

ALKALI CATION SELECTIVITY AND SURFACE CHARGE OF 2:1 CLAY MINERALS

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Abstract—A critical demand in environmental modeling and a desirable but elusive goal of research on the ion exchange properties of the charged solid surface has been to determine the selectivity coefficient from fundamental properties of the ions and surface. We developed a Hard and Soft Acid and Base (HSAB) Model to describe exchangeable cation selectivity on solid surfaces. Our previous work has shown that the model quantitatively describes alkali cation exchange on clay minerals in terms of the absolute electronegativity and softness of the exchangeable cations and two fitting parameters: α and β . This study was conducted to determine the relationship between α and β and surface charge characteristics of 2:1 clays. The layer charge and cation selectivity of seven smectites and one vermiculite were used. The regression of $\log K_{\text{v}}^{\circ}$ against four combinations of charge properties was performed and the appropriate relationship between α , β , and surface charge was selected based on both statistical criteria (R^2) and their consistency with the assumptions of the HSAB model. The selected model was then cross-validated using separate cation exchange data from the literature. It was found that α and β are linearly related to the amount of charge arising from mineral tetrahedral and octahedral sites, respectively. These results make it possible to predict the alkali cation selectivity of 2:1 clay minerals from their chemical composition data and the alkali cation properties.

Key Words—Hard/soft acid/base model, Ion exchange, Isomorphic substitution, Layer charge, Lewis acid, Lewis base, Smectite, Surface complexation, Vermiculite.

INTRODUCTION

Cation exchange, a major process responsible for the retention of mineral nutrients and toxic contaminants in the vadose zone, affects both plant growth and water quality. Although it is well-known that the cation-selective behavior of clay minerals is the consequence of a ternary interaction between cation, water, and the mineral surface (Sposito, 1984), we do not yet completely know (1) the relationship between cation selectivity and cation properties on a given surface, or (2) the relationship between cation selectivity and surface properties.

To provide a link between the cation selectivity and the properties of both cations and surfaces, Xu and Harsh (1990a) recently developed a quantitative explanation based on the Hard and Soft Acid and Base (HSAB) Principle. The HSAB Principle was first introduced by Pearson (1963, 1968) to generalize various types of ion-ligand interactions. According to this concept, cations and ligands are generally Lewis acids and bases, respectively, of different softness. For example, monovalent metal cations, Li, Na, K, Rb, and Cs are hard acids, while Ag and Tl are soft acids. The OH⁻ and H₂O are hard bases, whereas the thiol group (RS⁻) is a soft base. The HSAB Principle states that a hard

acid prefers to coordinate with a hard base, whereas a soft acid prefers to coordinate with a soft base.

Based on the HSAB principle, Misono *et al.* (1967) developed a dual parameter equation which predicts the stability constants of solution complexes from so-called “hardness” and “softness” of both cations and ligands. We extended this approach to surface exchange reactions with two basic assumptions (Xu and Harsh, 1990a). The first assumption is that negatively-charged surface functional groups can be regarded as ligands. The second assumption is that the stabilities of cation-surface complexes are responsible for differences in cation selectivity (Sposito, 1984). We proposed the following equation (the HSAB model) for monovalent cation exchange (Xu and Harsh, 1990a):

$$\log K_{\text{v}}^{\circ} = \alpha(\chi_{\text{M}} - \chi_{\text{ref}}) + \beta(S_{\text{M}} - S_{\text{ref}}) \quad (1)$$

where $\log K_{\text{v}}^{\circ}$ is the logarithm of Vanselow selectivity at 0.5 mole fraction; χ and S refer to the absolute electronegativity and the absolute softness of the cations, respectively; and the subscripts “M” and “ref” refer to replacing cation and reference cation, respectively. The coefficients α and β are two fitting parameters related to surface properties. The success in applying this model to the alkali cation selectivity on smectites, vermiculite, Si gel, Zr oxide, and cation exchange resins (Xu and Harsh, 1990b) suggests that the selectivity of various monovalent cations on a given surface is determined by the absolute electronegativity and softness of exchangeable cations.

