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Isopropanol dehydration via extractive distillation using low transition temperature mixtures as entrainers

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ABSTRACT

Low transition temperature mixtures (LTTMs), also known as deep eutectic solvents, show properties that make them suitable as entrainers for extractive distillation. Two different low transition temperature mixtures were considered as potential entrainers for the extractive distillation of the azeotropic mixture (isopropanol + water). (Lactic acid + choline chloride) (2:1) and (glycolic acid + choline chloride) (3:1) were selected for this work. (Vapor + liquid) equilibrium measurements of the pseudo-binary systems (isopropanol + LTTM) and (water + LTTM) were measured at different concentrations of LTTM in a pressure range of 10 to 100 kPa. (Vapor + liquid) equilibrium data of the pseudo-ternary system (isopropanol + water + LTTM) were also measured at constant pressure (100 kPa) and constant LTTM molar fraction of 0.05 and 0.1. It was found that these LTTMs cannot break the azeotrope at those concentrations. However, the azeotrope was displaced to a much higher isopropanol concentration. The NRTL model was successfully applied to fit the experimental data.

1. Introduction

Isopropanol (IPA) is a bulk chemical mainly used as solvent or as a chemical intermediate for the production of mono-isopropyl amine or isopropyl acetate. Mixtures of IPA and water that need to be dehydrated can be found in the production of IPA by indirect hydrogenation or by fermentation of cellulosic materials as well as byproducts in many other processes where IPA is involved. The (IPA + water) mixture presents an azeotrope at 87.5 wt%; therefore, the IPA dehydration by ordinary distillation is basically impossible [1]. Several alternative dehydration processes have been reported: azeotropic distillation [2–5], pervaporation [6–17], (liquid + liquid) extraction [18–20], reactive distillation [21,22], adsorption [23,24], and extractive distillation [25–37].

Extractive distillation is distillation in the presence of a separation agent, also called an entrainer, which interacts differently with the components of the original mixture and, therefore, alters their relative volatilities [38]. The main characteristics of a separation agent are: higher boiling point than the components of the original mixture, miscibility with the mixture, recyclability, low toxicity, and biodegradability [39]. Different salts [26,33,36,37] and ionic liquids (ILs) [40] were reported to be feasible separation agents in the extractive distillation of the (IPA + water) mixture.

The usage of salts as separation agents displays several advantages, such as selective association properties, as well as less energy consumption and small amounts of separation agent needed. The main disadvantages of salts are solid handling, corrosion, and pollution [33]. ILs were also reported to show good selective association properties, and because they are liquid, the handling problem is overcome. However, their main drawbacks for large-scale applications are their price, the complexity of the synthesis, and the amount of separation agent required [40]. Low transition temperature mixtures (LTTMs), discovered in 2003 [41], seem to be a promising alternative to ILs because they share many of their properties, but they can be prepared more easily and cheaply. Originally, LTTMs were called deep eutectic solvents (DESs), but this name does not cover the complete class of solvents, because many mixtures do not show an (eutectic) melting point, but a glass transition instead.

LTTMs were recently found to be a feasible alternative to organic solvents in different applications such as electrochemistry, material preparation, catalytic reactions, biomass deconstruction, biodiesel processing, and separation processes such as (liquid + liquid) extraction [42,43]. LTTMs are a mixture of one or more hydrogen bond donors (HBDs) and one or more hydrogen bond acceptors (HBAs) that together, in the proper ratio, have much lower melting point than the individual components. LTTMs generally present properties such as low vapor pressure, wide liquid range, water compatibility, biodegradability, non-flammability, and most

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importantly, easy and cheap preparation by mixing natural and readily starting materials [43]. All of these are desired properties for an entrainer in extractive distillation.

The target of this work is to determine if LTTMs can be used as entrainers in the separation of the azeotropic mixture (IPA + water) via extractive distillation. In order to demonstrate that, (vapor + liquid) equilibrium (VLE) data of the corresponding pseudo-binary and pseudo-ternary systems were measured, where the LTTM was treated as single component. Two LTTMs were selected with this purpose: (1) (glycolic acid + choline chloride) (molar ratio = 3:1) (GC 3:1) and (2) (lactic acid + choline chloride) (molar ratio = 2:1) (LC 2:1). Both LTTMs were used as entrainers in the IPA dehydration at different concentrations. The molecular structures of the LTTMs are illustrated in table 1. The NRTL model was used to fit the experimental data. Also during the NRTL fitting, the LTTMs were treated as a single compounds (HBD + HBA pair).

