Estimation of Thermodynamic Models for Azeotropic Systems Using Data Assessment and Thermodynamic Consistency Test

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ABSTRACT

Knowledge of precise vapor-liquid equilibria is a requirement to the detailed design of distillation equipment. However, such data is limited, and usually not available when new systems are under consideration, because it is complex and laborious to obtain the data experimentally. Predictive methods are therefore valuable for process evaluation and design. In this paper five binary azeotropes namely Acetone-water, Acetone-methanol, Ethanol-water, Ethanol-benzene, and Methanol-water were taken. The experimental vapour liquid equilibrium data determination for this system was carried out using Othmer type ebuilliometer in laboratory scale at atmospheric pressure. For the theoretical prediction of VLE five activity coefficient models namely NRTL, UNIQUAC, UNIFAC and modified form of florry-huggins equations (SRS and TCRS) have been employed. The parameters for the five systems of four models namely NRTL, UNIQUAC SRS and TCRS were computed using Newton Raphson technique. UNIFAC model was adopted using Analytical solution of group contribution (ASOG) method. Also these models are validated using thermodynamic consistency test. The performance of these models are tested and reported.

Keywords : Vapour Liquid Equilibrium, Azeotrope, Non Ideal System, Activity Coefficient Model, Thermodynamic Consistency

I. INTRODUCTION

Separation of chemical in to the constituents is an art for millennia [Seader, and Henley, 2006]. Chemical Engineers are more concerned with separations process. Separation methods include distillation, absorption, liquid-liquid extraction, leaching, drying and crystallization etc [Geankoplis, 2003]. Distillation, which is the most widely, used separation technique in the chemical process industries [Vivek Julka, *et al.,* 2009] accounts for about 3% of the world energy consumption. Also it has substantial advantages over the other processes applied in order to separate a mixture, such extraction, crystallization, semi permeable membranes etc. Distillation process is based on the fact that the composition of the boiling liquid and that of the vapour over it differ. Thus, if the boiling temperature is low (e.g., air separation), it is necessary to use low temperature refrigerants and conduct the process at a higher pressure. If it is high (e.g., in separation of heavy oil fractions or metals), high temperature heat carries or fire preheating have to be used and the process is run under vacuum [Mohamad Azamudin, 2010]. Because of the high energy demand of these processes the optimal design and operation of the distillation equipments are important from economic and also environmental points of view [Laszlo, 2013]. The presence of azeotropic mixture however complicates the design of ordinary distillation principles [Gadekar, *et al.,* 2004]. It is impossible to conduct the distillation process in the case of azeotropic composition. Azeotropes or

close-boiling mixtures [Narayanan, 2004]. The molecular interactions when two or more components are mixed may cause the mixture to form certain "inseparable" compositions where the vapor and liquid compositions at equilibrium are equal within a given pressure and temperature range. These specific mixture compositions are called azeotropes. The defining condition of an azeotropic mixture and the physical phenomena leads to nonideality. Nonideal mixtures exhibit positive ($\gamma_i > 1$) or negative ($\gamma_i < 1$) deviations from Raoult's law [Hilmen, 2000]. If these deviations become so large that the vapor pressure exhibits an extremal point at constant temperature, or, equivalently, an extremal point in the boiling temperature at constant pressure [Swietoslawski, 1963]. Azeotropes play an important role in vapor-liquid equilibrium separation processes. For efficient design of distillation equipment or any other separation processes which are diffusional in nature requires quantitative understanding of vapour liquid equilibria. In Vapour liquid equilibrium phases are expressed through vapour phase fugacity coefficients and the liquid phase activity coefficients. At low or modest pressures fugacity coefficient can be estimated easily for very simple mixtures or ideal solutions, but for non-ideal mixtures, estimation of liquid phase activity coefficient is quite difficult [Managobinda, 2010]. In the present work five azeotropic systems namely acetone-methanol, chloroform-methanol, acetone-water, ethanol-benzene and methanol-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.

II. EXPERIMENTATION

2.1.1 Materials and Methods

All the chemicals (acetone, benzene, ethanol, and methanol) were supplied by the Indian Scientific Chemical Industries Pvt. Ltd., Chennai, India. The purities of all reagents are confirmed to be analytical grade by gas chromatography and were found to be 0.998 mass fractions for ethanol, methanol 0.997 mass fractions for acetone, benzene. The water used in the experiment is deionised water which is prepared in the laboratory.

2.1.2 Experimental Procedure

Othmer VLE still (see fig.1) 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 $\times$ 0.25 mm ID $\times$ 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.
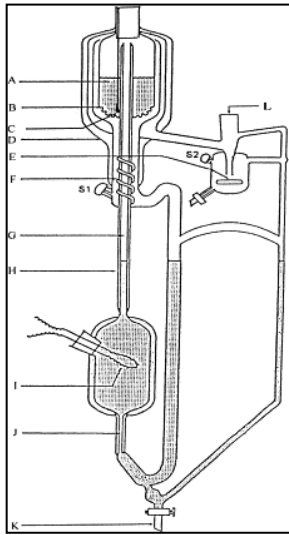
Figure 1. Schematic diagram of vapour liquid equilibrium still A: SS wire mesh packing; B: drain holes; C: Pt-100 bulb; D: pressure jacket; E: magnetic stirrer; F: SS mixing spiral; G: insulated Cottrell pump; H: pressure jacket; I: internal heater; J: capillary; K: drain valve; S1: liquid sampling point; S2: vapour sampling point; L: condenser is attached here.

