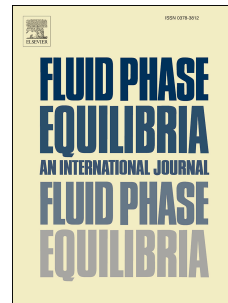


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Experimental study of the LL, VL and VLL equilibria of water + 1-butanol + 2-octanol at 101.3 kPa

Jorge Garcia-Cano, María Dolores Saquete, Nuria Boluda, Amy Houston



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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

3 Jorge Garcia-Cano, María Dolores Saquete, Nuria Boluda and Amy Houston.

4 University of Alicante, P.O. Box 99, E-03080 Alicante, Spain

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.

44 2.- MATERIAL AND METHODS

45 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 $\mu\text{S}/\text{cm}$ conductivity goes through another ion-
 55 exchanger resin reaching after this step a conductivity lesser than 2 $\mu\text{S}/\text{cm}$. Ethanol
 56 has been employed as an internal standard to improve quantification during sample
 57 analysis.

58 *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 |

59

60 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

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

83 To measure the temperature of the equilibrium vapour under boiling conditions, a Pt-
 84 100 sensor coupled to a Coprico thermometer (Model 3202) was employed. Its
 85 certificate of calibration (scale ITS 90 [4]) certifies a measured temperature uncertainty
 86 of 0.006 K. The pressure in the equipment was controlled to within an uncertainty of 0.1
 87 kPa at 101.3 kPa through a Fischer M101 phase equilibrium control system.

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

95

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 |

96

97 3.- RESULTS AND DISCUSSION

98 3.1. LLE determination

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

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Table 3: LLE Composition Results at 303.15K for the Ternary System of Water (1) + 1-Butanol (2) + 2-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 $u(P)=2\text{kPa}$. The temperature uncertainty is 0.5K.
 109 ^a was checked against Karl Fischer titration

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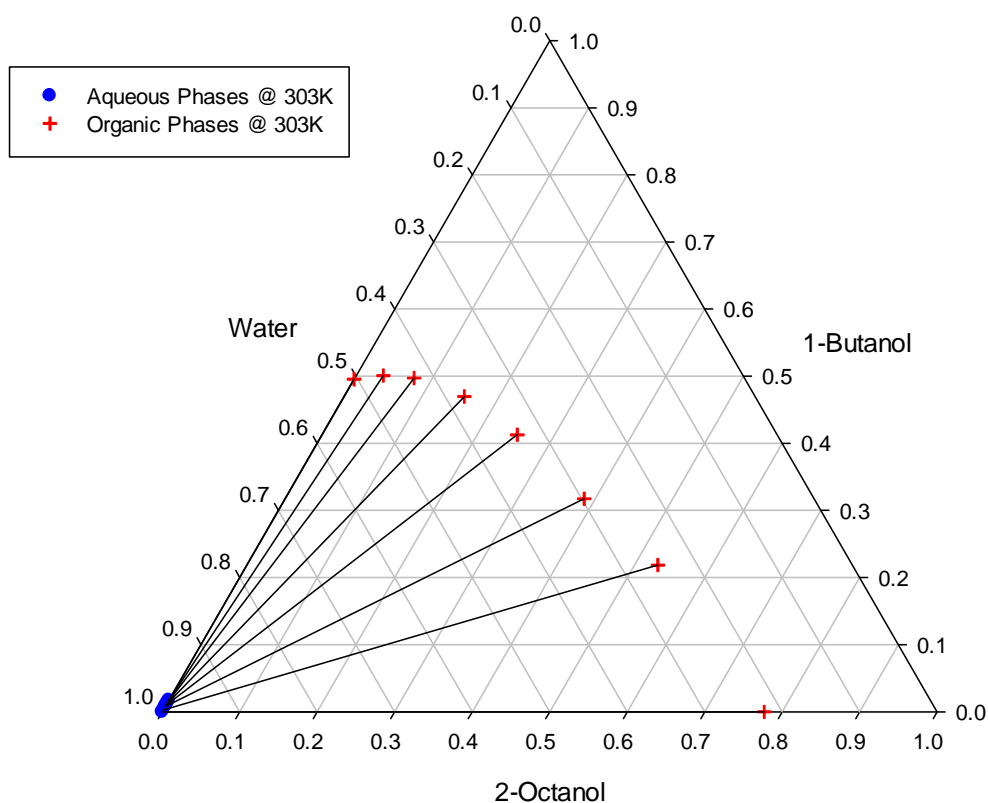
111 Table 4: LLE Composition Results at 313.15K for the Ternary System of Water (1) + 1-Butanol (2) + 2-
112 Octanol (3) in Mole Fraction at 101.3 kPa

