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EXCHANGE REACTIONS IN THE CA-MG-NA-MONTMORILLONITE SYSTEM

GIORA RYTWO,[1,2] AMOS BANIN,[1] AND SHLOMO NIR[1]

[1] The Seagram Center for Soil and Water Sciences, The Faculty of Agriculture, The Hebrew University of Jerusalem Rehovot 76100, Israel

[2] MIGAL Galilee Technological Center, Kiryat Shmona, 10200, Israel

Abstract—The exchange reactions of Na, Ca and Mg on montmorillonite are revisited employing recently developed analytical and theoretical approaches. The fractional adsorption of the cations has been determined by displacing them from the adsorbed state in one step, using a low concentration of an organic cation of large binding affinity. The analysis of displaced and solution cations employed inductively coupled plasma emission spectrometry. An adsorption model was employed in the analysis of the data. The procedure consists of solving the electrostatic Gouy-Chapman equations and calculating adsorbed amounts of the cations as the sum of the cations residing in the double layer region, and the cations chemically bound to the surface, in a closed system. The model also accounts explicitly for cation complexation in solution. Thus the calculations also considered the adsorption of $CaCl^+$ and $MgCl^+$, which eliminated the apparent increase of the cation exchange capacity (CEC) with divalent cation concentration. The model could explain and yield predictions for our measured adsorbed amounts as well as previously published data, in the binary and ternary systems of Ca/Mg/Na, provided that the fraction of surface sites occupied by calcium did not exceed 0.4. For a larger coverage of surface sites by calcium, a fit of the experimental data required an order of magnitude increase in the binding coefficients of the divalent cations in the binary system Ca/Na and in the ternary system Ca/Mg/Na.

Key Words—Cation Adsorption Model, Ca^{2+} Adsorption, Mg^{2+} Adsorption, Montmorillonite, Solution Complexes.

INTRODUCTION

This paper presents the results of a study on the adsorption of Ca^{2+} and Mg^{2+} to montmorillonite in suspensions containing pairs of cations Ca/Na or Mg/Na or the triads of Ca/Mg/Na. Since Ca^{2+} and Mg^{2+} are the most abundant divalent cations in soils, it is important to obtain a quantitative understanding of their adsorption to soils, and in particular to clays. Particularly important in arid-zone soils exposed to salinization and sodification stress is the understanding of the competitive adsorption of sodium with the divalent cations. Since smectite montmorillonite is a predominant mineral in many soils of the arid and the semi-arid regions (for example, Banin and Amiel 1969) it is customarily used as a model-mineral for such ion exchange experimental and modelling studies.

Previous studies on the adsorption to montmorillonite of Ca and Na were reported by Bolt (1955), Banin (1968), Banin and Lahav (1968), Maes and Cremers (1977), Shainberg et al. (1980) and adsorption of Mg was reported by Bolt (1955). Ternary systems were studied only in a few cases (Sposito et al. 1983b). The studies of Blackmore and Miller (1961), Rowell (1963), Banin (1968), Lahav and Banin (1968) and Emerson and Bakker (1973) showed correlations between the molar ratios of Ca to Na on the surface of the clay and the formation of tactoids.

The question of the preference of Ca^{2+} over Mg^{2+} for adsorption to montmorillonite was discussed in Sposito et al. (1983a, 1983b, 1983c) and Levy et al. (1983). Sposito et al. (1983a) found that in a perchlorate medium, the apparent total adsorbed cations was independent of the exchanger composition and equal to 0.97 ± 0.06 mol_c kg^{-1} (average for Na-Ca and Na-Mg exchanges). In a chloride medium, the apparent total adsorbed charges increased with the amount of calcium or magnesium adsorbed, up to 1.28 mol_c kg^{-1} as the clay became saturated with a divalent cation. These results were interpreted as an evidence for the adsorption of Ca^{2+} or Mg^{2+} complexes in the chloride medium experiments. In the current study we confirm this possibility of adsorption of solution complexes of the type ($M^{++}Cl^-$) by detailed model calculations, which yield only small variations in the cation exchange capacity (CEC) of the clay.

The current study involves the application of new experimental and theoretical procedures to these exchange systems. Experimentally, we have determined the amounts of adsorbed cations in clay treated with various proportions of the ions. A solution with low concentration of an organic cation of large binding affinity, was used to displace the adsorbed ions in a single desorption step (Rytwo et al. 1991). This procedure increased significantly the precision of the ion exchange measurements. The analysis of the results was done in the framework of a model (Nir 1984, 1986) that had already been employed for the study of adsorption to montmorillonite of Li^+, Na^+, K^+, Cs^+

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(Nir et al. 1986), and Cd^{2+} (Hirsch et al. 1989). The three main elements in this model are: (1) consideration of specific binding, whereby it assumes that the adsorbed cations consist of (a) cations tightly bound to the surface and (b) cations residing in the double layer region; (2) the electrostatic Gouy-Chapman equations are solved for a solid/liquid system containing several cations of various valencies, and particles whose surfaces are charged and partially neutralized by cation binding; and (3) the concentration of surface sites in the solid/liquid system is explicitly included in the computation, thus accounting for concentration of cations in solution during the adsorption/desorption process.

Theoretical Model

We present the principal equations and define the model main parameters.

The symbols M^+ and M^{2+} denote cations that can bind to singly charged negative sites, P^-, on the surface of the clay. The binding reaction for a monovalent cation is:

$$P^- + M^+ \leftrightarrow (PM)^0 \quad [1]$$

giving a binding coefficient:

$$K = (PM)^0/(P^-)(M^+) \quad [2]$$

The binding coefficient is a measure of the strength of complexation between a surface site and a cation.

