ION-PAIR FORMATION IN STRONTIUM CHLORIDE AND STRONTIUM HYDROXYDE SOLUTIONS UNDER SUPERCRITICAL WATER REACTOR OPERATING CONDITIONS

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Abstract

The proposed Generation IV nuclear reactor design is a "combined cycle" that would have supercritical water flowing through the reactor core and directly into the turbines. To model the behaviour of fission products in the event of a fuel failure, we are examining the aqueous chemistry of strontium salts in high temperature water. We have measured the molar conductivity of solutions of strontium chloride and strontium hydroxide as low as 10^{-5} mol kg^{-1} from 100 °C to 350 °C and 20 MPa with a unique high-precision flow-through AC electrical conductance instrument to determine the ion-association constants in these solutions. The results from measurements at the same conditions show that the formation of $Sr(OH)^+$ and $Sr(OH)_2{}^0$ ion-pairs is greater than for $SrCl^+$ and $SrCl_2{}^0$ ion pairs, and that the neutral species are substantial at concentrations above 10^{-3} mol kg^{-1} at 350 °C. These new formation constant data are required to determine whether the neutral $Sr(OH)_2{}^0$ may be sufficiently soluble in supercritical steam to be carried to the high pressure turbines. The molar conductivities at infinite dilution, $\Lambda°$, were found to be a simple exponential function of the solvent viscosity, which can be used to estimate ionic mobilities and diffusion in crevices under supercritical water reactor conditions.

1. Introduction

The Generation IV CANDU® Supercritical-Water-Cooled Reactor (SCWR) is a conceptual design for a novel, extremely energy-efficient advanced reactor that would come on line after 2025. The Gen IV concept would produce supercritical water (SCW) at temperatures as high as 650 ºC to generate electricity, hydrogen and district heating. The reactor and fuel channel concepts have been described by Torgerson *et al.* [1]. The use of super-critical water to carry heat from the reactor core to the turbine will generate much more extreme water chemistry conditions than those in current CANDU-6 design or the new Advanced CANDU 1000 reactor, which operate from 250 to 325 ºC. In addition to extreme temperature, two other key differences in the SCWR design will produce very significant chemistry control and materials challenges. First, while the current generation of CANDU reactors use separate primary and secondary coolant circuits to isolate the radioactive reactor core from boiler water, the CANDU-SCWR concept uses a direct cycle circuit in which the primary coolant will be in contact with radioactive fuel at temperatures from 250 to 650 ºC. Second, the proposed SCWR would replace the gas-annulus insulation system which surrounds the pressure tubes [1] with a system in which removable ceramic insulators will be placed inside the pressure tubes. The consequence of these design features is that contaminants from condenser leaks and make-up water will come in contact with the fuel bundles and pressure tubes in the reactor core. As a result, these contaminants can concentrate in the pores and crevices of the ceramic insulation together with corrosion products, actinides and fission products from (rare) fuel failures. There, the radioactive corrosion products and fission products may react with contaminants to form volatile species that are sufficiently soluble in supercritical steam to be transported to the turbines where they would cause high radiation fields. The long-term viability of the Gen IV CANDU-SCWR concept depends on the ability of designers to predict and control water chemistry, in order to minimize radionuclide transport and corrosion associated with the new design.

Because the SCWR will operate at pressures of 25-30 MPa, well above the critical pressure of water (P_c = 22 MPa), no boiling will take place and there will be no "steam" phase. Instead, the coolant will undergo a transition from "water-like" to "steam-like" densities (from ~0.8 to 0.1 $g \cdot cm^{-3}$) as it passes from sub-critical to super-critical conditions through the critical temperature at T_c = 373 ºC, as shown in Figure 1. Operating experience in supercritical thermal power stations has shown that the region of most importance is the range from 275 to 450 ºC and 25 MPa, the so-called "pseudo transition zone" [2]. This is a frontier region of hydrothermal chemistry, both because the SCWR will produce a unique water chemistry, not previously seen in the primary coolant circuits of pressure-tube reactors, and because most quantitative studies of aqueous solutes do not extend above 300 ºC. Above 450 ºC, water is sufficiently steam-like that solid-gas thermodynamic models are likely to be adequate.

