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Experimental and Theoretical Study of Phase Equilibria in Aqueous Mixtures of Lactic Acid with Benzyl Alcohol and *p*-Xylene at Various Temperatures

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Liquid-liquid equilibria for the (water + lactic acid + benzyl alcohol or *p*-xylene) ternary systems were investigated at atmospheric pressure and in the temperature range from 298.15-318.15 K. The studied systems exhibit two types of liquid-liquid equilibrium (LLE) behavior. The system consisting of benzyl alcohol displays type-1 LLE behavior, while a type-2 behavior is exhibited by the other system. The quality of the experimental tie line data was determined using the Othmer-Tobias and Hand equations. Distribution coefficients and separation factors were calculated over the biphasic region. The experimental tie line data were regressed using the UNIQUAC and NRTL models and the binary interaction parameters were obtained.

INTRODUCTION

Lactic acid (LA) or 2-hydroxypropanoic acid is a chiral carboxylic acid that has various applications in food, pharmaceutical, and cosmetic industries [1-3]. This acid is widely used as a monomer for producing polylactic acid, a biodegradable polymer with a large potential market [4]. LA is a colourless viscous liquid and is soluble in water and many polar organic solvents. This acid is mainly produced by chemical and fermentation processes [5,6]. However, there is a great interest in the LA production from fermentation, as this method can generate a pure optical isomer (*i.e.* L-(+)- or D-(-)) [7,8]. For recovery of the acid, the next step is the use of liquid extraction process, which is one of the most important ones. Up to now, many organic solvents have already been tested to improve the recovery of LA from water [9-15]. However, more LLE studies are still needed for various industrial purposes.

In this study, two aromatic compounds were selected as organic solvents, *i.e.* benzyl alcohol and *p*-xylene. To the best of our knowledge, the solubility and tie line data of the (water + L-(+)-LA + benzyl alcohol or *p*-xylene) systems have not been reported in the available literature. To compare the extracting capabilities of the solvents used in this work, the distribution coefficients and separation factors are determined. The reliability of the experimental data is determined using the Othmer-Tobias [16] and Hand [17] equations. The experimental data are correlated using the UNIQUAC [18] and NRTL models [19].

EXPERIMENTAL

Material

Benzyl alcohol (mass fraction > 0.998) and *p*-xylene (mass fraction > 0.99) were supplied from Carlo Erba and Merck, respectively. L-(+)-lactic acid containing 85 wt% was obtained from Chem-Lab. All chemicals were used as received without further purification. The purity of the acid

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was confirmed through acidimetric titration with 1 N NaOH. The stated purity of the solvents was checked using the refractive index method. Deionized and double distilled water was used in the preparation of all mixtures. The refractive index and density data of the chemicals used in this study along with the literature values are listed in Table 1 [20-22]. The molecular structure of the used solvents is shown in Fig. 1.

Apparatus

The refractive indices and densities of the solutions were determined at $T = 298.15$ K using an Abbe Refractometer (Model CETI) and DA-210 (Kyoto electronic) density meter. The instruments were initially calibrated before being used. The uncertainty in refractive index and density measurements were ±0.0002 and ±0.03 Kg m^{-3}, respectively. The temperature of the instruments was estimated to be accurate to ±0.01 K that was checked with a digital thermometer (Lutron TM-917). All weightings were carried out with an AND electronic analytical balance (HR-200) with an accuracy of ± 0.0001 g.

Solubility and Tie Line Measurements

The solubility data were determined by the cloud point titration method in a 50 ml equilibrium glass cell with a water jacket to maintain isothermal conditions [23]. The

Table 1. The Measured and Literature Values for the Refractive Index (n_D) and Density (ρ) of the Pure Components at $T = 298.15$ K and $p = 101.3$ kPa[a]

Component	Mass fraction Purity	Source	n_D		ρ (Kg m^{-3})	
			Exp.	Lit.	Exp.	Lit.
Lactic acid	0.85	Chem-Lab	1.4251	1.4394[b] [20]	1202.15	1207.00[b] [20]
Benzyl alcohol	> 0.998	Carlo Erba	1.5374	1.53837 [21]	1040.98	1041.27 [21]
p-Xylene	> 0.99	Merck	1.4928	1.49325 [21]	856.18	856.61 [21]
Water	Deionized and redistilled	-	1.3324	1.33250 [22]	997.05	997.00 [22]

[a]Uncertainties u are u (T) = 0.01 K, u (p) = 0.4 kPa, u (n_D) = 0.0002, and u (ρ) = 0.03 Kg m^{-3}. [b] Data determined for lactic acid with mass purity 0.90 and $T = 293.15$ K.

Benzyl alcohol   *p*-Xylene
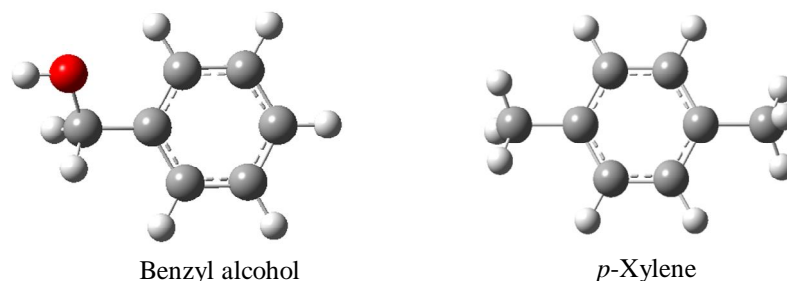
Fig. 1. Molecular structures of the solvents used in this study.

temperature of the cell was maintained with an accuracy of within ±0.01 K. The binary mixtures of either (water + acid) or (solvent + acid) were prepared gravimetrically and introduced into the cell and titrated against the third component. The titration endpoint was determined visually by observing the transition from a homogeneous to a heterogeneous mixture. The reliability of the method depends on the precision of addition of the third component into the cell that was carried out using a Brand Transferpette micropipette with an accuracy of ±0.001 ml. All experiments were repeated at least three times to acquire high accuracy. Moreover, waiting approximately 5 min at the end point and observing the stability of cloudiness is important to confirm the results. The average of these readings was taken for the component compositions. The uncertainty in the mass fraction of the solubility data was estimated to be better than ±0.0008. The solubility data for the studied ternary systems are given in Table 2.

