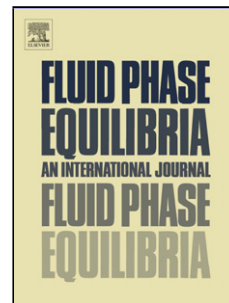


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Phase equilibria of the water + 1-butanol + toluene ternary system at 101.3 kPa

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Highlights

The phase equilibria of the system water + 1-butanol + toluene have been studied.

Isothermal liquid-liquid equilibrium data at 313.15 K was determined.

Isobaric vapour-liquid-liquid equilibrium data at 101.3 kPa was also determined.

Data obtained has been checked against literature data and those predicted with binary interaction parameters.

All experimental data have been correlated with thermodynamic models.

Abstract

Isobaric vapour-liquid and vapour-liquid-liquid equilibrium data for the water + 1-butanol + toluene ternary system were measured at 101.3 kPa with a modified VLE 602 Fischer apparatus. In addition, the liquid-liquid equilibrium data at 313.15 K were measured and compared with data from other authors at different temperatures. The system exhibits a ternary heterogeneous azeotrope whose temperature and composition have been determined by interpolation. The thermodynamic consistency of the experimental vapour-liquid and vapour-liquid-liquid data was checked by means of the Wisniak's L_i/W_i consistency test. Moreover, the vapour-liquid and the liquid-liquid equilibrium correlation for the ternary system with NRTL and UNIQUAC models, together with the prediction made with the UNIFAC model, were studied and discussed.

Keywords

Water; 1-butanol; Toluene; Liquid-Liquid Equilibrium; Vapour-Liquid-Liquid Equilibrium

1. Introduction

Butanol has traditionally been an important industrial chemical that has had a variety of applications, especially as a raw material in the chemical and plastics industries. However, there is now increasing interest in the use of biobutanol as a transport fuel given its many advantages [1]. In fact, a number of companies (such as BP-DuPont and Abengoa) are now investigating novel alternatives to traditional production process, which would enable

biobutanol to be produced on an industrial scale [2]. Traditionally it has been produced by fermentation (known as ABE process [3]); however, in recent years new biochemical and thermochemical routes have been investigated to improve the production yields and the recovery costs. [4, 5]

In this respect, several research efforts are being made regarding the fermentation process [6, 7] but another key fact is the purification of butanol. Since the purification step is one of the most energy consuming in the production of butanol, it is important to develop a separation sequence to produce pure butanol. Different techniques, such as distillation, liquid-liquid extraction, adsorption or pervaporation, are being investigated [8 - 11].

Nowadays, different combinations of separation techniques are under study and it could be helpful to have a complete set of experimental data to improve this kind of process development.

The present work was undertaken as a part of thermodynamic research on the separation of 1-butanol + water mixtures using different solvents, hydrocarbons commonly present in gasoline.

The purpose of our research is to develop a process that could cheapen the production costs of water-free butanol to be used as an additive in gasoline or, even, as a fuel. In this case, it would entail using toluene as an extractant either for liquid-liquid extraction or for azeotropic distillation.

Toluene can be a suitable entrainer, not only because it generally forms ternary heterogeneous azeotrope with 1-butanol and water, but also because it is generally present in gasoline, therefore reducing the butanol purity constraints in the entrainer recovery system.

To analyse the technical and economic viability of this option, it is really important to have reliable thermodynamic data to develop new sustainable processes. To study the distillation as well as the extraction processes, it will be necessary to obtain thermodynamic equilibrium data for not only the liquid-liquid equilibrium (LLE), but also for the vapour-liquid (VLE) and especially the vapour-liquid-liquid equilibrium (VLLE). Furthermore, a great effort is being made in the development of new thermodynamic models and EOSs and it is important to have reliable experimental data to check the accuracy of the models.

In this paper, we study the isothermal liquid-liquid equilibrium at 313.15 K and the isobaric vapour-liquid and vapour-liquid-liquid equilibrium at the atmospheric pressure for the water + 1-butanol + toluene ternary system. The liquid-liquid equilibria of the water + butanol + toluene system were previously determined at temperatures in the 293 – 303.15 K range by different authors but none of them analyse the temperature influence beyond 303.15 K. To compile the experimental data the isothermal liquid-liquid correlation and the isobaric vapour-liquid correlation was done using the NRTL and the UNIQUAC activity coefficient thermodynamic models. Results were compared with the prediction made by the group-contribution UNIFAC thermodynamic model.

This ternary system is a type II system following Treybal classification [12], that is to say, one binary pair almost immiscible at any composition (water + toluene), one binary pair with a limited miscibility gap (water + 1-butanol) and the third binary pair is completely miscible (1-butanol + toluene). It has three binary azeotropes -two heterogeneous and one homogeneous- and one ternary heteroazeotrope which is the lowest boiling specie of the whole system.

2. Experimental

2.1. Chemicals

All chemicals used in the experiments are listed in Table 1. 1-Butanol, toluene and 2-propanol (used as internal standard) were used as supplied by the provider without further treatment after the chromatographic analysis failed to show significant impurities. The Karl-Fischer titration method was used to determine the water content of the chemicals. Ultrapure water used was purified using a MiliQ Plus system.

2.2. Apparatus and procedures

2.2.1. Determination of Liquid-Liquid Equilibria

Liquid-liquid equilibrium measurements for the ternary mixture were performed at constant temperature. To determine the LLE at a constant temperature of 313.15 K, the procedure consisted in preparing mixtures of known composition with a METTLER AJ150 precision balance. These mixtures were placed in a thermostatic bath stirring intensively and setting for a long time at constant temperature to ensure that equilibrium was reached. After equilibrium was reached, samples were taken from both phases and were analyzed.

2.2.2. Determination of Vapour-Liquid and Vapour-Liquid-Liquid Equilibria

A glass Labodest (model 602) VLE apparatus was used in the determinations. This commercial unit (*Fischer Labor und Verfahrenstechnik*) has been modified by Gomis et al. [13] by means of an ultrasonic homogenizer coupled to the boiling flask. The ultrasound system applied ensures a good dispersion of partly miscible liquid phases, thus making the modified apparatus perfectly suited for the determination of VLE and VLLE data. In addition, it was necessary to improve the mixing of the recirculating liquid and vapour phases in the mixing chamber.

The equilibrium temperature was measured with a Pt100 sensor coupled to a digital thermometer (model 3002) with an uncertainty of 0.06 K according to its certificate of calibration (scale ITS 90) [14]. For the pressure measurement, a Fischer M101 phase equilibrium control system was used. This equipment is periodically checked against a Fortin barometer. The pressure in the still was 101.3 kPa, measured and controlled to within an accuracy of 0.1 kPa. The effect of pressure fluctuations on the temperature has been quantified and corresponds to 0.03K/kPa.

2.3. Analysis

Liquid and vapour phases obtained during the experimental determination were measured by gas chromatography.

Sampling was carried out using different methods depending on the phase treated:

- Vapour phase: a gaseous sample is injected automatically into the gas chromatograph using a UW Type, 6-port valve from Valco Instruments Co.
- Homogeneous liquid phase: a syringe is used to extract a sample from the liquid leaving the separator chamber and it is put it into a vial.
- Heterogeneous liquid phases: a small amount of the liquid coming from the separation chamber of the instrument (to separate gas and liquid phases) was diverted to a tube using a solenoid valve. Inside this tube, the dispersed liquid phases enter and separate into two layers at their bubble point since the tube is placed in a thermostatic bath at the boiling point temperature of the mixture. The tubes stay in the bath long enough to assure that liquid-liquid equilibrium is reached. A sample of each layer was taken and placed in a vial.