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Table 1. The origin and the absolute values of layer charge of the 2:1 minerals studied.

Minerals	Origin	Data sources ¹	Negative charge			Average charge	
			Tetrah.	Octah.	Total	Tetrah.	Octah.
(per half unit cell)							
<i>Smectites</i>							
Arizona (Cheto SAz-1) ²	Apache, AZ	26	0.07	0.48	0.54	0.07	0.47
		12	0.07	0.50	0.57		
		12	0.07	0.42	0.49		
		16	0.07	0.36	0.42		
		21	0.07	0.48	0.54		
		23	0.00	0.56	0.56		
Bayard Belle Fourche	Bayard, NM Belle Fourche, SD	24	0.09	0.52	0.61	0.00	0.43
		26	0.00	0.43	0.43		
		24	0.14	0.23	0.37		
		12	0.14	0.24	0.38		
		16	0.06	0.25	0.29		
		22	0.09	0.21	0.30		
Cameron ² Camp Berteau ²	Cameron, AZ Camp Berteau, Morrocco	21	0.15	0.23	0.38	0.19	0.32
		21	0.10	0.24	0.34		
		5	0.06	0.37	0.43		
		16	0.00	0.34	0.34		
		12	0.08	0.36	0.44		
		6	0.00	0.34	0.34		
Chambers ²	Chambers, AZ	4	0.00	0.38	0.38	0.05	0.36
		5	0.15	0.44	0.59		
		25	0.07	0.36	0.43		
		11	0.10	0.37	0.47		
		9	0.18	0.37	0.55		
		12	0.02	0.46	0.48		
Otay	San Diego, CA	21	0.11	0.40	0.51	0.11	0.38
		21	0.11	0.38	0.49		
		7	0.14	0.38	0.52		
		19	0.01	0.48	0.49		
		24	0.14	0.45	0.59		
		5	0.05	0.54	0.59		
Polkville	Smith, MS	8	0.08	0.53	0.61	0.04	0.49
		21	0.02	0.60	0.62		
		21	0.02	0.46	0.48		
		24	0.06	0.38	0.44		
Utah bentonite ²	Plymouth, UT	12	0.05	0.35	0.40	0.05	0.36
		12	0.18	0.32	0.50		
Upton Wyoming (SWy-1) ²	Upton, WY Crook, WY	21	0.20	0.26	0.46	0.19	0.29
		11	0.14	0.25	0.39		
Hectorite	Hector, CA	26	0.11	0.22	0.33	0.14	0.25
		24	0.10	0.21	0.31		
		3	0.11	0.20	0.31		
		19	0.11	0.22	0.33		
		12	0.13	0.20	0.33		
		12	0.09	0.21	0.30		
		12	0.06	0.24	0.30		
		2	0.08	0.26	0.34		
		19	0.03	0.28	0.31		
		1	0.00	0.31	0.31		
		0.11	0.21	0.31	0.11		
<i>Vermiculites</i>							
Llano vermiculite ²	Llano, TX	10	0.98	0.00	0.97	0.85	0.00
		14	0.75	0.00	0.75		
		20	0.86	0.00	0.86		
		20	0.82	0.00	0.82		
		23	0.80	0.00	0.80		
Transvaal	South Africa	13	0.62	0.00	0.62	0.62	0.00

¹ Data sources are (1) Ames *et al.*, 1958; (2) Brindley, 1980; (3) Brindley and Ertem, 1971; (4) Calvet and Prost, 1971; (5) Cicel and Machajdik, 1981; (6) Durand *et al.*, 1972; (7) Earley *et al.*, 1953; (8) Eberl *et al.*, 1986; (9) Faucher and Thomas,

