Liquid-liquid, vapor-liquid and vapor-liquid-liquid equilibrium data for the water-n-butanol-cyclohexane system at atmospheric pressure: experimental determination and correlation

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The temperature and the composition of the vapor-liquid-liquid equilibrium (VLLE), and the vapor-liquid equilibrium (VLE) of a ternary mixture of water – n-butanol – cyclohexane were measured at atmospheric pressure (101.32 kPa) in a modified dynamic recirculating still. As found in the literature, the experimental data obtained reveal a ternary azeotrope at 341.86 K with a mole-fraction composition of 0.281, 0.034 and 0.685 water, n-butanol and cyclohexane, respectively. The liquid-liquid equilibrium (LLE) compositions were measured at a constant temperature of 313.15 K and compared with data in the literature collected at other temperatures. Thermodynamic consistency of all the experimental data was demonstrated. The universal

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quasichemical (UNIQUAC) and the non-random two-liquid (NRTL) thermodynamic models were used to correlate the VLE and LLE data while the original universal functional (UNIFAC) model was used to compare the predicted data.

Keywords: Water, n-Butanol, Cyclohexane, Liquid-Liquid Equilibrium, Vapor-Liquid-Liquid Equilibrium, Experimental data.

INTRODUCTION

For 20 years, but especially since the advent of the Kyoto protocol (1997), the governments of many nations have been taking measures to reduce their greenhouse gas (GHG) emissions. These polluting emissions result from mankind's consumption of fossil fuels (such as coal or petrol) for a variety of purposes. In fact, the transport sector is widely acknowledged to be a major contributor to global warming: it accounts for around a third of all final energy consumption in the European Environment Agency member countries, and for more than a fifth of greenhouse gas emissions[1]. As a result, if countries desire to reduce their GHG emissions to meet the new regulations, substituting some of the fossil fuel burned in this sector with biofuels seems to be a viable option. In addition, the use of biofuels seems to be an alternative option to deal with the decrease in reservations of fossil fuels. Biomass can be exploited in fermentation to obtain alcohols such ethanol and butanol from this renewable source of hydrocarbons. These products have had a number of uses (medicine, chemistry) in the past; but, nowadays, they are also viewed as fuel substitutes or as additives to increase the octane number of nafta mixtures. There are further benefits to using these substances including, but not limited to, a reduced dependence

on other regions for fuel, improved preservation of nature and better agricultural practices. A sign of the rise in importance of biofuels is that Europe allocated 44% of its investment in energy to renewable energies and 14% to biofuels in the period 2007-2011[2].

In 2003 companies such as BP and DuPont announced their intention of combining forces to promote the use of biobutanol as an alternative to bioethanol. In 2009, BP and DuPont formed Butamax Advanced Biofuels[3] whose researchers have put the spotlight on the benefits of using this new biofuel instead of bioethanol. Among others properties, butanol contributes to approximately 86% of gasoline's energy content, whereas ethanol's contribution is only 67%. In addition, because butanol's properties more closely resemble those of gasoline, it is possible to use it as a fuel directly without having to change many of the vehicle engine's components. Moreover, as water affinity is lower in the case of butanol, the phase separation that can happen with ethanol in storage and vehicle fuel tanks is at a diminished risk of occurrence. Furthermore, since its vapor pressure is lower than ethanol's, evaporation losses are reduced and it is easier to blend. Last but not least, bioethanol plants can be adapted for biobutanol production with only a few modifications to certain stages such as fermentation or distillation.

Biobutanol produced by traditional ABE fermentation or by means of newer techniques developed during biomass studies, has the disadvantage of containing undesirable impurities. It is necessary to first separate the biobutanol from the other substances (especially water) before it can be used in many of its downstream applications. Various techniques are usually employed to accomplish this, such as adsorption, distillation, liquid-liquid extraction, pervaporation and gas stripping[4].

In order to acquire better knowledge about these systems' thermodynamic behavior and to study the distillation and extraction processes, accurate experimental phase equilibrium data are

needed. Not only is it necessary to obtain liquid-liquid equilibrium (LLE) data, but also the vapor-liquid (VLE) and, especially, the vapor-liquid-liquid equilibrium (VLLE) data in order to obtain the azeotropic compositions and, above all, design industrial processes. An entrainer that is typically used in industry for the dehydration of alcohols is cyclohexane. Thus, it might be interesting to determine if cyclohexane would be a suitable entrainer in the case of butanol separation. To this end, a comprehensive experimental study on the isobaric VLLE and VLE of the water – n-butanol –cyclohexane system at atmospheric pressure is needed, if it is desired to use cyclohexane as solvent. Unfortunately such a study is not present in the literature. In fact, the only literature data available for this system are liquid-liquid equilibrium data at various temperatures[5,6,7].

The above system exhibits a totally miscible pair at atmospheric pressure, n-butanol – cyclohexane, and two partially miscible pairs, water – n-butanol and water – cyclohexane. The mutual solubility of the water – n-butanol pair is much greater than that of the water – cyclohexane pair Furthermore, two heterogeneous binary azeotropes are present (water – n-butanol and water – cyclohexane), one homogeneous binary azeotrope (n-butanol – cyclohexane) is present as well, and has a ternary heterogeneous azeotrope at a very low concentration of n-butanol[8].

Because of a lack of experimental data, the equilibrium data for this system -needed to design and simulate the distillation process- are calculated from predictions made by thermodynamic models such as UNIFAC, or by the UNIQUAC or NRTL models, whose model parameters are based only on binary data (LLE and VLE) correlations. Therefore, if improvements in the simulation are to be made, experimental data are needed to assess the accuracy of these predictions.

