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On the driving force of cation exchange in clays : Insights from combined microcalorimetry experiments and molecular simulation

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Abstract

We study the origin of the ionic exchange enthalpy in montmorillonite clays using microcalorimetry measurements and molecular simulation. We first determine the standard reaction enthalpy for well-defined interlayer water contents. We then show by a detailed analysis based on thermodynamic cycles that replacing Na^+ ions by Cs^+ in the interlayer of montmorillonite clays is an endothermic process, and that the overall exchange is exothermic only because it is dominated by the exothermic replacement of Cs^+ by Na^+ in the aqueous phase. This conclusion from ionic exchange enthalpies supports the one of a recent study of the ionic exchange free energy by Teppen and Miller [*Soil. Sci. Soc. Am. J.*, **70**, 31 (2006)] and contradicts long-held views on the role of ion-clay interactions in determining the ionic exchange thermodynamics. This calls for a paradigm shift for the origin of this exchange: The driving force is the "hydrophobicity" of Cs^+ compared to Na^+ and not its affinity for clay surfaces.

PACS numbers:

Keywords: clay, ionic exchange, thermodynamics, molecular simulation, microcalorimetry

1. INTRODUCTION

Clays are layered aluminosilicate minerals found in large amount in the Earth's upper crust and are involved in many industrial and environmental processes. In particular, their retention properties have made clayey materials possible candidates to act as barriers for the disposal of toxic and radioactive waste. In smectite clays such as montmorillonite, the layers bear a permanent negative charge compensated by counterions located between them (inter-layer space). These counterions are the origin of two interesting features : clay swelling and ionic exchange. The former refers to the entrance of water into the interlayer, while the later involves the replacement of natural counterions like Na^+ in the clay interlayer by other ions initially in the aqueous solution in contact with the mineral, and the concomitant release of Na^+ in the solution [1–8]. The swelling properties of clays have been studied extensively, both experimentally [9–16] and theoretically [17–27] and are now relatively well understood. In the context of the geological disposal of nuclear waste, it is particularly important to understand the retention of radioactive traces by the geological medium. Although several mechanisms are at play for the retention of ions by clays [28–30], ionic exchange is predominant for some of them, in particular Cs^+ , a long-lived radioisotope of which ($^{137}\text{Cs}^+$) is expected to be one of the main contributors to the long term radioactivity [31]. In order to predict how cationic radioactive species are retained by clays, it is therefore important to have a good understanding of the thermodynamic properties of ionic exchange, i.e. the associated free energy, which controls the thermodynamic constant of the reaction, and enthalpy, which controls its variations with temperature via the van't Hoff equation. This is particularly important in the context of geological disposal of nuclear waste, since the radioactive parcels will heat the surrounding medium.

Several measurements of the equilibrium constants for ionic exchange in clay minerals, particularly in those of the montmorillonite type, have been reported [3–8], but the enthalpies of exchange were much less frequently determined [1, 2, 6, 7, 32]. One difficulty for rigorously defining thermodynamic quantities of reaction in the case of ionic exchange is that the water content in the interlayer may vary between the initial and final states. This is one of the reasons why the exchange enthalpy and free energy depend on the degree of exchange α . It is therefore important to distinguish the exchange of traces ($\alpha \rightarrow 0$ for traces of Cs^+ in a Na-clay) from the complete exchange ($\alpha \rightarrow 1$ for the exchange from homoionic Na-clay

to homoionic Cs-clay) [32]. Furthermore, the ionic selectivity, from which ionic exchange free energies are computed, is measured for clay suspensions. In many practical situations, however, clays constitute a solid phase (with a fixed, low water content) and the ions (e.g. traces of radioactive ions in the underground) are dissolved in the aqueous phase in contact with this solid. One thus needs to consider the water content in the clay phase when discussing the thermodynamics of ionic exchange.

According to the current paradigm for ionic exchange in clays, specific interactions between the ions and the clay surface, or the hydration properties of ions in the clay interlayer, are the driving force for the ionic exchange. The origin of clay selectivity for alkaline ions according to the series $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ has been explained by a number of arguments : the size of hydrated cations, compared to the interlayer spacing [33–35], their ability to lose a water molecule at the clay surface, thus forming a stronger inner-sphere complex [6, 36], their hydration state in the interlayer [37] or their polarizability that influences the formation of surface complexes [35, 38, 39]. These microscopic features are then thought to weight in favour of the interactions of clay interlayers with larger alkaline cations. However, considering only the clay phase to infer properties of the ionic exchange can lead to erroneous conclusions. This fact was emphasized by Teppen and Miller, who analysed the free energy of ionic exchange of small alkaline ions for larger ones, using molecular simulation supported by the analysis of experimental data from the literature [40]. They showed that the contribution of the clay phase to the ionic exchange free energy is in fact very unfavourable ($\Delta G \gg 0$) and that it is the hydration free energy difference, i.e. the contribution of the water phase, that leads to an overall exchange of small alkaline ions for larger ones (e.g. Na^+ for Cs^+).

In the present paper, we investigate (a) the influence of the interlayer water content on the exchange enthalpy and (b) the origin of this enthalpy. Both issues are addressed by considering thermodynamic cycles involving exchange enthalpies in solution, immersion enthalpies of clays, and hydration enthalpies of cations. This strategy is particularly efficient to investigate the ionic exchange process, because all these quantities are directly measurable by microcalorimetry experiments. It should be noted that, contrary to immersion enthalpies, immersion free energies are not measurable directly, which means that a similar analysis of the exchange free energy for well-defined interlayer water contents would be difficult, if possible at all. We analyse the contribution of the clay phase (at well defined interlayer

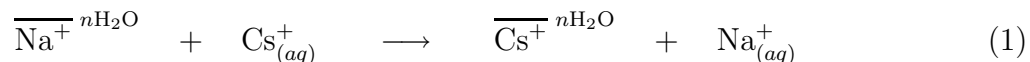
water contents) and that of the aqueous solution to the ionic exchange enthalpy. We support our experimental study by directly computing by molecular simulation the contribution of the clay phase to the exchange enthalpy. From this combined experimental and theoretical analysis we demonstrate that replacing Na^+ ions by Cs^+ in the interlayer of montmorillonite clays is an endothermic process, and that the overall exchange is exothermic only because it is dominated by the exothermic replacement of Cs^+ by Na^+ in the aqueous phase.

