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HARD AND SOFT ACID-BASE MODEL APPLIED TO BIVALENT CATION SELECTIVITY ON A 2:1 CLAY MINERAL

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Abstract—We applied the hard and soft acid-base (HSAB) model (Xu and Harsh 1990a, 1990b) to bivalent cation exchange on a purified Ca-montmorillonite. As a result, a satisfactory model is proposed to describe the gradual selectivity of exchange with Ca for 4 of the 6 metals studied (Cd, Cu, Pb, Zn). The selectivity is predicted as a function of the differences of electronegativity and softness of the metals. The deviation of Ni and Co data from the predicting model is interpreted in terms of hydration (Ni and Co being the most strongly hydrated ions). The fitting parameters of the model, α and β, are related to the electronegativity and softness characteristics of the surface, respectively. Their ratio gives information on the nature of bonding. Results suggest that covalent bonding modifies electrostatic interactions, which in turn affect selectivity, with an increasing influence of covalent bondings in the order: Pb < Cd < Zn < Cu.

To balance the lack of representativity of the model for the small molar fraction (N_M), we propose to associate to the HSAB model an equation describing the variation of the Vanselow selectivity coefficient as a function of the molar fraction of metal on clay.

Key Words—Bivalent Cations, Covalent Bonding, Electronegativity, HSAB, Montmorillonite, Selectivity Coefficient, Softness.

INTRODUCTION

The prediction of cation retention by minerals is of great interest in environmental and soil science. In this respect, clay minerals may fix metals through ionic exchange (Gaines and Thomas 1953; Van Bladel et al. 1993; Gorgeon 1994) or surface complexation (Goldberg and Glaubig 1986; Zachara et al. 1988; Stadler and Schindler 1993). This property is at the basis of geochemical barriers against diffuse aquatic pollutions such as observed 1) in suspended matters from wastewaters and polluted rivers (Helios-Rybika and Kyziol 1991; Viraraghavan and Kapoor 1994; Bertin and Bourg 1995), 2) in soils near smelter complexes (John et al. 1975; Nwankwo and Elinder 1979) or 3) in sediments from settling basins, near motorways (Hewitt and Rashed 1992; Lee et al. 1996). Furthermore, this property could be important for designing simple and low-cost cleaning systems for industrial effluents (Brigatti et al. 1995) and wastewaters (Auboiroux et al. 1996).

Metals sorption by clays has been studied by numerous authors (Farrah et al. 1980; Tiller et al. 1984; Hirsch et al. 1989; Halen et al. 1991; Van Bladel et al. 1993; Siantar and Fripiat 1995; Helios Rybicka et al. 1995). The various approaches grade from empirical to theoretical studies with special reference to the thermodynamic treatment of ionic exchange. In this article, an experimental contribution is presented to compare the fixation of 6 metals (Cd, Co, Cu, Ni, Pb and Zn) on a purified Ca-montmorillonite. The increasing selectivity, from Ni to Pb, is interpreted using the HSAB concept (Pearson 1963, 1968a, 1968b). Based on the Lewis definition of acids as electron acceptors and bases as electron donors, this concept states that "a hard acid prefers to coordinate with a hard base, whereas a soft acid prefers to coordinate with a soft base." Sullivan (1977) and Sposito (1984) proposed this concept as an explanation of exchangeable metal selective fixation on clay minerals. Later, Xu and Harsh (1990a, 1990b, 1992) developed a quantitative predicting model based on the assumption that the stability of surface complexes determines the selectivity. This model explains the selectivity in term of electronegativity and softness of the exchanged cations, and the characteristics of the surface exchanger, described by 2 parameters α and β. They verified the validity of their model for monovalent cation exchange using several surface exchangers (vermiculite, smectites, hydrous Zr oxides, silica gel and ion-exchange resins).

In this study, experimental results have been rationalized using the HSAB model proposed by Xu and Harsh (1990b) in order to check its possible relevance for explaining bivalent cations selectivity.

THE HSAB MODEL FOR CATION SELECTIVITY

When discussing the behavior of a sequence of metals, cation selectivity is an appropriate concept. It is defined as the measurement of the relative affinity of a surface for different cations. Various models of cation selectivity on clays have been proposed to explain

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observed selectivity sequences: 1) models with an assumption of no covalent bonding between cation and surface (Eisenman 1962; Nir 1986) and 2) the HSAB model, which introduces a softness term accounting for the effects of covalent interactions.

Following the HSAB concept introduced by Pearson (1963, 1968a, 1968b), the softness calculations given by Misono et al. (1967) and the first applications to clay selectivity by Sullivan (1977) and Sposito (1984), Xu and Harsh developed a model whose main conclusions are summarized below. Using the Misono et al. (1967) general equation for the determination of the stability constant (K) of a complex, the following equation is derived by Xu and Harsh (1990a):

$$\log K_{ex} = \alpha(\chi_M - \chi_{ref}) + \beta(S_M - S_{ref}) \quad [1]$$

In this expression, (M) and (ref) refer respectively to a cation M and the reference cation (initially present on clay); χ_M and χ_{ref} are absolute electronegativities values; S_M and S_{ref} are absolute softness values; and α and β are surface-dependent variables that are determined for a given exchanger at constant ionic strength, temperature and pressure. These coefficients represent the influence of surface properties on ion exchange.

