

Potassium–calcium exchange in electropositive oxisols: description of exchange sites

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Abstract

Potassium–calcium exchange was studied in batch experiments carried out with 2 oxisols exhibiting positive charge balance. The experimental data were quantitatively described with the Rothmund–Kornfeld formulation of the Gaines–Thomas approach, and the permanent and variable surface negative charges were measured using the caesium-adsorption method. For both soils, no appreciable involvement of permanent negative charges was observed in the potassium–calcium exchange, which, in turn, seemed to occur solely on the variable negative charges. The preference for potassium over calcium exhibited by both soils was well described by the Rothmund–Kornfeld formulation of the Gaines–Thomas approach. It was hypothesised that the exchange sites could be divided into 2 groups with different potassium selectivities. The proportions and selectivities of these exchange site groups were estimated combining the Rothmund–Kornfeld formulation with the Dufey–Delvaux multisite model. For both soils, there was excellent agreement between experimental and modelled data and it was possible to estimate the amounts of exchange sites (cmol_e/kg) presenting greater and lower potassium selectivity. The existence of variable negative charge pools more accessible to K than to Ca ions but not evenly accessible to the former was considered as a possible cause of the non-ideal behaviour of the studied soils in relation to the potassium–calcium exchange.

Additional keywords: caesium-adsorption method, Dufey–Delvaux multisite model, Gaines–Thomas, permanent negative charges, Rothmund–Kornfeld formulation.

Introduction

Adsorption processes play a central role in the dynamics of ions in soils. Both the availability of plant nutrients and leaching of ions through the soil profile are highly dependent on ionic retention phenomena. Thus, the quantitative parameters that describe ion adsorption by the soil solid phase must always be accounted for when modelling the ion fate in soils.

Considering the electrostatic adsorption of cations, it is commonly observed that some cationic species are preferentially adsorbed by the soil solid phase (Bolt 1967). Furthermore, soils normally behave as non-ideal exchangers, since they present adsorption sites that show different affinities for the same cation (Goulding and Talibudeen 1980). These aspects can be incorporated into multicomponent transport models using selectivity coefficients, which can be determined in batch competitive adsorption studies (Bond and Phillips 1990).

After the seminal work of Vanselow (1932), other thermodynamic (e.g. Argersinger *et al.* 1950) and quasi-thermodynamic (e.g. Gaines and Thomas 1953) approaches were developed for describing cation exchange reactions. However, even before the publication

of Vanselow (1932), Rothmund and Kornfeld had developed an empirical, simple, and extrapolation-exempted mathematical procedure to treat data from competitive adsorption studies (Bond 1995).

Although competitive adsorption studies involving all cations of interest would be more adequate from the standpoint of the similarities with natural systems, the mathematical treatment of experimental data becomes more complex or even unfeasible as the number of cations increases. However, the easy mathematical treatment associated with the Rothmund–Kornfeld formulation of cation exchange allows for more precise predictions of the cation distribution on the exchanger in ternary systems using binary exchange data with minimal computational effort (Bond and Verburg 1997).

In Brazil almost 60% of the land is covered by oxisols (Schaefer 2001), whose clay mineralogy comprises mainly kaolinite, gibbsite, hematite, goethite, titanium oxides, and hydroxyinterlayered vermiculite (Schwertmann and Herbillon 1992). Although variable surface charges are predominant in these highly weathered soils, permanent charges can also be found (Tessens and Zauyah 1982; Sposito 1983).

The reactivity of permanent negative charges towards cation adsorption increases as the isomorphic substitution of Si^{4+} by Al^{3+} in the silicon tetrahedra sheets of the soil phyllosilicates predominates over the substitution of Al^{3+} by Fe^{2+} or Mg^{2+} that takes place in their aluminium octahedra sheets. Furthermore, the physical conformation of the cation exchange sites derived from permanent charges (i.e. ditrigonal cavities in the silicon tetrahedral surface faces with diameter of ~ 0.26 nm) favours potassium adsorption because the K ion diameter is quite similar to that of the ditrigonal cavities (Sposito 1984).

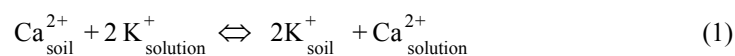
Anderson and Sposito (1991) developed a method for measuring permanent and variable surface negative charges of phyllosilicates based on the preference of the ditrigonal cavities for Cs^+ over Li^+ and on the much lower selectivity of ionisable surface groups for Cs^+ . This method was later described by Zelazny *et al.* (1996) with a few modifications. According to Anderson and Sposito (1991), besides variable negative charges, the caesium-adsorption method measures only the permanent negative surface charges that can make part of cation exchange reactions (i.e. accessible permanent charges).

Most of the current knowledge of potassium–calcium exchange was acquired in studies carried out with temperate climate soils (Goulding 1983). On the other hand, the description of potassium–calcium exchange in tropical soils is limited almost to those rich in allophanic materials (Escudey and Galindo 1988; Escudey *et al.* 1997). Therefore, the present study had the following objectives: (i) investigate the involvement of permanent and variable negative charges of 2 electropositive oxisols in potassium–calcium competitive adsorption; and (ii) describe the features of potassium–calcium exchange in these soils using the Rothmund–Kornfeld formulation of the Gaines–Thomas approach and its combination with the exchange site distribution model derived by Dufey and Delvaux (1989).

Theoretical considerations

Rothmund–Kornfeld formulation of the Gaines–Thomas approach

The potassium–calcium exchange equilibrium can be represented by the following equation:



According to the Gaines and Thomas (1953) approach, the thermodynamic equilibrium constant (K_t^{GT}) of this exchange reaction is given by:

$$K_t^{GT} = \frac{(g_K^{GT} N_K)^2 (\gamma_{Ca} M_{Ca})}{(g_{Ca}^{GT} N_{Ca}) (\gamma_K M_K)^2} \quad (2)$$

where g_K^{GT} and g_{Ca}^{GT} are the respective adsorbed activity coefficients of the K and Ca ions; N_K and N_{Ca} are the respective equivalent fractions of K^+ and Ca^{2+} on the exchanger; γ_K and γ_{Ca} are the activity coefficients of K^+ and Ca^{2+} in the equilibrium solution; and M_K and M_{Ca} are the K^+ and Ca^{2+} molarities in the equilibrium solution.

