

# Liquid-Liquid Equilibrium Data for Butan-2-ol - Ethanol - Water, Pentan-1-ol - Ethanol - Water and Toluene - Acetone - Water Systems

Tinuade Jolaade Afolabi, and Theresa Ibibia Edewor

**Abstract**—Experimental liquid-liquid equilibria of butan-2-ol - ethanol - water; pentan-1-ol - ethanol - water and toluene - acetone - water ternary systems were investigated at (25°C). The reliability of the experimental tie-line data was ascertained by using Othmer-Tobias and Hand plots. The distribution coefficients (D) and separation factors (S) of the immiscibility region were evaluated for the three systems.

**Keywords**—Distribution coefficient, Liquid-liquid equilibrium, separation factors, thermodynamic models

## I. INTRODUCTION

**L** IQUID-liquid extraction (LLE) is a method used in the recovery of key component from multicomponent streams using an immiscible solvent [1]–[5]. The two streams are contacted and separated. There are certain situations where LLE is favorable compared to other methods of separation, for example, in streams where components have similar relative volatilities or in cases where vacuum distillation may be required. In such cases, LLE is often more cost effective than distillation [6].

Recent research has been done to determine the ability to recover light alcohols from dilute aqueous solution using high molecular weight solvent extraction [7]–[9]. A complete phase diagram was obtained by determining solubility and tie line data when experimental LLE of water - acetic acid - butyl acetate system were studied at (298.15, 303.15 and 308.15) K [7]. Kirbasalar et al [9] also ascertained the reliability of the experimental tie line data using Othmer-Tobias and Hand plots for water - ethanol - 1-nonanol and water - ethanol - 1-decanol systems. Many researchers have described the use of liquid-liquid extraction to selectively remove ethanol from water [10]–[12]. The equilibrium condition between the organic and aqueous phases was found to be a very important aspect of the liquid-liquid extraction process and the variables most generally considered for the process are: (a) physical properties (density difference between liquid phases and boiling point), (b) chemical properties (distribution coefficient, selectivity and flammability) availability and cost [13]–[15].

Ternary liquid-liquid equilibria are usually determined by either the method of analysis or the method of titration. The method of analysis consists simply of letting a ternary

mixture separate into two liquid phases and determining the compositions of the two phases in equilibrium by analyzing for two components. In the method of titration the binodal curve is first established using the cloud point method. Once the binodal curve is known, the concentration of only one of the components in each phase is sufficient information to determine a tie line [16].

The availability of relevant liquid-liquid equilibrium data is necessary for both the design and the simulation of extraction processes. This work, therefore investigated the use of liquid-liquid extraction to selectively remove ethanol by water for butan-2-ol - ethanol - water and pentan-1-ol - ethanol - water systems and acetone for toluene - acetone - water system at (25°C) and their suitability for future use reported.

## II. EXPERIMENTAL SECTION

### A. Materials

Analytical grade ethanol, butan-2-ol, pentan-1-ol, acetone and toluene (purities > 99.5%) were purchased and used without further purification. Refractive indexes were measured with an Abbe refractometer (model M.46) by Hilger and Watts limited, London. It was fitted with thermo-prism surrounded by water jackets and the prism surfaces were cleaned with acetone before and after every measurement.

The temperature of the prism was controlled within  $\pm 0.002^\circ\text{C}$  by the circulation of cooling water in a controlled environment. The instrument has a scale ranging from 1.300 to 1.700 with each scale division being equal to 0.001.

### B. Procedure

The binodal curves for the butan-2-ol - ethanol - water; pentan-1-ol - ethanol - water and toluene - acetone - water systems were determined by the cloud-point method. The saturation points of the immiscible pairs; Butan-2-ol (j) - Water (s), Pentan-1-ol (j) - Water(s), Toluene (j) - Water (s) were determined by adding small drops of component j to 20 ml of component s and vice-versa until another phase is formed. The refractive index values were measured and the compositions calculated. Samples of the heterogeneous systems of component j and s were prepared at different compositions between the saturation points and titrated with the solute, i (ethanol or acetone) to turbidity. Also, the refractive index was measured and the composition calculated using eq. 1. The calculated composition was plotted on a triangular graph as the binodal or solubility curve. Also, the compositions

T. J. Afolabi is with the Department of Chemical Engineering, Ladoké Akintola University of Technology, Ogbomosho, Nigeria (e-mail: tjafolabi@lautech.edu.ng; phone no. 234-36669764)

T. I. Edewor is with Chemistry Department, Ladoké Akintola University of Technology, Ogbomosho, Nigeria (e-mail: ibitheresa@yahoo.com)