Xu and Harsh (1990a) showed that the electronegativity term ($\chi_M - \chi_{ref}$) in Equation [1] represents the effect of electrostatic interactions on selectivity, whereas the softness term ($S_M - S_{ref}$) represents the influence of covalent interactions. Then, α and β will provide an estimation of the influence of exchanger structure on the respective parts played by electronegativity and softness on surface affinity for metals.

The determination of α and β is based on the experimental exchange isotherms. The amounts of heavy metals fixed and Ca^{2+} released by clays are assumed to be the difference between initial and final concentrations in the bulk solution. The metal amount fixed by 1 g of clay is then:

$$q_M = \frac{([M^{2+}]_{initial} - [M^{2+}]_{final})}{M_M \times m_{clay}} \times V \quad [2]$$

where M_M and $[M^{2+}]$ are the atomic weight and the molarity of the cation M, m_{clay} is the weight of clay and V is the volume of solution used for each run.

The molar fraction (N) of cations M and Ca on clay are:

$$N_M = \frac{q_M}{q_M + q_{Ca}} \quad [3]$$

and:

$$N_{Ca} = 1 - N_M \quad [4]$$

The molar fraction (X) of cations in equilibrium solutions is determined as:

$$X_M = \frac{[M^{2+}]}{[M^{2+}] + [Ca^{2+}]} \quad [5]$$

and:

$$X_{Ca} = 1 - X_M \quad [6]$$

For each particular exchange, the Vanselow selectivity coefficient (K_v) is defined as follows:

$$K_v = \frac{N_M}{N_{Ca}} \frac{X_{Ca}}{X_M} \quad [7]$$

Log K_v values can be fitted to a polynomial function of N_M in the form:

$$\log K_V = A_0 + A_1 N_M + A_2 N_M^2 + A_3 N_M^3 + \cdots \quad [8]$$

where A_0, A_1, A_2, A_3, . . . are constants.

Babcock and Duckart (1980) state that it is possible to relate the equilibrium exchange constant K_{ex} to the selectivity coefficient K_v. Considering the exchange of 2 cations, A and B, on an exchanger X, one has:

$$aAX + bB_{(aq)} \Leftrightarrow bBX + aA_{(aq)} \quad [9]$$

with:

$$K_{ex} = \frac{f_{BX}^b}{f_{AX}^a} K_v^0 \quad [10]$$

where K_v^0 is the selectivity coefficient determined for the standard state and f_{AX} and f_{BX} are activity coefficients on the exchanger for A and B, whereas a and b are stochiometric coefficients for A and B in the equation describing the exchange reaction. Defining the standard state at $N_i^0 = 0.5$, one has $K_{ex} = K_v^0$ (Babcock and Duckart 1980).

The coefficients α and β are determined by fitting the log K_v^0 values to the general equation proposed by Xu et Harsh (1990a) (Equation [1]) using a 2-variable linear regression with y intercept set to zero.

MATERIALS, METHODS AND DATA ANALYSIS

Samples

Adsorption studies are often performed on natural materials such as soils and bentonites. This procedure is good for characterizing interactions between cations and soils, but gives only broad information on retention mechanisms. Carbonates, oxides, hydroxides and organic compounds, which are present in natural materials, are known to fix cations as well as clays significantly (Benjamin and Leckie 1981; Trichet et al. 1987; Bruemmer et al. 1988; Liu et al. 1993; Rose and Bianchi-Mosquera 1993; Kanungo 1994; Lee et al. 1997). Consequently, to eliminate any possible contribution of other minerals during adsorption experiments, we used a purified clay (SPV Wyoming montmorillonite, Comptoir des minéraux, France). A sedimentation/centrifugation procedure was performed during 7 successive exchanges with 1 M NaCl solutions. The montmorillonite was later Ca-saturated by

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Table 1. Chemical analyses of the purified Ca-montmorillonite.

SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MgO (%)	FeO (%)	TiO_2 (%)	MnO (%)	CaO (%)	Na_2O (%)	K_2O (%)	P_2O_5 (%)	LOI (%)
52.63	18.42	3.09	2.17	2.78	0.13	0.005	2.31	0.023	0.016	0.05	17.30

LOI = Loss on Ignition.

7 exchanges with 1 *M* $CaCl_2$ solutions. The Ca-clay was then washed/dialyzed in deionized water until excess Cl^- was totally eliminated, (that is, undetected by the $AgNO_3$ test). The clay was then air-dried and powder-crushed. The X-ray diffraction (XRD) analysis showed that the clay was purified (without peaks of the impurities that were present in the natural material, for example, quartz and feldspar).

The chemical analysis of the purified Ca-montmorillonite is given in Table 1. The structural formula was deduced from this analysis:

$$Ca_{0.364}K_{0.003}Na_{0.006}[Si_{7.735}(Al, Fe(III))_{0.265}]$$

$$[(Al, Fe(III))_{3.268}Mg_{0.475}Fe(II)_{0.341}Ti_{0.014}Mn_{0.001}P_{0.006}]$$

$$O_{20}(OH)_4$$

The charge density deduced from this formula is 0.37 charge per half unit cell with about 0.26 originating from octahedral substitutions and 0.11 from tetrahedral substitutions. These values are in agreement with the literature (Xu and Harsh 1992).

