

# Solubility and Tie Line Data for Ternary System of (water + phenol + isobutyl acetate) at $T=308.2\text{ k}$

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**Abstract**— This study demonstrates experimental solubility and tie-line data for the (water + phenol + isobutyl acetate) system at  $T = 308.2\text{ K}$  and atmospheric pressure. This ternary system exhibits type-2 behavior of LLE. To evaluate the extracting capability of the solvent, distribution coefficients and separation factors were calculated. The consistency of the experimental data was determined through the Othmer–Tobias and Bachman equations. The experimental data were correlated using the NRTL and UNIQUAC models, and binary interaction parameters were obtained. The average root mean square deviation values between the experimental and calculated data show the capability of these models.

**Keywords**— Liquid–liquid equilibrium, NRTL, Phenol, ternary system

## I. INTRODUCTION

**L** IQUID–liquid equilibrium (LLE) data are needed for design and operation of extraction processes. The LLE studies of ternary systems have been the subject of much attention in recent years.

Phenols are similar to alcohols but form stronger hydrogen bonds. Thus, they are more soluble in water than are alcohols and have higher boiling points. Phenol (phenylic acid) is a white, poisonous, crystalline solid at room temperature that melts at  $41^\circ\text{C}$ . It is a widely used chemical in the manufacture of plastics or related materials, detergents, and drugs [1]–[3]. Also, it has many important applications for the production of phenolic resins in various industries. Phenol forms a binary azeotrope with water at 9.2 wt % of phenol, which is hard to separate by distillation. Moreover, the removal of phenol and phenolic compounds from wastewater has taken on great environmental interest over the last years [4], [5]. Therefore, recovery of phenolic compounds from aqueous solution using liquid–liquid extraction method is industrially and economically important [6].

Precise LLE data are needed in the evaluation of industrial units for solvent extraction processes. Some researchers have

been reported about solubility and equilibrium for the aqueous solutions of phenol with various organic solvents [7], [8]. Many solvents have been tested, and the phase equilibrium data of the related systems are presented in the literature. Mainly, alcohols, carbonate [9], alkyl carbonates [10], ketones [11], esters [12], [13], aliphatic, and aromatic hydrocarbons [14]–[16] have been used for extraction of phenol from water.

More LLE data for the ternary aqueous mixture of phenol with organic solvents recently have been reported by authors of this paper [17]. The organic solvents were 1-octanol, 2-ethyl-1-hexanol, and cyclohexanone. In this research, isobutyl acetate (IBA) was chosen as an organic solvent for recovery of phenol from water at  $T = 308.2, \text{ K}$  and the phase compositions were measured.

In order to evaluate the extracting ability of the solvent for the separation of phenol from water, distribution coefficients and separation factors were determined from the tie-line data. The experimental tie-line data were correlated to test consistency with the Othmer–Tobias [18] and Bachman [19] equations. The experimental LLE data were correlated with the non-random two-liquid (NRTL) [20] and UNIQUAC [21] models and the values of the interaction parameters were obtained.

## II. EXPERIMENTAL

### A. Materials

The phenol and isobutyl acetate with stated mass fraction purities higher than 0.99 were purchased from Chem-lab and Merck, respectively. Deionised water was used throughout all experiments. All materials were used as received without any further purification. Some measured physical properties for the chemicals used in this study along with the literature values are listed in Table 1.

### B. Apparatus and procedure

Refractive indices and densities of the pure liquids were measured at  $T = 298.2\text{ K}$  using an Abbe Refractometer (model CETI,  $\pm 0.0002$ ) and a DA210 density meter (Kyoto electronic,  $\pm 0.05\text{ kg.m}^{-3}$ ), respectively. All weighting was carried out with an electronic analytical balance (model HR-200,  $\pm 0.0001\text{ g}$ ).

