

USE OF MOLE OR EQUIVALENT FRACTIONS IN DETERMINING THERMODYNAMIC PARAMETERS FOR POTASSIUM EXCHANGE IN SOILS¹

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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_v or k_c) 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 (ΔG^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_v).

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. Equivalent fractions are purely formal quantities that are not associated with ac-

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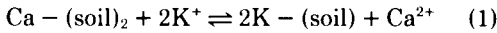
tual chemical species, except in the special case of univalent ions. Goulding (1983) surveyed the literature and compared thermodynamic parameters using the Gaines and Thomas and the Argersinger conventions. He concluded that there were differences in the magnitude of g , f , k_v , and k_c , but the 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



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

$$k_v = \frac{\bar{N}_K^2 a_{Ca}}{\bar{N}_{Ca} a_K^2} \quad \text{Vanselow} \quad (2)$$

$$k_c = \frac{E_K^2 a_{Ca}}{E_{Ca} a_K^2} \quad \text{Gaines and Thomas} \quad (3)$$

where \bar{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

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

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

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

the equations proposed by Argersinger et al. (1950)

$$\ln f_{Ca} = E_K \ln k_v - \int_0^{E_K} \ln k_v dE_K \quad (6a)$$

$$2 \ln f_K = -(1 - E_K) \ln k_v$$

$$+ \int_{E_K}^1 \ln k_v dE_K \quad (6b)$$

Moreover, because

$$\ln K_{eq} = \ln k_v - \ln f_{Ca} + 2 \ln f_K \quad (7)$$

Eq. (6) leads to the result

$$\ln K_{eq} = \int_0^1 \ln k_v dE_K \quad (8)$$

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

$$\ln g_{Ca} = E_K (\ln k_c - 1)$$

$$- \int_0^{E_K} \ln k_c dE_K \quad (9a)$$

$$2 \ln g_K = (1 - E_K)(1 - \ln k_c)$$

$$+ \int_{E_K}^1 \ln k_c dE_K \quad (9b)$$

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 Goulding (1983), k_v is related to k_c by

$$k_v = k_c \frac{u^u}{v^v} (uE_B + vE_A)^{v-u} \quad (11)$$

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_v 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

$$\ln K_v = \ln K_c + \int_0^1 f(E) dE_K - (u - v) \quad (13)$$

where

$$\begin{aligned} & \int_0^1 f(E) dE_K \\ &= \int_0^1 \ln \frac{u''}{v''} \\ &+ \int_0^1 (v-u) \ln [uE_K + vE_{Ca}] dE_K \quad (14) \\ &= u \ln u - v \ln v \\ &+ [-u \ln u + v \ln v + (u-v)] \\ &= u - v \end{aligned}$$

Thus

$$\ln K_v = \ln K_c = \ln K_{eq} \quad (15)$$

It therefore follows that

$$\Delta G_v^0 = \Delta G_c^0 = -RT \ln K_{eq} \quad (16)$$

Experimental procedures

Surface horizons of a Chester loam (fine-loamy, mixed, mesic Typic Hapludults) and a Matapeake silt loam (fine-silty, mixed, mesic Typic Hapludults) were used in this study. The Matapeake 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 Ca²⁺ using a 0.50 M CaCl₂ solution, and excess salts were removed by washing the soils with deionized water until a negative test of Cl⁻ was obtained using AgNO₃. Triplicate 1-g, air-dried, Ca-saturated samples were uniformly applied onto Buchner funnels equipped with 0.45- μ m filter paper. Different solutions of various KCl and CaCl₂ concentrations but of a constant ionic strength ($I = 0.01$) were prepared; equivalent fractions of K⁺ or Ca²⁺ 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 Ca²⁺ and K⁺ in the leachates were equal to those in the original solutions. After equilibrium was attained, entrained salts were removed by wash-

ing the soils with 0.10 L of deionized water. The soils were then leached with 0.35 L of a 1.0 M NH₄Cl solution, and the leachate was analyzed for K⁺ and Ca²⁺ 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 (ΔG^0), using the Argersinger 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_c) 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-

