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Vapor-liquid equilibrium of 3-ethoxy-1,2-propanediol + water/ethanol/diethyl ether/glycerol/1,2-propanediol at different pressures

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Keywords: VLE; vapor pressure; 3-ethoxy-1,2-propanediol; ethanol; diethyl ether; glycerol; 1,2-propanediol.

Highlights

-Vapor pressure of 3-ethoxy-1,2-propanediol has been determined at different temperatures

-Isobaric vapor-liquid equilibria of systems involving 3-ethoxy-1,2-propanediol were determined at different pressures

-UNIQUAC, NRTL, Wilson and UNIFAC were employed to compare with experimental data-

Abstract

The large availability of glycerol on the market and EU directives in the field of automotive fuels prompt Eni S.p.A to develop a technology for producing biofuels from glycerol. This work focuses on determining isobaric vapor-liquid equilibrium data at different pressures of binary systems constituted by 3-ethoxy-1,2-propanediol, an intermediate product, and some of the other compounds involved in the reactions: water, ethanol, 1,2-propanediol, diethyl ether and glycerol. Moreover, the vapor pressure curve of 3-ethoxy-1,2-propanediol was determined at different temperatures. Finally, different thermodynamic models (UNIFAC, UNIQUAC, NRTL and Wilson), were tested against the experimental data to analyze their possible use when designing separation processes of 3-ethoxy-1,2-propanediol.

1. Introduction

The enforcement of the Kyoto Protocol by the EU has led to the enactment of directives, known as the 20/20/20 package, to counteract global warming. The Renewable Energy Directive (RED 2009/28/CE) requires the introduction in fossil fuels of increasing quantity of biofuels up to 10% (on heating value base) by 2020. Revision of RED, also known as "ILUC Directive" feedstocks, considers a cap of 7% for biofuels from the so called food crops, and foster the use of "advanced" biofuels (i.e. biomass from urban waste, algae, raw glycerine waste effluents, lignocellulosic biomass, etc.) by fixing a minimum level of 0.5% by 2020 [1]. More recently, EU commission has further raised the level of fuels from renewable sources in fossil fuel [2] up to 14% by 2030. Currently, commercially available technology for producing gasoil from renewable sources is largely based on production of FAME (Fatty Acid Methyl Esters) generally known as biodiesel [3].

Biodiesel is produced from the triglycerides contained in vegetable oils [4] such as sunflower, rapeseed or soybean. Triglycerides are reacted with monoalcohols, mainly methanol and to a lower extend ethanol, through a catalytic transesterification. The reaction leads to the corresponding methyl or ethyl esters of fatty acids and glycerol as byproducts [5]. The glycerol produced accounts for approximately 10 % of the biodiesel produced: for each 3.8 L of biodiesel produced a 0.3 kg amount of glycerol byproduct is formed [6]. As a consequence of the increasing consumption of biodiesel, the worldwide production of glycerin has passed from $600 \cdot 10^3$ tonnes in 2006 to $2.6 \cdot 10^6$ tonnes in 2014. The surplus of glycerol production has led to strong reduction of the selling price dropped from 1200 US\$/ton to less than 70 US\$/ton [5]. The high availability and the low price makes the glycerol a good candidate for advanced biofuel production.

Eni has developed a technology for the production of fuel components starting from glycerol as reported in ref. [7 - 9] where are involved compounds such as ethanol, diethyl ether, water or 1,2-propanediol.

The process consists of a number of steps where the separation/purification of the intermediate products and final compounds is needed. Vapor-Liquid equilibrium data usable to design the separation steps are in our case scarcely available in literature and consequently an experimental activity was carried out to fill the gap.

This work focuses on firstly obtaining the vapor pressure curve for 3-ethoxy-1,2-propanediol (3-MEP) since in the literature only few data are available [10 - 15] and some of the data in the literature show some inconsistencies between them. In a second part, the work has been centered on the obtaining of isobaric vapor-liquid equilibrium data for five binary systems involved during the purification of the products of the transformations of glycerol: 3-ethoxy-1,2-propanediol + ethanol / diethyl ether / water / glycerol / 1,2-propanediol systems at two or three different pressures each one. To the extent of our knowledge no equilibrium data is available in the literature for these binary mixtures. The experimental data have been correlated using the UNIQUAC, NRTL and Wilson models and have been compared with predictions made with the UNIFAC model.

