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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}

carried out at 22 ± 2 °C with a mean solid/liquid ratio of 62.5 g L^{-1} for ISA and EDTA and 50.0 g L^{-1} for phthalate and oxalate. The sample was spiked with the ^{14}C-tracer and then agitated in a Turbula mixer for either 24 h or up to 2 months. At the time of sampling, the tubes were centrifuged at 50,000*g* for 1 h and a fraction of the supernatant was sampled and the tracer activity determined by liquid scintillation counting (Packard TRICARB 2500 with ultima gold™ cocktail from Perkin Elmer) taking radioactive decay into account. The distribution coefficients R_d (mL g^{-1}) were calculated using the following equation:

$$R_d = \left(\frac{C_0}{C} - 1\right) \times \frac{V}{m} = \left(\frac{A_0}{A} - 1\right) \times \frac{V}{m} \quad (1)$$

with C_0/C being the initial/residual concentration in solution (mol L^{-1}); A (CPM) the activity; V (mL) the solution volume; and m (g) the clayrock dry mass.

2.4. Diffusion experiments

The methodology has been detailed in (Bazer-bachi et al., 2006; Descostes et al., 2008). Preparation and equilibration of the diffusion cells were carried out in an anoxic glove box. The experiments were performed at room temperature (22 ± 2 °C). The through-diffusion cells consists of two polypropylene reservoirs (up and downstream: 175 and 130 mL, respectively), a polypropylene sample holder, two stainless steel filterplates or two polyether ether ketone grids (PEEK). The clayrock disks in the diffusion cells were equilibrated with the porewater solution by contacting for a period of 48 h to 7 day, then replacing the solution in the chambers. This was carried out three times followed by one last equilibration step lasting two weeks which was sufficient to reach equilibrium. The solution was then replaced by a new solution spiked with the desired tracer (initial concentrations and activities are listed in Table 2). Both compartments were periodically sampled and the solution volume was renewed by addition of synthetic water (downstream) or spiked solution (upstream). Solution samples were counted by liquid scintillation couting (Packard TRICARB 2500, with Ultima Gold™ cocktail).

The analysis of the results was based on Fick's second law for one-dimensional reactive transport (Crank, 1975):

$$\frac{\partial C}{\partial t} = \frac{D_e}{\varepsilon_a + \rho K_d}\frac{\partial^2 C}{\partial x^2} = \frac{D_e}{\alpha}\frac{\partial^2 C}{\partial x^2} \quad (2)$$

where C is the radioactivity per volume unit (Bq m^{-3}); t, the time (s); D_e, the effective diffusion coefficient (m^2 s^{-1}); ε_a, the diffusion-accessible porosity; ρ, the bulk dry density (kg m^{-3}); K_d, the sorption distribution ratio (m^3 kg^{-1}); and α, the rock capacity factor (also called apparent porosity). Boundary and initial conditions are the same as those used by Descostes et al. (2008, 2012), except for the decreasing upstream concentration due to diffusion flux. Full analytical solutions for through-diffusion and reservoir-depletion configurations were obtained in the Laplace space. These were subsequently numerically inverted to provide the time-dependent solution (Moridis, 1998). The analysis of the results was performed by a least-square fitting of the model to the incoming daily flux in the downstream reservoir, using an analytical solution of Eq. (2). This solution was also compared with a numerical solution using the ALLIANCES platform and the CAST3M code (Montarnal et al., 2007). Results from both methods were found to be consistent.

Table 2
Total concentration and activity of organics introduced in upstream solutions of through-diffusion experiments. The volume of the upstream compartment is 175 ± 2 mL.

Through-diffusion experiment	ISA	EDTA	Phthalate	Oxalate
[Orga]$_{t=0}$ Upstream compartment				
C_{TOT} (mol L^{-1})	1.0×10^{-3}	27×10^{-3}	1.2×10^{-4}	1.7×10^{-5}
^{14}C (MBq L^{-1})	2.21	5.05	5.15	2.37
^{14}C (MBq)	0.382	0.873	0.891	0.415

