

Measurement, Correlation and Prediction of LLE Data for the Ternary System Water + Lactic Acid + Diethyl Ether at 293.2 K

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In this study, tie-line points and solubility data were experimentally measured for the ternary mixture (water + lactic acid + diethyl ether) at $T = 293.2$ K and atmospheric pressure. UNIFAC calculations predicted that lactic acid and diethyl ether do not form an azeotrope. The mass fractions of organic and aqueous layers were determined by acid-base and the Karl Fisher titrations. Cloud point method verified that the LLE behavior of the studied system is Type-1. The reliability of the tie-line points was demonstrated by the Othmer-Tobias and Hand plots. Thermodynamic correlation of tie-line data was done by NRTL model and the obtained binary interaction parameters were tested after validation. The experimental and correlated data had very good accordance (rmsd = 0.88%). Extraction quality of diethyl ether was investigated using the calculation of distribution coefficients and separation factors over the immiscibility area. Separation factors decreased from 1.93 to 1.13 when aqueous mass fraction of lactic acid increased from 0.070 to 0.305. However, distribution coefficient increased from 0.07 to 0.12 in the same region. The study shows that the extraction of lactic acid is possible in all investigated feeds at 293.2 K.

Keywords: Lactic acid, Liquid-liquid equilibrium, Thermodynamic modeling

INTRODUCTION

Carboxylic acids are produced by chemical synthesis or fermentation processes in which a dilute solution of the acid is remaining. Solvent extraction is a conventional method for purification and separation of the acids from water. Different kinds of solvents could be used for separation process provided that the parameters of selected solvent would be suitable. Obtained liquid-liquid equilibrium data could also be used in the design of the separation process, thermodynamics modeling and prediction of similar systems [1-10].

Lactic acid (LA) is a water-soluble carboxylic acid. It is broadly applied in food and pharmaceutical manufacturing. Polylactic acid, an eco-friendly polymer, is prepared by

pure lactic acid. Throughout the fermentation process of lactic acid, pH of aqueous solution decreases. This slows down acid production. Then, removal of lactic acid from fermentation broth augments the production yield [11-14].

Many solvents were chosen for the separation of LA from aqueous phase [15-20]. Robert B. Weiser *et al.* [15] confined their experiments to calculate the distribution coefficients of some solvents and did not measure the composition of other components. Ternary systems containing water/lactic acid and 1-butanol [16,18], 1-octanol, 1-nonanol, 1-decanol [17], 2-butanol, 1-pentanol, 1-hexanol, 1-heptanol [18], methyl isobutyl ketone [19], benzyl alcohol and p-xylene [20] were investigated by researchers. Limited categories of solvents, besides alcohols, have been explored for the separation of lactic acid from water so far.

Diethyl ether (DEE) has not been yet chosen as

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extractant for the separation of lactic acid from aqueous phase. Due to its favorable properties, DEE seems a suitable choice for this goal. The boiling point of DEE (34.6 °C) is much lower than that of water, and its latent heat of vaporization is about six times less than water (368 J g⁻¹ for DEE *versus* 2260 J g⁻¹ for water), making DEE a favorable choice in solvent recovery treatments. The density of DEE is 0.71 g ml⁻¹ and the difference between the densities of water and DEE is suitable for separation of phases. The parameters mentioned are very important in separation process [10]. DEE has been applied in solvent extraction process for separation of methanol, ethanol, 1-propanol [21,22], acetic acid and propionic acid from water [23]. DEE was a proper solvent in extraction of the studied alcohols and acids. Reported distribution coefficients and separation factors of diethyl ether in all previous investigated systems were acceptable.

Since the ordinary distillation may be impossible when the mixture forms an azeotrope, then at least, the theoretical investigation of the possibility of azeotrope formation between selected solvent and extract seems necessary [24]. The universal functional activity coefficient (UNIFAC) is one of the most trustable prediction models to predict VLE and LLE data for binary mixtures [25-28].

