

Equilibrium diagram of the water + K_2SO_4 or Na_2SO_4 + 1-propanol or 2-propanol systems at boiling conditions and 101.3 kPa

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Highlights

- Experimental determinations at 101.3 kPa of the solid-liquid-liquid-vapor, liquid-liquid-vapor, solid-liquid-vapor and liquid-vapor equilibrium for the water + Na_2SO_4 + 1-propanol and 2-propanol ternary systems.
- Experimental determinations at 101.3 kPa of the solid-liquid-vapor and liquid-vapor equilibrium for the water + K_2SO_4 + 1-propanol and 2-propanol ternary systems.
- Experimental data prediction with UNIQUAC using AQSOL software.

Keywords

Water; 1-Propanol; 2-Propanol; Na_2SO_4 ; K_2SO_4 ; Isobaric; Solid-liquid-liquid-vapor; Phase diagram; UNIQUAC

Abstract

Thermodynamically consistent phase equilibrium data at 101.3 kPa and boiling conditions were determined for the ternary systems water + Na_2SO_4 + 1-propanol, water + Na_2SO_4 + 2-propanol, water + K_2SO_4 + 1-propanol and water + K_2SO_4 + 2-propanol. In contrast to the systems with Na_2SO_4 , the salting-out effect of K_2SO_4 was not sufficient to split the miscible propanol + water mixture into two liquid phases. The UNIQUAC equation extended to electrolytes for the liquid phase activity coefficients was used to predict the phase equilibria of all the systems. The model reproduced the experimental results quite well, except for the ternary system water + K_2SO_4 + 1-propanol. In this case the model predicted liquid-liquid splitting into two liquid phases, when there is not.

1. Introduction

The salting-out effect that occurs when a salt is added to a partially or completely miscible mixture permits modification of the properties of the mixture, affecting the mutual solubility of the compounds in the mixture. Its effects are varied and of great industrial interest. The presence of an electrolyte causes a significant change in the composition of the water + solvent equilibrium by altering the structure of hydrogen bonds and other intermolecular forces. Especially sensitive to this effect is the liquid-liquid equilibrium due to the change in mutual solubilities of the water + solvent produced by the salt and the relative liquid-vapor equilibrium, in this case to the change in the boiling temperature of the mixture.

The study of the operations of separation and purification of mixtures involving water, electrolytes and organic solvents is very important because the effects caused by salts in aqueous mixtures can be applied to very varied systems [1–3]. Thus, extractive distillation using salts can be applied to different systems, since small concentrations of salt considerably increase the relative volatility of the most volatile component, thus facilitating its separation

[4–6]. On the other hand, saline effects have many other practical applications, allowing solvents to be recovered from their aqueous solutions by salting out.

Furthermore, when a salt is added to a mixture, such as water + propanol where the compounds are completely miscible, the salting-out effect could result in the resultant mixture splitting into two phases both rich in water, giving rise to an aqueous two-phase system (ATPS). These ATPSs permit the design of separation processes of molecules that require a mild environment to remain stable, such as biomolecules. The selection of the mixture to form the ATPS useful for a feasible separation depends on several factors: the type of alcohol, the type of splitting agent (salt), the operating temperature, and the properties of the molecule to be separated (affinity with the different phases), etc. The equilibrium data of the splitting of the liquid phases are needed in order to perform the design calculations of these processes. In addition, it is necessary to know the liquid-vapor equilibrium data in presence of salt because the last stage of the process is often the recovery of the solvent by evaporation or distillation.

In previous works, the solid-liquid-liquid-vapor (SLLV) equilibrium diagrams of mixtures of water and 1-propanol or 2-propanol with different monovalent salts such as NaCl [7–8], KCl [9] or NH₄Cl [10–11] have been studied under boiling conditions at 101.3 kPa. The objective of this work is to study the SLLV equilibrium of water + salt + alcohol systems where the considered salts are divalent. The salts chosen for the study were sodium sulfate (Na₂SO₄) and potassium sulfate (K₂SO₄) and the alcohols were 1-propanol and 2-propanol. The SL equilibrium data obtained will allow design calculations of processes such as crystallization with a mixed solvent to obtain solid Na₂SO₄ or K₂SO₄ using the salting-out effect [12]. The LL equilibrium data are necessary for extraction in ATPS systems [13] and as previously mentioned the LV data are necessary for the final separation of the solvent by evaporation or distillation.

Therefore, the equilibrium diagrams of the water + Na₂SO₄/K₂SO₄ + 1-propanol/2-propanol systems have been determined at boiling temperatures and 101.3 kPa. No studies of the equilibrium of these four systems at boiling temperatures have been found in the literature although there are several works with equilibrium determinations at lower temperatures [12–16]

2. Experimental

2.1. Chemicals

The compounds used in this work, along with their provenance and purity, are presented in Table 1. The purities of 2-propanol and 1-propanol were verified by gas chromatography and their water contents were obtained by Karl Fischer coulometry technique. In addition, ultrapure water was obtained *in situ* from drinkable water after two ultrafiltration, one reverse osmosis and one ion-exchange resin steps, after which the water reached a conductivity less than 2 μS/cm.