2.5. Electro spray ionization mass spectrometry

The speciation of the dissolved organic molecules was determined by Electro Spray Ionization Mass Spectrometry (ESI-MS, Nogueira et al., 2009) on a LCT Premier equipped with an Electro-Spray source (Micromass, Manchester, UK) in negative W mode. The capillary voltage was set at 2500 V and the sample cone voltage at 30 V. The desolvation and source temperatures were set at 150 and 100 °C respectively. A syringe injection pump (Harvard Apparatus, Cambridge, MA) delivered the solvent at a constant flow rate of 10 μL min^{-1}. Measurements were performed on 10 mM solutions of ISA, EDTA and phthalate, and a saturated solution of oxalate ($C_{sat} \sim 2.4 \times 10^{-5}$ mol L^{-1}) in synthetic porewater (pH adjusted between 7 and 8). A volume of 20 μL of these organic solutions was diluted in 2 mL of methanol before measurement. Samples were then directly introduced into the ion source using a 250 μL glass syringe with a stainless steel needle (Hamilton Co., Reno, NV). Data were acquired by operating the data system in a total ion current (TIC) acquisition mode and several scans were summed to obtain the final spectrum.

3. Results

3.1. ESI-MS and speciation in solution

Speciation of organic molecules in the porewater solution was calculated using PhreeqC Chemical Code V2.17 (Parkhurst and Appelo, 1999; Gaucher et al., 2006) using Andra's Thermo_Chimie_8 database (Duro et al., 2012), completed with selected data on organics from the Minteq V4 PhreeqC database and reference (Hummel et al., 2005). In this section, the fully protonated ISA molecule which only display two labile protons at pH ~ 7–8 will be noted H_2ISA. The main aqueous species expected in 10 mM solutions of EDTA, H_2ISA, and phthalate are respectively: Mg-EDTA^{2-}/Ca-EDTA^{2-}: 72/28%, HISA$^-$/CaHISA$^+$: 92/8%, and Phtal.$^{2-}$/Mg-Phthal.$^{2-}$/Ca-Phthal.$^{2-}$/Na-Phthal.$^{2-}$: 69/12/12/7%. Solutions saturated with oxalate ([Ox] ~ 2×10^{-5} mol L^{-1}) present the following species: MgOx, CaOx, Ox^{2-}: 53/24/20%. The ratios between species remain almost unchanged when varying parameters such as pH from 7.0 to 8.5, CO_2 partial pressure from $10^{-3.5}$ to $10^{-1.9}$ atm, or total organic concentration from 10^{-2} to 10^{-9} mol L^{-1}.

Calculations were compared to the ESI-MS measurements of 10 mM solutions of EDTA, ISA, phthalate, and a saturated solution of oxalate, in artificial porewater. ESI-MS spectra are presented in Fig. 1. The peaks resulting from synthetic pore water are given in supplementary data. The main peaks observed for the EDTA solution correspond to complexed forms with calcium and magnesium, [M-EDTA]$^{2-}$, and possibly sodium. This result confirms the affinity between EDTA and cations leading to negatively charged species complexes. The major species observed for the ISA solution is also anionic, *e.g.* HISA$^-$, in good agreement with the previous speciation calculations. NaISA$^-$ is also observed in the spectra but no thermodynamic data is available to allow taking this species into account. CaHISA$^+$ is not observed as the ionization is performed in negative W mode. A single negative species is observed for phthalate, without cation complexation: HPhthal$^-$ (m/z = 165.51 uma). Phthal^{2-} was not observed at m/z = 82.3 uma. This may come from formation of a weak ion pair with protons in water, or by phthalate protonation during the dilution in methanol. The measurements on