The objective pursued with this paper was, on the one hand, to complete the VLE and the VLLE experimental databases, but also that of the LLE at 313.15 K, by means of a determination of the water – n-butanol – cyclohexane system at a constant pressure of 101.3 kPa. In addition, with a view to using the experimental data in simulations of separation processes of the above mentioned compounds, the data has been correlated by means of the activity coefficient models NRTL and UNIQUAC.

EXPERIMENTAL

Chemicals. All the chemicals, purchased from Merck, were of analytical grade (w=0.998 for n-butanol and w=0.995 for cyclohexane). 2-propanol was used as the internal standard for chromatographic analysis (w=0.995). Moreover, the organic solvents were analyzed by gas chromatography, which showed that no other compounds were present other than trace water. The water content of all the chemicals, determined using the Karl Fischer titrator, was low. The results of this titration (in mass %) were 0.004, 0.05 and 0.06 for cyclohexane, n-butanol and 2-propanol, respectively. A MiliQPlus system was used to obtain the ultrapure water.

Apparatus and procedures

For LLE data

The procedure and equipment used to determine the LLE at a constant temperature of 313.15 K was described in detail in a previous work[9], where the chromatographic analysis of the mixtures was carried out under different conditions. The oven of the Shimadzu GC14B was kept at 463.15 K, the temperature of the TCD (Thermal Conductivity Detector) was 483.15 K and the helium flow rate was 40 mL min^{-1}. On the other hand, the temperature of the FID (Flame

Ionization Detector) of the Thermo Trace chromatograph (by Thermo Fischer) with DB624 column (30 m, 0.25 mm, 1.4 μm) was 523.15 K. The oven possessed a programmable temperature ramp that was started at 313.15 K and raised at 40 K min-1 up to 473.15 K. The helium flow rate was set to 1 mL min^{-1}, split ratio 50:1.

For VLLE and VLE data

The experimental apparatus is a commercial unit (Labodest model 602) designed and built in Germany by Fischer Labor und Verfahrenstechnik which has been modified by Gomis et al. [9,10], who coupled an ultrasonic homogenizer to the boiling flask to obtain good mixing of the vapor and liquid phases as well as good separation of the phases once the equilibrium has been reached. The ultrasound system employed ensures good dispersion of the partly miscible liquid phases, making the modified apparatus perfectly suited for the determination of VLLE data.

Sampling was carried out by different methods depending on the phase being deal with:

(a) The gaseous phase was sampled using a UW Type, 6-port valve from Valco Instruments Co., which injected the samples automatically into the Shimadzu GC14B to avoid the problem of having to sample from the mixture of two liquid phases that formed once the vapor condensed. To obtain quantitative results, an external standard method was used.

(b) Liquid samples representative of the homogeneous region were extracted using a syringe from the liquid leaving the separator chamber and put into a vial together with the internal standard.

(c) In the case of the liquid phase in the heterogeneous region, a small amount of the liquid coming from the separation chamber of the instrument (to separate gas and liquid phases) was diverted into a tube using a solenoid valve. Once inside the tube, the dispersed liquid phases

separated into two layers at their bubble point since the tube had been placed in a thermostatic bath at the boiling point temperature of the mixture. The tubes were kept in the bath long enough to ensure that liquid-liquid equilibrium was reached. A sample of each layer was taken and placed in a vial along with a small amount of an internal standard.

A detailed description of the apparatus used to determine the VLLE and VLE data was given in previous papers[9,10]. The analytical conditions were the same as in the LLE determination.

For mole fractions above 0.01, the relative standard uncertainty u_r (uncertainty/measurand) in mole-fraction measurements was 0.02. Organic compounds in the aqueous phase and water in the organic phase with mole fractions below 0.01 were accompanied by relative uncertainties that reached up to 0.2: for a mole fraction of 0.0001 of cyclohexane, the smallest mole fraction measured.

RESULTS AND CORRELATION

In order to observe the influence of temperature on the ternary liquid-liquid equilibrium, experimental data have been obtained at 313.15 K. These data are shown in Table 1. For purposes of comparison with literature data, Figure 1 shows how these experimental results compare with the union curves of the experimental data obtained by Letcher et al.[5] and Plackov and Stern[6] (compiled by Skrzecz[11]), who determined the LLE data for the system under consideration at 298.15 K. In addition, the LLE data obtained at a constant temperature of 308.15 K by Hu et al.[7] are plotted in this figure. As it would be expected, it can be asserted that the LLE is not very dependent on temperature in this range since there are no significant differences between the experimental data presented in this paper and those obtained by the other researchers.

These experimental LLE data obtained at 313.15 K were correlated using the UNIQUAC and NRTL thermodynamic models. The non-randomness parameter α was fixed at a value of 0.2 for the NRTL model correlations. The process simulator CHEMCAD 6[12] was used to perform all the calculations and correlations, and the regression parameters sets obtained as well as the deviations are collected in Table 2. The composition mean deviations are the mean of the differences between the experimental composition of one component in one phase and the calculated data. The calculated data use the experimental composition of one phase to calculate the other one. The temperature mean deviation is the mean of the differences between the experimental boiling temperature and the calculated ones. Furthermore, plotted together in Figure 2 are the experimental binodal curve, those calculated using NRTL and UNIQUAC with the binary interaction parameters obtained from the correlation, and the curve predicted by UNIFAC LLE (with parameters from the CHEMCAD database). As can be seen, the calculated values agree well with the experimental data, so these thermodynamic models give a reliable prediction of LLE for this system at 313.15 K.