In the present study, the liquid-liquid equilibrium data of the ternary system water/LA/DEE was measured at $T = 293.2$ K and 102.5 kPa. Before any experimental operation, the probability of azeotrope formation between lactic acid and diethyl ether was investigated. The measured tie-line points were regressed by the Othmer-Tobias [29] and Hand [30] equations and the reliability of experimental points was investigated. NRTL (non-random two-liquid) thermodynamic model of Renon and Prausnitz [31] was then applied to correlate the reliable points. Binary interaction parameters were optimized and validated parameters were used for the prediction of more tie-lines. The extraction ability of DEE as an extracting agent of the lactic acid was judged using the calculation of distribution coefficients (D) and separation factors (S).

EXPERIMENTAL

Materials

Diethyl ether was prepared from Merck while L-(+)-

lactic acid was purchased from Chem-Lab Company. The weight fraction purities of the used chemicals were of 0.99 and 0.85, orderly. Diethyl ether does not need further purification but lactic acid could not be used directly for preparation of the aqueous solution and needs treatment. All aqueous feed solutions (prepared from mixing water and lactic acid) were boiled for 10 h under reflux before addition of diethyl ether. Lactic acid molecules form dimers in concentrated solutions (about 25% of the total concentration) and the mentioned treatment hydrolyses the dimers. The resulting solutions were applied for preparation of aqueous phases for the extraction studies. Aqueous feeds containing lactic acid were titrated with 0.5 M NaOH to determine the acid concentration in initial feed. Double distilled water (conductivity < 0.9 $\mu\text{s cm}^{-1}$) was prepared in the laboratory of Kimia Teyf Khazar company and applied throughout all experiments.

Apparatus and Procedure

The Karl-Fisher titrations were performed by a Metrohm-870 KF Titrino plus Karl-Fisher titrator. The temperature of the experiments was kept constant with an accuracy of ± 0.1 K and a Testo-735 digital thermometer was used to check the temperature. All the weightings were done *via* a Precisa electronic analytical balance (model LS120A) with an accuracy of ± 0.0002 g. A Brand Transferpette micropipette with an accuracy of ± 0.001 ml was used for cloud point titration.

Solubility data for determination of biphasic region were obtained by cloud-point method [32]. In this method, two miscible components with different weight fractions were visually titrated by third immiscible component. Water-LA and DEE-LA were miscible pairs that were titrated with DEE and water, respectively. End point in cloud point titration is an abrupt change from a homogeneous to a heterogeneous mixture. A water-jacketed glass cell was used to titrate mixtures and the mixtures were magnetically blended together. The averages of three-times repetition of the cloud point titrations were recorded as the solubility data and inserted in Table 1. The standard uncertainty of solubility points was estimated to be better than ± 0.005 .

Tie-line point measurements of the ternary system (water + lactic acid + diethyl ether) were carried out at $T = 293.2$ K. Six feeds containing water, lactic acid and

Table 1. Solubility Ccurve Data in Mass Fractions (w_i) for (Water + Lactic Acid + Diethyl Ether) at $T = 293.2 \text{ K}^a$

w_1	w_2	w_3	w_1	w_2	w_3
Right side of diagram			Left side of diagram		
0.937 ^b	0.000	0.063	0.344	0.384	0.272
0.882	0.042	0.076	0.308	0.360	0.332
0.807	0.099	0.094	0.263	0.300	0.437
0.747	0.145	0.108	0.223	0.242	0.535
0.706	0.176	0.118	0.167	0.173	0.660
0.669	0.203	0.128	0.103	0.098	0.799
0.626	0.237	0.137	0.079	0.067	0.854
0.588	0.267	0.145	0.067	0.053	0.880
0.549	0.296	0.155	0.054	0.036	0.910
0.500	0.333	0.167	0.040	0.018	0.942
0.444	0.361	0.195	0.026 ^b	0.000	0.974
0.391	0.382	0.227	-	-	-

^aStandard uncertainties u are $u(T) = 0.1 \text{ K}$, $u(P) = 0.5 \text{ kPa}$ and $u(w) = 0.005$. ^bMutual solubilities.

diethyl ether were mixed for 2 h in a water-jacketed glass cell. After 2 h of settling, two layers formed that were completely clear. Lactic acid of organic phase (upper layer) was titrated for every 30 min after stopping the stirrer. After 2 h, no change was observed in LA concentration. Once reaching the equilibrium, upper (etheric) and lower (aqueous) layers were sampled for acid-base and Karl-Fisher titrations. It is worth noting that the solvent in upper layer is DEE while water is the solvent of lower phase.

