	Y	γ_1 Exp	NRTL			UNIQUAC			UNIFAC			SRS			TCRS		
				γ_1	y_1	y_1 Error %	γ_1	y_1	y_1 Error %	γ_1	y_1	y_1 Error %	γ_1	y_1	y_1 Error %	γ_1	y_1	y_1 Error %
62.8	0.1390	0.1003	0.5760	0.3665	0.0638	36.3908	0.6026	0.1049	4.5862	0.7105	0.1237	23.3300	0.4751	0.0827	17.5473	0.5325	0.0927	0.0927
62.5	0.2338	0.2100	0.7242	0.4708	0.1365	35.0061	0.5952	0.1726	17.8173	0.8408	0.2438	16.0841	0.6132	0.1778	15.3414	0.6680	0.1937	0.1937
64.5	0.3162	0.3123	0.7462	0.5888	0.2464	21.1015	0.6147	0.2572	17.6432	0.8775	0.3672	17.5792	0.7045	0.2948	5.6035	0.6792	0.2842	0.2842
67.5	0.3888	0.4103	0.7246	0.6420	0.3635	11.4062	0.6798	0.3849	6.1905	0.8520	0.4824	17.5725	0.7676	0.4346	5.9224	0.6970	0.3946	0.3946
68.5	0.4582	0.5002	0.7264	0.7054	0.4857	2.9124	0.7736	0.5327	6.4824	0.8310	0.5722	14.3782	0.8624	0.5938	18.6959	0.7025	0.4837	0.4837
66.5	0.5299	0.6100	0.8159	0.8791	0.6572	7.7324	0.8660	0.6474	6.1259	0.9023	0.6746	10.5847	0.9932	0.7425	21.7153	0.7805	0.5835	0.5835
64.5	0.6106	0.7103	0.8790	0.9880	0.7984	12.3953	0.9191	0.7427	4.5540	0.9252	0.7476	5.2438	1.0354	0.8367	17.7870	0.8982	0.7258	0.7258
62.5	0.7078	0.8003	0.9115	0.9984	0.8765	9.5214	0.9361	0.8218	2.6864	0.9360	0.8217	2.6739	1.0317	0.9057	13.1700	0.9374	0.8229	0.8229
61.5	0.8302	0.9001	0.9033	0.9297	0.9264	2.9138	0.8969	0.8937	0.7187	0.8999	0.8967	0.3854	0.9587	0.9553	6.1243	0.8871	0.8839	0.8839
60.5	0.9075	0.9510	0.9023	0.9084	0.9574	0.6782	0.8851	0.9328	1.9158	0.8962	0.9445	0.6855	0.9322	0.9825	3.3101	0.8894	0.9373	0.9373
				Error Percentage		14.0058			6.8721			10.857			12.5217			4.4082

Table 2.Experimental andmodel prediction of VLE benzene-cyclohexane system at 101.325 kPa

T	X	Y	γ_1 Exp	NRTL			UNIQUAC			UNIFAC			SRS			TCRS		
				γ_1	y_1	y_1 Error %	γ_1	y_1	y_1 Error %	γ_1	y_1	y_1 Error %	γ_1	y_1	y_1 Error %	γ_1	y_1	y_1 Error %
79.5	0.0505	0.0991	1.9989	2.4509	0.1215	22.6034	2.1302	0.1056	6.5590	2.8342	0.1405	41.7759	1.5211	0.0754	23.9152	1.4322	0.0711	28.3551
79.5	0.2641	0.3414	1.3168	1.7222	0.4465	30.7850	1.4661	0.3801	11.3356	1.5367	0.3984	16.6959	1.4773	0.3830	12.1851	1.1294	0.2928	14.2355
78.5	0.4728	0.4713	1.0473	1.2679	0.5705	21.0481	1.1328	0.5097	8.1476	1.0674	0.4803	1.9096	1.1497	0.5173	9.7602	0.9565	0.4304	8.6781
74.5	0.6418	0.5500	1.0214	1.1860	0.6386	16.1090	1.0869	0.5852	6.4000	0.9550	0.5142	6.5090	1.0852	0.5843	6.2454	0.9626	0.5183	5.7636
72.5	0.7643	0.6197	1.0306	1.1511	0.6921	11.6830	1.0741	0.6458	4.2117	0.9700	0.5832	5.8899	1.0312	0.6200	0.0484	0.9687	0.5824	6.0190
72.5	0.8635	0.6980	1.0275	1.1103	0.7542	8.0515	1.0580	0.7187	2.9656	1.0031	0.6814	2.3782	0.9809	0.6663	4.5415	0.9660	0.6562	5.9885
73.5	0.8913	0.7275	1.0045	1.0748	0.7783	6.9828	1.0335	0.7484	2.8728	0.9816	0.7108	2.2955	0.9576	0.6934	4.6872	0.9455	0.6847	5.8831
73.5	0.9368	0.7980	1.0484	1.0948	0.8333	4.4235	1.0776	0.8202	2.7819	1.0322	0.7856	1.5538	0.9972	0.7590	4.8872	0.9924	0.7553	5.3508
75.5	0.9602	0.8580	1.0316	1.0716	0.8912	3.8694	1.0584	0.8802	2.5874	1.0211	0.8492	1.0256	1.0019	0.8332	2.8904	0.9900	0.8233	4.0442
79.5	0.9992	0.9890	1.0082	1.0194	0.9999	1.1021	1.0043	0.9851	0.3943	1.0193	0.9998	1.0920	1.0077	0.9884	0.0606	1.0194	0.9999	1.1021
				Error Percentage		12.6658			4.8256			8.1125			6.9221			8.5420