Table 3 and Table 4 collect, respectively, the experimental VLLE data of the ternary system studied and the VLE data corresponding to the homogeneous region. They contain the compositions (mole fraction) of the liquid phases (x_i) and the vapor phase (y_i) as well as their bubble point temperatures (T in K). The Wisniak L-W consistency point to point test[13] was applied to test for thermodynamic consistency and did not reveal any substantial inconsistencies in the experimental VLLE and VLE ternary data. Using the Antoine parameters A_i, B_i and C_i for water, n-butanol and cyclohexane taken from the literature[14, 15,16] and given in Table 5, all the L/W ratios obtained were between 0.96 and 1.00. Figure 3 shows the VLLE data, including several tie-lines, the vapor line and the non-isothermal binodal curve at 101.3 kPa. In this

respect, Kudryavtseva et al.[17] in 1973 determined experimentally by distillation that this system exhibited a ternary azeotrope. The composition of this ternary azeotrope was x_1 =0.294, x_2 = 0.044 and x_3 = 0.662 mole fraction of water (1), n-butanol (2) and cyclohexane (3), respectively, at a temperature of 341.83 K. The experimental data collected, the temperature of the binary water – cyclohexane azeotrope and the evolution of the vapor curve temperatures as the n-butanol concentration increases, as well as the VLLE data, signal the presence of a minimum boiling point ternary azeotrope. This ternary azeotrope can be calculated by interpolation to obtain x_1 =0.282, x_2 = 0.037 and x_3 = 0.681 mole fraction of water (1), n-butanol (2) and cyclohexane (3) at 341.86 K. The azeotrope calculated by interpolation is similar to the one obtained by Kudryavtseva et al. The tie line corresponding to the above ternary azeotrope has also been calculated by experimental data interpolation and has the following composition by mole fraction: the organic phase is x_1 =0.008, x_2 = 0.045 and x_3 = 0.947 and the corresponding aqueous phase is x_1 =0.995, x_2 = 0.005 and x_3 <0.0001 of water (1), n-butanol (2) and cyclohexane (3), respectively.

Figure 4 shows the VLE data corresponding to the homogeneous region of the system studied. It is worth pointing out that within the homogeneous region almost all of the liquid mixtures that appear in Figure 4 are in equilibrium with a vapor phase that is inside the heterogeous region.

As in the case of the LLE data, to analyze the suitability of the experimental data in order to simulate industrial processes, for example, biobutanol dehydration using cyclohexane, some correlations were done with the VLE data. The data used in the correlations were taken from the literature, on the one hand, e.g. the binary VLE data for the n-butanol – cyclohexane[18], water – n-butanol[14] and water – cyclohexane[19] systems, and from the experimental VLE data shown in Tables 3 and 4, on the other. The UNIQUAC and NRTL models were chosen for this purpose

with the objective function being the sum of $(x_{calc} - x_{exp})^2$. The parameters obtained from these correlations are summarized in Table 6 and 7. The heterogeneous region is not very well reproduced with the parameters generated by the UNIQUAC model. The region calculated using this parameter set is larger than the experimental one; however, the vapor line obtained is consistent with the experimental data. A similar situation arises in the case of the NRTL model. The heterogeneous region it predicts is also larger than the experimental one; however, the predicted vapor line is quite an accurate representation of the experimental data. So both binary interaction parameter models, NRTL and UNIQUAC, predict a larger heterogeneous region than actually exists.

If the original UNIFAC model is used to predict the VLLE, it is observed that the experimental non-isothermal binodal curve is higher than the predicted one, however, a vapor line results that is well predicted. Even though the UNIFAC model does not accurately replicate the heterogeneous region of the system studied, it fits the experimental data more closely than NRTL and UNIQUAC using the parameter sets obtained here. These differences between experimental and predicted data are shown in Figure 5.

In order to determine the reliability of the VLE, Table 8 lists the temperature and composition of the heterogeneous binary azeotrope water – n-butanol, the homogeneous binary azeotrope n-butanol – cyclohexane and the ternary heterogeneous azeotrope. Data corresponding to the heterogeneous binary azeotrope water – cyclohexane were not included because only minor discrepancies were observed.

Despite the fact that the heterogeneous region is not very well predicted by any of the models used, the predicted vapor line is an accurate representation of the experimental data to within a small standard deviation.

CONCLUSIONS

The ternary system water – n-butanol – cyclohexane exhibits a liquid-liquid equilibrium that is very little influenced by temperature in the range studied. The ternary system water – n-butanol – cyclohexane exhibits two partially miscible pairs: water – cyclohexane and water – n-butanol. The correlation of the experimental data by means of the UNIQUAC and NRTL models compares favorably with the experimental data.

In addition, the VLE and VLLE data of the same system at 101.1 kPa reveal one homogeneous binary azeotrope, two heterogeneous binary azeotropes, and a ternary heterogeneous azeotrope. The ternary azeotrope calculated by interpolation of experimental data is compatible with the literature data.

Using models such as NRTL or UNIQUAC to do experimental data correlations produce results that are not satisfactory, since it is hard to obtain a unique set of parameters that reproduces properly both VLLE and VLE data. The correlations using these models generate parameters that reproduce a bigger heterogeneous area than actually exists; however, the vapor line and calculated azeotropes obtained are consistent with the experimental data.

Overall, the UNIFAC model obtains the best fit of the experimental data, despite the fact that the heterogeneous region it produces is smaller than actually exists.

In conclusion, the experimental data obtained so far highlight the necessity of coming by more experimental equilibrium data, and for a variety of other systems if an improvement in industrial separation process simulations is to be achieved.

