

Potassium-Calcium Exchange in a Multireactive Soil System: II. Thermodynamics¹

P. M. JARDINE AND D. L. SPARKS²

ABSTRACT

Thermodynamics of K exchange were investigated in Ca-saturated samples from the Ap horizon of an Evesboro soil from Delaware. At 283 and 298 K the selectivity curves ($\ln k$, vs. \bar{X}_K) showed preference for K at low values of N_K (mole fraction of K in solution) and for Ca at higher values. This selectivity reversal may be attributed to exchange sites of varying reactivity for K and Ca ions and supports the hypothesis of the multireactive nature of the soil. Although K was selectively bound at low N_K , the soil exhibited an overall Ca preference as noted by the positive standard free energy values (ΔG°). The standard enthalpy of exchange (ΔH°) was negative, which indicated very strong binding of K ions with some sites of the soil. This may be associated with the presence of vermiculitic clay minerals that predominated in the $<2\text{-}\mu\text{m}$ clay fraction. A thermodynamic investigation was also initiated on the various size fractions of the soil (i.e., sand, silt, and clay) and on soil that was treated with cetyltrimethylammonium bromide (CTAB) or NaOCl-DCB. These treatments explained the differences in ionic selectivity observed in the Evesboro soil.

Additional Index Words: Selectivity curves, free energy of exchange, enthalpy of exchange, entropy of exchange.

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IONIC EXCHANGE EQUILIBRIA on clays and on soils have been characterized using thermodynamic principles (Keay and Wild, 1961; Laudelout et al., 1968; Jensen and Babcock, 1973; Sposito, 1981; Babcock and Duckart, 1980). While investigating K-Ca exchange on kaolinite, Jensen (1973) and Udo (1978) found that large negative ΔG° values described the process. The preference of kaolinite for K ions was attributed to specific interactions of the cation with edge sites of the mineral. The large charge density associated with edge sites would tend to create high exergonic values for the exchange of such cations (van Bladel and Menzel, 1969). Negative ΔG° values were

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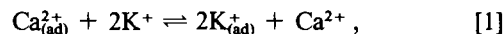
also found by Hutcheon (1966) for the formation of a Ca-clay from K-saturated montmorillonite.

The validity of thermodynamics on cation exchangers that exhibit several groups of binding sites is discussed by Barrer and Klinowski (1979). van Bladel and Gheyi (1980), investigating Ca-Na and Ca-Mg exchange equilibria on calcareous soils, found the Ca preference of the soil was strongly affiliated with the organic phase. Potassium exchange equilibria in many soils using several counter ions was investigated by Deist and Talibudeen (1967). The strong K preference of these soils was related to the large quantity of vermiculitic clay minerals that existed in the $<2\text{-}\mu\text{m}$ fraction. Goulding (1981) also found strong potassium retention in soils that contained substantial quantities of 2:1 clay minerals as well as strong Ca preference in soils that had high organic matter contents. Goulding and Talibudeen (1979) investigated the effect of particle size on K-Ca exchange selectivity in sandy clay soil. They noted that ΔG° became more negative with a decrease in particle size. This implied that K selectivity increased as the clay content increased. El-Sayed et al. (1970), investigating the thermodynamics of Cu-Ca exchange on a bentonite clay, noted a selectivity reversal for the cations at 298K. The apparent switch-over in preference was attributed to different binding sites on the mineral. Accordingly, the objectives of this study are to establish thermodynamic parameters on the Evesboro soil and to explain the differences in ionic selectivity observed in this multireactive soil system.

MATERIALS AND METHODS

Theoretical Considerations

Thermodynamic parameters for K-Ca exchange using the approach suggested by Argersinger et al. (1950) were studied. Considering the following reversible reaction,



we may express the thermodynamic equilibrium constant K as follows:

$$\frac{a_{\text{K}(\text{ad})}^2 a_{\text{Ca}}}{a_{\text{Ca}(\text{ad})} a_{\text{K}}^2} = K \quad [2]$$

where $a_{(\text{ad})}$ = the activity of the cation on the exchanger phase, and a = the activity of the cation in the solution phase.