For each specific ionic composition of both solution and exchanger phases, the selectivity coefficient (K_c^{GT}) is calculated by:

$$K_c^{GT} = \frac{N_K (\gamma_{Ca} M_{Ca})}{N_{Ca} (\gamma_K M_K)^2} \quad (3)$$

From Eqns 2 and 3 we have:

$$K_t^{GT} = \frac{g_K^{GT^2}}{g_{Ca}^{GT}} K_c^{GT} \quad (4)$$

The application of the Gibbs–Duhem equation (Guggenheim 1967) on Eqn 4 allows the derivation of equations that enable the calculations of the thermodynamic equilibrium constant and the activity coefficients of adsorbed ions. These equations are given by:

$$\ln K_t^{GT} = 1 + \int_0^1 \ln K_c^{GT} dN_K \quad (5)$$

$$2 \ln g_K^{GT} = (1 - N_K)(1 - \ln K_c^{GT}) + \int_{N_K}^1 \ln K_c^{GT} dN_K \quad (6)$$

$$\ln g_{Ca}^{GT} = N_K (\ln K_c^{GT} - 1) - \int_0^{N_K} \ln K_c^{GT} dN_K \quad (7)$$

The Rothmund–Kornfeld formulation of cation exchange is based on the empirical observation that there is a linear relationship between the logarithm of the ratio of adsorbed cation amounts, raised to their respective stoichiometric coefficients, and the logarithm of the ratio of cation activities in the equilibrium solution, also raised to their respective stoichiometric coefficients (Bond 1995). Considering Eqn 1 and using the Gaines–Thomas equivalent fractions for the expression of the adsorbed cation amounts, the Rothmund–Kornfeld equation is expressed by:

$$k = \frac{N_K^2}{N_{Ca}} \left(\frac{\gamma_{Ca} M_{Ca}}{\gamma_K^2 M_K^2} \right)^n \quad (8)$$

where k and n are empirical constants for the particular cation pair and exchanger. If Eqn 8 is obeyed, a plot of $\log(N_K^2/N_{Ca})$ v. $\log(\gamma_K^2 M_K^2/\gamma_{Ca} M_{Ca})$ should yield a straight line with slope n and intercept $\log k$.

The constants k and n can be used to calculate the thermodynamic equilibrium constant (K_t^{RK}) and the activity coefficients of adsorbed ions (g_K^{RK} and g_{Ca}^{RK}). Considering Eqn 1, these parameters can be calculated by the following equations (Bond 1995):

$$\ln K_t^{RK} = \frac{1}{n} (1 + \ln k) \quad (9)$$

$$g_K^{RK} = N_K^{(1/n)-1} \exp\left(\frac{N_{Ca}}{2n}\right) \quad (10)$$

$$g_{Ca}^{RK} = N_{Ca}^{(1/n)-1} \exp\left(\frac{-N_K}{n}\right) \quad (11)$$

It can be observed from Eqn 3 that the calculation of K_c^{GT} is not possible when $N_K = 0$ ($M_K = 0$) or when $N_K = 1$ ($N_{Ca} = 0$). This leads to the need for extrapolations at $N_K = 0$ and $N_K = 1$ in order to calculate K_t^{GT} , g_K^{GT} , and g_{Ca}^{GT} (Eqns 5, 6, and 7, respectively). This procedure involves uncertainties whose magnitudes depend on the shapes of the curves, conferring less precision to the K_t , g_K , and g_{Ca} values. On the other hand, the fact that the Rothmund–Kornfeld empirical constants k and n are obtained fitting the Eqn 8 to all experimental points, including $N_K = 0$ and $N_K = 1$, potentially gives more accuracy to the K_t , g_K , and g_{Ca} estimates when they are calculated using Eqns 9, 10, and 11, respectively.

Standard Gibbs free energy of exchange (ΔG°)

The overall selectivity of the exchanger phase by one ion, at constant temperature and pressure, is commonly expressed through ΔG° values, which can be calculated using the following equation (Sparks 1995):

$$\Delta G^\circ = -RT \ln K_t \quad (12)$$

where R is the universal gas constant (8.314 J/K mol), T is the absolute temperature, and K_t is the thermodynamic equilibrium constant.

Exchange site description

A generalised thermodynamic treatment of multisite adsorption has been presented by Sposito (1981) and Harmsen (1982) and can be used for modelling the different potassium selectivities shown by exchange sites. According to Dufey and Delvaux (1989) and considering Eqn 1, the potassium equivalent fraction on the exchanger can be calculated by:

$$N_K = \sum_{i=1}^m \alpha_i \left[\frac{K_{V,i} KAR^2}{4 + K_{V,i} KAR^2} \right]^{1/2} \quad (13)$$

where m is the number of site classes, α_i is the fraction of the total soil negative charge that is due to sites of type i , $K_{V,i}$ is the individual Vanselow selectivity coefficient of sites i , and KAR (potassium adsorption ratio) is the activity ratio $(K^+)/(Ca^{2+})^{1/2}$ in the equilibrium

solution. The KAR values can be calculated from both the potassium equivalent fraction in the solution (X_K) and total cationic concentration (CT, mol_c/L), according to the equation:

$$\text{KAR} = (2\text{CT})^{1/2} \frac{X_K}{(1 - X_K)^{1/2}} \frac{\gamma_K}{\gamma_{\text{Ca}}^{1/2}} \quad (14)$$

Material and methods

Soil characterisation

The competitive adsorption of potassium and calcium ions was performed using 2 highly weathered soil samples, which were collected in the B horizons of a Rhodic Acrudox and a Xanthic Acrustox (Soil Survey Staff 1998) located in the north of the São Paulo State, Brazil. The soil samples were air-dried and crushed to pass through a 2-mm sieve before analyses.

