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Sorption and diffusion of organic acids through clayrock: Comparison with inorganic anions

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SUMMARY

Organic complexing species are known to affect radionuclide mobility in the environment. The migration behaviour of several organic ligands was evaluated in the context of a proposed French radioactive waste repository in the Callovo-Oxfordian clayrock formation (COx). This study focuses on four anthropogenic acids (ethylenediaminetetraacetate, isosaccharinate, phthalate, oxalate) that are used in the nuclear fuel cycle or that occur as hydrosoluble degradation products of waste materials. Batch sorption and diffusion experiments were performed with COx clayrock samples using ^{14}C-labelled radiotracers. The observed effective diffusion coefficients were low ($D_e \sim 1–6 \times 10^{-12}$ m^2 s^{-1}), an order of magnitude lower than that of tritiated water in the same material, and roughly the same as values for inorganic anions such as I^-, Cl^- and SO_4^{2-}. The observed correlation of D_e with molecular mass, $M^{-1/3}$, differs significantly from that observed for cations. The organic ligands displayed significant affinity for the COx clayrock, with distribution ratios measured in batch experiments, $R_d = 1–30$ L kg^{-1}, which are much higher than usually observed for anionic species. While this result was confirmed by through-diffusion experiments, the K_d values obtained by fitting diffusion modelling were significantly lower than those measured in the batch experiments.

1. Introduction

Clay-rich sedimentary formations (clayrock) are under consideration as potential host rocks for construction of deep geological repositories for long-lived, high and intermediate level radioactive wastes, an example being the Callovo-Oxfordian formation (Meuse/Haute-Marne, France). The host formation constitutes the principal barrier for limiting radionuclide (RN) transfer towards the biosphere, mainly due to diffusive properties and the capacity of the clayrock to adsorb most radionuclides (Andra, 2005). Organic matter released from containers and waste packages, and subsequent degradation products, can alter RN uptake and transport in the geological barrier, as well as on cement materials used in vault construction (Hakanen and Ervanne, 2006; Read et al., 1998). Many studies have been carried out focusing on the influence of organic ligands on RN solubility, sorption and mobility in cement environments (Stockdale and Bryan, 2013) and in clayrocks (Maes et al., 2011; Poinssot and Geckeis, 2012). Numerous studies are also dedicated to the sorption of small organics on clayey materials (see for example Drouin et al., 2010), but only few data are available on diffusion-driven migration in clayey materials (Martens et al., 2010 studied the migration of ^{14}C-labelled natural organic matter (NOM) through boom clayrock). Such investigations are, however, crucial in order to assess the actual organic transport through the geosphere.

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Anthropogenic organic matter can have various origins: (i) organic complexants such as ethylenediaminetetraacetic acid (EDTA) used in decontamination processes; (ii) organic species (formic, acetic, oxalic, citric, isosaccharinic (ISA) acids...) resulting from radiolytic and alkaline degradation of bitumen, ion exchange polymers, cellulose; and (iii) additives used to improve the physical and rheological properties of concrete. Small acids are even naturally present in ground waters, as soluble degradation products of natural organic matter (Huclier-markai et al., 2010). In this study the focus is on four organic complexants (ISA, EDTA, phthalic and oxalic acid) which all possess carboxylic functional groups, but have different mass, shape and charge.

A thermodynamic database exists for EDTA and oxalate complexes in (Hummel et al., 2005). Numerous studies have been carried out on the effects of EDTA on RN sorption or migration, among which: diffusion of Metal/EDTA complexes in water (Furukawa et al., 2007), Pu/EDTA in soil (Hakem et al., 2001), U/EDTA through Clashach sandstone (Read et al., 1998), Sr/EDTA in partially-saturated, heterogeneous sediments (Pace et al., 2007) and sorption of Zn–Pb/EDTA on kaolinite (Darban et al., 2000). These studies focus on the influence of EDTA complexation on the transport of cation, whereas the transfer parameters of EDTA itself are not quantified.

Oxalate is also well-described in the literature in terms of complexation equilibria and effects on metal sorption (e.g. uranium and europium sorption on α-alumina (Alliot et al., 2005a), Co^{2+} sorption on kaolinite (Shakir et al., 1993), Ca^{2+} and Cu^{2+} sorption on goethite (Ali and Dzombak, 1996)). Oxalate sorption on various substrates has been extensively studied (e.g. on α-alumina (Alliot et al., 2005b), goethite (Mesuere and Fish, 1992) illite, kaolinite and montmorillonite (Kubicki et al., 1999)). On the other hand, few studies present measurements of oxalate complex migration and none, to our knowledge, investigate oxalate diffusion in clayrock.

The effect of ISA on Eu(III) and Th(IV) sorption on calcite was described by Tits et al. (2002), on undegraded hardened cement pastes at high pH by Wieland et al. (2002). The degradation of co-contaminant, such as ISA, and at low pH (7–8) with emphasis on their environmental fate was less discussed (Keith-Roach, 2008). To the best of our knowledge, no data exists for ISA migration in clay media.