2. Experimental

2.1. Materials

The chemicals used were of the high purity and purchased from trustful sources. They are shown in table 2. Deionized MilliQ water was used in all the studied mixtures ($\geqslant 18.2$ M$\Omega \cdot$ cm). The water content was measured by using Karl Fischer moisture analysis, type Metrohm795. The water content was between 0.4 and 0.7 wt% in all cases.

2.2. LTTMs preparation

LTTMs were prepared by following procedure already reported [44]. Mixtures were prepared using a Mettler AX205 balance with a precision of ±0.02 mg. Both HBD and HBA were added to a flask and heated while stirring. The uncertainty in the molar mixing ratio is (±2%). This is based on the uncertainty of the balance reading and the purity of the constituents used. The temperature was controlled using a thermostatic bath with temperature controller

TABLE 1
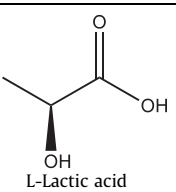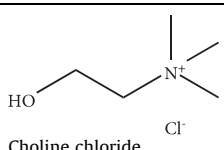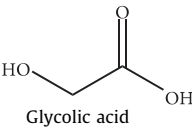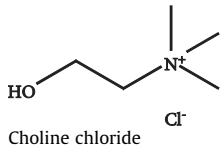HBD and HBA structure and molar ratio for the selected LTTMs.

HBD	Molar ratio	HBA
L-Lactic acid	2:1	Choline chloride
Glycolic acid	3:1	Choline chloride

TABLE 2
Chemicals used in this work.

Name	Source	Purity (w%)
Isopropanol	VWR	$\geqslant 98$
Glycolic acid	Sigma Aldrich	$\geqslant 99$
L-lactic acid	Purac	$\geqslant 99$
Choline chloride	Sigma Aldrich	$\geqslant 98$

(IKA ETS-D5). GC 3:1 was prepared at 343.15 (±0.1) K, while LC 2:1 was produced at 333.15 (±0.1) K.

2.3. VLE determination

Experimental VLE data were obtained using an all-glass ebulliometer (i-Fisher LABODEST® VLE 602D). Pressure and equilibrium temperature were determined with an accuracy of ±0.1 kPa and ±0.5 K. All solutions were prepared gravimetrically by an electronic balance (Mettler Toledo AX 205) with a readability of ±10^{-4} g. For the VLE measurements of the pseudo-ternary systems, after the equilibrium was reached, a sample of the vapor phase and a sample of the liquid phase were taken. Then, a certain amount of the system was removed and a new mixture of (IPA + LTTM) or (water + LTTM) was added, keeping the LTTM concentration constant.

The composition of the condensed vapor phase (IPA + water) was analyzed using a Varian CP-3800 gas chromatograph (GC) equipped with a flame ionization detector and a Varian CP-SIL 5CB column. The GC method is described in table 3. No presence of entrainer was detected in the vapor phase.

In the liquid phase, the IPA mole fraction was determined using the same GC method (where the low-volatile LTTM was captured in a liner placed before the column), while the water content was analyzed using Karl Fischer moisture analysis, type Metrohm795, the LTTM concentration was determined via a mass balance calculation.

3. Results and discussion

3.1. Binary VLE data

The VLE data of the pseudo-binary systems (IPA + LTTM) and (water + LTTM) were measured in a pressure range of 10 to 100 kPa at LTTM molar fractions of 0.05 and 0.1. Experimental data for (IPA + LC 2:1), (IPA + GC 3:1), (water + LC 2:1) and (water + GC 3:1) are displayed in table 4. A representation of these data is shown in figure 1. In order to calculate the activity coefficient, modified Raoult's law (equation (1)) was used.

$$\gamma_i = \frac{y_i P}{x_i p_i^0}, \tag{1}$$

where γ_i is the activity coefficient, y_i and x_i are the vapor and liquid mole fractions of component i, P is the total pressure and p_i^0 is the pure component vapor pressure. The vapor mole fraction of water and IPA in the binary system with LTTM is $y = 1$, because no presence of LTTM was detected in the vapor phase due to its low volatility. The pure component vapor pressure was calculated using the Antoine equation. Antoine parameters for IPA and water were taken from literature [45].