The paper is organized as follows. We first introduce the thermodynamic quantities associated with the ionic exchange and the thermodynamic cycles allowing us (a) to determine well-defined standard reaction enthalpies and (b) to characterize the relative contribution of the clay and aqueous phase to the overall exchange thermodynamics. We subsequently describe the experimental systems and methods, and present the results of microcalorimetry measurements. Then the molecular simulation systems and methods are presented. After validating their choice by studying the free energy associated with the exchange of traces, we present the simulation results on the complete exchange enthalpy. Finally, we discuss the experimental and simulation results and demonstrate how their combination supports our conclusions.

2. IONIC EXCHANGE THERMODYNAMICS

2.1. Ionic exchange reaction

The reaction of ionic exchange between clays at a given water content and ions in a dilute aqueous solution can be written as:



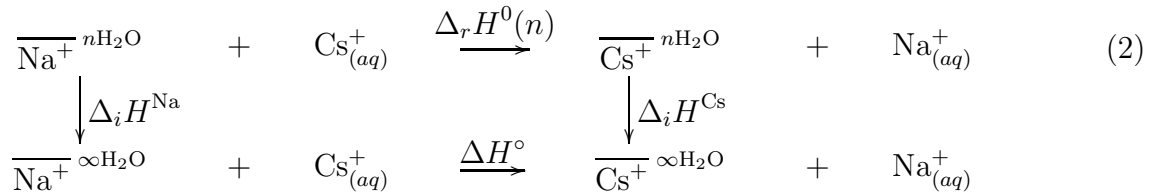
As the reaction proceeds, the degree of exchange α varies from 0 (exchange of traces of Cs^+ in a Na-clay) to 1 (complete exchange from homoionic Na-clay to homoionic Cs-clay). In order to define reaction quantities, it is necessary to carefully define the initial and final reference states and ensure that mass (including water) is conserved during the reaction. The standard reaction enthalpy, for the complete exchange from MNa to MCs with the same water content (n water molecules per cations), is $\Delta_r H^0(n)$. Table I summarizes the different thermodynamic quantities and the notations used in this paper. All previous experimental studies of the thermodynamics of ionic exchange were conducted on clays dispersed in water,

i.e. in equilibrium with an aqueous phase, but in which the interlayer water content is unknown and might even differ between the initial and final states. Here we study $\Delta_r H^0(n)$ (a) by combining thermodynamic data on ionic exchange for clays dispersed in solution and on immersion of clays with a known water content, as measured by microcalorimetry, and (b) by computing directly enthalpy differences using molecular simulation.

2.2. Thermodynamic states and water content

In order to define reaction quantities, it is necessary that the number of water molecules remains constant. Experimentally, however, the clay water content depends both on the nature of the counterion and on the water chemical potential. Well-defined water contents can be obtained by equilibrating dry clay powders with atmospheres of controlled relative humidity [9, 10]. It is well known that only a few hydration states are thermodynamically stable : they correspond approximately to 6-7 H₂O per cation (monolayer), both for MNa- and MCs, and 12-14 H₂O per cation (bilayer), only for MNa. Intermediate water contents correspond to mixtures of mono- and bilayers. For very low relative humidities, a lower water content can be obtained, down to 1.4 H₂O per cation for MNa, and 1.0 H₂O per cation for MCs.

Moreover, the exchange enthalpy can be measured directly only in the case of a clay suspension, i.e. in equilibrium with an aqueous solution, symbolized by the $\infty\text{H}_2\text{O}$ superscript in the cycle below. In that case, the water content inside the clay phase is unknown and the measured ΔH° , expressed per mole of cation, is not a reaction quantity because the water content might be different for MNa and MCs. In order to obtain experimentally the reaction enthalpy $\Delta_r H^0(n)$ corresponding to n H₂O per cation, we introduce the following thermodynamic cycle:



where $\Delta_i H$ is the enthalpy released upon immersion of a clay with a known water content into liquid water. We measure this immersion enthalpy by microcalorimetry as a function of counterion and water content, and combine it with ΔH° for the exchange in solution to

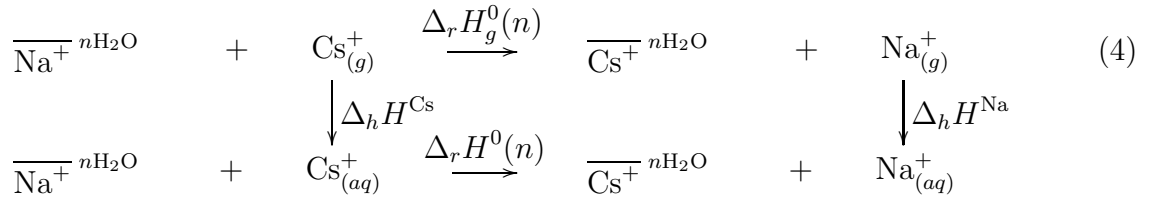
obtain the ionic exchange enthalpy for well-defined water content as:

$$\Delta_r H^0(n) = \Delta H^\circ - \Delta\Delta_i H \quad (3)$$

where $\Delta\Delta_i H = \Delta_i H^{\text{Cs}} - \Delta_i H^{\text{Na}}$. We will explain in section 3 how we determine experimentally the immersion enthalpies for clays with n water molecule per cations.

