

Exploring Phase Behavior and Thermodynamic Modeling of Ternary System Water + Lactic Acid + Propylene Carbonate at Different Temperatures

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This study presents experimental measurements of tie-line and solubility points for the ternary mixtures (water + lactic acid + propylene carbonate) at temperatures of 298.2 and 308.2 K and 101.7 kPa. HPLC measurements were employed to determine the mass fractions of solvent and water layers. The cloud point method was utilized to verify the Type-1 liquid-liquid equilibrium (LLE) behavior of the studied system. To ascertain the reliability of the tie-line points, Othmer-Tobias and Hand plots were analyzed. The thermodynamic correlation of tie-line data was achieved using the NRTL model, and the resulting binary interaction parameters were rigorously validated. Excellent agreement was observed between experimental and correlated data, with a root-mean-square deviation (rmsd) of only 0.3%. The study further explored activity coefficients calculated *via* the NRTL equation, revealing significant negative deviations for lactic acid and positive deviations for water and propylene carbonate from Raul's law. The extraction quality of propylene carbonate was investigated through the figuring of distribution coefficients and separation factors across the non-miscible region. Interestingly, separation factors increased from 1.07 to 1.11 when the lactic acid mass fraction in the aqueous layer increased from 0.036 to 0.105. However, distribution coefficients increased from 0.12 to 0.18 in the same investigated area. The study concludes that the extraction of the acid is viable in all examined feeds at 298.2 K.

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

INTRODUCTION

Carboxylic acids are commonly obtained through chemical synthesis or fermentation processes, resulting in dilute acid solutions. Solvent extraction is a traditional technique used for purifying and separating acids from water. Various solvents can be used for the separation process, provided their parameters are suitable. Liquid-liquid equilibrium (LLE) data obtained from such processes can also aid in designing separation processes, thermodynamic modeling, and predicting similar systems [1-8].

2-Hydroxypropanoic acid, or lactic acid (LA), a carboxylic acid that dissolves in water, is commonly utilized in the food industry and has many pharmaceutical applications. Polylactic acid, an environmentally friendly polymer, is derived from pure lactic acid. In the fermentation

process of LA, the pH of the water-based solution decreases, resulting in a slower production of acid. Consequently, removing lactic acid from the fermentation broth improves the overall production yield [9-13].

Numerous solvents have been examined in the quest to separate lactic acid from the water-rich phase [14-20]. However, the exploration of solvents for this purpose has been primarily focused on a restricted range of categories, with alcohols being the main focus.

Propylene carbonate or 4-methyl-1,3-dioxolan-2-one (PC) has not been explored as an extractant for separating lactic acid from the aqueous phase, yet. However, considering its advantageous characteristics, the PC seems to be a promising option for this purpose. In various solvent extraction processes, propylene carbonate has already demonstrated successful separation of different chemical compounds from water [21-27]. The unique properties of PC, such as a higher boiling point than water and a suitable

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density difference, make it an attractive solvent for separation processes. In addition, propylene carbonate possesses desirable attributes such as low toxicity, low vapor pressure, low viscosity, and low flammability. These parameters play a crucial role in solvent selection, as they help optimize the final prices of LLE extraction [9]. It is worth noting that, the boiling points of propylene carbonate (242 °C) and lactic acid (122 °C) differ significantly, allowing for separation through the distillation process. Subsequently, following a successful liquid-liquid extraction (LLE) separation, distillation processing can be employed to recover propylene carbonate for reuse.

The current research involved conducting experiments to measure the liquid-liquid equilibrium (LLE) data of the ternary system consisting of water, LA, and PC. These measurements were carried out at temperatures of 298.2 K and 308.2 K, under atmospheric pressure of 101.7 kPa. The purpose of this study was to gather data on the phase behavior of the system at different temperatures. The reliability of the obtained tie-line points was confirmed using the Othmer-Tobias and Hand [28] equations. The NRTL (non-random two-liquid) model of Renon and Prausnitz [29] was applied to correlate the tie-line data and obtain binary interaction parameters, which were subsequently validated and used for predicting additional tie-lines. The study also investigates the extraction efficiency of propylene carbonate as an extracting agent for lactic acid by calculating distribution coefficients and separation factors.

EXPERIMENTAL

Chemicals

The chemical compounds used in this research are

described in Table 1. Propylene carbonate from Merck and L-(+)-lactic acid from Chem-Lab Company were used for the study. Propylene carbonate did not require further purification, while lactic acid needed treatment before preparation of the aqueous solution because dense aqueous solutions of lactic acid (L-LA) typically consist of oligomers, which could influence the phase equilibrium and the investigated liquid-liquid extraction (LLE). Therefore, it is essential to perform hydrolysis on the oligomers to convert them into monomers prior to preparing the mixtures [19]. All aqueous feed solutions were boiled under reflux for 10 hours prior to the addition of propylene carbonate to hydrolyze the dimers formed by lactic acid molecules in concentrated solutions.

Oligomers are often present in dense lactic acid (L-LA) aqueous solutions, which can have an impact on the phase balance and the studied liquid-liquid equilibrium (LLE). Therefore, it is necessary to hydrolyze these oligomers into monomers before preparing mixtures. However, it has been reported that lactic acid solutions with low concentrations (less than 20 wt%) only contain LA monomers. The supplier stated that the concentration of untreated lactic acid in water ranges from 88-92%. However, the presence of oligomers may cause a decrease in the actual concentration of the acid. By conducting an acid-base titration, it was determined that the mass percent of unhydrolyzed L-LA is 78 wt% in water solution. To achieve the ideal conditions for hydrolyzing the oligomers, a preliminary test solution was created by diluting the original L-LA aqueous solution with water. Specifically, a volume of 20 ml of untreated L-LA aqueous solution was diluted to 100 ml. The resulting diluted solution, at a ratio of 1:5, was then heated under reflux at a temperature of 90 °C for a duration of 10 h to facilitate the hydrolysis of the

Table 1. Specifications of the Chemicals Used in this Study

Chemical	Supplier	CAS number	Mass fraction purity	Analysis method ^a	Purification method
L-(+)-Lactic acid	Chem-Lab Company	79-33-4	88-92	GC	Reflux
Propylene carbonate	Merck	108-32-7	99.7	GC	-
Water	-	7732-18-5	> 99.9	Conductometry	-

^aStated by the supplier. The purity of the solvents was confirmed by gas chromatography (GC).

oligomers. The hydrolysis process, including both the temperature and time, displayed a satisfactory level of efficiency in this particular study.

For all experiments, high-performance liquid chromatography (HPLC)-grade water was utilized. The temperature was carefully controlled and maintained at ± 0.1 K using a Testo-735 digital thermometer. This ensured precise temperature control throughout the experimental process. The solubility curves were determined by titrating mixtures of water and PC with LA until the turbidity disappeared. This process was used to obtain the central part of the curves. In the regions where the curve and the sides of the triangle are close and have similar slopes, binary mixtures of either water + LA or PC + LA were titrated against the third component. The transition from homogeneity to cloudiness was observed during this titration process. The weightings were performed using a Precisa electronic analytical balance (model LS120A) with an accuracy of ± 0.0002 g. To determine the endpoints of the tie lines, the conjugate phases were independently analyzed to ensure they were in equilibrium. Mixtures containing known masses of water, LA, and PC within the heterogeneous region were introduced into an extraction cell. The mixture was vigorously stirred for a minimum of 4 h and then left undisturbed for 4 h to allow the formation of distinct raffinate (aqueous) and organic (solvent) layers. These layers were then analyzed to determine the end points of the tie-lines. A Brand Transferpette micropipette, accurate to ± 0.001 ml, was utilized for cloud point titration. Density measurements were carried out using a DA210 (Kyoto electronic) density meter. Given the elevated vapor pressure of the chemicals used in this study, the measurements at the endpoint remain unaffected by variations in climate conditions such as atmospheric pressure changes. Local meteorological data was utilized to document the environmental pressure throughout the experiments. The pressure applied in this study was the atmospheric pressure changed to 101.7 kPa.

