

Accepted Manuscript

Effect of temperature on the phase-separation ability of KCl in aqueous two-phase systems composed of propanols: Determination of the critical temperature and extension of the results to other salts

Jorge Garcia-Cano, Alejandro Gomis, Alicia Font, Vicente Gomis

PII: S0021-9614(19)30129-6
DOI: <https://doi.org/10.1016/j.jct.2019.04.016>
Reference: YJCHT 5794

To appear in: *J. Chem. Thermodynamics*

Received Date: 5 February 2019
Revised Date: 11 April 2019
Accepted Date: 20 April 2019

Please cite this article as: J. Garcia-Cano, A. Gomis, A. Font, V. Gomis, Effect of temperature on the phase-separation ability of KCl in aqueous two-phase systems composed of propanols: Determination of the critical temperature and extension of the results to other salts, *J. Chem. Thermodynamics* (2019), doi: <https://doi.org/10.1016/j.jct.2019.04.016>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



Effect of temperature on the phase-separation ability of KCl in aqueous two-phase systems composed of propanols: Determination of the critical temperature and extension of the results to other salts

Jorge Garcia-Cano, Alejandro Gomis, Alicia Font, Vicente Gomis*

University of Alicante, PO Box 99, E-03080 Alicante, Spain

Keywords water, propanol, KCl, ATPs, SLLV

Highlights

- Vapor-liquid-liquid equilibrium data were determined.
- Vapor-liquid-solid and vapor-liquid-liquid-solid equilibrium data were determined.
- The effects of changes to the salt or propanol isomer are studied.
- The LCST has been determined for the system water + KCl + 1-propanol
- The effect of temperature on the LCST has been studied.

Abstract

The phase-forming ability of KCl in propanols has been investigated, aiming to assess its utility in aqueous two-phase extraction. Equilibrium data of the different equilibrium regions (SLLV, SLV, LLV, and LV) of aqueous two-phase systems (ATPSs) of water + KCl + 1-propanol and water + KCl + 2-propanol have been determined at the boiling temperatures of the mixtures and 101.3 kPa. In addition, the lowest critical solution temperature (LCST) for the water + KCl + 1-propanol system was measured to be 271.2 K, and the equilibrium behavior of the system in the vicinity of the LCST (at 268.1 and 273.1 K) was also determined. Finally, using various methods such as the effective excluded volume (EEV) theory, Setchenov-type equations, and the plait point of the liquid-liquid region, different salt and alcohol systems have been studied and classified according to their ability to produce ATPSs.

1. Introduction

An aqueous two-phase system (ATPS) consists of a mixture of different compounds that splits into two liquid phases under certain conditions of temperature and concentrations of the components. Each of the two liquid phases contains a large amount of water and is enriched in different components, depending on its liquid-liquid equilibrium [1].

*Corresponding author. Tel.: +34 965903365.
E-mail address: vgomis@ua.es (V. Gomis).

Since water is the solvent in both phases, ATPSs can provide adequate and non-destructive conditions for the separation and recovery of labile biomolecules (proteins, enzymes, DNA, or RNA) and also of biological particles (cells, bacteria, and viruses) [1, 2, 3].

The predominant compound in each phase may vary depending on the type of ATPS prepared. Traditionally, the solvents used in this type of system have been mixtures of two polymers or of a polymer and a salt. However, the application of ATPS employing polymer-based solvents is limited by the high viscosity of the mixture that forms the two liquid phases, the difficulty of their separation, and the tendency to form emulsions.

Salt + alcohol ATPS are considered a promising alternative because these components are much cheaper than polymer or copolymer blends, and they circumvent the aforementioned disadvantages of the polymer + polymer or polymer + salt mixtures. It is well known that the short-chain alcohols methanol, ethanol, 1-propanol (1P), 2-propanol (2P) and *tert*-butanol are completely miscible in water at any temperature above the freezing point. However, the presence of certain salts in sufficient concentration can cause splitting of the mixture into two liquid phases [4-12], both containing a high concentration of water. This can lead to an ATPS that could be used in the aforementioned separations.

Recently, many authors have determined equilibrium data of ATPSs consisting of water + 1P or 2P + different inorganic salts at or near room temperature [4 - 6]. The most common experimental methodology is to determine the solubility curve to estimate the size of the liquid-liquid region of the mixtures. Some authors have also included tie lines. However, in many of the published studies, the equilibrium diagram of the system has not been complete because the solid-liquid (SL) or solid-liquid-liquid (SLL) equilibrium regions have not been determined.

To study how temperature affects the splitting of the mixture into two liquid phases, some authors [4 - 11] have conducted measurements at different temperatures, but all in a narrow range of only 10-25 K and only in certain parts of the equilibrium diagram. The differences observed were small, in many cases even within the level of uncertainty of the measurements, which does not allow clear conclusions about the effect to be obtained.

In addition, the literature on solid-liquid-liquid-vapor equilibrium (SLLV) systems is scarce [13], and the relatively small amount of experimental data obtained at the boiling temperature of such systems are incomplete. Furthermore, in some cases, the data presented important inconsistencies [14]. For example, there are only a few water + inorganic salt + propanol systems that have reliable and complete data for the different regions of the equilibrium diagram at their boiling temperatures [13 - 15].

Consequently, the models that can be used to fit these systems, such as the OLI-MSE model [16], the extended UNIQUAC model for electrolytes [17], and the elec-NRTL model [18], are not based on sufficient and reliable equilibrium data to permit accurate estimation of the interaction model parameters.

KCl is a salt that is able to split completely miscible mixtures of water and propanol into two liquid phases at certain temperatures. The systems water + KCl + 1-propanol (W + KCl + 1P) and water + KCl + 2-propanol (W + KCl + 2P) therefore, are two ATPSs for which data are inconsistent and incomplete regarding how their phase equilibrium diagrams vary from the lower critical solution temperature (LCST) that leads to phase splitting to the boiling temperature, as will be discussed further on. Since the solubility of KCl in water varies

significantly with temperature (from 21.74% weight fraction of the salt at 273.1 K to 36.05% at 373.1 K [19]), it is expected that temperature exerts an important effect on the ability of KCl to split the water + propanol mixture into two liquid phases

Previous experimental equilibrium studies of the W + KCl + 1P system at 101.3 kPa: SLL and liquid-liquid (LL) equilibrium data have been reported at 298.15 K [20-24], and SLLV and liquid-liquid-vapor (LLV) equilibrium data have been reported at the boiling temperatures of the mixtures [25, 26]. No LCST has been reported for this system.

Three of the five reports involving experimentally determined equilibrium data for this system at 298.15 K exhibited similar results. However, two of these reports showed some discrepancies, one regarding the aqueous phases [23] and the other one regarding the organic phases [24], the compositions of which differed significantly from those in the other three studies. The comparison of these data is provided as supplementary material.

Experimental data were also reported at the boiling temperature of this system [25, 26]. Based on the criteria for consistency in SLLV equilibrium data [14], the data from Lin et al. [25] does not seem consistent since liquid mixtures whose composition corresponds to that of a tie line should have the same boiling temperature as the tie line itself. All points belonging to the SLLV region should boil at the same temperature; however, this was not the case based on their data. The same inconsistencies as in the temperature data can be observed in the data of the composition of the vapor in equilibria with points corresponding to a liquid phase. Therefore, these results are unacceptable as it is provided as supplementary material.

Finally, Johnson and Furter [26] only studied solutions saturated in KCl (in the SLV and SLLV regions). Although the boiling temperature and vapor composition of all samples containing two liquid phases and one solid phase should not change since they are in the SLLV region, the authors reported small differences, of 0.6 K in the boiling temperature and 0.02 mole fraction in the vapor composition.

Previous experimental equilibrium studies of the W + KCl + 2P system at 101.3 kPa: SLL and LL equilibrium data of the W + KCl + 2P system have been reported at different temperatures in the range of 283.1 K - 353.1 K [20, 22, 24, 27-31]. The small differences between some of the published data are shown as supplementary material.

From the experimental data, it can be inferred that there is a LCST in the range of 297.6 [26] - 298.4 K [25] with a critical plait point composition at this temperature of 0.848, 0.047 and 0.1047 mole fraction of water, KCl and 2-propanol respectively. Below this temperature, KCl is unable to split the W + 2P mixture into two liquid phases.

Finally, no SLLV, LLV, or SLV equilibrium data have been found for this system at boiling temperatures.

Taking all these considerations into account, in this work we complete the equilibrium data for the two ATPS containing KCl and propanol. We determined the LV, SLV, LLV, and SLLV equilibria data at 101.3 kPa and at boiling conditions for both ATPSs W + KCl + 1P and W + KCl + 2P, for which the currently published data are unacceptable. Moreover, for the system with 1P, we obtained its LCST and the SL, SLL, and LL equilibrium diagrams at two temperatures close to that of the LCST. Combining our results with the previously reported data, we will provide a base of equilibrium data for both systems over a wide range of temperatures, which

will allow analysis of the effect of temperature on the phase separation ability of KCl in ATPSs containing 1-propanol or 2-propanol.

2. Experimental methods

2.1 Chemicals

Table 1 presents the characteristics and source of all the chemical compounds used. Ethanol was employed for quantification purposes as an internal standard. The ultrapure water employed was obtained on-site using a Milli-Q Plus system. The water contents of the compounds used were determined by the coulometric Karl Fischer titration technique.