2.2 Experimental procedure

The procedure employed in this work is explained in detail in a previous work [7]. In order to determine equilibrium data, a Fischer Labodest VLLE 602 coupled to an ultrasonic probe was employed. Mixtures of water, salt (Na_2SO_4 or K_2SO_4) and 1- or 2-propanol were placed inside the equipment. The pressure inside the distillation still was controlled and fixed at 101.3 kPa by means of a Mensor High-Speed Pneumatic Pressure Controller model CPC3000 with an accuracy of 0.01 kPa. Subsequently, the mixture was heated with enough power to reach the boiling point. The temperature of the vapor was measured with a Pt100 sensor with an accuracy of 0.006 K.

The equipment used the Gillespie method with two recirculations: one for the vapor phase and one for the non-vapor phases. This can be composed of a single liquid, two liquid phases, a solid + a liquid or a solid + two liquids. To avoid temperature changes in the latter due to its cooling in the return duct, this was maintained at a controlled temperature close to that of boiling by means of an electric resistance around the tube.

Once the temperature was stable, samples of the condensed vapor and the other returning phases were extracted from the equipment acting on the solenoid valves. The vapor phase was analyzed in a Shimadzu GC-14B gas chromatograph using He as carrier gas. The stationary phase was a Porapak Q packed column. The temperatures were fixed: 543 K in the oven, 563 K in the injector and 563 K in the thermal conductivity detector, whose current was 100 mA.

The other phase(s), which were composed by a sole liquid phase, two liquid phases, a liquid and a solid salt phase or even two liquid phases and a solid phase were introduced inside a septum cap tube and placed inside a thermostatic bath at the boiling temperature so that the phases were in the same equilibrium state as inside the equipment. Two samples from each one of the liquid phases were collected from the tube using syringes heated to a temperature close to boiling to avoid precipitation of the salt. One of them was used for the determination of the water/alcohol ratio by chromatography and the other one for the determination of the salt content.

Taking into account that 305.6 K is the temperature at which the crystalline sodium sulfate decahydrate changes to give a sulfate liquid phase and an anhydrous solid phase [17], the aqueous phase samples containing Na_2SO_4 were kept at more than 323 K to ensure that any salt that precipitated in the vials before being injected was anhydrous and so there was no change in the water/alcohol ratio in the sample to be analyzed.

The water and propanol salt-free content were determined in the same chromatograph and conditions as the vapor phase.

The salt content was determined by gravimetric analysis. For some samples (i.e., the liquid phases with high propanol content) the weighted amount of salt was very low. To increase the accuracy in the measurement of the salt concentration of these samples, the weighted salt was dissolved in a known amount of water and the Na or K concentrations determined by ICP-OES technique using a Perkin Elmer model 7300 DV using a wavelength of 766.49 nm to measure the potassium content and 589.92 nm for the sodium content.

The uncertainty in all the measurements is given in the tables of results.

3. Results

Tables 2–5 show the experimental equilibrium data (mole fractions) for each system at the boiling temperature (T) and 101.3 kPa. Each Table has been divided into different sections depending of the phases in equilibrium: liquid-vapor (LV), solid-liquid-vapor (SLV), liquid-liquid-vapor (LLV) and solid-liquid-liquid-vapor (SLLV). The consistency of the experimental data was analyzed by interpolation of the diagrams of boiling temperature isotherms and the iso-composition of alcohol in the vapor phase of each system. As an example, Figure 1 shows these diagrams for the system water + Na₂SO₄ + 1-propanol. The isothermal and iso-composition figures of the four systems demonstrate that the presented data are consistent between them.

As can be seen in the four equilibrium diagrams shown in Figure 2, where part of the experimental data has been represented, there are important differences between the systems containing K₂SO₄ and Na₂SO₄. No liquid-liquid equilibrium was observed for systems with K₂SO₄ at the boiling conditions, and therefore these systems cannot be used as ATPSS since the salting-out effect of K₂SO₄ is not enough to split the miscible propanol + water mixture into two liquid phases. However, for certain concentrations, Na₂SO₄ is able of splitting the alcohol + water mixture into two aqueous phases, each one containing more than 50 mol% water. Nevertheless, it should be pointed out that the region containing two liquids is quite narrow at the boiling temperature.

The solubility of K₂SO₄ is less than 0.021 mole fraction in both systems for all the water + propanol mixtures. Obviously, the solubility of the salt is not high enough, even when the boiling conditions are met, to produce a sufficient instability in the mixture for the salting-out effect to induce a phase splitting. However, in the systems with Na₂SO₄, a mole fraction of 0.02 of Na₂SO₄ is high enough to separate the water and propanol mixtures into two liquid phases. It seems that sodium has a higher salting-out power than potassium when the sulfate anion is present.

As mentioned in the introduction, no studies of the equilibrium of these four systems at boiling temperatures have been found in literature. However, there are several works with equilibrium determinations of the four systems at temperatures below the boiling temperatures, where obviously compositions of vapor in equilibrium cannot be obtained.

