

Development of a database of the electrical conductivity of H₂O-NaCl fluids: A molecular dynamics study

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Introduction: Fluids in the earth's crust would have large effects on the occurrence of earthquake and volcanic eruptions. To delineate distribution of the fluids in the earth's crust is requisite to understand the effects of the fluids on the earthquake and volcanic activities. The distribution of the fluids has been expected to be revealed by electromagnetic observation, e.g. magnetotellurics. Electrical conductivity distribution in the crust is considered to roughly correspond to the fluids distribution because of the high electrical conductivity of fluids relative to solids. To develop a plausible model of the fluids distribution to explain the electromagnetic observations, we have to construct a database of the electrical conductivities of fluids over the wide range of pressure (P), temperature (T), and electrolyte concentrations (c). The experimental approaches to measure the electrical conductivities of aqueous NaCl solution have been difficult at high P , T and c conditions and we can get only the data at $P < 4000$ bars, $T < 1100$ K and $c < 0.1$ m (mol/kg) [1]. Classical molecular dynamics (MD) simulations are useful to obtain the physical properties of fluids at high P , T and c conditions and to understand the underlying atomic-scale mechanism of the electrical conductivities. The phases of water and aqueous NaCl solutions at the P - T conditions of the Earth's crust are in liquid and supercritical states. The aims of this study are to make a reliable water model to simulate water in liquid and supercritical phases and to construct a database of electrical conductivity of aqueous NaCl solution at high temperature and pressure conditions.

Computational Methods: We have developed a flexible and polarizable water model based on our previous flexible model [2]. In our new model, the point charges are located on the hydrogen atoms and on the lone pairs of the oxygen atom. The point charges are fluctuated during the MD simulations. The MD simulations were performed using the code MXDORTO with some modifications.

Results and Discussion: Electrical conductivity of aqueous NaCl solution should depend on the density, viscosity, dielectric constant, and salt concentration (mol/kg) [1]. The density and salt concentration are the parameters of the number of ions per unit volume. In the atomic-scale view, the decrease of the viscosity corresponds to the increase of the ionic mobility. Since the viscosity sharply decreases with the increase of the temperature and shows no large dependence on P and T at $T > 600$ K, the density, salt concentration and dielectric constant are the most important parameters at $T > 600$ K. To construct a reliable water model for the supercritical phases, we should check the reproducibility of the physical properties compared with experimental results. Here we compared the structure, density, dielectric constants, and electrical conductivity of aqueous NaCl solutions in supercritical phases with some experiments. The radial distribution functions between atoms in the solution were good agreement with the experiments at 673 K and 3400 bar. The densities of 0.1 m NaCl solution and dielectric constants of water at $T = 573 \sim 973$ K and $P = 2000 \sim 5000$ bar were reasonable compared with the experiments. In this study, we explain the underlying mechanism of the change of the electrical conductivity of aqueous NaCl solution in the supercritical phase from atomistic view and try to construct the useful equations for the electrical conductivity of aqueous NaCl solution in the supercritical phase.

[1] Quist, A.S. and Marshall, W.L. (1968) JPC 72 684-703. [2] Kumagai, N., Kawamura, K. and Yokokawa, T. (1994) Mol. Simul. 12 177-186.

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