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Complexation of Eu^{3+} with a polycarboxylate based concrete superplasticizer in chloride media

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ABSTRACT

In this work, we present a complexation study of Eu^{3+} with a commercial polycarboxylate based concrete superplasticizer Glenium® 51 in NaCl media at low to medium ionic strengths. The complexation is investigated using time-resolved laser fluorescence spectroscopy (TRLFS) at $pH_m = 5.1 \pm 0.1$. With the charge neutralization model, conditional stability constants log K'_m were determined for ionic strengths up to I_m (NaCl) = 2.47 mol kg^{-1} H_2O^{-1}. Eu^{3+} only forms one complex with this complexant under these conditions. The conditional stability constants decrease significantly at elevated ionic strengths by almost three orders of magnitude. Thus, the Eu^{3+}-Glenium® 51 complex formation is reduced at high ionic strengths. The determination of the conditional stability constants allows to extrapolate to the stability constant at zero ionic strength by using the specific ion interaction theory (SIT). A $log\ K_m^0 = 8.54 \pm 0.9$ has been determined, which highlights the strong complexation properties of the superplasticizer. Moreover, this novel study presents first insights into the interaction of Glenium® 51 with Eu^{3+} at various ionic strengths. Since Eu^{3+} is used as a surrogate for trivalent actinides, these results are very important for understanding actinide behavior in cementitious systems present at the geotechnical barrier of a repository in clay rock formations of Northern Germany containing pore and formation waters with elevated ionic strength.

1. Introduction

The storage of nuclear waste will be realized in deep geological formations applying a so-called multi-barrier system [1]. The geotechnical barrier in nuclear waste repositories consists of cementitious materials as components of waste containers or structural materials at the interface of backfilling. The physicochemical properties of these cementitious materials are altered by addition of chemical admixtures, which improve the dispersion of cement particles in water [2], hydration [3], strength [4], durability [5] and reduce creep, shrinkage and thermal strains [6]. One important subcategory of these admixtures are superplasticizers. These organic compounds are commonly classified as sulphonated naphthalene-formaldehyde polycondensates [7], modified lignosulphonates or polycarboxylate-ether [8] based macromolecules. Glenium® 51 (Fig. 1) is a commercially available polycarboxylate-ether based superplasticizer, which is synthesized by radical copolymerization of methacrylic and a ω-methoxy polyethylene glycol methacrylate ester.

In case of water intrusion into the nuclear waste repository, cement degradation processes will occur. In consequence, superplasticizers or their degradation products might be released as the cement degradation progresses. In regards to the safety of nuclear waste disposal, the interaction of these compounds with radionuclides, especially uranium and transuranium elements (Np, Pu, Am, Cm) are of high importance. The conditions in the near field of the repository are expected to be reducing [9]. Thus, Pu, Am, and Cm will be present as trivalent ions. Several solubility studies have been conducted with Eu^{3+} [10], Th^{4+} [11] and Am^{3+} [11] in cementitious systems containing superplasticizers. Eu^{3+} is established as a surrogate for the trivalent actinides because of its excellent spectroscopic properties. A previous study by Fröhlich et al. established the use of the charge neutralization model for the complexation of Eu^{3+} with Glenium® 51 at low ionic strength (I_m (NaCl) = 0.10 mol kg^{-1} H_2O^{-1}) [8]. However, there is a lack of complexation data at elevated ionic strengths in chloride media. Medium ionic strengths of up to 3 m are characteristic for pore and

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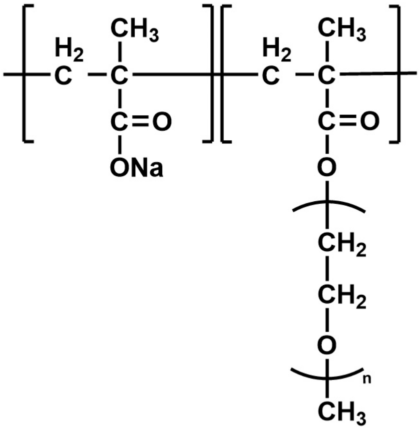

Fig. 1. Structural motif of Glenium® 51.

formation waters of clay rock formations in Northern Germany. These are considered as a potential site for a nuclear waste repository (site model NORTH) in Germany. Thus, the present work provides novel insights into the complexation of Eu^{3+} with the superplasticizer Glenium® 51 at various ionic strengths up to medium ionic strengths of I_m (NaCl) = 2.47 mol kg^{-1} H_2O^{-1} using time-resolved laser fluorescence spectroscopy (TRLFS). Through these complexation studies, $log\,K_m^0$ at zero ionic strength is determined. The $log\,K_m^0$ value is essential when modeling actinide behavior under various near-field conditions present at nuclear waste repositories.

2. Experimental section

2.1. Materials and instruments

TRLFS measurements. TRLFS measurements were performed using a Nd:YAG (Surelite II laser, Continuum) pumped dye laser system (NarrowScan D-R; Radiant Dyes Laser Accessories GmbH). Eu^{3+} was excited at a wavelength of 394.0 nm. A spectrograph (Shamrock 303i, ANDOR) with 300, 1199 and 2400 lines per millimeter gratings was used for spectral decomposition. The fluorescence emission was detected by an ICCD camera (iStar Gen III; ANDOR) in the wavelength range of 570–620 nm. All measurements were performed with a delay time of 1 μs to discriminate scattering light and short-lived organic fluorescence.

