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Effect of DTPA on europium sorption onto quartz – batch sorption experiments and surface complexation modeling

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Abstract

Sorption of radionuclides on mineral surfaces retards their migration in the environment of a repository. Presence of organic ligands, however, affects sorption and consequently influences their transport behavior. In this study, we quantify the sorption of Eu(III) onto quartz surfaces as a function of pH in the absence and presence of diethylenetriaminepentaacetic acid (DTPA). Batch sorption experiments show a pH-dependent sorption of Eu(III) on quartz. The presence of DTPA results in slightly higher sorption of Eu(III) at neutral to slightly acidic pH and considerably lower sorption at alkaline conditions. Sorption experiments were simulated using the Diffuse Double Layer Model (DDLDM) with single sorption sites ($\equiv\text{QOH}$) and monodentate surface complexation. The reactions were established based on the aqueous speciation calculation under the experimental conditions, and the thermodynamic constants of surface reactions were obtained and refined by numerical optimization. Results of surface complexation modeling show the formation of a surface species $\equiv\text{QOHEuDTPA}^{2-}$, explaining the elevated sorption of Eu(III) at neutral to slightly acidic pH. In contrast, dissolved EuDTPA^{2-} complex species are present at alkaline pH, resulting in an enhanced mobility of Eu(III).

Keywords:

Sorption, Europium, Radionuclides, Diethylenetriaminepentaacetic acid, Surface complexation modeling

26 **1 Introduction**

27 Radionuclide migration in natural aqueous systems is a critical process in the long-term safety assessment
28 of nuclear waste repositories. Sorption and desorption on mineral surfaces and complexation with organic
29 ligands are major processes controlling the mobility of actinides and lanthanides in the subsurface.
30 Therefore, quantitative experimental data on effects of organic complexing ligands are required for a
31 fundamental and mechanistic understanding of migration. This is a prerequisite for both the prediction of
32 radionuclide transport and the successful remediation of a contaminated environment.

33 In this context, several studies were conducted to investigate effects of organic complexing ligands on
34 sorption of lanthanides and actinides on mineral surfaces (Fairhurst et al., 1995; Takahashi et al., 1998;
35 Alliot et al., 2005; Lippold et al., 2005; Pathak and Choppin, 2007; Schott et al., 2012; Ye et al., 2014).
36 Specifically, it was found that organic ligands are able to elevate as well as to suppress the sorption of
37 radionuclides in dependence on pH and ionic strength. The two major groups of organic complexing
38 ligands to be considered are: (a) polycarboxylic acids including citric acid and oxalic acid and (b)
39 aminopolycarboxylic acids such as EDTA, NTA and DTPA (Choppin, 1995). Alliot et al. (2005) studied
40 the effects of small organic ligands such as oxalate, acetate and carbonic acid on sorption of Am(III) onto
41 α -alumina and found that these complexing ligands are able to prevent sorption. In another study, Pathak
42 and Choppin (2007) showed that oxalate enhanced sorption of Eu(III) on silica due to the formation of
43 ternary surface complexes, whereas acetate, citrate and EDTA reduced sorption of Eu(III) due to the
44 formation of a binary complex ligand/Eu(III) in solution. Only few studies were performed to investigate
45 the influence of aminopolycarboxylic acids on sorption of radionuclides onto minerals. Most of them are
46 focused on EDTA (Sylwester, 2001) and NTA (Reinoso-Maset et al., 2012).

47 Surface complexation models (SCMs) can describe sorption of radionuclides onto mineral surfaces under
48 variable geochemical conditions. They include surface properties such as the format of electrical
49 interfacial layers and define surface/dissolved complexes based on theoretical calculations and/or
50 spectroscopic studies. A couple of studies have quantified and modeled the sorption of Eu(III) and
51 trivalent actinides on quartz and silica in the absence of organic ligands (Wang et al., 2001; Kuta et al.,

