

Equation-of-state and electrical conductivity of NaCl-bearing fluids in the deep Earth: insights from molecular simulations

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SUMMARY

The next generation of mineral and energy system discoveries in Australia will be made under deeper cover or water and require knowledge of the deep earth. Primarily, these discoveries will be driven by understanding the lithospheric properties and resource transport that underpin the systems. Nevertheless, our lack of good understanding of the physical-chemical properties of lithospheric scale mineral systems hinders our interpretation of available data and makes predictive models difficult to use. These properties are very difficult to measure in the laboratory but are accessible through molecular dynamic simulations.

We used molecular dynamics simulations to investigate the chemical and physical properties of the NaCl-bearing fluids over wide range of temperature (25-1000 °C), pressure (1-60 kbar) and salinity (0-10 m) using high-performance computers. The equation-of-state, ion association and diffusion constant of NaCl solutions were predicted and fitted into an electrical conductivity model. By integrating predictive geophysical properties with large-scale models, this study will develop essential guides that underpin interpretation of geophysical data for mineral exploration.

Key words: deep Earth fluids; NaCl; electrical conductivity; geophysical properties; mineral exploration

INTRODUCTION

The sustainability of the industry depends on the discovery of new mineral orebodies at much greater depth in order to replace diminishing ore reserves in mature, well-explored terranes. To achieve this, a quantitative understanding of the minerals and fluids in the deep Earth that lead to the formation of ore deposits. To understand solubility of metals in ore-forming fluids, and the mechanism of ore deposition, it is necessary to determine the nature of the metal speciation, mineral properties and their stability and geophysical response as a function of variables such as temperature, pressure and fluid composition (Seward and Barnes, 1997). The chemical interpretation of geophysically relevant properties (e.g. electrical conductivity or seismic velocity) of mineral systems under cover are essential in mineral exploration (Kearey et al., 2013). The knowledge of physical properties of deep geological fluids enables us to improve the interpretation of geophysical data and build reactive transport models for better prediction and targeting in mineral exploration.

Metals are transported within the deep Earth at high pressures and temperatures by fluids possessing a complex chemical makeup. It is well known that sodium chloride (NaCl) is the major component of aqueous fluids in many ore-forming systems. Equation-of-state (EOS) of NaCl solutions under magmatic-hydrothermal conditions is important for understanding ion association and metal complexation in ore-forming fluids. Current experimental and theoretical studies of EOS of NaCl solutions only cover the pressures up to 5 kbar; however, many evidences show that high-pressure (10-50 kbar) supercritical fluids play an important role in dissolving and transporting metals (e.g., fluids rise from upper mantle to the Earth's crust, fluids form during subduction processes; Sanchez-Valle, 2013).

Australia has some of the most comprehensive geophysical data sets in the world (Kennett et al., 2018). Nevertheless, the value of these data and interpretative tools are currently restricted by inadequate knowledge of the physical properties of the fluids and rocks that influence the measurements. Aqueous fluids in ore-forming systems are also usually electrically conductive due to the dissolved salts which are partially dissociated into ions. For example, electrical conductivities obtained from magnetotelluric surveys could inform our understanding of the nature and abundance of metals and fluids present in these systems (Guo and Keppeler, 2019), in which NaCl is one of the most important salts in aqueous fluids and responsible for electrical conductivities. The interpretation of such data is presently severely hampered by insufficient data on fluid conductivity at high pressures and temperatures due to the difficulty of experimental measurements.

Molecular dynamics (MD) simulations are emerging as a powerful tool for predicting physical and chemical properties of the aqueous fluids and minerals that characterise ore-forming systems, yet these techniques require complex simulations and access to supercomputing facilities.

Previous studies (Driensner et al., 1998; Sherman and Collings, 2002) have demonstrated that classical MD is able to predict the EOS of NaCl solutions correctly. Our recent theoretical studies (Mei et al., 2013-2018) have also demonstrated that molecular modelling could provide an accurate picture of metal complexation and thermodynamic properties in hydrothermal fluids, adding new insights into how mineral systems are formed at a molecular level. In this study, we performed classical MD simulations to map the density and the EOS of NaCl fluids at pressure up to 1000 °C, 60 kbar, and calculated the ion association of Na⁺ and Cl⁻ in high T-P conditions up to NaCl concentration of 10 M. We also calculated the ion diffusion constant of Na-Cl at a wide-range of T-P conditions, and combine with experimental measurements to fit electrical conductivity of NaCl-bearing fluids at the wide-range of temperatures and pressures required for the formation and current conditions of mineral systems.