HPLC Measurements

Mutual solubilities of the binary system (water + propylene carbonate) and tie-line point measurements of the ternary system (water + lactic acid + propylene carbonate) were conducted at 298.2 K and 308.2 K, with the mass fractions of lactic acid and propylene carbonate in each layer

obtained through High-Performance Liquid Chromatography (HPLC). The Young Lin HPLC, specifically the YL Acme 9000 model, equipped with a UV-visible detector (UV-Vis), was utilized. High-performance liquid chromatography (HPLC) grade methanol was employed for the preparation of the internal standard. The separation of organic compounds from both the organic and aqueous phases was carried out using a Teknokroma Brisa C18 column (15 cm \times 4.6mm i.d. 5 μ m). The temperature of the column was maintained at 298.2 K temperature. The mobile phase (MP) consisted of a mixture of HPLC grade water, methanol, and acetonitrile in a ratio of 60:30:10 (v/v/v), while the pH of the MP was consistently adjusted to 3 using orthophosphoric acid with a mass purity of 85%. The flow rate was set at 1 ml min^{-1} , and the detection wavelength was set at 230 nm. Additionally, a fixed injection volume of 20 μ l was used for all samples. The retention times for lactic acid (LA) and propylene carbonate were observed to be 1.93 and 10.53 min, respectively. All injections were repeated three times. The mass fraction of water was determined using the mass balance equation ($w_1 + w_2 + w_3 = 1$).

RESULTS AND DISCUSSION

Solubility Data

The phase boundary data to identify the biphasic region were acquired through the cloud-point method. This involved visually titrating two miscible components with varying weight fractions using a third immiscible component. The average of three repetitions of the cloud point titrations was recorded as the solubility data. The solubility data were recorded as the average of three repetitions of cloud point titrations and subsequently inserted into Table 2. Data of the table are presented in mass fraction and w_1 , w_2 and w_3 are mass fractions of water, LA, and PC, respectively. The estimation of standard uncertainties of recorded solubility data (determined through the utilization of Eq. (1)) was better than ± 0.0069 and were calculated using the following equation for each mass fraction:

$$s(w_i) = \left(\frac{\sum_{k=1}^n (w_{i,k} - \bar{w}_{i,k})}{n(n-1)} \right)^{1/2} \quad (1)$$

In this context, $w_{i,k}$, $\bar{w}_{i,k}$, and n denote the mass fraction,

average value of the measurement, and the overall count of measurements, respectively.

After calculating the uncertainties of mass fractions, the uncertainty of each component is estimated by averaging the calculated uncertainties of its mass fractions in both phases using the following equation:

$$u(w_i) = \frac{\sum s(w_i)}{2 \times 6 \times 2} \quad (2)$$

The values in the denominator are from 2 systems, 6 tie lines, and 2 phases, for each component.

Among the three distinct component pairs, namely water-lactic acid and propylene carbonate-lactic acid, complete miscibility was exhibited, signifying a seamless blend, while the final pairing of water and propylene carbonate displayed partial miscibility with each other. This particular behavior aligns with the characteristics denoted as Type I within the liquid-liquid equilibrium paradigm.

Validate the HPLC Measurements

To validate the HPLC measurements, a graphical comparison was made between the mutual solubilities obtained through the HPLC method and the corresponding

Table 2. The Phase Boundary Data in Mass Fractions (w_i) for (water (1) + Lactic Acid (2) + Propylene Carbonate (3)) at $T = 298.2$ K and 308.2 K and 101.7 kPa^a

w_1	w_2	w_3	w_1	w_2	w_3
The left side of the diagram			The right side of the diagram		
<i>T = 298.2 K</i>					
0.0789	0.0000	0.9211 ^b	0.4765	0.1260	0.3975
0.1051	0.0205	0.8744	0.5488	0.1202	0.331
0.1414	0.0466	0.8120	0.6156	0.1105	0.2739
0.1623	0.0616	0.7761	0.6678	0.0919	0.2403
0.1903	0.0810	0.7287	0.7226	0.0595	0.2179
0.2163	0.0872	0.6965	0.7762	0.0279	0.1959
0.3225	0.1129	0.5646	0.8136	0.0000	0.1862 ^b
0.3750	0.1250	0.5000			
<i>T = 308.2 K</i>					
0.7573	0.0000	0.2427 ^b	0.3334	0.1027	0.5639
0.7016	0.0373	0.2611	0.3044	0.0972	0.5984
0.6629	0.0603	0.2768	0.2659	0.0868	0.6473
0.6199	0.0813	0.2988	0.2105	0.0718	0.7177
0.5761	0.0938	0.3301	0.1832	0.0624	0.7544
0.5387	0.1023	0.3590	0.1588	0.0492	0.7920
0.4985	0.1083	0.3932	0.1356	0.0333	0.8311
0.4552	0.1092	0.4356	0.1234	0.0263	0.8503
0.3992	0.1120	0.4888	0.1101	0.0181	0.8718
0.3658	0.1092	0.5250	0.1047	0.0155	0.8798
			0.1022	0.0104	0.8874
			0.1002	0.0055	0.8943
			0.0991	0.0000	0.9009 ^b

^aStandard uncertainties u are $u(T) = 0.1$ K, $u(P) = 0.5$ kPa and $u(w) = 0.0053$. ^bMutual solubilities measured by HPLC; $u(w) = 0.0041$.

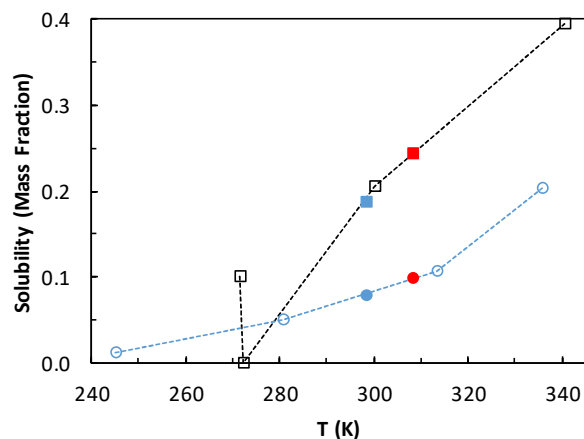


Fig. 1. Mutual solubilities of water and propylene carbonate in different temperatures; dashed lines: obtained from the literature [30] and HPLC measurements: (○) water in PC and (□) PC in water, blue and red filled are at 298.2 and 308.2 K, respectively.

data from the literature. Figure 1 illustrates this comparison. The calculated global standard uncertainty for all tie-lines, determined using Eq. (1), exceeded ± 0.0036 .