The activity coefficient shows the deviation from the ideal solution. Positive deviations commonly involve repulsive forces between the molecules. Subsequently, negative deviations mean attractive forces between the molecules. Greater deviations from

TABLE 3
GC conditions employed for analysis of the condensed vapor phase.

Column type	CP-SIL CB (30 m; 0.25 mm; 0.25 μm)
Detector type	FID
Detector temperature	523 K
Injector temperature	423 K
Injection volume	1 μL
Carrier gas	He
Flow rate (constant)	2.0 cm$^3 \cdot$ min^{-1}
Split ratio	200

TABLE 4

Experimental VLE data (temperature, T; pressure, P; liquid mole fraction, x; activity coefficients, γ) of the pseudo-binary systems (IPA (1) + LC 2:1 (2)), (IPA (1) + GC 3:1 (2)), (water (1) + LC 2:1(2)) and (water (1) + GC 3:1(2)) at constant LTTM molar fraction in a pressure range of 10 to 100 kPa.[a]

P/kPa	T/K	γ_1	P/kPa	T/K	γ_1	P/kPa	T/K	γ_1	P/kPa	T/K	γ_1
	IPA (1) + LC 2:1 (2)						IPA (1) + GC 3:1 (2)				
	$x_2 = 0.05$			$x_2 = 0.1$			$x_2 = 0.05$			$x_2 = 0.1$	
10.0	307.2	1.02	10.0	307.3	1.08	10.0	307.2	1.02	10.0	306.8	1.11
15.0	314.4	1.04	15.0	314.4	1.09	15.0	314.4	1.03	15.0	314.0	1.12
20.0	319.7	1.04	20.0	319.7	1.10	20.0	319.9	1.04	20.0	318.9	1.15
25.0	324.0	1.06	30.0	327.8	1.11	25.0	324.2	1.04	30.0	326.8	1.16
30.0	327.6	1.05	40.0	333.7	1.11	30.0	327.8	1.04	40.0	332.3	1.19
40.0	333.3	1.07	50.0	338.5	1.12	40.0	333.8	1.05	50.0	337.6	1.16
49.8	338.2	1.07	60.0	342.5	1.12	50.0	338.7	1.05	60.0	341,8	1.16
60.0	342.0	1.09	70.0	346.1	1.12	60.0	342.8	1.05	69.9	345.5	1.15
69.9	345.6	1.09	80.0	349.0	1.13	70.0	346.3	1.05	80.0	348.6	1.16
80.0	348.5	1.10	89.9	352.0	1.13	80.0	349.5	1.06	90.0	351.4	1.16
90.0	351.8	1.08	100.0	354.5	1.13	89.9	352.3	1.06	101.3	354.3	1.16
99.9	354.2	1.09				101.2	355.3	1.06			
	Water (1) + LC 2:1(2)						Water (1) + GC 3:1(2)				
10.0	319.5	1.02	10.0	320.5	1.02	10.0	320.0	0.99	10.0	319.7	1.06
15.0	327.3	1.03	14.9	328.2	1.04	15.0	328.1	1.00	15.0	327.3	1.10
20.0	333.8	1.02	20.0	334.2	1.06	20.0	333.8	1.02	20.0	333.3	1.10
24.9	338.3	1.04	30.0	342.4	1.10	25.0	338.7	1.02	30.0	341.0	1.12
30.0	342.3	1.05	40.0	349.1	1.10	30.0	342.2	1.05	40.0	349.1	1.11
40.0	349.1	1.05	50.0	354.6	1.11	40.0	349.3	1.04	50.0	354.5	1.11
49.9	354.5	1.05	60.0	359.2	1.11	50.0	354.8	1.04	60.0	358.9	1.12
60.0	359.1	1.05	70.0	363.2	1.11	60.0	359.3	1.04	70.0	363.2	1.11
70.0	362.4	1.08	80.0	366.7	1.11	70.0	363.2	1.05	80.0	366.3	1.12
80.0	365.7	1.09	90.0	369.9	1.12	80.0	366.7	1.05	90.0	369.8	1.11
89.9	368.6	1.10	100.0	371.6	1.16	90.0	369.7	1.06	100.0	371.8	1.15
100.0	371.1	1.12				101.3	372.8	1.06			