So, Taboada et al. [12] determined the solubility curves at 290.15, 308.15 and 318.15 K for the water + K₂SO₄ + 1-propanol system. Midlarz et al. [14] presented similar data at 293.15, 303.15, 313.15 and 323.15 K for the water + K₂SO₄ + 2-propanol system. In both works it was observed that the increase in temperature slightly decreased the size of the solid-liquid region and the solubility of the salt in the water + propanol mixture increased. The experimental data presented in this work were obtained at temperatures higher than those, but they follow the trends in by the data of the previously published works.

In respect to the systems with Na₂SO₄, Brenner et al. [15] determined solid-liquid-liquid data at different temperatures in the range 296.65–353.15 K for the system with 1-propanol and at 302.15–353.15 K for the system with 2-propanol. Their SLL equilibrium data at 353.15 K are

represented in Figure 2. Mills and Smith [16] also determined liquid-liquid equilibrium data for the system with 2-propanol at 313.15 and 333.15 K. As in the systems with K_2SO_4 , the temperatures used in the present work are higher than those but follow the trends of the previous data within the uncertainty of the measurements as can be seen in Figure .

In previous works, the equilibrium diagrams of water + NaCl/KCl/ NH_4Cl + 1-propanol or 2-propanol systems [7–11] were determined at boiling temperatures and 101.3 kPa. All these systems, where monovalent salts were involved, showed liquid-liquid phase splitting at the boiling point and even at lower temperatures, giving rise to ATPSs. Apart from the fact that all these systems presented phase splitting, while those with K_2SO_4 did not, the salt concentration range in the systems with Na_2SO_4 where two liquid phases were present was somewhat lower. Accordingly, it seems that the amount of monovalent salt required to produce phase splitting is higher, which is in accordance with the fact that a mole of a non-monovalent salt produces more moles of ions in the liquid phases compared to monovalent salts.

On the other hand, the mutual solubility of water and 1-propanol or 2-propanol when a salt is added to produce an ATPS could be related to the length of the liquid-liquid tie line of the invariant solid-liquid-liquid-vapor mixture. In all these systems, the propanol content of the richest water phase is low, with mole fraction always lower than 0.031. The propanol content of the other phase varies between values higher than 0.5 mole fraction for systems with NaCl, KCl or NH_4Cl to values with Na_2SO_4 of 0.463 for 1-propanol and only 0.360 for 2-propanol, showing that those monovalent salts produce a lower mutual solubility of water and propanol. This fact could have an impact on an ATPS process since a low quantity of salt can split the mixture into two liquid phases with a high amount of water in each one. This is especially useful for the extraction of some biological molecules that can be denatured with salt.

4. Modeling

Finally, the UNIQUAC model extended to electrolytes with parameters from reference [18] and using the AQSOL software was used to calculate the equilibrium diagrams of the four systems at the boiling temperatures. As shown in Figure 3, the different equilibrium regions (one SLLV, one LLV, one LV and two SLV regions) for the two systems with Na_2SO_4 were perfectly calculated. For the system with 2-propanol and K_2SO_4 the model also calculated correctly the existence of only two regions: one LV and one SLV. The values of concentrations in the different phases and temperatures also agree well with the experimental values for all of them.

In contrast, the number and shape of the equilibrium regions were not calculated correctly for the system water + K_2SO_4 + 1-propanol under boiling conditions. The model calculated the existence of a four-phase SLLV region with one solid, two liquid and one vapor phase in equilibrium at 361.2 K and consequently an LLV region with two liquid and one vapor phase in equilibrium. However, these regions did not exist on this system, since it has been experimentally shown that K_2SO_4 is not able to split the water + 1-propanol mixture into two liquid phases at the boiling point. Therefore, the experimental low critical solution temperature (LCST) for this system was greater than 361.2 K. The LCST predicted by the model with the interaction parameter used was determined by calculating the equilibrium diagram of the system at different temperatures and looking for the lowest temperature at which the

equilibrium diagram presents two liquid phases. The obtained LCST was 322.2 K, at least 39 K lower than the experimental value. Therefore, the parameters of the model should be reviewed based on the experimental data reported in this work. The new parameters should correctly reproduce the LCST in order to calculate correctly the shape of the equilibrium diagram of this system at any temperature.

Conclusions

Reliable and consistent experimental phase equilibria data have been determined for four different systems containing water, a bivalent salt (Na_2SO_4 or K_2SO_4) and a propanol (1-propanol or 2-propanol).

Both systems, with water + Na_2SO_4 + 1-propanol or 2-propanol, present five different regions: one SLLV, one LLV, two SLV and one LV. In contrast, both systems with water + K_2SO_4 + 1-propanol or 2-propanol show only two regions: one SLV and one LV, and therefore these systems cannot be used as ATPSS since the salting-out effect of K_2SO_4 is not sufficient to split the miscible propanol + water mixture into two liquid phases. However, for certain concentrations, Na_2SO_4 is capable of splitting the alcohol + water mixture into two aqueous phases, each one containing more than 50 mol% water.