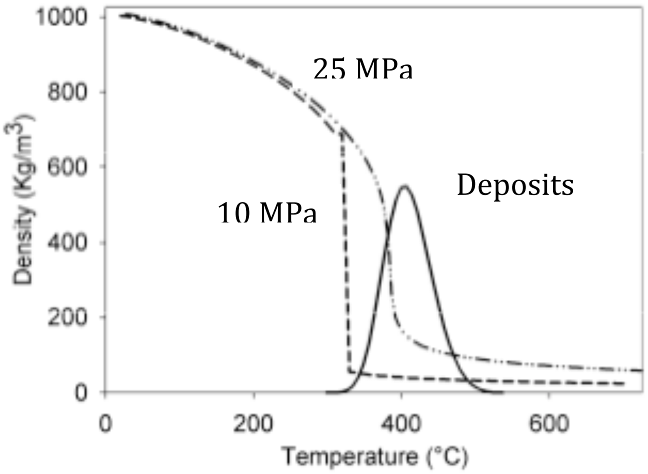

Figure 1: Density of water as a function of temperature at 10 MPa, typical of CANDU-6 steam generators, and 25 MPa proposed for the CANDU-SCWR. The solid line indicates the predicted region for corrosion product deposition.

The formation of neutral complexes increases with temperature, and can become important under near-critical and supercritical conditions. The most important region is from 300 to 450 ºC where the properties of water change dramatically, and solvent compressibility effects exert a huge influence on solvation. This is reflected in the dielectric constant of water, plotted in Figure 2 at p = 25 MPa, which falls from ε = 79 at 25 ºC to ε = 15 at 350 ºC. The effect of the low dielectric constant is to stabilize the neutral complexes of activated corrosion products, fission products and actinides, relative to charged species. As a result, species such as $[Me^{n+}(X^-)_n]^0(aq)$ (with Me^{n+} = Co^{2+}, Fe^{2+}, Ni^{2+}, Cs^+, Sr^{2+}, UO_2^{2+}… and X = OH^-, Cl^-, CO_3^{2-}, SO_4^{2-}…) are expected to dominate in the supercritical region. The concern for all Gen IV SCWR designs is that radioactive neutral species may be sufficiently soluble in supercritical water to be carried to the turbines.

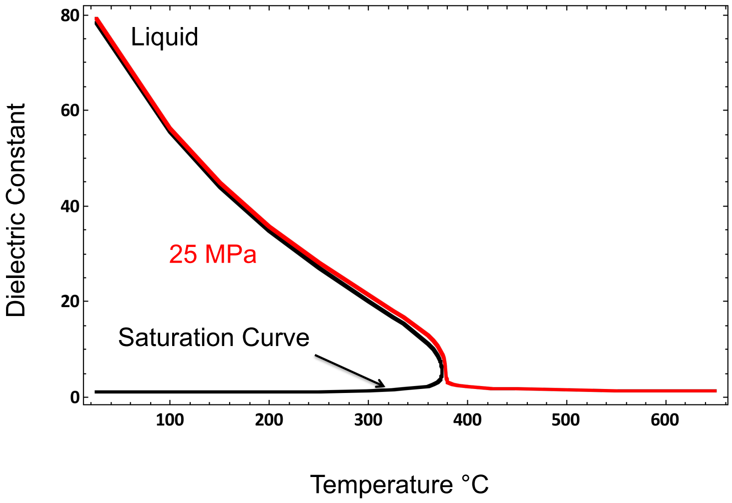

Figure 2: The dielectric constant of water and steam at steam saturation pressure, and water and supercritical water at 25 MPa *vs*. temperature.

The principal limitations in the existing understanding are (i) lack of thermodynamic and kinetic data for inorganic species above 250 ºC; (ii) lack of data for associated ion-pairs, hydrolyzed species and complexes above 250 ºC; (iii) shortcomings in theoretical models in the region $325 < T < 450$ ºC where both ions and ion-pairs co-exist; (iv) unknown species or reaction products that may exist at very high temperatures, $300 < T < 650$ ºC.

This paper reports preliminary results of an experimental study to determine the association constants of strontium with hydroxide and chloride at temperatures up to 350 °C, using a state-of-the-art high-pressure flow AC conductance apparatus [3]. The systems [$Sr(OH)_2$ + H_2O] and [$SrCl_2$ + H_2O] were chosen because of their importance to modeling fission product transport in SCWR reactors, and because they are soluble in near-critical water and so may be used as model systems for other M^{2+} species.