Treating the exchanger as a nonideal solid solution and assuming the activity of adsorbed water to be negligible (Högfeldt, 1952; Gaines and Thomas, 1953; Sposito, 1981), we may express the activity of the cations on the exchanger and in solution as follows:

$$a_{K(ad)}^2 = f_K^2 \bar{N}_K^2 \text{ and } a_{Ca(ad)} = f_{Ca} \bar{N}_{Ca} \quad [3]$$

$$a_K^2 = \delta_{KCl}^4 m_K^2 \text{ and } a_{Ca} = \delta_{CaCl_2}^3 m_{Ca} \quad [4]$$

where

f = activity coefficient of the cation on the exchanger phase,

\bar{N} = mole fraction of the cation on the exchanger phase,

δ = mean activity coefficient of the salt in the solution phase, (δ was determined by the Debye-Hückel equation), and

m = molality of the cation in the solution phase.

Thus, Eq. [2] assumes the form:

$$\frac{f_K^2 \bar{N}_K^2 \delta_{CaCl_2}^3 m_{Ca}}{f_{Ca} \bar{N}_{Ca} \delta_{KCl}^4 m_K^2} = \frac{f_K^2}{f_{Ca}} k_v = K \quad [5]$$

where k_v = Vanselow selectivity coefficient.

Applying the Gibbs-Duhem equation to this binary system and combining with Eq. [5], we may obtain the following using a mole fraction of unity as the standard state for adsorbed ions (Argersinger et al., 1950):

$$\ln K = \int_0^1 \ln k_v d\bar{X}_K \quad [6]$$

where \bar{X}_K = equivalent fraction of potassium on the exchanger phase.

From exchanger isotherms (e.g., \bar{N}_K vs. N_K), where N_K is the mole fraction of K^+ in the solution phase, selected values of \bar{N}_K and N_K may be used in combination with appropriate δ and m values to determine k_v as indicated by Eq. [5]. The equilibrium constant K may then be calculated by plotting $\ln k_v$ as a function of \bar{X}_K and determining the area under the curve by applying the trapezoidal rule. Knowledge of K allows calculation of ΔG° , the standard free energy of exchange, ΔH° , the standard enthalpy of exchange, and ΔS° , the standard entropy of exchange as shown in Eq. [7] through [9], respectively:

$$\Delta G^\circ = -RT \ln K \quad [7]$$

$$d \ln K / dT = \Delta H^\circ / RT^2 \quad [8]$$

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ) / T \quad [9]$$

The general treatment given by Gaines and Thomas (1953) differs from the approach given above (except for the special case of homovalent exchange) in that the Gaines and Thomas approach is derived totally in terms of equivalent fractions. Since the activity of a cation does not become equal to its equivalent fraction in the limiting cases of Raoult's law, exchange isotherms and selectivity coefficients for heterovalent exchange based on the equivalent fraction are subject to misinterpretation with regard to relative ion affinities for a surface (Högfeldt, 1952; Moore, 1972; Sposito and Mat-

tigod, 1979; Babcock, 1981). Thus, the Gaines and Thomas treatment on heterovalent systems provides only a general idea about ion selectivity and the physical causes for the behavior of an ion on a surface.

EXPERIMENTAL PROCEDURES

Basic Characterization Analysis

Bulk samples were taken from the Ap horizon of an Evesboro loamy sand (mesic, coated Typic Quartzipsamments) from Sussex County, Delaware, air-dried, and ground to pass through a 2-mm sieve. The selected chemical, mineralogical, and physical properties of the Evesboro soil are provided in Table 1.

Thermodynamics of Exchange on Evesboro Soil

Prior to the thermodynamic studies, subsamples of the Evesboro soil were Ca-saturated using procedures given previously (Sparks and Jardine, 1981). One-gram samples were placed in suspension with deionized water and incorporated onto 0.45- μ m Gelman filter pads using low-pressure suction. Once the soil was filtered free of the deionized water, one of eight different solutions, all at constant ionic strength ($I=0.1$) but varying KCl and $CaCl_2$ concentrations (Jensen and Babcock, 1973), was leached through the soil using low-pressure suction. The soil was leached with several liters of solution for 16 to 24 h until equilibrium was ascertained. Equilibrium was attained when the concentration of K and Ca of the leachate equaled the concentration of the initial K-Ca solution. Once equilibrium was established, two 25-mL aliquots of deionized water were leached through the soil to remove entrained salts. The hydrolysis of Ca was considered and found not to be a problem. The extent of Ca and K adsorption at equilibrium was determined by leaching the soil with 250 mL of a 1N NH_4Cl solution. Calcium and potassium were analyzed by atomic absorption spectrophotometry. All studies were conducted under isobaric, isothermal conditions of 1 atm, and 283, 298 and 313 \pm 0.5 K, respectively.