2.2 Experimental procedure

The experimental procedure employed for the determination of equilibrium data for both systems was analogous to that explained in a previous paper [14]: A modified Fischer Labodest still coupled with an ultrasonic probe in the boiling chamber was employed to enhance mass transfer between the phases. The pressure inside the instrument was controlled by means of a Fisher M101 phase equilibrium control system. A Pt100 sensor coupled to a digital thermometer (Hart Scientific 5615) was used to measure the temperature of the vapor phase.

The additional energy provided by the ultrasonic probe is compensated by decreasing the electrical power supplied to the immersion heater of the equipment. The electrical power is reduced in such a way that the sum of the two contributions generates a vapor flowrate that produces 1-2 drops/s of condensed liquid, which is the recommended value for the operation without ultrasounds.

Once the equilibrium state was reached, two samples were collected; one sample of the condensed vapor from one side, and another sample containing the other phase(s) (one liquid phase, two liquid phases, one liquid phase + one solid phase, or two liquid phases + one solid phase, depending on the initial mixture) in equilibria with the vapor.

During the LLV determinations, supersaturated state of the salt was never observed. The aqueous phases of the samples from these determinations always contained less salt than the SLLV aqueous phases.

The liquid-solid sample collected was introduced into a hermetic tube that was placed inside a thermostatic bath at a controlled temperature equivalent to the boiling equilibrium temperature. Two samples from each liquid phase were extracted subsequently: one for salt content determination by means of a gravimetric method, and another to determine the water and propanol contents via gas chromatography (GC). A known amount of ethanol was added to each GC sample for quantification purposes and to prevent phase splitting due to cooling of the sample outside of the thermostatic bath. The gas chromatograph employed was a Shimadzu GC14A with a Porapack Q packed column, coupled with a thermal conductivity detector (TCD). The carrier gas was He, with a flow rate of 25 mL/min. The temperature in the oven was maintained at 463.15 K, while those of the detector (100 mA current) and injector were set to 483.15 K.

3. Experimental results

Equilibrium diagrams at 101.3 kPa and boiling temperatures

Table 2 presents the experimental equilibrium data obtained for the water + KCl + 1-propanol system. The table is divided into different sections, with each one corresponding to a different region in the equilibrium diagram. In the same way, Table 3 presents the experimental data for the system with 2-propanol.

As mentioned in the introduction, Johnson and Furter [26] determined the effect of KCl on the SLV equilibrium at 100 kPa, but only for solutions that were saturated in the salt. Fig. 1 presents a comparison of their experimental data with our data, by presenting the curves of temperature and mole fraction of 1-propanol in the vapor phase each against the composition of the liquid (mole fraction of 1-propanol) on a salt-free basis. As seen, our data points correspond to those from the literature, except for the point representing the aqueous phase in the SLLV region. For this point, the mole fraction of 1-propanol in our results was lower than that reported previously. Since the authors of the previous report [26] did not consider that the liquid splits into two phases, we think that the sampling of the phases was not performed correctly in their work.

As has been shown in previous articles [14], the best way to demonstrate that the experimental data are consistent is to draw the diagrams of boiling temperature isotherms and iso-composition of the vapor phase by interpolating the experimental data. So, Figs. 2, 3, 4 and 5 show these two equilibrium diagrams for both systems, the data for which were obtained by interpolation of the data presented in Tables 2 and 3. Evidently, the SLLV region remained invariant, and the isotherms and vapor iso-composition lines of the SL and LL regions were straight lines.

As in the previously studied systems (W + NaCl + 1P, W + NaCl + 2P, W + NH₄Cl + 1P and W + NH₄Cl + 2P) [13-15, 32], the boiling temperatures of the binary azeotrope of water + alcohol, the plait point of the LLV region, and the invariant SLLV mixture are very similar. This feature explains why a large fraction of the mixtures in each of the systems boil within a very narrow range of temperatures, of only 1 K.

A comparison between Figs. 2 and 4 indicates that the shapes of the vapor iso-concentration curves of both systems are very similar. However, there are significant differences in the shape of the boiling temperature isotherms in the two systems, due to the different position of the binary azeotropic point with respect to the LLV region. From the curves for the system with 2-propanol, it can be seen that the boiling point of binary mixtures of water + 2-propanol in the range of 0.1-0.5 mole fraction of 2-propanol decreased slightly when salt was added, until the solution became saturated with salt. This feature, which in principle could be considered an anomaly, should occur in all the systems in which the binary azeotrope is displaced with respect to the position of the LLV region.

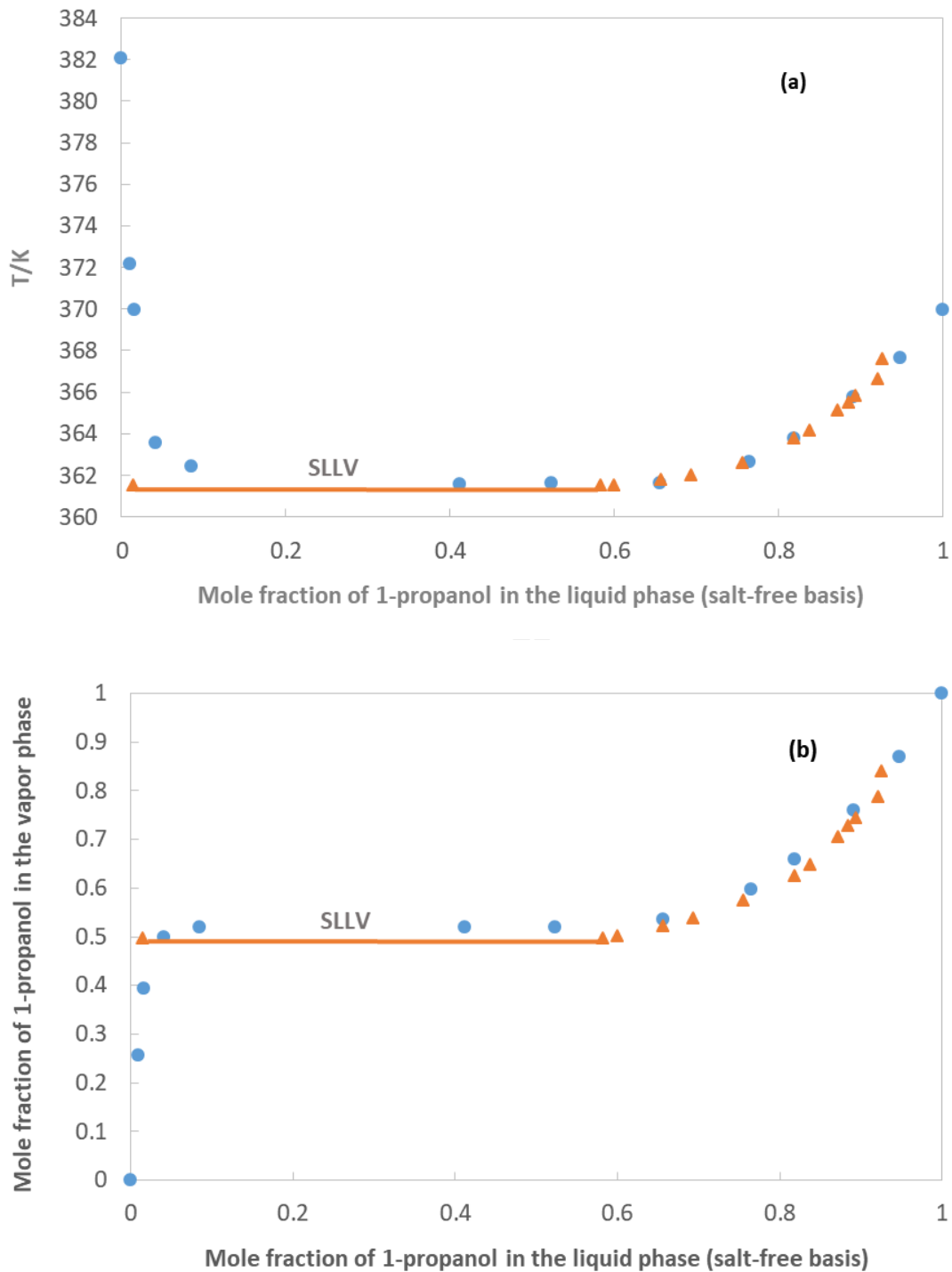


Fig. 1. Comparison of the experimental data obtained in this work with those from Johnson and Furter [26]: a) boiling temperature of the liquid (T_x); b) vapor composition (xy). \blacktriangle , this work; \bullet , Johnson and Furter [26].