2. Experimental Section

Aqueous stock solutions of strontium hydroxide and strontium chloride were prepared by mass from their salts. Details are given elsewhere [4]. $Sr(OH)_2$ solutions were kept under positive argon pressure in order to prevent bicarbonate contamination from atmospheric CO_2 (g). Stock solutions were diluted to concentrations from ~10^{-5} mol·kg^{-1} to ~0.1 mol·kg^{-1} by mass to a relative precision of ± 0.01 percent and stored either in sealed Pyrex glass bottles (in the case of $SrCl_2$) or sealed Nalgene plastic bottles (in the case of $Sr(OH)_2$).

A schematic diagram of the high-temperature, high-pressure conductance flow cell [3] used for this work is presented in Figure 3. Briefly, the cell consists of a 60 cm long temperature-controlled platinum inlet tube (1.0 mm i.d.; 1.6 mm o.d.) that leads into a platinized cup (4.6 mm i.d.; 5.2 mm o.d.), which serves as the outer electrode for the cell. The inner electrode is a platinum rod (1.6 mm o.d.), electrodeposited with platinum black, and is a direct extension of the platinum tube which carries the exiting solution away from the cell. The entire electrode assembly is contained in a titanium cell body, which sits in a large air oven capable of controlling temperature to ± 0.15 K over several hours. The electrical insulation between the two electrodes is provided by a sapphire disk and ceramic spacer. The complex impedance of the cell containing aqueous solutions was measured at frequencies from 100 Hz to 100 kHz using a programmable RCL meter (Fluke Model PM6304).

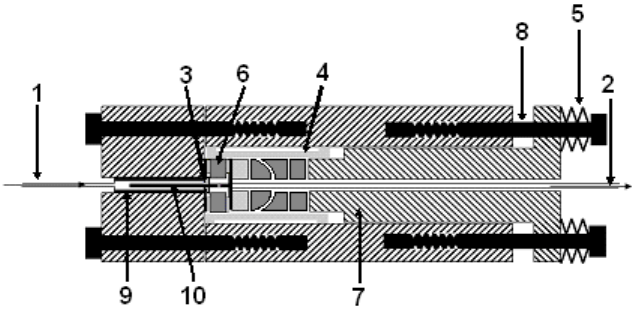

Figure 3: Schematic of the AC flow conductance cell: (1) platinum inlet tube; (2) platinum outlet tube; (3) diamond frit; (4) ceramic spacer; (5) Belleville washers; (6) sapphire insulator; (7) titanium ram; and (8) steel screws, (9) platinium outer electrode, (10) platinium inner electrode.

The pressure seal inside the cell is maintained by compressing annealed thin gold disks which sit between the sapphire insulator and a titanium end-cap, using a system of bolts and Belleville washers. The pressure of the flowing solutions was controlled with the HPLC injection system, described below. Temperature was measured with a platinum resistance standard (Hart Scientific, Model 5612) to an accuracy of ± 0.02 K and pressure was measured with a digital pressure transducer (Paroscientific Inc. Model 760-6K) to an accuracy of ± 0.01 MPa.

The injection system for the conductance equipment was very similar to that reported by Méndez De Leo and Wood [5], shown in Figure 4. Briefly, the sample to be injected was contained in a HPLC injection loop with a capacity of 50 mL. Dual piston pumps were used to inject degassed and de-ionized water into the high-pressure flow system. Pump 1, which was controlled through a computer with Hewlett Packard VEE Version 6.1 software, was used to pressurize the sample loop, or it bypassed the cell and flowed directly to waste while a sample injection was being made. Pump 2, which was always turned on, was used to inject a continuous flow of water through the cell, then to push the sample into the conductance cell. Two computer-controlled valves determined whether solution from the injection loop or water from the reservoir flowed through the conductance cell. Experiments were conducted at a flow rate of 0.5 $mL \cdot min^{-1}$. Solutions and solvent were purged with helium and kept under a positive argon pressure for the duration of the experimental runs. A peristaltic pump, under computer-control and connected to a 14-port valve was used to fill the loop with solutions.