Correction of pH. An Orion Star (Fisher Scientific) pH meter and a micro glass combination electrode (Mettler Toledo) was used for the pH measurements. Before measurement, the electrode was calibrated at pH = 4.00 ± 0.01; 7.00 ± 0.01 and 10.01 ± 0.01 with NIST standard buffer solutions (Fisher Scientific). For each ionic strength at $I_m > 0.1$, the measured pH_{exp} of the solution is an operational value that has to be corrected according to the following equations [12]:

$$A_{NaCl} = -0.0988 + 0.1715 \bullet m_{NaCl} + 0.0113 \bullet (m_{NaCl})^2$$

$$pH_m = pH_{exp} + A_{NaCl}$$

Titration. Sodium chloride (Merck, Purity >99 %) was of analytical grade and used without further purification. For all dilutions, MilliQ water was used. The polycarboxylate-ether based superplasticizer Glenium® 51 was purchased from BASF Construction Solutions GmbH. Glenium® 51 is a light brown liquid with a relative density of 1.10 ± 0.02 g/cm^3 (at 20 °C), a $pH_m = 6.6 \pm 0.1$ and a chloride content <0.1 %. For the Eu^{3+} stock solution, Eu_2O_3 (with a purity of 99.9 %) has been dissolved in 0.1 M $HClO_4$, resulting in a concentration of $Eu^{3+} = 1.065 \bullet 10^{-3}$ M. The TRLFS samples were prepared by adding 2.25 μL of the Eu^{3+} stock solution to 1194 μL of an aqueous solution with I_m(NaCl) = 0.11 mol kg^{-1} H_2O^{-1} to 2.47 mol kg^{-1} H_2O^{-1}, resulting in an Eu^{3+} concentration of $2 \bullet 10^{-6}$ M. For the titration, the respective ionic strength and the $pH_m = 5.1 \pm 0.1$ is held constant, while the Glenium® 51 concentration was varied for the spectroscopic speciation. Therefore, Glenium® 51 stock solutions of 22.88 g L^{-1} were prepared for each ionic strength. All TRLFS samples were measured in SUPRASIL-Quartz glass cuvettes (Hellma Analytics, 10 mm • 10 mm).

3. Results and discussion

3.1. Complexation study of Eu^{3+} with Glenium® 51 in chloride media

The complexation of Eu^{3+} with Glenium® 51 at various ionic strengths from I_m(NaCl) = 0.11–2.47 mol kg^{-1} H_2O^{-1} has been investigated by TRLFS. Fig. 2 (A) shows a selection of normalized emission spectra of Eu^{3+} as a function of the Glenium® 51 concentration at low ionic strength (I_m(NaCl) = 0.11 mol kg^{-1} H_2O^{-1}). The pH_m value in all steps was kept constant at $pH_m = 5.1 \pm 0.1$. Without the addition of Glenium® 51, the solvent species of Eu^{3+} is characterized by two emission bands at λ = 592 ($^5D_0 \rightarrow {}^7F_1$) and 616 nm ($^5D_0 \rightarrow {}^7F_2$) with a intensity ratio of $^7F_1/^7F_2 = 1.9$ [13]. With increasing Glenium® 51 concentration, a strong change in intensity and signal splitting (λ = 615.8 and 612.3 nm) is observed for the $^7F_2$ emission band ($^7F_1/^7F_2 = 0.48$ at [Gle] = 0.4 g L^{-1}). This clearly indicates that an Eu^{3+}-Glenium® 51 complex is formed. At [Gle] ≥ 0.4 g L^{-1}, the spectrum does not change anymore, indicating a quantitative formation of the Eu^{3+}-Glenium® 51 species. The fluorescence lifetime of this species is τ = 235 ± 24 μs (c. f. Fig. S1). Overall, the observed Eu^{3+}-Glenium® 51 spectrum is identical to the previous one reported by Fröhlich et al. [8]

At a higher ionic strength of I_m(NaCl) = 1.01–2.47 mol kg^{-1} H_2O^{-1}, a similar change of the emission spectra with increasing Glenium® 51 concentration is observed. This indicates the formation of a structurally similar or even identical Eu^{3+}-Glenium® 51 complex species. However, significantly higher Glenium® 51 concentrations are required for the formation of this complex, compared to the system at lower ionic strength, indicating a less favorable complex formation at higher ionic strength. This is clearly expressed by the spectral trends at different ionic strengths (I_m(NaCl) = 0.11; 1.01; 2.02 and 2.47 mol kg^{-1} H_2O^{-1}), as shown in Fig. 2.

For the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions, the species distribution for each normalized emission spectrum is determined by peak deconvolution. The single component spectra used for this iterative process as well as an example for peak deconvolution are given in Fig. S2 and S3 in the Supporting Information. With increasing Glenium® 51 concentration, the total intensity of the emission spectra increases. The increase in total intensity is due to a higher quantum yield of the Eu^{3+} – Glenium® 51 complex compared to the Eu^{3+} solvent species. This can be quantified by determination of the fluorescence intensity factor (f_i factor). The f_i factor is determined from the total peak area of the emission spectra of the Eu^{3+} solvent species and the Eu^{3+} – Glenium® 51 complex normalized to the pulse energy of the laser. It is used to calculate the molar fractions (χ_i) of the different species using Eq. 1:

$$\chi_i \bullet f_i = I_{i,rel} \tag{1}$$

χ_i is the fraction of species i acquired via peak deconvolution. The f_i factors determined for all ionic strengths are summarized in Table S1. Fig. 3 shows the Eu^{3+} speciation at $pH_m = 5.1 \pm 0.1$ as a function of the Glenium® 51 concentration at low to medium ionic strength. In all speciation diagrams, the point of equal fraction is depicted via a dotted line. It is clearly visible that the point of equal fraction is shifting to higher Glenium® 51 concentrations with increasing ionic strengths. This confirms the earlier assessment that the Eu^{3+}-Glenium® 51-complex formation is successively repressed with increasing ionic strength.

