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Sorption of Eu on Na- and Ca-montmorillonites: Experimental investigations and modelling with cation exchange and surface complexation

M. H. BRADBURY* and B. BAEYENS

Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

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Abstract—The 2-site protolysis no electrostatics surface complexation and cation exchange (2SPNE/CE) model used in previous work to model the sorption of Ni and Zn on Na- and Ca-montmorillonites was applied to sorption edges and isotherms measured for Eu on these two montmorillonite forms. The aim was to further test the applicability of the sorption model on a trivalent element with a more complex aqueous chemistry. An additional reason for choosing Eu was that it is considered to be a good chemical analogue for other lanthanides and trivalent actinides. With site types, site capacities, and protolysis constants fixed at the values in the Ni/Zn studies, all of the measured sorption edge data could be modelled using cation exchange and the monodentate surface species, $\equiv\text{S}^{\text{SO}}\text{Eu}^{2+}$, $\equiv\text{S}^{\text{SO}}\text{EuOH}^+$ and $\equiv\text{S}^{\text{SO}}\text{Eu}(\text{OH})_3^-$, on the strong site type. However, an additional modelling study showed that the same data were almost equally well described by considering bidentate surface complexes, $(\equiv\text{S}^{\text{SO}})_2\text{Eu}^+$ and $(\equiv\text{S}^{\text{SO}})_2\text{Eu}(\text{OH})_2^-$, and cation exchange. To model the sorption isotherm measurements up to $\text{pH} = 7.2$, only one additional weak site surface complex was required, $\equiv\text{S}^{\text{W}1}\text{O}\text{Eu}^{2+}$ for the monodentate case and $(\equiv\text{S}^{\text{W}1}\text{O})_2\text{Eu}^+$ for the bidentate case. Selectivity coefficients are given for Eu^{3+} – Ca^{2+} and Eu^{3+} – Na^+ exchange on the planar sites and surface complexation constants for monodentate and bidentate Eu surface species on the edge sites of montmorillonite. Copyright © 2002 Elsevier Science Ltd

1. INTRODUCTION

In a series of publications by Baeyens and Bradbury (1997) and Bradbury and Baeyens (1997, 1999), the sorption behaviour of the transition metals Ni and Zn on conditioned Na- and Ca-montmorillonites was examined in detail. Conditioning and characterisation procedures used to prepare SWy-1 Na- and Ca-montmorillonites¹ titration data together with Ni and Zn sorption edges and isotherms measured over a wide range of pH, ionic strengths, and metal concentrations were described in the above references. These sorption data were interpreted in terms of cation exchange and surface complexation mechanisms (e.g., Schindler et al., 1987; Zachara et al., 1993). The 2-site protolysis no electrostatics surface complexation and cation exchange (2SPNE/CE) model was developed and incorporated into the chemical equilibrium code MINEQL (Westall et al., 1976). The resulting code, MINSORB, was used successfully to model over 20 sets of titration, sorption edge, and sorption isotherm data.

The same basic sorption model parameters, i.e., $\equiv\text{SOH}$ site types and capacities, protolysis constants, and cation exchange capacities deduced for Na-montmorillonite were used to model the sorption data for Ca-montmorillonite. It was found that the intrinsic surface complexation constants determined for Ni on Na- and Ca-montmorillonites were slightly different; the constants for the Ca system were, on average, 0.2 to 0.4 log units weaker. The same was also true for Zn. Finally, it was demonstrated that there was good internal consistency between the

selectivity coefficients used to quantify the contribution of cation exchange to the overall sorption in the Na- and Ca-montmorillonite systems.

To further test the applicability of the 2SPNE/CE model, sorption edges and isotherms were measured for Eu on the Na and Ca forms of SWy-1 montmorillonite. Europium was chosen because it is a trivalent element with a fairly complex aqueous speciation in the pH region of interest (3–10) and because it is often taken as a chemical analog for trivalent actinides. In the modelling, the same basic system parameters as applied previously in Bradbury and Baeyens (1997, 1999) were used, i.e., the $\equiv\text{SOH}$ site types and site capacity values, protolysis constants, and cation exchange capacities were fixed at the outset.

2. EXPERIMENTAL

2.1. Materials

SWy-1 Na-montmorillonite was thoroughly washed with 1 mol/L NaClO_4 to remove all soluble salts and/or sparingly soluble minerals such as calcite and to convert the clay into the homo-ionic Na-form. The 0.5 μm size fraction was separated by successive washings with de-ionised water pre-equilibrated with conditioned clay combined with centrifugation. Soluble hydroxy-aluminium compounds were removed by an acid treatment ($\text{pH} = 3.5$) followed by phase separation and neutralisation ($\text{pH} = 7$). Sub-batches of clay suspensions were prepared at appropriate NaClO_4 or $\text{Ca}(\text{NO}_3)_2$ concentrations using dialysis methods. The conditioned Na- and Ca-montmorillonite suspensions were stored in the dark at 4°C. Typical background electrolyte compositions after equilibration with the corresponding Na- and Ca-montmorillonites are presented for NaClO_4 and $\text{Ca}(\text{NO}_3)_2$ solutions, respectively, in Table 1.

2.1.1. Physico-chemical characterisation of conditioned Na-montmorillonite

Mineralogic analysis: Mineralogic analyses for conditioned Na-montmorillonite were determined by X-ray diffraction methods. Mont-

* Author to whom correspondence should be addressed (mike.bradbury@psi.ch).

¹ SWy-1 Na-montmorillonite: Crook County, Wyoming Na-montmorillonite obtained from the Source Clay Minerals Repository, University of Missouri-Columbia, USA.

Table 1. Chemical analysis of 0.1 mol/L NaClO₄ and 0.066 mol/L Ca(NO₃)₂ solutions equilibrated with conditioned Na- and Ca-montmorillonites respectively at pH = 7.

Element	Concentration (mol/L) in 0.1 M NaClO ₄	Concentration (mol/L) in 0.066 M Ca(NO ₃) ₂
Na	1 × 10 ⁻¹	3 × 10 ⁻⁴
K	6 × 10 ⁻⁶	2 × 10 ⁻⁵
Mg	1 × 10 ⁻⁵	2 × 10 ⁻⁵
Ca	5 × 10 ⁻⁶	6.6 × 10 ⁻²
Sr	8 × 10 ⁻⁸	8 × 10 ⁻⁶
Ba	2 × 10 ⁻⁸	8 × 10 ⁻⁸
Mn	2 × 10 ⁻⁷	3 × 10 ⁻⁷
Zn	4 × 10 ⁻⁸	7 × 10 ⁻⁸
Fe	2 × 10 ⁻⁷	3 × 10 ⁻⁷
Si	4 × 10 ⁻⁵	4 × 10 ⁻⁵
Al	5 × 10 ⁻⁶	5 × 10 ⁻⁶

morillonite was present at ~97 wt.%, illite and quartz at ~1 wt.%, and other minerals such as albite, K-feldspar, calcite, dolomite and kaolinite/chlorite were below the detection limit of 0.5 wt.%.

