

# A 298 K thermodynamic model for $\{UO_2^{2+}-H^+-Na^+-ClO_4^- -OH^-\}_{aq}$

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Uranium(VI) is a component of nuclear wastes in oxidizing environments. HClO<sub>4</sub> and NaClO<sub>4</sub> are used to adjust pH and as non-complexing, ‘swamping electrolytes’ for constant ionic strength experiments involving uranyl and other actinide species. Hence, a Pitzer ion-interaction model is presented for the UO<sub>2</sub><sup>2+</sup>-H<sup>+</sup>-Na<sup>+</sup>-ClO<sub>4</sub><sup>-</sup>-OH<sup>-</sup> system at 298 K and 0.1 MPa. Six 'binary' parameters were fit to activity coefficient data for the NaClO<sub>4</sub>(aq) and UO<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>(aq) systems from infinite dilution to solid saturation (Fig. 1). The Oakes and Rai (2001) model [1] was used for HClO<sub>4</sub>(aq). Osmotic coefficients for {H<sup>+</sup>-UO<sub>2</sub><sup>2+</sup>-ClO<sub>4</sub><sup>-</sup>}(aq) are reproduced to 13 mol·kg<sup>-1</sup> ionic strength without any mixing parameters. The latter result contrasts with an existing [2] large theta<sub>H,UO2</sub> value derived using complex mixtures rather than common-ion systems from which this parameter is more rigorously determined. Our theta<sub>Na,UO2</sub> parameter was fit to osmotic coefficients for {Na<sup>+</sup>-UO<sub>2</sub><sup>2+</sup>-ClO<sub>4</sub><sup>-</sup>}(aq) to 16 mol·kg<sup>-1</sup> ionic strength. Two mixing parameters were fit to the {H<sup>+</sup>-Na<sup>+</sup>-ClO<sub>4</sub><sup>-</sup>}(aq) system. Our theta<sub>H,Na</sub> parameter is a revision of the Pitzer and Mayorga (1973) [3] and Harvie et al. (1984) value [4] (PM/HMW) and reproduces the properties for {HCl + NaCl}(aq) without the PM/HMW psi<sub>H,Na,Cl</sub>. Dimensionless standard state chemical potentials for schoepite (nominally UO<sub>2</sub>(OH)<sub>2</sub>·H<sub>2</sub>O) and (UO<sub>2</sub>)<sub>2</sub>(OH)<sub>2</sub><sup>2+</sup> were also derived in conjunction with the NEA value for UO<sub>2</sub><sup>2+</sup>. Twelve Pitzer parameters and seven state chemical potentials reproduce the 298 K, 0.1 MPa schoepite solubility (Fig. 2) and activity coefficients in {H<sup>+</sup>-Na<sup>+</sup>-UO<sub>2</sub><sup>2+</sup>-ClO<sub>4</sub><sup>-</sup>}(aq) mixtures for pH < 6.

## References

- [1] Oakes, C. S. and Rai, D. (2001) *J. Chem. Eng. Data* **46**, 875-884.
- [2] Xiong, Y. and Wang, Y. (2021) *Radiochim. Acta* **109**, 177-185.
- [3] Pitzer, K. S. and Mayorga, G. (1973) *J. Phys. Chem.* **77**, 2300-2308.
- [4] Harvie, C. E., Møller, N., and Weare, J. H. (1984) *Geochim. Cosmochim. Acta* **48**, 723-751.
- [5] Babko, A. K., Kodenskaya, V. S. (1960) *Zh. Neorg. Khim.* **5**, 2568-2574.
- [6] Gayer, K. H. and Leider, H. (1955) *J. Am. Chem. Soc.* **77**, 1448-1450.
- [7] Fujiwara, K., Yamana, H., Fujii, T., Kawamoto, K. Sasaki, T., and Moriyama, H. (2005) *J. Nucl. Sci. Tech.* **42**, 289-294.

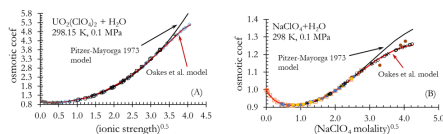


Figure 1. Comparison of our model and that of Pitzer and Mayorga (1973) to experimental osmotic coefficients for UO<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>(aq) (A) and NaClO<sub>4</sub>(aq) (B) at 298 K and 0.1 MPa.

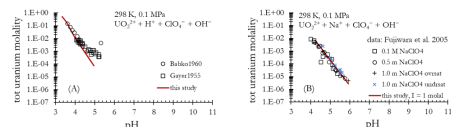


Figure 2. Model and experimental solubilities of schoepite in HClO<sub>4</sub>(aq) (A) and NaClO<sub>4</sub>(aq) (B) at 298 K and 0.1 MPa for pH < 6. The model schoepite solubility in NaClO<sub>4</sub>(aq) shows no ionic strength effect consistent with the data. The model schoepite solubility in HClO<sub>4</sub>(aq) is shown for the Gayer and Leider (1955) solution compositions.