2. Experimental

2.1. Chemicals

In Table 1 are presented the different compounds used. The water used was obtained from purified running water after two reverse osmosis steps and one ion exchange resin step and reached a conductivity lower than 2 $\mu\text{S}/\text{cm}$. The water content of the compounds was measured using a coulometric Karl Fischer analysis (737 Coulometer Metrohm). The compounds were used without further purification since GC analysis did not reveal significant impurities.

The 3-ethoxy-1,2-propanediol was analyzed by means of GC-mass and showed several impurities such as ethanol, water, 3-pentanol, 1-hydroxy-2-propanone or 2-ethyl-4-ethoxymethyl-1,3-dioxolane. As the sum of the areas of all the impurities was less than 1 % of the total area, the 3-ethoxy-1,2-propanediol was used as provided. A chromatogram of this compound is presented in figure 1.

Table 1. Provenance table of the compounds used.

IUPAC name	CAS	Other name	Provider	Purity (mass fraction)	Water content (mass fraction)
3-ethoxy-1,2-propanediol	1874-62-0	3-MEP, 3-monoethoxy-propanediol	ENI	>0.99	<0.0005
ethanol	64-17-5	ethyl alcohol	VWR	>0.998	<0.001
diethyl ether	60-29-7	ether, ethyl ether	Merck	>0.997	<0.002
1,2,3-propanetriol	56-81-5	glycerol, glycerin	Alfa Aesar	>0.99	<0.002
1,2-propanediol	57-55-6	propylene glycol	VWR	>0.99	<0.002

Figure 1. GC/MS of 3-ethoxy-1,2-propanediol

2.2. Procedure

2.2.1. Vapor pressure determination

To obtain the vapor pressure of 3-MEP a Fischer Labodest 602 still based on the Gillespie principle was used. This equipment was coupled to a control unit Fischer Minitron (VLE) that enabled to set the pressure inside the still at a desired value using two pressure sensors each for a different working range (2 - 1040 mbar abs and 900 - 4000 mbar abs). The uncertainty of the pressure measurement was 0.2 mbar for pressures in the range 1-100 mbar, 0.5 mbar in the range 200-800 mbar and 1 mbar for the highest pressures (1013-2026 mbar). During the experiment, the equipment was filled with the compound under investigation. To avoid further reactions that could occur during the determination at high temperatures between the compound and the oxygen contained in the air, the gases contained inside the equipment were evacuated until the pressure reached a value lower than 1 mbar and then filled with an inert gas such as Helium up to atmospheric pressure. This emptying/filling step was repeated several times to minimize as much as possible the oxygen remaining inside the equipment and to produce the desorption of the gases contained in the compound whose vapor pressure has to be determined.

The compound was heated in the boiling chamber in order to reach its boiling temperature at the set pressure. Once reached the boiling temperature heating was adjusted to keep the compound at the boiling temperature and produce one to two droplets of condensed vapor per second. A flux of cooling water went through both condensers (the vapor-return branch and the liquid-return one) to minimize losses of the compound. At that moment the temperature of the vapor in the separation chamber was measured with a Pt-100 sensor coupled to a Fischer Minitron (VLE) controller whose measurement uncertainty was 0.1 K (resolution 0.01 K). The pressure was controlled during the whole experiment and the temperature was measured continuously. Once the temperature remained constant at a fixed pressure both values were collected. Subsequently, the pressure set point was changed to determine other (temperature, pressure) datum.

During the vapor pressure measurements, the 3-MEP was in the equipment at boiling conditions for a whole period of more than 40 hours. Then, samples from both the liquid and the vapor phase were taken during the last vapor pressure experiment and subsequently analyzed by GC-mass analysis. These chromatograms were compared to that of the initial compound. All of the compounds present in the latter samples were also present in the initial reagent. The sum of the areas of the impurities still accounted for less than 1% of the total area although it was observed a slightly different distribution of the impurities between the compositions of the vapor and the liquid in equilibria.