52 2011; Britz, 2018). Wang et al. (2001) published an SCM for sorption of Am(III) on amorphous silica.
53 They used a Diffuse Double Layer Model (DDLML) in which the effect of changing aqueous speciation on
54 the formation of surface complexes was taken into account. By means of laser-induced fluorescence
55 spectroscopy, Kuta et al. (2011) performed a molecular dynamics simulation to predict sorption of Eu(III)
56 onto α -quartz and showed that both inner- and outer-sphere complexes of lanthanide ions formed on
57 surface edge sites of quartz. Britz (2018) compared a DDLML, a Basic Stern Model (BSM), and a Non-
58 Electrostatic Double Layer Model (noEDLM) to explain sorption of Eu(III) onto quartz and suggested a
59 monodentate, bidentate, and a combination of mono- and bidentate binding on the surface edge sites.
60 However, few works aimed to model and predict sorption of lanthanides on mineral surfaces in ternary
61 systems with complexing organic ligands.

62 In this work, we investigated the influence of diethylenetriaminepentaacetic acid (DTPA), which is used
63 as a decontamination agent during operation of a final repository (Sharma et al., 2010; Randall et al.,
64 2011), on the sorption of Eu(III) to quartz sand to derive implications for the mobility of radionuclides in
65 case of release together with organic complexants. Quartz is a widespread mineral with a relatively simple
66 structure. It is the predominant constituent of many soils and rocks which are involved in many physical,
67 chemical and biological processes in subsurface environments. For this reason, quartz was chosen as a
68 representative sorbent in this study. Because of their similar chemical behavior, it is widely accepted that
69 trivalent lanthanides are, to some extent, suitable as analogues of trivalent actinides such as Am(III),
70 Cm(III) or Pu(III) (Choppin, 1995). We quantified and predicted the effects of pH and ligand
71 concentration on Eu(III) sorption by conducting a series of batch sorption experiments in the pH range
72 between 3 and 9. Speciation calculations were conducted to determine the Eu(III) and Eu(III)-DTPA
73 species present in solution under the experimental conditions. A DDLML was applied to explain sorption of
74 Eu(III) and the influence of DTPA on Eu(III) sorption on quartz surfaces. Surface complexation reactions
75 were established based on the speciation calculation, and surface complexation parameters were estimated
76 and optimized from data fitting.

77 **2 Materials and methods**

78 2.1 Materials

79 Quartz sand with a grain size of 0.2 - 0.8 mm was obtained from Merck KGaA, Germany. It was washed
80 three times with 0.01 M NaClO₄ (Merck, Germany) and three times with deionized water to remove
81 impurities. A 10 mL stock solution of 2×10^{-4} mol/L Eu(NO₃)₃ (Merck, Germany) in ultrapure water (≥ 18
82 MΩ/cm) was spiked with ¹⁵²Eu as a radiotracer (POLATOM, Poland) at an activity of 0.3 MBq. The
83 solution was adjusted to pH 3 to avoid formation of colloids, precipitation, and sorption on walls. DTPA
84 (acid form) was provided by Sigma Aldrich, Germany. The pH of the stock solution (10^{-2} mol/L DTPA)
85 was adjusted to 6.5. NaClO₄ was used as a background electrolyte at a concentration of 0.01 M.

86

87 2.2 Experimental

88 Batch sorption experiments were performed in 50 mL polypropylene plastic tubes containing 0.2 g quartz
89 sand and 20 mL 10^{-6} M [¹⁵²Eu]Eu(III) in 0.01 M NaClO₄ with an activity concentration of 0.03 kBq/L.
90 The pH of the suspensions was varied between 3.5 and 9 using HClO₄ and NaOH for adjusting.
91 Experiments were done in the absence and in the presence of DTPA ([DTPA]/[Eu] = 0.5, 1, 2, 10, and 30).
92 Additional experiments at pH 6.5 and 8.5 and [DTPA]/[Eu] = 0.2, 0.7, and 6 were done to study sorption
93 of Eu(III) as a function of DTPA concentration. For the experiments done in the presence of organic
94 ligand, the DTPA stock solution was added to the suspension lastly. After rotating the suspensions for
95 about 40 h with an end-over-end shaker (ROTATHERM), the pH of the solutions were measured again,
96 and the samples were centrifuged at 5000 rpm for 10 min to separate quartz from supernatant. The
97 equilibration time was verified to be sufficient for surface complexation reactions in kinetic sorption
98 experiments with Eu(III) and Eu(III)/DTPA mixtures at pH 6 over a period of 100 h.
99 The amount of Eu(III) sorption on quartz was determined by counting the decays of ¹⁵²Eu in 8 mL samples
100 of the respective initial solutions and of the supernatant solutions after sorption. Count rates were
101 measured for 5 minutes with a gamma counter 1480 Wallac Wizard 3" (Perkin Elmer, USA), set at the full
102 energy range of 0 - 2 MeV as Eu was the only radionuclide in the sample. The percentage of Eu(III)
103 sorption was determined as:

104
$$\% \text{ sorbed} = \left[\frac{A_i - A_f}{A_i} \right] \times 100$$

105 where A_i and A_f are the initial and final count rates in the aliquots (before and after sorption, respectively).

106

107 2.3 Modeling

108 The aqueous chemical speciation of Eu(III), DTPA, and 1:1 Eu(III)-DTPA were calculated by means of
109 the geochemical speciation code PHREEQC (Version 3.4 (Parkhurst, 2013)). The Nagra/PSI Chemical
110 Thermodynamic Database (Thoenen et al., 2014), which contains thermodynamic data for a range of
111 lanthanides and actinides, was used to calculate the Eu(III) speciation. Additional equilibrium constants
112 for DTPA acidity and Eu(III)-DTPA complexation (Grimes and Nash 2014), which are not contained in
113 the database, were used in the model. Surface complexation reactions were described on the basis of the
114 Diffuse Double Layer Model (DDLDM) of Dzombak and Morel (1990). We assumed monodentate surface
115 complexation of the metal on a single edge site of quartz sand ($\equiv\text{QOH}$). Surface reactions were defined
116 based on the aqueous species, and the equilibrium constants ($\log k$) of surface complexation reactions
117 were optimized from fitting the simulated sorption curves to the experimental data using the parameter
118 estimation code PEST (Doherty, 2018) coupled with PHREEQC. The optimization of $\log k$ values for the
119 surface complexation reactions was done for the binary sorption system (no DTPA) and the ternary system
120 at $[\text{DTPA}]/[\text{Eu}] = 1$. A weighted residuals model was used to find the best fit. The defined thermodynamic
121 constants were then used to calculate sorption of Eu on quartz in the ternary sorption system at
122 $[\text{DTPA}]/[\text{Eu}] = 0.5, 2, \text{ and } 10$. Both surface complexation modeling as well as speciation modeling were
123 performed for equilibrium conditions, and no kinetic processes were considered.

124

125 3 Results and discussion

126 We quantified sorption of Eu(III) onto quartz sand in dependence on pH and DTPA concentration by
127 conducting a series of batch sorption experiments and surface complexation modeling.

128

129 3.1 Aqueous speciation

130
131 In the absence of DTPA, the ionic form of europium (Eu^{3+}) as well as the europium hydroxyl complexes
132 EuOH^{2+} , $\text{Eu}(\text{OH})_2^+$, and $\text{Eu}(\text{OH})_3$ are the dominant Eu(III) species in the studied pH range (Fig. 1a).
133 Figure 1b depicts the species distribution of DTPA. The change in Eu speciation in the presence of DTPA
134 at equal concentration is shown in Fig. 1c. It is evident that at $3.5 < \text{pH} < 9$ in the presence of organic
135 ligand the total amount of Eu is present in complexed form with DTPA (EuDTPA^{2-} is the only Eu aqueous
136 species formed). The acidity constants for DTPA as well as the stability constants for Eu-DTPA
137 complexation used in the speciation modeling were determined by potentiometric titration by Grimes and
138 Nash (2014), listed in Table 1.

