



# Influence of anions and cations on the phase behavior of ternary salt solutions studied by high pressure differential scanning calorimetry



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## ARTICLE INFO

### Article history:

Received 17 August 2015

Received in revised form 27 October 2015

Accepted 28 October 2015

Available online 1 December 2015

### Keywords:

Salt solutions

Electrolyte solutions

Precipitation

Liquid immiscibility

## ABSTRACT

The knowledge of the phase behavior of salt solutions at elevated temperatures and pressures is important for processes using hot compressed water as the process medium, such as supercritical water gasification (SCWG) and supercritical water oxidation (SCWO). Furthermore hydrothermal salt solutions play an important role in geochemical processes in the Earth's crust. We studied ternary solutions related to biomass for obtaining relevant data for the conversion of wet biomass to synthetic natural gas (SNG) in a SCWG process. The experiments were conducted using isochoric high-pressure differential scanning calorimetry (HP-DSC) at a fixed average fluid density of 300 kg/m<sup>3</sup>, a fixed concentration of 0.1 mol/kg(H<sub>2</sub>O) and molar ratios between the two salts of 100:1–1:100. We investigated salts with Na<sup>+</sup>, K<sup>+</sup> and Mg<sup>2+</sup> as cations and SO<sub>4</sub><sup>2-</sup>, HPO<sub>4</sub><sup>2-</sup> and CO<sub>3</sub><sup>2-</sup> as anions.

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## 1. Introduction

Over the past 30 years two groups of processes have been developed, which use hot compressed water as the process medium. The first group is the so called supercritical water oxidation (SCWO) [1–3], which is used to process hazardous waste. The second one is the supercritical water gasification (SCWG), where either a hydrogen-rich gas or synthetic natural gas (SNG) are produced, typically from biomass feedstock [4]. Currently research is conducted at the Paul Scherrer Institute on a catalytic SCWG process [5], which is dedicated to the production of SNG from micro-algae, manure, fermentation residue or other high moisture waste streams.

In the SCWG as well as in the SCWO process the management of the inorganic components plays an important role [6–10]. The solubility of salts in water at conditions corresponding to pressures and temperatures above the critical point of pure water are typically low, which leads to salt precipitation and thus to blocking of the plants. Furthermore in catalytic SCWG processes the salts can lead to fouling or poisoning of the catalyst. Hence, an effective removal of the inorganic constituents from the process stream is the key to successful operation of SCWG and SCWO plants. In addition, the recovery of nutrients such as potassium and phosphorus

would offer the possibility to produce value-added products such as fertilizers.

In this study we chose the ions which are abundant in biomass (K<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>) or might occur during biomass processing due to hydrolysis/thermolysis reactions (CO<sub>3</sub><sup>2-</sup>, HPO<sub>4</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>).

The phase behavior of the salt solutions of interest is crucial to determine if a salt can be removed from the process stream. Schubert et al. [6–8] found that so called type 1 salt solutions can be recovered as a concentrated brine, whereas so called type 2 salt solutions typically lead to scaling and blocking of the plant as they precipitate as “sticky” solids. Furthermore they found that mixtures of two salts can exhibit either type 1-like or type 2-like behavior, depending on the salts and their molar ratio in the mixture.

The classification into type 1 and type 2 was originally proposed by Valyashko (see e.g. [11,12]), who derived a set of comprehensive phase diagrams for binary solutions with one volatile compound (which is water in our case) and one non-volatile compound (e.g. a salt). Both types are further subdivided, depending on the presence and type of liquid-immiscibility in the phase diagram.

The binary phase diagrams of type 1 [12] are characterized by a continuous three-phase line (vapor–liquid–solid, V–L–S) ranging from the triple point of pure water to the triple point of the salt, and a continuous critical line which connects the critical point of water with the critical point of the salt. This means that critical phenomena, where the gas phase and the liquid phase become equal, are absent in the presence of a solid phase. The aqueous solutions of three salts in this study (K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>HPO<sub>4</sub>, and K<sub>2</sub>HPO<sub>4</sub>) exhibit a phase behavior of the so called type 1d (Fig. 1) [13,14],

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which in addition to the above mentioned properties also has a liquid–liquid immiscibility. This immiscibility starts at the lower critical end-point N ( $G=L_1=L_2$ ) (where a dilute liquid phase  $L_1$  and a concentrated liquid phase  $L_2$  are equal in composition), and ends at the upper critical endpoint R ( $G=L_1=L_2$ ), where the dilute liquid phase  $L_1$  and the gas phase  $G$  become equal in composition.

The other main type of phase diagrams, the type 2 systems, [12] exhibit a decreasing solubility with increasing temperature, which leads to an intersection of the  $G-L-S$  line with the critical line in a lower (in terms of pressure and temperature) critical endpoint  $p$  ( $G=L-S$ ) and an upper critical endpoint  $Q$  ( $G=L-S$  or  $L_1=L_2-S$ , as the dilute phase in this region is more liquid like than gas like). In between those two points either a single fluid or a fluid in equilibrium with a solid phase are present, meaning that  $G-L$  critical phenomena are present in this region in equilibrium with a solid phase. The aqueous solutions of the remaining salts used in this study ( $Na_2SO_4$ ,  $K_2SO_4$ , and  $MgSO_4$ ) belong to the subtype 2d' (Fig. 1) [12,15], which exhibits a metastable liquid immiscibility of the d-type as described above. Earlier studies on the  $K_2SO_4-Li_2SO_4-H_2O$  system [16,17] and the  $Na_2SO_4-K_2SO_4-H_2O$  system [18] showed that this metastable immiscibility can be stabilized in ternary solutions.

