

A Comparative Study on Water and Ethanol Separation Mixture by Different Solvents: New Experimental and Correlation Data

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This paper describes our interest in ethanol separation and the enhancement of the obtained interaction parameters. The binodal curves and tie-line data for the ternary systems of water + ethanol + 1-octanol, water + ethanol + 4-methyl-2-pentanone, and water + ethanol + ethyl acetate were investigated at 293.15 K. All these three ternary systems followed a type-1 liquid-liquid equilibrium diagram. Furthermore, the extraction capabilities of these solvents were tested by the separation factor (S), which was found to be greater than 1 in all ternary systems, with the separation factors varying between 3.52 and 18.37. In addition, it was found that the values of the distribution coefficient (D) of ethanol were not constant over the entire composition of the two-phase region (D values varied between 0.777 and 0.928), which confirmed the extraction of ethanol. The ternary system water + ethanol + ethyl acetate was found to be the best option in terms of the distribution coefficient and separation factor. Othmer-Tobias and Hand plots were used to determine the reliability of the experimental tie-line data. In addition, the non-random two-liquid (NRTL) model was used to correlate the experimental data, and the model parameters were obtained using a genetic algorithm (GA). The results showed that there was a strong agreement between the experimental and calculated tie-lines, with root-mean-square deviation (RMSD) values below 1.72%.

Keywords: Liquid-liquid equilibrium, Ethanol, Cloud point, NRTL, Genetic algorithm

INTRODUCTION

As a result of the rise in oil prices on the world market and the damaging effects of oil pollution on the environment, ethanol has received increasing attention and been gradually used as a transportation fuel. This has made ethanol addition an attractive alternative in transportation fuels, especially when anhydrous ethanol, as an additive, is mixed with gasoline in petrol engines, sometimes referred to as gasohol [1,2]. According to the literature statistics, there has been a rapid growth in ethanol production since 2012. For example, in 2020, the United States, by producing more than 15.80 billion gallons of ethanol, was the first producer

of ethanol in the world [3,4].

Studying the liquid-liquid equilibrium (LLE) of mixtures is of great importance for both basic and applied purposes, such as the design of the extraction and distillation processes. There are several methods to produce ethanol from biomass, such as sugarcane, corn, switchgrass, etc. [5,6]. For instance, the ethanol used industrially is a mixture of 95% ethanol and 5% water and is prepared by distilling the solution produced from the fermentation of sugars [7,8]. However, it is not possible to obtain over 95% purity by distillation due to the azeotropic point [9,10]. In this case, the most essential unit operation in chemical engineering, which is liquid-liquid extraction through decantation, is required to provide high purity [11-15].

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Due to its importance, many researchers have reported thermodynamic data on water/ethanol mixture with different solvents and temperatures. Andrés *et al.* [16] reported data on isobaric vapor-liquid-liquid equilibrium (VLLE) of water + methyl tert-butyl ether (MTBE) + ethanol system at temperatures ranging from 325.6-328.6 K and found that the LLE for the mentioned mixture was type 1. Arce *et al.* [17] measured the VLE for water + ethanol + 1-octanol at 101.32 kPa and proposed a simplified approach to obtain lower root-mean-square deviations (RMSDs) between the calculated and experimental data. Although in their study, the increase observed in the RMSD for the ternary system was slight, their proposed approach worked only with miscible binary subsystems. Luis *et al.* [18] also reported the separation of water + ethanol mixture using ethyl myristate at 298.15 K, 313.15 K, and 333.15 K.

Another study by Chang-Chuan *et al.* [19] reported the LLE of the water + ethanol + ethyl acrylate system and identified it as type 1, which confirmed the results reported by Andrés *et al.* [16]. Chang-Chuan *et al.* found that by increasing the temperature, the immiscibility region decreased in size. All the studies reviewed in the literature reported that the non-random two-liquid model (NRTL) model was one of the most suitable thermodynamic models.

Cháfer *et al.* [20] reported LLE data on the 4-methyl-2-pentanone (MIBK) + ethanol + water system at temperatures ranging between 283.2 and 323.2 K. They concluded that MIBK was capable of separating azeotropic mixtures.

