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Calcium-Magnesium Exchange on Wyoming Bentonite in the Presence of Adsorbed Sodium[1]

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ABSTRACT

The exchange of magnesium for calcium at 298 K on Wyoming bentonite was investigated in a 50 mol m^{-3} perchlorate background maintained at pH 7. The charge fraction of Na^+ in the aqueous solution phase was controlled at the values of 0.74 or 0.87 during the exchange experiments, resulting in average exchangeable sodium percentages (ESP) of either 16 or 36% on the clay. The Vanselow selectivity coefficient for Ca → Mg exchange was equal to 1.0 and was independent of exchanger composition at both ESP values. This result implied that, under the conditions of the exchange experiments, the clay exhibited equal affinities for Ca^{2+} and Mg^{2+} regardless of the quantity of adsorbed sodium present.

Additional Index Words: **cation exchange, exchange selectivity, saline soils, sodic soils, ternary cation exchange systems.**

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A WORKING HYPOTHESIS of long-standing importance to the assessment of irrigation water quality is embodied in the concept of the sodium adsorption ratio (SAR). This well-known parameter for the prediction of the exchangeable sodium percentage (ESP) in irrigated soils relies on the assumption, perhaps adopted in part for analytical convenience, of identical exchange selectivities of Ca^{2+} and Mg^{2+}. Although the success of the SAR as a predictor of ESP in field and laboratory studies has been significant (U.S. Salinity Laboratory Staff, 1954; Bingham et al., 1979; Oster and Sposito, 1980; Sheta et al., 1981; Alperovitch et al., 1981; Bresler et al., 1982), its underlying hypothesis of indifference with respect to calcium and magnesium exchange cannot be expected to apply in all circumstances. As pointed out by Bresler et al. (1982, p. 17), the validity of this hypothesis hinges on the idea that cation charge is the sole determining factor in cation exchange, whereas it is known that other properties, such as ionic radius and polarizability, play an important role in exchange selectivity in soils (see, e.g., Sullivan, 1977).

In a recent study of Na → Ca, Na → Mg, and Ca → Mg exchange on Wyoming bentonite in a noncomplexing perchlorate background, Sposito et al. (1983b) found that the exchange isotherm for Mg^{2+} in Ca → Mg exchange was congruent with the nonpreference isotherm. This result showed clearly that, under the conditions of the experiments (pH 7 and 50 mol m^{-3} perchlorate), the montmorillonite surface exhibited equal affinities for Mg^{2+} and Ca^{2+}. The slight preference for Ca^{2+} over Mg^{2+} often noted in exchange experiments involving montmorillonite (see, e.g., Rahman and Rowell, 1979; Alperovitch et al., 1981) then could be attributed, in principle, to a somewhat greater affinity of the clay for charged complexes of Ca^{2+} over those of Mg^{2+}, which would tend to form in aqueous solutions containing chloride and other common monovalent anions (Sposito et al., 1983a, 1983b).

The experiments of Sposito et al. (1983b) lend support to the hypothesis underlying the concept of SAR but are limited in scope since they pertain to Ca → Mg exchange at zero ESP. It is also necessary to examine this exchange reaction at ESP values in the range of concern to the chemistry of arid zone soils. In this article, the results of Ca → Mg exchange experiments on montmorillonite carried out in a 50 mol m^{-3} perchlorate background at ESP values < 40% will be reported. The principal objective of the experiments was to determine whether montmorillonite exhibits equal exchange selectivity toward calcium and magnesium in the presence of low quantities of adsorbed sodium. It appears that no systematic experimental investigation of this kind concerning the ternary exchange system Na-Ca-Mg on montmorillonite has been published heretofore.

