**Thermodynamic study of potassium-calcium exchange in**
**Typic Rhodustalf, Aeric Ochraqualf and Entic Chromusterts**
**using mole and equivalent fraction concept**

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**Abstract**

Thermodynamics of K exchange was investigated at three different temperatures (283°K, 298°K and 313°K) in Ca-saturated samples from the Ap horizon (0-15 cm) of red earth (fine loamy mixed hyperthermic Typic Rhodustalf), Karail (fine mixed hyperthermic family of Entic Chromustert) and alluvial (fine loamy mixed hyperthermic family of Aeric Ochraqualf) soils of eastern Uttar Pradesh. Thermodynamic parameter ($\Delta G^\circ$) using Argersinger’s mole fraction concept and Gaines and Thomas’s equivalent fraction concept were compared. With both the conventions the selectivity coefficients $k_v$ or $k_e$ decreased and varied with increasing fractional K-saturation which is indicative of non-ideality of K-Ca exchange and the presence of heterogenous sites for K-Ca exchange. The negative standard free energy ($\Delta G^\circ$) values suggests spontaneity of K-Ca exchange and overall preference of K+ on soil surface. The standard enthalpy ($\Delta H^\circ$) of exchange were negative which indicated strong binding of K+ with soil sites. The standard entropy of exchange ($\Delta S^\circ$) values suggest that K-Ca exchange created an environment that was more ordered in its molecular make up. Even though selectivity coefficients using the two conventions did not compare well in magnitude and the curves were similar and showed analogous trend. Moreover, when the selectivity coefficients were reduced to common thermodynamic parameters such as $\Delta G^\circ$, the two conventions not only resulted in similar inferences on ion behaviour but also in the same magnitude of values at a given temperature.

**Additional Keywords:** Selectivity coefficients, standard free energy, standard enthalpy, standard entropy.

**Introduction**

Thermodynamic principles have been used frequently to characterize exchange equilibria on clay and on soil surfaces (Argersinger *et al.* 1950; Gaines and Thomas 1953). These principles have been used to obtain exchange coefficients and thermodynamic parameters for various cation exchange systems (Hutcheon 1966; Poonia *et al.* 1986; Bansal 1990; Deist and Talibudeen 1967; Jensen 1973; Udo 1978). While investigating K-Ca exchange on kaolinite, Udo (1978) found that large negative $\Delta G^\circ$ described the process. Negative $\Delta G^\circ$ was found also reported by Hutcheon (1966) for formation of K-form from Ca montmorillonite. Large negative $\Delta H^\circ$ values were reported by Deist and Talibudeen (1967), which indicated that exchange reactions were not energy consuming. To describe thermodynamics of ion exchange in clay mineral and soils both Argersinger (Argersinger *et al.* 1950) and/or Gaines and Thomas (Gaines and Thomas 1953) conventions are usually employed. But in soil chemistry literature Gaines and Thomas’s convention is more widely used than Argersinger method.

Sposito and Mattigod (1979) have questioned the use of Gaines and Thomas convention for calculating thermodynamic parameters with particular reference to heterovalent exchange. Accordingly the objective of this study is to first establish the standard thermodynamic parameters for K-Ca exchange on the experimental soils in order to explain the
differences in ionic selectivity observed in the soil system and secondly to investigate how the thermodynamic parameters differ both in magnitude and trend using the two conventions and to discuss how these differences affect the inference on ion behaviour during exchange for the soils studied.

**Materials and methods**

**Theoretical consideration**

Considering the following reversible reaction,

\[
\text{Ca-(Soil)}_2 + 2\text{K}^+(\text{aq}) \rightleftharpoons 2\text{K-(Soil)} + \text{Ca}^{2+} (\text{aq})
\]

The selectivity coefficients according to Vanselow (1932) and Gaines and Thomas (1953) are as follows:

\[
k_v = \frac{\overline{N}_K^2 \cdot a_{Ca}^2}{N_{Ca} \cdot a_K^2} \quad \text{Vanselow 1932} \quad .... (2)
\]

and

\[
k_c = \frac{E_K^2 \cdot a_Ca^2}{E_{Ca} \cdot a_K^2} \quad \text{Gaines and Thomas 1953} \quad .... (3)
\]

where \(\overline{N}\) and \(E\) are the mole and equivalent fractions of \(K^+\) and \(Ca^{2+}\) in the adsorbed phase and \(a\) is the activity of the cations in solution.