As depicted in the figure, there is a slight variation between the literature data and the HPLC measurements, confirming the accuracy of the method applied for measuring propylene carbonate (PC) in both phases. The validation of lactic acid (LA) HPLC measurements was performed by comparing the HPLC data with acid-base titration, yielding excellent agreement between the results. Moreover, the HPLC method enables the simultaneous measurement of both PC and LA, thereby reducing measurement uncertainties.

Experimental Tie-Line Points

Figures 2a and 2b illustrate a triangular diagram that encompasses the empirically derived tie-line coordinates, showcasing the liquid-liquid equilibrium (LLE) characteristics inherent to the examined systems comprised of water, lactic acid, and propylene carbonate, all operating under the conditions of $T = 298.2$ K and 308.2 K and prevailing barometric pressure (101.7 kPa). The tabulated data presented in Table 3 involves both mass and mole fractions pertaining to the tie-line points. In the table, w_{11} ,

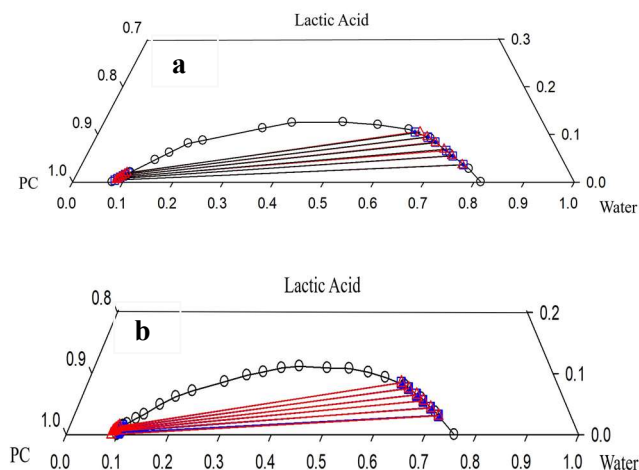


Fig. 2. Ternary phase diagram (mass fraction) for (water + lactic acid + propylene carbonate) at (a) $T = 298.2$ K and (b) $T = 308.2$ K and 101.7 kPa; (○) cloud point data, (□) experimental tie-line points, (Δ) NRTL correlated points ($\alpha = 0.1$).

w_{21} and w_{31} are mass fractions of water, lactic acid, and propylene carbonate in aqueous phase and w_{13} , w_{23} , and w_{33} are mass fractions of water, LA and PC in the organic phase. For the purpose of thermodynamic modeling and the validation of binary interaction parameters, the mole fractions were computed from the mass fractions through elementary calculations, given their utilization in this context. Notably, the precision of numerical values has been refined from four decimal places to three, due to the application of molecular weights that are expressed to three decimal places.

To ensure the accuracy of water mass fractions obtained from the mass balance equation, the Karl-Fischer titration method was also used to measure the water content of separated solutions. The results (Supplementary data file) showed that there are small differences between two series of mass fractions (less than 2%).

Based on the figures presented, it is evident that the tie-line slopes indicate a preference for water in both temperatures. This indicates that lactic acid has a higher affinity to dissolve in water compared to propylene carbonate. As a result, the distribution coefficients of LA are below one.

Table 3. Tie-line Data in Mass and Mole Fractions for (Water + Lactic Acid + Propylene Carbonate) at 298.2 K and 308.2 K and 101.7 kPa^a

<i>T</i> (K)	<i>w</i> ₁₁ or <i>x</i> ₁₁	<i>w</i> ₂₁ or <i>x</i> ₂₁	<i>w</i> ₃₁ or <i>x</i> ₃₁	<i>w</i> ₁₃ or <i>x</i> ₁₃	<i>w</i> ₂₃ or <i>x</i> ₂₃	<i>w</i> ₃₃ or <i>x</i> ₃₃
	<i>Aqueous phase</i>			<i>Organic phase</i>		
	<i>Mass Fractions</i>					
	0.7608	0.0364	0.2028	0.0819	0.0042	0.9139
	0.7304	0.0549	0.2147	0.0861	0.0073	0.9066
	0.7118	0.0662	0.2220	0.0900	0.0101	0.8999
	0.6811	0.0840	0.2349	0.0940	0.0127	0.8933
	0.6609	0.0943	0.2448	0.0970	0.0163	0.8867
	0.6299	0.1051	0.2650	0.1017	0.0189	0.8794
298.2	<i>Mole Fractions</i>					
	0.946	0.009	0.045	0.336	0.003	0.661
	0.937	0.014	0.049	0.348	0.006	0.646
	0.931	0.017	0.051	0.359	0.008	0.633
	0.921	0.023	0.056	0.370	0.010	0.620
	0.914	0.026	0.060	0.378	0.013	0.609
	0.903	0.030	0.067	0.390	0.015	0.595
	<i>Mass Fractions</i>					
	0.7104	0.0319	0.2577	0.1001	0.0033	0.8966
	0.6887	0.0445	0.2668	0.1009	0.0049	0.8942
	0.6685	0.0557	0.2758	0.1016	0.0073	0.8911
	0.6508	0.0656	0.2836	0.1024	0.0095	0.8881
	0.6301	0.0762	0.2937	0.1029	0.0117	0.8854
	0.6112	0.0854	0.3034	0.1035	0.0142	0.8823
308.2	<i>Mole Fractions</i>					
	0.9320	0.0084	0.0597	0.3865	0.0026	0.6109
	0.9248	0.0120	0.0632	0.3886	0.0038	0.6077
	0.9179	0.0153	0.0668	0.3903	0.0056	0.6041
	0.9115	0.0184	0.0701	0.3923	0.0073	0.6004
	0.9038	0.0219	0.0743	0.3935	0.0089	0.5975
	0.8964	0.0250	0.0785	0.3950	0.0108	0.5942

^aStandard uncertainties *u* are *u*(*T*) = 0.1 K, *u*(*P*) = 0.5 kPa, *u*(*w_w*) = 0.0021, *u*(*w_{LA}*) = 0.0024, *u*(*w_{PC}*) = 0.0033.

Investigation of Tie-lines Quality

The integrity and dependability of the acquired tie-line data were rigorously assessed employing two distinct equations, namely the Othmer-Tobias equation (Eq. (3)) and the Hand equation (Eq. (4)) [28]. These equations are tailored to facilitate a comprehensive analysis of two out of the three prevailing mass fractions within the system. The formulations of these equations are presented below:

$$\ln\left(\frac{(1-w_{33})}{w_{33}}\right) = A + B \ln\left(\frac{(1-w_{11})}{w_{11}}\right) \quad (3)$$

$$\ln\left(\frac{w_{21}}{w_{11}}\right) = A' + B' \ln\left(\frac{w_{23}}{w_{33}}\right) \quad (4)$$

Here, the symbols *A*, *B*, *A'*, and *B'* denote the respective parameters specific to the Othmer-Tobias and Hand

equations, in that sequence. The results of linear regressions have been tabulated in Table 4. As can be seen, R square values could prove the quality of measured data.

