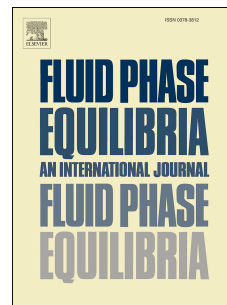# Accepted Manuscript

Experimental study of the LL, VL and VLL equilibria of water + 1-butanol + 2-octanol at 101.3 kPa

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1 Experimental study of the LL, VL and VLL equilibria of water + 2 1-butanol + 2-Octanol at 101.3 kPa

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5

6 ABSTRACT

7 Equilibrium data for the water + 1-butanol + 2-octanol system is determined in this
8 work. Liquid-liquid equilibrium (LLE) data are obtained at 303.15K and 313.15K, with a
9 view to investigating the influence of temperature.

10 Vapour-liquid-liquid equilibrium (VLLE) and vapour-liquid equilibrium (VLE) data of the
11 same system are also determined at 101.3 kPa, by means of a modified Fisher
12 Labodest recirculating still that is coupled to an ultrasonic probe. Additionally, the
13 heterogeneous binary azeotrope of the pair water + 2-octanol is determined.

14 Correlation parameters are obtained from the experimental results for use in the
15 universal quasichemical (UNIQUAC) and non-random two-liquid (NRTL)
16 thermodynamic models in CHEMCAD 7. The UNIQUAC, NRTL and original universal
17 functional group activity coefficient (UNIFAC) models are then, in turn, used to predict
18 the LLE and VLLE data from these correlation parameters.

19 KEYWORDS

20 Water, 1-butanol, 2-octanol, liquid-liquid, vapour liquid, vapour-liquid-liquid

21 1.- INTRODUCTION

22 Butanol is a fuel of natural origin that is gaining great relevance at the moment due to
23 the advantages it displays with respect to ethanol.

24 Now that butanol is becoming a substitute for bioethanol, companies are trying to
25 develop other methods of producing it that differ from the traditional ABE (Acetone-
26 Butanol-Ethanol) fermentation. Yet other usual industrial production methods are often
27 the Oxo process and Guerbet reaction [1].

28 It is for this reason that the Spanish company Abengoa undertook a technological
29 development project in 2013 that converts bioethanol, already produced by the
30 company, into butanol by means of the catalyzed Guerbet reaction [1]. This reaction
31 obtains longer molecular chains from others involving shorter chains, via a catalytic
32 dimerization.

33 Since this dimerization is not selective, other alcohols (C3-C8) may appear that can
34 adversely affect the subsequent purification processes of butanol, because the existing
35 equilibria between phases can be modified by the various species that are present.
36 Based on this fact, it would be desirable to have access to equilibrium data for butanol
37 in the presence of those long chain alcohols.

38 In this work, we study the vapour-liquid equilibria (VLE) and the vapour-liquid-liquid
39 equilibria (VLLE) of water + 1-butanol + 2-octanol at 101.3 kPa, as well as its liquid-
40 liquid equilibria (LLE) at 303.15K and 313.15K. Since octanol is among the long chain
41 alcohols that might be produced during the dimerization reactions, it would be
42 convenient to obtain equilibrium data for the above ternary system. At the time of
43 writing it has not been possible to find equilibrium data on this system in the literature.

2.- MATERIAL AND METHODS

2.1. Chemicals

46 The chemical compounds that were employed in this work, along with their purity and
47 provenance, are presented in table 1. In addition, their water content was checked
48 against the Karl Fischer titration technique. The compounds were used as supplied by
49 the provider, without any subsequent purification. Water was obtained in situ. The
50 water obtaining follows a 4 step process. Water from the drinking water network goes
51 through two reverse osmosis processes, the second one reaching 21 bar of osmotic
52 pressure. The water product from these reverse osmosis is fed into an Ellix Milipore
53 equipment, composed by a further reverse osmosis step and an ion-exchanger resin
54 step. This water product with less than 5 µS/cm conductivity goes through another ion-
55 exchanger resin reaching after this step a conductivity lesser than 2 µS/cm. Ethanol
56 has been employed as an internal standard to improve quantification during sample
57 analysis.

Table 1.- Specifications of chemical compounds used

Chemical	Provider	Purity (mass fraction)	Water content (mass fraction)(by Karl Fischer titration)	Purification method	Analysis method
1-Butanol	Merck	>0.995	<0.001	none	GC
2-Octanol	Merck	>0.980	<0.001	none	GC
Ethanol	VWR chemicals Prolabo	>0.9997	<0.001	none	GC

2.2. Apparatus and procedures

61 The procedure employed in the experimental determination has been explained in
62 detail in several previous works [2]. For LLE at temperatures below the boiling point,
63 known weighed global mixtures of water, 1-butanol and 2-octanol were prepared inside
64 sealed-cap tubes that, in turn, were submerged in a thermostatic bath at the
65 corresponding temperature. In a first step, the tubes were shaken vigorously to
66 increase mass transfer and help achieve equilibrium among all the phases.
67 Subsequently, stirring was stopped to permit decanting. Afterwards, samples from both
68 phases were extracted with syringes from the tubes, and introduced in vials along with
69 a known amount of ethanol (for quantification and to avoid phase splitting at a later
70 stage). Those vials were analyzed via gas chromatography (GC).

71 For the VLE and VLLE, we used a Fischer Labodest instrument whose boiling chamber
72 was retrofitted with an ultrasonic probe to facilitate phase mixing. It was also employed
73 on a previous occasion to obtain accurate VLLE data [3]. After the Cotrell pump, the
74 vapour in equilibrium with the liquid (or liquid phases) was diverted by means of a

peristaltic pump through a heated pipe, which avoided vapour condensation and subsequent phase splitting in the case of a heterogeneous vapour, to a six-way valve that, in turn, could be activated to inject an amount of vapour sample into the GC injector for analysis. On the other hand, the liquid was collected through a valve. In the case of a heterogeneous liquid, the collected sample was put into a tube inside a thermostatic bath. The controlled temperature of the bath in this case corresponded to the boiling temperature of the sample. The remaining steps of the procedure were the same as in the LLE determination.

To measure the temperature of the equilibrium vapour under boiling conditions, a Pt-100 sensor coupled to a Coprico thermometer (Model 3202) was employed. Its certificate of calibration (scale ITS 90 [4]) certifies a measured temperature uncertainty of 0.006 K. The pressure in the equipment was controlled to within an uncertainty of 0.1 kPa at 101.3 kPa through a Fischer M101 phase equilibrium control system.

To perform the analysis, two gas chromatographs were employed. The vapour, homogeneous liquid and organic phases were passed through a Shimazu GC-14A with a thermal conductivity detector (TCD). In the case of the acqueous phases where the amount of both butanol and octanol were small, an Agilent GC-7820A, with a TCD and a flame ionization detector (FID) in series, was used. The analytical conditions of both chromatographs are presented in table 2. Additionally, the amount of water in the organic phase was checked against the Karl Fischer technique.

Table 2.- Chromatographic conditions

	Shimadzu GC-14A	Agilent GC-7820A
Column	Porapack Q	Porapack Q
He Flowrate	23.7 mL/min	25 mL/min
Detector	TCD	TCD/FID
Column Temperature	503 K	503 K
Injector Temperature	523 K	523 K
Detector Temperature	523 K	523 K

3.- RESULTS AND DISCUSSION

3.1. LLE determination

The final composition of each phase, as obtained at the different temperatures, are given in tables 3 and 4.The LLE of the binary water + 1-butanol at both temperatures, have been reproduced from Ref. [5]. They are also shown as ternary plots in Figs. 1 and 2.

104

105 Table 3: LLE Composition Results at 303.15K for the Ternary System of Water (1) + 1-Butanol (2) + 2-
106 Octanol (3) in Mole Fraction at 101.3kPa

Aqueous Phase Composition			Organic Phase Composition		
x_1	x_2	x_3	$x_1{}^a$	x_2	x_3
0.9999	0.0000	0.000118	0.2231	0.0000	0.7769
0.9973	0.0027	0.000100	0.2512	0.2186	0.5303
0.9927	0.0082	0.000063	0.2862	0.3175	0.3858
0.9913	0.0088	0.000059	0.3354	0.4127	0.2519
0.9908	0.0103	0.000048	0.3749	0.4698	0.1551
0.9867	0.0131	0.000030	0.4264	0.4971	0.0766
0.9860	0.0143	0.000019	0.4641	0.5010	0.0349
0.983[5]	0.017[5]	0.000[5]	0.504[5]	0.496[5]	0.000[5]

107 The composition relative standard uncertainty is $u_r(x) = \frac{u}{x}$ is 2% except $u_r(x_3) = 20\%$ in the aqueous
108 phase. The pressure uncertainty is u(P)=2kPa. The temperature uncertainty is 0.5K.
109 [a] was checked against Karl Fischer titration

110

111 Table 4: LLE Composition Results at 313.15K for the Ternary System of Water (1) + 1-Butanol (2) + 2-
112 Octanol (3) in Mole Fraction at 101.3 kPa
113

Aqueous Phase Composition			Organic Phase Composition		
x_1	x_2	x_3	x^a	x_2	x_3
0.9999	0.0000	0.000130	0.2297	0.0000	0.7703
0.9949	0.0049	0.000096	0.2645	0.2207	0.5148
0.9946	0.0053	0.000096	0.3171	0.3297	0.3532
0.9934	0.0066	0.000086	0.3421	0.4137	0.2442
0.9908	0.0092	0.000067	0.3893	0.4608	0.1499
0.9896	0.0111	0.000064	0.4439	0.4866	0.0697
0.9894	0.0119	0.000056	0.4718	0.4965	0.0319
0.981[5]	0.019[5]	0.000[5]	0.516[5]	0.484[5]	0.000[5]

114 The composition relative standard uncertainty is $u_r(x) = \frac{u}{x}$ is 2% except $u_r(x_3) = 20\%$ in the aqueous
115 phase. The pressure uncertainty is u(P)=2kPa. The temperature uncertainty is 0.5K.
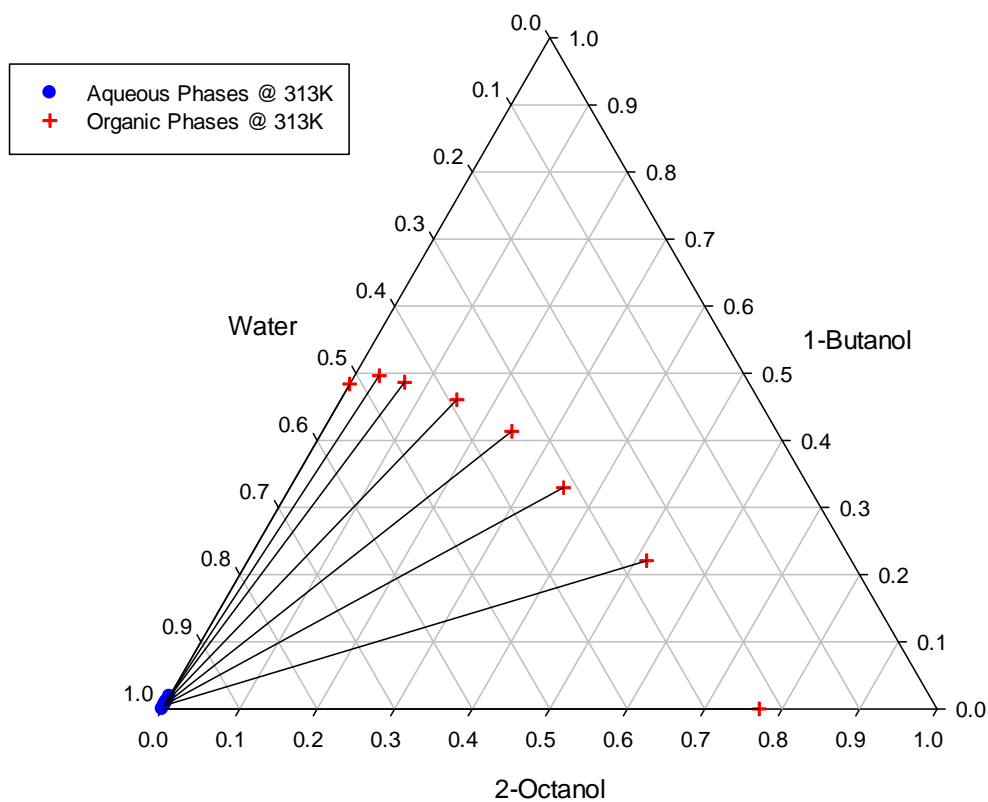116 [a] was checked against Karl Fischer titration

117

4

118
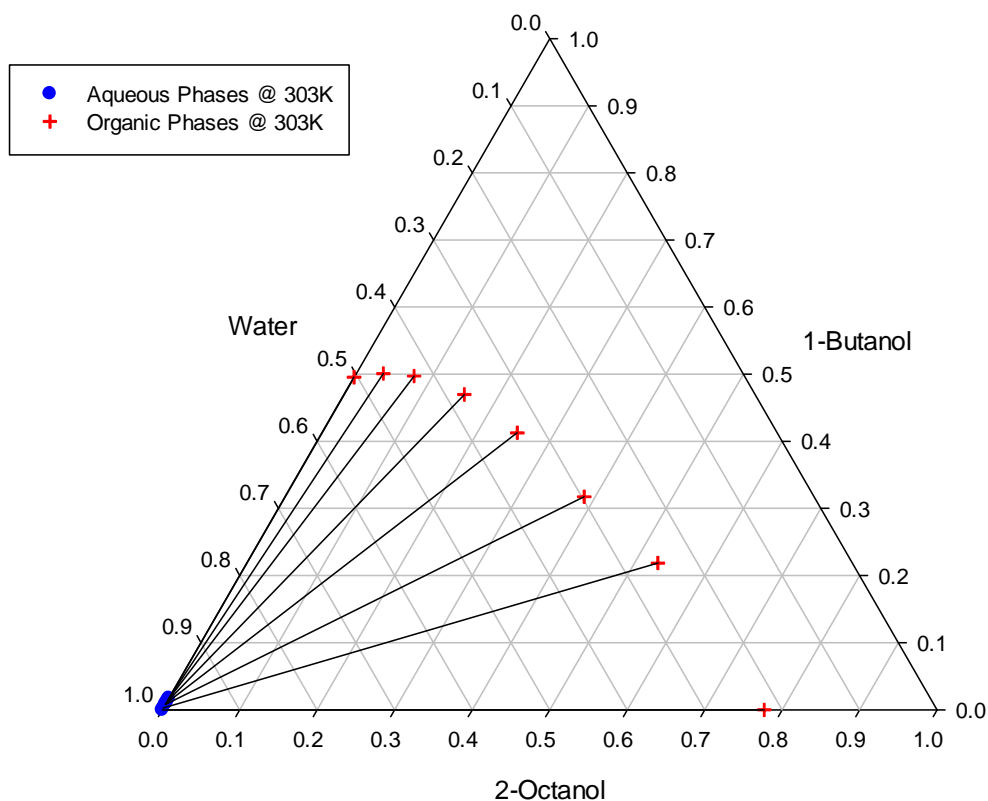
Figure 1: LLE Results for the System of Water + 1-Butanol + 2-Octanol at 303.15K with the Organic
Phases (red crosses) and Aqueous Phases (solid blue circles) joined by tie lines (black).

121

Figure 2: LLE Results for the System of Water + 1-Butanol + 2-Octanol at 313.15K with the Organic
Phases (red crosses) and Aqueous Phases (solid blue circles) joined by tie lines (black).

124

125 From these ternary plots it is evident that the organic phases, represented by the red
126 markers, follow a general trend which, at both temperatures, is very similar. The same
127 can be said for the aqueous phases. The points representing the aqueous phase follow
128 an approximately linear relationship, even though this is difficult to visualize because
129 the points are concentrated in a small area of the plot as a result of the high water
130 content of these phases.

131 A direct comparison with other experimental data was not possible for the water + 1-
132 butanol + 2-octanol system as no published liquid-liquid equilibrium information was
133 found.

134 However, data do exist in the literature for the LLE of the binary pairs water+1-butanol
135 and water+2-octanol. In a previous work [5] we compared our experimental data for
136 water+1-butanol, at several temperatures, with values from the literature. On the other
137 hand, the binary LLE for water + 2-octanol was also determined experimentally in other
138 works [6, 7, 8]. In Fig. 3 we show the compositions, at different temperatures, of the
139 organic and aqueous phases in the LLE of water+2-octanol obtained in all the sources
140 we have consulted. As can be seen, at 303.15K and 313.15K, we obtain similar results
141 as Stephenson [6]. Additionally, the evolution of our experimental data with
142 temperature is the same as the trend followed by the data in the literature, even for the
143 LLE at the boiling temperature (this can be seen in table 7 below).

144
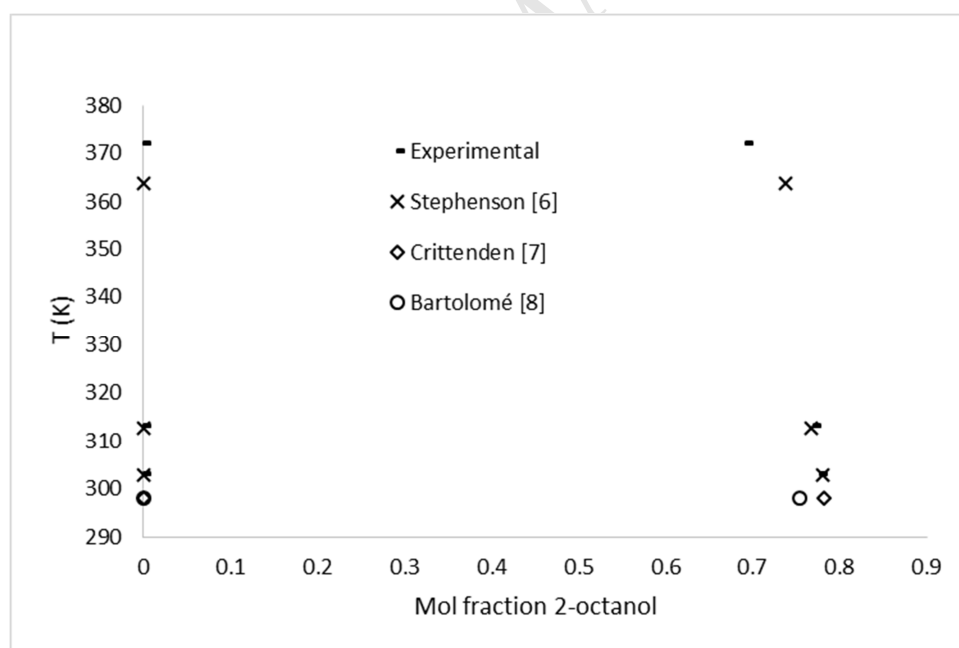
145

146 Figure 3. Comparison with literature data of the LLE for the water+2-octanol system at different
147 temperatures. The compositions are given in mole fraction.

148

149 The experimental LLE data obtained at both temperatures was correlated using the
150 UNIQUAC and NRTL thermodynamic models. A preset value of 0.2 was used for the
151 non-randomness parameter, α, in the NRTL model correlations as recommended in the
152 literature [9]. CHEMCAD 7 [10] was used to carry out all the predictions and
153 correlations, with the resulting regression parameters and deviations shown in tables 5

6

154 and 6. The mean deviations in composition are the mean of the absolute differences
155 between the experimental composition of one component in one phase and the
156 calculated data. The binodal curve was predicted at 303.15K and 313.15K using the
157 NRTL and UNIQUAC models, with the parameters shown in table 5. The resulting
158 curves are compared with the experimental data in Figs. 4 and 5, respectively. In
159 addition, the binodal curve corresponding to each temperature, was also predicted
160 using the classic UNIFAC model[11] via parameters from the CHEMCAD database.
161 These two curves also shown in Figs. 4 and 5, respectively.
162
163
164 Table 5: LLE Correlation Parameters where B_{ij} Represents the Binary Interaction Parameter for the NRTL
165 Model (K), α is the Non-Randomness Parameter for the NRTL Model and $U_{ij} – U_{jj}$ & $U_{ji} - U_{ii}$ are the Binary
166 Interaction Parameters for the UNIQUAC Model (K)

i	J	B_{ij}	B_{ji}	α	$U_{ij} – U_{jj}$	$U_{ji} – U_{ii}$
Water	1-Butanol	1821.67	-376.65	0.2	316.20	-29.61
Water	2-Octanol	2478.45	41.82	0.2	249.61	211.80
1-Butanol	2-Octanol	2297.66	-1153.07	0.2	-343.77	400.06

167
168 Table 6: Mean Deviations of Molar Composition from LLE Correlations for Water (1) and 1-Butanol (2) in
169 the Organic Phase (1) and Aqueous Phase (2)

Model	D_x_{11}	D_x_{12}	D_x_{21}	D_x_{22}
NRTL	0.0039	0.0042	0.0103	0.0067
UNIQUAC	0.0020	0.0021	0.0045	0.0021

170
171
172 The UNIQUAC, NRTL and UNIFAC model predictions were similar to the experimental
173 data for the two temperatures. UNIQUAC and NRTL produce a binodal curve that is
174 rather closer to the experimental points than the UNIFAC prediction, which, in turn,
175 produces a slightly smaller heterogeneous region. In Figures 4 and 5 the tie lines
176 calculated with UNIQUAC model with the parameters from Table 5. As can be seen the
177 tie lines agree well with the experimental ones. These thermodynamic models give a
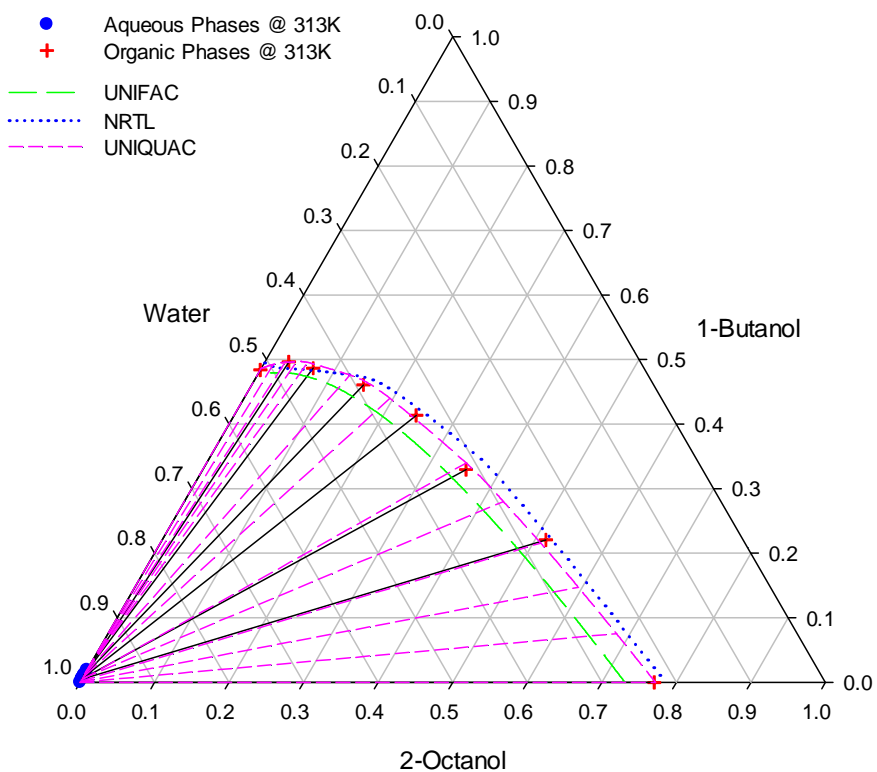178 reliable prediction of LLE for this system at both 303.15K and 313.15K.

179

180
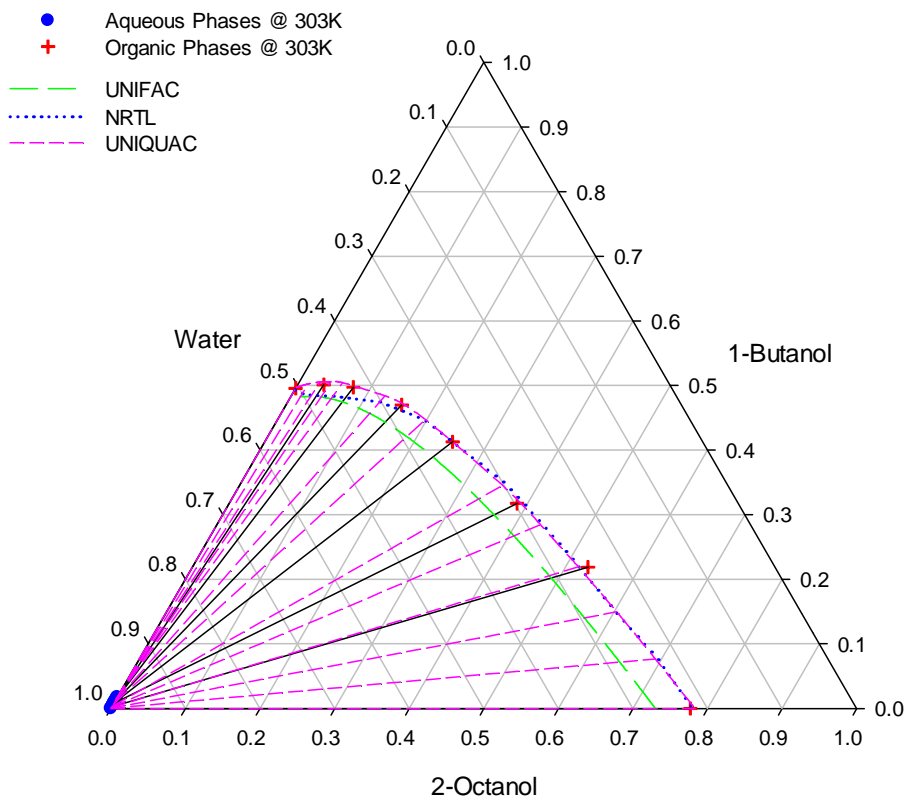
181
182 Figure 4: Comparison of Experimental LLE Data (red and blue markers) for the Ternary System of Water +
183 1-Butanol + 2-Octanol at 303.15K with Predictions of the NRTL (blue dotted line), UNIQUAC (short pink
184 dashed line) and UNIFAC (long green dashed line) Models

185
186 Figure 5: Comparison of Experimental LLE Data (red and blue markers) for the Ternary System of Water +
187 1-Butanol + 2-Octanol at 313.15K with Predictions of the NRTL (blue dotted line), UNIQUAC (short pink
188 dashed line) and UNIFAC (long green dashed line) Models

189

8

190
191
3.2. VLE & VLLE Determination

193 The experimental VLLE data are shown in table 7, corresponding to the heterogeneous
194 region, while table 8 collects the final values corresponding to the VLE data in the
195 homogeneous region. The compositions of each phase are expressed in mole fraction
196 and their bubble point temperature, *T*, is also reported. The VLE and VLLE results are
197 presented as ternary plots in Figs. 6 and 7. The VLLE of the water+1-butanol system at
198 101.3kPa was obtained in a previous work [3]

199
200
201
202

203 Table 7: VLLE Data for the Water (1) + 1-Butanol (2) + 2-Octanol (3) Ternary System, giving the Liquid
204 Phase Mole Fraction *x* and the Vapour Phase Mole Fraction *y* at Temperature *T* and a Pressure of 101.3
205 kPa

Organic Phase			Aqueous Phase			Vapour			
x_1	x_2	x_3	x_1	x_2	x_3	y_1	y_2	y_3	T (K)
0.3078	0.0000	0.6922	0.9998	0.0000	0.000241	0.9654	0.0000	0.0346	371.99
0.3112	0.0281	0.6607	0.9992	0.0006	0.000216	0.9400	0.0267	0.0333	371.68
0.3200	0.0789	0.6011	0.9980	0.0018	0.000170	0.9196	0.0499	0.0305	371.31
0.3185	0.1604	0.5211	0.9967	0.0032	0.000145	0.8633	0.1119	0.0248	370.07
0.3313	0.2061	0.4626	0.9957	0.0042	0.000156	0.8397	0.1394	0.0208	369.57
0.3332	0.2946	0.3723	0.9940	0.0059	0.000137	0.8075	0.1778	0.0147	368.55
0.3445	0.3276	0.3279	0.9933	0.0065	0.000164	0.8006	0.1873	0.0121	368.24
0.3636	0.3631	0.2733	0.9927	0.0072	0.000122	0.7829	0.2076	0.0095	367.85
0.3813	0.3926	0.2262	0.9906	0.0093	0.000107	0.7766	0.2163	0.0072	367.49
0.4069	0.4093	0.1838	0.9904	0.0095	0.000100	0.7681	0.2258	0.0061	367.15
0.4311	0.4288	0.1400	0.9902	0.0097	0.000096	0.7564	0.2397	0.0039	366.86
0.4439	0.4544	0.1018	0.9896	0.0103	0.000085	0.7541	0.2426	0.0033	366.53
0.4537	0.4544	0.0920	0.9886	0.0113	0.000076	0.7510	0.2459	0.0030	366.44
0.4905	0.4527	0.0569	0.9884	0.0116	0.000074	0.7497	0.2485	0.0018	366.28
0.5490	0.4304	0.0207	0.9865	0.0134	0.000072	0.7457	0.2536	0.0007	365.90
0.638[3]	0.362[3]	0.000[3]	0.979[3]	0.021[3]	0.000[3]	0.754[3]	0.246[3]	0.000[3]	365.73[3]

206 T is in K with a standard uncertainty of 0.06 K, the pressure standard uncertainty is 0.1 kPa and
207 composition relative standard uncertainty $u_r(x) = \frac{u}{x}$ is 2%

208
209
210

211 Table 8: VLE Data for the Water (1) + 1-Butanol (2) + 2-Octanol (3) Ternary System, giving the Liquid
212 Phase Mole Fraction *x* and the Vapour Phase Mole Fraction *y* at Temperature *T* and a Pressure of 101.3
213 kPa

	Liquid Phase			Vapour Phase			
	x_1	x_2	x_3	y_1	y_2	y_3	T (K)
1	0.3524	0.4859	0.1617	0.7590	0.2378	0.0033	368.04
2	0.2920	0.5533	0.1547	0.7458	0.2524	0.0019	369.34
3	0.2821	0.5845	0.1334	0.7410	0.2575	0.0014	370.00
4	0.2267	0.6623	0.1110	0.7076	0.2914	0.0010	371.57
5	0.1829	0.7349	0.0821	0.6589	0.3403	0.0008	373.77
6	0.1521	0.7892	0.0587	0.5986	0.4009	0.0004	375.83

7	0.1225	0.8359	0.0415	0.5276	0.4720	0.0003	377.99
8	0.1218	0.7567	0.1215	0.5661	0.4327	0.0012	378.10
9	0.1152	0.7219	0.1629	0.5564	0.4418	0.0019	379.15
10	0.1068	0.6990	0.1943	0.5521	0.4448	0.0031	379.97
11	0.1072	0.6495	0.2433	0.5701	0.4261	0.0037	380.74
12	0.0973	0.5745	0.3283	0.5883	0.4063	0.0053	382.90
13	0.0857	0.5055	0.4089	0.5914	0.4008	0.0078	384.92
14	0.0847	0.4632	0.4521	0.5755	0.4128	0.0117	388.19
15	0.0698	0.4045	0.5257	0.5683	0.4164	0.0153	391.11
16	0.0639	0.3422	0.5938	0.5865	0.3963	0.0172	393.91
17	0.0660	0.2808	0.6533	0.5912	0.3885	0.0203	397.70
18	0.0532	0.2371	0.7097	0.5922	0.3801	0.0277	401.82
19	0.0578	0.2151	0.7271	0.6078	0.3645	0.0277	405.32
20	0.0462	0.1700	0.7838	0.6122	0.3518	0.0360	410.45

214   T is in K with a standard uncertainty of 0.06 K, the pressure standard uncertainty is 0.1 kPa and

215   composition relative standard uncertainty $u_r(x) = \frac{u}{x}$ is 2%
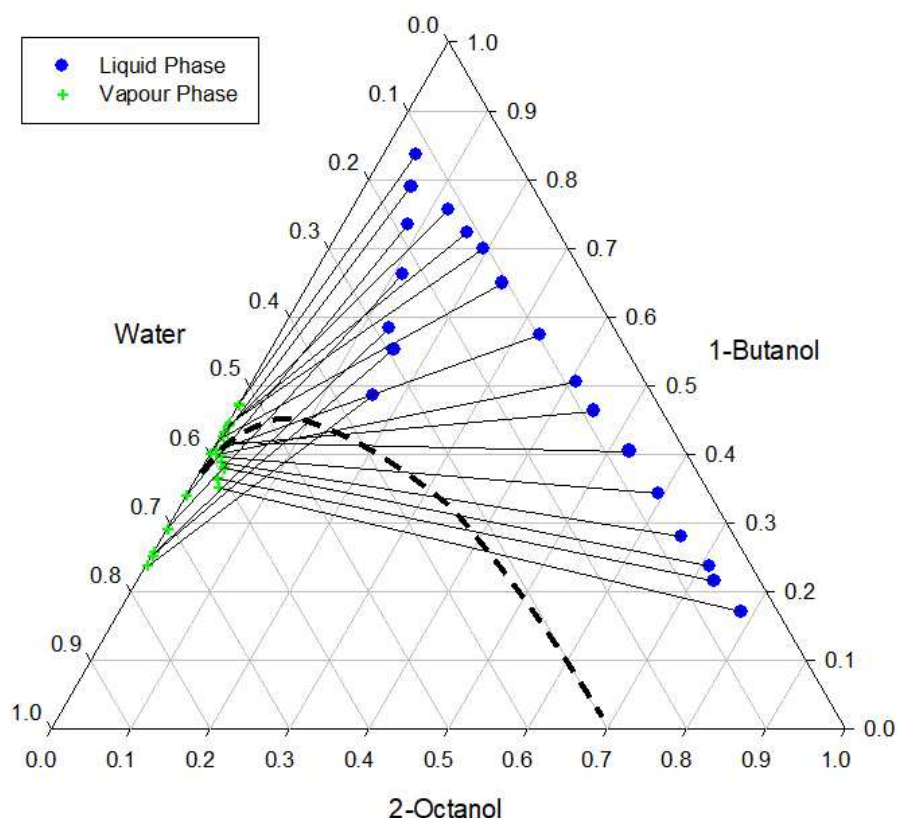
216
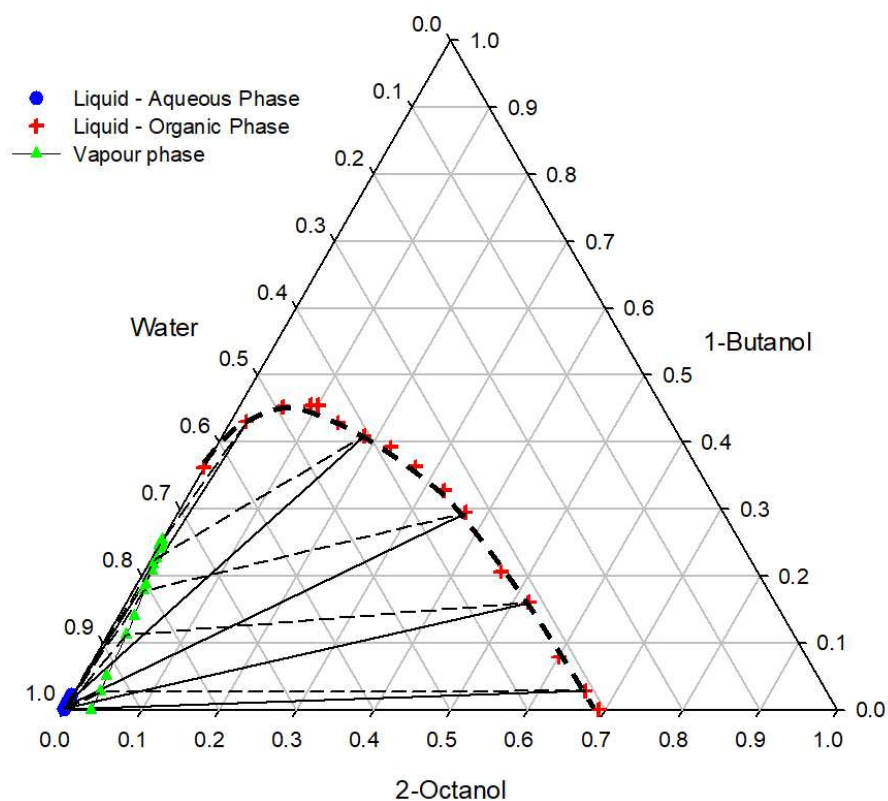
217

218   Figure 6: VLLE Ternary Diagram for the Water + 1-Butanol + 2-Octanol System at 101.3 kPa showing the
219   Organic Phase Liquids (red markers), Aqueous Phase Liquids (blue markers) and Vapours (green
220   markers) joined by tie lines (straight solid and dashed black lines) and the non-isothermal binodal curve
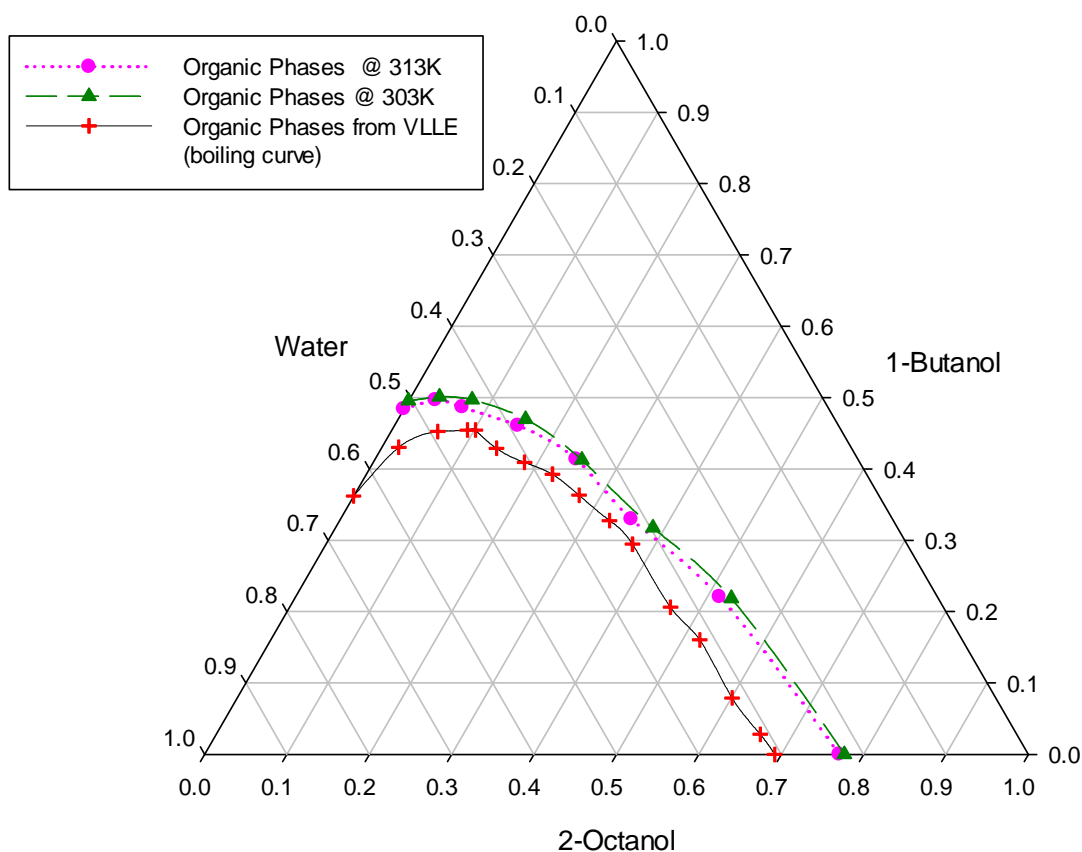221   (curved black line)

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Figure 7: VLE Ternary Diagram for the Water + 1-Butanol + 2-Octanol System at 101.3 kPa showing the
Liquid Phases (blue markers) and Vapours (green markers) joined by tie lines (straight solid black lines)
and the non-isothermal binodal curve (dashed black line)

From Fig. 6 one cannot conclude that the system contains a ternary azeotrope. This is
because all the triangles formed by the organic phase – aqueous phase – vapour tie
lines point in the same direction, and the bubble point temperatures in table 7 follow a
general rising trend with octanol content. The VLLE data also reveal the presence of
two heterogeneous binary azeotropes and these are given by the vapour compositions
in the water + 1-butanol and water + 2-octanol binary systems. We were unable to find
data on the binary azeotrope of the water+2-octanol system in the literature, and thus it
is not possible to make any comparison of its composition with previous works. Figure
7 shows that, for the points obtained, approximately half of the vapour phases which
are in equilibrium with a homogeneous liquid, are also confined to the heterogeneous
region. The vapours formed in both the VLLE and VLE determination were found to be
low in 2-octanol, with this being the least volatile compound in the system.

All the ternary points in Figs. 6 and 7 were tested for thermodynamic consistency using
the Wisniack L-W point-to-point test [12] for low pressure systems. All points passed
the test successfully for values between 0.94 and 1.00, indicating that there were no
substantial inconsistencies in the experimental VLE and VLLE data.

245

Figure 8: Comparison of the Heterogeneous Region from VLLE Determination (red crosses) with the
Boiling Curve (solid black line), LLE at 303.15K (green triangles – long dashed line) and LLE at 313.15K
(solid pink circles – dotted line) for the Ternary System of Water + 1-Butanol + 2-Octanol

249

To further assess the influence of temperature, the boiling curve, given by the organic
phases obtained during the VLLE determination, are plotted in Fig. 8 along with the
LLE binodal curves at 303.15K and 313.15K. If we compare the heterogeneous regions
at 303.15 and 313.15 K, a slight contraction in the size of the region is apparent in
going from the one to the other temperature. Moreover, just by looking at the figure, it
becomes clear that the organic phase curve at the boiling temperature leads to an even
greater reduction in the size of the heterogeneous region than the size difference
between the LLE at the two lower temperatures. In addition to this comparison between
the three temperatures, in the Fig. 9 has been represented the Txy diagram
qualitatively for the system studied. In this figure it can be seen the equilibrium regions
that exist at the temperatures around the boiling condition at 101.3 kPa. There exist
two distillation regions separated by the Separatrix also called the vapor curve that
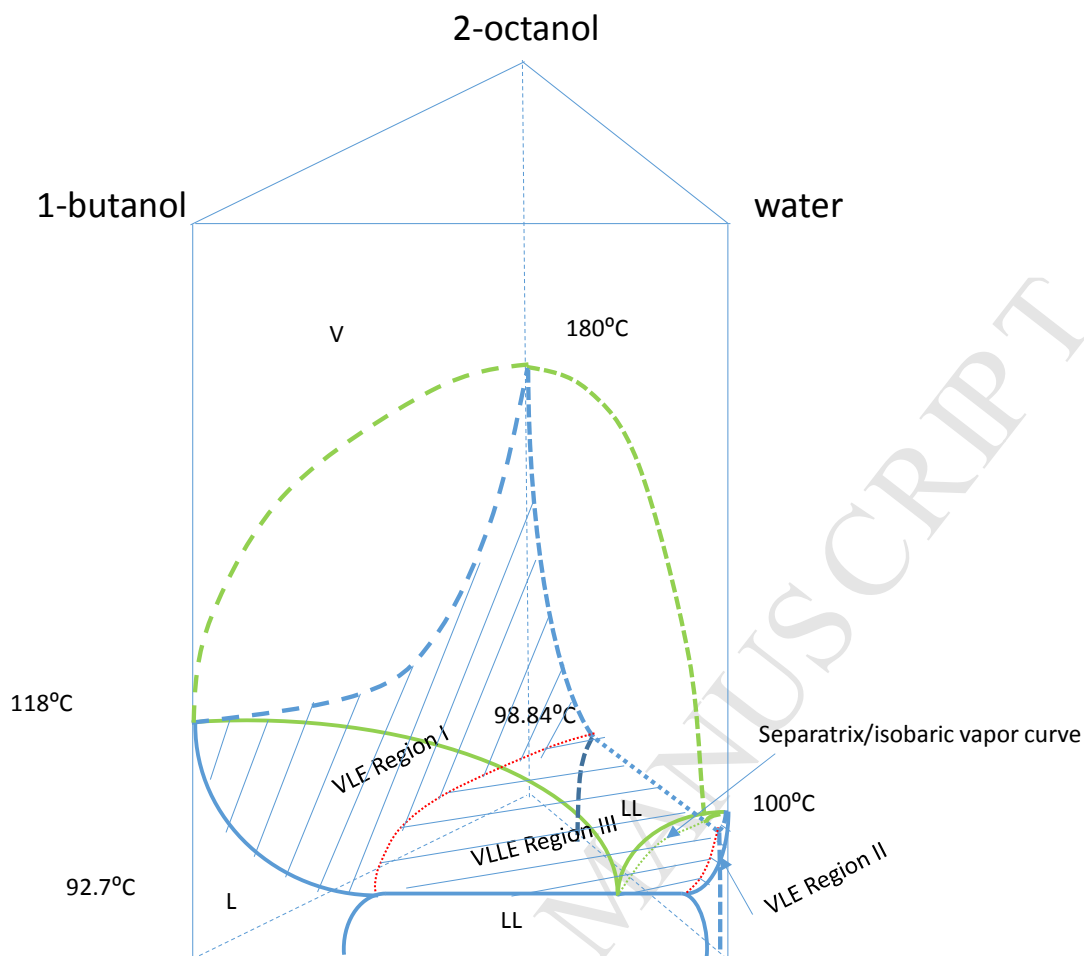goes from one heterogeneous binary azeotrope to the other one.

Figure 9: Schematic 3D bubble point surface for water + 1-butanol + 2-octanol at 101.3 kPa.

The experimental VLE and VLLE data were correlated in the same way as the LLE data, using the NRTL and UNIQUAC models to obtain binary interaction parameters, and then their associated deviations, through CHEMCAD 7. The results of these correlations are shown in tables 9 and 10. In this case, the data calculated in the correlation made use of the experimental liquid phase composition in order to find the composition of the vapour phase. The composition mean deviations are therefore the mean of the absolute differences between the experimental composition of one component in the vapour phase and the calculated data. The temperature mean deviation is then the mean of the differences between the calculated boiling temperature and its experimental value. The final non-randomness parameters, α, were obtained by iteration through minimization of the NRTL deviations. The UNIQUAC, NRTL and UNIFAC models were used to predict the experimental VLLE data and the resulting plots of the organic phases and vapour phases can be found in Fig. 10.