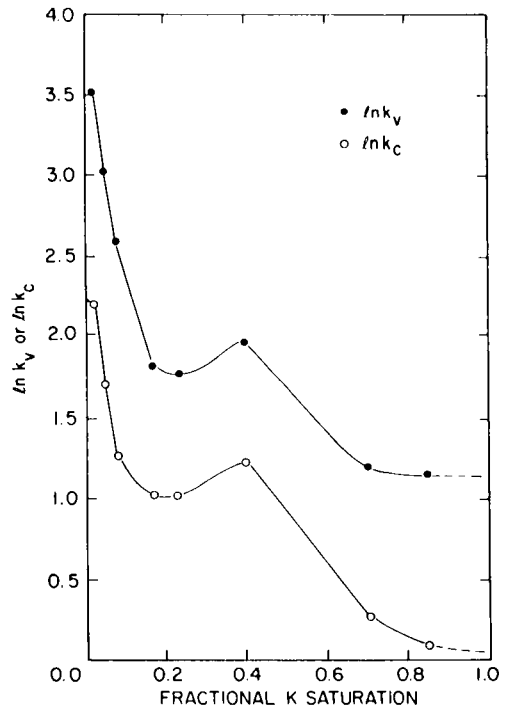


FIG. 1. Natural logarithm of Vanselow selectivity coefficients and Gaines and Thomas selectivity coefficients (k_c) as a function of fractional K saturation on Chester loam at 298K.

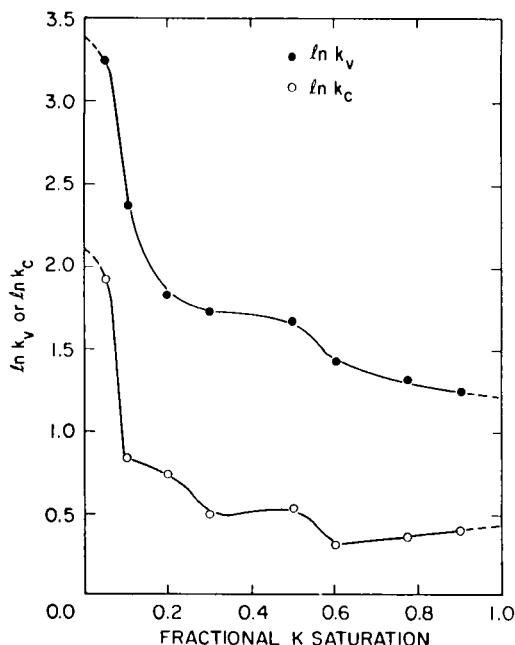


FIG. 2. Natural logarithm of Vanselow selectivity coefficient (k_v) and Gaines and Thomas selectivity coefficients (k_c) as a function of fractional K saturation on Matapeake silt loam at 298K.

sen 1973; Babcock 1963; Mehta et al. 1983) and is indicative of a decreasing specificity for K^+ ions by the two soils with an increase in K^+ saturation. The observation that k_v decreases with increasing F_K can also be related to differing sites for K reactivity in the soils, which could cause selectivity alterations during an exchange reaction (Goulding 1983; Jardine and Sparks 1984a, b). Previous studies (Jardine and Sparks 1984a, b) on Delaware soils showed that sites that were readily accessible for cation exchange reactions showed a preference for Ca^{2+} ions and sites that were difficultly accessible showed a preference for K^+ ions. This hypothesis was proved by conducting both kinetic and thermodynamic investigations.

In both soils, k_v varied for each value of F_K , which further indicates the heterogeneous sites present in the soils. Jensen (1973), for example, studying K-Ca exchange on a smectite, found that k_v was almost constant at F_K values >0.6 , which he ascribed to exchange on permanently charged, homogeneous sites of the clay. With kaolinite, there was a constant drop of k_v with F_K , which was attributed to reactions at exposed edges. The soils we investigated contain signifi-

cant quantities of kaolinite, which could explain the decrease in k_v as F_K increases.