The mass fractions of lactic acid in each layer (w_{21} for aqueous layer and w_{23} for etheric layer) were obtained by acid-base titration. The water content of the etheric (w_{13}) and aqueous (w_{11}) layers were achieved *via* Karl-Fisher method [33]. The mass fraction of diethyl ether (*i.e.* w_{31} and w_{33} for water and etheric layer) was achieved by the mass balance equation ($\sum w_i = 1$). The global standard uncertainty

of all tie-lines was better than ± 0.004 .

RESULTS AND DISCUSSION

Possibility of Azeotrope Formation

As we know, an azeotrope mixture has a fixed boiling point whose proportions could not be varied by ordinary distillation. So, formation of an azeotrope in a mixture complicates the purification process. Since in this study we aimed to purify lactic acid by diethyl ether, then, the possibility of azeotrope formation between lactic acid and diethyl ether was investigated using a UNIFAC predictive method [24]. The predictions results are plotted in Fig. 1. As can be seen from the figure, LA and DEE do not form any kind of azeotrope. The dotted red and blue lines do not meet each other in any point, then the studied binary mixture has no constant boiling point in any mole fraction of lactic acid.

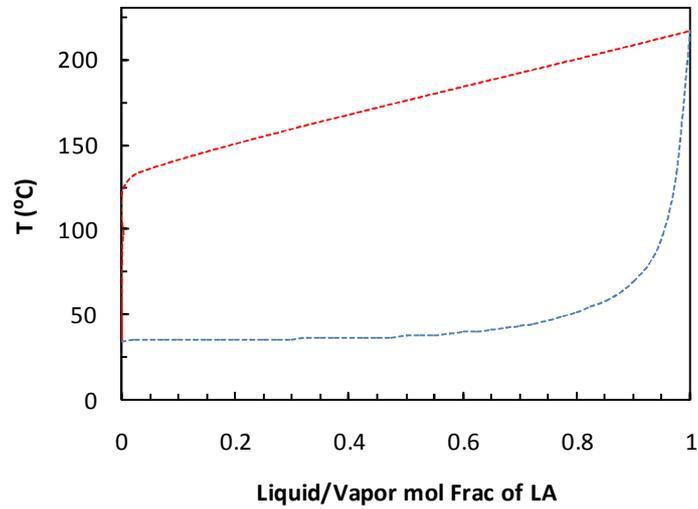


Fig. 1. Predicted results for the system of lactic acid-diethyl ether using UNIFAC model. Mole fraction of LA in: (dotted red line) vapor phase, and (dotted blue line) liquid phase.

