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Thermodynamics of the complexation of neptunium (V) with halides in aqueous solution at elevated temperatures

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Introduction

Deep geological salt rock formations are in discussion to serve as host rock for a repository of high-level nuclear waste. This approach requires a well-founded knowledge of the geochemical behaviour of the radionuclides in diluted to concentrated salt solutions to model their potential migration and retention in the near- and far-field of the repository over long time scales. In the past a broad variety of complexation reactions of actinides in their most important oxidation states were studied. The thermodynamic functions ($\log \beta_j^0$, $\Delta_r H_m^0$, $\Delta_r S_m^0$, $\Delta_r C_{p,m}^0$) and modelling parameters ($\epsilon_T(i, k)$) are summarized in the NEA thermodynamic database.¹ However, most data are only available for 25 °C or fixed ionic strength.^{2a,b} Temperatures up to 200 °C are expected in the near-field of a repository for high-level nuclear waste, which will significantly alter the thermodynamics of the geochemical reactions of the radionuclides in solution. Thus, detailed thermodynamic data at 25°C as well as at increased temperatures are mandatory for a comprehensive long-term safety assessment.

Results and Discussion

In this work the complexation of NpO_2^{+} with F^- and Cl^- was studied as a function of the temperature (20 – 85 °C) and the ionic strength ($I_m(\text{NaClO}_4) = 0.5 - 4.0 \text{ mol kg}^{-1}$) using near infrared (NIR) absorption spectroscopy. Systematic evaluation of the spectroscopic results clearly confirms the formation of two distinct complex species $[\text{NpO}_2(\text{L})_2]^{1-n}$ ($n = 1, 2$) for $\text{L} = \text{F}^-$ and Cl^- . Applying the specific ion interaction theory (SIT) and the integrated Van't Hoff equation the thermodynamic functions ($\log \beta_j^0$, $\Delta_r H_m^0$, $\Delta_r S_m^0$) and the binary ion-ion-interaction parameters ($\epsilon_T(i, k)$) for the different complexation reactions are obtained. With increasing temperature the chemical equilibrium shifts towards the complexed Np(V) species for both ligands. The thermodynamic stability constants increase by 0.5 - 1 orders of magnitude with increasing temperature. Furthermore, all complexation reactions show positive values of $\Delta_r H_m^0$ and $\Delta_r S_m^0$. Thus, the reactions are endothermic and driven by the high gain of entropy.

References

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