

A thermodynamical study on the complex formation of Cm(III) with methacrylate

Daniel R. Fröhlich^{a,*}, Petra J. Panak^{a,b}

^a Ruprecht-Karls-Universität Heidelberg, Physikalisch-Chemisches Institut, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany

^b Karlsruher Institut für Technologie, Institut für Nukleare Entsorgung, P.O. Box 3640, 76021 Karlsruhe, Germany

ARTICLE INFO

Handling Editor: Melissa A. Denecke

Keywords:

Curium

Methacrylate

Complexation

Thermodynamics

TRLFS

Elevated temperature

Nuclear waste disposal

ABSTRACT

Time-resolved laser fluorescence spectroscopy (TRLFS) is used to investigate the complexation of Cm(III) with methacrylate in NaCl solution as a function of the temperature (20–60 °C), ionic strength (0–2.5 mol/kg) and ligand concentration (0–0.2 mol/kg). The aqueous speciation of Cm(III) is obtained by deconvolution of the experimental emission spectra using pure component spectra of all Cm(III) species involved under the given experimental conditions. By applying the specific ion interaction theory (SIT), the temperature-dependent thermodynamic stability constants ($\log K_n^0(T)$, $n = 1, 2$) are determined by extrapolating the conditional stability constants to zero ionic strength. Additionally, the binary ion interaction coefficients ($\epsilon(i, j)$) for the interaction between Cl^- and the complex species $[\text{Cm}(\text{Meth})_n]^{3-n}$ ($n = 1, 2$) are calculated. The temperature dependency of $\log K_n^0$ in combination with the integrated Van't Hoff equation provides the molal standard reaction enthalpies and entropies ($\Delta_r H_m^0$, $\Delta_r S_m^0$) of the respective complexation reactions confirming that both, the formation of $[\text{CmMeth}]^{2+}$ and $[\text{Cm}(\text{Meth})_2]^+$ are endothermic and entropy driven. At temperatures ≥ 70 °C, an additional Cm(III) species is formed that is attributed to the thermally induced polymerization of methacrylate.

1. Introduction

Cementitious materials will be essential constituents of the engineered barriers in nuclear waste repositories in geological formations. The physical properties of these materials are optimized by addition of various organic admixtures, e.g. superplasticizers (Ferrari et al., 2011). The different classes of superplasticizers include modified lignosulphonates, polycarboxylate-ether based macromolecules, sulphonated naphthalene-formaldehyde and sulphonated melamine-formaldehyde polycondensates. During long storage times, these organic macromolecules might degrade either chemically after water intrusion into the repository or radiolytically as a result of the radioactive decay of the high-level waste material. As a result, small organic molecules might be released as degradation products from the cementitious material and serve as potential complexing agents for radionuclides, thus impacting their migration behaviour.

With respect to the long-term radiotoxicity, plutonium and the minor actinides (Np, Am, Cm) are particularly important. These actinides can occur in various oxidation states depending on the geochemical conditions. The near-field of the waste repository will most likely be dominated by reducing conditions as a result of the corrosion of the steel canisters. Therefore, +3 (Pu, Am, Cm) and +4 (Np) will be

the most important oxidation states of the above mentioned actinides. The migration of these cations will be determined by various geochemical processes, including sorption and diffusion, dissolution and precipitation equilibria, and complexation reactions with dissolved organic and inorganic complexing agents.

The effect of different superplasticizers on the geochemical behaviour of various lanthanides (Fröhlich et al., 2017; Wieland et al., 2014; Young et al., 2013) and actinides ((Kitamura et al., 2013; Wieland et al., 2014; Young et al., 2013) has been studied earlier, covering complexation reactions (Fröhlich et al., 2017), sorption (Wieland et al., 2014; Young et al., 2013) and dissolution processes (Kitamura et al., 2013). The present study focuses on complexation reactions of Cm(III) as a representative trivalent actinide with methacrylate as a potential degradation product of polycarboxylate superplasticizers which are standardly synthesized using either acrylic or methacrylic acid (e.g. Kinoshita et al., 1995; Plank et al., 2008; Plank and Winter, 2008; Winnefeld et al., 2007).

