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Effects of ionic strength and fulvic acid on the adsorption of Tb^{3+} and Eu^{3+} onto clay

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ABSTRACT High salinity and natural organic matter are both known to facilitate migration of toxic or radioactive metals in geochemical systems, but little is known on their combined effect. We investigated complexation of Tb^{3+} and Eu^{3+} (as analogues for trivalent actinides) with fulvic acid and their adsorption onto clay in the presence of NaCl, $CaCl_2$ and $MgCl_2$ at ionic strengths up to saturation. ^{160}Tb, ^{152}Eu and ^{14}C were employed as radiotracers, allowing invesitigations at very low concentrations according to probable conditions in far-field scenarios of nuclear waste repositories.

A composite approach (linear additive model) was tested for suitability in the prediction of K_d values for solid-liquid distribution of Tb(III) and Eu(III) in the ternary system of metal ion, clay and fulvic acid based on the constituent binary subsystems. The model was found suitable in reproducing the influence of fulvic acid as a function of ionic strength for bivalent electrolyte cations. In this analysis, it could be shown that high ionic strength does not further enhance the mobilizing potential of humic matter.

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1. Introduction

Clay is a potential host rock formation for a repository for highly radioactive waste. The storage of radioactive waste demands for evidence of security over a long period. The migration behavior of radionuclides in natural aquifer systems is influenced by their interaction with rock and colloid surfaces and by the solvent composition (Geckeis and Rabung, 2008). However, the influence of high ionic strength on reactions in this ternary system has not been examined so far and previous results for low saline clay formations cannot be transferred to high saline pore waters (Bossart, 2007; Marquardt, 2011). Another issue focusses on the influence of natural organic matter, especially humic substances, on migration and mobilization of radionuclides (Křepelová et al., 2007; Marquardt, 2011; Reich et al., 2007; Sachs and Bernhard, 2005). Complexation, redox reactions, agglomeration and adsorption processes are the dominating retention processes of actinides in aquifer systems (Geckeis and Rabung, 2008). To quantify the retention of radionuclides, distribution coefficients for a known aquifer/rock-system can be derived from adsorption isotherms.

The retention of actinides in rock is counteracted at high ionic strength and low pH (Geckeis and Rabung, 2008). Humic substances are deemed to mobilize actinides in the far field of a repository by formation of inner sphere complexes (Bradbury et al., 2005; Sachs et al., 2007) at moderate pH (Reich et al., 2007).

Competing effects may be caused by metal cations in the aquifer, also influencing the adsorption behavior of humic substances onto clay minerals (Křepelová et al., 2007; Křepelová et al., 2008; Schmeide and Bernhard, 2010). Whereas low salinity does not affect complexation reactions of humic substances (Joseph et al., 2011), competition for binding sites may occur at high concentrations of electrolytes (Tipping, 2002).

Conceptual models consider processes in the ternary system of solid surface, metal and organic matter by means of stability constants and distribution coefficients K_d. The latter are obtained from the linear part of adsorption isotherms. Relatively simple model approaches are based on a pseudo-two-phase-system consisting of solid phase and humic substance, where the reactant is partitioned (see for a review (Lippold and Lippmann-Pipke, 2009)). Their basic assumption is that dissolved organic matter is not adsorbed, which is, however, not valid under specific geochemical conditions.

The linear additive model (Zachara et al., 1994) describes the ternary system of solid phase, metal and humic substance by interactions in three binary subsystems as shown in Figure 1.

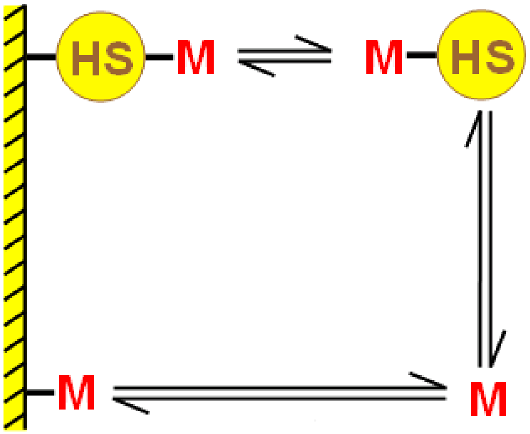

Figure 1. Linear additive model for adsorption of metals (M) onto solid surface phases (S) in the presence of humic substances (HS). Likely processes (sorption, desorption, complexation and dissociation) are indicated by bi-directional arrows.