Based on previous studies, the ternary systems of water + ethanol + 1-octanol, water + ethanol + MIBK, and water + ethanol + ethyl acetate were investigated at 293.15 K and atmospheric pressure. The cloud point titration method was used to obtain the phase diagram of the above-mentioned ternary systems. Also, the tie-lines with 1-octanol, MIBK, or ethyl acetate, as solvents, in the phase diagram of water + ethanol mixtures were determined [21-24]. Moreover, the distribution coefficient (D) and the separation factor (S) were calculated to evaluate the ability of the above-mentioned solvents in the recovery process [23,25-27]. The experimental results obtained from the LLE data were correlated with the NRTL activity coefficient model by applying a GA to optimize the calculated interaction parameters between each pair of components through the

minimization of the objective function [28-33]. The GA was also used to minimize the RMSD values so that the experimental data of the studied ternary systems could be modeled more accurately.

The results of this study, by offering thermodynamic data and a better understanding of molecular interaction parameters, will be useful in designing and simulating the separation processes of water + ethanol mixtures. Furthermore, this study offers a comparison between the most used solvents in industries, a comparison which is not available in the literature and can facilitate studies on LLE systems. In addition, to the best of the authors' knowledge, there is no published study comparing the LLE data of water and ethanol mixture with those of the three solvents mentioned in the present study at 293.15 K. The NRTL model, along with the GA optimization method, was used to correlate the ternary systems.

EXPERIMENTAL

Chemicals

All chemicals were used without purification. In the laboratory, double distilled water was prepared and used in all the experiments. Ethanol (99.8%) was purchased from Sigma-Aldrich. Furthermore, 1-octanol, ethyl acetate, and MIBK were obtained from Sigma-Aldrich with a mass purity of 99%, 99.5%, and 99%, respectively. More information on chemicals used in this study is given in Table 1.

Apparatus and Experimental Procedure

The binodal curves and the tie-line data of the ternary systems were determined by the cloud point titration method. The aforementioned method employed in this study was suggested by recent research [36,39-41]. The initial mixtures, including water + ethanol + 1-octanol, water + ethanol + MIBK, and water + ethanol + ethyl acetate, were prepared at 293.15 K using an electronic balance (Nahita, model 5023) with an accuracy of ± 0.001 g. Molar fractions were determined with an average uncertainty of less than 0.002.

The solutions were kept in an equilibrium glass vessel jacket and magnetically stirred with a magnetic stirrer (Nahita, model 690/1). A thermostat held at $T = 293.15$ K

Table 1. The Specifications of the Chemicals Used in the Present Study

Component	CAS-N	Supplier	Molecular weight (g mol ⁻¹)	Formula	Refractive index (n _D)	
					Exp.	Lit.
Water	7732-18-5		18.02	H ₂ O	1.3335	1.3334 [34]
Ethanol	64-17-5	Sigma	46.07	C ₂ H ₆ O	1.3635	1.3621 [35]
1-Octanol	111-87-5	Sigma	130.23	C ₈ H ₁₈ O	1.4275	1.4298 [36]
Ethyl acetate	141-78-6	Sigma	88.11	C ₄ H ₈ O ₂	1.3775	1.3745 [37]
MIBK	108-10-1	Sigma	100.16	C ₆ H ₁₂ O	1.3995	1.3980 [38]

The maximum standard deviation calculated μ (n_D) was less than 0.002; μ (T) = ± 0.1 K.