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FIGURES

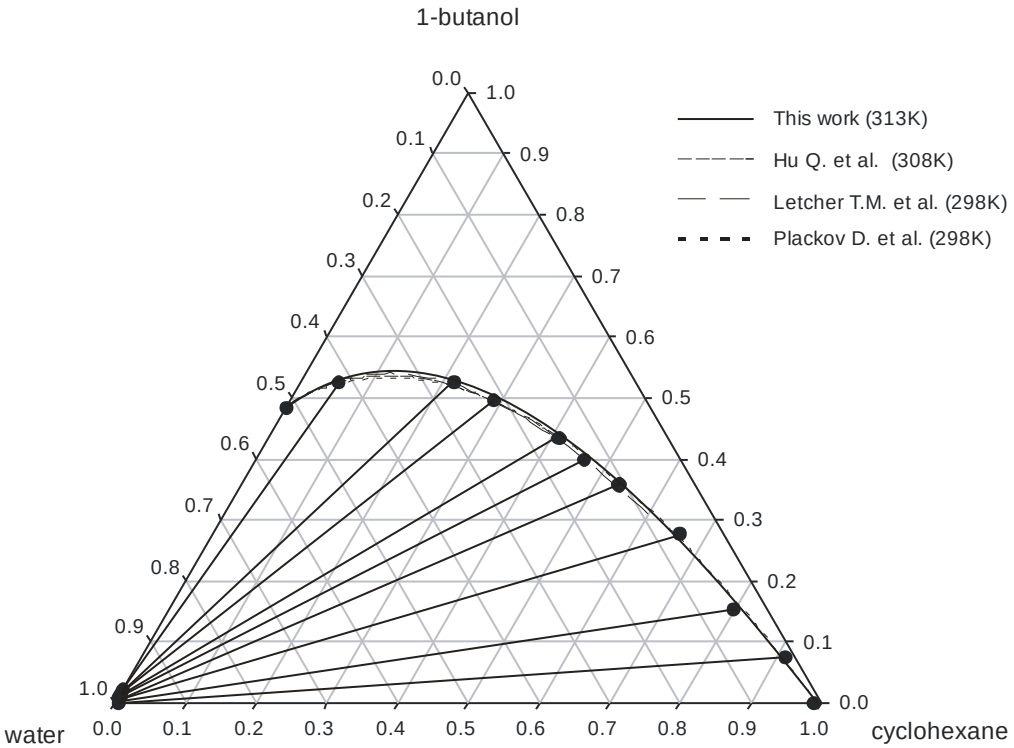


Figure 1. LLE data (mole fraction) for the water–n-butanol– cyclohexane system at 313.15 K versus those obtained by other authors at 298.15 K and 308.15 K.

● Experimental data; ——— This work experimental binodal curve at 313.15 K; – – – Letcher et al.[5] at 298.15 K; -----.Plackov and Stern[6] at 298.15 K and - - - - Hu et al.[7] at 308.15 K.

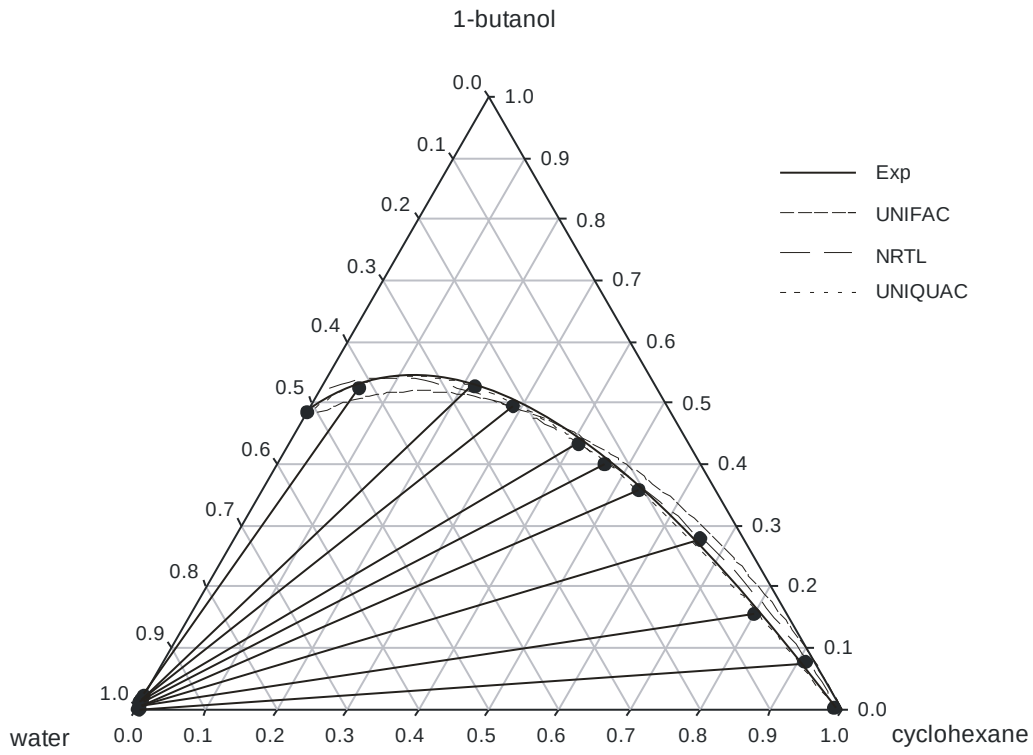


Figure 2. Comparison of the LLE data (mole fraction) for the water–n-butanol–cyclohexane ternary system at 313.15 K.