Divalent cations can react with one surface site yielding a charged complex, or they can associate to form a neutral complex, by binding to a negatively divalent charged site, P^{2-}, defined formally $(P^{2-}) = (P^-)/2$. The corresponding binding coefficient K_1 is defined as:

$$K_1 = (P^-M^{2+})^+/(P^-)(M^{2+}) \quad [3]$$

whereas for neutral complexes:

$$P^{2-} + M^{2+} \leftrightarrow (P^{2-}M^{2+})^0 \quad [4]$$

$$K_2 = (P^{2-}M^{2+})^+/(P^{2-})(M^{2+}) \quad [5]$$

As pointed out (Nir 1986), data for adsorption of the cations could be fit when using either K_1 or K_2. Experimental verification of the modes of binding requires the measurement of additional quantities, such as the surface potential and the concentration of divalent cations at which charge reversal occurs, or results of adsorption beyond the CEC. This was recently done in a study employing divalent organic cations (Rytwo et al. 1996). In Equations [1] to [5] the concentrations are given in units of M and the unit of the binding coefficients is M^{-1}.

The solution includes cations M^+, M^{2+}, and anions A^+, A^{2+}, as well as additional species such as $(M^{2+}A^-)^+$ and $(M^{2+}A^-_2)^0$ or $(M^{2+}A^{2-})^0$. For instance, in the current work we have accounted explicitly for the occurrence of solution complexes, such as $Mg^{2+}Cl^-)^+$. Divalent cations can also form the surface complex $(P^-M^{2+}A^-)^0$.

The concentration of the cation M^{z+} at the surface is:

$$M^{z+}(0) = S^{z+}Y_0^z \quad [6]$$

where $Y_0 = \exp[-ez\Psi_{(0)}/kT]$, e is the absolute magnitude of an electronic charge, z is the valence of the given ion, which is positive for a cation and negative for an anion, $\Psi_{(0)}$ is the surface potential, k is the Boltzmann factor, T is the absolute temperature and S^{z+} is the molar concentration of that cation in the equilibrium solution, far away from the surface.

We calculate analytically the excess concentration of mono and divalent cations in the double layer region above their bulk concentrations (see Nir et al. 1978).

The reduction in surface charge density is explicitly taken into account according to Equations [1] to [6]. The computational procedure is an iterative process based on Equations [1] to [6], using the Gouy-Chapman equation for the surface charge density, and the closeness of the system (Nir 1984, 1986; Hirsch et al. 1989).

EXPERIMENTAL

Materials

Wyoming montmorillonite SWy-1 obtained from the Source Clays Repository of The Clay Minerals Society was used. The CEC of this clay was 0.764 mmole g^{-1} (van Olphen and Fripiat 1979), and its specific surface area (SSA) was measured as in Carter et al. (1965) and equaled 756 m^2g^{-1}. These data yield an area per charged site of the clay of 1.64 nm^2. Methylene blue (MB) as chloride salt, and analytical grade $CaCl_2$ were purchased from Merck (E. Merck, Darmstadt, Germany). Analytical grade NaCl and $MgCl_2$ were purchased from BDH (BDH Chemicals Ltd., Poole, England). All chemical reagents were used without further treatment or purification.

Preparation of Homoionic Clays

Homoionic Na-montmorillonite was prepared from the SWy-1 clay using the batch procedure as follows: A 1% suspension of clay in 1 M NaCl solution was agitated for 24 h at 25 °C. The equilibrated solution was separated from the clay by centrifugation (30 minutes at 14,000 rpm) in a Kontron Centrikon H 401 centrifuge. This procedure was repeated four times. The precipitate was washed three times, by the centrifugation method with distilled water and freeze-dried in a Christ Alpha 4-1 lyophilizer. The cation exchange capacity of the Na saturated montmorillonite was 0.81 mmole g^{-1} (Rytwo et al. 1991). With the SSA specified above, it yields an area per charged site of 1.55 nm^2.

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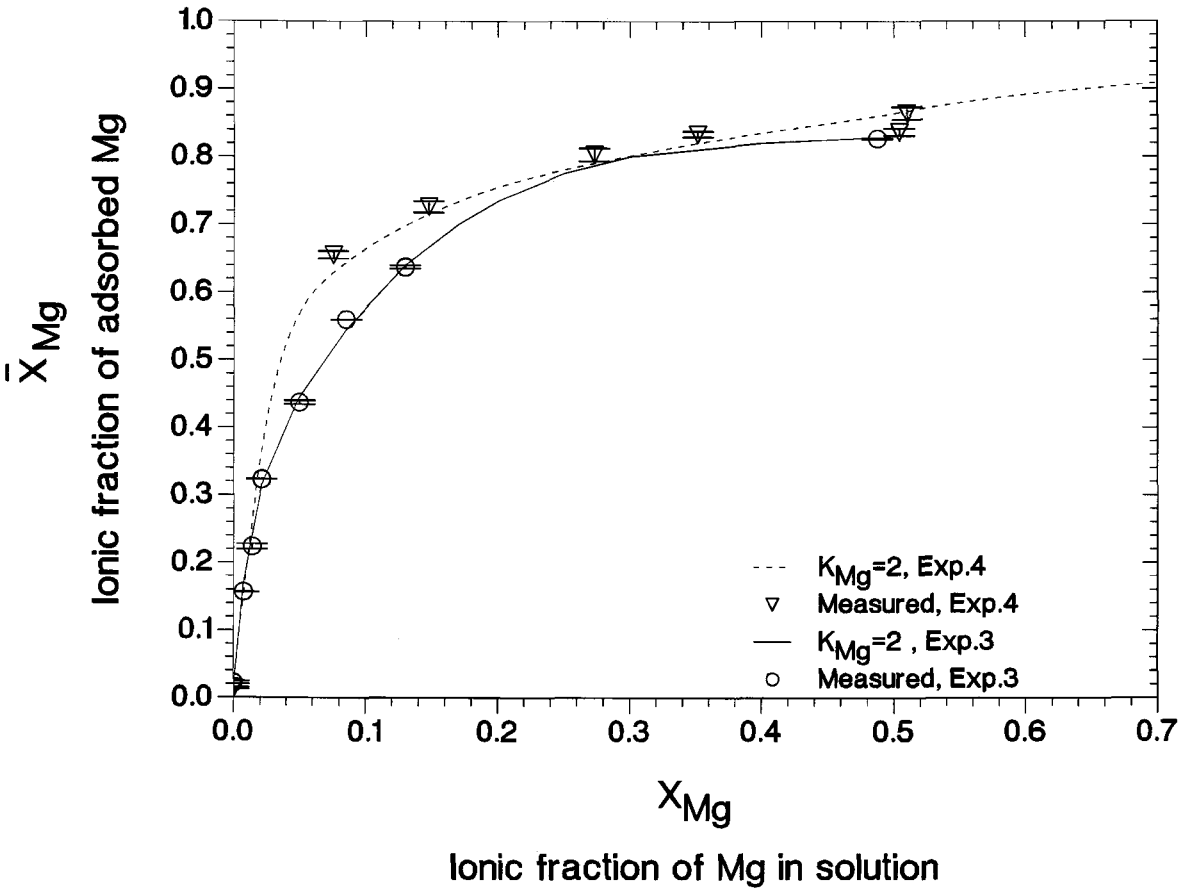