As stated by Eberl (1980), "one would like to predict the sorptive properties of a clay for all ions simply by characterizing the clay." Several attempts have been made to determine the relationship between cation selectivity and surface properties (Laudelout *et al.*, 1968; Maes and Cremers, 1977, 1978; Eberl, 1980), but none has been totally successful. For example, Maes and Cremers (1978) showed a linear relationship between the standard free energy of Na-Cs exchange and the surface charge density on Otay, Bayard, and the untreated and the charge-reduced Camp Berteau montmorillonites. However, the linear relationship held only for clays with predominantly octahedral substitution; a negative deviation from linearity was observed when tetrahedral substitution was significant. In addition, it is not known if the selectivity of exchangeable cations besides Na and Cs will have the same dependence on surface charge density.

The two fitting parameters, α and β , in the HSAB model are cation-independent constants and have been shown to be related only to surface properties at a given pH, ionic strength, temperature, and pressure (Xu and Harsh, 1990a, 1990b). The purpose of the present study is to determine the relationship between α and β and the surface charge properties of 2:1 clay minerals to obtain a selectivity model based on parameters that may be obtained independently from exchange data. The resulting model links the cation selectivity with both cation and surface properties.

MATERIALS AND METHODS

The origin and layer charge of the 2:1 clay minerals used in this study are listed in Table 1. In this following section we describe how the clay was prepared, how cation selectivity and layer charge were obtained, which model was tested against the measured selectivity and surface charge, and how the model was cross-validated.

Clay preparation

The 0.2- to 0.5- μm size-fraction of Na-saturated clay was prepared following the procedure described by Xu and Harsh (1990b), except that the clay suspension was pretreated with alkaline NaCl and acidic NaCl solutions to remove free Si oxides and free aluminum oxides, respectively. Briefly, 10 g clay were suspended in 1 liter 1 M NaCl and the appropriate amount of 1 M NaOH was added to bring the suspension pH to 10. The suspension then was shaken for 8 h before the clay was separated from the solution by centrifugation. This procedure was repeated three more times. After the

last treatment, the clay was washed with 1 M NaCl until the pH of the supernatant was the same as that of the 1 M NaCl solution.

The treated clay was resuspended in 1 liter 1 M NaCl solution. The suspension pH was adjusted to 4 with 1 M HCl and the suspension was shaken for 8 h before the clay was separated from the solution by centrifugation. This procedure was also repeated three more times.

After the last acid treatment, the clay was washed with deionized water until the clay was well-dispersed and the electrical conductivity of the supernatant solution was less than 0.2 dS m^{-1} . The 0.2- to 0.5- μm size fraction was separated and collected by centrifugation (Jackson, 1973). It was then washed with 1 M NaCl three more times and stored in 1 M NaCl solution.

Layer charge

To determine the layer charge of Wyoming (SWy-1), Arizona (SAz-1), and Cameron montmorillonites, the Na-saturated clay was digested in a closed vessel by HF (Lim and Jackson, 1982). The content of silica was determined by the molybdenum-blue method (Hallmark *et al.*, 1982), and Al, Ca, Mg, Na, K, Mn, and total Fe were determined by atomic absorption spectrophotometry. Ferrous iron content was determined colorimetrically (Stucki, 1981) and Fe(III) content was assumed to be the difference between the total Fe and Fe(II) contents.

The layer charge of SWy-1, SAz-1, and Cameron montmorillonite was calculated from the total element analysis. The assumptions made for this calculation are (1) all Si, Al, Fe, Mn, and Mg are structural elements of the clay and Na is an exchangeable cation; and (2) only Al substituted for Si in the tetrahedral layer. Calcium was not detected in any samples verifying that the clay was actually Na-saturated; however, the total element analysis revealed 0.7 mole kg^{-1} K in the Na-saturated Cameron clay sample. X-ray diffraction showed that K-feldspar was the only significant potassium-bearing mineral in that sample. Layer charge was then calculated using the total element analysis data corrected for this contaminant phase.