It describes the solid/liquid distribution of a metal in the presence of humic substances. The distribution coefficient K_d of the metal in the ternary system depends on the binary interactions, assuming that they are independent of each other. The linear additive model assumes linear adsorption isotherms over the entire concentration range of metal and humic substance. A further prerequisite is that the intrinsic adsorption properties of the solid are not affected by the humic substance (Lippold and Lippmann-Pipke, 2009; Liu et al., 2011; Samadfam et al., 1998; Zachara et al., 1994).

In the present study, we investigated the adsorption of Tb^{3+} and Eu^{3+} as analogues for trivalent actinides (Cm, Am) onto clay in an aqueous system with ionic strengths up to 4 M, additionally containing fulvic acid. We used natural clay material from the Opalinus clay formation (Mont Terri, Switzerland) and fulvic acid as a surrogate of high-molecular-weight clay organic. ^{160}Tb(III), ^{152}Eu(III) and ^{14}C were used as radioactive tracers. NaCl, $CaCl_2$ and $MgCl_2$ as main electrolyte constituents of clay pore waters were used for adjusting the ionic strength.

Main obejective of this work was to answer the question as to whether the mobilizing potential of natural organic matter may be enhanced at the conditions of highly saline systems. Synergistic as well as antagonistic effects are conceivable. Modelling shall provide information on general principles in the distribution behavior of metals in ternary systems with clay and humic or humic-like substances. So the effect of high ionic strength on contaminant mobility in the presence of humic material can be described, providing a basis for numerical transport modelling.

2. Materials

^{160}Tb (half-life 72.3 d) was produced at the TRIGA Mark II reactor at the University of Mainz (Germany) and used in the form of a stock solution of 10^{-4} M [^{160}Tb]terbium in 0.1 M $HClO_4$. ^{152}Eu was purchased as [^{152}Eu]$EuCl_3$ stock solution in 0.1 M HCl from POLATOM (Poland).

An Opalinus clay sample (BHE-241) from the Mont Terri rock laboratory (Switzerland) was used as a 4.8 $g \cdot L^{-1}$ suspension. Major mineral phases are kaolinite and illite, determined by XRD (Marquardt, 2011). The specific surface area was determined to be 28 $m^2 \cdot g^{-1}$ (N_2-BET) (NAGRA, 2002), reported values for the cation exchange capacity vary between 11.1 and 16.0 meq per 100 g (Marquardt, 2011; NAGRA, 2002). The grain size was 100 nm – 10 µm. The exact mineralogical compositon of Opalinus clay is given elsewhere (Marquardt, 2011; NAGRA, 2002).

The fulvic acid was isolated from surface water collected on the moor *Kleiner Kranichsee* (near Carlsfeld, Germany). Purification was carried out according to the recommendations of the International Humic Substances Society (Aiken, 1985). The average molecular weigth was determined to be 38 kDa by size exclusion chromatography, the total acidity was found to be 8.46 $meq \cdot g^{-1}$ by potentiometric titration.

All other chemicals were of analytical grade and used without further pretreatment. Solutions were prepared using ultrapure Milli-Q water and all experiments were carried out at ambient conditions.

2.1 Adsorption experiments

Variable amounts of NaCl, $CaCl_2$ or $MgCl_2$ in the range of 0 - 4 mol·L^{-1} were added to the clay suspension. The pH was adjusted to 5 or 7 by using HCl. Stock solutions of [^{160}Tb]terbium (for pH 5) or [^{152}Eu]europium (for pH 7) were added to yield a concentration of 10^{-6} M (42 Bq·mL^{-1} ^{160}Tb, 930 Bq·mL^{-1} ^{152}Eu). Fulvic acid solutions, adjusted to pH 5 or 7, were added to the clay suspension resulting in a concentration of 40 mg·L^{-1}. After reaching equilibrium (24 h), the remaining [^{160}Tb]terbium or [^{152}Eu]europium concentration in the supernatant was determined after centrifugation (45 min 7000 rpm), using a gamma counter WIZARD 3" (PERKIN-ELMER, USA).