Thermodynamics of Exchange on Various Size Fractions

Prior to the thermodynamic studies, subsamples of the Evesboro soil were fractionated into their various size fractions (e.g., sand 2 mm–50 μ m, silt 50–2 μ m, clay <2 μ m). Initially, the organic matter was removed from the soil samples with three washings of hot 10% NaOCl solution (pH 9.5), followed by three washings with 2% Na_2CO_3 (pH 9.5) and deionized water. The soil was then treated twice with appropriate quantities of 0.3M Na citrate, 1M $NaHCO_3$, and crystalline $Na_2S_2O_4$ and shaken for 16 h per treatment to remove Fe oxides (Mehra and Jackson, 1960). This treatment will hereafter be referred to as DCB. At this point, a portion of the soil sample was removed, washed with deionized water, then Ca saturated by standard methods. The NaOCl-DCB treated soil was then analyzed by the thermodynamic method described previously. The remaining portion of the soil sample was fractionated into its various size fractions. The sand was removed from the silt and clay using a 300-mesh sieve and pH 10 water. The separation of the silt from the clay was achieved through centrifugation. Each of the fractions was Ca saturated as before and analyzed by the thermodynamic method described previously.

Thermodynamics of Exchange on Soil Treated with CTAB

The application of cetyltrimethylammonium bromide (CTAB) to the Evesboro soil was discussed earlier (Jardine

Table 1—Selected chemical, mineralogical, and physical properties of Evesboro soil.

Horizon	Particle size analysis			Or-ganic matter	CEC mol($1/2$ Mg $^{2+}$) kg $^{-1}$	Mineral suite†	
	Sand	Silt	Clay			<2- μ m clay fraction	2 to 50- μ m silt fraction
	%						
Ap	86.9	10.6	2.5	1.4	23.9	VC $_1$, KK $_2$, MI $_3$, QZ $_4$	QZ $_1$, FE $_2$, GI $_3$, KK $_4$, VC $_1$

† VC = chloritized vermiculite, KK = kaolinite, MI = mica, QZ = quartz, FE = feldspar, GI = gibbsite. Subscript 1 = most abundant; 4 = least abundant.

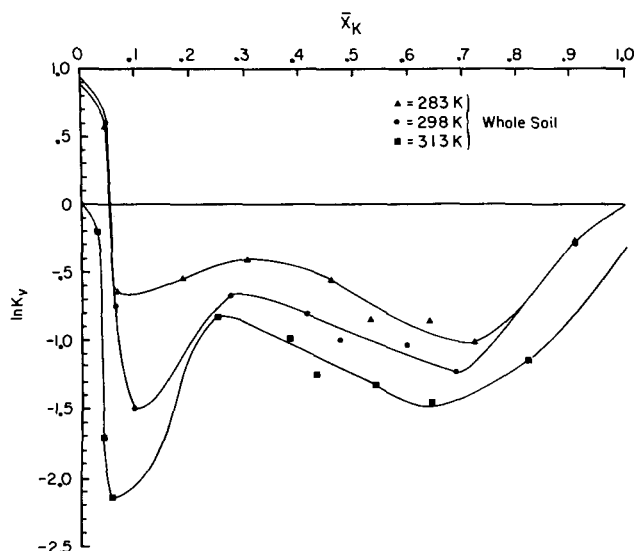


Fig. 1—Selectivity curves for K-Ca exchange on the Evesboro soil at three temperatures.

and Sparks, 1984). The CTAB-treated soil was also analyzed by the thermodynamic method described earlier.

RESULTS AND DISCUSSION

Thermodynamics of Exchange on Evesboro Soil

Since the kinetics of K adsorption and desorption were reversible on the Evesboro soil (95 to 97% of all K adsorbed could be subsequently desorbed), the application of thermodynamic principles to the soil is justified. Figure 1 illustrates the selectivity curves ($\ln k_v$ vs. \bar{x}_K) for K-Ca exchange on the Evesboro soil at 283, 298, and 313 K. At 283 and 298 K, the selectivity curves show preference for K at low values of N_K (mole fraction of potassium in solution) and for Ca at higher values. This selectivity reversal may be attributed to exchange sites of varying reactivity for K and Ca ions and supports the hypothesis of the multireactive nature of the soil (Jardine and Sparks, 1984).