Layer charge for the other minerals was obtained from the literature. For Upton Wyoming and Chambers montmorillonites, both exchange data and chemical analysis were obtained from Gast (1972). For others, the tetrahedral and octahedral charges were calculated from the total elemental analysis data from

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1954; (10) Foster, 1963; (11) Gast, 1972; (12) Grim and Guven, 1978; (13) Kittrick, 1973; (14) Laird, 1987; (15) Lagaly, 1982; (16) Mattigod and Sposito, 1978; (17) Merriam and Thomas, 1956; (18) Norrish, 1973; (19) Senkayi *et al.*, 1985; (20) Shirozu and Bailey, 1966; (21) Schultz, 1969; (22) Sterte and Shabtai, 1987; (23) Van Olphen and Fripiat, 1979; (24) Weaver and Pollard, 1973; (25) Weir, 1965; (26) this study.

² These are the minerals used to develop Eqs. (3) and (5).

literature. If more than one value existed for a mineral, the average charge value was calculated from the data that fit within the 95% confidence interval (Table 1).

Cation selectivity

Exchange isotherms for all four pairs of cations (Na-Li, Na-K, Na-Rb, and Na-Cs) on Cameron montmorillonite were determined following the procedure described in a previous paper (Xu and Harsh, 1990b). Briefly, after the Na-saturated clay was equilibrated with an appropriate mixture of 0.01 M NaCl and 0.01 M MCl (M = alkali cation) at 298 K and 1 atm, the solution and clay were separated by centrifugation. The cations were extracted with 1 M NH₄OAc. The concentrations of the exchange and reference (Na) cations in the equilibrating solution and NH₄OAc extract were measured by flame emission spectroscopy. The Vanselow selectivity coefficients (K_v) were calculated (Sposito *et al.*, 1981) and $\log K_v$ was fit to a polynomial function of the mole fraction of exchangeable cation. The $\log K_v$ at 0.5 mole fraction ($\log K_v^0$) was determined by interpolation (Xu and Harsh, 1990b). The measured $\log K_v^0$ is -0.12, 0.63, 1.17, and 1.60 for Na → Li (Na replaced by Li), Na → K, Na → Rb, and Na → Cs, respectively.

The K_v^0 for SWy-1, SAz-1, and Llano vermiculite (VTx-1) were obtained from a previous paper by the same authors (Xu and Harsh, 1990b) and those for Upton Wyoming montmorillonite, Chambers montmorillonite from Gast (1972), and Camp Berceau montmorillonite from Martin and Laudelout (1963) were obtained from the exchange isotherms determined at the same ionic strength (0.01 M), temperature (298 K), and pressure (1 atm) as described above. The K_v^0 for Utah bentonite from Krishnamoorthy and Overstreet (1949) was determined at the same temperature and pressure as above but at a slightly smaller ionic strength (0.007 M).

Model development

According to the chemical suppositions of the HSAB model, the absolute electronegativity and softness of the cations and surface determines the stability of surface coordination complexes and the selectivity differences among cations (Xu and Harsh, 1990b). For a cation (e.g., M^{z+}), the absolute electronegativity and the absolute softness can be calculated from its ionization potential (I) [$\chi = (I_{z+1} + I_z)/2$ and $S = 2/(I_{z+1} - I_z)$] (Pearson, 1987)]. No general model exists for surfaces.

Qualitatively, we might expect that electrostatic interactions depend on the total amount of fixed charge as well as the location of the fixed charge (octahedral vs tetrahedral layer charge). We might also expect that the softness of a surface will depend on the location of the charge. For example, relative to tetrahedral charge, the charge arising from the octahedral layer will be

more de-localized on the surface, allowing more polarization of surface oxygens involved in coordination (Sposito, 1984). Therefore, a surface with predominant octahedral charge should be softer than one with predominant tetrahedral charge.

