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KINETICS AND MECHANISMS OF ION EXCHANGE ON SOIL CONSTITUENTS

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KINETICS AND MECHANISMS OF ION EXCHANGE ON SOIL CONSTITUENTS

by

Richard Ayoro Ogwada

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Plant Science

June, 1986

KINETICS AND MECHANISMS OF ION EXCHANGE ON SOIL CONSTITUENTS

by

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ABSTRACT

A study was conducted to evaluate kinetics methodologies and the feasibility of using kinetics to determine thermodynamic parameters for K-Ca exchange on soils and clay minerals. Additionally, the elucidation of rate-limiting steps for ion exchange was performed using different kinetics techniques. Thermodynamic parameters using the Argersinger (mole fraction) and Gaines and Thomas (equivalent fraction) conventions were compared, in magnitude and trend. Selectivity coefficients and surface phase activity coefficients using the two conventions did not compare in magnitude, however, they showed similar trends when these coefficients were reduced to common thermodynamic parameters, such as the equilibrium constant (K_{eq}) and the standard free energy (ΔG^o) of exchange, the two conventions not only resulted in similar inferences on ion behavior but also in the same magnitude of values at a given temperature.

To evaluate the use of kinetics to determine thermodynamic parameters, the Argersinger convention was employed for the equilibrium approach while a kinetics approach was studied using miscible displacement, batch and vortex mixed batch techniques.

Except for the vigorously mixed vortex method, the thermodynamic parameters for the two approaches did not compare. However, when diffusion was greatly reduced as the rate-limiting step, as with the vigorously mixed vortex method, the data indicated that a kinetic approach can be successfully used to gather thermodynamic information about ion exchange processes.

The order of reduction of the influence of diffusion on K-Ca exchange by the kinetic methods evaluated was: vortex>batch=stirred>miscible displacement>static. Using an additive resistance relations model, rate-determining steps under static conditions were elucidated. Both film and intraparticle diffusion were found to be rate-determining on vermiculite. In kaolinite and the Chester soil, film diffusion was the rate-limiting step.

CHAPTER 1

INTRODUCTION

High crop yields usually require high amounts of soil potassium (K) or high application rates of potassium fertilizer. In the middle of the 17th century, J. R. Glauker in the Netherlands, first suggested the use of saltpeter (KNO_3) as the "principle" of vegetation. Saltpeter was derived from the leaching of coral soils. The recognition of essentiality of K to plant growth goes back to the work of von Liebig published in 1840 (Russell, 1961).

The average K content of the earth's crust is about 2.3%. Of the major and secondary elements, K is usually the most abundant in soils (Reitemeier, 1951). Igneous rocks of the earth's crust have higher K contents than sedimentary rocks. In the upper 0.2 m of the soil profile, the total content of K found in the mineral form is about 98% while about 2% is in the soil solution and exchangeable phases (Schroeder, 1978; Bertsch and Thomas, 1985).

Mineral bound K is mainly present in K-feldspars and micas. Considerable quantities exist in secondary micaceous minerals. The K-feldspars are tectosilicates. One out of every four silica tetrahedra is replaced by an Al tetrahedron. Some of the minerals in this group include sanidine, orthoclase, and microcline. They have the same ideal chemical composition, $KAlSi_3O_8$, but with increasing order of stability. The quantities of K-bearing feldspars in soils vary with the intensity and capacity of weathering reactions. In strongly weathered soils, K-feldspars are usually present in only small amounts (van der Plas, 1966). Feldspars are commonly present in the silt and sand fractions of young to moderately weathered soils (Somasiri et al., 1971).

Micas are phyllosilicates consisting of two major groups, dioctahedral and trioctahedral, represented by muscovite and biotite, respectively. Nonexchangeable K^+ in phyllosilicates is not bonded covalently within the crystal structures of the soil mineral particles, but is held between adjacent tetrahedral layers of dioctahedral and trioctahedral micas, vermiculite, and intergrade clay minerals (Rich, 1972). In micaceous minerals, the surface charges are satisfied by K^+ ions in the interlayer, which are bound tightly to the adjacent layers through coulombic forces.

The rate of K^+ release from soil minerals varies. Biotite weathers more rapidly than muscovite and releases K^+ more easily (Kittrick, 1966; Sparks and Huang, 1985). Although muscovite is the most resistant of the micas, muscovite may weather at a more rapid rate due to its smaller particle size. The K plane is the weakest part of the crystalline structure. Therefore, micas may physically split into thin sheets and K^+ is then exposed as exchangeable ions.

The degree of K^+ fixation depends on the kinds of minerals present and among other factors, the level of K in the soil solution. Minerals such as weathered micas and vermiculite fix K^+ under both dry and moist conditions, whereas montmorillonite fixes K^+ usually only under dry conditions. Phyllosilicates differ in charge density. The strength of bonding between adjacent layers through intervening K^+ ions increases with charge density. Vermiculites and micas, which have relatively high charge density (Bailey, 1980), hold K^+ with a much greater tenacity than does montmorillonite which has relatively lower charge density.

Hydroxy-interlayered vermiculites and smectites occur in soils as a product of weathering (Rich, 1968, 1972). The presence of polymeric hydroxy-Al interlayers reduce K^+ fixation, since the polymeric ions balance the negative charges on the surface and at the same time keep the layers expanded (Rich and Obenshain, 1955; Rich, 1964).

Relatively few "pure" kaolins exist in soils (Komarneni, 1978; Talibudeen and Goulding, 1983). A number of researchers have shown that kaolins show an affinity for K^+ over Ca^{2+} (Jensen, 1973; Udo, 1978). However, this is probably due to impurities in the kaolins such as vermiculite and mica both of which exhibit a pronounced affinity for K^+ over Ca^{2+} (Talibudeen and Goulding, 1983; Jardine and Sparks, 1984a,b).

Organic colloids possess negative charges derived from the dissociation of carboxyl and phenolic hydroxyl groups (Huang, 1980). These functional groups adsorb K^+ ions from the soil solution (Naylor and Overstreet, 1969).

Current interest in the K chemistry and fertility of soils has switched from measurements of amounts of exchangeable K^+, which are often not reliable indicators of the quantity of K^+ that is actually available to plants, to measurements of the rates at which K^+ mobility occurs in soils. Recent attention has focused on: (1) the rate of adsorption and desorption of exchangeable and solution K^+ on soils and clay minerals (Jardine and Sparks, 1984a,b); (2) and the rate of release of K^+ from initially nonexchangeable forms (Cooke, 1979, Martin and Sparks, 1983).

The study of K^+ exchange on clay minerals and soils can be approached from either a thermodynamic or kinetic viewpoint. In surveying the soil chemistry literature, one will undoubtedly find that most of the studies on K^+ exchange have been of an equilibrial rather than a dynamic nature. Although the former studies have proved valuable in understanding the often elusive behavior of K^+ in heterogeneous systems, they do not convey information about the rates or mechanisms of K^+ exchange processes. Moreover, thermodynamic investigations on soil K^+ are often not applicable to field conditions. While one can achieve a quasi-state equilibrium in K^+ exchange in the laboratory, these conditions are seldom if ever attained under field conditions.

Agricultural soils are nearly always in a state of disequilibrium with regard to K^+ transformations. Soils that have been intensively cropped and fertilized with optimal K^+ fertilizer additions for many years belong in this group because equilibrium is precluded by periodic additions of fertilizers (Sparks, 1985, 1986; Sparks and Huang, 1985). Goulding (1983b), in an excellent review on thermodynamics of K exchange on clay minerals and soils, stated quite well the limitation in using thermodynamics to study K^+ reactions under field conditions when he said:

> "When referring to the thermodynamics of K exchange, workers invariably mean exchange equilibria and thus equilibrium thermodynamics. The attainment of equilibrium in the laboratory is entirely possible, but in the field the exchange of K^+ between soil and solution is a dynamic equilibrium, if it is an equilibrium at all."

Cooke (1979) has noted that one of the most important areas of agricultural research now and in the future is modeling of soil-plant processes. Certainly, cation exchange and in particular the dynamics of adsorption and release of K^+ in soils must be an intergral part of this research on modeling. To increase the efficiency of K^+

fertilizer applications, and to predict the fate of applied K^+ with time, one must have an understanding of the dynamic reactions between the phases of soil K^+.

Accordingly, my main objective was to critically examine both thermodynamic and kinetics approaches for studying K^+ exchange on soils and clay minerals. Many researchers have been uncertain as to whether one should use equivalent or mole fractions when studying ion-exchange equilibrium. Therefore, the first objective of this study was to investigate how thermodynamic parameters for K exchange differ both in magnitude and in trend using equivalent and mole fraction conventions and how these differences impact on basic conclusions dealing with ion preference. The second objective was to critically evaluate the use of kinetics for determining thermodynamics of ion exchange in soils. Lastly, I wished to evaluate the effects of kinetics methodologies on adsorption rate coefficients and energies of activation for adsorption of K and to derive a model that would assist in the elucidation of the rate-limiting steps for ion exchange processes on soils and clay minerals.

CHAPTER 2

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

2.1 Literature Review

The Argersinger (Argersinger et al., 1950) or Gaines and Thomas (Gaines and Thomas, 1953) conventions are usually employed to describe thermodynamics of ion exchange on 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 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 on 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 (k_c) 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). They defined the adsorbed activity coefficients as $f = a/N$.

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 in the case of homovalent exchange, the g values calculated using the Gaines and Thomas convention are not true activity coefficients since 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 which 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 which are not associated with actual chemical species, except in the special case of univalent ions. Goulding (1983b) 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_v, and k_c but the overall conclusions and trends would be similar using the two conventions.

Since 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 this 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.

2.2 Materials and Methods

2.2A. Theoretical Considerations

Considering the following reversible binary exchange reaction,

$$\text{Ca} - (\text{soil})_2 + 2\text{K}^+ \rightleftharpoons 2\text{K}\text{-}(\text{soil}) + \text{Ca}^{2+}, \qquad [2.1]$$

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

$$k_v = \frac{\bar{N}_K^2 \, a_{Ca}}{\bar{N}_{Ca} \, a_K^2} \qquad \text{Vanselow} \qquad [2.2]$$

$$k_c = \frac{E_K^2 \; a_{Ca}}{E_{Ca} \; a_K^2} \qquad \text{Gaines and Thomas} \qquad [2.3]$$

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:

$$k_v = K_{eq} \frac{f_{Ca}}{f_K^2} \qquad [2.4]$$

$$k_c = K_{eq} \frac{g_{Ca}}{g_K^2} \qquad [2.5]$$

where f and g are the activity coefficients of the adsorbed cations. For the K^+-Ca^{2+} exchange reaction described by Eq. [2.1], activity coefficients of the adsorbed ions can be defined using the equations proposed by Argersinger _et al_., (1950):

$$\ln f_{Ca} = E_K \ln k_v - \int_0^{E_K} \ln k_v dE_K \qquad [2.6a]$$

$$2\ln f_K = -(1-E_K) \ln k_v + \int_{E_K}^{1} \ln k_v \; dE_K \qquad [2.6b]$$

Moreover, since,

$$\ln K_{eq} = \ln k_v - \ln f_{Ca} + 2 \ln f_K \qquad [2.7]$$

Eq. [2.6] leads to the result,

$$\ln K_{eq} = \int_0^1 \ln k_v \, dE_K \qquad [2.8]$$

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

$$\ln g_{Ca} = E_K (\ln k_c - 1) - \int_0^{E_K} \ln k_c \, dE_K \qquad [2.9a]$$

$$2 \ln g_K = (1-E_K)(1-\ln k_c) + \int_{E_K}^1 \ln k_c \, dE_K \qquad [2.9b]$$

The equilibrium constant is then given as:

$$\ln K_{eq} = 1 + \int_0^1 \ln k_c \, dE_K \qquad [2.10]$$

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

$$k_v = k_c \frac{u^u}{v^v} (uE_B + vE_A)^{v-u} \qquad [2.11]$$

where v and u are the valencies of K^+ and Ca^{2+}, respectively. Equation [2.11] can also be described as

$$\ln k_v = \ln k_c + f(E) \qquad [2.12]$$

If one lets K_v represent the equilibrium constant calculated using k_v and K_c that calculated using k_c, combination of Eqs. [2.8], [2.10], and [2.12] results in:

$$\ln K_v = \ln K_c + \int_0^1 f(E)\, dE_K - (u-v) \qquad [2.13]$$

where

$$\int_0^1 f(E)\, dE_K = \int_0^1 \ln \frac{u^u}{v^v} + \int_0^1 (v-u) \ln [uE_K + vE_{Ca}]\, dE_K$$

$$= u\ln u - v\ln v + [-u\ln u + v\ln v + (u-v)]$$

$$= u-v \qquad [2.14]$$

Thus,

$$\ln K_v = \ln K_c = \ln K_{eq} \qquad [2.15]$$

It therefore follows that

$$\Delta G^o{}_v = \Delta G^o{}_c = -RT \ln K_{eq} \qquad [2.16]$$

2.3 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 8.5% which is predominately chloritized vermiculite and mica; an organic matter content of 1.3%; and a cation exchange capacity (CEC) of 4.90 cmol kg^{-1}. The Chester soil has: a clay content of 28.0% which is mainly kaolinite; an organic matter content of 3.3%; and a CEC of 6.8 cmol kg^{-1}.

Equilibrium studies were conducted by first saturating the soils with Ca^{2+} using a 0.50 $\underline{M}$ $CaCl_2$ solution. Triplicate 1 g air-dried Ca-saturated samples were uniformly applied onto Buchner funnels which were equipped with 0.45 μm filter paper. Different solutions of varying 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 concentrations 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_4Cl solution and the leachate was analyzed for K^+ and Ca^{2+} using atomic absorption spectrophotometry. The studies were conducted at 283, 298, and 308 K.

Using the data from the above experiments, equilibrium selectivity coefficients, adsorbed activity coefficients, equilibrium constants and standard free energies of exchange (ΔG^0) were calculated using the Argersinger and Gaines and Thomas conventions.