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The solubility curves were determined by the cloud point method in an equilibrium glass cell. The temperature of the cell was controlled by a water jacket and maintained with a digital thermometer (Lutron TM-917, ±0.1 K). At each system, the third component was progressively added using a microburet. The end-points were determined by observing the turbidity. All the measurements were repeated at least three times. The average of these readings was taken for the component compositions. The uncertainty in the mass fraction of the solubility data was estimated to be better than ±0.0001. For the tie-line data measurements, a 250 cm<sup>3</sup> glass cell connected to a thermostat that controlled temperature was used. The equilibrium data were determined by preparing the ternary mixture of known compositions. This mixture was agitated vigorously for at least 4 h, and then left to settle for 5 h for complete phase separation. When the equilibrium was attained, samples of both phases were carefully analysed to determine their compositions.

TABLE I  
SOURCE, PURITY, REFRACTIVE INDEX (N), AND DENSITY (P) OF THE PURE COMPONENTS AT T = 298.2 K

component	n		ρ/(kg.m <sup>-3</sup> )	
	Exp.	Lit.	Exp.	Lit.
Phenol	1.5395 <sup>b</sup>	1.5395[7] <sup>b</sup>		1.3456 <sup>c</sup>
isobutyl acetate	1.3456	1.3456[20]	1.3456	1.3456[21] <sup>a</sup>
Water	1.3456	1.3456[19]	1.3456	1.3456[19]

<sup>a</sup> Measured at T = 293.15 K.

<sup>b</sup> Measured at T = 304.15 K.

<sup>c</sup> Provided by the supplier.

TABLE II  
EQUATIONS FOR REFRACTIVE INDEX (N) AS A FUNCTION OF PHENOL AND WATER MASS FRACTIONS (I.E. W<sub>2</sub> AND W<sub>1</sub>, RESPECTIVELY) IN THE ORGANIC AND AQUEOUS PHASES AT T = 308.2 K.<sup>A</sup>

	Equation	R <sup>2</sup>
<i>T = 308.2</i>		
phenol <sub>(org)</sub>	$n = 0.1490 w_2 + 1.3840$	0.9995
phenol <sub>(aq)</sub>	$n = 0.1662 w_2 + 1.3318$	0.9959
water <sub>(aq)</sub>	$n = 0.1989 w_1 + 1.5287$	0.9908

<sup>A</sup> Standard uncertainties u are u(T) = 0.1 K, u(n) = 0.0001, and u(w) = 0.0001

Details of the analysis have been previously reported in [22], [23]. In this paper, water content of the organic layer was measured by the Karl–Fisher method [24] using Metrohm-870 KF Titrino plus Karl–Fisher titrator. Concentration analyses of water and phenol were carried out for the aqueous phase using refractive index measurements. The refractive indices of the prepared standard samples lying on the binodal curves were measured used for building standard curves. Equations for refractive index (n) as a function of phenol mass fraction (w<sub>2</sub>) in both the phases, the mass fractions of water in the aqueous phase (w<sub>1</sub>) at T = 308.2 K are given in Table 2. The estimated uncertainty of all measured compositions is better than ±0.0001. The

uncertainty of the tie-line compositions were estimated according to the procedure suggested by Taylor and Kuyatt [25].

### III. RESULT AND DISCUSSION

#### A. Experimental LLE data

Equilibrium composition for the system (water + phenol + IBA) in the temperature of 308.2 K and atmospheric pressure is given in Table 3. The solubility curves for the investigated system is shown *T* = 308.2 in Figure 1.

TABLE III  
SOLUBILITY CURVE DATA IN MASS FRACTIONS (W<sub>2</sub>) FOR {WATER (1) + PHENOL (2) + IBA (3)} AT T = 308.2 K.<sup>a</sup>

w <sub>1</sub> (water)	w <sub>2</sub> (phenol)	w <sub>3</sub> (IBA)
0.0243	0.0000	0.9757
0.0275	0.0982	0.8743
0.0363	0.1946	0.7691
0.0439	0.2863	0.6698
0.0520	0.3787	0.5693
0.0606	0.4690	0.4704
0.0783	0.5496	0.3721
0.1058	0.6201	0.2741
0.1474	0.6812	0.1714
0.2061	0.7146	0.0793
0.3189	0.6811	0.0000
0.9873	0.0000	0.0127
0.9792	0.0157	0.0051
0.9658	0.0309	0.0033
0.9511	0.0469	0.0020
0.9380	0.0607	0.0013
0.9260	0.0735	0.0005
0.9079	0.0921	0.0000

<sup>a</sup> Standard uncertainties u are u(T) = 0.1 K and u(w) = 0.0001.