Table 4. Results of Regressions Using Othmer-Tobias and Hand Equations

Equation	T (K)	A or A'	B or B'	R^2
Othmer-	298.2	0.147	2.047	0.988
Tobias	308.2	-1.866	0.332	0.996
Hand	298.2	-0.667	0.520	0.993
	308.2	1.141	0.753	0.997

Evaluation of Separation Efficiency

The discriminative ability of propylene carbonate in extracting lactic acid from water was subjected to a comprehensive assessment through the computation of distribution coefficients for water (Eq. (5)) and lactic acid (Eq. (6)), as well as separation factors (Eq. (7)). These evaluations were performed employing the acquired tie-line extremities, presented in mass fractions. The outcome of

these computations has been meticulously incorporated within Table 5.

$$D_1 = \frac{w_{13}}{w_{11}} \quad (5)$$

$$D_2 = \frac{w_{23}}{w_{21}} \quad (6)$$

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

In order to assess the extraction capability of PC in extracting LA from water, calculations were performed to determine the solute distribution coefficient (D_2), water distribution coefficient (D_1), and separation factor (S). These calculations were conducted to evaluate the efficiency of PC in separating LA from water.

The table indicates that all separation factors are close to one, confirming the feasibility of the separation process for all examined feed concentrations. Density measurements have also been included in the table, revealing that the organic and aqueous phases can readily separate due to their significantly different densities.

The larger D_2 is, the less solvent is used for extraction, but it is not necessary for its value to be greater than one. S is

Table 5. Feed Fractions (f), Distribution Coefficients (D), Separation Factors (S), and Densities (d) of Aqueous and Organic Layers at $T = 298.2$ K and $T = 308.2$ K and 101.7 kPa^a

f_1	f_2	D_1	D_2	S	$d_{aq}(kg\ m^{-3})$	$d_{org}(kg\ m^{-3})$
$T = 298.2\ K$						
0.486	0.024	0.108	0.115	1.072	1055.2	1182.7
0.478	0.037	0.118	0.133	1.128	1068.0	1183.2
0.473	0.045	0.126	0.153	1.207	1076.0	1183.6
0.464	0.059	0.138	0.151	1.095	1089.1	1183.9
0.458	0.067	0.147	0.173	1.178	1097.3	1184.9
0.452	0.077	0.161	0.180	1.114	1108.0	1185.1
$T = 308.2\ K$						
0.489	0.022	0.141	0.103	0.734	1053.2	1167.0
0.482	0.030	0.147	0.110	0.752	1066.7	1168.3
0.475	0.039	0.152	0.131	0.862	1073.2	1169.5
0.469	0.048	0.157	0.145	0.920	1087.3	1170.1
0.463	0.056	0.163	0.154	0.940	1094.3	1171.7
0.458	0.065	0.169	0.166	0.982	1104.5	1172.4

^aStandard uncertainty in density measurements $u(d) = 1.5\ kg\ m^{-3}$.

a factor that must be greater than one to complete the extraction.

The difference in densities between the phases can contribute to a reduction in resting time. In this study, the resting time was approximately half an hour, which is significantly shorter (about 4 to 8 times) compared to other studies on liquid-liquid extraction (LLE) [14-26]. This property of propylene carbonate is crucial as it facilitates the separation process. Figure 3 illustrates how the resting time was determined by analyzing the mass fraction of lactic acid in both the aqueous and organic phases simultaneously. Data of the figure were obtained using a preliminary test and the acid concentrations were measured by acid-base titration.

Samples were taken from both aqueous and organic phases in 10-minute intervals and titrated with NaOH 0.1 M solution. Then, using the tie-lines and mass fraction of LA values plotted from the results, it could be found the time required for the mixture to rest. This will be continued until there is no change in the mass fraction of LA and this is where the equilibrium zone has reached. Then, it could be considered that time as the balance, where it has been allocated about four times the obtained time to the rest of the mixture to be sure (4 h in this study).

Figures 4a and 4b depict the graphical representation of computed separation factors and distribution coefficients pertaining to lactic acid (LA) as a function of the mass

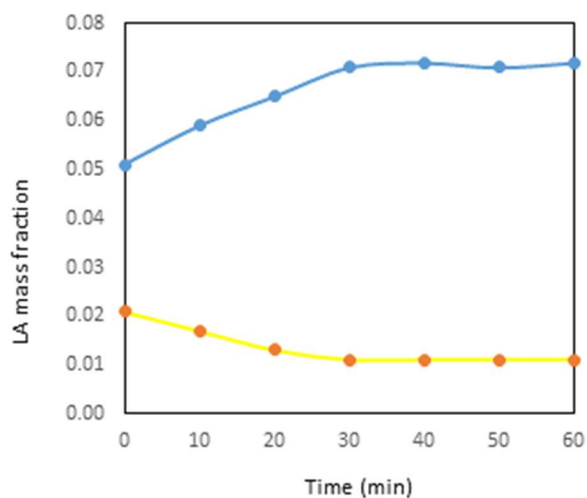


Fig. 3. Calculation of resting time using LA mass fraction measurements.

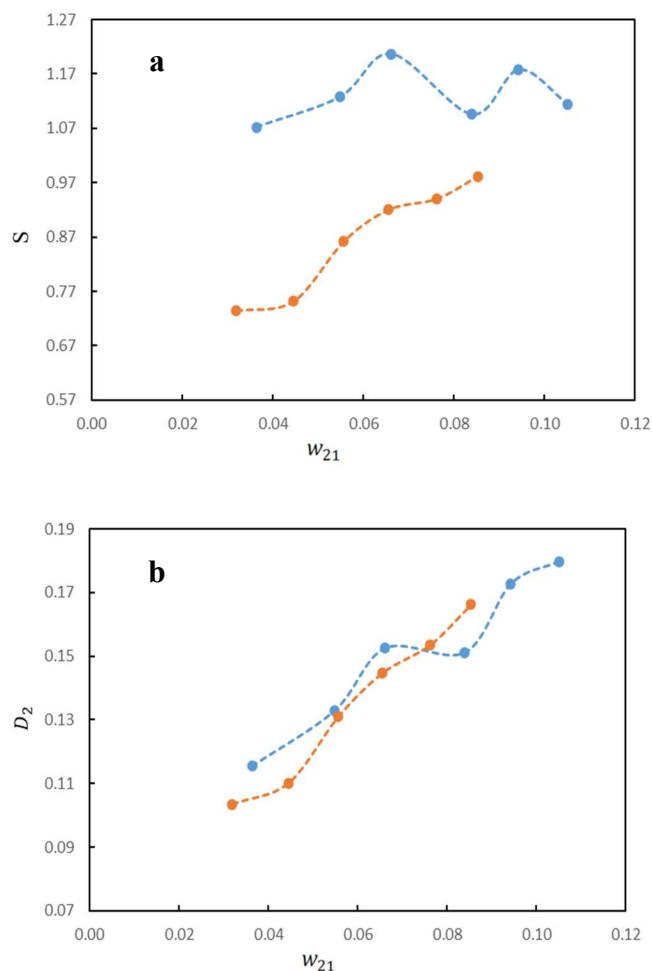


Fig. 4. Plots of (a) the separation factor (S) and (b) the distribution coefficient of LA (D_2) as a function of the mass fraction of the acid in the aqueous phase; (●) 298.2 K, (●) 308.2 K.

fraction of the acid within the aqueous layer. Within the concentration range under investigation, it becomes evident that all separation factors exceed unity, thereby indicating the potential efficacy of propylene carbonate in the separation of LA from the aqueous layer. Nevertheless, it is worth noting that the extraction quality experiences a diminishment when scrutinized from the perspective of separation factors.