Given these qualitative assumptions, α and β are regarded as functions of the charge properties. Beginning with the simplest possibility that α and β may be simple linear functions of surface charge parameters, we attempted to obtain these parameters from linear regression with the following equation:

$$\log K_v^0 = (a_0 + a_1 V_1 + a_2 V_2)(\chi_M - \chi_{ref}) + (b_0 + b_1 V_1 + b_2 V_2)(S_M - S_{ref}) \quad (2)$$

where a_0 , a_1 , a_2 , b_0 , b_1 and b_2 are constants. The following four combinations of surface charge variables (V_1 and V_2) were tested:

- (1) V_1 = the absolute value of total layer charge per half unit cell (ϵ_{to}), no V_2 ;
- (2) $V_1 = \epsilon_{to}$, V_2 = the octahedral charge fraction (F_{oc});
- (3) V_1 = the absolute value of tetrahedral charge per half unit cell (ϵ_{te}), V_2 = the absolute value of octahedral charge per half unit cell (ϵ_{oc});
- (4) V_1 = the tetrahedral charge fraction (f_{te}), $V_2 = f_{oc}$.

We used eight binary exchange data sets on minerals specified in Table 1 to obtain the constants defined in Eq. (2).

Cross validation of the model

To validate the chosen model, we used data sets from 11 different clay minerals for which selectivity coefficients had been obtained for one or more alkali metal ion pairs. These data sets were completely independent from those used to develop the model. The experimental temperature, pressure and ionic strength are the same as those for model development (25°C, 1 atm, and 0.01 M, respectively) with the following exceptions. The ionic strength for Na → Rb on Utah bentonite is 0.009 M (Kunishi and Heald, 1968). The ionic strength for Na → K, Na → Rb, and Na → Cs on attapulgite is 0.014 M (Marshall and Garcia, 1959). The ionic strength for Na → K on both Utah bentonite and Belle Fourche montmorillonite is between 0.02 and 0.001 M (Tabikh *et al.*, 1960).

RESULTS AND DISCUSSION

α , β and layer charge

The regression of $\log K_v^0$ against each combination of variables is listed in Table 2. Table 2 indicates that the model which has only one independent variable, ϵ_{to} , has the smallest R^2 value. An F-test showed that adding f_{oc} into the model significantly improved the fit of the model to the data. This suggests a model of ϵ_{to} alone is not as good as a two-variable model.

All of the two-variable models fit well to data at a

Table 2. Summary of regression analyses of Eq. (2).

		$\log K^{\circ} = (a_0 + a_1V_1 + a_2V_2)(\chi_M - \chi_{ref}) + (b_0 + b_1V_1 + b_2V_2)(S_M - S_{ref})$						
V_1	V_2	a_0	a_1	a_2	b_0	b_1	b_2	R^2 (d.f.) ¹
ϵ_{to}		0.193	-0.364		68.8	-83.3		0.812 (40)
ϵ_{to}	f_{oc}	-0.077	-0.060	0.189	-43.0	41.8	78.3	0.930 (40)
ϵ_{te}	ϵ_{oc}	0.012	-0.160	0.121	-4.22	-2.16	112	0.936 (40)
f_{te}	f_{oc}	-0.244	0.144	0.325	-3042	3040	3089	0.903 (40)

¹ d.f. refers to degree of freedom.

level of significance <0.001 (Table 2). We chose the ϵ_{te} and ϵ_{oc} as the independent variables for further modeling because the resulting model had the largest R^2 value and for their consistency with the HSAB theory which is discussed later. Now we can express α and β in terms of the $\epsilon_{te} = \epsilon_{oc}$:

$$\alpha = 0.012 - 0.160 \epsilon_{te} + 0.121 \epsilon_{oc} \quad (3)$$

$$\beta = -4.22 - 2.156 \epsilon_{te} + 112 \epsilon_{oc} \quad (4)$$

Eq. (4) indicates that the tetrahedral charge, relative to the octahedral charge, had a very small influence on β . Statistical analysis showed that β could be equally well obtained with only one parameter, ϵ_{oc} , as follows:

$$\beta = -5.86 + 116 \epsilon_{oc} \quad (5)$$

The simple relation between ϵ_{oc} and β is represented graphically in Figure 1.