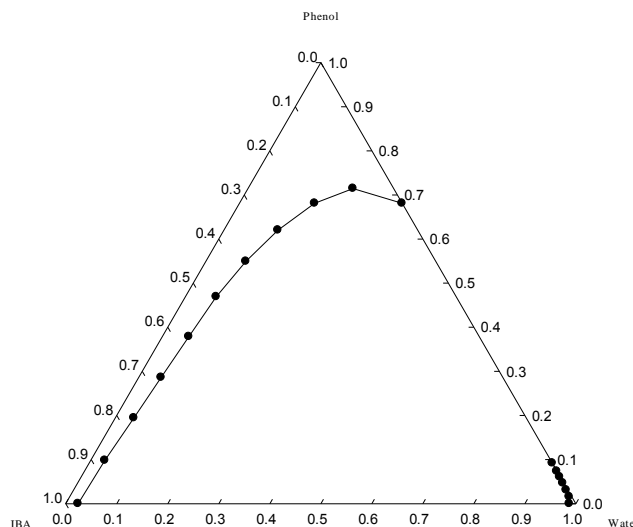


Fig.1. Solubility curve for the [water (1) + phenol (2) + IBA (3)] system at T = 308.2 K

The experimental tie-line data for the ternary system at T = 308.2 k are listed in Table 4. The LLE diagram is also shown in Figures 2. Since the (phenol + IBA) mixture is the only liquid pair that is completely miscible, this ternary system

behaves as type-2 LLE [26], and therefore, the phase diagrams show no plait points.

TABLE IV  
EXPERIMENTAL TIE-LINE DATA IN MASS FRACTIONS ( $w_2$ ) AND REFRACTIVE INDICES (n) FOR {WATER (1) + PHENOL (2) + IBA (3)} At  $T = 308.2$  K.<sup>a</sup>

Aqueous phase			
$w_1$ (water)	$w_2$ (phenol)	$w_3$ (solvent)	n
0.9884	0.0018	0.0098	1.3321
0.9834	0.0078	0.0088	1.3331
0.9774	0.0150	0.0076	1.3343
0.9698	0.0241	0.0061	1.3358
0.9633	0.0319	0.0048	1.3371
0.9588	0.0373	0.0039	1.3380
Organic phase			
$w_1$ (water)	$w_2$ (phenol)	$w_3$ (solvent)	n
0.0332	0.1966	0.7702	1.4133
0.0442	0.3174	0.6384	1.4313
0.0526	0.4040	0.5434	1.4442
0.0610	0.4664	0.4726	1.4535
0.0717	0.5141	0.4142	1.4606
0.0792	0.5510	0.3698	1.4661

<sup>a</sup> Standard uncertainties u are u(T) = 0.1 K, u(n) = 0.0001, and u(w) = 0.0001.

