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Unveiling the complexity of salt(s) in water under transcritical conditions

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Abstract:

Processes using water at sub- and supercritical conditions ($T > 300^{\circ}\text{C}$) are used in industrial wastewater treatment, chemical recycling of wastes, biomass conversion and also in material synthesis, because of their rapidity and high efficiency. However, the salts injected or generated during the processes can lead to complex multiphasic water-salts systems with a behavior far to be understood in all the cases. Drastic changes of physics and chemistry of the systems are expected from water intrinsic properties; however, the formation of new phases, sometimes unexpected, near the critical point of water (374°C ; 22.1 MPa) also has a direct effect on the properties of the system. It is thus important to be conscious of the existence of these new phases to have the best control as possible on the physico-chemistry occurring inside the reactor. The aim of this review paper is to give an overview of these poorly-known new phases and to show that they are more encountered in SCW than it is thought.

1. Introduction

Water, referred also as « Blue Gold », is the most vital chemical specie on Earth but also one of the most interesting in terms of the evolution of properties as a function of p and T . At ambient conditions, water exhibits a high dielectric constant, due to the capacity of water molecules to form hydrogen bonds, conferring it a high polarity and thus an elevated capacity of dissolution of inorganic salts. When reaching its supercritical conditions, *i.e.* $T > 374^{\circ}\text{C}$ and $p > 22.1$ MPa, water presents intermediate properties between liquid and vapor. SuperCritical Water (SCW) is then characterized by a fall of its viscosity, surface tension, density and dielectric constant (see Figure 1). These specific properties open the way of numerous possible applications such as material synthesis [1-4], recycling of chemical wastes and industrial wastewater [5-10] and also biomass conversion [8,11,12], processes displaying high chemical degradation rate and efficiency in a very short residence time. The weak polarity of SCW enables the dissolution of organic compounds [13], not possible at ambient conditions, but also decreases consequently the solubility of inorganic salts [14]. Although this drop of solubility is beneficial for material synthesis by enabling the formation of size-controlled crystalline nanoparticles, it has heavy consequences on continuous treatment and/or recycling processes because of solid precipitation into reactors, clogging the process [15-20]. Consequently, applications with inorganic salts in near- and supercritical hydrothermal environment are limited: the full understanding of salt behavior in SCW is the only way to overcome this limitation.

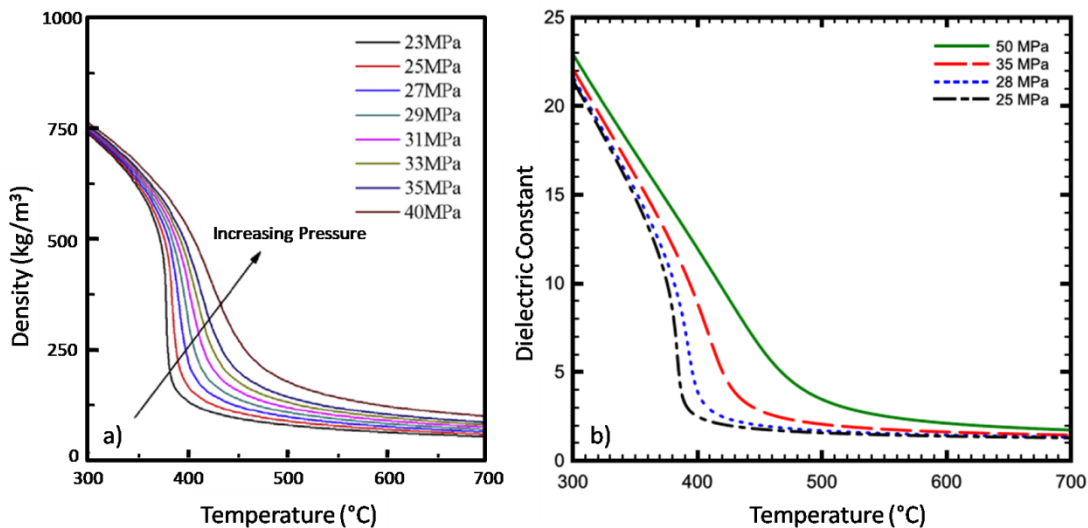


Figure 1: Evolution of water a) average density and b) dielectric constant as a function of temperature for several pressures. Graph a) was reprinted with permission from [21], Copyright (2020) Elsevier, and graph b) was reprinted with permission from [22], Copyright (2020) Elsevier.

The water-salt system is intrinsically linked to the study of ions-water interactions and benefits from several strong theoretical and experimental background when considered at ambient conditions. But the understanding of these complex interactions quickly fades when dealing with high temperature and high pressure conditions such as supercritical water. However, comprehension of ions-water interactions pass through the understanding of SCW behavior and particularly its structural mechanisms, directly related to its solvation capacity. Thereby, X-ray and neutron diffraction and diffusion [23,24], nucleus magnetic resonance [25] and spectroscopy [24,26] experiments have shown that, despite of the apparent low density of SCW, there is persistence of some hydrogen bonds in the supercritical domain, generating clusters of water molecules [27] and leading to local density inhomogeneities [28,29] (see Figure 2). Consequently, the evolution of density presented in Figure 1a) actually represents the average density of water and does not reflect the local phenomena occurring in SCW, as well as the dielectric constant in Figure 1b), which is a macroscopic parameter. Moreover, it has been also proved that these dynamical local density inhomogeneities are particularly expanded near the critical point, leading to areas containing dissolved ions (high density areas) and regions where solvation is impossible (low density areas).

These phenomena could be directly related to the existence of two domains in the supercritical region, characterized by two different dynamical regimes: gas-like and liquid-like domains [30,31]. These two domains are demarcated by the coexistence of response function extrema of several thermodynamic quantities, such as compressibility coefficients, the isobaric heat capacity and the Joule-Thomson coefficient, as well as the speed of sound, at particular (T, p) coordinates defining a line in the (T, p) diagram, called Widom line [32]. The passage from the liquid-like to the gas-like regions, and thus through the Widom line, is a smooth transition called pseudoboiling process [33]. This pseudoboiling engenders nanoscale density fluctuations of the supercritical fluid [31,34] and large variation of thermodynamic properties in the vicinity of the Widom line [33]. Thus, in these conditions, the quite known ion-water interactions change drastically and become difficult to predict, leading to complex systems with multiple phases, and sometimes, unexpected behaviors.