For measuring the adsorption of fulvic acid onto clay, ^{14}C-radiolabelled fulvic acid was prepared by azo-coupling with [^{14}C]aniline (Mansel and Kupsch, 2007). A detailed description of the procedure is given elsewhere (Lippold and Lippmann-Pipke, 2014). The [^{14}C]fulvic acid (40 mg·L^{-1}; 150 Bq·mL^{-1}) was added to the 4.8 g·L^{-1} clay suspension with variable amounts of NaCl, $CaCl_2$ or $MgCl_2$ (0 – 4 mol·L^{-1}) at pH 5 and pH 7. After equilibration for 24 h and centrifugation, the remaining concentration of [^{14}C]fulvic acid was determined by liquid scintillation counting on a Tri-Carb 3110TR (PERKIN-ELMER, USA), using Ultima Gold scintillation cocktail (PERKIN-ELMER, USA).

2.2 Complexation experiments

Solutions of 40 mg·L^{-1} fulvic acid, 10^{-6} M [^{160}Tb]terbium (pH 5) or [^{152}Eu]europium (pH 7) and variable amounts of NaCl, $CaCl_2$ or $MgCl_2$ in a range of 0 – 4 mol·L^{-1} were shaken for an hour and then centrifuged (7000 rpm) with "Vivaspin 2" 2 kDa ultrafilters (Sartorius, Germany). The remaining [^{160}Tb]terbium or [^{152}Eu]europium concentration in the filtrate (non-complexed fraction) was determined with a gamma counter WIZARD 3" (PERKIN-ELMER, USA).

3. Modelling adsorption in ternary systems

With the given results, it should be possible to predict the effect of ionic strength on the interactions in the ternary system of clay/metal/fulvic acid on the basis of the adsorption and complexation data in the constituent binary systems.

The solid-liquid distribution coefficient for metal adsorption $K_{\mathrm{d}}^{\mathrm{M/S}}$ (L·g^{-1}) is given by Eq. (1):

$$K_{\mathrm{d}}^{\mathrm{M/S}} = \frac{\Gamma_{\mathrm{M}}}{c_{\mathrm{M}}} \tag{1}$$

with Γ (mol·g^{-1}) denoting the amount of adsorbed metal M and c (mol·L^{-1}) denoting the concentration of free metal in solution.

Accordingly the distribution coefficient for adsorption of fulvic acid $K_{\mathrm{d}}^{\mathrm{FA/S}}$ (L·g^{-1}) is equal to:

$$K_{\mathrm{d}}^{\mathrm{FA/S}} = \frac{\Gamma_{\mathrm{FA}}}{c_{\mathrm{FA}}} \tag{2}$$

For simplicity, metal-fulvate complexation is likewise given as a distribution coefficient $K_{\mathrm{d}}^{\mathrm{M/FA}}$ (L·g^{-1}), calculated according to Eq. (3):

$$K_{\mathrm{d}}^{\mathrm{M-FA}} = \frac{c_{\mathrm{M-FA}}}{c_{\mathrm{M}}\, c_{\mathrm{FA}}} \tag{3}$$

where $c_{\mathrm{M\text{-}FA}}$ is the concentration of metal bound to fulvic acid.

According to the linear additive model, these distribution coefficients are independent of each other, and Eqs. (1 – 3) can be combined to Eq. (4) where $K_{\mathrm{d}}^{\mathrm{LAM}}$ (L·g^{-1}) is the solid-liquid distribution coefficient of the metal (free and as fulvate complex) in the ternary system:

$$K_{\mathrm{d}}^{\mathrm{LAM}} = \frac{K_{\mathrm{d}}^{\mathrm{M/S}} + K_{\mathrm{d}}^{\mathrm{FA/S}}\ K_{\mathrm{d}}^{\mathrm{M/FA}}}{1 + K_{\mathrm{d}}^{\mathrm{M/FA}}} \tag{4}$$

4. Results and Discussion

4.1 Adsorption of Tb(III), Eu(III) and fulvic acid onto clay in binary systems

Figure 2 shows the adsorption of Tb(III) (pH 5) and Eu(III) (pH 7) onto Opalinus clay represented as logarithmical solid-liquid distribution coefficient $K_{\mathrm{d}}^{\mathrm{M/S}}$ as a function of ionic strength. With increasing ionic strength I (up to almost saturated solutions, $I = 4$ M for NaCl, $I = 12$ M for $CaCl_2$ and $MgCl_2$), K_{d} values strongly decrease, most pronounced for the bivalent cations. At a pH of 5, metal adsorption is stronger suppressed than at pH 7, which is explained by the lower adsorption capacity of clay resulting from protonation.

