USE OF MOLE OR EQUIVALENT FRACTIONS IN DETERMINING THERMODYNAMIC PARAMETERS FOR POTASSIUM EXCHANGE IN SOILS

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We investigated K-Ca exchange equilibria in two soils at three different temperatures. Thermodynamic parameters using the Argersinger and Gaines and Thomas conventions were compared. With both conventions, the selectivity coefficients \( k_\text{r} \) or \( k_\text{e} \) decreased and varied with increasing fractional potassium saturation \( (F_K) \). This is indicative of nonideality of K-Ca exchange and the presence of heterogeneous sites for exchange. The difference between adsorbed-ion activity coefficients obtained by the two conventions was small at lower \( F_K \), but increased at higher \( F_K \). Inflexions, maxima, and minimum values for the activity coefficients occurred at virtually the same \( F_K \) for both soils. Even though the selectivity and adsorbed-ion activity coefficients using the two conventions did not compare in magnitude, the curves were similar and showed an analogous trend. When these coefficients were reduced to the common thermodynamic parameters, such as the equilibrium constant \( (K_{eq}) \) and the standard free energy \( (\Delta G^0) \) of exchange, the two conventions not only resulted in similar inferences of ion behavior, but also in the same magnitude of values at a given temperature.

The Argersinger (Argersinger et al. 1950) or Gaines and Thomas (Gaines and Thomas 1953) conventions are usually employed to describe thermodynamics of ion exchange in clay minerals and soils. In the soil chemistry literature, the Gaines and Thomas convention has been more widely used than the Argersinger method. Hutcheon (1966) first applied the Gaines and Thomas method specifically to potassium (K) exchange, using montmorillonite as a relatively simple exchanger. Talibudeen and coworkers (Deist and Talibudeen 1967a, b; Coulter and Talibudeen 1968; Talibudeen 1972; Goulding and Talibudeen 1980) used Gaines and Thomas’ equations to study K exchange in soils and clay minerals. The Argersinger method was used by Jensen and coworkers (Jensen 1973; Jensen and Babcock 1973) and by Jardine and Sparks (1984a) to investigate K reactions on soils and clay minerals. Gaines and Thomas (1953) calculated the selectivity coefficient and adsorbed activity coefficients using equivalent fraction \( (E) \) terms. They defined the adsorbed activity coefficients \( (g) \) as \( g = a/E \), where \( a \) is the activity and \( E \) is the equivalent fraction of the ion in the adsorbed phase. However, Argersinger et al. (1950) used the Vanselow (1932) terminology of mole fraction \( (N) \) in calculating the adsorbed activity coefficients \( (f) \) and the selectivity coefficient \( (k) \).

Recently, Sposito and Mattigod (1979) and Babcock and Doner (1981) have questioned the use of the Gaines and Thomas convention for calculating thermodynamic parameters. They point out that, except for homovalent exchange, the \( g \) values calculated using the Gaines and Thomas convention are not true activity coefficients, for they are defined in terms of equivalent fractions rather than mole fractions. An activity coefficient is, by definition, always the ratio of the actual activity to the value of the activity under those limiting conditions when Raoult’s law applies (Sposito and Mattigod 1979). Therefore, in solid solutions, such as exchanger phases, an activity coefficient always is the ratio of an actual activity to a mole fraction. Sposito (1981) points out that the ratio of an activity to an equivalent fraction is only a formal parameter that cannot be interpreted directly in terms of a thermodynamic reference state, as can adsorbed activity coefficients calculated from mole fractions. Equivalents are purely formal quantities that are not associated with ac-

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tual chemical species, except in the special case of univalent ions. Gouding (1983) surveyed the literature and compared thermodynamic parameters using the Gaines and Thomas and the Argersinger conventions. He concluded that there were differences in the magnitude of $g_i$, $f_i$, $k_i$, and $k_c$, but the overall conclusions and trends would be similar using the two conventions.

Because most researchers have employed the Gaines and Thomas convention for calculating thermodynamic parameters for various binary exchange processes, the above arguments should not be ignored. Accordingly, the objective of our study was to investigate how the thermodynamic parameters for K exchange differ both in magnitude and in trend using the two conventions and to discuss how these differences impact on basic conclusions dealing with ion preference.