Texture was determined by the pipette method (Gee and Bauder 1986), organic carbon by the Walkley and Black method (Nelson and Sommers 1982), exchangeable Al by 1 M KCl extraction (Bertsch and Bloom 1996), and potential acidity ($\text{H}^+ + \text{Al}^{3+}$) by shaking 2 g of soil for 15 min with 40 mL of $\text{Ca}(\text{OAc})_2$ 0.5 M buffered at pH 7, filtering the suspensions through Whatman 42 filter, and titrating 25 mL of the extracts with 0.025 M NaOH using 1% phenolphthalein as the indicator (EMBRAPA 1997). The Si, Fe, and Al contents associated with secondary minerals were determined after extraction with boiling H_2SO_4 1:1 at a 1:20 soil (g)/solution (mL) ratio (EMBRAPA 1997) and used for the calculation of the weathering indices Ki ($\text{SiO}_2/\text{Al}_2\text{O}_3$, mol/mol) and Kr ($\text{SiO}_2/(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$, mol/mol). Dithionite- and oxalate-extractable Fe (Fe_d and Fe_o) were determined according to Burman *et al.* (1996) in the clay fraction (<2 μm) separated by gravity settling (Jackson 1969).

Soil pH was measured in water at a 1:2.5 soil (g)/water (mL) ratio (EMBRAPA 1997) and the point of zero salt effect (PZSE) was calculated from potentiometric titration data (van Raij and Peech 1972) using the mathematical–computational approach outlined by Alves *et al.* (2002).

The permanent and variable surface negative charges were measured using the caesium-adsorption method described by Zelazny *et al.* (1996), with some modifications that allowed the charge measurements to be made at the same values of soil pH and ionic strength (I) as the potassium–calcium competitive adsorption studies. Thus, duplicate 2-g soil samples and 20 mL of 0.01 M CsCl were added to 50-mL centrifuge tubes, shaken for 30 min, and centrifuged. The supernatants were discarded, 20 mL of 0.01 M CsCl was added to the tubes, and the tubes were shaken and centrifuged. These procedures were repeated until the Cs^+ concentration in the supernatants was the same as that of the added solution. When this was observed, the supernatants were discarded and the soil slurries were successively washed with 20 mL of 95% ethanol by shaking for 1 min until the supernatant did not show the presence of Cl^- after the addition of 1 drop of 1 M AgNO_3 . Afterwards, the soils were dried at 65°C for 48 h to enhance the adsorption of Cs^+ ions on the permanent negative charges by inner-sphere complexation (Sposito 1984). For the displacement of Cs^+ from variable-charge sites, 0.5 g of oven-dried Cs-saturated soil and 25 mL of 0.01 M LiCl were added to 50-mL pre-weighed centrifuged tubes, shaken, and centrifuged and the supernatants were saved for Cs^+ measurement. The tubes were weighed to quantify the volumes of the entrapped solutions, whose density was considered to be 1 kg/L. The displacement of Cs^+ from permanent charges was carried out through four 30-min successive extractions with 15 mL of 1 M NH_4OAc . The supernatants from the extractions were combined and saved for Cs^+ analysis. The LiCl and NH_4OAc extracts were analysed for Cs^+ by flame atomic emission spectroscopy after the addition of K (as KCl) to suppress the Cs ionisation. The charge values measured in the oven-dried soil samples were corrected for the air-dried samples using gravimetric factors determined from the weight losses of 2 g of air-dried samples after drying at 65°C for 48 h.

The mineralogical composition of the soil clay fractions was evaluated qualitatively through X-ray diffraction (XRD) analysis. For the deferrified clays, oriented slides of Mg-saturated and K-saturated clay dried at 25°C were analysed in a Phillips PW 1830 diffractometer using monochromated $\text{CuK}\alpha$ radiation at 40 mA and 40 kV. The scans were obtained between 5 and 30°2 θ at a speed of 1.2°2 θ /min. The XRD patterns of the heated K-saturated clays (350°C and 550°C) and Mg-saturated clays treated with ethylene glycol were recorded using the same procedure. The XRD analyses were also performed on non-oriented powder samples of the soil clay fractions after their treatments with boiling 5 M NaOH for concentration of iron oxides (Kämpf and Schwertmann 1982). The patterns were recorded with a Siemens D5000 computer oriented diffractometer using monochromated $\text{CoK}\alpha$ radiation at 25 mA and 35 kV. The scans were

Table 1. Set of solutions used in the K⁺–Ca²⁺ competitive adsorption study
 X_K , equivalent fraction of potassium in solution, given by $X_K = [K^+]/([K^+] + [Ca^{2+}])$ where the terms in brackets represent the K⁺ and Ca²⁺ concentrations in the solution, both expressed in mol/L; CT, total cationic concentration

Solution	X_K	K ⁺	Ca ²⁺ (mol/L)	CT
1	0.000	0.0000	0.00666	0.00666
2	0.143	0.0010	0.00600	0.00700
3	0.333	0.0025	0.00500	0.00750
4	0.500	0.0040	0.00400	0.00800
5	0.778	0.0070	0.00200	0.00900
6	0.895	0.0085	0.00100	0.00950
7	0.931	0.0090	0.00066	0.00966
8	1.000	0.0100	0.00000	0.01000

obtained from 20 to 45°2θ at a speed of 0.6°2θ/min, and both peak positions and raw areas were determined using the software EVA 3.09.

Potassium–calcium competitive adsorption

The potassium–calcium exchange was studied following the batch procedure used by Udo (1978) with some modifications. Duplicate 2-g soil samples and 20 mL of KCl–CaCl₂ solutions (Table 1) were added to 50-mL pre-weighed centrifuge tubes, shaken for 30 min, and centrifuged. The supernatants were discarded, 20 mL of KCl–CaCl₂ solutions was added to the tubes, and the tubes were shaken and centrifuged. These procedures were repeated until the K⁺ and Ca²⁺ concentrations in the supernatants were the same as the added solutions. When this was verified, the supernatants were discarded, the tubes were weighed, and 2 successive extractions with 20 mL of 1 M NH₄OAc were performed. The extract concentrations of K⁺ and Ca²⁺ were determined, respectively, by flame emission and atomic absorption spectroscopies. Finally, the adsorbed amounts of K⁺ and Ca²⁺ were calculated discounting the amounts of these ions present in the entrapped solutions.