113

| Aqueous Phase Composition | | | Organic Phase Composition | | |
|---------------------------|----------------------|----------------------|---------------------------|----------------------|----------------------|
| x_1 | x_2 | x_3 | x_1^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 $u(P)=2\text{kPa}$. The temperature uncertainty is 0.5K.
 116 ^a was checked against Karl Fischer titration

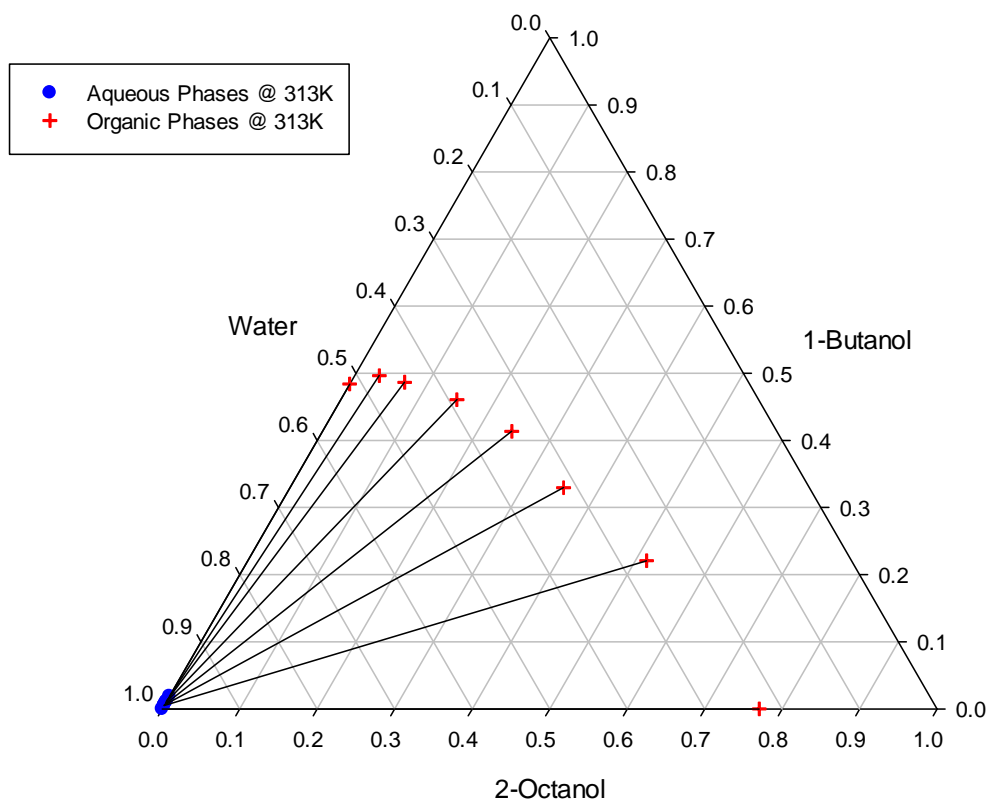
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Figure 1: LLE Results for the System of Water + 1-Butanol + 2-Octanol at 303.15K with the Organic Phases (red crosses) and Aqueous Phases (solid blue circles) joined by tie lines (black).



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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).