Iron extractions: The content of iron (hydr)oxides in conditioned Na-montmorillonite was determined using the oxalate extraction method for amorphous iron (Schwertmann, 1964) and the dithionite-citrate-bicarbonate extraction procedure for total iron (Mehra and Jackson, 1960). The results from such extraction tests showed that ~50% of the ~14 mmol kg⁻¹ total extractable iron was in the amorphous form.

Inventories: Conditioned Na-montmorillonite suspensions were shaken end-over-end in 0.5 mol/L HNO₃ Titrisol solutions for 1 d. Samples were centrifuged and the supernatant solutions analysed by plasma-emission spectroscopy (Applied Research Laboratory ARL 3410D ICP-AES). The aim of these tests was to displace all sorbed cations from the clay after conditioning. The most significant result was that Zn and Mn were present at levels of ~0.8 and ~0.4 mmol kg⁻¹, respectively.

Cation exchange capacity: From over 45 independent measurements on various clay batches of conditioned Na-montmorillonite, the cation exchange capacity (CEC), determined using the ²²Na isotopic dilution method, was found to be 0.870 ± 0.035 eq. kg⁻¹.

Surface area: Conditioned Na-montmorillonite suspensions were dialysed to reduce the NaClO₄ concentration to ~10⁻⁵ mol/L and then freeze-dried before degassing for 2 h at 200°C under a N₂ cover gas before the measurements. The N₂-BET surface areas were determined to be ~3.5 × 10⁴ m² kg⁻¹ from multipoint adsorption isotherms using a Micromeritics Gemini 2360 surface area analyser.

2.2. Europium

Eu belongs to the lanthanide group of elements, and only the trivalent oxidation state is stable in water. The ionic radii are almost the same for all the trivalent lanthanides and Am³⁺, which results in a chemically similar behaviour. Eu is often chosen for sorption investigations because it is easy to work with in the laboratory. The tracer most commonly used, ¹⁵²Eu, is a β/γ-emitter, whereas Am is an α-emitter. (The handling of α-emitters requires far more safety precautions.)

The solubility of europium hydroxide is strongly dependent on pH with a solubility product, log K_{so} = 17.6, for the amorphous phase. Because the ionic radius of Eu is fairly large at 0.95 Å (Weast, 1980), hydrolysis in solutions does not become appreciable until pH ~ 6 is reached. Above this pH, the aqueous speciation is relatively complex, even in such a simple system as the one modelled here. Fig. 1 shows the hydrolysis of Eu in 0.1 mol/L NaClO₄ using thermodynamic data given in Table 2. As can be seen from Fig. 1, the dominant europium species are Eu³⁺ (pH < 8) and Eu(OH)₃⁰ (pH > 9). In the pH range from ~7 to ~10, the mono- and dihydroxy species are present at significant levels. The sorption experiments were carried out in inert atmosphere glove boxes to avoid complexation of Eu³⁺ with carbonate.

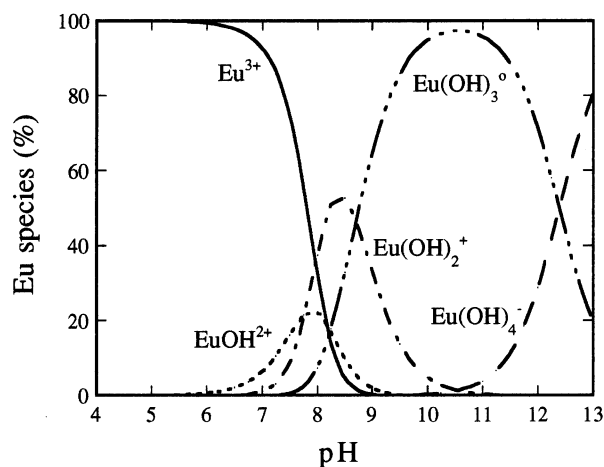


Fig. 1. Eu speciation in 0.1 mol/L NaClO₄ as a function of pH. The thermodynamic constants used are those given in Table 2.

2.3. Procedures and Techniques

The preparatory experiments carried out before the sorption tests, and the methodology used for the sorption measurements themselves, are the same as those reported in Baeyens and Bradbury (1997) for Ni/Zn sorption on Na-montmorillonite. The main aspects are briefly outlined below for completeness.

All experiments were carried out in controlled N₂ atmosphere glove boxes (CO₂ ~ 2 ppm, O₂ ~ 2 ppm) where sampling and pH measurements were made on a WTW Microprocessor 535 pH meter using Orion 8103 combination pH electrodes.

Radiotracer solutions of ¹⁵²Eu were purchased from Amersham International, and radionuclide assays were performed using either a Canberra Packard Tri-Carb 2250 CA liquid scintillation analyser or a Packard Minaxi 5530 auto gamma counter.

Buffers (Perrin and Dempsey, 1974) were used at concentrations of ~2 × 10⁻³ mol/L in the sorption edge and isotherm experiments to maintain constant pH conditions. A series of separate tests showed unambiguously that there was no significant influence of these buffers on sorption in the range of experimental conditions used.

For the sorption edge measurements on Na- and Ca-montmorillonites, the initial Eu concentrations were 10⁻⁷ mol/L and <10⁻⁸ mol/L, respectively. In all of the sorption isotherm measurements, the maximum initial Eu concentration used was at least one order of magnitude less than the solubility limit calculated for Eu(OH)_{3,solid} (Table 2). This condition was chosen to ensure that the starting Eu solutions were stable.

2.3.1. Eu sorption edge and isotherm measurements

Before the sorption experiments, kinetic tests were performed at trace Eu concentrations in buffered suspensions of conditioned mont-

Table 2. Aqueous thermodynamic data (I = 0; T = 298.15 K) used in the Eu modelling studies on Na- and Ca-montmorillonites. (Thermodynamic data taken from Hummel et al., 2002.)

Formation	log K ⁰
Eu ³⁺ + H ₂ O ⇌ Eu(OH) ²⁺ + H ⁺	-7.64
Eu ³⁺ + 2H ₂ O ⇌ Eu(OH) ₂ ⁺ + 2H ⁺	-15.1
Eu ³⁺ + 3H ₂ O ⇌ Eu(OH) ₃ ⁰ + 3H ⁺	-23.7
Eu ³⁺ + 4H ₂ O ⇌ Eu(OH) ₄ ⁻ + 4H ⁺	-36.2
Eu ³⁺ + NO ₃ ⁻ ⇌ Eu(NO ₃) ₂ ⁺	1.33
Solubility product	log K _{so}
Eu(OH) _{3,solid} + 3H ⁺ ⇌ Eu ³⁺ + 3H ₂ O	17.6

morillonite as a function of pH for between 1 and 18 d. No kinetic effects were observed, i.e., equilibrium was reached within 1 d.

