

Potassium-Calcium Exchange in a Multireactive Soil System: I. Kinetics¹

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ABSTRACT

The kinetics of K exchange were investigated in Ca-saturated samples from the Ap horizon of an Evesboro soil from Delaware. Biphase kinetics characterized the first-order plots for K adsorption and desorption at 283 and 298 K with the two simultaneous reactions being attributed to exchange sites with varying reactivity for K and Ca ions. The rapid reaction was ascribed to exchange sites of the soil that are readily accessible to cation exchange reactions, whereas the slow reaction was attributed to exchange sites that are difficultly accessible to cation exchange reactions. Confirmation of the biphase kinetics was achieved through the use of cetyltrimethylammonium bromide (CTAB). Parabolic diffusion plots for K adsorption and desorption at 283 and 298 K indicated that an intraparticle diffusion process may be rate limiting for the difficultly accessible sites of the soil. The initial deviation from linearity of the parabolic plots for K desorption suggested that film diffusion may be rate limiting for desorption on readily accessible sites of the soil that form strong bonds with Ca ions. At 313 K the initial rapid kinetics of exchange was no longer present, and the exchange process was described by a single first-order reaction. The parabolic plots at 313 K suggested that this phenomenon could possibly be attributed to the finite rate at which the polymer structure of soil organic matter changes in response to the adsorption and desorption of the two reacting cations.

Additional Index Words: biphase kinetics, adsorption by entropy effect, film diffusion, intraparticle diffusion, surface diffusion.

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A NUMBER OF RESEARCHERS have investigated kinetic reactions on pure clays and soils (Way, 1850; Gedroiz, 1914; Mortland, 1958; Sawhney, 1966; Kuo and Lotse, 1974a, 1974b; Sparks et al., 1980a, 1980b). Sawhney (1966) described the uptake of Cs on vermiculitic clay minerals as a pseudo first-order reaction where diffusion of the cation into the interlayer space was the rate-controlling process. First-order kinetics were also found to describe the desorption of phosphate from kaolinite (Bar-Yosef and Kafkafi, 1978). Key and Wild (1961) investigated the exchange of numerous univalent and divalent cations with Na⁺ on a vermiculite and suggested that intraparticle diffusion was the rate-controlling mechanism governing the adsorption velocity of the cations. Numerous other investigators have noted that K release from micaceous minerals was diffusion controlled and the kinetics of exchange conformed to the parabolic diffusion law (Barshad, 1951; Rausell-Colom et al., 1965; Chute and Quirk, 1967; Feigenbaum et al., 1981).

The kinetics of K adsorption and desorption in heterogeneous soil systems have also been shown to con-

form to first-order kinetics and to the parabolic law (Sivasubramaniam and Talibudeen, 1972; Sparks et al., 1980a, 1980b; Sparks and Jardine, 1981). Salim and Cooksey (1980), investigating the adsorption of Pb²⁺ on river muds, found that the rate of exchange conformed to first-order kinetics. Application of the parabolic law indicated that the adsorption process could not be fully explained by either film diffusion or by intraparticle diffusion. The kinetics of phosphate adsorption and desorption in soils has also been shown to conform to first-order kinetics and to exhibit a diffusion-controlled exchange (Amer et al., 1955; Kuo and Lotse, 1974b; Evans and Jurinak, 1976; Vig and Dev, 1979). Chien and Clayton (1980), investigating phosphate sorption and release in soils, found that the Elovich equation was superior to the first-order rate approach, since the former method tended to combine simultaneous first-order reactions into one linear slope.

It has been theorized that soils contain sites of differing reactivity for K ions (Bolt et al., 1963; Sawhney, 1966; Goulding and Talibudeen, 1979). Bolt et al. (1963) theorized the existence of three different types of binding sites for K exchange on illite. The authors attributed rapid kinetics of exchange to external planar sites, slow kinetics of exchange to interlattice exchange sites, and intermediate kinetics of exchange to interlattice edge sites. Goulding and Talibudeen (1979) also alluded to three different types of K binding sites in their soil system. Accessible K was attributed to external surface reactions, peripheral K was ascribed to that in the interlayers of clay minerals, and matrix K was theorized to be from mica interstratifications. Beckett and Nafady (1967) characterized different binding sites in a soil system using various organic compounds. Cetyltrimethylammonium bromide (CTAB) was used to block external surface sites and leave sites associated with clay mineral interlayers intact. The different sites associated with the soil matrix should exhibit different reaction rates; thus, multiple rate coefficients may exist. The objective of this study is to evaluate the kinetics of K-Ca exchange in a multireactive soil system.