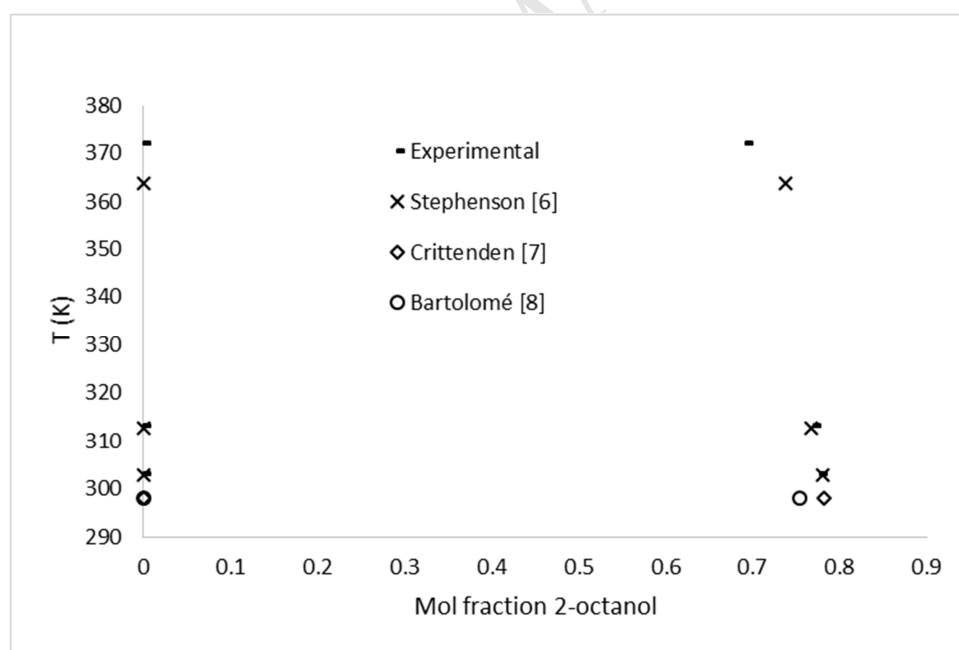
124

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).

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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.

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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

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.

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Table 5: LLE 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 $U_{ij} - U_{ji}$ & $U_{ji} - U_{ij}$ are the Binary Interaction Parameters for the UNIQUAC Model (K)

| <i>i</i> | <i>J</i> | B_{ij} | B_{ji} | α | $U_{ij} - U_{ji}$ | $U_{ji} - U_{ij}$ |
|-----------|-----------|----------|----------|----------|-------------------|-------------------|
| 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 |

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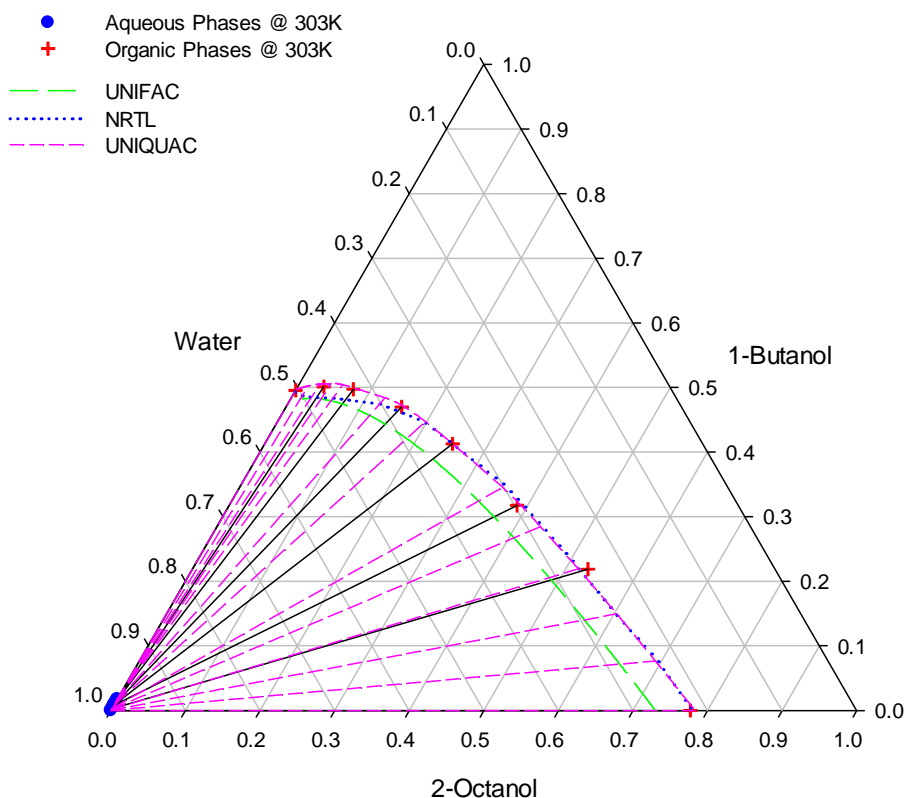
Table 6: Mean Deviations of Molar Composition from LLE Correlations for Water (1) and 1-Butanol (2) in the Organic Phase (1) and Aqueous Phase (2)

| Model | D_{x11} | D_{x12} | D_{x21} | D_{x22} |
|---------|-----------|-----------|-----------|-----------|
| NRTL | 0.0039 | 0.0042 | 0.0103 | 0.0067 |
| UNIQUAC | 0.0020 | 0.0021 | 0.0045 | 0.0021 |