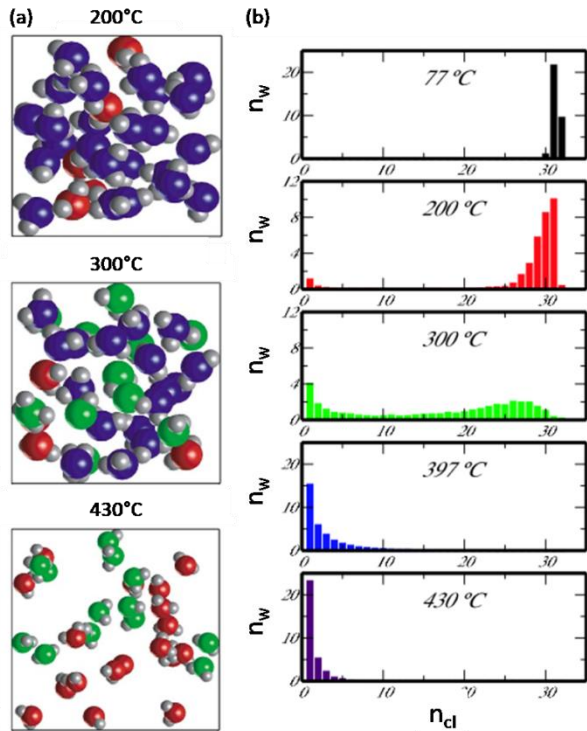


Figure 2: Simulation results obtained by Sit *et al.* considering 32 inequivalent water molecules in a periodic cubic supercell, at 30 MPa. (a) Snapshots from the simulations at 200, 300, and 430°C. Color of molecules represents their connectivity. Blue: water molecules in clusters with six or more molecules; green: water molecules in clusters with two to five molecules; red: monomers. (b) Number of water molecules n_w belonging to a cluster of size n_{cl} , at different temperatures.

Note that authors proved the good agreement between simulation and experimental data (obtained by x-ray inelastic scattering). Reprinted with the permission from [35], Copyright (2020) American Physical Society.

In this review, attention will be focused on the most common inorganic salts, injected in reactors or obtained by precipitation in SCW experiments, and on the complexity they bring to the system under sub- and supercritical conditions. The first part will be dedicated to generalities regarding water-salts systems under supercritical conditions and to the importance of water-salt multiphase systems. Then the particular cases of molten salt phase in supercritical conditions will be introduced, showing that although salts are mostly seen as a limitation, the understanding of their behavior in these conditions could also lead to new opportunities for many hydrothermal applications. The intense complexification of multiphase systems when dealing with salt mixtures will also be approached in the second part of the review. Finally, in the last part, the impact of the complexity of water-salts system on its chemico-physical properties will be discussed, leading to a questioning of certain concepts and models and showing the need to establish new *in-situ* measurement methods to improve our understanding of these media.

2. Multiphase water-salts systems in sub- and supercritical conditions

The solubility of salts in water is directly dependent of the pressure and the temperature: when the supercritical conditions for water are approaching and/or reached, the solubility decreases and salts tend to precipitate (see Figure 3(d)). The system can then be described as a fluid (water) - solid (salt) system. In that case, the phase behavior with water is ruled by the nature of the salt, depicting a particular binary phase diagram. Binary diagrams, thermodynamically compatible with a fluid-solid system, were selected by V.M. Valyashko [36-38] from the fluid-fluid interaction diagrams previously proposed by Scott and Van Konynenburg [39]. Two main behaviors are highlighted: type I and type II salts. In both cases, salt concentration, represented by x in Figures 3 (a) and (b), has an important impact on the critical point of aqueous solutions (see the example of NaCl solutions in Table1).

Table 1: Effect of the NaCl concentration C of an aqueous solution on its critical point (T_c , p_c) reported by Bischoff *et al.* [40]

| C (mol/L) | T_c (°C) | p_c (MPa) |
|-------------|------------|-------------|
| 0 | 374 | 22.1 |
| 0.38 | 400 | 28.1 |
| 1.03 | 430 | 36.3 |

For each value of x corresponds a new couple (T_c , p_c) depicted by the binary critical curve in the phase diagrams [24,40]. The relation between this curve and the saturation curves assigns the salt type. Type I salts are characterized by a continuous critical curve uninterrupted by the saturation curves in the supercritical domain: a two-phase fluid forms between the saturation and the critical curves (see Figure 3(a) and (c)). On the contrary, for the type II salts the critical curve is interrupted by the saturation curves (see Figure 3(b)): critical behavior occurs in saturated solutions forming a supercritical fluid and a solid phase. Considering small thermodynamic variations and topological transformations from these two possible interaction diagrams, numerous subdiagrams can be constructed, enabling the classification of most of the salts in supercritical water [36].