MATERIALS AND METHODS

Wyoming Bentonite

Montmorillonite SWy-1, obtained from the Source Clays Repository of the Clay Minerals Society, was used in this study. The unit cell formula for this Crook County, Wyoming, bentonite is (Sposito et al., 1983a)

$$M^{+}_{0.62}(Si_{7.80}Al_{0.20})[Al_{3.28}Fe(III)_{0.30}Fe(II)_{0.04}Mg_{0.38}]O_{20}(OH)_4 ,$$

where M^+ denotes 1 mol of monovalent exchangeable cation charge. The procedures employed to purify the clay and prepare it in the sodium-saturated form have been described in detail by Sposito et al. (1981).

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Exchange Experiments

Sodium-montmorillonite samples were reacted at 25.0 ± 0.3°C with ternary mixed salt solutions of $NaClO_4/Ca(ClO_4)_2/Mg(ClO_4)_2$ following the general procedure described by Sposito et al. (1981). In one series of exchange experiments, the pH value was maintained at 6.8 ± 0.2, with a total perchlorate concentration of 55.2 ± 0.8 mol m^{-3} and a charge fraction of Na^+ in the aqueous solution phase ($\tilde{E}_{Na}$) equal to 0.740 ± 0.003. In another series of experiments, the pH value was maintained at 7.0 ± 0.1, the perchlorate concentration at 53.5 ± 0.6 mol m^{-3}, and the charge fraction of Na^+ in the aqueous solution phase at 0.870 ± 0.003. Perchlorate was chosen as the background anion in these experiments because it does not complex Na^+, Ca^{2+}, or Mg^{2+} significantly at concentrations $< 10^3$ mol m^{-3} (see Frost et al., 1982, and the review given therein). The exchange experiments were carried out in sixfold replication, with reaction times varying between 24 and 60 h.

Chemical Analysis

Clay Concentration—The concentration of Na-montmorillonite in the stock suspension was determined as described by Sposito et al. (1981). For the experiments with a Na^+ charge fraction of 0.74 in the aqueous solution phase, the clay concentration was 26.7 ± 0.4 g of clay/kg of suspension; for the experiments at a charge fraction of 0.87, the clay concentration was 25.2 ± 0.2 g of clay/kg of suspension.

Supernatant Composition—Each of the six replicate supernatant solutions in an exchange experiment was analyzed for Na by flame emission and for Ca and Mg by flame absorption on a Perkin-Elmer Model 5000 atomic absorption spectrophotometer. Fisher Certified Reference Solutions were used in the preparation of all standard curves.

Clay Slurry Analysis—The clay slurries recovered in each experiment were analyzed for their content of Na, Ca, Mg, and water as described by Sposito et al. (1983a).

Data Analysis

The surface excesses and moles of adsorbed charge of Na, Ca, and Mg were calculated as described by Sposito et al. (1981). The total adsorbed metal cation charge, Q_o, was calculated with the following equation:

$$Q_o = \Gamma_{Na} + 2(\Gamma_{Ca} + \Gamma_{Mg}) \equiv q_{Na} + q_{Ca} + q_{Mg}, \quad [1]$$

where Γ_M is a surface excess of metal M (M = Na, Ca, or Mg) in moles per kilogram of clay, and q_M is the corresponding number of moles of adsorbed metal charge per kilogram of clay.

Vanselow selectivity coefficients for Na → Ca, Na → Mg, and Ca → Mg exchanges were calculated with the experimental composition data and the following equation (Sposito, 1981, Chap. 5; Chu and Sposito, 1981):

$$^{c}K_{ij}^{T} = \frac{x_j^{Z_i}(i)^{Z_j}}{x_i^{Z_j}(j)^{Z_i}}, \quad (i, j = 1,2,3), \quad [2]$$

where x is a mole fraction of a metal *species* in the exchanger phase, ( ) refers to an activity of a metal *species* in the aqueous solution phase, and i or j refer to cations of valence Z_i or Z_j. The superscript T denotes a ternary cation exchange system and the designations 1 = Na^+, 2 = Ca^{2+}, and 3 = Mg^{2+} are understood in Eq. [2]. The activities in Eq. [2] were calculated as products of molar concentrations and single ion activity coefficients estimated with the Davies equation (Sposito, 1981, 1984).