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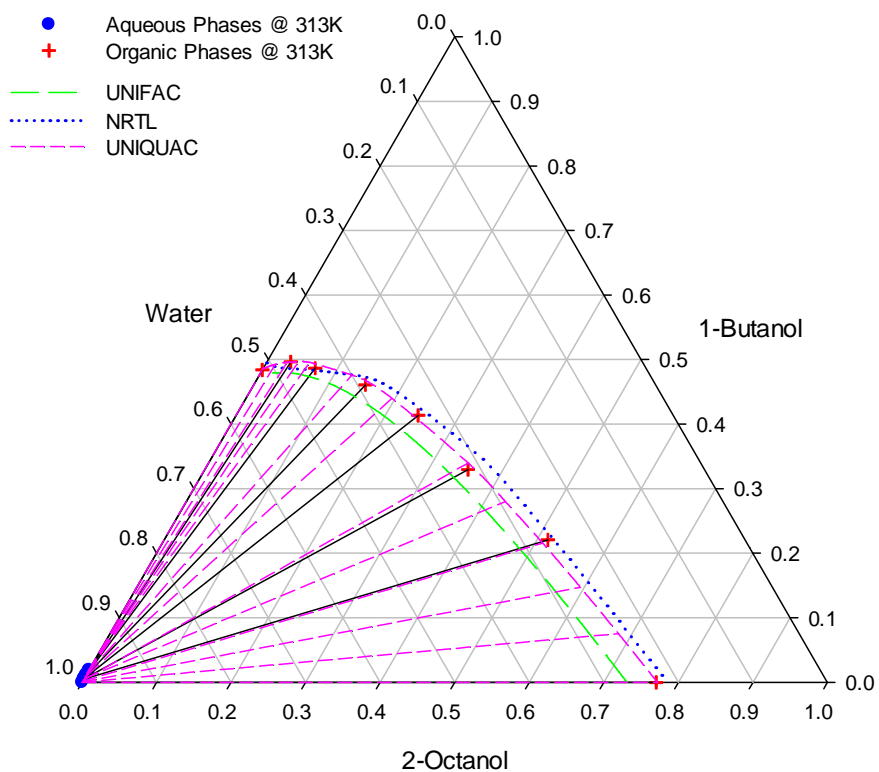
172 The UNIQUAC, NRTL and UNIFAC model predictions were similar to the experimental
 173 data for the two temperatures. UNIQUAC and NRTL produce a binodal curve that is
 174 rather closer to the experimental points than the UNIFAC prediction, which, in turn,
 175 produces a slightly smaller heterogeneous 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.

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



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

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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]

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

| Organic Phase | | | Aqueous Phase | | | Vapour | | | T (K) |
|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|-----------------------|
| x_1 | x_2 | x_3 | x_1 | x_2 | x_3 | y_1 | y_2 | y_3 | |
| 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%