Tie-lines for the studied systems were determined at $T =$ (298.15, 308.15 and 318.15) K. The experimental tie line data were determined by preparing the ternary mixtures of the known compositions of water, acid, and the solvent. The mixtures were placed in the extraction cell (250 ml glass cell) and were vigorously agitated by a magnetic stirrer for 4 h, and then left to settle for phase separation. For the system containing benzyl alcohol, settle time was 4 h, however, this time was 5 h for the system containing p-xylene.

At equilibrium, each system was separated into two liquid phases with a clear interface. Sampling was taken by a glass syringe from of each layer and the samples were carefully analyzed to determine their compositions. The concentrations of LA in both phases (w_{21} and w_{23}) were measured by NaOH titration. The amount of water in the organic layer (w_{13}) was measured by the Karl-Fisher method [24] using Metrohm-870 KF Titrino plus Karl-Fisher titrator. The water contents in the aqueous phase (w_{11}) was performed using refractive index measurements [25]. The refractive index values as a function of w_{11} lying on the solubility curves at each temperature are presented in Table 3. The mass of solvent in both phases (w_{31} and w_{33}) were evaluated by knowing masses of water and acid in each phase and using the equation of $\sum w_i = 1$. The estimated

uncertainty of all measured compositions is better than ± 0.001.

RESULTS AND DISCUSSION

Experimental Tie-line Data

The experimental tie-line data for the studied ternary systems at each temperature are given in Table 4. The corresponding data are plotted and shown in Figs. 2-4. As seen, for these systems, the temperature effect on the immiscibility regions is small. Because (LA + benzyl alcohol) and (LA + water) are two liquid pairs that are completely miscible, the (water + LA + benzyl alcohol) ternary system displays type-1 behavior of LLE. The other system exhibits type-2 phase behavior, where the two liquid pairs (LA + p-xylene) and (p-xylene + water) are partially miscible.

To specify the ability of the organic solvents (benzyl alcohol or p-xylene) in the extraction of LA, separation factor ($S = D_2/D_1$) were calculated from the experimental data. It is defined as:

$$S = \frac{\text{Distribution coefficient of solute}}{\text{Distribution coefficient of water}} = \frac{w_{23}/w_{21}}{w_{13}/w_{11}} \quad (1)$$

w_{13}, and w_{23} are the mass fractions of water and the acid in the organic-rich layer, respectively. w_{11} and w_{21} are the mass fractions of water and the acid in the aqueous-rich layer, respectively.

The distribution coefficients and separation factors, for each system, are given in Table 5. The variation of experimental separation factor as a function of w_{21} for the studied systems at $T = 298.15$ K is shown in Fig. 5. The results indicate that the separation factors are greater than 1. However, this quantity for the system containing benzyl alcohol is higher than that of p-xylene in the temperature range studied. It could be due to structural differences between these two solvents. p-Xylene is a non-polar and non-HBD aromatic solvent with very low dielectric constant (ε = 2.3) and zero permanent dipole moment. Benzyl alcohol is a polar aromatic solvent (ε_{BA} = 13, μ_{BA} = 1.7 D). Therefore, p-xylene is less water-soluble than benzyl alcohol and has lower distribution coefficient of water (D_1).

Table 2. Experimental Solubility Data in Mass Fraction for [Water (1) + Lactic Acid (2) + Benzyl Alcohol or *p*-Xylene (3)] at *T* = (298.15, 308.15 and 318.15) K and *p* = 101.3 kPa[a]

T = 298.15 K		T = 308.15 K		T = 318.15 K	
w_1 (water)	w_2 (LA)	w_1 (water)	w_2 (LA)	w_1 (water)	w_2 (LA)
water + LA + benzyl alcohol					
0.9575	0.0000	0.9528	0.0000	0.9481	0.0000
0.9138	0.0415	0.9071	0.0410	0.9002	0.0411
0.8663	0.0819	0.8622	0.0812	0.8539	0.0805
0.8208	0.1203	0.8180	0.1209	0.8033	0.1175
0.7752	0.1590	0.7716	0.1580	0.7513	0.1542
0.7247	0.1912	0.7199	0.1914	0.6861	0.1866
0.6530	0.2237	0.6505	0.2223	0.6175	0.2119
0.5752	0.2435	0.5627	0.2391	0.5270	0.2229
0.4837	0.2490	0.4701	0.2427	0.4326	0.2224
0.3521	0.2345	0.3569	0.2326	0.3893	0.2207
0.2980	0.2205	0.3003	0.2201	0.3217	0.2136
0.2507	0.2003	0.2564	0.1991	0.2707	0.1955
0.2124	0.1748	0.2154	0.1702	0.2372	0.1692
0.1794	0.1441	0.1865	0.1431	0.2063	0.1394
0.1499	0.1119	0.1555	0.1111	0.1749	0.1076
0.1263	0.0756	0.1263	0.0765	0.1508	0.0748
0.1038	0.0394	0.1017	0.0386	0.1254	0.0385
0.0865	0.0000	0.0886	0.0000	0.1051	0.0000
water + LA + *p*-xylene					
0.9925	0.0000	0.9915	0.0000	0.9894	0.0000
0.9514	0.0422	0.9482	0.0433	0.9481	0.0423
0.9081	0.0845	0.9045	0.0849	0.9057	0.0847
0.8669	0.1267	0.8639	0.1276	0.8630	0.1263
0.8219	0.1685	0.8213	0.1692	0.8185	0.1677

Table 2. Continued

0.7825	0.2091	0.7822	0.2085	0.7771	0.2102
0.7372	0.2522	0.7385	0.2530	0.7366	0.2528
0.6958	0.2957	0.6945	0.2939	0.6935	0.2937
0.6525	0.3369	0.6512	0.3350	0.6522	0.3362
0.6101	0.3772	0.6097	0.3786	0.6089	0.3763
0.5722	0.4164	0.5714	0.4162	0.5679	0.4194
0.5249	0.4613	0.5255	0.4608	0.5243	0.4598
0.4829	0.5023	0.4853	0.5040	0.4842	0.5021
0.4412	0.5418	0.4416	0.5426	0.4394	0.5416
0.3991	0.5830	0.3980	0.5851	0.3969	0.5811
0.3586	0.6225	0.3564	0.6247	0.3548	0.6242
0.3150	0.6660	0.3142	0.6678	0.3135	0.6625
0.2733	0.7067	0.2719	0.7070	0.2719	0.7050
0.1467	0.8312	0.1464	0.8295	0.1462	0.8286
0.0040	0.0225	0.0048	0.0274	0.0055	0.0310
0.0025	0.0000	0.0037	0.0000	0.0050	0.0000

[a]Average standard uncertainties u are u (T) = 0.01 K, u (p) = 0.4 kPa, and u (w) = 0.0008.