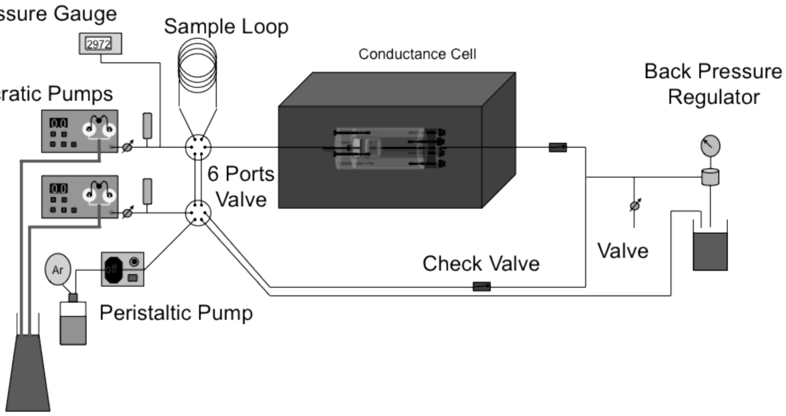

Figure 4. Schematic of the conductance flow circuit.

The result of these measurements was a series of values for the real and imaginary impedance, $Z_{\mathrm{Re}}(\omega)$ and $Z_{\mathrm{Im}}(\omega)$ as a function of frequency, ω:

$$Z(\omega) = Z_{\mathrm{Re}}(\omega) - j \cdot Z_{\mathrm{Im}}(\omega) \tag{1}$$

where Z is the complex impedance, and Z_{Re} and Z_{Im} are the real and imaginary components of the impedance. To obtain the solution resistance at infinite frequency, R_{s}, we extrapolated our impedance data with the function $Z_{\mathrm{Re}} = R_{\mathrm{s}} + \mathrm{a}(\omega)^{-\mathrm{n}}$, in which the exponential term n is a fitting factor [3-5]. The experimental conductivity of the solution ($\kappa_{\mathrm{s}}^{\mathrm{obs}}$), was calculated from R_{s}.

$$\kappa_{\mathrm{s}}^{\mathrm{obs}} = k_{\mathrm{cell}} / R_{\mathrm{s}} \tag{2}$$

The cell constant k_{cell} was determined before each set of runs by measuring the conductivity for a series of six KCl standard solutions (10^{-4} to 10^{-2} $\mathrm{mol \cdot kg^{-1}}$) at 298.15 K and 20 MPa at the same frequency settings as the test solutions. The experimental conductivities of our solutions, $\kappa_{\mathrm{soln}}^{\mathrm{exp}}$, were corrected for impurities within the solvent by subtracting the average of the two experimental values for H_2O, $\kappa_{\mathrm{w}}^{\mathrm{exp}}$, for each run, relative to the theoretical value for water, κ_{w}:

$$\kappa = \kappa_{\mathrm{soln}}^{\mathrm{exp}} - \kappa_{\mathrm{w}}^{\mathrm{exp}} + \kappa_{\mathrm{w}} \tag{3}$$

Equivalent molar conductivities, Λ^{exp}, were calculated from the corrected specific conductivities, κ, using the relationship:

$$\Lambda^{\mathrm{exp}} = \kappa / N \tag{4}$$

with

$$N = \sum_c c_c \cdot z_c = \sum_a c_a \cdot |z_a| \tag{5}$$

where κ is in SI units of $\mathrm{S \cdot m^{-1}}$, concentration, c, is in $\mathrm{mol \cdot m^{-3}}$ and normality, N, is in $\mathrm{molEq \cdot m^{-3}}$). In this study, these were converted to units of $\mathrm{S \cdot cm^{-1}}$ and $\mathrm{mol \cdot cm^{-3}}$, respectively.

3. Conductance Results

Typical results are plotted in Figures 5 and 6. Equivalent molar conductivities $\Lambda(SrCl_2)$ versus square root of the molar concentration from 25 °C to 350 °C at 20 MPa are shown in Figure 5. In the dilute region, steeper slope corresponds to a greater degree of ion-pair formation. The degree of ion association becomes much larger with increasing temperature. At the highest temperature investigated, the lowest concentration was $2.8 \cdot 10^{-5}$ $mol \cdot L^{-1}$, and the degree of ion association is still significant. Figure 6 compares the equivalent molar conductivities of $Sr(OH)_2$ with $SrCl_2$ at 325 °C and 20 MPa. The similar values at low concentration show that both salts are more or less fully dissociated at ~ 10^{-5} mol L^{-1}. The steeper slope of $\Lambda(Sr(OH)_2)$ vs $\Lambda(SrCl_2)$ clearly shows that the hydroxide ions pairs are more stable than chloride, and have a larger formation constant.

