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Thermodynamics of neptunium(V) complexation with sulfate in aqueous solution

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ABSTRACT

The complexation of NpO_2^+ with sulfate is studied in aqueous solution using absorption spectroscopy. The total ligand concentration (Na_2SO_4), ionic strength ($NaClO_4$), and temperature (T = 20–85 °C) is varied, yielding detailed information on the thermodynamics of the complexation reaction. A single complex species ($NpO_2(SO_4)^-$) is identified by peak deconvolution of the absorption spectra. The molar fraction of the complex species increases with increasing temperature. The conditional stability constants log $\beta'_1(T)$ are calculated and extrapolated to zero ionic strength for each temperature condition with the specific ion interaction theory (SIT). The determined log $\beta_1^0(T)$ values increase by approximately one logarithmic unit in the studied temperature range. Furthermore, the log $\beta_1^0(T)$ values are linearly correlated with the reciprocal temperature. Thus, fitting the data according to the integrated Van't Hoff equation yields the standard reaction enthalpy ($\Delta_r H_m^0$) and entropy ($\Delta_r S_m^0$) of the formation of the $NpO_2(SO_4)^-$ complex. The results show an endothermic reaction which is solely driven by the reaction entropy. In addition, the binary SIT ion-ion interaction coefficient $\varepsilon(Na^+, NpO_2(SO_4)^-)$ of the complex species is determined.

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1. Introduction

The application of nuclear fission for the generation of electrical power results in the accumulation of radioactive waste. One of the main issues in this context is the safe disposal of this nuclear waste. Besides uranium and fission products, plutonium and minor actinides (Np, Am, Cm) are present in the waste due to neutron capture reactions in the reactor. Because of the long half-lives of the actinides the disposal of high-level radioactive waste requires an effective isolation from the biosphere over very long timescales. The disposal option preferred worldwide is the final emplacement of the waste in deep geological formations. The long-term safety assessment of a nuclear waste repository requires the consideration of different incident scenarios, including the intrusion of water and subsequent dissolution of the radioactive waste. Besides reactions at liquid-solid interfaces (e.g. dissolution of the waste matrix and solubility of the radionuclides, sorption processes, etc.), complexation reactions with different ligands in the aqueous phase may influence the redox properties and the geochemical behaviour of the actinides considerably. Detailed knowledge of these processes is of major relevance for a reliable modelling of the migration behaviour of the actinides over very long time scales. Therefore, thermodynamic data like standard-state stability constants (log β_n^0), standard reaction enthalpies ($\Delta_r H^0$) and entropies ($\Delta_r S^0$) are required.

The actinides U – Am are redox active metals and exist as An(III) to An(VI) within the thermodynamic stability field of water. Within the An(V) series the pentavalent Np(V) is thermodynamically most stable and highly soluble in aqueous solution. Thus, the complexation of Np(V) with inorganic ligands in natural ground waters (e.g. OH^-, CO_3^{2-}, SO_4^{2-}, Cl^-, F^-, etc.) is of major relevance [1–3].

The present work focuses on the complexation of Np(V) with sulfate at T = 20–85 °C. Sulfate is available in natural ground waters, in pore waters of clay rocks and in brines from rock salt formations [4,5]. In the past considerable effort was made to study the complexation of different actinides with SO_4^{2-} [6–16]. Nonetheless, the complexation of Np(V) with SO_4^{2-} is not fully described. Most of the available studies were performed only at a fixed ionic strength and/or at ambient temperature [17–22]. Furthermore, the literature data deviate significantly from each other. For example the log $\beta'_{1,25^\circ C}(NpO_2(SO_4)^-)$ obtained by solvent extractions differ by up to 0.7 orders of magnitude ($I_m = 1.0$ mol kg^{-1} $NaClO_4$) [19,23,24]. The literature data were critically reviewed and are summarized in the NEA-TDB [1,3]. The NEA-TDB recommends a value of log $\beta^0_{25^\circ C}(NpO_2(SO_4)^-) = 0.44 \pm 0.27$ for the formation of $NpO_2(SO_4)^-$ [1,3]. This value is based on two older solvent extraction