Although K was selectively bound at low N_K , the soil exhibited Ca preference at all three temperatures as noted by the positive standard free energy (ΔG°) values (Table 2). The positive value implied that the driving force for the formation of a K soil from a Ca soil is not favored. The overall Ca preference of the soil may possibly be attributed to the organic phase of the soil. Strong binding of Ca to organic matter has been noted by numerous authors (Naylor and Overstreet, 1969; van Bladel and Gheyi, 1980). The validity of this hypothesis will become more apparent later. The ΔG° values became increasingly positive as temperature increased (Table 2). This implies that Ca ions become increasingly preferred on the soil exchange sites as the temperature rises. This conforms with the Le-Chatelier-Bran principle that states that exothermic reactions are impeded with additions of heat and endothermic reactions are enhanced by heat additions (Dickerson, 1969). Since heats of exchange for uptake of the preferred cation are generally exothermic (Table 2), a decrease in selectivity of K with increasing temperature can be expected.

The standard enthalpy of exchange (ΔH°) was de-

Table 2—Thermodynamic parameters for K-Ca exchange on Evesboro soil, soil treated with CTAB or NaOCl-DCB, and the various size fractions of the Evesboro soil under isothermal conditions.

Sample	Temperature	ΔG°	ΔH°	ΔS°
		— J mol ⁻¹ —	— J mol ⁻¹ K ⁻¹ —	
Whole soil	283	+1 247	-15 900	-60.7
	298	+1 925	-15 900	-59.8
	313	+3 071	-15 900	-60.7
CTAB-treated soil	283	+ 510		
	298	+1 008		
NaOCl-DCB treated soil	298	+ 172		
Silt	298	+ 364		
Clay	298	-2 839		

termined from the van't Hoff equation using three points with an r value of 0.986. The ΔH° value for the soil was negative, which indicated very strong binding of K with some sites of the soil (Table 2). The exothermic process indicated that heat was given off as the chemical bonds between Ca and K with the soil exchange sites were broken and formed, respectively. Also, the negative ΔH° is related to the heat release associated with the changing hydration status of the cations as they are adsorbed and desorbed from the soil surface. The ΔH° value was also several orders of magnitude larger than ΔG° values, suggesting that the bonding of K ions to these highly selective sites was extremely strong. The low ΔG° values imply that a small amount of heat in the standard state is left for the system to do useful work; thus, K ions have a limited molecular motion when in contact with these sites. Such a restriction suggests formation of strong bonds between K ions and some exchange sites of the soil.

Standard entropy values (ΔS°) were negative, indicating that K-Ca exchange produced a condition that was more ordered in its molecular arrangement (Table 2). This would be expected for the formation of a K soil from that of a Ca soil since the total entropy change of an aqueous soil system may be regarded as the sum of two terms: a configurational entropy term and a term encompassing the entropy of ion hydration. The adsorption of a monovalent ion and subsequent desorption of a divalent ion would both result in an entropy decrease. The adsorption of K ions onto the exchanger would cause a decrease in the configurational entropy of the soil since monovalent ions have fewer ways in which to arrange themselves on a given quantity of exchange sites compared with divalent ions (Laudelout et al., 1968). The desorption of Ca ions into the bulk solution would in turn cause a decrease in the entropy of hydration, since Ca ions structurally order water molecules (Hutcheon, 1966; Sparks and Jardine, 1981). The summation of these two factors would result in a net negative ΔS° value (Table 2). For reactions involving the exchange of two different sized cations, as in this study, it is more likely that the entropy term associated with ion hydration plays the predominate role in determining the total entropy change for the reaction (Laudelout et al., 1968). Also, the entropy term associated with ion hydration most likely dominates in exchange processes occurring on vermiculitic clay minerals (Gast and Klobe, 1971). The large ΔS° values obtained for the heterovalent ex-

change of K-Ca on the Evesboro soil may be related primarily to the exchange sites of organic matter and chloritized vermiculite.