Sorption edge measurements (sorption at trace radionuclide concentrations (generally $<10^{-7}$ mol/L) determined as a function of pH at a fixed ionic strength) were carried out at solid-to-liquid (S:L) ratios between 1 and 2 g L⁻¹ under inert atmosphere conditions in 40 mL polypropylene centrifuge tubes. After labelling with ¹⁵²Eu and shaking end-over-end for at least 2 d, the samples were centrifuged in a Beckman L7 Ultracentrifuge at 95,000 g (max.) for 1 h before returning them to the glove box for sampling of the supernatant solutions and pH measurements. Duplicate samples, together with the standards, were counted for long enough periods to give a 1 sigma (or better) error in the radio assay.

For the sorption isotherm determinations, a series of Eu(NO₃)₃ solutions covering the concentration range required was made up at the desired pH in a buffered NaClO₄ or Ca(NO₃)₂ background electrolyte and labelled with ¹⁵²Eu. A similar procedure to that described above was then followed.

Based on an assessment of wall sorption effects, and of the maximum absolute error calculated by considering the maximum error in each operation in batch sorption experiments at the highest and lowest sorption values, and on sets of repeat measurements, a realistic uncertainty in these measured sorption values was estimated to be a factor of ± 1.6 . This factor has been applied to all of the sorption data presented.

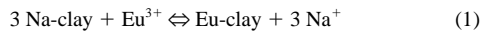
3. SORPTION MODEL DESCRIPTION

The multisite sorption model, combining surface complexation and cation exchange used to describe the uptake of aqueous metal species on montmorillonite, is described briefly below together with the associated assumptions and simplifications.

3.1. Cation Exchange

The permanent negative charge on clay mineral surfaces arising from isomorphous substitution is compensated by an excess of aqueous cations held closely by electrostatic attraction around the outside of the Si-Al-Si units. Electrostatically bound cations can exchange with other cations in solution in reactions which are fast, stoichiometric and reversible (Grim, 1953; Van Olphen, 1963; Bolt et al., 1976). In principle, the sorption due to cation exchange is independent of pH except at low pH and where dissolution of the clay leads to the release of competing cations.

The well-established and widely used approach of representing cation exchange reactions in terms of a selectivity coefficient (Vanselow, 1932; Gaines and Thomas, 1953; Bolt, 1967) obtained by the application of the mass action law has been used, e.g.,



Following the Gaines and Thomas (1953) convention, the thermodynamic constant, K, for the reaction can be defined as:

$$K = \frac{N_{\text{Eu}}}{N_{\text{Na}}^3} \cdot \frac{f_{\text{Eu}}}{f_{\text{Na}}^3} \cdot \frac{(\text{Na})^3}{(\text{Eu})} \cdot \frac{\gamma_{\text{Na}}^3}{\gamma_{\text{Eu}}} = \frac{E_{\text{Eu}} K_c}{N_{\text{Na}}^3} \cdot \frac{f_{\text{Eu}}}{f_{\text{Na}}^3} \quad (2)$$

where K = thermodynamic exchange constant; $\frac{E_{\text{Eu}} K_c}{N_{\text{Na}}^3}$ = selectivity coefficient; N_{Eu} and N_{Na} = equivalent fractional occupancies, defined as the equivalents of Eu (or Na) sorbed per unit mass divided by the CEC; f_{Eu} and f_{Na} = surface region activity coefficients; (Na) and (Eu) = aqueous concentrations (mol/L); and γ_{Eu} and γ_{Na} = aqueous phase activity coefficients.

A selectivity coefficient can be derived from experimental data in the following way:

$$\frac{E_{\text{Eu}} K_c}{N_{\text{Na}}^3} = \frac{N_{\text{Eu}}}{(\text{Eu})} \cdot \frac{\text{CEC}}{\text{CEC}} \cdot \frac{(\text{Na})^3}{N_{\text{Na}}^3} \cdot \frac{\gamma_{\text{Na}}^3}{\gamma_{\text{Eu}}} \quad (3)$$

The solid liquid distribution coefficient; R_d^{Eu} = Eu concentration on solid (mol kg⁻¹)/Eu equilibrium concentration in solution (mol/L), can be expressed as follows,

$$R_d^{\text{Eu}} = \frac{N_{\text{Eu}}}{(\text{Eu})} \cdot \frac{\text{CEC}}{3} \quad (4)$$

At trace Eu concentrations, $N_{\text{Na}} \sim 1$ and Eqn. 3 can be re-arranged to give:

$$\frac{E_{\text{Eu}} K_c}{N_{\text{Na}}^3} = R_d^{\text{Eu}} \cdot \frac{3}{\text{CEC}} \cdot (\text{Na})^3 \cdot \frac{\gamma_{\text{Na}}^3}{\gamma_{\text{Eu}}} \quad (5)$$

The selectivity coefficient, $\frac{E_{\text{Eu}} K_c}{N_{\text{Na}}^3}$, calculated from the experimental sorption edge measurements (see section 4.1), equals the thermodynamic constant K multiplied by the ratio of the surface activity coefficients, $f_{\text{Na}}^3/f_{\text{Eu}}$; see Eqn. 2. Surface activity coefficients are not well-known quantities and may well vary as a function of the relative occupancies (Gaines and Thomas, 1953; Bolt, 1982). $\frac{E_{\text{Eu}} K_c}{N_{\text{Na}}^3}$ can only be regarded as a constant at trace Eu concentrations ($N_{\text{Na}} \rightarrow 1$, $f_{\text{Na}} \rightarrow 1$) or under the condition that $f_{\text{Na}}^3/f_{\text{Eu}}$ remains constant as the occupancy of Eu changes. In the latter case, the sorption due to cation exchange as a function of sorbate concentration would then remain constant.

3.2. Surface Complexation

The pH-dependent component of sorption on montmorillonite is described by sorbate uptake on the amphoteric surface hydroxyl groups ($\equiv\text{SOH}$ sites) situated at clay platelet edges (e.g., Sposito, 1984; Davis and Kent, 1990). Similar to the proposals presented for oxides by Dzombak and Morel (1990), strong ($\equiv\text{S}^{\text{S}}\text{OH}$) and weak ($\equiv\text{S}^{\text{W}}\text{OH}$) site types are considered, with the difference that two weak site types ($\equiv\text{S}^{\text{W}1}\text{OH}$ and $\equiv\text{S}^{\text{W}2}\text{OH}$) were required to describe the titration behaviour of montmorillonite. (The $\equiv\text{S}^{\text{W}1}\text{OH}$ and $\equiv\text{S}^{\text{W}2}\text{OH}$ sites have the same capacities but different protolysis constants.) The $\equiv\text{S}^{\text{S}}\text{OH}$ and $\equiv\text{S}^{\text{W}1}\text{OH}$ type sites are assumed to have the same protolysis constants, and as discussed in Bradbury and Baeyens (1997), surface complexation reactions occur predominantly on these sites. The $\equiv\text{S}^{\text{S}}\text{OH}$ sites have a much smaller capacity but form considerably stronger complexes with metals and dominate the sorption at trace concentrations. (See the summary of data given in Table 3.)