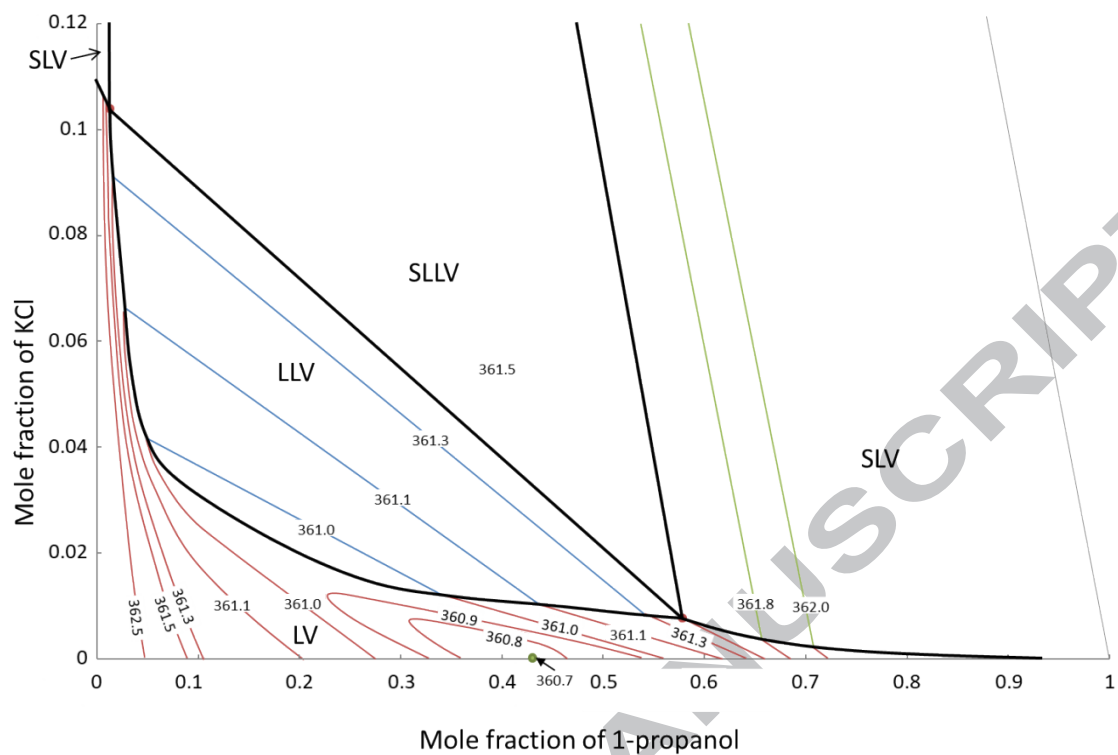


Fig. 2. Water + KCl + 1-propanol. Boiling temperature isotherms at 101.3 kPa. Values shown on the curves = T/K = boiling temperature.

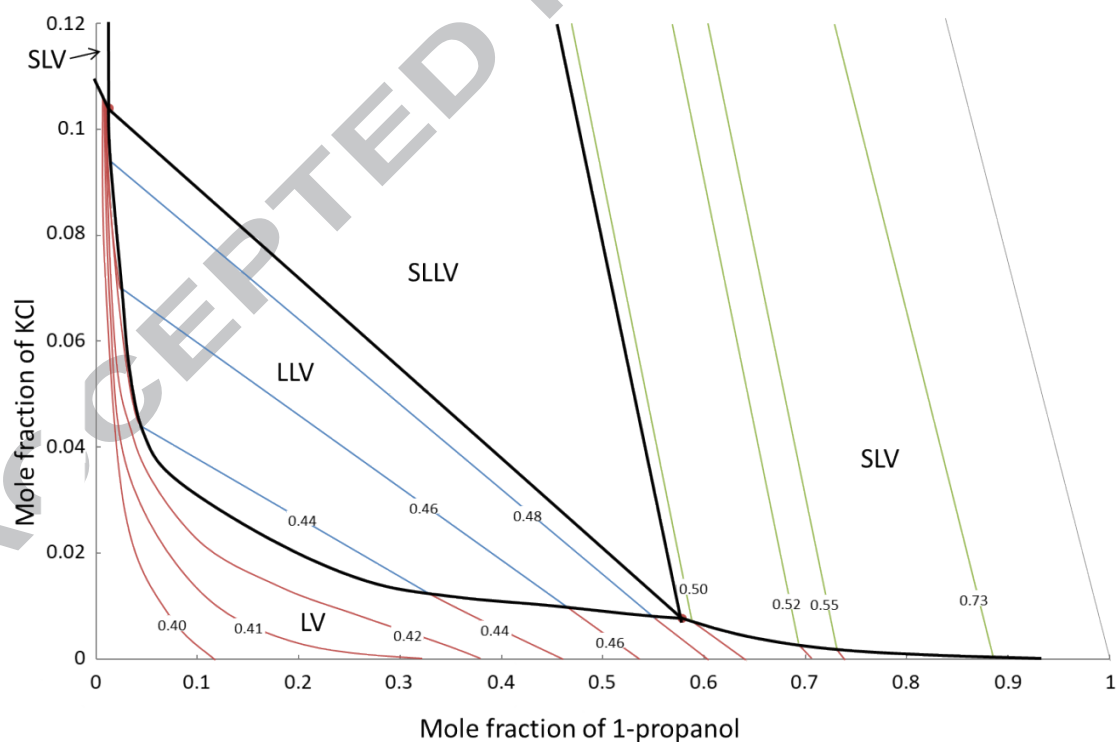


Fig. 3. Water + KCl + 1-propanol. Curves of iso-concentration of 1-propanol in the vapor phase at 101.3 kPa. Value shown on the curves = mole fraction of 1-propanol in the vapor phase.

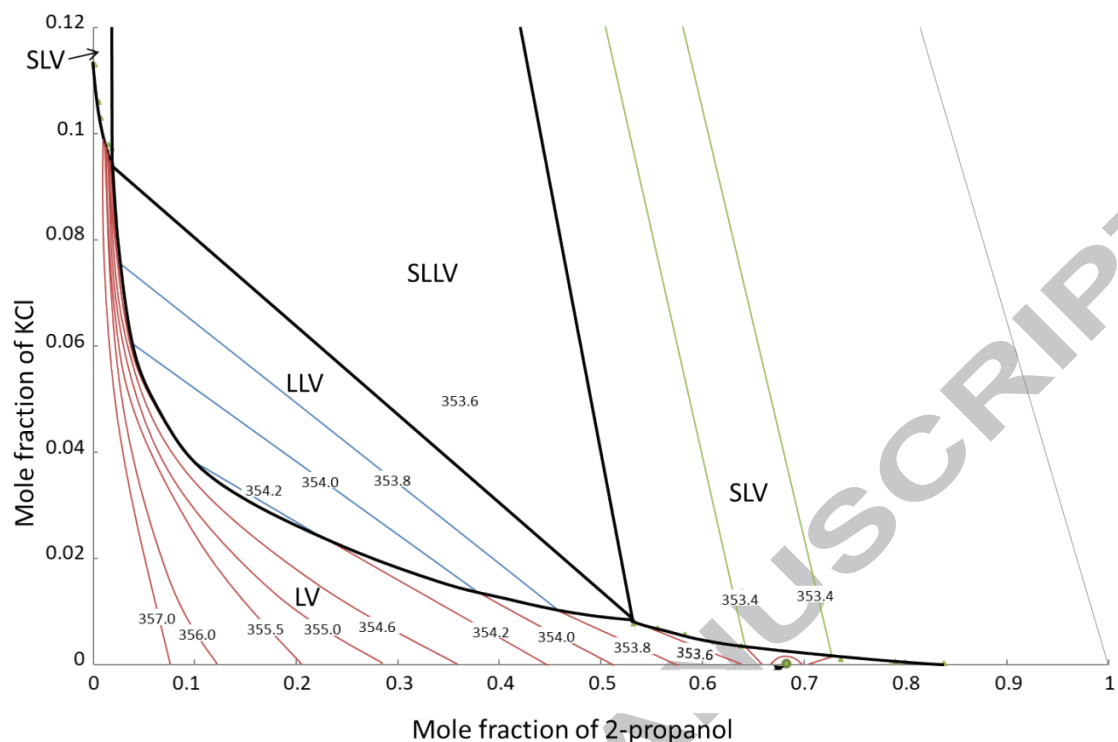


Fig. 4. Water + KCl + 2-propanol. Boiling temperature isotherms at 101.3 kPa. Value shown on the curves = T/K = boiling temperature.

