

# Equilibrium diagrams of water + NaCl or KCl + 2-methyl 2-propanol at the boiling temperature and 101.3 kPa

*Alejandro Gomis, Jorge Garcia-Cano, Juan Carlos Asensi, Vicente Gomis\**

Chemical Engineering Department, University of Alicante, PO Box 99, E-03080 Alicante, Spain

## KEYWORDS

Water; 2-methyl 2-propanol; NaCl; KCl; Solid-liquid-liquid; Solid-liquid-liquid-vapor; Phase diagram, boiling temperature

## ABSTRACT

Experimental equilibrium data of the systems water + NaCl or KCl+ 2-methyl 2-propanol are determined experimentally at boiling conditions and 101.3 kPa. The results obtained permit a study of the shape and different regions of their equilibrium diagrams. A comparison with similar diagrams of other alcohols is made, demonstrating that the ability of NaCl and KCl to split the water + alcohol mixture into two liquid phases increases with temperature and that NaCl splits the alcohols from water in the following order: 2-methyl 2-propanol >1-propanol> 2-propanol.

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

## INTRODUCTION

It is well-known that the presence of an electrolyte causes a significant change in the liquid-Vapor (LV) and liquid-liquid (LL) equilibrium of systems containing water + organic solvents. The mechanism by which this occurs involves an alteration of the intermolecular forces, especially hydrogen bonding. This effect of the salt on the LV equilibrium suggests a potential application as a separation technique in many industrial processes including extractive distillation or regeneration of solvents. Obviously, for design calculations, it is necessary to have the equilibrium phase diagram of the involved mixed solvent electrolyte system.

In the 1970s, Furter et al. (1-3) reported LV equilibria of several mixed solvent electrolyte systems and made an attempt to devise a theory of the salt effect on the LV equilibrium. Since then, experimental studies on the effects of the salt on the LV equilibrium and, correspondingly, the literature available on these systems, have remained scant (4), and the relatively small amount of existing experimental data is incomplete, with some even containing important inconsistencies (5, 6).

Two examples of such mixed solvent electrolyte systems are the ternary mixtures water + NaCl or KCl + 2-methyl 2-propanol (tert-butyl alcohol (TB)). The pair water + 2-methyl 2-propanol is completely miscible and presents a minimum boiling azeotrope at 101.3 kPa and  $352.8 \pm 0.3$  K, with a mole fraction of 2-methyl 2-propanol of  $0.64 \pm 0.02$  (obtained as mean value and standard deviation of the twelve azeotropic data values reported in (7)).

Moreover, the presence of salt (NaCl or KCl) can split the above miscible system into two liquid phases at 298.1 K (8). However, the influence of the salts on the equilibria of these systems, with

respect to the shape of the various regions of their equilibrium diagrams, or the effect on the azeotropic mixture water + 2-methyl 2-propanol, has not been addressed in the literature.

In this work, we report experimental LV (liquid-vapor), LLV (liquid-liquid-vapor), SLV (solid-liquid-vapor) and SLLV (solid-liquid-liquid-vapor) equilibrium data for water + NaCl + 2-methyl 2-propanol and water + KCl + 2-methyl 2-propanol at 101.3 kPa. The results obtained permit a study of the shape and various regions of these two systems' isobaric phase diagrams, as well as a comparison with similar diagrams of other alcohols, all with a view to contributing to a greater understanding of these mixed solvent electrolyte systems.

## MATERIALS AND METHODS

### Chemicals

Ultrapure water with conductivity less than 1  $\mu\text{S}/\text{cm}$  was obtained by means of a MiliQPlus system. The other chemicals used in this work are summarized and described in table 1. Ethanol appears because it served as an internal standard for quantitative chromatographic analysis.

### Experimental Method

All the LV, LLV, SLV and SLLV phase equilibrium determinations were carried out using a modified vapor-liquid Fischer Labodest unit (Fischer Labor und Verfahrenstechnik). This unit consists of a dynamic Gillespie still equipped with two internal recirculations: one for the vapor phase and the other for the liquid (in the case of LV), liquid+solid (SLV), two liquids (LLV) or two liquids and a solid (SLLV). The modification and operation of the unit is detailed in a previous paper (9). It has also been fitted with an ultrasonic transducer to enhance mixing,

dispersion and mass transfer of the various phases and has been tested successfully on solids (5-6).