The complexation is described by the following complexation model:

$$Eu^{3+} + Gle_{eq} \rightleftharpoons EuGle_{eq} \tag{2}$$

The stability constant is calculated according to the law of mass

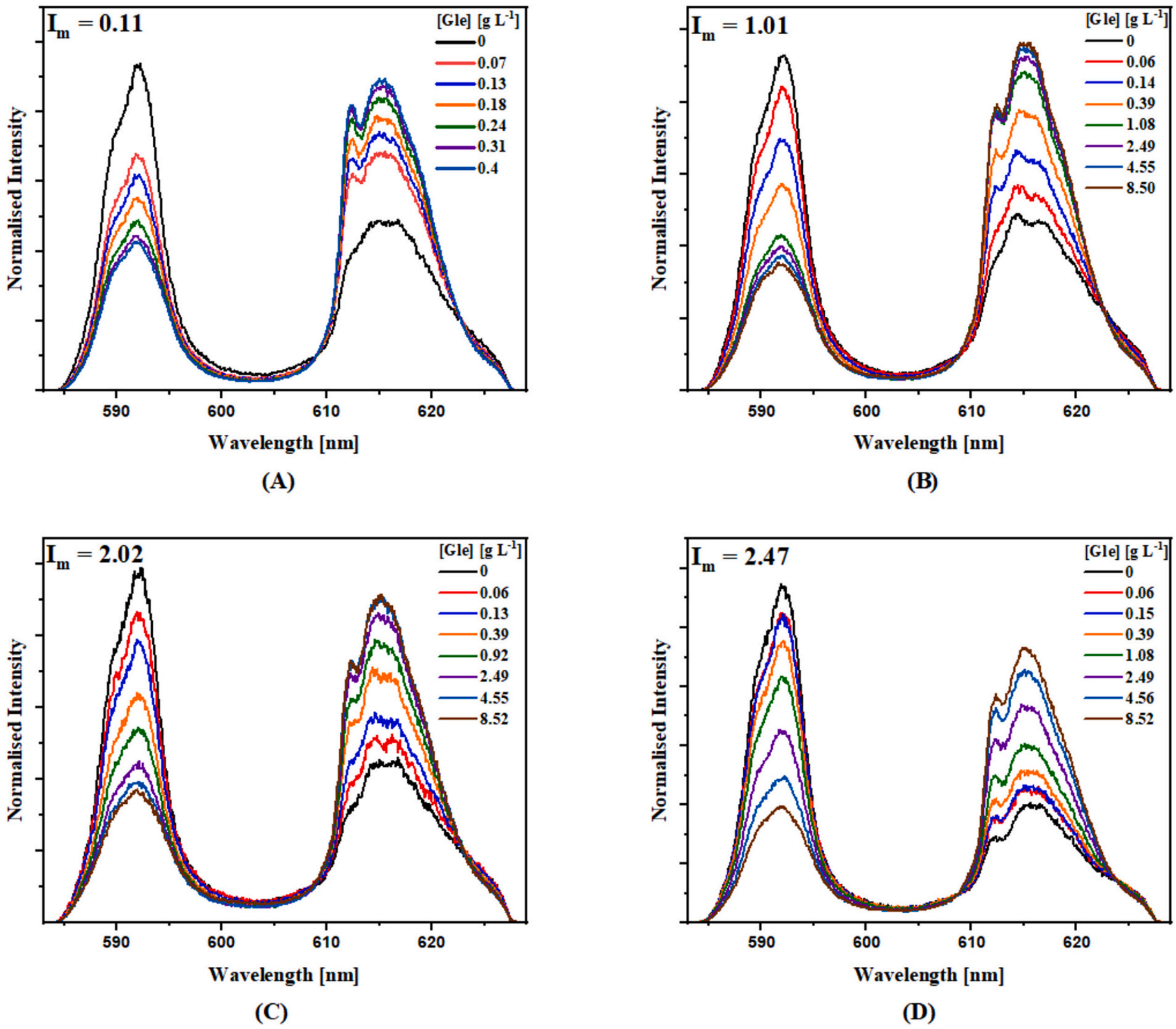

Fig. 2. Normalized Eu^{3+} emission spectra of Eu^{3+} and the Eu^{3+}-Glenium® 51 complex at $pH_m = 5.1 \pm 0.1$ as a function of the Glenium® 51 concentration at various ionic strengths. $[Eu] = 2\bullet10^{-6}$ M. (A): I_m (NaCl) = 0.11 mol kg^{-1} H_2O^{-1}. (B): I_m (NaCl) = 1.01 mol kg^{-1} H_2O^{-1}. (C): I_m (NaCl) = 2.02 mol kg^{-1} H_2O^{-1}. (D): I_m (NaCl) = 2.47 mol kg^{-1} H_2O^{-1}.