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studies which are assumed to be the most reliable [23,24]. Recent studies on the Np(V) sulfate complexation are not considered. Rao et al. applied spectrophotometry and calorimetry at T = 10–70 °C to determine a log $\beta^0_{1,25^\circ C}$ ($NpO_2(SO_4)^-$) = 1.03 ± 0.25, which increases by 0.2 logarithmic units in the studied temperature range [18]. In two different calorimetric studies by Rao et al. a log $\beta^0_{25^\circ C}$ ($NpO_2(SO_4)^-$) = 0.97 is reported [17,22]. The stability constant increases by 0.5 logarithmic units with increasing temperature. The stability constants determined in these recent studies are by approximately 0.5 orders of magnitude higher than the value recommended by the NEA-TDB. In all studies the formation of only the $NpO_2(SO_4)^-$ complex was observed, except for the solvent extraction study by Xia et al. describing the formation of the 1:2 complex ($NpO_2(SO_4)_2^{3-}$) even at low ligand concentrations ($[SO_4^{2-}] \approx 0.3$ mol L^{-1}) [22]. An EXAFS study on the coordination mode of sulfate with Np(V) by Hennig et al. describes the formation of two $NpO_2(SO_4)^-$ isomers [25]. One isomer exhibits a mono dentate coordination of the ligand, while the second one is coordinated in a bidentate manner. However, the EXAFS results confirm the solely formation of the 1:1 complex. Higher complexes of Np(V) with SO_4^{2-} were not observed. Although several stability constants are available in the literature a direct comparison is not possible as the reported values are conditional stability constants determined at different conditions (pH, I_m, T). An extrapolation of the reported conditional data to $I_m = 0$ is not possible due to the missing SIT specific binary ion-ion interaction coefficients for the NpO_2^+-SO_4^{2-} system.

In the present paper the impact of ionic strength and temperature on the complexation of Np(V) with sulfate is studied. The results are evaluated with the specific ion interaction theory (SIT) yielding thermodynamic standard-state stability constants, standard reaction enthalpies ($\Delta_r H^0_m$) and entropies ($\Delta_r S^0_m$) as well as binary ion-ion interaction coefficients.

2. Experimental section

2.1. Sample preparation

All concentrations are given on the molal concentration scale (mol kg^{-1} H_2O; “m”) to avoid changes of the concentration upon heating due to changes of the solution density. The chemicals used for the preparation of the solutions are reagent grade or higher and purchased from Merck Millipore. Ultrapure water (Milli-Q academic, Millipore) is used for sample preparation. An isotope pure Np(V)-237 stock solution (5.9×10^{-3} mol kg^{-1} H_2O) is used to prepare the samples with an initial Np(V) concentration of 2.5×10^{-4} mol kg^{-1} H_2O. The oxidation state of Np in the stock solution is validated by absorption spectroscopy. Details on the preparation of the Np(V) stock solution are given elsewhere [26]. The used chemicals and their purities are listed in Table S1 in Supplementary information. The total proton concentration in the samples is adjusted to $[H]^+_{total} = 5.0 \times 10^{-5}$ mol kg^{-1} H_2O with $HClO_4$. The sulfate concentration is increased by successive titration. The titration solutions are prepared by dissolving solid Na_2SO_4 in water. The proton concentrations of the titration solutions are identical to that of the samples. Four different titration series at ionic strengths of $I_m(NaClO_4)$ = 1.00, 2.01, 3.01, and 4.10 mol kg^{-1} H_2O are performed. The ionic strength of the sample and the titration solutions is adjusted by addition of solid $NaClO_4 \cdot H_2O$.

