

Structure, stability and distribution of neutral water clusters in high-temperature low-density fluids

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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 molecular components, however, do not exist as "anhydrous" molecular moieties but as hydrated clusters. Our current understanding of the interaction of water with such 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 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 results for the clustering equilibrium constant K_p for the reaction $H_2O + nH_2O = H_2O \cdot (H_2O)_n$ in the temperature range 298-1000K at 1bar and at water vapor saturation pressures for $n < 5$, using the high-level *ab initio* complete basis set theory (CBS-QCI/APNO) procedure [1]. Our newly calculated values for K_p are in good agreement with those obtained from thermal conductivity measurements [2], high temperature IR measurements [3, 4], as well as those obtained from second virial coefficient data [5]. For example, water dimerization enthalpies and entropies obtained in this study are -14.5 kJ·mol⁻¹ and -77.0 J·K⁻¹·mol⁻¹, respectively, and are in excellent agreement with TC measurement [2] ($\Delta H = -15.0 \pm 2.1$ kJ·mol⁻¹ and $\Delta S = -77.8 \pm 5.4$ J·K⁻¹·mol⁻¹). Calculations for larger clusters with up to five water molecules indicate that clustering equilibrium constants decrease with increasing temperature, however, it appears that while water cluster abundances at 1bar depend chiefly on the temperature-dependent changes of the equilibrium constant only, at vapor-liquid equilibrium abundances of higher clusters are governed by the shifting balance between the competing contributions of the equilibrium constant and the exponential water monomer term.

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Chemical evolution of groundwater in the unsaturated zone

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Evapotranspiration of recharge water is widely cited as the dominant geochemical process in the unsaturated zone. This implies groundwater will have similar ion ratios, but greater ion concentrations than its recharge source (i.e. rainwater or surface water). However, hydrogeochemical studies commonly note large discrepancies between ion ratios in meteoric water, surface water and groundwater [1-3]. In addition to evapotranspiration a number of unsaturated zone geochemical processes are responsible for this observation and ultimately, the effects on groundwater quality.

This study presents element/chloride ratios of rainwater, unsaturated zone soil pore water and groundwater from a semi-arid catchment in central New South Wales, Australia. Br/Cl, SO₄/Cl, NO₃/Cl, Ca/Cl, and K/Cl ratios are elevated in rainwater relative to groundwater. Variations in these ratios indicate the geochemical evolution from rainwater to groundwater occurs in the upper 1 metre of the unsaturated zone. Increases in ion concentrations with depth can be attributed to evapotranspiration, while variation in ion ratios is the result of biogeochemical processes, nutrient cycling and cation exchange. Nutrient cycling during groundwater recharge appears to be a significant process responsible for ion ratios measured in groundwater.

[1] Davis, S. N., Whittemore, D. O. & Fabryka-Martin, J., (1998) *Ground Water* **36**, 338-350. [2] Gibbs, R. J. (1970) *Science* **170**, 1088-1090. [3] Herczeg, A. L., Simpson, H. J. & Mazor, E. (1993) *Journal of Hydrology* **144**, 59-84.