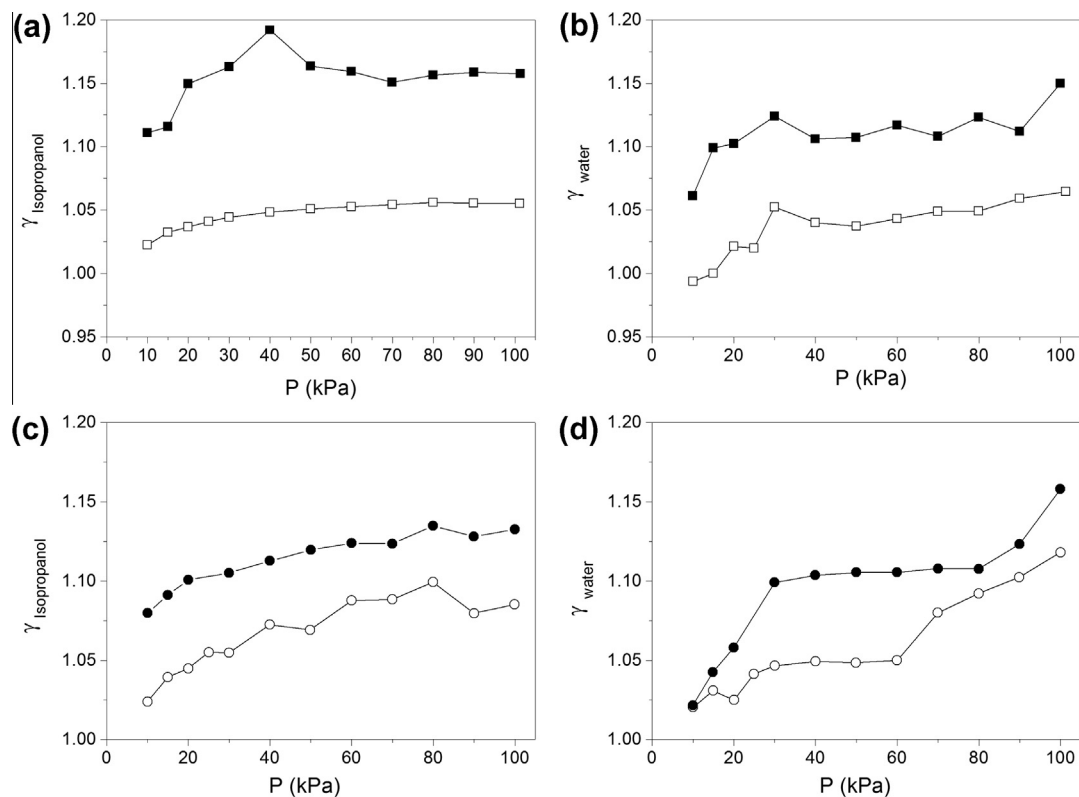[a] Standard uncertainties u are $u(T) = 0.5$ K, $u(P) = 0.1$ kPa, $u(x) = 0.001$.

FIGURE 1. (a) Experimental activity coefficients for the binary system (IPA + GC 3:1) at constant entrainer molar fraction of 0.05 (□) and 0.1 (■). (b) Experimental activity coefficients for the binary system (water + GC 3:1) at constant entrainer molar fraction of 0.05 (□) and 0.1 (■). (c) Experimental activity coefficients for the binary system (IPA + LC 2:1) at constant entrainer molar fraction of 0.05 (○) and 0.1 (●). (d) Experimental activity coefficients for the binary system (water + LC 2:1) at constant entrainer molar fraction of 0.05 (○) and 0.1 (●).

TABLE 5
Values of the binary interaction parameters for the NRTL model obtained from the correlation of the experimental VLE data for the pseudo-binary mixtures at constant LTTM molar fraction of 0.05 and 0.1 and the weighted sum of squares (WSS(P)) for the fits.

Comp. i	Comp. j	a_{ij}	a_{ji}	b_{ij}	b_{ji}	c_{ij}	WSS (P)
Water	LC 2:1 ($x_2 = 0.05$)	−15.11	3.13	8874.7	−2495.7	0.3	$2.23 \cdot 10^{-10}$
IPA	LC 2:1 ($x_2 = 0.05$)	−15.37	−13.20	10,821	3610.5	0.3	$7.33 \cdot 10^{-10}$
Water	LC 2:1 ($x_2 = 0.1$)	22.20	1.72	−4119.0	−1688.0	0.3	$1.71 \cdot 10^{-10}$
IPA	LC 2:1 ($x_2 = 0.1$)	8.074	−16.77	−1229.4	7031.7	0.3	$5.89 \cdot 10^{-10}$
Water	GC 3:1 ($x_2 = 0.05$)	−48.50	−13.32	22,779	3451.1	0.3	$1.50 \cdot 10^{-10}$
IPA	GC 3:1 ($x_2 = 0.05$)	12.80	−26.14	−2458.7	8526.5	0.3	$1.38 \cdot 10^{-10}$
Water	GC 3:1 ($x_2 = 0.1$)	15.93	5.17	−218.38	−2350.1	0.3	$1.85 \cdot 10^{-10}$
IPA	GC 3:1 ($x_2 = 0.1$)	10.10	−2.07	−1166.5	65.50	0.3	$8.61 \cdot 10^{-11}$