2.1.3 Low pressure VLE data reduction

There are different methods available for the regression of isothermal and isobaric VLE data. The gamma/phi (γ-φ) formulation of VLE or more commonly known as the combined method was used in this work to regress the VLE data [Ngema, 2010]. The combined method uses an equation of state to calculate the fugacity coefficients that describe the vapour phase non-idealities, while an activity coefficient model is used to calculate the activity coefficients that describe the liquid phase non-idealities. The gamma/phi method relies upon liquid phase activity coefficient models to represent VLE data, and give accurate result for non ideal solution [Kannan, 2003] which is given by

$$\varphi_i y_i P = \gamma_i x_i P_i^{Sat} \tag{1}$$

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; φ_i is fugacity coefficient and γ_i is activity coefficient.

2.1.4 Fugacity Coefficient

At low to moderate pressure (0 to 10 atm), fugacity coefficient can be calculated by the following equations [Rao, 1997].

$$\ln \varphi_i = (B^0 + \omega B^1) P_r / T_r \tag{2}$$

$$f_i = \varphi_i P \tag{3}$$

$$B_0 = 0.083 - 0.422 / T_r^{1.6} \tag{4}$$

$$B^1 = 0.139 - 0.172 / T_r^{4.2} \tag{5}$$

φ_i is fugacity coefficient; B^0 & B^1 are virial coefficients; ω is accentric factor; P_r is reduced pressure; T_r is reduced temperature.

2.3 ACTIVITY COEFFICIENT MODELS

2.3.1 NRTL (Non-Random Two Liquid) Model

The non random two liquid (NRTL) equation proposed by Renon [Renon and Prausnitz, 1968] is applicable to partially miscible as well as completely miscible systems. The equations for the activity coefficients are

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \tag{6}$$

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] \tag{7}$$

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

2.3.2 UNIQUAC (UNIversal Quasi-Chemical) model

The UNIQUAC equation was developed by Abrams and Prausnitz [Anderson and Prausnitz, 1978] 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

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \Sigma_j x_j l_j \tag{8}$$

$$\ln \gamma_i^R = q_i [1 - \ln (\Sigma_j \theta_j \tau_{ji}) - \Sigma_j \frac{\theta_j \tau_{ij}}{\Sigma_k \theta_k \tau_{kj}} \tag{9}$$

$$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1) \tag{10}$$

$$r_i = \Sigma_k v_k^i R_k \tag{11}$$

$$q_i = \Sigma_k v_k^i Q_k \tag{12}$$

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}.

2.3.3 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 [Fredenslund, *et al.,* 1977]. The combinatorial term is evaluated using equation (8) 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 [Fredenslund, *et al.,* 1975]

$$\ln \gamma_i = \ln \gamma_i \text{ (combinatorial)} + \ln \gamma_i \text{ (residual)} \tag{13}$$

$$\ln \gamma_i \text{ (residual)} = \Sigma_k v_k^i [\ln \Gamma_k - \ln \Gamma_k^i] \tag{14}$$

$$\ln \Gamma_K = Q_k [1 - \ln (\Sigma_m \phi_m \Psi_{mk}) - \Sigma_m \frac{\phi_m - \Psi_{km}}{\Sigma_n \phi_n \Psi_{nm}}] \tag{15}$$

$$\Psi_{mn} = \exp - \left[\frac{u_{mn} - u_{nn}}{RT} \right] = \exp \frac{- a_{mn}}{T} \tag{16}$$

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

2.4 MODIFIED FORM OF FLORY – HUGGINS EQUATION

2.4.1 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 [Sabarathinam, and Sivaprakash, 2002]

$$\ln\gamma_1 = -\ln(x_1 + x_2 L_{12}) - x_2[A_{12} - A_{21}] - (\ln L_{12} + \ln L_{21})$$

$$\left[\varphi_1 \varphi_2 + x_2 \varphi_2 \frac{\partial \varphi_1}{\partial x_1} + x_2 \varphi_1 \frac{\partial \varphi_2}{\partial x_1} \right] \tag{19}$$

$$\ln\gamma_2 = -\ln(x_2 + x_1 L_{21}) - x_1[A_{12} - A_{21}] - (\ln L_{12} + \ln L_{21})$$

$$\left[\varphi_1 \varphi_2 + x_1 \varphi_2 \frac{\partial \varphi_1}{\partial x_1} + x_1 \varphi_1 \frac{\partial \varphi_2}{\partial x_1} \right] \tag{20}$$

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

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

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

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

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.

2.4.2 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 [18]

$$\ln \gamma_1 = -\ln(x_1 + x_2 L_{12} \exp(x_1 \delta_{12})) +$$

$$x_2[A_{ij} - A_{ji}] - x_1 x_2^2 \delta_{12}(A_{ij} - A_{ji}) - (\ln L_{12} + \ln L_{21} + \delta_{12}(x_1 - x_2))$$

$$\left[\varphi_1 \varphi_2 + x_2 \varphi_2 \frac{\partial \varphi_1}{\partial x_1} + x_2 \varphi \frac{\partial \varphi_2}{\partial x_1} \right] - 2x_2 \varphi_1 \varphi_2 \delta_{12}$$

(23)

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

$$(A_{12} - A_{21}) - (\ln L_{12} + \ln L_{21} + \delta_{12}(x_1 - x_2))$$

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

(24)

$$\text{where} \quad L_{ij} = \frac{V_j}{V_i} \exp \left[\frac{\lambda_{ij} - \lambda_{ii}}{RT} \right]$$

(25)

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

(26)

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

(27)

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

(28)

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

(29)

2.5 ERROR ANALYSIS

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

$$REy_1 = \frac{\left| y_1 \text{ Experiment al} - y_1 \text{ Calculated} \right|}{y_1 \text{ Experiment al}} \times 100$$

