Ion Exchange Equilibria Involving Alumīnum in a Kaolīnītīc Ùltisöl

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ABSTRACT

Cation exchange equilibria in an acid Ultisol profile involving K-Al, Ca-Al, K-Ca, Na-K, and Na-Ca exchanges were studied. Selectivity coefficients, surface activity coefficients and free energy changes were computed using the thermodynamic formulations.

In exchange equilibria involving Al, the magnitude of selectivity coefficients $K_s$ was affected by pH, surface composition, and hydrolysis of Al. In equilibria not involving Al, good reversibility for K-Ca, Na-K and Na-Ca exchanges was obtained. Potassium was selectively adsorbed in all horizons of the profile. The overall selectivity sequence follows the order of $K > Al > Ca > Na$.

Additional Index Words: selectivity coefficients, surface activity coefficients, free energy change; K-Al, Ca-Al, Na-K, Na-Ca, and K-Ca exchanges.


I

ON EXCHANGE DATA in highly weathered soils are scanty. Singh and Talibudeen (1971) studied the K-Al exchange in some latosols (Ultisols and Oxisols) from Malaysia and found that in seven of the nine soils studied, K was adsorbed more strongly than Al; while the reverse was the case from the remaining two soils. Nye et al. (1961) reported that for the exchange between K and Al on smectite, Kaolinite and two North Carolina soils (Ultisols), the preference of Al over K by the exchange sites may reverse depending upon the salt concentration used for displacement and the degree of saturation of K on the exchange complex. This was not the case of the Al-Ca exchange where Al was always preferred.

In the high rainfall region of West and Central Africa, the coarse-textured, kaolinitic Ultisols and Oxisols are the major soils in the region. Exchangeable Al generally comprises more than 50% of the total exchangeable cations in the soil. Soil acidity and loss of nutrient elements through leaching are probably among the major factors limiting more intensive crop production. Studies on ion-exchange equilibria in these soils, particularly those involving Al, are therefore of fundamental importance in order to better understand the nutrient leaching phenomenon as well as correcting Al toxicity by liming. This paper reports on cation exchange in a representative Ultisol profile (Typic Paleudult) from southern Nigeria involving exchanges of K-Al, Ca-Al, K-Ca, Na-Ca, and Na-K.

MATERIALS AND METHODS

Profile samples were taken at 20-cm increments from International Institute of Tropical Agriculture (IITA) high rainfall (2,400 mm) substation at Onne, near Port Harcourt, Nigeria. The soil is classified as Typic Paleudult; coarse loamy, siliceous, isohyperthermic family according to Soil Taxonomy classification. Minerals present in the clay fraction are predominantly kaolinite and small amount of goethite throughout the profile. Relevant properties of the Onne profile are given in Table 1. Samples were air dried and sieved through a 2-mm sieve.

Exchange equilibria at 25°C and constant ionic strength were achieved as follows:

A series of 5-g soil samples were repeatedly saturated in preweighed polyethylene centrifuge tubes with 30-ml portions of 1 N KCl, CaCl₂, or NaCl solutions and equilibrating for 4 hours. After the last desaturation, the soil samples were washed 5 times with 30-ml portions of 10⁻⁴ M solutions of the corresponding chlorides. Correction was made by weighing the 10⁻⁴ M solution entrapped after the last desaturation. Mixed solutions (25 ml) of the two exchanging cations in varying ratios and at a total concentration of 10⁻⁴ M were then added to the soil and shaken on a reciprocal shaker for 48 hours. The equilibrium solutions were then analyzed after centrifugation. The cations on the exchange phase were extracted three times with 30-ml portions of unbuffered 1 N NH₄Cl and collected in 100-ml volumetric flasks. Correction was again made for the entrapped equilibrium solution. In a previous study (Gallez, et al., 1979), little or no adsorption of chloride was observed in these kaolinitic Ultisols within the pH range used in this experiment.

Sodium and potassium in NH₄Cl-extracts were measured on an EEL Flame photometer, calcium and magnesium were determined on a Perkin-Elmer 403 Atomic Absorption Spectrophotometer in presence of 1% La solution. Aluminum was measured with the modified aluminum method (Hsu, 1964) and the oxine chloroform method (Eckman and Laudelout, 1960). The procedure described by Lindsay et al., (1959) and Rhodes and Lindsay (1978) was used for calculating the Al ion activity in solution. Because we were dealing with very dilute Al concentrations (10⁻⁸-10⁻⁹ M), and the pH values were below 5.0, only the first stage hydrolysis involving Al and Al(OH)₄⁺ ions was considered.