2.3 Results and Discussion

2.3A. 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. 2.1-2.2 for the two soils. With both conventions, the selectivity coefficients decreased with increasing F_K. This has been observed before (Babcock, 1963; Bolt et al., 1963; Jensen, 1973; Mehta et al., 1983) and is indicative of a

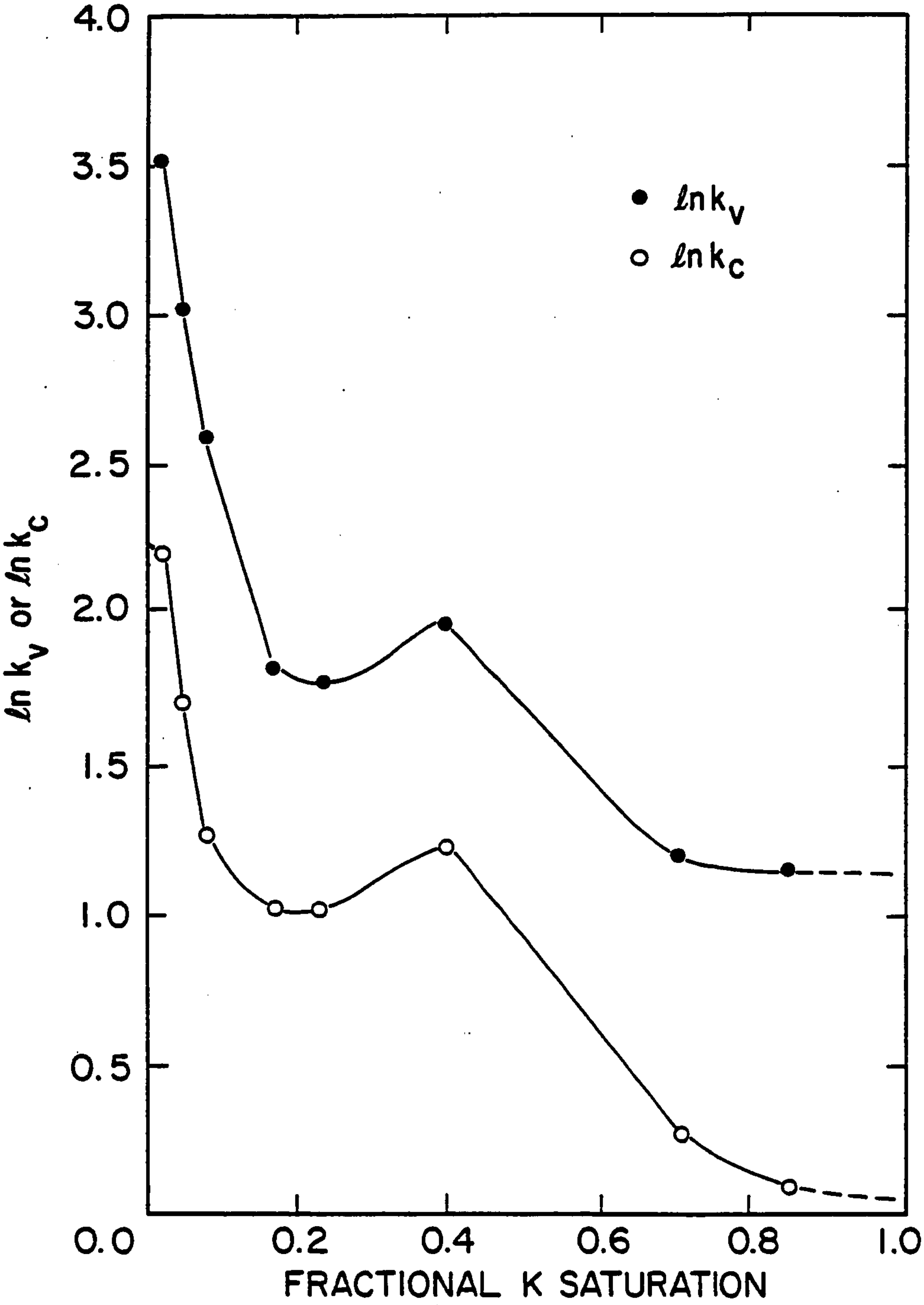

Fig. 2.1. Natural logarithm of Vanselow selectivity coefficients (k_v) and Gaines and Thomas selectivity coefficients (k_c) as a function of fractional K saturation on a Chester loam at 298 K.

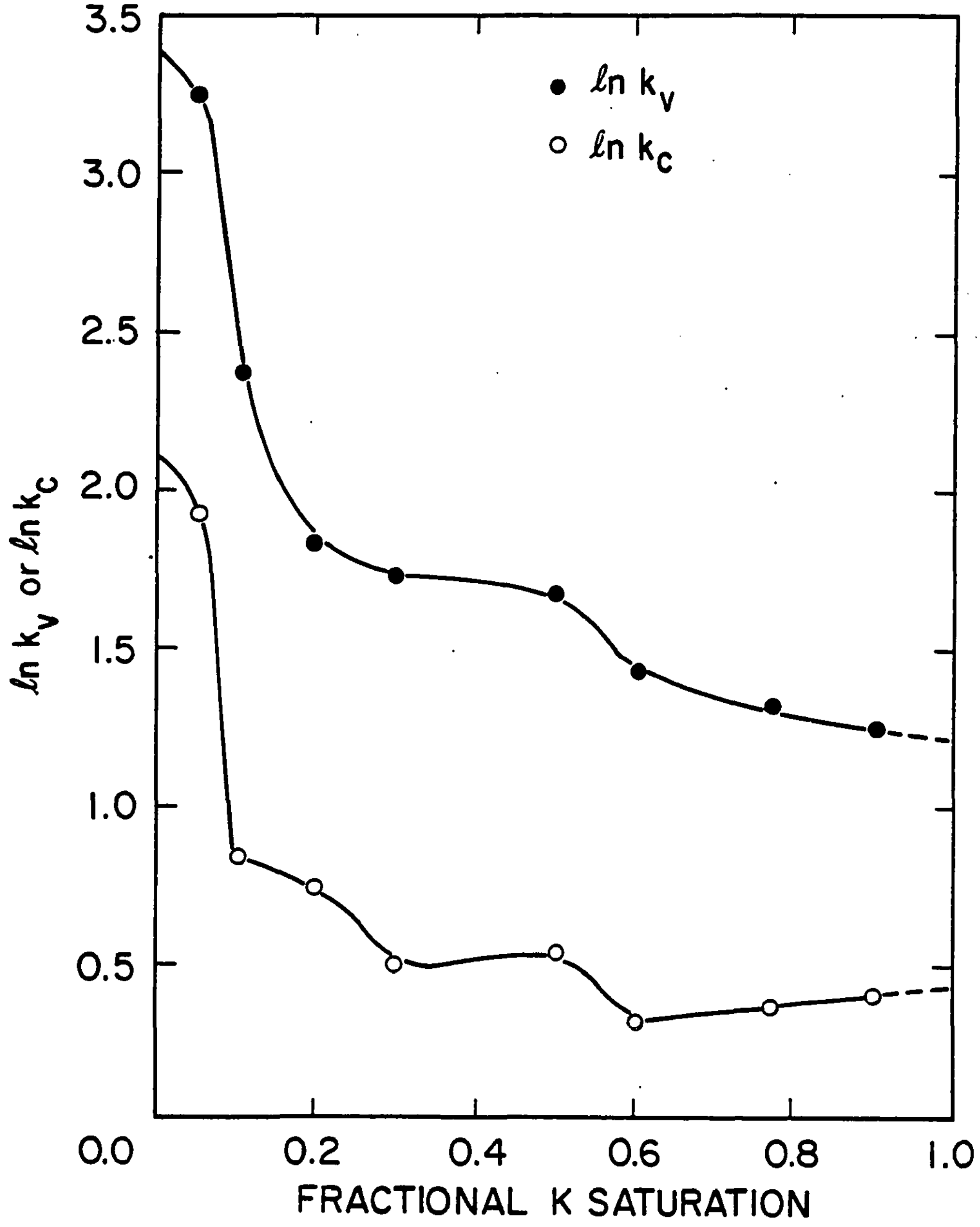

Fig. 2.2. Natural logarithm of Vanselow selectivity coefficient (k_v) and Gaines and Thomas selectivity coefficient (k_c) as a function of fractional K saturation on Matapeake silt loam at 298 K.

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). In previous studies (Jardine and Sparks, 1984a,b) on Delaware soils, it was shown 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 proven 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 investigated contain significant 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 pointed, 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. 2.1-2.2). This is not surprising since 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 these 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 of the soils (Figs. 2.1-2.2). 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. [2.8] and [2.10]. Even though the selectivity coefficients using the Vanselow and Gaines and Thomas conventions did not compare in magnitude, the curves were similar and showed a similar trend.

2.3B. 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 1953) adopted the convention that when the exchanger is saturated with K^+, f_K or g_K is unity, and when the exchanger is saturated with Ca^{2+}, f_{Ca} or g_{Ca} is unity. This leads to the application of the Gibbs-Duhem equation resulting in Eqs. [2.6] and [2.9]. The data obtained at 298K using two sets of equations are given in Fig. 2.3 for the two soils studied.

The curves obtained using the Vanselow and Gaines and Thomas conventions showed a significant difference in magnitude for 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 on the other hand, 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

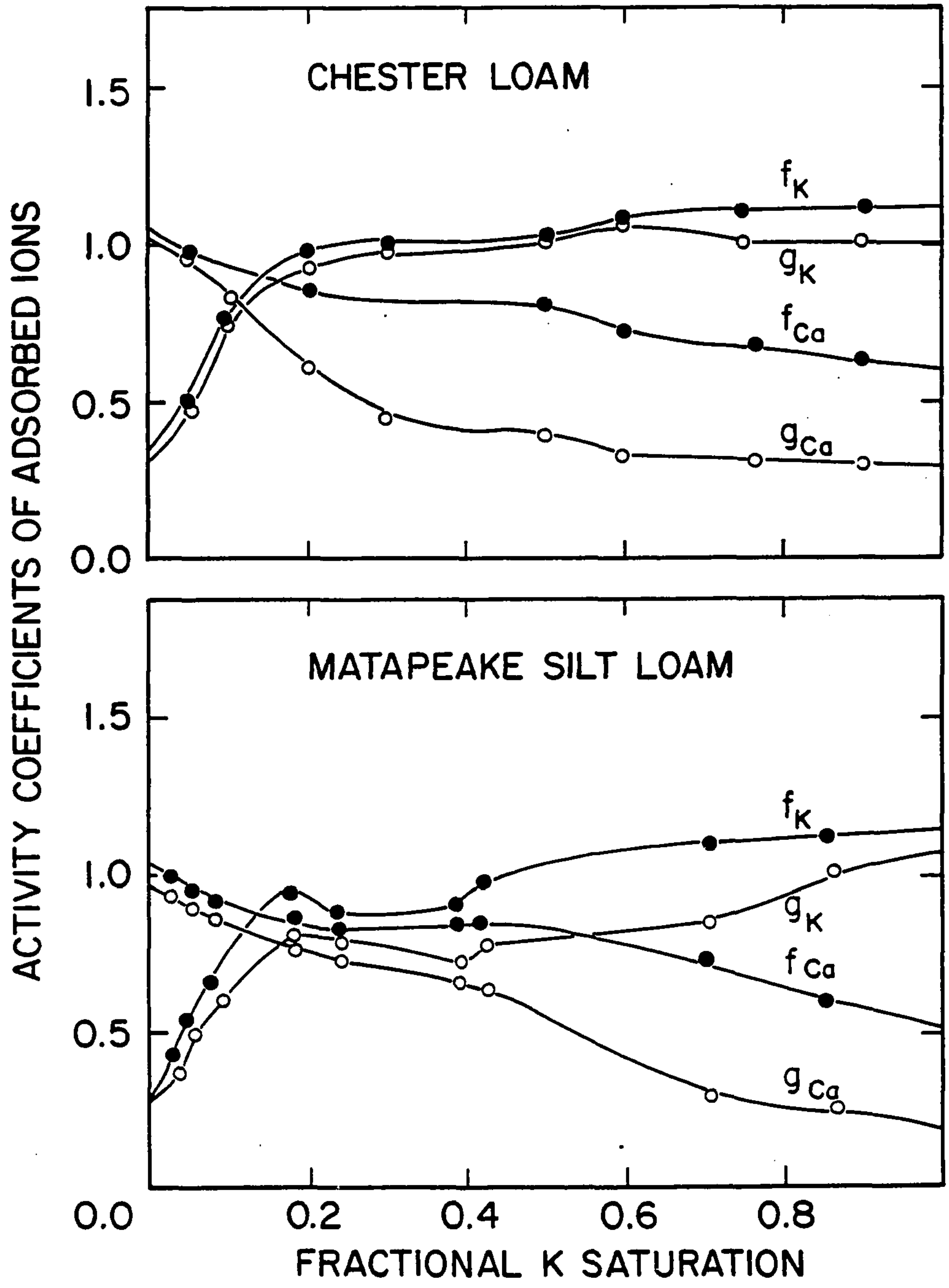

Fig. 2.3. Activity coefficients of adsorbed ions calculated using mole fraction (f_i) or equivalent fraction (g_i) versus fractional K saturation of the adsorbed phase for the two soils studied.

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. 2.3). 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.

Inflexions, and maxima and minima values for the activity coefficients using the two conventions occurred at virtually the same F_K for both soils (Fig. 2.3). It is also clear from Fig. 2.3 that while the f_i and g_i differ significantly in magnitude, the overall trend and shape of the curves is 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. [2.4] and [2.5] that since 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 of 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.