Table 3. Equations for Refractive Index (n_D) as a Function of Water Mass Fractions (w) in the Aqueous-rich Phase at T = (298.15, 308.15 and 318.15) K and p = 101.3 kPa[a]

System	T (K)	Equation[b]	R^2
water + LA + benzyl alcohol	298.15	$n_D = - 0.0686\ w_{11} + 1.4041$	0.997
	308.15	$n_D = - 0.0659\ w_{11} + 1.4002$	0.995
	318.15	$n_D = - 0.0642\ w_{11} + 1.3963$	0.996
water + LA + p-xylene	298.15	$n_D = - 0.0895\ w_{11} + 1.4162$	0.996
	308.15	$n_D = - 0.0879\ w_{11} + 1.4116$	0.995
	318.15	$n_D = - 0.0856\ w_{11} + 1.4039$	0.996

[a]Standard uncertainties u are u (T) = 0.01 K, u (p) = 0.4 kPa, u (n_D) = 0.0002, and u (w) = 0.001.
[b]The estimated standard error of slope and intercept coefficients of the linear plot are 0.0022 and 0.0016.

Table 4. Experimental Tie-line Data in Mass Fraction for (Water + Lactic Acid + Benzyl Alcohol or *p*-Xylene) at T = (298.15, 308.15 and 318.15) K and p = 101.3 kPa[a]

Aqueous phase mass fraction			Organic phase mass fraction		
w_1 (water)	w_2 (LA)	w_3 (solvent)	w_1 (water)	w_2 (LA)	w_3 (solvent)
water + LA + benzyl alcohol					
T = 298.15 K					
0.886	0.064	0.050	0.104	0.037	0.859
0.830	0.113	0.057	0.129	0.077	0.794
0.772	0.162	0.066	0.148	0.108	0.744
0.697	0.205	0.098	0.177	0.140	0.683
0.604	0.238	0.158	0.216	0.176	0.608
0.507	0.249	0.244	0.258	0.204	0.538
T = 308.15 K					
0.890	0.056	0.054	0.104	0.035	0.861
0.826	0.113	0.061	0.129	0.080	0.791
0.783	0.149	0.068	0.160	0.115	0.725
0.696	0.202	0.102	0.190	0.148	0.662
0.621	0.229	0.150	0.224	0.177	0.599
0.522	0.242	0.236	0.269	0.207	0.524
T = 318.15 K					
0.879	0.058	0.062	0.124	0.037	0.839
0.822	0.104	0.074	0.154	0.079	0.767
0.750	0.155	0.095	0.183	0.116	0.701
0.703	0.178	0.119	0.207	0.140	0.653
0.575	0.218	0.207	0.251	0.180	0.569
water + LA + *p*-xylene					
T = 298.15 K					
0.825	0.166	0.009	0.005	0.004	0.991
0.718	0.270	0.012	0.006	0.006	0.988
0.637	0.351	0.012	0.008	0.007	0.985
0.577	0.411	0.012	0.010	0.008	0.982
0.532	0.454	0.014	0.010	0.008	0.982
0.486	0.498	0.016	0.010	0.009	0.981

Table 4. Continued

			$T = 308.15$ K		
0.820	0.170	0.010	0.004	0.002	0.994
0.718	0.274	0.008	0.006	0.004	0.990
0.626	0.361	0.013	0.008	0.005	0.987
0.578	0.410	0.012	0.010	0.006	0.984
0.514	0.471	0.015	0.011	0.007	0.982
0.482	0.506	0.012	0.011	0.007	0.982
			$T = 318.15$ K		
0.824	0.161	0.015	0.004	0.003	0.993
0.726	0.263	0.011	0.006	0.005	0.989
0.639	0.348	0.013	0.009	0.006	0.985
0.591	0.393	0.016	0.010	0.007	0.983
0.526	0.456	0.018	0.010	0.008	0.982
0.496	0.489	0.015	0.012	0.009	0.979

[a]Standard uncertainties u are u $(T) = 0.01$ K, u $(p) = 0.4$ kPa, and u $(w) = 0.001$.

Moreover, distribution coefficient of the acid (D_2) in *p*-xylene is also very small, and therefore, it might be a reason for its observed separation factor values. It is found that benzyl alcohol could be considered as a better solvent for extraction of the acid from water.

The experimental distribution coefficient and separation factors obtained in this work and those reported in the previous publications [11,14] for the similar ternary systems are compared in Table 6.

Consistency of Experimental Data

The quality of the measured tie-line data of the studied systems was confirmed by applying the Othmer-Tobias ($\ln[(1 - w_{33})/w_{33}] = A + B \ln[(1 - w_{11})/w_{11}]$) [16] and the Hand ($\ln(w_{21}/w_{11}) = A' + B' \ln(w_{23}/w_{33})$) [17] plots; where w_{33} is the mass fraction of the solvent in the organic-rich phase, and A, B, A' and B' are the parameters of the Othmer-Tobias and the Hand correlation equations, respectively. For each system, these parameters were obtained by the least-squares method and are given in Table 7. As seen in Figs. 6 and 7,

the linearity of the plots indicate the degree of reliability of the experimental LLE data.

Correlated LLE Data

The experimental tie-line results obtained in this work were correlated using the NRTL and UNIQUAC models. In the present work, the optimum value of the non-randomness, α, for the systems containing benzyl alcohol and *p*-xylene were fixed at 0.3 and 0.2, respectively, which produced better goodness-of-fits. The UNIQUAC structural parameters (r and q) were taken from literature [26] (Table 8). The correlated data for the ternary systems at each temperature are given in Table 9. Figures 2-4 show a comparison between the correlated and experimental tie-line data. The experimental tie-line data were used to determine the UNIQUAC (a_{ij}) and NRTL (b_{ij}) binary interaction parameters between each pair of components (Table 10) [27].