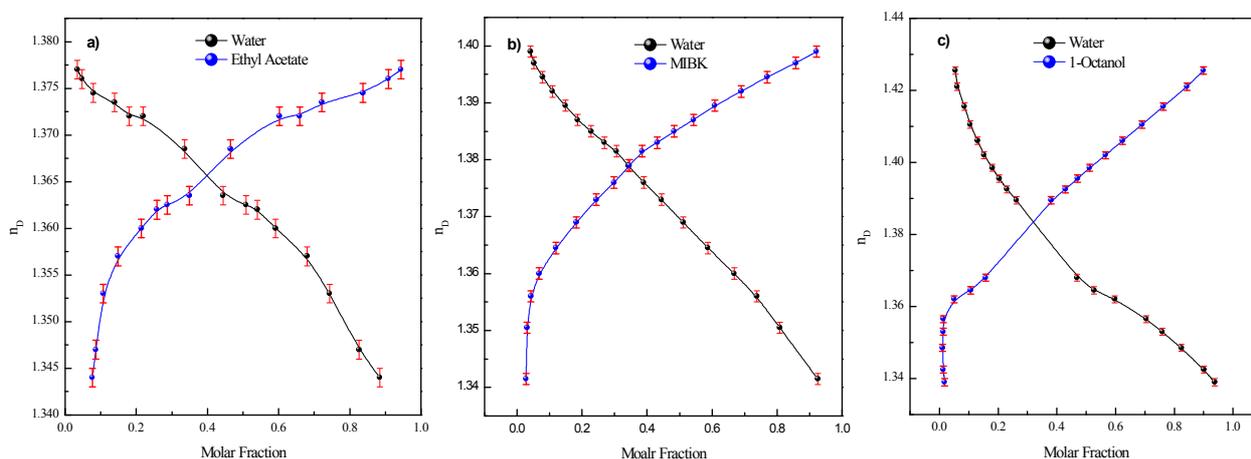


Fig. 1. a) Refractive indices for the system water + ethanol + 1-octanol, b) Refractive indices for the system water + ethanol + MIBK, and c) Refractive indices for the system water + ethanol + ethyl acetate. The solid lines represent the calibration curves.

regulated the temperature of the mixture in the equilibrium vessel to maintain the desired temperature within ±0.01 K.

The equilibrium tie-line data were obtained by preparing a mixture with known total composition in a jacketed glass vessel magnetically stirred. The mixture was kept at a fixed temperature for 4 h (293.15 ± 0.1 K). All prepared mixtures were left to settle for 24 h, allowing them to separate into two phases at equilibrium. Then, samples from both organic and aqueous phases were carefully taken with a syringe (2 ml) for further analysis [38].

After the examination of the upper and lower phases of

each sample, two refractive indices were measured to determine their composition [42]. Therefore, the third composition can be determined using the following formula:

$$\sum x_i = 1 \tag{1}$$

Figure 1 shows refractive indices for the three ternary mixtures as a function of the compositions. Two calibration curves were built from the experimental data for water + ethanol + 1-Octanol, water + ethanol + MIBK, and water + ethanol + ethyl acetate.

Table 2. Experimental Tie-Line data (Molar Fractions) for Water (1) + Ethanol (2) + Solvent (3) at 293.15 K and Atmospheric Pressure

Aqueous phase			Organic phase			S	D ₂
<i>x</i> ₁	<i>x</i> ₂	<i>x</i> ₃	<i>x</i> ₁	<i>x</i> ₂	<i>x</i> ₃		
Water + ethanol + 1-octanol							
0.829	0.162	0.009	0.067	0.159	0.773	12.126	0.986
0.765	0.224	0.011	0.102	0.184	0.715	6.196	0.822
0.743	0.242	0.015	0.117	0.221	0.662	5.813	0.913
0.722	0.260	0.018	0.134	0.250	0.616	5.164	0.961
0.652	0.316	0.032	0.180	0.307	0.512	3.522	0.973
Water + ethanol + MIBK							
0.926	0.049	0.025	0.047	0.045	0.908	18.371	0.928
0.876	0.096	0.028	0.052	0.077	0.872	13.591	0.800
0.832	0.135	0.033	0.062	0.115	0.823	11.530	0.854
0.802	0.164	0.034	0.068	0.128	0.805	9.202	0.777
0.789	0.176	0.035	0.074	0.140	0.786	8.535	0.797
0.761	0.200	0.039	0.090	0.173	0.737	7.366	0.868
0.701	0.254	0.045	0.145	0.233	0.622	4.443	0.920
Water + ethanol + ethyl acetate							
0.872	0.055	0.074	0.031	0.016	0.953	8.383	0.299
0.829	0.091	0.080	0.045	0.037	0.919	7.495	0.402
0.755	0.146	0.099	0.082	0.089	0.829	5.599	0.609
0.728	0.161	0.111	0.113	0.118	0.768	4.733	0.736

The maximum standard deviation ($\mu(x)$) and temperature ($\mu(T)$) calculated was less than 0.002 and ± 0.1 K at atmospheric pressure.

RESULTS AND DISCUSSION

LLE Experimental Results

To ensure high accuracy, the experimental error was calculated according to the Guide to the Expression of Uncertainty in Measurement (GUM) and using the standard deviation [43]. The results confirmed the reliability of the LLE data. In this study, the standard deviation is shown directly under Tables 1 and 2, and the calculations were made using Eqs. (2) and (3).

$$\bar{X}_i = \frac{1}{n} \sum_{k=1}^n X_{i,k} \quad (2)$$

$$S(x_i) = \sqrt{\frac{1}{(n-1)} \sum_{k=1}^n (X_{i,k} - \bar{X}_i)^2} \quad (3)$$

Where n is the series of measurements of the same point.