Thermodynamics of Exchange on Size Fractions and Soil Treated with CTAB or NaOCl-DCB

A thermodynamic investigation was also initiated on the various size fractions of the soil and on whole soil that was treated with CTAB or NaOCl-DCB. These treatments were conducted to explain the differences in ionic selectivity observed in the soil. As would be expected, a thermodynamic characterization of the sand fraction provided no useful information in describing the behavior of the cations on the soil surface. This fraction comprised 86.9% of the soil and was assumed to have no significant contribution to the total soil CEC.

The selectivity curves and exchange isotherms for the clay fraction and the whole soil at 298 K are shown in Fig. 2 and 3, respectively. The clay fraction of the soil comprised 25% of the total soil CEC. The selectivity curves and the ΔG° value (Table 2) show that the clay fraction has a strong preference for K ions. The large initial peak at low N_K on the clay selectivity curve (Fig. 2) indicates that binding sites with high affinity for K ions exist. The high selectivity for K is related to chloritized vermiculite and kaolinite, which predominate in this fraction (Table 1). Both of these minerals have been shown to exhibit strong attractive forces with K ions (Jensen, 1973; Udo, 1978; Sparks et al., 1980a, 1980b; Sparks and Jardine, 1981; Jardine and Sparks, 1984). The thermodynamics of K-Ca exchange were performed on a pure kaolinite clay (Jardine and Sparks, 1984) to serve as a reference for interpreting the Evesboro clay selectivity curves. The

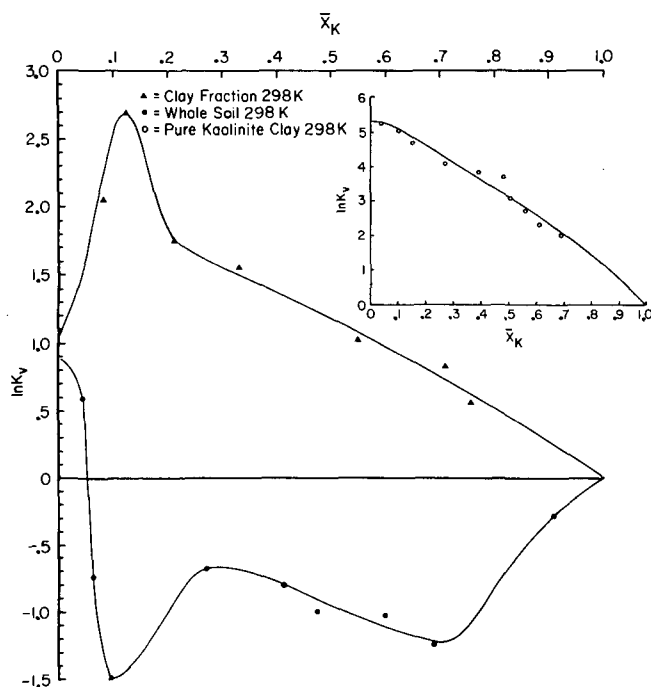


Fig. 2—Selectivity curves for K-Ca exchange on the Evesboro soil and the clay fraction of the soil at 298 K. The inset shows the selectivity curve for K-Ca exchange on a pure kaolinite clay at 298 K.

trends appear fairly similar for the two clay samples except for the strong initial peak at low N_K for the Evesboro clay. This may be related to the chloritized vermiculite in the latter, which exhibits stronger attractive forces for K ions relative to kaolinite. The loss of the Ca preference peaks that are prevalent in the whole soil selectivity diagram (Fig. 2) is related primarily to the extraction of organic matter and silt.

The selectivity curves for the silt fraction, which comprised approximately 10% of the total soil CEC, and the whole soil at 298 K are shown in Fig. 4. The magnified initial peak at low N_K for the silt selectivity curve indicates that binding sites with strong preference for K ions exist. This may possibly be attributed to the small quantity of chloritized vermiculite and kaolinite found in this fraction (Table 1). The loss of the Ca preference peak at about $\bar{X}_K = 0.10$ in the silt fraction is also apparent from the selectivity diagrams and from the ΔG° values (Table 2). The loss of Ca preference at this region is probably related to the extraction of the organic phase that was initiated prior to particle size fractionation. The hypothesis that the peak at $\bar{X}_K = 0.10$ is attributable to the organic matter of the soil will become more apparent as our discussion proceeds. The secondary Ca preference peak, which exhibited a minimum at approximately $\bar{X}_K = 0.65$ to 0.70 for both the silt and the whole soil, was much more difficult to characterize. This portion of the selectivity curve may possibly be related to large organic polymers, which are not adequately removed by NaOCl, or attributable to feldspar minerals, which were present in significant quantities in the silt fraction. Since feldspars differ in their relative affinities for ions, it is difficult to prove that the feldspars present in the silt fraction of the Evesboro soil prefer Ca ions relative to K ions. Marshall (1964) found that anorthite had a greater affinity for Ca ions than Na ions.