A surface complexation reaction representing, for example, the sorption of Eu on the strong sites may be written as:



In a non-electrostatic model, the corresponding intrinsic surface complexation constant, K_{int} , can be expressed as:

$$K_{\text{int}} = \frac{[\equiv\text{S}^{\text{S}}\text{OEu}^{2+}]}{[\equiv\text{S}^{\text{S}}\text{OH}]} \cdot \frac{f_{\text{SOEu}}}{f_{\text{SOH}}} \cdot \frac{\{\text{H}^+\}}{\{\text{Eu}^{3+}\}} \quad (7)$$

where { } terms are aqueous activities and [] terms are concentrations. Following the discussions given in Dzombak and Morel (1990), the same assumption concerning surface activity coefficients is made here,

Table 3. Summary of site types, site capacities, protolysis constants and Zn/Mn surface complexation constants determined for Na-montmorillonite (Bradbury and Baeyens, 1997) and used in the calculations for Eu sorption modelling on Na- and Ca-montmorillonites.

Site types	Site capacities
$\equiv\text{S}^{\text{S}}\text{OH}$	2.0×10^{-3} mol kg ⁻¹
$\equiv\text{S}^{\text{W}1}\text{OH}$	4.0×10^{-2} mol kg ⁻¹
$\equiv\text{S}^{\text{W}2}\text{OH}$	4.0×10^{-2} mol kg ⁻¹
Cation exchange	8.7×10^{-1} eq. kg ⁻¹
Surface complexation formation reactions	log K_{int}
$\equiv\text{S}^{\text{S}}\text{OH} + \text{H}^+ \Leftrightarrow \equiv\text{S}^{\text{S}}\text{OH}_2^+$	4.5
$\equiv\text{S}^{\text{S}}\text{OH} \Leftrightarrow \equiv\text{S}^{\text{S}}\text{O}^- + \text{H}^+$	-7.9
$\equiv\text{S}^{\text{W}1}\text{OH} + \text{H}^+ \Leftrightarrow \equiv\text{S}^{\text{W}1}\text{OH}_2^+$	4.5
$\equiv\text{S}^{\text{W}1}\text{OH} \Leftrightarrow \equiv\text{S}^{\text{W}1}\text{O}^- + \text{H}^+$	-7.9
$\equiv\text{S}^{\text{W}2}\text{OH} + \text{H}^+ \Leftrightarrow \equiv\text{S}^{\text{W}2}\text{OH}_2^+$	6.0
$\equiv\text{S}^{\text{W}2}\text{OH} \Leftrightarrow \equiv\text{S}^{\text{W}2}\text{O}^- + \text{H}^+$	-10.5
$\equiv\text{S}^{\text{S}}\text{OH} + \text{Zn}^{2+} \Leftrightarrow \equiv\text{S}^{\text{S}}\text{OZn}^+ + \text{H}^+$	1.6 (1.2)
$\equiv\text{S}^{\text{S}}\text{OH} + \text{Mn}^{2+} \Leftrightarrow \equiv\text{S}^{\text{S}}\text{OMn}^+ + \text{H}^+$	-0.1 (-0.4)

Values in parenthesis are for Ca-montmorillonite (Bradbury and Baeyens, 1999).

Table 4. Summary of the monodentate surface complexation constants and selectivity coefficients characterising the sorption of Eu on Ca- and Na-montmorillonites using the 2SPNE/CE model.

Surface complexation formation reactions	log K_{int} Ca-montmorillonite	log K_{int} Na-montmorillonite
$\equiv\text{S}^{\text{S}}\text{OH} + \text{Eu}^{3+} \Leftrightarrow \equiv\text{S}^{\text{S}}\text{OEu}^{2+} + \text{H}^+$	0.8	1.8
$\equiv\text{S}^{\text{S}}\text{OH} + \text{Eu}^{3+} + \text{H}_2\text{O} \Leftrightarrow \equiv\text{S}^{\text{S}}\text{OEuOH}^+ + 2\text{H}^+$	-5.7	-5.4
$\equiv\text{S}^{\text{S}}\text{OH} + \text{Eu}^{3+} + 3\text{H}_2\text{O} \Leftrightarrow \equiv\text{S}^{\text{S}}\text{OEu}(\text{OH})_3^- + 4\text{H}^+$	-22.6	-22.1
$\equiv\text{S}^{\text{W}1}\text{OH} + \text{Eu}^{3+} \Leftrightarrow \equiv\text{S}^{\text{W}1}\text{OEu}^{2+} + \text{H}^+$	-1.2	-0.5
Cation exchange reaction	$K_{\text{c}} (I = 0)$	
$3\text{Na-Clay} + \text{Eu}^{3+} \Leftrightarrow \text{Eu-Clay} + 3\text{Na}^+$	30	
$2\text{Na-Clay} + \text{Ca}^{2+} \Leftrightarrow \text{Ca-Clay} + 2\text{Na}^+$	4.1*	
$3\text{Ca-Clay} + 2\text{Eu}^{3+} \Leftrightarrow 2\text{Eu-Clay} + 3\text{Ca}^{2+}$	13	

* Value taken from Baeyens and Bradbury (1995).

i.e., the ratio of the surface activity coefficients in the mass action equations describing the surface complexation reactions is taken to be unity.

The 2SPNE/CE model was developed and used successfully to describe the sorption of Ni and Zn on montmorillonite in the Na and Ca forms under a very wide range of chemical conditions (Bradbury and Baeyens, 1997, 1999). A major feature of this modelling exercise was that an electrostatic term was not required in the mass action equations describing protolysis and surface complexation reactions used to reproduce the experimental data. That is to say, electrostatic effects may be involved in protolysis and aqueous metal species uptake on the $\equiv\text{SOH}$ sites, but unlike the case of oxides, electrostatic terms are apparently of secondary importance in the model description of sorption on montmorillonite.

The reasons that an electrostatic term in the model is not required are unclear. A possible explanation might lie in the nature of the different site types contributing to the overall surface charge (Bradbury and Baeyens, 1995). The surface charge of clay minerals is not only determined by the charge state of the $\equiv\text{SOH}$ type edge sites, but also by a fixed permanent negative surface charge. The relevant electrical potential at the surface at any given pH might then be a combination of these two surface site types, one pH dependent and the other not. The permanent negative charge amounts to ~ 0.87 eq. kg^{-1} , whereas the maximum charge arising from the $\equiv\text{S}^{\text{W}1}\text{OH}$ type sites, which are important for surface complexation reactions up to $\text{pH} \sim 10.5$, is $\pm 4 \times 10^{-2}$ eq. kg^{-1} when all $\equiv\text{S}^{\text{W}1}\text{OH}$ sites are protonated or deprotonated. Thus, the magnitude and sign of the overall surface charge are effectively determined by the permanent charge and are essentially fixed, except for a pH-dependent contribution from the $\equiv\text{S}^{\text{W}1}\text{OH}$ type sites, which amounts to a maximum of $< \pm 5\%$ of the total. Thus, the net effect is that the magnitude of the electrostatic term remains essentially constant as a function of pH. Under such conditions, an explicit representation of an electrostatic term would not be needed in the model, and the pH-dependent coulombic term would be included in the binding constant.