Similar procedure was followed with the isothermal LLE samples.

The internal standard method was used; the addition of the standard prevents phase split that might occur on changing the temperature once separation of the phases has taken place. For this reason, 2-propanol (which is completely miscible with water, 1-butanol and toluene) was also added to the sampling vials. A further description of the sampling procedure and the equipment configuration is given in previous papers [13, 15].

Depending on the composition of the sample, the analytical technique was different: water, 1-butanol and toluene of the organic phase were analyzed by gas chromatography with a TCD (Thermal Conductivity Detector). Water was compared with results obtained from the Karl-Fischer titration method (Metrohm 737 KF Coulometer). In the aqueous phase, water was analyzed using TCD, and 1-butanol and toluene with FID (Flame Ionization Detector). The temperature was 493.15 K for the TCD and 523.15 K for the FID.

The analysis of both vapour and liquid phases were carried out using a Shimadzu GC14B gas chromatograph. A 2m x 3mm 80/100 Porapack Q packed column was used to separate the components. Oven and detector temperature were set to 473.15 K and 493.15 K, respectively. The aqueous phase of the heterogeneous samples was analyzed with a Thermo Trace gas chromatograph by Thermo Fischer with a DB 624 column. The detector temperature in this case was 523.15 K, whereas the initial temperature of the oven was 313.15 K and was raised to 473.15 K in increments of 40 K min⁻¹.

The relative uncertainty of the mole fraction measurements has been estimated at 2% if the mole fractions are greater than 0.01. For water in the organic phase, and organic compounds in the aqueous phase when the mole fractions are lower than 0.01, the relative uncertainty increases until it reaches approximately 20% for a 0.0001 mole fraction of toluene.

3. Results and discussion

3.1. Liquid-liquid equilibrium data

Table 2 shows the experimental LLE tie-lines obtained at a constant temperature of 313.15 K for the water + 1-butanol + toluene system studied. Different research groups previously determined the LLE equilibrium data of this ternary system. In fact, Shanahan [16] measured only the saturation curve at a constant temperature of 293.15 K; Letcher and Siswana [17] and Kim et al. [18] reported both the saturation curve and the LLE at a constant temperature of 298.15 K; and, finally, Fuoss [19] did the same at a constant temperature of 303.15 K using the conductance method and assuming that the water-rich phase was toluene free. These LLE data have been compiled and analyzed by A. Skrzecz [20].

To contrast the recent acquired data with those published previously, a graphical representation of the experimental data obtained and those extracted from literature is shown in Figure 1. As can be seen in this figure, in this temperature range (293 – 313.15 K) the LLE equilibrium does not vary very much with temperature.

Using the process software CHEMCAD 6 [21], the LLE data at 313.15 K have been calculated using the group contribution UNIFAC LLE thermodynamic model. As can be observed in Figure 2, the shape and wide of the heterogeneous region as well as the slope of the tie lines is very similar to the experimental ones. However, in an attempt to find the best fit to reproduce the experimental data as accurately as possible, the LLE tie lines at 313.15 K have been correlated using the UNIQUAC and NRTL models. In the case of the NRTL model the α parameter value was fixed to 0.2, according to the procedure followed in DECHEMA. The parameters obtained reproduce the phase equilibrium at this temperature quite well. The regression parameters

and the deviations obtained are summarized in Table 3 and the calculated binodal curves with all the models have been included in Figure 2.

3.2. Vapour-liquid and vapour-liquid-liquid equilibrium data

A complete analysis of the homogeneous region of the ternary system has been done and the VLE data is presented in Table 4 and Figure 3. It is worth noting that almost all liquid mixtures from the homogeneous region in Figure 3 have a vapour phase that, once condensed, would belong to the heterogeneous region splitting into two liquid phases. In fact, the analysis of these vapour mixtures has been more reliable since one of the main advantages of the equipment used is that it can be directly injected into the chromatograph.

In a similar way, 23 VLLE tie-lines describe the heterogeneous region in detail. Equilibrium temperatures versus composition in both phases have been collected in Table 5. Figure 4 includes the vapour line and the non-isothermal binodal curve obtained at a constant pressure of 101.3 kPa. Comparing this data with the experimental LLE data at 313.15 K and those obtained by different authors at different temperatures [16-19], it can be concluded that the size of the heterogeneous region of this system is not very sensitive to temperature in the range of 293.15 K to 362.96 K except in the vicinity of the water + 1-butanol pair.

In 1976, Arzhanov et al. [22] studied the vapour-liquid equilibrium of the ternary system covering the whole composition triangle as can be seen in Figure 5. In this figure the experimental liquid boiling envelope and the homogeneous VLE points have been plotted. It can be seen that the vapour-liquid equilibrium of the heterogeneous region does not match the vapour curve as would be expected. Due to the error encountered, these data would not be considered for comparison. Toikka and Tarasova [23], analyzed the 4 vapour compositions that have also been included in Figure 5. It can be seen that these points lie on the experimental vapour curve here presented here, supporting the reliability of the new data. Data from Arzhanov et al. and Toikka and Tarasova have been extracted from the Dortmund Data Bank (DDB).

The experimental VLLE and VLE data were tested by the point to point Wisniak L_i/W_i consistency test [24] and were found to be thermodynamically consistent since all the values of L_i/W_i are between 0.97 and 1.00 and the test declares as consistent the data whose values range between 0.92 and 1.08. To calculate the L_i/W_i values, the vapour pressures were calculated with the Antoine equation, whose parameters A_i , B_i and C_i for water, 1-butanol and toluene were taken from literature [25, 26] and are given in Table 6.

The distillation experiments of Kudryavtseva in 1973 [27, data extracted from 28] showed a ternary azeotrope for a composition of 0.532, 0.080 and 0.388 mole fraction for water (1), 1-butanol (2) and toluene (3), respectively, and a temperature of 356.45 K.

Observing carefully the ternary diagram presented in Figure 3, it can be seen that some vapour compositions are above its liquid-liquid tie-line in equilibrium. However, other points are below its tie-line. This fact points out the existence of a ternary azeotrope since there must be a point whose vapour composition lies on the liquid-liquid tie-line. Using this property, the composition of the ternary azeotrope can be deduced by interpolation. A complete description of the calculation procedure can be found in previous references [12, 14]. In addition, the temperature of the vapour curve presents a minimum at this point. In this particular case, the vapour composition will be $x_1 = 0.530$, $x_2 = 0.075$ and $x_3 = 0.395$ mole fraction of water (1), 1-butanol (2) and toluene (3) and the temperature will be 356.53 K. This vapour composition is in equilibrium with two liquid phases whose compositions have also been calculated by interpolation too. The organic phase is $x_1 = 0.034$, $x_2 = 0.149$ and $x_3 = 0.817$ and the aqueous phase is $x_1 = 0.995$, $x_2 = 0.005$ and $x_3 = 0.0003$ for water (1), 1-butanol (2) and toluene (3) respectively.

3.2.1. VLE and VLE Prediction with literature parameters

It is well known that for systems of type II, if the mutual solubility (LLE) data are known for the two partially miscible pairs, and if reasonable VLE data are known for the miscible pair, the ternary equilibria can be predicted [29].