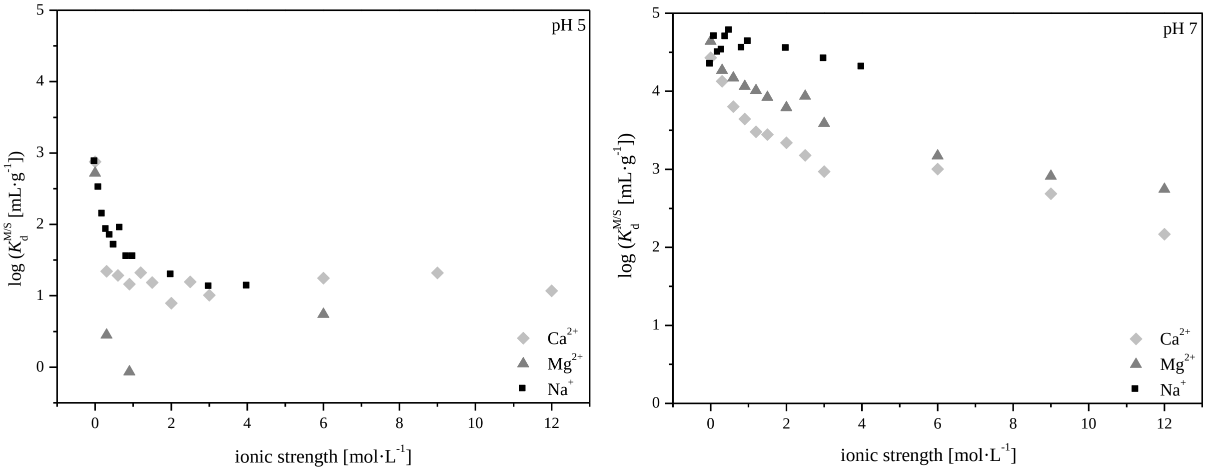

Figure 2. Adsorption of Tb(III) (pH 5) and Eu(III) (pH 7) onto Opalinus clay in the presence of NaCl, $CaCl_2$ and $MgCl_2$.

In Figure 3, adsorption of fulvic acid onto Opalinus clay at pH 5 and 7 in the presence of NaCl, $CaCl_2$ and $MgCl_2$ is shown as a function of ionic strength. Adsorbed amounts are relatively insensitive to increasing ionic strength. Adsorption of fulvic acid is slightly higher at pH 5 since repulsion by negative charge on fulvic acid and clay surface is reduced by protonation (Lippold and Lippmann-Pipke, 2009).