Non-preference exchange isotherm

The non-preference isotherm for the heterovalent exchange ($\Delta G^\circ = 0$) was calculated using data in Table 1 and the equation proposed by Sposito (1981):

$$N_K = \left[1 + \frac{2}{\tau CT} \left(\frac{1}{X_K^2} - \frac{1}{X_K} \right) \right]^{-1/2} \quad (15)$$

where $\tau = \gamma_K^2 + \gamma_{Ca}^{2+}$. The values of γ_{K^+} and $\gamma_{Ca^{2+}}$ were calculated using the extended Debye–Hückel equation (Wolt 1994).

Results and discussion

Soil characterisation

The results of the soil characterisation analyses are given in Table 2. The data revealed that the Rhodic Acrudox sample was very clayey (clay >600 g/kg), whereas the Xanthic Acrustox had medium texture (clay <350 g/kg, sand >150 g/kg) (EMBRAPA 1999). The studied soils have similar pH values (5.50 and 5.69) and no exchangeable Al³⁺. Therefore, for both soils, the (H⁺+Al³⁺) values represent the amounts of the covalent-bonded H⁺ dissociated from surface ionisable groups at pH 7, being greater for the Rhodic Acrudox due to its higher clay and organic matter contents. The comparison of pH and PZSE values indicates that for both soils the net variable surface charge was positive (pH < PZSE) (van Raij and Peech 1972).

Table 2. Soil properties

C, organic carbon; Al^{3+} , exchangeable Al; $\text{H}^+ + \text{Al}^{3+}$, potential acidity; PZSE, point of zero salt effect; σ_p , accessible permanent negative surface charge; σ_v , variable negative surface charge; Ki, weathering index given by $1.7 (\text{SiO}_2/\text{Al}_2\text{O}_3)$ (EMBRAPA (1997)); Kr, weathering index given by $1.7 (\text{SiO}_2)/(\text{Al}_2\text{O}_3 + 0.64\text{Fe}_2\text{O}_3)$ (EMBRAPA 1997); Fe_o/Fe_d , ratio between ammonium oxalate and dithionite extractable iron in the clay fraction

Soil	Sand	Silt (g/kg)	Clay	C (g/kg)	Al^{3+} (cmol _c /kg)	$\text{H}^+ + \text{Al}^{3+}$ (cmol _c /kg)	pH	PZSE	Fe_o/Fe_d
Rhodic Acrudox	44	309	647	4.9	0.0	3.7	5.50	6.07	0.06
Xanthic Acrustox	419	157	324	2.0	0.0	1.9	5.69	6.96	0.03
	σ_p	σ_v (cmol _c /kg)	$\sigma_p + \sigma_v$	Fe_2O_3 (H_2SO_4 digestion, g/kg)	Al_2O_3	SiO_2	Ki	Kr	
Rhodic Acrudox	0.54	1.00	1.54	323.9	313.5	90.5	0.49	0.30	
Xanthic Acrustox	0.46	0.89	1.35	121.5	181.5	90.5	0.85	0.60	

Unlike most of the world's soils, in which Si is more abundant than Al, oxisols usually present the opposite relationship due to weathering, whose degree is characterised in the Brazilian Soil Classification System (EMBRAPA 1999) through the indexes Ki and Kr; the lower Ki and Kr values, the more weathered the soil. The low Ki values of the studied soils (Table 2) reflect the occurrence of intense Si losses and the relative accumulation of Fe and Al in both of them, whereas Kr values < 0.75 indicate predominance of oxides over kaolinite in their clay fractions (EMBRAPA 1999).

Low Fe_o/Fe_d ratios (Table 2) indicate predominance of well-ordered over poorly ordered iron oxides in the clay fractions of both soils. The ratio of hematite to hematite + goethite clay contents (Hm/Hm+Gt), calculated according to Resende *et al.* (1987) from XRD patterns of iron oxide concentrated clays, was 0.85 for the Rhodic Acrudox and 0 for the Xanthic Acrustox, indicating that the former can be classified as hematitic (Hm/Hm+Gt > 0.6) and the latter as goethitic (Hm/Hm+Gt < 0.2) (EMBRAPA 1999).

The XRD analyses carried out in the deferrified clay showed that kaolinite and gibbsite were the main constituents of this fraction for both soils. However, only for the Xanthic Acrustox could the presence of hydroxyinterlayered vermiculite be ascertained, which agrees with the high resistance to weathering of this mineral (Schwertmann and Herbillon 1992). The XRD patterns of the iron oxide concentrated clays indicated the presence of goethite, hematite, anatase, and maghemite in the Rhodic Acrudox. On the other hand, goethite was the only crystalline iron oxide found in the Xanthic Acrustox clay fraction, which also comprised rutile and anatase. Finally, for both soils, no 2:1 clay mineral line was observed in the XRD patterns of the iron oxide concentrated clays.

The results of the caesium-adsorption method show that in both soils the variable negative charges represented nearly 65% of the total surface negative charges at the soil pH and I of 0.01 mol/L (Table 2). Although the XRD patterns showed that the hydroxyinterlayered vermiculite clay content of the Xanthic Acrudox was greater than that of the Rhodic Acrudox, the amount of permanent negative charges determined in the former was slightly smaller. This can be ascribed to the 2-fold greater clay content of the Rhodic Acrudox, whose measured permanent charges may indicate the presence of XRD-undetectable amounts of hydroxyinterlayered vermiculite in its clay fraction. Furthermore, for both soils, small amounts of permanent negative charges could be ascribed to their contents of kaolinite, whose permanent and variable negative charges can