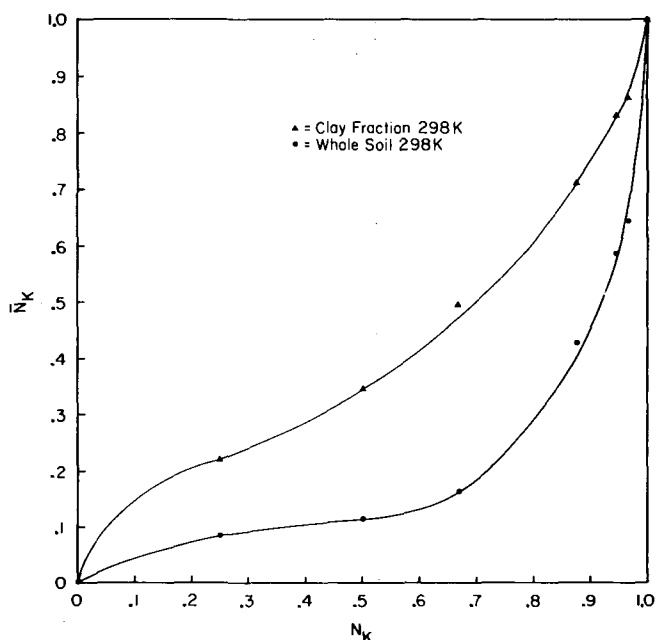


Fig. 3—Exchange isotherms for K-Ca exchange on the Evesboro soil and the clay fraction of the soil at 298 K.

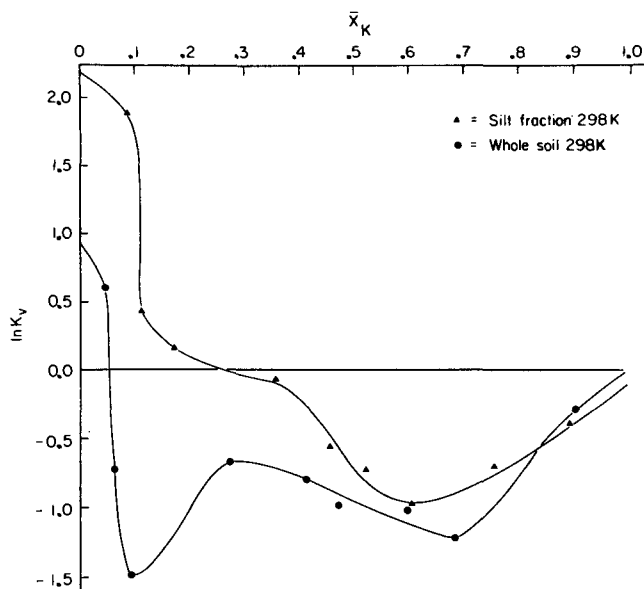


Fig. 4—Selectivity curves for K-Ca exchange on the Evesboro soil and the silt fraction of the soil at 298 K.

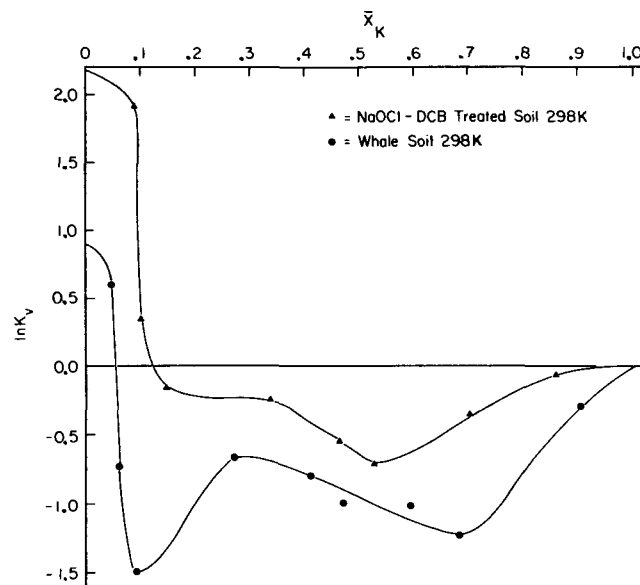


Fig. 5—Selectivity curves for K-Ca exchange on the Evesboro soil and soil treated with NaOCl-DCB at 298 K.

