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Review Article

Measurement and Correlation of the Liquid-Liquid Equilibria of Tertiary-Butyl Alcohol – Water – Benzene System at 30°C and 1 Atmosphere Pressure

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Abstract

The Liquid-Liquid equilibria of Tertiary-Butyl Alcohol – Water – Benzene System were measured experimentally at 30°C and 1atm pressure. The experimental binodal curve compositions were obtained using the cloud point method. The compositions of the two equilibrium phases were analysed using Agilent 7820A series Gas Chromatograph. The consistency of the experimental data was determined using the Hand, Othmer-Tobias and Bachman- Brown correlation equations while the plate point was determined using the Treybal's method. The effectiveness of the solvent in the extraction was determined by calculating the distribution coefficients and separation factors. The experimental tie-line data were correlated with the Universal Quasi-Chemical (UNIQUAC) and Non-Random Two Liquid (NRTL) activity coefficient models. Also, the deviation between the experimental and calculated equilibrium compositions were calculated using the root mean squared deviation equation. The UNIQUAC predicted data gave a closer resemblance to the experimental.

Keywords: Liquid-Liquid Equilibrium, UNIQUAC, NRTL, Plait point, Consistency test, Tertiary-Butyl Alcohol – Water – Benzene.

1. INTRODUCTION

Separation and purification of chemicals for industrial and domestic uses are of great interest to engineers and scientists because the process industry deals with enormous amounts of mixtures. Several techniques employed in the purification of mixtures depend on the chemical and physical properties of the components of the mixtures. The design and development of separation processes rely on the liquid-phase equilibrium data of aqueous mixtures with organic solvents, particularly the liquid-liquid equilibria (LLE) of ternary mixtures which are used to evaluate industrial units for solvent extraction processes (Ghanadzadeh, Ali *et al.*, 2009). The binodal curve and tie-line data are needed for optimized operation of the recovery systems (Mohsen-Nia *et al.*, 2009), and the precise interpretation of phase equilibria and thermodynamic behaviour of ternaries is fundamental in improving solvent extraction techniques (Ghanadzadeh, Ali *et al.*, 2009).

Tertiary-butyl alcohol (TBA) is a high-volume solvent because of its numerous commercial uses: as a fuel oxygenate used to replace tetra-ethyl lead as an anti-knock agent in gasoline, as a denaturant for ethanol and other alcohols, in the manufacture of food essences and perfumes, in nitrocellulose lacquers and latex production, numerous cosmetics, fragrances, deodorants, hair and skin care products, etc (Clark, 2001). TBA and Water form an azeotrope at normal pressure, hence, simple distillation cannot be used to separate the components (Perrin, D. D.; Armarego, 1988). An effective method of purification of TBA during production has continued to pose great challenges to the industry, since azeotropic distillation is expensive.

Simasatitkul *et al.*, (Simasatitkul *et al.*, 2017) had proposed a recovery process consisting of extractive distillation and conventional distillation columns with hexyl acetate as its most suitable solvent

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among three solvents of 3-octanone, hexyl acetate and 2-heptanone. Huiyuan & Songlin (2006) suggested using cyclohexane as an entrainer in a heterogeneous azeotropic batch distillation to separate tert-butyl alcohol from water. In their work, cyclohexane formed ternary and binary heterogeneous azetropes with the original components. These processes, though expensive, offer some thermodynamic insights in the recovery of t-butanol from aqueous solutions.

Solvent extraction has proved advantageous in separation techniques when components to be separated are only small fractions of the mixture, when the boiling points of the components are very close, or they form azeotropes, and also when the system is not thermally stable (Wankat, 2006). The main objective of this study is to measure the LLE of t- Butanol-Water-Benzene system at 30°C and 1 atmosphere pressure, hence provide the thermodynamic process data for the recovery of TBA with the solvent Benzene. The experimental tie-line data have been correlated with the UNIQUAC (Abrams & Prausnitz, 1975) and NRTL (Renon & Prausnitz, 1968) activity coefficient equations to assess their predictive quality.

2. EXPERIMENTAL

2.1 Materials

Tertiary Butanol ($(CH_3)_3COH$) and Benzene (C_6H_6) manufactured by Loba Chemie PVT Ltd and distilled water (H_2O) were used in this work and their properties are shown in table 1. The purity of the components was checked by gas chromatography and the results didn't show any appreciable deviation from pure t-butanol (>98%) and benzene (>99%). The components were used without further treatment or purification.