(30)

2.6 VLE CONSISTENCY

The Gibbs duhem equation relates the chemical potential of the components in a mixture to another. When applied to liquid phase and written in the terms of activity coefficients, the isothermal and isobaric form for a binary system is [Philip Jackson and Richard Wilsak, 1995]

$$X_1 d \ln \gamma_1 + X_2 d \ln \gamma_2 = 0$$

(31)

This total differential can be manipulated into various forms each giving rise to different thermodynamic consistency test. Of all the thermodynamic consistency tests the integral test is probably the best known. It was proposed by RedlichKister in 1948 [Redlich, and Kister, 1948]. In this work the thermodynamic consistency of measured (vapour + liquid) equilibrium data is validated using integral test it is given by

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2} \, dx_1 = 0$$

(32)

The limits of integrations cover the entire composition range. The integral test can be applied rigorously to isothermal and isobaric activity coefficient. The graphical implication is straight forward. If $\ln \gamma_1/\gamma_2$ is plotted against x_1, the area above the axis should equal to area below it.

2.7 RESULT AND DISCUSSION

VLE data for the five binary systems namely Acetone-water, Acetone-methanol, Ethanol-water, Ethanol-benzene, and Methanol-water were determined and the results are represented in tables 1-5. The experimental data are compared with literature and found to be in good agreement. Vapour phase ideality was characterized by fugacity coefficient calculation using equations (2-5) from the calculations the fugacity coefficient was found to be closer to unity. Hence it is reasonable to consider that the vapour phase is ideal. The activity coefficient (γ_1) calculated from the experimental VLE using Equation (1) for the five azeotropic systems is also incorporated in tables 1-5. Since the numerical values of activity coefficient (γ_1) are greater than unity for all the systems the liquid phase feature strong non ideality. 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 [Luben and Wenzel, 1988]. Also all the five azeotropic systems show positive deviation from ideality (minimum boiling azeotropes). This is because the dissimilar molecular structures of five azeotropic systems exert repulsive forces other than

attractive forces. The repulsive forces results in higher concentration of molecules in vapour phase than in the liquid phase with higher activity coefficient (γ).

Table 1. Experimental and Models Predicted VLE of Acetone-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 %
74.80	0.0615	0.5981	5.3329	7.1565	0.8026	46.2730	3.6431	0.4085	31.7003	6.4157	0.7195	20.2976	2.9835	0.3346	44.0561	4.8927	0.5487	8.2594
68.53	0.1253	0.7401	3.9265	4.6083	0.8686	12.2947	3.4671	0.6535	11.7011	4.3850	0.8265	11.6741	3.6254	0.6833	7.6746	4.1039	0.7735	4.5129
65.26	0.1492	0.7616	3.7636	4.2806	0.8662	8.7371	3.4217	0.6924	9.0861	4.1022	0.8301	8.9942	3.9332	0.7959	4.5036	3.9368	0.7966	4.5955
63.59	0.2124	0.7912	2.8986	2.7045	0.8558	2.5893	2.7045	0.7382	6.6986	3.0437	0.8308	5.005	3.2086	0.8758	10.692	3.0563	0.8342	5.4347
60.75	0.3214	0.8204	2.1797	2.1942	0.8258	0.3980	2.0318	0.7647	6.7893	2.1918	0.8249	0.5485	2.353	0.8856	7.9473	2.2029	0.8291	1.0604
59.95	0.4201	0.8369	1.7468	1.6588	0.7947	2.2749	1.6209	0.7765	7.2171	1.7007	0.8147	2.6526	1.8296	0.8765	4.7317	1.6975	0.8132	2.8318
59.12	0.4961	0.8387	1.5240	1.4096	0.7757	4.3408	1.4241	0.7837	6.5577	1.4714	0.8097	3.4577	1.5741	0.8662	3.2788	1.4736	0.8109	3.3146
58.29	0.6126	0.8592	1.3000	1.1889	0.7857	3.5359	1.2184	0.8052	6.2849	1.2297	0.8127	5.412	1.2747	0.8424	1.9553	1.2325	0.8145	5.2025
57.49	0.6971	0.8712	1.1900	1.0964	0.8026	3.1261	1.1373	0.8325	4.4421	1.1322	0.8288	4.8668	1.1296	0.8269	5.0849	1.1318	0.8285	4.9012
56.68	0.7838	0.8895	1.1107	1.0411	0.8337	2.7981	1.0911	0.8737	1.7762	1.0724	0.8587	3.4626	1.0464	0.8379	5.8010	1.0711	0.8577	3.5750
56.30	0.8923	0.9233	1.0260	1.0082	0.9073	1.0146	1.0342	0.9307	0.7960	1.0191	0.9171	0.6768	0.9949	0.8953	3.0378	1.0186	0.9166	0.7310
			Error percentage			7.9438			8.4590			6.0952			8.9785			4.0380

