

Liquid-Liquid Equilibria for Ternary Mixtures of (Water + Carboxylic Acid+ MIBK), Experimental, Simulation, and Optimization

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Abstract—In this work, Experimental tie-line results and solubility (binodal) curves were obtained for the ternary systems (water + acetic acid + methyl isobutyl ketone (MIBK)), (water + lactic acid+ methyl isobutyl ketone) at $T = 294.15\text{K}$ and atmospheric pressure. The consistency of the values of the experimental tie-lines was determined through the Othmer-Tobias and Hands correlations. For the extraction effectiveness of solvents, the distribution and selectivity curves were plotted. In addition, these experimental tie-line data were also correlated with NRTL model. The interaction parameters for the NRTL model were retrieved from the obtained experimental results by means of a combination of the homotopy method and the genetic algorithms.

Keywords—Liquid-liquid equilibria, homotopy methods, carboxylic acid, NRTL.

I. INTRODUCTION

MANY attempts have been made to describe the solvent extraction of carboxylic acids from aqueous fermentation solutions. The (liquid–liquid) equilibrium (LLE) measurements and phase behaviour of ternary systems including carboxylic acids has been the subject of much research in recent years [1]–[5]. LLE data of the related systems are not only needed for the design of an efficient and productive extraction system, but they are also indispensable in calibration and verification of analytical models.

In the present work, liquid–liquid equilibrium data have been obtained for three different systems, namely, (water + acetic acid + methyl isobutyl ketone), (water + lactic acid+ methyl isobutyl ketone) at 294.15K and at atmospheric pressure. The distribution coefficients and separation factors were obtained from experimental results and are also reported. The tie lines were determined and were correlated by the methods of Othmer-Tobias and Hand on a mass-fraction basis. The experimental results are compared with values predicted by NRTL.

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II. EXPERIMENTAL SECTION

A. Chemicals

Acetic acid, lactic acid, dichloromethane and methyl isobutyl ketone were purchased from Merck and were of 99, 99, 98, and 99% mass purity, respectively. The chemicals were used without further purification. Deionized and redistilled water was used throughout all experiments.

B. Analytical Methods

The Solubility curve was determined by the cloud point method [6] using a thermostated cell, equipped with a magnetic stirrer and isothermal fluid jacket. The cell was kept in a constant-temperature bath maintained at $21 \pm 0.1^\circ\text{C}$. The cell was filled with homogeneous water + carboxylic acid mixtures prepared by weighing, using a Nahita YP402N balance with a precision of 10^{-2}g . The solvent was titrated into the cell from a microburet with an uncertainty of $\pm 0.01\text{cm}^3$. The end point was determined by observing the transition from a homogeneous to a heterogeneous mixture. This pattern was convenient to provide the aqueous-rich side of the curves. The data for organic-rich side of the curves were therefore obtained by titrating homogeneous solvent + carboxylic acid binaries with water until the turbidity had appeared. The maximum error in the calculation of the compositions of the bimodal curve was estimated to be 10^{-2} . Next, the refractive indexes of these ternary mixtures are measured by using a Nahita Modèle 690/1 refractometer. Each measurement was taken on three occasions.

For the tie-line measurement, an equilibrium cell was immersed in a thermostat controlled at the desired temperature ($\pm 0.1^\circ\text{C}$). The pure components were added, and the mixture was stirred for at least 3 h with a magnetic stirrer. The two-phase mixture was allowed to settle for at least 3. Samples were taken by syringe from the upper and lower mixtures. The refractive indexes of both phases at equilibrium were measured to later determine their compositions.

III. MODELS THERMODYNAMIC

The NRTL model was used to correlate the experimental data in this work, the NRTL model was expressed by:

$$\ln \gamma_i = \frac{\sum_{j=1}^n \tau_{ji} G_{ji} x_j}{\sum_{k=1}^n G_{ki} x_k} + \sum_{j=1}^n \frac{x_j G_{ij}}{\sum_{k=1}^n G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_{i=1}^n x_i \tau_{ij} G_{ij}}{\sum_{k=1}^n G_{kj} x_k} \right) \quad (1)$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \quad \alpha_{ji} = \alpha_{ij}$$

The effective interaction parameter τ_{ji} is defined by:

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{R.T} = \frac{A_{ji}}{T}$$

The LLE experimental data were used to determine the optimum NRTL binary interactions parameters. The thermodynamic model was fitted to experimental data using the Newton homotopy formulation [7].