RESULTS AND DISCUSSION

Calcium–Magnesium Exchange

The primary laboratory data on the ternary exchange experiments appear in the first six columns of Table 1. In this table, c refers to an equilibrium molinity (moles per kilogram of solution, see Whitfield, 1979, p. 161) and q_M (M = Na, Ca, or Mg) is an adsorbed cation charge. The last column in the table gives values of the total adsorbed metal cation charge. For the experiments performed with $\tilde{E}_{Na}$ = 0.74, the mean value of Q_o was 1.01 ± 0.05 mol_c kg^{-1}, whereas for the experiments at $\tilde{E}_{Na}$ = 0.87, Q_o = 0.97 ± 0.05 mol_c kg^{-1}. These two Q_o values are in good agreement with one another and with the Q_o values determined

Table 1—Experimental data on Na^+-Ca^{2+}-Mg^{2+} exchange at 298 K on Wyoming bentonite in perchlorate background.

c_{Na}	c_{Ca}	c_{Mg}	q_{Na}	q_{Ca}	q_{Mg}	Q_o
mmol kg^{-1}			mol_c kg^{-1}			
			$\tilde{E}_{Na}$ = 0.74			
39.6 ± 0.1	0.00	7.18 ± 0.06	0.20 ± 0.06	0.00	0.85 ± 0.06	1.05
40.6 ± 0.2	0.793 ± 0.008	6.40 ± 0.06	0.14 ± 0.09	0.071 ± 0.005	0.79 ± 0.06	1.00
40.8 ± 0.06	1.448 ± 0.003	5.73 ± 0.05	0.10 ± 0.03	0.145 ± 0.005	0.76 ,0.07	1.01
41.1 ± 0.1	2.150 ± 0.008	5.05 ± 0.04	0.10 ± 0.07	0.25 ± 0.02	0.62 ± 0.04	0.97
39.7 ± 0.2	2.83 ± 0.02	4.36 ± 0.03	0.20 ± 0.06	0.37 ± 0.01	0.52 ± 0.02	1.10
40.1 ± 0.3	3.51 ± 0.02	3.64 ± 0.02	0.15 ± 0.08	0.45 ± 0.01	0.42 ± 0.01	1.02
40.1 ± 0.4	4.23 ± 0.02	2.91 ± 0.04	0.16 ± 0.07	0.55 ± 0.01	0.29 ± 0.02	1.00
40.3 ± 0.2	4.91 ± 0.03	2.21 ± 0.03	0.17 ± 0.08	0.59 ± 0.04	0.25 ± 0.02	1.01
40.4 ± 0.2	5.63 ± 0.02	1.54 ± 0.02	0.15 ± 0.07	0.64 ± 0.02	0.14 ± 0.02	0.93
45.9 ± 0.2	5.33 ± 0.03	0.707 ± 0.005	0.23 ± 0.08	0.63 ± 0.03	0.076 ± 0.006	0.94
40.8 ± 0.2	7.02 ± 0.03	0.00	0.10 ± 0.09	0.93 ± 0.03	0.00	1.03
			$\tilde{E}_{Na}$ = 0.87			
46.46 ± 0.05	0.00	3.485 ± 0.006	0.30 ± 0.08	0.00	0.73 ± 0.01	1.03
46.70 ± 0.07	0.350 ± 0.004	3.150 ± 0.009	0.4 ± 0.1	0.070 ± 0.003	0.43 ± 0.02	0.90
46.7 ± 0.3	0.690 ± 0.003	2.79 ± 0.01	0.4 ± 0.1	0.143 ± 0.003	0.46 ± 0.01	1.00
45.3 ± 0.2	1.032 ± 0.004	2.47 ± 0.01	0.3 ± 0.1	0.203 ± 0.008	0.40 ± 0.02	0.90
46.43 ± 0.05	1.369 ± 0.008	2.14 ± 0.01	0.4 ± 0.2	0.27 ± 0.01	0.34 ± 0.01	1.01
46.7 ± 0.1	1.728 ± 0.004	1.74 ± 0.01	0.3 ± 0.1	0.304 ± 0.008	0.331 ± 0.009	0.94
47.5 ± 0.2	2.06 ± 0.01	1.363 ± 0.007	0.38 ± 0.07	0.41 ± 0.02	0.273 ± 0.005	1.06
46.2 ± 0.4	2.37 ± 0.01	1.016 ± 0.005	0.3 ± 0.2	0.45 ± 0.01	0.20 ± 0.01	0.95
46.0 ± 0.1	2.73 ± 0.01	0.68 ± 0.01	0.3 ± 0.1	0.53 ± 0.02	0.14 ± 0.01	0.97
46.0 ± 0.1	3.07 ± 0.02	0.340 ± 0.002	0.29 ± 0.06	0.56 ± 0.02	0.066 ± 0.005	0.92
46.6 ± 0.5	3.443 ± 0.009	0.00	0.4 ± 0.2	0.61 ± 0.02	0.00	1.01