Table 3.Experimental and model prediction of VLE methyl acetate-methanol system at 101.325 kPa

T	X	Y	γ_1 Exp	NRTL			UNIQUAC			UNIFAC			SRS			TCRS		
				γ_1	y_1	y_1 Error %	γ_1	y_1	y_1 Error %	γ_1	y_1	y_1 Error %	γ_1	y_1	y_1 Error %	γ_1	y_1	y_1 Error %
56.5	0.05645	0.2155	3.8746	4.4141	0.2455	13.9443	4.576	0.2545	18.1368	4.3215	0.2403	11.5336	2.4381	0.1356	37.0496	5.1388	0.2858	32.6310
55.5	0.1273	0.3420	2.8240	3.0785	0.3728	9.0204	3.3354	0.4039	18.1125	3.1032	0.3758	9.8976	2.2384	0.2710	20.7432	3.6540	0.4425	29.3985
54.5	0.2521	0.4770	2.0604	2.1879	0.5065	6.1949	2.3521	0.5445	14.1639	2.1318	0.4935	3.4767	1.8389	0.4257	10.7431	2.5175	0.5828	22.1924
55.5	0.4355	0.5755	1.3891	1.4558	0.6031	4.8107	1.5476	0.6411	11.4048	1.3341	0.5527	3.9591	1.4140	0.5858	1.7987	1.6549	0.6856	19.1459
53.5	0.5550	0.6290	1.2788	1.3241	0.6512	3.5357	1.3934	0.6853	8.9554	1.198	0.5892	6.3275	1.3592	0.6685	6.2933	1.4814	0.7286	15.8410
52.5	0.6230	0.6570	1.2334	1.2718	0.6774	3.1126	1.3246	0.7055	7.3850	1.1392	0.6068	7.6328	1.3264	0.7065	7.5372	1.4071	0.7495	14.0823
54.5	0.7125	0.6916	1.0570	1.0884	0.7121	2.9641	1.1305	0.7396	6.9433	1.0005	0.6546	5.3397	1.1506	0.7528	8.8548	1.1899	0.7785	12.5650
52.5	0.8550	0.7852	1.0741	1.0922	0.7984	1.6811	1.1224	0.8205	4.5020	1.052	0.7690	2.0625	1.1334	0.8285	5.5202	1.1573	0.8460	7.7496
53.5	0.9555	0.9025	1.0659	1.0785	0.9132	1.1810	1.088	0.9212	2.0669	1.0539	0.8924	1.1234	1.0915	0.9242	2.4019	1.1025	0.9335	3.4292
54.5	0.99599	0.9989	1.0922	1.0885	0.9955	0.3493	1.0776	0.9855	1.35036	1.0806	0.9883	1.0650	1.0801	0.9878	1.1151	1.0721	0.9805	1.8508
				Error Percentage		4.6794			9.3021			5.2418			10.2057			15.8886

Table 4.Experimental and model prediction of VLE tetrahydrafuran-water system at 101.325 kPa