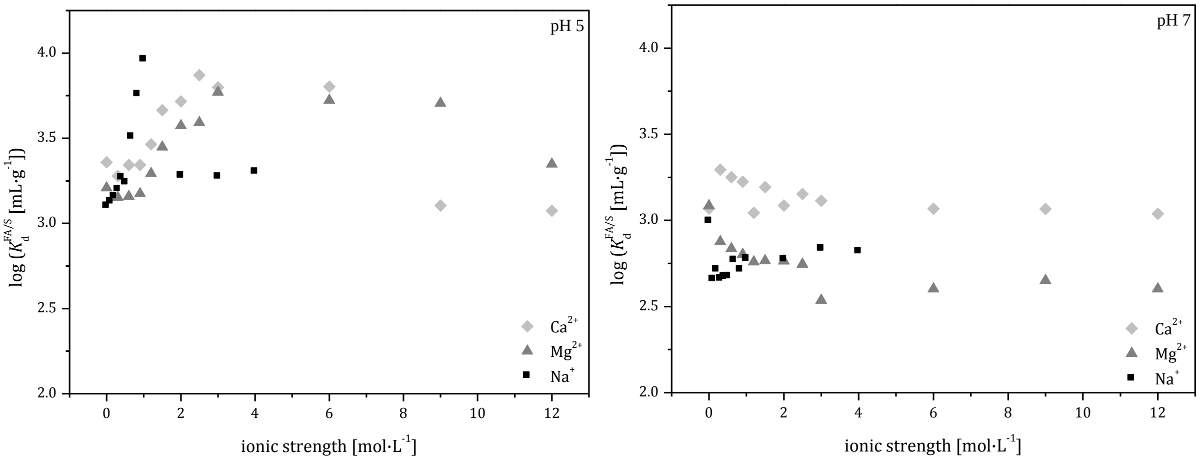

Figure 3. Adsorption of fulvic acid onto Opalinus clay at pH 5 and 7 in the presence of NaCl, $CaCl_2$ and $MgCl_2$.

4.2 Complexation of Tb(III) and Eu(III) with fulvic acid

The dependence of Tb(III) or Eu(III)-fulvate complexation on ionic strength is shown in Figure 4. For better comparison, these data are likewise given as distribution coefficients $K_\mathrm{d}^\mathrm{M/FA}$, considering the fulvic acid colloids as a pseudo solid phase. Complexation of Tb(III) and Eu(III) is strongly suppressed with increasing ionic strength and is significantly lower at pH 5 than at pH 7. The pH dependence is caused by the protonation of fulvic acid which leads to blocking of ligands (Lippold et al., 2005).

Again, the influence of ionic strength is higher for the bivalent cations Ca^{2+} and Mg^{2+}. Both show strong interferences on the complexation which can be explained by competition or shielding effects.

To verify the accuracy of the separation of free and fulvic-bound metal via ultrafiltration, possible sources of experimental errors were taken into consideration. (I) The membrane of the ultrafilters may be transmissible for small fulvic acid molecules, pretending lower complexed fractions. (II) ^{160}Tb or ^{152}Eu may be adsorbed at the membrane, pretending higher complexed fractions. (III) A possible perturbation of the complexation equilibrium due to the up-concentration of fulvic acid during the filtration process may lead to changes in the results. The issues (I) and (II) proved to be insignificant in preliminary tests. Complexation was also investigated by time-resolved laser fluorescence spectroscopy (TRLFS) as an alternative method. Very similar results were obtained, showing that issue (III) is not important as well. The TRLFS studies have also shown that a formation of chloro complexes for Tb(III) and Eu(III) at high ionic strength is negligible.

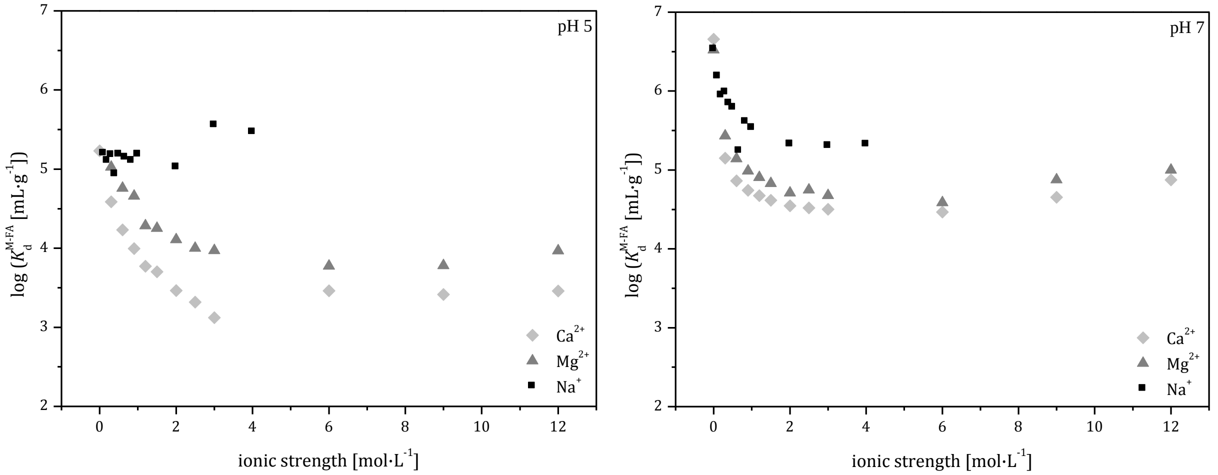

Figure 4. Complexation of Tb(III) or Eu(III) with fulvic acid as a function of ionic strength at pH 5 and 7 in the presence of NaCl, $CaCl_2$ and $MgCl_2$.