The aqueous speciation of Cm(III) is tracked as a function of the ligand concentration, ionic strength and temperature using time-resolved laser fluorescence spectroscopy (TRLFS). The species distribution which is obtained via deconvolution of the emission spectra is evaluated using the specific ion interaction theory (SIT) and the Van't

* Corresponding author.

E-mail address: daniel.froehlich@partner.kit.edu (D.R. Fröhlich).

Hoff equation to determine the temperature dependent stability constants ($\log K^0(T)$) for the formation of different Cm(III)-methacrylate species and the molal standard reaction enthalpies ($\Delta_r H_m^0$) and entropies ($\Delta_r S_m^0$) of the related complexation reactions. The obtained data will complement existing thermodynamic databases which are indispensable with respect to long-term safety assessment of nuclear waste disposal. This is also the first time, temperature dependency of the complexation between a trivalent actinide and an unsaturated monocarboxylic ligand is studied in detail.

2. Experimental section

2.1. Sample preparation

All concentrations are given in mol/kg H₂O. The sample solutions are prepared using a 2×10^{-7} m Cm(III) stock solution in diluted HClO₄ with the isotopic distribution: 89.7% Cm-248, 9.4% Cm-246, 0.3% Cm-244, and 0.6% Cm-243/245/247. In all samples, the total Cm(III) concentration is held constant at 5×10^{-9} m. One batch of samples is prepared by varying the ionic strength ($I = 0.5$ – 2.5 m) at a constant methacrylate concentration of 0.01 or 0.05 m. The ionic strength is adjusted by adding solid NaCl. The second batch of samples is prepared at constant ionic strength ($I = 1$ m) varying the ligand concentration between 0 and 0.2 m. The methacrylate concentrations are adjusted by adding either solid sodium methacrylate or aliquots of a 1.0 m solution. The total proton concentration is adjusted with 0.01 m HCl and held constant in all samples ($[H^+]_{\text{total}} = 9 \times 10^{-5}$ M). All chemicals were purchased from Merck or Sigma/Aldrich.

2.2. TRLFS

TRLFS measurements are performed with a pulsed Nd:YAG (Surelite II, Continuum, USA) pumped dye laser system (NarrowScan, Radiant Dyes Laser & Accessories GmbH, Germany) with a pulse energy between 1 and 3 mJ at a repetition rate of 10 Hz using the dye Exalite 398. The detector system consists of an iStar Gen II ICCD camera and a Shamrock SR-303i spectrograph (both ANDOR Technology PLC, Northern Ireland). The sample solutions are measured in quartz cuvettes (Hellma, Germany) embedded in a copper block. The temperature of the block is controlled using a water bath thermostat (K6-mpc-NR, Peter Huber Kältemaschinenbau GmbH, Germany). Curium is excited at 396.6 nm. Emission spectra are recorded in the range of 570–630 nm using the 1200 lines/mm grating of the spectrograph. By measuring the Cm(III) fluorescence in time-grated mode with an initial delay time of 1 μ s, short lived fluorescence of organic impurities and scattering light are excluded.

3. Results and discussion

3.1. Fluorescence spectra

Two temperature series of emission spectra of Cm(III) in the presence of 0.005 and 0.05 m methacrylate are presented in Fig. 1. Due to the continuous decrease of the fluorescence intensity with increasing temperature, spectra are normalized with respect to the total peak area. The decrease is the result of a successive population of higher energetic states (Tian et al., 2011). It is visible, that the position of the emission band shifts with increasing temperature and ligand concentration. This change is correlated with a successive shift of the equilibrium from the aqueous Cm(III) towards complexes with methacrylate ($[Cm(Meth)_n]^{3-n}$). Evaluation of all measured spectra reveals four different species; besides the Cm(III) aquo ion, pure component spectra of the methacrylate complexes ($[Cm(Meth)_n]^{3-n}$, $n = 1$ – 3) are extracted. This extraction process is performed by hand without usage of any evaluation software. At first, the spectrum of the $[CmMeth]^{2+}$ complex is obtained at moderate temperature and low ligand concentration by