Table 1: Physicochemical Properties of t-Butanol, Water and Benzene Used

	Molecular Weight (g/mol)	Density (g/ml)	Assay (%)
t-Butanol	74.120	0.780	+98.500
Distilled Water	18.020	1.000	+99.800
Benzene	78.110	0.877	+99.000

2.2 Apparatus and Procedure

The Cloud-point method (Lo, T. H.; Baird, M. H.; Hanson, 1983) was used in determining the binodal curve at 30°C ± 0.1°C measured with an OEHLER thermometer model 609327 which uses a temperature sensor in an equilibrium cell.

Binary mixtures of t-Butanol and water, or t-Butanol and Benzene were titrated with Benzene or Water respectively with continuous shaking after each drop of the titrant. The end point was the first perceptible cloudiness which was left for 4 minutes to see if it was stable. Each measurement was repeated three times and the average compositions were recorded with deviation from the average value being less than 0.1%.

In determining the tie lines, ternary mixtures of known compositions were prepared; 25 ml Water and 25 ml Benzene were mixed with 5 to 30ml t-Butanol. Each mixture was prepared in an equilibrium cell, immersed in a thermostat (30°C ± 0.1°C) to control the temperature and stirred using a magnetic stirrer for 2 hours after which it was left to settle for 4 hours when two stable clear phases appeared indicating equilibrium.

2.3 Analysis

The collected samples were analyzed using Agilent 7820A Series Gas Chromatograph (GC) in a split/splitless inlet mode, coupled to a DB-624 (60m×320umx1.8um) Capillary Column suitable for separation of benzene and alcohols and equipped with a Flame Ionization Detector (FID). The GC inlet was set at 250ºC, a temperature high enough to volatilize the compounds in the sample; the injection was set to split the sample by 30:1. Nitrogen gas used as the carrier gas was set at a flowrate of 1.8ml/min. The run was an isothermal run with an oven temperature of 120ºC and a total run time of 9mins. The FID was set at 250ºC with Air, Hydrogen and Nitrogen flow rates of 400, 40 and 20mL/min while the Injection Volume was 1µl. Methanol was used as an internal standard for t-butanol and benzene. All calculations were as per the average response (area) of the components injected. The analysis was carried out three times and the average results obtained. Concentrations were computed as mass fractions of the components.

3. RESULTS AND DISCUSSION

3.1 Mutual Solubility and Tie-Line Data

The experimental data for the binodal curve of t-Butanol – Water – Benzene system at 30°C and 1 atm in mass fraction are shown in table 2, where x_i denotes the mass fraction of the *i*th component. The compositions of the experimental tie-lines for the system are presented in table 3, in which x_{a1} and x_{a2} denote the mass fraction of component a in water(1)-rich phase and the mass fraction of component a in solvent(2)-rich phase respectively.

Table 2: Experimental binodal curve data for t-Butanol (1) – Water (2) – Benzene (3) system at 30°C and 1 atm in Mass Fraction

x_1	x_2	x_3
0.0997	0.8972	0.0031
0.1991	0.7965	0.0044
0.2948	0.688	0.0172
0.3864	0.5797	0.0339
0.4711	0.4711	0.0578
0.5429	0.3619	0.0952
0.5846	0.2506	0.1648
0.5478	0.1369	0.3153
0.385	0.0428	0.5722
0.0985	0.0148	0.8867
0.1951	0.0244	0.7805
0.2913	0.0291	0.6796
0.381	0.0476	0.5714
0.4673	0.0654	0.4673
0.5333	0.1111	0.3556
0.5691	0.187	0.2439
0.5776	0.278	0.1444
0.4147	0.5392	0.0461

Table 3: Experimental tie-line compositions for t-Butanol (1) – Water (2) – Benzene (3) system at 30°C and 1atm in Mass Fraction

	Water Rich Phase			**Solvent Rich Phase**		
	(x_{11})	**(x_{21})**	**(x_{31})**	**(x_{12})**	**(x_{22})**	**(x_{32})**
A	0.1038	0.8962	0.0000	0.1109	0.0134	0.8757
B	0.1496	0.8504	0.0000	0.2515	0.0289	0.7196
C	0.1754	0.8246	0.0000	0.4035	0.0354	0.5611
D	0.2017	0.7983	0.0000	0.4783	0.0723	0.4494
E	0.2106	0.7894	0.0000	0.5123	0.0894	0.3983

3.2 Experimental Data Consistency Test

The consistency and reliability of the experimental tie-lines were ascertained with the Bachman-Brown (Brown, 1948), Hand (Hand, 1930) and Othmer-Tobias (Othmer & Tobias, 1942) correlations. Timedjeghdine *et al.*, (2016), Roy *et al.*, (2006), Torabi *et al.*, (2021), Kim & Park (2005) and several authors have also used same correlations in checking the reliability of their experimental tie-line data.