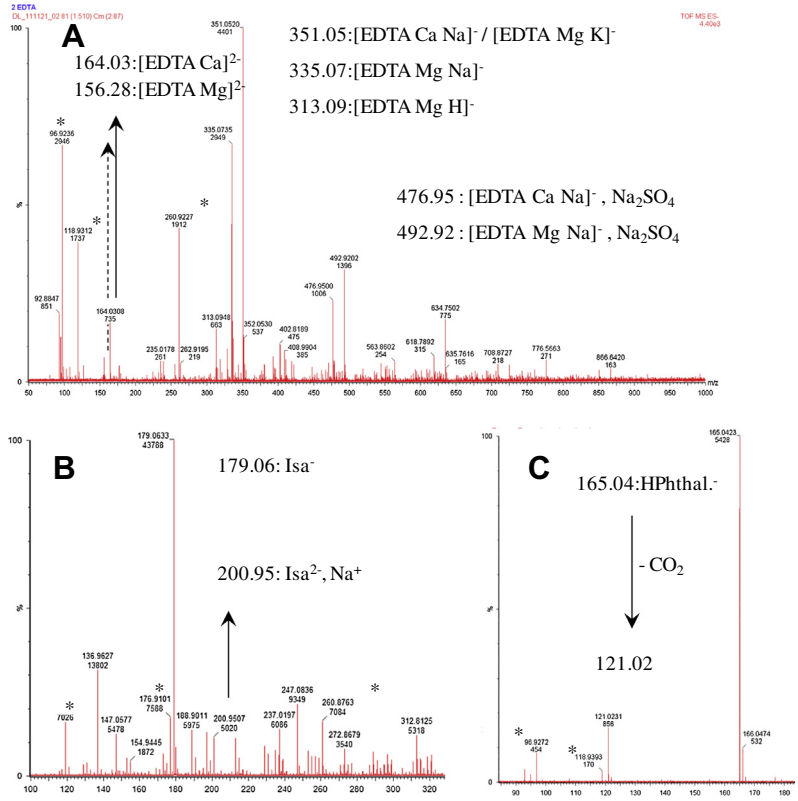

Fig. 1. Electro spray ionization mass spectra of organic solutions in porewater solutions. (A) EDTA, 10 mM, (B) ISA, 10 mM, (C) Phthalate, 10 mM. *Peaks corresponding to ions clusters observed in poral water without organic in negative W mode (anions detection).

oxalate sample gave no signal, even at higher concentration (50 μL in 500 μL of MeOH). This result agrees with the calculation indicating low oxalate solubility and a majority of neutral species (Ca-Ox, Mg-Ox).

Further interpretation is difficult, especially because calculations are limited to complexes with thermodynamic constants available in the literature. Information is particularly rare concerning structures with various cations, e.g. $[EDTACa/Mg, Na]^-$ or bigger ion clusters. It is therefore difficult to conclude whether or not such species are representative of the solution or adducts formed during ESI-MS experiment as discussed by Schug and McNair (2003). Still, ESI-MS measurements were performed on samples from the downstream reservoir in diffusion experiments with EDTA and ISA. The results were similar to measurements performed on the upstream compartment indicating that no degradation occurred during the two years experiment. Indeed, it is very unlikely that a degradation of acids occurred by oxidation or bacterial activity leading to CO_2/H_2O only without molecules displaying an intermediate molecular weight. This also demonstrates that the speciation imposed to acids by the initial porewater was not affected by diffusion through the clayrock.

3.2. Sorption experiments

Sorption of organics on COx clayrock was studied as a function of solution concentration. The isotherms, $R_d(\text{Orga.}) = f[\text{Orga.}]$, are represented in Fig. 2. The high values observed for $[\text{Ox.}] > 2.4 \times 10^{-5}$ mol L^{-1} correspond to the precipitation of a Ca-Ox solid phase. The results presented are those corresponding to a long period (at least 40 days). This duration ensures that the system reached equilibrium, usually observed within the first 48 h for sorption of organics. Low R_d values, from 0.1 to 30 L kg^{-1}, were measured for the range of studied concentrations, but these values are much higher than sorption usually observed for anions such as Cl^-, I^- and SO_4^{2-}, on the COx clayrock (Bazer-bachi et al., 2006, 2007; Descostes et al., 2008; Savoye et al., 2012).

The decrease in R_d values at high concentration is characteristic of the saturation of surface sites. Results over a large concentration range (10^{-8} to 10^{-1} mol L^{-1}) could be modelled using a one-site Langmuir isotherm. This result is surprising considering the many phases and sorption sites present in the natural material. Such an isotherm is described by Eq. (3)

$$C_{ads} = S_{max} \times \frac{K_{ads} \times C_{eq}}{1 + K_{ads} \times C_{eq}} \quad (3)$$

where C_{ads} is the concentration of the adsorbed molecule on the solid phase (mol kg^{-1}); C_{eq}, the equilibrium concentration in solution (mol L^{-1}); K_{ads}, the adsorption constant (L mol^{-1}); and S_{max} the maximum amount of organic sorbed (mol kg^{-1}) representative of the saturation of surface sites. At low concentrations, i.e. for $K_{ads} \times C_{eq} \ll 1$, the isotherm becomes linear giving a constant distribution ratio: $R_d \sim K_{ads} \times S_{max}$. The parameter values obtained by least square fitting of the data are presented in Table 3. Fitting of the oxalate curve gives only one parameter (R_d) because CaOx precipitation occurs before saturation of sorption sites. The maximum amount of species sorbed is roughly the same for ISA and phthalate: $8.8 \times 10^{-4}/9.4 \times 10^{-4}$ mol kg^{-1} respectively while a higher value is obtained for EDTA: $S_{max} = 2.54 \times 10^{-1}$ mol kg^{-1}. Concerning R_d values, the highest sorption was observed for ISA ($R_d = 30$ L kg^{-1}). Phthalate presented the lowest affinity for the clayrock ($R_d = 1.4$ L kg^{-1}), which is nevertheless still higher than the usual values for inorganic anions. EDTA and oxalate gave intermediate values, similar to results from other studies, but few data exist for clayey materials (Table 3). Interpretation and physical meaning of the sorption values are discussed in the last section.