The selectivity curves for NaOCl-DCB treated soil at 298 K are illustrated in Fig. 5. As might be expected, the extraction of organic matter and Fe oxides from the soil resulted in a 65% loss in CEC. Once again the large initial peak implying strong binding of K ions to certain sites of the soil was present. Also, the Ca preference peak at $\bar{X}_K = 0.10$ was no longer present and supports the hypothesis that the peak is attributable to the organic phase of the soil. The secondary Ca preference peak that exhibited a minimum at about $\bar{X}_K = 0.60$ to 0.70 was also still apparent but was much less dramatic than that observed for the whole soil and the silt fraction (Fig. 1 and 4). This is probably related to the increased percentage of clay that occurs when various fractions of the whole soil are eliminated. This is verified by the fact that the ΔG° value for the NaOCl-DCB treated soil falls between the ΔG° values obtained for the clay and silt (Table 2).

The thermodynamics of K-Ca exchange on soil treated with CTAB was also performed (Fig. 6, Table 2). It was previously determined from ion exchange kinetics that CTAB was selectively adsorbed onto the readily accessible sites of the soil and had no effect on the interlayer sites (Jardine and Sparks, 1984). This is verified as well from ion exchange equilibria data since CTAB effectively eliminated 40% of the exchange sites associated with the soil. Figure 6 illustrates the selectivity curves for the soil treated with CTAB and the whole soil at 298 K. The magnified initial peak at low N_K for the CTAB-treated soil indicates that the percentage of highly selective sites for K has been increased. This might be expected since CTAB does not affect the interlayer sites of clay minerals that are highly specific for K ions (Fig. 2). Since CTAB also does not affect the difficultly accessible sites of organic matter (Jardine and Sparks, 1984), the Ca preference peaks still prevail over the majority of the selectivity diagram (Fig. 6). Even though the Ca preference peaks are present, their magnitude is significantly reduced,

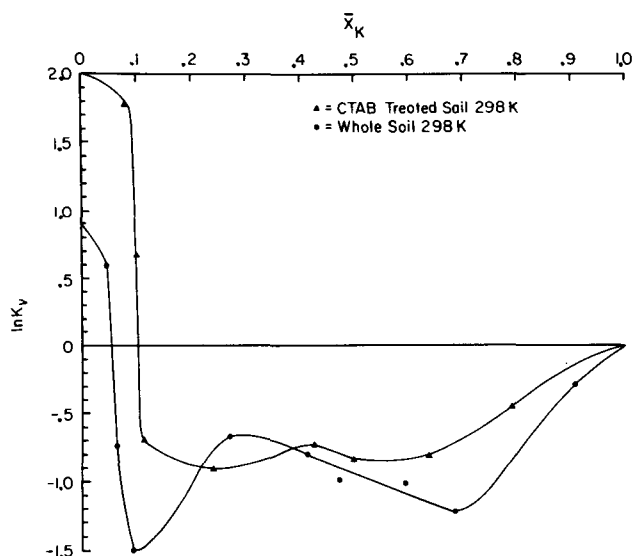


Fig. 6—Selectivity curves for K-Ca exchange on the Evesboro soil and soil treated with CTAB at 298 K.

indicating that CTAB is eliminating readily accessible sites of the soil that prefer Ca ions. This might be expected since the readily accessible sites of the soil are primarily related to the external surfaces of organic matter (Jardine and Sparks, 1984). Similar results were obtained at 283 K. At 313 K the CTAB molecule did not bind to the soil as noted by an insignificant drop in CEC. This is probably related to the increased solubility of the molecule as well as structural changes occurring in organic matter at this higher temperature. The ΔG° values at 283 and 298 K (Table 2) are significantly less positive than those of the whole soil at similar temperatures. This further supports the idea that CTAB eliminates readily accessible exchange sites from the Evesboro soil that would normally prefer Ca ions relative to K ions.

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