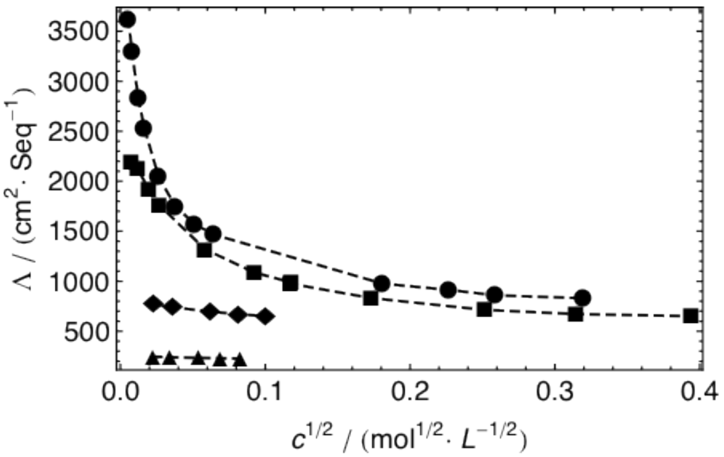

Figure 5. Equivalent Molar Conductance of Aqueous $SrCl_2$ Solutions *vs*. Concentration at 20 MPa: (▲) 25°C, (◆) 100°C, (■) 325°C, (●) 350°C.

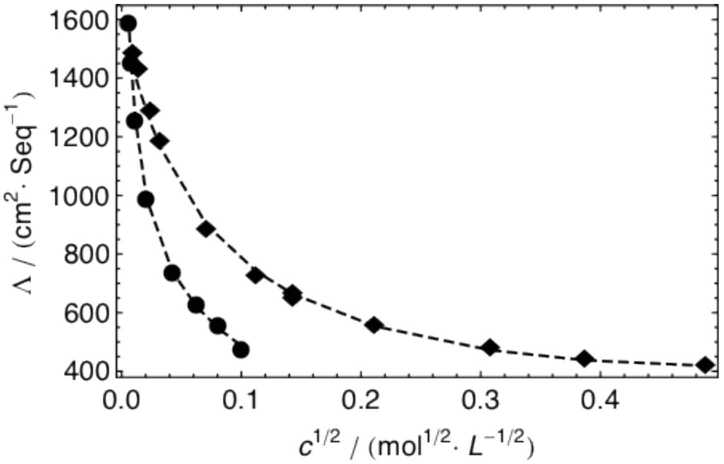

Figure 6. Experimental equivalent molar conductance of aqueous $SrCl_2$ (◆) & $Sr(OH)_2$ (●) solutions *vs*. concentration at 325°C and at 20 MPa . (---) TBBK Fit.

4. Data Analysis

Following the method developed by De Leo and Wood [5], the Turq-Blum-Bernard-Kunz ("TBBK") conductance model [6] was used to model the experimental concentration-dependent equivalent conductivities of our solutions. The analysis included both the first and second complexation steps for aqueous $Sr(OH)_2$ and $SrCl_2$ solutions, and the autoprotolysis of water.

$$H_2O \rightleftharpoons H^+(aq) + OH^-(aq) \qquad K_w \qquad (6)$$

$$Sr^{2+}(aq) + OH^-(aq) \rightleftharpoons Sr(OH)^+(aq) \qquad K_{1OH} \qquad (7)$$

$$Sr(OH)^+(aq) + OH^-(aq) \rightleftharpoons Sr(OH)_2^o(aq) \qquad K_{2OH} \qquad (8)$$

$$Sr^{2+}(aq) + Cl^-(aq) \rightleftharpoons SrCl^+(aq) \qquad K_{1Cl} \qquad (9)$$

$$SrCl^+(aq) + Cl^-(aq) \rightleftharpoons SrCl_2^o(aq) \qquad K_{2Cl} \qquad (10)$$

The TBBK conductance model [6] uses the Mean Spherical Approximation (MSA) theory to calculate the equivalent conductivity of the electrolyte solution. To be consistent, the speciation in solution was also determined using the MSA model for the activity coefficients of the ionic species.