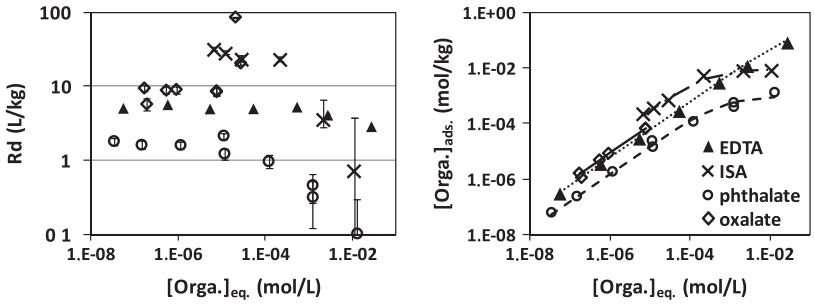

Fig. 2. Experimental results for sorption of organic acids, EDTA, ISA, oxalate, phthalate on COx argillite. Sampling time superior to 40 days. (Left) Distribution ratio (R_d) as a function of organic concentration at equilibrium. (Right) Experimental concentration of sorbed species (mol kg^{-1}) as a function of concentration in solution (mol L^{-1}) and corresponding results modelled using a Langmuir one-site isotherm.

3.3. Diffusion experiments

Normalised cumulated radioactivities in the downstream compartment ($Q_{down}(t)/Q_{up}(t=0)$) and incoming daily fluxes ($F_{down}(t) = [Q_{down}(t+dt) - Q_{down}(t)]/S \times dt$) are given for each ligand in Fig. 3. EDTA was observed in the downstream reservoir after 40 days, much earlier than ISA, which confirms the stronger affinity of ISA for clayrock than EDTA. Results for oxalate and phthalate are very similar indicating little effect of the aromatic ring. Two parameters (D_e and α) can be adjusted by least squares fitting of the flux curves (Fig. 3 and Table 4). Very low effective diffusion coefficients, from 1 to 5×10^{-12} m^2 s^{-1}, were obtained. These values are at least an order of magnitude lower than that for diffusion of tritiated water. Effective diffusion constants obtained for carboxylic acids in COx clayrock are in the same range as values for inorganic anions like chloride, sulphate or iodide.

The corresponding rock capacity factors range from 0.27 for EDTA to 2.57 for ISA respectively (cf. Table 4). Rock capacity factors previously observed in similar samples for non-sorbing anions were roughly equal to the accessible porosities: $\varepsilon_a(I^-, Cl^-) \sim \alpha(I^-, Cl^-) < 0.08$ (Bazer-bachi et al., 2006; Descostes et al., 2008) while the α values for the carboxylic acids are higher than the total porosity measured with HTO. This result confirms the sorption of organics observed in batch experiments. In the case of sorbing species, the rock capacity factor, α, obtained by through-diffusion experiment, gives a second estimation of the sorption using Eq. (4):

$$K_d = \frac{(\alpha - \varepsilon_a)}{\rho} \quad (4)$$

where K_d is the distribution ratio, ε_a is the accessible porosity assumed to be the same than that measured for anions $\varepsilon_a \sim 0.08 \pm 0.02$ and $\rho \sim 2.4$ kg L^{-1} the clayrock dry density. It was not possible to adjust experimental data with only De as a parameter and (K_{ads}, S_{max}) taken from batch results. Since a flux curve allows the adjustment of only two parameters, we then adjusted (D_e, α), assuming a linear sorption. In the case of oxalate, ISA and phthalate, upstream concentrations are low (<10^{-3} mol L^{-1}), and the use of a constant (K_d) instead Eq. (3) gives a reasonable approximation. In the case of EDTA, upstream concentrations are higher and K_d value obtained by Eq. (4) may slightly underestimate the sorption at trace level. This underestimation does not affect the further discussion.