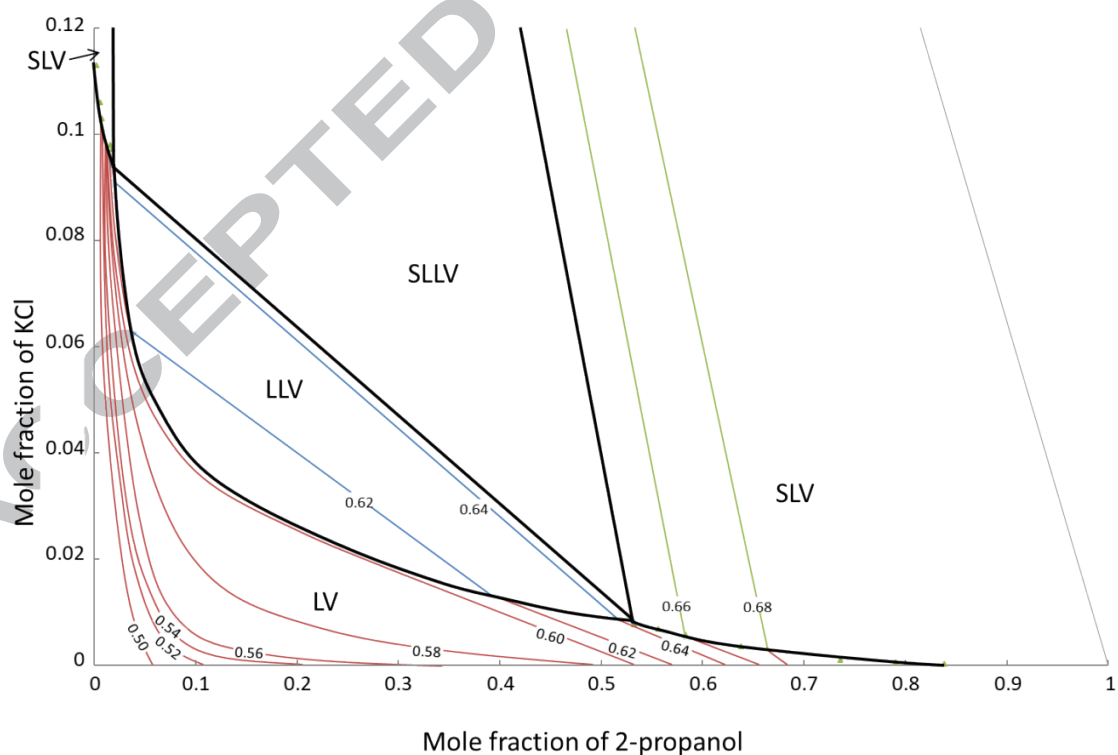


Fig. 5. Water + KCl + 2-propanol. Curves of iso-concentration of 2-propanol in the vapor phase at 101.3 kPa. Parameter shown on the curves = mole fraction of 2-propanol in the vapor phase.

LCST and equilibrium diagrams at nearby temperatures

As mentioned previously, the system W + KCl + 2P is an ATPS which cannot split into two phases if the temperature is lower than the LCST (297.6 [28] - 298.4 K [27]). Similarly, the LCST for the system with 1-propanol was determined to be 271.2 K with a critical plait point composition at this temperature of 0.802, 0.026 and 0.172 mole fraction of water, KCl and 1-propanol respectively. Equilibrium diagrams of the system W + KCl + 1P were thus determined at two temperatures close to the LCST, one slightly higher (273.1 K) and the other lower (268.1 K). Table 4 shows the results obtained for each of the regions of this system. In order to study the effect of temperature, the experimental data are represented in Figs. 6 a and b, alongside that corresponding to the boiling temperatures (data of Table 2) and that at 298.15 K taken from the literature [20] (Fig. 6 c).

At 268.1 K, which is below the LCST, only a homogeneous liquid region and a solid-liquid region exist. At 273.1 K, a temperature above the LCST, the LL region appeared, and became larger as the temperature was increased, up to the boiling point. Consequently, the length of the SLL tie line as well as salt content increased as the temperature increased, which is in accordance with the increase in solubility of KCl in water at higher temperatures.

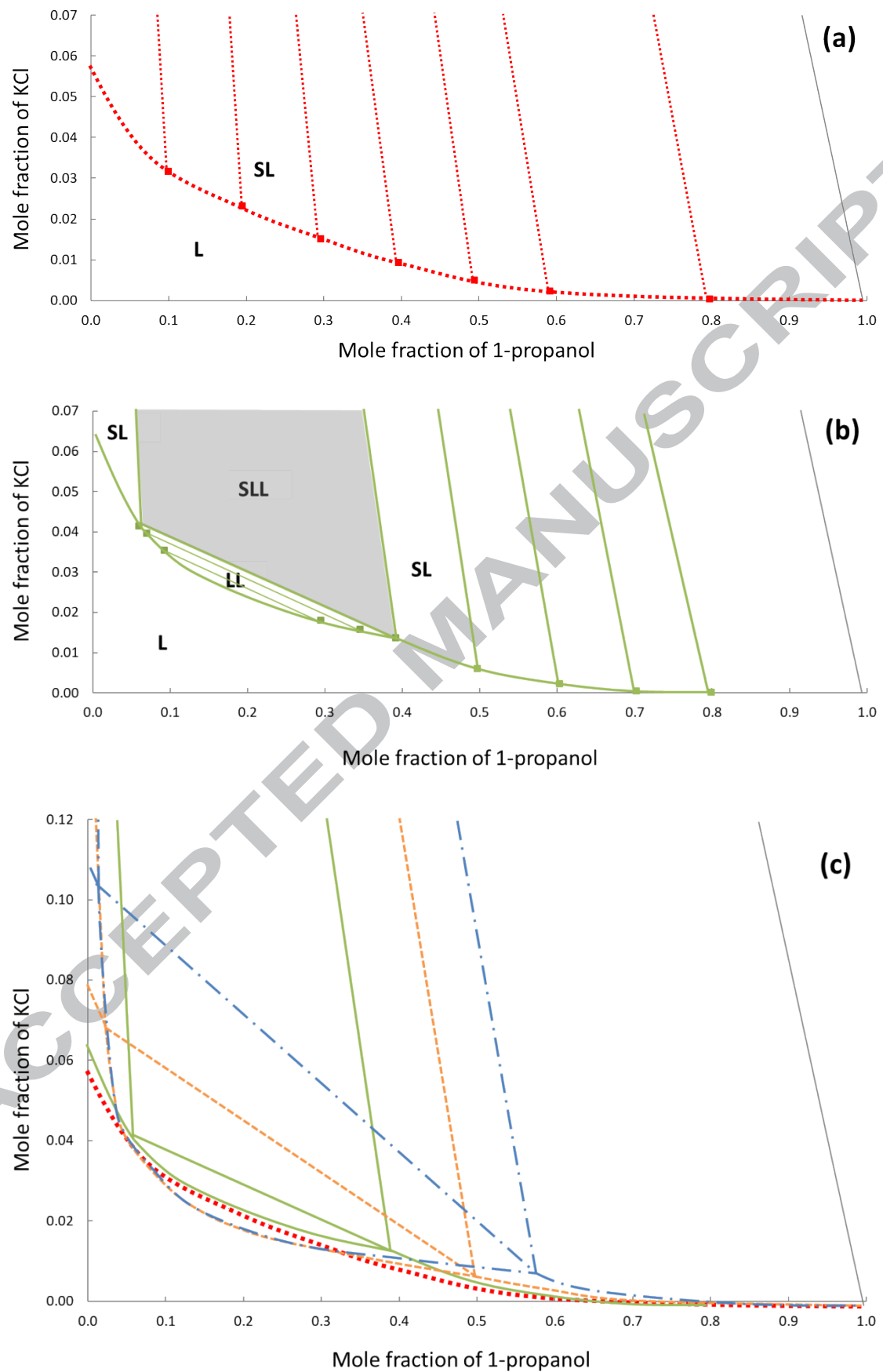


Fig. 6. Equilibrium regions of the system water + KCl + 1-propanol at different temperatures at 101.3 kPa. a) boundaries at 268.1 K, below the LCST; b) boundaries at 273.1 K, above the LCST;

c) boundaries at different temperatures T. T = 268.15 K; — T = 273.15 K; - - - T = 298.15 K; - . . T = boiling temperatures.

The system with 2-propanol exhibited similar behavior: the size of the LL region increased with an increase in temperature. This system has a higher LCST than that of 1-propanol, and the concentration of salt necessary to split the mixture into two liquid phases is also higher, which implies that it is more difficult for the 2-propanol system to form two liquid phases.

4. Application of the extended UNIQUAC model.

The phase equilibrium diagram of each system has been calculated using the extended UNIQUAC model with the available parameter values [17]. The model with the available parameter values correctly predicted the shapes of the different regions and even the boiling temperatures. As an example, Fig. 7 presents these regions for the system with 2-propanol as determined by the experimental and calculated data.

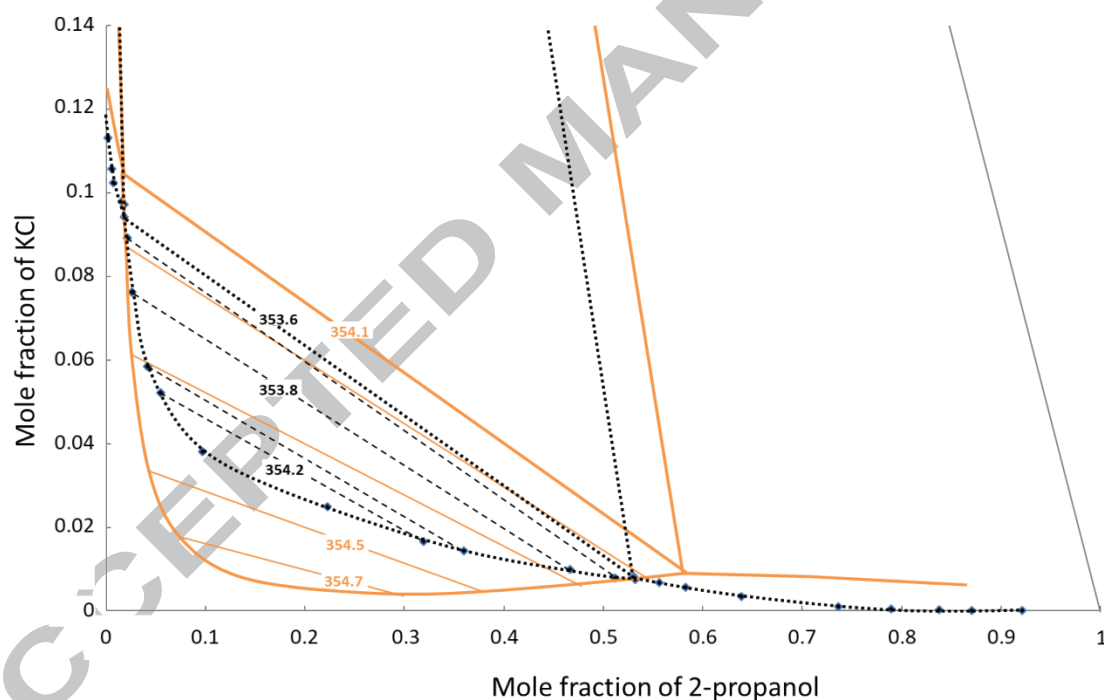


Fig. 7. Experimental and calculated equilibrium regions of the system water + KCl + 2-propanol at boiling temperature at 101.3 kPa. Value shown on the tie lines = T/K = boiling temperature. This work: - . .; Extended UNIQUAC model: —