Eq. (3) indicates that tetrahedral and octahedral charge are both important in determining α . In the HSAB model, $\alpha(\chi_M - \chi_{ref})$ accounts for the contribution of "purely" electrostatic interactions to the cation selectivity (Xu and Harsh, 1990a, 1990b). The dependence of α on both types of charge indicates that both tetrahedral and octahedral sites influence the strength of electrostatic interactions between the surface and cations. According to Eq. (3), increasing ϵ_{te} will increase the electrostatic contribution to K° when $\chi_M - \chi_{ref} < 0$ (e.g., a cation replaced by another cation with larger dehydrated radius, such as Na replaced by Cs). Eq. (3) states that the more easily dehydrated cation's electrostatic interaction with the surface will increase as tetrahedral charges increase. This is consistent with purely electrostatic models of ion exchange (e.g., Eberl, 1980).

On the other hand, increasing ϵ_{oc} makes a positive contribution to α and lowers $\log K^{\circ}$ when $\chi_M - \chi_{ref} < 0$, implying that the difference in dehydrated radius becomes the more important factor in determining cation selectivity as octahedral charge increases. The difference in the influence of tetrahedral charge from that of octahedral charge is related to the fact that water molecules form stronger hydrogen bonds with the surface oxygen atoms at tetrahedral sites and are less easily displaced than at sites receiving their charge from octahedral substitution (Doner and Mortland, 1971; Farmer and Russell, 1971; Cariati *et al.*, 1983). Intervening water molecules preclude the formation of inner

sphere complexes and, hence, the participation of covalent bonding. In addition, increasing ϵ_{te} makes the surface harder and increases the electrostatic component of bonding; whereas increasing ϵ_{oc} makes the surface softer and decreases the electrostatic component of bonding.

In the HSAB model, $\beta(S_M - S_{ref})$ accounts for the contribution of covalent bonding to cation selectivity. The coefficient for ϵ_{oc} is positive in Eq. (5) because increasing the number of softer (i.e., octahedral) sites results in greater covalent character in the cation-surface oxygen bond. The fact that β is not a function of tetrahedral charge is entirely consistent with our previous supposition that inner sphere complexes with covalent character are not generally formed at sites of tetrahedral substitution (Xu and Harsh, 1990a, 1990b). This is mainly due to the high localization of the charge and low polarizability of the surface oxygen atoms at these sites (Sposito, 1984).

Cross validation

In Figure 2, we plotted $\log K^{\circ}$ s calculated from χ and S and surface charge variables according to Eqs. (1), (3), and (5) [$\log K^{\circ}$ (Predicted)] against their measured values [$\log K^{\circ}$ (Measured)]. A regression analysis gives:

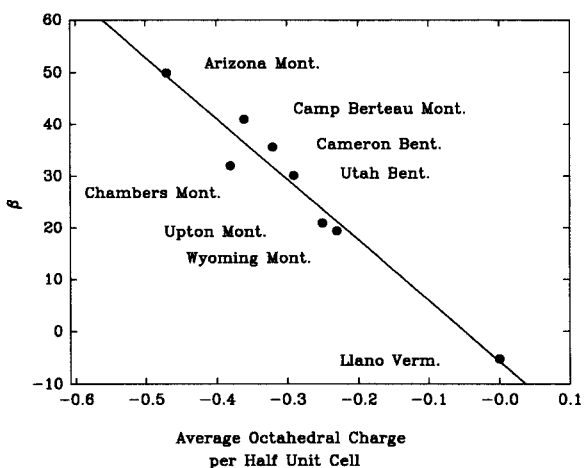


Figure 1. The dependence of β on the negative octahedral charge.