2.3. Origin of the ionic exchange enthalpy

According to the current paradigm for ionic exchange in clays, specific interactions between the ions and the clay surface or/and the hydration properties of ions in the clay interlayer are the driving force for the ionic exchange. Only a single analysis of the ionic exchange free energy by Teppen and Miller [40] emphasized the importance of also considering the contribution of the aqueous phase. There are indeed two contributions to the standard reaction enthalpy: on the one hand the ion-clay and ion-water interactions in the clay phase, on the other hand the ion-water interactions in the aqueous phase. This can be understood in terms of the following thermodynamic cycle, in which we introduce the exchange reaction with ions in the gas phase, where there are no interactions, used as a reference state.



This thermodynamic cycle involves the hydration enthalpy of both cations $\Delta_h H^{\text{Na}}$ and $\Delta_h H^{\text{Cs}}$, the standard ionic exchange reaction with the gas phase $\Delta_r H_g^0(n)$ and that with the aqueous phase $\Delta_r H^0(n)$. From this cycle we deduce the relation :

$$\Delta_r H_g^0(n) = \Delta_r H^0(n) + \Delta\Delta_h H \quad (5)$$

where $\Delta\Delta_h H = \Delta_h H^{\text{Cs}} - \Delta_h H^{\text{Na}}$. After determining $\Delta_r H^0(n)$ by microcalorimetry (see section 3), we will be in a position to estimate the clay contribution $\Delta_r H_g^0(n)$ to the enthalpy for the exchange of ions between clays of fixed water content, and thus to investigate this quantity for well-defined reference states. In parallel to this indirect experimental determination we will also compute directly $\Delta_r H_g^0(n)$ using molecular simulation (see section 4).

Notation	Definition
H, F, G	Enthalpy, Helmholtz free energy, Gibbs free energy
$\Delta_h X$	Hydration quantity ($X = H, F, G$) for the introduction of a gas into liquid water
$\Delta_i X$	Immersion quantity for the introduction of a solid phase into liquid water
$\Delta_r X^\circ$	Standard reaction quantity
ΔX°	Exchange quantity for clay dispersed in solution, per mole of cation
$\Delta_r X^\circ(n)$	Standard reaction quantity for the exchange of ions between clay with n H ₂ O and the aqueous phase
$\Delta_r X_g^\circ(n)$	Standard reaction quantity for the exchange of ions between clay with n H ₂ O and the gas phase

TABLE I: Notations used for thermodynamic quantities.

3. MICROCALORIMETRY EXPERIMENTS

3.1. Materials

Homoionic Na- and Cs-montmorillonite clays (MNa and MCs, respectively) were prepared from ANDRA's reference Wyoming bentonite (MX80). The bentonite was first purified : after removal of impurities (quartz, feldspars, etc.) by sedimentation of a suspension in deionized water, the clay solution was centrifuged several times and the upper part containing particles $< 2\mu\text{m}$ was collected. Then homoionic MNa was obtained by ion-exchange : the clay was suspended in 1 M aqueous NaCl and dialyzed to remove the excess salt. Conductivity measurements were used to check the presence or absence of salt in the dialyte. This ion-exchange procedure was repeated twice. The absence of Cl^- ions in the dialyte was confirmed by the AgNO_3 test. The homoionic Cs-montmorillonite was obtained from the Na-montmorillonite following the same procedure with 1 M aqueous CsCl. The purified clays were then dried under vacuum at 100°C , and placed in a silicagel desiccator where their mass remained constant. Their purity was checked by X-ray diffraction. Dried samples were then placed in a desiccator containing saturated saline solutions, which control the relative humidity (RH). With saturated solutions of K_2CO_3 and KCl, the relative humidity is of 43% and 85%, respectively. The mass of the samples is stabilized within a few days.

3.2. Microcalorimetric measurements

Immersion enthalpies of MNa and MCs at different relative humidities have been measured at 298 K using the Microsolution 2265 unit of the isothermal microcalorimeter TAM 2277 (Thermometric - TA Instruments). Samples of 5 to 25 mg are placed in three microcartridges which fit tightly in the measurement cell. The immersion process is started by the successive fall of the cartridges into 15 mL of water placed in a 20 mL vessel stirred by a propeller at 60 rpm. Figure 1 illustrates the typical shape of the resulting thermogram. The return to baseline after immersion of a clay sample takes a time reflecting the time constant of the microcalorimeter, of the order of 10 minutes, which is longer than the hydration process itself. Immersion enthalpies (in mJ/mg) are computed by integrating the thermogram peaks using the Digitam software (Thermometric). They are given in kJ/mol of cation in table II. Three to six immersions were carried out for each montmorillonite sample, with given counterion and hydration state. The reproducibility of the measurements is very good for RH=43% and 85%, however there is more variability for the samples prepared at RH=0%. This is due to the fact that the immersion enthalpy varies significantly with the water content when the latter is small [9, 10], and that the water content of the driest samples can increase during the preparation of the microcalorimetry experiment.

HR (%)	$\Delta_i H^{\text{Na}}$ (kJ.mol ⁻¹)	$\Delta_i H^{\text{Cs}}$ (kJ.mol ⁻¹)
0	-37±4	-21±4
43	-25±1	-5±1
85	-8±1	-4±1

TABLE II: Experimental immersion enthalpies for Na- and Cs-montmorillonite, as a function of the relative humidity (RH). Results are given per mole of cation.