For general soil properties, soil pH was determined on a Beckman Expandomatic pH meter using a combination electrode. Clay content was measured by the hydrometer method using Calgon dispersion (Bouyoucos, 1951). Exchangeable Ca, Mg, K, and Na were determined by neutral 1 N NH₄OAc extraction (Black, 1965) and exchange acidity (Al+H) by unbuffered 1 N KCl extraction (Black, 1965). The sum of the NH₄OAc-extractable bases and KCl-extractable acidity is called "effective cation exchange capacity" or ECEC. Aluminum and total acidity (AH+H) in the natural profile were also determined by

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extraction with AgTU (Chhabra et al., 1975). The extract was titrated with NaOH to phenolphthalein end-point. Total free Fe oxides was determined by the method of Mehra and Jackson (1960) using a dithionite–citrate–NaHCO₃ system (DCB). "Amorphous" Fe was determined by the oxalate extraction (Schwertmann, 1964). "Active Al" was measured by the procedure given by Tweneboah et al., (1969) using 0.5 M CaCl₂ at pH 1.5. Minerals in the clay fraction were identified by X-ray diffraction and thermal analysis (Jackson, 1975).

### RESULTS

#### CEC of the Soil

The values of CEC (or sum of NH₄Cl-exchangeable cations) though relatively small, are somewhat dependent on the kind of cations present on the soil (Table 2). The change in CEC as a function of cation loading of a given cation is shown in Table 3. The CEC values decrease with Al loading in the Ca-Al exchange. However, for the K-Al and K-Ca exchange, CEC values remained fairly constant with varying cation composition on the exchange phase. The mean CEC values (Table 2) were used for calculating the selectivity coefficients.

#### Exchange Equilibria and Selectivity Coefficients

The ion exchange reaction can be presented in a general form as:

\[ b \text{ A}^a + a \text{ B}^b \text{Z} = b \text{ A}^a \text{Z} + a \text{ B}^b \]  

[1]

where \(a\) and \(b\) are the valency of cation A and cation B, respectively. \(Z\) represents the ion exchanger.

Selectivity coefficients according to Gaines and Thomas (1953) for the above reaction can be defined as:

\[ K_e = \frac{N_A^{a^b} m_B^a \gamma_B^a}{N_A^{a^b} m_B^a \gamma_B^a} \]  

[2]

where \(N\) is the equivalent ionic fraction on the soil and \(m\) is the molality in the equilibrium solution. At \(10^{-4}\)N solution concentration, the small difference between molality and molarity can be disregarded.

Theoretically, the mean molal activity coefficients of the whole salt components should be present in the above equation. The contribution of these coefficients becomes more important in heterovalent exchange. Due to the lack of these coefficients, ionic activity coefficients, \(\gamma\) (Debye-Huckel) were introduced and the thermodynamic formulations of Gaines and Thomas (1953) were used in the present study for the calculation of the equilibrium constant and surface activity coefficients. Change in solvent activity (water activity) is not taken into account. The formulation introduces reference states characteristics for the surface region, i.e. the exchanger in a single ionic form (monoionic soil) in contact with the pure solvent (water).
The following equations are obtained for the equilibrium constant (K) and the surface activity coefficients (f).

\[
\ln \frac{A}{B}K = (b - a) + \int_0^1 \ln K_c \, dN_A \quad [3]
\]

\[
\ln f_A^b = N_B (b - a) - N_B \ln K_e + \int_0^1 N_A \ln K_c \, dN_A \quad [4]
\]

\[
\ln f_B^a = - N_A (b - a) + N_A \ln K_c - \int_0^1 N_A \ln K_e \, dN_A \quad [5]
\]

The equilibrium constant is related to the free energy change by the common equation:

\[
\Delta G^o = -RT \ln K. \quad [6]
\]

The exchange isotherms (Fig. 1) at 10^{-2}N concentration show a sequence of preferential adsorption which follows the order: Al>Ca>K>Na. The selectivity sequence as indicated by the selectivity coefficients, K_c, for all horizons of the profile follows the order: K>Al>Ca=Na (Fig. 2 and 3).

The preference of an ion exchanger for one of the two counter ions is determined by the ratio of the equivalent fractions of the two counter ions in the exchanger and the equilibrium solution. For heterovalent exchange, it is strongly dependent on the solution concentration (Helfferich, 1962). The apparent contradiction between the preference sequence (Fig. 1) and the selectivity sequence (Fig. 2 and 3) is therefore due to the concentration-valency effect (Helfferich, 1962).