For this reason, we have tested some binary interaction parameters (BIPs) sets obtained from binary equilibrium data to predict the VLE of the system studied. We have found in DECHEMA four different recommended BIPs sets (obtained from binary data of different reliable sources) for the three pairs:

- VLE BIPs for the water + 1-butanol pair at 101.3 kPa [30].
- LLE BIPs for the water + 1-butanol pair at 373.15 K [31].
- VLE BIPs for the 1-butanol + toluene pair at 101.3 kPa [32].
- LLE BIPs for the water + toluene pair at 298.15 K [31].

An analysis was performed with regard to the correlation of the binary water + 1-butanol. None of the correlated BIPs from binary data published in the DECHEMA Database was capable of accurately reproducing the VLE data and the LLE data simultaneously. Figures 6a and 6b show the experimental data and that predicted with UNIQUAC. It is worth noting that the VLE parameters predict a wider heterogeneous region of the water + 1-butanol binary (Figure 6a). When the LLE parameters are used (Figure 6b), the heterogeneous region is well predicted, however the vapour composition and the temperature differ considerably from the experimental data. Similar graphs are obtained using the NRTL model.

Using the UNIQUAC model the ternary azeotrope is not predicted with these parameters sets. This reinforces the idea of the necessity to do a correlation of the ternary data to improve the VLE prediction.

On the other hand, a prediction of VLE has been made using the UNIFAC (original) model. In this case, the heterogeneous region predicted is more similar in shape to experimental data than with the other models but the non-isothermal binodal curve is still larger than experimental data shows. To illustrate these comparisons Figure 7 represents the experimental data for the VLE and those predicted with this model.

3.2.2. VLE and VLE Correlation

A correlation of VLE and VLE data was carried out in order to have a BIPs set capable of properly reproducing the phase equilibrium of the system. Both models, UNIQUAC and NRTL, were used to do the correlation. The data used to calculate the BIPs were the bibliographic VLE data of water + 1-butanol [33] and 1-butanol + toluene [32]; the ternary azeotrope obtained by Kudryatseva [27] together with the homogeneous VLE data and the VLE data extracted from VLE data (extracting VLE data matching each liquid composition with its vapour in equilibrium) presented in this paper. Table 7 collects the results obtained by the correlations of the two models used. The prediction done with the parameters of Table 7 together with the experimental data have been represented in Figure 7. As it can be seen in the figure, the vapour curve calculated with both models is very similar.

With both models, significant differences in the heterogeneous region are shown especially in the region near the water + 1-butanol pair. The UNIQUAC model generates a heterogeneous region larger than the experimental data shows. However the vapour line calculated accurately reproduces the experimental data. The NRTL model estimates a more extended heterogeneous region but not as large as the UNIQUAC model does. However, the vapour curve and the boiling temperatures agree well with the experimental data.

With the parameters shown in Table 7, the binary and ternary azeotropes have been calculated using NRTL and UNIQUAC and have been predicted with UNIFAC. In Table 8 these results are presented together with the experimental azeotropes found in literature. UNIQUAC BIPs calculate azeotropes with a closer composition and temperature to the experimental ones than the NRTL model. UNIFAC model prediction only improves the correlation results in the binary 1-butanol + toluene azeotrope.

4. Conclusions

Toluene has been proposed as an extractant for the separation of the 1-butanol + water binary system either by azeotropic distillation or by liquid-liquid extraction. For this reason, liquid-liquid equilibrium data at 303.15 K and vapour-liquid and vapour-liquid-liquid data at 101.3 kPa have been determined for the ternary system. All data were proved thermodynamically consistent using the Wisniak L_i/W_i point-to-point consistency test.

These data have been compared and analyzed with data previously determined by other authors. In this system, temperature has a negligible effect on the solubility curve in the 293 – 313.15 K range. In contrast, in the vicinity of the water + 1-butanol pair temperature significantly influences the solubility of water in butanol.

The temperature and composition of the ternary azeotrope have been inferred by interpolation and agree well with data previously obtained. The organic and aqueous phase compositions in which the azeotrope splits once condensed have also been determined.

These data have been correlated using the UNIQUAC and NRTL models by means of the commercial software package CHEMCAD. It has not been possible to find a set of parameters that properly reproduces the VLE and VLLE data.

With either the UNIQUAC or NRTL model, a larger heterogeneous region than the experimental one is predicted near the water + 1-butanol pair. However the vapour curve is quite well predicted with all the models studied. An analysis of the correlation of this pair has been done and it has not been possible to find a BIPs set capable of accurately reproducing the VLE and the LLE data. This observation reinforces the idea of the necessity to find new models or modify existing ones with a view to obtain new ones with more flexibility that could reproduce more accurately systems like the one studied in this paper.

To conclude, the experimental data obtained do fill the gap in literature but highlight the need to obtain more phase-equilibrium experimental data of different systems in order to improve the simulations of industrial processes.

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Figures

Figure 1. Liquid–liquid equilibrium data (mole fraction) for the water + 1-butanol + toluene system at 313.15K and those obtained by other authors.

Experimental data at 313.15 K; Liquid-liquid tie lines; Shanahan at 293.15 K [15]; Letcher et al. at 298.15 K [16]; Kim et al. at 298.15 K [17]; Fuoss at 303.15 K [18].

Figure 2. Comparison of the LLE data (mole fraction) of the water + 1-butanol + toluene ternary system at 313.15K.

Experimental data. Calculated data: predicted using the UNIFAC LLE model; calculated with the NRTL model (Table 3); calculated with the UNIQUAC model (Table 3).

Figure 3. VLE (mole fraction) diagram for the water + 1-butanol + toluene ternary system at 101.3kPa:

liquid phase; + vapour phase; non-isothermal binodal curve; vapour-liquid tie lines.

Figure 4.

VLE (mole fraction) diagram for the water + 1-butanol + toluene ternary system at 101.3kPa:

liquid phase; + vapour phase; non-isothermal binodal curve; vapour curve; vapour-liquid tie lines; liquid-liquid tie lines

Figure 5. VLE (mole fraction) diagram for the water + 1-butanol + toluene ternary system at 101.3kPa:

non-isothermal binodal curve; vapour curve.

Arzhanov liquid phase; + vapour phase; vapour-liquid tie lines

Toikka and Tarasova vapour phase

Figure 6. RCM and non-isothermal binodal curve of the ternary system at 101.3kPa predicted by means of the DECHEMA recommended BIPs for VLE water + 1-butanol (a) and LLE water + 1-butanol (b).

Figure 7. Comparison of the VLLE data of the water + 1-butanol + toluene ternary system at 101.3kPa.

Experimental data. Calculated data: predicted using the UNIFAC model; calculated with the NRTL model (Table 7); calculated with UNIQUAC (Table 7).

Tables

Table 1 Specifications of chemical compounds.

Chemical	Provider	Initial purity (mass fraction)	Water content (mass fraction)	Purification method	Analysis method
1-Butanol	Merck	> 0.998	0.0007	none	GC ^a
Toluene	Merck	> 0.999	0.0005	none	GC ^a
2-Propanol	Merck	> 0.995	0.0005	none	GC ^a

^a GC = Gas chromatography.