TABLE I  
BINODAL CURVE DATA AS MASS FRACTION OF BUTAN-2-OL (1) -  
ETHANOL (2) -WATER (3) SYSTEM AND THE CORRESPONDING  
REFRACTIVE INDEX VALUES

$w_1$	$w_2$	$w_3$	Refractive index
0.000	0.000	1.000	1.331
0.163	0.000	0.837	1.348
0.189	0.030	0.781	1.350
0.236	0.032	0.731	1.354
0.313	0.041	0.646	1.360
0.378	0.041	0.582	1.364
0.430	0.038	0.532	1.368
0.484	0.036	0.480	1.370
0.558	0.028	0.414	1.374
0.606	0.019	0.375	1.378
0.658	0.000	0.342	1.380
1.000	0.000	0.000	1.397

TABLE II  
BINODAL CURVE DATA AS MASS FRACTION OF PENTAN-2-OL (1) -  
ETHANOL (2) -WATER (3) SYSTEM AND THE CORRESPONDING  
REFRACTIVE INDEX VALUES

$W_1$	$W_2$	$W_3$	Refractive index
0.000	0.000	1.000	1.331
0.000	0.020	0.980	1.333
0.210	0.073	0.717	1.350
0.224	0.132	0.644	1.355
0.235	0.222	0.543	1.359
0.239	0.289	0.472	1.366
0.249	0.338	0.413	1.370
0.227	0.403	0.370	1.373
0.236	0.474	0.290	1.377
0.210	0.607	0.183	1.383
0.170	0.720	0.110	1.389
0.000	0.901	0.099	1.396
1.000	0.000	0.000	1.401

of component j and s were plotted against the refractive index values on a rectangular graph. This was used to determine the composition of the tie lines.

$$x_i = \frac{v_i \rho_i}{\sum_i v_i \rho_i} \quad (1)$$

where:  $x_i$  mass fraction of component i  $v_i$  Volume of component i  $\rho_i$  Density of component i  $M_i$  Molecular weight of component i

The procedure was repeated for the other two ternary systems: water (s) - pentan-1-ol (j) - ethanol (i) and water (s) - toluene (j) - acetone (i) and the measurement is as shown in Tables I, II and III.

Tie lines data were obtained by preparing ternary mixtures of known overall composition lying within the two-phase region. Samples were shaken vigorously and left for 24 h to settle and attain equilibrium state under isothermal conditions. The refractive index values of resulting two phases after attainment of equilibrium were measured using the refractometer. This procedure was repeated for the three ternary systems. The composition of each phase was determined from plots of refractive index with composition for the three ternary systems extracted from Tables I, II and III.

### III. RESULTS AND DISCUSSION

The experimental data on the phase equilibria of butan-2-ol - ethanol - water; pentan-1-ol - ethanol - water and toluene

TABLE III  
BINODAL CURVE DATA AS MASS FRACTION OF TOLUENE (1) -  
ACETONEL (2) -WATER (3) SYSTEM AND THE CORRESPONDING  
REFRACTIVE INDEX VALUES

$w_1$	$w_2$	$w_3$	Refractive index
0.000	0.000	1.000	1.331
0.592	0.060	0.347	1.367
0.622	0.097	0.281	1.372
0.641	0.123	0.236	1.376
0.646	0.145	0.209	1.378
0.652	0.163	0.185	1.379
0.669	0.172	0.159	1.381
0.662	0.200	0.138	1.384
0.658	0.233	0.109	1.389
0.288	0.645	0.067	1.391
0.000	1.000	0.000	1.493

- acetone - water ternary system at (25°C) are summarized in Tables I, II and III while the corresponding experimental binodal/ solubility curves are given in Figures 1, 2 and 3.

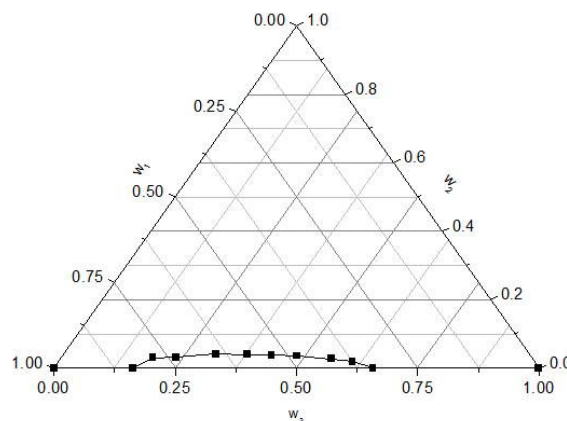


Fig. 1. Binodal curve for Butan-2-ol (1) - Ethanol (2) - Water (3) System at (25°C)

The phase behaviour of the three systems can be attributed to type I [2]. This type is characterized by the total miscibility between two pairs and partial miscibility in the third pair as shown in the Figures. For example, in butan-2-ol - ethanol - water system, the liquid pairs, ethanol - butn-2-ol and ethanol - water are miscible while butan-2-ol - water pair dissolves to a limited extent. Addition of the solute, ethanol to the mixture tends to make butan-2-ol and water more soluble until the plait point is reached where the two phase become one.