Table 2—Natural logarithms of Vanselow selectivity coefficients and exchanger composition data.†

$\ln {}^cK_{13}^T$	$\ln {}^cK_{12}^T$	$\ln {}^cK_{23}^T$	E_1	E_2	E_3
1.13	1.45	0.32	0.141	0.071	0.788
1.85	2.14	0.29	0.103	0.143	0.754
1.97	2.01	0.043	0.108	0.258	0.634
0.823	0.728	−0.095	0.190	0.337	0.473
1.41	1.31	−0.102	0.144	0.442	0.414
1.29	1.02	−0.27	0.157	0.553	0.290
1.09	1.04	−0.057	0.167	0.584	0.249
1.21	1.01	−0.21	0.159	0.688	0.153
0.699	0.611	−0.088	0.248	0.671	0.081
0.376	−0.006	−0.38	0.427	0.080	0.493
0.477	0.245	−0.23	0.384	0.146	0.470
0.643	0.439	−0.20	0.340	0.224	0.436
0.318	0.113	−0.20	0.397	0.265	0.338
0.708	0.784	0.076	0.316	0.328	0.357
0.510	0.522	0.012	0.357	0.385	0.258
0.541	0.579	0.038	0.344	0.453	0.202
0.675	0.736	0.061	0.322	0.536	0.143
0.722	0.778	0.056	0.316	0.612	0.072

† 1 = Na, 2 = Ca, 3 = Mg; E_i (i = 1, 2, 3) is a charge fraction on the clay.

previously in the binary exchanges, Na → Ca (Q_o = 1.03 ± 0.05 $mol_c\ kg^{-1}$), Na → Mg (Q_o = 0.9 ± 0.1 $mol_c\ kg^{-1}$), and Ca → Mg (Q_o = 0.96 ± 0.07 $mol_c\ kg^{-1}$), on Wyoming bentonite in a 50 mol m^{-3} perchlorate background (Sposito et al., 1983a, 1983b). The cation exchange data in Table 1 confirm, for the ternary system, the finding in studies of binary unibivalent cation exchange that the total adsorbed metal cation charge shows no tendency to increase with increasing bivalent metal saturation of a montmorillonite exchanger in a *perchlorate* background at fixed pH value (Sposito et al., 1981, 1983a, 1983b).

Table 2 lists the natural logarithms of the ternary Vanselow selectivity coefficients calculated with the data in Table 1 and Eq. [2]. The last three columns in the table give the composition of the exchanger phase in terms of the charge fractions, E_i (i = 1, 2, 3), where