2.2.2. Vapor-liquid equilibrium determination.

In the same equipment used for the vapor pressure determination, a mixture of the system to be studied was introduced in the mixing chamber. The mixture was heated until it boiled at the set pressure and the vapor temperature measured. Once these variables remained constant within the uncertainty, both samples, the condensed vapor and the returning liquid in equilibrium with the condensed vapor, were collected and

analyzed. The analyses were performed in an Agilent 7820A gas chromatograph with a thermal conductivity detector (TCD) and a flame ionization detector (FID) in series after a Supelco Analytical 6ft x 1/8 in x 2.1 mm SS packed column with "Porapak Q". Helium was used as carrier gas at 25 mL/min flow. The temperature of the oven was fixed at constant temperature of 493.15 K. The injector and TCD temperature was set at 513.15 K while the FID temperature was maintained at 523.15 K.

3. Results.

3.1. Vapor pressure

The boiling temperatures at the different pressures studied are presented in Table 2. Boiling temperatures at pressures higher than 1013 mbar were not determined as these boiling temperatures would surpass the temperature limit of the equipment. Using these data, the parameters of the Antoine's equation can be regressed. A sole regression was performed for the whole temperature range. In table 3, the values for the parameters of the Antoine equation: $\log P^{\circ} \text{ (mbar)} = A - [B/(T(K)+C)]$ and the standard deviation of the calculated pressure with these parameters (SD) are presented.

Table 2. Boiling temperature of 3-ethoxy-1,2-propanediol at different pressures

T / K	P / mbar
377.6	10.0
390.5	20.0
394.9	25.0
409.8	50.0
426.3	100.0
444.6	200.0
465.0	400.0
478.3	600.0
488.2	800.0
496.8	1013.0

Standard uncertainty: $u(T)=0.1$ K, $u(P)=0.2$ mbar for pressures in the range 1-100 mbar, 0.5 mbar in the range 200-800 mbar and 1 mbar for the highest pressures (1013 mbar).

Table 3. Antoine's parameters* for the 3-ethoxy-1,2-propanediol.

A	B	C	Temperature range	SD (mbar)
7.464	1711.864	-112.88	380 K-497 K	1.23

*Antoine equation. $\log(P(\text{mbar}))=A-B/(T(K)+C)$

To visualize the goodness of the regressed Antoine's parameters sets, Figure 2 shows the experimental vapor pressure of the 3-ethoxy-1,2-propanediol at different temperatures. In the same figure the $P=f(T)$ curves are represented for the parameter set in Table 3. In the same table the standard deviation (SD) of the pressure calculated with the Antoine equation parameters and the experimental data are shown. As can be

seen in this Figure 2, the equation using the parameters for the whole temperature range is able to reproduce quite accurately the vapor pressure. Data taken from the literature are also represented. Most of the data are mutually consistent. Nevertheless the data of Cross et al. [14] at 1013 mbar differs by more than 10 K from those of Garcia et al. [15] or this work.

Figure 2. Vapor pressure of 3-MEP at different temperatures. Vapor pressure calculation using the regression parameters set [table 3].

3.2. Vapor-liquid equilibrium

References for the experimental vapor-liquid equilibrium data of the systems investigated in this work are summarized in table 4. Tables from 5 to 9 show the boiling temperature and the compositions in mole fraction of the liquid and the vapor for the different pressures. The same data are shown graphically in Figures 3-7 with their smoothing curves. The order of tables and figures ranges from the most volatile component, diethyl ether, to the heaviest, glycerol.

In each figure the shape of the curves at the different pressures is very similar. The five binary pairs are totally miscible and don't have azeotropes and the separation of 3-MEP from the other compounds in a distillation column would be simple. On the other hand, there are significant differences between the shapes of the equilibrium diagrams of the different systems. Those with the more volatile compounds (Figures 3 and 4) are characterized by a wide region of compositions of liquids boiling all at almost the same temperature and giving a vapor composition of almost the pure volatile compound.

Table 4. Summary of the systems studied and location of the experimental data table and figure where the Txy equilibrium has been represented. Tb⁰= boiling temperature at 1 atm.

System		Pressure / mbar	Table	Figure
Compound 1	Compound 2			
Diethyl ether (Tb ⁰ = 307.8K)	3-MEP	1013 2026	5	3
Ethanol (Tb ⁰ =351.5K)	3-MEP	1013 2026	6	4
Water (Tb ⁰ =373.15 K)	3-MEP	100 1013 2026	7	5
1,2-propanediol (Tb ⁰ =461.3K)	3-MEP	10 20	8	6
Glycerol (Tb ⁰ =563.15K)	3-MEP	25 50 100	9	7

Table 5. Vapor-liquid equilibrium of the diethyl ether (1) + 3-MEP (2) system in mole fraction at 1013 mbar and 2026 mbar.

