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Isobaric vapor-liquid-liquid-solid equilibrium of the water + NaCl + 1-butanol system at 101.3 kPa.

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Highlights

- Vapor-liquid-liquid and vapor-liquid equilibrium data are determined
- Vapor-liquid-solid and vapor-liquid-liquid-solid equilibrium data are determined
- Results are compared with literature data
- The influence of salt on water + 1-butanol equilibria is studied
- The influence of temperature is also studied.

Keywords

Water; 1-butanol; NaCl; Isobaric; Vapor-liquid-liquid-solid; Equilibrium data;

Abstract

A mixture of water + NaCl + 1-butanol at 101.3 kPa is studied in order to determine the influence of salt on its experimental vapor-liquid-liquid-solid equilibrium. A detailed analysis of the evolution with temperature of the different equilibrium regions is carried out. The study is conducted at a constant pressure of 101.3 kPa in a recirculating still that has been modified by our research group.

The changes in the 1-butanol/water composition ratio in the vapor phase that are provoked by the salt are studied as a function of equilibrium region. In addition, the mutual solubility of 1-butanol and water is assessed in the liquid-liquid and solid-liquid regions.

1. Introduction

The phase diagrams of liquid-liquid (L–L E), vapor-liquid (V–L E) and even solid-liquid (S–L E) equilibria have been widely studied [1-4]. However, if the equilibrium in question is between a solid, a vapor and two liquid phases the situation is not as well understood. In fact, there is scant literature on this type of system. For instance, it is not even mentioned among all the phase equilibria types in the well-known book by John E. Ricci [5].

The study of the vapor-liquid-liquid-solid equilibrium (VLLSE) in systems with electrolytes is complex due to the number of phases involved. Consequently, there are no complete studies that examine the shape of the different equilibrium surfaces and regions. In addition there is a lack of reliable VLLSE data, in part due to the difficulty of finding equipments capable of separating and analyzing the different phases in equilibrium. On the other hand, due to the importance of the application of such systems, different groups are working on the development of more flexible and reliable thermodynamic models that can be used to improve industrial processes. However, experimental data are needed to check the predictions and correlations of the models.

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Regarding the water + alcohol + salt systems, the experimental data available in literature does not cover all of the regions [6-12]. In fact, it is difficult to find data of solid-liquid-liquid-vapor because the different authors tend to avoid the equilibrium determination of the liquid-liquid region.

To analyze the SLLV equilibrium diagram of these systems, as an example, consider a ternary system A+B+C in which C is a solid salt and A and B are two partly miscible liquids at a specified temperature $T_0$. We first consider, in turn, the three different binary subsystems that constitute it.

**A+B binary:** Consider figure 1a as an example of the equilibrium diagram at constant pressure for a partly miscible binary system A+B. Water+1-butanol could be an example of such a system [13-14] and it can be seen in the figure 1a. A has a boiling point ($T_{bA}$) represented by the point $e_A$, with a lower boiling temperature than that of B ($T_{bB}$) represented by $e_B$. Points a and b correspond to the solubility at $T_0$ of B in A rich phase and A in B rich phase respectively. At the temperature $T_z$ (the boiling temperature of the binary heterogeneous azeotrope represented by the point $z$) the mutual solubility of A and B have changed slightly (because of temperature changes) and now correspond to a’ and b’. The points a, a’, b, b’, z, $e_A$ and $e_B$ and the lines which join them define characteristic regions of the system: two regions consisting of one liquid (L), one region of two liquids (L-L), two regions of liquid-vapor (L-V) and one region of only vapor (V).

**Figure 1:** Equilibrium diagrams of binary systems near boiling conditions [13-14].
**Figure 1a.** Txy diagram of a partially miscible binary system at constant pressure.

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**Figure 1b.** Txy diagram of a binary system A+C at constant pressure, where A is water and C is NaCl [15-16].