$$E_i = q_i/Q_o\,, \quad (i = 1, 2, 3)\,, \qquad [3]$$

and the designations 1 = Na, 2 = Ca, 3 = Mg apply. Values of the natural logarithm of the selectivity coefficient for Ca → Mg exchange, ${}^cK_{23}$, appear in the third column of the table. For the experiments at $\tilde{E}_{Na}$ = 0.74, E_1 = 0.16 ± 0.04 and ${}^cK_{23}$ = 0.99 ± 0.2 (ln ${}^c\bar{K}_{23}$ = −0.010). For the experiments at $\tilde{E}_{Na}$ = 0.87, with data listed in the lower one-half of Table 2, E_1 = 0.36 ± 0.04 and ${}^cK_{23}$ = 0.93 ± 0.2 (ln ${}^c\bar{K}_{23}$ = −0.073). The two average values of ${}^cK_{23}$ in the ternary cation exchange system are not significantly different from ${}^cK_{23}$ = 1.0 ± 0.2, determined by Sposito et al. (1983b) for Ca → Mg exchange at E_1 = 0.0. These results show that, under the conditions of pH and perchlorate concentration in the experiments and within the precision of the data, calcium-magnesium exchange on Wyoming bentonite is not affected by the presence of adsorbed Na^+ at ESP values < 40%.

A suspension of Na/Ca/Mg–montmorillonite at an ionic strength near 50 mol m^{-3}, with less than about 20% of the total adsorbed metal cation charge accounted for by Na^+, comprises well-developed quasicrystals with bivalent exchangeable cations residing primarily in the interlayer regions and whatever Na cations are present relegated primarily (but not solely)

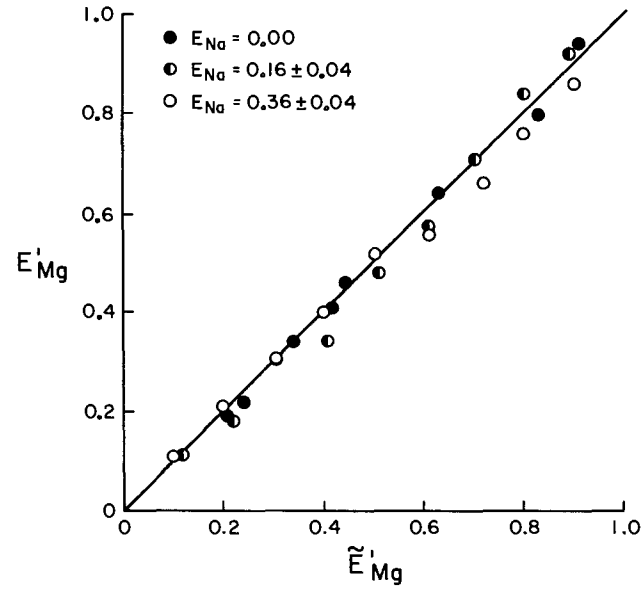

Fig. 1—A graph of the variable E_{Mg} vs. $\tilde{E}_{Mg}$ (Eq. [4]) for three values of E_{Na}.

to external surfaces. This distribution of the cations is the result of pronounced differences in monovalent-bivalent exchange selectivity between the two kinds of surface, interlayer and external (Shainberg et al., 1980). It is reasonable, therefore, that Ca-Mg exchange on montmorillonite under the conditions of the present experiments would involve principally the exchange sites that show preference for bivalent cations. This being the case, the quantity of adsorbed Na^+ should exert little influence on Ca-Mg exchange selectivity.

Figure 1 illustrates this concept through a plot of the two variables

$$E'_{Mg} = q_{Mg}/(q_{Ca} + q_{Mg})\,,$$
$$\tilde{E}'_{Mg} = c_{Mg}/(c_{Ca} + c_{Mg})\,, \qquad [4]$$

where E'_{Mg} is the fraction of adsorbed bivalent metal cation charge accounted for by Mg^{2+} and $\tilde{E}'_{Mg}$ is a similar quantity for bivalent cation charge in the aqueous solution phase. For Ca → Mg exchange in a *binary* system (E_{Na} = 0), a graph of $\tilde{E}'_{Mg}$ vs. $\tilde{E}'_{Mg}$ is an exchange isotherm (Sposito, 1981, Chap. 5). Figure 1 shows that the relationship between the Mg fraction of the total bivalent cation charge on the exchanger and that in aqueous solution is, within the precision of the data, independent of the value of E_{Na} in the range 0 to 0.4. The solid line in Fig. 1 represents the thermodynamic nonpreference isotherm for a *binary* exchange system. That the data points follow the line closely is in agreement with the mean values of selectivity coefficient ${}^cK_{23}$ given above (Sposito, 1981, Chap. 5).