Table 2 Experimental (liquid - liquid) equilibrium data for the system water (1) +1-butanol (2) + toluene (3) for mole fractions x at the temperature $T = 313.15$ K.²

Organic phase			Aqueous phase		
x_1	x_2	x_3	x_1	x_2	x_3
0.008	---	0.992	1.000	---	0.0001
0.019	0.096	0.885	0.994	0.006	0.0001
0.087	0.310	0.603	0.991	0.009	0.0001
0.131	0.380	0.489	0.990	0.010	0.0001
0.162	0.421	0.417	0.989	0.011	0.0001
0.187	0.451	0.362	0.989	0.011	0.0001
0.253	0.501	0.246	0.988	0.012	0.0001
0.287	0.517	0.197	0.987	0.013	0.0001
0.330	0.522	0.148	0.987	0.013	0.0001
0.383	0.530	0.088	0.986	0.014	0.0001
0.442	0.505	0.053	0.985	0.015	0.0001
0.500	0.487	0.013	0.984	0.016	0.0000

0.516 0.484 --- 0.981 0.019 ---

[†] Standard uncertainty u is $u(T) = 0.1$ K, and relative uncertainty u_r is $u_r(x) = 0.02$.

Table 3 Parameters and mean deviations of the LLE correlation. A_{ij} (K) NRTL binary interaction parameters. $U_{ij} - U_{ii}$ (K) UNIQUAC binary interaction parameters. Mean deviations of water (1) and butanol (2) in organic phase (1) and aqueous phase (2).

i	j	A_{ij}	A_{ji}	α	$U_{ij}-U_{jj}$	$U_{ji}-U_{ii}$
Water	1-Butanol	1463.370	-294.840	0.2	303.080	-23.403
Water	Toluene	1488.963	1272.934	0.2	332.224	731.265
1-Butanol	Toluene	-975.748	1226.281	0.2	91.070	-79.364
		Mean Deviation	D_{X11}	D_{X21}	D_{X12}	D_{X22}
		NRTL	0.0097	0.0072	0.0048	0.0051
		UNIQUAC	0.0039	0.0029	0.0013	0.0015

Table 4 Experimental (vapour - liquid) equilibrium temperatures T , liquid mole fractions x and vapour mole fractions y for the system water (1) +1-butanol (2) + toluene (3) x at pressure $p = 101.3$ kPa.

Liquid phase			Vapour phase			T (K)
x_1	x_2	x_3	y_1	y_2	y_3	
0.022	0.633	0.346	0.111	0.422	0.467	376.91
0.027	0.688	0.285	0.141	0.435	0.424	377.28
0.029	0.915	0.056	0.144	0.698	0.157	384.81
0.030	0.800	0.171	0.176	0.508	0.315	379.13
0.030	0.741	0.229	0.159	0.466	0.374	377.80
0.033	0.844	0.122	0.173	0.559	0.267	381.06
0.035	0.739	0.226	0.162	0.483	0.355	378.06
0.050	0.801	0.149	0.224	0.496	0.280	378.37
0.050	0.837	0.112	0.265	0.509	0.226	379.25
0.057	0.359	0.583	0.415	0.168	0.417	368.81
0.060	0.601	0.340	0.330	0.275	0.395	370.42
0.063	0.918	0.019	0.296	0.641	0.063	381.70
0.064	0.868	0.068	0.291	0.555	0.154	379.86
0.064	0.899	0.037	0.309	0.587	0.104	380.90
0.064	0.452	0.484	0.362	0.219	0.419	368.37
0.065	0.867	0.068	0.319	0.523	0.158	379.09
0.070	0.524	0.407	0.388	0.222	0.390	369.65

0.071	0.472	0.456	0.389	0.212	0.399	366.90
0.076	0.710	0.213	0.381	0.292	0.326	372.41
0.091	0.817	0.092	0.414	0.391	0.195	375.73
0.103	0.776	0.121	0.444	0.334	0.222	372.23
0.115	0.621	0.263	0.445	0.230	0.324	368.76
0.127	0.858	0.016	0.480	0.476	0.044	376.64
0.130	0.718	0.152	0.498	0.265	0.237	369.17
0.139	0.836	0.026	0.519	0.413	0.068	374.76
0.163	0.754	0.083	0.518	0.321	0.161	369.87
0.170	0.799	0.030	0.548	0.378	0.074	372.61
0.177	0.775	0.049	0.602	0.293	0.105	367.93
0.184	0.779	0.037	0.586	0.322	0.092	370.27
0.195	0.609	0.196	0.517	0.217	0.266	364.74
0.203	0.687	0.110	0.546	0.261	0.192	366.79
0.212	0.529	0.260	0.547	0.157	0.296	360.51
0.212	0.566	0.222	0.547	0.169	0.283	362.43
0.213	0.658	0.130	0.564	0.220	0.216	364.27
0.226	0.633	0.141	0.567	0.210	0.224	363.42
0.259	0.582	0.159	0.576	0.181	0.243	361.76
0.266	0.679	0.055	0.621	0.262	0.118	365.94
0.268	0.559	0.173	0.573	0.170	0.257	360.88
0.278	0.505	0.217	0.568	0.145	0.286	359.19
0.290	0.644	0.066	0.630	0.233	0.137	364.07
0.333	0.598	0.068	0.642	0.202	0.156	363.00
0.363	0.559	0.078	0.636	0.188	0.175	361.64
0.400	0.513	0.087	0.629	0.177	0.194	360.71

¹ Standard uncertainty u are $u(T) = 0.05\text{K}$, $u(p) = 0.1\text{kPa}$, and relative uncertainty u_r are $u_r(x) =$ and $u_r(y) =$.

Table 5 Experimental (vapour - liquid - liquid) equilibrium temperatures T , liquid mole fractions x and vapour mole fractions y for the system water (1) +1-butanol (2) + toluene (3) x at pressure $p = 101.3\text{ kPa}$.³

Organic Phase	Aqueous phase	Vapour phase
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	x_1	x_2	x_3	x_1	x_2	x_3	y_1	y_2	y_3	T (K)
BIN	0.012	---	0.988	1.000	---	0.0003	0.561	0.000	0.439	357.34
1	0.014	0.012	0.974	1.000	0.000	0.0003	0.548	0.015	0.437	357.15
2	0.014	0.044	0.941	0.998	0.001	0.0003	0.536	0.038	0.426	357.18
3	0.025	0.102	0.873	0.996	0.003	0.0003	0.527	0.066	0.408	356.59
4	0.033	0.135	0.833	0.995	0.005	0.0003	0.528	0.073	0.399	356.54
5	0.034	0.156	0.810	0.995	0.005	0.0002	0.531	0.077	0.392	356.53
6	0.054	0.196	0.750	0.994	0.006	0.0002	0.531	0.084	0.384	356.57
7	0.054	0.234	0.712	0.994	0.006	0.0003	0.530	0.089	0.381	356.59
8	0.077	0.264	0.659	0.993	0.007	0.0002	0.534	0.093	0.373	356.64
9	0.095	0.313	0.592	0.993	0.007	0.0002	0.536	0.097	0.367	356.76
10	0.145	0.366	0.489	0.992	0.008	0.0002	0.542	0.104	0.354	356.89
11	0.156	0.404	0.440	0.992	0.008	0.0001	0.545	0.108	0.346	357.04
12	0.204	0.461	0.335	0.991	0.009	0.0001	0.548	0.117	0.335	357.37
13	0.264	0.496	0.240	0.990	0.010	0.0001	0.561	0.130	0.310	357.85
14	0.299	0.506	0.196	0.989	0.011	0.0001	0.562	0.138	0.299	358.17
15	0.375	0.497	0.128	0.988	0.012	0.0001	0.586	0.152	0.262	358.69
16	0.404	0.494	0.101	0.987	0.013	0.0001	0.603	0.159	0.238	359.20
17	0.436	0.483	0.081	0.987	0.013	0.0001	0.613	0.165	0.222	359.76
18	0.478	0.468	0.054	0.986	0.014	0.0001	0.633	0.176	0.191	360.55
19	0.515	0.451	0.033	0.986	0.014	0.0001	0.661	0.194	0.145	361.53
20	0.537	0.440	0.024	0.985	0.015	0.0000	0.690	0.204	0.107	362.49
21	0.549	0.432	0.019	0.984	0.016	0.0000	0.697	0.211	0.092	362.96
BIN	0.638	0.362	---	0.979	0.021	---	0.754	0.246	---	