The model also predicted the LCST for both systems. For the system with 1-propanol the calculated LCST was 258.8 K (experimental LCST = 271.2 K, obtained in this work) and that for the system with 2-propanol was 273.8 K (experimental LCST = 297.6 [28] - 298.4 K [27]); both predicted values were much lower than the experimentally determined values. For example, Fig. 8 shows the effect of temperature in this mixture, calculated using the thermodynamic model for the system with 2P. At 273.15 K, which is lower than the calculated LCST, there are only regions corresponding to one liquid phase (L) and solid-liquid (SL). However, at 283.15 K, SLL and LL regions appeared. There were large differences between the experimental and

calculated LCSTs, but considering the inaccuracy of the previously reported experimental data, it is suggested that this model has a great potential to fit this kind of data.

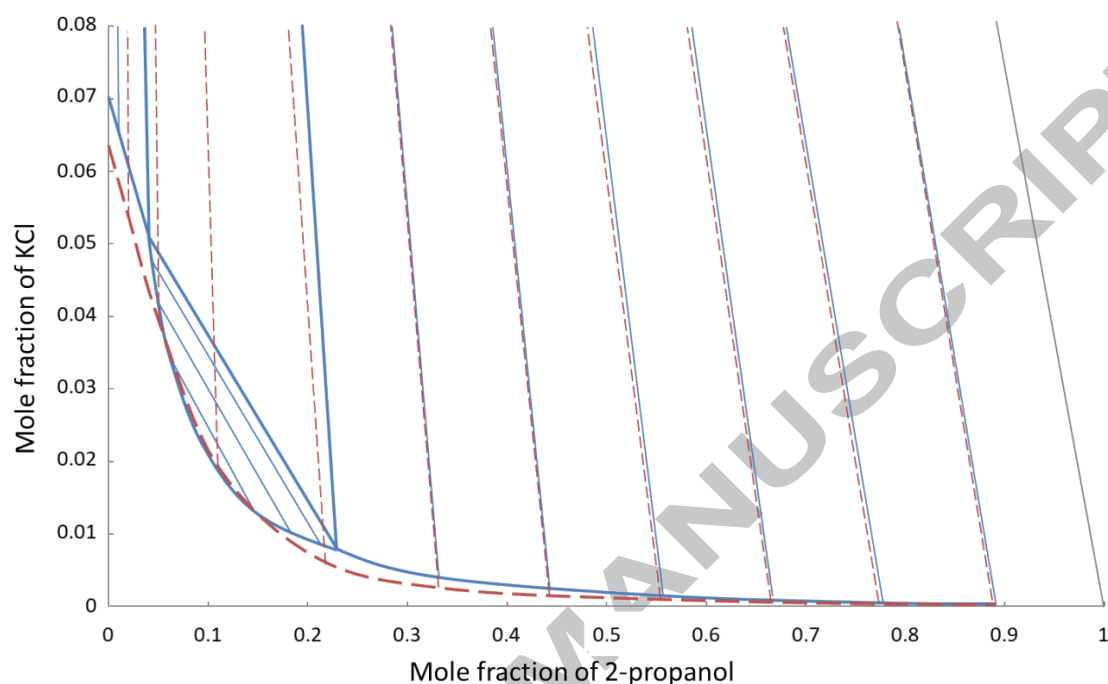


Fig. 8. Calculated phase boundaries with the extended UNIQUAC model of the system water + KCl + 2-propanol at 283.15 K (—) and 273.15 K (---).

The scarcity and the low reliability of the experimental data used to obtain the model parameters led to these inaccurate results. This reinforces the idea that there is a need for reliable experimental data that are suitable for the development of new models, or for new interaction parameters that are capable of accurately reproducing the experimental phase equilibria. Thus, it would be useful to reassess the thermodynamic binary interaction parameters for such systems.

5. Comparison between similar systems

In a previous study [33], it was shown that the ability of a salt to split a mixture of alcohol + water into two liquid phases increased with temperature. For this reason, the equilibrium data obtained at the boiling temperature of this system were chosen for comparison. The comparison involves the experimental data presented in this work for the systems W + KCl + 1P and W + KCl + 2P and those for the systems W + NaCl + 1P [13], W + NaCl + 2P [14], W + NH₄Cl + 1P [15], and W + NH₄Cl + 2P [32]. With these data, it is possible to analyze how variations in the alcohol, propanol isomer, and cation of the salt affect the behavior of ATPS at the boiling temperatures of the respective systems.

Effective excluded volume (EEV) theory

The effective excluded volume (EEV) of each of the different salts, determined using the model developed by Guan et al. [34] has been applied to each of the different water + alcohol systems. The basic assumptions underlying this model are, first, that at the macroscopic level, any molecular species is randomly distributed in solution, and second, that the compositions pertaining to the binodal curve correspond to a geometrically saturated solution of one solute in the presence of another. The EEV can be imagined as the minimum space in an alcohol molecule in which an individual salt could be accepted without causing instability and phase splitting. The model was first applied to water + polymer systems, but Wang et al. [35] extended its application to water + salt + alcohol ATPSs. After adapting the model of Guan et al. [34], Equation 1 can be used to determine the composition of the mixture at the points belonging to the binodal curve, where V_{213}^* is the scaled EEV, w_i is the weight fraction of component i , and M_i is the molecular weight of component i .

$$\ln\left(V_{213}^* \frac{w_2}{M_2}\right) + V_{213}^* \frac{w_1}{M_1} = 0 \quad (1)$$

The scaled EEV can be used to assess the capacity of a salt to produce an ATPS. Its value is related to the salting-out ability of the salt. In the same way, the scaled EEV values for a given salt can provide information about the ease with which a water + alcohol mixture would split in the presence of a given amount of salt. Fig. 9 presents the points belonging to the binodal curve at boiling temperature and 101.3 kPa for six systems involving three different salts and the two propanol isomers. In the same figure, the parametric binodal curves at four EEV values (160, 190, 240, 300) have been drawn. As seen, the organic phases can generally (except for the W + NH₄Cl + 1P) be characterized by an EEV value. Nevertheless, the salt contents of the aqueous phases increased at higher rates than the EEV model tended to predict, not following the same parametric curves as those of the organic phases, implying that the model fails to simultaneously represent both the organic and aqueous phases in these systems. Considering the limitations of the model, the experimental data have been fitted with the model using the least squares method, the scaled EEV values have been calculated, and the results are presented in Table 5. For all the systems studied, the scaled EEV values for NaCl were similar or slightly higher than those for KCl. NH₄Cl had a lower EEV value than the other two salts, for the systems involving both alcohols studied.

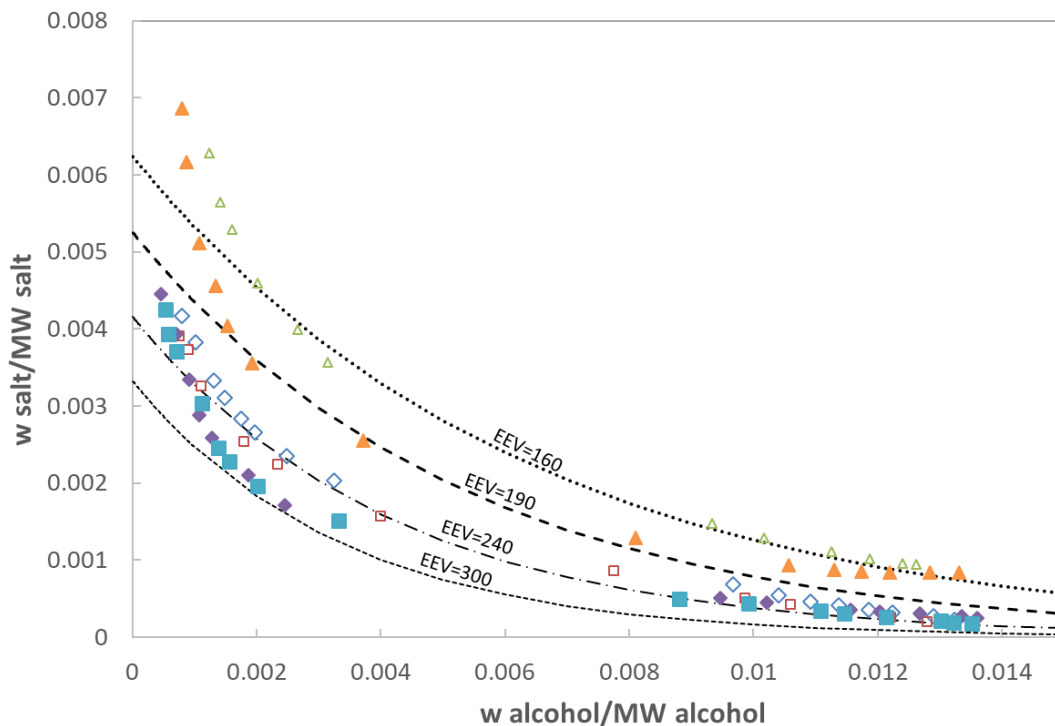


Fig. 9. Experimental binodal curves at boiling temperatures and 101.3 kPa, and binodal curves calculated using the EEV model. \triangle , water + 2-propanol + NH_4Cl ; \blacktriangle , water + 1-propanol + NH_4Cl ; \diamond , water + 2-propanol + NaCl ; \blacklozenge , water + 1-propanol + NaCl ; \square , water + 2-propanol + KCl ; \blacksquare , water + 1-propanol + KCl .