Lastly, numerous studies exist in the field of water research concerning phthalate derivatives and phthalic esters, although few deal with sorption or complexation of ortho-phthalic acid. For example, sorption of phthalic acid was quantified on boehmite (γ-AlOOH) and goethite (α-FeOOH) by Persson et al. (1998), and its effect on Cu^{2+} and Ca^{2+} sorption was studied by Kubicki et al. (1999). A sorption mechanism on hematite is discussed by Hwang et al. (2007). Migration of phthalic acid complexes in soil or clayey materials remains to be investigated.

A large scale modelling of the effects of organic acids on RN behaviour cannot be carried out without information on behaviour of the ligands themselves in natural materials. The objective of this work was to determine transport parameters of EDTA, ISA, ortho-phthalic and oxalic acids in the COx clayrock. To this aim, we performed both sorption and diffusion experiments with ^{14}C-labelled molecules. Such data are required to quantify the diffusivity of small complexing ligands in the far-field.

2. Methods and materials

2.1. Clayrock characterisation and preparation

Experiments were carried out on a single core sample (sample number EST16517) obtained from a depth of −501.8 to 502.0 m in the EST207 borehole (Savoye et al., 2011) at site of the Andra Underground research laboratory (Meuse/Haute-Marne, France). Samples were protected from oxidation of pyrite minerals by direct placement in anoxic aluminium containers under N_2. Once in the lab, the outermost 5 mm of the core sample were removed using a diamond wire saw under anoxic conditions. The remaining rock was used for batch experiments. Each core was then sliced parallel to the bedding plane to produce a 1 cm thick section and 3.5 cm diameter disk. Samples for batch experiments were produced by grinding the rock to a fine powder and sieving to <63 μm, all in an anoxic glove box (PO_2/P_0 < 2 ppm). The powder was then rinsed with synthetic porewater solution with a composition detailed in Table 1. Powder and porewater were mixed in polypropylene centrifugation tubes with a solid/liquid ratio of 0.25 g mL^{-1}. The tube was sealed, taken out of the glove box and agitated in a Turbula mixer for 72 h. The tube was then centrifuged at 10,000 g during 30 min, the supernatant removed and the solution renewed. This mixing step was repeated three times during 24–48 h in order to equilibrate the clay mineral surface with the synthetic porewater, following the protocol detailed by Descostes and Tevissen (2004). Finally the powder was rinsed with ethanol in order to eliminate the excess of salts and water and stored in a vacuum-oven at 60 °C.

2.2. Chemicals and radiotracer synthesis

High purity salts were used to prepare all solutions: disodium Na_2H_2EDTA (Fluka #03679 purity >99%), disodium oxalate (Na_2Ox. Sigma–Aldrich #100956140 purity >99.5%), phthalic acid (H_2Phtal. Merck #224 G 445711, purity >99.5%). Sodium NaISA salt was used to avoid high calcium concentrations. This salt was obtained by passing a cold solution (4 °C) of dissolved $Ca(ISA)_2$ (20 g in 2 L of Milli-Q water) through a cation exchange resin column. The proton excess in Na_2H_2EDTA and $H_2Phtalate$ was balanced by NaOH addition. The pH was then adjusted with concentrated NaOH or HCl standard solutions.

Sorption and diffusion experiments were carried out with ^{14}C-labelled radiotracers in synthetic porewater. The use of ^{14}C-radiolabelled tracers was necessary because of the presence of natural organic matter in the clay, which made ligand quantification by TOC analysis impossible and also to improve the detection limits required for diffusion experiments. ^{14}C-EDTA and ^{14}C-Oxalate were commercially available from Sigma, #30,471-9 and #03,004-^{14}C respectively. The ^{14}C-IsoSaccharinic and ^{14}C-phthalic acids were synthesised (cf. supplementary data for details).

2.3. Sorption experiments

Sorption experiments were carried out using sealed polycarbonate centrifugation tubes (PC) and synthetic porewater bubbled with a N_2/CO_2 mixture to limit oxidation. Experiments were

Table 1
Synthetic porewater compositions used in this study. Composition was refined for the most recent experiments (phthalate oxalate). In both case pH = 7.15/8.0 ± 0.1 when $pCO_2 = 10^{-1.9}/10^{-3.5}$ atm respectively.

Ions Ligand	$[Na^+]$ (mol L^{-1})	$[K^+]$ (mol L^{-1})	$[Ca^{2+}]$ (mol L^{-1})	$[Mg^{2+}]$ (mol L^{-1})	$[Sr^{2+}]$ (mol L^{-1})	$[Cl^-]$ (mol L^{-1})	ΣCO_2 (mol L^{-1})	$[SO_4^{2-}]$ (mol L^{-1})
EDTA ISA	3.56×10^{-2}	1.48×10^{-3}	8.79×10^{-3}	7.00×10^{-3}	1.26×10^{-4}	3.36×10^{-2}	2.20×10^{-3}	1.69×10^{-2}
Phthalate Oxalate	4.56×10^{-2}	1.03×10^{-3}	7.36×10^{-3}	6.67×10^{-3}	2.0×10^{-4}	4.10×10^{-2}	3.34×10^{-3}	1.56×10^{-2}