Values measured by through-diffusion (noted K_d) and by batch experiments (noted R_d) are compared in Table 4. R_d and K_d values follow a similar trend: $R_d(Cl^-, I^-) \ll R_d(EDTA) < R_d(phthalate) < R_d(oxalate) < R_d(ISA)$ for batch experiments and $K_d(Cl^-, I^-) \ll K_d(phthalate) < K_d(EDTA) < K_d(oxalate) < K_d(ISA)$ for diffusion experiments. The only exception is the order of values for EDTA and phthalate which are very close. Unexpectedly high R_d/K_d ratios, from 6 up to 80, were obtained. These values are much higher than previously observed for anions or cations (Bazer-bachi et al., 2007; Melkior et al., 2005). The origin of such high values is still under investigation and discussed in the next section.

Variations in upstream activity were too small to be exploited. Upstream activities measured during through-diffusion are compared to the model using previous (D_e, α) values and presented in Fig. 3. This comparison is used to verify the mass balance during the experiments. A good agreement was observed in the case of phthalate and ISA experiments with less than 1% and 5% differences between experimental data and modelled ΔQ_{up}. The upstream activity for EDTA after 450 days decreased by 14%. This is slightly higher than the 10% expected from modelling and does not affect the determination of diffusive parameters. Only the ^{14}C-oxalate activity decreased much faster than expected, about 45% in 250 days against the predicted 7%. This decrease affects the measurement by changing the concentration gradient between upstream and downstream compartment. Thus, a second modelling was performed with $Q_{upstream} = 0.280$ MBq instead of 0.406 MBq in order to prevent an overestimation of transport

Table 3
Sorption parameters obtained by modelling the experimental isotherms using a one-site Langmuir model. Results of other studies found in the literature have been included for comparison. Values in bold are solid solution distribution coefficients (R_d).

Sorption experiment	ISA	EDTA	Phthalate	Oxalate	Solid phase
Log [K_{ads} (L × mol^{-1})]	3.54	1.39	3.18	No saturation	COx clayrock
[S_{max}] (mol × kg^{-1})	8.8×10^{-3}	2.54×10^{-1}	9.4×10^{-4}		
$R_d = K \times [S_{max}]$ (L × kg^{-1})					
(This work)	**30**	**6.2**	**1.4**	**8.4**	
Pace et al. (2007)		**75–100**			Clay
		3–5			Sand
		Sr^{2+} tracer			
Kubicki et al. (1999)			**2.5–4.7**	**Not detailed**	Kaolinite, Illite, Montmorillonite
			pH 3/6		
Alliot et al. (2005a,b)				**1–10**	α-alumina
Mesuere and Fish (1992)				**5–20 × 10^2**	Goethite
				pH ~ 8	

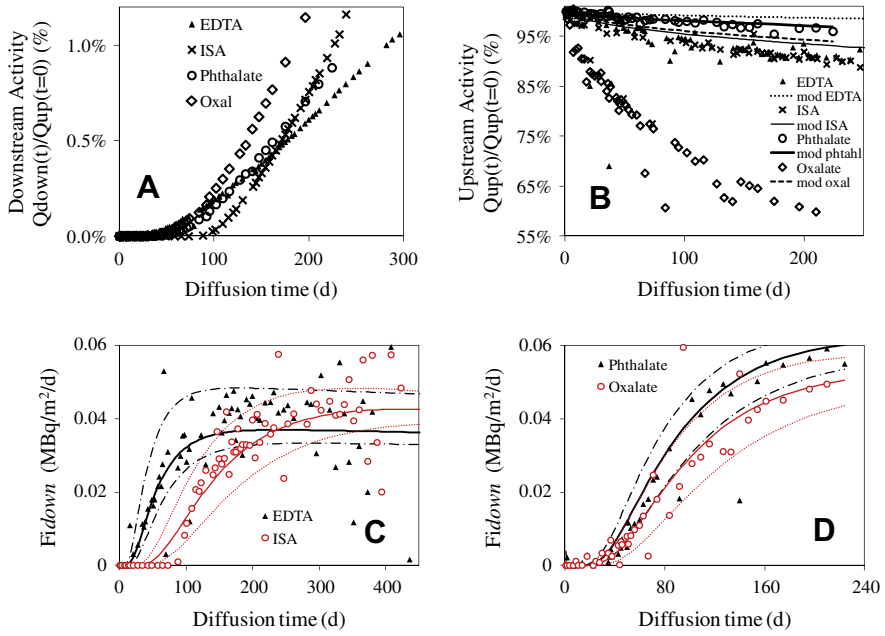

Fig. 3. (A and B) Cumulated radioactivities respectively in the downstream (Q_{down}) and upstream (Q_{up}) compartments of through-diffusion cells. Activities (Bq), were normalised by the initial activity in the upstream compartment Q_{up} ($t = 0$) in order to compare results from different cells. Curves in (B) represents modelled data, calculated with (D_e, α) values taken from downstream flux. (C and D) represent the incoming daily fluxes for ^{14}C-organics through the clayrock in diffusion cells. Solid curves represent best fit using equation and dotted curves represent adjustment used for the estimation of uncertainties.