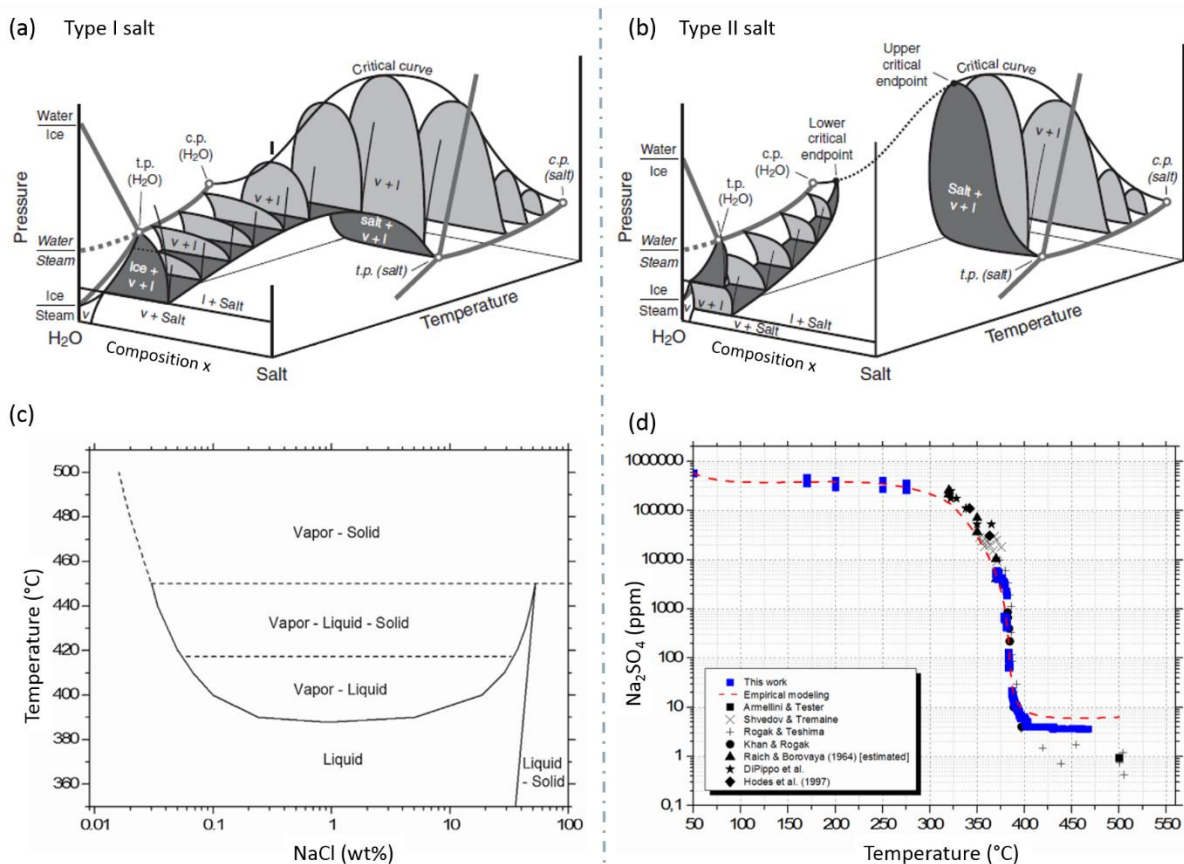


Figure 3: General P-T-x phase diagrams for (a) a type I salt and (b) a type II salt, with x the composition. In the case of a type I salt (a), the binary critical curve is continuous and presents no intersection with the saturation curves, contrary to the type II salt (b) showing a binary critical curve interrupted by the saturation curves leading to the existence of two critical end points. Abbreviations: t.p., triple point; c.p., critical point.

Reprinted with permission from [41]. Copyright (2020), Wiley. (c) Schematic phase diagram of the binary system H₂O-NaCl, representing the behavior of one of the most know type I salt in water, reprinted with the permission from [42], Copyright (2020), Elsevier. (d) Solubility curve of the type II salt Na₂SO₄ in water as a function of temperature, measured at 25 MPa, showing the typical abrupt change of solubility of salts in water when reaching the supercritical conditions. This figure is reprinted with permission from [43], Copyright (2020), Elsevier.

However, the categorization of salts into these two types of behavior remains delicate and is still controversial. Two main classifications are proposed. Marshall classification [44] separates salts based on their solubility near the water critical point: type I salts present a higher solubility than type II salts. Concurrently, Valyashko classification [45] not only takes into account the solubility of the salt into water but also considers a correlation between the type of a salt and its melting temperature. Salts are then classified as a type I salt if its melting temperature is lower than 800-1000°C and as a type II salt if its melting temperature is higher than 700-800°C. Valyashko also mentioned that for a given cation (anion) the salt solubility in supercritical water increases with the size of the associated anion (cation). However, posterior studies of the effect of the ion nature on the salt solubility in supercritical water made by Schubert *et al.* [46] proves that the solubility of NaNO₃ is higher than the one of KNO₃, itself higher than the solubility of Ca(NO₃)₂. The solubility of these salts is thus decreasing when the ionic radius of the ionic alkali metal is increasing, which is inconsistent with Valyashko's prediction. Consequently, these salts classifications can be taken as a working base but should be taken with a pinch of salt; only experimental data in supercritical water could validate the type I –type II classification.

The behavior of Sodium Chloride salt, classified by Marshall and Valyashko as a type I salt, provides an excellent example of an empirical phase diagram reconstruction. This mixture has been studied in supercritical water [14,42,47,48] and the binary NaCl-H₂O phase diagram was determined at 25 MPa [40,49]. These studies show the coexistence of a low-density water vapor phase characterized by a low NaCl concentration with a highly concentrated liquid phase giving rise to a diphasic domain between 390 and 450°C. Direct observation of these two phases are shown in [50] using a high temperature and high pressure optically accessible cell. At higher temperatures the salt begins to precipitate and the system reaches a vapor-solid domain. Nevertheless, Voisin *et al.* [42] shown that the precipitation occurs much before 450°C and unveiled a triphasic vapor-liquid-solid domain existing from about 415 to 450°C [42], revealing the complexity of the phase diagram of the binary NaCl-H₂O system (see Figure 3(c)). In SuperCritical Water Oxidation (SCWO), for instance, several salts are susceptible to be formed in reactors, like carbonates, phosphates, nitrates and sulfates. The system can then be described as a binary, ternary or higher system [15]. As for the binary systems, Valyashko used the method of continuous topological transformation to determine the phase diagram of ternary salt-water-salt systems, based on the idea of continuous transitions between fluid phase diagrams [51]. However, the validity of these reconstructed diagrams needs to be validated experimentally and only few studies were performed on mixtures of salts. These studies revealed that the behavior of these systems is particularly difficult to predict due to the existence of several effects encountered in sub- and supercritical water. Indeed, it was shown that the mixture in water of two salts presenting a common ion has a direct effect on the solubility of the salts: a decrease of the solubility of the less soluble salt leading to its precipitation is observed [52]. This effect, called "common ion effect", reflects the principle of Le Chatelier predicting that an excess of reagent, here the common ion, in a chemical equilibrium displaces this equilibrium towards the formation of products, in this case the precipitation of the less soluble salt. Modification of salts solubility could also be observed in mixtures of type I and type II salts: Valyashko predicted the solubility of a type II salt would be increased with temperature by addition of a type I salt [36,37,51]. This assumption was

validated by Dipippo *et al.* for the system NaCl-H₂O-Na₂SO₄ up to 550°C and 25 MPa [53]; an extensive description of these studies can be found in the paper in reference [42]. Finally, when the salts dissolved in water do not share a common ion, a different precipitation mechanism of salts from the initial ones can occur, favoring, when the nature of the ions enables it, the formation of type I salts [46,54,55]. This ion-exchange phenomenon leads to the transformation of a ternary system into a higher order system, much more complicated to model and making the behavior of the initial mixture impossible to predict. Last but not least, the existence of a highly concentrated liquid phase can also play an important role on the solubility of salts. Actually, salts precipitating from the aqueous solution can efficiently be dissolved in a second liquid phase with a high concentration in salt enabling a higher solubility of these salts than without presence of this highly concentrated liquid phase [56]. This mechanism has been recently highlighted by Voisin *et al.* for the NaCl-H₂O-Na₂SO₄ system, where a liquid phase highly concentrated in NaCl is generated at supercritical conditions (see Figure 3(c)) and, thanks to its high polarity and density, dissolves the Na₂SO₄ solid precipitate arising from the SCW phase [42] (see Figure 4).