METHOD AND RESULTS

Molecular dynamics simulations

We used the classical MD code MOLDY (Refson, 2000) to perform the simulations of NaCl in fluids. In classical MD, the inter-atomic interactions are described by empirical potentials fitted from experiments and quantum mechanics calculations, which is a promising approach to conduct MD simulations at large scales. MD simulations were performed at 25-1000 °C, 1-60 kbar using NPT ensembles. Periodic boundary conditions were applied on simulation boxes with 1000-1100 H₂O molecules and 18-180 NaCl pairs to represent NaCl molality of 0-10 m (for example, as shown in Figure 1). The SPC/E potential for water and empirical Lennard-Jones potential for Na⁺ and Cl⁻ was used in the calculations (Berendsen et al., 1987; Smith and Dang, 1994, Sherman and Collings, 2002). A time step of 0.25 fs was applied for all the simulations. All simulations were run for 400 ps, with the trajectories collected at every 0.025 ps after 25ps.

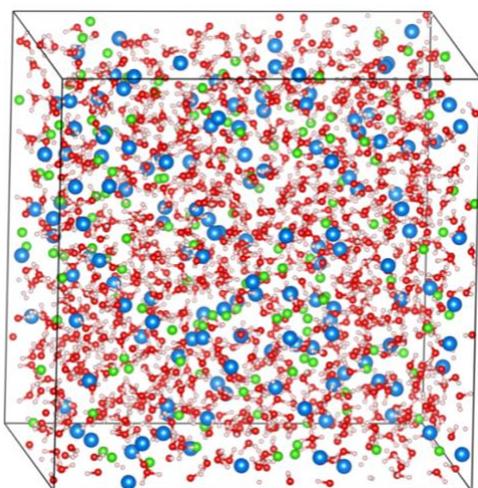


Figure 1. A snapshot of the MD simulation of 8 M NaCl brine at 625 °C, 15 kbar. Atom colours are blue, green, red and pink for sodium, chlorine, oxygen and hydrogen, respectively.

Density and equation of state

In each NPT MD run, the unit cell matrix information was collected with trajectories after 25 ps, and for all simulations, the unit cell matrix shows good convergence in the next 375 ps MD simulations. We used the average of unit cell to calculate the molar volume and density. Figure 2 shows the results of density calculated by MD simulations, and the comparison with previous experimental and theoretical studies (i.e., SOWAT model by Driesner, 2007; Driesner and Heinrich, 2007). The predicted EOS data are in good agreement with the SOWAT model, especially at 25°C and 625°C, and the density of NaCl brines in the range of ~1-1.2 g/cm³ (Figure 2). At lower density range (325 °C, 1kbar), although the predicted density values are slightly lower than the SOWAT model, the EOS predicted by the MD simulations still show the same trend as in previous studies.

There is insufficient EOS data at extreme T-P conditions (i.e., 1000 °C, 60 kbar) from previous studies for comparison to our MD results; however, our results show the same trend of density change as a function of NaCl molality at each T-P condition.

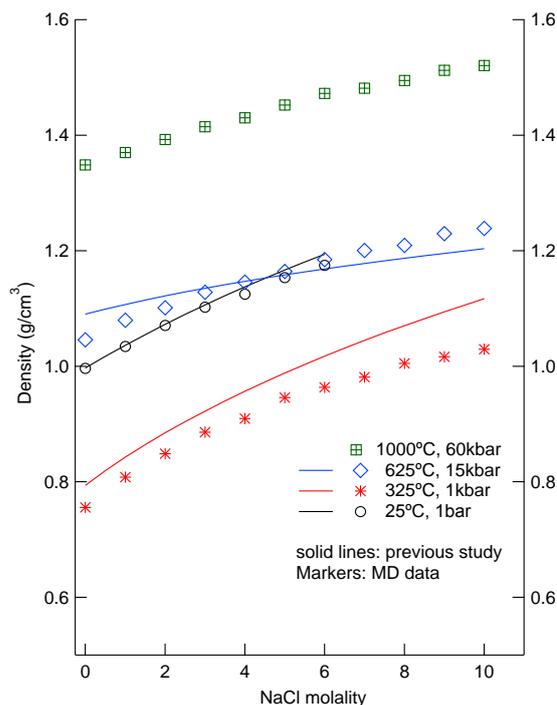


Figure 2. Density of NaCl fluids calculated from MD simulations and the comparison with previous studies (Driesner, 2007; Driesner and Heinrich, 2007).