Conversely, distribution coefficients exhibit a consistent upward trend, resulting in the utilization of less solvent and the mitigation of environmental contamination. In aqueous solutions of lower concentration, separation factors assume

higher values, owing to the organic solvent remaining unsaturated with lactic acid molecules. In contrast, within more concentrated aqueous solutions, an intensified transfer of LA molecules to the organic layer occurs, subsequently leading to the incremental rise of distribution coefficients. However, it's crucial to recognize that LA molecules tend to attract water molecules toward them, thereby contributing to the decline of separation factors as the concentration of aqueous solutions progresses from dilute to concentrated states. This underscores the heightened effectiveness of the separation process within dilute aqueous solutions.

The discernible impact of the additional hydroxyl group in lactic acid is of paramount significance in influencing the magnitude of separation factors and distribution coefficients. This hydroxyl (-OH) group positioned on the alpha carbon renders lactic acid a polar acid, distinguishing it from propionic and acetic acids, which are linear short-chain carboxylic acids. Consequently, the presence of this supplementary functional group engenders a greater propensity for hydrogen bonding interactions between lactic acid and water, culminating in the reduction of both distribution coefficients and separation factors.

The findings from D_2 and S indicate that lactic acid molecules migrate to the organic phase, while the solvent phase restricts the entry of water molecules into the propylene carbonate layer. Similar results have been observed in numerous liquid-liquid extraction (LLE) studies, particularly those involving relatively polar extracts and solvents.

Figures 5a and 5b show the distribution coefficients and separation factors of previously studied solvents in (LA+ Solvent + Water) system [14,15,19] in comparison with propylene carbonate. As can be seen, PC molecule has similar behavior like 2-butanol in the presence of LA in the aqueous system [15].

Lactic acid is a polar molecule and tends to dissolve in water as a polar solvent, while the extractant does not have to be as polar as water to form a biphasic region. As seen in Fig. 5a, the D_2 values are smaller than unity for many extractants, indicating that lactic acid has distribution coefficients lower than one in numerous liquid-liquid extraction (LLE) systems. However, the crucial factor for a successful extraction is that separation factors are larger than 1, which has been observed in this study.

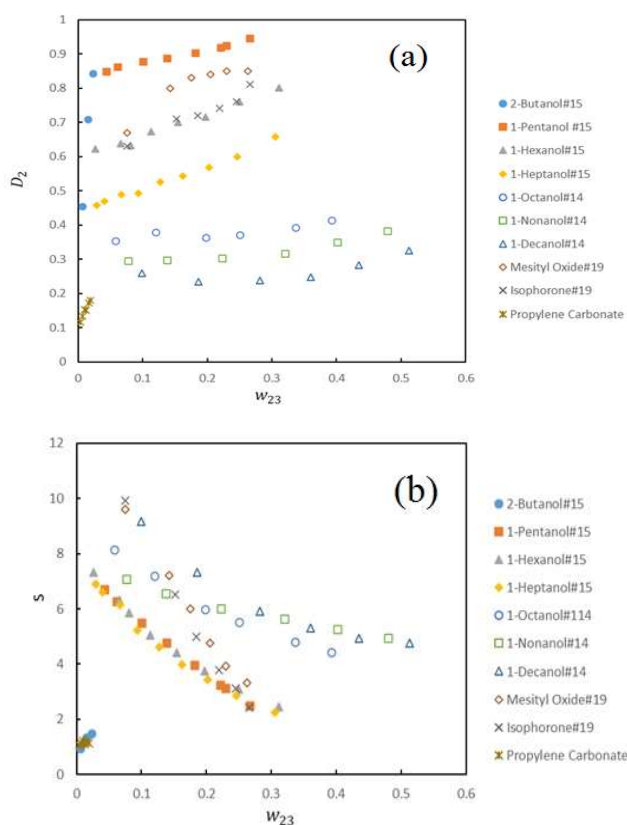


Fig. 5. The (a) distribution coefficients and (b) separation factors of previously studied solvents in the (Water + LA + Solvent) system in comparison with Propylene Carbonate at $T = 298.2$ K.

Thermodynamic Modeling

In instances where experimental data is accessible, the optimization of binary interaction parameters can be achieved through thermodynamic modeling. These optimized parameters subsequently facilitate the prediction of tie-line data, particularly within the examined biphasic range. In the context of this investigation, the nonrandom two-liquid (NRTL) model, as proposed by Renon and Prausnitz [29], was employed for the purpose of establishing correlations with the measured tie-line data and deriving the requisite binary parameters. It is noteworthy that a predetermined value for the non-randomness parameter (α) was set at 0.1 0.2 and 0.3. Upon a comprehensive comparison of the correlated data, the most dependable outcomes were achieved when α was configured at 0.1. The resulting correlated tie-line data for the analyzed system which were

done using an optimizing function of MATLAB software [31], have been systematically presented within Table 6, serving to encapsulate the culmination of this modeling endeavor.

In the pursuit of refining the NRTL model and generating the requisite binary interaction parameters, the optimization process hinged upon the utilization of the objective function as follows:

$$OF = \sum_{k=1}^M \sum_{j=1}^2 \sum_{i=1}^3 (w_{ijk}^{exp} - w_{ijk}^{cal})^2 \quad (8)$$

The value of w_{ijk}^{cal} represents the mass fraction of components that has been calculated, while w_{ijk}^{exp} represents the corresponding experimental mass fraction. The subscript "k" denotes the tie-line, "j" refers to the phase, and "i" pertains to the components. The variable M represents the total number of tie lines. The outcomes of this modeling endeavor have been visually represented in Fig. 1, providing a comprehensive depiction of the attained results. The culmination of the optimization procedure manifests in the form of the optimal NRTL binary interaction parameters, systematically outlined in Table 7.

Table 6. The Calculated NRTL ($\alpha = 0.1$) Tie-line Data in Mass Fraction for (Water + Lactic Acid + Propylene Carbonate) at $T = 298.2$ K and 308.2 K

w_{11}	w_{21}	w_{31}	w_{13}	w_{23}	w_{33}
Aqueous phase			Organic phase		
$T = 298.2$ K					
0.7588	0.0359	0.2053	0.0849	0.0043	0.9108
0.7283	0.0553	0.2164	0.0875	0.0073	0.9052
0.7063	0.0685	0.2251	0.0898	0.0097	0.9005
0.6820	0.0826	0.2354	0.0926	0.0128	0.8945
0.6595	0.0948	0.2457	0.0958	0.0161	0.8881
0.6404	0.1045	0.2551	0.0989	0.0194	0.8817
$T = 308.2$ K					
0.7110	0.0312	0.2577	0.0877	0.00037	0.9086
0.6898	0.0438	0.2664	0.0894	0.0055	0.9050
0.6694	0.0554	0.2752	0.0913	0.0075	0.9013
0.6517	0.0651	0.2833	0.0930	0.0093	0.8977
0.6307	0.0758	0.2935	0.0954	0.0117	0.8930
0.6118	0.0850	0.3032	0.0978	0.0140	0.8882