TABLE 6
Experimental VLE data (temperature, T; LTTM-free liquid mole fraction, x'; vapor mole fraction, y; relative volatility, α) of the pseudo-ternary systems (IPA (1) + water (2) + GC 3:1) and (IPA (1) + water (2) + LC 2:1) at 100 kPa and constant LTTM molar fraction.[a]

x'_1	y_1	T/K	α	x'_1	y_1	T/K	α
			IPA (1) + water (2) + GC 3:1 (3)				
		$x_3 = 0.05$				$x_3 = 0.1$	
0.000	0.000	372.0		0.000	0.000	371.8	
0.026	0.448	360.4	29.92	0.028	0.463	360.9	30.22
0.053	0.490	357.3	17.26	0.056	0.515	357.2	18.09
0.105	0.538	354.3	9.89	0.111	0.544	355.4	9.54
0.158	0.575	353.4	7.22	0.167	0.547	355.4	6.04
0.211	0.589	353.2	5.36	0.222	0.597	353.4	5.18
0.263	0.616	353.0	4.49	0.278	0.611	353.0	4.08
0.316	0.629	353.1	3.67	0.334	0.650	353.2	3.71
0.525	0.656	352.8	1.72	0.389	0.668	353.1	3.16
0.578	0.682	352.9	1.56	0.445	0.690	353.1	2.78
0.630	0.687	352.9	1.29	0.487	0.687	353.1	2.30
0.683	0.725	353.0	1.23	0.541	0.711	353.2	2.09
0.735	0.759	353.0	1.14	0.594	0.729	353.1	1.83
0.788	0.785	353.1	0.99	0.666	0.750	353.0	1.51
0.840	0.832	353.4	0.94	0.722	0.783	353.1	1.39
0.893	0.894	353.6	1.01	0.777	0.824	353.1	1.34
0.946	0.941	354.0	0.91	0.833	0.836	353.3	1.02
0.973	0.963	354.3	0.73	0.889	0.887	353.6	0.98
1.000	1.000	355.2		0.944	0.940	353.9	0.92
				0.972	0.970	354.1	1.14
				1.000	1.000	354.3	
			IPA (1) + water (2) + LC 2:1 (3)				
0.000	0.000	371.1		0.000	0.000	371.5	
0.053	0.488	357.3	17.12	0.027	0.430	359.2	27.19
0.106	0.545	354.5	10.17	0.053	0.470	357.4	15.87
0.158	0.558	354.1	6.72	0.102	0.505	354.6	9.00
0.264	0.585	353.5	3.93	0.146	0.525	353.2	6.45
0.316	0.607	353.3	3.34	0.186	0.551	353.2	5.36
0.369	0.611	353.2	2.69	0.222	0.561	353.1	4.49
0.422	0.635	353.1	2.39	0.252	0.555	353.1	3.70
0.527	0.670	352.9	1.82	0.295	0.583	353.1	3.33
0.580	0.683	352.9	1.57	0.54	0.608	352.6	1.33
0.632	0.717	352.9	1.47	0.57	0.621	352.6	1.23
0.684	0.725	352.9	1.22	0.62	0.650	352.6	1.12
0.737	0.754	353.0	1.09	0.68	0.692	352.6	1.06
0.790	0.788	353.1	0.99	0.73	0.715	352.6	0.91
0.843	0.835	353.3	0.95	0.79	0.740	352.6	0.77
0.896	0.884	353.8	0.89	0.84	0.780	352.8	0.67
0.948	0.939	354.2	0.84	0.89	0.853	352.9	0.68
0.974	0.962	354.3	0.68	0.95	0.924	353.2	0.68
1.000	1.000	354.6		0.97	0.975	353.3	1.08
				1.00	1.000	353.6	

[a] $u(T) = 0.5$ K, $u(P) = 0.1$ KPa, $u(x') = 0.001$, $u(x_3) = 0.001$ and $u(y) = 0.005$.

ideality make it easier to find significant changes in the relative volatilities and, therefore, break the azeotrope.