This means that the ability of the salt to split the ATPS studied, as indicated by the EEV values, follows the order $\text{KCl} > \text{NaCl} > \text{NH}_4\text{Cl}$. With higher EEV values, a lower amount of the salt is needed to split the same water + alcohol mixture. The order determined is in accordance with that determined by Hofmeister [36].

Comparing the different alcohols by considering the same salt, the EEV values for 1-propanol were similar or slightly larger than those for 2-propanol. This means that the 1-propanol + water mixture forms an ATPS at a slightly lower salt content compared to that of the system with 2-propanol.

Setchenov-type equation

In order to study the effect of a salt on the non-electrolyte solubility, the Setchenov equation can be employed. In recent years, this equation has been modified to assess the salting-out abilities of salts in ATPS comprised of polymers or alcohols [5, 37-39]. In this case, the Setchenov-type equation used herein is shown as follows:

$$\ln\left(\frac{x_{\text{salt top phase}}}{x_{\text{salt bottom phase}}}\right) = \beta + k(x_{\text{alcohol bottom}} - x_{\text{alcohol top}}) \quad (2)$$

where x is the mole fraction of the corresponding component, k is the salting-out coefficient, and β is the constant related to the activity coefficient. Fitting the liquid-liquid tie lines of the different systems to Equation 2 is possible to obtain the k and β parameters characteristic of

the system. Fig. 10 presents a graphical representation of the data for the systems studied, and performing linear regression enables the parameters to be obtained.

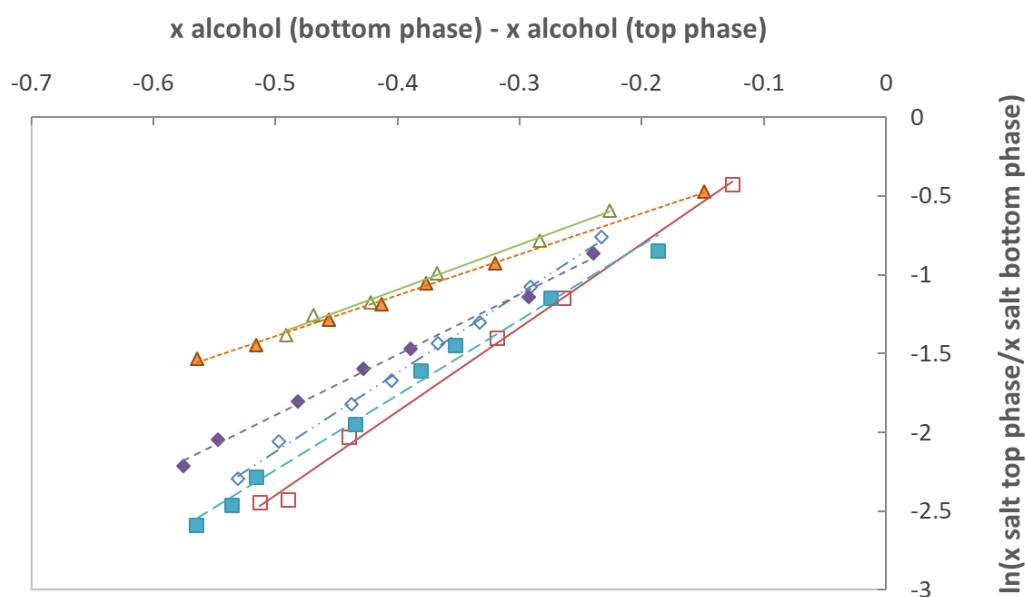


Fig. 10. Experimental binodal LL equilibrium points at boiling temperatures of the studied systems. \triangle , water + 2-propanol + NH_4Cl ; \blacktriangle , water + 1-propanol + NH_4Cl ; \diamond , water + 2-propanol + NaCl ; \blacklozenge , water + 1-propanol + NaCl ; \square , water + 2-propanol + KCl ; \blacksquare , water + 1-propanol + KCl .

In Table 6, the values of the parameters obtained for each system and the correlation coefficients (R^2) are presented. As can be seen in Fig. 10, the tie line data from the studied systems involving NH_4Cl had a linear dependence on the alcohol composition difference in the two phases. However, the data for the other systems exhibited slight curvatures. The NH_4Cl systems exhibited the lowest k coefficients, indicating that an increase in the amount of NH_4Cl produces a new tie line corresponding to a higher increase in the difference between the alcohol contents of the two phases than in the systems involving the other salts. However, more NH_4Cl is needed, in comparison to the other salts studied, to produce the same partial miscibility between the water and the alcohol.

Determination of the plait point

A characteristic point of the systems in which a heterogeneous LL mixture exists is the plait point, which corresponds to the point on the tie line where the composition of both phases is the same. The Hand equation permits the plait point to be obtained via extrapolation of the experimental tie line data [40]. After applying this method, Table 7 shows the compositions corresponding to the plait points for all the systems at their boiling temperatures and 101.3 kPa.

From the data presented in Table 7, it can be seen that the systems with NH_4Cl have plait points corresponding to the highest salt contents, which verifies the order of salting-out power

determined herein and reported previously by Hofmeister [36], where NH_4Cl salt has the lowest salting-out power among the studied salts.

Conclusions

The ATPSs studied, water + KCl + 1-propanol and water + KCl + 2-propanol, exhibited similar behavior regarding the shape and evolution of the different equilibrium regions. The LL region increased in size as the temperature increased, due to the increase in solubility of the salt. Several differences were apparent between the systems involving 1-propanol and 2-propanol. First, the LCST was higher for the 2-propanol system than that for the 1-propanol system, with the water + 2-propanol mixture requiring a higher temperature to split in the presence of a salt. As the temperature was increased to above the LCST, LL regions appeared and became larger as the temperature was increased further up to the boiling point. Second, the proportion of propanol in the binary water + propanol azeotrope was higher for the system with 2-propanol than that for the system with 1-propanol. This caused the direction of the variation in boiling temperature in the LL equilibrium region to change as the salt content corresponding to the tie-line composition increased.

In order to classify the salts and alcohols studied, both in this work and in previous studies, in terms of their ability to form an ATPS, three different techniques have been used: the EEV model; adjustment of the LL equilibrium data with a Setchenov-type equation; and determination of the plait point of the LL equilibrium region at boiling temperature. The salts studied followed the order of salting-out ability reported by Hofmeister [36] ($\text{K}^+ > \text{Na}^+ > \text{NH}_4^+$), meaning that lower concentrations of the salts with K^+ are required to cause phase splitting, in comparison to those of the salts with Na^+ and especially those with NH_4^+ . As for the alcohols, the ATPS with 1-propanol underwent phase splitting at lower temperatures and lower salt contents than the systems with 2-propanol.

The extended UNIQUAC model, employing the parameter values presented in the literature, was able to qualitatively predict the different equilibrium regions of the mixtures present at their boiling temperatures. Nevertheless, some quantitative differences were observed. It is advised that new parameters for this model be determined using the new and consistent experimental data that have been presented herein.

Acknowledgments

The authors wish to thank Dr. Kaj Thomsen for his collaboration and help with the AQSOL software used for calculations. In addition, we would like to thank the "Dirección General de Investigación Científica y Técnica" DGICYT, of Spain for the financial support under project CTQ2014-59496.

References

[1] P. A. Albertsson, *Partition of Cell Particles and Macromolecules*, 3rd ed.; John Wiley & Sons: New York, 1986.