Table 7. Optimized Binary Interaction Parameters of the NRTL ($\alpha = 0.1$) Model for the Ternary System (Water + Lactic Acid + Propylene Carbonate) at $T = 298.2$ K and 308.2 K

		b_{ij}/K	b_{ji}/K	τ_{ij}	τ_{ji}	rmsd %
$T = 298.2$ K	1-2	-2795.49	3123.16	-9.37	10.47	0.30
	1-3	1610.05	-495.06	5.40	-1.66	
	2-3	-48.87	198.93	-0.16	0.67	
$T = 308.2$ K	1-2	-2889.30	2905.17	-9.37	9.43	0.56
	1-3	1532.02	-460.50	4.97	-1.49	
	2-3	-45.45	205.61	-0.15	0.67	

The derived binary parameters are presented in two distinct formulations: the energy parameter (b_{ij}) and the dimensionless parameter (τ_{ij}), thereby encapsulating the fundamental characteristics that underpin the interaction between the components under scrutiny. The related Eqs. ((9)-(11)) of thermodynamic modeling are given below:

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

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} \quad (10)$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) (\alpha_{ji} = \alpha_{ij}) \quad (11)$$

The inputs for this analysis consist of mole fractions and the temperature under examination. The software will then optimize the values of a_{ij} and b_{ij} to determine the most suitable activity coefficients. For this particular investigation, the a_{ij} values were set to zero, and temperature-dependent binary interaction parameters (b_{ij}) were derived.

To assess the efficacy of the modeling process and the capability of the acquired interaction parameters to predict tie-line data, an initial step involved the computation of root-mean-square deviation (rmsd) values. The calculation of rmsd values was executed using the formula stipulated by Eq. (12), which is articulated as follows:

$$rmsd = \sqrt{\frac{\sum_{k=1}^n \sum_{j=1}^2 \sum_{l=1}^3 (w_{ijk}^{exp} - w_{ijk}^{cal})^2}{6n}} \quad (12)$$

In the equation denoted by Eq. (11), the variable " n " represents the count of tie-line data points, and " w_{ijk}^{exp} " and " w_{ijk}^{cal} " correspond to the measured and calculated outcomes, respectively. The subscripts " i ," " j ," and " k " signify the components, phases, and tie-line data points ($k = 1, 2, \dots, n$), in that sequence.

The rmsd values generated by the NRTL model for the examined system at the temperature $T = 298.2$ K have been systematically compiled within Table 7. These rmsd values substantiate the caliber of the thermodynamic modeling process and underscore the accomplishment of an effective fit. On the whole, the rmsd value falls well below the acceptable threshold of 0.3%.

The subsequent step undertaken to ensure the robustness of the modeling process involved employing a graphical user interface software developed by Reyes-Labarta [32,33]. Within this software framework, compositions were employed in the form of mole fractions, and dimensionless binary interaction parameters (τ_{ij}) were incorporated. Through this software, the optimized binary interaction parameters underwent validation by means of calculating excess Gibbs energy based on these parameters.

The alignment of binary parameters with experimental data was evaluated by assessing the plot of $G^M(L)/RT$ against the mole fraction of any given component. This plot was expected to exhibit tangency if the binary parameters corresponded accurately with the experimental data. Examples of such $G^M(L)/RT$ plots for tie-lines 1 and 6 are depicted in Figs. 6a and 6b. As is evident from these figures, both plots clearly demonstrate the coherence of the utilized binary interaction parameters.

An additional test to ascertain the accuracy of these binary parameters encompassed the utilization of a miscibility boundary plot [34], depicted in Fig. 7. This visualization effectively illustrates the estimated miscibility regions based on the optimized binary interaction parameters. As observed in the figure, pairs like water-LA and LA-PC occupy the homogeneous region, whereas the water-PC pair is situated within the heterogeneous part. This predictive outcome harmonizes with the experimental results of the studied binary mixtures, thus substantiating the validity of the interaction parameters.

Once the binary interaction parameters have been validated, we can have confidence in the activity coefficient obtained from Eq. (8). These calculated activity coefficients are presented in Table 8. Examining the table, it is evident that the activity coefficients of water in the aqueous phase (γ_w^{aq}) and propylene carbonate in the organic phase (γ_{PC}^{org}) are close to unity, which is expected as they are solvents in their respective media. However, both of these activity coefficients display small positive deviations from Raoult's law. On the other hand, the activity coefficients of lactic acid (γ_{LA}^{aq} and γ_{LA}^{org}) exhibit significant negative deviations, whereas the activity coefficients of propylene carbonate in the aqueous phase (γ_{PC}^{aq}) and water in the organic phase (γ_w^{org}) demonstrate relatively large positive deviations.

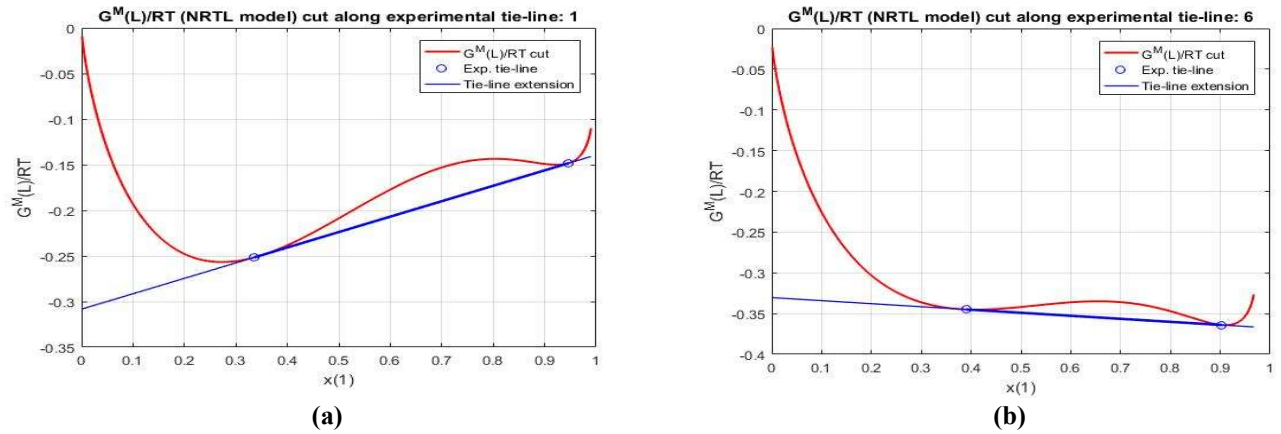


Fig. 6. Plot of $G^M(L)/RT$ versus mole fraction of water; (a) tie-line #1 and (b) tie-line #6.