The association constants of strontium with the hydroxide ion (K_{1OH} and K_{2OH}) and the chloride ion (K_{1Cl} and K_{2Cl}), derived from fitting our experimental conductance data with the TBBK model, are plotted in Figues 7 and 8. The association constants were regressed by a nonlinear, least-squares technique (Levenberg-Marquardt). The weights in the least-squares fit were estimated from statistical uncertainties of the experimental impedance measurements. The method requires only the ionic radii and limiting conductivities of the species in the model at the temperature and pressure of each measurement. These were determined by methods similar to those of Mendez De Leo and Wood [3]. Details are given elsewhere [4]. The limiting equivalent conductivity at infinite dilution for Sr^{2+} was determined by conductance measurements on aqueous $Sr(CF_3SO_3)_2$ as the trifluoromethansulfonate ion is known to be non-complexing. Values for the ionization constant of water (K_w) was taken from Bandura and Lvov [7].

Sharyagin et al. [8] have shown that the conductance of mixtures of aqueous electrolytes can be calculated from the conductivities of the single salt solutions using this TBBK model with an accuracy of about 1% at molalities up to about 0.1 $mol\cdot kg^{-1}$. The precision of our fitted model lies within the statistical uncertainties of our measurements, consistent with this observation. We believe the overall accuracy of the conductivity data is ± 2% or better, and that the fitted equilibrium constants are accurate to ± 5% or better.

5. Discussion

5.1 Strontium Association and Solubility under SCWR Conditions

The ion association constants in Figs. 7 and 8 show that, at all temperatures, $Sr(OH)_2$ forms more ion-pairs than $SrCl_2$. The formation constant for $Sr(OH)^+$ is stronger than that for $SrCl^+$ by one order

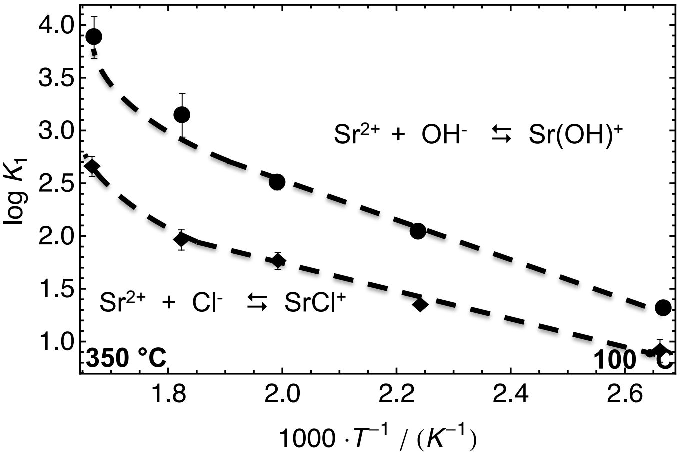

Figure 7. The 1st association constant of $SrCl_2$ (◆) and $Sr(OH)_2$ (●) *vs.* temperature, log K_1 *vs.* $1/T$.

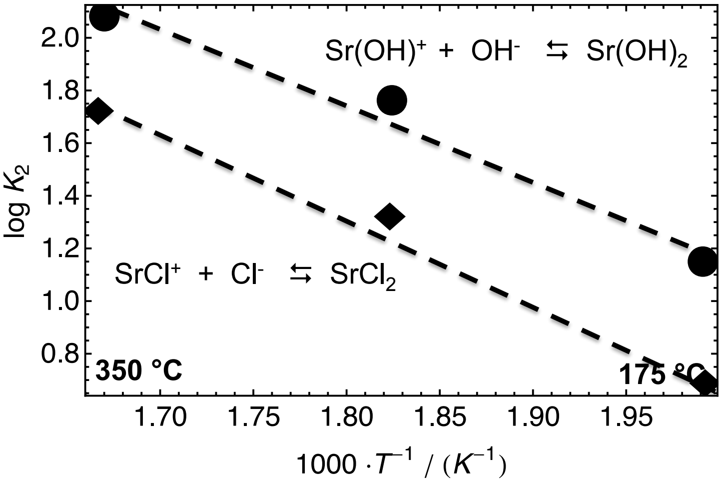

Figure 8. The 2nd association constant of $SrCl_2$ (◆) and $Sr(OH)_2$ (●) *vs.* temperature, log K_2 *vs.* $1/T$.