The Bachman-Brown correlation is defined as

$$\frac{x_{32}}{x_{21}} = M_3 x_{32} + W_3 \qquad (1)$$

The Hand correlation is defined as

$$\ln\left(\frac{x_{11}}{x_{21}}\right) = W_1 + M_1 \ln\left(\frac{x_{12}}{x_{32}}\right) \qquad (2)$$

The Othmer-Tobias correlation is defined as

$$\ln\left(\frac{1-x_{32}}{x_{32}}\right) = M_2 \ln\left(\frac{1-x_{21}}{x_{21}}\right) + W_2 \qquad (3)$$

W_i and M_i are the ith correlation coefficients, x_{cl} is the mass fraction, where the first index refers to components t-Butanol (1), Water (2) and Benzene (3) and the second index refers to the phases (1= water-rich phase, 2= solvent-rich phase).

Figures 1-3 show the consistency plots of the Bachman-Brown's, Hand's and Othmer-Tobias' correlations respectively. Table 4 shows that the Bachman-Brown's model has the highest R-squared value and the experimental tie-line data may be taken to be thermodynamically consistent and reliable.

Table 4: Correlation Factors and Coefficients for the Hand, Othmer-Tobias and Bachman-Brown Equations for the System

Model Type	**M**	**W**	R^2
Hands	0.3549	-1.4052	0.994
Othmer-Tobias	2.8431	4.1227	0.994
Bachman-Brown	0.9965	0.1155	0.997

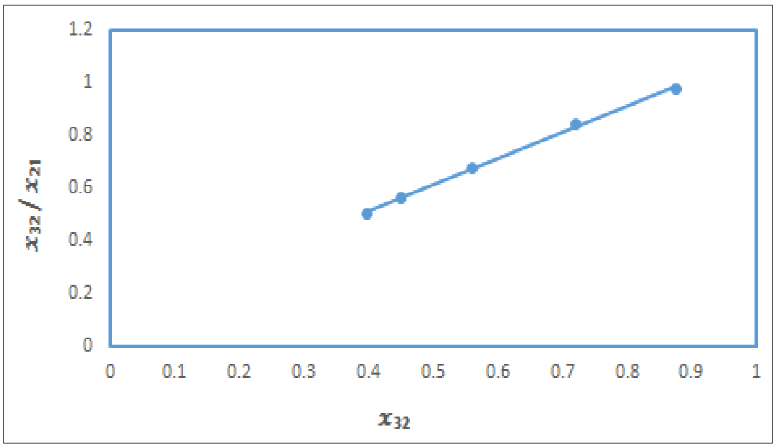

Fig. 1: Bachman-Brown's consistency plot for the t-Butanol –Water – Benzene System at 30°C

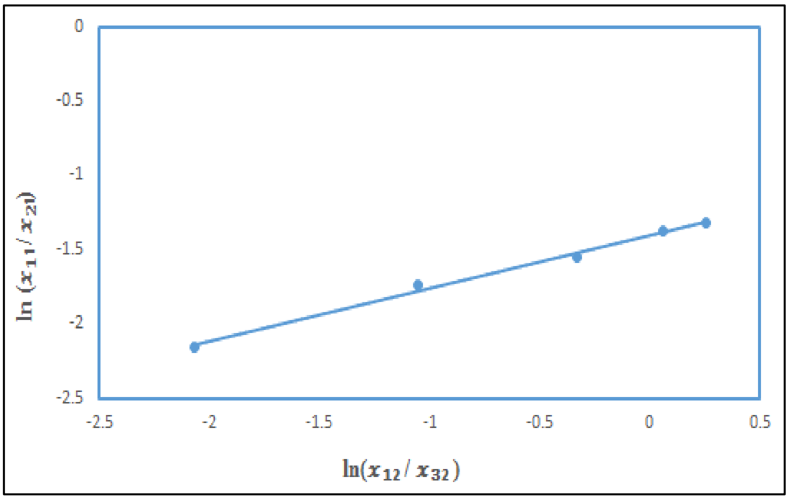

Fig. 2: Hand's consistency plot for the t-Butanol –Water – Benzene System at 30°C