MATERIALS AND METHODS

Theoretical Considerations

With the use of a miscible displacement technique, the apparent adsorption and desorption rate coefficients (k'_a and k''_a , respectively) can be determined from first-order kinetic equations as derived below.

Apparent Adsorption Rate Coefficient (k'_a)

$$d(K_t/K_\infty) = k_a(K_\infty - K_t) dt \quad [1]$$

where

K_t = amount of K on the exchange sites of the soil at time t ,

K_∞ = amount of K on the exchange sites of the soil at equilibrium, and

k_a = absolute velocity coefficient for the adsorption process.

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Separating variables:

$$[d(K_t/K_\infty)]/[(1 - K_t/K_\infty)] = k_a K_\infty dt \quad [2]$$

Integration of the form $dx/1+x = \ln(1+x)$ yields

$$\ln(1 - K_t/K_\infty) = k_a K_\infty t \quad [3]$$

or

$$\log(1 - K_t/K_\infty) = k'_a t \quad [4]$$

where

$$k'_a = k_a K_\infty / 2.303$$

Apparent Desorption Rate Coefficient (k'_d)

For the desorption reaction,

$$d(K_t/K_0) = -k_d K_t dt \quad [5]$$

where

K_0 = amount of K on the exchange sites of the soil at zero time,

K_t = amount of K on the exchange sites of the soil at time t , and

k_d = absolute velocity coefficient for the desorption process.

On integration with boundary conditions:

$t = 0, (K_t/K_0) = 1; t = \infty, K_t/K_0 = 0$, one obtains

$$\ln(K_t/K_0) = -k_d t \quad [6]$$

or

$$\log(K_t/K_0) = -k'_d t \quad [7]$$

where

$$k'_d = k_d / 2.303$$

It should be mentioned that the absolute velocity coefficients for the adsorption and desorption process in solution (k_a and k_d , respectively) are comprised of numerous diffusional and chemical reaction rates. It is appropriate to suggest that for the adsorption process

$$k_a \propto r_1 + r_2 + r_3 \quad [8]$$

where

r_1 = reaction rate associated with film diffusion;

r_2 = reaction rate associated with intraparticle diffusion, or, independently, the reaction rate associated with surface diffusion; and

r_3 = chemical reaction rate.

Depending on the type of system that is being studied, one or more of the above rates (e.g., r_1, r_2, r_3) may be negligible or absent. The reaction rate that is slowest will be the rate-limiting kinetic parameter and will have the greatest impact on the observed velocity coefficient k_a . Analogous expressions can be obtained for the desorption process.

Energies of Activation

From the Arrhenius equation, energies of activation for K adsorption and desorption (E_a and E_d , respectively) can be determined as shown by Sparks and Jardine (1981).

Parabolic Equation

The parabolic diffusion equation for K exchange may be stated as follows (Sivasubramaniam and Talibudeen, 1972):

$$K_t/K_\infty = (4/\pi^{1/2}) (Dt/a^2)^{1/2} - (Dt/a^2) \quad [9]$$

where

K_t = quantity of K on the exchange sites of the soil at time t ,

K_∞ = quantity of K on the exchange sites of the soil at equilibrium,

a = radius parameter, and

D = diffusion coefficient.

Thus, a plot of K_t/K_∞ vs. $t^{1/2}$ should provide a linear relationship if the reaction conforms to Fickian diffusion.