Table 3. K⁺–Ca²⁺ exchange equilibrium data of the studied soils

X_K , equivalent fraction of potassium in solution, given by $X_K = [K^+]/([K^+] + [Ca^{2+}])$ where the terms in brackets represent the K⁺ and Ca²⁺ concentrations in the solution, both expressed in mol/L; N_K , equivalent fraction of potassium on the exchanger, given by $N_K = K^+_{ads}/(K^+_{ads} + Ca^{2+}_{ads})$ where K^+_{ads} and Ca^{2+}_{ads} represent the respective amounts of K⁺ and Ca²⁺ on the exchanger, both expressed in cmol_c/kg

X_K	Rhodic Acrudox				X_K	Xanthic Acrustox			
	N_K	K^+_{ads}	Ca^{2+}_{ads}	$(K^+ + Ca^{2+})_{ads}$ (cmol _c /kg)		N_K	K^+_{ads}	Ca^{2+}_{ads}	$(K^+ + Ca^{2+})_{ads}$ (cmol _c /kg)
0.000	0.000	0.00	1.10	1.10	0.000	0.000	0.00	0.99	0.99
0.143	0.114	0.12	0.93	1.05	0.143	0.151	0.14	0.79	0.93
0.333	0.241	0.26	0.82	1.08	0.333	0.302	0.28	0.64	0.92
0.500	0.333	0.34	0.68	1.02	0.500	0.415	0.38	0.54	0.92
0.778	0.540	0.56	0.48	1.04	0.778	0.656	0.62	0.33	0.95
0.895	0.684	0.73	0.34	1.07	0.895	0.775	0.74	0.22	0.96
0.931	0.753	0.79	0.26	1.05	0.931	0.837	0.77	0.15	0.92
1.000	1.000	1.06	0.00	1.06	1.000	1.000	0.93	0.00	0.93
Mean ± s.d.				1.06 ± 0.02					0.94 ± 0.03

also be measured by the caesium-adsorption method as shown by Schroth and Sposito (1997).

Involvement of permanent and variable negative charges in the potassium–calcium exchange

For both soils, the sum of the adsorbed amounts of K⁺ and Ca²⁺ at equilibrium was effectively constant for all X_K values (Table 3), indicating practically the same occupation of cation exchange sites at different concentrations of K⁺ and Ca²⁺ in the equilibrium solutions (Table 1).

Considering that the variable surface charges are dependent on the solution pH and ionic strength (Gillman 1981) and that both the negative charge measurements and the potassium–calcium exchange studies were carried out at the same pH and I values, it is possible to compare the mean potassium–calcium exchange site occupations and the amounts of negative surface charges measured by the caesium-adsorption method. The variable negative surface charge (σ_v) values (1.00 ± 0.02 cmol_c/kg for the Rhodic Acrudox and 0.89 ± 0.01 cmol_c/kg for the Xanthic Acrustox) were, for both soils, quite similar to the mean amounts of K⁺ + Ca²⁺ on the exchanger phase at equilibrium (1.06 ± 0.02 cmol_c/kg for the Rhodic Acrudox and 0.94 ± 0.03 cmol_c/kg for the Xanthic Acrustox) (Table 3). These numerical similarities and the smaller values of the permanent negative surface charges (σ_p) (0.54 ± 0.02 cmol_c/kg for the Rhodic Acrudox and 0.46 ± 0.01 cmol_c/kg for the Xanthic Acrustox) may suggest that σ_p had an inappreciable involvement in the potassium–calcium exchange.

Some operational aspects of the caesium-adsorption method may explain these results. Both the alcoholic washing, which replaces water molecules that were solvating Cs⁺ by less-effective solvating molecules of ethanol, and the sample heating, which removes the ethanol-solvating shell, enhance the inner-sphere complexation of Cs⁺ with the permanent negative charges (Sposito 1984; Anderson and Sposito 1991). Therefore, these procedures probably enable the Cs ions to displace from permanent negative charge cations that, under the experimental conditions of the potassium–calcium exchange, behaved as non-exchangeable cations. Although Anderson and Sposito (1991) obtained good correspondence between the charge measurements using the caesium-adsorption method and the charge properties of reference clay minerals, there is no experimental evidence that

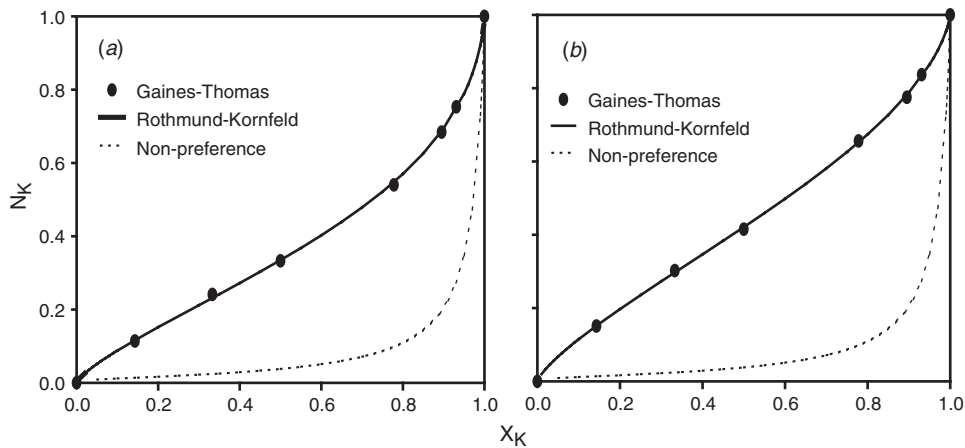


Fig. 1. Measured cation exchange isotherms (points) and fitted Rothmund–Kornfeld relationships (Eqn 8) (solid lines): (a) Rhodic Acrudox, (b) Xanthic Acrustox.

the σ_p values measured by this method consist of permanent negative charges that can be involved in cation exchange reactions under natural conditions. In fact, the authors argued that because no existing method can quantify the accessible permanent negative charge, it was not possible for them to provide direct experimental evidence for the validity of the proposed macroscopic method.