Exchange enthalpies for clays dispersed in water at 298 K were obtained as explained in ref. [32]. The exchange enthalpy depends on the degree of exchange α , with values ranging from -15 ± 0.5 kJ/mol of cation for $\alpha \rightarrow 0$ (which corresponds to traces of Cs⁺ in a MNa) to -4.1 ± 0.2 kJ/mol for $\alpha \rightarrow 1$. The standard reaction enthalpy is obtained by integrating these values between $\alpha = 0$ and 1, with the result $\Delta H^0 = -7.5 \pm 1.0$ kJ/mol. The standard state corresponds to clay in solution at infinite dilution, where the interlayer is in equilibrium

with the solution has an unknown water content.

3.3. Immersion enthalpy as a function of water content

We have shown using the thermodynamic cycle (2) how the exchange enthalpy $\Delta_r H^0(n)$ can be deduced from the exchange enthalpy in solution ΔH° and the immersion enthalpies $\Delta_i H^{\text{Na}}$ and $\Delta_i H^{\text{Cs}}$ via Eq. 3. These immersion enthalpies must be determined as a function of the water content n . As mentioned in section 2, the experimental hydration states correspond to clays in equilibrium with vapor at a given relative humidity. Only a few hydration states are thermodynamically stable and most conditions correspond to mixtures of these states. Table III reports the proportion of each state as a function of the relative humidity, as estimated by Bérend *et al.* for Na- and Cs-Wyoming montmorillonite (Clay Spur 26 from Ward’s Natural Science) [10].

RH (%)	Na			Cs		
	dry (%)	mono (%)	bi (%)	dry (%)	mono (%)	bi (%)
0	100	0	0	100	0	0
43	50	50	0	40	60	0
85	0	20	80	20	80	0

TABLE III: Proportion of hydration states: dry (1-2 water molecules per cation), monolayer (6-7) and bilayer (12-14) as a function of the relative humidity (RH) of the atmosphere in equilibrium with the clay. These values are estimations from Bérend *et al.* [10].

Although obtained for samples of a different montmorillonite, prepared under slightly different conditions, these results can be used together with table II to estimate the value of the immersion enthalpy $\Delta_i H(n)$ for $n = 1$ and 6. The values for RH=0% correspond to the values for $n = 1$, thus $\Delta_i H^{\text{Na}}(n = 1) = -37 \pm 4$ kJ/mol and $\Delta_i H^{\text{Cs}}(n = 1) = -21 \pm 4$ kJ/mol. Then we can deduce the values for $n = 6$ (monolayer), since we have $\Delta_i H^{\text{Na}}(\text{RH} = 43\%) = 0.5\Delta_i H^{\text{Na}}(n = 1) + 0.5\Delta_i H^{\text{Na}}(n = 6)$. This yields $\Delta_i H^{\text{Na}}(n = 6) = -13 \pm 6$ kJ/mol, and a similar calculation gives $\Delta_i H^{\text{Cs}}(n = 6) = +6 \pm 4$ kJ/mol. Note that the main contribution to the uncertainty comes from the estimation of the water content, and not

from the microcalorimetric measurements of immersion enthalpies. The positive sign for the immersion of MCs in the monohydrated state is consistent with the fact that MCs does not swell. This also holds for K-montmorillonite and a positive sign was found in that case by molecular simulation results [23].

3.4. Complete exchange enthalpy

From the immersion enthalpies for $n = 1$ and 6 , which are stable states for both counterions, and the exchange enthalpy in solution ΔH° we now obtain the standard reaction enthalpy using Eq. (3). This yields $\Delta_r H^0(1) = -7.5 - [-21 + 37] = -23.5 \pm 9$ kJ/mol and $\Delta_r H^0(6) = -7.5 - [6 - (-13)] = -26.5 \pm 11$ kJ/mol. The main contribution to the uncertainty comes again from the estimate of the water content for a given relative humidity, and not from the measurements of enthalpies by microcalorimetry. We repeated the same analysis using the experimental immersion enthalpies of Bérend *et al.* [9]. In that case Eq. (3) yields -39.5 ± 7 kJ/mol for $n = 1$, and -16.5 ± 15 kJ/mol for $n = 6$. Despite the relatively large uncertainties, both sets of data lead to consistent results : They clearly indicate that the ionic exchange is exothermic. Note that the ionic exchange enthalpy for $n = 1$ and 6 are more negative than the value obtained in solution ($\Delta H^\circ = -7.5$ kJ/mol of cation). This underlines the need to consider carefully the water content in clays when analysing thermodynamic quantities.

4. MOLECULAR SIMULATION

Molecular simulation allows to compute the energy and enthalpy of a system from the interactions between the atoms, and thus gives access to differences in thermodynamic quantities that are not easily accessible by direct measurement. For example, the reaction energy $\Delta_r U_g^0(n)$ of the ion-exchange reaction between a) the clay at a well-defined water content of n water molecules per cations, and b) ions in the gas phase (which can be used as a reference state for the ions) is obtained by subtracting the energy of the MNa system to that of the MCs system (there are no interactions for isolated ions in the gas phase). Similarly, the hydration enthalpy difference $\Delta\Delta_h H$ for Na^+ and Cs^+ is obtained by computing the enthalpy of the ions in water (again, there is no contribution of the gas phase). Ionic exchange free

energies can also be computed using the thermodynamic integration method [41, 42], as will be explained in section 4.4.2.