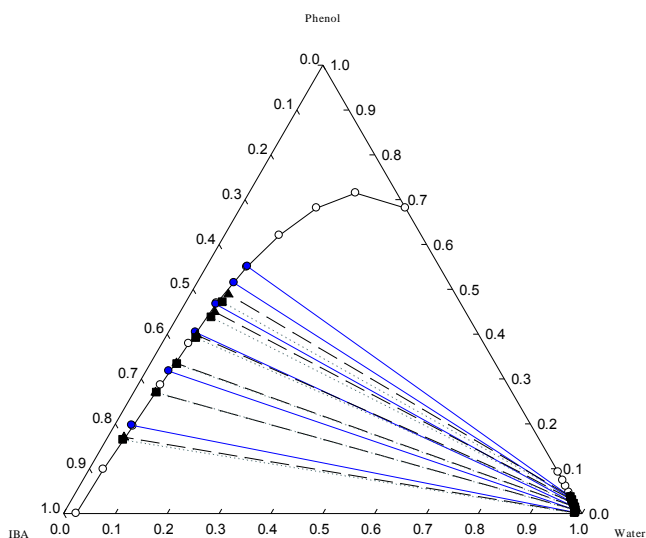


Fig. 2 Ternary diagram for the [water (1) + phenol (2) + IBA (3)] system at  $T = 308.2$  K; (○) experimental solubility curve, (●) experimental tie-line data, (---▲---) calculated NRTL data, (····■····) calculated UNIQUAC data.

**B. Distribution coefficient and separation factor**

In order to evaluate the extracting capability of IBA at each temperature for the separation of phenol from aqueous solutions, the separation factor ( $S$ ) was calculated. The separation factor is defined as the ratio of distribution coefficients of phenol ( $D_2$ ) to water ( $D_1$ )

$$S = \frac{w_{23}/w_{21}}{w_{13}/w_{11}} = \frac{D_2}{D_1}$$

where  $w_{13}$ , and  $w_{23}$  are the mass fractions of water and phenol in the organic phase, respectively.  $w_{11}$ , and  $w_{21}$  are the mass fractions of water and phenol in the aqueous phase, respectively] The distribution

coefficients and separation factors for  $T = 308.2$  k are given in Table 5.

TABLE V  
DISTRIBUTION COEFFICIENTS FOR WATER ( $D_1$ ) AND PHENOL ( $D_2$ ) AND SEPARATION FACTORS (S) At  $T = 308.2$  K.

$D_1$	$D_2$	S
0.0401	15.9640	398.1316
0.0469	15.3731	327.7927
0.0559	14.3093	256.0358
0.0710	12.4854	175.7463
0.0814	12.2559	150.5638
0.0904	11.9272	131.9472

The variation of experimental separation factor of phenol as a function of the mass fraction of the solute in aqueous phase ( $w_{21}$ ) is shown in Figure 3. For the investigated ternary system, the experimental results indicate that these solvent have high separation factor, thereby indicating the ability of the solvent to extract phenol from water.. In general, the average uncertainty for S was less than 0.05.

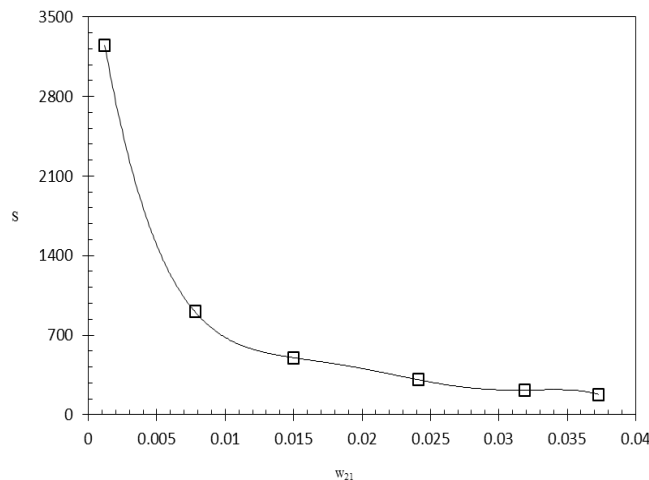


Fig. 3 Separation factor (S) plotted against the mass fraction of phenol in the aqueous phase at  $T = 308.2$  k.

**C. Consistency of tie-line data**

The reliability of experimentally measured tie-line data can be determined by applying the Othmer-Tobias [18] (equation (1)) and Bachman [19] (equation (2)) correlation equation.

$$\ln \left( \frac{1-w_{33}}{w_{33}} \right) = A + B \ln \left( \frac{1-w_{11}}{w_{11}} \right) \tag{1}$$

$$w_{23} = A' + B' \left( \frac{w_{33}}{w_{11}} \right) \tag{2}$$

Where  $w_{33}$  is mass fraction of solvent in the solvent-rich phase; A, B, A' and B' are the parameters of the Othmer-Tobias and the Bachman correlations, respectively. These parameters are listed in Table 6 and shown in Figures 4 and 5, respectively. The correlation factor ( $R^2$ ), and the linearity of the plots indicates the degree of consistency the measured LLE results in this work.