- [2] H. Walter, D. Brooks, D. Fisher, Partitioning in Aqueous Two-phase Systems: Theory, Methods, Uses, and Applications to Biotechnology, Academic Press, New York, 1985.
- [3] H. Hustedt, K.H. Kroner, M.R. Kula, I.H. Walter, D. Brooks, D. Fisher (Eds.), Partitioning in Aqueous Two-phase Systems, Academic Press, New York, 1985. pp. 529–587.
- [4] W. Guo, J. Ma, Y. Wang, J. Han, Y. Li, S. Song, Liquid–liquid equilibrium of aqueous two-phase systems composed of hydrophilic alcohols (ethanol/2-propanol/1-propanol) and $MgSO_4/ZnSO_4$ at (303.15 and 313.15)K and correlation. *Thermochim. Acta* 2012, 546, 8–15.
- [5] E. Nemati-Kande, H. Shekaari, S. A. Jafari, Liquid–liquid equilibrium of 1-propanol, 2-propanol, 2-methyl-2-propanol or 2-butanol+sodium sulfite+water aqueous two phase systems. *Fluid Phase Equilib.* 2012, 329, 42–54.
- [6] S. M. Arzideh, K. Movagharnejad, M. Pirdashti, Influence of the Temperature, Type of Salt, and Alcohol on Phase Diagrams of 2-Propanol + Inorganic Salt Aqueous Two-Phase Systems: Experimental Determination and Correlation. *J. Chem. Eng. Data.* 2018, 63, 8, 2813-2824.
- [7] J. Wang, Y. Zhang, Y. Wang, Liquid–Liquid Equilibria for 1-Propanol (or 2-Propanol)–Water Systems Containing Potassium Fluoride. *J. Chem. Eng. Data* 2002, 47, 110-112.
- [8] H. Katayama, K. Kitagawa, Liquid–Liquid Phase Equilibria of (1-Propanol or 2-Propanol + Water) Containing Dipotassium Hydrogen Phosphate. *J. Chem. Eng. Data* 2006, 51, 2103-2106.
- [9] A. Salabat, M. Hashemi, Temperature Effect on the Liquid–Liquid Equilibria for Some Aliphatic Alcohols + Water + K_2CO_3 Systems. *J. Chem. Eng. Data* 2006, 51, 1194-1197.
- [10] E. Nemati-Knade, H. Shekaari, S. A. Jafari, Thermodynamic study of aqueous two phase systems for some aliphatic alcohols +sodium thiosulfate+water. *Fluid Phase Equilib.* 2012, 321, 64-72.
- [11] E. Nemati-Kande, H. Shekaari, M. T. Zafarani-Moattar, Binodal Curves and Tie-Lines of Aliphatic Alcohols + Diammonium Hydrogen Citrate + Water Ternary Systems: Measurement and Modeling. *J. Chem. Eng. Data* 2012, 57, 1678–1688.
- [12] J. Timmermans, Critical Solubility Temperatures of Ternary Mixtures. *Z. physik. Chem.* 1907, 58, 129-31.
- [13] J. Garcia-Cano, V. Gomis, J. C. Asensi, A. Gomis A. Font, Phase diagram of the vapor-liquid-liquid-solid equilibrium of the water + NaCl + 1-propanol system at 101.3 kPa. *J. Chem. Therm.* 116, 2018, 352-362
- [14] J. Garcia-Cano; A. Gomis; A. Font; M. D. Saquete; V. Gomis, Consistency of experimental data in SLLV equilibrium of ternary systems with electrolyte. Application to the water + NaCl + 2-propanol system at 101.3 kPa. *J. Chem. Thermo.* 2018, 124, 79-89
- [15] A. Gomis, J. Garcia-Cano, A. Font, V. Gomis, SLLE and SLLVE of the water + NH_4Cl + 1-propanol system at 101.3 kPa. *Fluid Phase Equilib.* 2018, 465, 51-57
- [16] P.Wang, Anderko A., R.D. Young, A speciation-based model for mixed solvent electrolyte systems. *Fluid Phase Equilib.* 2002, 203, 141-176

- [17] K. Thomsen, M. C. Iliuta, P. Rasmussen, Extended UNIQUAC model for correlation and prediction of vapor-liquid-liquid-solid equilibria in aqueous salt systems containing non-electrolytes. Part B. Alcohol (ethanol, propanols, butanols)-water-salt systems. *Chem. Eng. Sci.* 2004, 59, 3631-3647
- [18] C.C. Chen, Y. Song, Generalized electrolyte-NRTL model for mixed-solvent electrolyte system. *AIChE J.* 2004, 50, 1928-1941
- [19] R. Cohen-Adad, J.W. Lorimer, Solubility Data Series, International Union of Pure and Applied Chemistry (IUPAC). Vol. 47 Pergamon Press, Oxford, 1991.
- [20] V. Gomis, F. Ruiz, G. de Vera, E. Lopez, M.D. Saquete, Liquid-liquid-solid equilibria for the ternary systems water – sodium chloride or potassium chloride – 1-propanol or 2-propanol. *Fluid Phase Equilib.* 1994, 98, 141-147.
- [21] T.-J. Chou, A. Tanioka, H.-C. Tseng, Salting Effect on the Liquid-Liquid Equilibria for the Partially Miscible Systems of n-Propanol-Water and i-Propanol-Water. *Ind. Eng. Chem. Res.* 1998, 37, 2039-2044.
- [22] H.-Y. Guo, M.-C. Hu, Q.-G. Zhai, S.-N. Li, Y.-C. Jiang, M.-X. Wang, Liquid-liquid-solid Equilibrium for Two Quaternary Systems Potassium Chloride +Rubidium Chloride + ½-Propanol + Water at 25degC. *Chin. J. Chem.* 2008, 26, 2179-2184
- [23] J. Chen; Y. Zhong; J. Han; M. Su; X. Shi, Liquid-liquid equilibria for water + 1-propanol (or 1-butanol) + potassium chloride + ammonium chloride quaternary systems at 298.15 K. *Fluid Phase Equilib.* 2015, 397, 50-57.
- [24] G. Khayati, A. Gholitabar, Liquid-Liquid Equilibrium of Hydrophilic Alcohols with Three Different Salts of Chloride: Experimental and Correlation . *J. Chem. Eng. Data* 2016, 61, 1454-1461.
- [25] Ch.-L. Lin, L.-S. Lee, H.-Ch. Tseng, Phase Equilibria for Propan-1-ol + Water + Sodium Chloride and + Potassium Chloride and Propan-2ol + Water + Lithium Chloride and + Lithium Bromide, *J. Chem. Eng. Data* 1993, 38, 306-309.
- [26] A. I. Johnson, W. F. Furter, Salt Effect in Vapor-Liquid Equilibrium, Part II. *Can. J. Chem. Eng.*, June, (1960) 78-86.
- [27] V. Gomis, F. Ruiz, N. Boluda, M.D. Saquete, The influence of temperature on the liquid-liquid-solid equilibrium of the ternary system water-potassium chloride-2-propanol. *Fluid Phase Equilib.* 1997, 130, 223-229.
- [28] K.K. Il'in, D.G. Cherkasov, S.A. Yukushev, Polythermal study of salting-out of isopropyl alcohol from aqueous solutions with potassium chloride and bromide. *Russian Journal of General Chemistry* 1998, 68, 227-233.
- [29] Y. Zhong, J. Chen, J. Han, M. Su. Y. Li, A. Lu, The influence of temperature on liquid-liquid-solid equilibria for (water + 2-propanol + KCl +NH₄Cl) quaternary system. *Fluid Phase Equilib.* 2016, 425, 158-168.
- [30] G.W. Ferner, M.G. Mellon, Analytical Uses of 2-Propanol. *Ind. Eng. Chem. Anal. Ed.* 1934, 6, 345

- [31] P.M. Ginnings, Z.T. Chen, Ternary Systems: Water, Isopropanol and Salts at 25 C. J. Am. Chem. Soc. 1931, 53, 3765-3769.
- [32] A. Gomis, J. Garcia-Cano, A. Font, V. Gomis, Influence of the temperature on the equilibrium phase diagram of the ternary system water + ammonium chloride + 2-propanol at 101.3 kPa. J. Chem. Therm. 2019, 131, 33-39.
- [33] A. Gomis, J. Garcia-Cano, J. C. Asensi, V. Gomis, Equilibrium Diagrams of Water + NaCl or KCl + 2-Methyl 2-Propanol at the Boiling Temperature and 101.3 kPa. J. Chem. Eng. Data 2018, 63, 4107-4113.
- [34] Y. Guan, T.H. Lilley, T.E. Treffry, A new excluded volume theory and its application to the coexistence curves of Aqueous Polymer Two-Phase Systems. Macromolecules 1993, 26, 3971-3979.
- [35] Y. Wang, Y. Yan, Sh. Hu, J. Han, X. Xu, Phase diagrams of ammonium sulfate + Ethanol/1-propanol/2-propanol + water Aqueous Two-Phase Systems at 298.15 K and correlation. J. Chem. Eng. Data 2010, 55, 876-881.
- [36] F. Hofmeister. Arch. Exp. Pathol. Pharmacol. 1888, 24, 247-260.
- [37] R. Duraiyya, S. Arumugam, S. Settu, Equilibrium phase behavior of poly (ethylene glycol) 4000 and biodegradable salts at various temperatures [(20, 30, and 40) °C]. J. Chem. Eng. Data 2012, 57, 1112-1117.
- [38] C. Yu, J. Han, Y. Wang, Y. Yan, S. Hu, Y. Li., X. Zhao, Liquid-liquid equilibrium composed of imidazolium tetrafluoroborate ionic liquids + sodium carbonate aqueous two-phase systems and correlation at (288.15, 298.15, and 308.15) K. Thermochim. Acta 2011, 23, 221-226.
- [39] S.C. Lo, R.N. Ramanan, B.T. Tey, T.Ch. Ling, P.L. Show, Ch.W. Ooi, , Liquid-liquid equilibrium of alcohols + ammonium/potassium/sodium acetate +water systems: experimental and correlation. J. Chem. Eng. Data 2015, 60, 2848-2857.
- [40] R. E. Treybal. Liquid extraction (2 ed.). McGraw-Hill, New York, 1963.