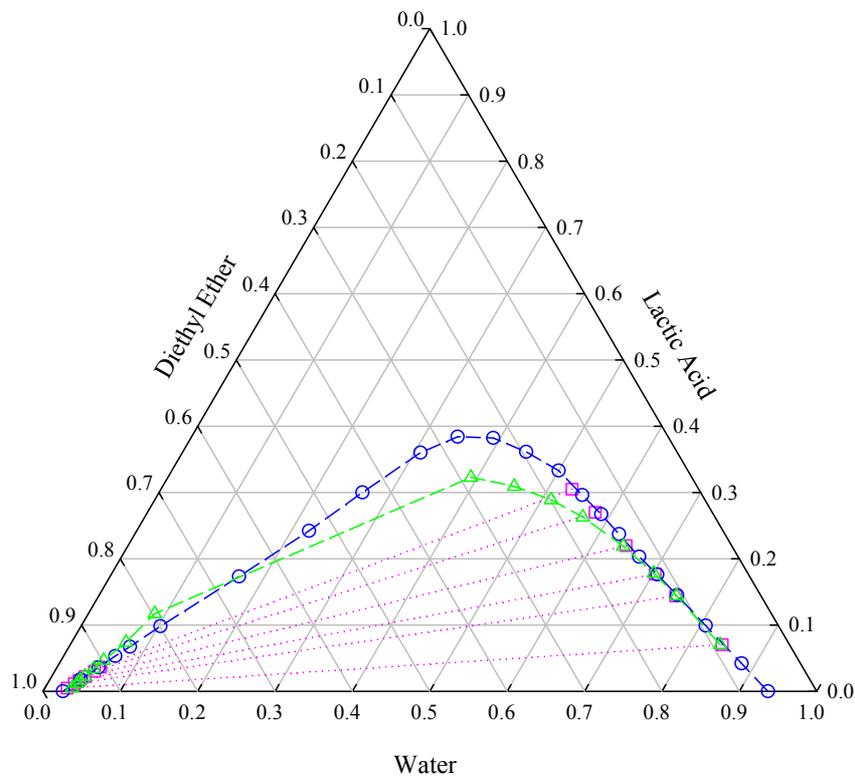


Fig. 2. Ternary phase diagram for LLE of [water (1) + lactic acid (2) + diethyl ether (3)] at $T = 293.2$ K; (\circ) obtained cloud points, (\square) experimental tie-lines, (Δ) NRTL calculated points ($\alpha = 0.3$).

Experimental LLE Results

Figure 2 shows the triangle diagram containing the measured tie-line points and LLE behavior of the system (water + lactic acid + diethyl ether) at $T = 293.2$ K and barometric pressure. Tie-line points in mass and mole fractions are also inserted in Table 2. Mole fractions were obtained from mass fractions using simple calculations as mole fractions were used in thermodynamic modeling and validation of obtained binary interaction parameters. Significant digits were reduced from 4 decimals to 3 because of using molecular weights with 3 decimals. Among three pairs of components, water-lactic acid and diethyl ether-lactic acid were completely miscible and the last pair (water-diethyl ether) had partial miscibility in each other. This performance could be attributed to the Type I behavior of LLE.

The quality and reliability of obtained tie-line points were checked by the Othmer-Tobias (Eq. (1)) [29] and Hand (Eq. (2)) [30] equations. Both equations focus on the simultaneous investigation of two of the three mass fractions. The equations are as follow:

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

$$\ln\left(\frac{w_{21}}{w_{11}}\right) = A' + B' \ln\left(\frac{w_{23}}{w_{33}}\right) \quad (2)$$

where A, B, A' and B' are the parameters of the Othmer-Tobias and the Hand equations, orderly. The Othmer-Tobias and the Hand plots, the related parameters and R squares are inserted in Figs. 3 and 4, respectively. As presented in the figures, the measured tie-line endpoints seems reliable in mass and mole fractions as all calculated R squares are greater than 0.98.

The selectivity of diethyl ether for extraction of lactic acid from water was investigated by calculating distribution coefficients of water ($D_1 = w_{13}/w_{11}$) and LA ($D_2 = w_{23}/w_{21}$) and separation factors ($S = D_2/D_1$ via the obtained tie-line endpoints in mass and mole fractions. The calculated factors are inserted in Table 2. Separation factors calculated by mole and mass fractions are the same but distribution coefficients (D_1 and D_2) have differences because molar weight of water is much less than that of lactic acid and

diethyl ether.

The diagram of computed separation factors and distribution coefficients of LA as a function of the mass fraction of the acid in aqueous layer is shown in Fig. 5. Although all separation factors in the concentration range of study are larger than 1 and LA could be effectively separated from the aqueous layer by diethyl ether, the quality of extraction decreases from separation factor point of view. Despite this, distribution coefficients regularly increase leading to less use of solvent and less environmental pollutions. In dilute aqueous solutions, the separation factors are higher, because the organic solvent is not saturated with lactic acid and in the more concentrated aqueous solutions, more LA molecules are transferred to organic layer causing the distribution coefficients increase point by point but LA molecules pull water molecules to them and this cause of decreasing of separation factors from dilute to concentrated aqueous solutions. Then, separation process is more effective in dilute aqueous solutions. The additional hydroxyl group in lactic acid has a strong effect on the value of separation factors and distribution coefficients. The -OH group in alpha carbon makes LA a polar acid rather than propionic and acetic acids. This additional group causes more hydrogen bonding between LA and water and decreases the values of both distribution coefficients and separation factors rather than linear short chain carboxylic acids.