The average error in the calculated molar fractions and temperature of the ternary systems water + ethanol + 1-Octanol, MIBK, or ethyl acetate were less than ± 0.002 and just ± 0.1 K, respectively [43]. In addition, the experimental solubility data from the binodal curve diagrams of the ternary systems were analyzed and graphically represented in separate triangular diagrams, as can be seen in Figs. 2-4. A graphical representation of the miscibility curve with the experimental and calculated tie-lines is shown in Figs. 2-4. Based on the LLE diagrams, the systems were identified as Treybal's Type-I [44,45]. This finding is in agreement with those of Cháfer *et al.* [20] and Arce *et al.* [17]. The envelope of the immiscibility region decreased in the following order: 1-octanol > MIBK > ethyl acetate. The tie-line data for all the three studied ternary systems were

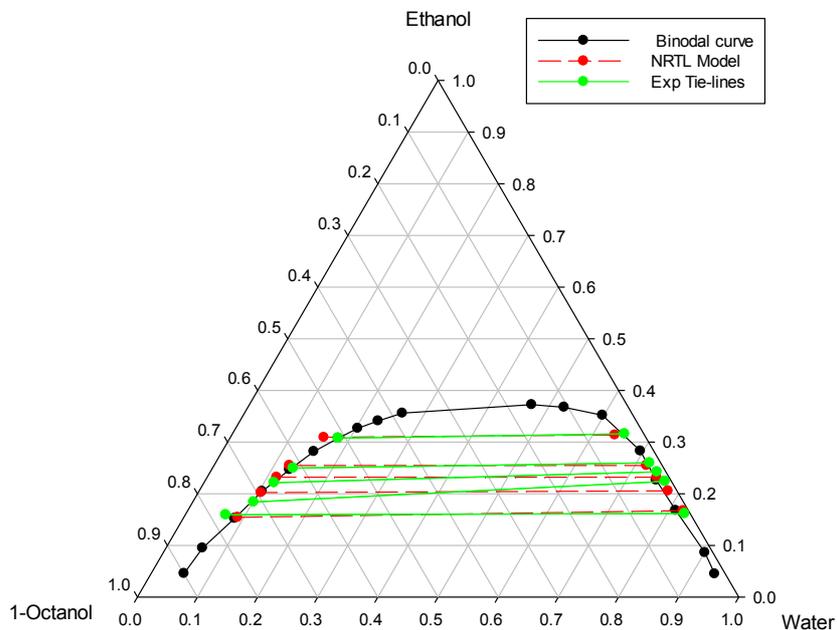


Fig. 2. The LLE phase diagram of water (1) + ethanol (2) + 1-octanol (3) system at 293.15 K and atmospheric pressure.

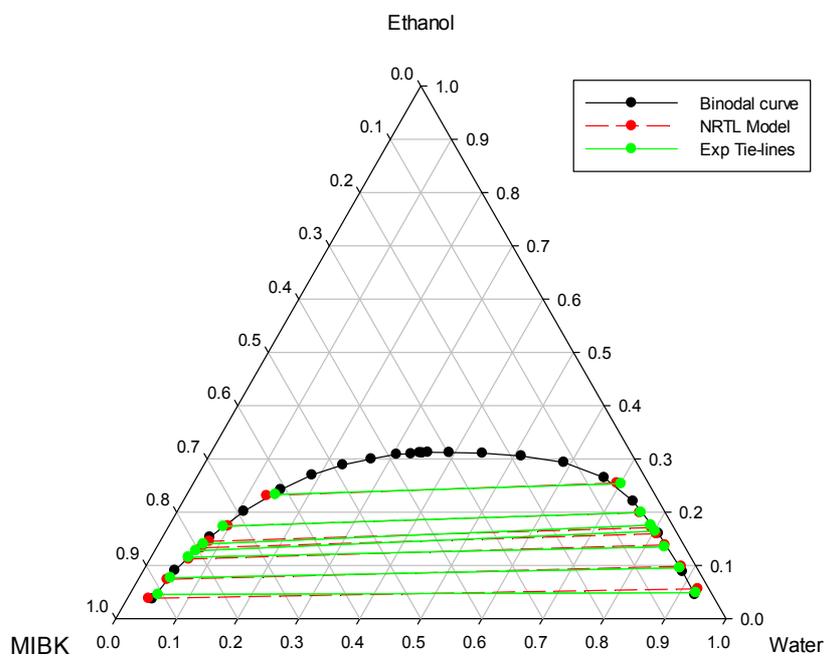


Fig. 3. The LLE phase diagram of water (1) + ethanol (2) + MIBK (3) system at 293.15 K and atmospheric pressure.