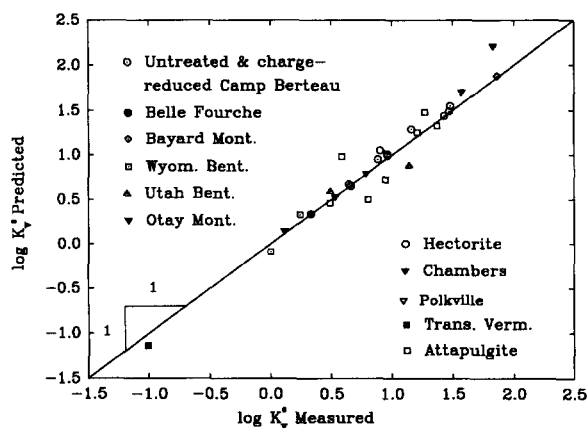


Figure 2. The comparison of the measured $\log K_v^o$ with the $\log K_v^o$ predicted from the amount of tetrahedral and octahedral charge for the following exchange reactions (with the source of exchange data in parentheses). Attapulgitte: Na \rightarrow K (Na replaced by K), Na \rightarrow Rb, Na \rightarrow Cs (Marshall and Garcia, 1959; Merriam and Thomas, 1956); Belle Fourche mont.: Na \rightarrow K (Shainberg *et al.*, 1987); Bayard mont.: Na \rightarrow Cs (Eliason, 1966); untreated and charge-reduced Camp Berteau mont.: Na-Cs (Maes and Cremers, 1978); Chambers mont.: Na \rightarrow Cs (Cremers and Thomas, 1968) and Li \rightarrow Na (Gast and Klobe, 1971); hectorite: Na \rightarrow Cs (Maes and Cremers, 1978); Otay mont.: Na \rightarrow K (Shainberg *et al.*, 1987) and Na \rightarrow Cs (Maes and Cremers, 1978); Polkville mont.: Na \rightarrow K (Shainberg *et al.*, 1987); Transvaal vermiculite: Na \rightarrow Li (Gast and Klobe, 1971); Utah bentonite: Na \rightarrow K (Tabikh *et al.*, 1959) and Na \rightarrow Rb (Kunishi and Heald, 1968); Upton mont.: Na \rightarrow K (Shainberg *et al.*, 1987); Wyoming bentonite: Na \rightarrow Li (Tabikh *et al.*, 1960).

$$\log K_v^o (\text{Predicted}) = 0.005 + 1.037 \log K_v^o (\text{Measured})$$

$$R^2 = 0.943 \quad (n = 34) \quad (6)$$

with the 95% confidence interval of its intercept as 0.005 ± 0.310 . Forcing the intercept to zero, we obtain a slope of 1.053 with a 95% confidence interval from 0.989 to 1.095; therefore, at the 95% confidence level, the slope is not different from 1 and the predicted values from the two-variable model with ϵ_{te} and ϵ_{oc} do not differ statistically from the measured values.

When the same was done for the model with ϵ_{to} and f_{oc} , we found the predicted values were more scattered ($R^2 = 0.910$) and the model overestimated the $\log K_v^o$ by 16%. And the model with f_{te} and f_{oc} was even worse ($R^2 = 0.689$, overestimating $\log K_v^o$ by 29%). This result confirmed that the model with ϵ_{te} and ϵ_{oc} as variables is the best one among the models tested.

The highest $\log K_v^o$ values in Figure 2 were obtained with Na-Cs exchange on Bayard and Otay montmorillonites. Compared with exchange of Na against other alkali cations, Na-Cs exchange produces the largest difference in the softness term of Eq. (1) ($S_{Cs} - S_{Na}$). The Bayard and Otay clays have the highest values of ϵ_{oc} and highest β among minerals tested. The high $\log K_v^o$ is, thus, consistent with the Principle of Hard and Soft Acids and Bases (Pearson, 1963, 1968) which states

that soft-soft interactions are more stable than soft-hard interactions.