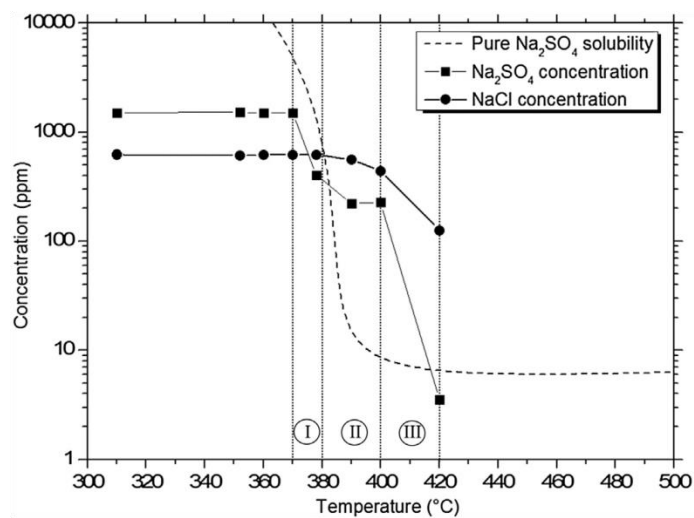
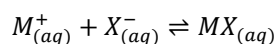


Figure 4: Solubility curves as a function of temperature obtained for an aqueous solution of NaCl (type I) and Na₂SO₄ (type II) salts at 25 MPa. Dashed curve represents the solubility curve obtained for a solution of pure Na₂SO₄ at 25 MPa. The comparison of Na₂SO₄ solubility curves evidences that for the salts mixture solution precipitation of Na₂SO₄ occurs at lower temperature than for pure Na₂SO₄ (domain I). This difference can be explained by the common ion effect, favoring the precipitation of Na₂SO₄ salt. The concentration of Na₂SO₄ is then stabilized in the domain II at a value 10 times higher than the solubility of pure Na₂SO₄. This domain corresponds to the beginning of the NaCl diphasic domain leading to the appearance of a dense concentrated liquid phase. Part of the Na₂SO₄ precipitate is dissolved in this highly concentrated phase, preventing the complete precipitation. Above 400°C (domain III), the saturation concentration in the highly concentrated phase is reached and both salts precipitation occurs. The impact of a type I salt (NaCl) on the solubility of a type II salt (Na₂SO₄) is here clearly evidenced and is in coherence with Valyashko predictions. Figure reprinted with the permission from [42]. Copyright (2020), Elsevier.

Taking into account the previous phenomena, experiments combining salts having one common ion were done by Reimer *et al.* and an ionic solubility scale has been extracted from their results [57]. Concerning the cations, solubility decreases in the sequence $K^+ > Na^+ > Mg^{2+}$ (study performed with SO_4^{2-}) in coherence with the one observed by Schubert *et al.* [46]. For the anions, the following order was evidenced: $HPO_4^{2-} > SO_4^{2-} > CO_3^{2-}$ (study performed with K^+ and Na^+). These trends are explained by the authors as a dependency of the salt solubility on the charge over the radius ratio: the smaller the ionic radius is, the stronger is the electronic interaction between ions leading to ions association and clustering before precipitation at higher temperature. In addition, in polyatomic ions,

as CO_3^{2-} and SO_4^{2-} , the number of coordination sites could play a key role on the solubility: higher the number of coordination is, more the solubility will increase. This important work could lead to the determination of a general empirical rule for salt solubility in sub- and supercritical water: the solubility of a salt is increasing when the charge to radius ratio of its ions decreases and when their number of coordination sites increases.

The ion association phenomena seems to be an important factor when dealing with the solubility of salts, it is then important to understand it at supercritical conditions to be able to predict the solubility of a mixture of salts in supercritical water. At ambient conditions, salts in water are entirely dissociated into solvated ions. Water polarity screens electrostatic interactions between ions, preventing them to precipitate. In supercritical conditions, the structure of water changes: the number of hydrogen bonds is considerably reduced causing a drastic drop of the dielectric constant. The screening effect of the water molecules decreases and enables two oppositely charged ions to get closer to each other via attractive electrostatic forces (see Figure 5). These gatherings form contact ion pairs (CIP) in solution, defined as:



Although we focus here on sub- and supercritical conditions, CIP have been reported to also be present in solution near room temperature in highly concentrated liquid phases or saturated [58-62].

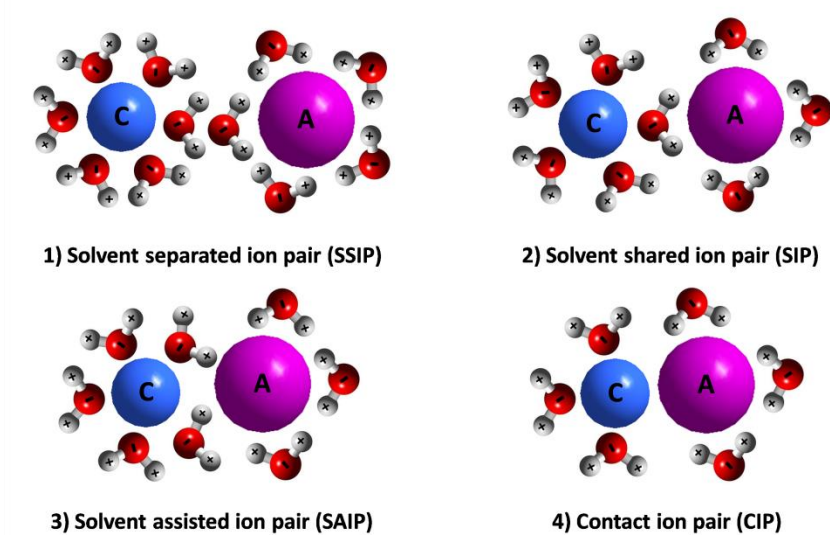


Figure 5: Schematic representation of the formation process of contact ion pair (CIP) in water. C stands for cation and A for anion.