Table 2. Experimental and Models Predicted VLE of Acetone-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 %
65.5	0.0561	0.1673	2.1859	1.7931	0.1372	17.9916	1.8659	0.1428	14.6443	2.5171	0.1926	15.1225	2.9686	0.2272	35.8039	1.6242	0.1243	25.7023
64.5	0.1154	0.2939	1.9277	1.7632	0.2688	8.5403	1.7881	0.2726	7.2473	1.9788	0.3016	2.6199	2.4584	0.3748	27.5263	1.6752	0.2554	13.0996
63.5	0.1885	0.4094	1.6979	1.5546	0.3748	8.4513	1.7485	0.4215	2.9555	1.7724	0.4273	4.3722	1.9833	0.4782	16.8050	1.7988	0.4337	5.9355
62.5	0.3197	0.5235	1.3224	1.2504	0.4949	5.4632	1.3964	0.5527	5.5778	1.3858	0.5485	4.7755	1.4721	0.5827	11.3085	1.4494	0.5737	9.5893
61.5	0.3945	0.5678	1.2011	1.1584	0.5475	3.5752	1.2444	0.5882	3.5928	1.2294	0.5811	2.3423	1.3027	0.6158	8.4536	1.3616	0.6436	13.3497
58.5	0.5742	0.6452	1.0360	1.0024	0.6242	3.2548	1.0483	0.6528	1.1779	1.0650	0.6632	2.7898	1.0659	0.6638	2.8828	1.1764	0.7326	13.5461
54.5	0.7335	0.7325	1.0550	1.0302	0.7152	2.3617	1.0292	0.7145	2.4573	1.0635	0.7383	0.7918	0.9850	0.6838	6.6484	1.1591	0.8047	9.8566
52.5	0.8132	0.7856	1.0941	1.1194	0.8037	2.3039	1.0626	0.7629	2.8895	1.1034	0.7922	0.8401	0.9839	0.7064	10.0814	1.1750	0.8436	7.3828
51.5	0.8845	0.8354	1.1079	1.1391	0.8588	2.8010	1.0814	0.8153	2.4060	1.0976	0.8275	0.9456	0.9861	0.7435	11.0007	1.1600	0.8746	4.6923
50.5	0.9438	0.8946	1.1519	1.1781	0.9148	2.2579	1.1284	0.8762	2.0567	1.1400	0.8852	1.0507	1.0633	0.8257	7.7017	1.1927	0.9262	3.5323
50.5	0.9978	0.9837	1.1981	1.1799	0.9687	1.5248	1.2041	0.9885	0.4879	1.1882	0.9755	0.8335	1.1421	0.9376	4.6863	1.1981	0.9836	0.0101
			Error Percentage			5.3205			4.1357			3.3167			12.9908			9.6997

Table 3. Experimental and Models Predicted VLE of Ethanol-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 %
92.5	0.0170	0.1589	5.4644	3.9141	0.1138	28.3826	7.0209	0.2041	28.4455	6.6402	0.193	21.46	8.6951	0.2528	59.0937	8.0401	0.2337	47.0736
90.5	0.0621	0.3789	3.8360	3.0797	0.3042	19.7170	4.5559	0.4500	18.7617	4.2968	0.4244	12.0054	5.0771	0.5015	32.3533	4.8221	0.4763	25.7026
88.5	0.0856	0.4375	3.4586	2.8659	0.3625	17.1428	3.9173	0.4955	13.2571	3.4476	0.4361	0.3200	4.3189	0.5463	24.8685	4.1562	0.5257	20.1600
86.0	0.1238	0.4805	2.8834	2.4778	0.4129	14.0686	3.2057	0.5342	11.1758	2.8135	0.4688	2.4349	3.5382	0.5896	22.7055	3.3234	0.5538	15.2549
84.5	0.1561	0.5219	2.6287	2.2294	0.4426	15.1944	2.8006	0.5560	6.5338	2.4903	0.4944	5.2692	3.1422	0.6238	19.5248	2.8899	0.5737	9.9252
84.5	0.2508	0.558	1.7493	1.5431	0.4922	11.7921	1.8538	0.5913	5.9677	1.6873	0.5382	3.5488	2.0729	0.6612	18.4946	1.9206	0.6126	9.7849
82.5	0.3075	0.5826	1.6081	1.4561	0.5275	9.4576	1.6813	0.6091	4.5485	1.5386	0.5574	4.3254	1.8574	0.6729	15.4994	1.7299	0.6267	7.5695
80.5	0.4065	0.6223	1.4040	1.3136	0.5822	6.4438	1.4179	0.6284	0.9802	1.3272	0.5882	5.4796	1.5627	0.6926	11.2968	1.4519	0.6435	3.4067
79.5	0.4979	0.6564	1.2573	1.1942	0.6234	5.0274	1.2509	0.6511	0.8074	1.1727	0.6122	6.7336	1.3685	0.7144	8.8360	1.2844	0.6705	2.1480
79.0	0.5198	0.6629	1.2404	1.1842	0.6328	4.5406	1.2255	0.6549	1.2068	1.1657	0.6229	6.0340	1.3477	0.7202	8.6438	1.2809	0.6845	3.2584
78.0	0.5923	0.6921	1.1823	1.1833	0.6926	0.0722	1.1582	0.6779	2.0517	1.1328	0.663	4.2045	1.2649	0.7404	6.9787	1.2019	0.7035	1.6471
77.0	0.6963	0.7495	1.1333	1.1233	0.7428	0.8939	1.0977	0.7259	3.1487	1.112	0.7353	1.8945	1.1835	0.7826	4.4162	1.1271	0.7453	0.5603
75.5	0.7572	0.7965	1.1762	1.1558	0.7826	1.7451	1.1367	0.7697	3.3647	1.1416	0.773	2.9504	1.2003	0.8127	2.0338	1.1290	0.7645	4.0175
74.5	0.9143	0.9243	1.1770	1.1759	0.9233	0.1081	1.1319	0.8888	3.8407	1.1555	0.9073	1.8392	1.1434	0.8978	2.8670	1.1292	0.8867	4.0679
			Error Percentage			9.6133			7.4350			5.6071			16.7922			11.0411