Thermodynamic Modeling

Binary interaction parameters could be optimized by thermodynamic modeling when experimental data are available. The optimized binary parameters could be used for prediction of tie-line data especially in the studied biphasic range. In this study, the nonrandom two-liquid (NRTL) model of Renon and Prausnitz [31] was applied to correlate measured tie-lines and obtain binary parameters. The value of the non-randomness (α) was fixed in 0.2 and 0.3. Comparing the correlated data, the most reliable results were obtained in $\alpha = 0.3$. The correlated tie-lines of the studied system are tabulated in Table 3.

For optimization of the NRTL model and producing the binary interaction parameters, the objective function introduced by Sorensen [34] was used. The results of modeling are illustrated in Fig. 1. The optimum NRTL

Table 2. Measured Tie-line Points in Mass and Mole Fractions, Separation Factors (S), and Distribution Coefficients of LA (D₂) and Water (D₁) for (Water + Lactic Acid + Diethyl Ether) at T = 293.2 K^a

W ₁₁ OR X ₁₁	W ₂₁ OR X ₂₁	W ₁₃ OR X ₁₃	W ₂₃ OR X ₂₃	D ₁	D ₂	S
Aqueous phase			Organic phase			
Mass fractions						
0.8426	0.0704	0.0292	0.0047	0.035	0.067	1.93
0.7459	0.1438	0.0351	0.0114	0.047	0.079	1.68
0.7027	0.1767	0.0385	0.0164	0.055	0.093	1.69
0.6436	0.2197	0.0436	0.0223	0.068	0.102	1.50
0.5787	0.2701	0.0517	0.0302	0.089	0.112	1.25
0.5313	0.3049	0.0562	0.0364	0.106	0.119	1.13
Mole fractions						
0.960	0.016	0.110	0.004	0.115	0.221	1.93
0.931	0.036	0.130	0.008	0.140	0.236	1.68
0.916	0.046	0.142	0.012	0.155	0.262	1.69
0.893	0.061	0.158	0.016	0.177	0.266	1.50
0.864	0.081	0.184	0.022	0.213	0.266	1.25
0.841	0.096	0.198	0.026	0.235	0.266	1.13

^aStandard uncertainties u are u(T) = 0.1 K, u(P) = 0.5 kPa, u(^w) = 0.004.

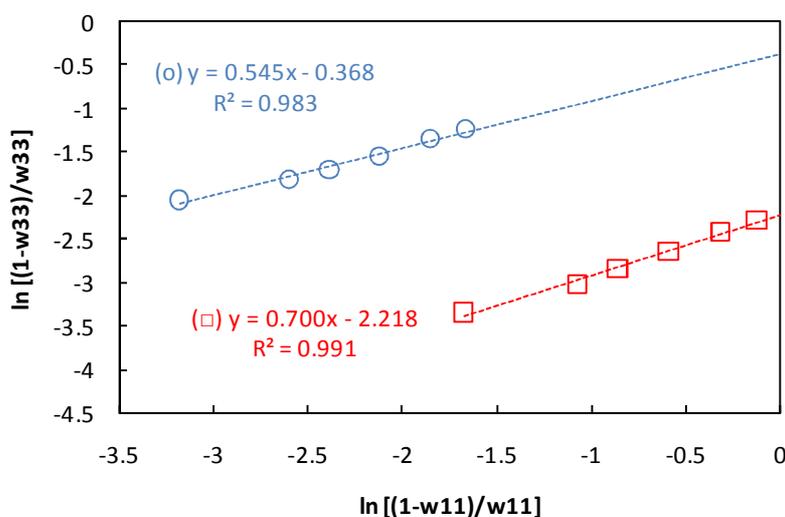


Fig. 3. The Othmer-Tobias plot of the [Water (1) + lactic acid (2) + diethyl ether (3)] ternary system at 293.2 K; (○) correlated by mole fractions, (□) correlated by mass fractions.