T	X	Y	γ_1 Exp	NRTL			UNIQUAC			UNIFAC			SRS			TCRS		
				γ_1	y_1	y_1 Error %	γ_1	y_1	y_1 Error %	γ_1	y_1	y_1 Error %	γ_1	y_1	y_1 Error %	γ_1	y_1	y_1 Error %
88.5	0.02601	0.6631	12.9383	14.468	0.7415	11.8232	13.910	0.7129	7.5101	8.6380	0.4427	33.2378	6.9815	0.3578	46.0413	5.7131	0.2928	55.8437
84.5	0.0521	0.7541	8.2262	8.9844	0.8236	9.2162	8.6462	0.7926	5.1054	6.9030	0.6328	16.0854	7.2521	0.6648	11.8419	6.2976	0.5773	23.4451
74.5	0.15792	0.7911	3.8286	4.0832	0.8437	6.6489	3.9990	0.8263	4.4495	3.7401	0.7728	2.3132	3.5659	0.7368	6.8638	3.4986	0.7229	8.6209
70.5	0.30995	0.8292	2.3147	2.4061	0.8619	3.9435	2.3221	0.8318	0.3135	2.3229	0.8321	0.3497	2.1596	0.7736	6.7052	2.2380	0.8017	3.3164
68.5	0.45504	0.8497	1.7212	1.7673	0.8724	2.6715	1.7039	0.8411	1.0121	1.7681	0.8728	2.7186	1.6261	0.8027	5.5313	1.6668	0.8228	3.1658
67.5	0.59721	0.8786	1.4001	1.4176	0.8895	1.2406	1.3588	0.8526	2.9592	1.4330	0.8992	2.3446	1.3310	0.8352	4.9396	1.3130	0.8239	6.2258
66.5	0.76213	0.8999	1.1605	1.1772	0.9128	1.4334	1.1371	0.8817	2.0224	1.1770	0.9126	1.4112	1.1385	0.8828	1.9002	1.0998	0.8528	5.2339
65.5	0.87201	0.9121	1.0619	1.0802	0.9278	1.7213	1.0773	0.9253	1.4472	1.0772	0.9252	1.4362	1.0861	0.9328	2.2694	1.0382	0.8917	2.2365
64.5	0.91394	0.9194	1.0551	1.0696	0.9319	1.3595	1.0801	0.9411	2.3602	1.0819	0.9426	2.5233	1.0864	0.9466	2.9584	1.0706	0.9328	1.4574
63.5	0.95502	0.9504	1.0787	1.0689	0.9417	0.9164	1.1025	0.9713	2.1979	1.1027	0.9715	2.2190	1.1042	0.9728	2.3558	1.0937	0.9636	1.3878
				Error Percentage		4.0974			2.9377			6.4639			9.4107			11.0933

Table 5 Estimated NRTL, UNIQUAC, SRS and TCRS parameters of four azeotropic systems

System	**NRTL J/mol K**		**UNIQUAC J/mol K**		**TCRS J/mol K**		**SRS J/mol K**	
	λ_{12}-λ_{11}	λ_{21}-λ_{22}	u_{12}-u_{22}	u_{21}-u_{11}	λ_{12}-λ_{11}	λ_{21}-λ_{22}	λ_{12}-λ_{11}	λ_{21}-λ_{22}
Acetone-Chloroform	-1145.053	2750.342	-2163.345	2011.632	3012.205	-1034.635	2277.836	-1136.324
Benzene-Cyclohexane	396.9232	4955.149	1108.235	1820.878	36916.148	31857.23	36916.14	31857.231
Methylacetate-Methanol	1695.919	1428.263	-617.4522	3236.160	34284.913	34669.596	34284.91	34669.596
THF-water	1089.321	3012.483	680.7241	3062.184	25931.384	84244.851	25931.38	84244.851

Table 6 Thermodynamic Consistency test of four azeotropic systems using RedlickKister method

System	**Area**				
	NRTL	**UNIQUAC**	**UNIFAC**	**TCRS**	**SRS**
Acetone-chloroform	0.13875	0.04125	0.07375	0.11501	**0.02125**
Benzene-cyclohexane	0.25125	**0.01750**	0.12875	0.1038	0.17750
Methylacetate-methanol	**0.00750**	0.06325	0.0200	0.07350	0.20690
THF-Water	0.00311	**0.00075**	0.00632	0.01125	0.01650