Experimental Procedures

Basic Characterization Analyses

Bulk samples were taken from the Ap horizon of an Evesboro loamy sand (Typic Quartzipsamments) from Sussex County, Delaware, air-dried, and ground to pass through a 2-mm sieve. The soil contained 86.9, 10.6, and 2.5% sand, silt, and clay, respectively, using the hydrometer method (Day, 1965). The organic matter content of the soil, as determined by the Walkley-Black method (Jackson, 1958), was 1.4%, and the CEC, as determined by Mg-Ca exchange, was 23.9 mmol ($1/2\text{Mg}^{2+}$) kg^{-1} . The mineral suite of the $<2\text{-}\mu\text{m}$ clay fraction was determined by x-ray diffraction using the procedures outlined previously (Sparks et al., 1980a), and was mainly chloritized vermiculite with smaller quantities of kaolinite and mica.

Kinetic Studies

Prior to the kinetic studies, subsamples of the Evesboro soil were Ca saturated using procedures given previously (Sparks and Jardine, 1981). The pH of the Ca-saturated samples, determined at a soil/water ratio of 1:2, was 5.9.

Clay minerals of vermiculite (Llano, Texas), montmorillonite (Gorgales County, Texas), and well-crystallized kaolinite (Washington County, Georgia) from the University of Missouri Source Clay Minerals Depository were also fractionated and Ca saturated using standard methods. The CEC of the clay minerals as determined by Mg-Ca exchange, was 2070, 702, and 11.5 mmol ($1/2\text{Mg}^{2+}$) kg^{-1} for vermiculite, montmorillonite, and kaolinite, respectively. Kinetics of K adsorption and desorption using miscible displacement were determined for the Evesboro soil and the standard clays using procedures outlined by Sparks and Jardine (1981). All studies were conducted under isobaric, isothermal conditions (1 atm; 283, 298, 313 \pm 0.5K, respectively) using a constant flow rate of 0.5 mL min^{-1} for the Evesboro soil and 1.0 mL min^{-1} for the standard clays. In this study and in an earlier work (Sparks et al., 1980b), it was found that flow rate had a negligible effect on the magnitude of the rate parameters. Potassium in solution was determined by atomic absorption spectrophotometry, and the concentrations of KCl and CaCl_2 used in the kinetic studies were chosen to mimic field conditions.

Confirmation of Biphase Kinetics

To confirm that the two simultaneous kinetic reactions of the Evesboro soil could be attributed to exchange sites of varying K reactivity and were not related to some kinetic artifact, the soil was treated with CTAB. The application of CTAB involved three successive washings of a 5-g Ca-saturated soil sample with a saturated aqueous solution of CTAB. The soil was then air-dried, and duplicate 1-g portions were analyzed kinetically as before.

RESULTS AND DISCUSSION

Potassium adsorption and desorption in the Evesboro soil conformed to first-order kinetics at all three temperatures (Fig. 1 and 2, respectively). At 283 and 298 K, two simultaneous first-order reactions existed with the first slope containing both a rapid reaction (rxn1) and a slow reaction (rxn2). The second slope