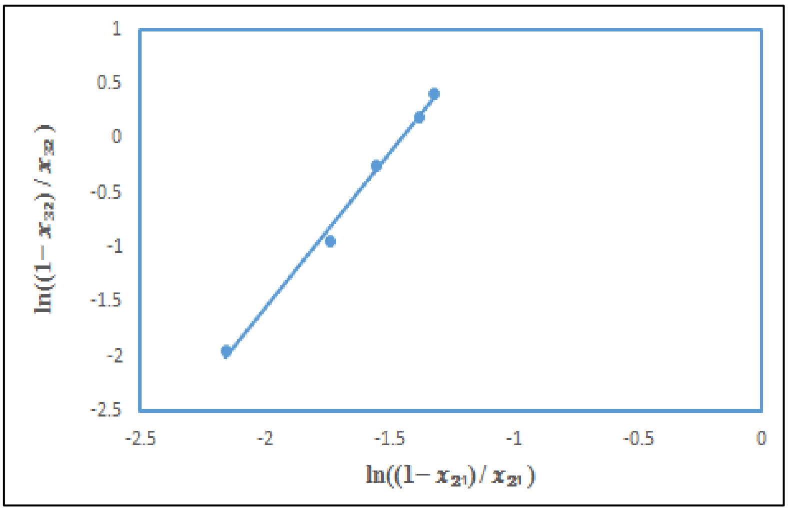

Fig. 3: Othmer-Tobias' consistency plot for the t-Butanol –Water – Benzene System at 30°C

3.3 Distribution Coefficient and Separation Factor

The distribution coefficient which is the measure of the difference in solubility between the two phases in equilibrium is given by

$$D_a = \frac{x_{a2}}{x_{a1}} \qquad (4)$$

Where D_a is the distribution coefficient for component a, x_{a1} is the mass fraction of component a in water-rich phase, x_{a2} is the mass fraction of component a in the solvent-rich phase.

The effectiveness of extraction of t-butanol by benzene in the t-butanol + water mixture is determined by the separation factors, which also show the ability of the solvent in the recovery process (Stoicescu *et al.*, 2011) . It is given as

$$S = \frac{D_1}{D_2} \qquad (5)$$

Benzene has the ability as a solvent to extract t-Butyl Alcohol from Water as shown by the high separation factors in table 5 which varied between 21.4704 and 71.2267, being most potent at low concentration of t-Butanol (figure 5). Figure 4 shows that the distribution coefficient of t-Butanol in the water-rich phase tends to increase with increasing concentration of t-Butanol in water.

Table 5: Distribution Coefficients of t-Butanol (D_1), Water (D_2) and Separation Factors (S) for t-Butanol – Water – Benzene System at 30°C and 1 atm

s/n	D_1 $(\frac{x_{12}}{x_{11}})$	D_2 $(\frac{x_{22}}{x_{21}})$	S $(\frac{D_1}{D_2})$
1	1.0684	0.015	71.2267
2	1.6812	0.034	49.4471
3	2.3005	0.043	53.5000
4	2.3713	0.0906	26.1732
5	2.4326	0.1133	21.4704

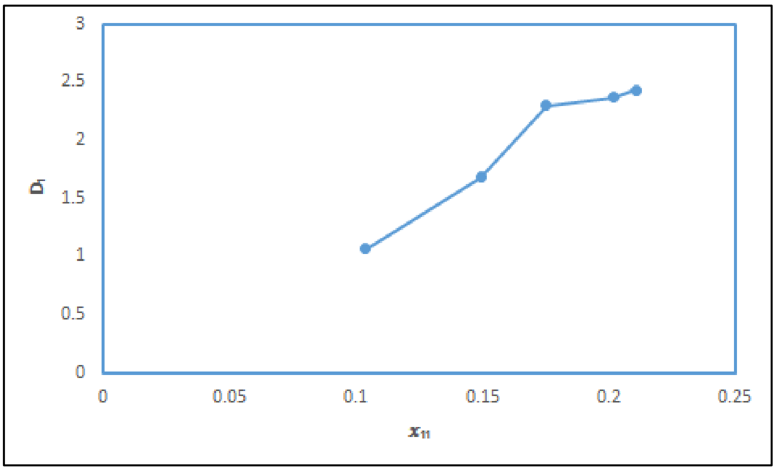

Fig. 4: Distribution coefficient plot of t-Butanol (D_1) and mass fraction of t-Butanol in the water-rich phase (x_{11})