Figure 1. Adsorption isotherm of Mg^{2+} to montmorillonite in the presence of Na^{+} (Experiments [1] and [2] in Materials and Methods). The suspension contained 13.25 g clay/L in Experiment [1] 10.5 g clay/L yielding a site concentration of 10.6 mM and in Experiment [2], yielding a site concentration of 8.4 mM.

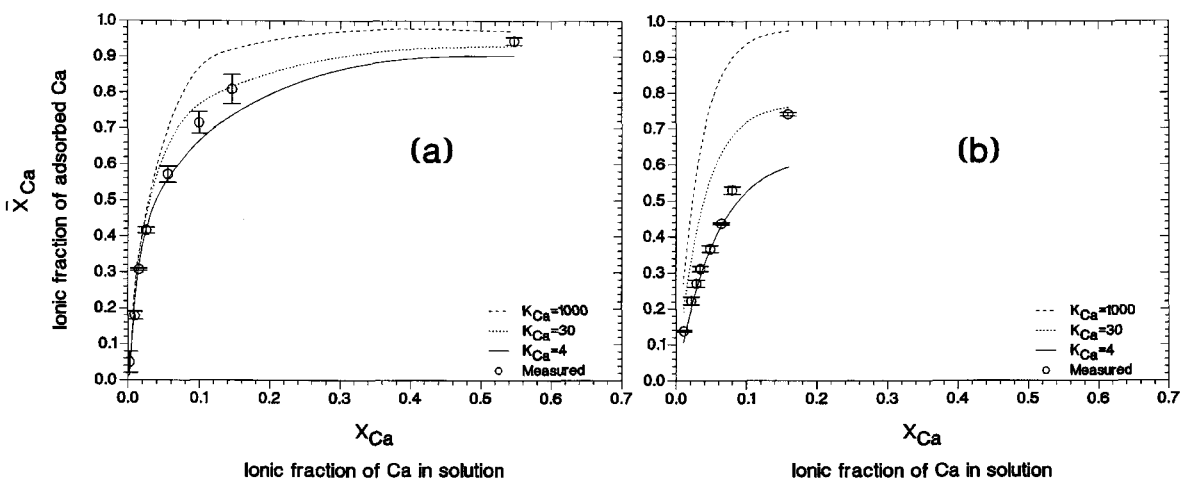


Figure 2. Adsorption isotherm of Ca^{2+} to montmorillonite in the presence of Na^{+} (Experiments [3] and [4] in Materials and Methods). The suspension contained 11 g clay/L in [a] and 9.4 g clay/L in [b]. The sums of cation concentrations in (a) were 20 mM_c and in (b) were 100 mM_c.

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Table 1. Measured and calculated data for the adsorption of Ca, Mg and Na to montmorillonite.

A. Measured results

No	Total added concentrations			Measured adsorbed amounts			Measured solution concentrations
	Ca	Mg	Na	Ca	Mg	Na	Ca
	mM			mole kg^{-1}			mM
1	7.5	10.88	3.13	0.203 ± 0.011	0.179 ± 0.003	0.020 ± 0.001	5.870 ± 0.120
2	10	8.38	3.13	0.267 ± 0.009	0.149 ± 0.005	0.025 ± 0.004	7.583 ± 0.245
3	12.5	5.88	3.13	0.285 ± 0.017	0.100 ± 0.003	0.019 ± 0.001	9.613 ± 0.200
4	7.5	10.88	13.13	0.190 ± 0.004	0.169 ± 0.002	0.037 ± 0.001	5.956 ± 0.078
5	10	8.38	13.13	0.265 ± 0.005	0.141 ± 0.001	0.043 ± 0.002	7.955 ± 0.121
6	12.5	5.88	13.13	0.306 ± 0.015	0.104 ± 0.001	0.046 ± 0.001	9.714 ± 0.044
7	7.5	10.88	23.13	0.215 ± 0.001	0.172 ± 0.004	0.060 ± 0.002	6.322 ± 0.052
8	10	8.38	23.13	0.226 ± 0.002	0.140 ± 0.003	0.061 ± 0.004	7.513 ± 0.129
9	12.5	5.88	23.13	0.305 ± 0.002	0.103 ± 0.001	0.066 ± 0.003	9.827 ± 0.199

B. Model calculations for the adsorption of Ca and Mg to montmorillonite. The error is calculated relative to the measured values, as: 100*(calculated-measured)/measured. Error = (100)(calculated-measured)/measured.

No	$K_{Ca} = 4M^{-1}$; $K_{Mg} = 2M^{-1}$				$K_{Ca} = 6M^{-1}$; $K_{Mg} = 2M^{-1}$			
	Ca		Mg		Ca		Mg	
	calc.	error	calc.	error	calc.	error	calc.	error
	$mole_c\ kg^{-1}$		$mole_c\ kg^{-1}$		$mole_c\ kg^{-1}$		$mole_c\ kg^{-1}$	
1	0.369	−8.9%	0.387	8.0%	0.409	0.8%	0.350	−2.5%
2	0.516	−3.4%	0.312	4.8%	0.556	4.1%	0.275	−7.8%
3	0.570	−0.1%	0.194	−2.8%	0.599	5.1%	0.166	−16.5%
4	0.340	−10.5%	0.351	3.8%	0.378	−0.3%	0.317	−6.4%
5	0.491	−7.4%	0.293	4.0%	0.533	0.5%	0.258	−8.6%
6	0.596	−2.6%	0.200	−3.6%	0.631	3.1%	0.172	−17.2%
7	0.358	−16.9%	0.367	6.7%	0.401	−6.8%	0.330	−3.7%
8	0.435	−3.9%	0.257	−7.9%	0.474	4.9%	0.226	−19.1%
9	0.579	−4.9%	0.193	−6.5%	0.618	1.3%	0.166	−19.8%