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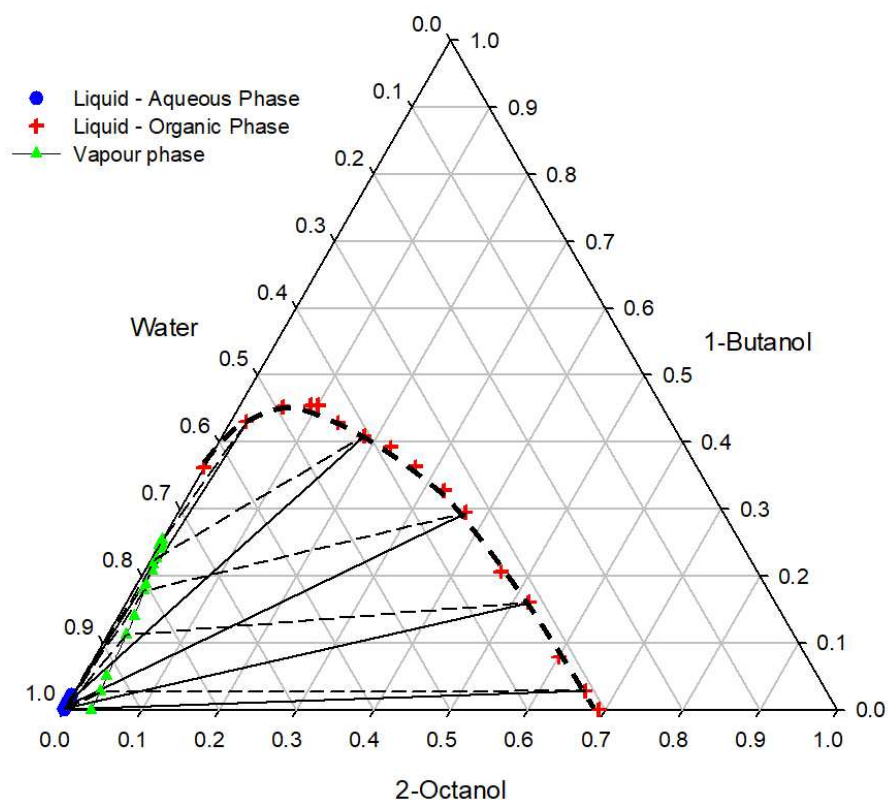
211 Table 8: VLE Data for the Water (1) + 1-Butanol (2) + 2-Octanol (3) Ternary System, giving the Liquid
212 Phase Mole Fraction x and the Vapour Phase Mole Fraction y at Temperature T and a Pressure of 101.3
213 kPa

| | Liquid Phase | | | Vapour Phase | | | T (K) |
|---|--------------|--------|--------|--------------|--------|--------|--------|
| | x_1 | x_2 | x_3 | y_1 | y_2 | y_3 | |
| 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%

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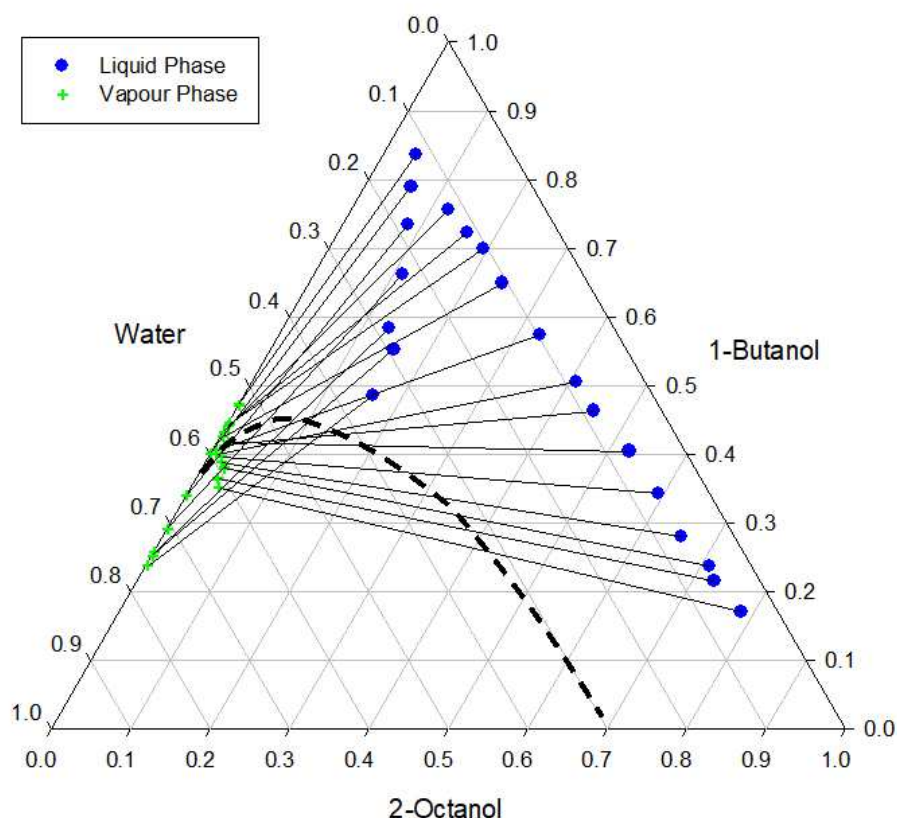
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218 Figure 6: VLE Ternary Diagram for the Water + 1-Butanol + 2-Octanol System at 101.3 kPa showing the
 219 Organic Phase Liquids (red markers), Aqueous Phase Liquids (blue markers) and Vapours (green
 220 markers) joined by tie lines (straight solid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