The selectivity coefficients (Fig. 2 and 3) generally vary with the cation loading on the soil, showing the nonideality of the exchange complex. The change in selectivity with depth for K-Ca exchange pair is clearly shown in Fig. 2a where the Ca affinity decreases with depth. However, the variation in K_c with depth is less pronounced in the exchange equilibria involving Al (Fig. 3). Because pH values in K-Al and Ca-Al systems are considerably lower than K-Ca system and vary from 3.7 to 4.8, comparisons of the selectivity data be-

<table>
<thead>
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<th>Horizon number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td>2.01</td>
<td>2.30</td>
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<tr>
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<td>-2.01</td>
<td>-1.31</td>
</tr>
<tr>
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<td>1.57</td>
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<td>2.13</td>
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<tr>
<td>Na-K (pH 5)</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>Na-Cs (pH 5)</td>
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<td>-</td>
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</table>
between Fig. 2 and 3 become less meaningful. The free energy changes corresponding to these equilibria are given in Table 4.

**DISCUSSION**

**Exchange Equilibria not Involving Al**

For K-Ca exchange, the selectivity for K increases with the decrease of K loading (Fig. 2a). This is also true for the Na-K exchange (Fig. 2b). The selectivity coefficients ($K_e$) for K-Ca exchange show higher selectivity for K which tends to increase with depth of the profile (Fig. 2a).

In agreement with selectivity data of Fig. 2a, the $\Delta G^0$ values given in Table 4, also show a somewhat increasing K selectivity or a decreasing Ca selectivity with depth for K-Ca exchange. The abnormal low selectivity of Ca for the surface soil (horizon 1) which contains relatively the largest amount of organic matter, could be due to organic exchange sites which are blocked by positively charged polynuclear hydroxy-Al polymers that cannot be displaced by KCl saturation (Juo and Kamprath, 1979).

Although limitations in applying thermodynamic calculations for heterogeneous systems, such as soils and clays are well recognized, the free energy change ($\Delta G^0$) has been frequently used for estimating selectivity sequences representing the entire range of surface composition (Singh and Talibudeen, 1971; Gaines and Thomas, 1953, 1955; Poonia and Talibudeen, 1977). The values of $\Delta G^0$ for the K-Ca, Na-Ca and Na-K exchange at pH 5 are given in Table 4. Application of the triangle rule (Hess' Law) on the exchanging pairs K-Ca, Na-Ca and Na-K for horizon 2 gives a difference of only 0.14 kcal eq$^{-1}$. This difference is probably within the experimental error. It is assumed, therefore, that the K-Ca exchange at pH 5 is reversible.

The K-Ca exchange at a more acidic condition (pH 3.3) for horizon 2 was also studied. A considerably lower selectivity of the soil for the Ca ion was observed comparing with the K-Ca exchange at pH 5.0. The ratio of adsorbed K to Ca was higher at pH 3.3 than at pH 5.0. A similar pH effect was reported by Pratt et al. (1962) for Na-Ca exchange in some acid surface soils. At low pH values such as pH 3.3, hydroxy-Al polymers or amorphous aluminum hydroxides may become depolymerized or solubilized and interfere with the exchange equilibria.

**Exchange Equilibria Involving Al**

The pH values of the exchange experiments involving Al were variable and occurred at lower pH values (pH 3.7 - 4.8) than the pH of the exchanges not involving Al (pH 5). The selectivity data for the K-Al exchange (Fig. 3) also show a high selectivity for K within the range of K loadings studied. The general shape of the K-Al selectivity curves for the various horizons are very similar. This may be partly attributed to the relatively uniform clay mineralogy and pH in the profile. Calculation of selectivity data at low K loading or at low Al loading were not possible due to lack of experimental data. Our data, however, differ considerably from those published by Singh and Talibudeen (1971) who found a very high K selectivity at low K loading for K-Al exchange on latosols from Malaysia.

It is known that the surface charge of Ultisols and Oxisols in West Africa is pH-dependent (Gallez et al., 1976). Such effect is depicted by the decrease in CEC in Ca-Al systems as a result of lowering pH at higher Al loading (Table 3). A strong change of selectivity with loading was also reported by Nye et al. (1961) for the K-Al exchange on montmorillonite and kaolinite. They found that the selectivity coefficient ($\ln K_{AI}$) uncorrected for activity coefficients in solution for kaolinite decreases from 6.9 to 2.4 with increasing K loading.