Table 4. Experimental and Models Predicted VLE of Ethanol-benzene 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 %
78.0	0.0187	0.1297	7.0951	8.0324	0.1468	13.1842	11.1504	0.2038	57.1318	2.9508	0.0539	58.4117	6.9391	0.1268	2.1952	4.5736	0.0836	35.4973
74.0	0.0523	0.2394	5.5072	5.8086	0.2525	5.4720	7.0465	0.3063	27.9448	3.3635	0.1462	38.9306	6.0406	0.2625	9.6816	4.5043	0.1958	18.2122
73.0	0.0993	0.3067	3.8719	4.2006	0.3327	8.4773	4.8706	0.3858	25.7906	2.8822	0.2283	25.5624	4.2006	0.3298	7.5380	3.4669	0.2746	10.4662
68.5	0.1567	0.3596	3.4788	3.7335	0.3858	7.2858	4.3225	0.4468	24.2491	2.9739	0.3074	14.5161	3.4421	0.3558	1.0552	3.4324	0.3548	1.3348
66.5	0.2345	0.3989	2.8115	2.9612	0.4201	5.3146	3.4249	0.4859	21.8099	2.6347	0.3738	6.29230	2.7497	0.3901	2.2046	3.0154	0.4278	7.2449
66.0	0.3241	0.4322	2.2527	2.3351	0.4479	3.6325	2.6453	0.5075	17.4224	2.2007	0.4222	2.31374	2.1784	0.4179	3.3006	2.4717	0.4742	9.7177
65.5	0.4500	0.4567	1.7524	1.7655	0.4601	0.7444	2.0023	0.5218	14.2544	1.8434	0.4804	5.18940	1.7274	0.4501	1.4284	1.9854	0.5174	13.2910
64.5	0.5228	0.4780	1.6498	1.5681	0.4543	4.9581	1.8405	0.5332	11.5481	1.7514	0.5074	6.15062	1.6354	0.4738	0.8659	1.8771	0.5438	13.7656
63.0	0.7101	0.5228	1.4202	1.3337	0.4909	6.1017	1.5371	0.5658	8.22494	1.5708	0.5782	10.5967	1.5056	0.5542	6.0160	1.6701	0.6147	17.5784
62.0	0.7866	0.5760	1.4775	1.3704	0.5342	7.2569	1.5266	0.5951	3.31597	1.6043	0.6254	8.57638	1.5448	0.6022	4.5601	1.6746	0.6528	13.3333
60.5	0.8743	0.6834	1.6882	1.6098	0.6516	4.6532	1.6167	0.6544	4.24348	1.7948	0.7265	6.30670	1.7333	0.7016	2.6731	1.7896	0.7244	5.9994
60.0	0.9230	0.7734	1.8516	1.8716	0.7817	1.0731	1.7610	0.7355	4.90044	1.9479	0.8136	5.19782	1.8774	0.7841	1.3906	1.9532	0.8158	5.4822
Percentage Error						5.6974			18.4030			15.6703			3.5758			12.6614

Table 5. Experimental and Models Predicted VLE of Methanol-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 %
96.4	0.0189	0.1234	1.8695	2.6641	0.1758	42.4635	2.0471	0.1351	9.4813	2.0132	0.1328	7.6175	1.1409	0.0753	38.9789	0.7242	0.0478	61.2641
93.5	0.0389	0.2230	1.8432	2.3048	0.2788	25.0224	1.8234	0.2206	1.0762	1.6667	0.2016	9.5964	1.5097	0.1826	18.1165	1.1871	0.1436	35.6053
91.2	0.0588	0.3104	1.8652	2.1406	0.3562	14.7551	1.9151	0.3187	2.6739	1.8575	0.3091	0.4188	1.7049	0.2837	8.6018	1.4711	0.2448	21.1340
89.3	0.0827	0.3665	1.6888	1.8655	0.4048	10.4502	1.8075	0.3922	7.0122	1.7138	0.3719	1.4733	1.7115	0.3174	13.3970	1.3069	0.2836	22.6193
87.7	0.1032	0.4228	1.6643	1.8061	0.4588	8.5146	1.8326	0.4655	10.0993	1.6704	0.4243	0.3548	1.5463	0.3928	7.0955	1.4255	0.3621	14.3566
84.4	0.1485	0.5117	1.4777	1.6643	0.5763	12.6245	1.6323	0.5652	10.4553	1.5058	0.5214	1.8956	1.3924	0.4821	5.7846	1.3366	0.4628	9.5563
81.7	0.1897	0.5729	1.4504	1.6073	0.6348	10.8046	1.5652	0.6182	7.9071	1.4837	0.5860	2.2866	1.3627	0.5382	6.0569	1.2865	0.5081	11.3108
78.0	0.3016	0.6765	1.1839	1.2710	0.7262	7.3466	1.2295	0.7025	3.8433	1.1872	0.6783	0.2660	1.1159	0.6376	5.7501	1.092	0.6239	7.7753
75.3	0.3982	0.7311	1.1058	1.1619	0.7681	5.0608	1.1272	0.7452	1.9286	1.1239	0.7430	1.6276	1.0628	0.7026	3.8982	1.0501	0.6942	5.0471
72.1	0.5120	0.7819	1.0148	1.0573	0.8146	4.1821	1.0328	0.7945	1.6114	1.0315	0.7947	1.6370	0.9914	0.7638	2.3148	1.0031	0.7728	1.1638
67.2	0.6015	0.8305	1.0331	1.0591	0.8513	2.5045	1.0435	0.8388	0.9993	1.0459	0.8407	1.2281	1.0111	0.8127	2.1432	1.0222	0.8217	1.0596
66.3	0.7127	0.8689	1.0993	1.1116	0.8786	1.1163	1.1081	0.8758	0.7941	1.1112	0.8782	1.0703	1.0790	0.8528	1.8529	1.0896	0.8612	0.8861
64.5	0.8257	0.9211	1.0416	1.0522	0.9304	1.0041	1.0312	0.9118	1.0150	1.0332	0.9136	0.8196	1.0295	0.9103	1.1778	1.0306	0.9113	1.0693
Error Percentage						11.2191			4.5305			2.3301			8.8591			14.8344