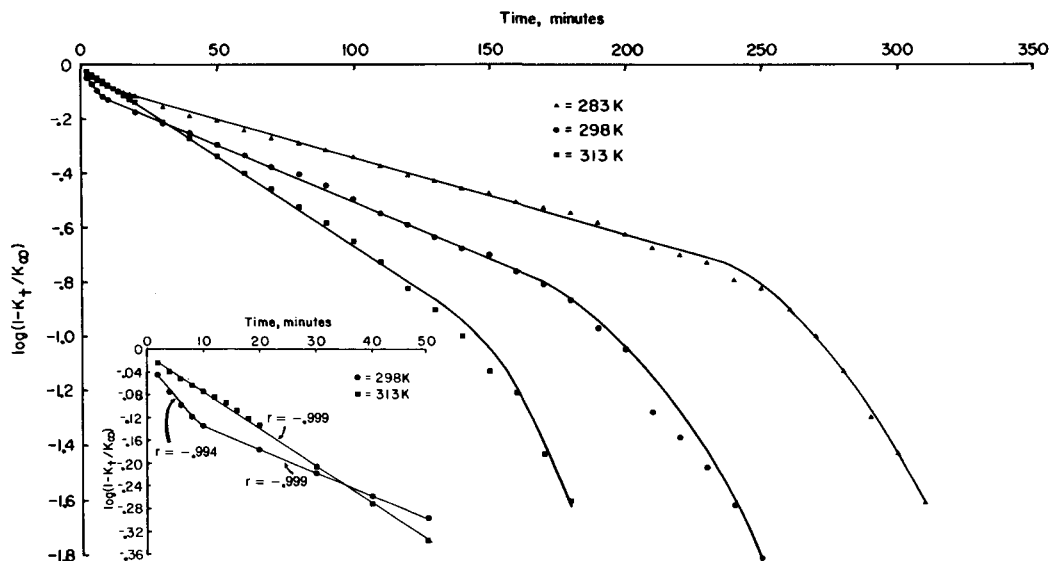


Fig. 1—First-order kinetics for K adsorption at three temperatures on Evesboro soil with inset showing the initial 50 min of the first-order plots at 298 and 313 K.

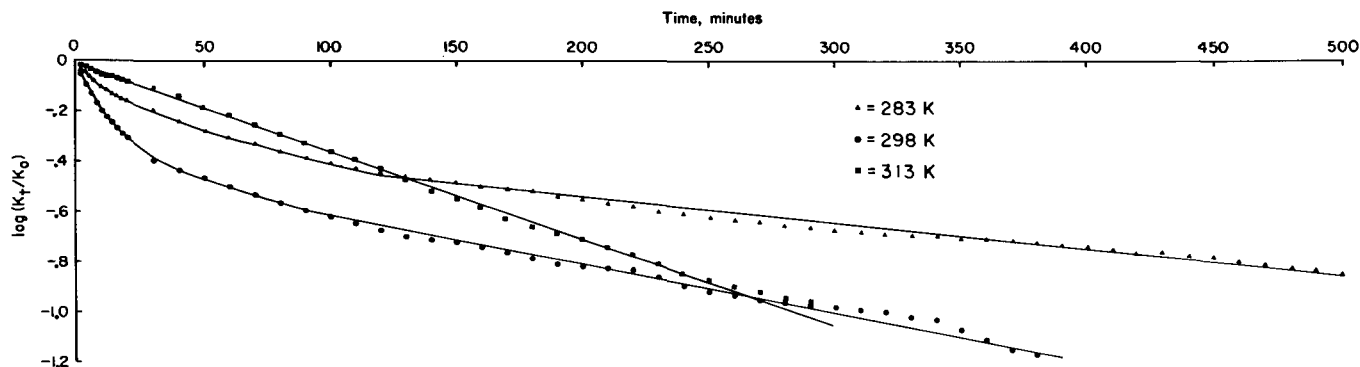


Fig. 2—First-order kinetics for K desorption at three temperatures on Evesboro soil.

described only the slow reaction (rxn2). The difference between the two slopes would yield the slope for rxn1. Reaction 1 conformed to first-order kinetics for 8 min, at which time it began to terminate, leaving rxn2 to proceed for many hours. As equilibrium was approached, deviation from first-order kinetics occurred, indicating that rxn2 was nearing completion. Similar deviations were noted by Boyd et al. (1947) and Sivasubramanian and Talibudeen (1972) when a relatively long time of contact was employed. Boyd et al. (1947) suggest that deviations from first-order kinetics as the equilibrium point is approached may be related to irregularities in particle size of the solid exchanger. Although this statement may have practical implications in soil systems, it must be remembered that the region of near equilibrium ($1 - K_t/K_\infty < 0.2$) is characterized by large experimental error (Boyd et al., 1947).