An exchanger phase shows ideal behavior if k_v is observed to be constant as the composition of the exchanger is varied. As Sposito and Mattigod (1979) clearly point out, the constancy of k_v , not k_c , with changes in F_K determine whether an exchanger phase is ideal. The Chester and Matapeake soils exhibited marked nonideality (Figs. 1 and 2). This is not surprising, for heterovalent exchange would normally involve a configurational interaction as two K^+ ions replace one Ca^{2+} ion, which precludes ideal behavior in the exchanger phase, even if the exchange were an athermal process (Guggenheim 1952; Sposito and Mattigod 1979). It would also appear from our studies and from previous investigations that ideality is associated not only with the nature of the exchanger itself, but also with the nature of the cations involved. Jensen and Babcock (1973) noted that nonideality was most pronounced when K^+ was involved in the exchange process. The effect of kind of ion on ideality of solid soil solutions deserves further study.

The k_c values were significantly lower than the k_v values for both soils (Figs. 1 and 2). The area under the curve given by k_c was one order of magnitude lower than that given by k_v . 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 mole 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

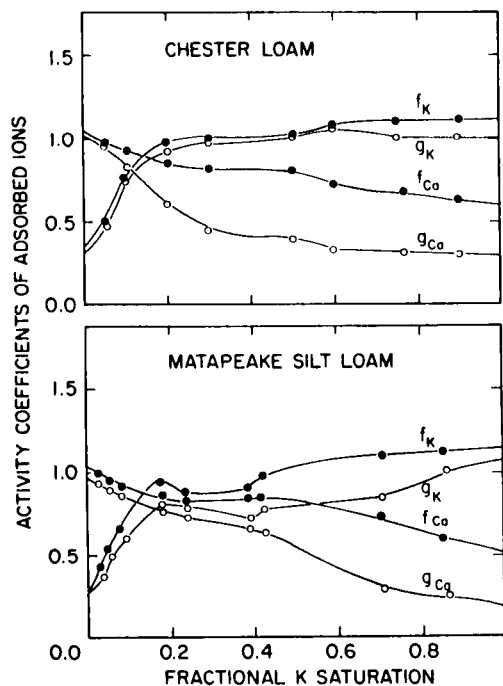


FIG. 3. Activity coefficients of adsorbed ions calculated using mole fraction (f_i) or equivalent fraction (g_i) versus fractional K saturation of the adsorbed phase for the two soils studied.

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).

Inflections, 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_{eq} is a constant and k_v or k_c varies with ionic composition of the soil colloid, it is therefore clear that all the variation of k_v or k_c with ionic composition is contained within a fraction f_{Ca}/f_K or g_{Ca}/g_K .

Other thermodynamic parameters

The equilibrium constants (K_{eq}) and standard free energy (ΔG^0) values were calculated from the experimental data using both conventions. These parameters are presented against change in temperature (Figs. 4 and 5). The K_{eq} 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_{eq} and k_v or k_c (Eqs. (8) through (15)). Because K_{eq} values obtained from the two conventions are

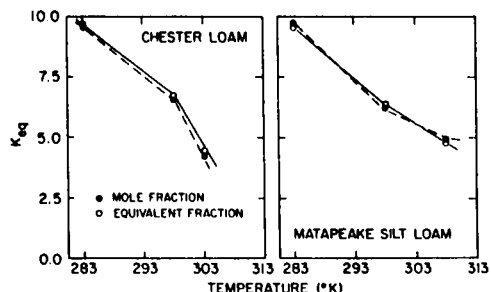


FIG. 4. Comparison of the thermodynamic equilibrium constants (K_{eq}) obtained using mole and equivalent fractions versus temperature for the two soils studied.

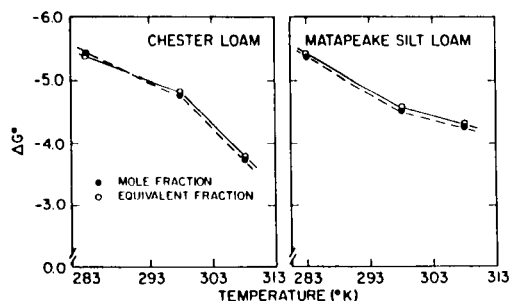


FIG. 5. Comparison of the standard free energy (ΔG^0) of exchange obtained using mole and equivalent fractions versus temperature for the two soils studied.

similar, it therefore follows from Eq. (16) that the calculated ΔG^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} and ΔG^0), they not only resulted in the same inferences concerning ion behavior, but they were of the same magnitude at a given temperature.

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