The theoretical cation exchange capacity (CEC_{theor}) is 102.2 meq/100 g. This value is in agreement with the CEC determined using adsorption of an ethylenediamine complex of Cu (Bergaya and Vayer 1997), giving an experimental CEC of 100 ± 5 meq/100 g of calcined material.

Reagents

Analytical reagent grade NaCl and $CaCl_2 \cdot 2H_2O$ (PROLABO) were used to purify the clay and to put it in Ca form. Analytical reagent grade $Ca(NO_3)_2 \cdot 4H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$ (PROLABO) and $Cd(NO_3)_2 \cdot 4H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Pb(NO_3)_2$ (MERCK), were used to obtain the different aqueous solutions.

Exchange Procedures

The Ca^{2+}/M^{2+} exchange isotherms were performed at constant ionic strength ($I = 3 \times 10^{-2} M$), (M^{2+} being Cd, Co, Cu, Ni, Pb, Zn). Experimental solutions were obtained by mixing solutions of 10^{-2} *M* $M^{2+}(NO_3)_2$ with 10^{-2} *M* $Ca(NO_3)_2$. The M^{2+} initial concentrations increased from 10^{-5} to 10^{-2} *M*.

Each exchange experiment was carried out by adding 500 mg of purified Ca-montmorillonite to 200 mL of solution in a polypropylene centrifuge bottle at room temperature. Suspensions were shaken for 16 h (overnight). At the end of the experiments, the pH of the suspensions was systematically measured. After separation by centrifugation (4500 RPM during 30 min), 20 mL of solution were collected and filtered through 0.22-μm Millipore filters. The Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+} and Ca^{2+} concentrations were determined using atomic absorption spectrometry (AAS) both in equilibrium and initial solutions (Hitachi Z-8100 apparatus with a polarized Zeeman background correction device and a dual-purpose flame-furnace facility). All of the experiments were duplicated to check the reproducibility of data.

Data Analysis

As discussed previously, we proposed to apply the HSAB model given by Xu and Harsh (1990a, 1990b) to check the influence of cation electronegativity and softness on bivalent/bivalent exchange selectivity on clays.

For each metal, the Vanselow selectivity coefficient (K_v) was calculated (Equation [7]) and the log K_v values were plotted as a function of the molar fraction on the clay surface (N_M). The different plots were fitted to a polynomial function of N_M (Equation [8]). The equilibrium exchange constant K_{ex} was determined from this polynomial function by taking the standard state for $N_{Ca} = N_M = 0.5$. In this particular case, $K_{ex} = K_v^0$.

The HSAB model was then calculated by fitting the log K_v^0 values to the general equation proposed by Xu et Harsh (1990a) (Equation [1]).

Although electronegativities are relatively well known with limited variations between different references (Parr and Yang 1989; Nagle 1990), softness values are less certain (Misono et al. 1967; Robles and Bartolotti 1984; Yang and Parr 1985; Parr and Pearson 1983; Parr and Yang 1989). Misono's scale is mostly empirical, whereas Parr's scale is derived from theoretical quantities that have definite physical meaning and are correlated with molecular-orbital theory (Pearson 1986). Xu and Harsh (1990b, 1992) used the softness values given by Parr and Pearson (1983). These values were updated by Parr and Yang (1989), and minor differences appear in the revised scales. Misono's as well as Parr's softness values were tested to fit experimental results.

Coefficients depending on clay surface electronegativity (α) and softness (β), were determined from a 2-variable linear regression of Equation [1] with *y* intercept set to zero.

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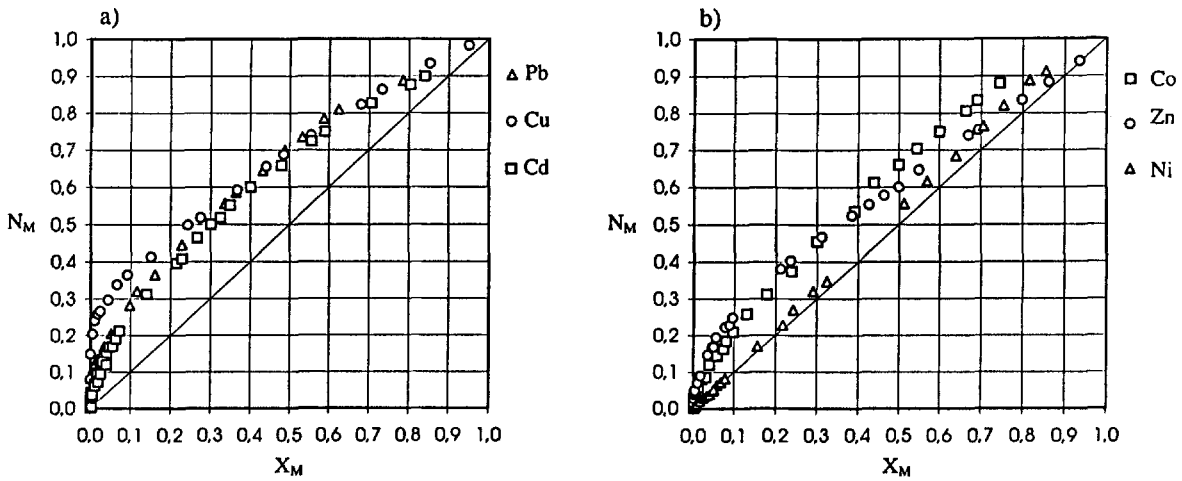