action:

$$K' = \frac{[EuGle]_{eq}}{[Eu^{3+}]_{eq} \bullet [Gle]_{eq}} \tag{3}$$

with $[Eu^{3+}]_{eq}$, $[Gle]_{eq}$ and $[EuGle]_{eq}$ being the concentrations of the solvated Eu^{3+}, the free ligand and the Eu^{3+}-Glenium® 51 complex. The "Metal Ion Charge Neutralization" model is used for further quantification [14]. According to this model, it is assumed that the lanthanide ion occupies a number of proton exchanges sites equivalent to its charge within the carboxylic macromolecular ligand [14]. The grade of deprotonation and thus the availability of the functional groups for complexation reactions depends on pH and ionic strength [14]. This is considered by using the loading capacity (LC) in Eq. (4):

$$LC = \frac{[Eu^{3+}]_{max}}{[Gle]_{total}} \tag{4}$$

$[Eu^{3+}]_{max}$ is the maximum metal ion concentration that can be bound to Glenium® 51 and $[Gle]_{total}$ [eq kg^{-1}] is the total Glenium® 51 concentration. $[Gle]_{total}$ is determined as follows:

$$[Gle]_{total} = \frac{(Gle) \bullet PEC}{Z} \tag{5}$$

PEC is the proton exchange capacity of Glenium® 51, (Gle) is the concentration of Glenium® 51 in g L^{-1} and Z the ionic charge of the metal ion (for Eu^{3+}, Z = 3). Fröhlich et al. determined the proton exchange capacity PEC via titration with a cationic poly-diallyl dimethyl ammonium chloride solution, resulting in 2366 μeq g^{-1} in 0.1 mol/L NaOH solution [8]. Combining eqs. (4) and (5) gives Eq. (6):

$$LC = \frac{Z \bullet [Eu^{3+}]_{max}}{PEC \bullet (Gle)} \tag{6}$$

The free Glenium® 51 concentration is calculated as follows:

$$[Gle]_{eq} = [Gle]_{total} \bullet LC - [EuGle]_{eq} \tag{7}$$

The combination of Eqs. (3), (6) and (7) leads to:

$$[Eu^{3+}]_{eq} = LC \bullet \frac{[Eu^{3+}]_{eq} \bullet [Gle]_{total}}{[EuGle]_{eq}} - \frac{1}{K'} \tag{8}$$

The LC values strongly depend on the ionic strengths and are determined by a linear regression plot of the free Eu^{3+} concentration $[Eu^{3+}]_{eq}$ versus $\frac{[Eu^{3+}]_{eq} \bullet [Gle]_{total}}{[EuGle]_{eq}}$ at each ionic strength. Examples for the determination of the LC are displayed in Fig. 4 (I_m (NaCl) = 0.11 and 2.47 mol kg^{-1} H_2O^{-1}) and Fig. S4 (I_m (NaCl) = 1.01 and 2.02 mol kg^{-1}