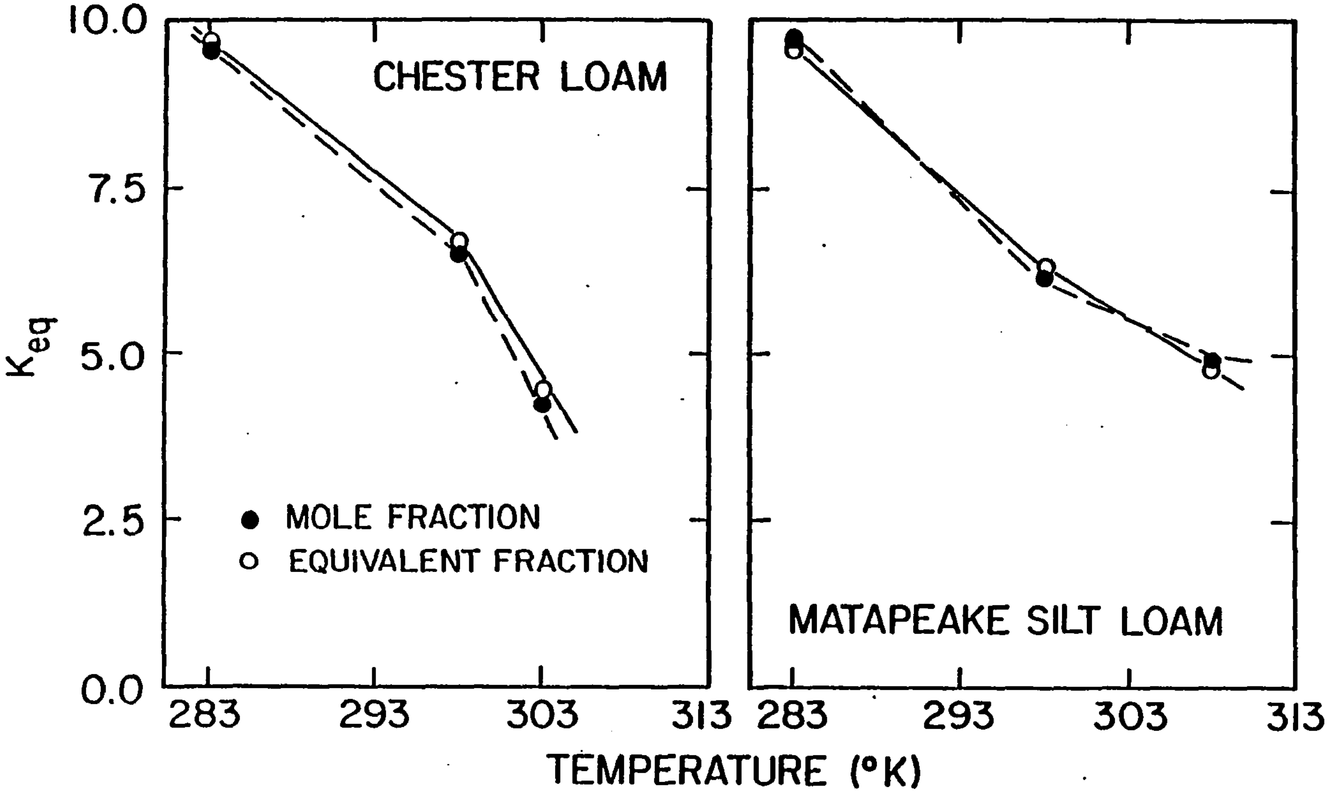

Fig. 2.4. Comparison of the thermodynamic equilibrium constant (K_{eq}) obtained using mole and equivalent fractions versus temperature for the two soils studied.

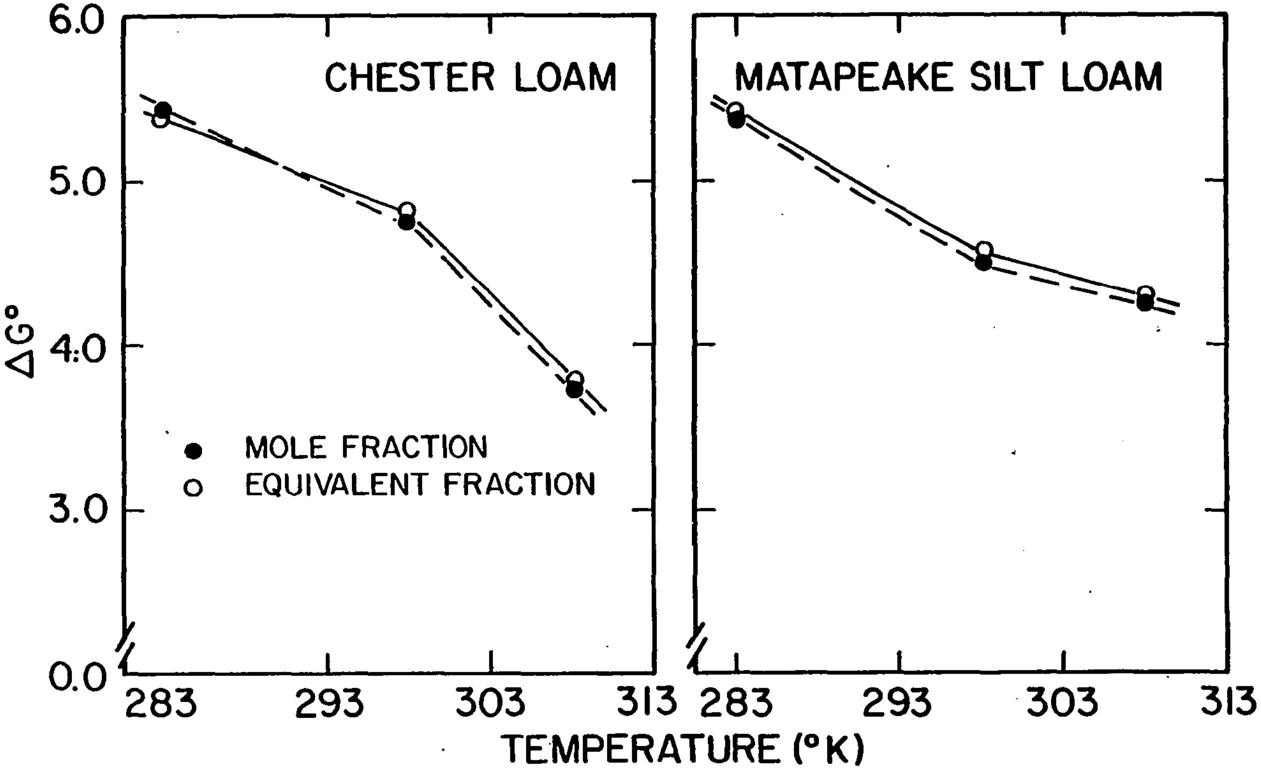

Fig. 2.5. Comparison of the standard free energy (ΔG^{o}) of exchange obtained using mole and equivalent fractions versus temperature for the two soils studied.

2.3C. Other Thermodynamic Parameters

The equilibrium constants (K_{eq}) and standard free energy (ΔG^o) values for k^+ exchange on soils were calculated from the experimental data using both conventions. These parameters are presented against change in temperature (Figs. 2.4-2.5). The K_{eq} values decreased with increasing temperature (Fig. 2.4) 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. 2.8-2.15). Since the K_{eq} values obtained from the two conventions are similar, it therefore follows from Eq. (2.16) that the calculated ΔG^o values using both conventions, at a given temperature, are similar. This is confirmed by the data presented in Fig. 2.5. The same values of K_{eq} or ΔG^o may not be obtained due to curve-extrapolation normally done to reach $F_K=0$ and $F_k=1$ (Figs. 2.1 and 2.2) when evaluating the integrals (Eqs. 2.8 and 2.10), however, the differences are always insignificant.

2.4 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. It was found that the activity coefficients of adsorbed ions and the selectivity coefficients obtained using the two 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 similar magnitude at a given temperature.

CHAPTER 3

A CRITICAL EVALUATION ON THE USE OF KINETICS FOR DETERMINING THERMODYNAMICS OF ION EXCHANGE

3.1 Literature Review

One can study ion exchange in soils and clay minerals from either a thermodynamic or a kinetics perspective. Most studies on the chemistry of soil K have been of a thermodynamic nature or were based on the law of mass action (Hutcheon, 1966; Deist and Talibudeen, 1967a; Jensen, 1973). However, recently Sparks and his coworkers (Sparks et al., 1980; Sparks and Jardine, 1981; Sparks and Rechcigl, 1982; Jardine and Sparks, 1984a; Carski and Sparks, 1985; Sparks, 1985, 1986) studied soil K exchange from a kinetics viewpoint.

Thermodynamic investigations on K have proved valuable, but they do not assist one in understanding the mechanisms and rates of K exchange on clay minerals and soils, nor are they often applicable to field conditions. Agricultural soils are nearly always in a state of nonequilibrium with regard to K reactions. Soils that have been intensively cropped and fertilized with optimal fertilizer additions for many years belong in this group, because equilibrium is precluded by periodic additions of K fertilizers (Sparks, 1985, 1986).

H. C. Thomas (1965) asked whether a relationship existed between the standard enthalpy of exchange for the solid phase ($\Delta H^o{}_s$) and the activation enthalpy, $\Delta H^{\ddagger}$, of an ion exchange reaction, where $\Delta H^o_s = \Delta H^{\ddagger} - \Delta H^o_\ell$ [3.1] and ΔH^o_ℓ is the standard enthalpy of exchange for the solution phase (Goulding, 1983b). He suggested that the best way to establish such a connection was through self-diffusion studies. Unfortunately, no further publication has appeared clarifying this idea or confirming the relationship.

It has been known for many years that a direct relationship exists between chemical equilibria and completely reversible reactions (Glasstone et al., 1941; Laidler, 1965). Keay and Wild (1961) used this approach to calculate the enthalpy and entropy of Na-Mg exchange on vermiculite from measurements of kinetics of Mg-Na and Na-Mg exchange. Sparks and Jardine (1981) first applied the relationship to K exchange studies, and they calculated apparent thermodynamic parameters for K-Ca exchange on a soil from measurements of the kinetics of this reaction. A miscible displacement technique (Sparks et al., 1981) was used to calculate the kinetics parameters. The magnitude of the apparent thermodynamic parameters determined by Sparks and Jardine (1981) compared well to pseudothermodynamic parameters calculated using Eyring's reaction rate theory. However, the authors did not calculate the thermodynamic parameters from classical exchange isotherm data and compare the results using the two theories. A comparison of this type for soils or clay minerals has not been published. Such a study would lend credence to both theories. However, Goulding (1983a) noted that the apparent thermodynamic parameters calculated by Sparks and Jardine (1981) compared in magnitude to a range of values found by Deist and Talibudeen (1967a,b) for British soils using exchange isotherm data.

Accordingly, the objective of this study was to determine the theoretical and practical implications of using a kinetics approach to calculate thermodynamic parameters for K-Ca exchange on soils. This was accomplished by comparing both in magnitude and trend the parameters using kinetics and equilibrium theories.

Several methods were employed for the kinetics approach while the Argersinger theory (Argersinger et al., 1950) was used for the equilibrium approach. A study of this type has not appeared in the soil chemistry literature.

3.2 Theoretical Considerations

3.2A. Equilibrium Approach

If one employs the classical theory of Argersinger et al. (1950) to the following exchange reaction,

$$\text{Ca-(Soil)}_2 + 2K^+ \rightleftharpoons \text{2K-Soil} + Ca^{2+} \qquad [3.2]$$

one finds that the thermodynamic equilibrium constant (K_{eq}) is given by

$$K_{eq} = \frac{a^2_{K(ad)}\, a_{Ca}}{a_{Ca(ad)}\, a^2_K} \qquad [3.3]$$

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

Treating the exchanger as a nonideal solid solution and assuming the activity of adsorbed water is negligible,

$$a^2_{K(ad)} = f^2_K\, \bar{N}^2_K \text{ and } a_{Ca(ad)} = f_{Ca}\, \bar{N}_{Ca} \qquad [3.4]$$

$$a^2_K = \gamma^4_{KCl}\, m^2_K \text{ and } a_{Ca} = \gamma^3_{CaCl_2} m_{Ca} \qquad [3.5]$$

where

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

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

γ = mean activity coefficient of the ions in the solution phase

m = molality of the cation in the solution phase

Thus, Eq. [3.3] assumes the form:

$$\frac{f^2_K\, \bar{N}^2_K\, \gamma^3_{CaCl_2} m_{Ca}}{f_{Ca} \bar{N}_{Ca} \gamma^4_{KCl} m^2_K} = K_{eq} \qquad [3.6]$$

or $$K_{eq} = \frac{f^2_K}{f_{Ca}} k_v \qquad [3.7]$$

where

k_v = Vanselow selectivity coefficient.

Applying the Gibbs-Duhem equation to this binary system and combining with Eq. [3.6], one may obtain the following using a mole fraction of unity as the standard state for adsorbed ions (Argersinger et al., 1950):

$$\ln K_{eq} = \int_0^1 \ln k_v \, dE_K \qquad [3.8]$$

where E_k is the equivalent fraction of K^+ on the colloid. Integrals are then evaluated graphically by plotting ln k_v against E_K. The area under the curve which equals ln K_{eq} can be obtained using the trapezoidal rule.

The standard free energy, ΔG^o; enthalpy, ΔH^o; and entropy, ΔS^o changes for K^+ exchange are then calculated from Eqs. [3.9]-[3.11],

$$\Delta G^o = -RT \ln K_{eq} \qquad [3.9]$$

$$\ln\left(\frac{K_{eq_2}}{K_{eq_1}}\right) = -\frac{\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad [3.10]$$

$$\Delta S^{o} = (\Delta H^{o} - \Delta G^{o})/T \qquad [3.11]$$

3.2B. Kinetics Approach

The general derivation of a kinetics model for cation exchange is based on the rate of the reaction in Equation [3.2]. One assumes at the outset that this rate can be expressed as (Denbigh, 1981; Sposito, 1985):

$$\frac{dE}{dt} = R_f - R_b \qquad [3.12]$$

where dE = extent of the reaction parameter, R_f is the rate of the forward reaction and R_b is the rate of the backward reaction in Eq. [3.2], e.g., the same reaction describes both the forward and backward processes in the K-Ca reaction.

The individual rates (R_f and R_b) will each depend on temperature, pressure, and the concentrations of the species in Eq. [3.2]. At equilibrium, the left side of Eq. [3.12] will vanish and R_{fe}/R_{be}, where "e" denotes the equilibrium conditions, will be some function of temperature, pressure, and the equilibrium composition of the exchanger and the aqueous solution phase. Since the activity coefficients of the species in Eq. [3.2] have the same kind of functional dependence, one may infer that R_{fe}/R_{be} is a function of T, P, and the species activities (Denbigh, 1981). However, this relationship applies also to the quotient of the right and left sides of Eq. [3.6] and therefore, one may conclude that, for example,

$$R_{fe}/R_{be} = F\,[(a_{K(ad)})_e^2(a_{Ca})_e \;/\; (a_{Ca(ad)})_e(a_K)_e^2 K_{eq}] \qquad [3.13]$$

in respect to Eq. [3.3].