Butan-2-ol - ethanol - water system has the smallest area of heterogeneity (the area bounded by the curve) while toluene - acetone - water system has the largest area of heterogeneity. This may be attributed to the difference in the degree of miscibility of the two base solvents since butan-2-ol - water has the highest degree of miscibility and toluene - water the least degree of miscibility out of the three base pairs. In other words, less solute will be needed to form homogeneous

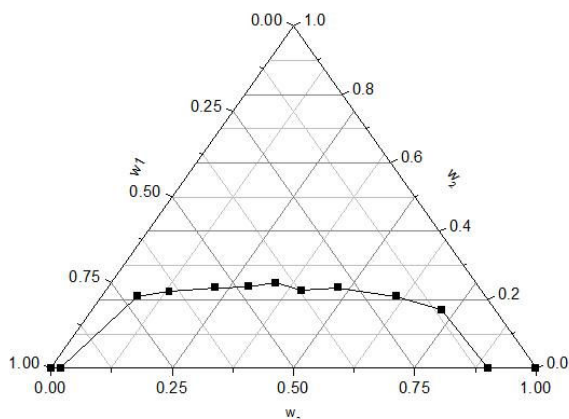


Fig. 2. Binodal curve for Butan-2-ol (1) - Ethanol (2) - Water (3) System at (25°C)

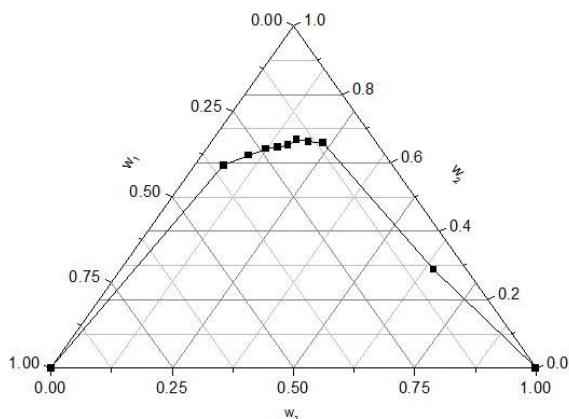


Fig. 3. Binodal curve for Butan-2-ol (1) - Ethanol (2) - Water (3) System at (25 °C)

ternary mixture for butan-2-ol - ethanol - water mixture while more acetone (solute) will be needed for toluene - acetone - water mixture since toluene is totally immiscible with water [2]. Also, this differences in area of heterogeneity among the three systems may be attributed to other factors especially physical properties of the system components. For example, the differences in interfacial tension and density of the solute and its carrier [6].

The tie lines data of the three ternaries are given in Tables IV, V and VI respectively.

Distribution coefficients,  $D_i$ , for butan-2-ol ( $i=1$ ) and ethanol ( $i=2$ ) and separation factors,  $S$ , were determined as

TABLE IV  
TIE LINES DATA AS MASS FRACTION OF THE BUTAN-2-OL (1) - ETHANOL (2) - WATER (3) SYSTEM

(Extract) Water layer			(Raffinate) Butan-2-ol layer		
$w_1$	$w_2$	$w_3$	$w_1$	$w_2$	$w_3$
0.165	0.035	0.800	0.362	0.035	0.604
0.189	0.037	0.774	0.396	0.037	0.567
0.202	0.038	0.760	0.413	0.038	0.550
0.215	0.038	0.747	0.421	0.038	0.541
0.254	0.040	0.706	0.479	0.040	0.481

TABLE V  
TIE LINES DATA AS MASS FRACTION OF THE PENTAN-1-OL (1) - ETHANOL (2) - WATER (3) SYSTEM

(Extract) Water layer			(Raffinate) Pentan-1-ol layer		
$w_1$	$w_2$	$w_3$	$w_1$	$w_2$	$w_3$
0.012	0.097	0.890	0.828	0.096	0.077
0.059	0.181	0.759	0.557	0.212	0.231
0.027	0.132	0.840	0.755	0.131	0.114
0.052	0.172	0.775	0.599	0.197	0.204
0.012	0.097	0.890	0.853	0.083	0.064
0.027	0.132	0.841	0.686	0.162	0.152