The HSAB Principle is further illustrated with the Na-Cs exchange data on charge-reduced Camp Berteau montmorillonite included in Figure 2. As we mentioned earlier, Maes and Cremers (1978) noted that the logarithm of cation selectivity for Na \rightarrow Cs exchange on untreated and a series of charge-reduced Camp Berteau clays was linearly related to their surface charge densities. By combining Eqs. (1), (3), and (5) and inserting the corresponding χ and S values [$\chi_{Na} = 26.2$, $\chi_{Cs} = 14.5$, $S_{Na} = 0.0474$, and $S_{Cs} = 0.1042$ (Xu and Harsh, 1990a)], we obtained:

$$\log K_{v(Na-Cs)}^o = 1.872 \epsilon_{te} + 5.173 \epsilon_{oc} - 0.473. \quad (7)$$

Because the surface charge of Camp Berteau montmorillonite originates almost completely from the octahedral layer (Table 1) and because charge reduction in Camp Berteau is accomplished by placing Li in the octahedral layer and neutralizing octahedral charge (Hofmann and Klemen, 1950; Calvet and Prost, 1971; Jaynes and Bigham, 1987), Eq. (7) can be reduced to

$$\log K_{v(Na-Cs)}^o = 5.173 \epsilon_{oc} - 0.473 \quad (8)$$

or

$$\log K_{v(Na-Cs)}^o = 5.173 \epsilon_{to} - 0.473. \quad (9)$$

If we assume that charge reduction does not significantly change the "molecular weight" and surface area of the treated mineral, Eq. (9) implies a linear relationship between the logarithm of cation selectivity and the surface charge density. Therefore, Maes and Cremers (1978) were illustrating the same relation we found between $\log K_v^o$ and ϵ_{oc} ; namely, a decrease in $\log K_v^o$ occurs with octahedral charge reduction because the number of "softer" sites available for surface complexation with the softer Cs is reduced.

Because Eq. (9) does not contain the ϵ_{te} term, it should be applicable only to montmorillonites with no significant tetrahedral charge. This is completely consistent with experimental results from Maes and Cremers (1978) who reported that the linear equation established among charge-reduced Camp Berteau montmorillonites predicts the cation selectivity of Na-Cs exchange on montmorillonite with little tetrahedral charge (e.g., Otay and Bayard montmorillonite). When the amount of tetrahedral charge is significant, Eq. (7) can be rewritten as:

$$\log K_{v(Na-Cs)}^o = 5.173 \epsilon_{to} - 3.301 \epsilon_{te} - 0.473. \quad (10)$$

Comparing Eq. (10) with Eq. (9), we know that a linear relationship based upon the charge-reduced Camp Berteau montmorillonites overestimates $\log K_v^o$ of other smectites by $3.301 \epsilon_{te}$. This explains the observation of Maes and Cremers (1978) that the measured $\log K_v^o$ is smaller than that predicted from surface charge density for Wyoming montmorillonite ($\epsilon_{te} > 0.3 \epsilon_{to}$).

Another interesting point shown in Figure 2 is that the selectivities of alkali cation exchange on attapulgite (Merriam and Thomas, 1956; Marshall and Garcia, 1959) also fit the model, although it is not a 2:1 clay mineral. On the other hand, the selectivity of alkali cation exchange on a natural zeolite did not fit the model (data not shown). This implies that the selectivity of alkali cations on aluminosilicates may be independent of the clay morphology except when steric factors intervene, as with zeolites (Sherry, 1979).

CONCLUSION

Under constant temperature (298 K), pressure (1 bar), and ionic strength (~ 0.01 M), the alkali cation selectivity of the 2:1 clays could be quantitatively predicted from the net tetrahedral and octahedral charge of the minerals, and the absolute electronegativity and softness of the exchangeable cations. All of these parameters are determined independently of the exchange isotherms. The success of this study lends support to the HSAB model as a valid description of the factors determining exchange selectivity and raises the hope of estimating the ion exchange properties of materials important in industrial and natural processes without performing exchange isotherms.

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