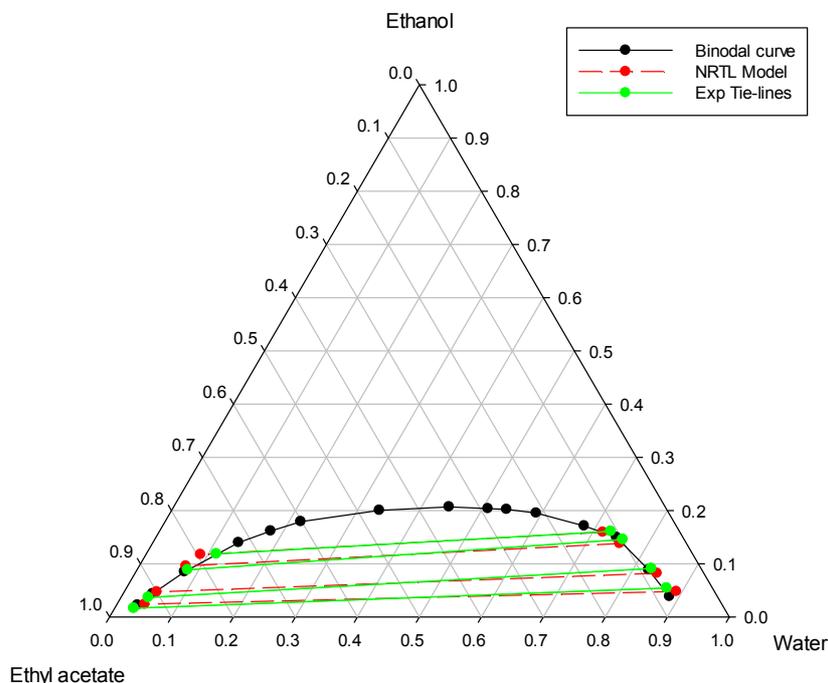


Fig. 4. The LLE phase diagram of water (1) + ethanol (2) + ethyl acetate (3) system at 293.15 K and atmospheric pressure.

obtained experimentally and are reported in Table 2.

Distribution Coefficient and Separation Factor

The distribution and separation coefficients of the studied systems are shown in Table 3. The efficiency of solvent extraction of ethanol can be expressed based on its separation factors, as shown in Eq. (4) [46-48]:

$$S = \frac{D_2}{D_1} \quad (4)$$

The efficiency of solvent extraction of ethanol can be defined based on its distribution coefficients, as shown in Eqs. (5) and (6), respectively [37,49]:

$$D_1 = \frac{x_{1e}}{x_{1r}} \quad (5)$$

$$D_2 = \frac{x_{2e}}{x_{2r}} \quad (6)$$

while x_{1e} and x_{2e} are the molar fractions of water and ethanol, respectively, in the extract phase, x_{1r} and x_{2r} are the

molar fractions of water and ethanol, respectively, in the raffinate phase. These coefficients provide an indication of the capacity of solvents to extract ethanol from water. The separation factors were found to be greater than 1 for all the studied ternary systems and varied between 3.52 and 18.37. The ternary system water + ethanol + MIBK had a separation factor (S) equal to 18.371, which was the highest compared to those of other solvents. The distribution coefficient (D) values of ethanol were not constant over the entire composition of the two-phase region and varied between 0.777 and 0.928. These results confirm that ethanol can be extracted *via* the aforementioned solvents.

The most suitable solvent based on the distribution coefficients and separation factors was MIBK, which had the highest separation factor based on the results related to the extraction capabilities of the solvents used in this study.