139 140 3.2 Sorption kinetics

141 Kinetic experiments have been performed in order to determine the time needed to reach equilibrium for
142 both binary and ternary ($[\text{Eu}]/[\text{DTPA}] = 1$) sorption systems at pH 6. The percentages of Eu(III) sorption
143 on quartz versus time are plotted in Fig. 2 for systems with and without organic ligand. Initially,
144 equilibration proceeds fast and then continues slowly till equilibrium is reached. Presence of DTPA affects
145 the rate of europium sorption. In general, the initial rapid sorption occurred within the first 2 h, and
146 equilibrium sorption was reached after 20 h and 36 h for Eu(III) and Eu-DTPA sorption systems,
147 respectively. A similar rate trend was reported by Pathak and Choppin (2007) for adsorption of Eu (10^{-5}
148 M) on silica at pH 6 in 0.2 M NaClO_4 (included in Fig. 2).

149 150 3.3 Batch sorption experiments

151 3.3.1 Sorption of Eu(III)

152 In Fig. 3a, sorption of Eu(III) onto quartz in the absence of DTPA is shown as a function of pH. The
153 results show a continuous increase in the percentage of Eu sorption with pH from 5 to 6.5. Above pH 6.5,
154 the total amount of Eu(III) is adsorbed. This behavior can be related to increasing ionization of surface

155 hydroxyl groups ($\equiv QO^-$) with increasing solution pH. In general, sorption of Eu(III) on oxides increases
156 with pH due to deprotonation of sorption sites (Wang et al., 2011; Qiu et al., 2018). Eu(III) bonding with
157 mineral surface hydroxyl groups reduces the negative charges of the ionized hydroxyl groups. By means
158 of time-resolved laser fluorescence spectroscopy (TRLFS), Stumpf et al. (2008) observed the formation of
159 inner-sphere complexes of Am(III) on deprotonated surface sites of quartz (QO^-) and found a similar pH-
160 dependent sorption behavior.

161

162 3.3.2 Effect of DTPA on Eu(III) sorption

163 In Fig. 3a, sorption of Eu(III) in the presence of DTPA onto quartz at ligand/metal ratios of 0.5, 1, 2, 10,
164 and 30 is shown as a function of pH. In general, presence of DTPA affects the shape of the sorption curve.
165 Results show that under slightly acidic conditions (pH 4-5), presence of DTPA slightly enhances Eu(III)
166 uptake (by ~ 5-10%). This was observed at [DTPA]/[Eu] ratios of 0.5 to 30 with similar effects. It can be
167 interpreted as sorption of Eu-DTPA complexes on the surface sites of quartz. Increase of metal sorption in
168 the presence of organic ligands at neutral to slightly acidic conditions was also found in a previous study
169 (Karimzadeh et al., 2017). By using TRLFS, Pathak and Choppin (2007) identified Eu-oxalate surface
170 species on silica at neutral pH. In addition, Ye et al. (2014) found that in the presence of fulvic acid and at
171 acidic to neutral pH, sorption of Eu(III) was enhanced due to the formation of a Eu-FA surface complex
172 on the surface edge sites of quartz. They found that fulvic acid forms a bridge between Eu ions and quartz,
173 thereby increasing metal uptake. However, our results show that in the presence of DTPA and above pH 5,
174 Eu(III) uptake is inhibited (Fig 3a). Compared to the binary sorption system, at [DTPA]/[Eu] = 0.5 and pH
175 > 6 the adsorbed amount of Eu is reduced by ~ 20%. By increasing the ligand/metal ratio from 0.5 to 30,
176 the percentage of adsorbed Eu decreases in dependence on the solution pH. At [DTPA]/[Eu] = 30 and pH
177 9, only 22% of Eu is adsorbed. Speciation modeling (Fig. 1) shows that at pH > 5, the total amount of
178 aqueous europium is present in complexed form with DTPA ($EuDTPA^{2-}$). Sorption of DTPA on quartz at
179 alkaline conditions does not take place due to its negative charge. Thus, the major influence of DTPA on
180 Eu sorption results from the formation of Eu-ligand complexes in solution. Under alkaline conditions, the

181 Eu(III) surface complex is weaker than the complex with DTPA in solution. Therefore, DTPA is able to
182 mobilize Eu and to reduce its sorption at high pH.