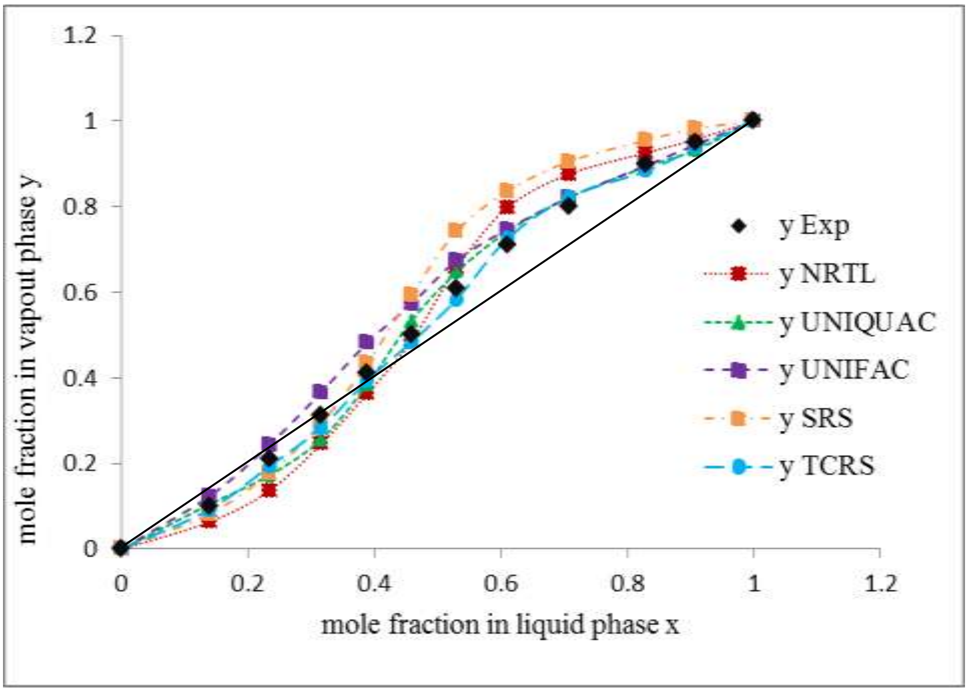

Figure 2. Experimental and correlated xy diagram of acetone-chloroform system at 101.325 kPa

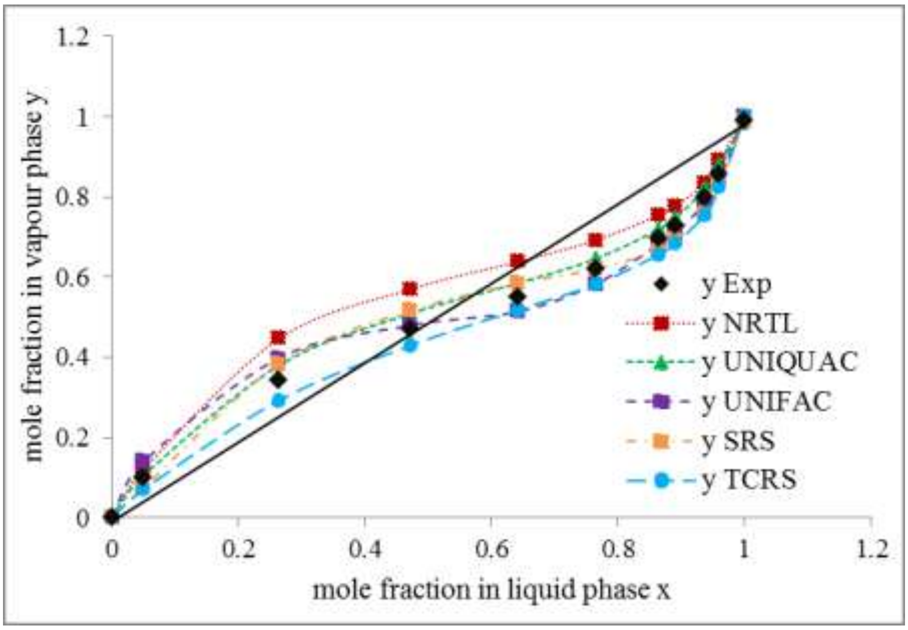

Figure 3. Experimental and correlated xy diagram of benzene-cyclohexane system at 101.325 kPa