Reliability of the Experimental Tie-Line Data

The reliability of the experimental tie-line data related to the studied ternary systems, including water + ethanol + 1-octanol, water + ethanol + MIBK, and water + ethanol +

Table 3. RMSD Values Obtained from the NRTL-GA Model in This Study and those From Re-Correlated Experimental Data Provided by Arce *et al.* and Cháfer *et al.*

System	RMSD	
	Literature	This study
Water + ethanol + MIBK	0.81%	0.02%
Water + ethanol + 1-octanol	4.1%	1.22%,

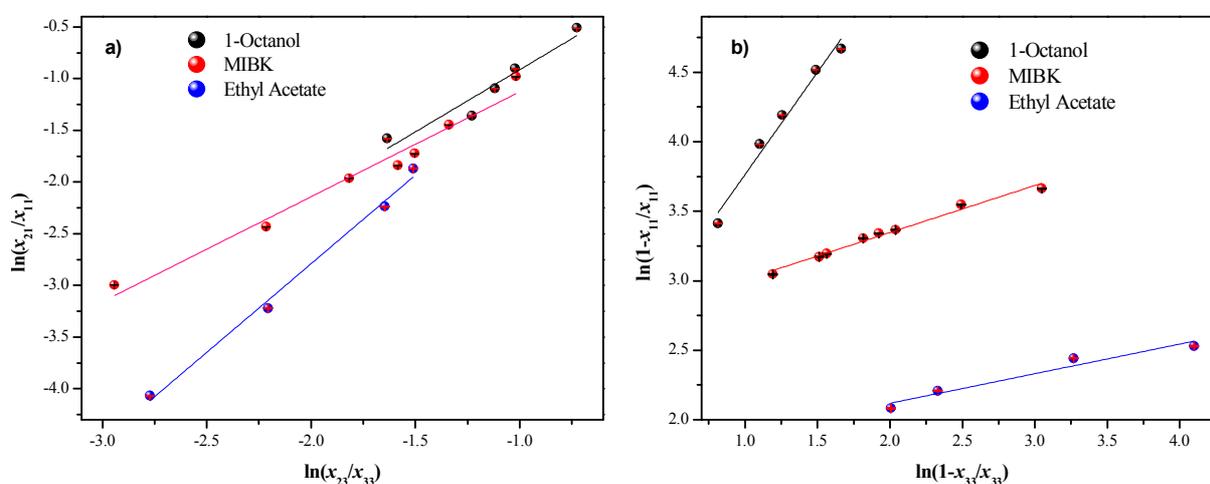


Fig. 5. a) Othmer-Tobias plots and b) Hand plots of the water + ethanol + 1-octanol, (water + ethanol + MIBK, and water + ethanol + ethyl acetate ternary systems at T = 293.15 K.

ethyl acetate) were verified by applying the Othmer-Tobias [50-52] and Hand [6,53] correlations, as shown in Eqs. (7) and (8):

$$\ln\left[\frac{1-x_{11}}{x_{11}}\right] = a_1 + b_1 \ln\left[\frac{1-x_{33}}{x_{33}}\right] \quad (7)$$

$$\ln\left[\frac{x_{21}}{x_{11}}\right] = a_2 + b_2 \ln\left[\frac{1-x_{23}}{x_{33}}\right] \quad (8)$$

Othmer-Tobias and Hand correlations for each of the three studied ternary systems are shown in Fig. 5.

Model Correlation and Parameter Estimation

The NRTL model was used to compare the experimental data for each of the three ternary systems at T = 293.15 K [54]. In the present study, the alpha parameter of the NRTL model was set at $\alpha = 0.2$. The activity

coefficients (γ_i) were calculated using Eqs. ((9)-(11) [55,56]:

$$\ln \gamma_i = \frac{\sum_{j=1}^n \tau_{ji} G_{ji} x_j}{\sum_{k=1}^n G_{ki} x_k} + \sum_{j=1}^n \frac{x_j G_{ij}}{\sum_{k=1}^n G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_{l=1}^n x_l \tau_{lj} G_{lj}}{\sum_{k=1}^n G_{kj} x_k} \right) \quad (9)$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \quad (10)$$

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} = \frac{A_{ji}}{T} \quad (11)$$

where subscripts i, j , and k refer to the components, A_{ij} is the binary interaction parameter, and α_{ij} represents the non-randomness of the NRTL model.