Figure 1. Exchange isotherms of a) Pb, Cu and Cd and b) Co, Ni and Zn on the Ca-montmorillonite of Wyoming (I = 0.03 M; T = 25 °C; P = 1 atm). X_M and N_M are respectively the molar fraction in solution and in clay.

RESULTS

Ca^{2+}/M^{2+} exchange isotherms for the purified Ca-montmorillonite, performed at I = 0.03 and 25 °C, are presented in Figure 1. On this plot, the diagonal line represents a nonselective exchange.

From the exchange isotherms, the metals can be separated into 3 classes as a function of their adsorption: 1) Ni, the less adsorbed cation, with an isotherm close to the nonselective isotherm, 2) Co and Zn, which present intermediate isotherms, 3) Cu, Pb and Cd, which present higher retention. Accordingly, the selectivity sequence is Cu ≅ Pb ≅ Cd > Co ≥ Zn > Ni.

It should be noted that adsorbed metal, as determined from the isotherms, may be fixed on different sites, that is: 1) planar charged sites (resulting from tetrahedral or octahedral substitutions) and 2) edge sites (resulting from the rupture of layers). As the experiments explored a limited pH range (4.8 to 5.5), it was impossible to investigate the pH dependence of metal adsorption and the possible contribution of edge sites as performed by Inskeep and Baham (1983), Schindler et al. (1987) or Gorgeon (1994).

Fitting Exchange Data to the HSAB Model

Vanselow selectivity coefficients were calculated from Equation [7] and fitted to a polynomial regression function (Equation [8]). Table 2 lists the ranges of X_M and N_M within which selectivity coefficients were fitted, the constants A_0 to A_4, the regression coefficients (R^2) and the K_v^0 values calculated from each regression with N_M = 0.5.

The log K_v^0 values are fitted to the general equation proposed by Xu et Harsh (Equation [1]). A first test revealed that it was not possible to obtain a linear regression with a correct significance when involving all 6 metals. Ni was identified as the factor inducing the poor fit when using Misono's softness values. Similarly, Ni and Co were found to cause the model to fail when using Parr's data. We decided to exclude the disruptive metals from model calculations; justifications are given in the Discussion section.

Table 2. Molar fraction of cations in solution (X_M) and in clay (N_M); coefficients in power series (A_0, A_1, A_2, . . .); regression coefficients (R^2); number of data used to calculate the regression and Vanselow selectivity coefficient (K_v^0) calculated for N_M = 0.5.

Ca → M	X_M range	N_M range	A_0	A_1	A_2	A_3	A_4	R^2	Number of data	K_v^0†
Ca → Cd	0.01 → 0.8	0.06 → 0.9	0.904	−2.177	2.485	−1.024	—	0.998	10	2.037
Ca → Co	0.01 → 0.7	0.06 → 0.8	0.870	−4.016	9.330	−8.632	2.667	0.996	8	1.914
Ca → Cu	0.006 → 0.7	0.2 → 0.8	3.357	−10.214	9.916	−2.762	—	0.990	12	2.421
Ca → Pb	0.02 → 0.8	0.1 → 0.9	1.145	−2.750	3.712	−1.668	—	0.990	9	3.090
Ca → Zn	0.01 → 0.7	0.07 → 0.7	0.969	−2.372	1.911	−0.398	—	0.995	10	1.656
Ca → Ni	0.008 → 0.8	0.006 → 0.9	−0.039	−0.094	1.546	−1.036	—	0.957	13	1.4825

† K_v^0 was obtained by setting N_M = 0.5 in the polynomial regression.

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Table 3. Application of Equation [1] to exchange data from isotherms, for whole metals or by omitting Ni and/or Co.

	Cations	α	β	R^2	|α/β|
Parr's softness values	All metals	−0.025	3.14	0.24	0.008
	Omit Ni	−0.020	4.14	0.51	0.005
	Omit Co	−0.030	3.16	0.39	0.009
	Omit Ni and Co	−0.025	4.39	0.99	0.006
Misono's softness values	All metals	0.027	0.34	0.73	0.081
	Omit Ni	0.021	0.33	0.83	0.066

Misono's scale and Parr's scale lead to large differences between calculated α and β values (Table 3); however, the conclusions (discussed later) concerning the relative contribution of covalent and electrostatic interactions deduced from the |α/β| ratios are similar. Consequently, we shall discuss only the results obtained using Parr's data, to be in agreement with Xu and Harsh calculations. The α and β values, the |α/β| ratios and regression coefficients (R^2) are listed in Table 3.