Modelling

Generally distillation columns are operated under varying conditions of temperature and pressure depending on the feed conditions and the desired quality of products. Obtaining VLE for such varying conditions experimentally is quite complex and expensive too. Hence theoretical estimation of VLE using activity coefficient models becomes inevitable. In this context five models namely NRTL, UNIQUAC, UNIFAC [Rao, 1997.] and two modified forms of Florry Huggins' model namely SRS and TCRS [Sabarathinam and Sivaprakash, 2002] were employed in the present study. Newton Raphson technique was used to make the computations with computer programming in Java software of 1.6 version. The parameters estimated are presented in table 6. Binary interaction parameters for UNIFAC method have been taken from the literature [Rao, 1997.].

Table 6. Estimated NRTL, UNIQUAC, SRC and TCRS parameters of five azeotropic systems

System	NRTL J/mol K		UNIQUAC J/mol K		SRS J/mol K		TCRS J/mol K	
	$\lambda_{12}-\lambda_{11}$	$\lambda_{21}-\lambda_{22}$	$u_{12}-u_{22}$	$u_{21}-u_{11}$	$\lambda_{12}-\lambda_{11}$	$\lambda_{21}-\lambda_{22}$	$\lambda_{12}-\lambda_{11}$	$\lambda_{21}-\lambda_{22}$
Acetone-water	2160.1319	18602.345	- 580.1319	1112.3450	3066.913	29.5959	5326.9130	- 2230.4040
Acetone-methanol	- 17460.218	- 51385.655	4769.778	19434.015	1646.530	-1633.5299	8046.530	- 8033.5299

Ethanol-water	- 1835.131	12920.345	-860.1319	1392.345	-1232.8499	3400.00	-1852.849	2780.00
Ethanol-benzene	-1920.1319	9922.3450	320.1319	852.3450	167.1500	4800.00	132.8499	4500.00
Methanol-water	699.8679	1542.3499	12399.868	-11867.654	21832.32	-16828.438	12980.279	-16430.404

The complete comparison of VLE predicted from the five models with the experimental data is presented in tables 1-5. The experimental and correlated x-y diagrams of five azeotropic systems using the five models are given in figures 2-6.
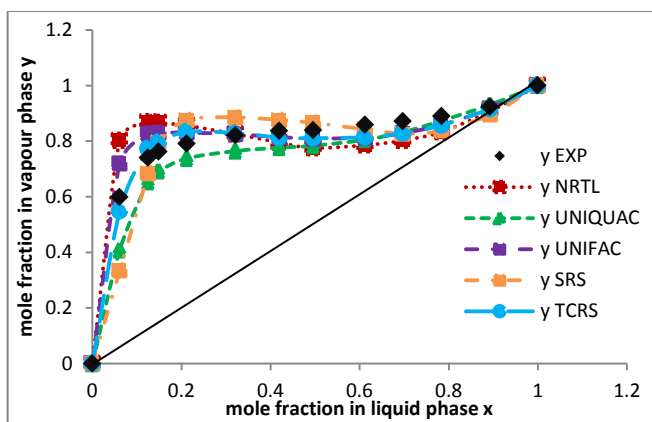
Figure 2. Experimental and Correlated xy Diagram of Acetone-water System at 101.325 kPa.
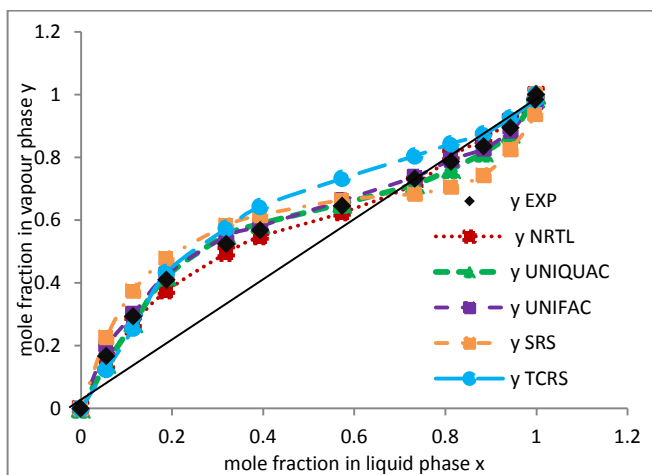
Figure 3. Experimental and Correlated xy Diagram of Acetone-methanol System at 101.325 kPa.
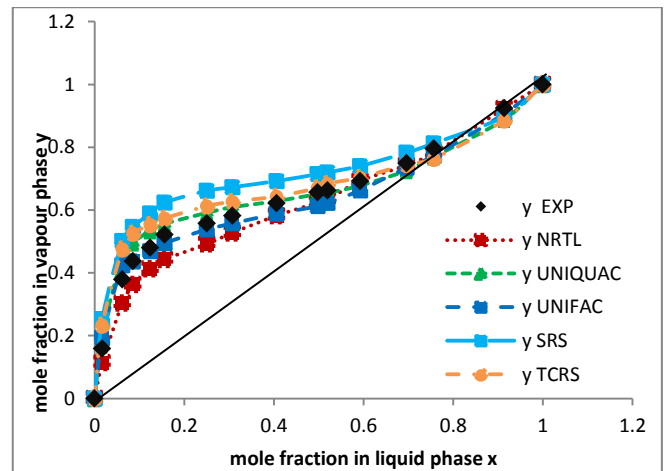
Figure 4. Experimental and Correlated xy Diagram of Ethanol-water System at 101.325 kPa.
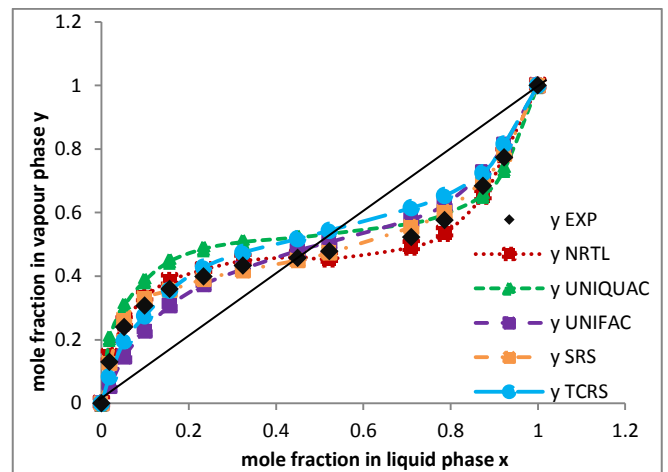
Figure 5. Experimental and Correlated xy Diagram of Ethanol-benzene System at 101.325 kPa.
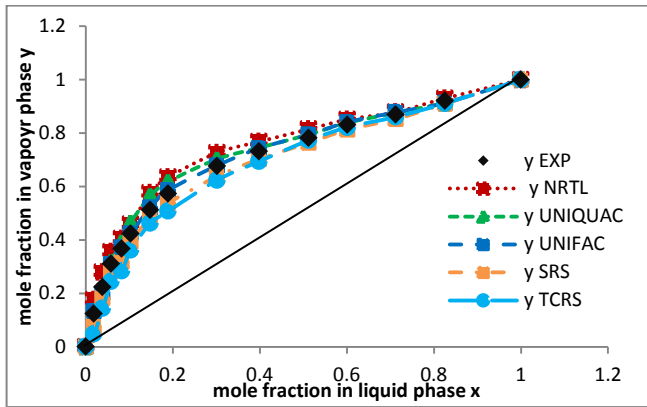
Figure 6. Experimental and Correlated xy Diagram of Methanol-water System at 101.325 kPa.