One of the major aims in the development of sorption models was to set up the simplest chemically reasonable model with the least number of variable parameters capable of describing and predicting sorption over a wide range of conditions. On this principle, no advantage could be seen in introducing an electrostatic term. Indeed, non-electrostatic surface complexation models, which in general imply that the chemical contribution to the adsorption free energy predominates over the electrostatic contribution, have been proposed and used successfully by numerous authors on different sorbents (e.g., Koss, 1988; Davis and Kent, 1990; Zachara and Smith, 1994; Hayes and Katz, 1996; Stumm and Morgan, 1996; Davis et al., 1998).

Outer sphere complexes of Eu on the edge sites are not considered in the model. As mentioned above, the relative capacities of the permanent charge sites and the maximum outer sphere complex capacity of the edge sites are well over an order of magnitude different. Modelling the cation exchange contribution to the overall sorption was achieved using a single selectivity coefficient. Good agreement with the data was found over a wide range of conditions: pH, background electrolyte concentrations, and sorbate concentration. Thus, on the basis of the

currently available experimental evidence, it was not considered a necessity to introduce an additional parameter describing the formation of outer sphere complexes.

3.3. MINSORB

In all of the fitting/modelling work described below, the computer code MINSORB was used. MINSORB is basically the geochemical speciation code MINEQL (Westall et al., 1976) containing a subroutine for calculating surface complexation via a non-electrostatic model. Cation exchange was incorporated into the code and included in all of the calculations given later using the selectivity coefficients presented in Table 4.

MINSORB is a relatively flexible code allowing speciation and sorption by cation exchange and surface complexation to be calculated simultaneously for mixtures of radionuclides in any given water chemistry on different solid phases. Aqueous activity coefficients are calculated using the Davies relation (Davies, 1962).

4. SORPTION RESULTS AND MODELLING

4.1. Eu Sorption Edge on Ca-Montmorillonite

The approach adopted to model the Eu sorption data on Ca- and Na-montmorillonites was the same and is illustrated here for the sorption edge measured on Ca-montmorillonite (Fig. 2). The procedures described below are a somewhat simplified version of the iterative process actually used (more details are given in Bradbury and Baeyens, 1997). To avoid unnecessary repetition, the measured sorption data are presented as symbols in the figures, together with the calculated sorption curves.

In the region of the sorption edge where the R_{d} is constant and independent of pH ($\text{pH} < 4.5$), the uptake of Eu is interpreted as being due to cation exchange on the permanently charged planar sites. The Eu-Ca exchange is described by:



An equation similar to Eqn. 5 in section 3.1 was then used to calculate a selectivity coefficient. The experimental data could be fitted with a $K_{\text{Ca}}^{\text{Eu}}$ of 13. Cation exchange was included in the calculations described in the following with the Eu-Ca selectivity coefficient fixed at this value.

Difficulties were encountered with the use of FITEQL (Herbelin and Westall, 1996). Instead, a stepwise approach to modelling the sorption edge was adopted by considering simple chemically reasonable surface complexation reactions in the order given below and finding a best fit by eye for part of the edge at each step. It was found that with sorption edges pre-

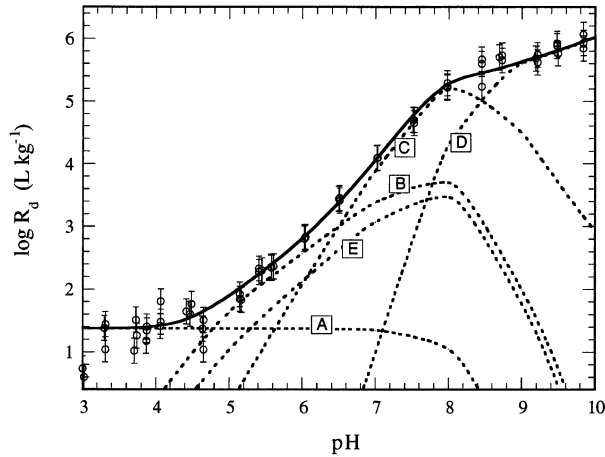


Fig. 2. Eu sorption edge on conditioned Ca-montmorillonite in 6.6×10^{-2} mol/L $\text{Ca}(\text{NO}_3)_2$. Total Eu concentration = 9.5×10^{-9} mol/L. S:L = 1.0 g L^{-1} . The continuous line is the best fit obtained with the 2SPNE/CE model and the parameters listed in Tables 2 and 4. The dotted lines illustrate the contribution of the different surface species to the overall sorption: (A) CE- Eu^{3+} ; (B) $\equiv\text{S}^{\text{SO}}\text{Eu}^{2+}$; (C) $\equiv\text{S}^{\text{SO}}\text{EuOH}^+$; (D) $\equiv\text{S}^{\text{SO}}\text{Eu}(\text{OH})_3^-$; (E) $\equiv\text{S}^{\text{W1O}}\text{O-Eu}^{2+}$.

sented in the $\log R_d$ vs. pH form, the fits to the data were rather sensitive to the surface complexation constants chosen, and fitting by eye worked quickly and well for the stepwise procedures used. The surface complexation constant fitted in one step was then fixed and carried over into the next calculation.

For example, up to $\text{pH} \sim 8$, the dominant aqueous species is the free Eu^{3+} cation (Fig. 1), and the first surface complexation reaction considered was:



It became immediately apparent that the rising edge of the

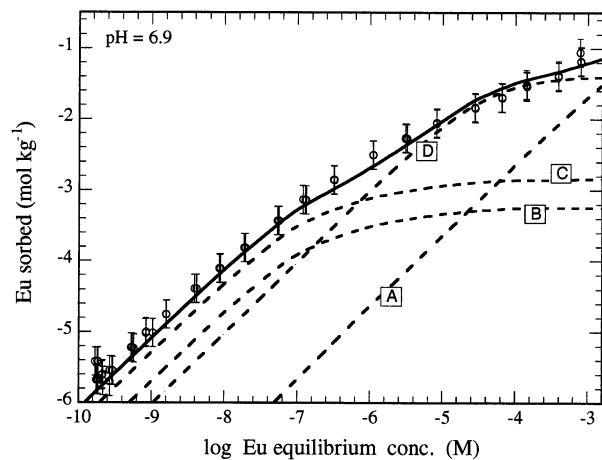
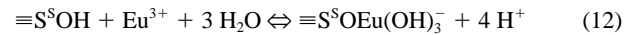
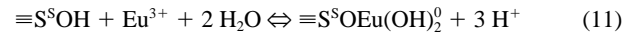


Fig. 3. Eu sorption isotherm data on conditioned Ca-montmorillonite at $\text{pH} = 6.9$ and $\text{Ca}(\text{NO}_3)_2 = 6.6 \times 10^{-2}$ mol/L. S:L = 1.0 g L^{-1} . The continuous line is the best fit to the data obtained using the 2SPNE/CE model and the parameters listed in Tables 3 and 4. The dotted lines illustrate the contribution of the different surface species to the overall sorption: (A) CE- Eu^{3+} ; (B) $\equiv\text{S}^{\text{SO}}\text{Eu}^{2+}$; (C) $\equiv\text{S}^{\text{SO}}\text{EuOH}^+$; (D) $\equiv\text{S}^{\text{W1O}}\text{O-Eu}^{2+}$.

sorption curve and the sorption plateau (Fig. 2) could not be fitted simultaneously with only this reaction: any approximate fit to the first resulted in a substantial underestimate in the second. Thus, a best fit to part of the edge was found, the surface complexation constant for Eqn. 9 was fixed, and then the process was repeated sequentially for Eqn. 10, 11, and 12:



An iterative procedure then followed to find the best fit to the data and fine-tune the surface complexation constants. The results are illustrated in Figure 2, where the best overall fit to the data is given by the continuous line, together with the calculated contributions of the individual surface species. Note that the rising slopes of the individual edges are proportional to the protons released in the respective surface complexation reactions. The decreases are due to the aqueous hydrolysis of the different Eu species (see Fig. 1). These two features explain why the overall Eu sorption edge requires a series of surface complexation reactions to successfully fit the experimental data.