IV. HOMOTOPY CONTINUATION METHOD

The phase equilibrium problem involves the separation of N_C components of molar fractions z into two phases I and II at a given temperature T and pressure P . The molar fractions of the components in the two phases are denoted as X_i^I and X_i^{II} , respectively.

$$X_i^I \beta + X_i^{II} (1 - \beta) - z_{i, Feed} = 0 \quad (2)$$

$$X_i^I \gamma_i^I - X_i^{II} \gamma_i^{II} = 0 \quad (3)$$

$$1 - \sum_i X_i^I = 0 \quad (4)$$

In these equations; X_i denote the mole fractions in phases I and II. β stands for the phase fraction of phase I. The γ_i denotes the activity coefficients to be calculated by using an appropriate activity coefficient model such as the UNIQUAC model which is discussed in the previous section.

In this work, a convex linear homotopy continuation method is used; this method is globally convergent method for the solution of nonlinear equations; i.e., this method can find the solution while moving from a known solution or a starting point to an unknown solution. The homotopy function of a linear combination of two functions $G(X)$, an easy function, and $F(X)$, a difficult function.

$$H(X,t) = tF(X) + (1-t)G(X) \quad (5)$$

where t is a homotopy parameter that is gradually varied from 0 to 1 as a path is tracked from $G(X)$ (known solution) to $F(X)$ (unknown solution) and X is the vector of independent variables, X_0 is the initial of X and a solution of $G(X)$.

For the Newton homotopy formulation, the function $H(x,t)$ in (4) within $G(X) = F(X) - F(X_0)$, can take a form as follows:

$$H(X, t) = F(X) - (1-t)F(X_0) \quad (6)$$

When using homotopy continuation method, it is not only convenient but effective as well, to initialize the ternary system with pure methyl isobutyl ketone and water [7].

V. RESULTS AND DISCUSSION

A. Experimental Binodal and Tie-Line Measurements

The compositions defining the binodal curve of the ternary systems, (water + acetic acid + methyl isobutyl ketone), (water + lactic acid + methyl isobutyl ketone) at 294.15K are listed in Table I in which x_i denotes the mass fraction of the i th component.

TABLE I
EXPERIMENTAL SOLUBILITY CURVE DATA

Water (1) + lactic Acid (2) + MIBK(3)			Water (1) + acetic Acid (2) + MIBK(3)		
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)
0.0381	0.10193	0.85997	0.05442	0.08568	0.8599
0.04867	0.1823	0.76903	0.09977	0.14958	0.75065
0.0716	0.26293	0.66547	0.13197	0.21641	0.65161
0.13891	0.33351	0.52758	0.17393	0.25353	0.57253
0.15017	0.436	0.41383	0.17689	0.28562	0.53749
0.17453	0.44773	0.37774	0.21962	0.31147	0.46891
0.19823	0.49105	0.31072	0.27109	0.3233	0.40561
0.40336	0.50359	0.09305	0.30428	0.34013	0.35559
0.47389	0.44374	0.08236	0.33147	0.34444	0.32409
0.51191	0.42608	0.06201	0.38999	0.34804	0.26198
0.61508	0.30717	0.07775	0.40931	0.34365	0.24704
0.7313	0.22826	0.04044	0.45495	0.34378	0.20127
0.81253	0.15217	0.0353	0.5357	0.33733	0.12696
0.8856	0.08292	0.03148	0.57931	0.30399	0.1167
			0.64281	0.26985	0.08734
			0.66787	0.23364	0.09849
			0.74114	0.19446	0.0644
			0.81661	0.12855	0.05484
			0.90065	0.07089	0.02846

Table II shows the experimental tie-line compositions of the equilibrium phases, for which x_{i1} and x_{i3} refer to the mass fractions of the i th component in the aqueous and solvent phases, respectively. The binodal curves and tie-lines are shown in Figs. 1 and 2.