Models deduced from the regression are significant when Ni and Co are neglected. Log K_{ex} on the purified Ca-Montmorillonite, at I = 0.03 M, T = 25 °C and P = 1 atm is given by the relation:

$$\log K_{ex} = -0.025(\chi_M - \chi_{Ca}) + 4.39(S_M - S_{Ca}) \quad [11]$$

The influence of analytical errors on the determination of α and β, was estimated by a procedure involving 16 tests, as described below.

Considering analytical errors on q_M values, explained by the dilutions (1/10 or 1/100) required to analyze initial and final solutions in the range of N_M considered, the validity of the HSAB model was checked by following a procedure implicating the (log K_v^0)$_{max}$ and (log K_v^0)$_{min}$ values determined graphically from experimental data. The following procedure has been used:

1) For each metal, visual determination, on [log K_v = $f(N_M)$] plots, of the highest and lowest possible log K_v^0 values for N_M = 0.5.

2) Application of the general relation (Equation [1]) to all the possible groupings of log K_{vmax}^0 and log K_{vmin}^0 values. The number of possible groupings is: $2 + C_1^4 + C_2^4 + C_3^4 = 16$ (with $C_p^n = n!/p!(n-p)!$).

3) Linear regression for the 16 combinations, and determination of α and β.

4) Recalculation using Equation [1] of the respective log K_v^0 values (log $K_{vrecalculated}^0$).

5) Determination of the relative errors with respect to the "recalculated log K_v^0" values given by the model.

This operation allows average errors on the log K_v^0 and the α and β values to be calculated. In our opinion, these errors represent an accurate estimation of the influence of analytical errors on the model calculation, because their determination is based on the limit values of log K_v^0. Table 4 illustrates the influence of analytical errors on log K_v^0, α, β and |α/β| values. Considering the limit conditions involved to appreciate the influence of analytical errors, one may consider that the α and β values given by the model are significant. Actually, the log K_v^0 values deduced for polynomial regressions are clearly more precise than the log $K_{v\ max}^0$ and log $K_{v\ min}^0$ values determined graphically.

DISCUSSION

Figure 2 plots for each metal the Log $K_v^0 - [\alpha(\chi_M - \chi_{Ca})]$ as a function of the difference of softness $(S_M - S_{Ca})$ for the experimental data and the model. Ni and Co, as expected from calculations, deviate from the model prediction. Xu and Harsh (1990b) made a sim-

Table 4. Logarithms of the Vanselow selectivity coefficient calculated from Equation [8]; recalculated logarithms of the Vanselow selectivity coefficient from Equation [11] and average errors on the α, β and log K_v^0 values determined by the 16 tests procedure.

	Log K_v^0	(Log K_v^0)$_{recalculated}$	Error† ± σ (%)
Cd	0.309	0.305	6.01 ± 3.92
Cu	0.384	0.378	11.24 ± 6.68
Pb	0.490	0.488	9.11 ± 6.07
Zn	0.219	0.241	7.04 ± 4.06

α	Error† ± σ (%)	β	Error† ± σ (%)	|α/β|	Error† ± σ (%)
−0.0245	53.02 ± 32.64	4.3948	23.92 ± 15.63	0.0056	61.41 ± 26.82

† Average errors in the 16 tests procedure with respect to the α, β and log K_v^0 values recalculated by the model.

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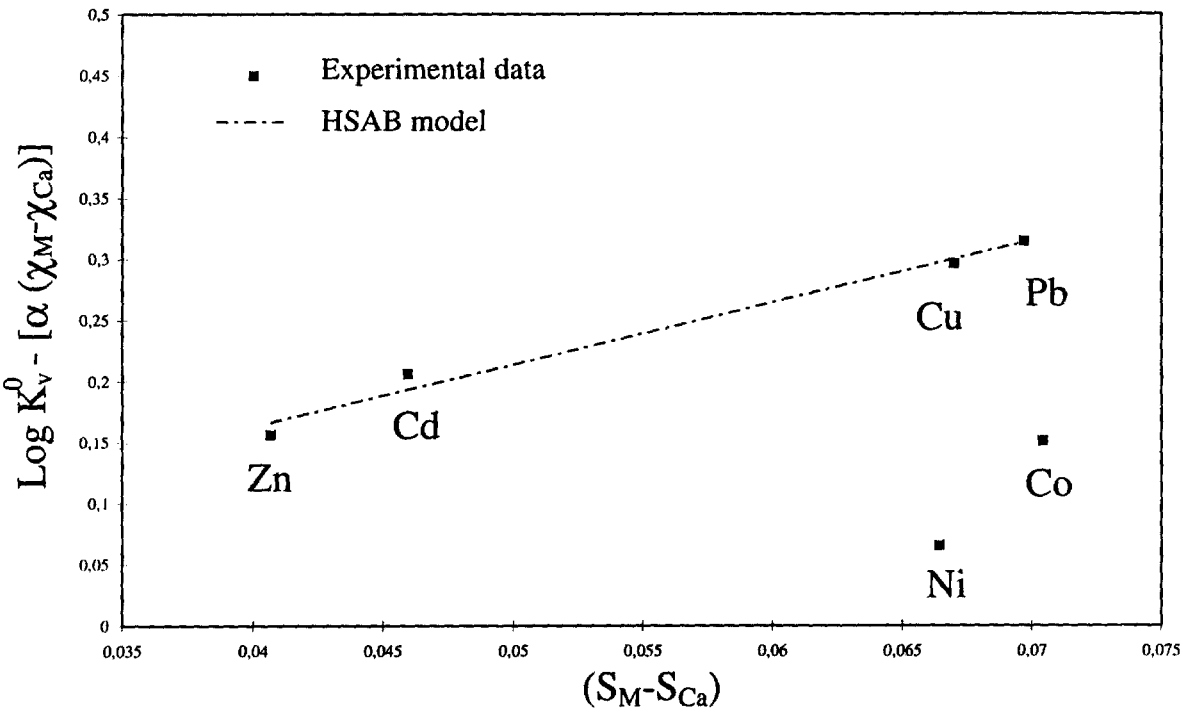