Table 1. Specifications of chemical compounds.

Chemical (CAS number)	Provider	Initial purity (mass fraction)	Water content KF ^a (mass fraction)	Purification method	Analysis method
KCl (7447-40-7)	VWR	> 0.999		none	
1-Propanol (71-23-8)	Merck	> 0.995	0.0006	none	GC ^b
2-Propanol (67-63-0)	Merck	> 0.995	0.0009	none	GC ^b
Ethanol (64-17-5)	VWR	> 0.998	0.0002	none	GC ^b

^a KF = Karl Fischer Technique

^b GC = Gas chromatography

Table 2. Equilibrium data (mole fraction) of the water + KCl + 1-propanol (1P) system at the boiling temperature (T) and 101.3 kPa.

	Salt	Liquid phase I		Liquid phase II		Vapor phase
T/K	KCl	KCl ²	1P ¹	KCl ²	1P ¹	1P ¹
SLLV						
361.50	1	0.104	0.013	0.0078	0.578	0.497
LLV						
360.99		0.035	0.077	0.015	0.264	0.434
360.99		0.044	0.045	0.014	0.320	0.438
361.02		0.051	0.035	0.012	0.388	0.446
361.03		0.055	0.031	0.011	0.412	0.448
361.12		0.070	0.026	0.010	0.461	0.458
361.28		0.088	0.017	0.009	0.533	0.475
361.32		0.094	0.014	0.008	0.550	0.480
SLV						
361.51	1	0.0070	0.596			0.501
361.78	1	0.0040	0.654			0.522
361.98	1	0.0029	0.692			0.539
362.61	1	0.0015	0.755			0.574
363.75	1	0.0008	0.818			0.626
364.17	1	0.0007	0.838			0.648
365.12	1	0.0005	0.872			0.706
365.50	1	0.0004	0.884			0.727
365.80	1	0.0003	0.894			0.743
366.61	1	0.0002	0.920			0.788
367.58	1	0.0003	0.926			0.840
LV						
360.77		0.0024	0.441			0.442
360.94		0.0025	0.267			0.414
360.90		0.0064	0.265			0.418
360.91		0.0119	0.257			0.429
360.94		0.0145	0.258			0.432
361.05		0.0019	0.192			0.409
361.01		0.0049	0.188			0.412
361.03		0.0090	0.188			0.416
360.98		0.0136	0.182			0.421
360.97		0.0205	0.184			0.431
361.20		0.0013	0.109			0.400
361.16		0.0053	0.105			0.406
361.18		0.0136	0.100			0.411

361.09	0.0210	0.097	0.417
360.99	0.0253	0.099	0.424
360.98	0.0294	0.090	0.431
362.42	0.0041	0.048	0.383
362.19	0.0107	0.045	0.385
362.10	0.0150	0.043	0.391
361.91	0.0197	0.041	0.396
361.77	0.0239	0.039	0.402
361.58	0.0307	0.035	0.408
361.50	0.0358	0.035	0.415
361.36	0.0471	0.032	0.429
361.07	0.0232	0.120	0.428
361.00	0.0147	0.194	0.427
360.96	0.0217	0.153	0.426

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

Relative standard uncertainties: $u_r(x) = \frac{u}{x}$ is 0.02, except for the mole fraction of KCl in the phases with $x_{\text{salt}} < 0.01$, in which its relative standard uncertainty is 0.05.

¹obtained by GC-TCD

²obtained by gravimetric analysis

Table 3. Equilibrium data (mole fraction) of the water + KCl + 2-propanol (2P) system at the boiling temperature (T) and 101.3 kPa.

T/K	Solid		Liquid phase I		Liquid phase II		Vapor phase
	KCl	KCl ²	2P ¹	KCl ²	2P ¹	2P ¹	
SLLV							
353.62	1	0.0943	0.0181	0.0082	0.531	0.648	
LLV							
354.14		0.0521	0.0544	0.0165	0.319	0.613	
354.04		0.0586	0.0416	0.0144	0.360	0.614	
354.21		0.0381	0.0969	0.0249	0.223	0.603	
353.81		0.0762	0.0259	0.0100	0.466	0.633	
353.68		0.0893	0.0215	0.0079	0.511	0.637	
SLV							
353.58	1	0.0076	0.532			0.654	
353.52	1	0.0068	0.556			0.656	
353.50	1	0.0057	0.583			0.659	
353.43	1	0.0035	0.638			0.674	
353.38	1	0.00098	0.736			0.720	
353.44	1	0.00049	0.790			0.752	
353.68	1	0.00017	0.838			0.793	
372.34	1	0.113	0.0019			0.271	
359.79	1	0.103	0.0075			0.567	
361.70	1	0.106	0.0056			0.530	
353.79	1	0.0973	0.0180			0.644	
353.88	1	0.0980	0.0156			0.647	
LV							
354.26		0.022	0.241			0.622	
359.86		0.071	0.012			0.562	
373.19		0.008	0.002			0.144	
359.28		0.069	0.015			0.557	
355.07		0.002	0.217			0.560	
356.14		0.004	0.098			0.538	
355.8		0.008	0.098			0.553	
355.57		0.011	0.096			0.554	
359.78		0.005	0.035			0.453	
359.69		0.011	0.034			0.468	
359.26		0.016	0.032			0.493	

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

Relative standard uncertainties: $u_r(x) = \frac{u}{x}$ is 0.02, except for the mole fraction of KCl in the phases with $x_{\text{salt}} < 0.01$, in which its relative standard uncertainty is 0.05.

¹obtained by GC-TCD

²obtained by gravimetric analysis

ACCEPTED MANUSCRIPT

Table 4. Equilibrium data (mole fraction) of the water + KCl + 1-propanol (1P) system at 268.1 and 273.1 K and 101.3 kPa.

T/K	Solid	Liquid phase I		Liquid phase II		
	KCl	KCl ²	1P ¹	KCl ²	1P ¹	
268.1			SL			
	1	0.0317	0.100			
	1	0.0232	0.195			
	1	0.0152	0.296			
	1	0.0093	0.396			
	1	0.0050	0.494			
	1	0.0024	0.592			
	1	0.0003	0.797			
273.1			SL			
	1	0.0060	0.497			
	1	0.0023	0.603			
	1	0.0004	0.702			
	1	0.0002	0.799			
			SLL			
	1	0.0415	0.0599	0.0137	0.392	
			LL			
			0.0397	0.0695	0.0159	0.345
			0.0354	0.0924	0.0180	0.295

Standard uncertainties: $u(T) = 0.3$ K, $u(P) = 2$ kPa

Relative standard uncertainties: $u_r(x) = \frac{u}{x}$ is 0.02, except for the mole fraction of KCl in the phases with $x_{\text{salt}} < 0.01$, in which its relative standard uncertainty is 0.05.

¹obtained by GC-TCD

²obtained by gravimetric analysis

Table 5. Calculated scaled EEV values for different water + salt + alcohol systems at their boiling temperatures and 101.3 kPa.

Alcohol	Salt	Scaled EEV
1P	KCl	231
2P	KCl	232
1P	NaCl	226
2P	NaCl	216
1P	NH ₄ Cl	163
2P	NH ₄ Cl	155

Table 6. Parameter values and regression coefficients of the Setchenov-type equation obtained using experimental VLL equilibrium data at 101.3 kPa for each water + salt + alcohol system studied.

Alcohol	Salt	β	k	R ²
1P	KCl	0.14	4.74	0.990
2P	KCl	0.26	5.32	0.997
1P	NaCl	0.03	3.84	0.996
2P	NaCl	0.39	5.01	0.997
1P	NH ₄ Cl	-0.09	2.59	0.998
2P	NH ₄ Cl	0.05	2.86	0.993

Table 7. Plait points (shown as the corresponding mole fractions of each component) of the water + salt + alcohol systems, calculated using the Hand equation.

Alcohol	Salt	x_{water}	x_{salt}	x_{alcohol}	T/K
1P	KCl	0.768	0.020	0.212	360.9
2P	KCl	0.806	0.029	0.165	354.3
1P	NaCl	0.764	0.019	0.217	361.0
2P	NaCl	0.767	0.029	0.204	354.1
1P	NH ₄ Cl	0.784	0.046	0.170	361.5
2P	NH ₄ Cl	0.749	0.061	0.190	354.3

Standard uncertainties: $u(T) = 0.3$ K

Relative standard uncertainties: $u_r(x) = \frac{u}{x}$ is 0.02 for water, 0.04 for the salt and 0.05 for the alcohol.

Highlights

- Vapor-liquid-liquid equilibrium data were determined.
- Vapor-liquid-solid and vapor-liquid-liquid-solid equilibrium data were determined.
- The effects of changes to the salt or propanol isomer are studied.
- The LCST has been determined for the system water + KCl + 1-propanol
- The effect of temperature on the LCST has been studied.

ACCEPTED MANUSCRIPT