To judge the precision of the correlations, the root-mean square error (*rmse*) values were utilized. The *rmse* value was calculated from the difference between the
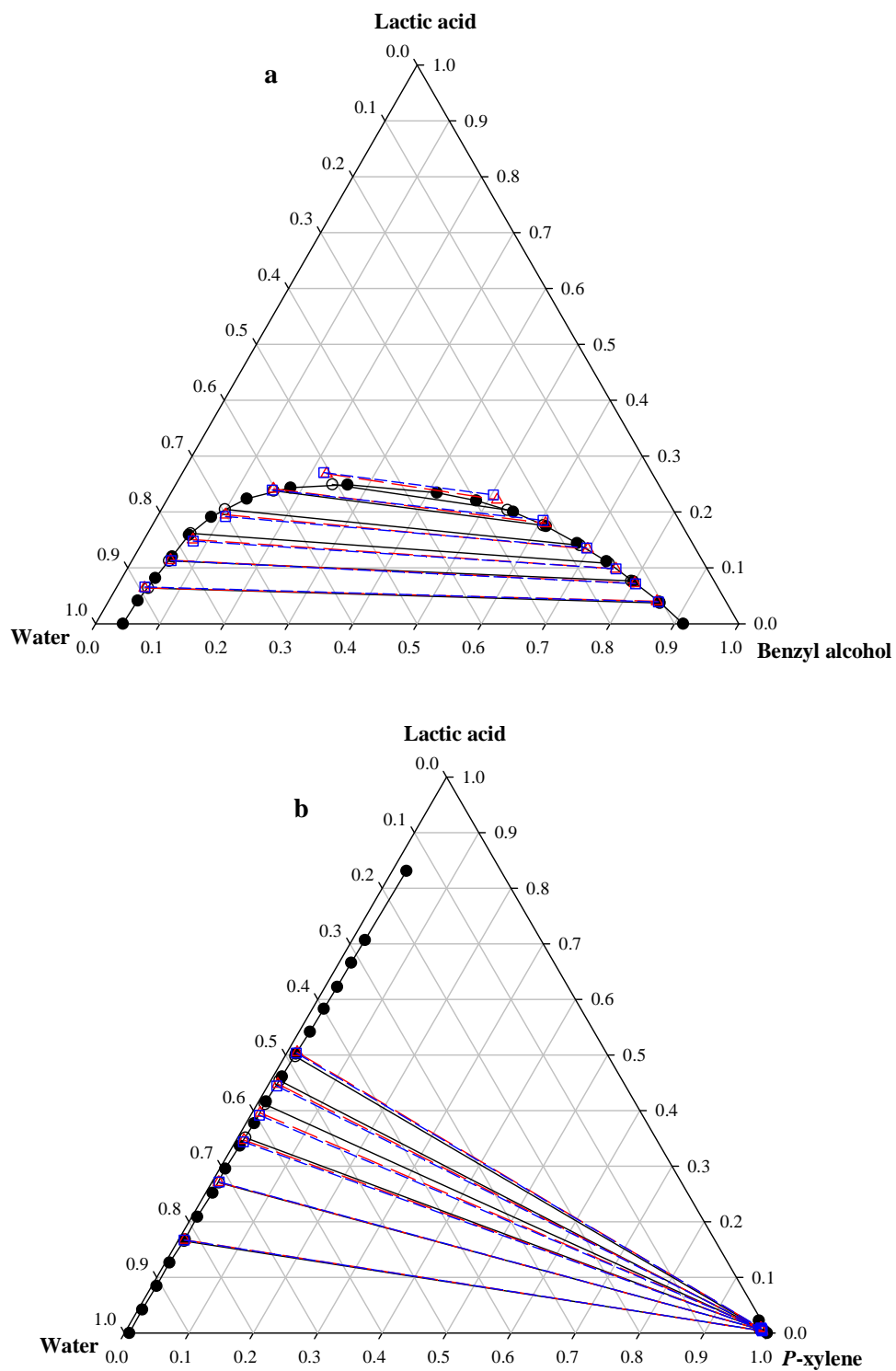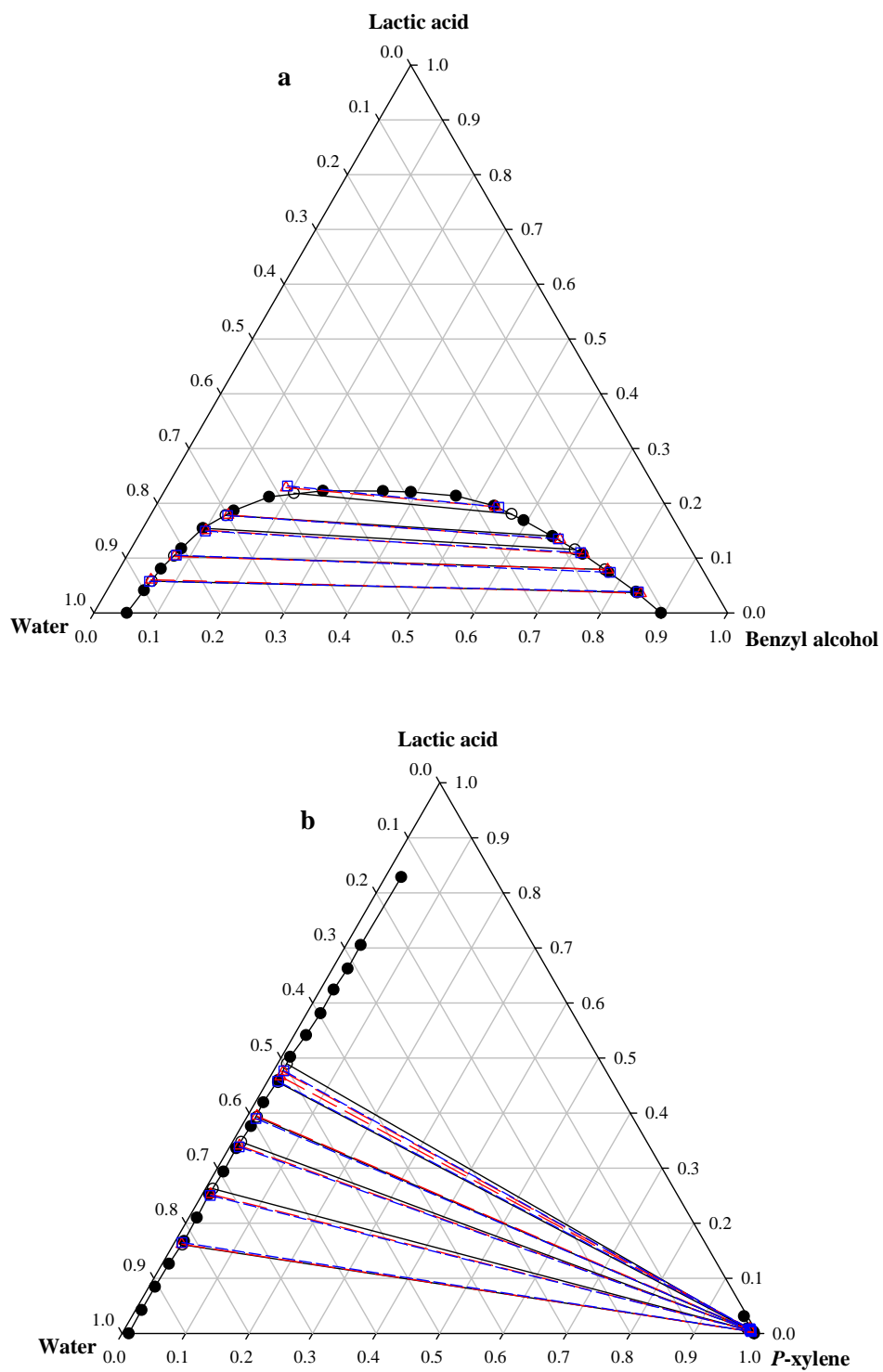
Fig. 2. Ternary diagram for the systems at T = 298.15 K; (•) solubility data points, (○) experimental tie-lines, (Δ) NRTL points, (□) UNIQUAC