To carry out an experiment, a mixture of water + salt + 2-methyl 2-propanol is placed in the boiling flask. There, it is heated at a pressure of 101.3 kPa, which is maintained by means of a pressure controller (Mensor CPC 3000) and a Fisher M101 phase equilibrium control system.

When equilibrium has been reached, the boiling temperature is measured using a digital thermometer (Hart Scientific 5615). Then, samples of the condensed vapor and of the liquid, liquid+liquid or solid+liquid+liquid flowing through the recirculation, are taken and separated at the boiling temperature (that is, if they contain more than one phase), and subsequently analyzed.

For this analysis, a liquid sample is introduced into a vial with a known amount of ethanol, which serves as an internal standard. The sample is then analyzed by gas chromatography to determine its water and 2-methyl 2-propanol content. Another aliquot of the liquid sample is collected and its salt concentration is determined after drying it to constant weight at 403.1 K.

The gas chromatograph is a Shimadzu GC14B equipped with a Thermal Conductivity Detector (TCD) using a 100 mA current. The separation of the compounds is performed in a 2 m x 3 mm 80/100 Porapak Q packed column. Glass wool is placed inside the glass insert to avoid NaCl and KCl entering the column. Helium is used as a carrier gas at a flow rate of 25 mL/min, and the temperatures of the oven, injector and detector are 463.15 K, 483.15 K and 483.15 K respectively.

The correct functioning of the equipment and appropriateness of the methodology have been verified by determining several LV equilibrium points for the binary system water + 2-methyl 2-propanol. The results exhibit perfect agreement with the experimental LV equilibrium data in the

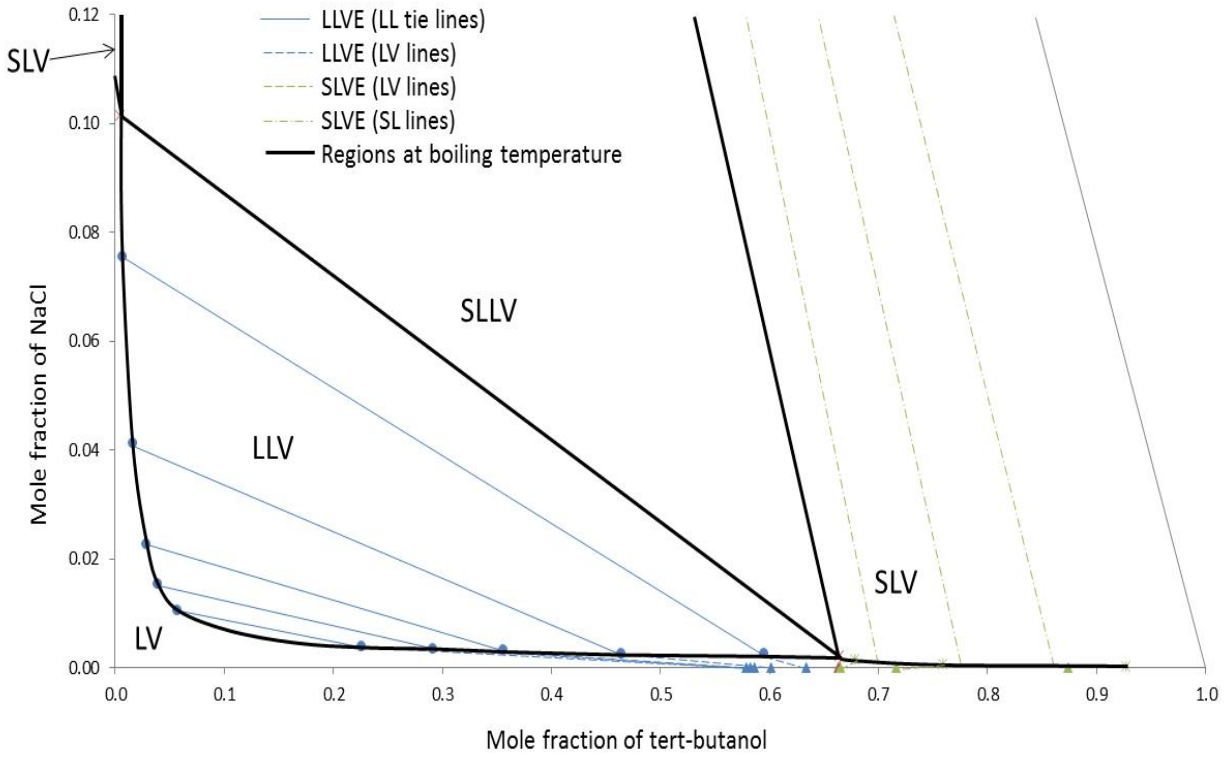
literature: an azeotropic temperature of 352.88 K for the mixture water + 2-methyl 2-propanol and an azeotropic composition of 0.65 mole fraction in 2-methyl 2-propanol, are obtained as can be seen in supplementary data.