The equilibrium constant can be evaluated according to the following equations:

\[
\ln K_{eq} = \int_0^1 \ln k_v \, dE \quad (\text{Vanselow et al., 1950}) \quad .... (4)
\]

\[
\ln K_{eq} = 1 + \int_0^1 \ln k_c \, dE \quad (\text{Gaines and Thomas, 1953}) \quad .... (5)
\]

Knowledge of \(K_{eq}\) allows calculations of \(\Delta G^o\), \(\Delta H^o\) and \(\Delta S^o\) as follows:

\[
\Delta G^o = -RT \ln K_{eq} \quad .... (6)
\]

\[
\frac{d \ln K}{dT} = \frac{\Delta H^o}{RT^2} \quad .... (7)
\]

\[
\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} \quad .... (8)
\]

**Experimental procedure**

**Thermodynamic Study : Equilibrium Approach** : The bulk ( \( \approx 200 \) g) of soil samples from the \( A_p \) (0-15 cm) horizons of red earth, alluvial and Karail (analogous to black soils) of eastern Uttar Pradesh were made homoionic with \( Ca^{2+} \) by repeated washing with 0.5 \( M \) \( CaCl_2 \) solution and excess salts were removed by washing the soils with deionized water until a negative test of \( Cl^- \) was obtained with \( AgNO_3 \). The selected physico-chemical properties of the soils used are presented in table 2. Different solution of various \( KCl \) and \( CaCl_2 \) concentrations but of constant ionic strength (\( I = 0.01 \)) were prepared. Equivalent fractions of \( K^+ \) and \( Ca^{2+} \) in the mixed solutions varied from 0 to 1.0. 1 g air dried Ca-saturated samples in triplicate were then equilibrated (1:20 soil to solution ratio) with the prepared solutions of chlorides (\( K^+ + Ca^{2+} \)) for 24 hours with intermittent shaking. After centrifugation at 10,000 r.p.m. for 10 min. the supernatant solutions were separated and concentrations of \( Ca^{2+} \) and \( K^+ \) were determined using atomic absorption spectrophotometer (Perkin Elmer; 2380 Model). The studies were conducted at 283, 298 and 313°K. From these data, the equilibrium constants, standard free energy, standard enthalpy, standard entropy of exchange...
were calculated using Gaines and Thomas (1953) convention as was applied by Udo (1978) and Argersinger (1950) convention as was applied by Jardine and Sparks (1984).

Results and discussion

According to Helfferich (1962), the preference of a given counterion is expressed in the selectivity coefficients. The selectivity coefficients (Fig. 1 & 2) with both the conventions for red earth and alluvial soil at different experimental temperatures were high, especially at low K-saturation, decreasing to a rather constant value as K-saturation increased. This has been observed before (Bolt et al. 1963; Jensen 1973; Babcock 1963; Udo 1978) and is indicative of decreasing specificity for K+ ions with an increase in K-saturation. The initial high values of the selectivity coefficients at low K-saturation suggest a preference of the soils of K+ relative to Ca2+ and also indicates the involvement of forces other than long range electrostatic ones. The variation of $k_c$ for each value of fractional K-saturation for all the soils indicates presence of heterogeneous sites in the soil system. It is observed particularly for the Karail soil, and to some extent in alluvial soils that K+ had a preference on soil surface at low fractional K-saturation zone, while reversal of preference occurred at high K-saturation values. This may be due to exchange sites of various reactivity for K+ ions supporting the hypothesis of multireactive nature of soil (Jardine and Sparks 1984).

The standard free energy change values ($\Delta G^o$) for all the soils at different temperatures were negative and increased with increasing temperature (Table 1). Negative value indicates spontaneity of exchange and an overall preference of K+ over Ca2+ on the soil surface. The $\Delta G^o$ becomes more negative with a decrease in particle size which, in turn, implies that K+ selectivity increases as clay content increases. In all the soil K+ preference decreased with an increase in temperature. This may be due to the fact that initially more hydrated Ca2+ ion than K+ ion become smaller in size at higher temperature due to reduction of Ca2+ ion hydration shell and hence can approach the surface more closely than at lower temperature thereby causing reduction in preference for K+ ion.