If our soils had appreciable natural amounts of K^+ and Ca^{2+} adsorbed on permanent negative charges or if appreciable amounts of K and Ca ions added to soils in the batch experiments were adsorbed onto those charges, the mean amounts of $K^+ + Ca^{2+}$ adsorbed at equilibrium state should be significantly greater than σ_v ; however, this was not the case. Even for variable negative charges, there may be the non-involvement of some cation exchange sites in the potassium–calcium adsorption. For both soils, the mean amounts of $K^+ + Ca^{2+}$ adsorbed at equilibrium (Table 3) were lower than the sums of σ_v plus $(H^+ + Al^{3+})$ (Table 2). Therefore, at the soil pH values, the K and Ca ions were not able to displace covalent-bonded H^+ from variable negative charges.

Rothmund–Kornfeld description of potassium–calcium exchange

The experimental cation exchange isotherms were positioned above the non-preference isotherm for mono-divalent exchange (Fig. 1), indicating, as pointed out by Jensen and Babcock (1973), that the oxisols evaluated in this study presented preferential adsorption of K^+ over Ca^{2+} , in agreement with well-known descriptions of potassium–calcium exchange carried out in soils worldwide (Jardine and Sparks 1984; Levy *et al.* 1988; Parfitt 1992).

Both Fig. 1 and data given in Table 4 show that the Rothmund–Kornfeld formulation provided an excellent fit to the experimental data for both soils, in agreement with the results of Bond (1995) and Escudey *et al.* (2001).

A functional relationship between the Gaines–Thomas selectivity coefficient and the equivalent fraction of potassium on the exchanger can be derived from Eqns 3 and 8 in terms of Rothmund–Kornfeld empirical parameters. This equation is given by:

$$K_c^{GT} = k^{1/n} \frac{N_K^{2(1-1/n)}}{(1 - N_K)^{1-1/n}} \quad (16)$$

Table 4. Empirical k and n Rothmund–Kornfeld parameters, thermodynamic equilibrium constants calculated after the Rothmund–Kornfeld formulation and the Gaines–Thomas approach, and respective free energies of exchange

R^2 , coefficient of determination of the linear form of Eqn 8 fitted to experimental data; K_t^{RK} and K_t^{GT} , thermodynamic equilibrium constants calculated with Eqns 9 and 5, respectively; ΔG° , free energy of exchange calculated with Eqn 12

Soil	k	Rothmund–Kornfeld			Gaines–Thomas		
		n	R^2	K_t^{RK}	K_t^{GT}	ΔG°	ΔG°
					(J/mol)	(J/mol)	
Rhodic Acrudox	5.67	0.76	0.99	37.3	–8966	37.8	–8999
Xhantic Acrustox	10.68	0.76	0.99	82.3	–10927	80.6	–10875

As shown in Fig. 2, the decrease in the potassium selectivity coefficient with an increase in the potassium saturation on the exchanger was adequately described by Eqn 16 for both soils with an excellent agreement between the K_c^{GT} values calculated using the k and n Rothmund–Kornfeld empirical parameters and those calculated according the Gaines–Thomas approach (Eqn 3). It can be inferred from these results that some sites possess a strong ability to adsorb K^+ at lower potassium concentrations in the equilibrium solution. After these sites become K^+ -saturated, other sites presenting less potassium selectivity begin to operate. The possible nature of the potassium-selective sites will be discussed later in this paper.

A K_t value greater than unity and, as a consequence, a negative value of ΔG° indicate that the exchanger phase has preference for the cation that was present in the solution before the cation exchange (Goulding 1983). Thus, data in Table 4 reiterate the conclusions that were drawn from the cation exchange isotherms, giving to them a numerical meaning and indicating again an excellent agreement between the K_t values calculated with the Rothmund–Kornfeld formulation (Eqn 9) and with the Gaines–Thomas approach (Eqn 5).

The activity coefficient of an adsorbed ion represents the degree of freedom that it has to leave the adsorbed state towards the unitary standard state of maximum freedom, and therefore reflects the heterogeneity of the exchange process (Goulding 1983). The behaviour of the potassium and calcium adsorbed activity coefficients described over the

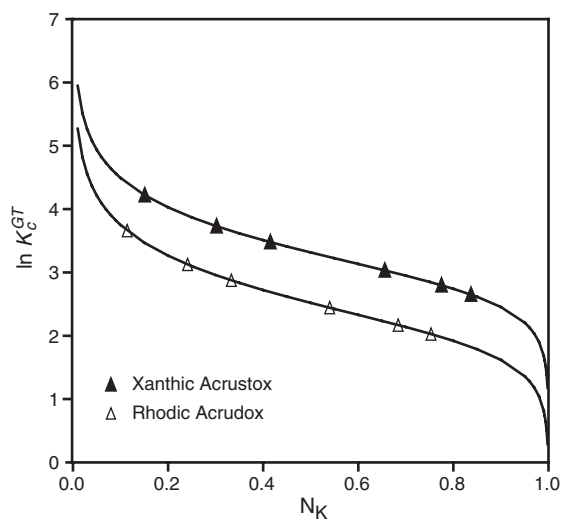


Fig. 2. Gaines–Thomas selectivity coefficients in logarithmic scale calculated using Eqn 3 (points) and calculated from the fitted Rothmund–Kornfeld k and n empirical parameters (Eqn 16) (lines).