It will be noticed that the surface species corresponding to Eqn. 11 does not appear, even though considered in the modelling exercise. The reason is that the contribution of this surface complexation reaction to the overall pH dependent sorption turned out to be unimportant compared with Eqn. 9, 10, and 12.

Note that the modelling was performed throughout at the actual S:L ratios and Eu inventories present in the measurement of the sorption edges (see figure captions).

4.2. Eu Sorption Isotherms on Ca-Montmorillonite

Two sorption isotherms were measured for the Eu/Ca-montmorillonite system at pH values of 6.9 and 6.0 in 6.6×10^{-2}

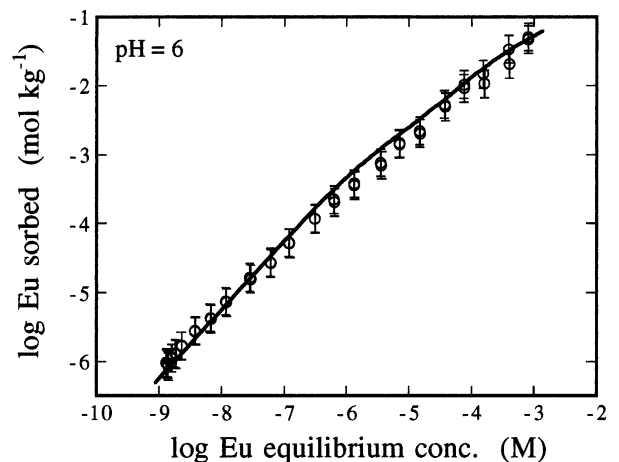


Fig. 4. Eu sorption isotherm data on conditioned Ca-montmorillonite at $\text{pH} = 6.0$ and $\text{Ca}(\text{NO}_3)_2 = 6.6 \times 10^{-2}$ mol/L. S:L = 1.0 g L^{-1} . The continuous line is the best fit to the data obtained using the 2SPNE/CE model and the parameters listed in Tables 3 and 4.

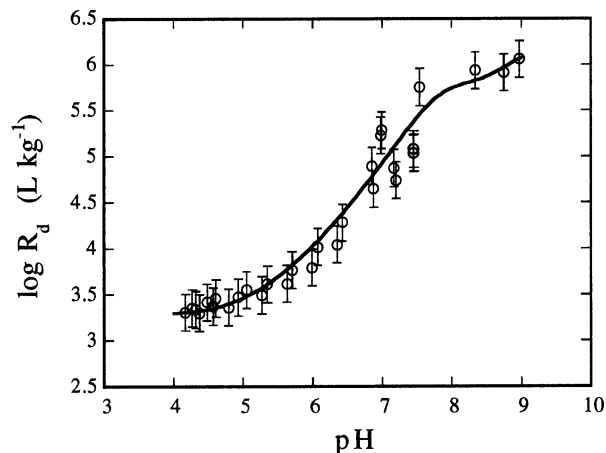
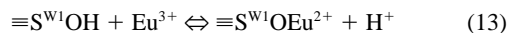


Fig. 5. Eu sorption edge on conditioned Na-montmorillonite in 0.1 mol/L NaClO₄, S:L = 1.5 g L⁻¹. Total Eu concentration = 1.3 × 10⁻⁷ mol/L. The continuous line is the best fit obtained with the 2SPNE/CE model and the parameters listed in Tables 3 and 4.

mol/L Ca(NO₃)₂ background electrolyte (Figs. 3, 4), respectively. The combination of electrolyte concentration and pH were chosen so as to give a wide range of Eu equilibrium concentrations, reduce the contribution of cation exchange, and ensure that sorption was occurring predominantly on the ≡S^{SOH} and ≡S^{W1OH} sites. At pH = 8, for example, the solubility of Eu is ~3 orders of magnitude lower than at pH ~7, assuming that the controlling solid phase is Eu(OH)_{3,solid}. This places quite severe restrictions on the maximum initial Eu concentrations which can be used if the stability of the solution is to be ensured (see section 2.2). Practically, the equilibrium Eu concentrations would be restricted to values of ~10⁻⁶ mol/L, and this implies that sorption would probably occur predominantly on the strong sites only.

If the surface complexation constants and Eu-Ca selectivity coefficient derived from the sorption edge data are fixed, it was found that only one additional parameter was required to fit the two sets of isotherm data. The additional reaction considered was:



The modelled curves are illustrated in Figs. 3 and 4. In Fig. 3, the contributions from the individual surface species are given. At Eu equilibrium concentrations above 10⁻⁶ mol/L, the sorption on the weak sites becomes dominant.

Part of the iterative procedure mentioned previously involved going back to the sorption edge data and refitting the

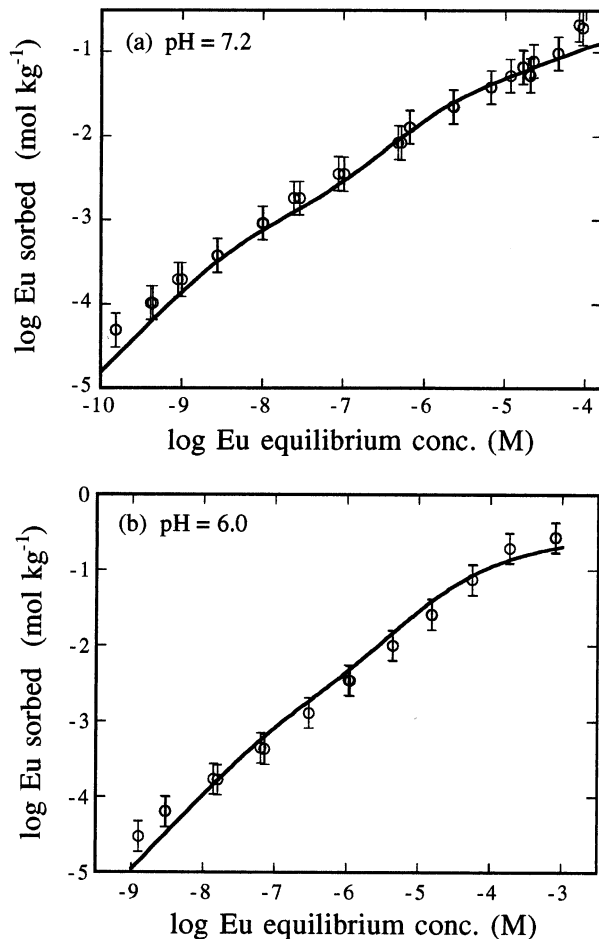


Fig. 6. Eu sorption isotherm data on conditioned Na-montmorillonite at (a) pH = 7.2 and (b) pH = 6.0 and NaClO₄ = 0.1 mol/L, S:L = 0.5 g L⁻¹. The continuous line is the best fit obtained with the 2SPNE/CE model and the parameters listed in Tables 3 and 4.

strong site surface complexation constants, taking into account the potential contribution of sorption on the weak sites. As can be seen in Figure 2, the ≡S^{W1OH} sites do apparently make a contribution to the sorption edge for the experimental conditions used. The contribution is by no means dominant in any pH range, but its presence cannot be ignored.