2.2. NIR absorption spectroscopy

Spectrophotometric measurements are conducted in the wavelength range of λ = 950–1050 nm using a Varian Cary-5G UV/Vis/NIR spectrophotometer. The temperature of the sample holder is set to T = 20, 30, 40, 50, 60, 70, 80, 85 °C controlled by a Lauda Eco E100 thermostatic system. The cuvettes (quartz glass with air tight screw caps, 1 cm path length, Hellma Analytics) are pre-equilibrated at the respective temperatures in a custom-made sample holder. Each sample is tempered for 15 min to ensure chemical equilibrium before measurement. Spectra are recorded with 0.1 nm data interval, a scan rate of 30 nm min^{-1} (average accumulation time: 0.1 s) and a slit width of 0.7 nm in double beam mode. The spectrum of the single complex species and the stability constants of the Np(V)-SO_4^{2-} complex are obtained by peak deconvolution and slope analyses of the mole fractions. The methods of peak deconvolution and slope analysis are described elsewhere [27]. All uncertainties of the stability constants log β, enthalpy ΔH, entropy ΔS and SIT binary ion-ion interaction coefficient $\Delta\varepsilon_{j,k}$ are given with a confidence level of 0.95.

3. Results and discussion

3.1. Absorption spectra

The absorption spectra of Np(V) as a function of $[SO_4^{2-}]_{tot}$ = 0–7.8×10^{-2} mol kg^{-1} H_2O at $I_m(NaClO_4)$ = 4.10 mol kg^{-1} H_2O and T = 20 and 85 °C are displayed in Fig. 1. At both temperatures, the absorption band shifts to higher wavelengths with increasing ligand concentration. At 20 °C and without sulfate a single absorption band at λ_{max} = 980.2 nm is observed. This band is attributed to the hydrated Np(V) aquo ion, $NpO_2(H_2O)_5^+$ [28,29]. With increasing concentration of SO_4^{2-} the absorption band is slightly shifted to higher wavelengths and a small shoulder appears at the bathochromic side. The red shift of the absorption band is accompanied by a broadening in the full width half maximum (FWHM) of the spectra. At 85 °C the changes of the features of the absorption band with increasing SO_4^{2-} concentration are more pronounced: the maximum of the absorption band shifts 1.8 nm to higher wavelengths. The formation of the shoulder at the bathochromic side and the broadening of the FWHM are also more distinct. These changes clearly indicate the formation of $NpO_2(SO_4)_n^{1-2n}$ complexes, which is fostered at increased temperatures. Comparison of the integral of the absorption bands, i.e. the total transition intensity of the Np(V) aquo ion and the total transition intensity of the absorption spectra at higher sulfate concentrations shows that the total integrated absorbance remains constant. This proves that the complex species and the solvated Np(V) have equal integrated extinction coefficients.

Fig. 2 shows the absorption spectra of the Np(V) aquo ion as a function of temperature and ionic strength. The absorption band shifts to lower wavelengths with increasing temperature by 0.02 nm per K. However, the FWHM remains constant at 7.4 nm (Fig. 2 (left)). This temperature dependent effect is observed at all ionic strengths. So far, this effect has not been mentioned in the literature. A similar hypsochromic shift is observed with increasing ionic strength. The absorption band shifts to lower wavelengths by 0.2 nm per 1 mol kg^{-1} $NaClO_4$ (Fig. 2 (right)). This effect is described in the literature and is attributed to changes in the outer hydration sphere of the Np(V) ion [30]. As the solvent polarity may also affect the energy of the electronic absorption the temperature-dependent blue shift of the Np(V) absorption spectra observed in the present work might also result from changes of the solvent polarity [31–34]. The hypsochromic shift of the absorption spectra is contrary to the bathochromic shift of the spectra caused by the complexation of Np(V) with sulfate. Due to this, the spectra have to be treated separately for each studied temperature and ionic strength, and single component spectra have to be determined for all experimental conditions.

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