183 Figure 3b shows the effect of DTPA concentration in mol/L on the amount of Eu(III) adsorbed per mass
184 of adsorbent (mol/g) at pH 6.5 and 8.5. Both curves exhibit two regions with different slopes. This figure
185 shows that with increasing DTPA concentration, the mobilizing effect of DTPA (the ability of DTPA to
186 keep Eu in the solution phase) sharply declines at equimolar ligand/metal ratio ($[DTPA] = [Eu] = 10^{-6} M$),
187 which confirms the 1:1 stoichiometry as it is shown in the aqueous speciation in Fig. 1c, too.

188

189 3.4 Surface complexation modeling

190 A surface complexation model was developed to explain Eu sorption in the absence of DTPA as well as
191 the effect of DTPA on Eu sorption onto quartz sand. A preliminary assessment of the possible mode of
192 Eu(III) complexation on quartz sorption sites suggested Eu binding in a monodentate and/or bidentate
193 manner (Stumpf et al., 2008; Kumar et al., 2012; Britz, 2018). Kumar et al. (2012) showed by TRLFS that
194 a monodentate surface complex of Eu is formed on silica surfaces. Monodentate binding of Eu on surface
195 sites of quartz was also proposed in the published surface complexation models (Ye et al., 2014; Britz,
196 2018). In our model, we assumed monodentate surface complexation of Eu on single edge sites of quartz
197 ($\equiv QOH^0$ and $\equiv QO^-$). It has been described in the literature that metal sorption onto crystalline quartz is
198 dominated by the edge sites (Britz (2018)). Based on the previous work (Stumpf et al. (2008)), the number
199 of sites at the quartz surface was set to 3.6 nm^{-2} and the specific surface area measured $0.165 \text{ m}^2/\text{g}$. The
200 surface parameters and the surface complexation reactions for the considered binary and ternary surface
201 complexes together with the estimated $\log k$ values are given in Table 2. In Fig. 4, the overall model fit
202 and the distribution of surface species for binary and ternary sorption systems are presented. The
203 thermodynamic constants for reactions 3, 4, 5, and 6 in Table 2 are optimized from the Eu sorption
204 experiments in the absence of DTPA. The modeling results presented in Fig. 4a show that in the absence
205 of organic ligand, surface reactions 4 and 5 reproduce the sorption edge of europium, and the
206 contributions of surface species $\equiv QOEu^{2+}$ and $\equiv QOHEu(OH)_3$ described by equations 3 and 5 are

207 negligible (less than 0.1% at their peak). This shows that the europium hydroxide species $\text{Eu}(\text{OH})^{2+}$ and
208 $\text{Eu}(\text{OH})_2^+$ are bound to deprotonated surface edge sites of quartz ($\equiv\text{QO}^-$, Fig. 1a). As shown in Fig. 4a, the
209 model predicts a small fraction of Eu hydroxide $\text{Eu}(\text{OH})^{2+}$ to be sorbed in form of $\equiv\text{QOEuOH}^+$ (9% at
210 peak at pH 6) and the major part of Eu to be sorbed as neutral surface species to form $\equiv\text{QOEu}(\text{OH})_2$.