Sodium-Calcium and Sodium-Magnesium Exchange

The data in the first two columns of Table 2 can be used to check the general equation for the thermodynamic exchange equilibrium constant in a ternary system as derived by Chu and Sposito (1981, Eq. [19]). For the case of Na → Ca exchange, this equation re-

duces to the expression

$$\ln K_{12} = \int_{\substack{(1,0,0)\\ \text{Any path}}}^{(0,1,0)} \ln {}^cK_{12}^T dE_2 + \int_{\substack{(1,0,0)\\ \text{Any path}}}^{(0,1,0)} \ln {}^cK_{13}^T dE_3 . \quad [5]$$

In the binary Na–Ca system, $E_3 \equiv 0$ and Eq. [5] takes on the standard form (Sposito, 1981, Chap. 5)

$$\ln K_{12} = \int_0^1 \ln {}^cK_{12}^B dE_2 , \quad [6]$$

where ${}^cK_{12}^B$ is the Vanselow coefficient in the binary system comprising cations 1 and 2. According to chemical thermodynamics, the left sides of Eq. [5] and [6] should be identical (Chu and Sposito, 1981).

To verify the composition and path independence of K_{12}, the integrals in Eq. [5] were evaluted along two separate paths: (a) (1, 0, 0) → (0.5, 0, 0.5) → (0.3, 0.7, 0) → (0, 1, 0) and (b) (1, 0, 0) → (0.15, 0, 0.85) → (0.25, 0.75, 0) → (0, 1, 0). The resulting values of ln K_{12} then were compared with the value of the integral in Eq. [6], obtained by fitting the Na → Ca exchange data in Table 2 of Sposito et al. (1983a) to the equation

$$\ln {}^cK_{12}^B = \sum_{n=0}^{6} B_n E_2^n \quad (r^2 = 0.98) \quad [7]$$

and integrating the right side term by term. The values of the coefficients B_n are listed in Table 3.

For the integration path (a), $E_2 = 0$ along the first leg and only an integral of ln ${}^cK_{13}^B$ with respect to E_3 must be evaluated. This was done by calculating ${}^cK_{13}^B$ with the Na → Mg exchange data in Table 3 of Sposito et al. (1983a), representing the selectivity coefficient with the regression equation

$$\ln {}^cK_{13}^B = -0.7118 + 1.7726E_3 \quad (r^2 = 0.90) \quad [8]$$

and inserting this expression into the second term on the right side of Eq. [5]. Along the second leg of the path of integration, the values of ln ${}^cK_{12}^T$ and ln ${}^cK_{13}^T$ in the lower half of Table 2 were fit to expressions having the same general form as Eq. [8]. Examination of the correlation coefficients for the regression indicated that the selectivity coefficients showed no significant dependence (at the 99% level) on exchanger composition. Therefore, the mean values

$$\ln {}^cK_{12}^T = 0.55 \pm 0.14 \quad \ln {}^cK_{13}^T = 0.47 \pm 0.29 \quad [9]$$

were introduced into Eq. [5] for the second leg. For the third leg of the path of integration, $E_3 = 0$ and only an integral of ln ${}^cK_{12}^B$ is involved. In this case, Eq. [7] was inserted into the first term on the right side of Eq. [5] to complete the calculation. The final result for ln K_{12} was

$$\ln K_{12} = \underset{\text{(Leg 1)}}{-0.134} + \underset{\text{(Leg 2)}}{0.153} - \underset{\text{(Leg 3)}}{0.075} = -0.056$$

$$[\text{Path (a)}] \quad [10a]$$

The natural logarithm of K_{12} also was calculated as outlined above for the integration path (b) with the help of the ternary exchange data in the upper half of Table 2. The final result for ln K_{12} was

$$\ln K_{12} = \underset{\text{(Leg 1)}}{0.035} - \underset{\text{(Leg 2)}}{0.112} - \underset{\text{(Leg 3)}}{0.050} = -0.127$$

$$[\text{Path (b)}] \quad [10b]$$

where Eq. [6] and [7] were employed along with the mean values from Table 2:

$$\ln {}^cK_{12}^T = 1.27 \pm 0.42 \quad \ln {}^cK_{13}^T = 1.26 \pm 0.53 \quad [11]$$

applicable to the second leg of the path of integration.