TABLE VI  
TIE LINES DATA AS MASS FRACTION OF THE TOLUENE (1) + ACETONE (2) + WATER (3) SYSTEM

(Extract) Water layer			(Raffinate) Toluene layer		
$w_1$	$w_2$	$w_3$	$w_1$	$w_2$	$w_3$
0.010	0.060	0.930	0.948	0.048	0.004
0.017	0.148	0.835	0.861	0.128	0.011
0.013	0.128	0.859	0.885	0.105	0.010
0.021	0.184	0.795	0.795	0.189	0.016
0.038	0.310	0.652	0.657	0.315	0.028
0.028	0.230	0.742	0.754	0.225	0.021
0.040	0.345	0.615	0.529	0.433	0.038
0.040	0.409	0.551	0.495	0.463	0.042
0.042	0.451	0.507	0.368	0.579	0.053
0.040	0.345	0.615	0.542	0.418	0.040

TABLE VII  
DISTRIBUTION COEFFICIENTS,  $D_i$  OF BUTAN-2-OL (1) - ETHANOL (2) AND SEPARATION FACTOR, WITH WATER (3) AS SOLVENT AT (25°C)

$D_1$	$D_2$	$S$
0.456	1.000	2.190
0.477	1.000	2.100
0.489	1.000	2.040
0.510	1.000	1.960
0.530	1.000	1.890

follows:

$$D_i = \frac{w_{i3}}{w_{i1}} \quad (2)$$

$$S = \frac{D_i}{D_j} \quad (3)$$

The distribution coefficients and separation factor for the three systems are given in Tables VII, VIII and IX.

#### A. Reliability of tie lines data

The reliability of experimentally measured tie lines data can be ascertained by applying the Othmer-Tobias and Hand correlation equations [7], [9]. The Othmer-Tobias and Hand correlation equations are given as eqs. 4 and 5, respectively.

TABLE VIII  
DISTRIBUTION COEFFICIENTS,  $D_i$  OF PENTAN-1-OL (1) - ETHANOL (2)  
AND SEPARATION FACTOR, WITH WATER (3) AS SOLVENT AT (25°C)

$D_1$	$D_2$	S
0.015	1.010	69.700
0.106	0.854	8.060
0.036	1.010	28.200
0.087	0.873	10.100
0.014	1.170	82.900
0.040	0.815	20.700

TABLE IX  
DISTRIBUTION COEFFICIENTS,  $D_i$  OF TOLUENE (1) - ACETONE (2) AND  
SEPARATION FACTOR, WITH WATER (3) AS SOLVENT AT (25°C)

$D_1$	$D_2$	S
0.011	1.250	119.000
0.020	1.160	58.700
0.015	1.220	82.900
0.026	0.974	36.900
0.058	0.984	17.000
0.037	1.020	27.600
0.076	0.797	10.500
0.081	0.883	10.900
0.114	0.779	6.830
0.074	0.825	11.200

$$\ln\left(\frac{1-w_3^b}{w_3^t}\right) = a_1 + b_1 \ln\left(\frac{1-w_1^t}{w_1^b}\right) \quad (4)$$

$$\ln\left(\frac{w_2^b}{w_3^b}\right) = a_1 + b_1 \ln\left(\frac{w_2^t}{w_1^t}\right) \quad (5)$$

where  $w_{ij}$  is the mass fraction of component i (1=organic solvent, 2 = ethanol, 3 = water) in the j (b=bottom, t = top) phases. The plot of Othmer-Tobias correlation of  $\ln\left(\frac{1-w_3^b}{w_3^t}\right)$  vs.  $\ln\left(\frac{1-w_1^t}{w_1^b}\right)$  was used to determine a and b coefficients. Similarly, the plot of the Hand correlation of  $\ln\left(\frac{w_2^b}{w_3^b}\right)$  vs.  $\ln\left(\frac{w_2^t}{w_1^t}\right)$  was used to determine a and b coefficients. (See Table X)

On the basis of the standard deviations,  $\delta_1$  and  $\delta_2$ , given in Table X, it can be concluded that eqs 4 and 5 can be satisfactorily used to correlate the tie lines data of the three systems studied.

$$\delta_i = \sqrt{\frac{\sum_{j=1}^N (w_{ji}^{cal} - w_{ji}^{expl})^2}{N}} \quad (6)$$

where:  $N$  is the number of tie lines and  $j = 1$  and 2.  $\delta_1$  and  $\delta_2$  represents the mass fraction standard deviation of water in the extract phase and solvent in the raffinate phase respectively.