The two simultaneous reactions may be attributed to sites of varying reactivity for K and Ca ions. Reaction 1 may be ascribed to exchange sites of the soil that are readily accessible to cation exchange reactions, whereas rxn2 may be attributed to exchange sites of the soil that are difficultly accessible to cation exchange reactions. The rapid reacting exchange sites (rxn1) accounted for approximately 35% of the total

CEC, whereas the slower reacting exchange sites (rxn2) accounted for approximately 65% of the CEC. The exchange sites associated with rxn1 can most likely be ascribed to the readily accessible sites of organic matter and kaolinite. Since the organic matter accounted for 65% of the total soil CEC, it is evident that some sites of the organic matter are also associated with rxn2. The difficultly accessible exchange sites of the organic matter may be related to its complex polymeric structure, which develops tortuous paths for diffusing cations (Theng, 1974; Moreale and van Bladel, 1979). The slow reacting sites associated with rxn2 may also be attributable to interlayer sites of the 2:1 vermiculitic clay minerals that predominated in the $< 2\text{-}\mu\text{m}$ clay fraction. At 313 K, biphasic kinetics no longer existed for K adsorption and desorption (Fig. 1 and 2, respectively) as evidenced by a single slope that correlated to exchange sites of the soil that are difficultly accessible to cation exchange reactions. The first 50 min of K adsorption at 298 and 313 K (Fig. 1) clearly shows the loss of the initial slope at the higher temperature.

Although not shown, K adsorption and desorption on the Evesboro soil were also fitted to the Elovich equation. A curvilinear response of the equation to K kinetics was noted. The nonlinear Elovich plot may

support the hypothesis of the multireactive nature of this soil. It has been suggested (Low, 1960; Atkinson et al., 1970; Chien and Clayton, 1980) that any "breaks" in the Elovich plot indicate a different reactivity of sites for the adsorption of ions on an irregular surface. The curvilinear nature of the Elovich plot must be viewed with caution however, since the Elovich equation was originally developed to describe the kinetics of chemisorption of gases on solid surfaces and not cation exchange reactions at solid-solution interfaces whose kinetics are typically controlled by diffusion.

Apparent Adsorption and Desorption Rate Coefficients (k'_a and k'_d , Respectively)

The k'_a and k'_d values for both rxn1 and rxn2 increased with increasing temperature (Table 1), and they are consistent with Bronsted's reaction rate theory that states that reaction rates should become higher with increasing temperature. The k'_d values were lower than the k'_a values for rxn2, which indicated K desorption was slower than K adsorption. The slower desorption kinetics can partly be ascribed to the interlayer sites of the 2:1 clay minerals that undergo partial collapse upon K adsorption (Sawhney, 1966; Sparks and Jardine, 1981). The difficultly accessible exchange sites of the organic matter may also play a role in the slower desorption kinetics. At 283 and 298 K, k'_d values were greater than k'_a values for rxn1, indicating that K desorption was more rapid than K adsorption (Table 1). These data indicate Ca ions are adsorbed more quickly on the readily accessible exchange sites of the soil relative to K ions.

Since the initial slope was absent at 313K, k'_a and k'_d values could not be calculated for rxn1. Although the initial slope could not be detected for the adsorption and desorption of K, the quantity of total adsorbed and desorbed K did not decrease. This implied that both readily accessible and difficultly accessible exchange sites were all actively participating in cation exchange reactions. An explanation of this phenomenon will be elaborated in a later section that discusses Fickian and non-Fickian diffusion.

First-order plots for the adsorption of K at 298 K and 1.0 mL min⁻¹ flow velocity for three standard clay minerals are provided for reference (Fig. 3). Among the three clays studied, kaolinite exhibited the most rapid reaction rate (Table 1) since its exchange capacity is due primarily to external surface and edge sites

Table 1—Apparent adsorption and desorption rate coefficients (k'_a and k'_d , respectively) for rxn1 and rxn2 in Evesboro soil and k'_a values for standard clays under isothermal conditions.