The AQSOL software that uses the extended UNIQUAC model has been proved able to predict quantitatively and qualitatively the different equilibrium regions present at boiling conditions for all the systems except for the water + K_2SO_4 + 1-propanol system. It would be helpful for future research to determine new parameters using the new consistent experimental data determined in this paper.

The results obtained can be used to design new ATPS separation processes, particularly for molecules with low tolerance to salt.

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TABLES

Table 1. Provenance of the compounds used.

Common name	Provider	Purity (mass fraction)	Water content KF ^a (mass fraction)	Purification method	Analysis method
1-propanol	Merck	>0.995	<0.001	none	GC ^b
2-propanol	Fischer Chemical	>0.998	<0.001	none	GC ^b
K ₂ SO ₄	VWR	>0.997		none	
Na ₂ SO ₄	Merck	>0.99		none	

^a KF = Karl Fischer Technique

^b GC = Gas chromatography

Table 2. SLLV, LLV, SLV and LV equilibrium data (mole fraction) of the water + Na₂SO₄ + 1-propanol system at 101.3 kPa

T/K	Solid	Liquid phase I		Liquid phase II		Vapor phase
	Na ₂ SO ₄	Na ₂ SO ₄	1-propanol	Na ₂ SO ₄	1-propanol	1-propanol
SLLV						
360.76	1	0.000336	0.463	0.0473	0.00587	0.456
LLV						
360.77		0.00058	0.421	0.0355	0.0110	0.456
360.82		0.00092	0.362	0.0266	0.0177	0.448
360.87		0.00146	0.311	0.0199	0.0265	0.443
360.90		0.00191	0.277	0.0168	0.0341	0.440
SLV						
360.84	1	0.000082	0.532			0.469
361.05	1	0.0000251	0.599			0.488
361.30	1	0.0000136	0.626			0.495
361.64	1	0.0000465	0.659			0.513
LV						
360.99		0.00236	0.192			0.421
361.30		0.00328	0.0889			0.423
361.64		0.00253	0.0674			0.410
361.43		0.0062	0.0568			0.418
361.79		0.0055	0.0472			0.412
362.25		0.0077	0.0336			0.400
361.08		0.0072	0.0789			0.419
361.34		0.0059	0.0631			0.418

T is in K with a standard uncertainty of 0.06 K, the pressure standard uncertainty is 0.1 kPa and composition relative standard uncertainty, $u_r = \frac{u}{x}$ is 2% except for the Na₂SO₄ in liquid phase I where the relative standard uncertainty is 5%.

Table 3. SLLV, LLV, SLV and LV equilibrium data (mole fraction) of the water + Na₂SO₄ + 2-propanol system at 101.3 kPa

T/K	Solid	Liquid phase I		Liquid phase II		Vapor phase
	Na ₂ SO ₄	Na ₂ SO ₄	2-propanol	Na ₂ SO ₄	2-propanol	2-propanol
SLLV						
354.41	1	0.00054	0.360	0.0456	0.00714	0.589
LLV						
354.87		0.00343	0.204	0.0213	0.0454	0.592
354.71		0.00173	0.267	0.0284	0.0217	0.597
354.59		0.00118	0.293	0.0328	0.0158	0.586
354.53		0.00078	0.332	0.0382	0.0113	0.591
354.38		0.00064	0.345	0.0416	0.00935	0.591
SLV						
354.35	1	0.00054	0.372			0.586
354.24	1	0.000292	0.395			0.595
353.84	1	0.000072	0.483			0.610
353.52	1	0.0000097	0.582			0.618
LV						
355.29		0.0146	0.0660			0.584
355.74		0.0128	0.0464			0.585
357.52		0.0105	0.0345			0.557
359.16		0.0095	0.0242			0.527
355.73		0.0094	0.0578			0.576
355.42		0.0091	0.0725			0.584
356.35		0.0084	0.0522			0.556
355.35		0.0090	0.0778			0.581
354.95		0.0072	0.136			0.574
356.12		0.00444	0.0767			0.572
359.19		0.00290	0.0388			0.541
356.49		0.00279	0.0746			0.568

T is in K with a standard uncertainty of 0.06 K, the pressure standard uncertainty is 0.1 kPa and composition relative standard uncertainty, $u_r = \frac{u}{x}$ is 2% except for the Na₂SO₄ in liquid phase I where the relative standard uncertainty is 5%.

Table 4. SLV and LV equilibrium data (mole fraction) of the water + K₂SO₄ + 1-propanol system at 101.3kPa.