4.1. System

The simulated clay system has the idealized composition $\text{Si}_8 (\text{Al}_{3.25} \text{Mg}_{0.75}) \text{O}_{20} (\text{OH})_4 \text{X}_{0.75}$ with X the counterion Na^+ or Cs^+ . Although no experiments for K^+ montmorillonite were undertaken in the present study, we also performed molecular simulations for this counterion. The simulation box of lateral dimensions $20.72 \times 17.94 \text{ \AA}^2$ contains two clay layers, both with 4×2 unit cells and a thickness of 6.54 \AA (distance between surface oxygen atoms from the same layer). Their atomic structure was taken from X-ray diffraction measurements [43]. The interlayer space contains the counterions and n water molecules per cation. Periodic boundary conditions in all directions are used so that the simulation box corresponds to infinite clay layers (no edges). A snapshot of the simulation box is represented in Fig. 2.

Interactions between atoms are modelled using pairwise potentials :

$$\mathcal{V}_{ij} = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} + 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (6)$$

with q_i the (partial) charge of atom i , and the pair Lennard-Jones (LJ) parameters ϵ_{ij} and σ_{ij} are calculated from the individual ϵ_{ii} and σ_{ii} using Lorentz-Berthelot mixing rules. \mathcal{V}_{ij} contains an electrostatic (Coulomb) term, and a 6-12 Lennard-Jones term. This force field is completely determined by the atomic parameters $\{q_i, \epsilon_{ii}, \sigma_{ii}\}$. Water molecules were described using the rigid SPC/E model [44]. The ions LJ parameters are taken from Åqvist [45]. They were developed to reproduce the experimental hydration energy when used in combination with the SPC water model (SPC/E is an extension of this model). The clay layers are treated as rigid bodies. The partial charges and LJ parameters for clay atoms are the one from Smith [46]. In this force field the LJ parameters for surface oxygen atoms are identical to that of SPC/E water oxygens. All partial charges and individual Lennard-Jones parameters are summarized in Electronic Annex 1. Long-range electrostatic interactions were computed using Ewald summation, and a cut-off of 8 \AA was used for the short-range LJ interactions.

4.2. Methods

We performed Monte-Carlo simulations in the NPT ensemble, i.e. at fixed number of particles, pressure $P = 1$ bar, and temperature $T = 298$ K. Thermodynamic quantities such as energy and enthalpy were computed by averaging their mechanical expressions $U = \sum_{i<j} \mathcal{V}_{ij}$ and $H = U + PV$ over microscopic configurations sampled from the NPT ensemble. For the clay systems we did not allow the rotation of the layers relative to each other, but only translational moves in the direction perpendicular to the surfaces, and in both directions along the surfaces. Only the pressure in the direction perpendicular to the clay surfaces is imposed (NP_zT ensemble). This is necessary to preserve the symmetry of the clay particle. We performed simulations for both Na^+ and Cs^+ counterions, and water contents of 1 (dry state), 6 (monolayer) and 12 (bilayer) water molecules per cations. Ions and solvent molecules are inserted randomly in the interlayers, and the system is first equilibrated at 1000 K for 10^5 steps. The temperature is then gradually decreased to 298 K. After 10^7 equilibration steps at this temperature, sampling of the energy and enthalpy is achieved for $5 \cdot 10^7$ to 10^8 steps. For the lowest hydration states, simulated annealings (i.e. repeating the above procedure via high temperatures) are used to ensure that the simulation correctly samples the whole phase space. The equilibrium interlayer distances obtained by NP_zT simulation are $\approx 10.8, 12.3,$ and 15.3 \AA for Na^+ with $n = 1, 6$ and 12 , respectively, and 12.2 and 12.9 \AA for Cs^+ with $n = 1$ and 6 , respectively. These results are in good agreement with X-ray diffraction data, except for the driest states for which smaller distances have been reported (see e.g. [10, 12]). In that case, even a single water molecule leads to a larger distance than for a completely dry state.

Simulations of aqueous ions consisted of a single ion and 252 water molecules in a cubic box. The equilibrium size of the box corresponds to a concentration of about 0.2 M. The fact that the simulation box is charged (there is no anion) is not a problem : it has been shown that it is equivalent to the same system with a uniform neutralizing background, and that there is only a shift in the electrostatic energy [47]. For a cubic box of size L , $\Delta E = -\alpha Q^2 / 8\pi\epsilon_0 L$, with Q the total charge of the box and α a (Madelung) constant. Thus the shift is identical for the simulations with Na^+ or Cs^+ and compensates when considering differences in energy (or enthalpy).

In addition to Monte-Carlo simulations in the NPT ensemble, we also performed molec-

ular dynamics simulations of the same systems in the NVT ensemble (at the equilibrium volume determined by the NPT simulations), using a modified version of the DLPOLY software package. These simulations were used to compute Helmholtz free energy differences by the thermodynamic integration technique [41, 42]. It consists in gradually turning one type of ion into another using a coupling parameter $\lambda \in [0, 1]$ which interpolates between the Hamiltonian $\mathcal{V}(\lambda = 0) = \mathcal{V}^{\text{Na}}$ of the system with Na^+ and that $\mathcal{V}(\lambda = 1) = \mathcal{V}^{\text{Cs}}$ with Cs^+ . Then the Helmholtz free energy difference between the two states is :

$$\Delta F^{\text{Na} \rightarrow \text{Cs}} = \int_0^1 \left\langle \frac{\partial \mathcal{V}}{\partial \lambda} \right\rangle_{\lambda} d\lambda \quad (7)$$