The formation of CIP in sub- and supercritical conditions can be predicted by *ab initio* numerical simulations or molecular dynamic simulations on 1:1 salts, as demonstrated by Chialvo *et al.* [63] about the Na^+ - Cl^- ion pair association. Experimentally, the quantity of CIP in solution can be determined by *in situ* conductivity measurements [64] as evidenced by Ho *et al.* for NaCl , KCl and KOH solutions [65,66]. Moreover, in some cases the association of ions leads to the formation of more complex entities with not necessary the final salt stoichiometry. This phenomenon was reported for MgSO_4 salt for which a liquid-liquid phase separation was evidenced at high temperature using Raman spectroscopy [67]. A MgSO_4 -rich liquid phase is then coexisting with a MgSO_4 -poor liquid phase and a vapor-saturated phase. This phase separation, also observed for aqueous UO_2SO_4 solutions [68](see Figure 6), could be explained by strong ions association leading to a complex association mechanism of the ions, forming

ionic pseudo-polymers before precipitation. However, this liquid-liquid-vapor domain is probably a metastable domain [51,69] where pseudo-ionic polymers could be formed and become prenucleus for precipitation. The experimental X-ray Absorption Spectroscopy (XAS) technique, including X-ray Absorption Near-Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy, can also be used to identify ion associations in solution as it enables the observation of the direct environment of the ions and its evolution. As an example, XAS technique enabled to observe the formation of $[\text{GaBr}_n(\text{H}_2\text{O})_{4-n}]_{(\text{aq})}^{3-n}$ complexes, with $n = 2, 3$ or 4 , as well as the existence of high-order tetrahedral Fe(II)-chloride complexes, respectively in a GaBr_3 solution [70] and an acidic chloride concentrated liquid phase [71] at supercritical conditions. EXAFS technique was also used to characterize a mixture of Ca^{2+} and Cl^- ions in supercritical water by Fulton et al. [72] and evidenced CIP formation with a decreasing of the number of water molecules around the ions and the shortening of the distance between Ca^{2+} and Cl^- ions.

Observation of ion associations, metastable ionic pseudo-polymers and liquid-liquid phase separation in the sub- and supercritical regions (ex: NaCl and MgSO_4 respectively) gives precious information to understand the link between structural properties of the fluid and its thermodynamic properties. These association mechanisms are still not well understood, particularly in supercritical conditions, because of the difficulty to evidence experimentally these ionic entities. Nevertheless, the apparition of a second liquid phase with a high salt concentration at sub- or supercritical conditions could reflect macroscopically the capacity of the salt to form ionic pairs and complex ionic entities microscopically. It could then be interesting to understand why some salts exhibit this CIP capacity up to the point of forming a metastable phase, but other salts do not. Answering this question could enable to improve the salt type classification.

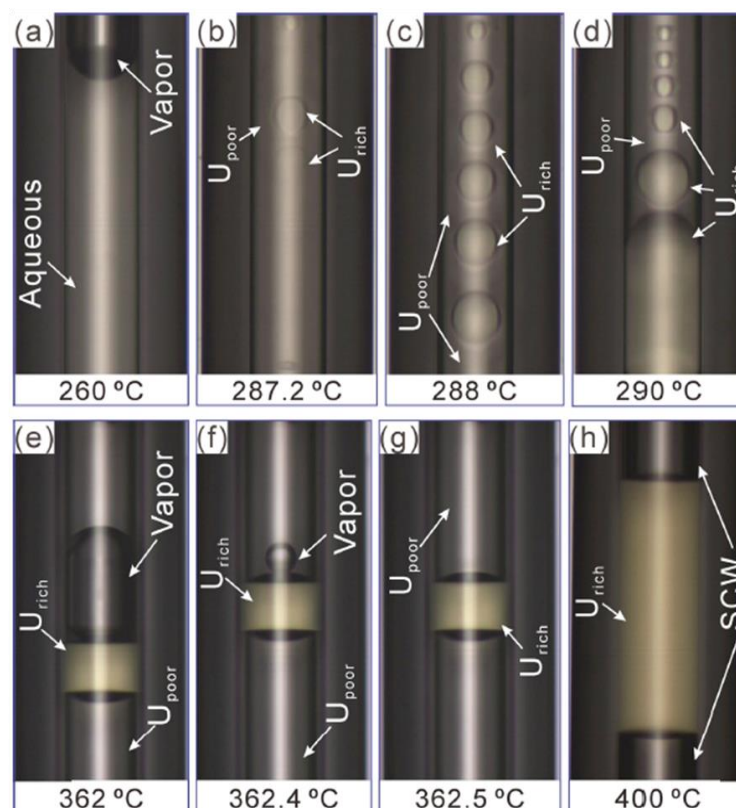


Figure 6: Photographs obtained by Wang *et al.* showing the phase separation in a UO_2SO_4 aqueous solution along the liquid-vapor curve [68]. At 287.2°C a new liquid phase is separated from the aqueous phase at saturated vapor pressure. Above 287.2°C , immiscible UO_2SO_4 -rich droplets (U_{rich}) develop and coalesce in a

UO₂SO₄-poor aqueous phase (U_{poor}). The U_{poor} phase is then converted into SCW at temperature above 374°C and U_{rich} phase and SCW coexist up to 420°C. Reprinted with permission from [68]. Copyright (2020), Elsevier.

Water-salts mixtures are thus complex systems with a behavior difficult to predict in sub- and supercritical regions. Despite this difficulty, models for water-salts phase diagrams are available thanks to Valyashko, providing a solid base for experimental studies. Attempts of classification of salts were also proposed, based on their solubility in water, but have to be improved by a better understanding of the ion association phenomena, mechanism seeming to be the crucial element determining salts solubility. Ion association and formation of contact ion pairs are also surely at the origin of the formation of additional highly concentrated liquid phases. We have shown that water-salts phase diagrams are complex but it can be even more complicated if one salt presents a precipitation temperature higher than its melting temperature. Indeed, in this case, when the saturation limit is reached, the precipitation of the salt occurs and is instantaneously followed by the fusion of the salt. A molten salt phase is then created, as observed for systems containing sodium nitrate and nitrite, lithium and potassium nitrate [73], potassium hydroxide or potassium phosphate [74] as well as sodium hydroxide [75] leading to a supplementary phase in the water-salt phase diagram.

3. Molten salts and reactive salts in sub- and supercritical water

3.1. Molten salt and HyMos technology

The molten salt phase is an ionic liquid phase where the main interactions are mainly electrostatic. This phase is characterized by a disordered structure. Nonetheless a short range order still exists in the phase and its structure can be viewed as intertwining quasi-lattices of cation sites and anion sites. The ions constituting the molten salt phase are poorly coordinated (10% lower than in crystals) and the cation-anion and anion-anion distances are very close to the distances in crystals at room temperature [76-78]. Molten salt phases are characterized by a high polarity, enabling the dissolution of various inorganic compounds. This high inorganic dissolution capacity as well as their high thermal stability and low vapour pressure make them widely used for various high temperature industrial applications. Many common salts exhibit high melting temperatures, way above the critical temperature of water. However, some others have a melting temperature below or near the critical temperature of water, usually between 300°C and 500°C (cf. Table 2). This is the case for nitrate salts (NaNO₃, KNO₃...) or hydroxides (NaOH, KOH...).