Adsorption Experiments

Clay suspensions were prepared by dispersing 5 g of Na-montmorillonite in 200 mL of distilled water. Appropriate amounts of Na, Ca and Mg solutions were added to 20 mL clay suspension, in the different experiments as follows:

1. $MgCl_2$ from 0 to 10 mM, keeping an approximate sum of total charge concentration of 20 mM_c with NaCl solution.
2. $MgCl_2$ from 0 to 50 mM, with NaCl concentrations varying between 20 and 0 mM.
3. $CaCl_2$ from 0 to 10 mM, keeping an approximate sum of total charge concentration of 20 mM_c with NaCl solution.
4. $CaCl_2$ from 0 to 10 mM, keeping an approximate sum of total charge concentration of 100 mM_c with Na solution.
5. Ca and Mg as chloride salts, at equal concentrations from 0 to 10 mM, keeping an approximate sum of charge concentration of 40 mM_c with NaCl solution.
6. Solutions of particular cation combinations such as high concentrations of Mg with low concentrations of Ca, or vice versa, were added.

The final volume was brought to 60 mL in 100 mL polyethylene bottles. The bottles were sealed and kept at 25 ± 0.5°C and continuous agitation was applied. All of the experiments were performed in triplicate. After 24 h of incubation, 10 mL of suspension were taken from each bottle and centrifugated at 15,000 rpm for 90 min. The supernatant was separated (supernatant A), and 10 ml of 12 mM MB solution were added to the sedimented clays to displace the adsorbed cations. The dye solution/clay system was agitated vigorously with the clay for 72 h. Then the suspensions were centrifugated for 60 min at 15,000 rpm, and supernatant B was separated. The concentrations of the soluble cations were determined in supernatant A, while the amount of cations adsorbed were determined in supernatant B. Elemental concentrations were determined using a Spectra inductively coupled plasma atomic emission spectrometer (ICPAES). Measurements of standards of inorganic cations dissolved in MB solutions of different concentrations showed that the presence of the dye did not interfere with the analysis of the inorganic ions (Rytwo et al. 1991).

RESULTS

We first presented the newly determined results of Mg and Ca adsorption in the binary system M^{++}/Na^{+} and in the ternary system Ca/Mg/Na. In the analysis, we ignored the possibility of solution complexes such as $CaCl^{+}$ or $MgCl^{+}$. In the second stage, we applied

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Table 1. Extended.

Measured solution concentrations		
Mg	Na	Calculated CEC
mM	mM	$mole_c\ kg^{-1}$
10.07 ± 0.147	6.439 ± 0.032	0.782 ± 0.020
7.528 ± 0.191	6.487 ± 0.029	0.856 ± 0.020
5.513 ± 0.067	6.448 ± 0.016	0.789 ± 0.039
9.973 ± 0.102	17.79 ± 0.234	0.756 ± 0.009
7.869 ± 0.075	17.82 ± 0.190	0.856 ± 0.014
5.422 ± 0.005	17.55 ± 0.194	0.866 ± 0.031
10.11 ± 0.134	29.09 ± 0.181	0.834 ± 0.013
7.612 ± 0.065	28.99 ± 0.095	0.792 ± 0.012
5.461 ± 0.071	28.64 ± 0.140	0.883 ± 0.007

$K_{Ca} = 40M^{-1}$; $K_{Mg} = 20M^{-1}$

Ca		Mg	
calc.	error	calc.	error
$mole_c\ kg^{-1}$		$mole_c\ kg^{-1}$	
0.397	−2.3%	0.375	4.5%
0.547	2.4%	0.297	−0.4%
0.596	4.6%	0.181	−9.3%
0.375	−1.1%	0.350	3.6%
0.535	1.0%	0.287	1.9%
0.642	4.9%	0.192	−7.4%
0.407	−5.4%	0.377	9.8%
0.488	7.9%	0.259	−7.1%
0.642	5.4%	0.191	−7.5%

the adsorption model to the data of Sposito et al. (1983a) for the binary systems Mg/Na and Ca/Na in the presence of the anion perchlorate, where the formation of solution complexes can be ignored (Lindsay 1979; Sposito et al. 1983a). We employed the association constants tabulated in Sposito et al. (1983a) in calculations that introduced binding coefficients for the adsorption of the monovalent complexes $MgCl^+$ and $CaCl^+$.

Application of the Adsorption Model to the Experimental Results

The adsorption isotherm for Mg^{2+} in the presence of Na^+ is shown in Figure 1, where the x-axis represents the ionic fraction of the tested cation in solution, X_{Me}, and the y-axis is its ionic fraction in the adsorbed phase, $\bar{X}_{Me}$:

$$X_{Me} = \text{metal concentration in solution } (mM_c) / \text{sum of cation concentration } (mM_c)$$

$$\bar{X}_{Me} = \text{amount of cation adsorbed } (mmole_c\ g^{-1}) / \text{CEC } (mmole_c\ g^{-1})$$

The calculated adsorbed ionic fractions are also shown (a continuous line). These calculations employed $K_{Na} = 1M^{-1}$ (Nir et al. 1986). The best fit for the observed fractions of surface sites occupied by Mg was obtained by setting $K_{Mg} = 2M^{-1}$. It is evident that model calculations can simulate and predict accurately the amounts of Mg and Na adsorbed to montmorillonite, using constant binding coefficients for the two ions. This suggests that the binding affinity for Na and Mg is almost constant throughout the adsorption range studied here, that is, 0.0-to-0.8 of the exchange capacity for each of the cations.