4.3 Adsorption of Tb(III) and Eu(III) onto clay in ternary systems with fulvic acid

Figure 5 shows the adsorption of Tb(III) and Eu(III) on Opalinus clay in the presence and absence of fulvic acid as a function of ionic strength for NaCl, $CaCl_2$ and $MgCl_2$. At pH 5, the presence of fulvic acid leads to increased adsorption of Tb(III) in general. In the case of $MgCl_2$, high ionic strength suppresses adsorption of Tb(III) on clay almost completely, whereas the ternary system with fulvic acid shows significant adsorption. Mineral-bound fulvic acid increases adsorption of metal ions at acidic conditions. With increasing ionic strength, complexation is suppressed and leads to lower adsorbed amounts. At pH 7, the effect of fulvic acid is reversed: Metal adsorption is decreased compared to the system without fulvic acid. Obviously, this changeover is a consequence of the pH-depedent adsorption behavior of the organic carrier (*cf.* Figure 3).

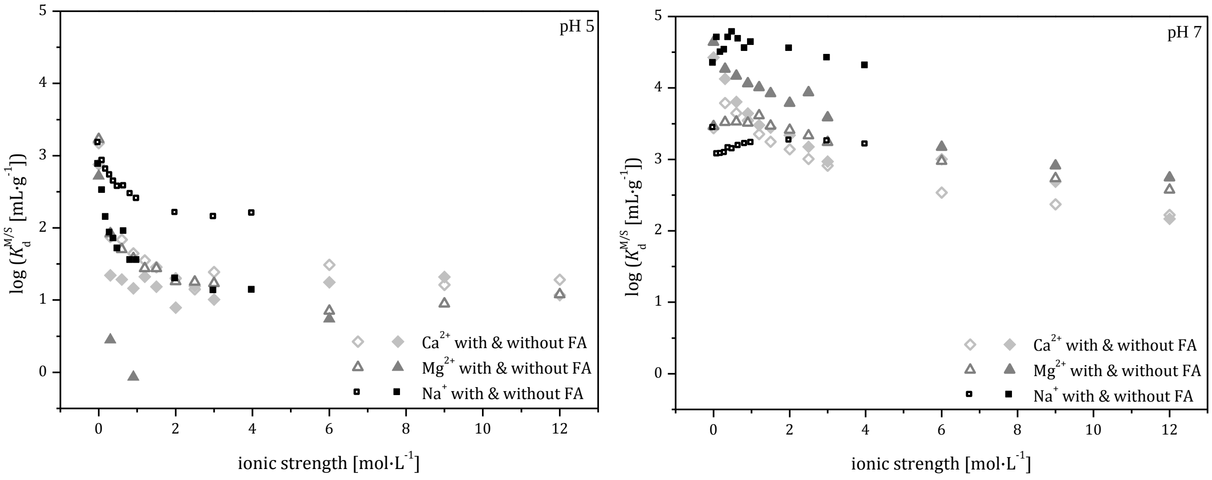

Figure 5: Adsorption of Tb(III) (pH 5) and Eu(III) (pH 7) on Opalinus clay in the presence (empty symbols) and absence (full symbols) of fulvic acid as a function of ionic strengths for NaCl, $CaCl_2$ and $MgCl_2$ as electrolytes.

Figure 6 shows the measured distribution coefficients for the co-adsorption of metal and metal-fulvate complex together with the corresponding $K_\mathrm{d}^\mathrm{LAM}$ values calculated according to Eq. (4).