The uncertainties were determined by a statistical calculation of repeated measurements. The temperature standard uncertainty ( $u$ ) in the SLLV determinations is 0.06 K. The composition ( $x_1 = x_2$ ) is 2% for all components except for the NaCl and KCl in the organic phases containing low concentrations of the salt. The relative uncertainty, in this case, is 5%.

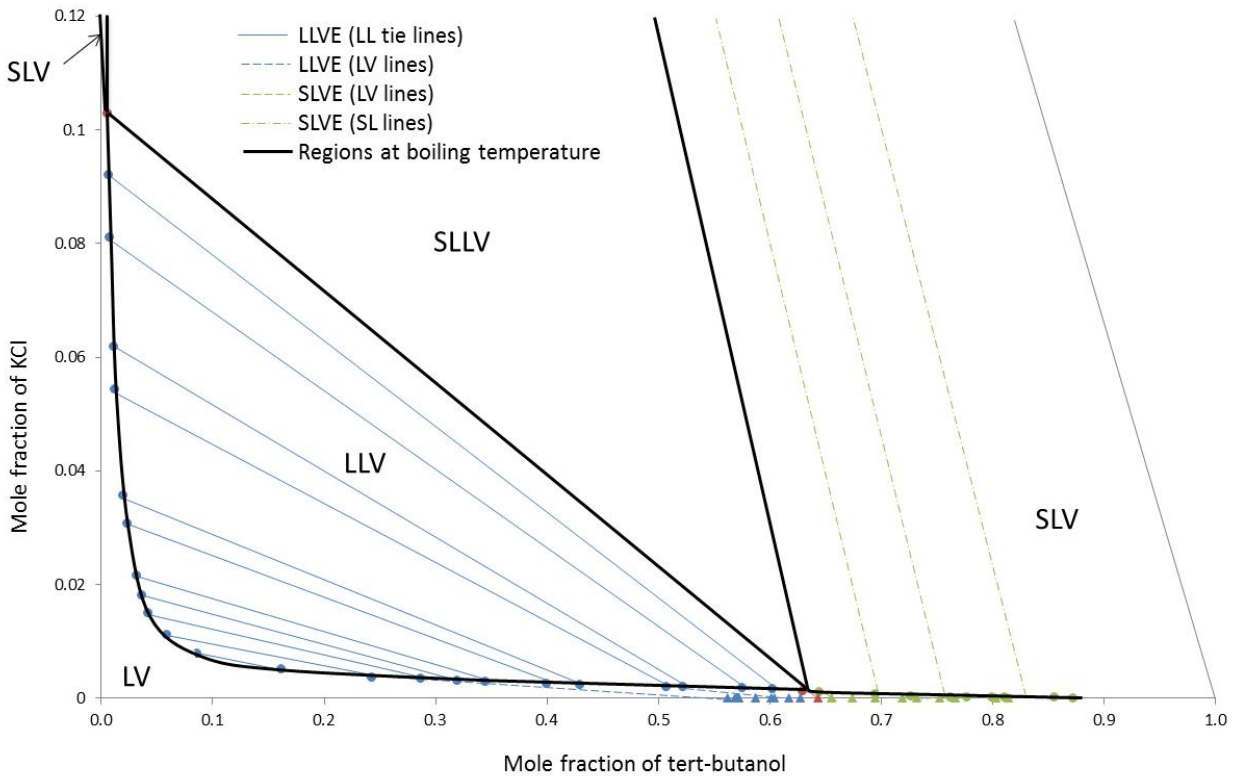
## RESULTS

Equilibrium data and boiling temperatures of different mixtures in each of the two systems are shown in tables 2 and 3. These tables are divided into different sections, corresponding to the different regions of the equilibrium diagram. The experimental data for two liquid phases and those saturated in salt are plotted in Figs. 1 and 2, which show the various boundaries of the LV, SLV, LLV and SLLV equilibrium regions, the tie lines of the LLVE region, and the lines joining several organic phases with the points that represent the vapor phase.

The results show that there is a very small difference of less than 1 K between some of the critical points in each system: the azeotropic temperature of the binary system water + tertbutanol is 352.8 K (7)); the temperatures of the LLV plait point in both systems are approximately 353.8 K; and the temperatures of the SLLV invariant are 352.9 K. Consequently, the presence of salt in all the mixtures, with a salt-free basis mole fraction of 2-propanol in the range 0.10-0.75, modifies the boiling temperatures of both systems only very slightly.



**Fig. 1.** Phase diagram (mole fraction) for the water + NaCl + 2-methyl 2-propanol (TB) system at the boiling temperature and 101.3 kPa. Continuous lines = LL tie lines. Dashed lines = LV lines. Dashed lines with dots = SL lines. ● = liquid compositions. ▲ = vapor compositions