The term in the integral is an ensemble average for a system at a fixed, intermediate value of λ . We have chosen a thermodynamic path in which all the *pair* LJ parameters vary linearly between that of Na and that of Cs :

$$\varepsilon_{\lambda,j} = \varepsilon_{\text{Na},j} + \lambda(\varepsilon_{\text{Cs},j} - \varepsilon_{\text{Na},j}) \quad (8a)$$

$$\sigma_{\lambda,j} = \sigma_{\text{Na},j} + \lambda(\sigma_{\text{Cs},j} - \sigma_{\text{Na},j}) \quad (8b)$$

where j corresponds to any other atom, and where the extreme pair parameters $\varepsilon_{\text{Na},j}$, $\varepsilon_{\text{Cs},j}$, $\sigma_{\text{Na},j}$, and $\sigma_{\text{Cs},j}$ are obtained from the Lorentz-Berthelot rules. We considered thermodynamic paths in which a single ion is changed from Na^+ to Cs^+ , Na^+ to K^+ , and K^+ to Cs^+ , both in pure water and in clay at a water content of 6 water molecules per cation, corresponding to a water monolayer. For each thermodynamic integration we performed a set of 11 simulations at different λ corresponding to a step $\Delta\lambda = 0.1$, in which we sampled $\langle \partial \mathcal{V} / \partial \lambda \rangle$ for at least 100 ps. Fig. 3 shows the variation of the average $\langle \partial \mathcal{V} / \partial \lambda \rangle$ as a function of λ for the thermodynamic integration from Na^+ to Cs^+ in aqueous solution (solid line) and in clay with $n_{\text{H}_2\text{O}} = 6$ water molecules per cation (dashed line). Numerical integration between $\lambda = 0$ and 1 yields the difference in hydration free energy $\Delta\Delta_h F$ and the enthalpy for the exchange of ions between clay and the gas phase $\Delta_r F^0(6)$, respectively.

4.3. Free energy for the exchange of traces

We first present the results of the thermodynamic integration approach, and use them to validate our choice of parameters to describe the energetic properties of clay, ions and water. In the aqueous ions simulations, the resulting free energy difference corresponds to

the hydration free energy difference $\Delta\Delta_h F$ for Na^+ , K^+ and Cs^+ . The results are reported in table IV.

$\Delta\Delta_h F$ (kJ.mol ⁻¹)	Simulation	Burgess	Marcus
$\text{Na}^+ \rightarrow \text{Cs}^+$	+124±2	+127	+117
$\text{Na}^+ \rightarrow \text{K}^+$	+72±2	+74	+72
$\text{K}^+ \rightarrow \text{Cs}^+$	+53±2	+53	+45

TABLE IV: Hydration free energy difference as obtained by thermodynamic integration. Our simulation results are compared to the values given in the thermodynamic databases compiled by Burgess [48] and Marcus [49].

We first notice that there is a good thermodynamic consistency between the results, i.e. that $\Delta\Delta_h F(\text{Na} \rightarrow \text{Cs}) = \Delta\Delta_h F(\text{Na} \rightarrow \text{K}) + \Delta\Delta_h F(\text{K} \rightarrow \text{Cs})$. Furthermore, the simulation results are in good agreement with the experimental data for $\Delta\Delta_h G \sim \Delta\Delta_h F$ (the difference $P\Delta V$ between these two is only a few kJ/mol) reported in [50]: +117, +72 and +45 kJ/mol, and even better with the values of ref. [48]: +127, +74 and +53 kJ/mol. The excellent agreement with the latter is not surprising, since the Lennard-Jones parameters for the cations were calibrated by Åqvist to reproduce these values when combined to the SPC water model [45], a variant of which (SPC/E) is used in this study. Therefore the force field used for our simulations reasonably represents the interactions between ions and water.

Transformation	$\Delta_r F_g^0(6)$ (kJ.mol ⁻¹)
$\text{Na}^+ \rightarrow \text{Cs}^+$	+120±2
$\text{Na}^+ \rightarrow \text{K}^+$	+68±2
$\text{K}^+ \rightarrow \text{Cs}^+$	+51±2

TABLE V: Free energy difference obtained by thermodynamic integration for ions in clay with 6 water molecules per cation.

The results for the thermodynamic integration for the exchange of a single ion in a MNa with 6 water molecules per counterions are reported in table V. We observe again a good thermodynamic consistency between the results. In addition, all values are positive and

relatively large, meaning that the replacement of an alkaline ion by a larger one in a MNa is clearly thermodynamically unfavourable. More precisely, the value of $\Delta_r F_g^0(6)$ corresponds to the exchange of ions between a MNa and the gas phase (see below). The value for the $\text{Na}^+ \rightarrow \text{Cs}^+$ exchange is in good agreement with the conclusion drawn by Teppen and Miller [40] from experimental data (+117 kJ/mol), and the one for the $\text{K}^+ \rightarrow \text{Cs}^+$ exchange is in good agreement with both their simulation results (+47 kJ/mol) and their conclusions drawn from experimental data (+54 kJ/mol). Since their simulation results were obtained using a different force field to represent ions and clay atoms, and a slightly different method to compute the free energy difference (free energy perturbation, see e.g. [42]), the similar conclusion to which we arrive, namely that the clay phase contributes unfavourably to the ionic exchange free energy, seems to be very robust. We can also conclude that the force field that we use gives a reasonable description of the thermodynamic properties of clay interlayers.

In the above-mentioned study, the authors considered the complete exchange from a K-clay to a Cs-clay, whereas here we consider the exchange of ionic traces in a MNa. This suggests that for a given water content, the short-range ion-clay and ion-water interactions are relatively independent of the nature of the other ions in the interlayer. Such an observation has already been made in simulations of Cs^+ in bihydrated Na-montmorillonite [51]: the structure of the inner-sphere Cs-surface complex was very similar to the one observed in monohydrated Cs-montmorillonite. It is therefore not surprising that energetic properties for the exchange of traces of Cs^+ in MNa show the same behaviour as for the complete exchange from homoionic MNa to homoionic MCs.

