Gold(I)-sulfite Complexation in Hydrothermal Fluids: a CPMD Study

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In our previous study, we highlighted that the anion species $[HSO_3]^-$ and $[SO_3]^{2-}$ would emerge as a consequence of H_2SO_3 ionization and exist in hydrothermal fluid environments. In this study, we explore the molecular interactions between both sulfite species and transition metal ions, in particular, gold(I), and their relevance in hydrothermal Au transport. Our present study aims to explore the structure and stability of gold(I)-bisulfite $[AuHSO_3]$ and gold(I)-sulfite $[AuSO_3]^-$ metal-ion complex species in aqueous solution, by undertaking Car-Parrinello molecular dynamic (CPMD) simulations. These CPMD simulations have been performed at ambient conditions (25 ^{o}C), and hydrothermal conditions (up to 350 ^{o}C). The present study aims at better understanding the speciation of the gold-(bi)sulfite system, with a particular focus on the propensity for Au^+ to attach onto SO_3^{2-} and HSO_3^- as a function of temperature. Our preliminary CPMD results indicate that $[AuSO_3]^-$ forms a linear complex with water according to H_2O-$[AuSO_3]^-$ (see figure) with the water molecule bound to the opposite side of the sulfite ligand. CPMD simulations at 25 ^{o}C show that $[AuSO_3]^-$ exists as a stable species for >30 ps, while maintaining a time-averaged Au-S distance of 2.258 ± 0.046 Å, which is slightly shorter than that of the disulfite complex $[Au(SO_3)_2]^{3-}$ (2.32 Å), the latter albeit calculated at the MP2/PCM level of theory [1]. At higher temperature, i.e. T= 350 ^{o}C, H_2O-$[AuSO_3]^-$ remains stable with a moderately extended Au-S distance of 2.287 ± 0.066 Å relative to that at 25 ^{o}C. Building upon these simulation results, we are also undertaking a series of distance-constrained simulations to determine the complexation constants pK of $[AuSO_3]^-$ in the aqueous phase, at ambient and high temperatures, using the thermodynamic integration approach. Our preliminary results predict a pK value of 19.8 for the gold(I) dissociation reaction $[AuSO_3]^- = Au^+ + SO_3^{2-}$, and this value represents, to the best of our knowledge, the first reported complexation constant for this ion pair. We are currently expanding this approach to include additional complexation constants for $[AuSO_3]^-$ and $[AuHSO_3]$ at ambient and hydrothermal conditions.

[1] Pokrovski, Tagirov, Schott, Hazemann, & Proux, (2009). *Geochim. Cosmochim. Acta*, 73, 5406-5427.