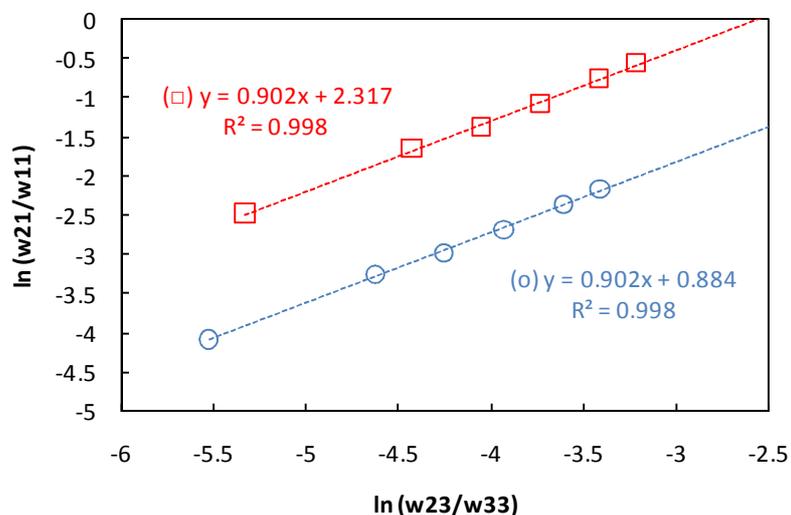


Fig. 4. The Hand plot of the [Water (1) + lactic acid (2) + diethyl ether (3)] ternary system at 293.2 K; (○) correlated by mole fractions, (□) correlated by mass fractions.

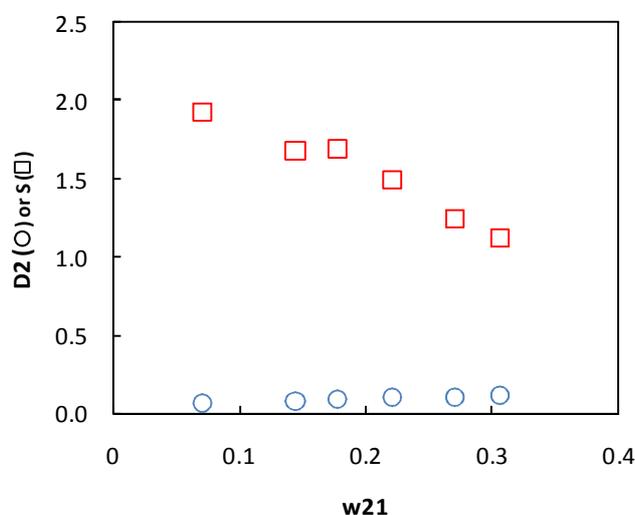


Fig. 5. Plot of the separation factor (S) and distribution coefficient of LA (D_2) as a function of mass fraction of the acid in the aqueous phase; (□) separation factor, and (○) distribution coefficient.

binary interaction parameters are given in Table 4. Obtained binary parameters are presented in two different forms of energy parameter (b_{ij}) and dimensionless parameter (τ_{ij}).

To evaluate the quality of modeling and the ability of obtained interaction parameters for prediction of tie-line points, in the first step, rmsd values (root-mean square

deviation) were calculated (Using Eq. (3)). The equation for calculation of rmsd values is as follow:

$$rmsd = \sqrt{\frac{\sum_{k=1}^n \sum_{j=1}^2 \sum_{i=1}^3 (W_{ijk}^{exp} - W_{ijk}^{cal})^2}{6n}} \quad (3)$$

In Eq. (3), n is the number of tie-line data and W_{ijk}^{exp} and

Table 3. The Calculated NRTL ($\alpha = 0.3$) Tie-line Data in Mass and Mole Fraction for (Water + Lactic Acid + Diethyl Ether) at T = 293.2 K

Correlated mass fractions				Correlated mole fractions			
W ₁₁	W ₂₁	W ₁₃	W ₂₃	X ₁₁	X ₂₁	X ₁₃	X ₂₃
0.840	0.070	0.035	0.005	0.959	0.017	0.126	0.004
0.747	0.144	0.038	0.012	0.933	0.036	0.136	0.008
0.700	0.178	0.040	0.016	0.915	0.048	0.144	0.012
0.640	0.219	0.043	0.023	0.893	0.061	0.154	0.016
0.566	0.263	0.049	0.034	0.866	0.076	0.169	0.022
0.512	0.289	0.055	0.047	0.847	0.085	0.180	0.027
0.840	0.070	0.035	0.005	0.959	0.017	0.126	0.004
0.747	0.144	0.038	0.012	0.933	0.036	0.136	0.008

