

The structure and stability of metal water clusters in high temperature low density fluids

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Metal-bearing low-density aqueous fluids occur ubiquitously close to and on the Earth's surface over a wide range of temperatures ranging from atmospheric water vapor up to high-pressure supercritical steam. These volatile metal species, however, do not exist as "anhydrous" moieties but as hydrated metal clusters. Our current understanding of the interaction of metals as well as metal halides with such water clusters in steam and/or low-density supercritical water and in magmatic gases is rudimentary. Quantum chemistry in combination with experiment can provide fundamental insight into the structures, corresponding energies and distribution of these metal water clusters in natural systems and play an important role in our understanding of solute-solvent interactions such as, for instance, in volatile-enriched ore fluids at high temperature.

The work here presents new theoretical results for the clustering equilibrium constants K for the reaction $M^+(H_2O)_n + H_2O = M^+(H_2O)_{n+1}$ ($M = Co, Ni, Cu, Zn$) in the temperature range 298-600K at 1bar and at water vapor saturation pressures for $n \leq 6$, using G3 and CBS- x *ab initio* theory procedures [1, 2]. Our newly calculated cluster geometries and values for K are in good agreement with those obtained from mass spectrometric measurements [3, 4] as well as those obtained from IR experiments [5]. For example, the stepwise binding enthalpies at 298K obtained in this study for $n=0$ and $n=1$ for the reaction $Cu^+(H_2O)_n + H_2O = Cu^+(H_2O)_{n+1}$ are $-159.1 \text{ kJ}\cdot\text{mol}^{-1}$ and $-161.9 \text{ kJ}\cdot\text{mol}^{-1}$, respectively, and are in good agreement with results from mass spectrometric measurements ($\Delta H_{0,1} = -160.6 \pm 7.5 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta H_{1,2} = -170.3 \pm 6.7 \text{ kJ}\cdot\text{mol}^{-1}$) [3]. Calculations for larger metal water clusters, i.e. for $Cu^+(H_2O)_n$, $Zn^+(H_2O)_n$ and $Ni^+(H_2O)_n$ with $n \leq 6$, indicate that stepwise binding enthalpies and entropies asymptotically approach values characteristic of bulk water (i.e., $-44.0 \text{ kJ}\cdot\text{mol}^{-1}$ for the enthalpy and $-118.8 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for the entropy of H_2O condensation).

[1] Mayhall *et al.* (2008) *JCP* **128**, 144122. [2] Montgomery *et al.*, 1999, *JCP*, **110**, 2822. [3] Dalleska *et al.* (1994) *JACS* **116**, 3519. [4] Magnera *et al.* (1989) *JACS* **111**, 4100. [5] Iino *et al.* (2007) *JCP* **126**, 194302.

Biological selenium remediation - A simple process complicated

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Different microbial groups can detoxify selenate by reducing it to insoluble elemental selenium. XANES spectroscopy demonstrated that methanogenic biofilms, accumulated elemental selenium during bioreactor operation, yet metal selenides and organic selenium compounds were produced as side products. Selenium speciation was sensitive to oxidation by ambient air. The liquid effluent of the bioreactor contained both colloidal dispersed elemental selenium particles and alkylated selenium compounds, as demonstrated by SPME-GC-MS. The alkylation was induced by minor temperature changes during reactor operation. The microbial reduction of selenate to elemental selenium appears to be a straightforward approach for bioremediation of selenium on first sight. The formation of colloidal / alkylated selenium species, the complexity of selenium solid phase speciation and its sensitivity to re-oxidation, however, result in complications anticipated for full-scale application.