¹ Standard uncertainty u are $u(T) = 0.05\text{K}$, $u(p) = 0.1\text{kPa}$, and relative uncertainty u_r are $u_r(x) =$ and $u_r(y) =$.

Table 6 Antoine equation parameters^a of the pure substances.

Compound	A	B	C	Temperature Range (K)
Water	7.1961	1730.63	-39.724	274.15 / 373.15
1-Butanol	6.546	1351.555	-93.34	295.65 / 390.85
Toluene	6.0783	1343.943	-53.773	308.52 / 384.66

^a Antoine Equation: $\log(p) = A - B / [T + C]$, with: $p(\text{kPa})$ and $T(\text{K})$

Table 7 Parameters and mean deviations from the VLE correlation. A_{ij} (K) NRTL binary interaction parameters. U_{ij} - U_{jj} (K) UNIQUAC binary interaction parameters. Mean deviations of temperature T (K) and vapour phase compositions for water (1) and 1-butanol (2).

i	j	A_{ij}	A_{ji}	α	U_{ij} - U_{jj}	U_{ji} - U_{ii}
Water	1-Butanol	1398.917	120.423	0.363	263.557	73.669
Water	Toluene	3192.485	561.478	0.152	459.942	726.283
1-Butanol	Toluene	-127.442	636.442	0.240	-77.660	227.327
Mean Deviation				D T	D y_1	D y_2
NRTL				1.06	0.0149	0.0140
UNIQUAC				0.75	0.0105	0.0120

Table 8 Temperature and composition (mole fraction) of the binary and ternary azeotropes for the system water (1) + 1-butanol (2) + toluene (3) at 101.3 kPa.

Heterogeneous binary azeotrope water (1) + 1-butanol (2)				
	Experimental ^[34]	NRTL	UNIQUAC	UNIFAC
x_1	0.750	0.760	0.751	0.760
x_2	0.250	0.240	0.249	0.240
T (K)	365.65	365.97	365.69	366.21
Heterogeneous binary azeotrope water (1) + toluene (3)				
	Experimental ^[35]	NRTL	UNIQUAC	UNIFAC
x_1	0.561	0.563	0.560	0.558
x_3	0.439	0.437	0.440	0.442
T (K)	357.34	357.77	357.64	357.55
Homogeneous binary azeotrope 1-butanol (2) + toluene (3)				
	Experimental ^[36]	NRTL	UNIQUAC	UNIFAC
x_2	0.327	0.304	0.321	0.328
x_3	0.673	0.696	0.679	0.672
T (K)	378.15	378.97	378.71	378.13
Ternary heterogeneous azeotrope water (1) + 1-butanol (2) + toluene (3)				
	Experimental ^[27]	NRTL	UNIQUAC	UNIFAC
x_1	0.532	0.542	0.541	0.530
x_2	0.080	0.085	0.081	0.096
x_3	0.388	0.373	0.378	0.374
T (K)	356.45	356.98	356.94	356.53