TABLE VI  
 OTHMER–TOBIAS AND BACHMAN EQUATIONS CONSTANTS AND THE CORRELATION FACTOR (R2) FOR THE {WATER (1) + PHENOL (2) + IBA (3)} System At T = 308.2 K.

Othmer–Tobias correlation			Bachman correlation		
A	B	R <sup>2</sup>	A'	B'	R <sup>2</sup>
4.5766	1.2815	0.9886	0.0215	1.0148	0.9999

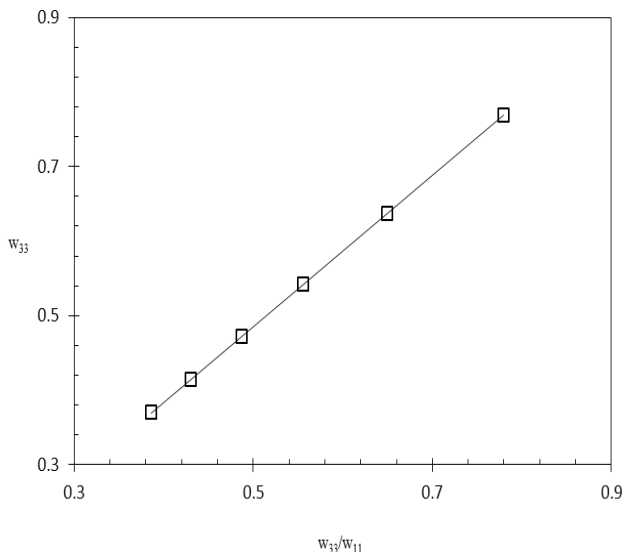


Fig. 6. Bachman plot for the {water (1) + phenol (2) + IBA (3)} system T = 308.2 K

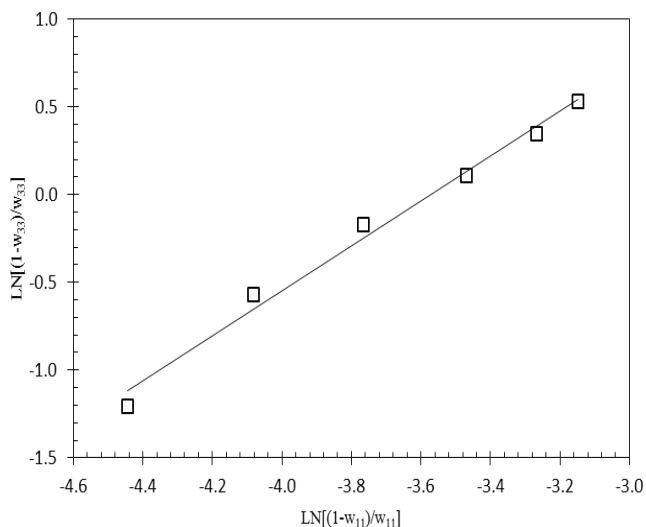


Fig. 7 Othmer-Tobias for the {water (1) + phenol (2) + IBA (3)} system at T = 308.2 K.

The experimental tie-line data for each ternary system were Correlated using the NRTL [20] and the UNIQUAC [21] models. The calculated data for the ternary systems at T = 308.2 K are listed in Table 7.

