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## Competitive adsorption of organic molecules on clay rock

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### Abstract

The processes governing adsorption of anthropogenic organic molecules on natural systems are complex. The presence of various phases in soils and mudstones may lead to various and simultaneous retention mechanisms. Adsorption experiments were performed on acetic, o-phthalic and citric acids on the Callovo-Oxfordian clay rock. Whereas the retention of inorganic species is dominated by clay minerals, small carboxylic acids were found to sorb on various phases or sites and not necessarily endured competition during co-adsorption. Data will be presented to illustrate the interest of various adsorption protocols to discriminate between mechanisms occurring beside adsorption onto soils and sediments: covalent bonding, chemical perturbation, phase dissolution, bacterial activity, etc..

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### 1. Introduction

The adsorption of chemicals and contaminants on mineral surfaces is an important process limiting their mobility in soils and sediments. It is then crucial to understand the underlying mechanisms for environmental issues, hazardous wastes management or decontamination processes. To this aim, competitive adsorption experiments are valuable tools for both understanding phenomenology of natural systems and designing industrial processes for wastes management. This study presents competitive adsorption of several carboxylic acids, performed in support of a larger study dedicated to adsorption on a clay rich sedimentary rock.

The chosen adsorbent was a sedimentary clay-rich rock, the Callovo-Oxfordian formation from the eastern Paris Basin) which is investigated by the French radioactive waste management agency (Andra). This material displays various phases (clay minerals, tectosilicates, carbonates, sulfurs, organic matter...), which makes adsorption mechanisms hard to predict with accuracy. Adsorption of inorganic ions is mostly dominated by ligand exchange

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and electrostatic interaction with clay minerals. Still adsorption may also occur on minor phases such as sulfurs, oxides and on organic matter by hydrophobic interaction and Van der Waals interactions.

The chosen adsorbates were small soluble carboxylic acids with various shapes and chemical functions. Since carboxylic acids are complexing agents, their species in solution might sorb simultaneously on clay minerals, oxides or even on hydrophobic domains depending on their speciation in solution and charge (anionic, cationic or uncharged).

We will present competitive adsorption experiments with three carboxylic acids, namely acetate, ortho-phthalate, and citrate, on Callovo-Oxfordian clay rock. The results helped to confirm or deny which chemical functions and solid phases are responsible for adsorption. Such an approach is useful for prediction of organic plume migration or confinement of hazardous wastes.

## 2. Materials and Methods

### 2.1. Sedimentary rock

The sedimentary rock comes from the Callovo-Oxfordian (COx) formation in the east of the Paris basin. Experiments were carried out on a clay-rich rock core (EST40471). It was collected from the borehole OHZ1705, argon-drilled downwards in the Meuse/Haute Marne Underground Research Laboratory, at a depth between 497.7 and 498.1 m below ground level. This sample is roughly composed of one third of clay minerals, one third of carbonates and one third of quartz. The composition of main minerals and minor phases is detailed in table 1.

Table 1. Composition of clay rock sample (EST40471 from borehole OHZ1705).

Composition of rock	Quantity (% mass)	Main minerals (% mass)
Clayey minerals	35 ± 5	Illite (~17 %) Interstratified illite-smectite (~17 %)
Carbonates	29 ± 2	Calcite (~25 %) Dolomite (~5 %)
Quartz	27 ± 5	Siderite and ferrous minerals (<2%)
Minor phases	< 5	Pyrite (<1%) Natural Organic Matter (< 1%)

Complementary petro-physical and chemical data of the COx rock can be found in literature<sup>1,2</sup>. Deep argillaceous rocks are reducing environments, so samples were protected from O<sub>2</sub> in sub-oxic glove box ([O<sub>2</sub>] < 2 ppm). The rock was ground to fine powder (< 63 µm) and equilibrated with a synthetic porewater (solid/liquid ratio, S/L = 0.25 kg L<sup>-1</sup>). This synthetic porewater was previously prepared by dissolution of salts with major ions (Na, K, Ca, Mg, SO<sub>4</sub>, Cl, HCO<sub>3</sub>). Composition of synthetic porewater was detailed in previous articles<sup>3,4</sup>. It was then mixed with clay powder (S/L ~ 0.05 kg L<sup>-1</sup>) for equilibration with trace elements (Fe, Al, Si, Mn). pH of synthetic porewater (~7.1 ± 0.2) was adjusted by bubbling gaseous nitrogen with CO<sub>2</sub> during 30 min (pCO<sub>2</sub> ~ 10<sup>-1.9</sup> atm).

### 2.2. Chemicals and radiotracers

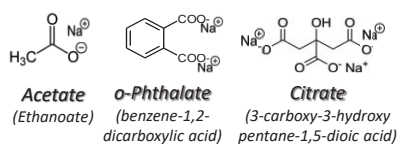


Fig. 1. Molecular structure of the carboxylic acids used in this study.

Three carboxylate ions were used as adsorbates in this study with different properties (Figure 1). Acetate is a small aliphatic acid, ortho-phthalate an aromatic dicarboxylate and citrate a multidentate hydroxy-carboxylate. Stable chemicals were prepared from high purity salts: sodium acetate (Merck, purity > 99%), phthalic acid (Merck, purity > 99.5%) and citric acid (Merck, purity > 99.7%). Adsorption experiments were performed with radiolabelled compounds to improve sensitivity and selectivity towards natural organic matter. Radiolabelled compounds were purchased from ARC: acetic acid [<sup>3</sup>H] sodium salt (ART 0202, 150 mCi/mmol), citric acid [<sup>14</sup>C] (MC-365, 112

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