4.3. Eu Sorption Edges and Isotherms on Na-Montmorillonite

One sorption edge and two isotherms were measured for the Eu/Na-montmorillonite system (Figs. 5, 6). The background

Table 5. Summary of the bidentate surface complexation constants characterising the sorption of Eu on Ca- and Na-montmorillonites using the 2SPNE/CE model.

Surface complexation formation reactions	log K _{int} Ca-montmorillonite	log K _{int} Na-montmorillonite
2≡S ^{SOH} + Eu ³⁺ ⇌ (≡S ^{SO}) ₂ Eu ⁺ + 2H ⁺	0.8	1.6
2≡S ^{SOH} + Eu ³⁺ + 2H ₂ O ⇌ (≡S ^{SO}) ₂ Eu(OH) ₂ ⁻ + 4H ⁺	-15	-14.8
2≡S ^{SOH} + Eu ³⁺ ⇌ (≡S ^{W1O}) ₂ Eu ⁺ + 2H ⁺	-3.0	-2.5

electrolyte in all three cases was a purified NaClO₄ solution at 0.1 mol/L. The isotherms were measured at pH values of 6 and 7.2. The modelling procedure was exactly the same as described above, and the calculated overall sorption curves are given by the continuous lines in the figures.

The Eu-Ca and Eu-Na selectivity coefficients and values for the surface complexation constants used to model Eu sorption in the Ca- and Na-montmorillonite systems are summarised in Table 4.

4.4. Bidentate Surface Species

Even though the sorption edges and isotherms given above were successfully modelled over a whole range of conditions, this does not enable any statement to be made about the uniqueness of the set of parameters deduced for the 2SPNE/CE model. In an attempt to look at potential alternatives, a further modelling study was undertaken in which bidentate surface species were considered. The same datasets as above were taken and modelled by the same procedures as described in sections 4.1 and 4.2.

The bidentate surface complexation reactions used to model Eu sorption edges and isotherms on Ca- and Na-montmorillonites, together with the corresponding constants, are summarised in Table 5. The solid lines in Figure 7a–f are the calculated curves. Only two surface species on the strong sites and one on the weak type 1 sites were required. The cation exchange data given in Table 4 were also used. (Curves calculated for monodentate surface species are shown in Figure 7a–f as dashed lines for comparison.)

In general, there is reasonable correspondence between the modelled curves and the experimental data. For the sorption edge on Ca-montmorillonite, the fit becomes less good at pH > 9. Some deviations from the isotherm measurements are evident at the highest Eu concentrations in all cases and at the lowest concentrations in one case (Na-montmorillonite, pH = 6).

5. DISCUSSION

In the analyses of the Eu sorption edge data for the Ca- and Na-montmorillonites, the regions below pH ~4.5 exhibited constant sorption and were modelled by cation exchange. From this modelling approach, the Eu-Ca and Eu-Na selectivity coefficients given in Table 4 were derived. Each selectivity coefficient was obtained from only one set of data, and consequently, it is not feasible on such a basis to make any judgement about the general applicability of the values. However, according to the work of Lewis and Thomas (1963) and Martin and Laudelout (1963), it is possible to calculate a $\frac{Ca}{Na}K_c$ value from the measured $\frac{Eu}{Na}K_c$ and $\frac{Eu}{Ca}K_c$ values. This provides a means of checking the consistency of the Eu selectivity constants with independently measured literature data for $\frac{Ca}{Na}K_c$. The equation relating the $\frac{Eu}{Na}K_c$, $\frac{Eu}{Ca}K_c$ and $\frac{Ca}{Na}K_c$ is:

$$\left(\frac{Ca}{Na}K_c\right)^3 = \frac{\left(\frac{Eu}{Na}K_c\right)^2}{\frac{Eu}{Ca}K_c} \quad (14)$$

and when the values for $\frac{Eu}{Na}K_c$, $\frac{Eu}{Ca}K_c$ are used, Eqn. 14 yields

$\frac{Ca}{Na}K_c = 4.1$. This is in excellent agreement with the previously reported value given in Baeyens and Bradbury (1995) (see Table 4). Such a good agreement is perhaps fortuitous, but the consistency is clearly demonstrated. Further, Van Bladel et al. (1972), Maes and Cremers (1977), and Sposito et al. (1983) report values of $\frac{Ca}{Na}K_c$ in various montmorillonite systems of 3.4 to 3.9, 3.7, and 3.4, respectively, for Ca fractional occupancies <0.3. In addition, the validity of the relation given in Eqn. 14 is further evidence that the interpretation of the Eu sorption data in Figs. 2 and 5 in terms of a cation exchange mechanism at pH < 5 is justified.

The contribution of cation exchange to the sorption edge is illustrated in Figure 2. Since only Eu³⁺ aqueous species are considered to cation exchange, this contribution to the overall sorption decreases rapidly as the Eu³⁺ concentration falls to zero due to hydrolysis. Eu sorption on Na-montmorillonite tends to increase with the inverse of the Na aqueous concentration raised to an exponent of three, whereas in Ca-montmorillonite and in Ca-dominated solutions, the exponent is three halves. Under conditions of low ionic strength, the uptake of Eu by cation exchange can become the dominant sorption mechanism over a wide pH range.

From Tables 4 and 5, it can be seen that for both the Eu monodentate and bidentate surface species, the binding constants in the Na-montmorillonite system are greater than for Ca-montmorillonite. The differences in the constants are significant but not enormous, varying from 0.3 log units to a maximum of 1.0 log unit. A similar trend in the monodentate surface complexation constants for the transition metals Ni and Zn for Na and Ca forms of montmorillonite was also observed. In the latter cases, the differences were smaller, being at maximum 0.4 log units. Put simply, Ni, Zn, and Eu sorb more strongly by surface complexation on Na-montmorillonite than on Ca-montmorillonite. It may be speculated that the surface-binding constants might be dependent on whether complexation is occurring with edge sites associated with a Na or Ca outer sphere complex.