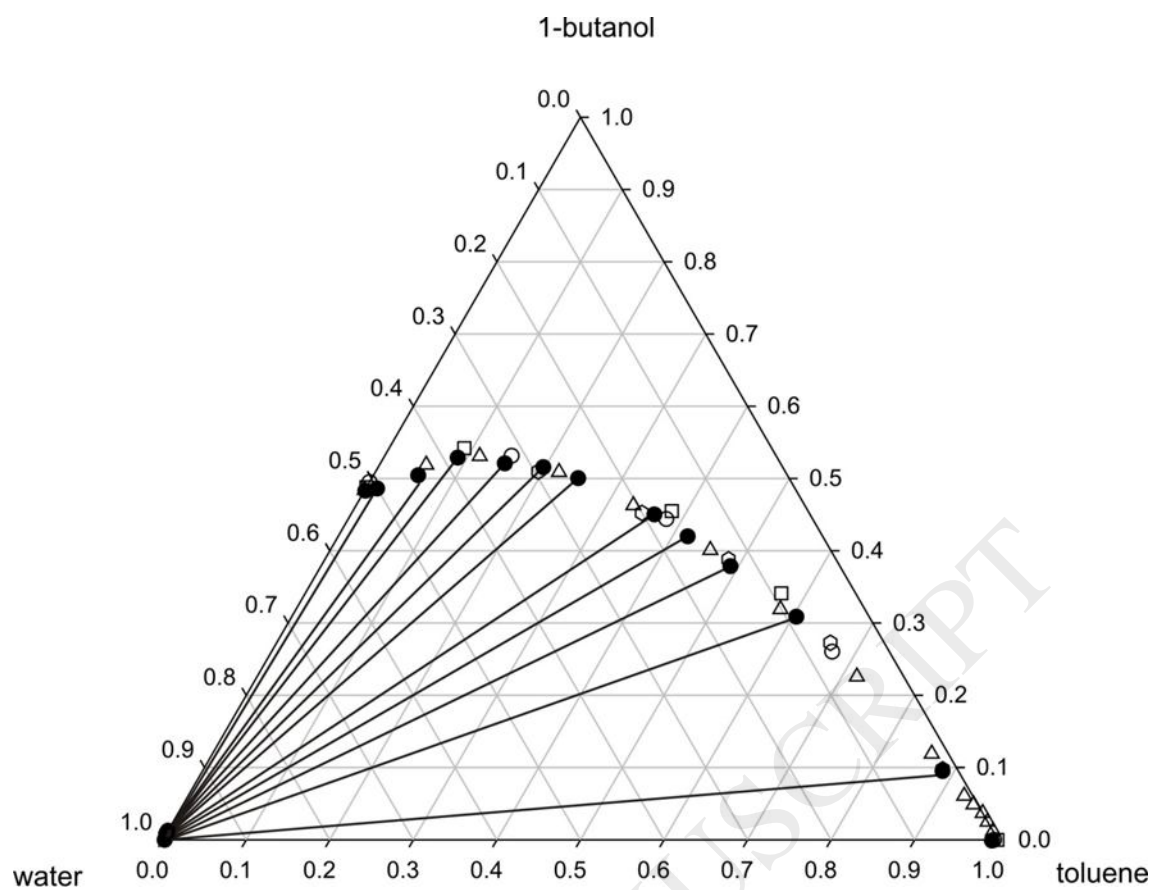


Fig. 1

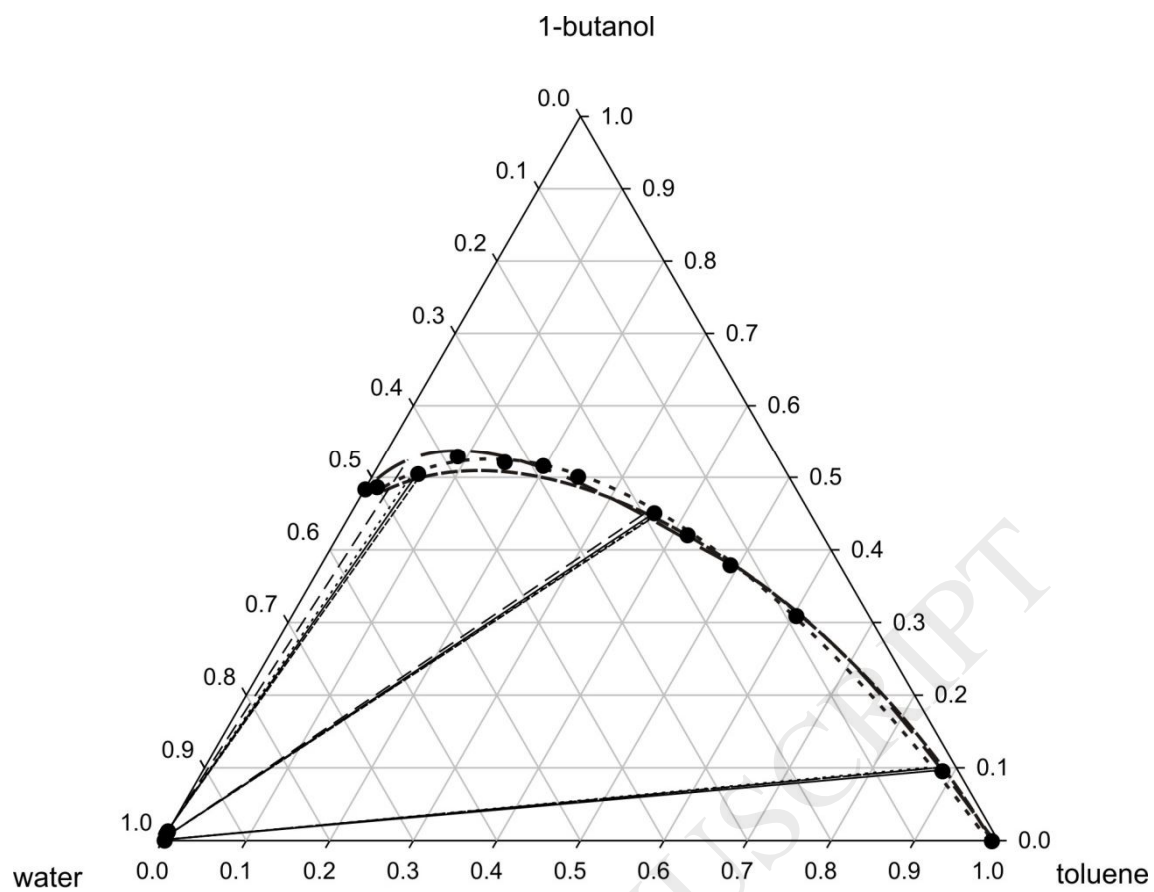


Fig. 2