A somewhat different behavior is observed for Ca^{2+} adsorption in the Ca/Na system (Figure 2). At low concentrations of Ca^{2+} a binding coefficient $K_{Ca} = 4\ M^{-1}$ can adequately simulate the experimental results. However, at higher Ca^{2+} concentrations the calculated values of fractions of surface sites occupied by Ca^{2+} are below the experimental values. To achieve reasonable simulation, it is necessary to increase the values of K_{Ca} to 30 M^{-1} or even higher, as the total Ca^{2+} concentration increases. Comparison of Figure 2a with Figure 2b indicates that the shift to higher adsorption affinity of Ca^{2+} to montmorillonite occurs when the fraction of surface sites occupied by Ca^{2+} reaches approximately 0.4. In Figure 2a (approximately 20 mM_c sum of cations) this fraction is reached at a total Ca^{2+} concentration of 3.1 mM, whereas in Figure 2b (approximately 100 mM_c sum of cations) this fraction is attained at 5 mM Ca^{2+}.

The measured fractions of surface sites occupied by Ca, Mg and Na, and the measured solution concentrations in the Ca/Mg/Na system are given in Table 1A. The calculated fractions of the different complexes are given in Table 1B for various values of the binding coefficients. For all concentrations, the Mg^{2+} results can be explained by constant values of the binding coefficients, $K_{Ca} = 4\ M^{-1}$ and $K_{Mg} = 2\ M^{-1}$. These values result in underestimates of the adsorbed amounts of Ca^{2+} in certain cases. The calculated adsorbed amounts of Na^+ are overestimated, with an absolute error of less than 5% (not shown). Due to the low amount of sodium adsorbed, small absolute errors may yield large relative errors (up to 60%). Keeping $K_{Mg} = 2M^{-1}$ and increasing K_{Ca} to $6M^{-1}$ improves the agreement between calculated and measured adsorbed amounts of Ca, but leads to large underestimates for the adsorbed amounts of Mg^{2+} without improving considerably the fit to Na^+ results. The set of binding coefficients which gave the best fit was $K_{Ca} = 40M^{-1}$ and $K_{Mg} = 20M^{-1}$. Phenomenologically this implies that the presence of Ca^{2+} promotes the adsorption of Mg^{2+} to montmorillonite.

Detailed data given in Table 2 show that the amount of adsorbed Na^+ is constituted of roughly equal contributions from direct binding to the surface and residence in the diffuse part of the double layer, whereas in the case of the divalent cations a larger fraction is a result of binding. The data also show the decrease

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Table 2. Selected experimental and calculated fractions of surface sites occupied by Ca^{2+}, Mg^{2+} and Na^{+} due to binding and residence in the double layer region.[1]

Sample number	1	2	3	4
Total Ca^{2+} concentration (mM)	1.07	2.10		
Total Mg^{2+} concentration (mM)			1.09	2.18
Total Na^{+} concentration (mM)	27.30	25.30	31.13	28.97
Experimental adsorbed fraction: Ca or Mg	0.180	0.416	0.157	0.316
Calculated adsorbed fraction: Ca or Mg	0.210	0.418	0.172	0.316
Calculated bound fraction: Ca or Mg	0.174	0.343	0.130	0.228
Calculated in double layer: Ca or Mg	0.036	0.075	0.042	0.088
Calculated bound fraction: Na	0.385	0.258	0.361	0.318
Calculated double layer: Na	0.348	0.269	0.322	0.268
$-\psi_0$ (mV)	94.4	86.9	92.7	86.4

[1] The full range of Mg^{2+} adsorption results appears in Figure 1 and the full range of Ca^{2+} adsorption results appears in Figure 2.

in the magnitude of surface potential in the presence of Ca or Mg. This effect was discussed at length in McLaughlin et al. (1971), Nir et al. (1978) and Nir (1986).

Maes and Cremers (1977) raised criticism regarding the use of the Gouy-Chapman double layer model rather than a simpler mass-action exchange model. Despite some resemblance in form of Figures 1 or 2 to results with mass action equations, we advocate explicit consideration of electrostatic equations. According to Equation [6] the concentration of cation M^{2+} at the surface might be several orders of magnitude above that in solution far away from the surface. Consequently, ignoring this difference can seriously affect the value of the binding coefficient deduced in Equations [1] to [5]. This has been established in numerous studies (McLaughlin et al. 1971; Nir et al. 1978, 1986; Hirsch et al. 1989). A notable example which emphasizes the importance of the combination of the Gouy-Chapman equation with the mass action equation is illustrated in the adsorption of organic monovalent cations in excess of the CEC, where according to Equation [6] $Y_0 < 1$. According to the Gouy-Chapman equation, Y_0 should increase in this case with an increase in ionic strength. Experimental results confirmed the prediction of the model that the adsorbed amounts of certain monovalent organic cations should increase with ionic strength for adsorption beyond the CEC (Margulies et al. 1988; Rytwo et al. 1995a). We agree with Maes and Cremers (1977) that the Gouy-Chapman equation is strictly applicable only for isolated surfaces. Sposito (1991) discussed additional limitations of the Gouy-Chapman equations stemming from the finite size of ions and ion-ion correlations, and also pointed out a particular effect of Cl^{-}.

The data in Figures 1 and 2 and Table 1 could also be fit by considering the adsorption of the monovalent complexes MCl^{+}, but overall, this extension did not result in an improvement of the fits (not shown). On the other hand, this extension did abolish the slight apparent increase of the CEC with an increase in divalent cation concentrations, as will be elaborated below.

Application of the Adsorption Model to the Results of Sposito et al. (1983a)

In Tables 3 and 4, the results of calculations using our model are compared with the adsorbed amounts determined by Sposito et al. (1983a) for Na^{+}-Mg^{2+} and Na^{+}-Ca^{2+} exchange on Wyoming bentonite in a 0.05M perchlorate background. The clay used in the above study differs somewhat from the one used in our experiments, yielding an area of 1.33 nm^2 (rather than 1.55 nm^2) per singly charged surface site. In all of the calculations we used an average concentration of 25 mM of clay surface sites, and first determined the total concentrations of the ions from the adsorbed and solution concentrations. Inspection of Tables 3 and 4 demonstrates that the employment of the previously determined binding coefficients, that is $K_{Na} = 1M^{-1}$, $K_{Mg} = 2M^{-1}$ and $K_{Ca} = 4M^{-1}$ yields good predictions for the adsorbed amounts.

