

Validation of linear density models for equilibrium constants in supercritical aqueous fluids

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The pressure (P) and temperature (T) conditions near the critical point (CP) of water present a major challenge for modeling the thermodynamic properties of solutes. This is due to the anomalous and therefore hardly predictable behavior of basic thermodynamic properties of solutes, such as partial molar volumes. A promising basis for the development of future thermodynamic models, which avoid the direct treatment of these anomalously behaving properties are linear relationships between the logarithm of water density ($\log(\rho_{\text{H}_2\text{O}})$) and the logarithm of equilibrium constants ($\log(K)$) at constant temperature [1]. Although such linear relationships have been known for decades, they still require validation, since the linear behavior derived from experiments is purely empirical. Previous studies using classical molecular dynamics (MD) simulations in conjunction with enhanced sampling methods show no linearity between $\log(K)$ and $\log(\rho_{\text{H}_2\text{O}})$ for NaCl in supercritical water (SCW) [2].

Here, we perform classical MD simulations of NaCl in SCW, using an alternative approach for validating the linearity between $\log(K)$ and $\log(\rho_{\text{H}_2\text{O}})$. This approach is based on the direct

determination of the volumetric properties underlying $\log(K)$, i.e., the reaction volume and the compressibility of the solvent. In addition, we perform a Voronoi tessellation based trajectory analysis to shed light into the short- and long-range (SR and LR) contributions of the NaCl reaction volume.

Our results confirm the constant $\log(K)$ vs. $\log(\rho_{\text{H}_2\text{O}})$ slope between $\sim 0.3 \text{ g/cm}^3$ and $\sim 0.8 \text{ g/cm}^3$.

At densities below $\sim 0.3 \text{ g/cm}^3$, $\log(K)$ levels off and forms an s-shaped curve with the significantly lower values calculated for vapor-like densities. This result is consistent with the early, theoretically based predictions of Pitzer [3]. The results of the Voronoi analysis provide additional insights for a better understanding of the importance of the compressibility-driven LR contributions to reaction volumes.

This work was funded within EU2020 project GEOPRO, grant agreement ID 851816. Simulations were performed on the JUWELS supercomputer at Jülich Supercomputing Centre (JSC).

[1] Dolejš (2013) Reviews in Mineralogy and Geochemistry 76, 35–79.