Equation [3.13] expresses a general relation between reaction rate and thermodynamics, predicated on Eq. [3.12] and the uniqueness of Eq. [3.2] as experimental facts of kinetics. If it is assumed further that F(x)=x on the right side of Eq. [3.13], then R_{fe}/R_{be} will equal the quotient of the right and left sides of Eq. [3.6]:

$$R_{fe}/R_{be} = (a_{K(ad)})_e^2\ (a_{Ca})_e \;/\; (a_{Ca(ad)})_e\ (a_K)_e^2 K_{eq} \qquad [3.14]$$

Equation [3.14] is expected whenever R_f and R_b depend on powers of the concentrations of the rectants and products in Eq. [3.2] and the power exponents are the stoichiometric coefficients of the four species involved (Denbigh, 1981). Even with this simplification of Eq. [3.12], it is necessary to assume that the mechanism of the cation exchange reaction at equilibrium does not change when $R_f \neq R_b$ in order that finite rate data can be used in the application of Eq. [3.14].

For the kinetic phase of this study, the following exchange reaction was studied:

$$Ca_{1/2}X(s) + K^+(aq) = KX(s) + 1/2Ca^{2+}(aq) \qquad [3.15]$$

The applicability of Eq. [3.12] to Eq. [3.15] depends on the assumption that the rate is not controlled by diffusion processes. Helfferich (1965, 1983) has noted that if the rate-controlling process is diffusion and not the reaction in Eq. [3.15], then no information about K_{eq} can be derived from an analysis of kinetics data. This hypothesis was tested in my experimental studies. Assuming the influence of diffusion is eliminated or practically so, the rates R_f and R_b can be modeled for K-Ca exchange using the equations:

$$R_f = k_a M_s q_{Ca} m_K \qquad R_b = k_d M_s q_K m_{Ca}^{1/2} \qquad [3.16]$$

where k_a and k_d are adsorption and desorption rate coefficients, respectively, M_s is the mass of the exchanger, q_i (i = Ca or K) is the number of moles of charge of metal i adsorbed by unit mass of the exchanger, and m_i is a molality (i = Ca or K). The rate of formation of KX(s) now can be expressed by the equation:

$$dE/dt = M_s(dq_K/dt) = M_s[k_a q_{Ca} m_K - k_d q_K m_{Ca}^{1/2}] \qquad [3.17]$$

If the rate of adsorption of K^+ is measured by miscible displacement (Sparks and Jardine, 1981) with m_K maintained constant and $m_{Ca} = 0$, then Eq. [3.17] reduces to Eq. [3.18]:

$$dq_K/dt = k'_a m_K(q_T - q_K) \qquad [3.18]$$

where $q_T = q_{Ca} + q_K$ is the cation exchange capacity and k_a' is now an apparent adsorption rate coefficient (Sparks et al., 1980). Equation [3.18] is a first-order rate equation with respect to K^+ (aq) and KX(s). If the rate of desorption is measured with m_{Ca} held constant and $m_K=0$ as in my experiment, Eq. [3.17] becomes:

$$dq_K/dt = -k_d' \, m_{Ca}^{1/2} q_K \qquad [3.19]$$

where k_d' is an apparent desorption rate coefficient (Sparks et al., 1980b) and which is first-order with respect to KX(s) but of fractional order with respect to Ca^{2+}(aq). Equations [3.18] and [3.19] lead to measurement of the coefficients k_a' and k_d' by standard kinetics analysis (Sparks and Jardine, 1981; Sparks, 1985, 1986; Sparks and Huang, 1985).

Once K_{eq} is determined through a kinetic approach, e.g., $k_a/k_d = K_{eq}$, ΔG^0 can be obtained using Eq. [3.9].

Using the Arrenhius and van't Hoff equations (Denbigh, 1981), energies of activation for K adsorption and for K desorption (E_{aa} and E_{ad}, respectively) can be determined as shown below (Sparks, 1985 1986):

$$d \ln k_a/dT = E_{aa}/RT^2 \qquad [3.20]$$

and for the desorption kinetic reaction,

$$d \ln k_d/dT = E_{ad}/RT^2 \qquad [3.21]$$

and from the van't Hoff equation, the enthalpy for K exchange (ΔH^0) can be determined:

$$d \ln K_{eq}/dT = \Delta H^o/RT^2, \text{ or} \qquad [3.23]$$

$$E_{aa} - E_{ad} = \Delta H^o \qquad [3.24]$$

The ΔS^o can then be determined using Eq. [11].

3.3 Experimental Procedures

The Ap horizons of a Chester loam (fine-loamy, mixed, mesic Typic Hapludult) and a Downer sandy loam (fine-loamy, mixed, mesic Typic Hapludult) were used in this study. Basic chemical, mineralogical, and physical properties of the soils were determined using standard methods outlined by Jardine and Sparks (1984a). The Chester loam contained 15.0, 57.0, and 28.0% sand, silt, and clay, respectively, 3.3% organic matter, had a CEC of 6.8 cmol kg^{-1}, and the <2 μm clay fraction contained mainly kaolinite and chloritized vermiculite with smaller quantities of vermiculite and gibbsite. The Downer sandy loam contained 76.5, 15.0, and 8.5% sand, silt and clay, respectively, 1.3% organic matter, had a CEC of 4.90 cmol kg^{-1}, and the clay fraction contained primarily chloritized vermiculite and kaolinite with smaller quantities of vermiculite and gibbsite.

3.3A. Equilibrium Studies

Equilibrium studies were conducted by first saturating the soils with Ca^{2+} using 0.5 M $CaCl_2$ and washing with deionized water until a negative test for Cl^- was received using $AgNO_3$. Triplicate 1 g dry Ca-saturated soil samples were uniformly applied onto Buchner funnels which were equipped with 0.45 μm filter paper. Eight different solutions of varying KCl and $CaCl_2$ concentrations but of a constant ionic strength of 0.01 were prepared. The equivalent fraction of K^+ or Ca^{2+} in the mixed solution varied from 0 to 1.00. The experiments were performed in a large, temperature controlled, incubator at 283, 298, and 308 K. The soil was leached at low pressure suction with about 400 mL of the solution or until the concentration of K^+ and Ca^{2+} in the leachate was equal to those concentrations in the original solution. After equilibrium, the entrained salts were removed by washing the soil with 100 mL of deionized water. The free water was removed by suctioning. To determine the extent of adsorbed K^+ and Ca^{2+} at equilibrium, the soil was leached with 350 mL of a 1.0 M NH_4Cl solution. The leachate was analyzed for K^+ and Ca^{2+} using atomic absorption spectrophotometry. Thermodynamic parameters were calculated using Eqs. [3.9] - [3.11].

3.3B. Kinetics Approach

The kinetics approach for determining thermodynamic parameters was investigated using three techniques: a miscible displacement method first proposed by Sparks et al., (1980), a batch, and a vortex mixed batch. These three techniques were used to determine how diffusion affects the comparison between thermodynamic parameters calculated using a kinetics approach and an equilibrium method.

The miscible displacement technique was employed by Sparks and Jardine (1981) to investigate the kinetics of K exchange in soil. The apparent kinetic rate coefficients (k_a' and k_d') were then used to calculate apparent thermodynamic parameters. However, the authors clearly referred to the equilibrium constant as an apparent K_{eq} (K_{eq}'). As noted earlier, they did not compare the thermodynamic parameters they calculated with those using exchange isotherm data.

With the miscible displacement (flow) technique, triplicate 1 g dry samples of the Ca-saturated soils were thinly spread onto a 0.45 μm nuclepore filter and then the filter was securely cupped. The filter was attached to a LKB Ultrorac II 2070 fraction collector and peristaltic pump. The studies were performed at the same temperatures used in the equilibrium studies.

For K adsorption kinetics, the Ca-saturated soils were leached with a 0.001 M KCl solution at a constant flow rate of 1 mL min^{-1}. Two-mL aliquots were collected at 2 min increments until an apparent equilibrium was attained. Then, the sample was leached with 100 mL of deionized water to remove any entrained solution and suctioned to remove any excess water. Potassium desorption was subsequently initiated using a 0.001 M $CaCl_2$ solution. Leaching was continued until no K^+ was detected in the leachates and K^+ in solution was analyzed as before. Apparent rate coefficients (k_a' and k_d') were calculated using first-order kinetic equations for flow techniques outlined by Sparks (1985, 1986) and thermodynamic parameters were calculated as given in Eqs. [3.9], [3.11], and [3.24].

The batch method consisted of placing triplicate 2 g Ca-saturated soil samples into 50 mL polyethylene centrifuge tubes. Then, 5 mL of a 0.001 M KCl solution were rapidly introduced into the tube and timing was begun. The mixture was then shaken on a reciprocating shaker at 180 rpm for time intervals of 5 s for the first min of the reaction, and then for 2 min intervals thereafter. This shaking speed was chosen to effect mixing but to cause minimal abrasion of the soil particles. The mixture was shaken by placing the tube at a 45^{0} angle to the moving plane of the shaker to ensure even mixing and to prevent the soil from adhering to the surfaces of the tube. The latter was observed when the tubes were placed directly on the shaker. After equilibration, the solution was immediately separated from suspension by pouring the mixture into a glass syringe which was attached to a nuclepore filter holder containing 0.45 μm filter paper. The leachate was collected in a plastic test tube [Fig. 3.1]. The maximum time required for the filtration step was about 5 s.

Desorption studies were conducted by using soils that were equilibrated with 0.001 M KCl. The K was desorbed using 0.001 M $CaCl_2$ and the procedures and times, given above. Adsorption and desorption rate coefficients were determined using first-order equations given by

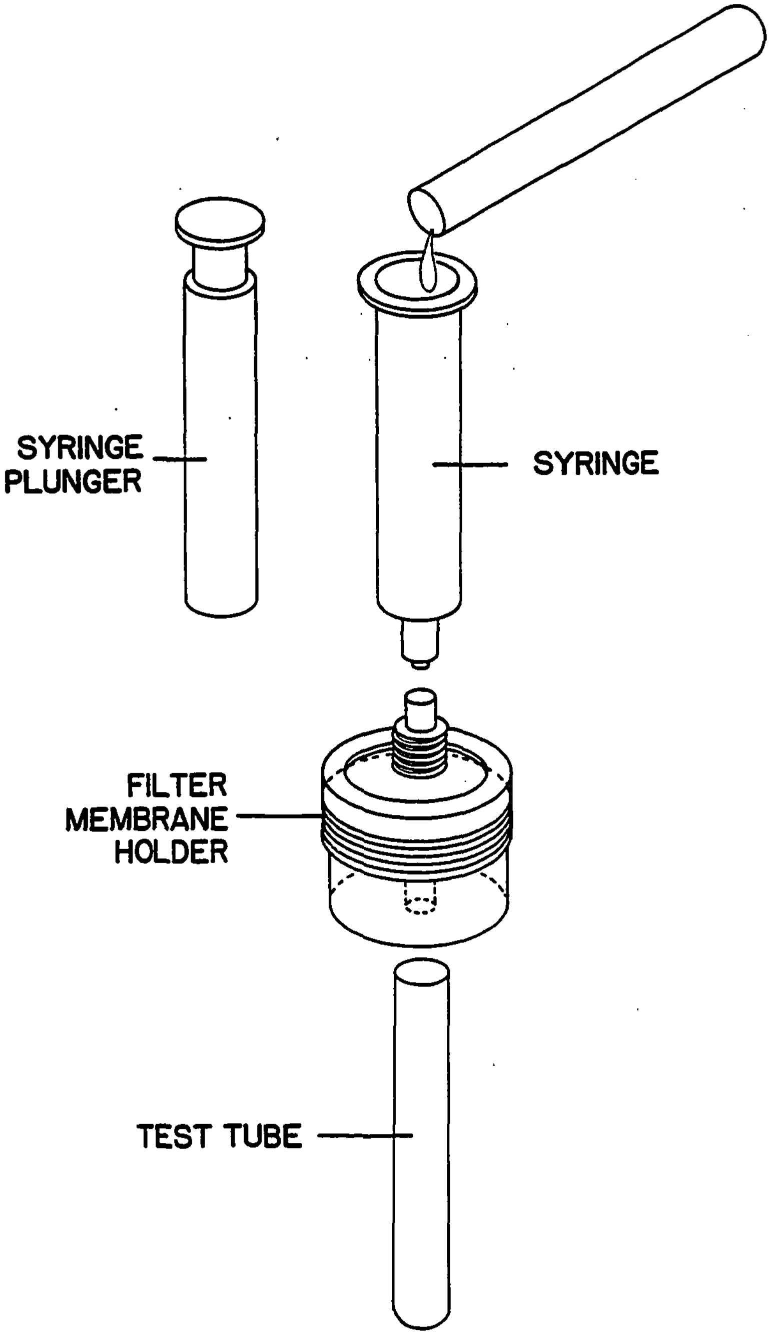

Fig. 3.1. Schematic diagram depicting various parts of the device used for rapid filtration in the batch and vortex batch kinetics.

Sparks (1985, 1986). The batch technique and the method of filtration described above were chosen to avoid centrifugation and thus, rapid exchange reactions could be observed. It usually takes at least five min of centrifugation to separate the solid from the liquid phases. Many exchange reactions are complete by this time or less (Jardine and Sparks, 1984a).

The vortex mixed batch technique was accomplished using the same procedure as for the batch technique except the soil and solution were rapidly mixed by vortexing rather than by equilibrating on a reciprocating shaker. Rate coefficients were calculated as with the batch technique and thermodynamic parameters were calculated for both batch methods using Eqs. [3.9], [3.11], and [3.24].

The filtrates from the miscible displacement, batch, and vigorously mixed vortex batch studies were analyzed for K^+ using atomic absorption spectrophotometry. All kinetics studies were run at 283, 298, and 308 K.