Figure 2. Illustration of the fit of the HSAB model with experimental data. The points represent data obtained from isotherms, the dashed line represents the HSAB model (Equation [11]). Ni and Co, which present a large deviation from the model, have been excluded from the calculation.

ilar observation for Ag^+ and Tl^+ selectivity on Wyoming montmorillonite, Arizona montmorillonite and Utah bentonite. These authors suggested that a negative deviation of log K_v^0 may be caused by a higher affinity of cations for water while a positive one will appear if the radius of the cation is smaller than expected (Xu and Harsh 1990b). The total deviation results from the sum of these 2 phenomena.

The negative deviation of Ni and Co may result from a stronger hydration of these cations. The hydration of ions is influenced by their ionic potential (I_p), (Sposito 1984; Langmuir 1997), an increasing ionic potential favoring the formation of outer-sphere complexes (hydrated cation), and increasing the importance of electrostatic interactions. Of the 6 studied metals, Ni and Co have the highest ionic potential (I_p = 2.90 and 3.08 respectively, radius data from CRC 1997) and tend to be more hydrated than the others. Their negative deviation from the "bivalent trend" could hence be explained by their higher hydration.

The influence of hydration on electronegativity and softness values would have to be investigated to proceed in the application of such models (Klopman 1968; Guse 1981; Makov 1995; Rashin and Honig 1985). Pearson (1997) showed that an acid-base reaction for the formation of a complex in water involves 4 acid-base interactions: 1) the interaction between the acid and water (which is considered both an acid or a base), 2) the interaction between the base and water, 3) the interaction between the acid and the base and 4) the interaction of water with itself, which is represented by a constant factor. The stability constant of the complex depends on the sum of these 4 interactions.

Although the subject of cation-water interactions in clay minerals has always attracted many researchers, the modeling of clay–water interactions is more recent and less data are available (Delville 1991; Skipper, Soper and McConnell 1991; Skipper, Refson and McConnell 1991). A recent review has been published on clay–water interface by Güven (1992).

|α/β| Value as Indicator of the Nature of Cation-Surface Interactions

As said previously, Xu and Harsh (1990b) use |α/β| ratio as an indicator of the relative influence of electrostatic and covalent interactions on metal selectivity.

For each exchange, it is possible to calculate the theoretical |α/β| value for which the contribution on log K_v^0 of the electronegativity term and the softness term, are equal, that is: $|\alpha/\beta|_{0.5}$. Table 5 summarizes the $\alpha_{0.5}$, $\beta_{0.5}$, $|\alpha/\beta|_{0.5}$ values and the respective percentage of electronegativity and softness terms on log K_v^0 values, determined for each exchange.

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Table 5. Theoretical $\alpha_{0.5}$, $\beta_{0.5}$ and $|\alpha/\beta|_{0.5}$ values, for which the contribution on log K_v^0 of the electonegativity and softness terms are equal and respective contribution of electronegativity and softness terms on log K_v^0 values.

	$\alpha_{0.5}$	$\beta_{0.5}$	$\lvert\alpha/\beta\rvert_{0.5}$	Electrostatic interactions	Covalent interactions
Cd	−0.036	3.32	0.011	33.7	66.3
Cu	−0.066	2.70	0.025	18.5	81.5
Pb	−0.031	3.64	0.009	39.7	60.3
Zn	−0.047	2.97	0.016	25.9	74.1

Table 6. The α, β, $|\alpha/\beta|$ and regression coefficient (R^2) values derived from Equation [1] for different molar fractions on clay (N_M).

N_M	α	β	R^2	$\lvert\alpha/\beta\rvert$
0.05	0.068	37.12	0.81	0.002
0.08	0.144	38.90	0.86	0.004
0.1	0.203	39.76	0.91	0.005
0.2	0.166	28.75	0.96	0.006
0.3	0.095	18.58	0.98	0.006
0.4	0.010	9.12	0.98	0.001
0.6	−0.038	2.02	0.91	−0.019

For all the metals, the $|\alpha/\beta|_{0.5}$ values are higher than the $|\alpha/\beta|$ value deduced from the model. This indicates that softness is the dominant factor determining log K_v^0 and hence that covalent interactions prevail on electrostatic interactions for determining the selectivity sequence. This result is confirmed for each metal by the respective contribution on log K_v^0 of electrostatic and covalent interactions.