points; a) (water + lactic acid + benzyl alcohol), b) (water + lactic acid + *p*-xylene).
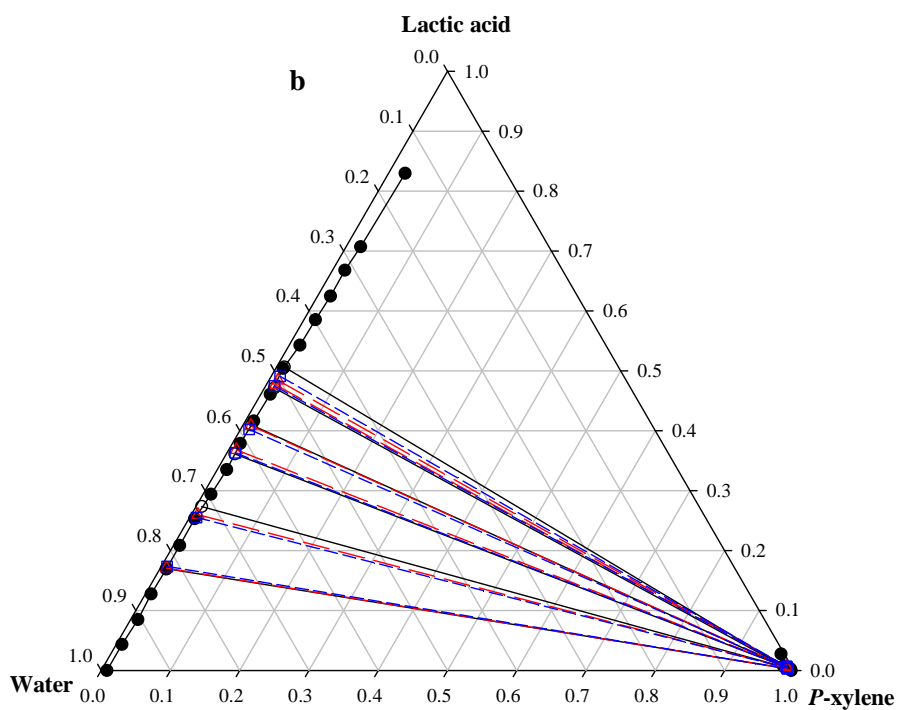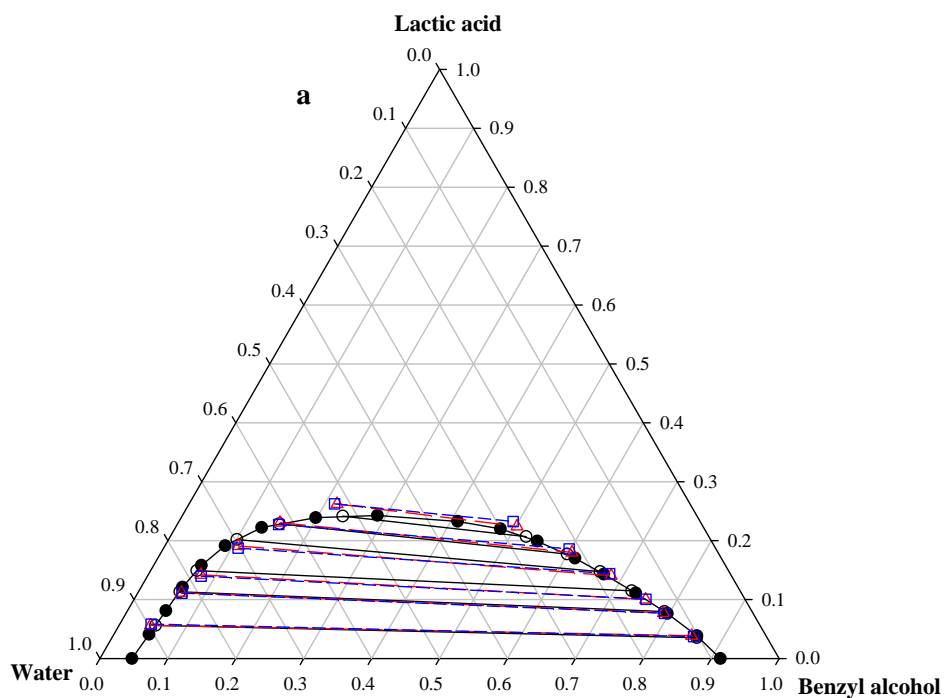
Fig. 3. Ternary diagram for the systems at T = 308.15 K; (•) solubility data points, (○) experimental tie-lines, (Δ) NRTL points, (□) UNIQUAC points; a) (water + lactic acid + benzyl alcohol), b) (water + lactic acid + p-xylene).