**MATERIALS AND METHODS**

**Theoretical considerations**

Considering the following reversible binary exchange reaction

$$\text{Ca} - \text{(soil)} + 2K^+ \rightleftharpoons 2\text{K} - \text{(soil)} + \text{Ca}^{2+}$$

we may express selectivity coefficients according to Vanselow (1932) and Gaines and Thomas (1953) as follows

$$k_v = \frac{N_{K^+}^{\text{soil}}a_{\text{Ca}^{2+}}}{N_{\text{Ca}^{2+}}a_{K^+}} \quad \text{Vanselow}$$

$$k_c = \frac{E_{K^+}^{\text{soil}}a_{\text{Ca}^{2+}}}{E_{\text{Ca}^{2+}}a_{K^+}} \quad \text{Gaines and Thomas}$$

where $N$ and $E$ are the mole and equivalent fractions, respectively, of $K^+$ and $Ca^{2+}$ in the adsorbed phase, and $a$ is the activity of the cations in solution.

Equilibrium constants ($K_{eq}$) can be related to the previous selectivity coefficients using the relationships below

$$k_v = K_{eq} \frac{f_{\text{Ca}^{2+}}}{f_{K^+}} \quad (4)$$

$$k_c = K_{eq} \frac{g_{\text{Ca}^{2+}}}{g_{K^+}} \quad (5)$$

where $f$ and $g$ are the activity coefficients of adsorbed cations. For the $K^+ - Ca^{2+}$ exchange reaction described by Eq. (1), activity coefficients of the adsorbed ions can be defined using the equations proposed by Argersinger et al. (1950)

$$\ln f_{\text{Ca}^{2+}} = E_{K} \ln k_v - \int_{0}^{k_v} \ln k_c \, dE_K \quad (6a)$$

$$2 \ln f_K = -(1 - E_K) \ln k_v + \int_{k_v}^{1} \ln k_c \, dE_K \quad (6b)$$

Moreover, because

$$\ln K_{eq} = \ln k_v - \ln f_{\text{Ca}^{2+}} + 2 \ln f_K$$

Eq. (6) leads to the result

$$\ln K_{eq} = \int_{0}^{1} \ln k_c \, dE_K \quad (8)$$

According to the Gaines and Thomas convention, activity coefficients, $g$, of adsorbed ions can be calculated as follows

$$\ln g_{\text{Ca}^{2+}} = E_{K} \ln k_v - \int_{0}^{k_v} \ln k_c \, dE_K \quad (9a)$$

$$2 \ln g_K = (1 - E_K)(1 - \ln k_v) + \int_{k_v}^{1} \ln k_c \, dE_K \quad (9b)$$

The equilibrium constant is then given as

$$\ln K_{eq} = 1 + \int_{0}^{1} \ln k_c \, dE_K \quad (10)$$

From the work of Hutcheon (1966), Sposito (1981), and Gouding (1983), $k_v$ is related to $k_c$ by

$$k_v = k_c \frac{u^v}{u^u} (uE_n + vE_u)^{v-u}$$

where $v$ and $u$ are the valencies of $K^+$ and $Ca^{2+}$, respectively. Equation (11) can also be described as

$$\ln k_v = \ln k_c + f(E) \quad (12)$$

If one lets $K_r$ represent the equilibrium constant calculated using $k_v$ and lets $K_c$ be that calculated using $k_c$, combining Eqs. (8), (10), and (12) results in

$$\ln K_r = \ln K_c + \int_{0}^{1} f(E) \, dE_K - (u - v)$$

(13)
where

\[
\int_{0}^{1} f(E) dE_k = \int_{0}^{1} \frac{u}{v} dE_k + \int_{0}^{1} (v - u) \ln[(uE_k + vE_{k_2})dE_k
\]

\]

\[
= u \ln u - v \ln v + \frac{[-u \ln u + v \ln v + (u - v)]}{v}
\]

Thus

\[
\ln K_c = \ln K_e = \ln K_{eq}
\]

It therefore follows that

\[
\Delta G^{\text{eq}} = \Delta G^{\text{eq}} = -RT \ln K_{eq}
\]

**Experimental procedures**

Surface horizons of a Chester loam (fine-loamy, mixed, mesic Typic Hapludults) and a Matapexke silt loam (fine-silty, mixed, mesic Typic Hapludults) were used in this study. The Matapexke soil has: a clay content of 41.8%, which is predominantly chloritized vermiculite and mica; an organic matter content of 1.66%; a cation exchange capacity (CEC) of 1.25 cmol kg\(^{-1}\), and a pH in water of 6.30. The Chester soil has: a clay content of 28.0%, which is mainly kaolinite; an organic matter content of 3.3%; a CEC of 2.55 cmol kg\(^{-1}\); and a pH in water of 5.93.