Eventually, it is possible to establish, using Parr's as well as Misono's softness values, a cation sequence following the electrostatic and covalent contributions to selectivity. This sequence is:

Increasing covalent interactions →

$$Pb < Cd < Zn < Cu$$

← Increasing electrostatic interactions

To be adsorbed in the clay interlayer, a bivalent cation must compensate 2 negative charges. Accordingly, the cation will be farther from each charge than is a monovalent cation, compensating only 1. However our values are similar to those obtained with monovalent cations by Xu and Harsh (1990b) on different montmorillonites. As alkali cations are considered harder than bivalent transition elements or heavy metals (Sullivan 1977; Sposito 1984), one may assume that the greater average separation of bivalent cations from the surface negative charges is compensated by their higher softness.

Representativity of the HSAB Model

The general equation (Equation [1]) established by Xu and Harsh (1990a) allows a selectivity model to be determined. It seems important to discuss its physical meaning. The fundamental contribution of this model is to take both electrostatic and covalent interactions into account. However, the model is based on 2 assumptions which, in our opinion, have to be discussed.

1) The α and β coefficients characterize the surface without distinction of different sites. This assumption may be valid in the case of oxides or ion resin surfaces, on which all the charge originates on the surface oxygens, but is debatable when clay surfaces are involved. Crystal-chemical arguments support this view through heterogeneity of charge distribution at clay surface, in relation to the irregular character of tetrahedral and octahedral substitutions (Fripiat et al. 1965; Schultess and Huang 1990; Gorgeon 1994). Moreover, different authors have suggested an heterogeneity in site type with differences of bonding energy between planar and edge sites (Peigneur et al. 1975; Inskeep and Baham 1983). The most energetically favorable sites would be occupied first (Inskeep and Baham 1983). More recently, quantum chemistry studies on phyllosilicates by Bleam (1990a, 1990b, 1993), presenting simulations of different clay surfaces, show local perturbations of the electrostatic potential, generated by tetrahedral or octahedral substitutions. The elevated energetic variability supports the hypothesis of heterogeneous planar sites.

2) Xu and Harsh choose $N_M = 0.5$ as a standard state, basing the model on the selectivity coefficient determined for this particular value. This implies that an entire exchange process can be represented by only 1 K_v value. Such an assumption is too restrictive, because extreme values are neglected by the model. The selectivity coefficient decreases as a function of cation concentration over the range of N_M (Wada and Kakuto 1980; Godfrin et al. 1989; Maza-Rodriguez et al. 1992; Staunton and Roubaud 1997). In the trace concentrations region ($N_M < 0.1$), K_v can reach very high values, which are not reflected by the model.

To complement the model empirically, in addition to calculation at $N_M = 0.5$, we computed α and β coefficients for other N_M values (N_M = 0.05, 0.08, 0.1, 0.2, 0.3, 0.4 and 0.6). A good fit is obtained for Cd, Cu, Pb and Zn for each regression. The different values of α, β and α/β obtained are listed in Table 6 and plotted as a function of N_M in Figure 3. Such a plot illustrates the dependence of selectivity on molar fraction. One may notice that the ratio α/β reaches a maximum values in the range $0.1 < N_M < 0.3$, suggesting that the contribution of electrostatic interactions on selectivity is maximum in this range of molar fractions. Conversely, the contribution of covalent bonding appears maximum when $N_M < 0.1$ and $N_M > 0.3$.

Polynomial regressions in the form were calculated to obtain α and β:

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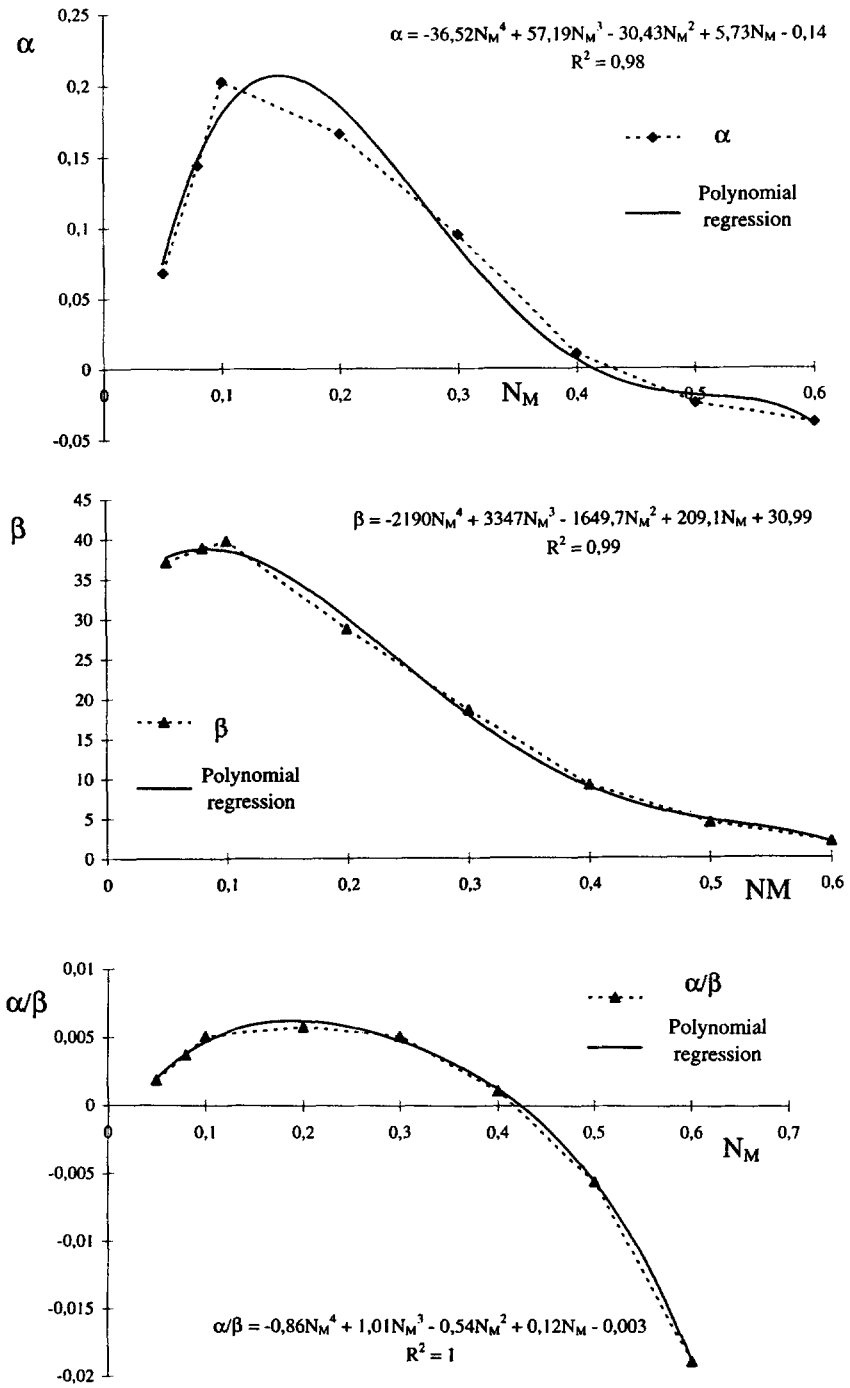


Figure 3. Plot of α, β and |α/β| as a function of the molar fraction in clay (N_M). The large variability of α and β illustrates the dependence of the Vanselow selectivity coefficient on N_M.

$$\alpha = (a_0 + a_1N_M + a_2N_M^2 + a_3N_M^3 + \ldots) \quad [12]$$

and:

$$\beta = (b_0 + b_1N_M + b_2N_M^2 + b_3N_M^3 + \ldots) \quad [13]$$

where a_0, a_1, a_2, a_3 and b_0, b_1, b_2, b_3 are constants. One may notice that these relations are empirical as they involve the selectivity coefficient (K_v) instead of the equilibrium contant (K_v^0).

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As a result, the variation of the logarithm of Vanselow selectivity coefficient for Cd, Cu, Pb and Zn can be described by the equation:

$$\log K_v = (-0.14 + 5.73N_M - 30.43N_M^2 + 57.19N_M^3 - 36.52N_M^4)(\chi_M - \chi_{Ca}) + (30.99 + 209.1N_M - 1649.7N_M^2 + 3347N_M^3 - 2190N_M^4)(S_M - S_{Ca}) \quad [14]$$

This relation, associated with the HSAB model equation, could be helpful to represent, with a higher accuracy, the selectivity at a clay surface in the trace region.

CONCLUSIONS

The HSAB model given by Xu and Harsh (1990a, 1990b) has been applied to bivalent cation exchange on a purified Ca-montmorillonite. For given ionic strength (I = 0.03 M), temperature (T = 25 °C) and pressure (P = 1 atm), the selectivity of bivalent exchanges has been predicted as a function of their electronegativity and softness, for 4 of the 6 studied metals (Cd, Cu, Pb, Zn) when using Parr's softness values (Equation [11]). Using Misono's softness values, it is possible to integrate Co in the model, Ni being always deviating. Nevertheless, we focused on the model established using Parr's softness values because of its higher physical significance.

The failure of Ni and Co to accommodate the HSAB model has been interpreted as a consequence of a higher hydration (Xu and Harsh 1990b). A better knowledge of the electronegativity and softness of metals with hydroxy-complexes would permit hydrolyzed cations to be integrated into the model.

The relative contribution of electrostatic and covalent interactions is determined by the fitting parameters α and β of the HSAB model. These contributions have been studied with respect to the hypothetical $|\alpha/\beta|_{0.5}$ ratio corresponding to an equivalent contribution of electrostatic and covalent bonding, and to the respective contribution of electronegativity and softness terms on log K_v^0 values. Data show a higher contribution of the latter with respect to the former.

Theoretical calculations are performed with N_M = 0.5. To increase the representativity of the model for the small N_M values, we propose to associate to the HSAB model an empirical equation describing the variation of the selectivity coefficient as a function of the molar fraction on clay.

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