TABLE II
EXPERIMENTAL TIE-LINE RESULTS IN MASS FRACTION FOR TERNARY SYSTEMS

Water-rich phase (aqueous phase)			Solvent-rich phase (organic phase)		
x_1 (water)	x_2 (solute)	x_3 (solvent)	x_1 (water)	x_2 (solute)	x_3 (solvent)
Water (1) + Lactic Acid (2) + MIBK(3)					
0,7666	0,19684	0,03656	0,01366	0,04214	0,9442
0,65676	0,28344	0,0598	0,03353	0,08687	0,8796
0,5917	0,33354	0,07476	0,03588	0,10308	0,86104
0,5785	0,34376	0,07774	0,043	0,1517	0,8053
0,42038	0,45952	0,1201	0,0439	0,1659	0,7902
Water (1) + Acetic Acid (2) + MIBK(3)					
0,9543	0,0314	0,0143	0,01934	0,03176	0,9489
0,8731	0,09115	0,03575	0,06239	0,09271	0,8449
0,83085	0,1256	0,04355	0,0796	0,1212	0,7992

0,7879	0,15815	0,05395	0,0955	0,1497	0,7548
0,7515	0,18284	0,06566	0,1123	0,1821	0,7056
0,6884	0,22319	0,08841	0,1231	0,2048	0,6721
0,6189	0,2706	0,1105	0,151	0,2334	0,6156

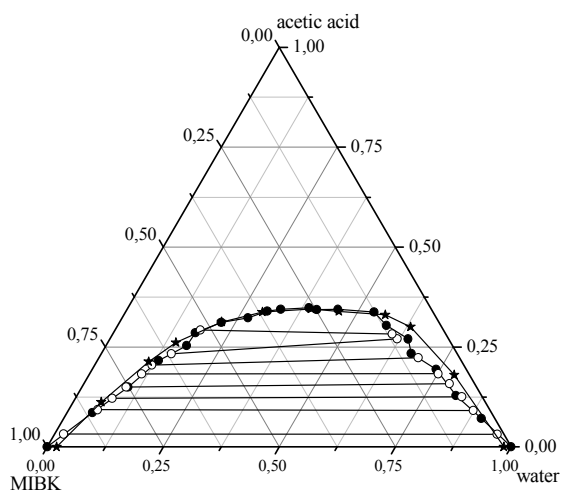


Fig. 1 Ternary diagram for LLE of {water (1) + Acetic acid (2) + MIBK (3)} at T = 294.15 K; —●— experimental solubility curve; —○— experimental tie-line data; —*— experimental tie-line data at 308.15 K [8]

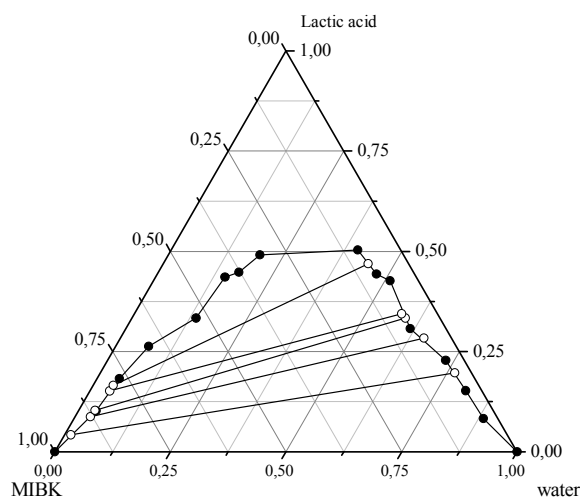


Fig. 2 Ternary diagram for LLE of {water (1) + lactic acid (2) + MIBK (3)} at T = 294.15 K; —●— experimental solubility curve; —○— experimental tie-line data

B. Distribution Coefficient and Separation Factor

The effectiveness of extraction of carboxylic acid by the solvent is given by its separation factor (S), which is an indication of the ability of the solvent to separate carboxylic acid from water.

$$S = \frac{D_2}{D_1} \quad (7)$$

where D_1 and D_2 are the distribution coefficients of water and carboxylic acid, respectively. The distribution coefficients, D_i , for water ($i = 1$) and carboxylic acid ($i = 2$) were calculated as follows:

$$D_i = \frac{x_i^3}{x_i^1} \quad (8)$$

where x_i^3 and x_i^1 are the mass fractions of component i in the solvent-rich and water-rich phases, respectively.