Fig. 4. Ternary diagram for the systems at T = 318.15 K; (●) solubility data points, (○) experimental tie-lines, (Δ) NRTL points, (□) UNIQUAC points; a) (water + lactic acid + benzyl alcohol), b) (water + lactic acid + *p*-xylene).

Table 5. Separation Factors (S) and Distribution Coefficients of Lactic Acid (D_2) and Water (D_1) at T = (298.15, 308.15 and 318.15) K and p = 101.3 kPa[a]

System	T (K)	D_1	D_2	S
water + LA + benzyl alcohol	298.15	0.118	0.581	4.9
		0.155	0.682	4.4
		0.192	0.668	3.5
		0.254	0.686	2.7
		0.358	0.740	2.1
		0.508	0.817	1.6
	308.15	0.116	0.628	5.4
		0.156	0.703	4.5
		0.204	0.770	3.8
		0.272	0.731	2.7
		0.360	0.775	2.2
		0.516	0.856	1.7
	318.15	0.141	0.638	4.5
		0.187	0.762	4.1
		0.244	0.749	3.1
		0.294	0.786	2.7
		0.436	0.826	1.9
water + LA + p-xylene	298.15	0.006	0.022	4.0
		0.008	0.021	2.4
		0.013	0.020	1.5
		0.016	0.018	1.1
		0.019	0.018	1.0
		0.021	0.019	0.9
	308.15	0.004	0.015	3.3
		0.008	0.014	1.7
		0.013	0.014	1.1
		0.017	0.014	0.8
		0.021	0.014	0.7
		0.024	0.014	0.6
	318.15	0.005	0.019	3.6
		0.009	0.018	2.1
		0.013	0.018	1.3
		0.016	0.018	1.1
		0.019	0.018	0.9
		0.023	0.018	0.8

[a]Average relative uncertainties u are u (T) = 0.01 K, u (p) = 0.4 kPa, and u (S) = 0.2.
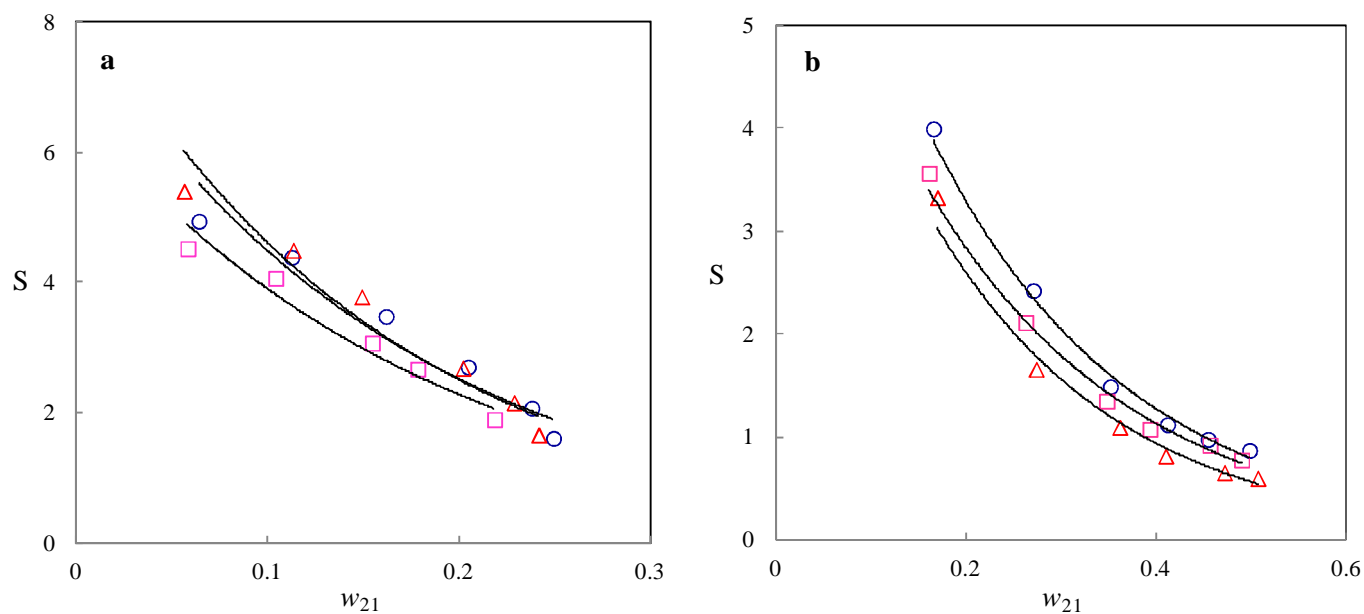
Fig. 5. Plot of the separation factor (S) of lactic acid as a function of mass fraction of the acid in the aqueous phase (w_{21}) for the system containing a) benzyl alcohol, or b) p-xylene, at different temperatures; (○) 298.15 K, (Δ) 308.15 K, (□) 318.15 K.
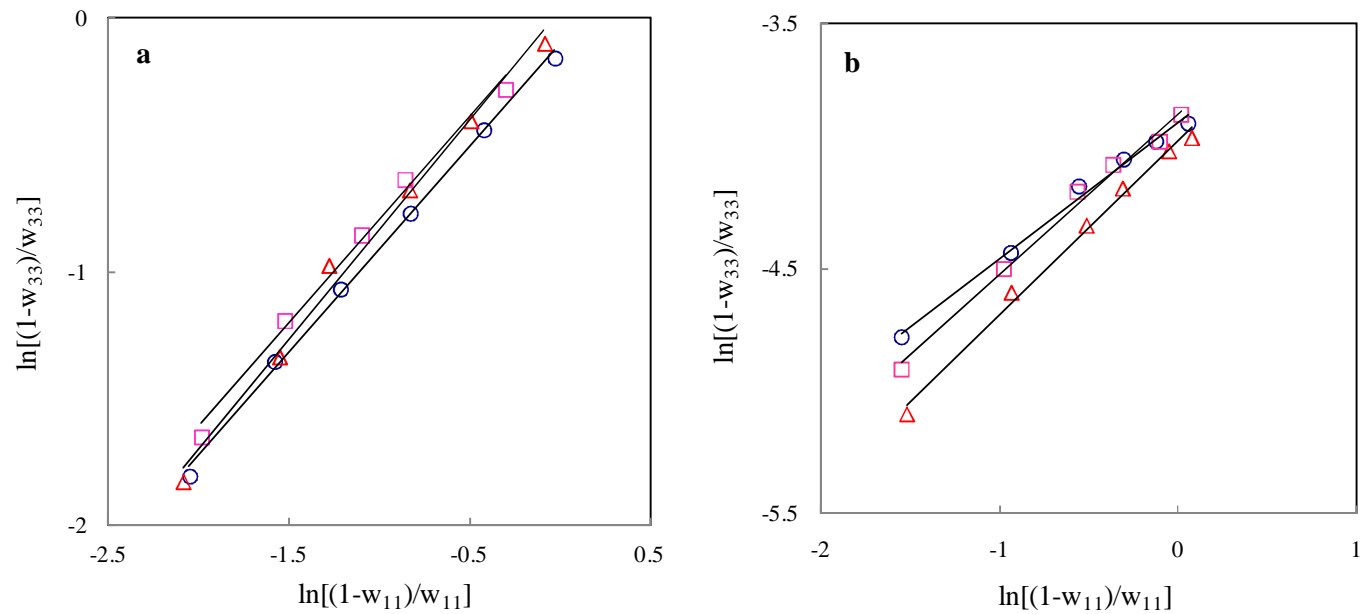
Fig. 6. Othmer-Tobias plot for the [water + lactic acid + a) benzyl alcohol or b) p-xylene] systems at different temperatures; (○) 298.15 K, (Δ) 308.15 K, (□) 318.15 K.