Equilibrium studies were conducted by first saturating the soils with Ca\(^{2+}\) using a 0.50 M CaCl\(_2\) solution, and excess salts were removed by washing the soils with deionized water until a negative test of Cl\(^-\) was obtained using AgNO\(_3\). Triplicate 1-g, air-dried, Ca-saturated samples were uniformly applied onto Buchner funnels equipped with 0.45-\(\mu\)m filter paper. Different solutions of various KCl and CaCl\(_2\) concentrations but of a constant ionic strength (I = 0.01) were prepared; equivalent fractions of K\(^+\) or Ca\(^{2+}\) in the mixed solutions varied from 0 to 1.00. The soil samples were then leached at a flow rate of 1.0 ml min\(^{-1}\) with about 0.4 L of the mixed solutions or until the concentration of Ca\(^{2+}\) and K\(^+\) in the leachates were equal to those in the original solutions. After equilibrium was attained, entrained salts were removed by washing the soils with 0.10 L of deionized water. The soils were then leached with 0.35 L of a 1.0 M NH\(_4\)Cl solution, and the leachate was analyzed for K\(^+\) and Ca\(^{2+}\) using atomic absorption spectrophotometry. The studies were conducted at 283, 298, and 308K.

Using the data from the above experiments, we calculated equilibrium selectivity coefficients, adsorbed activity coefficients, equilibrium constants, and standard free energies of exchange (\(\Delta G^{\text{eq}}\)), using the Argerisinger and Gaines and Thomas conventions.

**RESULTS AND DISCUSSION**

**Selectivity coefficients**

The relationship between selectivity coefficients and fractional K saturation (\(F_k\)) using Vanselow (\(k_v\)) and Gaines and Thomas (\(k_t\)) conventions is presented in Figs. 1 and 2 for the two soils. With both conventions, the selectivity coefficients decreased with increasing \(F_k\). This has been observed before (Bolt et al. 1963; Jen-

![Fig. 1. Natural logarithm of Vanselow selectivity coefficients and Gaines and Thomas selectivity coefficients (k) as a function of fractional K saturation on Chester loam at 298K.](image-url)
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![Graph showing the natural logarithm of Vanselow selectivity coefficient ($k_v$) and Gaines and Thomas selectivity coefficients ($k_c$) as a function of fractional K saturation on Matapeake silt loam at 298K.]

Figure 2.

The $k_v$ values were significantly lower than the $k_c$ values for both soils (Figs. 1 and 2). The area under the curve given by $k_v$ was one order of magnitude lower than that given by $k_c$. This is in accordance with Eqs. (8) and (10). Even though the selectivity coefficients using the Vanselow and Gaines and Thomas conventions did not compare in magnitude, the curves were similar and showed an analogous trend.

AdSORBED ACTIVITY COEFFICIENTS

Adsorbed activity coefficients correct the equivalent or molar fraction terms for departures from ideality. They thus reflect the change in the status, or fugacity, of the ion held at exchange sites and also the heterogeneity in the exchange process. Fugacity may be defined as the degree of freedom an ion has to leave the adsorbed state, relative to a standard state of maximum freedom of unity. Plots of adsorbed activity coefficients versus $F_K$ show how this “freedom” changes during the exchange process, which indicates the degree of exchange heterogeneity. Additionally, one can derive a quantitative indication of selectivity changes during an exchange reaction (Goulding 1983).

Three groups of authors (Ekedahl et al. 1950; Argersinger et al. 1950; Gaines and Thomas...
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Fig. 3. Activity coefficients of adsorbed ions calculated using mole fraction \( f_i \) or equivalent fraction \( g_i \) versus fractional K saturation of the adsorbed phase for the two soils studied.