——Experimental data; ● liquid phase. Calculated data: - - - - predicted using the UNIFAC model; — — — calculated with the NRTL model (Table 2); - - - - - calculated with the UNIQUAC model (Table 2).

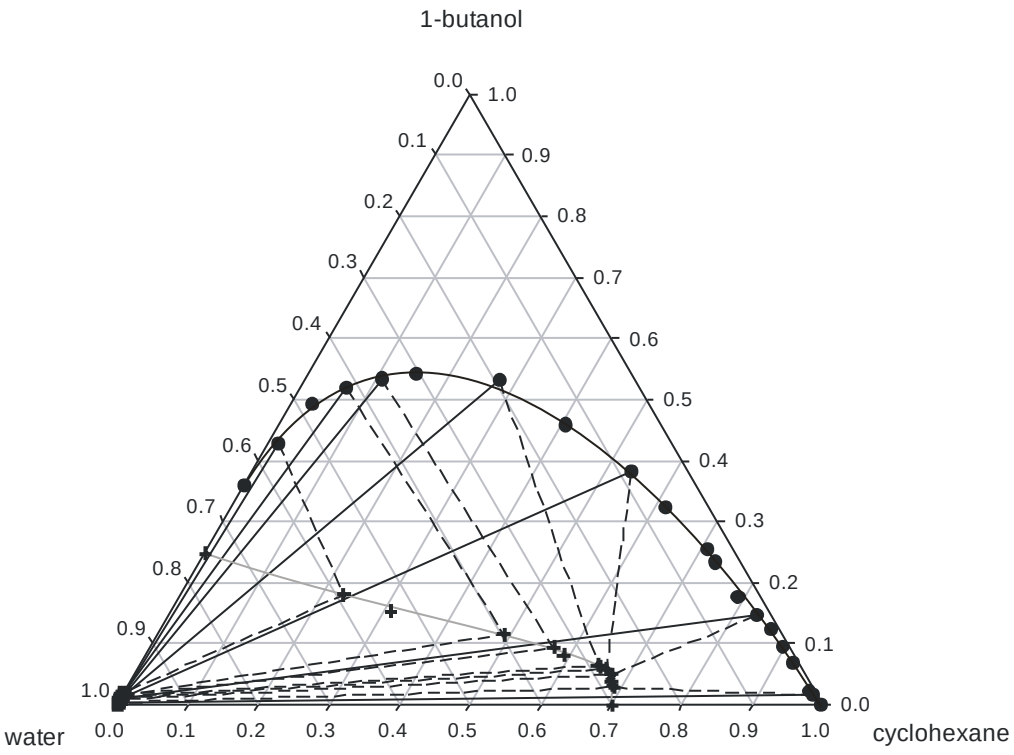


Figure 3. VLLE (mole fraction) diagram for the water–n-butanol– cyclohexane ternary system at 101.3 kPa:

● liquid phase; + vapor phase; ___non-isothermal binodal curve; ___ vapor line.

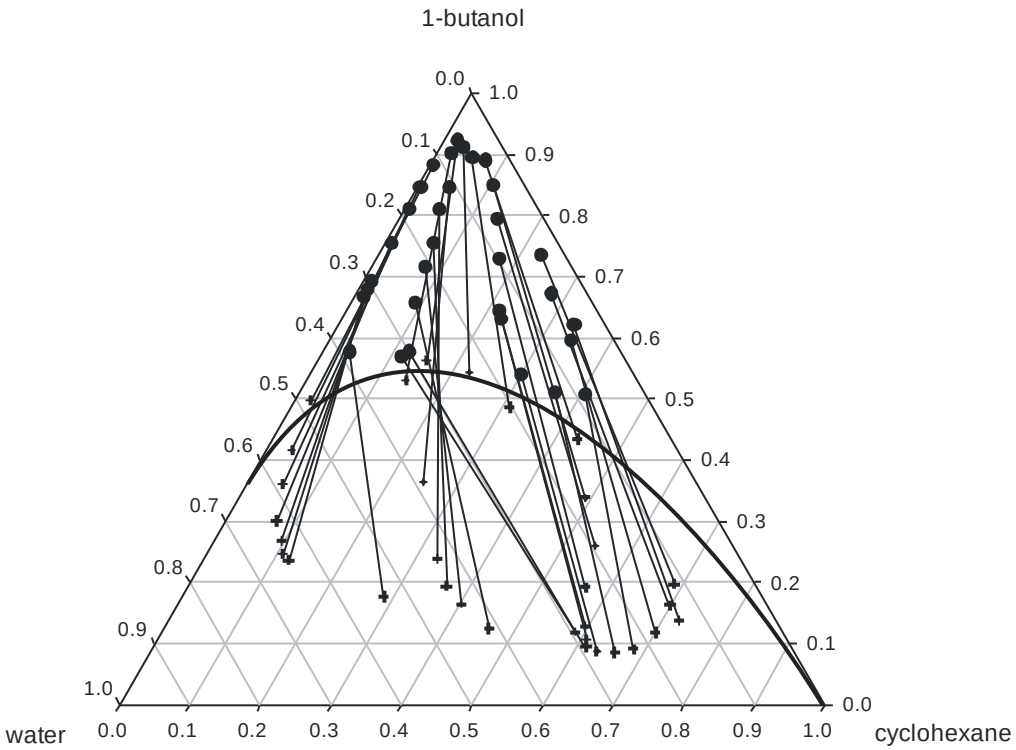


Figure 4. VLE (mole fraction) diagram for the water–n-butanol– cyclohexane ternary system at 101.3 kPa:

● liquid phase; + vapor phase; ▬ non-isothermal binodal curve.