| Temperature | Evesboro soil | | | |
|-------------|------------------------|-----------------|------------------------|-------|
| | rxn1 | rxn2 | rxn1 | rxn2 |
| | k'_a h ⁻¹ | | k'_d h ⁻¹ | |
| 283 | 0.257 | 0.174 | 0.510 | 0.057 |
| 298 | 0.448 | 0.269 | 0.908 | 0.108 |
| 313 | None | 0.398 | None | 0.193 |
| | Kaolinite | Montmorillonite | Vermiculite | |
| | k'_a h ⁻¹ | | | |
| 298 | 2.65 | 0.577 | 0.228 | |

that are readily accessible to cation exchange. As would be expected, vermiculite exhibited slow kinetics (Table 1) since its primary source of exchange capacity is interlayer sites, which impede many cation exchange processes. Montmorillonite exhibited reaction rates intermediate to those of the previous two clays (Table 1), which can be related to its freely expanding interlayer space. The k'_a value for rxn2 of the soil at 298K compares well with the k'_a value obtained on the standard vermiculite clay (Table 1). The fair correlation is probably related to the interlayer sites of chloritized vermiculite, which have been postulated to be partly responsible for exchange sites associated with rxn2 of the soil. Since difficultly accessible exchange sites of organic matter are also associated with rxn2, a direct and definitive comparison between the standard vermiculite clay and the chloritized vermiculite of the soil cannot be made. This is substantiated since k'_a values for rxn1 of the soil cannot be compared with those of the standard clays since rxn1 of the soil is probably very strongly influenced by organic matter.

Confirmation of Biphasic Kinetics

To document that the biphasic kinetics on the Evesboro soil are attributable to exchange sites of varying K and Ca reactivity and were not related to some kinetic artifact (i.e., column elution curves), CTAB was introduced onto the soil. The CTAB molecule is a long hydrocarbon chain (15 CH₂ groups) attached to a trimethylated nitrogen functional group. Thus, CTAB is a large, bulky molecule whose functional group is strongly hydrated (Franzen, 1955). The molecule, exhibiting both hydrophobic and hydrophilic characteristics, is bound to the soil surface primarily through electrostatic interactions with entropy effects contributing a secondary role in the molecule's overall affinity for the soil. Cetyltrimethylammonium bromide was shown by Beckett and Nafady (1967) to be selectively adsorbed on external surface sites of soil and to effectively eliminate these sites from cation exchange reactions. Although CTAB blocked external surface sites, Beckett and Nafady (1967) suggested the molecule did not affect those sites associated with interlayers of clay minerals.

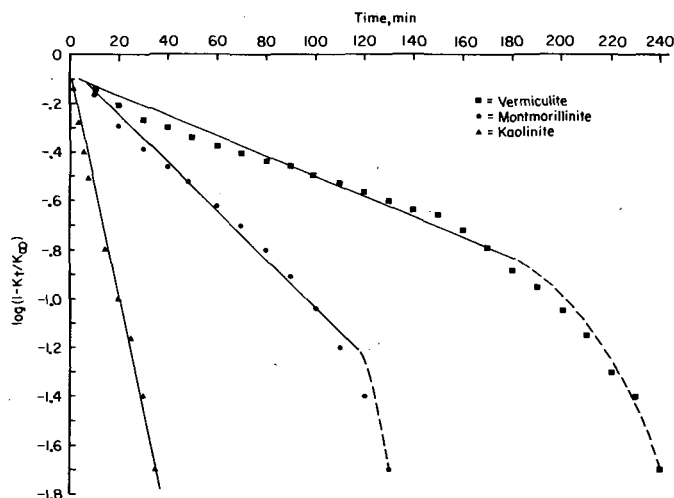


Fig. 3—First-order kinetics for K adsorption at 298 K on standard clays.

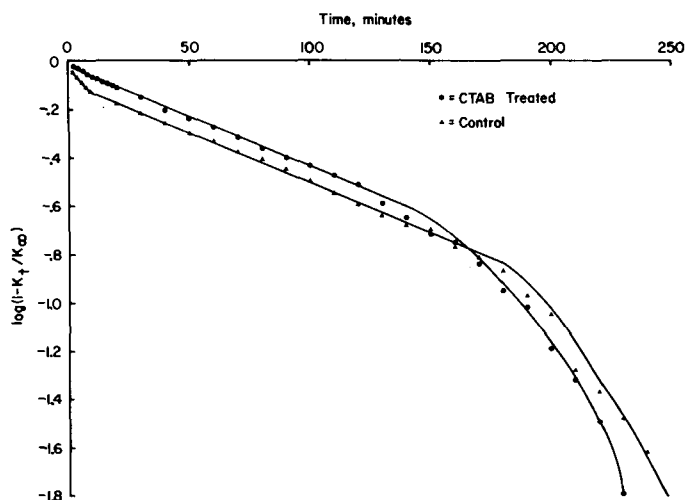


Fig. 4—First-order kinetics for K adsorption at 298 K on Evesboro soil treated with CTAB.