In figure 1 it is observed that the activity coefficient increases with the concentration of LTTM in all the pseudo-binary systems. Therefore, the boiling point of the most volatile compound was decreased upon LTTM addition. Reason is that the hydrogen bonding nature of the LTTMs creates weak interactions between the solvent and the solute. These weak interactions interfere with the hydrogen bonds already present in the most volatile component (IPA or water). Therefore, both the water and the IPA become relatively more volatile.

If the pressure is considered, it is observed that the higher the pressure, the larger the activity coefficient. Taking into account that the larger the activity coefficient, the better the performance of the LTTMs in the separation, a pressure of 100 kPa was selected as working condition in the pseudo-ternary experiments.

Furthermore, in figure 1(a) and (c) it is shown that GC 3:1 increases the activity coefficient of IPA more than LC 2:1 under the same conditions. Therefore, it is possible to say that the interactions between the IPA and the GC 3:1 are weaker (more repulsion) than the interactions between the IPA and the LC 2:1. In figure 1(b) and (d) it is shown that both LTTMs produce similar increments in the activity coefficient of the water; thus, both LTTMs produce similar repulsive forces.

Moreover, higher activity coefficients for the system containing (IPA + LTTM) than for the system containing (water + LTTM) (water volatility is less increased compared to IPA volatility) are desired in order to break the azeotrope. Therefore, figure 1(a) and (b) must be considered simultaneously, as well as figure 1(c) and (d). In all cases the activity coefficient of IPA and water are higher than one; consequently, a displacement of the azeotrope is expected. Only for GC 3:1 at molar fraction of 0.1 the activity coefficient of IPA is over the entire pressure range higher than the activity coefficient of water. Consequently, azeotrope breaking is only expected for this system.

The pseudo-binary systems were correlated using the non-random two liquid (NRTL) model. The parameters obtained with this model can later be used to predict the behavior of the pseudo-ternary systems. In the model, the LTTMs were treated as a single compound. The NRTL model is defined as follows:

$$ln\gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{kj}} \right), \qquad (2)$$

where:

$$G_{ij} = e^{(-\alpha_{ij}\tau_{ij})}, \qquad (3)$$

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T}, \qquad (4)$$

$$\alpha_{ij} = c_{ij} = c_{ji}. \qquad (5)$$

In equation (5) it is shown that the c_{ij} parameter is symmetrical. In this work it was fixed to 0.3 (this is the recommended value for nonpolar substances and nonpolar with polar non-associated liquids). The correlation was made with an Aspen Plus® regression, using the Maximum-Likelihood objective function and solved with the New Britt–Luecke algorithm. The estimated values of the binary parameters including the weighted sum of squares (WSS) between the experimental and calculated data points are shown in table 5.
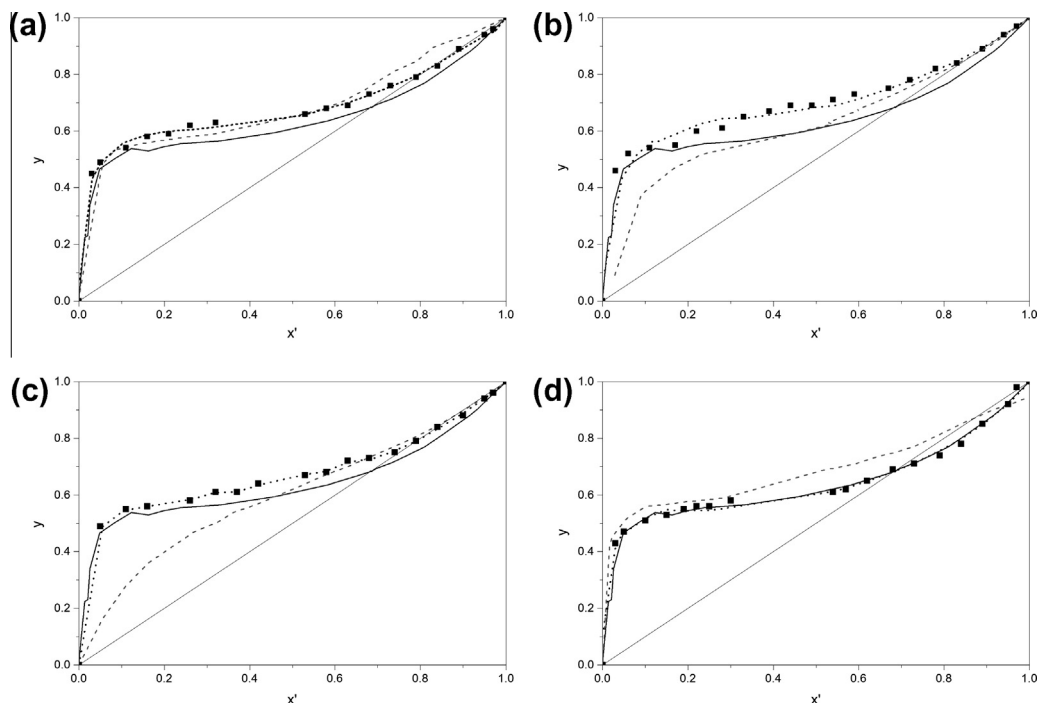
FIGURE 2. (a) Experimental $x'y$ diagram for (IPA + water + GC 3:1) at constant pressure (100 kPa) and LTTM molar fraction of 0.05. (b) Experimental $x'y$ diagram for (IPA + water + GC 3:1) at constant pressure (100 kPa) and LTTM molar fraction of 0.1. (c) Experimental $x'y$ diagram for (IPA + water + LC 2:1) at constant pressure (100 kPa) and LTTM molar fraction of 0.05. (d) Experimental $x'y$ diagram for (IPA + water + LC 2:1) at constant pressure (100 kPa) and LTTM molar fraction of 0.1. In all the graphs the solid squares (■) represent the experimental data, the solid line represent the VLE data of the azeotropic mixture (IPA + water), the grey dashed lines represent the prediction using the NRTL model and the black dotted line represent the fitting using the NRLT model.

TABLE 7

Values of the binary interaction parameters for the NRTL model obtained from the correlation of the experimental VLE data for the pseudo-ternary mixtures at constant LTTM molar fraction of 0.05 and 0.1 and the weighted sum of squares ($WSS(P)$) for the fits.

Comp. i	Comp. j	a_{ij}	a_{ji}	b_{ij}	b_{ji}	c_{ij}	WSS (P)
		IPA (1) + water (2) + GC 3:1 (3) (x_3 = 0.05)					
Water	GC 3:1	202.75	68.71	1000.7	−24,989	0.3	0.006
IPA	GC 3:1	195.48	−15.86	−3498.1	6257.3	0.3	
IPA	Water	−277.61	−2.72	103,793	1835.1	0.3	
		IPA (1) + water (2) + GC 3:1 (3) (x_3 = 0.1)					
Water	GC 3:1	2.31	68.51	−66.06	−204.81	0.3	0.001
IPA	GC 3:1	4.69	3.97	133.81	−113.81	0.3	
IPA	Water	1.85	3.25	−627.25	−409.58	0.3	
		IPA (1) + water (2) + LC 2:1 (3) (x_3 = 0.05)					
Water	LC 2:1	136.00	−28.26	−42,174	9129.8	0.3	0.0003
IPA	LC 2:1	138.33	121.58	4029.8	22,119	0.3	
IPA	Water	−12.79	42.61	4536.3	−14,349	0.3	
		IPA (1) + water (2) + LC 2:1 (3) (x_3 = 0.1)					
Water	LC 2:1	−35.94	119.95	13,666	−42,694	0.3	8.6e−5
IPA	LC 2:1	−215.46	−1.14	81,083	171.49	0.3	
IPA	Water	10.91	50.03	−3837.6	−16,318	0.3	

TABLE 8

The values of weighted sum of squares ($WSS(P)$) obtained in prediction of the pseudo-ternary systems VLE data using the binary interaction parameters from the correlation of the pseudo-binary systems VLE data.

System	WSS (P)
IPA (1) + water (2) + GC 3:1 (3) (x_3 = 0.05)	0.030
IPA (1) + water (2) + GC 3:1 (3) (x_3 = 0.1)	0.004
IPA (1) + water (2) + LC 2:1 (3) (x_3 = 0.05)	0.003
IPA (1) + water (2) + LC 2:1 (3) (x_3 = 0.1)	0.005

3.2. Ternary VLE data

The VLE data of the pseudo-ternary systems (IPA + water + LTTM) were measured at constant pressure of 100 kPa and constant LTTM molar fraction of 0.05 and 0.1. Experimental results for the system (IPA + water + GC 3:1) and for the system (IPA + water + LC 2:1) can be found in table 6.