1013 mbar			2026 mbar		
T / K	x ₁	y ₁	T / K	x ₁	y ₁
491.7	0.0009	0.072	512.0	0.002	0.258
477.8	0.0038	0.444	503.2	0.003	0.507
470.7	0.0042	0.675	485.4	0.011	0.664
454.2	0.0043	0.838	461.4	0.012	0.862
437.6	0.011	0.916	385.1	0.062	0.974
344.7	0.052	0.9988	347.7	0.092	0.9995
326.9	0.071	0.9996	337.9	0.155	0.9998
314.5	0.146	0.9999	332.5	0.166	0.9999
307.8	0.275	0.9999	329.3	0.210	0.9999
			327.7	0.323	0.99995

Standard uncertainty: u(T)=0.1 K and u(P)= 1 mbar. Relative standard uncertainty $u_r(x)=u(x)/x=0.02$

Table 6. Vapor-liquid equilibrium of the ethanol (1) + 3-MEP (2) system in mole fraction at 1013 mbar and 2026 mbar.

1013 mbar			2026 mbar		
T / K	x_1	y_1	T / K	x_1	y_1
491.8	0.010	0.142	477.5	0.0657	0.592
479.7	0.0126	0.234	460.1	0.0791	0.777
453.4	0.0378	0.566	450.9	0.0805	0.824
438.5	0.0596	0.730	445.2	0.113	0.863
407.9	0.127	0.958	442.1	0.116	0.867
355.4	0.245	0.994	432.1	0.147	0.893
352.7	0.403	0.997	399.7	0.207	0.983
351.7	0.491	0.999	374.8	0.344	0.994

Standard uncertainty: $u(T)=0.1$ K and $u(P)=1$ mbar. Relative standard uncertainty $u_r(x)=u(x)/x=0.02$

Table 7. Vapor-liquid equilibrium of the water (1) + 3-MEP (2) system in mole fraction at 100, 1013 and 2026 mbar.

100 mbar			1013 mbar			2026 mbar		
T / K	x_1	y_1	T / K	x_1	y_1	T / K	x_1	y_1
406.4	0.020	0.611	461.8	0.030	0.664	513.8	0.015	0.266
389.3	0.040	0.825	443.2	0.043	0.797	490.0	0.036	0.639
369.6	0.074	0.939	435.7	0.073	0.876	447.6	0.087	0.915
366.4	0.079	0.950	410.2	0.16	0.955	428.5	0.184	0.949
358.3	0.095	0.964	399.0	0.244	0.977	427.0	0.200	0.958
348.4	0.154	0.976	392.5	0.324	0.983	412.0	0.345	0.984
340.7	0.239	0.980	384.4	0.45	0.993	408.4	0.416	0.987
334.1	0.373	0.993	379.1	0.634	0.996	399.9	0.654	0.9951
325.5	0.599	0.996	376.9	0.763	0.9979	397.5	0.766	0.9973
322.9	0.775	0.9993	375.4	0.850	0.9987	395.8	0.849	0.9981
321.4	0.868	0.99995	374.5	0.924	0.9992	395.0	0.927	0.9989
320.5	0.935	0.9987	373.9	0.9663	0.9997	394.4	0.966	0.9996
320.0	0.963	0.9994	373.5	0.9841	0.9998	394.1	0.984	0.9999
319.7	0.980	0.9998						

Standard uncertainty: $u(T)=0.1$ K and $u(P)=0.2$ mbar at 100 mbar and $u(P)=1$ mbar at 1013 and 2026 mbar. Relative standard uncertainty $u_r(x)=u(x)/x=0.02$

Table 8. Vapor-liquid equilibrium of the 1,2-propanediol (1) + 3-MEP (2) system in mole fraction at 10 and 20 mbar.