That CTAB was selectively adsorbed onto the readily accessible sites of the soil is shown by the loss of the first slope and subsequent intersection of the second slope into the origin (Fig. 4). It is evident that CTAB selectively binds to these sites since k'_a values could not be calculated for rxn1 and the molecule effectively eliminated 38% of the exchange sites associated with the soil. The amount of sites blocked by CTAB compares very well with the total percentage of CEC associated with the readily accessible sites of the soil (i.e., 35%).

Since the k'_a values for rxn2 of the CTAB treated soil were within 3% of the control (i.e., 0.260 and 0.269 h^{-1} , respectively), it can be concluded that the difficultly accessible exchange sites of the soil are unaffected by CTAB additions. This is probably due to the large molecule being sterically hindered from entering the small interlayer spaces of the soil clay minerals and the restrictive spaces associated with the difficultly accessible sites of organic matter. It has been reasonably well documented that the biphasic kinetics on the Evesboro soil are attributable to exchange sites of varying K and Ca reactivity.

Application of the Parabolic Diffusion Law

Potassium adsorption and desorption in the Evesboro soil was applied to the parabolic diffusion law at all three temperatures (Fig. 5 and 6). At 283 and 298K (Fig. 5), the adsorption of K conformed well to parabolic kinetics, suggesting that intraparticle diffusion or surface diffusion may be rate limiting (Helfferich, 1969; Crank, 1976). The former diffusional process is a transport of the adsorbing ion through the liquid associated with difficultly accessible exchange sites of the soil and is characterized by activation energies of 21 to 42 kJ mol^{-1} (Reichenberg, 1957). The latter diffusional process involves the movement of the adsorbing ion along the walls of the difficultly accessible spaces and is characterized by an activation energy roughly equal to the heat of adsorption, ΔH° (Boyd et al., 1947). In the present study, the energies of activation for the adsorption and desorption of K (E_a and E_d , respectively) were 20 and 29 kJ mol^{-1} , re-

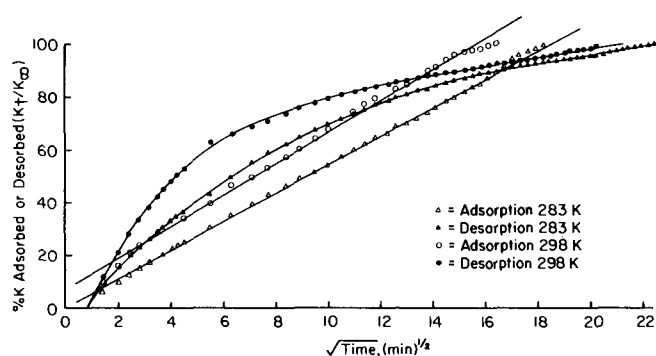


Fig. 5—Parabolic plots for K adsorption and desorption at 283 and 298 K for Evesboro soil.

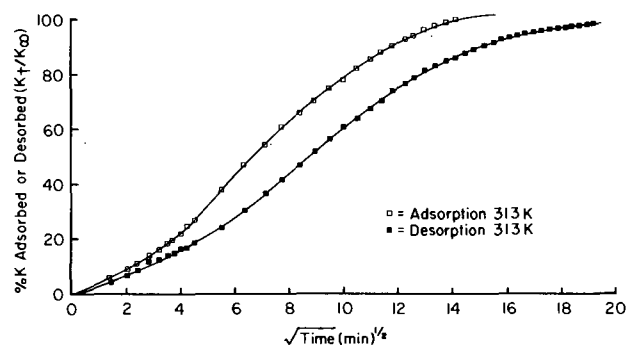


Fig. 6—Parabolic plots for K adsorption and desorption at 313 K for Evesboro soil.