Table 9: VLE and VLLE Correlation Parameters where B_{ij} represents the Binary Interaction Parameter for the NRTL Model (K), α is the Non-Randomness Parameter for the NRTL Model and $U_{ij} - U_{jj}$ & $U_{ji} - U_{ii}$ are the Binary Interaction Parameters for the UNIQUAC Model (K)

i	j	B_{ij}	B_{ji}	α	$U_{ij} - U_{jj}$	$U_{ji} - U_{ii}$
Water	1-Butanol	1427.54	244.97	0.36	255.79	138.09
Water	2-Octanol	2278.68	-303.72	0.17	22.30	420.91
1-Butanol	2-Octanol	524.79	-346.85	0.3	-158.84	231.64

283

284 Table 10: Mean Deviations from VLE and VLLE Correlations of Molar Composition in the Vapour Phase *y*
285 for Water (1) and 1-Butanol (2) and of Temperature *T*

Model	D_T/K	D_y_1	D_y_2
NRTL	0.90	0.0253	0.0179
UNIQUAC	0.95	0.0239	0.0172

286
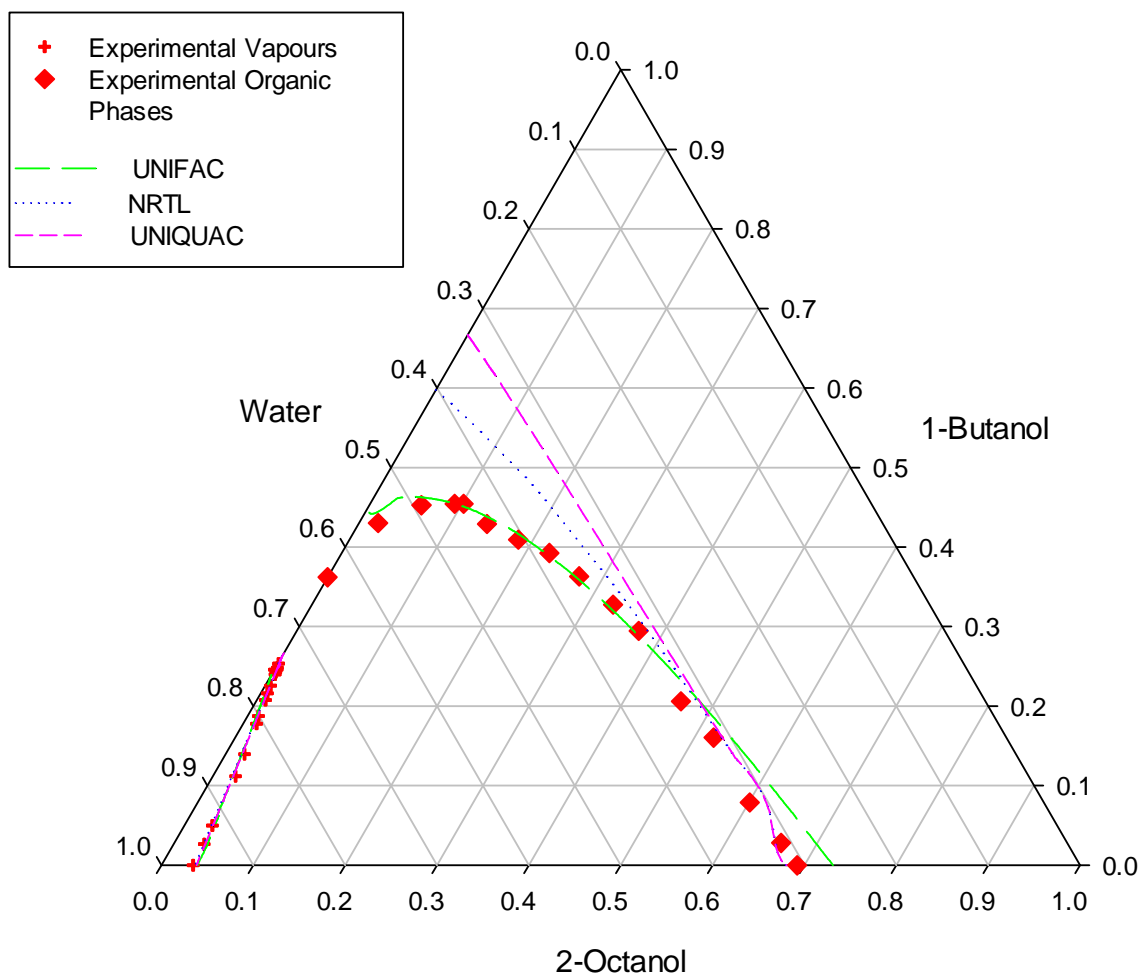
287

288 Figure 10: Comparison of Experimental VLLE Data (red markers for boiling curve) for the Ternary System
289 of Water + 1-Butanol + 2-Octanol with Predictions using the NRTL (blue dashes), UNIQUAC (short pink
290 dashes) and UNIFAC (long green dashes) Models

291 All three models successfully reproduced a vapour line that was close to the
292 experimental points, as indicated in table 10 by the low deviations in the calculated
293 vapour phases resulting from the correlation. Nevertheless the UNIFAC model was the
294 only one to reproduce a heterogeneous region that closely follows the experimental
295 points. The UNIQUAC and NRTL models both predicted a heterogeneous region that
296 was larger than the experimental one, with the correlation parameters given in table 9.
297 The UNIQUAC prediction gave the largest heterogeneous region and was furthest from
298 the experimental data. Of the three models that were tested on the VLLE data, only the
299 UNIFAC model would be suitable for process simulation and equipment design
300 purposes in the water + 1-butanol + 2-octanol system.

301

4.- CONCLUSIONS

LLE data was obtained at 303.15K and 313.15K, revealing that for the water + 1-butanol + 2-octanol system, an increase in temperature promoted mixing between the two immiscible liquid phases, which, in turn, produced a reduction in the size of the heterogeneous region. This conclusion was supported by the VLLE data when the binodal curve at the boiling temperature exhibited a further reduction in the size of the heterogeneous region.

The VLLE and VLE data also revealed the presence of two heterogeneous binary azeotropes in a system with two partially miscible pairs: water + 1-butanol and water + 2-octanol. The mole fraction composition of the latter azeotrope was 0.965 and 0.035 in water and 2-octanol, respectively.

The LLE, VLLE and VLE data were correlated using the NRTL and UNIQUAC thermodynamic models to obtain binary interaction parameters. The NRTL, UNIQUAC and UNIFAC models were then used to predict the experimental data of the water + 1-butanol + 2-octanol system. This revealed that UNIQUAC more closely reproduced the experimental points for the LLE while UNIFAC obtained the best fit of the VLLE experimental data.

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Highlights

- LLE, VLE and VLLE of the ternary mixture water + 1-butanol + 2-octanol have been measured.

- The UNIQUAC, UNIFAC and NRTL models provided good data correlation for LLE.

- UNIQUAC and NRTL from VLE data exhibited important discrepancies between predictions of the non-isothermal binodal curve and experimental data.

- The data do not reveal the existence of a ternary heterogeneous azeotrope.