In the next stage, we employed the stability constants tabulated in Sposito et al. (1983a) for the complexes $CaCl^{+}$ and $MgCl^{+}$ and calculated their fractional content. The calculations followed the procedure outlined in Hirsch et al. (1989). In these calculations, the use of the value $K_{CaCl^+} = K_{MgCl^+} = 50M^{-1}$ gave the best fit to the experimental adsorbed amounts of Mg and Ca in Sposito et al. (1983a), whereas the other binding coefficients used were the same as those in Figures 1 and 2 and Tables 3 and 4, that is $K_{Na} = 1M^{-1}$, $K_{Mg} = 2M^{-1}$, and $K_{Ca} = 4M^{-1}$. Inspection of Figures 3 and 4 indicate that the calculations simulate the experimental values fairly well. However, as in Figure 2 the calculated values underestimate the experimental amounts of adsorbed Ca^{2+} in the presence of larger Ca^{2+} concentrations.

Figures 3 and 4 illustrate that the apparent cation exchange capacity, Q, exceeds 1 $mol_c kg^{-1}$ by up to 20 to 30% as the concentration of the bivalent cation is increased at the expense of Na^{+}. However, the calcu-

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Table 3. Calculated and experimental data on Na^+-Mg^{2+} exchange on Wyoming bentonite in a 50 mM perchlorate bakground, at 298°K.[1]

Solution concentrations		Measured adsorbed amounts			Calculated adsorbed amounts		
c_{Na}	c_{Mg}	q_{Na}	q_{Mg}	Q	q_{Na}	q_{Mg}	CEC
mM		$mol_c\ kg^{-1}$					
49.50 ± 0.12	1.17 ± 0.01	0.53 ± 0.09	0.28 ± 0.01	0.81	0.62	0.29	0.91
47.40 ± 0.33	2.34 ± 0.01	0.30 ± 0.17	0.45 ± 0.02	0.75	0.45	0.46	0.91
44.00 ± 0.13	7.00 ± 0.05	0.22 ± 0.08	0.70 ± 0.04	0.92	0.28	0.66	0.94
23.68 ± 0.08	17.40 ± 0.24	0.06 ± 0.02	0.78 ± 0.05	0.84	0.10	0.84	0.94
18.50 ± 0.17	19.65 ± 0.08	0.06 ± 0.03	0.95 ± 0.02	1.01	0.08	0.87	0.95

[1] The corresponding number of adsorbed metal charges per kg clay is denoted by q. Experimental values for q_{Na} and q_{Mg} are taken from Sposito et al. (1983a). Q is the apparent total adsorbed metal charge, given by $q_{Na} + q_{Mg}$. Calculated values for q_{Na}, q_{Mg} and CEC, were obtained as described in the text, using the binding costants of $K_{Na} = 1M^{-1}$ and $K_{Mg} = 2M^{-1}$.

lated values of the CEC, which account explicitly for the adsorption of the monovalent cations $CaCl^+$, or $MgCl^+$, do not exceed 1 $mol_c kg^{-1}$ and are essentially the same as with 0.05M perchlorate background (Tables 3 and 4). The small variation in the calculated CEC values is due to anion exclusion, which is explicitly taken into account by the adsorption model (Nir 1986).

DISCUSSION

Constant values of K_{Na} and K_{Mg} yielded good predictions for the amounts of Na^+ and Mg^{2+} adsorbed to montmorillonite for a wide range of concentrations, in fact, the whole range was covered in our experiments. The same applies to the binary system Ca/Na, as long as the fraction of surface sites occupied by Ca^{2+} does not exceed 0.4. However, note that sensitivity tests of the binding coefficient (Figure 2) show that large changes in K_{M++} have little effect on predicted values when $\bar{X}_{Me} < 0.3$ or > 0.8.

One of the issues is whether the adsorption affinity of Ca^{2+} to montmorillonite is greater than that of Mg^{2+}. According to Sposito et al. (1983b), the Wyoming bentonite clay exhibits equal affinities for Ca^{2+} and Mg^{2+} in perchlorate background, whereas Sposito et al. (1983c) found a slight preference of Ca over Mg for adsorption to montmorillonite in a chloride solution. This preference was suggested to be a result of the formation of $CaCl^+$ complexes, which are more stable thermodynamically and have a greater affinity for the clay than $MgCl^+$. While the conclusions of the present study support the conclusions of Sposito et al. (1983a and b) regarding the formation of the complexes $CaCl^+$ and $MgCl^+$ and its adsorption, the binding coefficient found here, $K_{Ca} = 4M^{-1}$ is two-fold larger than K_{Mg}. In Table 5, we illustrate by model calculations that in many cases, including the range of concentrations used in Sposito et al. (1983a and b), the above two-fold difference in binding affinity may result only in small differences in the adsorbed amounts.

Three factors contribute to reduce the difference between the adsorbed amounts of Ca^{2+} and Mg^{2+} in the binary system $M^{++}Na^+$: (1) When the total amount of divalent cation in the system is below half of the amount of surface charges, this sets a limit on the adsorbed amount irrespective of the binding affinity; (2) Part of the adsorption which occurs due to residence in the double layer region, rather than actual binding, is independent of the binding affinity; and (3) A cation with a larger binding affinity, for example, Ca^{2+}, neutralizes a somewhat larger fraction of the surface sites

Table 4. Calculated and experimental data on Na^+-Ca^{2+} exchange on Wyoming bentonite in a 50 mM perchlorate background, at 298 °K.[1]

Solution concentrations		Measured adsorbed amounts			Calculated adsorbed amounts		
c_{Na}	c_{Ca}	q_{Na}	q_{Ca}	Q	q_{Na}	q_{Ca}	CEC
mM		$mol_c\ kg^{-1}$					
52.60 ± 0.64	0.59 ± 0.02	0.76 ± 0.04	0.27 ± 0.01	1.03	0.65	0.26	0.91
47.80 ± 0.07	1.11 ± 0.01	0.61 ± 0.08	0.35 ± 0.01	0.96	0.55	0.36	0.91
47.60 ± 0.33	2.33 ± 0.02	0.56 ± 0.30	0.44 ± 0.02	1.00	0.45	0.44	0.89
36.10 ± 0.43	7.05 ± 0.03	0.33 ± 0.10	0.67 ± 0.12	1.00	0.22	0.71	0.93
31.40 ± 0.50	9.77 ± 0.04	0.25 ± 0.12	0.79 ± 0.04	1.04	0.16	0.78	0.94
21.10 ± 0.06	13.70 ± 0.17	0.13 ± 0.02	0.89 ± 0.07	1.02	0.09	0.86	0.95
11.17 ± 0.05	19.54 ± 0.09	0.10 ± 0.01	0.90 ± 0.02	1.00	0.04	0.90	0.94