![Fig. 1. Gaines and Thomas's selectivity coefficients for (a) Red earth, (b) Alluvial and (c) Karail soils.](image-url)
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Fig. 2. Vanselow selectivity coefficients for (a) Red earth, (b) Alluvial and (c) Karali soils.

Table 1. Thermodynamic parameters for $K^+ - Ca^{2+}$ exchange

<table>
<thead>
<tr>
<th>Soil</th>
<th>Temperature °K</th>
<th>$\Delta G^\circ$ kJ mol$^{-1}$</th>
<th>$\Delta H^\circ$ kJ mol$^{-1}$</th>
<th>$\Delta S^\circ$ J mol$^{-1}$ K$^{-1}$</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Gaines &amp; Thomas approach</td>
<td>Argersinger approach</td>
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<tr>
<td>Red Earth</td>
<td>283</td>
<td>-9.58</td>
<td>-9.47</td>
<td>-49.0</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>-9.11</td>
<td>-8.83</td>
<td>-23.4</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>-8.22</td>
<td>-8.32</td>
<td>-48.1</td>
</tr>
<tr>
<td>Karail</td>
<td>283</td>
<td>-10.21</td>
<td>-10.19</td>
<td>-74.5</td>
</tr>
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<td></td>
<td>298</td>
<td>-9.44</td>
<td>-9.90</td>
<td>-31.2</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>-8.29</td>
<td>-8.02</td>
<td>-73.3</td>
</tr>
<tr>
<td>Alluvial</td>
<td>283</td>
<td>-9.35</td>
<td>-9.35</td>
<td>-89.6</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>-8.62</td>
<td>-8.68</td>
<td>-34.7</td>
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<tr>
<td></td>
<td>313</td>
<td>-6.66</td>
<td>-6.66</td>
<td>-89.6</td>
</tr>
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Table 2. Selected physico-chemical properties of soils

<table>
<thead>
<tr>
<th>Soil</th>
<th>pH</th>
<th>Organic carbon %</th>
<th>CEC cmol(p+)/kg$^{-1}$</th>
<th>Particle size analysis</th>
</tr>
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<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>Sand (%)</td>
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<tr>
<td>Red Earth</td>
<td>5.2</td>
<td>0.54</td>
<td>6.8</td>
<td>17.4</td>
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<tr>
<td>Karail</td>
<td>6.5</td>
<td>0.56</td>
<td>24.4</td>
<td>1.7</td>
</tr>
<tr>
<td>Alluvial</td>
<td>7.7</td>
<td>0.50</td>
<td>9.5</td>
<td>33.7</td>
</tr>
</tbody>
</table>
The $\Delta H^\circ$ values (Table 1) were all found to be negative suggesting very strong binding of K$^+$ ions with soil sites. The low negative value indicates physical nature of adsorption.

The fact that the bonding of K$^+$ ions to highly selective sites is extremely strong is indicated by the large $\Delta G^\circ$ values relative to $\Delta H^\circ$ (Table 1).

The overall entropy changes (Table 1) in all the soils were found to be negative at all reaction temperatures. The negative value of standard entropy changes ($\Delta S^\circ$) suggest that the adsorbate molecules were somewhat ordered on the adsorbent surface after completion of adsorption apparently due to its preferred configuration on the adsorbent surfaces.

From the present study it is evident that the selectivity coefficients obtained using both the conventions differed in magnitude (Figs. 1&2) but the same basic trends were observed. The decrease of selectivity coefficients with increasing K$^+$ saturation for all the soils indicates non-ideality of K-Ca exchange. The $k_c$ values were significantly lower than the $k_v$ values for all the soils at different experimental temperatures. The area under the curve was very close to one order of magnitude lower than that given by $k_v$. This is in accordance with equations 4 and 5.

Even though the selectivity coefficients using Vanselow and Gaines and Thomas's conventions did not compare well in magnitude, the curves were similar and showed analogous trend. Moreover, when the selectivity coefficients were reduced to common thermodynamic parameters like $\Delta G^\circ$ (Table 1) they not only resulted in similar conclusion on ion behaviour but also yielded same magnitude at a given temperature suggesting that any of the two conventions can be used to study the thermodynamics of K-Ca exchange.

References


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