3.4 Results and Discussion

3.4A. Kinetics Methods

Although not shown, K^+ adsorption and desorption conformed well to first-order kinetics using all three kinetics methods. This has been observed in several previous studies (Sparks et al., 1980; Sparks and Jardine, 1981; Sparks and Rechcigl, 1982; Jardine and

Sparks, 1984a; Sparks and Jardine, 1984; Carski and Sparks, 1985). The effect of method on k_a, k_d, E_{aa}, and E_{ad} values is shown in Table 3.1. With all three methods and at all temperatures, the k_d or k_d' values are lower than the corresponding k_a or k_a' values indicating that the rate of K^+ desorption was lower than for K^+ adsorption. This observation is further supported by the magnitude of the energy of activation values. Energies of activation vary inversely with the rate of exchange (Sparks, 1985, 1986). With each method, the E_{ad} values were higher than the E_{aa} values indicating that the rate of K^+ desorption was lower than for K adsorption, and that the energy needed to desorb K^+ is greater than that to adsorb K^+. These results can be explained by the predominance of vermiculitic minerals present in the two soils. In the K^+ adsorption process, a partial collapse of the interlayers occurs due to coulombic attractive forces being greater between the clay surfaces and the K^+ ions than between the individual K^+ ions. Consequently, K^+ desorption becomes a slower and more difficult exchange process than K^+ adsorption (Kittrick, 1966; Jardine and Sparks, 1984a).

The E_{aa} and E_{ad} values were quite low, particularly for the miscible displacement and batch techniques (Table 3.1) which suggests that diffusion controlled exchange is occurring (Boyd et al., 1947; Mortland and Ellis, 1959; Sparks and Jardine, 1981; Sparks, 1985, 1986). The E_{aa} and E_{ad} values were considerably higher with the vortex batch technique suggesting that the effect of diffusion was

Table 3.1 Effect of kinetic method on adsorption and desorption rate coefficients (k_a and k_d), respectively, and energies of activation (E_{aa} and E_{ad}), respectively, for adsorption in soils.

Temp.	Kinetic Method											
	Miscible Displacement				Batch				Vortex Mixed Batch			
K	k'_a	k'_d	E_{aa}	E_{ad}	k_a	k_d	E_{aa}	E_{ad}	k_a	k_d	E_{aa}	E_{ad}
	----min^{-1}----		--kJ mol^{-1}--		-----min^{-1}---		---kJ mol^{-1}--		----min^{-1}----		--kJ mol^{-1}--	
					Chester loam							
283	0.031	0.020			0.179	0.061			0.867	0.159		
298	0.036	0.026			0.225	0.086			2.331	0.500		
308	0.040	0.030			0.257	0.113			2.629	0.656		
			7.42	11.87			10.69	18.41			32.96	42.10
					Downer sandy loam							
283	0.054	0.025			0.189	0.076			1.871	0.162		
298	0.061	0.031			0.288	0.097			2.900	0.385		
308	0.069	0.038			0.312	0.211			3.981	0.643		
			7.42	12.47			14.85	30.29			22.39	40.92

diminished significantly. Mortland and Ellis (1959) found the E_{ad} for K^+ release from vermiculite, using a leaching technique, was 14.85 kJ mol^{-1}. They concluded that film diffusion was the rate-controlling step. This value is in the range found with the miscible displacement and batch techniques of this study. Boyd et al., (1947) found that E_{aa} values for Na^+ adsorption on exchange resins from dilute KCl solutions averaged 18.83 kJ mol^{-1} and also concluded film diffusion was rate controlling. Kuo and Lotse (1974) found adsorption of phosphorus on gibbsite and hematite was characterized by an E_{aa} value of 7.95 kJ mol^{-1}, again indicating diffusion-controlled exchange.

It is clear from the kinetic data in this study (Table 3.1) that the rate of K^+ adsorption and desorption is very dependent on the method chosen. The rate followed the order vortex batch>batch>miscible displacement. This same order was observed in the rate coefficients and energies of activation. For example, the k_a value for the Downer soil at 283 K is approximately 35 times greater when the vigorously mixed batch technique was used than when a miscible displacement was employed.

Most ion exchange reactions are conducted by a batch or column process. In both cases, there is usually some form of agitation of the liquid (stirring, shaking, or flowing) with the object of mixing the liquid and ensuring that its composition remains uniform up to the surface of the particles. Some researchers have assumed that shaking or stirring would eliminate or drastically reduce diffusion (Gonzales et al., 1982). However, for hydrodynamic reasons, there is usually a thin region around each particle in which such mixing is imperfect and the ions can only transverse this region by diffusion. This region may be referred to as the Nernst film (Boyd et al., 1947; Reichenberg, 1957).

The data in this study clearly show that diffusion is occurring in the miscible displacement and batch techniques and to a much reduced extent with the vigorously mixed vortex batch technique. It would appear that rapid agitation is required before the effect of diffusion on the rate process is significantly diminished. This kind of agitation is not present in most batch studies. The implications that diffusion has on using kinetics to obtain information about equilibrium processes of ion exchange in soils will be discussed later.

3.4B. Comparison of Equilibrium and Kinetics Approaches

Thermodynamic data obtained from the equilibrium and kinetics approaches are shown in Table 3.2. In both soils, the ΔG^0 values for K-Ca exchange were negative indicating an overall selectivity of K^+ over Ca^{2+}. The preference for K^+ is probably related to the vermiculitic clay minerals present in the soils which prefer K^+ over Ca^{2+} (Jardine and Sparks, 1984a). The two soils exhibited similar selectivity which would be expected due to their similar clay mineralogies and organic matter contents.

Table 3.2. Comparison of equilibrium and kinetic approaches for determining thermodynamics of potassium exchange in soils.

Temperature	Equilibrium Approach				Kinetics Approach Methods							
					Miscible Displacement				Batch			
K	K_{eq}	ΔG^o	ΔH^o	ΔS^o	K_{eq}	ΔG^o	ΔH^o	ΔS^o	K_{eq}	ΔG^o	ΔH^o	ΔS^o
		-kJ mol^{-1}		J $mol^{-1}K^{-1}$		-kJ mol^{-1}		J $mol^{-1}K^{-1}$		-kJ mol^{-1}		J $mol^{-1}K^{-1}$
					Chester loam							
283	9.59	-5.32		-38.72	1.55	-1.03		-9.14	2.93	-2.53		-16.80
298	6.77	-4.74		-38.69	1.38	-0.80		-9.58	2.62	-2.39		-16.52
308	4.24	-3.70		-40.83	1.33	-0.74		-9.44	2.27	-2.10		-16.83
			-16.28				-4.45				-7.72	
					Downer sandy loam							
283	9.81	-5.37		-50.72	2.16	-1.81		-12.09	2.49	-2.15		-36.73
298	6.43	-4.61		-50.72	1.97	-1.68		-12.22	2.76	-2.52		-33.64
308	5.27	-4.26		-50.21	1.82	-1.53		-12.15	1.48	-1.00		-37.45
			-19.73				-5.05				-15.44	

Table 3.2. (Continued)

Temperature	Kinetics Approach			
°K	Methods			
	Vortex Mixed Batch			
	K_{eq}	ΔG^o	ΔH^o	ΔS^o
		----kJ mol^{-1}---		J $mol^{-1} K^{-1}$
	Chester loam			
283	5.45	-3.99		-16.19
298	4.66	-3.82		-15.96
308	4.01	-3.57		-16.24
			-9.14	
	Downer sandy loam			
283	11.55	-5.76		-41.81
298	7.53	-5.00		-42.24
308	6.19	-4.67		-42.00
			-18.53	

In both soils, K^+ preference decreased with increasing temperature for all methods. The observation that ΔG^0 becomes less negative with an increase in temperature has been observed by several researchers (Udo, 1978; Sparks and Jardine, 1981; Bansal, 1982). Two hypotheses for this seem reasonable. Firstly, the Ca^{2+} ion is more hydrated than the K^+ ion. At higher temperatures, the Ca^{2+} ion hydration shell is reduced and it can approach the surface more closely than at lower temperatures, which could result in a slightly reduced preference for the K^+ ion. Secondly, the overall reaction for K-Ca exchange in the soils we studied using both the kinetic and equilibrium approaches was exothermic as evidenced by negative ΔH^0 values (Table 3.2). Increasing the temperature would therefore result in lowering the preference for the K^+ ion.

The negative ΔH^0 values for K-Ca exchange have been observed by others (Goulding and Talibudeen, 1979, 1980; Sparks and Jardine, 1981) which indicates a stronger binding strength for K^+ than for Ca^{2+}. The ΔS^0 values were all negative for both soils, and with all methods (Table 3.2) and indicated an ordered system.

The data in Table 3.2 show that thermodynamic parameters calculated using the equilibrium and kinetics approaches compare very well in trend, and give the same inferences of ion behavior for the two soils studied. However, except for the vigorously mixed vortex batch technique, the magnitude of the thermodynamic parameters for the two approaches compared poorly. The ΔG^0 values for both soils at all three temperatures calculated using the vigorously mixed vortex batch technique compared well to those calculated using the equilibrium approach. However, with both the batch and the miscible displacement methods, the comparison was poor. The ΔH^0 values using the vortex mixed kinetic technique and the equilibrium approach compared well, particularly in the Downer soil. The discrepancies are not surprising since Laudelout et al. (1968) even noticed differences in the magnitude of ΔH^0 measured by an equilibrium approach and those measured directly by calorimetry.

The large differences in the magnitude of the thermodynamic parameters using the equilibrium and the miscible displacement and batch approaches may be due to assumptions inherent in both theories. However, the more probable explanation for the discrepancies is the pronounced diffusion that exists particularly in the miscible displacement and batch kinetic methods (Table 3.1).

Helfferich (1965, 1983) noted that if the rate-controlling process is diffusion and not the reaction in Eq. [15], then no information about equilibrium can be derived from kinetic analyses. When diffusion is significantly reduced, as with the vigorously mixed vortex batch technique, it appears that a kinetic approach can be successfully used to gather thermodynamic information about a soil system (Tables 3.1-3.2). Under the extreme conditions of rapid mass transfer as found with the vortex batch system, the influence of diffusion is significantly reduced and the rate coefficients obtained approximate that of the reaction step.

These findings do not diminish the usefulness of the batch and the miscible displacement techniques for kinetic analyses. In fact, they would be preferred over the vigorously mixed vortex batch technique for such studies, since vigorous mixing may cause abrasion of soil particles, resulting in increased surface area and causing greater adsorption of some ions such as K^+. However, for equilibrium analyses, these two procedures would not be suitable if one wanted to quantitatively determine ΔG^0, ΔH^0, and ΔS^0 values due to diffusion effects.

3.5 Conclusions

Thermodynamics of K-Ca exchange were compared using equilibrium and kinetics approaches for two Delaware soils. The classical Argersinger theory was employed for the equilibrium approach while a kinetics approach was studied using miscible displacement, batch, and vigorously mixed batch techniques. These three techniques were used to determine how diffusion affects the comparison between thermodynamic parameters using kinetics and equilibrium approaches. Rate coefficients and energies of activation were profoundly affected by the type of kinetics technique employed and their magnitude was in the order: vortex mixed batch>batch>miscible displacement. Energies of activation for adsorption (E_{aa}) in the two soils ranged from 7.42 kJ mol^{-1} using the miscible displacement technique to 32.96 kJ mol^{-1} with the vortex mixed batch while energies of activation for desorption (E_{ad}) ranged from 11.87 to 42.1 kJ mol^{-1} for the two methods, respectively. The magnitude of the E_{aa} and E_{ad} values indicated pronounced diffusion effects in the miscible displacement and batch techniques which were greatly reduced with the vortex mixed batch method. Thermodynamic parameters (ΔG^0, ΔH^0, and ΔS^0) calculated using the equilibrium and kinetic approaches compared very well in trend, and gave the same inferences of ion behavior for the two soils studied. However, except for the vortex mixed batch technique, the magnitude of the thermodynamic parameters for the two approaches compared poorly. For example, the ΔG^0 values calculated using the equilibrium approach averaged 4.67 kJ mol^{-1} for the two soils while they averaged 4.92 kJ mol^{-1} with the vortex mixed batch, 2.12 kJ mol^{-1} with the batch and 2.12 kJ mol^{-1} with the miscible displacement techniques. The degree of comparison between the two approaches was directly related to the extent of diffusion controlled exchange. When the influence of diffusion was significantly reduced, as with the vigorously mixed batch technique, these data would indicate that a kinetic approach can be successfully used to gather thermodynamic information about a soil colloidal system.

CHAPTER 4

KINETICS OF ION EXCHANGE ON CLAY MINERALS AND SOIL: EVALUATION OF METHODS

4.1 Literature Review

One of the most important aspects of any kinetics study is the method one employs to measure rate parameters. Soil chemists have primarily used batch and miscible displacement or flow techniques to investigate kinetics of ion exchange on soils and clay minerals (Sparks, 1985, 1986).

Historic kinetics studies with soils and clay minerals have employed batch techniques. These involve placing an exchanger and the adsorbate in a vessel such as a centrifuge tube. The suspension is then agitated using a reciprocating shaker or it is stirred. Then, the suspension is usually centrifuged or filtered to separate a clear supernatant solution for subsequent analysis. The use of centrifugation to separate the phases in batch techniques to measure the rate of ionic reactions on clay minerals and soils has a major disadvantage. Unless filtration is used (Zasoski and Burua, 1978), centrifugation may require about five min to separate the solid from the liquid phases. Many exchange reactions are complete by this time or less (Harter and Lehmann, 1983; Jardine and Sparks, 1984a; Sparks and Huang, 1985; Sparks, 1985, 1986).

Flow or miscible displacement techniques have been used to a lesser extent to investigate the kinetics of reactions in clay minerals and soils (Sivasubramaniam and Talibudeen, 1972; Sparks et al., 1980; Sparks and Jardine, 1981; Jardine and Sparks, 1984a; Jardine et al., 1985; Sparks, 1985, 1986). However, flow techniques may be preferable to batch studies to study sorption-desorption phenomena on colloids, particularly if one wishes to relate kinetic studies to solute transport under field conditions (Murali and Aylmore, 1981; 1983a,b). Sparks et al., (1980) developed a miscible displacement technique to study kinetics of K adsorption by soils. Later, Jardine and Sparks (1984a) modified the technique so that aliquots of leachate could be taken at 2 min increments.