T/K	Solid	Liquid phase		Vapor phase
	K ₂ SO ₄	K ₂ SO ₄	1-propanol	1-propanol
SLV				
370.18	1	0.0212	0.00273	0.168
366.40	1	0.0189	0.00838	0.305
363.07	1	0.0136	0.0190	0.383
361.24	1	0.0100	0.0412	0.416
361.00	1	0.0072	0.0741	0.418
360.98	1	0.0053	0.118	0.419
360.90	1	0.00241	0.206	0.418
360.93	1	0.00154	0.253	0.420
360.82	1	0.00111	0.281	0.421
360.84	1	0.00059	0.322	0.423
360.76	1	0.000201	0.399	0.432
360.77	1	0.000096	0.446	0.440
360.82	1	0.0000476	0.537	0.461
361.31	1	0.0000405	0.648	0.507
362.97	1	0.0000226	0.785	0.605
364.77	1	0.0000241	0.865	0.696
LV				
372.77		0.0157	0.000724	0.0411
370.31		0.0127	0.00374	0.137
370.51		0.0098	0.00416	0.118
369.21		0.0077	0.00628	0.168
368.48		0.0060	0.00866	0.192
366.19		0.00278	0.0174	0.292
363.10		0.00262	0.0382	0.361
362.09		0.0072	0.0404	0.372
361.24		0.0067	0.0677	0.401

T is in K with a standard uncertainty of 0.06 K, the pressure standard uncertainty is 0.1 kPa and composition relative standard uncertainty, $u_r = \frac{u}{x}$ is 2% except for the K₂SO₄ where the relative standard uncertainty is 5%.

Table 5. SLV and LV equilibrium data (mole fraction) of the water + K_2SO_4 + 2-propanol system at 101.3kPa.

T/K	Solid	Liquid phase		Vapor phase
	K_2SO_4	K_2SO_4	2-propanol	2-propanol
SLV				
365.54	1	0.0188	0.00409	0.319
360.37	1	0.0144	0.0152	0.489
357.02	1	0.0098	0.0359	0.550
356.03	1	0.0064	0.0521	0.570
355.58	1	0.00465	0.0888	0.579
355.31	1	0.00289	0.135	0.583
355.16	1	0.00215	0.168	0.584
355.00	1	0.00119	0.208	0.587
354.82	1	0.00076	0.247	0.590
354.61	1	0.000427	0.298	0.594
354.47	1	0.000263	0.343	0.601
354.05	1	0.000130	0.423	0.614
353.86	1	0.000069	0.480	0.625
353.70	1	0.0000310	0.517	0.633
353.60	1	0.0000297	0.552	0.641
353.46	1	0.0000209	0.591	0.656
353.38	1	0.0000182	0.624	0.666
353.33	1	0.0000173	0.657	0.679
353.31	1	0.0000151	0.685	0.694
353.28	1	0.0000155	0.712	0.709
353.31	1	0.0000136	0.739	0.723
353.37	1	0.0000065	0.770	0.744
353.41	1	0.0000035	0.791	0.761
LV				
356.00		0.00503	0.0554	0.560
365.81		0.0115	0.00665	0.290
365.88		0.0098	0.00629	0.263
358.64		0.00061	0.0389	0.453
358.33		0.00203	0.0394	0.513
358.49		0.0051	0.0352	0.523
358.06		0.0065	0.0366	0.532
357.38		0.00120	0.0666	0.541
357.50		0.00248	0.0547	0.545
356.00		0.0054	0.0569	0.572
356.41		0.000461	0.0930	0.553
356.17		0.00179	0.0880	0.561
355.72		0.00362	0.0953	0.573
366.94		0.00074	0.0103	0.155

366.77	0.00268	0.0118	0.197
366.55	0.00425	0.00987	0.257
365.71	0.0077	0.0109	0.270

T is in K with a standard uncertainty of 0.06 K, the pressure standard uncertainty is 0.1 kPa and composition relative standard uncertainty, $u_r = \frac{u}{x}$ is 2% except for the K_2SO_4 where the relative standard uncertainty is 5%.