Na⁺/Cl⁻ Ion association

The radial distribution functions (RDF) for the Na-Cl pair and their integrals (reflecting the time averaged coordination numbers, CN) were calculated using VMD (Humphrey et al., 1996) to characterise the time averaged structural information to investigate the ion association between Na⁺ and Cl⁻ at different T, P and NaCl molality. Figure 3 shows the change of Na-Cl ion association with temperature using the Na-Cl in 5 M NaCl brines as an example.

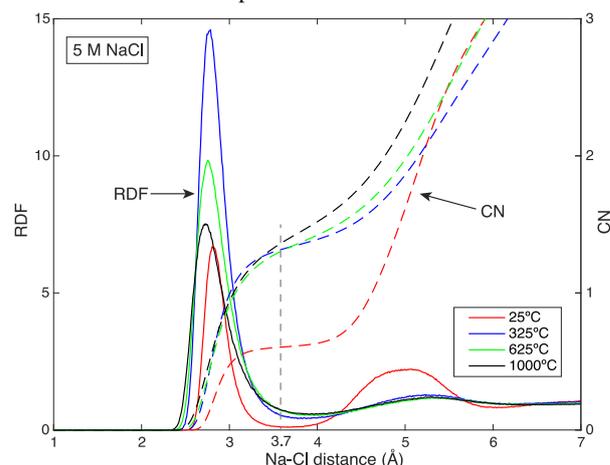


Figure 3. Radial distribution functions (RDF, left Y-axis, solid lines) of Na-Cl and their integrals (coordination number (CN), right Y-axis, dashed lines) at various temperatures.

At 25 °C, 1 bar, the integral of the Na-Cl RDF at 3.7 Å (this Na-Cl distance cutoff was chosen at the first minimum of Na-Cl RDF peak) gave a NaCl coordination number of 0.61, showing

reasonable (61%) Na-Cl ion association at room temperature in NaCl bearing fluids. As shown in Figure 3, at high temperatures, the NaCl coordination number reached higher values of ~1.3-1.4. Figure 4 shows the average coordination number of NaCl at different T-P and NaCl molality. Those more extensive Na-Cl ion associations were also reflected by the formation of Na_nCl_m clusters ($n+m > 3$), which were also confirmed by the peak at ~4.5 Å in the RDF of Na-Na and Cl-Cl for concentrated NaCl solutions at high temperature.

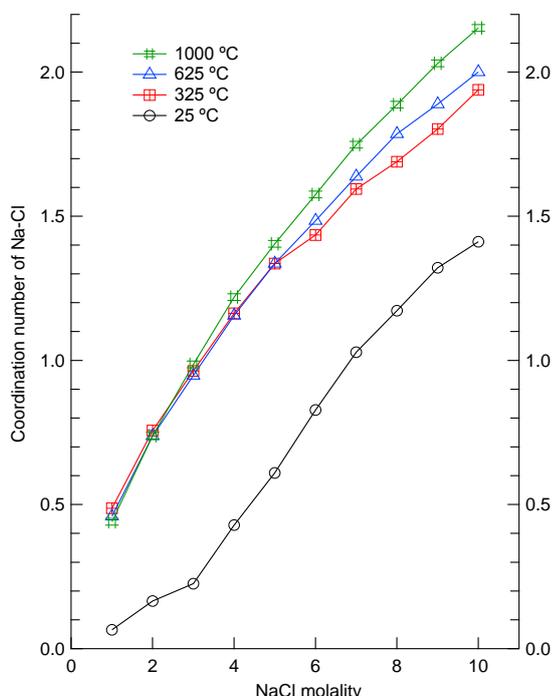


Figure 4. Average coordination number of NaCl at different T-P and NaCl molality.