Using such salts under supercritical water conditions means that when the solubility limit of the salt is reached, the salt precipitates and instantaneously forms a liquid molten salt phase, partially miscible with supercritical water. Instead of a solid – fluid equilibrium like usual salts in supercritical water cases, we end up with a fluid – fluid equilibrium. On one hand is the low density fluid composed of supercritical water and a fraction of dissolved salt, on the other hand is high density molten salt phase with a fraction of water, *i.e.* hydrous molten salt phase. This unique Hydrothermal Molten Salt (HyMoS) system re-addresses the questions of homogeneous systems in supercritical water conditions as a binary fluid system is formed. Much more than questioning the thermodynamic and hydrodynamic of a simple water-salt system, hydrothermal molten salts raise multiple other potential applications for supercritical water processes.

Table 2: List of alkaline and alkaline earth salts with a melting temperature lower than 500°C susceptible to be present as a molten salt phase in sub- and supercritical conditions. Melting temperatures presented here are determined at room pressure; they can be calculated for higher pressures using the reference [79]. Thereby, considering a melting temperature of 319.9°C for NaOH at ambient pressure [79], the calculated melting temperature for a pressure of 25 MPa is 322.2°C. More generally, the variation of the melting temperature of salts can be considered as negligible in the pressure range of the study (20-30 MPa), as proved experimentally by Petitet *et al.* for NaNO₃, with T_m(0.1 MPa)= 305.4°C and T_m(35.4 MPa)= 310.8°C and for LiOH, with T_m(0.1 MPa)= 466.7°C and T_m(30 MPa)= 467.9°C [80]. References in the Table: a: [81], b: [82], c: [76], d: [83], e: [80].

| Salt | T _m (°C) | Salt | T _m (°C) | Salt | T _m (°C) |
|------------------------------------|------------------------------------|-----------------------------------|------------------------------------|-----------------------------------|--|
| Ba(ClO ₃) ₂ | 414 ^a | KClO ₃ | 368 ^a | NaClO ₄ | 480 ^a |
| Ba(OH) ₂ | 408 ^a | KHCO ₂ | 167 ^c | NaCNS | 287 ^b |
| BeCl ₂ | 405 ^b -415 ^a | KHF ₂ | 238.8 ^a | NaHCO ₂ | 257.3 ^a |
| BeI ₂ | 480 ^a | KHSO ₄ | 215 ^c | NaHSO ₄ | 182 ^c |
| Ca(ClO ₃) ₂ | 340 ^a | KNH ₂ | 335 ^a | NaNH ₂ | 210 ^a |
| Cs ₂ O | 495 ^a | KNO ₂ | 438 ^a | NaNO ₂ | 284 ^a |
| Cs ₂ S ₂ | 460 ^b | KNO ₃ | 334 ^a | NaNO ₃ | 305.4 ^e -306.5 ^a |
| Cs ₂ S ₃ | 217 ^b | KOH | 360 ^d -406 ^a | NaOH | 318 ^d -323 ^a |
| Cs ₂ S ₅ | 210 ^b | KSCN | 173 ^c | Rb ₂ S ₂ | 420 ^a |
| CsCH ₃ CO ₂ | 191 ^c | LiCH ₃ CO ₂ | 291 ^b | Rb ₂ S ₃ | 213 ^a |
| CsHCO ₂ | 263 ^c | LiClO ₃ | 127,6 ^c | Rb ₂ S ₅ | 225 ^b |
| CsHF ₂ | 180 ^c | LiClO ₄ | 236 ^a | RbCH ₃ CO ₂ | 246 ^c |
| CsHSO ₄ | 218 ^c | LiCN | 160 ^c | RbHCO ₂ | 170 ^c |
| CsNH ₂ | 262 ^b | LiI | 469 ^a | RbHF ₂ | 210 ^c |
| CsNO ₃ | 414 ^a | LiNO ₂ | 200 ^c -222 ^a | RbHSO ₄ | 206 ^c |
| CsOH | 272 ^b | LiNO ₃ | 253 ^a | RbNO ₃ | 310 ^a |
| CsSCN | 206 ^c | LiOH | 462 ^d -473 ^a | RbOH | 301 ^d -385 ^a |
| KCH ₃ CO ₂ | 295 ^d -309 ^a | NaClO ₃ | 215 ^c -248 ^a | RbSCN | 184 ^c |

The first evident application to the preservation of a dense fluid phase at high temperature is the possibility to dissolve inorganic compounds, which could not be possible with supercritical water. This solubility capacity of molten salt in aqueous system has been proven by Borovaya and Ravich in the study of the solubility of NaCO₃ and Na₃PO₄ in aqueous solutions of NaOH at elevated temperatures for a wide range of NaOH concentration [84]. They evidenced that above 350°C, NaCO₃ and Na₃PO₄ solubility increases consequently for a sufficiently concentrated aqueous NaOH solution. At this temperature NaOH forms a molten salt phase dissolving salts which are only very slightly soluble in pure water. An additional phenomenon was highlighted by the authors: in the case of Na₃PO₄, for a certain interval of NaOH concentration the salt precipitating at low temperature is then redissolved in the molten phase above 325°C. With this work, Borovaya and Ravich revealed the high capacity of dissolution of molten salts in water systems. Nevertheless, the presence of molten salts in supercritical water was mainly seen as a problematic phenomenon up to recently mainly because of potential corrosion they can cause. The super-solvent potential of these phases in supercritical water systems was evidenced with the example of NaOH and Na₂SO₄ [75]. The experiment, carried out by Voisin *et al.*, consists in the deposition of solid Na₂SO₄ crystals on the walls of a continuous supercritical water tubular reactor followed by the injection of a NaOH/water solution. The experiment was realized between 400°C and 420°C at 25 MPa, *i.e.* above the melting temperature of NaOH (T_m = 320°C).