The distribution coefficients and separation factors for each system are given in Table III. Separation factors are greater than 1 for the systems reported here, which means that extraction of the studied carboxylic acids from water with MIBK is possible. The separation factor is not constant over the whole two-phase region. Selectivity diagrams on a solvent-free basis are obtained by plotting, $x_2^3 / (x_2^3 + x_1^3)$ versus $x_2^1 / (x_2^1 + x_1^1)$ for each carboxylic acid in Fig. 3. The selectivity diagram indicated that the performance of the MIBK for extraction of acetic acid is higher than lactic acid.

TABLE III
DISTRIBUTION COEFFICIENTS FOR WATER (D_1) AND CARBOXYLIC ACID (D_2), AND SEPARATION FACTORS (S)

D_1	D_2	S
Water (1) + Lactic Acid (2) + MIBK(3)		
0,01782	0,21408	12,01432
0,05105	0,30648	6,00319
0,06064	0,30905	5,09654
0,07433	0,4413	5,93697
0,09899	0,35381	3,57434
Water (1) + acetic Acid (2) + MIBK(3)		
0,02027	1,01146	49,90905
0,07146	1,01711	14,23374
0,09581	0,96497	10,07216
0,12121	0,94657	7,80945
0,14943	0,99595	6,66481
0,17882	0,9176	5,13143
0,24398	0,86253	3,53522
0,30584	1,03541	3,38545

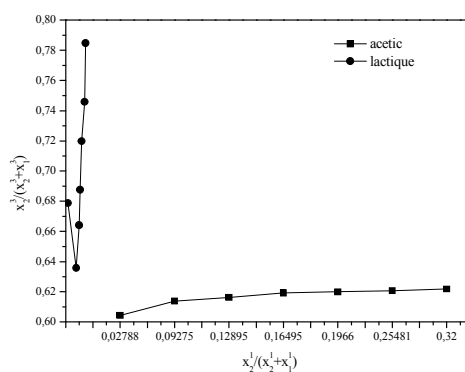


Fig. 3 Solvent-free basis selectivity diagram of systems for (●) Water-Lactic acid-MIBK, (■) Water-Acetic acid-MIBK

C. Othmer–Tobias and Hand Correlations

In this study Othmer-Tobias [9], Hand [10], correlations were used to ascertain the reliability of the experimental

results for each system, where x_{11} , mass fraction of water in the aqueous phase; x_{23} and x_{21} , mass fraction of carboxylic acid in organic and aqueous phases, respectively; x_{33} , mass fraction of solvents in organic phase; a , b , a' , and b' , the parameters of the Othmer-Tobias correlation and the Hand correlation, respectively,

The Othmer-Tobias correlation is:

$$\ln\left(\frac{(1-x_{33})}{x_{33}}\right) = a + b \ln\left(\frac{1-x_{11}}{x_{11}}\right) \quad (9)$$

The Hand correlation is

$$\ln\left(\frac{x_{21}}{x_{11}}\right) = a' + b' \ln\left(\frac{x_{23}}{x_{33}}\right) \quad (10)$$

The correlations are given in Figs. 4, 5, and the constants of the correlations are also given in Table IV. The correlation factor (R^2) being approximately unity and the linearity of the plots indicate the degree of consistency of the measured LLE values in this study.

TABLE IV
THE CORRELATION COEFFICIENTS AND CORRELATION FACTORS FOR THE OTHMER-TOBIAS AND HAND CORRELATIONS

System	Othmer-Tobias correlation			Hand correlation		
	a	b	R^2	a'	b'	R^2
Water-Acetic acid-MIBK	0,1774	1,0024	0,9935	1,3764	0,9961	0,9943
Water-Lactic acid-MIBK	1,3764	1,0898	0,9406	0,5993	0,6175	0,9671