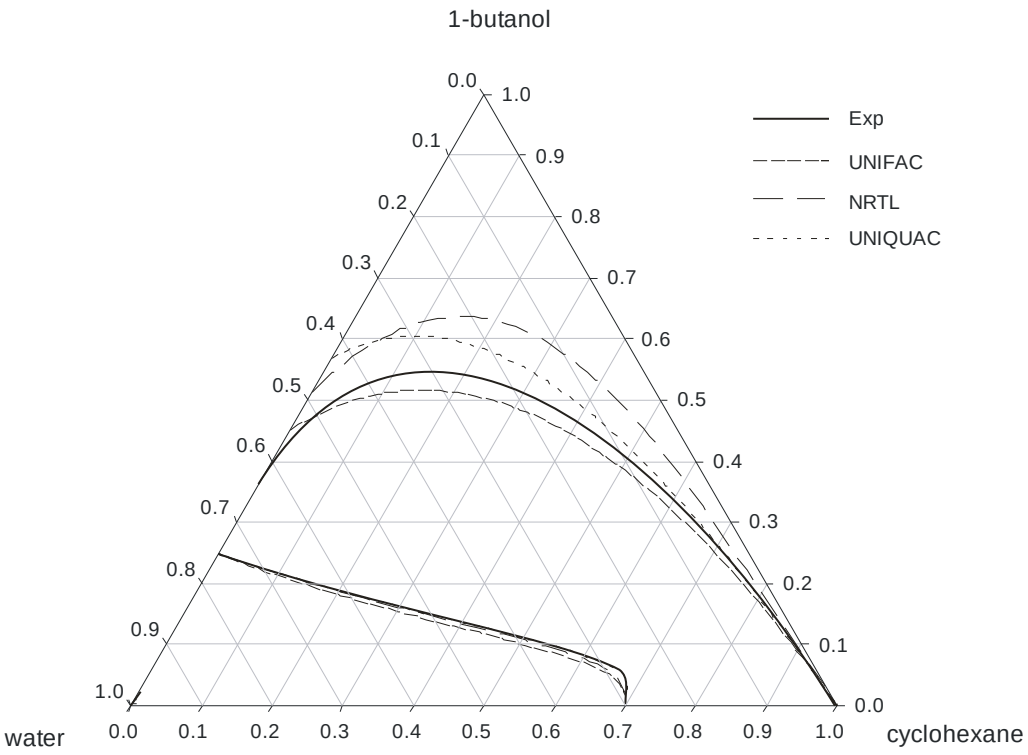
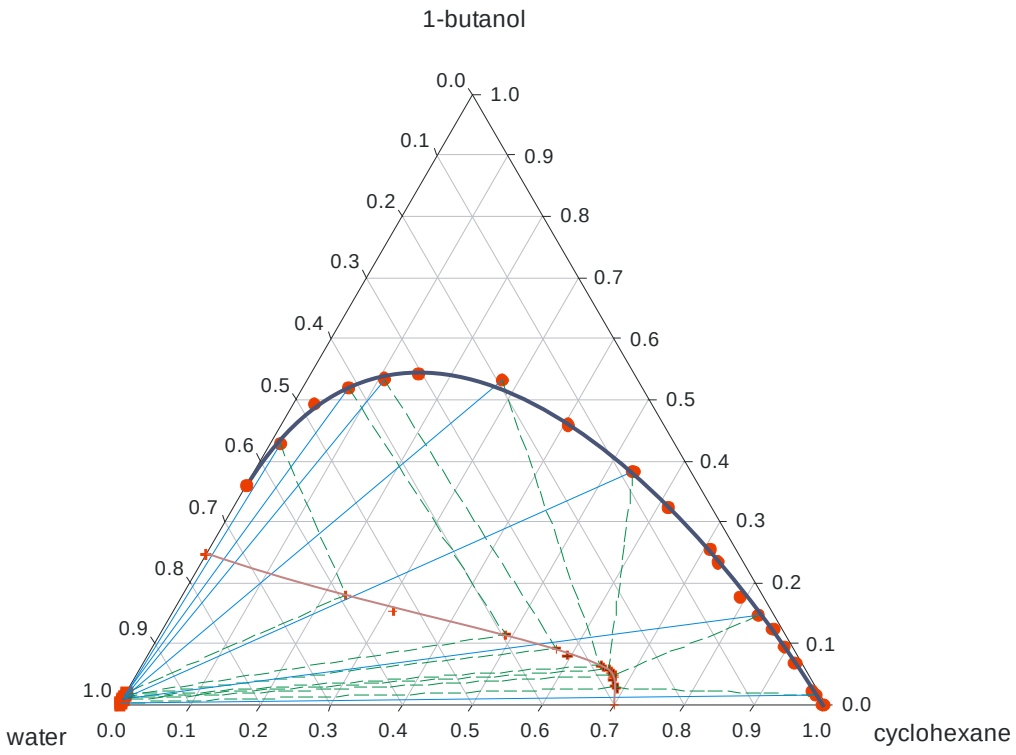


Figure 5. Comparison of the VLLE data of the water–n-butanol–cyclohexane ternary system at 101.3 kPa.

—— Experimental data. Calculated data: - - - - predicted using the UNIFAC model; — — — calculated with the NRTL model (Table 6); _ _ _ _ _ calculated with UNIQUAC (Table 7).


1-butanol
0.0
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water
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0.1
0.2
0.3
0.4
0.5
0.6
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1.0
cyclohexane

TOC

TABLES.