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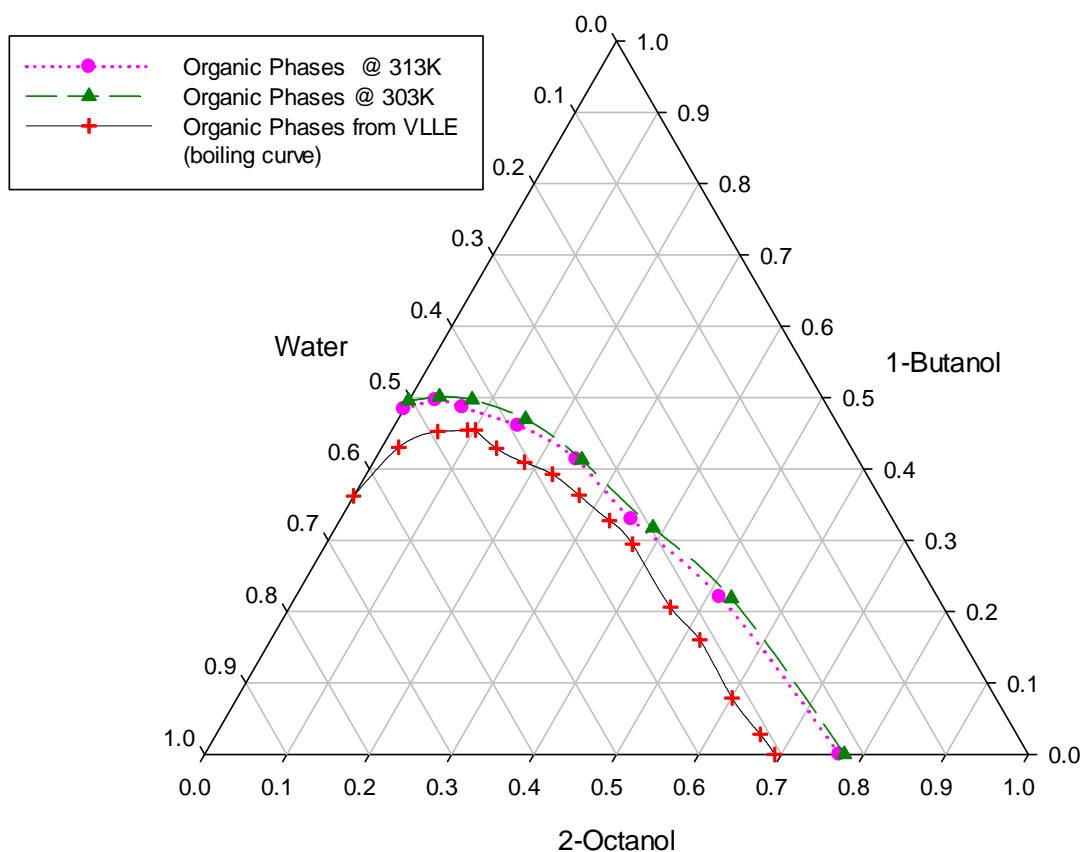


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226 Figure 7: VLE Ternary Diagram for the Water + 1-Butanol + 2-Octanol System at 101.3 kPa showing the
 227 Liquid Phases (blue markers) and Vapours (green markers) joined by tie lines (straight solid black lines)
 228 and the non-isothermal binodal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

229 From Fig. 6 one cannot conclude that the system contains a ternary azeotrope. This is
 230 because all the triangles formed by the organic phase – aqueous phase – vapour tie
 231 lines point in the same direction, and the bubble point temperatures in table 7 follow a
 232 general rising trend with octanol content. The VLLE data also reveal the presence of
 233 two heterogeneous binary azeotropes and these are given by the vapour compositions
 234 in the water + 1-butanol and water + 2-octanol binary systems. We were unable to find
 235 data on the binary azeotrope of the water+2-octanol system in the literature, and thus it
 236 is not possible to make any comparison of its composition with previous works. Figure
 237 7 shows that, for the points obtained, approximately half of the vapour phases which
 238 are in equilibrium with a homogeneous liquid, are also confined to the heterogeneous
 239 region. The vapours formed in both the VLLE and VLE determination were found to be
 240 low in 2-octanol, with this being the least volatile compound in the system.