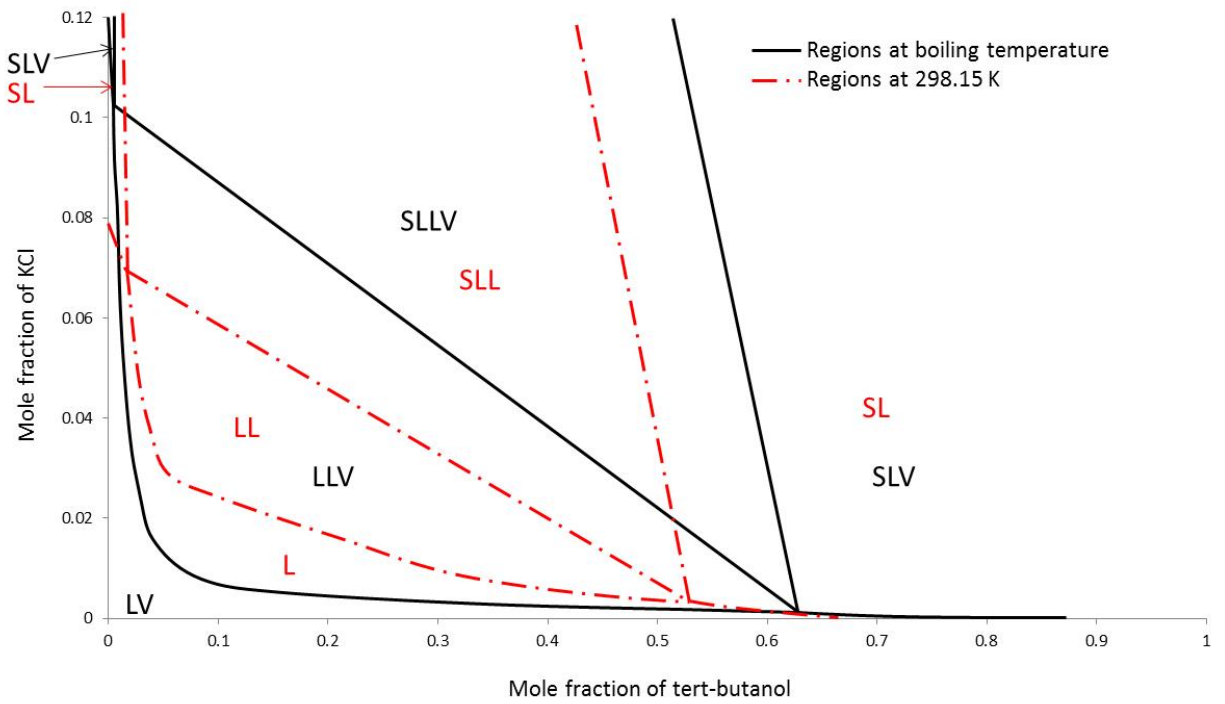
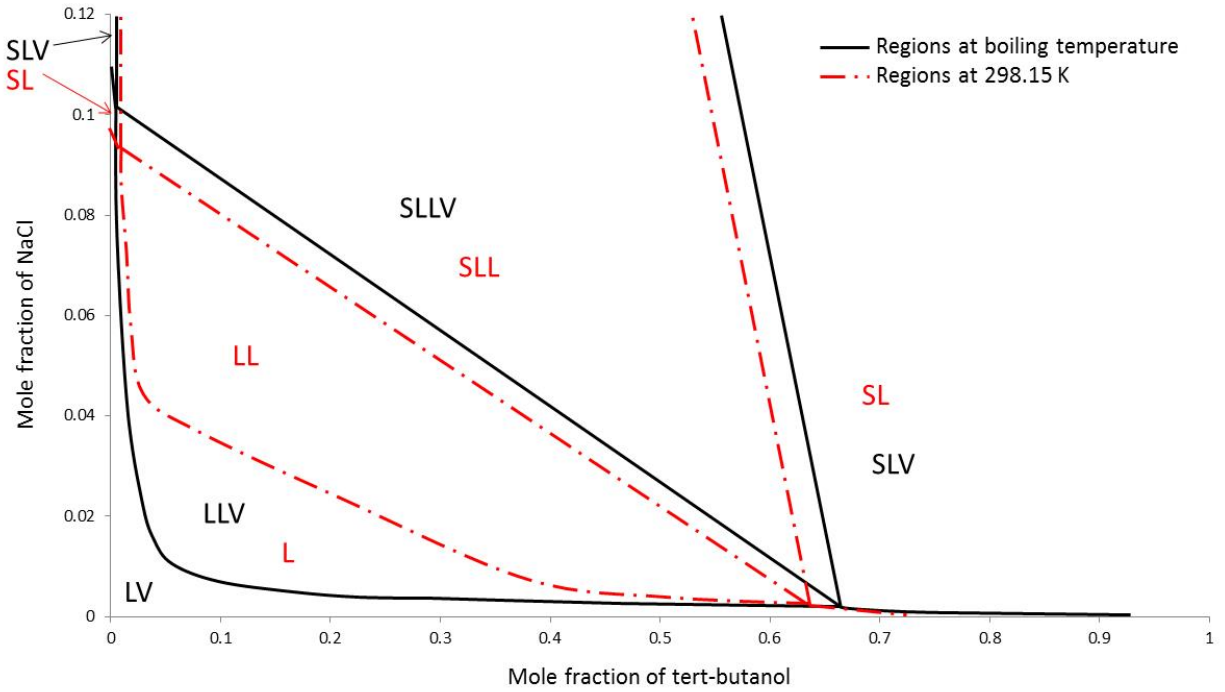


**Fig. 2.** Phase diagram (mole fraction) for the water + KCl + 2-methyl 2-propanol (TB) system at the boiling temperature and 101.3 kPa. Continuous lines = LL tie lines. Dashed lines = LV lines. Dashed lines with dots = SL lines. ● = liquid compositions. ▲ = vapor compositions

The location of the plait point of the two systems was estimated by the classical method of the intersection of the plot of the Hand equation and the solubility line (10): The results are shown in table 4. It also shows the plait points calculated by the same method for the systems with TB at 25° (8), and systems with NaCl and 1-propanol (1P) (5) and 2-propanol (2P) (11) at the boiling temperature.

**Effect of the temperature.** For each salt, Fig. 3 shows a comparison of equilibrium diagrams at low temperature (8) and at the boiling point. The shapes of the different regions are very similar in all of them. However, one can see how the temperature increases the size of the region corresponding to two liquid phases. In both cases, an increase in temperature lowers the concentration of salt that is needed to produce the splitting into two liquid phases. The effect also manifests through the value of the mole fraction of salt at the plait point, which is reduced by half for an increase of temperature from 298.15 K to the boiling temperature. Moreover, the size of the LLE region increases more in its upper area in the presence of  $K^+$  than  $Na^+$ , since the solubility of KCl in water rises more rapidly with temperature than in the case of NaCl.