Table 1. Liquid-liquid equilibrium data for the water (1) – n-butanol (2) – cyclohexane (3) ternary system in mole fraction *x* at the temperature T = 313.15 K[1].

	Organic Phase			**Aqueous Phase**		
	x_1	x_2	x_3	x_1	x_2	x_3
1	0.516	0.484	--	0.981	0.019	--
2	0.421	0.524	0.054	0.982	0.018	<0.0001
3	0.257	0.525	0.218	0.984	0.016	<0.0001
4	0.218	0.495	0.288	0.985	0.015	<0.0001
5	0.155	0.433	0.412	0.986	0.014	<0.0001
6	0.136	0.399	0.465	0.989	0.011	<0.0001
7	0.108	0.357	0.534	0.989	0.011	<0.0001
8	0.063	0.277	0.660	0.989	0.011	<0.0001
9	0.048	0.154	0.798	0.990	0.010	<0.0001
10	0.014	0.075	0.910	0.990	0.010	<0.0001
11	0.010	--	0.990	1.000	--	<0.0001

[1] Standard uncertainties *u* and standard relative uncertainties u_r are u(T) = 0.1 K, $u_r(x)$ = 0.02 except $u_r(x_3)$ = 0.2 in the aqueous phase.

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

i	**j**	$\mathbf{A_{ij}}$	$\mathbf{A_{ji}}$	α	$\mathbf{U_{ij}}$-$\mathbf{U_{jj}}$	$\mathbf{U_{ji}}$-$\mathbf{U_{ii}}$
Water	**n-Butanol**	1337.69	-235.61	0.2	219.39	24.85
Water	**Cyclohexane**	1456.94	998.39	0.2	275.17	743.05
n-Butanol	**Cyclohexane**	-935.27	680.02	0.2	23.14	-119.49
Mean Deviation			$\mathbf{D\_x_{11}}$	$\mathbf{D\_x_{12}}$	$\mathbf{D\_x_{21}}$	$\mathbf{D\_ x_{22}}$
		NRTL	0.0058	0.0060	0.0106	0.0090
		UNIQUAC	0.0047	0.0048	0.0059	0.0035

Table 3. Vapor-liquid-liquid equilibrium data for the water (1) – n-butanol (2) – cyclohexane (3) ternary system, for the liquid phase mole fraction x and the vapour phase mole fraction y at temperature T_b and pressure p = 101.3 kPa[2].

	Organic Phase			**Aqueous Phase**			**Vapour Phase**			***T* /K**
	x_1	x_2	x_3	x_1	x_2	x_3	y_1	y_2	y_3	
BIN	0.638	0.362	--	0.979	0.021	--	0.754	0.246	--	365.73
1	0.558	0.428	0.014	0.979	0.021	<0.0001	0.589	0.180	0.231	358.74
2	0.479	0.492	0.030	0.982	0.018	<0.0001	0.536	0.153	0.311	357.51
3	0.415	0.520	0.065	0.984	0.016	<0.0001	0.395	0.115	0.490	351.69
4	0.359	0.534	0.108	0.985	0.015	<0.0001	0.335	0.093	0.573	346.17
5	0.306	0.542	0.153	0.987	0.013	<0.0001	0.325	0.081	0.594	346.11
6	0.193	0.531	0.276	0.987	0.013	<0.0001	0.286	0.065	0.649	343.07
7	0.136	0.459	0.406	0.989	0.011	<0.0001	0.284	0.063	0.653	343.01
8	0.081	0.382	0.537	0.989	0.011	<0.0001	0.277	0.059	0.664	342.51
9	0.061	0.323	0.616	0.990	0.010	<0.0001	0.279	0.057	0.665	342.34
10	0.036	0.254	0.710	0.990	0.010	<0.0001	0.275	0.054	0.671	342.22
11	0.036	0.234	0.731	0.990	0.010	<0.0001	0.277	0.053	0.671	342.16
12	0.032	0.178	0.791	0.991	0.009	<0.0001	0.276	0.050	0.674	342.06
13	0.021	0.147	0.832	0.991	0.009	<0.0001	0.273	0.049	0.677	341.98
14	0.012	0.124	0.864	0.991	0.009	<0.0001	0.277	0.046	0.677	341.97
15	0.010	0.096	0.894	0.992	0.008	<0.0001	0.280	0.043	0.677	341.90
16	0.009	0.068	0.923	0.993	0.007	<0.0001	0.281	0.041	0.679	341.86
17	0.008	0.022	0.970	0.995	0.005	<0.0001	0.283	0.031	0.686	341.96
18	0.006	0.016	0.978	0.996	0.004	<0.0001	0.281	0.028	0.691	341.97
BIN	0.003	--	0.997	1.000	--	<0.0001	0.299	--	0.701	342.60

All compositions were measured experimentally except the composition of cyclohexane in the vapour phase which is determined by difference.

[2] Standard uncertainties u and standard relative uncertainties u_r are u(T) = 0.006 K, u(p) = 0.1 kPa, $u_r(y)$ = 0.02 and $u_r(x)$ = 0.02 except $u_r(x_3)$ = 0.2 in the aqueous phase

Table 4. Vapor-liquid equilibrium data (mole fraction) for the water (1) – n-butanol (2) – cyclohexane (3) ternary system, for the liquid phase mole fraction x and vapour phase mole fraction y at temperature T_b and pressure p = 101.3 kPa[3].