[1] The corresponding number of adsorbed metal charges per kg clay is denoted by q. Experimental values for q_{Na} and q_{Ca} are taken from Sposito et al. (1983a). Q is the apparent total adsorbed metal charge, given by $q_{Na} + q_{Ca}$. Calculated values for q_{Na}, q_{Ca} and CEC, were obtained as described in the text, using the binding costants of $K_{Na} = 1M^{-1}$ and $K_{Ca} = 4M^{-1}$.

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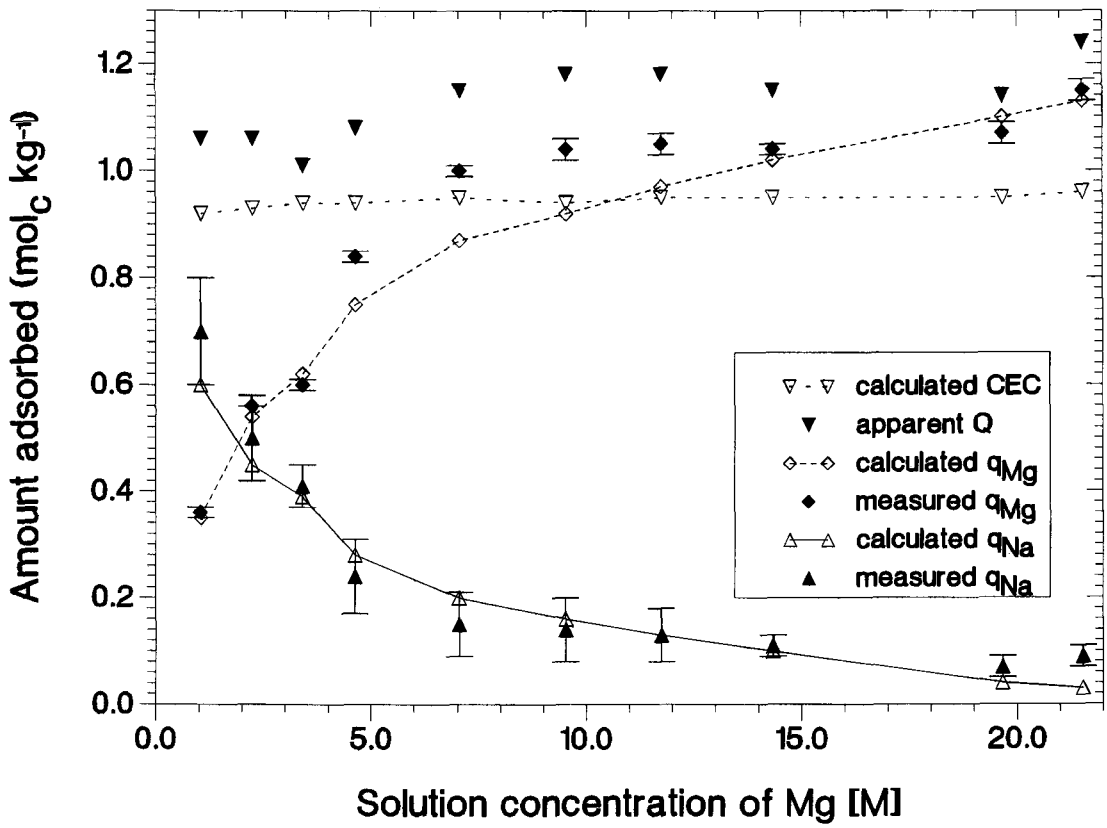


Figure 3. Na-Mg exchange at 298°K on Wyoming bentonite in a 0.05 M chloride background. The corresponding number of adsorbed metal charge per kg clay is denoted by q. Measured values for qNa and qMg are taken from Sposito et al. (1983a). Apparent Q is the apparent total adsorbed metal charge, assumed to be equal to the cation exchange capacity, as obtained by qNa + qMg. Calculated values for qNa, qMg and CEC were obtained as described in the text. The stability constant K_{MgCl^+} = 2.089 M^{-1}, was taken from Sposito et al. (1983a).

than a cation of smaller binding affinity, for example Mg^{2+}. This in turn results in a larger reduction in the magnitude of the surface potential φ_0, in the presence of Ca^{2+}. Consequently, a smaller enhancement will occur in the concentration of the divalent cation near the surface due to the factor $\exp[-2e\varphi_0/kt]$, where k is Boltzmann's factor, T is the absolute temperature and e is the magnitude of electronic charge. This decrease in $|\varphi_0|$ reduces the adsorption of Ca^{2+} to a larger degree than that of Mg^{2+}.

The results in Figures 1 and 2, and in particular, those in Table 1, for the adsorption in the ternary system Na/Ca/Mg support a larger binding affinity of Ca than Mg towards montmorillonite. Part of this difference in adsorption is due to a larger tendency of Ca^{2+} to form M_{Cl+} complexes, but in Figures 1 and 2 and Table 1, adsorption of these complexes comprises a minor part of the total adsorbed amounts.

The result that the binding affinity of Mg^{2+} is lower than that of Ca^{2+} is rationalized by the tightly bound hydration shell of Mg^{2+}, which has a relatively small crystallographic radius. In comparison to the values of 1, 2 and 4 M^{-1} for the binding coefficients of Na^+ Mg^{2+} and Ca^{2+}, respectively, the value of K_{Cs} is 200 M^{-1} (Nir et al. 1986). In the latter case the hydration shells are only loosely attached to the bulky bare ion. It is interesting that the binding coefficient of Cd^{2+} (10 M^{-1}, Hirsch et al. 1989) exceeds that of Ca^{2+}. However, as the fraction of surface sites occupied by Ca increases above 0.4, the effective binding coefficient of Ca increases significantly.