Consequently, when NaOH salt precipitates, it immediately forms a molten salt phase. This molten salt phase then dissolves the Na₂SO₄ salt and enables to clean the process. Moreover, no corrosion of the reactor was observed. Besides the great potential of removing precipitated salts in a continuous SCW process, the experiment also determined that the solubility of Na₂SO₄ in the molten NaOH phase is very high and consistent with the thermodynamic predicted by the Na₂SO₄-NaOH binary diagram, *i.e.* the obtained solubility corresponds to the composition ratio of the liquidus curve of the Na₂SO₄-NaOH binary diagram at the experimental temperature. This means that in addition to the newly discovered potential of HyMos in supercritical water, their properties and solubility capacities seem to be consistent with the already known high temperature binary diagrams, despite the presence of water. One could then use the existing databases of salts at high temperatures to predict and choose the right HyMoS to fit its application, without necessarily redetermining all its thermodynamic properties in supercritical water. However, the case of NaOH is quite simple: other potential molten salts could induce much more complexity in the phase diagram and in the chemistry of the system. Indeed, sodium hydroxide is a very common salt composed of two ions, which are frequently present in aqueous chemical systems. Therefore, any system involving sodium ions and a strong base in water could possibly lead to the formation of NaOH, thus a HyMoS system. This simple statement leads in contrast to complex consequences, as the study of a binary system composed of common sodium salt in supercritical water could end up as a study of a multiphasic system composed of molten NaOH, dissolved salt, supercritical water and solid salt.

3.2. Reactive salts: the sodium phosphate case study

In order to illustrate how a simple system such as salt in water can become much more complex when studied under supercritical water conditions, one can consider the case of the trisodium phosphate salt Na₃PO₄. Great solubility in water at ambient conditions and good biocompatibility make trisodium phosphate a common salt used in many applications such as cleaning agents, food additives or lubricants.

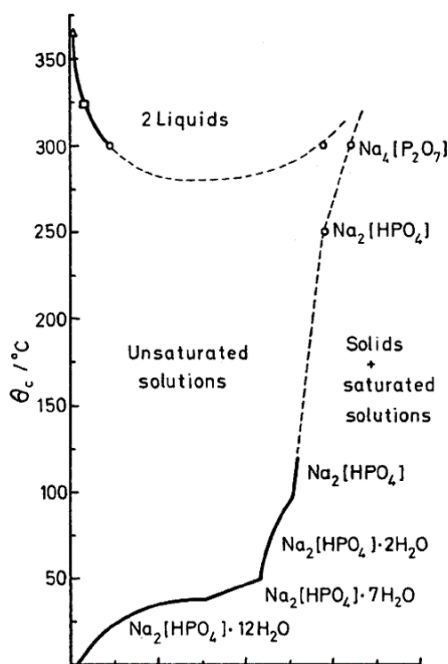
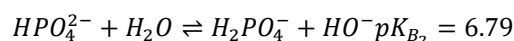
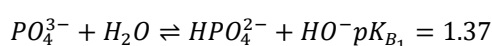


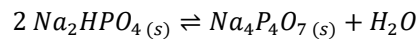
Figure 7: Binary diagram of Na₂HPO₄ - H₂O at high temperature, reprinted with permission from [84]. Copyright (2020), The Royal Society of Chemistry.

One specificity of Na₃PO₄ is its tri-acidity, which means depending on the pH value, the analysis of one salt can become a complex 3 salts study, according to the hydration reactions:



Following these chemical equilibriums, Na₃PO₄ is a strong basic salt, meaning that the dissolution of a reasonable quantity of Na₃PO₄ in water will induce the presence of a high concentration of sodium ions and hydroxide ions, thus potentially the formation of the NaOH molten phase when reaching the supercritical water conditions. This hypothesis is supported by the preferential precipitation of type I salt in systems containing type II salts (as seen in the previous section), leading to the favourable precipitation of NaOH (type I salt) rather than Na₃PO₄ (type II salt). Moreover, the melting temperature of Na₃PO₄ is quite high (1583°C) compared to the usual

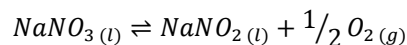
supercritical water conditions, but regarding HPO_4^{2-} the literature specifies a degradation temperature of 250°C. This degradation temperature actually expresses a dehydration mechanism to form a pyrophosphoric compound according to the following reaction:



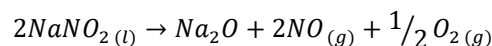
The pyrophosphoric compounds $\text{Na}_4\text{P}_2\text{O}_7$ possess a melting temperature of 988°C and is known for its great solubility in water, but is unstable under 250°C and decomposes into Na_2HPO_4 . This high temperature reaction implies that in addition to the equilibrium between the 4 acid-base forms of the phosphate salt and the potential presence of molten NaOH, a 6th compound can be formed *in situ* with additional questions regarding solubility, precipitation and behaviour with supercritical water. One binary diagram can be found in the literature regarding Na_2HPO_4 and water (see Figure 7), which specifies that above 250°C, after the formation of the pyrophosphoric compound, a liquid-liquid equilibrium occurs instead of solid precipitation [85], exactly like the NaCl or MgSO_4 cases previously described.

In the end, what looked like a simple binary equilibrium study between Na_3PO_4 and supercritical water becomes a difficult multiphasic study with dehydration reactions, potential liquid-liquid equilibrium, molten salt phase and solid salt precipitation. Without intentionally complicating the system, the question of the pH in supercritical water is more likely to lead to deep implications regarding the dehydration mechanism of the acidic forms of phosphoric acid, such as the example with the formation of the $\text{Na}_4\text{P}_2\text{O}_7$.

The sodium phosphate case is taken as an example here, but is far from being an isolated case. One could also look into the sodium nitrate system NaNO_3 which presents a low melting temperature (308°C), but also a degradation temperature reachable in SCW experiments (380°C) leading to the formation of nitrite compounds. NaNO_3 thermal degradation can be divided into several characteristics regions [86,87]. From the melting temperature to 450°C the quantity of nitrite formed is low. Then from 450°C up to 550°C, a nitrate-nitrite chemical equilibrium is established:



The quantity of formed nitrite is no more negligible as shown by Dell'Orco when trying to determine the solubility of NaNO_3 in supercritical water [73]. Above 550°C, the NaNO_2 formed by NaNO_3 degradation is undergoing decomposition as well, in accordance with the following reaction:



And finally, above 700°C all the nitrates are decomposed. These successive degradations prove the complexity of the NaNO_3 - H_2O system presenting a molten salt phase in supercritical conditions and becoming the ternary system NaNO_2 - H_2O - NaNO_3 above 450°C, with two molten salts, and becoming even more complex at higher temperatures.