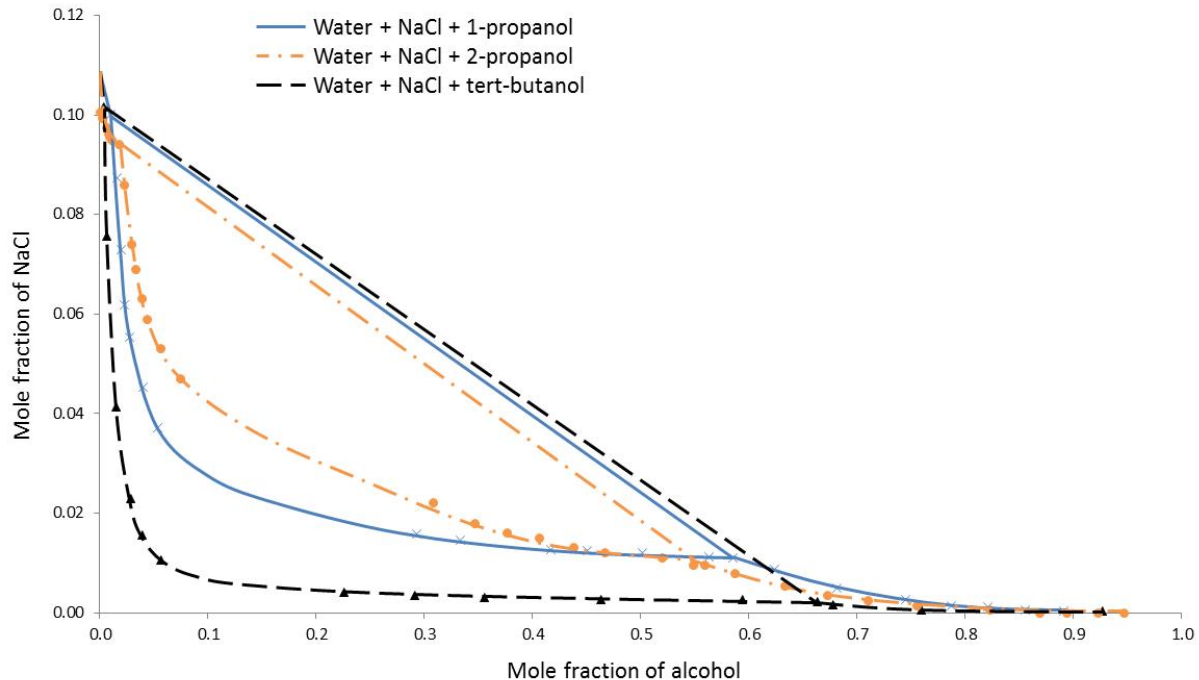




**Fig. 3.** Phase diagrams (mole fraction) for the water + NaCl or KCl + 2-methyl 2-propanol (TB) systems at 298.15 K and at the boiling temperature and 101.3 kPa. Continuous line = regions at boiling temperature. Dashed lines with dots = regions at 298.15 K

The above phenomenon was studied previously for the same alcohol and different salts (12-13), but at temperature difference of only 20 K. It was found that the effect of the temperature on the concerned systems was negligible or very small. However, in this work we find a marked increase in the ability of the salts to separate phases as the temperature rises.

**Effect of the alcohol.** The ability of NaCl to split the alcohol water mixture into two liquid phases, as a function of the identity of the alcohol, has been also studied. This ability increases in the order  $2P < 1P < TB$  as evidenced in Fig. 4. There, one can see how the region of two liquid phases grows in that order or, how the composition of the plait point shows that the concentration of salt necessary to split the alcohol-water mixture into two liquids, decreases from 0.0286 for 2-propanol to 0.0049 for 2-methyl 2-propanol. The longer carbon chain of TB causes the solubility of the alcohol in water to decrease a lot more in the presence of salt. With respect to 1P and 2P, in spite of possessing the same carbon number, the differences remain marked. This effect can be explained by considering the relative interaction strengths of alcohol-alcohol or alcohol-water molecules due to the differing polar nature and ability of water and alcohol to self and cross-associate. The boiling point of 1P is 15 K higher than that of 2P, which indicates that the alcohol-alcohol interaction is relatively stronger than the alcohol-water interaction in 1P. Consequently, less salt is needed to split the water + 1P mixture into two phases since a more stable and richer alcohol phase forms.