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



245

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

249

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

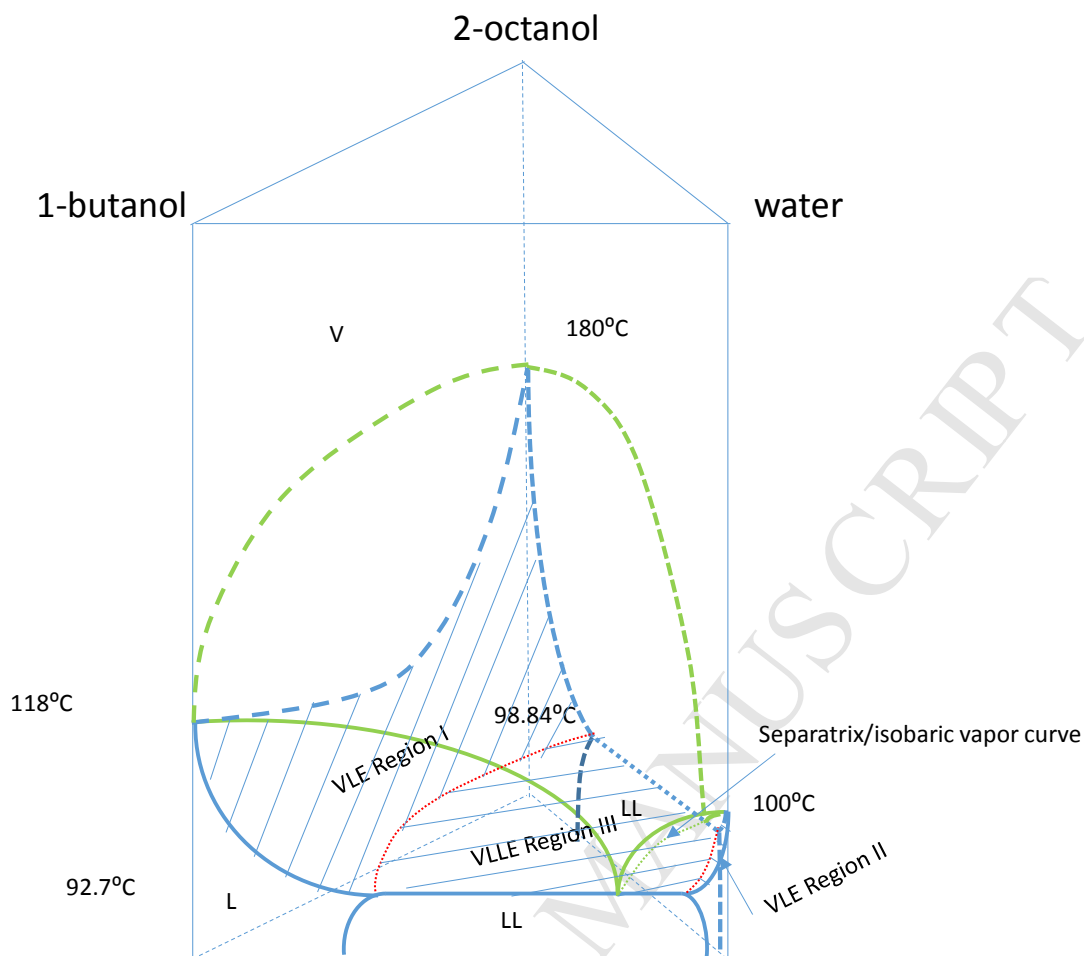


Figure 9: Schematic 3D bubble point surface for water + 1-butanol + 2-octanol at 101.3 kPa.