spectively. The difference between the E_a and E_d yields 9 kJ mol^{-1} which is the heat of adsorption, ΔH° , established through diffusional kinetics. The ΔH° established through thermodynamic equilibria (Jardine and Sparks, 1984) was 15 kJ mol^{-1} . Since these two parameters are dissimilar, it appears surface diffusion is probably not the rate-controlling mechanism in K adsorption for this soil. Generally when particle resistance (i.e., movement of the adsorbing ion along the walls of the difficultly accessible spaces) determines the adsorption velocity, surface diffusion is the rate controlling mechanism. For such a situation, it would be valid to suggest that true chemical heats of adsorption may be determined through the use of activation energies established by surface diffusion kinetics. Although this hypothesis has no substantial proof, it has previously been suggested by others (Keay and Wild, 1961; Sparks and Jardine, 1981; K.W.T. Goulding, personal communication). Since K adsorption at 283 and 298K conformed well to the parabolic law and was characterized by an E_a value of 20 kJ mole^{-1} , it is suggested that intraparticle diffusion may be the rate-determining process.

The desorption of K at 283 and 298 K (Fig. 5) followed a much different path than did the adsorption process. Initially a curvilinear response characterized the parabolic law and suggested that film diffusion was the initial rate-controlling process (Helfferich, 1962). This diffusional process is the transport of the adsorbing ion through the static liquid film that surrounds the constituents of the soil. As time proceeded, the diffusional process was linearly related to the parabolic law and suggested that intraparticle diffusion was now rate controlling. The initial curvilinear re-

sponse for the desorption of K may be related to the strong adsorption of Ca for the readily accessible sites of the soil. It has been postulated that these sites are primarily related to accessible exchange sites of soil organic matter. The strong preference of Ca for such sites is shown clearly by thermodynamic equilibria studies initiated on this soil (Jardine and Sparks, 1984). Strong adsorption on readily accessible exchange sites in the soil favors film diffusion-controlled adsorption rates (Boyd et al., 1947). Once the initial reaction involving K desorption from accessible exchange sites was complete, the exchange process was linearly related to the parabolic law. This might be expected since K desorption would be occurring from exchange sites that are difficultly accessible to cation exchange reactions. Conformity to the parabolic law and an E_d value of 29 kJ mol⁻¹ might suggest that the rate of K desorption from difficultly accessible exchange sites is intraparticle diffusion controlled.

The parabolic law was also applied to K adsorption and desorption at 313K (Fig. 6). The plots follow a definite sigmoidal trend, with inflection points occurring between 45 and 55% of equilibrium sorption. Deviations from Fickian behavior, such as these, may possibly be related to the finite rate at which the polymeric structure of soil organic matter may change in response to the adsorption and desorption of the two reacting cations (Crank, 1976). The increase in temperature to 313K causes the rate of cation diffusion toward the soil matrix to increase. Possibly the rate of diffusion is more rapid or comparable to the relaxation time of the organic polymers as they exchange K for Ca or vice versa. Such a situation would cause non-Fickian diffusion curves that are sigmoidal in shape and exhibit an inflection point at about 50% equilibrium sorption (Park, 1968). This hypothesis may serve as a possible explanation for the loss of the initial slope from first-order plots at 313K. In this situation, accessible sites from the organic phase (rxn1) are still actively exchanging, but due to the impeded relaxation time of the organic polymers, the process of exchange from these sites is retarded. Since the readily accessible sites of soil organic matter would probably be more affected by polymer relaxation than the difficultly accessible sites of organic matter, the anomalous effect may not have a large impact on the kinetics of exchange from the latter. However, this hypothesis is difficult to prove since one might expect a stepwise loss of slope from 283 to 298 K to its complete loss at 313 K.

Other possible reasons for the non-Fickian behavior of the diffusion process at 313 K may be associated with changing polymer structure on solubility or result from internal stresses on the polymer that are exerted by different portions of the soil matrix as diffusion proceeds.

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