The increase found in the binding coefficient of Ca in the Ca/Na system and Ca/Mg in the Ca/Mg/Na systems may be considered a phenomenological formulation of a complex situation. One possibility could be that the formation of tactoids (in contrast to isolated plates) due to Ca binding to the plates results in an elevation in the surface potential (Verwey and Overbeek 1948), which in turn results in a larger concentration of cations near the surface, depending on their valency. Consequently, the adsorption of divalent cations will increase at the expense of Na^+ as the distances between adjacent plates are reduced. However, this effect should result in similar enhancement of binding for both Ca^{2+} and Mg^{2+}. Still we observed that the Mg/Na system is explained by constant binding

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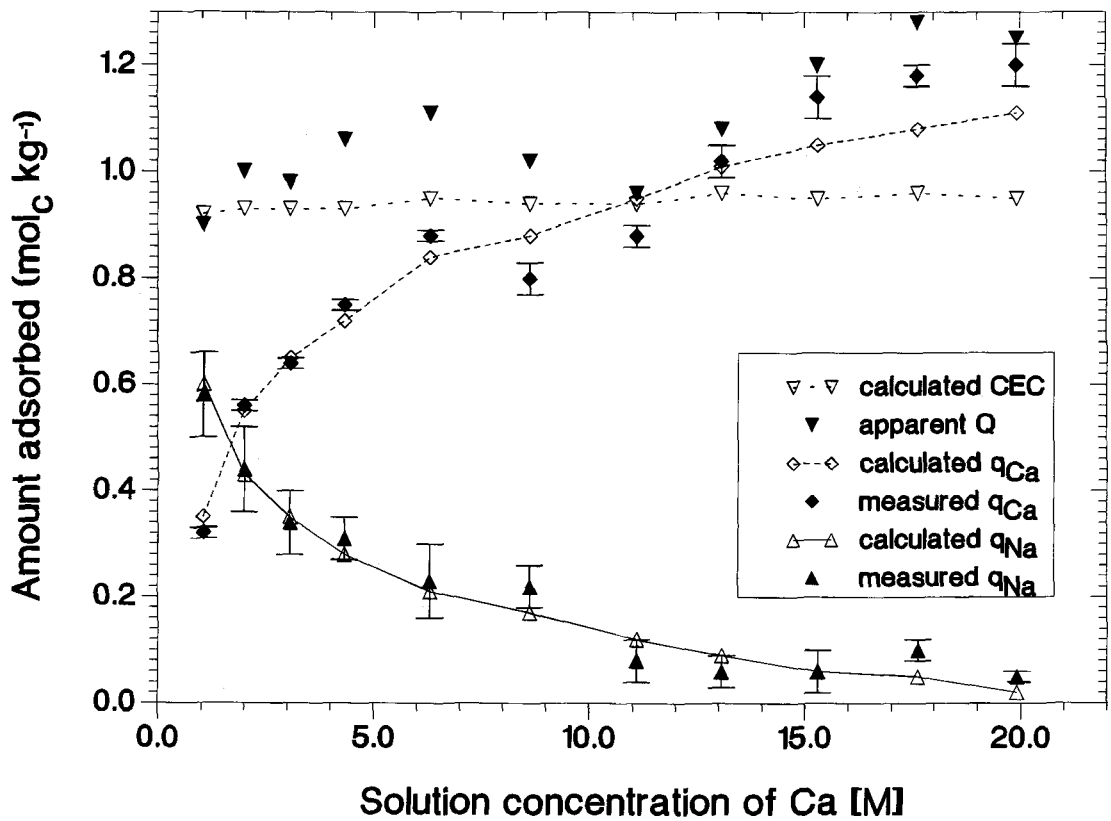


Figure 4. Na-Mg exchange at 298°K on Wyoming bentonite in a 0.05 M chloride background. The corresponding number of adsorbed metal charge per kg clay is denoted by q. Measured values for qNa and qCa are taken from Sposito et al. (1983a). Apparent Q is the apparent total adsorbed metal charge, given by qNa + qCa. Calculated values for qNa, qCa and CEC were obtained as described in the text. The stability constant K_{CaCl^+} = 2.63 M^{-1}, was taken from Sposito et al. (1983a).

coefficients. In the ternary system (Table 1), the binding coefficients of both Ca^{2+} and Mg^{2+} appear to increase by one order of magnitude. Hence, the enhancement in the binding of divalent cations in the ternary system might indeed be due to enhanced surface potential on the inner surfaces of tactoids, but the different pattern in the Mg/Na than in Ca/Na or Ca/Mg/Na systems implies that the formation of tactoids and the enhanced binding in Ca^{2+}-containing systems is a result of slightly decreased interparticle repulsion in these systems.

Table 5. Calculated fractions of adsorbed Ca or Mg per charged site of montmorillonite in the binary systems M^{++}/Na^+ or Ca^{++}/Mg^{++} assuming the absence of solution complexes.

Site concentration	Total added concentrations			Fraction of charges adsorbed per site	
	Na	Ca	Mg	Ca	Mg
	mM				
250	0	65	65	0.500	0.500
10		5	5	0.542	0.432
5		2.5	2.5	0.544	0.436
25	2	14	—	0.956	—
	2	—	14	—	0.952
	15	30	—	0.902	—
	15	—	30	—	0.886
	45	15	—	0.704	—
	45	—	15	—	0.662
	65	5	—	0.336	—
	65	—	5	—	0.310

In passing we speculate that the enhanced binding affinity of Ca^{2+} to montmorillonite, which is observed when higher fraction of the surface is occupied by Ca^{2+}, is largely due to the formation of a complex in which Ca bridges two opposing surfaces. The chance for the formation of such complexes increases as the fraction of the surface sites occupied by Ca is increased. Such a complex apparently does not exist in the case of the Mg^{2+} ion, which is surrounded by a tightly bound hydration shell. However, the binding of Mg^{2+} to montmorillonite in the presence of Ca^{2+} is then enhanced due to enhanced surface potentials on the internal faces of plates in a tactoid and perhaps also due to a certain degree of dehydration as a result of the presence of Ca^{2+} in the internal spaces of tactoids.

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