Liquid Phase			**Vapour Phase**			***T* /K**
x_1	x_2	x_3	y_1	y_2	y_3	
0.316	0.570	0.115	0.292	0.094	0.614	348.67
0.301	0.578	0.122	0.294	0.119	0.587	350.09
0.252	0.658	0.090	0.414	0.125	0.462	353.41
0.209	0.716	0.075	0.433	0.164	0.402	358.41
0.177	0.755	0.068	0.440	0.194	0.367	361.49
0.142	0.810	0.048	0.430	0.238	0.332	365.54
0.110	0.846	0.044	0.387	0.364	0.249	373.12
0.059	0.923	0.018	0.283	0.563	0.154	379.92
0.319	0.668	0.013	0.641	0.237	0.122	364.57
0.308	0.679	0.013	0.645	0.247	0.108	365.33
0.296	0.692	0.012	0.636	0.268	0.096	366.85
0.236	0.755	0.009	0.626	0.301	0.073	368.77
0.184	0.811	0.005	0.588	0.361	0.051	372.04
0.150	0.847	0.003	0.547	0.416	0.037	374.71
0.114	0.884	0.002	0.480	0.498	0.023	377.93
0.079	0.902	0.019	0.328	0.531	0.141	377.82
0.056	0.912	0.032	0.232	0.543	0.224	377.96
0.057	0.895	0.053	0.204	0.4860	0.310	376.19
0.035	0.891	0.074	0.134	0.434	0.432	373.92
0.046	0.850	0.104	0.170	0.339	0.491	368.69
0.067	0.795	0.137	0.196	0.260	0.544	363.77
0.096	0.730	0.174	0.244	0.192	0.565	358.64

All compositions were measured experimentally except the composition of cyclohexane in the vapour phase which is determined by difference.

[3] Standard uncertainties u and standard relative uncertainties u_r are u(T) = 0.006 K, u(p) = 0.1 kPa, $u_r(y)$ = 0.02 and $u_r(x)$ = 0.02.

0.139	0.644	0.217	0.275	0.128	0.596	352.99
0.144	0.631	0.225	0.285	0.106	0.609	351.06
0.161	0.541	0.298	0.280	0.087	0.633	348.12
0.129	0.511	0.362	0.256	0.085	0.659	347.19
0.086	0.508	0.407	0.226	0.091	0.684	348.06
0.063	0.596	0.341	0.181	0.118	0.701	351.66
0.045	0.622	0.334	0.138	0.138	0.724	353.66
0.051	0.672	0.277	0.138	0.163	0.699	356.26
0.035	0.736	0.228	0.115	0.197	0.688	360.17
0.384	0.578	0.038	0.537	0.177	0.287	358.61

Table 5. Antoine equation parameters[a] of the pure substances.

Compound	A	B	C	Temperature Range /K
Water[14]	7.1961	1730.63	-39.724	+274.15 / +373.15
n-Butanol[16]	6.5460	1351.555	-93.34	+295.65 / +390.85
Cyclohexane[15]	5.9763	1206.47	-50.014	+280.15 / +354.15

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

Table 6. Parameters and mean deviations of the VLE correlation. $\mathbf{A_{ij}}$ binary interaction parameters for the NRTL model (K). Mean deviations of temperature (D_T/K), and water (D_Y_1) and n-butanol (D_Y_2) molar compositions in the vapor phase.

i	**j**	$\mathbf{A_{ij}}$	$\mathbf{A_{ji}}$	**α**
Water	**n-Butanol**	1284.51	143.71	0.3634
Water	**Cyclohexane**	3398.65	807.30	0.1353
n-Butanol	**Cyclohexane**	-105.01	1003.30	0.2936
Mean Deviation		**D_T**	$\mathbf{D\_y_1}$	$\mathbf{D\_y_2}$
NRTL		1.38	0.0266	0.0133

Table 7. Parameters and mean deviations of the VLE correlation.$\mathbf{U_{ij}}$ **-** $\mathbf{U_{jj}}$ and $\mathbf{U_{ji}}$**–**$\mathbf{U_{ii}}$ binary interaction parameters for the UNIQUAC model (K). Mean deviations of temperature (D_T/K), and water (D_y_1) and n-butanol (D_y_2) molar compositions in the vapor phase.

i	**j**	$\mathbf{U_{ij}}$**-**$\mathbf{U_{jj}}$	$\mathbf{U_{ji}}$**-**$\mathbf{U_{ii}}$
Water	**n-Butanol**	213.66	106.10
Water	**Cyclohexane**	679.00	1273.31
n-Butanol	**Cyclohexane**	-79.22	314.22
Mean Deviation	**D_T**	**D_y_1**	**D_y_2**
UNIQUAC	1.13	0.0205	0.0121

Table 8. Temperature (T/K) and composition (mole fraction) of the binary and ternary azeotropes for the system water (1) – n-butanol (2) – cyclohexane (3) at 101.3 kPa.

Heterogeneous binary azeotrope water – n-butanol				
	EXPERIMENTAL	NRTL	UNIQUAC	UNIFAC
x_1	0.750	0.752	0.749	0.760
x_2	0.250	0.248	0.251	0.240
T	365.65	365.84	365.74	366.21

Homogeneous binary azeotrope n-butanol – cyclohexane				
	EXPERIMENTAL	NRTL	UNIQUAC	UNIFAC
x_2	0.090	0.097	0.080	0.092
x_3	0.910	0.903	0.920	0.908
T	352.75	352.42	353.28	352.59

Ternary heterogeneous azeotrope				
	EXPERIMENTAL	NRTL	UNIQUAC	UNIFAC
x_1	0.294	0.292	0.297	0.291
x_2	0.044	0.052	0.028	0.045
x_3	0.662	0.656	0.675	0.664
T	341.83	342.07	342.39	342.07