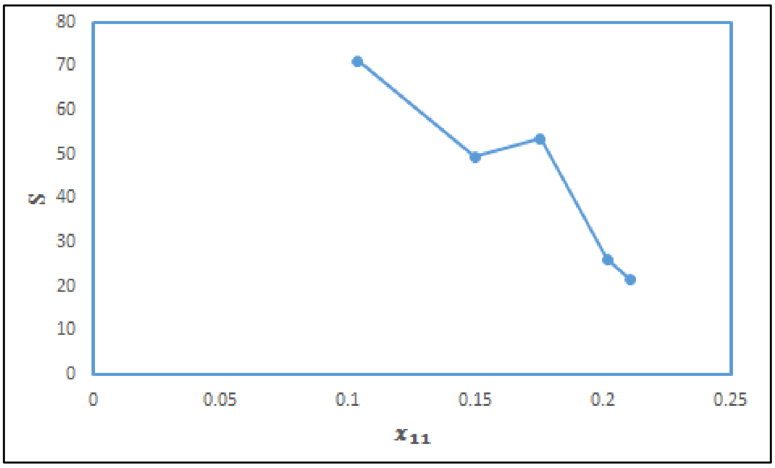

Fig. 5: Plot of separation factor (S) and mass fraction of t-Butanol in the water-rich phase (x_{11})

The method by Treybal *et al.*, (1946) with the Hand's coordinates has been used to estimate the plate point for the t-butanol-water-benzene system at 30°C and 1 atm; the point of intersection of the tie-line data and the solubility curve is the plate point as shown in figure 6. The plait point compositions in mass fractions are t-Butanol = 0.3662, water = 0.6037, benzene = 0.0301.

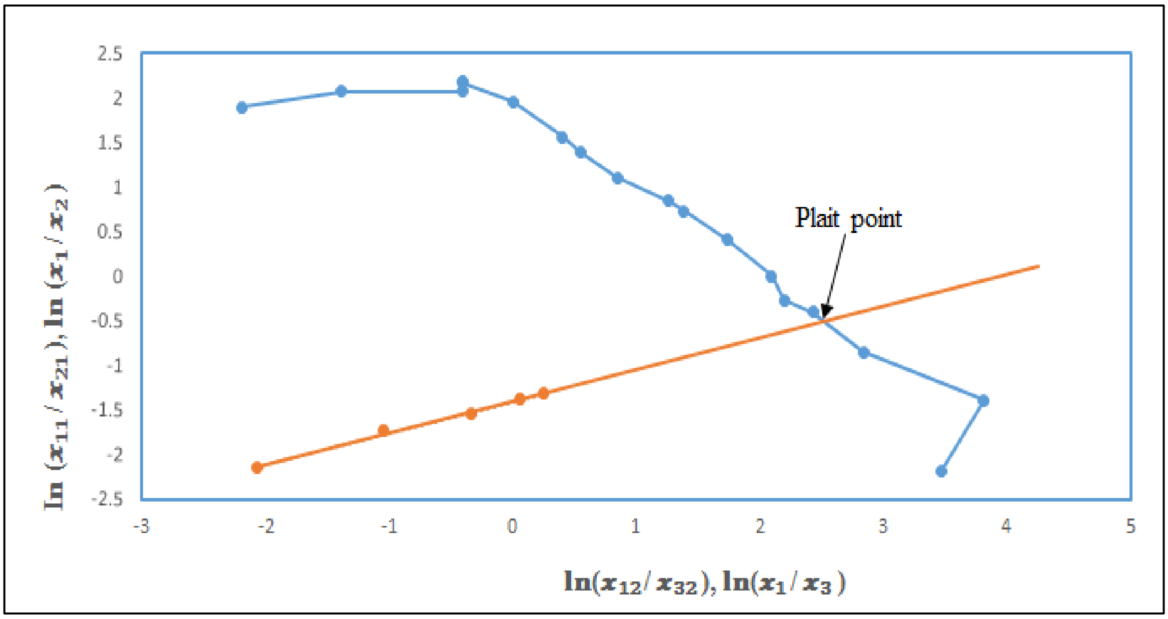

Fig. 6: Plait point estimation plot for t-butanol-water-benzene system at 30°C; Tie-line data (●), Binodal curve (●)