of magnitude, while the stepwise formation constant for $Sr(OH)_2$ from $Sr(OH)^+$ is stronger than that of $SrCl_2$ from $SrCl^+$ by about 0.5 orders of magnitude. Strontium fission products form as the oxide SrO(s) in the fuel pellets and hydrolyze to $Sr(OH)_2$ when exposed to coolant so that the dissolution reaction can be expressed as

$$\mathrm{Sr(OH)_2(s)} \rightleftharpoons \mathrm{Sr^{2+}(aq)} + \mathrm{2OH^-(aq)} \tag{11}$$

or as

$$\mathrm{Sr(OH)_2(s)} \rightleftharpoons \mathrm{Sr(OH)_2^0(aq)}\,. \tag{12}$$

Under bulk coolant conditions, the hydroxide concentration will be ~ 10^{-4} mol·kg^{-1}, while the concentration of chloride from condenser leaks will be much lower. As a result, it appears that the hydroxy complexes will be the dominant strontium species in solution. A full assessment of the risk of fission product carry-over to the turbines will require values for the solubility product of $Sr(OH)_2(s)$ from 250 to 650 °C using reaction 11 or 12, along with extrapolated values for the ion pair formation constants from the data plotted in Figs. 7 and 8, and an appropriate chemical equilibrium and transport model for simulating coolant chemistry along the reactor core and into the turbine. The results from this study provide a strong foundation for doing so.

5.2 Predictive Models for Thermodynamic Data under SCWR Operating Conditions

Recent advances in the understanding of water chemistry in hydrothermal conditions are summarized in a monograph by the International Association for the Properties of Water and Steam ("IAPWS") [9]. Semi-empirical models now exist for predicting the standard-state properties of aqueous electrolytes up to about 350 ºC and organic solutes up to 250 ºC [10,11]. The models and databases for simple anions and cations are based on robust physical models and good experimental data. The models for inorganic neutral species are more empirical. While parameters for transition metal complexes and other ion pairs are included in these databases, these are derived from correlations based on a very limited number of accurate high-temperature experimental studies and should be used with great caution in predicting activated corrosion product transport, even under sub-critical conditions. Theoretical models for the properties of neutral ion-pairs in supercritical water have been reviewed by Anderko *et al.* [12], however accuracy of these models is limited by a lack of experimental data and they are not applicable to dissociated ionic species. The database for fission product ion pairs and complexes is equally sparse.

Several chemical equilibrium and mass transport models are used by the electric power industry and the geochemical community, along with appropriate activity coefficient models, to model mass transport under sub-critical conditions. These include MULTEQ (EPRI), CHEMSOLVE (AECL), PROCHEM (OLI Systems), EQ3/EQ6 (US DOE), and others. Most of these are limited to temperatures below 350 °C. Models used for supercritical water are often limited to temperatures above 450 °C, because they are not based on Helmholtz free energy formalisms required to model classical near-critical behaviour in solutions containing both ions and ion pairs.

6. Conclusion

This work reports the first conductivity measurements on dilute aqueous solutions of $Sr(OH)_2$ and $SrCl_2$ at temperatures above 100 °C. Ion pair formation constants and limiting ionic conductivities have been derived from these results. The molar conductivities at infinite dilution, $\Lambda°$, were found to be a simple exponential function of the solvent viscosity, which can be used to estimate ionic mobilities and diffusion in crevices under SCWR conditions. Under SCWR conditions the formation of $SrOH^+$ and $Sr(OH)_2^0$ ion-pairs was established to be greater than $SrCl^+$ and $SrCl_2^0$ ion pairs, so that hydroxy complexes will be the dominant strontium species in solution. Neutral species were found to be substantial at 350 °C at concentrations above 10^{-3} mol·kg^{-1}, for both salts. These new formation constant data are an important first step to determine whether the neutral $Sr(OH)_2^0$ may be sufficiently soluble in supercritical steam to be carried to the high pressure turbines.

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