10 mbar			20 mbar		
T / K	x_1	y_1	T / K	x_1	y_1
376.6	0.011	0.02	389.6	0.01	0.021
371.2	0.115	0.222	383.6	0.128	0.254
365	0.294	0.523	377.2	0.333	0.563
361.6	0.461	0.722	373.4	0.481	0.719
358.8	0.623	0.841	370.8	0.635	0.824
357.4	0.719	0.870	369.1	0.727	0.877
356.0	0.799	0.9131	367.9	0.807	0.917
355.5	0.850	0.9403	367.2	0.860	0.9439
355.1	0.891	0.9582	366.7	0.896	0.9585
354.8	0.918	0.9706	366.3	0.9176	0.9717
353.7	0.9903	0.9978	365.4	0.9869	0.9967
353.5	0.9931	0.998	365.3	0.9994	0.9999
353.6	1	1	365.31	1	1

Standard uncertainty: $u(T)=0.1$ K and $u(P)=0.2$ mbar. Relative standard uncertainty $u_r(x)=u(x)/x=0.02$

Table 9. Vapor-liquid equilibrium of the glycerol (1) + 3-MEP (2) system in mole fraction at 25, 50 and 100 mbar.

25 mbar			50 mbar			100 mbar		
T / K	x_1	y_1	T / K	x_1	y_1	T / K	x_1	y_1
397.2	0.199	0.015	410.5	0.202	0.013	426.7	0.191	0.015
399.5	0.441	0.029	412.5	0.441	0.026	428.0	0.442	0.027
401.6	0.644	0.057	416.2	0.635	0.06	430.5	0.640	0.060
415.3	0.807	0.158	428.5	0.814	0.143	449.1	0.816	0.168
424.9	0.929	0.246	434.5	0.898	0.170	457.6	0.907	0.197
438.4	0.954	0.527	457.5	0.967	0.612	474.0	0.959	0.315

Standard uncertainty: $u(T)=0.1$ K and $u(P)=0.2$ mbar. Relative standard uncertainty $u_r(x)=u(x)/x=0.02$

Figure 3. Txy diagrams in mole fraction for the diethyl ether + 3-MEP system at 1013 mbar and 2026 mbar.

Figure 4. Txy diagrams in mole fraction for the ethanol + 3-MEP system at 1013 mbar and 2026 mbar.

Figure 5. Txy diagrams in mole fraction for the water + 3-MEP system at 100 mbar, 1013 mbar and 2026 mbar.

Figure 6. Txy diagrams in mole fraction for the 1,2-propanediol + 3-MEP system at 10 mbar and 20 mbar.

Figure 7. Txy diagrams in mole fraction for the glycerol + 3-MEP system at 25 mbar, 50 mbar and 100 mbar.

Calculations with thermodynamic models

Firstly, the equilibrium diagram of each system was calculated using UNIFAC and the Chemcad 7.0 software. The data base of compounds of the program does not contain the 3-MEP. For this reason, was necessary, in order to calculate the phase equilibria, to include its Antoine parameters and to divide into the following UNIFAC groups: (one CH, two CH₂, one CH₃, two -OH and one -CH₂-O-).

The results obtained for each system at each pressure show that both the curves corresponding to the liquids are always above the experimental points which means that the calculated bubble temperatures are higher than the experimental ones. With respect to the vapor curves, the differences between the experimental and calculated temperatures are smaller. Figures 8-12 show some of the results obtained for the different systems at only one pressure.

For these systems at the different pressures, it should be noted that the UNIFAC parameters used [16] always calculate that there is no splitting into two liquid phases at any region except for the diethyl ether + 3-MEP system at 1013 mbar. In this case, it calculates that for a small region between 0.802 and 0.999 mole fraction of diethyl ether the mixtures split into two liquid phases with a boiling temperature of 308.69 K. This fact does not occur experimentally because diethyl ether and 3-MEP are totally miscible at all temperatures.

Likewise, the determined experimental data were correlated using Wilson, UNIQUAC and NRTL thermodynamic models. The Chemcad 7.0 software was used to fit the

binary interaction parameters for each of the studied systems. A global correlation was performed for each of the systems: vapor-liquid equilibrium data at all the experimental pressures studied were correlated simultaneously.

Tables 10-12 show the parameters B_{ij} (K) and α for the NRTL model and the parameters $(U_{ij}-U_{ji})$ (K) for the UNIQUAC and Wilson model. Additionally, the mean deviation of the correlation of each model for the boiling temperature and the vapor composition are also presented in the tables. The Antoine parameters used are the one present in the Chemcad software's database except for the 3-ethoxy-1,2-propanediol whose employed parameters are the ones shown in Table 3.

The molecular values of r and q for 3-MEP to be used with UNIQUAC were calculated from the values of Q_k and R_k of each of the UNIFAC groups defining the molecule and applying a weighted average. The values calculated were $r = 5.3876$ and $q = 5.024$.

