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Water and ions in clays: Unraveling the interlayer/micropore exchange using molecular dynamics

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Abstract

We present the first microscopic description of the exchange of water and ions between clay interlayers and microporosity. A force field based on ab-initio calculations is developed and used in classical molecular dynamics simulations. The latter allow to compute the potential of mean force for the interlayer/micropore exchange for water, Na^+ and Cs^+ cations and Cl^- anions. For the simulated water content (water bilayer, with interlayer spacing 15.4 Å) and salt concentration in the micropore (0.52 mol dm^{-3}) the exchange is found to be almost not activated for water and cations, whereas the entrance of an anion into the interlayer is strongly unfavorable ($\Delta\mathcal{F} \sim 9k_BT$). Calculations of the diffusion tensor in the interlayer and in the micropore complete the study of the exchange dynamics.

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1. INTRODUCTION

Clays consist of negatively charged lamellae, compensated by (solvated) cations which can move in the interlayer spacings originating from the stacking of the mineral layers. These stacks form particles, which also aggregate to form larger structures with a corresponding porosity. Elucidating the transport mechanisms of water and ions through clays is particularly important, since clays are considered as suitable materials for the geological storage of toxic and radioactive waste (Bradbury and Baeyens, 2003; Dossier, 2005). The transport of a tracer through a clay sample is averaged over the whole porosity: interlayer, micropores (less than 2–3 nm), macropores ($\geqslant$100 nm) (Bourg et al., 2006). However a simple average assumes that the tracer can exchange easily between all types of porosities. To interpret the variations of the effective diffusion coefficient D_e with the tracer's charge, it is often argued that the porosity accessible to each species depends on its charge and size (Kato et al., 1995; Dossier, 2005). Due to the negative charge of clay layers, anions should be repelled by the external surfaces, and excluded from the interlayers. On the contrary, cations are attracted by the surfaces, and may exchange with the natural interlayer counterions. Ions can also be trapped on clay edge sites. Experimental evidence of anionic exclusion and cation exchange are generally indirect: inferred from macroscopic tracer diffusion, or batch measurement of selectivity constants (for exchange) (Kato et al., 1995; Bradbury and Baeyens, 2003; Dossier, 2005).

Molecular simulations have provided microscopic interpretations of experimental data, related to structural (Skipper et al., 1989, 1995a,b; Delville, 1992, 1993; Chang et al., 1995, 1997, 1998; Smith, 1998; Sposito et al., 1999; Park and Sposito, 2000; Ferrage et al., 2005a), thermodynamical (Boek et al., 1995a,b; de Siqueira et al., 1997; Shroll and Smith, 1999; Young and Smith, 2000; Hensen et al., 2001; Hensen and Smit, 2002; Whitley and Smith, 2004; Tambach

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et al., 2004a,b, 2006; Smith et al., 2006; Liu and Lu, 2006) and dynamical (Sutton and Sposito, 2001; Titiloye and Skipper, 2001; Marry et al., 2002; Marry and Turq, 2003; Malikova et al., 2004a,b, 2005, 2006) properties of clay interlayers. The microscopic structure of the water/mineral interface (Wang et al., 2004, 2005, 2006; Kirkpatrick et al., 2005), and adsorption onto clay basal surface (Greathouse and Cygan, 2005, 2006) were also investigated. In a recent paper, Teppen et al. have used microscopic simulations to gain insight into the mechanism of ionic exchange (Teppen and Miller, 2006). They demonstrated that the thermodynamic driving force of K^+ to Cs^+ exchange in montmorillonite is not related to any "selection" of Cs^+ by the interlayer but rather dominated by the free energy change in the aqueous phase. The ionic exchange reaction between a natural counterion (e.g., Na^+) and an ion in solution (possibly a radioactive ion, e.g., $^{137}Cs^+$), can be summarized as:

$$Cs^+_{aq} + Clay - Na^+ \rightarrow Na^+_{aq} + Clay - Cs^+ \qquad (1)$$

From a thermodynamical point of view, the study of ionic exchange requires only to consider the initial and final states. However, nothing can be learned on the ionic exchange *process* and its kinetics without considering explicitly the transition zone between the two states (interlayer and external porosity), which occurs at the clay edges. Indeed, an ion or a water molecule leaving the interlayer (where it diffuses in two dimensions along the clay sheets) for the micropore (where it diffuses in 3D) will experience the effect of the interface (close to the edges), and will cross it with a certain probability. This situation is depicted in Fig. 1. The overall Na^+ to Cs^+ ionic exchange is thus a twofold process: (1) Na^+ release into the micropore and (2) Cs^+ entrance into the interlayer. Both processes may or may not occur simultaneously, and might be later coupled to a change in interlayer water content, as the Cs/Na ratio evolves. Indeed, hydrated homoionic Cs-montmorillonite only exists in the monohydrated state, whereas Na-montmorillonite also exists in the bihydrated (even trihydrated) state. The purpose of the present study is to give microscopic insights into the ionic exchange and the anion exclusion processes, using molecular dynamics (MD) simulations. We will consider the interlayer/micropore exchange of each species separately, and focus on the early stages of the overall exchange (when the Cs/Na ratio is small, which is the relevant situation for radioactive contaminant transport), so that the interlayer water content corresponds to that of a Na-montmorillonite.

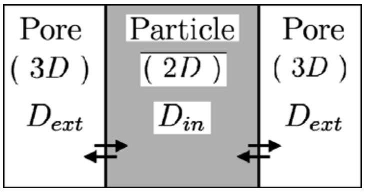

Fig. 1. Conceptual model for the dynamics of exchange between interlayer and micropore. Diffusion is in 2D in the interlayer, and 3D in the pore. A diffusing particle reaching the interface will cross it with a probability controlled by the free energy profile along the interface (see text). The arrows represent the interface crossing reactions.

Clarifying the transition between micropore and interlayer is very important to understand the respective contributions of each type of porosity to the overall water and ionic transport. Since no direct experimental data is available on this process on the microscopic scale, microscopic simulations are a reasonable alternative to study it. Such a study remains however a challenge, because it requires to include explicitly in the same simulation box both a clay particle (including interlayers and counterions) and a micropore (containing a bulk electrolyte solution), and a sound description of the particle edges must be adopted.

Clay edges have first been investigated using ab-initio simulations, with the focus on structure and acidity of edges sites (Bickmore et al., 2003; Churakov, 2006). Indeed, the interpretation of titration curves generally relies on a large number of fitting parameters (Tournassat et al., 2004), partially supported by semi-empirical approches like MUSIC (Hiemstra et al., 1996). Prediction of acidity constants from first principles aims at supporting the interpretation of these data, which are of great practical importance since they influence dramatically the retention of ions by clays. Such studies have been initiated on short pyrophyllite fragments in vacuum, and allowed to make some predictions on the relative acidity of edge sites (Churakov, 2006). More recently, the study of a confined water film on clay edges allowed to observe the proton exchange between acidic edge sites and water adsorbed on the surface (Churakov, 2007). The system required to study the interlayer/micropore exchange is at present completely out of reach of ab-initio simulations, for two reasons: the size of the system is too large (it involves too many atoms, see below), and the relevant timescale is too long (several nanoseconds). Therefore a simpler description should be adopted. To that end, we first developed a classical force field to describe the edges, based on density functional theory (DFT) calculations on a smaller system. This force field was then used to simulate a larger system containing both interlayer and microporosity, for long times (several nanoseconds).

The microscopic description of the system is not the only challenge. Indeed, the relevant framework to study the exchange kinetics needs to be carefully defined. The standard approach to describe a transition between two states is to evaluate the free energy profile along a reaction coordinate which characterizes the evolution of the process. For a chemical reaction a typical situation is the one illustrated in Fig. 2: it will occur if the system overcomes a free energy barrier $\Delta\mathscr{F}^{\#}_{1\rightarrow2}$; the reverse reaction needs to overcome $\Delta\mathscr{F}^{\#}_{2\rightarrow1}$, and the overall free energy change is $\Delta\mathscr{F}_{1\rightarrow2} = \Delta\mathscr{F}^{\#}_{1\rightarrow2} - \Delta\mathscr{F}^{\#}_{2\rightarrow1}$. When considering the transition between interlayer and micropore, several questions arise. (1) What is the relevant reaction coordinate to describe the exchange, and what is the shape of the free energy profile, depending on the considered molecule/ion? In particular, the presence of activation barriers ($\Delta\mathscr{F}^{\#}_{1\rightarrow2}$ or $\Delta\mathscr{F}^{\#}_{2\rightarrow1}$) is not *a priori* obvious. (2) How to describe the dynamics along this free energy profile? This implies the determination of the diffusion coefficient in different regions of the system (interlayer and micropore). We will show that