FIGURES

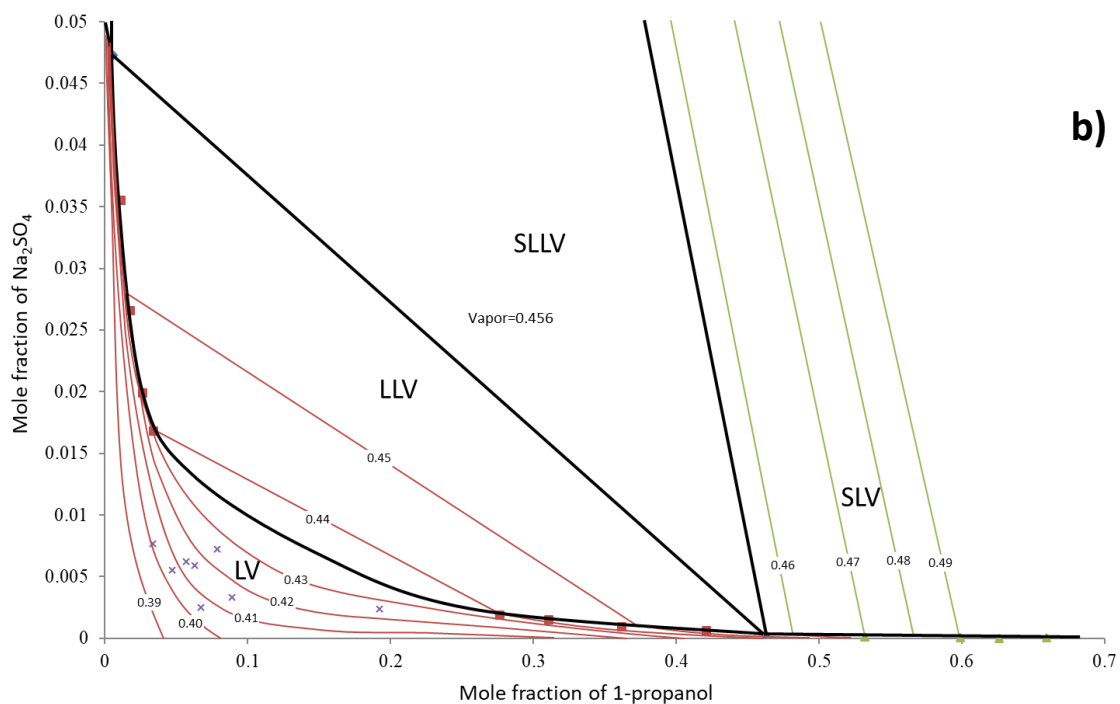
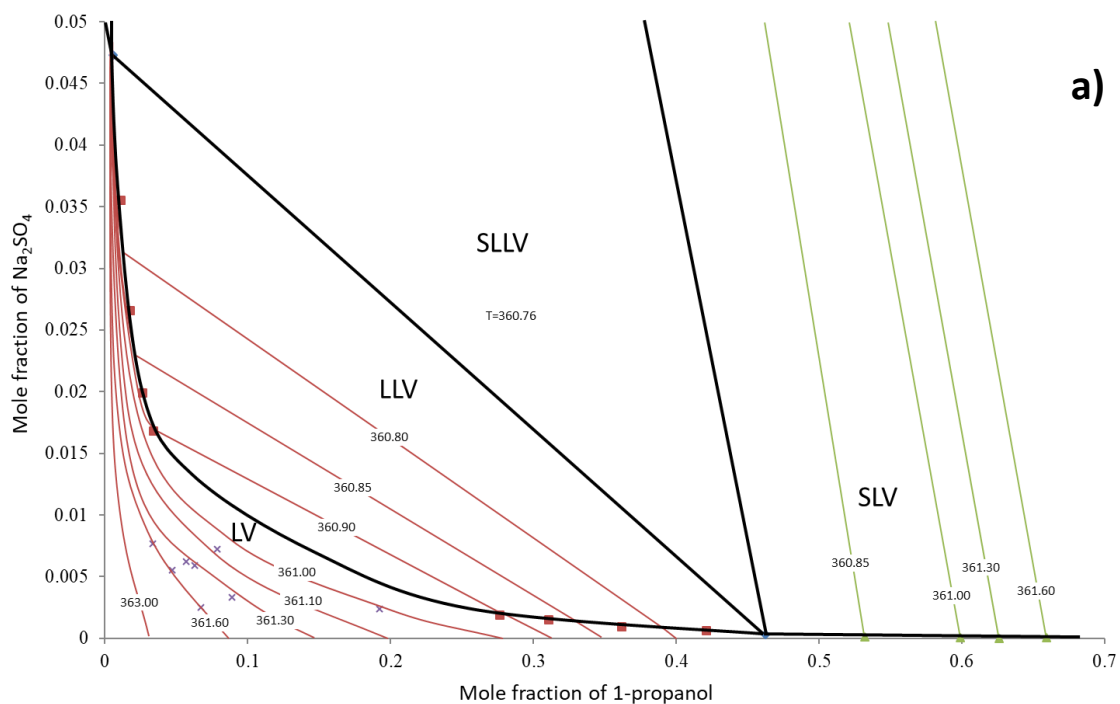


Figure 1. Phase equilibria representation of the water + Na_2SO_4 + 1-propanol system at 101.3 kPa. a) Isotherms representation. Parameter shown on the curves = boiling temperature (K). b) Iso-composition of alcohol in the vapor phase. Parameter shown on the curves = mole fraction of 1-propanol in the vapor phase.