For the sorption edges up to pH values of 8 to 8.5, and over almost the whole range of Eu equilibrium concentrations in the isotherm measurements, the sorption models with monodentate and bidentate surface complexes fit the experimental values relatively well (see Fig. 7). If Eu is considered as a chemical analog to trivalent actinides, then the environmentally relevant concentration range is sub-micromolar, and in argillaceous rocks containing smectites and in compacted bentonites, the pH certainly lies in the range 6 to 8.5. Thus, the pH and concentration ranges of most importance are those in which monodentate and bidentate surface species sorption models both fit the data best. (In general, the monodentate species approach provides a better fit to the experimental data, but not decisively so.) In addition, it cannot be ruled out that monodentate and bidentate surface species are dominant in different pH regions. Although monodentate surface complexes are in general considered more likely, the specific question regarding the sorption of Eu on montmorillonite still remains, i.e., whether the surface complexes are monodentates or bidentates. Questions of this type can only be resolved with the aid of advanced surface analysis techniques.

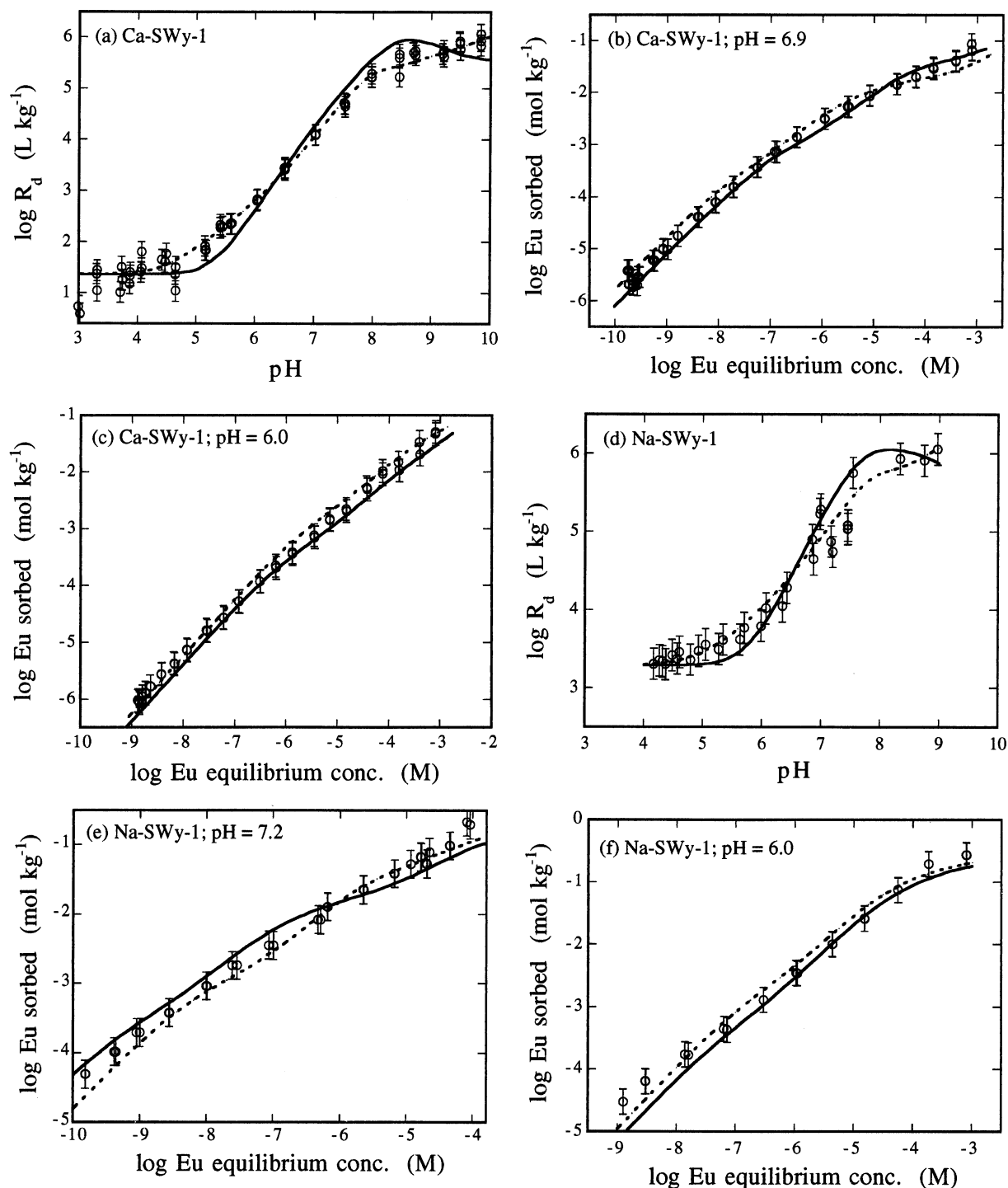


Fig. 7. Eu sorption edge and isotherm data on conditioned Na- and Ca-montmorillonites. The continuous lines are the best fits obtained with bidentate surface species, the 2SPNE/CE model, and the parameters listed in Tables 3, 4 (cation exchange), and Table 5. The dotted lines are the calculated curves for the monodentate surface species given for comparison.

6. SUMMARY

The 2SPNE/CE model has been used successfully to quantitatively model the sorption of the transition metals, Ni, Zn, Mn, and in this work, the lanthanide Eu, as a function of

concentration over a wide range of solution conditions for Na- and Ca-montmorillonites.

The site types, site capacities, and protolysis constants determined for Na-montmorillonite were fixed in the modelling for both montmorillonite forms and for all the above elements.

These system parameters may therefore be considered to be appropriate for any mixed Na/Ca montmorillonite.

As was found previously for the transition metals, no electrostatic term was required for modelling the uptake of Eu on Na/Ca montmorillonites in the presence of 1:1 and 2:1 background electrolytes, respectively.

Since the breadth of data from which the cation exchange selectivity coefficients, K_{Na}^{Eu} and K_{Ca}^{Eu} were deduced was not large, consistency checks were carried out. It was found that the internal consistency between the K_{Na}^{Eu} and K_{Ca}^{Eu} values and K_{Na}^{Ca} , determined in independent studies, was very good. In addition, since it was previously shown that K_{Na}^{Ca} , K_{Na}^{Ni} , K_{Ca}^{Ni} , K_{Na}^{Zn} and K_{Ca}^{Zn} constituted a consistent parameter set (Bradbury and Baeyens, 1999), then the Eu selectivity coefficients are, by inference, also consistent with the transition metal selectivity coefficients. This adds to the confidence in the K_{Na}^{Eu} and K_{Ca}^{Eu} values given.

The broad-based datasets (sorption edges and isotherms at different pH on different forms of montmorillonite in 1:1 and 2:1 background electrolytes) were modelled with Eu monodentate and bidentate surface species for both the Ca- and Na-montmorillonite forms in two separate studies. In both cases, more than one surface species was required to satisfactorily model the sorption edges and isotherms over the pH ranges investigated. Although the correspondence between modelled curves and experimental data using monodentate species was better, the possible formation of bidentate species cannot be ruled out.

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