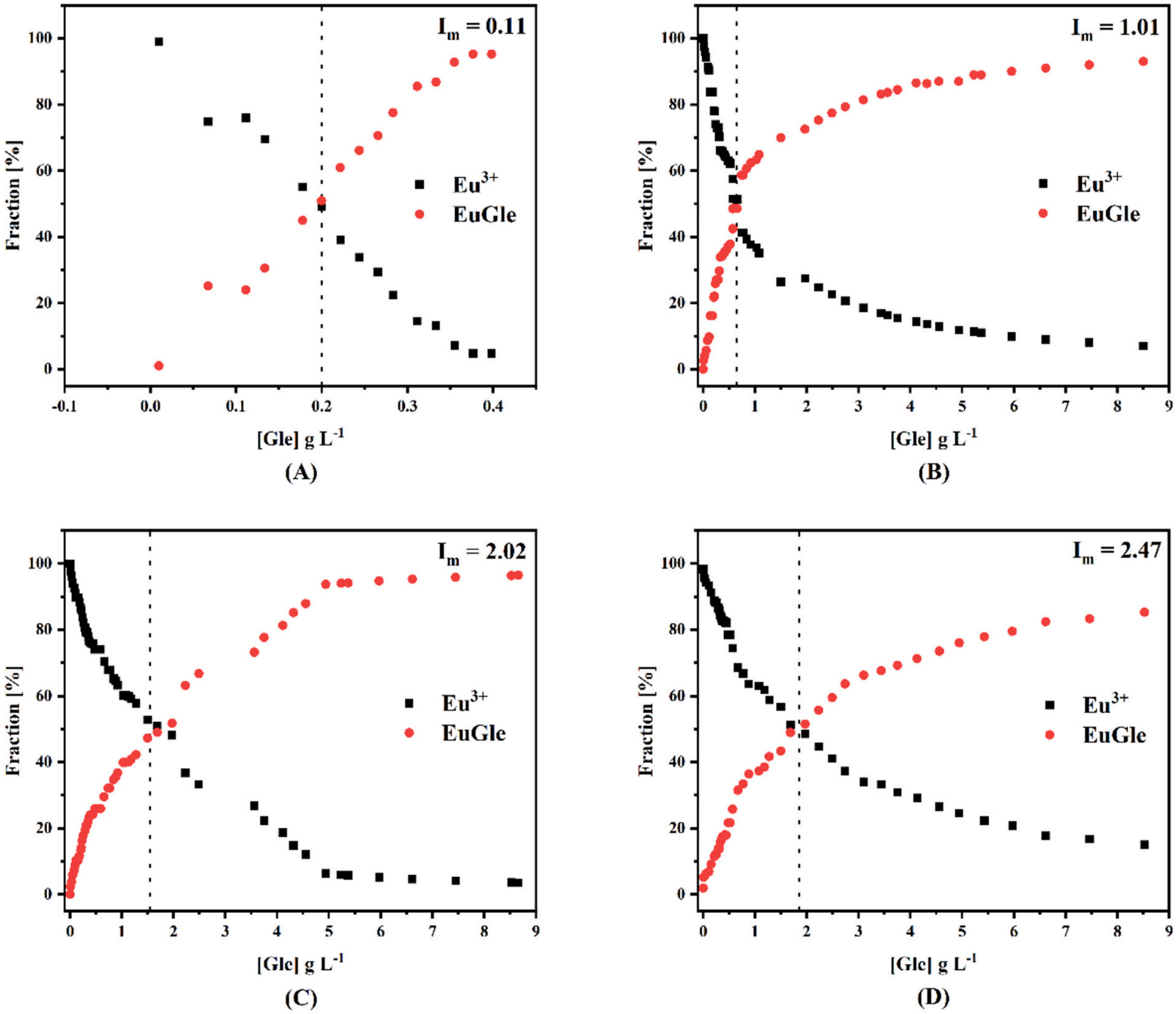

Fig. 3. Eu^{3+} speciation at $pH_m = 5.1 \pm 0.1$ as a function of Glenium® 51 concentration. [Eu] = $2 \bullet 10^{-6}$ M. (A): I_m (NaCl) = 0.11 mol kg^{-1} H_2O^{-1}. (B): I_m (NaCl) = 1.01 mol kg^{-1} H_2O^{-1}. (C): I_m (NaCl) = 2.02 mol kg^{-1} H_2O^{-1}. (D): I_m (NaCl) = 2.47 mol kg^{-1} H_2O^{-1}. Dotted line: Point of equal fraction.

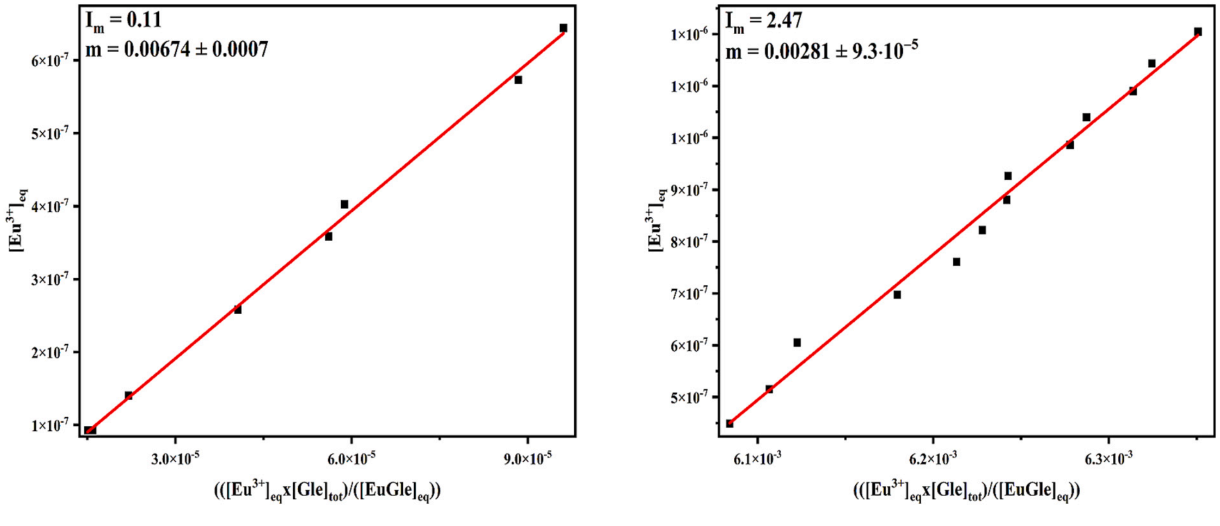

Fig. 4. Determination of the loading capacity of Glenium® 51 with Eu^{3+} at I_m (NaCl) = 0.11 mol kg^{-1} H_2O^{-1} and I_m (NaCl) = 2.47 mol kg^{-1} H_2O^{-1}.

Table 1

Stability constants of the complexation of Eu^{3+} with Glenium® 51 as a function of ionic strength.

I_m (NaCl) [mol kg^{-1} H_2O^{-1}]	Loading Capacity	$log\ K'_m$	Reference
0.11	0.00674	7.48 ± 0.8	p.w.
1.01	0.00471	5.99 ± 0.6	p.w.
2.02	0.00413	5.60 ± 0.6	p.w.
2.47	0.00281	4.80 ± 0.5	p.w.
0.10	0.0063	7.52 ± 0.33	Fröhlich et al. [8]

H_2O^{-1}). The LC values at each ionic strength are given in Table 1.