Table 8. Activity Coefficients Obtained for the System (Water + Lactic Acid + Propylene Carbonate) at $T = 298.2$ K and 308.2 K and 101.7 kPa

γ_w^{aq}	γ_{LA}^{aq}	γ_{PC}^{aq}	γ_w^{org}	γ_{LA}^{org}	γ_{PC}^{org}
$T = 298.2$ K					
1.00	2.55×10^{-3}	16.66	2.83	6.70×10^{-3}	1.12
1.01	2.54×10^{-3}	15.20	2.73	6.07×10^{-3}	1.14
1.02	2.59×10^{-3}	14.38	2.65	5.57×10^{-3}	1.16
1.03	2.25×10^{-3}	13.11	2.58	5.12×10^{-3}	1.18
1.04	2.37×10^{-3}	12.30	2.51	4.87×10^{-3}	1.21
1.05	2.15×10^{-3}	10.93	2.44	4.46×10^{-3}	1.23
$T = 308.2$ K					
1.05	1.38×10^{-3}	12.81	2.53	4.40×10^{-3}	1.20
1.04	1.36×10^{-3}	12.22	2.47	4.17×10^{-3}	1.22
1.03	1.52×10^{-3}	11.66	2.42	4.02×10^{-3}	1.24
1.02	1.56×10^{-3}	11.17	2.37	3.83×10^{-3}	1.26
1.01	1.53×10^{-3}	10.59	2.32	3.65×10^{-3}	1.28
1.00	1.55×10^{-3}	10.07	2.27	3.53×10^{-3}	1.30

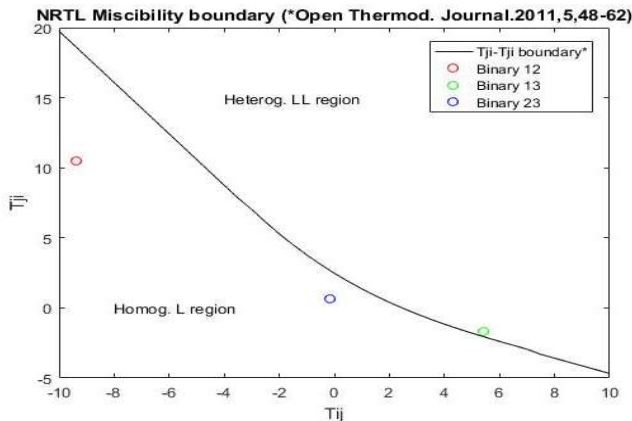


Fig. 7. Plot of Miscibility boundary estimated from optimized binary interaction parameters for the system [water (1) + LA (2) + PC (3)].

CONCLUSIONS

Experimental liquid-liquid equilibrium (LLE) data were meticulously acquired for the ternary system comprising water, lactic acid (LA), and propylene carbonate (PC), all at consistent temperatures of $T = 298.2$ K and 308.2 K and 101.7 kPa. This ternary system exhibited the characteristic Type-1 behavior within the domain of LLE phenomena. In the endeavor to establish correlations between the experimental tie-line data and to compute the phase compositions of the investigated mixtures, the NRTL model was judiciously employed. The outcomes of the thermodynamic modeling process were notably reliable for

the examined system. Within the scope of this study, the separation factors and distribution coefficients pertaining to the employed etheric solvent were meticulously determined. Notably, the experimental findings revealed that the separation factors for propylene carbonate exceeded unity across the range of acid concentrations investigated at 298.2 K. However, it was determined that the higher temperatures were unsuitable for the separation process. This observation underscores the solvent's pronounced ability to effectively purify the acid from water. The experimental data were in good agreement with the Othmer-Tobias and Hand equations due to the high R^2 values ranging from 0.988 to 0.997 which are close to 1. The validation of binary interaction parameters undertaken in this study yielded exceptional outcomes, attesting to the accuracy and credibility of the established model. The activity coefficient calculations revealed that lactic acid exhibits a pronounced negative deviation from Raul's law in both phases. Conversely, the other components, water and propylene carbonate, displayed positive deviations.

REFERENCES

- [1] Ayuso, M.; Mateo, S.; Belinchón, A.; Navarro, P.; Palomar, J.; García, J.; Rodríguez, F., Cyclic carbonates as solvents in the dearomatization of refinery streams: Experimental liquid-liquid equilibria, modelling, and simulation. *J. Mol. Liq.* **2023**, *380*, 121710, DOI: 10.1016/j.molliq.2023.121710.
- [2] Altway, S.; Tiwikrama, A. H.; Rahayu, S. D.; Ningrum, E. O.; Altway, A.; Pudjiastuti, L., Biological Buffer Effect on Liquid-Liquid Equilibria of Systems Containing n-Butanol+ Methyl Isobutyl Ketone + Water. *J. Chem. Eng. Data* **2023**, *68* (2), 384-392, DOI: 10.1021/acs.jced.2c00657.
- [3] Li, H.; Qin, H.; Jiang, S.; Wang, B.; Zeng, J.; Chen, K.; Fang, Y., Liquid-liquid equilibria of ternary water-ethyl acetate-1, 8-cineole system at different temperatures. *Fluid Ph. Equilibria* **2023**, *575*, 113911, DOI: 10.1016/j.fluid.2023.113911.
- [4] Gaikwad, S. G.; Pathak, A. A.; Mote, D. R.; Gogate, P. R.; Singh, S.; Modhera, B., Liquid-liquid equilibria of ternary mixtures containing Aniline + Toluene + water at elevated temperatures: measurements and correlation. *Sep. Sci. Technol.* **2023**, *1*, 1-8, DOI: 10.1080/01496395.2023.2232104.
- [5] Choe, H. J.; Song, K. H., Liquid-Liquid Equilibria for Pseudo-Ternary Systems of 1-Hydroxypropan-2-one + Water + Cyclic Terpene-Based Mixtures at 298.15 K. *J. Chem. Eng. Data* **2023**, *68* (2), 430-440, DOI: 10.1021/acs.jced.2c00737.
- [6] Hasan, M. J.; Yeganeh, F.; Ciric, A.; Chen, P.; Vasquez, E. S.; Ureña-Benavides, E. E., Liquid-liquid equilibria of water + ethanol + castor oil and the effect of cellulose nanocrystal/Fe₃O₄ and lignin/Fe₃O₄ nanoparticles. *J. Chem. Thermodyn.* **2023**, *180*, 107007, DOI: 10.1016/j.jct.2023.107007.
- [7] Sapkowski, M.; Hofman, T., Problems and limitations in the calculation of liquid-liquid equilibrium. *Fluid Ph. Equilibria* **2023**, *571*, 113823, DOI: 10.1016/j.fluid.2023.113823.
- [8] Fan, W.; Huang, H.; Li, Q.; Gao, J.; Xu, D.; Wang, Y., Liquid-liquid equilibria for separation of benzothiophene from model fuel oil: Solvent screening and thermodynamic modeling. *J. Chem. Thermodyn.* **2022**, *167*, 106693, DOI: 10.1016/j.jct.2021.106693.
- [9] Treybal, R. E.; *Mass Transfer Operations*. third ed., McGraw-Hill, New York, **1960**, p. 477-489.
- [10] Datta, R.; Henry, M., Lactic acid: recent advances in products, processes and technologies - a review. *J. Chem. Technol. Biotechnol.* **2006**, *81*, 1119-1129, DOI: 10.1002/jctb.1486.
- [11] Geanta, R. M.; Ruiz, M. O.; Escudero, I., Micellar-enhanced ultrafiltration for the recovery of lactic acid and citric acid from beet molasses with sodium dodecyl sulphate. *J. Membrane Sci.* **2013**, *430*, 11-23, DOI: 10.1016/j.memsci.2012.12.006.
- [12] Clark, A.; Milbrandt, T. A.; Hilt, J. Z.; Puleo, D. A., Mechanical properties and dual drug delivery application of poly(lactic-co-glycolic acid) scaffolds fabricated with a poly(b-amino ester) porogen. *Acta Biomater.* **2014**, *10*, 2125-2132, DOI: 10.1016/j.actbio.2013.12.061.
- [13] Bai, D.; Zhao, X.; Li, X.; Xu, S., Strain improvement of *Rhizopus oryzae* for over-production of L(+)-lactic acid and metabolic flux analysis of mutants. *Biochem.*