A graphical representation of the experimental data is shown in figure 2. Figure 2 is an $x'y$ diagram, where x' represents the IPA molar fraction in the liquid phase on a LTTM-free basis, and y represents the IPA molar fraction in the vapor phase (which is also LTTM-free, because of the low-volatility nature of the LTTM). The relative volatility can be defined as:

$$\alpha = \frac{y_i/x_i}{y_j/x_j} = \frac{\gamma_i p_i^0}{\gamma_j p_j^0}, \tag{6}$$

where x is the liquid mole fraction, y is the vapor mole fraction, γ is the activity coefficient, p^0 corresponds to the pure component vapor pressure and the subscript i and j refer to components i and j.

The relative volatility is a comparison between the vapor pressure of the components of a mixture. It indicates the difficulty in the separation of the components via distillation. If the relative volatility of the more volatile component is always larger than one, then the azeotrope is broken. Besides, the larger the relative volatility, the easier the separation. Moreover, if the relative volatility is at any point smaller than one, then the azeotrope is not broken.

As shown in figure 2, both LTTMs produce a positive displacement of the azeotropic point (to the pure IPA-side of the $x'y$-diagram), although the azeotrope is not broken in any case. In addition, when the effect of both LTTMs is compared, greater displacements are detected for GC 3:1 than for LC 2:1. Figure 2 shows that GC 3:1 at a molar fraction of 0.1 almost breaks the azeotrope. For the systems GC 3:1 and LC 2:1 at molar fraction of 0.05 a

displacement of the azeotrope have been noticed from 0.68 to 0.78 and 0.73 molar fraction, respectively. Finally, in the system LC 2:1 at molar fraction of 0.1 almost no effect of the entrainer is observed.

These results were also expected on basis of the binary measurements, where only the LTTM GC 3:1 at 0.1 molar fraction increased the IPA volatility more than the water volatility. This is the only system where the azeotrope is almost broken, although at concentrations higher than $x' = 0.89$ the compositions of vapor and liquid phase are nearly identical ($\alpha \approx 1$).

The pseudo-ternary systems were predicted using the NRTL model, with the binary parameters obtained from the pseudo-binary VLE experiments. The binary parameters for the (IPA + water) were taken from Aspen® database. It is observed that the prediction is accurate for LTTM molar fractions 0.05. However, when the LTTM molar fraction is increased, the accuracy of the predictions using the NRTL model for the systems containing LTTMs is lower. One of the main reasons why the prediction is not so accurate in these systems may be the consideration of the LTTM as a single component (neglecting any interactions between the LTTM constituents).

Therefore, the NRTL model was also used to fit the pseudo-ternary systems directly (without the use of the previously obtained binary parameters). Both the predicted (on basis of binary data) and the regressed (on basis of ternary data) VLE data using the NRTL model are graphically depicted in figure 2. In table 7, the parameters for the fitting are shown, together with the WSS of the difference between the regressed and the experimental data. In table 8, the WSS of the pseudo-ternary systems prediction are shown.

4. Conclusions

Two different LTTMs were tested as entrainers for the extractive distillation of the azeotropic mixture (IPA + water). Firstly, the VLE of the pseudo-binary mixtures was measured. It was found that both LTTMs increase the activity coefficient of IPA and water, but only the LTTM GC 3:1 at 0.1 molar fraction increased the IPA volatility more than the water volatility.

Secondly, the VLE of the pseudo-ternary systems (IPA + water + LTTM) were measured at a constant pressure of 100 kPa and a constant LTTM molar fraction of 0.05 and 0.1. It was found that the azeotropic compositions were displaced to much higher IPA concentrations, although the azeotrope was not broken in any case. The LTTM GC 3:1 at 0.1 molar fraction showed the highest displacement of the azeotrope (from 0.68 to 0.89), which was also expected on basis of the binary results.

Finally, the pseudo-binary systems were successfully correlated using the NRTL model. The obtained binary parameters were used to predict the behavior of the pseudo-ternary systems, but the prediction was not adequate in all cases. The ternary systems were also correlated using the NRTL model, where the fitting was found to be adequate.

Acknowledgments

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