According to the complexation model, Eu^{3+} is coordinated by one charge equivalent of Glenium® 51, forming a 1:1 Eu^{3+}-Glenium® 51 complex [8]. It is important to consider that the functional groups attached to Eu^{3+} do not have to belong to one single macromolecule (see definition of $[\mathrm{Gle}]_{\mathrm{total}}\left[\mathrm{eq\ kg}^{-1}\right]$, Eq. (5)). To verify the 1:1 Eu^{3+}-Glenium® 51 complex species, slope analyses are performed according to the following equation for each ionic strength:

$$\log\left(\frac{[\mathrm{EuGle}]_{\mathrm{eq}}}{[\mathrm{Eu}^{3+}]_{\mathrm{eq}}}\right) = log\ K' + \log\,[\mathrm{Gle}]_{\mathrm{eq}} \tag{9}$$

$\log\left(\frac{[\mathrm{EuGle}]_{\mathrm{eq}}}{[\mathrm{Eu}^{3+}]_{\mathrm{eq}}}\right)$ is plotted against $\log\,[\mathrm{Gle}]_{\mathrm{eq}}$, for which linear regressions yield slopes of 0.94 ± 0.15 for I_m(NaCl) = 0.11 mol kg^{-1} H_2O^{-1} (black), 0.95 ± 0.04 for I_m(NaCl) = 1.01 mol kg^{-1} H_2O^{-1} (blue), 0.96 ± 0.04 for I_m(NaCl) = 2.02 mol kg^{-1} H_2O^{-1} (red) and 1.01 ± 0.01 for I_m(NaCl) = 2.47 mol kg^{-1} H_2O^{-1} (green), respectively (c. f. Fig. 5). Comparing the concentration ratios in Fig. 5 for low and elevated ionic strengths, it is evident that with increasing ionic strength, higher concentrations of free Glenium® 51 are required to form the Eu^{3+}-Glenium® 51 complex.

To further quantify the complexation strength, conditional stability constants are determined at each ionic strength (see Table 1). The stability constant for the Eu^{3+}-Glenium® 51 formation decreases significantly with increasing ionic strength. Throughout the series, a decline of 2.7 orders of magnitude in stability is observed from I_m(NaCl) = 0.11 mol kg^{-1} H_2O^{-1} to I_m(NaCl) = 2.47 mol kg^{-1} H_2O^{-1}. At ionic strength I_m (NaCl) = 0.11 mol kg^{-1} H_2O^{-1}, a stability constant of $log\ K'_{0.11} = 7.48 \pm 0.8$ is determined, which is in excellent agreement with the obtained $log\ K'_m$ of Fröhlich et al..

The metal charge neutralization model was originally designed to determine stability constants for the complexation of trivalent ions with humic acids [14]. Humic acids are polycarboxylic macromolecules and thus, are expected to show a similar complexation behavior to Glenium® 51. In direct comparison, Glenium® 51 forms a complex with Eu^{3+}, which is approximately one order of magnitude stronger than the Eu^{3+}-

Table 2

Comparison of $log\ K'_m$ (this work) with literature data for structurally similar ligands.

	Method	I_m (NaCl) [mol kg^{-1} H_2O^{-1}]	$log\ K'_m$	Reference
Eu^{3+}-Glenium® 51 complex	TRLFS	0.11	7.48 ± 0.8	p. w.
Eu^{3+}-polyacrylate	TRLFS	0.10	5.87 ± 0.28	Fröhlich et al. [15]
Eu^{3+}-52IPEG4.5 complex	TRLFS	0.10	6.54 ± 0.10	Fröhlich et al. [16]
Eu^{3+}-Humic acid complex (Suwannee River)	Lanthanide Ion Probe Spectroscopy	0.10	6.4	Susetyo et al. [17]