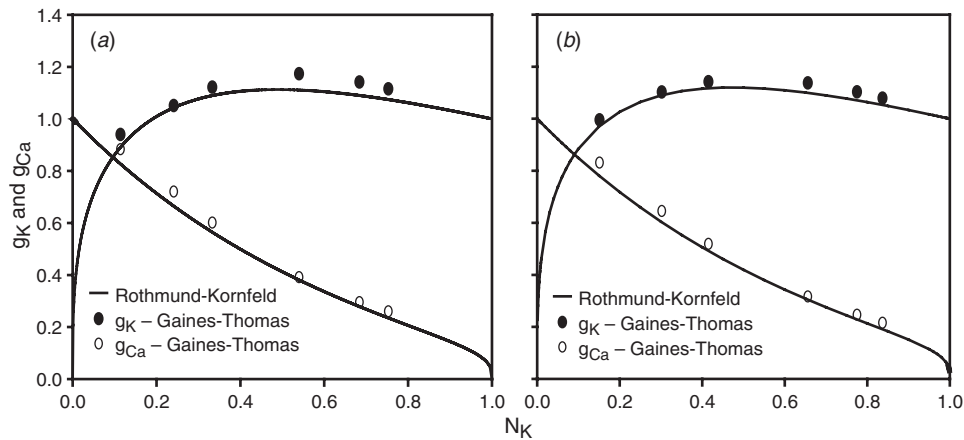


Fig. 3. Relationships between the activity coefficients of adsorbed ions and potassium saturation on the exchanger phase as calculated according to the Gaines–Thomas approach (Eqns 6 and 7) (points) and from the Rothmund–Kornfeld n parameter (Eqns 10 and 11) (lines): (a) Rhodic Acrudox, (b) Xanthic Acrustox.

whole range of N_K values using the Rothmund–Kornfeld formulation (Fig. 3a, b) showed that for both soils the potassium ions were more strongly held to the adsorption complex when the potassium saturation on the exchanger phase was low. Furthermore, it can be verified again that for both K^+ and Ca^{2+} there was a good correspondence between the activity coefficients of the adsorbed ions as calculated by the Rothmund–Kornfeld formulation (Eqns 10 and 11) and by the Gaines–Thomas approach (Eqns 6 and 7).

Distribution of the potassium-selective sites

The multisite model presented by Dufey and Delvaux (1989) (Eqn 13) assumes that the exchange reaction is governed by a single value of the Vanselow selectivity coefficient, K_v , for each group of exchange sites presenting the same affinity for potassium ions. Although Eqn 13 allows simulations for any number of exchange site groups, we chose the 2-site model for describing the distribution of the potassium-selective sites in our soils.

In the present study, the nonlinear fitting of the Dufey–Delvaux multisite model would be less precise or even impossible if it were carried out with only the experimental N_K and X_K values that can be used for this purpose. Thus, in order to improve the fitting results, we created a more comprehensive dataset by estimating N_K values with the Rothmund–Kornfeld equation (Eqn 8) from X_K values that ranged from 0.001 to 0.999 with a step of 0.001. The potassium and calcium molarities (M_K and M_{Ca}) required in Eqn 8 were also calculated from the same X_K values and for $I = 0.01$ mol/L using the following equations, which were derived from the equivalent fraction and ionic strength definitions applied to a KCl–CaCl₂ solution:

$$M_K = \frac{2X_K I}{3 - X_K} \quad (17)$$

$$M_{Ca} = \frac{I}{3} \left(1 - \frac{2X_K}{3 - X_K} \right) \quad (18)$$

Besides conferring smaller standard deviations for the parameter estimates, this approach allows the multisite model to explore with greater detail the changes of potassium

Table 5. Results of the nonlinear regression analysis carried out to fit the two-site model

$$N_K = \alpha_1 \left[\frac{K_{V1} KAR^2}{4 + K_{V1} KAR^2} \right]^{1/2} + \alpha_2 \left[\frac{K_{V2} KAR^2}{4 + K_{V2} KAR^2} \right]^{1/2}$$

Soil	Parameter	Estimate	Standard error	Confidence interval (95%)	
				Lower	Upper
Rhodic Acrudox	α_1	0.211	0.002	0.207	0.216
	K_{V1}	1527.583	44.170	1440.905	1614.261
	α_2	0.725	0.002	0.721	0.729
	K_{V2}	18.607	0.263	18.091	19.123
Xhantic Acrustox	α_1	0.240	0.003	0.235	0.245
	K_{V1}	2335.316	65.339	2207.096	2463.535
	α_2	0.712	0.002	0.707	0.716
	K_{V2}	35.102	0.468	34.183	36.021

selectivity with the N_K variations, since the Rothmund–Kornfeld k and n empirical parameters (Eqn 8) implicitly include the variations of the selectivity and exchanger-phase activity coefficients with the exchanger composition (Bond 1995). For each X_K value, the total cationic concentration (mol/L) was calculated as $CT = M_K + 2M_{Ca}$ and used in Eqn 14 for the KAR calculation. Nonlinear regression analysis (SAS 1994) was then carried out to fit the N_K and their respective KAR values to the Eqn 13 considering 2 groups of exchange sites ($m = 2$).

The 2-site model fitted very well to the adsorption data of both soils. Table 5 shows that most of 2-site model parameters had small standard deviations and narrow interval confidences, which for all of them did not include estimates equal to zero. Furthermore, the 2-site model predictions of N_K values were very similar to the experimental ones (Fig. 4).

The respective amounts of more and less potassium-selective sites were estimated by multiplying the mean amounts of exchange sites occupied by K^+ and/or Ca^{2+} at the equilibrium (Table 3) by the α_1 and α_2 2-site model parameters. Thus, for the Rhodic Acrudox, the more potassium-selective sites comprised nearly 0.22 cmol_c/kg, whereas the sites with lower potassium selectivity corresponded to nearly 0.77 cmol_c/kg. For the Xanthic Acrudox, ~0.23 cmol_c/kg consisted of exchange sites with greater potassium selectivity, whereas the less potassium-selective sites comprised nearly 0.67 cmol_c/kg. Although having quite different clay contents (647 g/kg for the Rhodic Acrudox and 324 g/kg for the Xanthic Acrustox), both soils presented identical amounts of cation exchange sites with higher potassium selectivity. However, the Vanselow selectivity coefficient associated with the more potassium-selective sites of the Xanthic Acrudox was greater than that associated with the same sites of the Rhodic Acrudox. Taking into consideration the similar soil pH values, these results indicate that the clay composition has more impact on soil potassium selectivity than has the clay content.