- Eng. J.* **2004**, *18*, 41-48, DOI: 10.1016/S1369-703X(03)00126-8.
- [14] Sahin, S.; Kırbaşlar, S. I.; Bilgin, M., (Liquid + liquid) equilibria of (water + lactic acid + alcohol) ternary systems. *J. Chem. Thermodyn.* **2009**, *41*, 97-102, DOI: 10.1016/j.jct.2008.07.014.
- [15] Domingues, L.; Cussolin, P. A.; da Silva, J. L.; de Oliveira, L. H.; Aznar, M., Liquid-liquid equilibrium data for ternary systems of water + lactic acid + C₄-C₇ alcohols at 298.2 K and atmospheric pressure. *Fluid Ph. Equilibria* **2013**, *354*, 12-18, DOI: 10.1016/j.fluid.2013.06.007.
- [16] Afolabi, T. J.; Alao, A. I., Liquid-liquid equilibria of water + lactic acid + methyl isobutyl ketone. *Fluid Ph. Equilibria* **2014**, *379*, 19-25, DOI: 10.1016/j.fluid.2014.06.010.
- [17] Gilani, H. G.; Gilani, A. G.; Peydeh, F. B.; Seyed Saadat, S. L.; Ahmadifar, S., Experimental and Theoretical Study of Phase Equilibria in Aqueous Mixtures of Lactic Acid with Benzyl Alcohol and p-Xylene at Various Temperatures. *Phys. Chem. Res.* **2016**, *4*, 489-505, DOI: 10.22036/pcr.2016.15062.
- [18] Shekarsaraee, S.; Naimi, A.; Bussary, B., Measurement, correlation and prediction of LLE data for the ternary system water + lactic acid + diethyl ether at 293.2 K. *Phys. Chem. Res.* **2021**, *9* (2), 181-192, DOI: 10.22036/PCR.2020.250264.1840.
- [19] Gilani, A. G.; Kashef, A.; Khanghah, B. M.; Nakhaee, A. H.; Ahadzadeh, A., Comparative study of liquid-liquid equilibria for aqueous mixtures of lactic acid with structurally similar cyclic and non-cyclic ketones. *J. Chem. Thermodyn.* **2023**, *179*, 106997, DOI: 10.1016/j.jct.2022.106997.
- [20] Alao, A. I.; Afolabi, T. J.; Agarry, S. E., Extraction of Lactic Acid from Fermentation Broth Using Long-Chain Alkanones. *J. Chem. Eng. Data* **2023**, *68* (3), 642-653, DOI: 10.1021/acs.jced.2c00651.
- [21] Shekarsaraee, S., Liquid-liquid equilibrium study for the system (water + phosphoric acid + propylene carbonate) at different temperatures. *J. Chem. Thermodyn.* **2017**, *104*, 16-23, DOI: 10.1016/j.jct.2016.09.008.
- [22] Shekarsaraee, S.; Nahzomi, H. T.; Nasiri-Touli, E., Phase diagrams for the system water/butyric acid/propylene carbonate at T = 293.2-313.2 K and p = 101.3 kPa. *Rus. J. Phys. Chem. A* **2017**, *91*, 2078-2084, DOI: 10.1134/S0036024417110267.
- [23] Annesini, M. C.; Gironi, F.; Marrelli, L.; Kikic, I., Liquid-liquid equilibria for ternary systems containing hydrocarbons and propylene carbonate. *J. Chem. Eng. Data* **1985**, *30* (2), 195-196, DOI: 10.1021/je00040a019.
- [24] Salem, A. B. S.; Hamad, E. Z., Liquid-liquid equilibrium of the five component system of n-hexane-n-heptane toluene-o-xylene propylene carbonate. *Fluid Ph. Equilibria* **1995**, *108*, 231-241, DOI: 10.1016/0378-3812(95)02686-9.
- [25] Rajapakse, N.; Finston, H. L.; Fried, V., Liquid-liquid phase equilibria in the propylene carbonate + methyl isobutyl ketone + water system. *J. Chem. Eng. Data*, **1986**, *31* (4), 408-410, DOI: 10.1021/je00046a010.
- [26] Golmohammadi, B.; Shekaari, H.; Zafarani-Moattar, M. T., Thermodynamic Properties of Ternary Systems Containing (LiCl and LiBr) + Propylene Carbonate+ Ionic Liquid (1-Alkyl-3-methylimidazolium Thiocyanate). *ACS Omega*, **2021**, *6* (42), 27874-27887, DOI: 10.1021/acsomega.1c03517.
- [27] Akkoyun, M.; Carrot, C.; Blottière, B., Ternary Diagrams of Poly (vinylidene fluoride) and Poly [(vinylidene fluoride)-co-hexafluoropropene] in Propylene Carbonate and Dimethyl Sulfoxide. *Macromol. Chem. Phys.* **2012**, *213* (5), 587-593, DOI: 10.1002/macp.201100595.
- [28] Li, Y.; Dong, S.; Wang, L.; Sun, X.; Zhao, W.; Xiang, S., The extraction of aromatics using n-methylpyrrolidone: Liquid-liquid equilibrium determination and mechanism exploration. *Chin. J. Chem. Eng.* **2023**, *In Press*, DOI: 10.1016/j.cjche.2023.05.016.
- [29] Cox, K. R.; Chapman, W. G., *The Properties of Gases and Liquids*, By Bruce E. Poling (University of Toledo), John M. Prausnitz (University of California at Berkeley), and John P. O'Connell (University of Virginia). McGraw-Hill: New York. **2001**, 768 pp. ISBN 0-07-011682-2, p. 8.17.

- [30] Catherall, N. F.; Williamson, A. G., Mutual solubilities of propylene carbonate and water. *J. Chem. Eng. Data* **1971**, *16* (16), 335-336, DOI: 10.1021/je60050a021.
- [31] McKinnon, K. I., Convergence of the Nelder--Mead simplex method to a nonstationary point. *SIAM. J. Optim.* **1998**, *9* (1), 148-158, DOI: 10.1137/S1052623496303482.
- [32] Reyes-Labarta, J. A., Graphical User Interface (GUI) for the representation of GM surfaces (using the NRTL model) and curves, including tie-lines and Hessian matrix. Institutional Repository of the University of Alicante (RUA)
hdl.handle.net/10045/51725
- [33] Marcilla, A.; Reyes-Labarta, J. A.; Olaya, M. M., Should we trust all the published LLE correlation parameters in phase equilibria? Necessity of their Assessment Prior to Publication. *Fluid Ph. Equilibria* **2017**, *433*, 243-252, DOI: 10.1016/j.fluid.2016.11.009.
- [34] Marcilla, A.; Labarta, J. A.; Serrano Cayuelas, M. D.; Olaya, M. D. M., GE models and algorithms for condensed phase equilibrium data regression in ternary systems: limitations and proposals. *Open Thermodyn. J.* **2011**, *5*, 48-62, DOI: 10.2174/1874396X01105010048.