The overall error percentages of the VLE for acetone-water system using five activity coefficient models (NRTL, UNIQUAC, UNIFAC, SRS and TCRS) are 7.9438, 8.4590, 6.0952, 8.9785, and 4.0380 respectively as indicated in table 1. It is observed that TCRS model have lesser error percentages than the other four models. Acetone-methanol system shows significant validity for the UNIFAC and UNIQUAC models with the least error percentage of 3.3167 and 4.1357 whereas the other models have more than 5 % (table 2.) Error occurred in UNIFAC model (5.6071 %) provide good representation of VLE for ethanol-water system when compared to other models (table 3). The SRS and NRTL model gave better results for the ethanol-benzene system yielding an error percentage of 3.5758 and 5.6974 (table 4). Of all the five models chosen, the UNIFAC and UNIQUAC models gives better result for methanol-water system with least error percentage of 2.3301 and 4.5305 (table 5).

Related outcome were observed with the Redlich-Kister method of thermodynamics consistency test (Eq. 32). This can be seen from the figures 7-11.
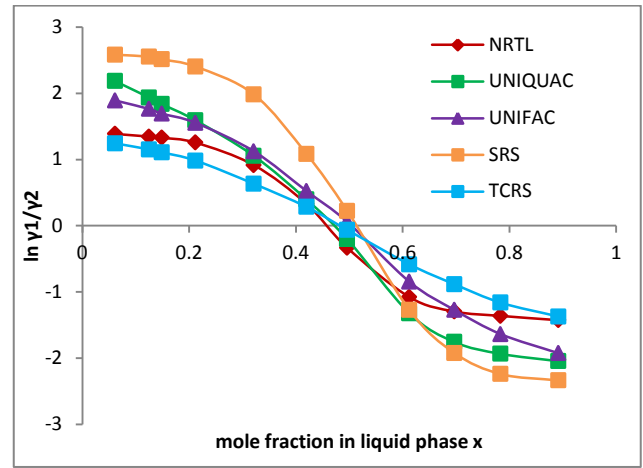
Figure 7. Thermodynamic Consistency test of Acetone-water System Using Redlich Kiester method for NRTL, UNIQUAC, UNIFAC, SRS and TCRS models.
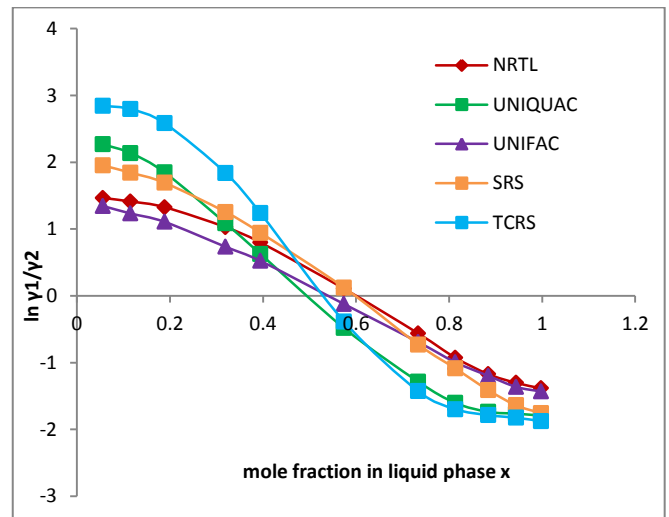