TABLE X  
THE COEFFICIENT OF OTHMER-TOBIAS AND HAND EQUATIONS  
OBTAINED USING LEAST SQUARE METHOD

System	Butan-2-ol - Ethanol - Water				Pentan-1-ol - Ethanol - Water				Toluene - Acetone - Water			
	a	b	$\delta_1$	$\delta_2$	a	b	$\delta_1$	$\delta_2$	a	b	$\delta_1$	$\delta_2$
Othmer-Tobias	- 0.77	-1.07	0.001	0.001	-1.03	0.64	0.007	0.017	-0.30	0.75	0.003	0.004
Hand	- 7.04	-1.69	0.004	0.002	-0.88	0.59	0.034	0.055	-0.34	0.76	0.008	0.010

#### IV. CONCLUSION

The binodal and tie line data of the three systems, butan-2-ol - ethanol - water; pentan-1-ol - ethanol - water and toluene - acetone - water systems were determined at (25°C). It was found that the tie line data of these systems could be satisfactorily described by the Othmer-Tobias and Hand correlation equations.

#### REFERENCES

- [1] W. L. Badger and J. T. Banchero, *Introduction to Chemical Engineering* Tata McGraw Hill Publishing Ltd. Delhi, 2000.
- [2] R. H. Perry and C. H. Chilton, *Perry's Chemical Engineering Handbook*, 7th ed. McGraw Hill Book Company, Australia, 1998.
- [3] P. J. Bailes, *Liquid-liquid Extraction Test System* Chemical Engineering Research Development, 1983, 61, 321.
- [4] R. E. Treybal, *Mass-Transfer Operations*; 3rd Edition;. McGraw Hill Book Company: New York, 1986
- [5] R. E. Kirk and D. F. Othmer, *Kirk-Othmer Encyclopedia of Chemical Technology*; 4th Edition Volume 1 and 8; Wiley-Interscience Publications, New York, 1992.
- [6] H. R. Null, *Phase Equilibrium in Process Design*; . Wiley Interscience Publications: New York, 1970
- [7] E. Ince and S. L. Kirbaslar, Liquid-liquid Equilibria of the Water-Acetic acid-Butyl acetate System. *Braz. J. Chem. Eng.*, vol. 19, no. 2, pp.243-254, 2002.
- [8] S. I. Kirbaslar, S. Cehreli, S.; D. Ustun and E. Keskinocak, Water-Ethanol-1-Dodecanol Ternary System *Turk J Engin Environ Sci.*, vol. 25, pp. 111-115, 2001.
- [9] S. I. Kirbaslar, S. Cehreli, S.; D. Ustun and E. Keskinocak, Equilibrium data on ethanol-water-solvent ternaries. *Braz. J. Chem. Eng.*, vol. 17, pp. 191-197, 2000.
- [10] C. Sola, C. Casas, F. Godia, M. Poch and A. Serra, Continuous Ethanol Production by Immobilised Yeast Cells and Ethanol Recovery by Liquid-Liquid Extraction *Biotechnology and Bio-engineering Symp.*, vol. 17, pp. 519-523, 1986.
- [11] M. Miner and G. Goma, Evaluation of Solvents for the Recovery of Clostridium Fermentation Products by Liquid-Liquid Extraction *Biotechnology and Bio-engineering Symp.*, vol. 15, pp. 611, 1985.
- [12] A. M. Dadgar and G. L. Foutch, Liquid-Liquid Extraction *Biotechnology and Bio-engineering Symp.*, vol. 15, pp. 612620, 1985.
- [13] F. Kollerup and A. J. Daugulis, Screening and Identification of Extractive Fermentation Solvents Using a Database *Canada J. Chem. Eng.*, vol. 63, pp. 919927, 1985.
- [14] F. Kollerup and A. J. Daugulis, Ethanol Production by Extractive Fermentation Solvents Identification and Prototype Development. *Canada J. Chem. Eng.*, vol. 64, pp. 596-606, 1986.
- [15] D. S. Jassal, Z. Zhang and G. A. Hill, In-situ Extractive and Purification of Ethanol Using Oleic Acid *Canada J. Chem. Eng.*, vol. 72, pp. 822-826, 1994.
- [16] F. R. Bevia, D. P Rico and V. G. Yagues, Determination Of Quaternary Liquid-Liquid Equilibrium Data Using Either Measurements Of A Single Physical Property or the Analysis of Only One of The Components. Application to the Quaternary System: Water-Ethanol-Chloroform-Toluene at 25C *Fluid Phase Equilibria*, 23, 269-292, 1985