4.4. Complete exchange enthalpy

The enthalpy for the complete $\text{Na}^+ \rightarrow \text{Cs}^+$ exchange is reported in table VI, as a function of the number of water molecules per cations: $n_{\text{H}_2\text{O}} = 1$ corresponds to the dry state, 6 to the monolayer state, and 12 to the bilayer state. Note that the latter is not experimentally stable in the Cs case [10]. As for the free energy, $\Delta_r H_g^0(n)$ corresponds to the exchange of ions between clay and the gas phase. These values are all positive and large. Furthermore, they increase as the water content increases. All these observations will be discussed and compared to experimental results in the next section.

$n_{\text{H}_2\text{O}}$	$\Delta_r H_g^0$ (kJ.mol ⁻¹)
1	+88±5
6	+101±3
12	+113±4

TABLE VI: Clay contribution to the standard enthalpy for the exchange reaction between a Na-Clay with n water molecules per cation and a Cs-Clay with n water molecules per cation (see the thermodynamic cycle 4). The values for $n = 1, 6$ and 12 correspond to the dry, monolayer and bilayer states, respectively - even if the latter is not experimentally stable in the Cs case. These simulation results should be compared to the experimental ones of table VII.

5. DISCUSSION

5.1. Origin of the ionic exchange enthalpy

The results for the contribution of the clay phase to the reaction enthalpy $\Delta_r H_g^0(n)$, computed from Eq. (5) using the values of $\Delta_r H^0(n)$ determined in section 3.3.4 and the experimental value of $\Delta\Delta_h H = +133$ kJ/mol [49], are reported in table VII. The same analysis using the experimental immersion enthalpies of Bérend *et al.* [10] yields $+93.5 \pm 7$ kJ/mol for $n = 1$, and $+116.5 \pm 15$ kJ/mol for $n = 6$.

$n_{\text{H}_2\text{O}}$	$\Delta_r H_g^0$ (kJ.mol ⁻¹)
1	+109.5 ± 9
6	+106.5 ± 11
∞	+125.5 ± 1

TABLE VII: Clay contribution to the standard enthalpy for the exchange reaction between a Na-Clay with n water molecules per cation and a Cs-Clay with n water molecules per cation (see the thermodynamic cycle 4). Results are obtained from the experimental immersion enthalpies, enthalpy for the exchange in solution and the proportions of each hydration states.

Experimental results therefore clearly indicate that interactions in the clay interlayer contribute unfavourably to the replacement of Na^+ cations by Cs^+ . This conclusion is further supported by the simulation results of table VI. The latter can be seen as more direct estimates of $\Delta_r H_g^0(n)$ since they are based on the computation of the internal energy from the microscopic interactions between atoms. The agreement between experimental and simulation results, though not quantitative for the lowest water content, is good. The uncertainty on the experimental results reported in table VII does not allow to identify the variations of $\Delta_r H_g^0(n)$ with water content, but the results based on the experiments of ref. [10] suggest an increase of $\Delta_r H_g^0(n)$ with increasing water content, as observed in simulations.

As mentioned in the introduction, the current paradigm for ionic exchange considers that its driving force is to be found in specific interactions between the ions and the clay surface, or in the hydration properties of the ions in the clay interlayer, that would be more favourable to Cs^+ than to Na^+ . However, our simulation results for the free energy clearly support the conclusion of Teppen and Miller [40] that the contribution of the clay phase to the ionic exchange free energy is in fact very unfavourable ($\Delta G \gg 0$) and that it is the hydration free energy difference, i.e. the contribution of the water phase, that leads to an overall exchange of Na^+ for Cs^+ . The driving force for the Na^+ to Cs^+ exchange in montmorillonite is thus the "hydrophobicity" of Cs^+ compared to Na^+ , and not its affinity for the clay surfaces. The same argument also explains the selectivity observed for alkaline earth cations in the order $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$, as was already suggested in ref. [40] as an extension of their analysis of alkaline cations.

Both our experimental and simulation results support the conclusion that the same holds for the ionic exchange enthalpy: replacing Na^+ ions by Cs^+ in the interlayer of montmorillonite clays is an endothermic process, and the overall exchange is exothermic only because it is dominated by the exothermic replacement of Cs^+ by Na^+ in the aqueous phase. An advantage of considering enthalpies is that they are measured directly by microcalorimetry, whereas experimental free energies in solution are deduced from exchange constants, and immersion or swelling free energies are not easily measured. Therefore enthalpy lends itself better to the direct comparison between experimental and simulation results.

5.2. Implications for the exchange of traces

We mentioned in the experimental section that the exchange enthalpy depends on the degree of exchange α . In the trace regime ($\alpha \rightarrow 0$), the value measured in solution by microcalorimetry is -15 ± 0.5 kJ/mol [32]. We could not obtain a direct estimate by simulation using the same approach as before, because the change in enthalpy associated with the replacement of one Na^+ by one Cs^+ in a simulation box containing only Na^+ counterions is small compared to the absolute value of the enthalpy in both systems, and even to the equilibrium fluctuations of the enthalpy. Therefore the uncertainty on the difference obtained by this approach is too large for the result to be meaningful. The evaluation of the free energy did not suffer from this problem, since it was based on a quantity ($\langle \frac{\partial \psi}{\partial \lambda} \rangle$) involving only the exchanged ion.