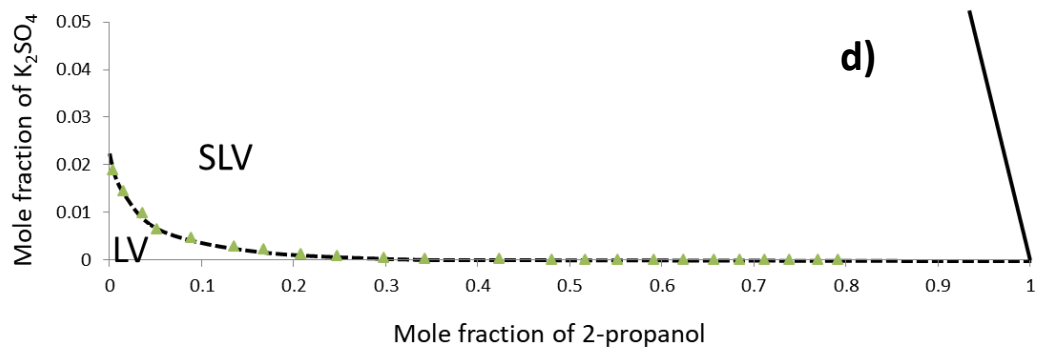
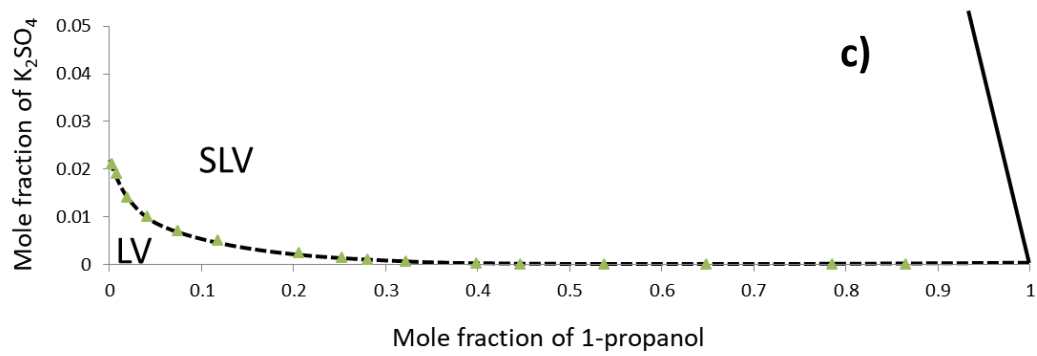
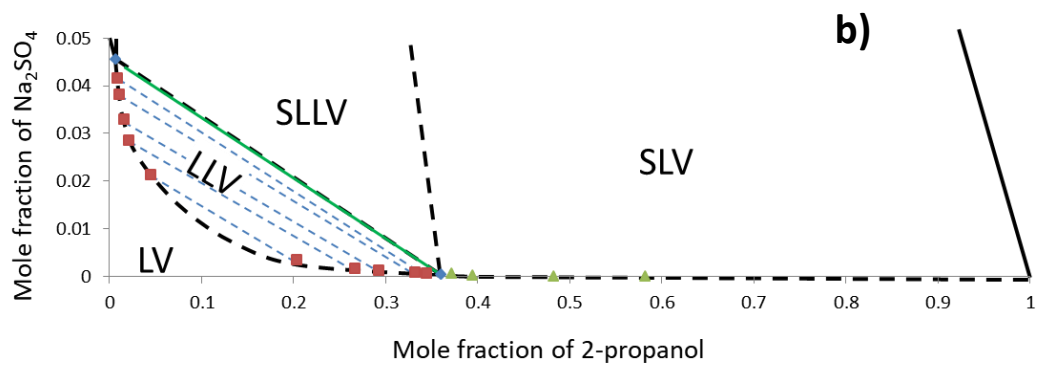
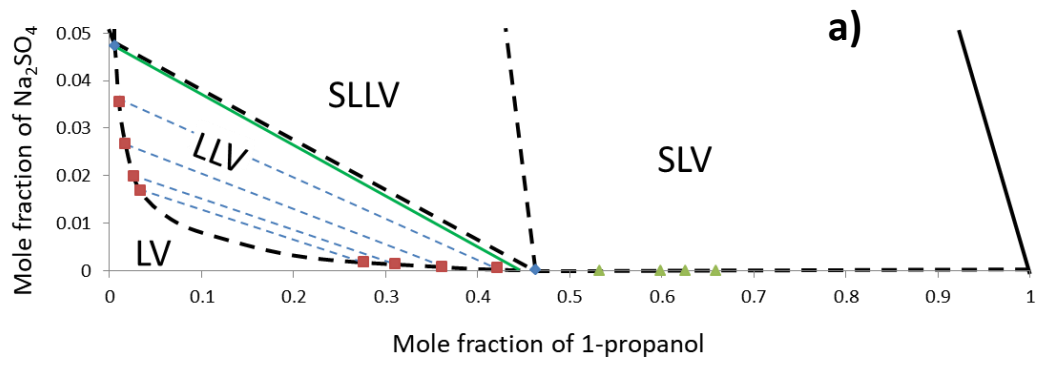


Figure 2. Experimental phase equilibria representation of the four ternary systems at 101.3 kPa. — — This work at boiling temperature; — : SLLV data from Brenner et al. [15] at 353.1 K. a) water + Na_2SO_4 + 1-propanol. b) water + Na_2SO_4 + 2-propanol. c) water + K_2SO_4 + 1-propanol. d) water + K_2SO_4 + 2-propanol.