Table 4. Correlated Results from the NRTL ($\alpha = 0.3$) Model and the Corresponding Binary Interaction Parameters (b_{ij} , b_{ji} , τ_{ij} and τ_{ji}) for the Ternary System

	b_{ij}^a/K	b_{ji}/K	τ_{ij}^a	τ_{ji}
1-2	-3494.03	936.76	-11.9169	3.194957
1-3	971.60	430.79	3.31377	1.469282
2-3	-172.37	-1683.89	-0.58791	-5.74315

^a $b_{ij} = \frac{(g_{ij} - g_{jj})}{R}$, ^b $\tau_{ij} = \frac{(g_{ij} - g_{jj})}{RT}$.

Table 5. The rmsd Values for Correlated Mass and Mole Fractions of Tie-line Data

Types of rmsd values	For correlated mass fractions	For correlated mole fractions
Overall rmsd%	0.88	0.72
Aqueous phase rmsd%	0.83	0.25
Organic phase rmsd%	0.29	0.68

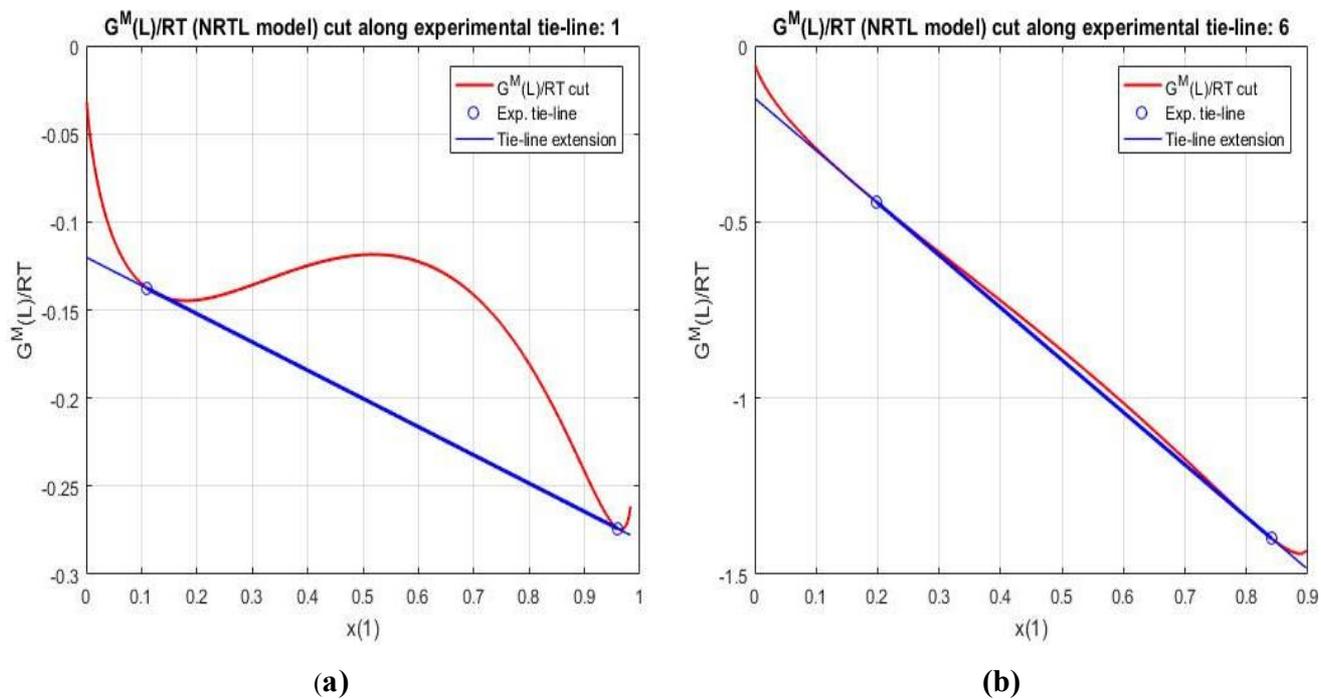


Fig. 6. Plot of $G^M(L)/RT$ versus mole fraction of water; (a) tie-line # 1 and (b) tie-line # 6.