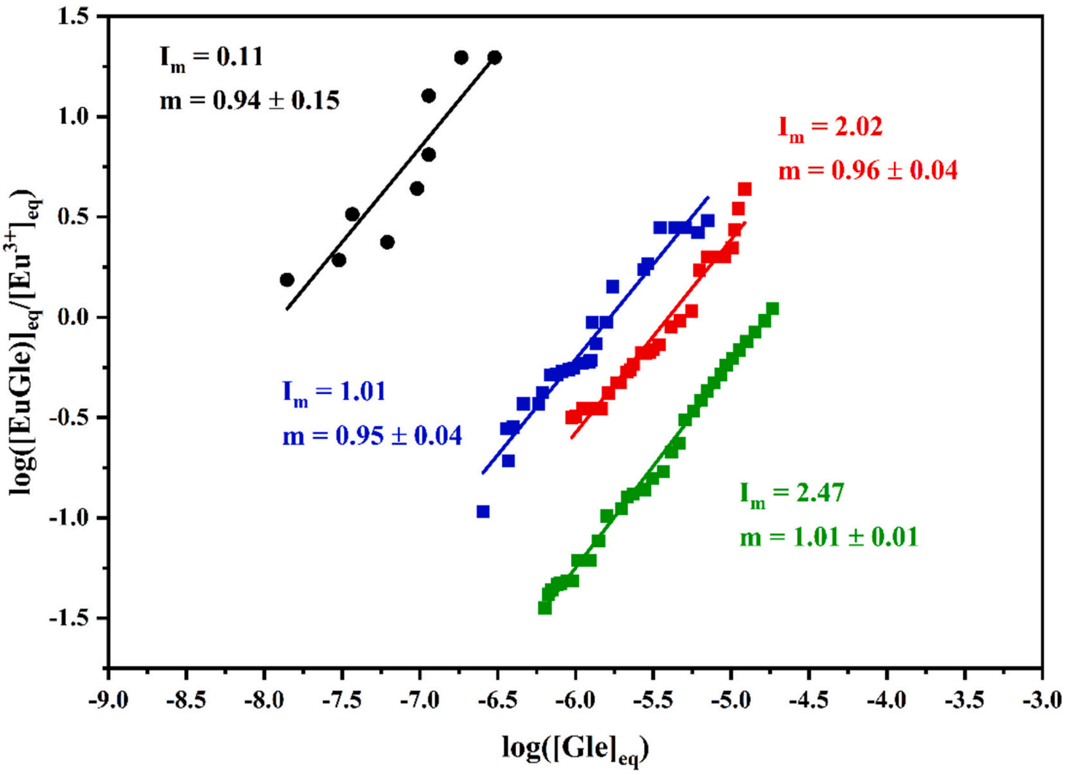

Fig. 5. Slope analyses for the formation of the Eu^{3+}-Glenium® 51-complex at I_m(NaCl) = 0.11 mol kg^{-1} H_2O^{-1} (black), I_m(NaCl) = 1.01 mol kg^{-1} H_2O^{-1} (blue), I_m(NaCl) = 2.02 mol kg^{-1} H_2O^{-1} (red) and I_m(NaCl) = 2.47 mol kg^{-1} H_2O^{-1} (green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Humic acid complex under similar experimental conditions (see Table 2). Compared to the structure of Glenium® 51, humic acids have a variety of additional functional groups such as phenol-, ether-, chinon- and aliphatic OH-groups, and are sterically more hindered, which might explain the higher complexation strength of the Eu^{3+}-Glenium® 51 complex.

Polyacrylate is composed of one carboxylic polymer chain and consequently can serve as a model ligand for complex polycarboxylates such as superplasticizers and humic acids. Nevertheless, the complexation of Eu^{3+} is stronger with Glenium® 51 than with polyacrylate at similar conditions (see Table 2). In contrast to Glenium® 51, polyacrylate is missing side chains and additional functional groups, which explains the higher stability constant of the Eu^{3+}-Glenium® 51 complex.

The anionic isoprenyl ether-based superplasticizer 52IPEG4.5 is a well characterized synthetic acrylate based polycarboxylate-ether superplasticizer with a molecular weight of ~69,000 g/mol, which was used in prior studies to determine thermodynamic and structural data [16]. Though a similar complexation behavior is expected, the stability constant for the formation of the Eu^{3+}-Glenium® 51 complex is somewhat higher. This might be due to the fact, that Glenium® 51 is a commercial admixture also containing other constituents than the polymer.

3.2. Specific ion interaction theory (SIT)

For implementation of thermodynamic data into thermodynamical databases, stability constants at standard state conditions are required. Thus, we determined log K^0 at zero ionic strength using the specific ion interaction theory (SIT). For $I_m \leq 4$, this model describes the activity coefficient γ of a species i in aqueous solution as follows:

$$\log \gamma_i = -z_i^2 \frac{A(T)\sqrt{I_m}}{1 + B(T)a_i\sqrt{I_m}} + \sum \boldsymbol{\varepsilon_{ik}(T)} \bullet m_k \tag{10}$$

Here, z_i is the charge of ion i, $\varepsilon\ (i,k)$ is the ion interaction coefficient of opposite charged ions i and k, while m_k (mol kg^{-1} H_2O^{-1}) is the molal concentration of ion k. $\frac{A(T)\sqrt{I_m}}{1+B(T)a_i\sqrt{I_m}}$ is the temperature dependent Debye-Hückel term D(T). In our case, I_m is the molal ionic strength and the values A(25 °C) = 0.5107 $kg^{0.5}$ $mol^{-0.5}$ and B(25 °C)a_i = 1.5 $kg^{0.5}$ $mol^{-0.5}$ are used for calculation [18]. The stability constant $\log K^0$ at zero ionic strength is derived from the conditional stability constants $\log K'_m$ according to:

$$\log K'_m = \log K^0 - \Delta z^2 \bullet \frac{0.5107\sqrt{I_m}}{1 + 1.5\sqrt{I_m}} + \Delta\varepsilon \bullet I_m \tag{11}$$

$$\Delta\varepsilon = \sum \varepsilon_{products} - \sum \varepsilon_{educts} \tag{12}$$

In case of defined organic or inorganic ligands, $\log K'_m - \Delta z^2 \bullet D(T)$ is plotted against I_m. However, in our case, the charge of the Eu^{3+}-Glenium® 51 is not known. Therefore, $\log K'_m$ is plotted against $\sqrt{I_m}$. Czerwinski et al. used this approach to determine log K^0 values for the Am(III) and Cm(III) with humic acids [18]. The regression analysis according to the SIT is depicted in Fig. 6 and provides $\log K^0$ (intercept with the y-axis), the ion interaction coefficient $\Delta\varepsilon$ and Δz^2. Using a non-linear least square fitting procedure according to Eq. (11), $\log K^0 = 8.54 \pm 0.9$, $\Delta\varepsilon = -0.53 \pm 0.05$ and $\Delta z^2 = 9.33 \pm 0.9$ are determined. There is no defined physical meaning of $\Delta\varepsilon$ and Δz^2 for our system since Glenium® 51 is a macromolecule with a multitude of functional groups. Hence, these values are only treated as operational parameters [19].