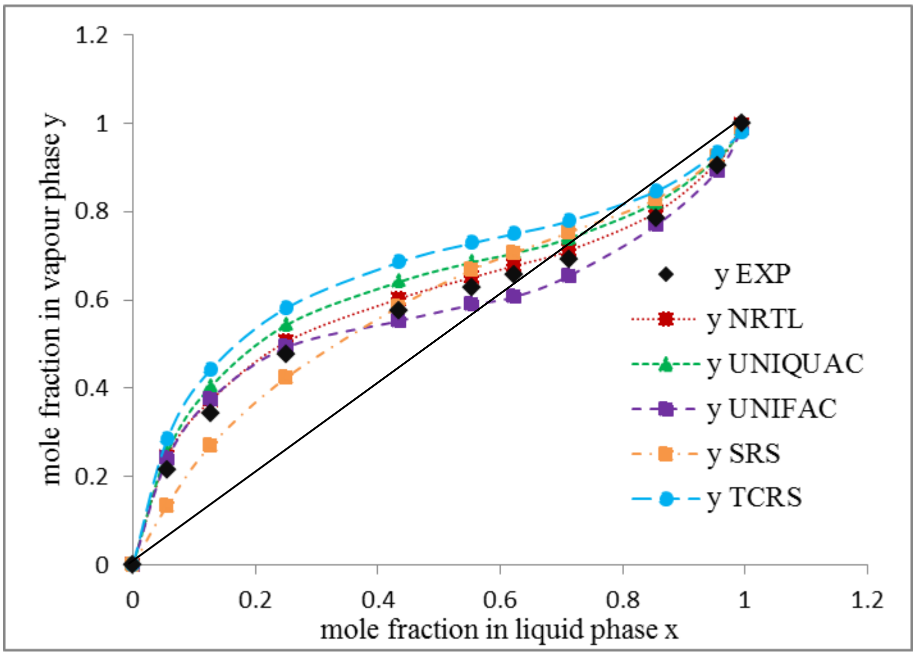

Figure 4. Experimental and correlaed xy Diagram of methyl acetate-methanol system at 101.325 kPa

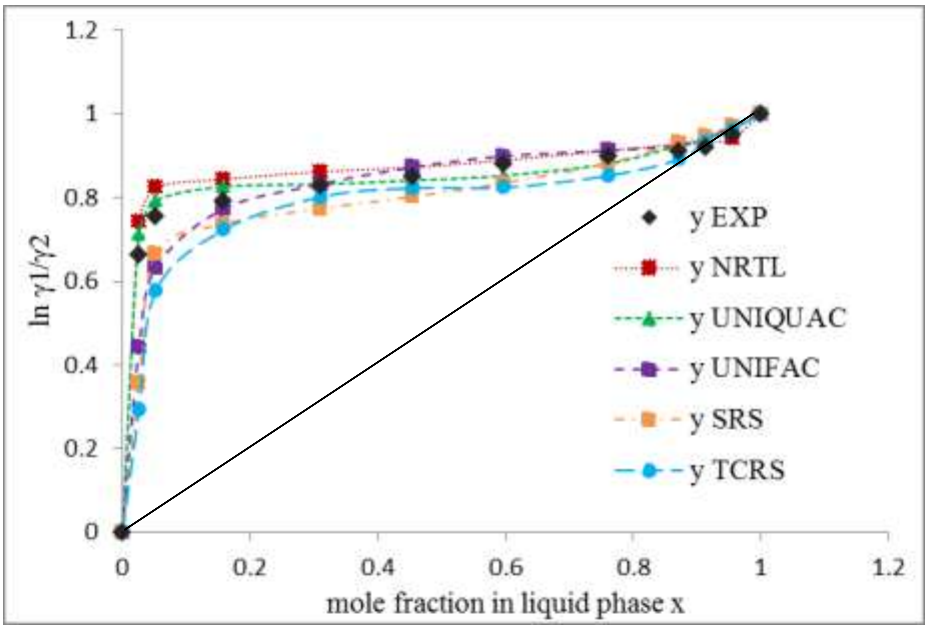

Figure 5. Experimental and correlated xy Diagram of tetrahydrafuran-water system at 101.325 kPa