Figure 8. Thermodynamic Consistency test of Acetone-methanol System Using Redlich Kiester method for NRTL, UNIQUAC, UNIFAC, SRS and TCRS models.
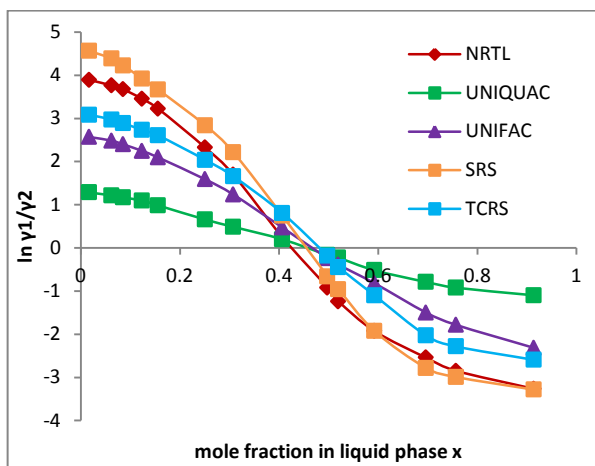
Figure 9. Thermodynamic Consistency test of Ethanol-water System Using Redlich Kiester method for NRTL, UNIQUAC, UNIFAC, SRS and TCRS models.
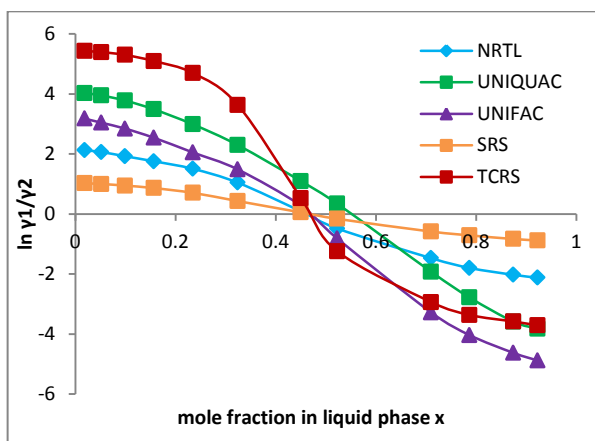

Figure 10. Thermodynamic Consistency test of Ethanol-benzene System Using Redlich Kiester method for NRTL, UNIQUAC, UNIFAC, SRS and TCRS models.
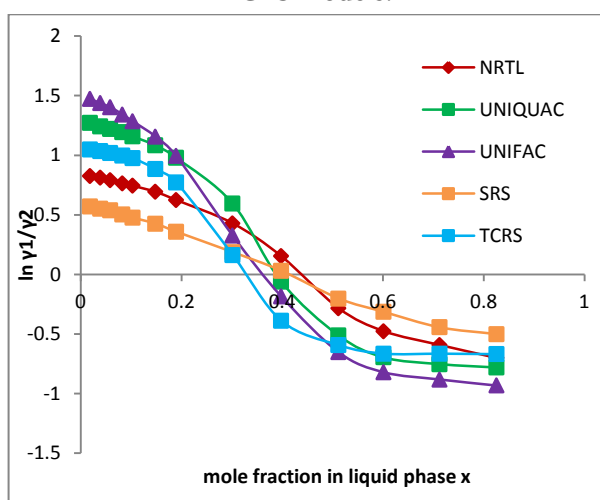

Figure 11. Thermodynamic Consistency test of Methanol-water System Using Redlich Kiester method for NRTL, UNIQUAC, UNIFAC, SRS and TCRS models.

These plots are made using activity coefficient from five models listed in tables 1-5. Area under the curve computed for these models are given in table 7.

Table 7 Thermodynamic Consistency test of five azeotropes system using RedlickKister method

System	Area Under the Curve				
	NRTL	UNIQUAC	UNIFAC	SRS	TCRS
Acetone-water	0.0791	0.09075	0.01625	0.4445	**0.00375**
Acetone-methanol	0.1789	0.08512	**0.03621**	0.2172	0.2005
Ethanol-water	**0.0158**	0.0221	0.0201	0.1173	0.1067
Ethanol-benzene	0.0165	0.4714	0.4041	**0.0054**	0.3823
Methanol-water	0.0409	0.0052	**0.0041**	0.0157	0.0560

From the table it can be observed that value of TCRS model close to zero for acetone-water system. In a similar approach the acetone-methanol system shows good thermodynamic consistency for UNIFAC and UNIQUAC activity coefficient models whereas the ethanol-water own good concurrence with UNIFAC model. For ethanol-water system SRS and NRTL model gives better result of VLE consistency. Correspondingly UNIFAC and UNIQUAC models show appreciable thermodynamic consistency for methanol-water system.

III. Conclusion

In case of VLE prediction of azeotropes, NRTL, UNIQUAC UNIFAC, SRS and TCRS models were tested for the systems namely Acetone-water, Acetone-methanol, Ethanol-water, Ethanol-benzene, and Methanol-water. The experimental VLE findings show that all the five systems show minimum boiling azeotropes (positive deviation from ideality). Major finding of the present work is the estimation of NRTL, UNIQUAC, SRS and TCRS parameters for the five systems. These parameters can be utilized for VLE calculation at any pressure conditions. This paper will be beneficial for distillation column design.

IV. Acknowledgement

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

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_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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