**A+C Binary:** Figure 1b shows the phase equilibria at constant pressure of water + NaCl binary system [15-16] (that can be an example of an A+C pair). The point e_A again represents the boiling point of A. The point h_A corresponds to the solubility of the salt C in A at temperature T_0. When the temperature increases the solubility of the salt in A changes: the greater the salt content in A, the higher the boiling temperature. The point j_A corresponds to the boiling point of a saturated liquid mixture of C in A and its boiling point is T_j. Again, these characteristic points and the lines which join them delineate characteristic regions of the system: a single liquid (L), a solid-liquid (S-L), a liquid-vapor (L-V) and one solid-vapor (S-V) region.

**B+C Binary:** A T-composition diagram such as the one shown in figure 1b can also be drawn for the B+C pair (a mixture of salt and another liquid compound might be an example). It would have similar equilibrium regions to A+C.
Figure 2. Schematic representation of the equilibrium diagram for the ternary A+B+C in a T-x-y prism.

**A+B+C Ternary:** Figure 2 is a schematic representation of the equilibrium diagram for the A+B+C ternary in a $Txy$ prism, with each of its three faces corresponding to a binary system. Figure 3 shows several constant-temperature cross sections of the prism to illustrate the evolution of the various equilibrium regions as the temperature increases.
Figure 3 (a-f). Evolution with temperature (increasing T) of the different equilibrium regions of a system with two partially miscible compounds (A and B) and a salt (C).
Figure 3c.

Figure 3d.
At temperature $T_0$, six different regions co-exist in figure 3a: one liquid-liquid (L-L), one solid-liquid-liquid (S-L-L), two solid-liquid (S-L) and two liquid regions (L). Here the point $h_A$ corresponds to the solubility of compound C (the salt) in A at $T_0$ (same point $h_A$ as in figure 1b).
In the same way $h_b$ corresponds to the solubility of $C$ in $B$. A split occurs in the solid-liquid-liquid region at point $p$: into the solid $C$, and at the liquid phases $m$ and $n$.

When the temperature reaches $T_z$, the azeotropic boiling point of the $A+B$ system, a vapor point appears that is in equilibrium with the two binary heterogeneous liquids (see figure 3b). The point $z$ corresponds to the binary azeotrope or $A+B$ pair. When the temperature increases a little more a new vapor-liquid-liquid region and two new vapor-liquid regions appear (see figure 3c).

At higher temperatures the liquid-liquid region and the two liquid regions shrink in size, while the size of the vapor-liquid-liquid and the two vapor-liquid regions increases and the size of the liquid-liquid region decreases until it disappears (figure 3d), and a new solid-liquid-liquid-vapor ($S$–$L$–$L$–$V$) region is formed.

When the temperature increases further a new solid-vapor region appears (see figure 3e), as well as two vapor-liquid-solid regions on either side of it. With higher temperatures, the solid-vapor region grows and pushes the vapor-liquid-solid, liquid-vapor and liquid-solid regions to the sides while shrinking the liquid regions.

Finally, one of the liquid regions disappears (see figure 3f) and the point is reached at which the salt-saturated compound $A$ boils. At this point, only solid-vapor, solid-liquid, single liquid and vapor-liquid regions remain since the boiling point of compound $B$ is higher. The temperature then produces the same effect of increasing the solid-vapor region while shrinking that of the liquid until only a solid-liquid-vapor point and a solid-vapor region are left, at which point the salt-saturated compound $B$ boils. At an even higher temperature only a solid-vapor region exists.

All of these figures illustrate a qualitative behavior that assumes that the sizes of the regions remain more or less constant with temperature. Actually, the solubility of the salt in the liquids changes with temperature and the salt can induce salting-in and/or salting out effects that move the borders of the regions out to one or the other side of the diagram. It is indeed a complex and difficult-to-study phenomenon since it involves a lot of equilibrium data (solid-liquid, solid-vapor, liquid-liquid, solid-liquid-liquid, liquid-liquid-vapor and liquid-vapor). There is very limited data available on this subject in the literature and hence obtaining phase equilibrium data would permit a better understanding of the phase behavior of such systems.

The objective of this work is to study all the constant-pressure equilibrium regions of one particular system. The chosen system that exhibits all of the abovementioned regions is water + NaCl + 1-butanol. It has a partially miscible water+1-butanol pair at 298 K. Sodium chloride is one of the most common salts in seawater.

2. Experimental

2.1. Chemicals

Ultrapure water with a conductivity of less than 1 $\mu$S/cm was obtained by means of a MiliQPlus purifying system. The remaining compounds, listed in table 1, were used as supplied. The 2-propanol was used as internal standard for quantitative chromatographic analysis. The NaCl
contains less than 0.01% in total solid impurities. The water content of the liquid compounds was checked against the Karl Fischer technique.

2.2. Apparatus and procedures

To reproduce the equilibrium of this system a modified Fischer vapor-liquid determination unit was used. This is a Fischer Labodest unit (Fischer Labor und Verfahrenstechnik) coupled with an ultrasonic transducer to permit a good mass transfer between phases. The operation of this equipment was described in a previous paper [17]. It employs an ultrasonic probe to enhance the mixing and dispersion of the phases. A mixture of water, 1-butanol and NaCl is placed inside the boiling flask where it is heated to the boiling point at a pressure of 101.3 kPa, which, in turn, is maintained by a Fisher M101 phase equilibrium control system. The temperature is measured using a Pt100 sensor coupled to a digital thermometer (model 3002) with a standard uncertainty of 0.06 K according to its certificate of calibration (scale ITS 90) [18]. The boiling mixture leaving the Cottrell pump is split into a vapor, on the one hand, and the liquids and solid, on the other, in the separation chamber. Some of the vapor is pumped out of the apparatus by means of a peristaltic pump and towards a six-port valve, which is used to inject the vapor into a chromatograph for analysis by a Thermal Conductivity Detector (TCD). The rest of the vapor is returned to the mixing chamber after condensation. The liquid and solid phases return to the mixing chamber through a tube from which a sample is siphoned off by means of a solenoid valve. This sample is put inside a glass tube and sealed with a septum cap.

The glass tube containing the sample is submerged inside a thermostatic bath at a constant temperature at the boiling point of the mixture. Depending on the composition region, different phases are present in the liquid sample. In the case of the single liquid - single solid region the liquid phase which is rich in 1-butanol is decanted, extracted from the tube and introduced into a vial with a known amount of 2-propanol. The 2-propanol is used as an internal standard and also prevents the sample from splitting into two phases when its temperature decreases from the bath temperature to that of the surroundings. The sample in the vial is then analyzed by gas chromatography to determine the water and 1-butanol content of the liquid phase. Another aliquot of the sample is taken from the tube to check its water content against the Karl Fisher Technique (Metrohm 737 KF Coulometer). Finally, yet another aliquot of the liquid phase is collected and put inside a tube together with a known amount of water and several droplets of HNO₃ solution. This sample is analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) to determine its Na content.

In the case of two liquid phases in equilibrium with each other (the liquid-liquid region), the upper layer in the tube in the thermostatic bath is the organic phase, which is analyzed by the same procedure outlined above. To analyze the aqueous phase, a sample of it is taken and put in a vial that is also analyzed by chromatography with a TCD. In this case, 2-propanol is not added since it now promotes phase splitting. Another known amount of the aqueous phase is collected and put inside an open cap tube. This tube is heated in an oven at 368.15K in order to drive off the water and butanol from the sample until it reaches a constant weight corresponding to the NaCl content of the sample.
When it comes to determining the vapor-liquid-liquid-solid equilibrium, a similar procedure is followed to that in the case of the two liquid phases. One has to ensure that during the sampling from the sampling valve both solid and liquid phases are collected. The solenoid valve is opened enabling a sample from the returning solid and liquid phases to the mixing chamber to be collected in a tube with septum sealing. However, when sampling the equilibrium liquid phases from the thermostatic bath, it has to be ensured that no solid at all is transferred to the vials when collecting liquid phase samples. This was accomplished by using cellulose acetate filters in the sampling syringe.

A Shimadzu GC14B gas chromatograph with a 2 m x 3 mm 80/100 Porapack Q packed column is employed for the analysis in this case. When the liquid samples are analyzed glass wool is put inside the glass insert to avoid NaCl from entering the column. Helium is used as carrier gas at a flow rate of 50 mL/min. The temperature of the oven is set to 493.15 K while the injector and the detector are set to 513.15 K. A 100 mA current is used. The ICP-OES is a Perkin Elmer, Model: 7300 DV (with dual vision).

Several standards containing different amounts of NaCl are prepared for the analysis with the ICP technique, but which contain the same proportion of water/butanol as the sample in order to avoid changes in the ICP signal due to changes in the medium of analysis.

The uncertainties were obtained from statistical calculation of repeated measurements. The temperature standard uncertainty (u) is 0.06 K, and the composition relative uncertainty (\(u_c = \frac{u}{w}\)) is 2% for all components except for the NaCl in the organic phase where the relative uncertainty is 5%. The bigger relative uncertainty for the NaCl composition is due to the fact that the measurement is near the detection limit.

3. Results

The equilibrium data and the boiling temperature of different samples from the three-phase region (V–S–1 L\(_{\text{org}}\)) are presented in table 2. Each of the rows in the table corresponds to the triangle Cmn of the three-phase region in figure 3f, with the vertices m and n representing the liquid and vapor phases that are in equilibrium with each other. The positions of these vertices change as the temperature increases as is shown in the other panels in figure 3. Accordingly, table 2 shows, at different temperatures, the phase compositions at the triangle vertices of the solid-organic liquid-vapor region.

The experimental data of the three-phase region (V–L\(_{\text{ac}}\)–L\(_{\text{org}}\)) are shown in table 3. The composition and boiling temperature of the binary azeotrope water + 1-butanol agree well with literature data [13-18]. Referring to the figures 3c and 3d, each line corresponds to the triangle V-L\(_{1}\)-L\(_{2}\), whose vertices represent the compositions of the equilibrium phases at a given temperature. Therefore, shown in table 3 are phase compositions corresponding to vapor-liquid-liquid region triangles at different boiling temperatures.

The four phase region (S–L\(_{\text{org}}\)–L\(_{\text{ac}}\)–V) equilibrium data are recorded in table 4 and correspond to the quadrilateral CL\(_{1}\)L\(_{2}\)V in figure 3e that exists only at a single temperature.

Finally, table 5 records several data points of the vapor-liquid equilibrium when the liquid is homogeneous. One of the points corresponds to the aqueous side of the diagram while the
others correspond to the butanol rich homogeneous liquid. The data in tables 2, 3 and 4 have been represented graphically in figure 4. As can be seen, the solubility of NaCl is low in the organic phases, with all of the points occurring near the water + 1-butanol edge. Conversely, it exhibits a much greater solubility in the aqueous phases, being located farther away from the water + 1-butanol edge. As shown in table 4, the maximum salt mass fraction that the organic phase can reach is 0.0036, while in the aqueous phase it can go up to a higher value, 0.2700.

**Figure 4.** a) Liquid-liquid-vapor, solid-liquid-vapor and solid-liquid-liquid-vapor equilibria for the water + NaCl + 1-butanol system at 101.3 kPa. b) Enlarged region (curved line separates regions)
On the other hand, the presence of salt decreases the solubility of water in butanol as well as that of butanol in water. This behavior can be appreciated in figure 4. As the salt concentration increases, the aqueous phases approach the water + salt edge, while the organic phases move towards the butanol + salt edge. Based on the data shown in the tables, the solubility of water in butanol decreases from the value of 0.2997, corresponding to the boiling-point mass fraction of water in the liquid organic phase when there is no salt present, down to the value of 0.0927 shown in table 4, corresponding to the mass fraction of water in the organic phase when the V–L–L–S equilibrium is in effect.

Figure 5. Liquid-liquid equilibrium for water + NaCl + 1-butanol system at 298.15 K [19] and at the boiling temperature, both at atmospheric pressure (Aqueous region side).

In order to analyze the influence of temperature on the L–L E, the data obtained in this work at the boiling temperature are plotted in the same figure as those from a previous work obtained at a constant temperature of 298.15 K [20] Other references [21-23] were used for comparison but have not been included in the figures for the sake of clarity. The comparison between LLE experimental data and all the literature data cited has been included as supporting information. Figure 5 shows the data for the aqueous phases, and figure 6 for the organic phases. As can be seen in figure 5, in both cases very similar data are obtained. The temperature has little influence on this part of the liquid-liquid region. The maximum NaCl concentration increases from 0.261 to 0.270 when the temperature increases from 298.15 K to 369.15 K. It can also be seen that an increase of the temperature slightly decreases the solubility of butanol in water. This behavior is consistent with the fact that the aqueous phase samples taken from the thermostatic bath did not split into two phases when the temperature descended.
Figure 6. L-L E and L-S E curves in NaCl for a water + 1-butanol mixture at 298.15 K [19] and at the boiling temperature at atmospheric pressure (Organic region side).

In figure 6, the organic-phase data corresponding to the solid-liquid equilibrium have also been plotted. Focusing on the behavior of the organic phases corresponding to the liquid-liquid equilibrium, it is observed that at the boiling point the organic phases occur closer to the salt composition axis than those corresponding to the temperature of 298.15 K. This indicates that an increase in the temperature substantially increases the solubility of water in the butanol. This behavior is consistent with a need to add 2-propanol to avoid organic phase splitting after a sample has been collected from the thermostatic bath. On the other hand, it is also observed that the maximum salt mass fraction that can be reached in the organic phase is higher at the boiling temperature. In fact, the maximum NaCl weight fraction at 298K corresponding to the S–L–L region is 0.0019, and at the boiling temperature it is 0.0036, nearly double the salt presence in the organic phase. Regarding the organic phases corresponding to the solid-liquid equilibrium, it is observed that the temperature has very little influence on them.

4. Conclusions

Vapor-liquid-liquid-solid equilibrium data has been determined for water + NaCl + 1-butanol at a constant pressure of 101.3 kPa. Additionally, a study has been carried out of the different equilibrium regions that appeared as the temperature was varied. With an increase in temperature, the L–L E region shrinks and other regions with vapor (V–L, V–S, V–L–L, S–L–V and S–L–L–V) appear.

The presence of NaCl changes the 1-butanol/water composition ratio in the vapor in different ways depending on the equilibrium region considered. In the case of the liquid-liquid regions, the water rich region is not very sensitive to temperature changes. By contrast, the organic rich region is rather temperature sensitive and an increase in temperature substantially increases the solubility of water in butanol.
The salt changes the shape of the equilibrium surfaces, which allows changing from one distillation region to another when obtaining pure components is the intention.

Acknowledgment
The authors thank the DGICYT of Spain for the financial support of project CTQ2009-13770 and CTQ2014-59496.

References


Tables

Table 1. Specifications of chemical compounds.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Provider</th>
<th>Initial purity (mass %)</th>
<th>Water content (ppm)</th>
<th>Purification method</th>
<th>Analysis method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Butanol</td>
<td>Merck</td>
<td>&gt; 99.8</td>
<td>650</td>
<td>none</td>
<td>GC a</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>Merck</td>
<td>&gt; 99.5</td>
<td>450</td>
<td>none</td>
<td>GC a</td>
</tr>
<tr>
<td>NaCl</td>
<td>VWR</td>
<td>&gt; 99.99</td>
<td>--</td>
<td>none</td>
<td>--</td>
</tr>
</tbody>
</table>

* GC = Gas chromatography

Table 2. Equilibrium data (weight fraction) corresponding to the three phase region (1S - 1L_{org} - 1 V) of the water + NaCl + 1-butanol system at 101.3 kPa. Solid composition is pure NaCl.

<table>
<thead>
<tr>
<th>T/K</th>
<th>Liquid</th>
<th>Vapor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water1</td>
<td>NaCl2</td>
</tr>
<tr>
<td>376.42</td>
<td>0.0311</td>
<td>0.0003</td>
</tr>
<tr>
<td>374.65</td>
<td>0.0413</td>
<td>0.0004</td>
</tr>
<tr>
<td>373.81</td>
<td>0.0474</td>
<td>0.0007</td>
</tr>
<tr>
<td>372.69</td>
<td>0.0503</td>
<td>0.0007</td>
</tr>
<tr>
<td>372.25</td>
<td>0.0495</td>
<td>0.0008</td>
</tr>
<tr>
<td>371.15</td>
<td>0.0600</td>
<td>0.0012</td>
</tr>
</tbody>
</table>

T is in K with a standard uncertainty of 0.06 K, pressure standard uncertainty is 0.1 kPa and composition relative uncertainty is \( u_r = \frac{u}{w} \) is 2% except for the NaCl in the organic phase where the relative uncertainty is 5%.

1 obtained by GC-TCD
2 obtained by ICP-OES
3 checked against Karl Fischer Technique
Table 3. Equilibrium data (weight fraction) corresponding to the three phase region (1 L$_{aq}$ - 1L$_{org}$ - 1 V) of the water + NaCl + 1-butanol system at 101.3 kPa.

<table>
<thead>
<tr>
<th>T/K</th>
<th>Water$^1$</th>
<th>NaCl$^2$</th>
<th>1-Butanol$^3$</th>
<th>Water$^{1,4}$</th>
<th>NaCl$^3$</th>
<th>1-Butanol$^4$</th>
<th>Water$^1$</th>
<th>1-Butanol$^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>365.72</td>
<td>0.9188</td>
<td>0.0000</td>
<td>0.0812</td>
<td>0.2997</td>
<td>0.0000</td>
<td>0.7003</td>
<td>0.4161</td>
<td>0.5839</td>
</tr>
<tr>
<td>365.75</td>
<td>0.9230</td>
<td>0.0222</td>
<td>0.0549</td>
<td>0.2220</td>
<td>0.0006</td>
<td>0.7774</td>
<td>0.4116</td>
<td>0.5884</td>
</tr>
<tr>
<td>365.78</td>
<td>0.9099</td>
<td>0.0441</td>
<td>0.0461</td>
<td>0.1976</td>
<td>0.0011</td>
<td>0.8013</td>
<td>0.4143</td>
<td>0.5857</td>
</tr>
<tr>
<td>366.02</td>
<td>0.9011</td>
<td>0.0633</td>
<td>0.0356</td>
<td>0.1838</td>
<td>0.0011</td>
<td>0.8154</td>
<td>0.4092</td>
<td>0.5908</td>
</tr>
<tr>
<td>366.24</td>
<td>0.8812</td>
<td>0.0906</td>
<td>0.0283</td>
<td>0.1655</td>
<td>0.0019</td>
<td>0.8327</td>
<td>0.4123</td>
<td>0.5877</td>
</tr>
<tr>
<td>366.41</td>
<td>0.8633</td>
<td>0.1127</td>
<td>0.0241</td>
<td>0.1582</td>
<td>0.0019</td>
<td>0.8399</td>
<td>0.4072</td>
<td>0.5928</td>
</tr>
<tr>
<td>366.49</td>
<td>0.7965</td>
<td>0.1906</td>
<td>0.0129</td>
<td>0.1242</td>
<td>0.0026</td>
<td>0.8732</td>
<td>0.4033</td>
<td>0.5967</td>
</tr>
<tr>
<td>366.99</td>
<td>0.7463</td>
<td>0.2477</td>
<td>0.0061</td>
<td>0.1127</td>
<td>0.0033</td>
<td>0.8840</td>
<td>0.3911</td>
<td>0.6089</td>
</tr>
<tr>
<td>367.54</td>
<td>0.7343</td>
<td>0.2602</td>
<td>0.0055</td>
<td>0.0966</td>
<td>0.0036</td>
<td>0.8998</td>
<td>0.3810</td>
<td>0.6190</td>
</tr>
</tbody>
</table>

T is in K with a standard uncertainty of 0.06 K, pressure standard uncertainty is 0.1 kPa and composition relative uncertainty is $u_r = \frac{u}{w}$ is 2% except for the NaCl in the organic phase where the relative uncertainty is 5%.

$^1$obtained by GC-TCD

$^2$obtained by gravimetric analysis

$^3$obtained by ICP-OES

$^4$checked against Karl Fischer Technique
Table 4. Equilibrium data (weight fraction) corresponding to the four phase region (1S - 1 L_{aq} - 1 L_{org} - 1 V) of the water + NaCl + 1-butanol system at 101.3 kPa.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Water&lt;sup&gt;1,4&lt;/sup&gt;</th>
<th>NaCl&lt;sup&gt;2,3&lt;/sup&gt;</th>
<th>1-Butanol&lt;sup&gt;4&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Organic Liquid</td>
<td>0.0927</td>
<td>0.0036</td>
<td>0.9037</td>
</tr>
<tr>
<td>Aqueous Liquid</td>
<td>0.7251</td>
<td>0.2700</td>
<td>0.0049</td>
</tr>
<tr>
<td>Vapor</td>
<td>0.3357</td>
<td>0.0000</td>
<td>0.6643</td>
</tr>
</tbody>
</table>

| Temperature (K) | 369.28 |

T is in K with a standard uncertainty of 0.06 K, pressure standard uncertainty is 0.1 kPa and composition relative uncertainty is \( u_r = \frac{u}{w} \) is 2% except for the NaCl in the organic phase where the relative uncertainty is 5%.

<sup>1</sup>obtained by GC-TCD

<sup>2</sup>obtained by gravimetric analysis

<sup>3</sup>obtained by ICP-OES

<sup>4</sup>checked against Karl Fischer Technique
Table 5. Equilibrium data (weight fraction) corresponding to the liquid-vapor regions at 101.3 kPa.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>Water(^1)</th>
<th>NaCl(^2)</th>
<th>1-butanol(^3)</th>
<th>Water(^4)</th>
<th>1-butanol(^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>371.76</td>
<td>0.0565</td>
<td>0.0009</td>
<td>0.9426</td>
<td>0.3527</td>
<td>0.6473</td>
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<td>374.24</td>
<td>0.0344</td>
<td>0.0003</td>
<td>0.9653</td>
<td>0.3422</td>
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</tr>
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<td>379.16</td>
<td>0.0238</td>
<td>0.0002</td>
<td>0.9760</td>
<td>0.2741</td>
<td>0.7259</td>
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<tr>
<td>366.89</td>
<td>0.1063</td>
<td>0.0023</td>
<td>0.8914</td>
<td>0.4035</td>
<td>0.5965</td>
</tr>
<tr>
<td>370.17</td>
<td>0.9784</td>
<td>0.0127</td>
<td>0.0089</td>
<td>0.6892</td>
<td>0.3108</td>
</tr>
</tbody>
</table>

\(^1\)obtained by GC-TCD  
\(^2\)obtained by gravimetric analysis  
\(^3\)obtained by ICP-OES  
\(^4\)checked against Karl Fischer Technique

T is in K with a standard uncertainty of 0.06 K, pressure standard uncertainty is 0.1 kPa and composition relative uncertainty is \(\frac{u_p}{w} = \frac{u}{w}\) is 2% except for the NaCl in the Liquids rich in 1-butanol where the relative uncertainty is 5%.