**Fig. 4.** Phase diagrams (mole fraction) for the water + NaCl + 1-propanol (continuous lines), 2 propanol (dashed lines with dots) or 2-methyl 2-propanol (dashed lines) systems at the boiling temperature and 101.3 kPa

**Application of the extended UNIQUAC model.** Finally, the extended UNIQUAC model and AQSOL software, with parameters taken from (14), have been used to calculate the equilibrium of both systems containing TB. The equilibrium diagrams obtained at 298.15 K are reproduced correctly, but at temperatures above 330 K, the results are unrealistic since the model estimates that both salts are very soluble in alcohol. The region representing the two liquid phases even disappears.

It should be noted that the various systems that were correlated in order to obtain the parameters employed here, include water + NaCl or KCl + TB at 298.15 K, but not at another temperature since

there are no previously published data available. In addition, there is no equilibrium data available for systems with TB containing the Cl<sup>-</sup> ion in combination with other cations, at temperatures above 300 K. It is therefore not surprising that the calculated results do not correctly predict the equilibria of those systems at such temperatures. Thus, based on the reliable experimental data reported here, it will be necessary to review the parameters of the model. The new parameters should correctly reproduce the influence of temperature on the shape of the equilibrium diagram.

## CONCLUSIONS

Equilibrium data representing the various regions of the phase diagrams of water + NaCl + 2-methyl 2-propanol and water + KCl+ 2-methyl 2-propanol, at boiling conditions and 101.3 kPa, have been determined experimentally.

The presence of these two salts splits a totally miscible mixture such as water + TB into two liquid phases and the extent of splitting increases with temperature. From 298.15 K to the boiling temperatures, less salt is needed to split the liquid mixture into two liquid phases. Comparing different alcohols, the ability of NaCl to split water + alcohol mixtures follows the order 2-methyl 2-propanol > 1-propanol > 2-propanol.

Finally, it will be necessary to review the interaction parameters of the extended UNIQUAC model, including equilibrium data at temperatures higher than 300 K, to correctly reproduce the behavior of these systems with rising temperature.

## Supporting Information

“Associated Content: [Experimental VLE data for water + tertbutanol binary system, comparison with azeotropic data from literature]

## ACKNOWLEDGMENT

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Table 1. Chemicals used

Chemical	Provider	Initial purity (mass %)	Analysis method	Water content KF <sup>a</sup> (mass %)	Purification method
NaCl	VWR	> 99.9			none
KCl	Merck	>99.5			none
2-Methyl 2-Propanol (TB)	VWR	> 99.9	GC <sup>b</sup>	0.02	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. Equilibrium data (mole fraction) of the water + NaCl + 2-methyl 2-propanol (TB) system at the boiling temperature (T) and 101.3 kPa.

T/K	Solid		Liquid phase I			Liquid phase II			Vapor phase	
	NaCl	Water <sup>1</sup>	NaCl <sup>2</sup>	TB <sup>1</sup>	Water <sup>1</sup>	NaCl <sup>2</sup>	TB <sup>1</sup>	Water <sup>1</sup>	TB <sup>1</sup>	
SLLV										
352.95	1	0.334	0.0022	0.664	0.895	0.102	0.0040	0.342	0.658	
LLV										
353.75		0.770	0.0040	0.226	0.933	0.0106	0.0567	0.423	0.577	
353.63		0.705	0.0036	0.291	0.946	0.0156	0.0388	0.420	0.580	
353.49		0.641	0.0031	0.356	0.949	0.0229	0.0283	0.416	0.584	
353.23		0.534	0.0027	0.464	0.943	0.0414	0.0155	0.401	0.599	
352.99		0.403	0.0024	0.595	0.918	0.0757	0.0061	0.370	0.630	
SLV										
352.96	1	0.321	0.0015	0.678				0.340	0.660	
353.07	1	0.240	0.00061	0.759				0.290	0.710	
354.27	1	0.073	0.00031	0.927				0.141	0.859	
LV										
354.01		0.946	0.0095	0.0445				0.419	0.581	
355.31		0.962	0.0156	0.0229				0.430	0.570	
354.31		0.960	0.0081	0.0319				0.426	0.574	
353.90		0.894	0.0052	0.101				0.424	0.576	
354.25		0.939	0.0034	0.0580				0.430	0.570	

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

$ur(x)=ux$  is 2% except for the NaCl in the phases with  $x_{salt} < 0.01$  where its relative standard uncertainty is 5%.