Table 4
Diffusive parameters (D_e, α) of organic acids, EDTA, ISA, oxalate, phthalate, obtained by through-diffusion experiments. Values in bold refer to the best fit of experimental results. Values between brackets indicate variation in experimental results. The extrapolated K_d was calculated considering Eq. (4) with $\varepsilon = 0.08$, $\rho = 2.41$ kg L^{-1}. K_d values are compared to R_d values obtained from batch experiments.

	Through-diffusion			Batch
	D_e	α	K_d	R_d
Species	(10^{-12} m^2 s^{-1})	(–)	(L kg^{-1})	(L kg^{-1})
EDTA	**0.94** (0.85–1.23)	**0.27** (0.27–0.30)	**0.08**	**6.2** (5.1–7.0)
ISA	**2.8** (2.65–3.1)	**2.57** (2.25–3.10)	**1.03**	**30** (14–32)
Phthalate	**2.1** (1.7–2.3)	**0.63** (0.60–1.20)	**0.23**	**1.4** (1.2–2.0)
Oxalate	**3.37** (3.2–3.65)	**1.76** (1.50–2.10)	**0.61**	**8.4** (8.2–9.0)
(max.)[b]	(<5.24)	(<2.8)	(<1.11)	
Cl^-[a]	**4–9**	$0.05 < \alpha < 0.09$	$\ll 0.1$	
I^-[a]	**3–7**	$0.07 < \alpha < 0.18$	<0.06	$\ll 0.1$
SO_4^{2-}[a]	**1.9**	**0.307**	**0.15** $< K_d <$ **0.37**	**0** $< R_d <$ **0.57** ± 0.16
HTO[a]	24–50	0.16–0.25	$\ll 0.1$	

[a] Taken from (Bazerbachi et al., 2006, 2007; Descostes et al., 2008; Savoye et al., 2012).
[b] Overestimation of oxalate parameters using modified upstream activity. $Q_{up} = 0.28$ MBq instead of 0.4.

parameters (Table 4). This higher uncertainty in the case of oxalate does not affect the discussion in the last section.

4. Discussion

4.1. Interpretation of sorption data

A significant sorption of ligands was evidenced by both sorption (R_d) and diffusion (K_d) experiments. These values confirm the affinity of carboxylic acids for COx clayrock despite the electrostatic repulsion by the negative permanent charge of clayey minerals. The differences between R_d and K_d values are still unexplained and several hypotheses may be considered. Among them, the effect of compaction and the enhancement of sorption by creation of new surfaces in crushed rock were discussed by Miller and Wang (2012). The authors suggested that in the case of weak electrostatic interactions, the effective specific surface area is almost identical for crushed and intact rocks. However, this similarity remains unclear for species sorbed with stronger interactions. These interactions may alter the chemistry of clay particles and thus the structure and sorption sites available in compacted systems. Other mechanisms to mention are the incorporation of organics in the solid by dissolution/precipitation, the chemical reactivity with NOM, or the slow oxidation of the solid by air ingress during the long-term diffusion experiments.

Another important phenomenon that may partially explain such result is the sorption irreversibility or slow desorption of organics. Adsorption/desorption hysteresis were quantified for numerous organics on soil/sediment systems (Pignatello, 1999). For example sorption of aromatic compounds on sand rich sediment was studied by Kan et al. (1994) indicating that a substantial fraction of the pollutants is bound by strong chemical interactions and resists desorption. Nowara et al. (1997) discussed similar results on carboxylic acids sorbed on soils with various clay contents. They attributed this behaviour to the adsorption between the mineral layers by ionic interactions, especially with montmorillonite. A