Consequently, beyond the apparent chemical simplicity of salt in water, the behaviour of salt in supercritical water conditions highlights how far we are to fully understand the interactions between ions, water and salts, and the extensive potential still unused of these systems.

4. Conclusions and perspectives

As it has previously been exposed in this work, the interactions involved between sub- and supercritical water and inorganic salts are complex, considering all the changes in properties simultaneously happening as a result of the high temperature and high pressure. These changes in water properties when reaching sub- and supercritical conditions are well documented, giving access to the evolution of density, viscosity, dielectric constant or even the dissociation constant (Figure 8) on a large range of temperature and pressure [88]. But the changes of these properties brought by the presence of a high concentration of salt are quite uncharted. Even when considering water at ambient conditions, theoretical models for ions-water interactions struggle to be in an accurate agreement with experimental data when reaching high concentration of salt, near the saturation point. Yet, this specific case becomes the norm in supercritical conditions, as the saturation limit for salt decreases drastically when the temperature increases, usually by several orders of magnitude. This means that the particular interactions between ions and water close to the saturation point are of main interest to understand the behaviour of salts in sub- and supercritical water.

It is known for a fact that these interactions can be counter-intuitive, such as the example of the formation of contact ion pairs and ionic pseudo-polymers previously discussed. However, some work directly correlated these phenomena with the appearance of a second liquid phase highly concentrated in salt, partially miscible with sub- or supercritical water [67,68]. This suggests that the ion – ion interactions in these conditions are far from being negligible and should be of main interest for future studies. The questions of the stability domain and properties of these particular highly concentrated liquid phases are undoubtedly crucial for the development of SCW processes dealing with inorganic charges. What we once considered as a homogeneous phase with deposited solid particle, is now a multiphasic system of at least two partially miscible liquids with very different physical and chemical properties. Thus, a deep reconsideration of the hydrodynamic and thermodynamic of such systems is necessary, especially for continuous flow processes where the system will edge towards a turbulent colloidal flow rather than a homogeneous one, with all the issues related to this domain. Thankfully, it also means that a whole new field of studies and research opens up for sub- and supercritical water applications involving inorganic salts. In addition, the unsuspected properties of hydrothermal molten salt (such as the example of NaOH) in supercritical water expand the potential applications using inorganic salts and the prospect of solving the current limitation due to solid precipitation. Hydrothermal molten salt also brings complexity, in the same way than the example of phosphate and nitrate salts and their self-reactivity when reaching subcritical conditions. But these considerations are a glance at the new opportunities offered by the water-salt system. The potential in terms of chemical reaction, catalysis or degradation and recycling is also broad, considering that supercritical media enables chemical reactions with metastable species and molten salt phase enables to maintain inorganic species dissolved.

However, hydrothermal molten salt and multiphasic liquids flow in sub- and supercritical water, giving the system a complex thermodynamics, also readdress several questions regarding the physical and chemical properties of this media. For example, one knows how important the question of pH can be for the prevention of reactor corrosion and for some specific chemical reactions and applications. Discussions about the evolution of acidity constant and pH values in supercritical water are far from being settled, but the general trend observed for pure water, in Figure 8, shows non-negligible pK_w and pH variations occurring during transcritical processes. pH of aqueous systems is of first concern for supercritical-water-cooled nuclear reactors and pH control agent, as LiOH salt, are added to the system to mitigate corrosion [90]. It is thus essential to know how the added salt behaves in the process (T,p) region and be aware of the possible complex multiphasic character of the system.

For example, LiOH salt, because of its low melting temperature, will form at high temperatures a molten salt phase, which is not taken into account in pH calculations for supercritical-water-cooling processes [91]. The idea of a liquid molten salt phase evolving alongside sub- or supercritical water adds a supplementary challenge to the question of pH in this media. Besides, it is more than likely that the question of ion pairing has a major influence on the pH and reactivity in these conditions. This issue has already been considered by Trémillon proposing, in order to quantify the acidity of the molten salt phase, the use of the Lux-Flood concept describing acid-base couples as oxo-acid - oxo-base couples and considering their O^{2-} potential rather than the H^+ potential. In addition, in the case of salt without oxygenated anions, the solvo-acidity concept can then be used, defined by the auto-dissociation equilibrium of the solvent [92].

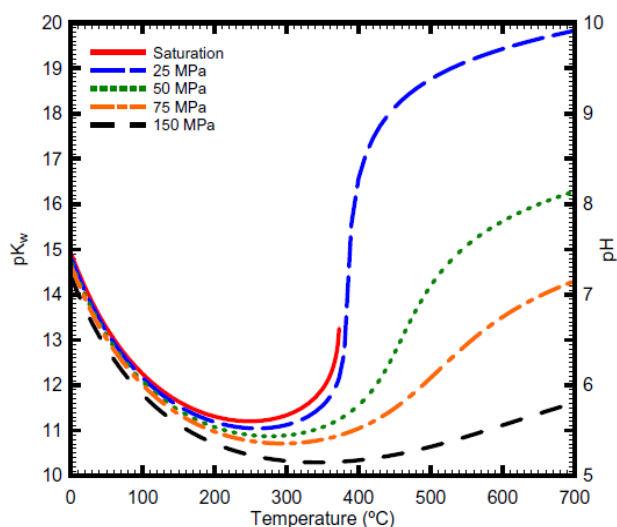


Figure 8: Evolution with temperature of the ionic product and pH of neutral water determined by Bandura *et al.* for different pressure values [89]. Figure picked from [22], illustrating the large change of water properties under high temperature and pressure. Reprinted with permission from [22]. Copyright (2020), Elsevier.

Therefore, it is of main interest to focus our efforts on the study and understanding of water-salt systems in sub- and supercritical water conditions, to improve our knowledge of these unexpected behaviours and to re-assess the driving-forces and nature of chemical reactions occurring in the reactor during transcritical processes. The main way to achieve this goal would probably be to develop and improve *in situ* techniques and continuous flow systems. As an example, *in situ* optical pH measurements associated with optical oxygen potential measurement techniques from power plants technologies (in the case of molten salt presence) might be able to probe the different phases of the system and determine their solvo-acidity. This valuable information would allow a better understanding and control of the reactor corrosion (choice of the most suitable material for building the reactor) and on the chemical reactions occurring during the process, enabling to enhance the quality of the desired synthesis or application. In this way, the supercritical community would benefit even more from all the theoretical background of other fields (electrochemistry, catalysis, colloids,...) and be at the crossroads of several chemical domains, enhancing the multidisciplinary of supercritical fluids research.

Declaration of Competing Interest

There is no conflict of interest.

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