A comparison of the methods used to obtain kinetic data is an important subject in soil chemistry research. Few reports have appeared in the soil chemistry literature on the effect of kinetics methodologies on kinetic parameters such as rate coefficients and energies of activation. The objective of this phase of my research was to conduct these studies by investigating the kinetics of K-Ca exchange on a sandy Delaware soil and on two standard clay minerals at three temperatures.

4.2 Materials and Methods

The Ap horizon of a Chester loam (fine-loamy, mixed, mesic Typic Hapludults), a Georgia well crystallized kaolinite, and a Llano vermiculite were used in this study. The clay minerals were obtained from the University of Missouri Source Clays Depository and were fractionated according to standard procedures (Jackson, 1979). Basic chemical, mineralogical, and physical properties of the Chester soil were determined using methods outlined by Jardine and Sparks (1984a). The soil contained 15.0, 57.0, and 28.0% sand, silt, and clay, respectively; had an organic matter content of 3.3%, had a CEC of 6.80 cmol kg^{-1}, and the <2 μm clay fraction contained mainly kaolinite and chloritized vermiculite with smaller quantities of quartz, mica, and gibbsite. This soil was chosen because it had mineralogical properties intermediate to kaolinite and vermiculite.

The effect of methodology on various kinetic parameters was investigated using five different techniques which are described below. Before the kinetic analyses, the Chester soil and the clay minerals were Ca-saturated with 1 M $CaCl_2$ and excess salt was removed with deionized water until a negative test for Cl^- was obtained using $AgNO_3$.

4.2A. Miscible Displacement Technique

This method is a slight modification of the one first proposed by Sparks et al. (1980). The miscible displacement technique has been successfully employed in a number of kinetic studies by Sparks and his coworkers with K (Sparks and Jardine, 1981; Sparks and Rechcigl, 1982; Jardine and Sparks, 1984a; Sparks and Jardine, 1984; Carski and Sparks, 1985) and by other researchers (Hodges, 1984; Jardine et al., 1985) with other ions. In this experiment, triplicate 2 g dry samples of Ca-saturated soil, kaolinite or vermiculite were uniformly spread onto a rebuilt Nuclepore filter holder containing a 0.45 μm filter membrane and it was securely cupped. The filter was then capped securely and attached to a fraction collector and a peristaltic pump. The experiments were performed at 283, 298, and 313 K. The Ca-saturated samples were leached with a 0.001 M KCl solution at a constant flow rate of 1.0 mL min^{-1}. Two-mL aliquots were collected at 2 min increments until an apparent equilibrium was attained or until the concentration of K^+ in the leachate was equal to that concentration in the original solution.

4.2B. Batch and Vortex Batch Techniques

The batch method consisted of placing 2 g of Ca-saturated soil or clay samples into 50 mL polyethylene tubes. Then, 15 mL of a 0.001 M KCl solution were rapidly introduced into the tube and timing was begun. The mixture was then shaken on a reciprocating shaker at

180 rpm for time intervals of 5 sec for the first 1 min of the reaction and then for two min intervals thereafter The mixture was shaken by placing the tube at a 45° angle to the moving plane of the shaker to ensure even mixing and prevent the soil from adhering to the surface of the tube. After shaking, the solution was immediately separated from the suspension by pouring the mixture into a glass syringe which was attached to a nuclepore filter holder containing 0.45 μm filter paper. The leachate was collected in a plastic test tube and the maximum time required for the filtration step was less than 5 sec.

The vortex batch technique was accomplished using the same procedure as for the batch technique except the soil and solution were vigorously mixed by vortexing. Vortex mixing was done at 5 sec intervals for the first 1 min and then 10 sec intervals thereafter until equilibrium was reached. Both batch and vortex batch studies were conducted at 283, 298, and 313 K. The leachates from the miscible displacement, batch, and vortex batch studies were analyzed for K using atomic absorption spectrophotometry.

4.2C. Static and Stirred Techniques Using a K-Specific Ion Electrode

Static and stirred studies were accomplished using an Orion K-specific ion electrode (Model 93-19) and an Orion Model 901 digital ionalyzer meter. In the static system triplicate 2 g Ca-saturated soil or clay samples were carefully weighed. Then, 30 mL plastic cups were filled with 20 mL of a 0.001 M KCl solution. The electrode was then introduced into the cup and an initial reading of the solution was taken. The soil or clay samples were then rapidly added to the cups and a timer was immediately started. The change in K^+ concentrations was recorded at 5, 10, 20 and 30 sec for the first 30 sec and then for 10 sec intervals thereafter. The stirred technique was accomplished similarly to the static system except all of the readings were taken while stirring the solution and the soil or clay sample. Readings in both methods were taken until equilibrium in K adsorption was reached. These studies were conducted at temperatures given earlier.

4.2D. Calculation of Rate Coefficients and Energies of Activation

The kinetics data for all five techniques conformed well to first-order expressions as described by Sparks (1985, 1986) and adsorption rate coefficients (Table 4.1) were calculated from the equations (Sparks, 1985, 1986) as shown below. Energies of activation for K adsorption (E_{aa}) (Table 4.2) were calculated using the Arrhenius equation (Sparks, 1985, 1986) for each of the kinetics methods (Table 4.1).

If the rate of adsorption of K^+ onto a colloidal surface follows first-order kinetics, then

$$d(K_t/K_\infty) = k_a\,(K_\infty - K_t)dt \qquad [4.1]$$

Table 4.1. Effect of kinetics method on adsorption rate coefficients (k_a) in systems studied.

	Kinetics Method				
Temperature	Static	Miscible Displacement	Batch	Stirred	Vortex Batch
K		k_a (min^{-1})			
283	0.030	0.033	1.304	1.321	1.444
298	0.034	0.037	2.383	2.838	3.482
313	0.037	0.045	3.764	3.784	4.981
		Chester loam			
283	0.025	0.031	0.179	0.192	0.867
298	0.027	0.036	0.225	0.250	2.331
313	0.031	0.042	0.260	0.293	3.240
		Vermiculite			
283	0.021	0.012	0.058	0.049	0.421
298	0.024	0.015	0.083	0.056	0.945
313	0.027	0.018	0.099	0.069	1.647

Table 4.2. Effect of kinetics method on energies of activation for adsorption (E_{aa}) in systems studied.

System	Static	Miscible Displacement	Batch	Stirred	Vortex Batch
	Kinetics Methods				
			--E_{aa} (kJ mol^{-1})--		
Kaolinite	5.05	7.57	26.06	26.01	30.59
Chester loam	5.25	7.46	9.19	19.92	32.58
Vermiculite	6.16	9.96	13.19	13.35	33.55

where K_t is the amount of K^+ on the colloid at time t, K_∞ is the amount of K^+ on the colloid at equilibrium, and k_a is the adsorption rate coefficient. Separating variables, integrating, and simplifying results in

$$\log (1-K_t/K_\infty) = -k_a t \qquad [4.2]$$

4.3 Results and Discussion

4.3A. Effect of Kinetics Methods on Adsorption Rate Coefficients

The K^+ adsorption rate coefficients (k_a) for kaolinite were higher than those for the Chester soil and vermiculite, irrespective of the kinetics method employed or the temperature studied (Table 4.1). However, the k_a values for kaolinite and the Chester soil were similar using the static and miscible displacement techniques. The higher k_a values observed for kaolinite would be expected since a relatively pure kaolin, as this one was, would exhibit only easily accessible planar surface sites for K^+ exchange (Goulding and Talibudeen, 1979; Jardine and Sparks, 1984a,b). The k_a values for the Chester soil (Table 4.1) were intermediate between those of kaolinite and vermiculite. The mineralogy of this soil was predominantly kaolinite but there was some chloritized vermiculite and mica. The Chester soil would therefore exhibit K^+ adsorption characteristics between kaolinite and vermiculite. Vermiculite showed the lowest k_a values of the systems we studied. This is primarily due to vermiculite having planar external, edge, and interlayer sites for K^+

adsorption (Jardine and Sparks, 1984a,b). Once some K^+ is adsorbed into the interlayers of vermiculite, a partial collapse occurs making further K^+ adsorption slow and diffusion-controlled (Sparks and Jardine, 1981; Sparks, 1985, 1986).

The magnitude of the k_a values for the three systems studied was clearly affected by the kinetics method employed (Table 4.1). Although not shown, the type of method also greatly affected the time required for equilibrium in K^+ adsorption to be reached in the three systems. For example, with kaolinite 60 min was required in the static system while only 0.58 min was required with the vortex batch method. Similar trends were also seen with the Chester soil and vermiculite. The time required for equilibrium to be reached in the three systems followed the order:
static>miscible displacement>batch>stirred>vortex batch.

Only for kaolinite did the k_a values of both the stirred and batch techniques approximate in magnitude, those of the vortex batch method. The magnitude of the k_a values for kaolinite reveal a very important aspect of agitation on adsorption of ions. The kaolinite we studied was relatively pure and only external adsorption surface sites were available for exchange. Thus, intraparticle diffusion processes were not operable and only film diffusion and reaction controlled phenomena could be rate-limiting. When the kaolinite mixture was perturbed, as in the batch or stirred system, the film radius around the kaolinite particles was probably significantly reduced and the mass transfer across the hydrodynamic film was rapid. Thus, the influence of film diffusion was greatly diminished, and the rate of K adsorption on kaolinite was primarily reaction-controlled. Therefore, the k_a values for the stirred and batch techniques approximated those of the vortex batch method (Table 4.1). In Chapter 3, it was shown that when a system is vigorously mixed, as with the vortex method, the effect of diffusion processes is greatly reduced so that chemical exchange is the primary rate-controlling process.

Unlike kaolinite, in the Chester soil and in vermiculite, both of which contain appreciable interlayer sites where K^+ adsorption could occur, the k_a values for the batch and stirred methods were not similar to those of the vortex batch. These data indicate that in systems where intraparticle diffusion could occur, the batch technique is not successful in eliminating the effect of diffusion as some researchers have previously thought.

The k_a values (Table 4.1) with the static method compared very well to those using miscible displacement. These observations lend more credence to the latter technique since they indicate that dilution is not a significant problem with the method we used. One of the primary advantages in using a miscible displacement technique, run at a very low flow rate is simulation of field conditions, particularly if one wishes to model solute transport phenomena in soils (Murali and Aylmore, 1981, 1983a,b; Sparks, 1985, 1986). The k_a

values using both static and miscible displacement techniques were significantly lower than those obtained using batch and stirred methods. This is because the influence of diffusion is predominant in the static and miscible displacement systems as will become more evident as we discuss the E_{aa} values for the five techniques. In the batch and stirred systems, the influence of diffusion is reduced due to perturbation.

4.3B. Effect of Kinetics Methods on Energy of Activation Values for K Adsorption (E_{aa})

The energy of activation (E_{aa}) measures the magnitude of the forces to be overcome during the process of ionic exchange (Laidler, 1965; Denbigh, 1966). Energies of activation vary inversely with the rate of exchange. Low E_a values indicate diffusion-controlled processes whereas high values indicate chemical exchange processes (Glasstone *et al*., 1941; Mortland and Ellis, 1959; Kuo and Lotse, 1974).

The E_{aa} values in our study ranged from 5.05 to 33.55 kJ mol^{-1} and their magnitude was strongly dependent on the kinetics technique employed (Table 4.2). The E_{aa} values were higher for the miscible displacement than for the static system. Except for the Chester loam, the E_{aa} values using the batch technique compared very well to the stirred method (Table 4.2) which indicates that the shaking involved with the batch technique has the same effects as stirring on reducing the influence of diffusion. For each system, the E_{aa} values were greater for the batch and stirred methods than for the static and miscible displacement techniques indicating that the influence of diffusion is decreased (Sparks, 1985, 1986).

Kaolinite, with only external surface sites, exhibited equal E_{aa} values for the stirred and batch techniques (26 kJ mol^{-1}) which was similar to the E_{aa} value using the vortex batch method (30.59 kJ mol^{-1}). The similarities in the E_{aa} values for kaolinite using batch, stirred, and vortex methods were also observed for the k_a values (Table 4.1) and indicate again that in systems where only external planar sites are present, shaking or stirring greatly reduced the effect of diffusion on the rate of adsorption.

In contrast, in the Chester soil and in vermiculite, where non-external sites for K^+ adsorption also exist, the E_{aa} values for the batch and stirred techniques indicated significant diffusion-controlled exchange (Table 4.2). They were not similar to the E_{aa} values using the vortex batch method. Thus, in systems like these, if one wants to greatly reduce the influence of diffusion, a batch technique would not be suitable.

4.3C. Critical Evaluation of Kinetic Methodologies

A number of kinetic methodologies have been investigated in this research to determine how they affect rate coefficients, energies of activation, and time required to reach equilibrium. Each of the techniques has advantages and disadvantages.

The rate of K^+ adsorption was rapid on kaolinite with equilibrium being reached in 60, 26, 5.6, 0.83 and 0.58 min for the static, miscible displacement, batch, stirred, and vortex batch methods, respectively. It is obvious that if one employs the typical batch technique whereby the soil and solution is shaken or stirred and then centrifuged, one will never observe many exchange reactions that are complete by 5 min or less (Harter and Lehmann, 1983; Jardine and Sparks, 1984; Sparks and Huang, 1985). Consequently, using a typical batch technique may be inappropriate if one is studying the kinetics of reactions on organic matter, kaolinite, montmorillonite, and other layer silicates that have readily accessible sites for exchange. However, if one uses the batch technique of Zasoski and Burau (1978), which is a filtration technique, or batch techniques similar to those used in this study, one can observe rapid exchange reactions.

The amount of shaking or stirring in a batch technique is obviously important. Only with kaolinite, was the influence of diffusion significantly reduced by using the batch technique (Tables 4.1-4.2). Thus, it would appear that unless extreme perturbation occurs, as in the vortex batch method, one cannot eliminate the influence of intraparticle diffusion processes which so often are rate-controlling in ion exchange processes (Helfferich, 1979).