mathematical resolution is discussed in (Crank, 1975) in the case of diffusion with various rates, λ and μ, for sorption and desorption respectively. If $\mu = 0$, the sorption, or chemical reaction, is irreversible and the solid acts as a sink for the solute. If $\mu \neq 0$, the flux of solute depends on the ratio $\mu a^2/D$ (where a is the diffusion length). The transport is then controlled either by the reversible reaction if $\mu a^2 \ll D$ or by the diffusion process if $D \ll \mu a^2$. In our case, at least two sorption/desorption mechanisms could occur simultaneously, with different rates $\mu_{irr.}$(slow or irreversible process) $\ll \mu_{rev.}$(fast and reversible process). The observed flux would then correspond to the fraction of solute that diffuses with a fast desorption compared to the time scale of the experiment ($t = 1$ year/$a = 1$ cm). Then, K_d measured by through-diffusion would be representative of the fast and reversible processes, and R_d measured by batch would represent all sorption processes ($R_d \gg K_d$), including fast, slow and non-reversible mechanisms. This assumption remains to demonstrate and experiments are currently being carried out to quantify the sorption kinetics and hysteresis. It is also crucial to determine if the sorption hysteresis corresponds to a slow desorption or an irreversible incorporation. Smith and Comans (1996) discussed similar issues in the case of ^{137}Cs remobilisation in sediments. They indeed observed an irreversible sorption of radiocaesium on short-time scale (several months) after a fallout event. However, this "fixed" caesium actually displayed a slow desorption rate and had to be considered explaining long-term environmental mobility of radiocaesium (years).

The macroscopic values obtained in this work may be used for assessing the environmental risk associated with the mobility of organics. Still, these results give no evidences at a microscopic scale. Several mechanisms may be mentioned to describe sorption of organics on mineral surfaces: ion exchange, cation bridging, ligand exchange, van der Waals bonding and hydrophobic effects. Ligand exchange involves the interaction between the carboxylic group and the hydroxyl groups of minerals. It is described as the dominant mechanism for the sorption of NOM on iron oxide (Gu et al., 1994) and for the sorption of carbonic, acetic and oxalic acid on α-alumina (Alliot et al., 2005b). Van der Waals interactions and ligand exchange were estimated to be responsible for 60% and 35% respectively of the adsorption of organic matter on montmorillonite by Arnarson and Keil (2000). Microscopic-scale characterisation of phthalate sorbed on hematite is given by Hwang et al. (2007), and of oxalate on goethite by Mesuere and Fish (1992). Mono and dicarboxylic acids were also studied on clayey minerals in (Kang and Xing, 2007; Kubicki et al., 1999) and evidences were obtained for both outer-sphere complexes (with weak electrostatic or van der Waals interactions) and inner-sphere complexes (with strong electrostatic or covalent bonds). The possibility of several mechanisms, leading to both strong and weak chemical bounds, would be consistent with the assumption of various rates of desorption. However, given the heterogeneity of clayrocks, further investigations are necessary to evaluate in the first place which phases are driving the sorption of organics on clay.

4.2. Diffusion in clay: anionic exclusion and size dependency

Effective diffusion coefficients for the organics are lower than that for HTO and close to values for anionic tracers such as halides (Table 4). No correlation was observed between the D_e for carboxylic acids and molecule charge or speciation. The lowest D_e value was measured for the highest molecular weight ($M_{Ca\text{-}EDTA} \sim 328$ g mol^{-1}) and the highest D_e value for the smallest molecule ($M_{Ca\text{-}Ox} \sim 112$ g mol^{-1}). This result leads us to consider the correlation between the size of the species and the diffusion parameters. Size effects in water can be described by a simplified interpretation of Stokes–Einstein law with spherical molecules, leading to Eq. (5)

$$D_0 = r^{-1}\frac{R \times T}{6\pi\eta \times N_a} = M^{-1/3}\frac{R \times T}{6\pi\eta \times N_a \times \left(\frac{3}{4\pi \times N_a \times \rho}\right)^{1/3}} \quad (5)$$

where D_0 is the diffusion coefficient in water (m^2 s^{-1}), R is the universal gas constant, T the temperature (K), η the viscosity of the medium, ρ (kg m^{-3}) the density of the molecule, Na the Avogadro constant (mol^{-1}), r (m) and M (kg mol^{-1}) the hydrated radius and molecular mass of the molecule. One can easily estimate the correlations between size and diffusion using equation $D_0 = f(r^{-1})$, or $D_0 = f(M^{-1/3})$ when the radii of hydrated species are not available.

The ratio: $D_0(A)/D_0(\mathrm{HTO})$ is useful to discuss the diffusion of solutes in water. The ratio: $\Pi = [D_e(A)/D_e(\mathrm{HTO})]/[D_0(A)/D_0(\mathrm{HTO})]$ isolates the effect of clay on the diffusion pathway (i.e. tortuosity and constrictivity as discussed by Van Brakel and Heertjes, 1974). Both ratios are represented in Fig. 4 as a function of r^{-1} or $M^{-1/3}$ and show two major trends.