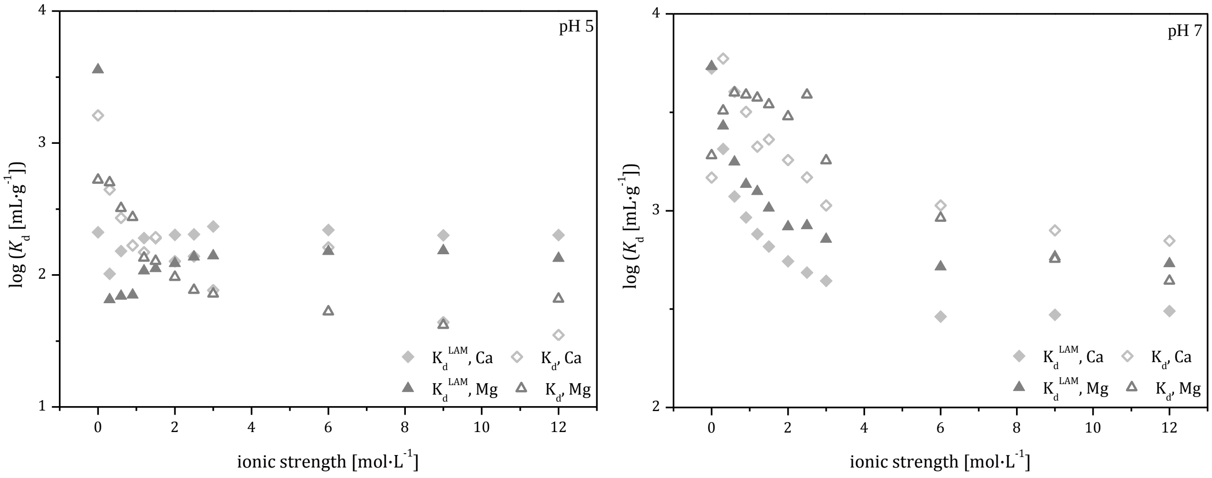

Figure 6. Adsorption of Tb(III) (pH 5) and Eu(III) (pH 7) on Opalinus clay in the presence of fulvic acid as a function of ionic strength for $CaCl_2$ and $MgCl_2$ as electrolytes. The full symbols show the calculated values according to the linear additive model (Eq. (4)).

The model reproduces the measured data for the bivalent cations quite well, especially for pH 7. Nonetheless, the prediction by the linear additive model leads to slightly lower (in case of pH 5) or higher (for pH 7) K_d values for the solid-liquid distribution ratio in the ternary system. Nonetheless, the predicted, not fitted modelled data show a similar trend as the measured values.

Overall, the additivity concept proved to be suitable for estimations on the effect of humic material on metal adsorption at variable solution conditions.

5. Conclusions

Fulvic acid strongly influences the adsorption of trivalent lanthanide ions by formation of metal-fulvate complexes. The results provide important information on the mobility behavior of metals in a ternary system with clay and fulvic acid and can be the basis for further transport investigations. High ionic strength, as found in the clay pore water in rock formations especially in northern Germany, suppresses adsorption of metals as well as their complexation with humic-like clay organics, which has significant implications on humic-bound metal transport.

In summary, this study has shown that a mobilization of metals caused by humic matter is not enhanced by high ionic strength. On the contrary, a mitigating effect was evidenced, based on the fact that complexation is suppressed while adsorption of humic matter is hardly influenced. At low pH, adsorption of metals on a clay surface is increased by fulvic acid due to the formation of surface complexes of the type S-FA-M. Their presence has been proven by the applicability of the linear additive model. This approach is a simple method to reconstruct adsorption data, proving or disproving the additivity of the binary equilibria in the ternary system. It was found to be suitable for predicting trends in the co-adsorption of metals and fulvic acid in dependence on ionic strength, in part nearly quantitatively.

Spectroscopic data would deepen the understanding of complex formation on the solid surface, including a possible presence of a certain amount of ternary surface complexes of the kind S-M-FA, which are not considered in the linear additive model. A further possible reason of deviations is that selectivities in complexation and adsorption within the polydisperse system of fulvic acid molecules are not taken into account. For instance, preferred adsorption of molecules with high metal loads would entail an underestimation by the model, since it operates with an averaged metal load, determined for the humic substance as a whole. Studies with fractionated humic material could serve to clarify the importance of selectivity effects.

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