1953) adopted the convention that when the exchanger is entirely in the K\(^+\) form, \( f_K \) or \( g_K \) is unity, and when the exchanger is entirely in the Ca\(^{2+}\) form, \( f_{Ca} \) or \( g_{Ca} \) is unity. This leads to the application of the Gibbs-Duhem equation resulting in Eqs. (6) and (9). The data obtained at 298K using two sets of equations are given in Fig. 3 for the two soils studied.

The curves obtained using the Vanselow and Gaines and Thomas conventions showed a significant difference in magnitude of the \( f_i \) and \( g_i \) values in the two soils. The difference between \( f_i \) and \( g_i \) was small at lower \( F_k \), but increased at higher \( F_k \). For the Chester soil, \( f_{Ca} \) and \( g_{Ca} \) decreased from unity, at Ca saturation, to 0.60 and 0.30, respectively, at K saturation. Values of \( f_K \) and \( g_K \), however, increased from 0.33 and 0.30, respectively, at Ca saturation to 1.10 and 1.00, respectively, at K saturation. Deist and Talibudeen (1967a) also observed that adsorbed activity coefficients for K\(^+\) exceeded 1 in some British soils using the Gaines and Thomas convention. The trends in activity coefficients versus \( F_k \) using the two conventions were similar in the Matapeake soil (Fig. 3). However, a more marked difference was observed in the behavior of Ca\(^{2+}\) and K\(^+\) ions for the Matapeake soil. Although the \( g_{Ca} \) and \( f_{Ca} \) decreased smoothly as \( F_k \) increased, \( g_K \) and \( f_K \) values varied greatly showing maxima, minima, and inflections. This behavior is perhaps a reflection of the different distribution of Ca\(^{2+}\) and K\(^+\) ions in the Gouy and Stern layers (Deist and Talibudeen 1967).

Inflexions, maxima, and minima values for the activity coefficients using the two conventions occurred at virtually the same \( F_k \) for both soils (Fig. 3). It is also clear from Fig. 3 that, though the \( f_i \) and \( g_i \) differ significantly in magnitude, the overall trend and shape of the curves are similar. The maxima and minima parts of the curves could represent homogeneous groups of cation exchange sites in the heterogeneous soil systems (Goulding 1980; Goulding and Talibudeen 1980).

The importance of the \( f_i \) or \( g_i \) values cannot be underestimated. One can see from Eqs. (4) and (5) that, because \( K_m \) is a constant and \( k_c \) or \( k \), varies with ionic composition of the soil colloid, it is therefore clear that all the variation of \( k_c \) or \( k \) with ionic composition is contained within a fraction \( f_{Ca}/F_k \) or \( g_{Ca}/g_k \).

**Other thermodynamic parameters**

The equilibrium constants \( (K_m) \) and standard free energy \( (\Delta G^\circ) \) values were calculated from the experimental data using both conventions. These parameters are presented against change in temperature (Figs. 4 and 5). The \( K_m \) values decreased with increasing temperature (Fig. 4), but the values obtained using the two conventions were virtually the same at a given temperature level. This observation clearly supports the mathematical relationship between \( K_m \) and \( k_c \) or \( k \) (Eqs. (8) through (15)). Because \( K_m \) values obtained from the two conventions are

Fig. 4. Comparison of the thermodynamic equilibrium constants \( (K_m) \) obtained using mole and equivalent fractions versus temperature for the two soils studied.
similar, it therefore follows from Eq. (16) that the calculated \( \Delta G^0 \) values using both conventions, at a given temperature, are similar. This is confirmed by the data presented in Fig. 5.

CONCLUSIONS

The Gaines and Thomas (1953) approach for calculating thermodynamic parameters for a cation exchange process uses the equivalent fraction concentration scale. The equivalent fraction has been equated to the normality scale, which is a purely formal quantity whose resulting parameters give no strict thermodynamic meaning in themselves (Sposito and Mattigod 1979). This work attempted to provide comparative data on the thermodynamic parameters using both equivalent and mole fraction concentration scales in heterovalent cation exchange processes in two soils. We found that both the activity coefficients of adsorbed ions and the selectivity coefficients obtained using the conventions differed in magnitude, but the same basic trends were observed. Moreover, when parameters were reduced to common thermodynamic parameters \( (K_{eq} \text{ and } \Delta G^0) \), they not only resulted in the same inferences concerning ion behavior, but they were of the same magnitude at a given temperature.

REFERENCES