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

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

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

T/K	Solid	Liquid phase I			Liquid phase II			Vapor phase	
	KCl	Water <sup>1</sup>	KCl <sup>2</sup>	TB <sup>1</sup>	Water <sup>1</sup>	KCl <sup>2</sup>	TB <sup>1</sup>	Water <sup>1</sup>	TB <sup>1</sup>
SLLV									
352.93	1	0.370	0.0013	0.629	0.892	0.103	0.0049	0.357	0.643
LLV									
352.95		0.396	0.0017	0.602	0.902	0.0921	0.0061	0.373	0.627
353.00		0.424	0.0018	0.575	0.911	0.0811	0.0076	0.383	0.617
353.09		0.476	0.0020	0.522	0.927	0.0619	0.0107	0.396	0.604
353.13		0.491	0.0020	0.507	0.934	0.0544	0.0114	0.399	0.601
353.31		0.569	0.0025	0.429	0.945	0.0358	0.0196	0.413	0.587
353.41		0.598	0.0027	0.399	0.946	0.0308	0.0233	0.429	0.571
353.50		0.653	0.0029	0.344	0.947	0.0217	0.0313	0.428	0.572
353.60		0.678	0.0031	0.319	0.945	0.0182	0.0364	0.430	0.570
353.66		0.711	0.0035	0.286	0.943	0.0150	0.0420	0.430	0.570
353.74		0.754	0.0037	0.242	0.930	0.0113	0.0583	0.432	0.568
353.80		0.834	0.0052	0.161	0.907	0.0080	0.0853	0.438	0.562
SLV									
353.79	1	0.128	0.00010	0.872				0.186	0.814
353.65	1	0.145	0.00017	0.855				0.197	0.803
353.33	1	0.189	0.00018	0.810				0.234	0.766
353.23	1	0.200	0.00021	0.799				0.248	0.752
353.18	1	0.222	0.00026	0.777				0.268	0.732
353.09	1	0.238	0.00029	0.762				0.281	0.719
353.01	1	0.274	0.00035	0.726				0.306	0.694
352.95	1	0.306	0.00071	0.694				0.326	0.674
352.94	1	0.354	0.0012	0.644				0.345	0.655
LV									
353.06		0.923	0.0730	0.0044				0.387	0.613
353.12		0.937	0.0559	0.0074				0.402	0.598
353.31		0.949	0.0398	0.0111				0.416	0.584
353.52		0.958	0.0229	0.0191				0.431	0.569
353.56		0.960	0.0202	0.0203				0.434	0.566
353.71		0.957	0.0147	0.0284				0.436	0.564
353.89		0.961	0.0098	0.0294				0.441	0.559
353.84		0.901	0.0062	0.0928				0.441	0.559
354.24		0.962	0.0045	0.0333				0.449	0.551

$u(T) = 0.06 \text{ K}$ ,  $u(P) = 0.1 \text{ kPa}$

$ur(x) = ux$  is 2% except for the KCl 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 4. Compositions of the plait point (mole fraction) of the systems water + salt + alcohol at 25° and at the boiling temperature (T). TB = 2-methyl 2-propanol, 1P = 1-propanol, 2P = 2-propanol

T(K)	salt	alcohol	x water	x salt	x alcohol
298.15	NaCl	TB	0.803	0.013	0.184
298.15	KCl	TB	0.798	0.013	0.189
353.85	NaCl	TB	0.809	0.0049	0.186
353.90	KCl	TB	0.850	0.0058	0.144
361.00	NaCl	1P	0.763	0.0195	0.217
354.10	NaCl	2P	0.767	0.0286	0.204

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