Table 6. The Highest Values of Separation Factors for the (Water + Lactic Acid + Solvent) Ternary Systems at $T = 298.15$ K and $p = 101.3$ kPa[a]

System	D_2	S	Literature
Water + LA + 1-butanol	2.402	4.33	[14]
Water + LA + 1-pentanol	2.693	6.73	[14]
Water + LA + 1-hexanol	2.455	7.33	[14]
Water + LA + 1-heptanol	2.091	6.92	[14]
Water + LA + 1-octanol	0.350	8.14	[11]
Water + LA + 1-nonanol	0.290	7.06	[11]
Water + LA + 1-decanol	0.260	9.14	[11]
Water + LA + benzyl alcohol	0.581	4.90	This study
Water + LA + p-xylene	0.022	4.00	This study

[a]Standard uncertainties u are u $(T) = 0.01$ K, and u $(p) = 0.4$ kPa.

Table 7. Coefficients of Othmer-Tobias and Hand Equations for the Ternary Systems of (Water + Lactic Acid + Benzyl Alcohol or p-Xylene) at $T = (298.15, 308.15$ and $318.15)$ K and $p = 101.3$ kPa[a]

T (K)	Othmer-Tobias correlation			Hand correlation		
	A	B	R^2	A'	B'	R^2
	water + LA + benzyl alcohol					
298.15	-0.104	0.808	0.998	0.175	0.902	0.998
308.15	0.024	0.860	0.992	0.060	0.890	0.997
318.15	0.021	0.815	0.992	0.013	0.888	0.996
	water + LA + p-xylene					
298.15	-3.902	0.560	0.991	8.244	1.769	0.994
308.15	-3.976	0.712	0.993	7.509	1.521	0.998
318.15	-3.867	0.659	0.991	6.941	1.484	0.996

[a]Standard uncertainties u are u $(T) = 0.01$ K, and u $(p) = 0.4$ kPa.
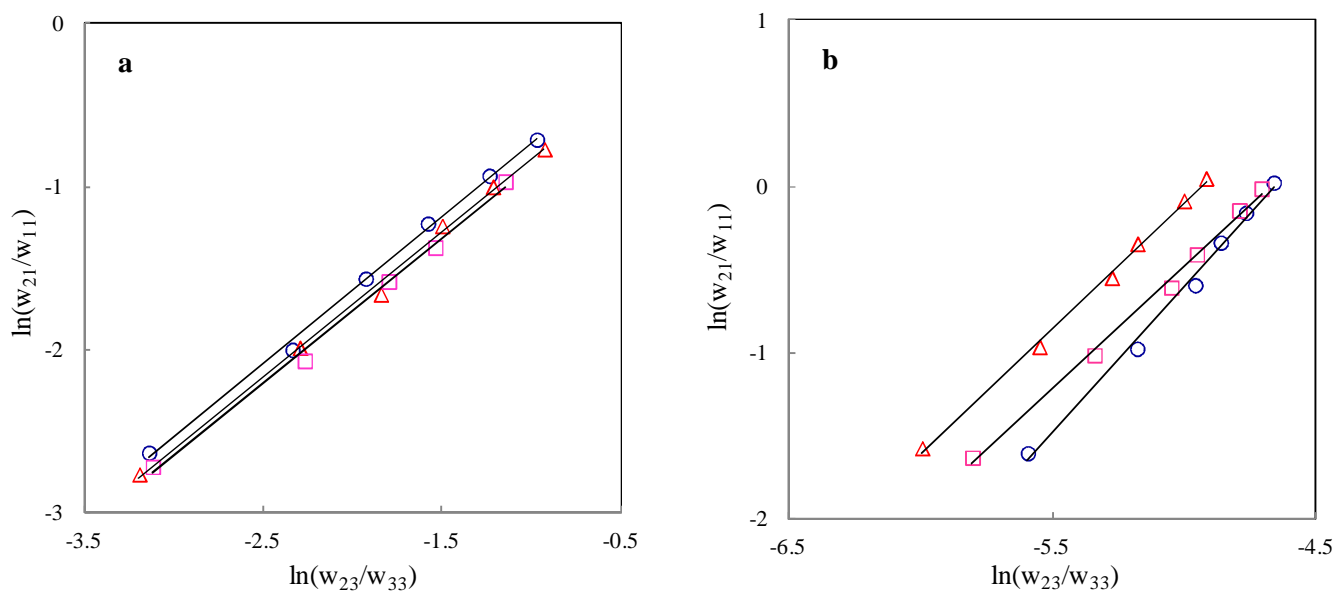
Fig. 7. Hand plot for the [water + lactic acid + a) benzyl alcohol or b) *p*-xylene] systems at different temperatures; (○) 298.15 K, (△) 308.15 K, (□) 318.15 K.

