First Principles Simulations of CuCl in High Temperature Water Vapor

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It is well-documented in the literature that aqueous vapors and low-density supercritical fluids play a very important role in metal transport within the earth. Experimental data suggests that the solubility of copper in these high-temperature vapors in controlled by the formation of hydrated clusters of the form CuCl(H2O)*n*, where the average number of water molecules in the cluster increases with increasing density [1]. However, the nature of these clusters is difficult to probe experimentally. Moreover, there are some discrepancies between the experimental data and prior simulation work [2]. We have performed first principles simulations to explore these clusters in more detail. At all densities we find an approximately linear H2O-Cu-Cl structure, in agreement with the earlier simulations, surrounded by a variable number of water molecules. The surrounding water molecules do not form a well-defined second solvation shell, but rather a loose network of hydrogen-bonded water with molecular CuCl on the outside edge of the water cluster. We find a broad distribution of hydration numbers, especially at higher densities. In contrast to previous simulation work, but in agreement with experimental data, we find that the average hydration number increases with increasing density.

References

[1]. Migdisov et al., *Geochim. Cosmochim. Acta,* **129**, 33-53 (2014).

[2]. Mei et al., *Geofluids*, **2018**, 4279124 (2018).