211 The thermodynamic constant for surface reaction 7 was estimated from fitting the modeling results to the
212 experimental data presented in Fig. 4c ($[\text{Eu}]/[\text{DTPA}] = 1$) and was then used together with the log k values
213 obtained for the binary sorption system to simulate sorption of Eu in the presence of organic ligand at
214 $[\text{DTPA}]/[\text{Eu}] = 0.5, 2, \text{ and } 10$ (Figs. 4b, 4d, and 4e). The DDLM provides a close fit to the experimental
215 data. Our model results show that in the presence of DTPA and at a ligand-to-metal ratio of 0.5 (Fig. 4b),
216 the surface species $\equiv\text{QOEuOH}^+$, $\equiv\text{QOEu}(\text{OH})_2$, and $\equiv\text{QOHEuDTPA}^{2-}$ are formed on the quartz surface
217 (surface reactions 4, 5, and 7, Table 2). However, at $[\text{DTPA}]/[\text{Eu}] \geq 1$, surface reactions 5 and 7 dominate
218 the Eu(III) sorption profile (Figs. 4c, 4d, and 4e), i.e., mainly the surface species $\equiv\text{QOEu}(\text{OH})_2$ and
219 $\equiv\text{QOHEuDTPA}^{2-}$ are formed if DTPA is present in excess. Figures 4b - 4e show that with increasing
220 $[\text{DTPA}]/[\text{Eu}]$ ratio in ternary sorption systems, the contribution of $\equiv\text{QOHEuDTPA}^{2-}$ in the sorption edge is
221 elevated and at $[\text{DTPA}]/[\text{Eu}] = 10$ the sorption curve of this surface species extends over the whole
222 studied pH range. At neutral to slightly acidic pH, DTPA can form a bridge between quartz surface and
223 Eu(III) and thus enhances Eu(III) sorption. This is well displayed in the modeling results. Figures 4b - 4e
224 show that the surface species $\equiv\text{QOHEuDTPA}^{2-}$ is formed mostly at $\text{pH} < 8$, where neutral surface hydroxyl
225 groups ($\equiv\text{QOH}^0$) are available. As mentioned before, due to the ionization of surface hydroxyl groups at
226 alkaline conditions, the quartz surface mostly consists of $\equiv\text{QO}^-$. At $\text{pH} > 7.5$, the surface species
227 $\equiv\text{QOEu}(\text{OH})_2$ dominates total Eu(III) sorption on deprotonated quartz surface edge sites ($\equiv\text{QO}^-$), i.e.,
228 surface reaction 5 constitutes the major part of Eu sorption.

229 In Fig. 5, experimental and modeling results of Eu sorption on quartz in the absence of organic ligand are
230 compared with the results provided by Pathak and Choppin (2007), Stumpf et al. (2008) and Ye et al.
231 (2014). All sorption curves show the same trend, and the shapes are comparable. Nevertheless, they
232 display slight differences in curvature and starting point, which is mostly due to differences in the

233 experimental conditions (initial metal concentration, background electrolyte concentration and solid/liquid
234 ratios). Furthermore, the lines are based on different modeling approaches. In contrast to our DDLM,
235 Stumpf et al. (2008) used the Basic Stern Model in combination with the charge distribution concept and
236 assumed bidentate surface complexation of Am(III) on single sites of quartz. However, the Eu sorption
237 profile obtained with our model is close to the sorption profile simulated by Stumpf et al. (2008). The
238 experimental results of Eu sorption onto silica provided by Ye et al. (2014) are more heterogeneous
239 compared to the results provided by Stumpf et al. (2008) and Pathak and Choppin (2007) and show a
240 noticeable Eu sorption at acidic conditions ($\text{pH} < 5$), which can be caused by minor surface impurities as it
241 is addressed by Britz (2018) and Lützenkirchen (1996). On the other hand, the model results provided by
242 Ye et al. (2014) show no Eu sorption under acidic conditions. A comparison of the surface complexation
243 parameters used in our model in binary and ternary sorption systems with those used in the selected
244 models explained above is provided in Table S1 (supporting data). Note that there are differences in the
245 modeling approaches, surface complexation reactions and surface parameters (e.g., surface area and site
246 density), which is reflected in the thermodynamic constants.

247

248 **4 Summary and conclusions**

249 We described the sorption behavior of Eu(III) on quartz, in the presence and absence of DTPA, by a
250 combination of experimental data and surface complexation modeling. DTPA reduces sorption of Eu(III)
251 at alkaline pH and therewith enhances its mobility due to the formation of Eu(III)-ligand complexes in
252 solution. At $[\text{Eu}]/[\text{ligand}]$ ratios > 1 , the mobilization effect of DTPA is higher than at $[\text{Eu}]/[\text{ligand}]$ ratios
253 < 1 , confirming the 1:1 stoichiometry. Under acidic conditions, DTPA slightly decreases the mobility of
254 Eu(III), indicating the formation of ternary surface complexes (Eu/ligand/quartz). The applied DDLM
255 successfully described the experimental data. These results show that mobility of trivalent lanthanides and
256 most likely actinides can be changed in the presence of aminopolycarboxylic acids. Their usage as a
257 decontamination agent in the operation phase of a nuclear waste repository should thus be avoided. The

258 obtained thermodynamic data are substantial for reactive transport models simulating long-term
259 radionuclide migration in the far-field of a repository.

260

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266

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