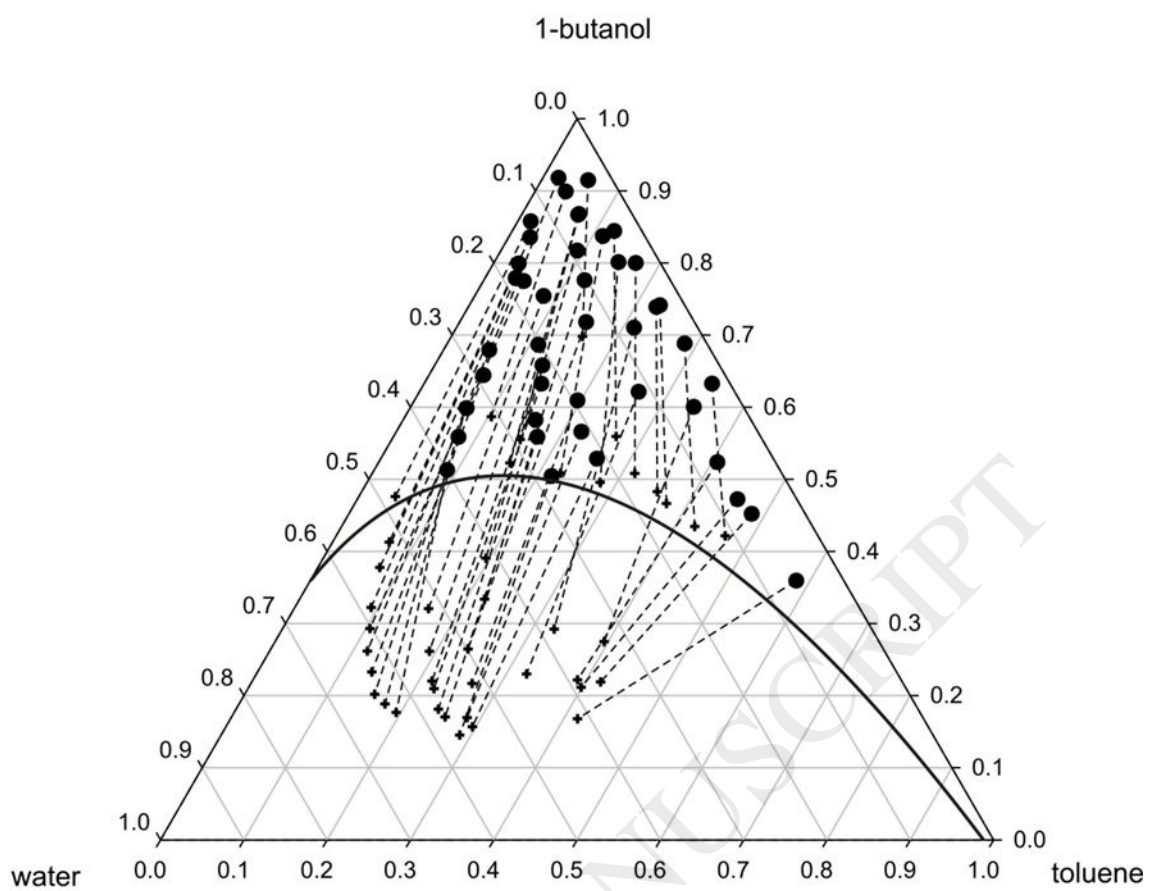


Fig. 3

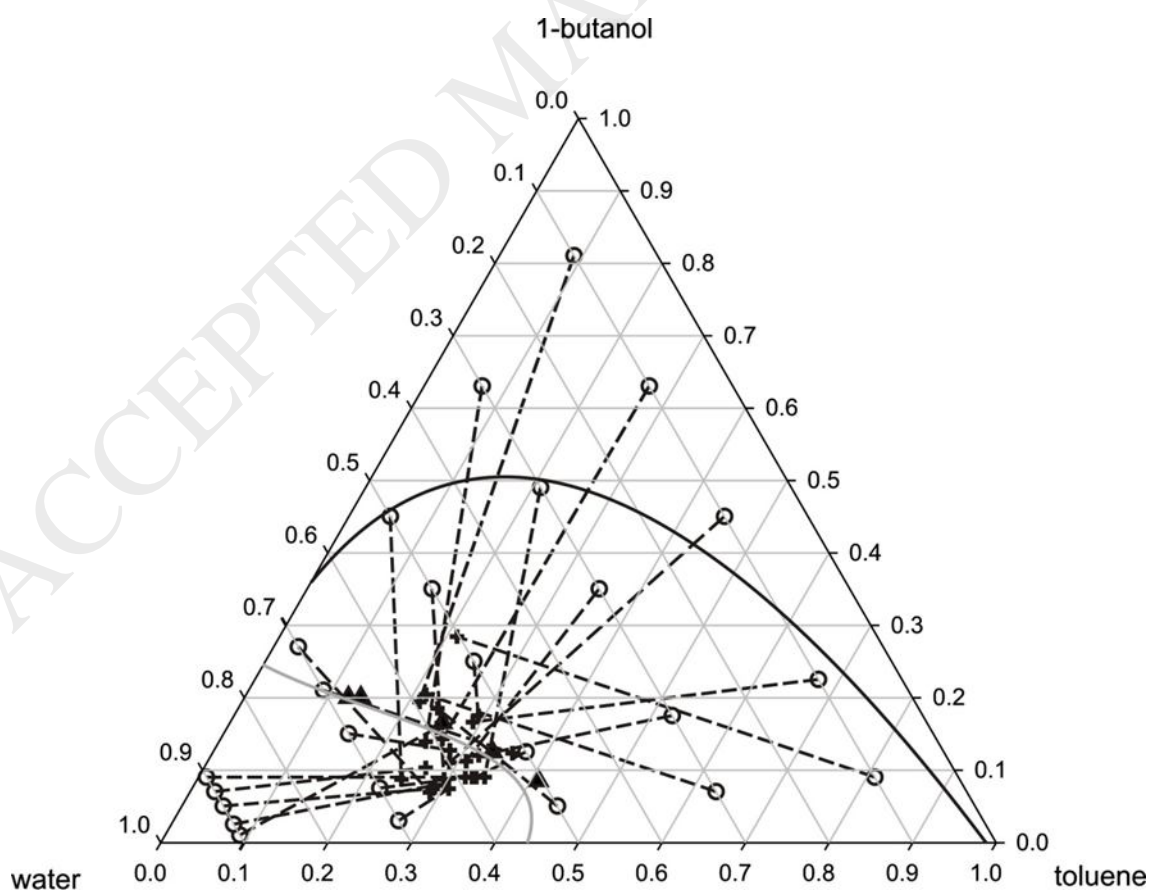
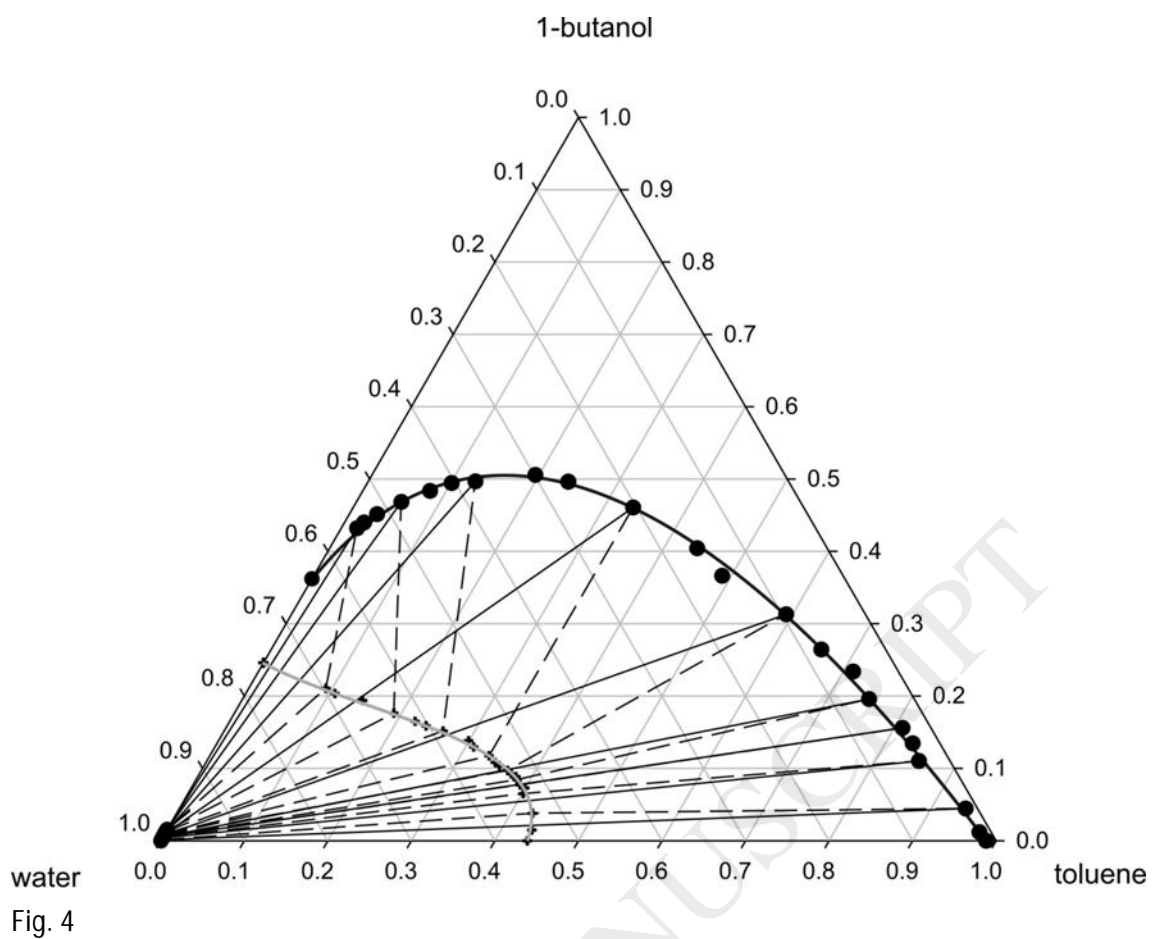