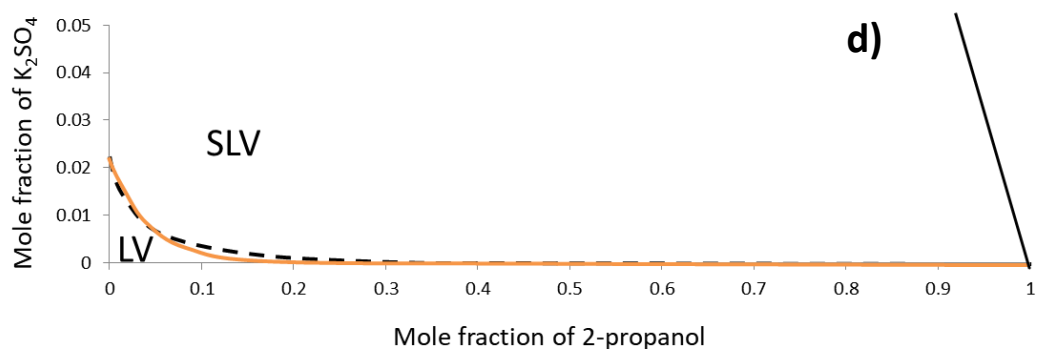
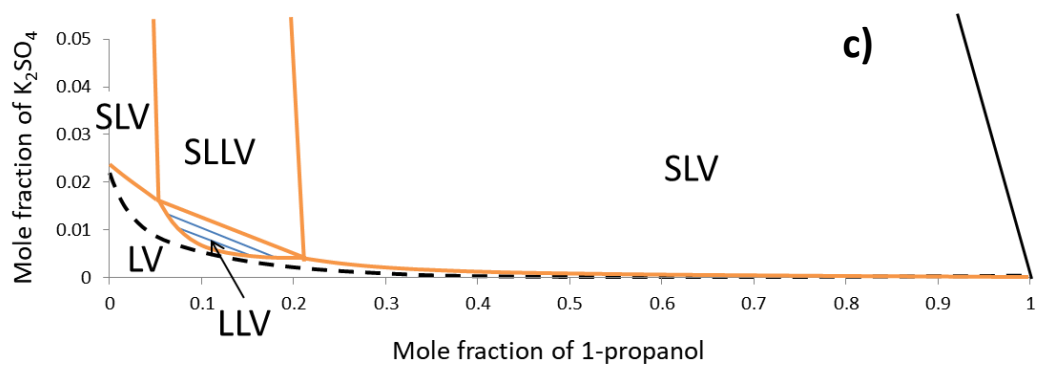
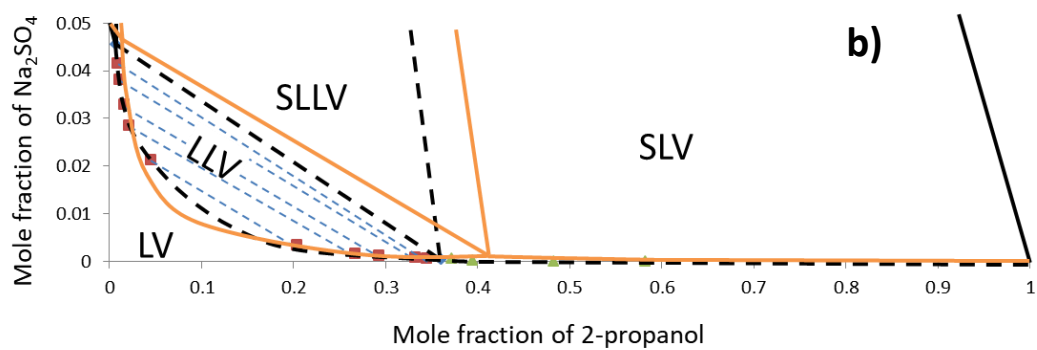
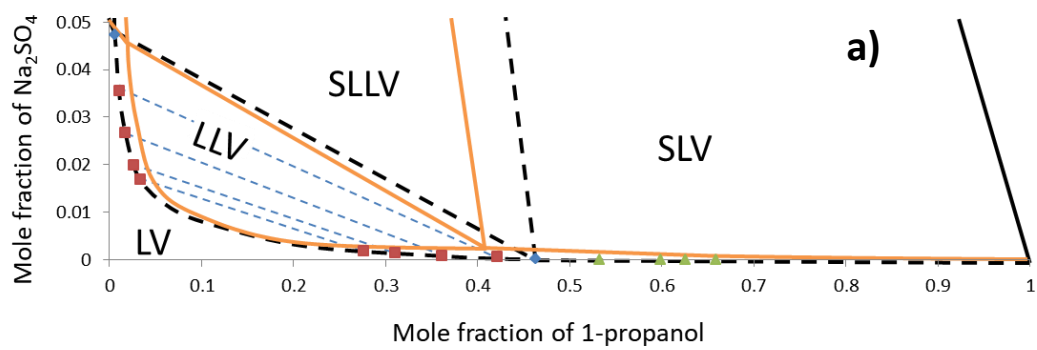


Figure 3. Phase equilibria representation of the four systems calculated with AQSO4 software. This work: - - ; Extended UNIQUAC model: — a) water + Na_2SO_4 + 1-propanol. b) water + Na_2SO_4 + 2-propanol. c) water + K_2SO_4 + 1-propanol. d) water + K_2SO_4 + 2-propanol.