Table 10. Wilson parameters, $(U_{ij}-U_{ji})$ (K), mean deviations of the boiling temperature and vapor composition (mole fraction) and liquid molar volume v (mL/mol) of the pure components.

i	j	$U_{ij}-U_{ji}$	$U_{ji}-U_{ii}$	$\Delta T / K$	Δy
Diethyl ether	3-MEP	492.00	244.01	11.9	0.042
Ethanol	3-MEP	284.29	-309.49	10.9	0.050
Water	3-MEP	521.26	710.98	4.4	0.025
1,2-propanediol	3-MEP	390.33	-390.77	1.0	0.034
Glycerol	3-MEP	1244.44	-180.93	1.9	0.037
v ethanol	v DEE	v water	v 12-PG	v glycerol	v 3 MEP
58.68	104.75	18.07	73.68	73.19	113.5

Table 11. UNIQUAC parameters, $(U_{ij}-U_{ji})$ (K) and mean deviations of the boiling temperature and vapor composition (mole fraction) for each system.

i	j	$U_{ij}-U_{ji}$	$U_{ji}-U_{ii}$	$\Delta T / K$	Δy
Diethyl ether	3-MEP	115.23	12.58	15.7	0.069
Ethanol	3-MEP	104.46	-46.32	9.5	0.050
Water	3-MEP	-41.39	317.54	3.8	0.022
1,2-propanediol	3-MEP	-174.58	155.77	1.0	0.034
Glycerol	3-MEP	137.68	-75.55	4.0	0.043

Table 12. NRTL parameters, B_{ij} (K) and mean deviations of the boiling temperature and vapor composition (mole fraction) for each system.

i	j	B_{ij}	B_{ji}	α	$\Delta T / K$	Δy
Diethyl ether	3-MEP	240.95	411.00	0.100	8.88	0.046
Ethanol	3-MEP	-57.97	33.23	0.340	10.9	0.048
Water	3-MEP	1380.39	-516.27	0.201	2.5	0.015
1,2-propanediol	3-MEP	-46.49	-9.70	0.303	1.0	0.034
Glycerol	3-MEP	316.76	199.52	0.263	3.0	0.041

It can be seen in these Tables 10-12 that the deviations are greater for systems in which the compound that forms the pair with 3-MEP is more volatile. Figures 8-12 show the experimental data compared with those calculated with Wilson, NRTL and UNIQUAC models using the parameters presented in Tables 10-12. The conclusions about the deviations are the same with important deviations in the Tx curve or in the Ty curve.

For systems with diethyl ether and ethanol, the Tx curve is very flat in a wide region.

Any better fit of that curve results in parameters that reproduce the experimental data but predict nonexistent immiscibility regions (as in the calculations with UNIFAC), thus not correctly reproducing the real type of system.

Figure 8. Txy diagram comparison in mole fraction for the diethyl ether + 3-MEP system at 1013 mbar between experimental and calculated data.

Figure 9. Txy diagram comparison in mole fraction for the ethanol + 3-MEP system at 1013 mbar between experimental and calculated data.

Figure 10. Txy diagram comparison in mole fraction for the water + 3-MEP system at 1013 mbar between experimental and calculated data.

Figure 11. Txy diagram comparison in mole fraction for the 1,2-propanediol + 3-MEP system at 20 mbar between experimental and calculated data.

Figure 12. Txy diagram comparison in mole fraction for the glycerol + 3-MEP system at 50 mbar between experimental and calculated data.

Conclusion

The vapor-liquid equilibrium of five binary systems studied at different pressures have been determined. They involve 3-ethoxy-1,2-propanediol and five other compounds (diethyl ether, ethanol, water, 1,2-propanediol and 1,2,3-propanetriol) with very different volatilities. The pairs of compound of each binary system are totally miscible at any temperature and do not show the presence of azeotrope. When thermodynamic models as Wilson, NRTL, UNIQUAC and UNIFAC are applied to fit and calculate the experimental vapor-liquid equilibrium large deviations are found depending on the system and pressure. The largest deviations are obtained with the systems with diethyl ether and ethanol which present a very flat T_x curve in a wide region. Any better fit of that curve results in parameters that reproduce the experimental data but predict nonexistent immiscibility regions thus not correctly reproducing the real type of system.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: