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# Influence of the temperature on the equilibrium phase diagram of the ternary system water + ammonium chloride + 2-propanol at 101.3 kPa

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## Highlights

- Multiphase equilibrium for water +  $\text{NH}_4\text{Cl}$  + 2-propanol
- Isothermal LL, SL and SLL equilibrium data at 298.1, 308.1, 313.1 and 333.1 K
- Isobaric LV, LLV, SLV and SLLV equilibrium data at the boiling temperature and 101.3 kPa
- The lowest temperature at which  $\text{NH}_4\text{Cl}$  can split water + 2-propanol into two liquid phases is 310.4 K
- Extended UNIQUAC have been used to model phase equilibrium including solid

## Keywords

Water; 2-Propanol;  $\text{NH}_4\text{Cl}$ ; Isobaric; Solid-liquid-liquid; Solid-liquid-liquid-vapor; Phase diagram

## Abstract

The phase equilibrium of the water +  $\text{NH}_4\text{Cl}$  + 2-propanol mixture, at a constant pressure of 101.3 kPa, has been determined isothermally at four temperatures, as well as at the boiling temperature. Transitions between the different regions of the isothermal equilibrium diagrams have been studied, and the lowest temperature at which the salt can split water+ 2-propanol mixtures into two liquid phases, is found to be 310.4 K. As the temperature is increased from this critical value, the two-liquid-phase region expands until the boiling temperature is reached.

Finally, the extended UNIQUAC model for electrolytes has been used to predict the equilibrium diagram of the system. Large discrepancies with the experimental results have been found, and it will, therefore, be necessary to review the parameters of the model based on the experimental data reported in this work.

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## 1. Introduction

Knowledge of the equilibrium phase diagram of mixed solvent electrolyte systems is important because these mixtures are ubiquitous in many industrial processes. However, the number of previous works on such systems is relatively small [1]. Consequently, the thermodynamic models that can be used to represent them, such as the OLI MSE model of Wang et al [2], the extended UNIQUAC model for electrolytes [3], or the electrolyte NRTL model of Chen et al. [4], do not include enough equilibrium data to permit the correct calculation of model parameters. Moreover, not only is the amount of previous experimental data insufficient and incomplete, but some of the published data [5, 6] also contain great inconsistencies as it is demonstrated in Ref. [7, 8].

One of these mixed solvent electrolyte systems is the ternary mixture water +  $\text{NH}_4\text{Cl}$  + 2-propanol. No equilibrium data for this system, at any temperature, can be found in the bibliography. 2-propanol is completely miscible with water, and, at room temperature,  $\text{NH}_4\text{Cl}$  cannot split this miscible system into two liquid phases as other salts do, e.g.,  $\text{LiCl}$  or  $\text{NaCl}$  [9, 10]. However, at higher temperatures, this becomes possible and  $\text{NH}_4\text{Cl}$  can split water + 2-propanol mixtures into an aqueous and an organic phase in mutual equilibrium.

In order to assess this fact and determine the lowest temperature at which phase splitting occurs, equilibrium diagrams at 101.3 kPa, and at different temperatures ranging from 298.1 K to the boiling temperatures, have been determined. Transitions between different regions of the diagrams have also been studied.

## 2. Experimental

### 2.1. Chemicals

The ultrapure water used in our experiments was collected from a MiliQPlus system. Its conductivity was measured to be less than 1  $\mu\text{S}/\text{cm}$ . Table 1 contains a summary and description of the other chemicals used in this work, and includes ethanol because it served in the quantitative chromatographic analysis as an internal standard. Table 1 summarizes the provenance and purity of the compounds used. This table also includes the concentration of water in the organics, which was determined in a Mettler Toledo DL31 Karl Fischer apparatus.

### 2.2. Apparatus and procedures

Phase equilibrium determinations at temperatures lower than the boiling temperature.

Liquid-liquid (LL), solid-liquid-liquid (SLL), and solid-liquid (SL) equilibrium measurements were performed at 298.1, 308.1, 313.1 and 333.1 K. The method used to carry out the determinations at the different temperatures, was reported in a previous paper [9]. In essence, the procedure consists of preparing mixtures of known overall composition of water, 2-propanol and ammonium chloride salt in 15 mL tubes sealed with septum, stirring vigorously and placing them in a thermostatic bath at a controlled constant temperature. The latter is measured to within an accuracy of 0.1 K by means of a calibrated mercury-in-glass type thermometer. The process of settling and mixing is then repeated several times over a period of at least one day, in order to guarantee that equilibrium is attained. After that, syringes at

the bath temperature are used to extract samples from the liquid phases and their compositions are analyzed by the methods described below.

Phase equilibrium at 101.3 kPa and boiling temperature. A modified vapor-liquid Fischer Labodest VLL 602 equipment unit (Fischer *Labor und Verfahrenstechnik*) was employed to determine the liquid-vapor (LV), liquid-liquid-vapor (LLV), solid-liquid-vapor (SLV), and solid-liquid-liquid-vapor (SLLV) equilibria at the boiling temperature. The modification is the addition of an ultrasonic probe to improve the mixing and dispersion of the various phases, which facilitates proper mass transfer between them, especially between the two liquid phases and the solid in the boiling flask. This permits the use of the original commercial equipment in the determination of the SLLV equilibrium. A previous paper [11] describes the operation of the equipment.

Due to the large variation in solubility with temperature of  $\text{NH}_4\text{Cl}$ , unlike in previous works, it has also been required to add a controlled electrical heating resistance around the return pipe joining the separation chamber with the mixing chamber. The external temperature controlled by the electrical resistance was fixed at 373.15 K. This prevents salt precipitation in the duct which might become clogged up by a slight temperature decrease of the stream that flows through it.

To start with the experimental data determination, a three component mixture is added inside the mixing chamber and the boiling chamber where it is then heated at a pressure of 101.3 kPa, which, in turn, is fixed by means of a pressure controller (Mensor CPC 3000). A Pt100 sensor coupled to a digital thermometer (Hart Scientific 5615) is used to measure the boiling temperature.

Once equilibrium has been reached, a sample of the vapor and liquid phases are collected and analyzed by a previously described methodology [5]. The correct functioning of the equipment and appropriateness of the methodology were verified by determination of several LV equilibrium points of the binary system water + 2-propanol. The results exhibit perfect agreement with the experimental LV equilibrium data in the literature.

Method of analysis. The concentrations of the components in the liquid and vapor phases were determined by gas chromatography (GC). An amount of the liquid was put inside a vial with a weighed amount of internal standard for analysis. Ethanol was used for this purpose. Later the sample was analyzed by GC to measure its 2-propanol and water composition ratio. In case of the liquid phase, another aliquot from the sample was taken and the concentration of salt therein was determined after it had been dried to constant weight at 353.1 K. We also verified that the loss of  $\text{NH}_4\text{Cl}$ , due to its volatility, was negligible at that temperature.

A Shimadzu GC14B gas chromatograph with a 2 m x 3 mm 80/100 Porapack Q packed column and Thermal Conductivity Detector (TCD) was used to execute the analysis. For the liquid samples containing salt, glass wool was placed in the glass insert of the GC injector to trap the  $\text{NH}_4\text{Cl}$  and thus prevent the salt from reaching the chromatographic column. The carrier gas was Helium, at a flow rate of 25 mL/min. The oven worked at a constant set temperature of

463.15 K, while in the detector and injector the temperature was 483.15 K. The detector current was 100 mA.

A statistical calculation of repeated experimental measurements was used to obtain the experimental uncertainties. In the experiments at the boiling temperature, the standard uncertainty ( $u$ ) was 0.06 K for the temperature and 0.1 kPa for the pressure. The relative uncertainty in the composition ( $u_r = \frac{u}{x}$ ) was 2% for all components, except for the  $\text{NH}_4\text{Cl}$  in the phases with low concentrations of salt. In this case, the relative uncertainty was 5%.

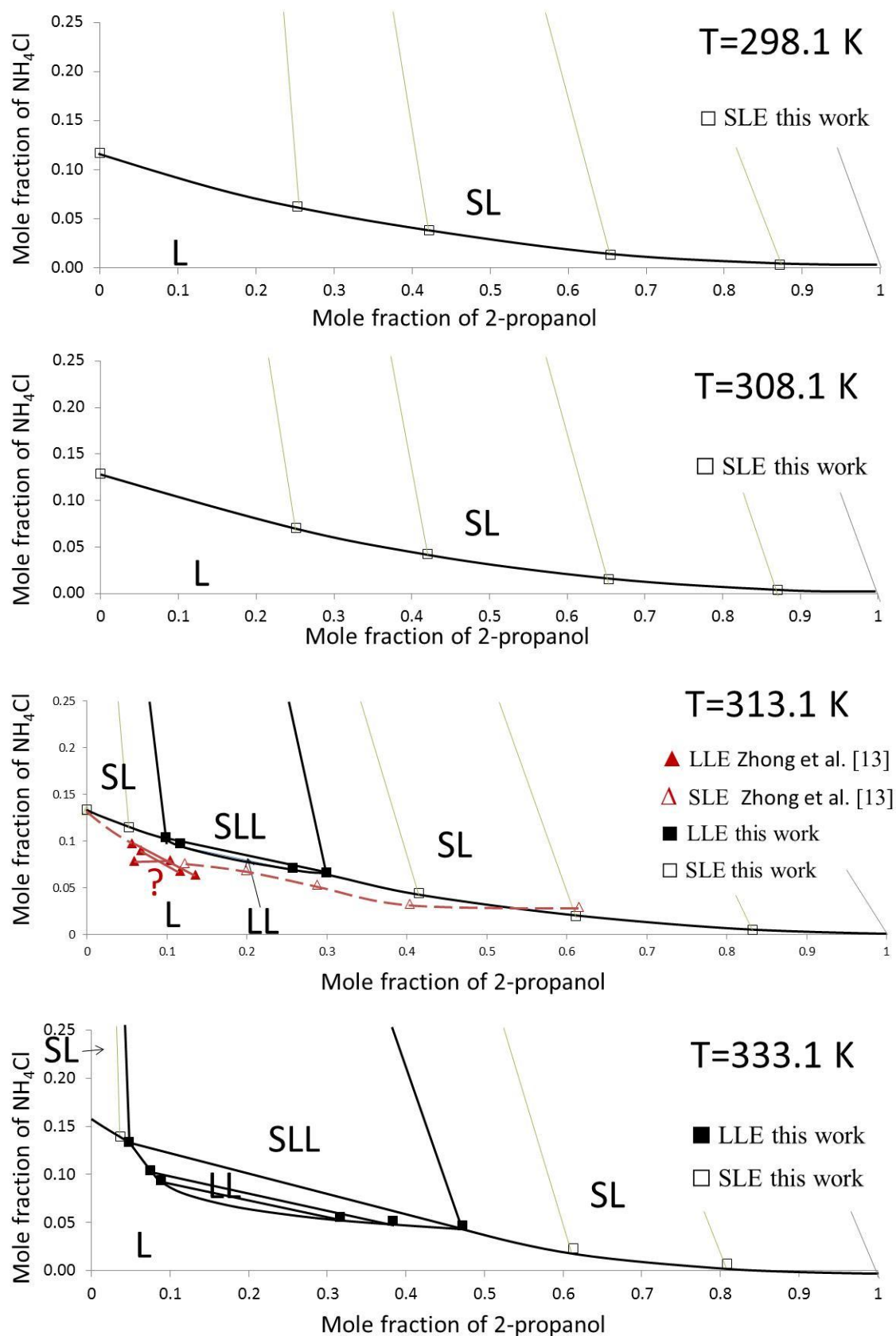
### 3. Results

#### 3.1 Experimental results.

The equilibrium data obtained at temperatures below the boiling point are shown in Table 2. For each of the temperatures, experimental data of the different regions of the system have been determined. As it is shown in the isothermal diagrams of Figure 1, the system only has one heterogeneous SL region at 298.1 and 308.1 K. However the system exhibits different heterogeneous regions at 313.1 and 333.1 K: SL, SLL and LL. At  $310.4 \pm 0.1$  K, the equilibrium diagram presents a very narrow region of two liquid phases for which no tie lines have been obtained. The temperature 310.4 K is the lowest temperature at which water +  $\text{NH}_4\text{Cl}$  + 2-propanol can split into two liquid phases. As the temperature is increased from this critical temperature, the size of the LL phase region expands until the boiling temperature is reached.

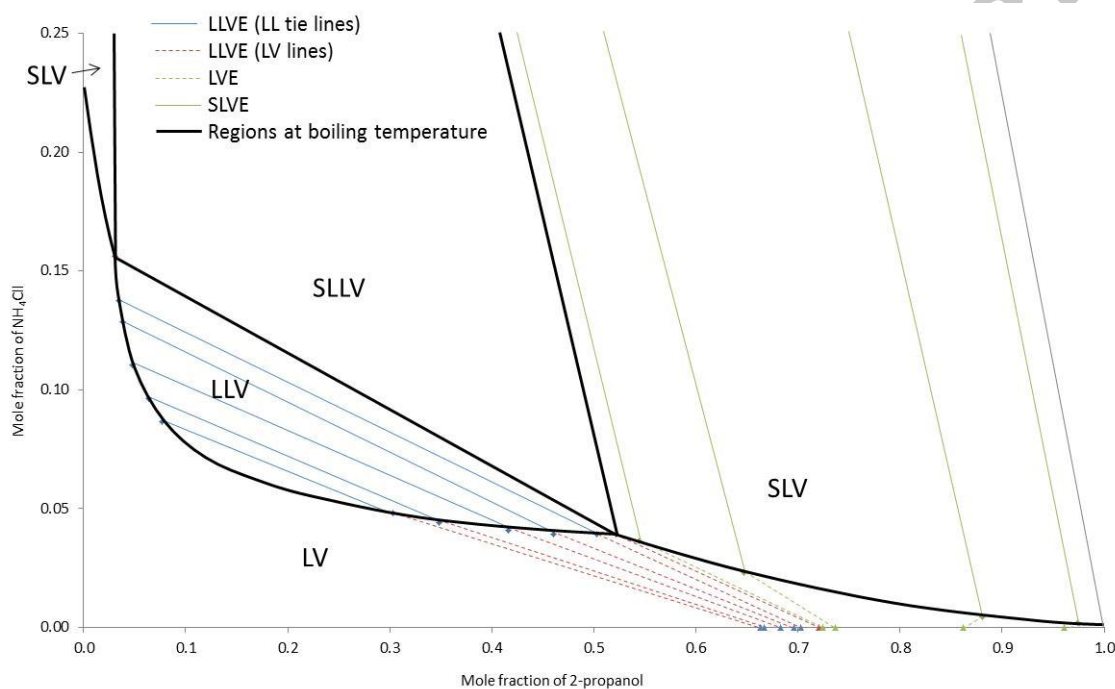
This behavior is similar to that of the system water – potassium chloride – 2-propanol where it was determined 298.4 K as the minimum temperature to split the mixture into two liquid phases [12]

Zhong et al [13] also determined some LL and SLV equilibrium data of this system at different temperatures. They obtained a lower critical solution temperature of  $310.3 \pm 0.1$  K that produces phase splitting which coincides with ours to within uncertainty. However, there are undoubtedly mistakes in their tables containing the equilibrium data. Figure 1 (at  $T=313.1$  K) shows their data, with evident errors such as tie lines that cross each other and an inconsistency between their own LL and SL equilibrium data.



**Fig. 1.** Phase diagram (mole fraction) for the water +  $\text{NH}_4\text{Cl}$  + 2-propanol system at different temperatures.

The boiling temperatures and the equilibrium data of the studied mixtures are shown in Table 3. It has been divided into different sections corresponding to the different regions of the phase diagram of the system. The boundaries of the LV, SLV, LLV and SLLV regions are plotted in Figure 2, where solid tie lines are used in the LLV and SLV regions and dashed lines to join the liquid phases with the compositions of the vapors in equilibria. The shape of the equilibrium diagram is similar to those of previous studied systems containing a completely miscible pair water-alcohol [7, 8]

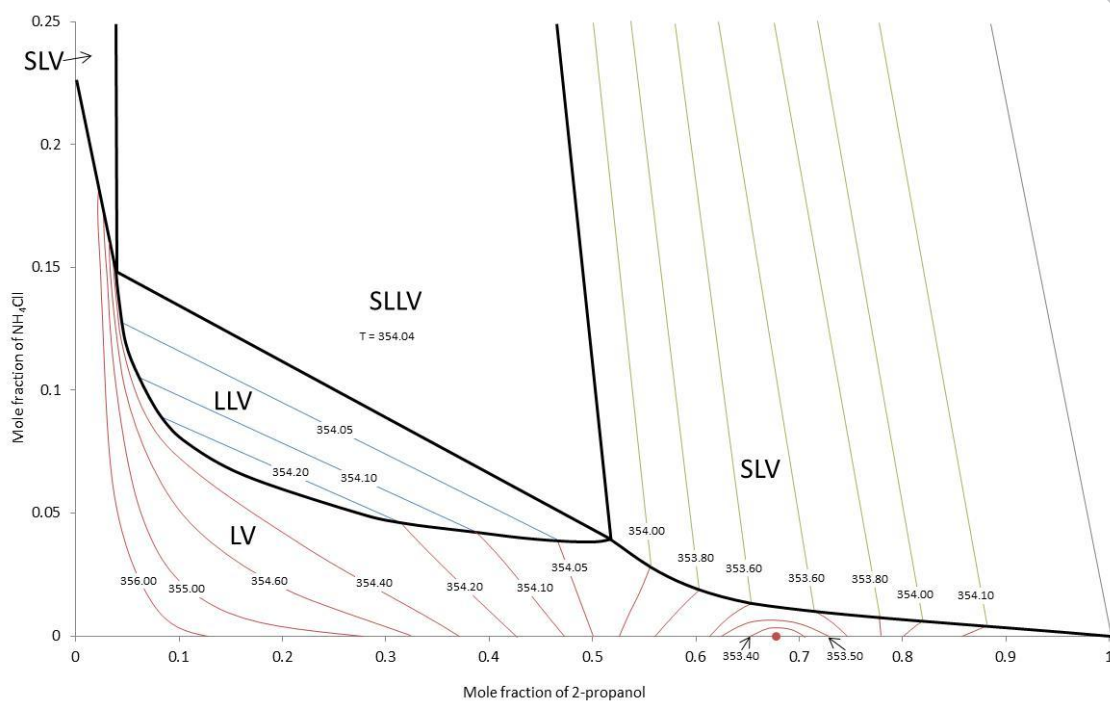


**Fig. 2.** Phase diagram (mole fraction) for the water +  $\text{NH}_4\text{Cl}$  + 2-propanol system at boiling temperature and 101.3 kPa.

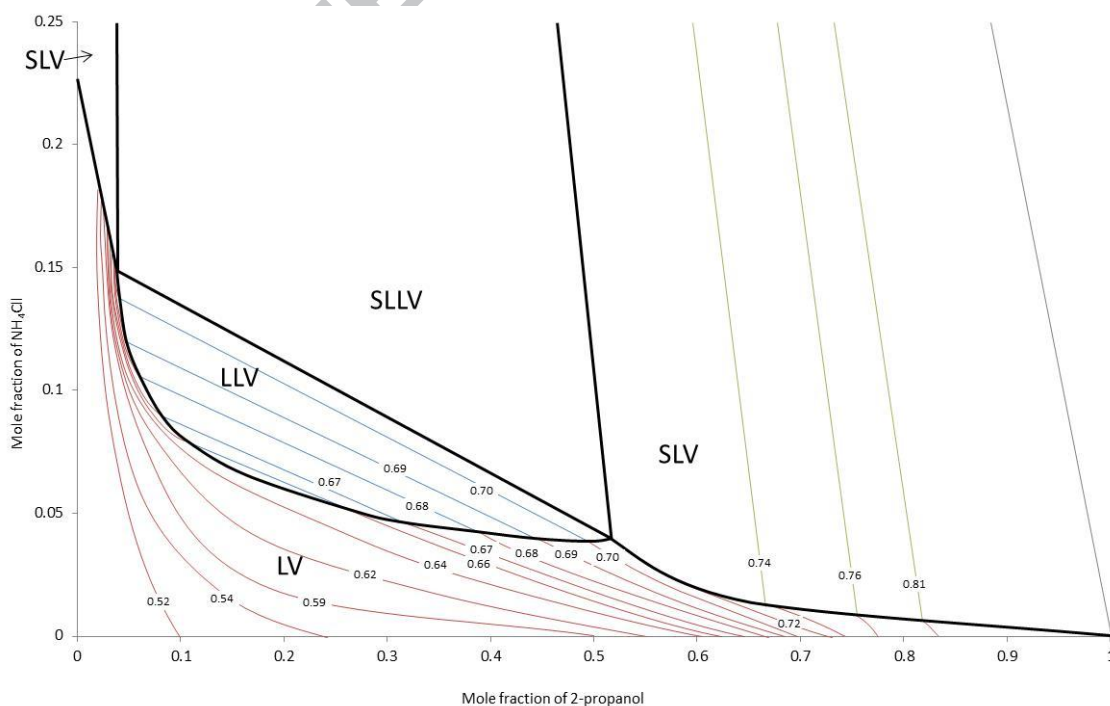
From an interpolation of the data in Table 3, we have drawn Figures 3 and 4, showing the boiling temperature isotherms and the iso-concentration curves of 2-propanol in the vapor phase. As was demonstrated previously [7], the construction of these figures constitutes the best way to check the consistency of the data. The figures show how the results are completely consistent since the SLLV region remains invariant and the vapor iso-concentration lines and the isotherms are straight lines in the LLV and SLV regions.

Figure 3 also shows that there is a very small difference of less than 1 K between some of the critical points of the system: the azeotropic temperature of the binary system water + 2-propanol is 353.28 K [14]), the temperature of the LLV plait point is approximately 354.3 K, and the temperature of the SLLV invariant is 354.04 K. Therefore, the presence of salt in all the mixtures, with a salt-free basis mole fraction of 2-propanol in the range 0.25-0.75, modifies their boiling temperatures only very slightly. Consequently, the fluctuations in boiling temperatures during the experimental measurement are very small in spite of the determinations are done in a dynamic system with ultrasounds.

Another characteristic that can be deduced from these figures, and be considered anomalous, is the slight decrease in the boiling point of many mixtures after salt has been added. All the mixtures that are in the range 0.07-0.50 in 2-propanol exhibit this characteristic of a decreasing boiling point when salt is added.



**Fig. 3.** System water +  $\text{NH}_4\text{Cl}$  + 2-propanol at 101.3 kPa: Boiling temperature isotherms (K).



**Fig. 4.** System water +  $\text{NH}_4\text{Cl}$  + 2-propanol at 101.3 kPa: Curves of iso-concentration of 2-propanol in the vapor phase (mole fraction).

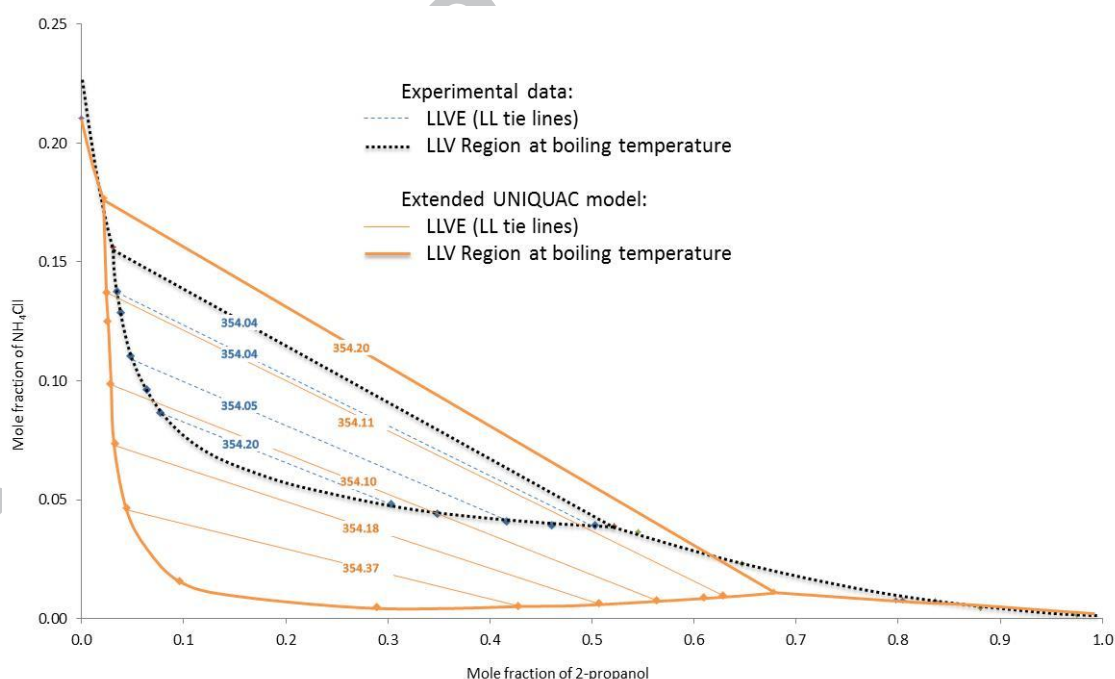


### 3.2. Calculated results with the extended UNIQUAC model

The extended UNIQUAC model and AQSOL software, with parameters taken from Ref. [3], have been used to calculate the equilibrium of the system. It should be noted that the various systems that were correlated in order to obtain these parameters, did not include water +  $\text{NH}_4\text{Cl}$  + 2-propanol, since there are no previously published data available for this system at any temperature. Therefore, the extended UNIQUAC model has merely been used as a predictive tool.

Figure 5 shows the results of the calculation and also compares them with the data in Table 3. At the boiling temperature, the model and parameters reproduce correctly the boiling temperatures and even the shape of the different regions. However, there are important differences between the sizes of the experimental and predicted LLV regions, since the model predicts that in order to form a mixture with two liquid phases, less salt would be needed than in practice. Furthermore, the model does not correctly predict the shape of the diagram of the system at low temperatures either, when salt is not able to split the mixture water + 2-propanol into two liquid phases, as was shown previously. At these temperatures, the model predicts that the equilibrium diagram has the same shape as in Figure 5.

Therefore, based on the reliable experimental data reported here, it will be needed to review the parameters of the model. The new parameters should correctly reproduce the influence of temperature on the shape of the equilibrium diagram.



**Fig. 5.** System water +  $\text{NH}_4\text{Cl}$  + 2-propanol at 101.3 kPa: Experimental and calculated by means of the extended UNIQUAC model [3] equilibrium data (mole fraction). On each tie line, the boiling temperatures (K) are shown.

#### 4. Conclusions

The phase equilibrium of the system water +  $\text{NH}_4\text{Cl}$  + 2-propanol has been determined experimentally at 101.3 kPa: isothermally at four temperatures, and also at the boiling point. Transitions between the different regions of the isothermal equilibrium diagrams have been studied, and the lowest temperature at which the salt can split water + 2-propanol mixtures into two liquid phases has been found to be 310.4 K. When the temperature is increased from this critical value, the two-liquid-phase region expands until the boiling temperatures are reached.

Our results show that all the mixtures with compositions close to the invariant SLLV mixture, the binary azeotrope water + 2-propanol, or the plait point of the LLV region, have boiling points that lie within a 1 K range. Consequently, the presence of salt in all the mixtures, with a salt-free basis mole fraction of 2-propanol in the range 0.25-0.75, does not significantly modify their boiling temperatures.

Another characteristic that can be deduced from the equilibrium data, and be considered anomalous, is the slight decrease in the boiling point of many mixtures upon the addition of salt. All the mixtures that are in the range 0.07-0.50 in 2-propanol exhibit this characteristic of a decreasing boiling point when salt is added.

Finally, the extended UNIQUAC model for electrolytes has been used to predict the equilibrium diagram of the system. Large discrepancies with the experimental results have been found, and it will, therefore, be necessary to review the parameters of the model based on the experimental data reported in this paper.

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## TABLES

**Table 1.**

Details of the chemical compounds used in this work.

Chemical	Provider	Initial purity (mass %)	Analysis method	Water content KF <sup>a</sup> (mass %)	Purification method
NH <sub>4</sub> Cl	Acros Organics	> 99.6			none
2-Propanol (2P)	Merck	> 99.5	GC <sup>b</sup>	0.09	none
Ethanol	VWR	> 99.8	GC <sup>b</sup>	0.02	none

<sup>a</sup> KF = Karl Fischer Technique<sup>b</sup> GC = Gas chromatography

**Table 2.**

System water + NH<sub>4</sub>Cl + 2-propanol (2P): isothermal equilibrium data (mole fraction) at different temperatures and 101.3 kPa.

T/K	Solid	Liquid phase I			Liquid phase II		
	NH <sub>4</sub> Cl	Water <sup>1</sup>	NH <sub>4</sub> Cl <sup>2</sup>	2P <sup>1</sup>	Water <sup>1</sup>	NH <sub>4</sub> Cl <sup>2</sup>	2P <sup>1</sup>
298.1							SL
	1	0.685	0.0624	0.253			
	1	0.540	0.0381	0.422			
	1	0.332	0.0135	0.655			
308.1	1	0.126	0.0032	0.871			
							SL
	1	0.678	0.0705	0.251			
	1	0.538	0.0423	0.420			
313.1	1	0.331	0.0154	0.654			
	1	0.126	0.0040	0.870			
							SL
	1	0.833	0.115	0.0523			
	1	0.540	0.0449	0.415			
	1	0.369	0.0201	0.611			
	1	0.163	0.0052	0.832			
	1	0.797	0.105	0.0982	0.633	0.0669	0.300
333.1							LL
		0.786	0.0975	0.116	0.671	0.0712	0.257
							SL
	1	0.824	0.139	0.0368			
333.1	1	0.364	0.0231	0.613			
	1	0.184	0.0071	0.809			
							SLL
	1	0.818	0.134	0.0477	0.481	0.0472	0.472
							LL
		0.821	0.104	0.0749	0.564	0.0517	0.384
	0.818	0.0942	0.0883	0.628	0.0561	0.316	

Standard uncertainty ( $u$ ):  $u(T) = 0.5$  K,  $u(P) = 2$  kPa

$u_r(x) = \frac{u}{x}$  is 2% except for the NH<sub>4</sub>Cl in the phases with  $x_{\text{salt}} < 0.01$  where its relative standard uncertainty is 5%.

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

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

**Table 3.**

System water + NH<sub>4</sub>Cl + 2-propanol (2P): Isobaric equilibrium data (mole fraction) at the boiling temperature (T) and 101.3 kPa.

T/K	Solid	Liquid phase I			Liquid phase II			Vapor phase	
	NH <sub>4</sub> Cl	Water <sup>1</sup>	NH <sub>4</sub> Cl <sup>2</sup>	2P <sup>1</sup>	Water <sup>1</sup>	NH <sub>4</sub> Cl <sup>2</sup>	2P <sup>1</sup>	Water <sup>1</sup>	2P <sup>1</sup>
SLLV									
354.04	1	0.813	0.156	0.0309	0.439	0.0391	0.522	0.280	0.720
LLV									
354.20		0.837	0.0867	0.0765	0.648	0.0480	0.303	0.337	0.663
354.15		0.839	0.0964	0.0642	0.608	0.0441	0.348	0.333	0.667
354.05		0.841	0.110	0.0481	0.543	0.0409	0.416	0.317	0.683
354.05		0.833	0.128	0.0387	0.500	0.0394	0.461	0.304	0.696
354.04		0.828	0.137	0.0342	0.458	0.0391	0.503	0.297	0.703
SLV									
354.03	1				0.423	0.0366	0.540	0.285	0.715
353.86	1				0.332	0.0230	0.645	0.263	0.737
354.10	1				0.115	0.0043	0.881	0.138	0.862
355.05	1				0.0235	0.0019	0.975	0.0394	0.961
LV									
355.77		0.886	0.0112	0.102				0.485	0.515
354.59		0.839	0.0569	0.104				0.366	0.634
354.64		0.836	0.0450	0.119				0.388	0.612
354.36		0.750	0.0509	0.199				0.350	0.650
354.52		0.747	0.0252	0.228				0.391	0.609
354.34		0.723	0.0427	0.234				0.358	0.642
354.34		0.726	0.0388	0.235				0.358	0.642
354.34		0.707	0.0403	0.253				0.356	0.644
354.15		0.611	0.0359	0.353				0.338	0.662
354.04		0.563	0.0303	0.407				0.337	0.663

Standard uncertainty (u): u(T) = 0.06 K, u(P) = 0.1 kPa

$u_r(x) = \frac{u}{x}$  is 2% except for the NH<sub>4</sub>Cl in the phases with  $x_{\text{salt}} < 0.01$  where its relative standard uncertainty is 5%.

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

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