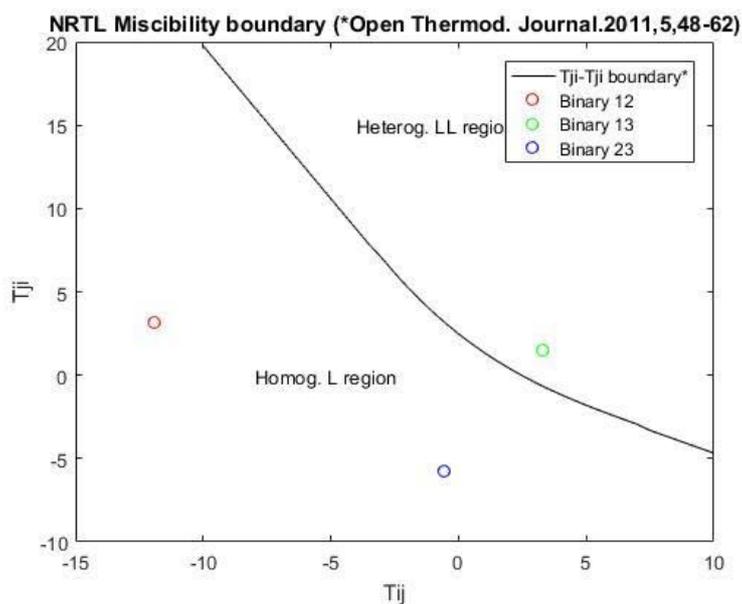


Fig. 7. Plot of miscibility boundary estimated from optimized interaction parameters for the system [water (1) + LA (2) + DEE (3)].

W_{ijk}^{cal} express the measured and correlation results. The subscript i, j and k refer to components, phases and tie-line data ($k = 1, 2, \dots, n$), respectively. The rmsd values of NRTL model for the investigated system at $T = 293.2$ K are listed in Table 5. The rmsd values prove the quality of thermodynamic modeling, indicating an appropriate fitting. Overall rmsd values for mass and mole fractions are lower than 1%. The rmsd values for aqueous and organic layers were also calculated. For correlated mass fractions, tie-line data of organic phase show closer results to the experimental points while for the correlated mole fractions, aqueous phase compositions show better results.

The second step to ensure the quality of modeling is using a graphical user interface software developed by Reyes-Labarta [35,36]. In this software, compositions must be in mole fractions and dimensionless binary interaction parameters (τ_{ij}) should be applied. Using this software, optimized binary interaction parameters could be validated by calculation of excess Gibbs energy from binary parameters. If the binary parameters are coherent with experimental data, the plot of $G^M(L)/RT$ against the mole fraction of any component would be tangent. Figures 6a and 6b are example of G^M plots for tie-lines 1 and 6. As can be seen from the figures, both plots show that the used binary interaction parameters are coherent. The other test for ensuring the accuracy of binary parameters is using the miscibility boundary plot [37]. Figure 7 shows the miscibility region estimated by optimized binary interaction parameters. As can be seen from the figure, water-LA and LA-DEE pairs are in the homogeneous part while water-DEE pair is in the heterogeneous part. This prediction is compatible to the experimental results for the binary mixtures and proves the validity of interaction parameters.

CONCLUSIONS

Experimental LLE data for the (water + LA + DEE) ternary system were obtained at $T = 293.2$ K and barometric pressure. The ternary system shows type-1 behavior of the LLE. The NRTL model was used to correlate the experimental tie-line data and to calculate the phase compositions of the investigated mixtures. The thermodynamic model gave reliable results for the studied

system. The separation factors and distribution coefficients for the etheric solvent applied in this work were determined. The experimental results showed that the separation factors for DEE are larger than one for the studied acid concentration range in this work, which indicates the ability of the solvent to purify the acid from water. Binary interaction parameters were validated and showed excellent results.

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