The question then becomes how much shaking or stirring should occur with a batch technique. If mixing is inadequate, the rate of reaction will be diffusion limited. However, vigorous mixing, which many investigators have used and which would be similar to the vortex batch method, can cause abrasion of the exchanger particles leading to high rates of reaction and alterations in the surface chemistry of the particles (Barrow and Shaw, 1979). Barrow and Shaw (1979) studied the rate of phosphate adsorption by soil and found that under prolonged agitation, breakdown of soil particles occurred, increasing surface area, and causing greater phosphate adsorption. The abrasion of colloidal particles could be a serious problem when studying most ionic reactions, but particularly with K^+ since release could occur from K-bearing minerals.

Miscible displacement or flow techniques are not a panacea for kinetics analyses of ion exchange processes. However, they have a number of benefits. Using the miscible displacement technique in this study, one can measure ionic reactions at two min increments. As noted earlier, many exchange processes are complete in 5 min or less. Additionally, a miscible displacement or flow technique better simulates solute transport in soils.

The amount of solution in contact with colloidal particles is also an important attribute of a flow or miscible displacement technique. Supplied with a solution of the same concentration, soil particles with solution flowing past them will be exposed to a greater mass of ions (concentration x flow rate x time) than the soil particles in a static system (concentration x solution volume) by the time equilibrium is established. More importantly, with solution flowing through the soil system, the solution not only brings in more ions, but also removes the desorbed ions of other species that were present originally at potential sorption sites (Akratanakul et al., 1983). This is particularly important in studying K^+ reactions since small amounts of K^+ in the equilibrium solution will prevent further release of adsorbed K which, consequently, results in marked hysteresis (Martin and Sparks, 1983). With the miscible displacement technique employed in this study, one can obtain almost complete reversibility in K^+ exchange because desorbed K^+ ions are being constantly removed (Jardine and Sparks, 1984a). Additionally, the number of introduced ions that can be adsorbed also depends on how easily they can be exchanged with other ions of different kinds already adsorbed by the soil surfaces, thus affecting the magnitude of the heat of adsorption.

With a closed system, exchange cannot be complete without increasing the concentration of the replaced ions in the bulk solution. This would, in turn, drive these ions back into the adsorbed phase. However, in an open, flow system, the exchange can be complete, as the replaced ions are continuously carried out of the system while more of the introduced ions can take their place.

However, along with the advantages of a flow technique, one must also recognize some disadvantages. Dilution errors can exist with the original miscible displacement technique of Sparks et al. (1980) which could cause errors, particularly in systems which are known to adsorb very small quantities of ions such as with B sorption on sandy soils (Evans, 1983; Carski and Sparks, 1985). Fortunately, in these systems, the dilution problem can be eliminated by using a modified miscible displacement technique developed by Carski and Sparks (1985) or by using the technique outlined in this study in which dry soil is initially placed on the Nuclepore filter.

Other disadvantages of the miscible displacement and static techniques are the pronounced diffusion-controlled exchange, which presents problems if one is attempting to use kinetics to calculate thermodynamic parameters. In Chapter 3 of this study, it is shown that if diffusion is rate-limiting, one cannot use kinetics to determine thermodynamic parameters. However, even in the batch and stirred batch techniques (Tables 4.1-4.2), diffusion is rate-limiting, particularly in systems where non-external sites for adsorption are present. This would be the case in many soils.

4.4 Conclusions

The effect of kinetics methodology on adsorption rate coefficients (k_a) and energies of activation (E_{aa}) of ion adsorption were investigated using five different techniques. These techniques were: miscible displacement, batch, static, stirred, and vortex batch. Kinetics of K^+ adsorption were studied on Ca-saturated kaolinite, a Chester soil (fine-loamy, mixed mesic Typic Hapludults), and vermiculite. The k_a values were highest for kaolinite and lowest for vermiculite. The higher k_a values observed for kaolinite would be expected since a relatively pure kaolin would exhibit only easily accessible planar surface sites for K^+ exchange. The k_a values for the Chester soil were a reflection of the intermediate mineralogical properties of this soil between kaolinite and vermiculite. The type of kinetics technique greatly affected the time required for equilibrium to be attained in K^+ adsorption. From greatest to least time, the order was: static>miscible displacement>batch>stirred>vortex batch. Both static and miscible displacement techniques yielded the lowest k_a and E_{aa} values for all three colloids. This is primarily because these methods represent systems where the influence of diffusion on the rate of K^+ adsorption is at its maximum. Only for kaolinite did the k_a and E_{aa} values of both the stirred and batch techniques approximate, in magnitude, those of the vortex method. With the Chester soil and vermiculite, which contain appreciable interlayer sites, the stirred and batch techniques yielded k_a and E_{aa} values much lower than those of the vortex batch method. These results indicate that in colloids where more significant intraparticle diffusion occurs, the batch or stirring technique is not effective in eliminating the influence of diffusion.

CHAPTER 5

KINETICS OF ION EXCHANGE ON CLAY MINERALS AND SOIL: ELUCIDATION OF RATE-LIMITING STEPS

5.1 Literature Review

One of the most important aspects of any kinetics study is the elucidation of rate-limiting steps. This task is difficult in any system, but particularly with ion exchange studies on soils and clay minerals. The rate determining step in ion exchange is usually the interdiffusion of counter ions (Boyd et al., 1947; Helfferich, 1983). This was first recognized by G. Schulze as early as 1915 (Boyd et al., 1947). However, until recently, the importance of his work was overlooked. Much of our current knowledge about rate-limiting steps involving ion exchange comes from the elegant research of G. E. Boyd and coworkers (Boyd et al., 1947). They were the first to embark on a thorough analysis of ion exchange kinetics and to apply the concept of "film thickness" or the "Nernst film" which ions must diffuse across in ion exchange.

Ion exchange phenomena in soils and other heterogeneous systems involve mass transfer and chemical kinetics processes (Boyd et al., 1947; Helfferich, 1983). For actual chemical adsorption to occur, ions have to be transported to the active fixed sites of the soil particles. The film of water adhering to and surrounding the particle and the hydrated interlayer spaces in the particle are both zones of low concentration. These zones are constantly being depleted by adsorption of ions to the adsorption sites (Froment and Bischoff, 1979). The concentration of these interface zones has to be compensated for by the bulk concentration.

Most kinetic studies have only succeeded in general terms in differentiating between diffusion and chemical reaction controlled adsorption steps. A linear relation between concentration of ion adsorbed on an exchanger and the square root of time of adsorption or the parabolic law has been ascribed by numerous investigators to diffusion-controlled exchange (Boyd et al., 1947; Weber et al., 1963; Chute and Quirk, 1966; Salim and Cooksey, 1980; Jardine and Sparks, 1984a. Jardine and Sparks (1984a) found that adsorption of K at 283 and 298K conformed well to parabolic kinetics, suggesting that intraparticle diffusion was rate limiting.

The magnitude of activation energies (E_{aa}) has also been used to differentiate between reaction and diffusion-controlled processes. Low E_{aa} values indicate diffusion-controlled exchange since pure chemical exchange is characterized by high E_{aa} values (Laidler, 1965).

Salim and Cooksey (1980) found an E_{aa} value of 5.77 kJ mol^{-1} for Pb adsorption on sediment samples. Kuo and Lotse (1974) found adsorption of P on gibbsite and hematite was characterized by an E_{aa} value of 7.95 kJ mol^{-1}. These low E_{aa} values were attributed to diffusion-limited exchange. Similar results suggesting diffusion is rate limiting have been obtained for K exchange on soils and clay minerals by Sparks and coworkers (Sparks and Jardine, 1981; Jardine and Sparks, 1984).

Differentiating between chemical exchange and diffusion as rate limiting steps has been relatively easy since with most studies involving soils or clay minerals diffusion is rate limiting. Unfortunately, differentiating between film and intraparticle diffusion rate processes has been arduous and relatively uninvestigated. In many cases, ion adsorption is limited by both types of diffusion, particularly when the rate of ion transfer by both types is the same (Helfferich, 1962; Helfferich, 1983).

The objective of this study is to use combined observed rate coefficients under static, stirred, and vortex conditions to quantify film diffusion, intraparticle diffusion, and reaction rate resistances for K adsorption processes on a Delaware soil and on standard clay minerals. This information will be used to elucidate rate-limiting steps in these systems.

5.2 Theoretical Considerations

5.2A. Definition of Rate-Limiting Steps

Consider a one dimensional-horizontal adsorption process. The adsorption of ions from solution by soil particles occurs in a series rather than a parallel-reaction mode with three main consecutive steps. First, there is transport of ions by diffusion across the solution film adhering around the particles which is film diffusion. The second step, with the exception of adsorption which occurs on the planar and edge sites of the soil particles, is the diffusion of ions through hydrated interlayer spaces of the particles. This is referred to as intraparticle diffusion. The last step is the actual adsorption of a cation on the interior surfaces bounding the interlayer and capillary spaces of the particle. This is termed as the chemical reaction step. More detailed descriptions of these steps have been given by Vermeullen et al., (1984) and by Sparks (1985, 1986). Since these processes are sequential steps, the slower of the three is rate-controlling. In many instances, the process is controlled by both types of diffusion (Helfferich, 1962; Zogorski, 1976).

5.2B. Proposal of Combined Additive Resistances

First, let us consider a reactive species A in a solution, in contact with soil particles and its concentration at the interface where reaction is taking place is C_A. The rate of the reaction at the surface will therefore depend on the concentration at the interface which is itself directly dependent on the rate of the actual adsorption mechanism at the surface or interlayer sites. If we assume a first-order reaction, the rate is defined as,

$$r_A = k_r C_A \qquad [5.1]$$

where

r_A = rate of reaction of A at the soil colloid sites

k_r = rate of coefficient for the reaction

The depletion of C_A at the interface has to be compensated by diffusion from the bulk solution. The usual algebraic equation for this process is given in terms of an appropriate driving force (Frank-Kamenetskii, 1969; Froment and Bischoff, 1979) as,

$$j_A = k_{dif} (C_o - C_A) \qquad [5.2]$$

where

j_A = mass flux with respect to the fixed particle surfaces

k_{dif} = mass transfer coefficient

C_o = concentration of A in the bulk solution.

Under the steady state conditions, the rate of diffusion of A from the bulk solution to the interface is approximately equal to the rate of adsorption of A, and this can be used to eliminate the unmeasured interface concentration, C_A. Thus,

$$r_A = j_A = r \qquad [5.3]$$

where

r = rate of reaction of A under the steady state conditions.

Combining of Eqs. [5.1] and [5.2] gives,

$$C_A = \frac{k_{dif}\, C_o}{k_r + k_{dif}} \qquad [5.4]$$

and

$$r = \frac{k_{dif}\, k_r}{k_r + k_{dif}} C_o = k_o C_o \qquad [5.5]$$

where

$$k_o = \frac{k_{dif}\, k_r}{k_r + k_{dif}} \qquad [5.6]$$

This relation can assume a simple form. Instead of the reaction rate coefficient (k_r), mass transfer coefficient (k_{dif}) and experimentally observed rate coefficient (k_o), one can use the reciprocals of the coefficients such that:

$$1/k_o = 1/k_r + 1/k_{dif} \qquad [5.7]$$

One now has both kinetic and diffusional resistances which are additive. However, ion adsorption processes on soils or clay minerals occur in a series rather than in a parallel-reaction mode. As noted earlier, the diffusion steps include both film and intraparticle processes. One can therefore assign two resistances to the diffusion resistance,

$$1/k_{dif} = 1/k_I + 1/k_f \qquad [5.8]$$

where k_I is the intraparticle diffusion rate coefficient and k_f is the film diffusion rate coefficient. Equations [5.7] and [5.8] can be combined to give,

$$1/k_o = 1/k_r + 1/k_I + 1/k_f \qquad [5.9]$$

The greatest of these resistances (smallest of the rate coefficients) will be the rate-determining step under static adsorption conditions.

5.2C. Proposal of Combined Kinetic Techniques

The observed diffusion and reaction rate coefficients can be obtained from specific experiments. To quantify the rate coefficients on the right-hand side of Eq. [5.9], kinetic experiments could be conducted such that the global rate is preferably determined by the film diffusion, intraparticle diffusion or reaction steps. In the laboratory, these steps can be simulated separately by conducting experiments using static, stirred or vortex batch adsorption systems. Therefore, to these systems we accordingly assign additive resistance relations as follows:

Static system

$$1/k_{os} \cong 1/k_r + 1/k_I + 1/k_f \qquad [5.10]$$

Stirred system

$$1/k_{ot} \cong 1/k_r + 1/k_I \qquad [5.11]$$

Vortex batch system

$$1/k_{ov} \cong 1/k_r \qquad [5.12]$$

where k_{os}, k_{ot}, and k_{ov} are observed rate coefficients in the static, stirred, and vortex batch adsorption systems, respectively.

The rate-coefficients obtained experimentally from these three systems represent the full spectrum of the rate-limiting steps in ion adsorption processes. Algebraic combination of these observed rate coefficients from each of the systems can be used to quantify and isolate the rate controlling step in the static system. These suggestions are made based on the assumption that the static system has all of the three resistances. Such an assumption seems plausible based on the work in Chapter 3. Due to agitation in the stirred system, the influence of the film diffusion resistance which was prevalent in the static system is greatly reduced by uniform mixing and rapid mass transfer across the hydrodynamic film. Therefore, the stirred system is assigned only the reaction and intraparticle resistance relations. It is also assumed that using the vortex batch technique, mass transfer is maximized and is at its highest rate which limits the formation of a concentration gradient in the film or hydrated interlayer spaces of the particles. Thus, in the vortex batch system, it is assumed that the observed rate coefficient approximates that of the reaction step in the static system and only one resistance relation has been assigned to this system. This seems justified based on studies in Chapter 3.