3.4 LLE Model Correlation

At Liquid-Liquid equilibrium, the fugacities of the component *i* in both phases are equal and the mass fractions x_i^E , x_i^R of the phases (extract phase and raffinate phase respectively) were determined by combining equations (6) and (7):

$$(\gamma_i x_i)^E = (\gamma_i x_i)^R \qquad (6)$$

$$\sum x_i^E = \sum x_i^R = 1 \qquad (7)$$

Where γ_i^E and γ_i^R are the corresponding activity coefficients of component *i* in extract phase and raffinate phase respectively.

The universal quasi-chemical equation (UNIQUAC) of Abrams and Prausnitz (Abrams & Prausnitz, 1975) and the non-random two liquid equation (NRTL) of Renon and Prausnitz (Renon & Prausnitz, 1968) were used in correlating the experimental tie-line compositions. The UNIQUAC structural parameters q and r in table 6 were chosen from literature while the binary interaction parameters for the UNIQUAC and NRTL models shown in tables 7 and 8 respectively were obtained by data regression using Aspen plus V8.6. The regression was implemented using the Britt- Luecke (Britt & Luecke, 1973) algorithm. The binary parameters were calculated by minimization of deviations between experimental data and models calculated values. The maximum likelihood objective function was used and new sets of parameters were determined iteratively until the evaluated objective function was smaller than the prescribed tolerance.

The predicted tie-line compositions for both UNIQUAC and NRTL models obtained from the flash calculations performed using Aspen plus version 8.6 simulator are presented in table 9, but the UNIQUAC and NRTL equations used are shown in Appendix A.

Table 6: UNIQUAC Structural Parameters for t-Butanol, Water and Benzene

	q	**r**
t-Butanol	3.0480	3.4528
Water	1.4000	0.9200
Benzene	2.4000	3.1905

Table 7: UNIQUAC binary interaction parameters for t-butanol-water-benzene system at 30°C and 1 atm

	b_{ij}		
	t-Butanol	**Water**	**Benzene**
t-Butanol	---	-76.9627	-265.1
Water	-53.4074	---	-357.308
Benzene	95.86205	-629.112	---

Table 8: NRTL binary interaction parameters for t-Butanol-Water-Benzene system at 30°C and 1 atm

		t-Butanol	Water	Benzene
a_{ij}	t-Butanol	---	7.189096	-1.96345
	Water	-0.61884	---	-2.2957
	Benzene	-0.32717	8.845502	---
b_{ij}	t-Butanol	---	-1441.51	1076.101
	Water	236.293	---	1551.991
	Benzene	128.6074	-1186.75	---
c_{ij}	t-Butanol	---	---	---
	Water	0.298234	---	---
	Benzene	0.369842	0.294215	---

Table 9: Experimental and Predicted tie-line compositions for t-Butanol (1) – Water (2) – Benzene (3) system at 30°C and 1 atm in Mass Fraction

Water Rich Phase									Solvent Rich Phase								
x_{11}^{exp}	x_{11}^{UNIQ}	x_{11}^{NRTL}	x_{21}^{exp}	x_{21}^{UNIQ}	x_{21}^{NRTL}	x_{31}^{exp}	x_{31}^{UNIQ}	x_{31}^{NRTL}	x_{11}^{exp}	x_{11}^{UNIQ}	x_{11}^{NRTL}	x_{21}^{exp}	x_{21}^{UNIQ}	x_{21}^{NRTL}	x_{31}^{exp}	x_{31}^{UNIQ}	x_{31}^{NRTL}
0.1038	0.1061	0.1111	0.8962	0.8924	0.8733	0.0000	0.0015	0.0156	0.1109	0.1103	0.1090	0.0134	0.0134	0.0131	0.8757	0.8763	0.8779
0.1496	0.1542	0.1632	0.8504	0.8434	0.8176	0.0000	0.0024	0.0192	0.2515	0.2505	0.2486	0.0289	0.0282	0.029	0.7196	0.7213	0.7224
0.1754	0.1834	0.1943	0.8246	0.8134	0.7846	0.0000	0.0032	0.0211	0.4035	0.3967	0.3954	0.0354	0.0545	0.0559	0.5611	0.5488	0.5487
0.2017	0.2020	0.2156	0.7983	0.7943	0.7624	0.0000	0.0037	0.0220	0.4783	0.4768	0.4767	0.0723	0.0774	0.0762	0.4494	0.4458	0.4471
0.2106	0.2121	0.2274	0.7894	0.7839	0.7501	0.0000	0.0040	0.0225	0.5123	0.5120	0.5133	0.0894	0.0908	0.0871	0.3983	0.3972	0.3996