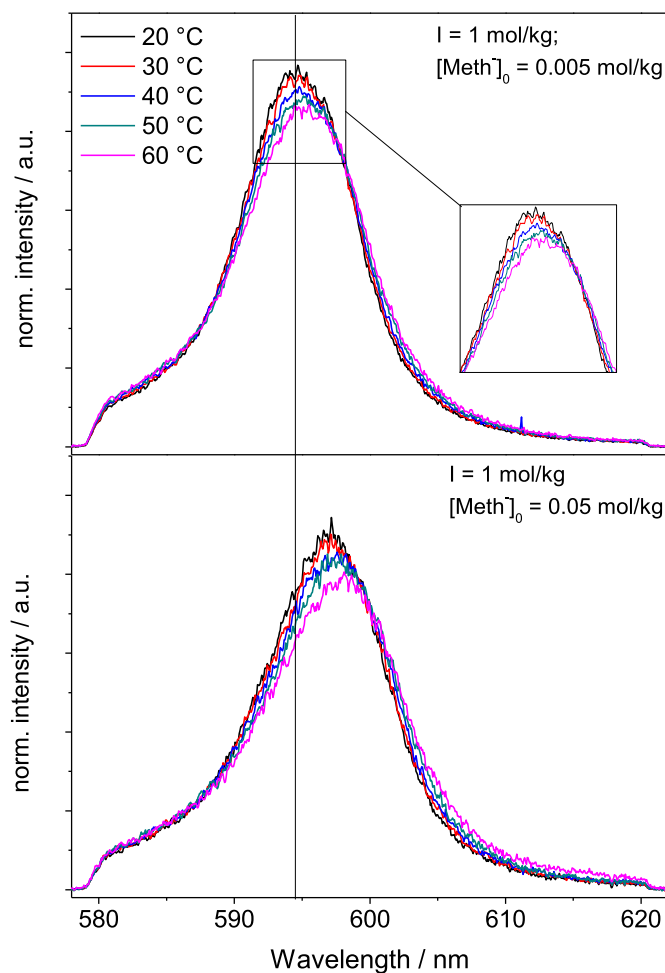


Fig. 1. Emission spectra of Cm(III) in 1.0 m NaCl solution in the presence of 0.005 m (top) or 0.05 m methacrylate (bottom) as a function of the temperature (20–60 °C). All spectra are normalized to equal peak area.

subtraction of an appropriate share of the Cm(III) aquo ion, followed by normalization of the residue with respect to the total peak area. Using the spectrum of the Cm(III) aquo ion and the $[CmMeth]^{2+}$ complex, the pure component spectrum of the $[Cm(Meth)_2]^+$ species is derived similarly at higher ligand concentration and temperature. Due to the relative low amounts of $[Cm(Meth)_3]$ formed at the given experimental conditions, this species has to be extracted at very high ligand concentration and temperature. Following this procedure, it is assumed that the pure component spectra do not vary significantly with increasing temperature. The correctness of this deconvolution process is ensured by performance of slope analyses (see chapter 3.2).

Fig. 2 presents the different pure component emission spectra, with maxima located at 593.5, 596.6, 599.0, and 602.0 nm. A shift of ≈ 3 nm for each ligand entering the coordination sphere of Cm(III) is typical for monocarboxylates and has been reported earlier (Skerencak et al., 2013; Fröhlich et al., 2013, 2014, 2015). The weak signal/noise ratio of the spectrum of the $[Cm(Meth)_3]$ species is a result of the low amounts of this species at the given experimental conditions. A visible change in the fluorescence intensity for the different Cm(III) species was not observed ($F_i = 1$). Applying temperatures of 70 °C and higher leads to a significant change of the emission spectra which does not fit the evolution of the spectra with increasing temperature at $T < 70$ °C. As an example, spectra of one sample at 20 °C, 90 °C, and 20 °C after 15 min at 90 °C are shown in Fig. 3. At 90 °C the emission spectrum is visibly broadened and a new species (maximum at 602–603 nm) is observed. After cooling back to room temperature, the spectrum which is previously obtained at 20 °C cannot be reproduced. This effect is attributed

Download English Version:

<https://daneshyari.com/en/article/8863131>

Download Persian Version:

<https://daneshyari.com/article/8863131>

[Daneshyari.com](https://daneshyari.com)