Table 8. The UNIQUAC Structural Parameters (*r* and *q*) for Pure Components [26]

Components	*r*	*q*
Water	0.92	1.40
Lactic acid	3.65	3.50
Benzyl alcohol	3.55	3.15
p-xylene	6.62	5.83

Table 9. Calculated UNIQUAC and NRTL Tie-line Data in Mass Fraction for (Water + Lactic Acid + Benzyl Alcohol or *p*-Xylene) at *T* = (298.15, 308.15 and 318.15) K

Aqueous phase mass fraction				Organic phase mass fraction			
w_{11}		w_{21}		w_{13}		w_{23}	
UNIQ.	NRTL	UNIQ.	NRTL	UNIQ.	NRTL	UNIQ.	NRTL
water + LA + benzyl alcohol							
T = 298.15 K							
0.890	0.892	0.066	0.064	0.105	0.107	0.039	0.040
0.826	0.826	0.113	0.114	0.124	0.125	0.071	0.072

Table 9. Continued

0.774	0.773	0.148	0.151	0.142	0.142	0.098	0.098
0.702	0.700	0.192	0.195	0.169	0.168	0.136	0.134
0.606	0.602	0.239	0.241	0.212	0.211	0.185	0.180
0.510	0.507	0.271	0.269	0.266	0.265	0.231	0.222
			$T = 308.15$ K				
0.895	0.897	0.058	0.056	0.107	0.110	0.037	0.039
0.824	0.824	0.111	0.112	0.130	0.132	0.077	0.077
0.781	0.780	0.140	0.142	0.146	0.146	0.101	0.100
0.703	0.700	0.187	0.191	0.178	0.177	0.144	0.140
0.623	0.619	0.227	0.231	0.216	0.215	0.186	0.180
0.523	0.520	0.262	0.262	0.275	0.274	0.232	0.224
			$T = 318.15$ K				
0.883	0.880	0.058	0.060	0.122	0.119	0.038	0.036
0.817	0.821	0.105	0.103	0.148	0.150	0.074	0.079
0.749	0.748	0.149	0.151	0.177	0.173	0.110	0.107
0.700	0.699	0.178	0.179	0.199	0.197	0.135	0.134
0.579	0.582	0.232	0.229	0.264	0.269	0.193	0.194
			water + LA + *p*-xylene				
			$T = 298.15$ K				
0.824	0.823	0.167	0.167	0.008	0.008	0.004	0.004
0.717	0.718	0.272	0.271	0.008	0.008	0.006	0.006
0.643	0.641	0.344	0.347	0.008	0.008	0.007	0.007
0.595	0.591	0.392	0.396	0.008	0.008	0.007	0.008
0.541	0.538	0.444	0.448	0.008	0.008	0.008	0.008
0.481	0.479	0.504	0.505	0.008	0.008	0.009	0.009
			$T = 308.15$ K				
0.818	0.820	0.173	0.171	0.008	0.008	0.003	0.003
0.735	0.730	0.255	0.260	0.008	0.008	0.004	0.004
0.625	0.620	0.363	0.368	0.008	0.008	0.005	0.005
0.585	0.579	0.402	0.409	0.008	0.008	0.006	0.006
0.512	0.502	0.475	0.484	0.007	0.007	0.006	0.006
0.496	0.510	0.491	0.477	0.007	0.007	0.007	0.006
			$T = 318.15$ K				
0.823	0.825	0.165	0.162	0.008	0.008	0.003	0.003
0.736	0.734	0.251	0.253	0.008	0.008	0.005	0.005
0.646	0.645	0.339	0.341	0.008	0.008	0.006	0.006
0.594	0.590	0.390	0.395	0.008	0.008	0.007	0.007
0.526	0.517	0.458	0.467	0.008	0.008	0.008	0.008
0.507	0.509	0.477	0.475	0.008	0.008	0.008	0.008

Table 10. Correlated Results from the UNIQUACand NRTL Models and the Corresponding
Binary Interaction Parameters (a_{ij} and a_{ij})/K and (b_{ij} and b_{ij})/K of the Systems

Model	i - j	a_{ij} ($b_{ij)}$	a_{ji} (b_{ji})	*rmse* (%)
water + LA + benzyl alcohol				
UNIQUAC	1-2	-510.96	482.48	
	1-3	-225.06	0.57	1.04
	2-3	374.85	-211.11	
NRTL	1-2	-1225.00	-325.65	
	1-3	1446.05	96.64	0.98
	2-3	-291.89	-1255.70	
water + LA + *p*-xylene				
UNIQUAC	1-2	-379.20	466.84	
	1-3	-213.62	-4.20	0.56
	2-3	337.11	-43.99	
NRTL	1-2	-830.29	-559.32	
	1-3	1463.43	104.82	0.46
	2-3	-297.94	-1297.94	

experimental and calculated mass fractions according to the following equation:

$$\text{rmse} = \left\{ \frac{1}{6n} \left(\sum_{k=1}^{n} \sum_{j=1}^{2} \sum_{i=1}^{3} \left(w_{ijk}^{\text{exp}} - w_{ijk}^{cal} \right)^2 \right) \right\}^{\frac{1}{2}} \qquad (2)$$

where n is the number of tie-lines, w^{exp} indicates the experimental mass fraction, and w^{cal} is the calculated mass fraction. The binary interaction parameters along with *rmse* values for the studied systems are given in Table 10. For these ternary systems, both the models perform well in the correlations of the LLE data.

CONCLUSIONS

The LLE data for the (water + lactic acid + benzyl alcohol) and (water + lactic acid + *p*-xylene) ternary systems were obtained at $T = (298.15, 308.15$ and $318.15)$ K. The experimental results show that the system containing benzyl alcohol exhibits type-1 behavior of LLE and the other system displays type-2.

The temperature effect on the separation factors of both systems is small. A comparison of the extracting abilities of the solvents was made with respect to the separation factor values. This factor is found to be greater than 1 ($S > 1$) for

the systems investigated, which means that extraction of LA by these solvents is possible. The system containing benzyl alcohol has the advantage of higher acid distribution coefficient and separation factor.

The UNIQUAC and NRTL thermodynamic models were used to correlate the experimental LLE data. The corresponding optimized binary interaction parameters were determined. The average *rmse* values indicate that both models give good correlation for the investigated systems.

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