It was again Valyashko who derived and classified ternary phase diagrams from the above mentioned binary ones. In general, ternary phase diagrams with one volatile compound (pure water in our case) and two non-volatile compounds (two different salts) are determined by their binary boundary phase diagrams [12], which were described above. With varying the molar fraction of one salt between 0 and 1 relative to the second salt, phase behavior will change gradually from the behavior of the binary subsystem of the second salt to the one of which the concentration is increased. Due to the increased number of degrees of freedom the critical endpoints of the binary subsystems will be represented as critical lines in the ternary phase diagrams. The transformation from one boundary type to another can lead to multiple critical endpoints such as the so called  $pQ$  ( $G=L-S$ ) critical endpoint (in case one or both of the boundary subsystems is of type 2), where type 2 behavior turns into type 1 behavior [12], or the  $NR$  ( $L_1=L_2=G$ ) critical endpoint, where a liquid immiscibility of the d-type starts/ends (in case one or both of the subsystems have a d-type immiscibility).

Many ternary phase diagrams have been investigated in the group of Valyashko, mainly at concentrations above 5 wt.% and at temperatures above 390 °C [13,16,17,19–23]. To our knowledge a study is missing investigating the influence of the different anions and cations on the phase behavior in ternary solutions, especially in the low concentration range, which is relevant for hydrothermal processing of biomass.

In an earlier study [18] we showed that it is possible to differentiate between the different types of phase behavior using the heating and the cooling mode of a Differential Scanning Calorimeter at isochoric conditions. Other studies used thermal analysis as well to investigate phase transitions in hydrothermal systems [24–28].

## 2. Methods

The salt solutions were prepared gravimetrically based on  $(100 \pm 0.01)$  g of deionized water (in-house supply, conductivity  $< 5 \mu S/cm$ ) plus the respective combination of salts (weighed with an accuracy of 0.1 mg). In case of the use of a hydrated salt, the amount of water was reduced accordingly. The ternary samples were prepared at molar ratios (salt formula based) of 100:1, 10:1, 1:1, 1:10, and 1:100 at a total salt concentration of 0.1 mol/kg ( $H_2O$ ).

For example  $(17.3 \pm 0.1)$ , mg of  $K_2SO_4$  were added to a solution of  $(1406.3 \pm 0.1)$  mg  $Na_2SO_4$  in  $(100 \pm 0.01)$  g water to yield a ternary solution with a  $Na^+:K^+$  ratio of 100:1 at the above mentioned total salt concentration.

The obtained solutions were weighed into single-use Incoloy crucibles (SETARAM, France), suitable for use up to 500 bar and 600 °C, with an inner volume of  $(128.6 \pm 0.5) \mu L$  (95% confidence interval), as determined gravimetrically by fully filling with water at 25 °C. The salt solutions were transferred into the crucibles using an adjustable volume pipette (Eppendorf, Germany) and weighed using an analytical balance. Typically several attempts are needed to obtain the target sample mass of 38.6 mg. As described earlier [18], a liquid sample mass of  $(38.6 \pm 0.1)$  mg yields an average fluid (gas and liquid) density of  $(300 \pm 1) kg/m^3$  in the crucible. The gas phase consists of air at room temperature, with increasing amounts of vapor upon increasing temperature during the measurement.

Note that the volume expansion of the crucibles due to the thermal expansion of the material and the stress due to the increasing vapor pressure of the contained solution are neglected here. The influence of the air in the gas phase is also neglected, as the partial pressure of 1 bar of air is much smaller than the vapor pressure of the fluid ( $> 100$  bar) at the temperatures at which the phase transitions occur.

The experiments were carried out on a Sensys DSC (SETARAM, France), which has a high precision Calvet-style sensor and was calibrated using indium, tin, lead and zinc reference samples (SETARAM, France). After an equilibration period of 1 h, the runs were carried out in both heating and cooling mode at a heating rate of 0.1 K/min, in order to be able to distinguish between the different types of phase behavior. For the samples containing  $Na_2HPO_4$  and  $MgSO_4$  heating and cooling rates of 1 K/min were applied to resolve the signals. The obtained heat flow curves were evaluated using the Calisto software (AKTS, Switzerland), using the glass transition tool to determine the dissolution or heterogenization temperatures.

During the course of our investigation we discovered that for systems containing either  $MgSO_4$  or  $Na_2HPO_4$ , higher heating/cooling rates of 1 K/min (compared to 0.1 K/min) were needed to reveal the signals of solid precipitation or liquid immiscibility. This is also due to the signal intensity being linearly dependent from the heating rate in thermal analysis.

In our earlier investigation [18] the measurement error for the temperature at a heating/cooling rate of 0.1 K/min was generally around  $\pm 0.2$  °C. As a higher heating/cooling rate most likely will induce a larger error, a maximum error for the measured phase transition temperatures can be estimated to  $\pm 1-2$  °C.

The values for the boundary binary systems were either interpolated from our earlier work [18] ( $Na_2SO_4-H_2O$ ,  $K_2SO_4-H_2O$ , and  $K_2HPO_4-H_2O$ ) or, in case of  $MgSO_4-H_2O$  and  $Na_2HPO_4-H_2O$ , newly measured.

## 3. Results

As described in an earlier contribution [18] the signals in the heat flow curves of isochoric measurements of hydrothermal salt solutions can be interpreted as follows: In the heating mode step-like signals in endothermic direction correspond to liquid immiscibilities, whereas endothermic peak-like signals occur upon solid precipitation. In the cooling mode of the calorimeter both signals look step-like; the peak shape in the heating mode occurs due to supersaturation (see also Abdulagatov et al. [25]). The measurements in the cooling mode were more consistent in terms of deviations in multiple measurements. Hence the phase transition temperatures were determined in the cooling mode, whereas the nature of the phase transitions was obtained from the signals in the heating mode.

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