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 $U_{ij} - U_{ji}$ & $U_{ji} - U_{ii}$ are the Binary Interaction Parameters for the UNIQUAC Model (K)

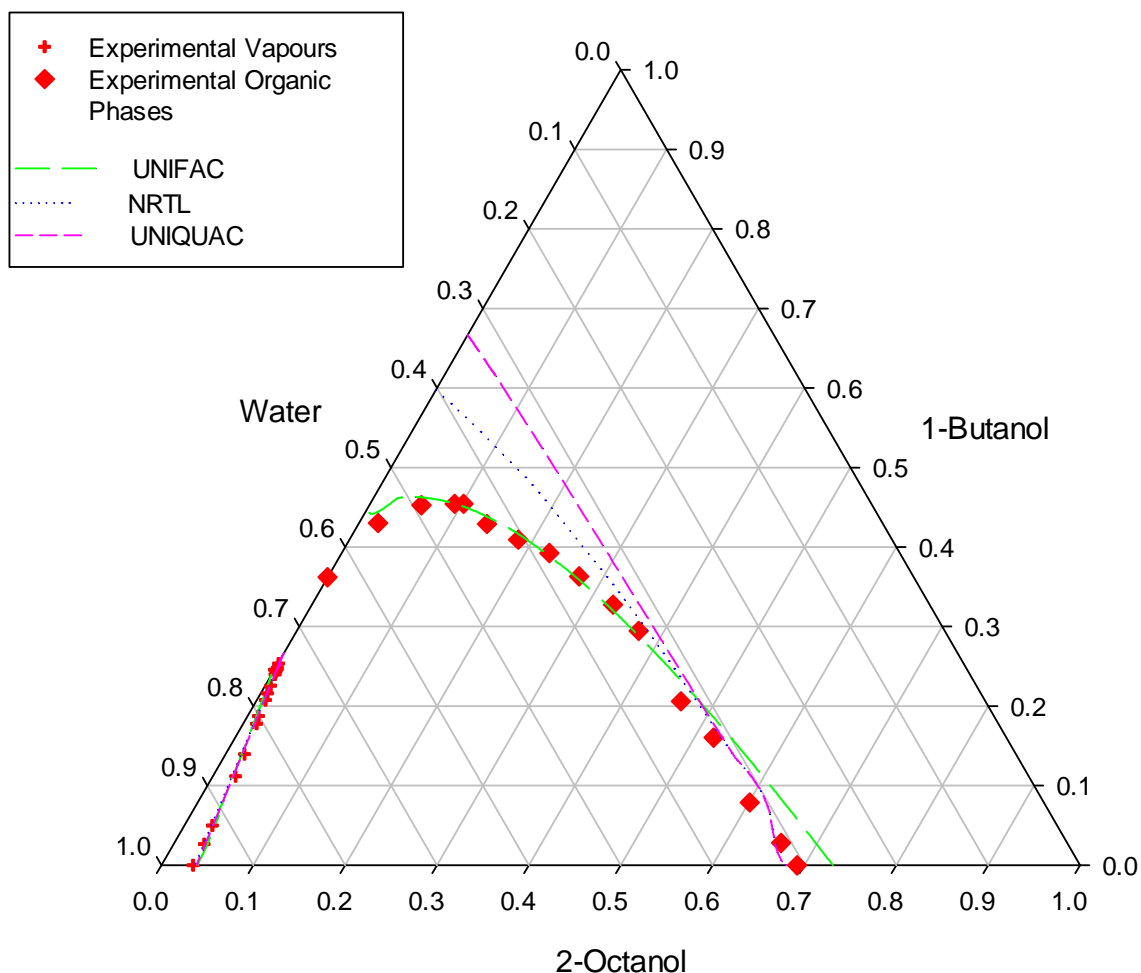
| i | j | B_{ij} | B_{ji} | α | $U_{ij} - U_{ji}$ | $U_{ji} - U_{ii}$ |
|-----------|-----------|----------|----------|----------|-------------------|-------------------|
| Water | 1-Butanol | 1427.54 | 244.97 | 0.36 | 255.79 | 138.09 |
| Water | 2-Octanol | 2278.68 | -303.72 | 0.17 | 22.30 | 420.91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

283
284
285

Table 10: Mean Deviations from VLE and VLLE Correlations of Molar Composition in the Vapour Phase y 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

302 4.- CONCLUSIONS

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

309 The VLLE and VLE data also revealed the presence of two heterogeneous binary
310 azeotropes in a system with two partially miscible pairs: water + 1-butanol and water +
311 2-octanol. The mole fraction composition of the latter azeotrope was 0.965 and 0.035 in
312 water and 2-octanol, respectively.

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

319

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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.