TABLE VII  
 CALCULATED UNIQUAC AND NRTL TIE-LINE VALUES IN MASS FRACTION (W<sub>i</sub>) FOR (WATER + PHENOL + IBA) At T = 308.2 K.

w <sub>1</sub> (water)		w <sub>2</sub> (phenol)	
NRTL	UNIQUAC	NRTL	UNIQUAC
Aqueous phase			
0.9842	0.9839	0.0020	0.0021
0.9830	0.9829	0.0082	0.0082
0.9784	0.9785	0.0148	0.0148
0.9716	0.9718	0.0231	0.0229
0.9645	0.9647	0.0311	0.0310
0.9586	0.9585	0.0377	0.0377
Organic phase			
0.0391	0.0367	0.1700	0.1655
0.0456	0.0480	0.2699	0.2709
0.0561	0.0581	0.3349	0.3344
0.0690	0.0683	0.3974	0.3924
0.0778	0.0746	0.4496	0.4384
0.0830	0.0779	0.4889	0.4721

Figure 2 also compare the calculated tie-lines from the NRTL and UNIQUAC models with the experimental results. The values r and q (the UNIQUAC structural parameters) used for this ternary system were taken from reference [27] and are presented in Table 8. In the present work, the value of the non-randomness was fixed at 0.25. The corresponding sets of binary interaction parameters were evaluated for each of the components over all of the tie-lines. The NRTL and UNIQUAC binary interaction parameters for the ternary systems of (water + phenol + IBA) at T = 308.2 K are shown in Tables 9 and 10, respectively. The root-mean-square deviation (RMSD) value was calculated from the difference between the experimental and calculated mass fractions according to the following equation:

$$RMSD = \sqrt{\frac{\sum_{k=1}^n \sum_{j=1}^n \sum_{i=1}^n (w_{ijk}^{exp} - w_{ijk}^{cal})^2}{6n}} \tag{3}$$

Where n is the number of tie-lines, w<sup>exp</sup> indicates the experimental mass fraction, w<sup>cal</sup> the calculated mass fraction, and subscript i indexes components, j indexes phases and k = 1, 2, ..., n (tie-lines).

TABLE VIII  
 The UNIQUAC Structural Parameters (r And q) For Pure Components [22].

components	r	q
Isobutyl acetate	4.8300	4.1900
Phenol	3.54647	2.71600
Water	0.92000	1.40000

The average root-mean-square deviations are presented in Tables 9 and 10 for NRTL and UNIQUAC models for (water + phenol + IBA). It can be seen that both models presented good agreement between the measured and calculated mass fractions for the studies system.

TABLE IX

NRTL ( $\alpha = 0.25$ ) BINARY INTERACTION PARAMETERS ( $b_{ij}$  And  $b_{ji}$ ) And RMSD VALUES FOR THE TERNARY SYSTEM.

$i-j$	$b_{ij}^*/k$	$b_{ji}/k$	RMSD%
$T = 308.2$			
1-2	2811.48	1620.47	3.48
1-3	1930.48	1008.88	
2-3	2288.05	2532.17	

$$* b_{ij} = \left( \frac{b_{ij} - b_{ji}}{\alpha} \right)$$

TABLE X

UNIQUAC BINARY INTERACTION PARAMETERS ( $b_{ij}$  And  $b_{ji}$ ) And RMSD VALUES FOR THE TERNARY SYSTEM.

$i-j$	$b_{ij}^*/k$	$b_{ji}/k$	RMSD%
$T = 308.2$			
1-2	793.04	2064.21	3.89
1-3	-91.64	1168.60	
2-3	954.98	1393.39	

$$* b_{ij} = \left( \frac{b_{ij} - b_{ji}}{\alpha} \right)$$

#### IV. CONCLUSION

Tie-line data for the (water + phenol + IBA) ternary system were obtained at  $T = 308.2$  K. The ternary system exhibits type-2 behavior of the LLE. The consistency of tie-line data was verified by applying the Othmer–Tobias and Bachman equations. The linearity of the plots indicates the consistency of the experimental data. The separation factors and distribution coefficients for the organic solvent used in this work were calculated. The experimental results indicate that IBA has high separation factors, indicating the ability of this solvent to extract phenol from water. It can be concluded that it can be considered as reliable organic solvent for the extraction of phenol from aqueous solutions.

The UNIQUAC and NRTL ( $\alpha = 0.25$ ) models were satisfactorily used to correlate the experimental data and to calculate the phase compositions of the mixtures studied. The corresponding optimized binary interaction parameters were also calculated. Both the models give relatively good results for the system investigated..

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