However, the enthalpy for the exchange of traces can be estimated under the assumption that ions in the interlayer behave independently of the nature of the surrounding cations. This assumption is reasonable and consistent with previous molecular simulation results. In [51], it was shown that Cs^+ ions in a bihydrated heteroionic Na/Cs-clay adopt the same coordination mode as in the -experimentally unstable- bihydrated homoionic MCs : three surface oxygen atoms were included in the first coordination shell of the ion, as also observed on monohydrated homoionic MCs. The value of the enthalpy can then be approximated by $\Delta_r H^0(12) = \Delta_r H_g^0(12) - \Delta \Delta_h H = +113 - 133 = -20 \pm 4$ kJ/mol. Since $\Delta_r H_g^0(n)$ increases with the water content, the choice of the -thermodynamically stable- bilayer state provides a lower bound on the value for suspended clays (for which the larger water content is unknown). This estimate is in good agreement with the value measured by microcalorimetry.

Finally, we can compare these results to the enthalpy deduced from the measurements of clay selectivities at various temperatures using the Van't Hoff relation. Liu *et al.* have reported a value of -18 ± 2 kJ/mol [52], and Tertre *et al.* -19 ± 5 kJ/mol [53]. The assumptions on Cs^+ in MNa and on the water content seem therefore to be reasonable. The fact that independent routes (direct measurement or simulation on the one hand and selectivity measurements at different temperatures on the other hand) lead to the same value of the trace exchange enthalpy give further support to the above discussion. Since the ionic exchange reaction is exothermic, it is a priori unfavoured by an elevation of temperature. However the relatively low value of the exchange enthalpy implies that temperature has only

a weak influence on the retention of Cs^+ by clays, as was already concluded in [32].

6. CONCLUSION

We have studied the origin of the ionic exchange enthalpy in montmorillonite clays using microcalorimetry measurements and molecular simulation. We have first determined the standard reaction enthalpy for well-defined interlayer water contents. We have then shown by a detailed analysis based on thermodynamic cycles that replacing Na^+ ions by Cs^+ in the interlayer of montmorillonite clays is an endothermic process, and that the overall exchange is exothermic only because it is dominated by the exothermic replacement of Cs^+ by Na^+ in the aqueous phase. This conclusion supports the one of a recent study of the ionic exchange free energy [40] and contradicts long-held views on the role of ion-clay interactions in determining the ionic exchange thermodynamics. This calls for a paradigm shift for the driving force of this exchange: The driving force is the "hydrophobicity" of Cs^+ compared to Na^+ and not its affinity for clay surfaces. This analysis has a broader range than the case of clays, and might explain the relative homogeneity of specific effects observed in many contexts according to "Hofmeister series" [54]: One should not forget the role of the hydration energy (i.e. the contribution of the water phase), even if specific interactions with the substrates come into play. The present study does not tell us about the role of the nature of the counterions on the kinetics of the exchange. This would require to take into account clay particle edges explicitly [55]. Moreover, particle edges provide other sites for the retention of cations [28–30]. In particular, the understanding of the effect of pH on the sorption of cations on these edge sites might benefit from the combined theoretical and experimental approach followed in the present paper.

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FIG. 1: Thermogram obtained upon the successive immersions of three MNa (RH=43%) samples in water. Peak c: calibration. Peak 1: 13.0 mg yields $\Delta_i H^{\text{Na}} = 23.9$ mJ/mg. Peak 2: 17.0 mg yields $\Delta_i H^{\text{Na}} = 23.2$ mJ/mg. Peak 3: 23.4 mg yields $\Delta_i H^{\text{Na}} = 23.5$ mJ/mg.

FIG. 2: The simulation box contains to Montmorillonite layers, one in the center, the other cut in two halves at the top and bottom of the box, and corresponds to a periodic stack of infinite layers. Counterions (blue) and water molecules are in the interlayer space. Al atoms are represented in green, Si atoms in yellow, O atoms in red and H atoms in white.

FIG. 3: Average $\langle \partial \mathcal{V} / \partial \lambda \rangle$ as a function of λ , for the thermodynamic integration from Na^+ to Cs^+ in aqueous solution (solid line) and in clay with $n_{H_2O} = 6$ water molecules per cation (dashed line). Standard deviations are smaller than the symbols. The integrals are the difference in hydration free energy $\Delta \Delta_h F$ and the enthalpy for the exchange of ions between clay and the gas phase $\Delta_r F_g^0(6)$, respectively.

Figure 1

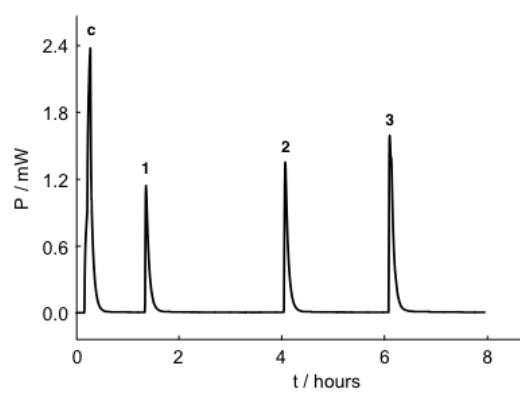


Figure 2

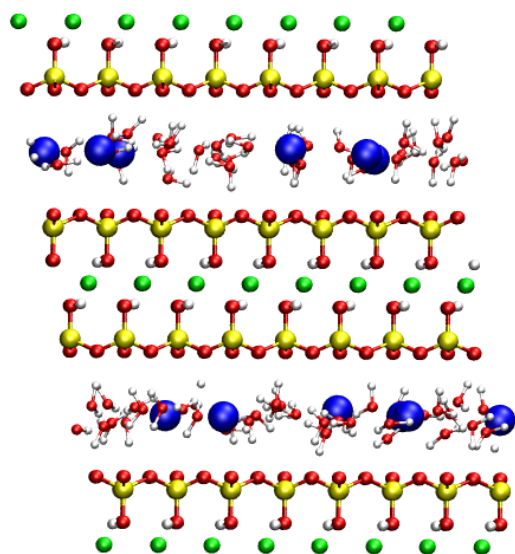


Figure 3