Potassium selectivity in electropositive oxisols

Ionic selectivity is dependent on both intrinsic ion properties and exchanger characteristics. Although it is well known that the smaller size, polarisability, and hydration energy of the potassium ions favour their preferential adsorption over calcium (Shainberg and Kemper 1963; Goulding 1983), the complex nature of the soil solid phase makes it impossible to

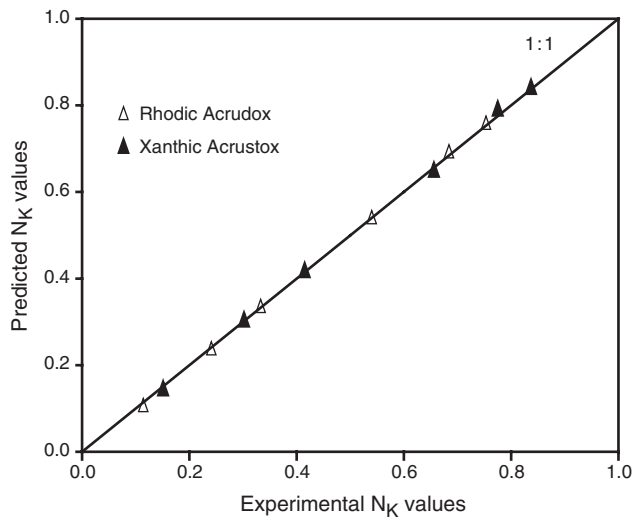


Fig. 4. Relationship between the experimental values of potassium saturation on the exchanger phase and the predicted values given by the 2-site model.

precisely assign the exchanger features responsible for the preferential adsorption of K^+ . However, some assumptions can be made.

Considering that soil sesquioxides have points of zero charge between 5.0 and 9.0 (Parks 1965) and that the soil pH values were 5.50 and 5.69, most of the oxide surface hydroxyls of our soils were protonated (OH_2^+), and thus carrying few negative charges available for cation adsorption. The major involvement of electrostatic forces in the adsorption of K and Ca ions by variable charge soils (Ji and Li 1997) allows the argument that this positive charge balance disfavors calcium adsorption, obeying the double-layer model derived by Eriksson (1952) for electrostatic mono-divalent exchange, in which the preferential adsorption of the divalent cation increases as the net negative surface charge of the exchanger also increases. The decrease in the preferential adsorption of K^+ after the removal of iron oxides from oxisols reported by Ji and Li (1997) appears to reinforce this assumption. Furthermore, the electrostatic repulsion itself is more intense for divalent ions such as calcium than for monovalent ones.

Organic matter, hydroxyinterlayered vermiculite, and kaolinite were the main sources of negative charges in the studied soils and therefore their exchanger features related to potassium–calcium exchange must also be considered. Although organic matter seems to decrease the soil preference for potassium relative to calcium by increasing the negative surface charge density (Goulding and Talibudeen 1984; Jardine and Sparks 1984), its interactions with 2:1 soil phyllosilicates appear also to increase the proportion of potassium-accessible adsorption sites, lowering the calcium selectivity (Poonia and Niederbudde 1990). The preferential adsorption of K^+ by kaolinite relative to calcium is almost always ascribed to the presence of trace amounts of 2:1 clay minerals as impurities in the kaolinite samples used in the potassium–calcium exchange experiments (Ferris and Jepson 1975; Goulding and Talibudeen 1980; Levy *et al.* 1988).

The main exchanger feature accounting for the preferential adsorption of potassium relative to calcium by 2:1 phyllosilicates is the presence in their structures of regular exchange sites (i.e. planar surface charges) with lower potassium selectivity and wedge-shaped zones or frayed-edge exchange sites that show high affinity for potassium

(Beckett and Nafady 1967; Saha *et al.* 2001). In this exchange site scheme, the K^+ ions enter the wedge zones preferentially because they lose their hydration shells more easily than the strongly hydrated Ca ions, which, in turn, are screened out. In addition, when the wedge zones become more saturated with K^+ ions, the selectivity is then determined by the planar surface sites, which have relatively lower affinity for K^+ . Thus, the potassium selectivity decreases as K^+ saturation increases. For vermiculite, this potassium-selective site distribution is in close agreement with the results of the microcalorimetric measurements carried out by Goulding and Talibudeen (1980) and with those from the infrared studies performed by Badreddine *et al.* (2002).

Although our results suggest that the charge type *per se* (i.e. permanent or variable negative charge) does not seem the direct cause of the non-ideal behaviour of both studied soils in relation to the potassium–calcium exchange, it is possible to hypothesise that this exchange feature may be mainly due to the existence in these soils of variable negative charge pools, which, although being more accessible to K^+ than to Ca^{2+} , are not evenly accessible to the former. Therefore, in such an exchange complex where the existence of 2 pools is considered, the 2-site model seems appropriate for describing the distribution of the potassium-selective sites. However, more research is needed for evaluating these suppositions.

Conclusions

The electropositive oxisols evaluated in this study behaved as non-ideal exchangers and presented preferential adsorption of potassium over calcium for all proportions of these cations on the exchanger phase. For both soils, the permanent negative charges measured by the caesium-adsorption method seem to be involved in undetectable amounts in the potassium–calcium exchange, which instead took place solely on the variable negative charges. More research is needed to better assess the involvement of the permanent negative charges of oxisols in the cation exchange reactions. The Rothmund–Kornfeld formulation of the Gaines–Thomas approach allowed an excellent macroscopic description of the potassium–calcium exchange in both soils, and its combination with the Dufey–Delvaux multisite model provides a good tool for modelling the exchange site distribution with greater precision using fewer experimental data. Although we modelled the distribution of 2 groups of potassium-selective sites, precise simulations considering more than 2 exchange site groups can also be done using fewer experimental data when the Rothmund–Kornfeld empirical equation is combined with the Dufey–Delvaux multisite model in exchange systems presenting constant ionic strength. The significance of this approach for cation transport modelling should be assessed in future research. The methods used in this study did not allow the assigning of precise causes of the preferential adsorption of potassium exhibited by the studied soils. It is probable that the heterogeneous nature of the cation exchange sites towards potassium adsorption may be due to the existence of variable negative charge pools, which, although being more accessible to K^+ than to Ca^{2+} ions, may not be evenly accessible to the former. However, further investigation is needed for evaluating this hypothesis.

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