Firstly a correlation appears between $D_0(A^-)/D_0(\mathrm{HTO})$ and $M^{-1/3}$ for anions. Additional data were added for organics and detailed in supplementary data. Larger/heavy anions display lower diffusion coefficients and small anions diffuse faster. This assumption is verified for many organic species in various solvents (Valencia and González, 2012). For large molecules such as organics, the total charge and the solvation will have less of an effect than the size of the diffusing species. This may explain why the number of negative charges per organic molecule appears to play a rather subordinate role on diffusivity. An exception to this size dependency is observed for halides, for which the strength of the hydration shell strongly affects the motion in water as discussed by (Zhou et al., 2002).

Secondly, the ratio Π is lower than 1, in the range [0.1–0.25] for both organic and inorganic anions. This result is indicative of the anionic exclusion discussed by (Descostes et al., 2008). No clear correlation between Π and $M^{-1/3}$ is evidenced given the uncertainties and the size effects do not appear to be linked to the clay structure. Results obtained by Melkior et al. (2007) for alkaline cations are given for comparison in (Fig. 4). Diffusion of cations in water is also correlated with hydrated radii. The high values of the ratio Π indicate an enhancement of the macroscopic flux of cations in COx clayrock due to surface mobility of the sorbed cation (Gimmi

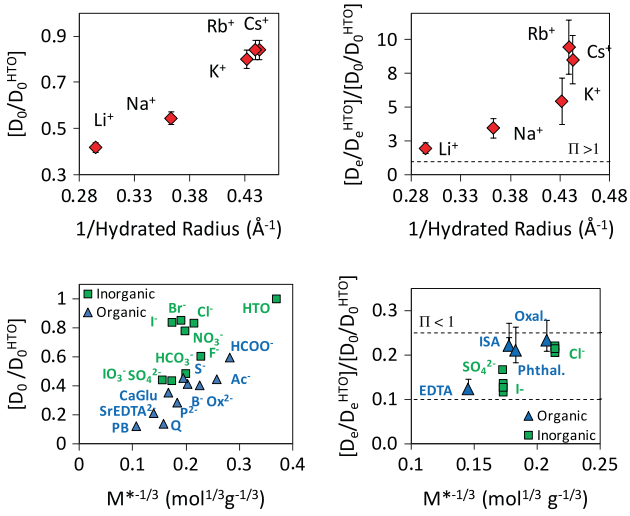

Fig. 4. Effect of molecular size and clayrock on ions diffusion. (Left) Diffusion of ions in water (D_0/D_0^{HTO}). (Right) Contribution of COx clayrock to the effective diffusion: $\Pi = [D_e/D_e^{HTO}]/[D_0/D_0^{HTO}]$. Results are taken from (Bazer-bachi et al., 2006, 2007; Descostes et al., 2008; Savoye et al., 2012) for inorganic anions and from (Melkior et al., 2007; Zheng and Zaoui, 2011) for alkaline cations. The hydration number of inorganic anions was taken into account to calculate molecular mass (M^*). Additional data added for organics are detailed in supplementary data.

and Kosakowski, 2011). Small cations display more interactions with clay minerals (higher K_d values) and are more sensitive to the cationic "acceleration", inducing a correlation between Π and r^{-1}. Since small values of Π are observed for organics and without correlation, it is likely that almost no surface diffusion occurs despite the significant macroscopic sorption.

5. Conclusion

The macroscopic transport parameters of four organics ligands, namely EDTA, ISA, phthalate and oxalate, were measured on COx clayrock. Distribution ratio between solid and liquid was estimated by both sorption in batch and through-diffusion experiments. The organic ligands displayed significant affinity for the COx clayrock. The values measured in batch experiments, R_d = 1-30 L kg^{-1}, are much higher than usually observed for inorganic anions. This result was confirmed by through-diffusion experiments, but the K_d values obtained by fitting diffusion modelling were significantly lower than those measured in the batch experiments. The diffusion of organic and inorganic anions is mostly driven by anionic exclusion and, to a lesser extent, by a size dependency. Size effects may be evaluated for organics from diffusion values in water (D_0) as a first approximation. Despite a significant sorption, the carboxylic acids display an anionic exclusion comparable to inorganic anions ($0.1 < \Pi < 0.25$). The mobility of organics is not enhanced by clayrock and "surface mobility" remains only evidenced for cations. The values obtained may be useful to estimate transport of small acids in natural environments such as sedimentary rocks.

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Appendix A. Organic synthesis and additional data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhydrol.2014.02.002.

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