Diffusion constant

The self-diffusion constants of Na^+ and Cl^- were calculated from the mean-square displacement (MSD) using a build-in utility in MOLDY package. In the MSD calculation, each species defined in the simulation, namely, H_2O , Na^+ , Cl^- were calculated separately. At 25 °C, from our MD calculations, the self-diffusion constant of water molecules in pure water is $2.75 \times 10^{-5} \text{ cm}^2/\text{s}$, which is very close to the experimental value ($2.27 \times 10^{-5} \text{ cm}^2/\text{s}$, Tanaka, 1978). The self-diffusion constant of water molecules in 1 M NaCl solution is $2.29 \times 10^{-5} \text{ cm}^2/\text{s}$, also close to experimental measurement of $2.12 \times 10^{-5} \text{ cm}^2/\text{s}$. For Na^+ and Cl^- , as shown in Figure 4, there are large amount of ion association between Na^+ and Cl^- ions, but we cannot separate the free ions and NaCl clusters during the MSD calculation. Here we consider the total concentration of Na to show the trend of change of diffusion and compare with the ion association effect. Figure 5 shows the results of self-diffusion constants of Na at different T-P and NaCl molality calculated from MD simulations. Overall, the self-diffusion constant of Na decreases with NaCl concentration, while at high temperature, this effect becomes relatively smaller compare to at 25 °C. Sherman and Collings (2002) suggested that the ion association and the formation of large Na_nCl_m clusters lower the average diffusion constant of Na and Cl, which is consistent with the Na-Cl ion association investigated in this study (Figure 4).

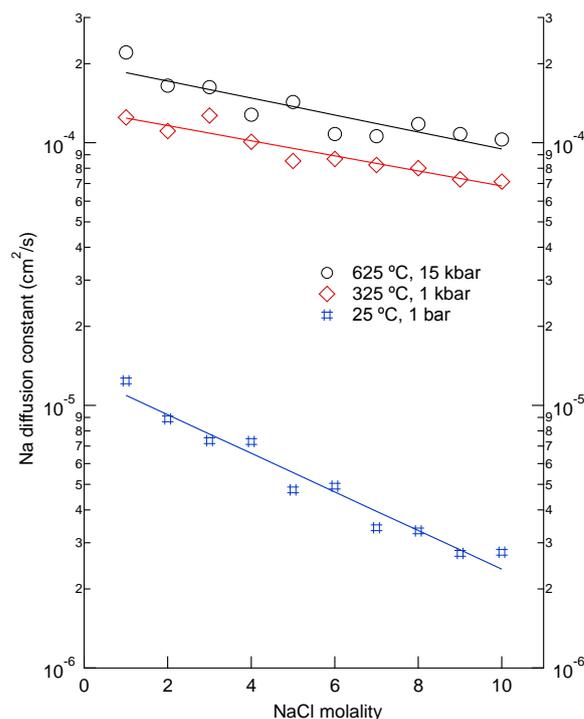


Figure 5. Self-diffusion constants of Na at different T-P and NaCl molality.

Electrical conductivity

The limiting conductance (Λ_0) of NaCl electrolyte is calculated using equation:

$$\Lambda_0 = \Lambda_0^+ + \Lambda_0^- = \frac{eF}{k_B T} (D_0^+ + D_0^-)$$

where e is the electronic charge, F is the Faraday constant, k_B is Boltzmann's constant and D_0^+/D_0^- are the diffusion constants for the individual ions calculated using MD simulations (Sherman and Collings, 2002). The Λ_0 of 1M NaCl solution at 25 °C, 1 bar calculated from MD simulation is $112.72 \text{ S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$, close to the molar conductivity value of $126.45 \text{ S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ for NaCl at infinite dilution at 25 °C (Malmberg, 1965). We also considered the Na-Cl ion association when calculating the conductivity of NaCl at high concentration.

CONCLUSIONS

In this study, we conducted molecular dynamics simulation to calculate the density, ion association and diffusion constant of NaCl fluids at pressure up to 1000 °C, 60 kbar, and used simulation results to predict molar conductivity Λ_0 of NaCl at the wide-range of temperatures and pressures required for the formation of mineral systems. The results show that the ion association of Na-Cl has a major effect in the diffusion constant and conductivity, which has been investigated quantitatively in this study. The new model of EOS and electrical conductivity will fill the gap of physical fluids property measurements under different T-P conditions and will lead to a better interpretation of geophysical data. By applying molecular dynamics simulation to calculate the diffusion of ions in ore-forming fluids, we are able to predict the electrical conductivity properties of a typical brine in mineral systems.

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