Since Eu^{3+} is a surrogate for trivalent actinides, the interaction of trivalent actinides, such as Cm(III) or Am(III) with Glenium® 51, is expected to be similar. Unfortunately, there is no literature data available for trivalent actinides. However, comparable complexation studies of Cm(III) and Am(III) with humic acid from the Gorleben aquifer system have been conducted as a function of ionic strength by TRLFS and UV–Vis spectroscopy [18]. These studies have been performed in $NaClO_4$ solutions. From I_m ($NaClO_4$) = 0.10 to 2.50 mol kg^{-1} H_2O^{-1}, only a small decline of the stability constants from $\log K'_{0.10} = 6.23 \pm 0.11$ to $\log K'_{2.50} = 6.10 \pm 0.07$ was observed [18]. This decrease of the stability constant of about 0.13 orders of magnitude is within the uncertainties of the determined stability constants. Comparing this to our system, it is evident that we observed a much stronger decrease (2.7 orders of a magnitude) of the stability constants in NaCl media. This is in line with the higher complexation strength of chloride in comparison to perchlorate. Comparing our log K^0 at zero ionic strength to the Cm(III) humic acid system ($\log K^0 = 6.52 \pm 0.06$) [18], the formation of Eu^{3+}-Glenium® 51 at zero ionic strength is favored by two orders of magnitude.

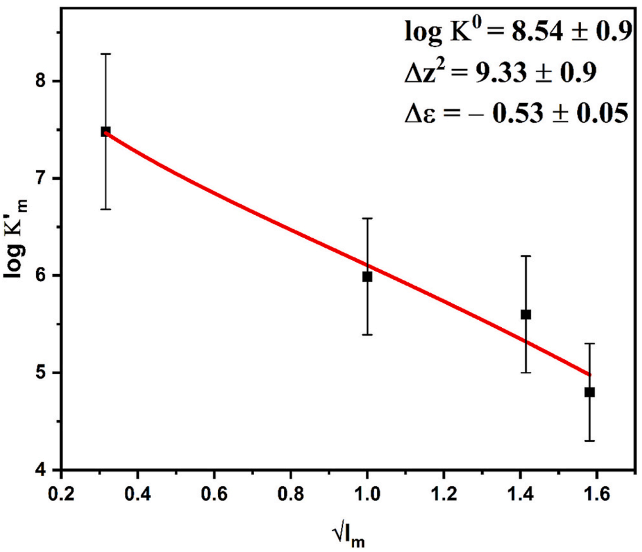

Fig. 6. Plot of $\log K'_m$ vs. $\sqrt{I_m}$ and non-linear least square fitting according to the SIT equation (Eq. (11) at T = 25 °C for the formation of the Eu^{3+}-Glenium® 51-complex.

4. Conclusions

In our work, we present a systematic complexation study of Eu^{3+} with the polycarboxylate based concrete superplasticizer Glenium® 51. Using time-resolved laser fluorescence spectroscopy, the complexation as function of the ligand concentration and ionic strength from I_m(NaCl) = 0.11 mol kg^{-1} H_2O^{-1} to I_m(NaCl) = 2.47 mol kg^{-1} H_2O^{-1} is investigated. Our results show, that higher ionic strengths repress the formation of the Eu^{3+}-Glenium® 51 complex, which results in a significant decline of the stability constant by 2.7 orders of magnitude from $\log K'_{0.11} = 7.48 \pm 0.8$ to $\log K'_{2.47} = 4.80 \pm 0.5$. The stability constants at various ionic strengths are obtained using the Metal Ion Charge Neutralization model and are extrapolated to determine the stability constant $\log K^0$ at zero ionic strength. By using the Specific Ion Interaction Theory, we determined $\log K^0 = 8.54 \pm 0.9$, which highlights the superb complexation properties of the superplasticizer Glenium® 51 towards trivalent ions.

Cementitious materials are used for geotechnical barriers for nuclear waste repositories. Through long-term natural water intrusion into the repository, cement degradation processes may occur causing superplasticizers or their decomposition products to be released. The clay formations located in Northern Germany contain pore and formation waters with ionic strengths up to 3 mol kg^{-1} H_2O^{-1}. Therefore, studying the complexation of trivalent actinides with superplasticizers as a function of ionic strength is of high importance. Since Eu^{3+} is a surrogate for trivalent actinide ions such as Pu(III)/Am(III)/Cm(III), an important step of achieving a better understanding on the impact of ionic strength on actinide complexation behavior with Glenium® 51 is accomplished.

Furthermore, the determination of the *log* K_m^0 value allows to extrapolate the complexation reaction to various near-field conditions of other nuclear waste repositories.

CRediT authorship contribution statement

Sema Özyagan: Writing – original draft, Visualization, Investigation, Formal analysis, Data curation. **Raoul E. Gillmeister:** Investigation, Data curation. **Thomas Sittel:** Writing – review & editing, Supervision. **Andrej Skerencak-Frech:** Writing – review & editing. **Petra J. Panak:** Writing – review & editing, Validation, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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Associated content

Supporting Information available: TRLFS spectra.

Declaration of competing interest

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.rechem.2025.102399.

Data availability

Data will be made available on request.

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