Accordingly, the parameters for Eq. [5.10] can be calculated as follows:

$$1/k_f \cong 1/k_{os} - (1/k_r + 1/k_I) \qquad [5.13]$$

or

$$1/k_f \cong 1/k_{os} - 1/k_{ot} \qquad [5.14]$$

and

$$1/k_I \cong 1/k_{ot} - 1/k_r \qquad [5.15]$$

or

$$1/k_I \cong 1/k_{ot} - 1/k_{ov} \qquad [5.16]$$

As mentioned above $1/k_{os}$, $1/k_{ot}$ and $1/k_{ov}$ are parameters obtained from respective experiments and therefore $1/k_f$ and $1/k_I$ are the only unknowns to be calculated from Eqs. [5.14] and [5.16].

In summary, a model was developed which assumed that the adsorption of ions from solution by soil particles occurs in a series rather than a parallel-reaction mode. Thus, a mass transfer process and chemical reaction occur consecutively. Under the steady state approximation, the rate of mass transfer is approximately equal to the rate of the reaction, so that an instantaneous change in the concentration of C_A with time approaches zero. Under such conditions, only some of the processes or reaction that constitute the overall mechanism are at equilibrium. The overall reaction need not be at equilibrium.

5.3 Experimental Procedures

The Ap horizon of a Chester loam (fine-loamy, mixed mesic Typic Hapludults), a Georgia well-crystallized kaolinite, and a Llano vermiculite were used in this study. The clay minerals were obtained from the University of Missouri Source Clays Depository and were fractionated before analysis using standard techniques (Jackson, 1964). The CEC of the kaolinite and vermiculite as determined by Mg-Ca exchange, was 11.5 and 2070 (mmol (1/2 Mg^{2+}) kg^{-1}, respectively (Jardine and Sparks, 1984a,b). Basic physicochemical and mineralogical properties of the Chester soil were reported earlier (Chapter 2 of this study). Prior to the kinetic studies, the clay minerals and soil were Ca-saturated using procedures given previously (Sparks and Jardine, 1981).

Rate-limiting steps for K^+ adsorption on the clay minerals and Chester soil under static conditions were quantified from observed rate coefficients (Eqs. 5.13-5.16) using the static, stirred, and vortex techniques given earlier. The lowest rate coefficient (greater resistance value) indicates the rate-limiting step. The rate coefficients were determined at 283, 298, and 313 K and energies of activation for K^+ adsorption (E_{aa}) were determined using the Arrhenius equation.

The quantitative relationship between the rate of mixing or agitation and the rate coefficients was also investigated. Additionally, the effect of mixing on the specific surface areas of the adsorbents was studied. The specific surface area of stirred and vortex mixed samples at various mixing rates was determined using the ethylene glycol monoethyl ether procedure given by Mortland and Kemper (1965). The mixing rates of the stirring and vortex mixer devices were measured using a stroboscopic light (Strobatac Type 1531).

5.4 Results and Discussion

5.4A. Effect of Mixing Rates on Specific Surface Area and Rate Coefficients

The effect of mixing rates in the stirred and vortex batch systems on specific surface area and rate coefficients is shown in Table 5.1 for the Chester soil. Under stirred conditions, surface area remained constant in the 285-478 rpm range and increased abruptly thereafter. Under stirred conditions, k_a values increased between the 0-370 rpm range, leveled off between 370-478 rpm and then showed an abrupt increase after the mixing rate reached 640 rpm.

Since the specific surface area of the Chester loam remained constant up to 478 rpm, the increase in the k_a values observed from 0 to 370 rpm is probably due to increased reduction of film diffusion as the rate-limiting step. Intraparticle diffusion is therefore likely the rate-limiting step after one attains a mixing rate of 370 rpm since the k_a values remain constant from 370 to 478 rpm. The increase in the k_a values observed after > 640 rpm has nothing to do with the rate-limiting step, but rather with increased surface area of the soil (Table 5.1). The latter could be ascribed to the abrasion of the colloidal particles caused by the magnetic stirring rod at the high stirring rates. The leveling off of the k_a values in the 370-478 rpm range influenced our choice of a mixing rate of 435 rpm under stirred conditions (Chapter 4).

Even though mixing rates were several orders of magnitude higher with vortex mixing than with stirring (Table 5.1), very little difference was observed in the specific surface area of the soil using the two methods. However, the k_a values obtained using vortex mixing were considerably higher than those obtained under stirred conditions. The lowest mixing rate one could obtain with the vortex mixer used in this study was 2240 rpm. Both the surface area and the k_a values remained constant at the 2240 to 2318 rpm mixing range. Because of the latter observation, it was assumed that at this mixing range, intraparticle diffusion which was rate-limiting at 435 rpm under stirred conditions, had ceased to be rate-limiting and the k_a values obtained at the 2240-2318 rpm mixing rates approximated those of the reaction rate step.

This latter assumption is supported in the earlier work (Chapter 3). It was found that only when a vortex method was used, could one obtain thermodynamic parameters using a kinetics approach that compared with those parameters calculated according to an equilibrium approach. With batch and miscible displacement techniques, the thermodynamic parameters calculated using a kinetic approach did not compare to an equilibrium approach. This was attributed to the influence of diffusion in both the batch and miscible displacement techniques. With the vortex batch method,

Table 5.1. Effects of degree of agitation on specific surface area and rate of K^+ adsorption on Chester Loam.

Mixing Rates	Specific Surface Area	Rate Coefficient
rpm	m^2g^{-1}	$k_a(min^{-1})$
	Stirred	
0	53.54	0.027
285	53.66	0.048
330	53.65	0.081
370	53.66	0.251
435	53.66	0.250
478	53.68	0.251
640	55.44	0.315
870	61.11	0.341
	Vortex Batch	
2240	53.69	2.330
2290	53.78	2.330
2318	53.79	2.329
2420	55.43	3.501
2490	55.59	3.512
2625	56.88	3.610
2770	56.89	3.611

diffusion effects were dramatically reduced and the thermodynamic parameters compared well using the kinetics and equilibrium approaches.

5.4B. Rate-Limiting Steps for Kaolinite

The data in Table 5.2 suggest that the rate controlling process for K^+ adsorption on kaolinite, under static conditions, is film diffusion. The rate coefficients for film diffusion (k_f) for the three temperatures ranged from 0.031 - 0.037 min^{-1} while intraparticle diffusion rate coefficients (k_I) were much higher ranging from 15.06 - 15.74 min^{-1}. The magnitude of the k_I values indicates that intraparticle diffusion hardly exists, and does not have an important bearing on the rate of K^+ adsorption.

These results would be expected since the kaolinite used in this study was quite "pure" as evidenced by the low CEC (11.5 mmol kg^{-1}). The K^+ adsorption data for kaolinite, the Chester loam, and vermiculite were applied to the parabolic diffusion law equation which relates the quantity of K^+ adsorbed to $(time)^{1/2}$ and measurements of the correlation coefficient (r) and standard error of the estimate (SE) were calculated (Table 5.3). This equation has been used by a number of researchers to investigate the dynamics of K^+ reactions in clay minerals and soils (Barshad, 1954; Mortland and Ellis, 1959; Chute and Quirk, 1966; Sparks et al., 1980; Feigenbaum et al., 1981; Sparks and Jardine, 1984; Havlin and Westfall, 1985). Conformity of

Table 5.2. Rate coefficients for film diffusion, intraparticle diffusion, and chemical reaction rate processes for K adsorption under static conditions.

Adsorbent	Temperature	Rate Coefficients		
		k_f	k_I	k_r
	K	min^{-1}		
Kaolinite	283	0.031	15.060	1.444
	298	0.034	15.361	3.482
	313	0.037	15.739	4.981
Chester Loam	283	0.029	0.247	0.837
	298	0.030	0.280	2.331
	313	0.035	0.322	3.240
Vermiculite	283	0.037	0.055	0.421
	298	0.042	0.060	0.945
	313	0.044	0.072	1.647

Table 5.3. Correlation coefficient (r) and standard error of estimate (SE) of colloids studied using the parabolic diffusion equation.

	r	SE
Kaolinite	0.9603	4.017
Chester loam	0.9791	2.872
Vermiculite	0.9909	1.249

kinetics data to the parabolic diffusion equation indicates that intraparticle diffusion may be rate-limiting (Boyd et al., 1947; Mortland and Ellis, 1959; Jardine and Sparks, 1984; Sparks and Jardine, 1984).

The parabolic diffusion law did not describe K^+ adsorption on kaolinite well as evidenced by lower r values and higher SE values than was observed for the Chester loam and particularly for vermiculite. This poor conformity further indicates that the rate-limiting process for K^+ adsorption on kaolinite is not intraparticle diffusion. This is precisely the conclusion derived from the data in Table 5.2.

Relatively pure kaolinite should have only external planar surface sites exposed for K^+ exchange, and thus only film diffusion-controlled exchange should occur. Several investigators have previously shown that kinetics data do not conform well to the parabolic diffusion law (Chute and Quirk, 1967; Sparks et al., 1980; Jardine and Sparks, 1984a; Sparks and Jardine, 1984) which indicates that intraparticle diffusion is not rate-limiting (Boyd et al., 1947).

However, the insignificance of intraparticle diffusion on kaolinite may not apply to all kaolins since many of them contain impurities such as smectites and micas. Talibudeen and Goulding (1983) used differential heats of K-Ca exchange to study charge heterogeneity in kaolins. The heat values, coupled with entropies of exchange values, suggested that 0.1-10% vermiculite, mica and smectite clay minerals were present--presumably interstratified with kaolinite layers. Thus, depending on the source, the k_I values for kaolinite may not always be as high as was obtained in this study.

The energies of activation for K^+ adsorption (E_{aa}) on kaolinite for the reaction, film diffusion, and intraparticle diffusion steps were estimated from the k_r, k_f, and k_I values, respectively. The E_{aa} values for film and intraparticle diffusion were very low, 4.31 and 1.07 kJ mol^{-1}, respectively, while the E_{aa} for the reaction step was about 31 kJ mol^{-1}. The low E_{aa} values for film and intraparticle diffusion are characteristic of those values quoted for diffusion processes (Mortland and Ellis, 1959; Kuo and Lotse, 1974; Jardine and Sparks, 1984a). Since the chemical reaction process is more sensitive to temperature changes than diffusional processes, one would expect relatively higher E_{aa} values for the former process (Table 5.4).

5.4C. Rate-limiting Steps for Chester Loam

Similarly to kaolinite, the rate of K^+ adsorption under static conditions for the Chester loam was also film diffusion limited (Table 5.2). This is evidenced by significant differences between k_f and k_I values (Table 5.2). The estimated k_I values were on the average, 8.7 times higher than the k_f values, indicating that film diffusion was the rate-determining step. The mineralogical composition of the <2 μm

Table 5.4. Energies of activation of rate-limiting steps for K^+ adsorption under static conditions.

System	Rate-limiting steps		
	Film diffusion	Intraparticle diffusion	Reaction
	kJ mol^{-1}		
Kaolinite	4.31	1.07	30.51
Chester loam	4.57	6.50	32.58
Vermiculite	4.25	6.51	33.55

clay fraction of the Chester soil was predominantly kaolinite with smaller quantities of quartz, chlorotized vermiculite, mica and gibbsite so it is not surprising that the rate-limiting step for the Chester soil is film diffusion. As with kaolinite, the parabolic diffusion law did not describe K^+ adsorption well indicating intraparticle diffusion was not rate limiting (Table 5.3).

The E_{aa} values of the two diffusional steps for the Chester loam were low but slightly higher than those for kaolinite (Table 5.4). The E_{aa} values for the reaction step for Chester loam were about 33 kJ mol^{-1}. This was five times as high as the E_{aa} value for intraparticle diffusion and seven times that of film diffusion.

5.4D. Rate-Limiting Steps for Vermiculite

There were no significant differences between the k_I and k_f values for K^+ adsorption on vermiculite (Table 5.2). This suggests that both film diffusion and intraparticle diffusion were rate limiting steps. It has been noted earlier that in many cases ion adsorption is limited by both film and intraparticle diffusion particularly when the rate of ion transfer by both types is the same (Boyd _et al_., 1947; Helfferich, 1962).

The parabolic diffusion law equation described the kinetics of K adsorption on vermiculite well indicating that intraparticle diffusion may have been the predominant rate-limiting step. This equation has previously been found by some researchers to describe the kinetics of K exchange on vermiculite (Chute and Quirk, 1966; Jardine and Sparks, 1984a; Sparks and Jardine, 1984). However, Mortland and Ellis (1959) using a flow technique to investigate the K release kinetics from vermiculite, found that K release increased as flow rate increased. Thus, the authors concluded that film diffusion was rate-limiting.

As with kaolinite and Chester loam, the E_{aa} value for the reaction step in the vermiculite system was several orders of magnitude higher than those for film and intraparticle diffusion (Table 5.4). As seen for the Chester loam, the E_{aa} values of the intraparticle diffusion step were slightly higher than those for film diffusion. This suggests that greater forces must be overcome for K adsorption to occur in interlayers rather than on particle surfaces (Jardine and Sparks, 1984a).

5.4 Conclusions

Kinetics of K^+ adsorption were investigated on kaolinite, a Chester loam soil and vermiculite using static, stirred, and vortex batch techniques. The objective of this study was to elucidate the rate-limiting steps for K^+ adsorption on the clay minerals and soil. It was hypothesized that it is possible under laboratory conditions to set up a system in which the global rate is limited by mass transfer (under static conditions), in which only the intraparticle diffusion step is rate-limiting (stirred system) and a system in which the rates of film and intraparticle diffusion are both relatively rapid, presumably rendering the reaction step to be rate-controlling (vortex batch). Additive resistance relations were derived and assigned to the three proposed experimental methods according to the above stated assumptions. Observed rate coefficients obtained from static, stirred and vortex batch systems were combined and used to calculate rate coefficients for film diffusion (k_f) in a static system. Film diffusion and intraparticle diffusion rate coefficients were approximately the same in vermiculite, indicating that both steps were rate-determining. In kaolinite and the Chester soil, film diffusion was found to be the rate-limiting step. These conclusions were also verified using the parabolic diffusion equation. The k_I values were on the average 8.7 times as great as k_f values in the kaolinite system, indicating that intraparticle diffusion was not important for kaolinite. Since chemical reactions are more sensitive to temperature changes than diffusion processes, higher (E_{aa}) values were observed for the reaction step than for intraparticle or film diffusion steps.

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