Figure 7 compares the experimental and predicted (UNIQUAC & NRTL) binodal tie lines. The UNIQUAC gave a better result in terms of the recovery of t-Butanol in solvent than the NRTL with an average deviation of 0.60% of t-Butanol data in the solvent compared with the experimental. On the other hand, the NRTL gave an average deviation of 1.01%. The root mean square deviation (RMSD) between the experimental and predicted data is 0.0057 and 0.0181 for UNIQUAC and NRTL predicted, respectively.

The root-mean-square deviation (RMSD) can be taken as a measure of precision of the LLE correlations (Ghanadzadeh *et al.*, 2008). It is given by

$$RMSD\% = 100\sqrt{\frac{\sum_{k=1}^{n}\sum_{j=1}^{2}\sum_{i=1}^{3}(x_{ijk}^{exp} - x_{ijk}^{cal})^2}{6n}} \qquad (8)$$

Where n is the number of tie-lines, x^{exp} indicates the experimental mass fraction, x^{cal} is the calculated mass fraction, and the subscript i indexes components, j indexes phases and k = 1, 2, . . . , n (tie-lines).

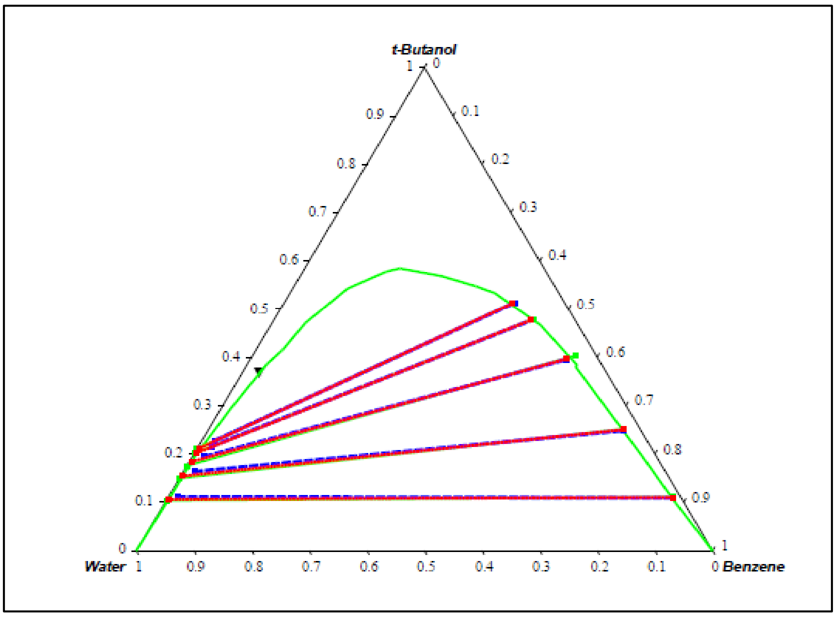

Figure 7: Estimated plait point (▲), experimentally obtained (—— green), UNIQUAC Predicted (…. red) and NRTL predicted (----blue) tie lines of the Liquid-Liquid Equilibria of t-Butanol – Water – Benzene System at 30°C and 1 atm

The predicted values by UNIQUAC model gave a closer resemblance to the experimental values as confirmed by the lower RMSD. However, both UNIQUAC and NRTL equations tend to describe the behaviour of the ternary system fairly well.