In this study, the objective function developed by

Table 4. The NRTL-GA Binary Interaction Parameters Values for Water + Ethanol + 1-Octanol, Water + Ethanol + MIBK, and Water + Ethanol + Ethyl Acetate Ternary Systems

Ternary system	NRTL parameters			RMSD
	i-j	Aij	Aji	
Water + ethanol + 1-octanol	1-2	3125.6	194.6	1.22%
	1-3	2126.6	461.0	
	2-3	-0073.6	1711.6	
Water + ethanol + MIBK	1-2	753.3	-709.6	0.68%
	1-3	942.1	666.7	
	2-3	3551.8	-510.4	
Water + ethanol + ethyl acetate	1-2	-790.7716	350.3929	1.72%
	1-3	659.6591	605.2463	
	2-3	-348.2514	71.3470	

Sorensen *et al.* [23,48,57] was used, and it was defined as the sum of the square of the error between the experimental and calculated compositions of all the components over the whole set of tie-lines, as given in Eq. (12):

$$\min F = \sum_{k=1}^m \sum_{j=1}^2 \sum_{i=1}^n w_{ik}^j (x_{ik}^{cal}(j) - x_{ik}^{exp}(j))^2 \quad (12)$$

The accuracy of the model correlation was assessed by the RMSD between the experimental and correlated data, as defined in Eq. (13) [23,31]:

$$RMSD = \left[\frac{-F}{2mn} \right]^{0.5} \quad (13)$$

where “m” and “n” are the total number of tie-lines and components, respectively [58]. The consistency of the correlated data consistency with the experimental data for the three studied ternary systems, including water + ethanol + 1-octanol, water + ethanol + MIBK, and water + ethanol + ethyl acetate, was plotted, and the distribution coefficients are shown in Figs. 2-4. Previously, a ternary system of water + ethanol + 1-octanol was studied as VLE by Arce *et al.* [17]. Moreover, Cháfer *et al.* [20] provided data on the LLE ternary system of water + ethanol + MIBK at as in the present study.

The RMSD values provide a consistent method for

evaluating the difference between the correlated values and the experimental data. The closer the experimental results are to the model correlations, the smaller the RMSD values will be. In order to compare the results of this study with those of previous studies and to better understand the effect of temperature on the ternary systems, the RMSD values calculated in this study, which used an NRTL model and a GA to optimize the obtained interaction parameters, are listed alongside with the re-correlated experimental data provided by Arce *et al.* and Cháfer *et al.* [20], as shown in Table 3.

The RMSD value reported by Cháfer *et al.* [20] for LLE of the ternary system MIBK + ethanol + water at 298.2 K was 0.81% while in this study, the value determined by the proposed NRTL model, along with the GA optimization, was 0.02%. In addition, the RMSD value obtained in our study was equal to 1.22% while Arce *et al.* [17] reported an RMSD value of 4.1% for the system and 4.5% for their proposed simplified system. Based on the reported data in Table 3, the utilization of a GA improved the optimization of interaction parameters and correlated more closely with the experimental data with a low RMSD value.

After verifying the validity of the proposed NRTL-GA model based on the available literature, the binary interaction parameters were estimated for the NRTL-GA model and are shown in Table 4.

The interaction parameter values were estimated based

on the experimental LLE data by minimizing a suitable objective function with constrained minimization using the GA of MATLAB (2009b) optimization toolbox [26]. The correlated results showed good agreements with the experimental data for all the three chemical systems, namely, water + ethanol + 1-octanol, water + ethanol + MIBK, and water + ethanol + ethyl acetate. The obtained RMSD values were less than 1.72%, as shown in Table 2. This supports the ability of the NRTL-GA optimization model to accurately correlate the experimental data.

CONCLUSIONS

The LLE data of three chemical systems, including water + ethanol + 1-octanol, water + ethanol + MIBK, and water + ethanol + ethyl acetate, were measured and correlated at 293.15 K and atmospheric pressure. These ternary systems followed type-I LLE phase diagram. The extraction abilities of the solvents, measured by distribution coefficients and the separation factors, showed that the system water + ethanol + MIBK had a higher separation factor. Furthermore, both Othmer-Tobias and Hand correlations were used to verify the thermodynamic consistency of the experimental tie-lines. The validity of the NRTL-GA model was tested by correlating the obtained results with the experimental results reported in the literature. The results showed that there was a strong agreement between the measured and correlated tie-lines, with the RMSD values being less than 1.72%.

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