In Ca-Al systems (Fig. 3) the results show strong selectivity of Al over Ca. Large variations in the magnitude of $K_e$ with Al loading are again observed especially for the three upper horizons of the profile. Horizons 4 and 5 depict a rather different selectivity pattern. The higher selectivity for Al at low Al loading (horizons 1, 2, and 3) could be due to the presence of low and high energetic sites. However, such relationship was less pronounced in the K-Al exchange (Fig. 3). The equilibria may be also affected by the pH which decreases with increasing Al loading. Thus, the variation in $K_e$ with Al loading is probably the result of both changes in pH and surface composition. The $\Delta G^0$ values are also summarised in Table 4. The selectivity sequence follows K>Al>Ca. The change in $\Delta G^0$ as a function of depth is not so clear as in the case of the K-Ca exchange.

**Surface Activity Coefficients and Al Hydrolysis**

Deist and Talibudeen (1976) interpreted the surface activity coefficients in terms of the relative freedom of movement of the adsorbed ions in soil and clay systems. They suggested that ions in the Stern layer would have a smaller activity coefficient than ions in the Gouy-Chapman layer. Surface activity coefficients ($f$) shown in Fig. 4 reveal some points of interest. For heterovalent exchange the cation with high valency is preferentially adsorbed in the Stern layer (i.e. K-Al, Ca-Al, and K-Ca exchanges). In the case of homovalent exchange the degree of hydration becomes a more important factor affecting the distribution of the cation. Thus, for Na-K exchange K ions are occupying the Stern layer while Na ions are distributed in the diffuse double layer (Fig. 4a). For K-Al and Ca-Al exchange, the low $f_{AI}$ values at low Al loading indicate that Al ions are mostly occupying the Stern layer (Fig. 4). The increase in $f_{AI}$ with increasing Al loading suggests that an increasing number of Al ions are distributed in the Gouy-Chapman layer as Al loading increases.

The peculiar $f_{AI}$ and $f_{Ca}$ curves for horizons 4 and 5 in Ca-Al exchange (Fig. 4c) may be explained partly by the discrepancy between total exchangeable Al and total titratable acidity in the natural profile obtained from a separate experiment (Fig. 5). There is good agreement between exchangeable Al and titratable acidity for the first three layers (0-60 cm) of the profile. But for horizons 4 and 5 a significant difference appears and the total acidity becomes less than the total exchangeable Al. On the other hand, the pH (water) remains constant while the pH values of the
AgTU extracts (Chhabra et al. 1975) and the KCl
and is probably in Al(OH)\(^+\) form in the subsoil horizons.

The hydrolysis of Al in the subsoil apparently has a more pronounced effect on the Ca-Al equilibria than on the K-Al equilibria (Fig. 3 and 4). The reason for Al hydrolysis in the subhorizon is not known.

Some comments should be given on the calculation of the surface activity coefficients. Firstly, errors from the solution activity coefficients calculated from the Debye-Huckel approximation, especially in the heterogeneous ion exchange, can affect the calculation of f values. Secondly, the limiting slopes of the exchange isotherms were taken to be the slopes of the line extrapolated through the origin. Therefore, the value of the surface activity coefficient in the regions of low surface loading is doubtful.

CONCLUSION

Results from this study show that cation exchange equilibria involving Al in the kaolinitic Ultisol are affected by pH, surface composition and hydrolysis of Al. In equilibria not involving Al, good reversibility was obtained. The over-all selectivity sequence follows the order of K>Al>Ca=Na.

The Ca-Al exchange isotherm at low ionic strength shows that Al activity in solution becomes extremely low (< 10\(^{-5}\)M) when exchangeable Al saturation falls below 40%. The high Al selectivity at high Ca loading suggests that exchangeable Ca will be easily displaced by Al ions which may reappear in the soil solution of a limed Ultisol as a result of subsequent use of acidifying fertilizers. Thus, to maintain a high degree of exchangeable Ca in the kaolinitic Ultisols in the high rainfall tropics, one needs to maintain high concentrations of Ca ions in the soil solution through frequent applications of lime or other Ca amendments. Results from a liming experiment conducted on the same soil at IITA Onne station conformed with this conclusion. A high rate of Ca leaching from the limed surface soil and the lack of Ca retention by the subsoil horizons were observed three years after lime application (D.K. Friesen and A.S.R. Juo, unpublished).

On the other hand, the high K selectivity throughout the profile suggests that K fertilizer can be used very effectively. Further attempts are being made to predict the distribution and leaching of cation in this soil using data obtained from column leaching and lysimeter studies.

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LITERATURE CITED