Fig. 5

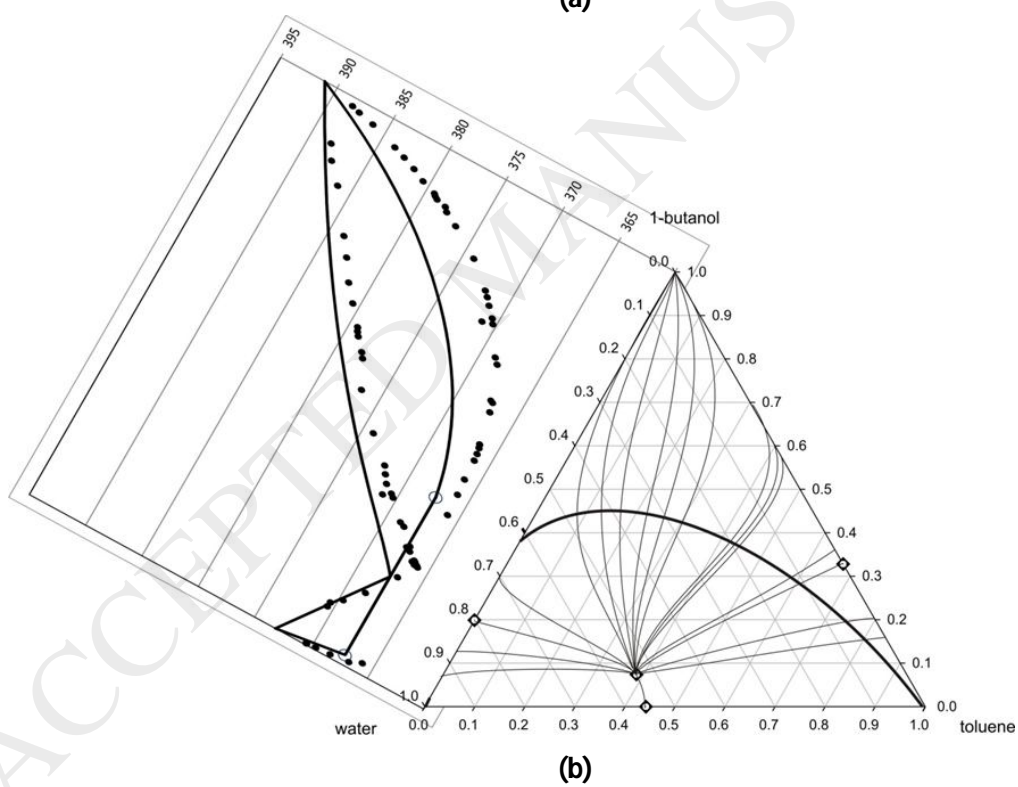
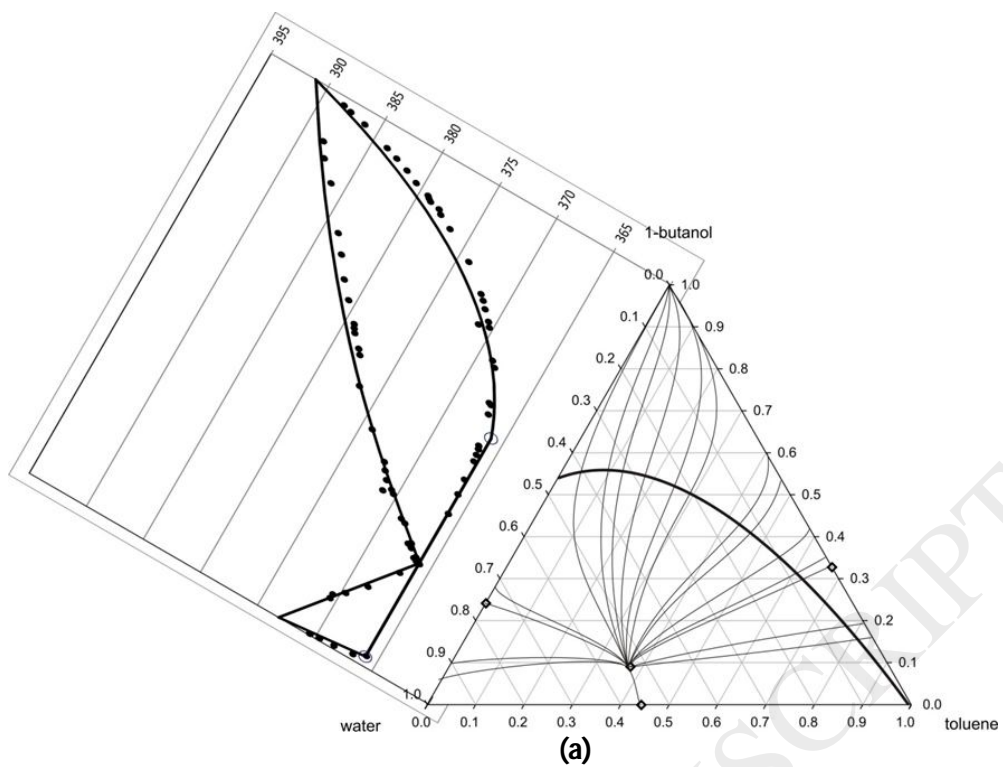


Fig. 6

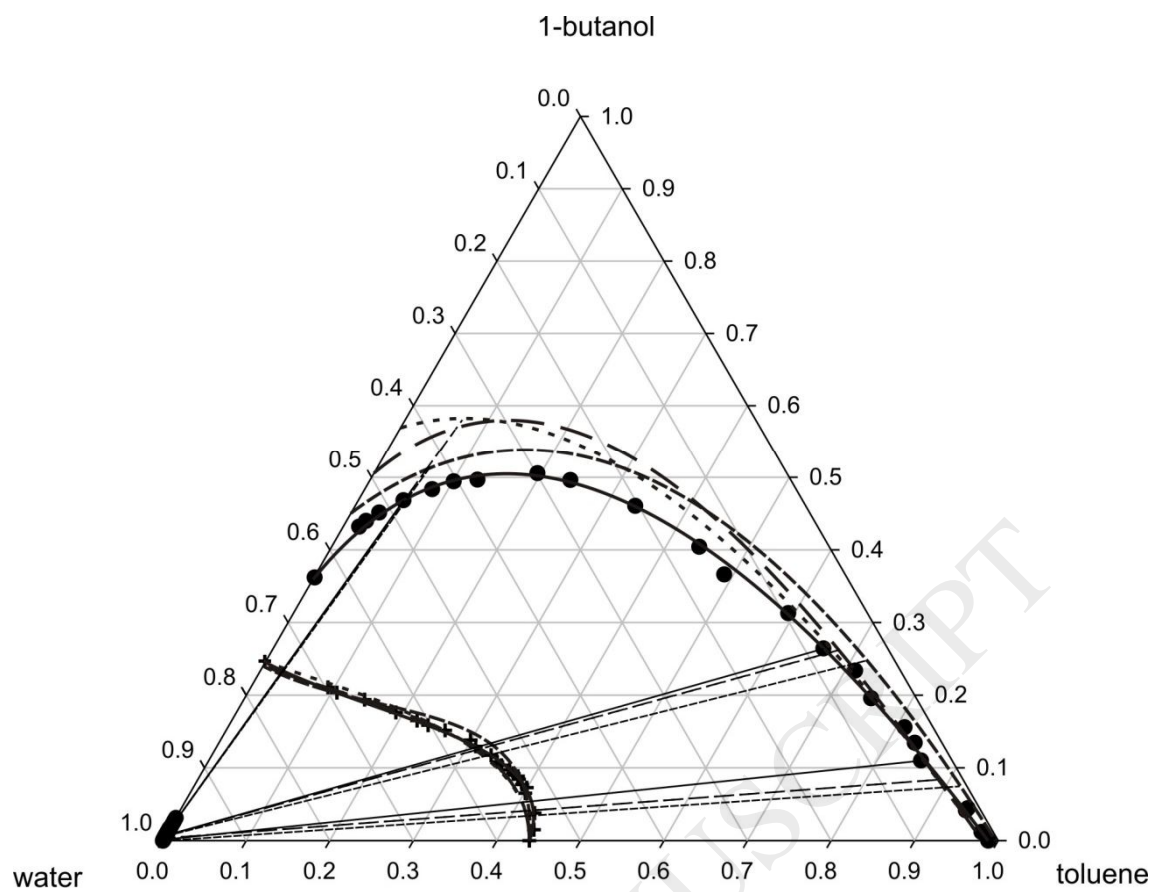


Fig. 7