These values of ln K_{12} can be compared with that found directly after introducing Eq. [7] into Eq. [6], i.e.,

$$\ln K_{12} = 0.039 . \quad [10c]$$

Equations [10] led to the values 0.95, 0.88, and 1.04, for K_{12}. These results are in very good agreement, given the precision of the exchanger composition data. A similar, nonredundant calculation could not be performed for ln K_{13} because the expression analogous to Eq. [5] for this parameter (Chu and Sposito, 1981, Eq. [19]) is

$$\ln K_{13} = \int_{\substack{(0,0,1)\\ \text{Any path}}}^{(1,0,0)} \ln {}^cK_{13}^T dE_1 + \int_{\substack{(0,0,1)\\ \text{Any path}}}^{(1,0,0)} \ln {}^cK_{23}^T dE_2 . \quad [12]$$

Since $dE_1 \approx 0$ and ln ${}^cK_{23}^T \approx 0$ in the present experiments, the data in Table 2 cannot be used to help evaluate ln K_{13}.

Besides their thermodynamic consistency, as epitomized in Eq. [5] and [6], the data in the first two columns of Table 2 indicate that

$$\ln {}^cK_{12}^T \approx \ln {}^cK_{13}^T \quad [13]$$

at any exchanger composition (cf. also Eq. [8] and [11]). Equation [13] follows directly from the closure relation (Chu and Sposito, 1981):

$$2 \ln {}^cK_{12}^T + \ln {}^cK_{23}^T = 2 \ln {}^cK_{13}^T \quad [14]$$

and the fact that ln ${}^cK_{23} \approx 0$ in the present experiments. However, Eq. [13] does not imply that ln ${}^cK_{12}^T$ and ln ${}^cK_{13}^T$ are constants. Indeed, Eq. [8] and [11] indicate that these two parameters are larger at $E_{Na} = 0.16$ than they are at $E_{Na} = 0.36$. This decrease in bivalent cation selectivity with increasing sodium saturation of the exchange sites is probably the result of an incipient breakdown of the quasicrystals that accompanies an increase of E_{Na} above 0.2 (see, e.g., Dufey and Banin, 1979).

Table 3—Numerical values of the coefficients B_n in Eq. [7].

n	B_n	n	B_n	n	B_n
0	1.0001	3	32.4619	5	84.8210
1	−1.5371	4	−74.2044	6	−34.4080
2	−8.0645				

CONCLUSIONS

In a 50 mol m^{-3} perchlorate background at 25°C and pH 7, the exchange of Mg^{2+} for Ca^{2+} on Wyoming bentonite is characterized by a Vanselow selectivity coefficient equal to 1.0, regardless of the presence of adsorbed Na^+, up to an ESP of about 40%. This behavior is consistent with the hypothesis that, at low ESP values, Ca → Mg exchange takes place primarily on sites exhibiting strong preference for bivalent cations, such as those in the interiors of quasicrystals. Under these conditions, the influence of adsorbed Na^+ is likely to be small. On the other hand, the influence of adsorbed Na^+ on the Vanselow selectivity coeffi-

cients for Na → Ca and for Na → Mg exchange on a Na/Ca/Mg-montmorillonite should reflect a perturbation of the quasicrystal structure by an increasing ESP. This effect was illustrated in the present experiments by a decrease in ${}^{c}K_{12}^{T}$ and ${}^{c}K_{13}^{T}$ from values near 3.5 to values near 1.6 as E_{Na} increased from 0.16 to 0.36.

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