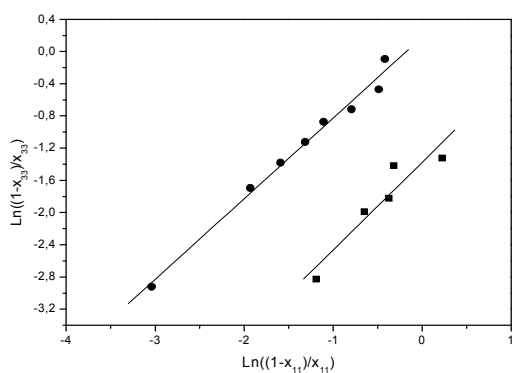


Fig. 4 Othmer-Tobias plots of: (●)Water-Acetic acid-MIBK and (■)Water-Lactic acid-MIBK ternary systems

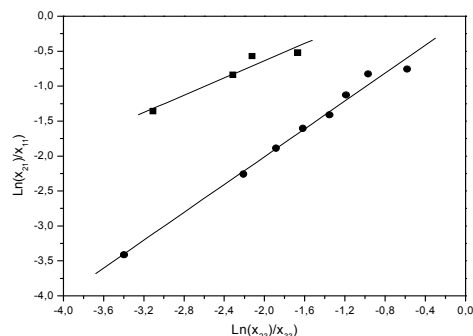


Fig. 5 Hand plots of: (●) Water-Acetic acid-MIBK and (■) Water-Lactic acid-MIBK ternary systems

VI. OPTIMIZATION PROCEDURE

The NRTL model was used to correlate the raw experimental LLE values. In the present work, the value of the non-randomness parameter of the NRTL equation, α , was fixed at 0.2. The objective function developed by Sorensen [11] was used to optimize the equilibrium models. The objective function is the sum of the squares of the difference between the experimental and calculated data. The objective function can be defined as:

$$\min F = -\sum_{k=1}^m \sum_{j=1}^2 \sum_{i=1}^n w_{ik}^j (x_{ik}^{cal}(j) - x_{ik}^{exp}(j))^2 \quad (11)$$

The observed results were used to determine the optimum NRTL (Δg_{ij}) binary interaction energy between an i - j pair of molecules or between each pair of compounds (tables 5). The interaction parameters values obtained with genetic algorithm (GA).

The quality of the correlation is measured by the root-mean square deviation (RMSD). The RMSD value was calculated from the difference between the experimental and calculated mole fractions according to the following equation:

$$RMSD = \sqrt{\frac{\sum_{k=1}^n \sum_{j=1}^2 \sum_{i=1}^s (x_{ijk} - \hat{x}_{ijk})^2}{6n}} \quad (12)$$

where n is the number of tie-lines, x indicates the experimental mole fraction, \hat{x} is the calculated mole fraction, and the subscript i indexes components, j indexes phases and $k = 1, 2, \dots, n$ (tie-lines).

The RMSD values in the correlation by NRTL models for the systems studied at $T = 394.15K$ are listed in Table V.

TABLE V

NRTL ($\alpha = 0.2$) BINARY INTERACTION PARAMETERS (Δg_{ij} AND Δg_{ji}) AND RMSD VALUES FOR LLE DATA OF THE TERNARY SYSTEMS AT T=294.15 K

i-j	Δg_{ij}	Δg_{ji}	RMSD
Water (1) + Lactic Acid (2) + MIBK(3)			
1-2	-1433.04	-1182.796	
1-3	-1433.04	-1495.601	4.657.10 ⁻²
2-3	2570.381	856.7449	
Water (1) + Acetic Acid (2) + MIBK(3)			
1-2	623.9883	-238.045	
1-3	802.9326	-238.6706	8.580.10 ⁻²
2-3	2521.114	805.4741	

VII. CONCLUSIONS

The experimental tie-line data of, (water + acetic acid + methyl isobutyl ketone) and (water + lactic acid+ methyl isobutyl ketone) at T = 294.15K and atmospheric pressure. The NRTL model was used to correlate the experimental data. The RMSD values between observed and calculated mass percents for the systems water-lactic-MIBK, water-acetic acid-MIBK were 4.657%, 8.580% respectively

It is apparent from the separation factors and experimental tie-lines that MIBK is found to be preferable solvent for separation of acetic and lactic acid from aqueous solutions.

The combining Homotopy continuation and Genetic algorithms can be applied to predict liquid-liquid equilibrium and binary interaction parameters, respectively for other liquid-liquid systems as well as vapor-liquid systems.

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