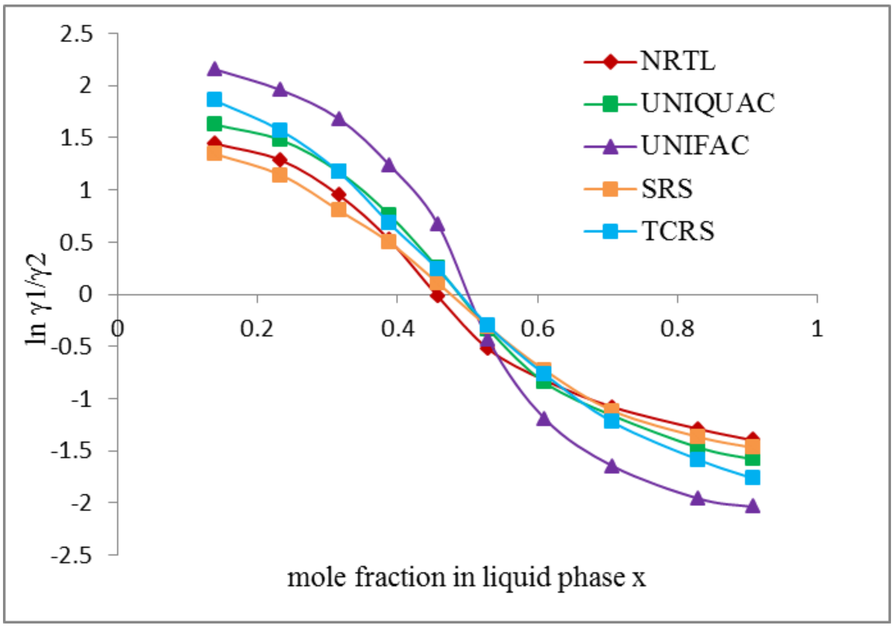

Figure.6 Thermodynamic consistency test of acetone-chloroform system using Redlich Kiester method for NRTL,UNIQUAC,UNIFAC,SRS and TCRS models.

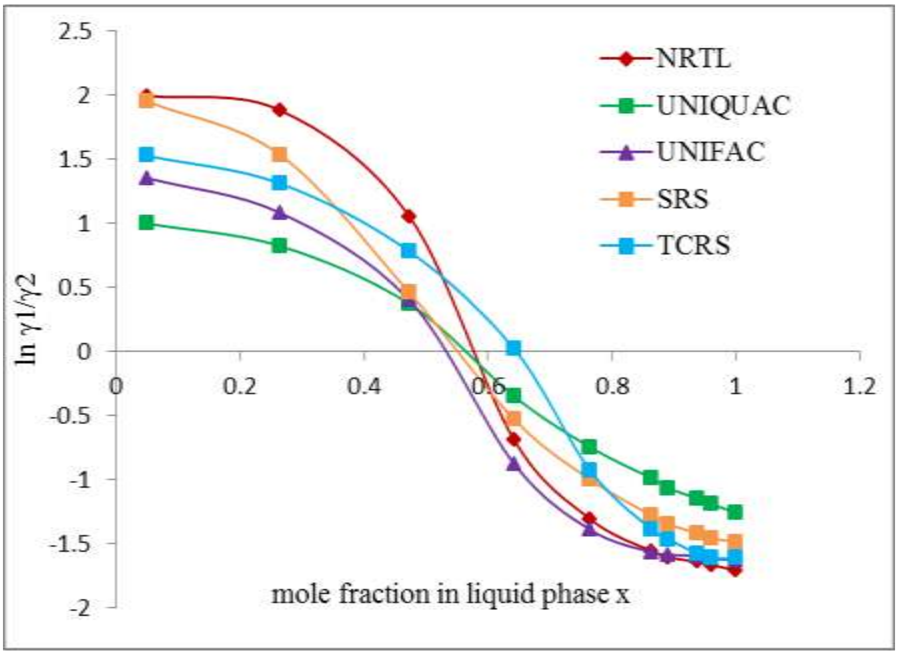

Figure.7 Thermodynamic consistency test of benzene-cyclohexane system using Redlich Kiester method for NRTL,UNIQUAC,UNIFAC,SRS and TCRS models