4. CONCLUSION

The liquid-liquid equilibria of t-Butanol-Water-Benzene were measured experimentally at 30°C and 1 atm pressure, and correlated with the universal-quasi chemical (UNIQUAC) and non-random two liquid (NRTL) activity coefficient equations, and the binary interaction parameters were regressed using Aspen plus version 8.6. The experimental tie-lines data were determined with Agilent 7820A series gas chromatography. The effectiveness of recovery by the solvent was determined by the separation factors. The thermodynamic consistency of the experimental data was tested by the Hand's, Othmer-Tobias' and Bachman-Brown correlation equations. A comparison of the predicted tie-lines with the experimental gave a root-mean-square deviation (RMSD) of about 0.0057 for UNIQUAC- predicted and 0.0181 for NRTL-predicted. The predicted values by UNIQUAC model gave a closer resemblance to the experimental values. However, both UNIQUAC and NRTL equations tend to describe the behaviour of the ternary system fairly well.

APPENDICES

Appendix A

The universal quasi-chemical (UNIQUAC) equation for the liquid phase activity coefficient is given as:

$$\ln \gamma_i = In\left(\frac{\Phi_i}{x_i}\right) + 0.5zq_i In\left(\frac{\theta_i}{\Phi_i}\right) + l_i - \frac{\Phi_i}{x_i}\sum_{j=1}^{c} x_j l_j + q_i\left[1 - In\left(\sum_{j=1}^{c}\theta_j\tau_{ji}\right) - \sum_{j=1}^{c}\frac{\theta_j\tau_{ij}}{\sum_{k=1}^{c}\theta_k\tau_{kj}}\right] \tag{A1}$$

Where;

Segment fraction, $\Phi_i = \frac{x_i r_i}{\sum_{i=1}^{c} x_i r_i}$ (A2)

Area fraction, $\theta_i = \frac{x_i q_i}{\sum_{i=1}^{c} x_i q_i}$ (A3)

$$\tau_{ij} = \exp\left(a_{ij} + {}^{b_{ij}}/_{T} + c_{ij}\ln T + d_{ij}T + {}^{e_{ij}}/_{T^2}\right) \equiv \exp\left[\frac{b_{ij}}{T}\right] \tag{A4}$$

$$l_j = 0.5z(r_j - q_j) - (r_j - 1) \tag{A5}$$

r and q are known as the UNIQUAC structural parameters, τ_{ij},τ_{ik} and τ_{jk} are the adjustable parameters in the UNIQUAC equation for the binary systems. z is the coordination number usually set equal to 10. b_{ij} and b_{ji} are the UNIQUAC binary interaction parameters.

The non-random two liquid (NRTL) equation is an activity coefficient-based equation is given as:

$$\ln \gamma_i = \frac{\sum_j x_j\tau_{ji}G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}}\left[\tau_{ij} - \frac{\sum_m x_m\tau_{mj}G_{mj}}{\sum_k x_k G_{kj}}\right] \tag{A6}$$

Where, $G_{ij} = \exp(-\propto_{ij}\tau_{ij})$ (A7)

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} + e_{ij}\ln T + f_{ij}T \tag{A8}$$

$$\propto_{ij} = \propto_{ji} \equiv c_{ij} \tag{A9}$$

γ_i is the activity coefficient of component i, x_j – mass fraction of component j, T – Temperature (K), $\propto_{ij}$ – Non-random constants of the NRTL equation. The binary interactions a_{ij}, b_{ij}, eij, and f_{ij} are unsymmetrical, that is, a_{ij} may not be equal to a_{ji}.

AUTHOR CONTRIBUTIONS

The manuscript was written through contributions of all authors.

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ABBREVIATIONS

GC, gas chromatography; NRTL, non-random two liquids; UNIQUAC, universal quasi-chemical; FID, flame ionization detector; RMSD, root mean square deviation; LLE, liquid-liquid equilibrium; R², coefficient of determination.

Nomenclature and Units

D	Distribution coefficient	—
S	Separation factor	—
x	Mass fraction	—
C	Concentration	g/mol
V	Volume	mL
γ	Activity coefficient	—
q	Relative surface area per molecule	—
r	Relative molecular volume	—
τ_{ij},τ_{ik} , τ_{jk}	Adjustable parameters in the UNIQUAC equation for the binary systems	—
z	Coordination number	—
a_{ij}	UNIQUAC binary interaction parameters	Kelvin
θ_i	Area fraction	—
Φ_i	Segment fraction	—
$\propto_{ij}$	Non-random constants of NRTL model	—
M_1, N_1	Hand correlation constants	—
M_2, N_2	Othmer-Tobias correlation constants	—
M_3, N_3	Bachman-Brown correlation constants	—
LLE	Liquid-Liquid Equilibria	—

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