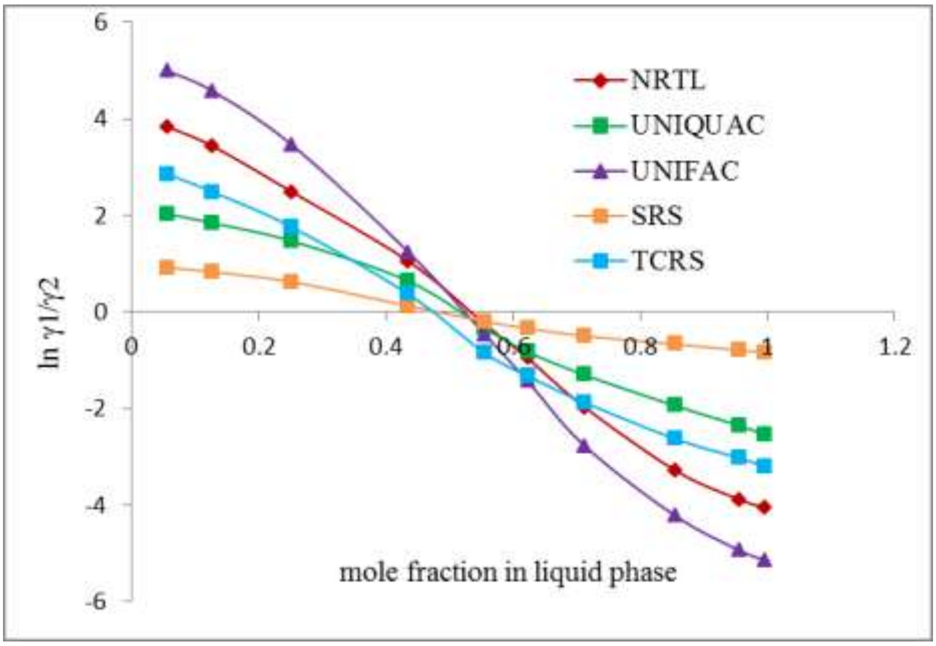

Figure.8 Thermodynamic consistency test of methylacetate-methanol system using Redlich Kiester method for NRTL,UNIQUAC,UNIFAC,SRS and TCRS models.

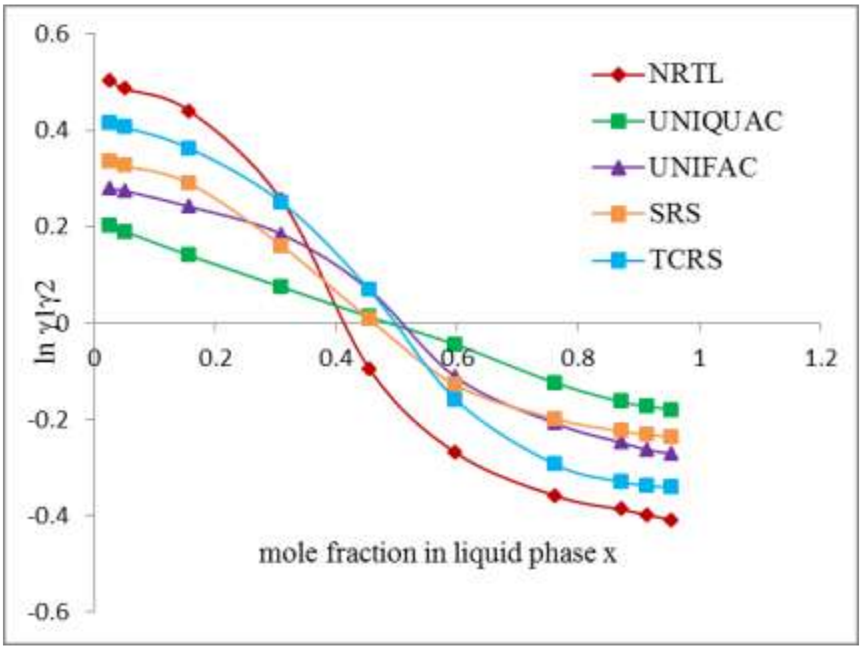

Figure.9 Thermodynamic consistency test of tetrahydrafuran-water system using Redlich Kiester method for NRTL,UNIQUAC,UNIFAC,SRS and TCRS models.

4. Conclusion

In case of VLE prediction of azeotropes, NRTL, UNIQUAC UNIFAC, SRS and TCRS models were tested for the systems acetone-chloroform, benzene-cyclohexane, methyl acetate-methanol and tetrahydrafuran-water. The experimental VLE findings show that acetone-chloroform forms maximum boilingazeotrope and the other three systems are minimum boiling azeotropes. Major finding of the present work is the estimation of NRTL, UNIQUAC, SRSand TCRS parameters for the four systems. These parameters can be utilized for VLE calculation at any pressure conditions.

Nomenclature

B^0& 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
Qi = 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_k & 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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