

# Kinetics of Ion Exchange on Clay Minerals and Soil: II. Elucidation of Rate-limiting Steps<sup>1</sup>

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## ABSTRACT

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. We 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). We derived and assigned additive resistance relations 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 ( $k_f$ ), intraparticle diffusion ( $k_i$ ), and reaction kinetics ( $k_r$ ) 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 the rate-limiting step. These conclusions were also verified using the parabolic diffusion equation. The  $k_f$  values were on the avg 8.7 times as great as  $k_i$  values in the kaolinite system, indicating that intraparticle diffusion

was not important for kaolinite. Higher energies of activation for adsorption ( $E_{ad}$ ) were observed for the reaction step than for intraparticle diffusion or film diffusion steps. These findings were expected since chemical reactions are more sensitive to temperature changes than diffusion processes.

*Additional Index Words:* additive resistance, diffusion, reaction kinetics, K-ion selective electrode, energies of activation.

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ONE OF THE MOST IMPORTANT aspects of any kinetic 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; Sparks, 1985, 1986). 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.

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Ion exchange phenomena on soils and other heterogeneous systems involve mass transfer and chemical kinetic processes (Boyd et al., 1947; Helfferich, 1983; Sparks, 1985, 1986). 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 sites (Froment and Bischoff, 1979). The decrease in concentration of ions in these interface zones is compensated by diffusion of ions from the bulk solution.

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 (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; Sparks et al., 1980; Jardine and Sparks, 1984; Sparks, 1985, 1986). Jardine and Sparks (1984) found that adsorption of  $K^+$  at 283 and 298 K conformed well to parabolic kinetics, suggesting that intraparticle diffusion was rate limiting.

The magnitude of activation energies ( $E_{aa}$ ) have 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<sup>-1</sup> 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<sup>-1</sup>. 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; Ogwada and Sparks, 1986a, b).

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 soil processes. 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 in a Delaware soil and in standard clay minerals. This information will be used to elucidate rate-limiting steps in these systems.

## MATERIALS AND METHODS

### Theoretical Considerations

#### Definition of Rate-limiting Steps

In this paper, we shall consider a one-dimensional horizontal adsorption process. The adsorption of ions from so-

lution 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 (film diffusion). The second step, with the exception of adsorption that occurs on the planar and edge sites of the soil particles, is the diffusion of ions through hydrated interlayer spaces of the particles (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 (the chemical reaction step). More detailed descriptions of these steps have been given by Vermeulen 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).

#### Proposal of Combined Additive Resistances

Consider a reactive species A in a solution in contact with soil particles. Its concentration at the interface where the 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 at interlayer sites. Assuming a first-order reaction, the rate is defined as

$$r_A = k_r C_A \quad [1]$$

where  $r_A$  = rate of reaction of A at the soil colloid sites and  $k_r$  = rate 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, 1979; Froment and Bischoff, 1979) as,

$$j_A = k_{dif} (C_o - C_A) \quad [2]$$

where  $j_A$  = mass flux with respect to the fixed particle surfaces,  $k_{dif}$  = mass transfer coefficient, and  $C_o$  = concentration of A in the bulk solution.

Under 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,

$$r_A \cong j_A = r \quad [3]$$

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

Combining Eq. [1] and [2] gives,

$$C_A = k_{dif} C_o / (k_r + k_{dif}) \quad [4]$$

and

$$r = [k_{dif} k_r / (k_r + k_{dif})] C_o = k_o C_o \quad [5]$$

where

$$k_o = k_{dif} k_r / (k_r + k_{dif}) \quad [6]$$

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

$$1/k_o = 1/k_r + 1/k_{dif} \quad [7]$$

One now has both kinetic and diffusional resistances that are additive. However, ion adsorption processes in soils or clay minerals are assumed to 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,

$$1/k_{dif} = 1/k_l + 1/k_f \quad [8]$$

Table 1. Effect of degree of agitation on surface area and rate of K<sup>+</sup> adsorption on Chester loam.

Mixing rates	Specific surface	Rate coefficient
rpm	10 <sup>4</sup> m <sup>2</sup> kg <sup>-1</sup>	k <sub>a</sub> , min <sup>-1</sup>
	<u>Stirred</u>	
0	5.35	0.027
285	5.37	0.048
330	5.37	0.081
370	5.37	0.251
435	5.37	0.250
478	5.37	0.251
640	5.54	0.315
670	6.11	0.341
	<u>Vortex batch</u>	
2240	5.37	2.330
2290	5.38	2.330
2318	5.38	2.329
2420	5.54	3.501
2490	5.56	3.512
2625	5.69	3.610
2700	5.69	3.611

where  $k_i$  is the intraparticle diffusion rate coefficient and  $k_f$  is the film diffusion rate coefficient. Equations [7] and [8] can be combined to give

$$1/k_o = 1/k_r + 1/k_i + 1/k_f. \quad [9]$$

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

#### 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. [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 (Ogwada and Sparks, 1986b). Therefore, to these systems we accordingly assign additive resistance relations as follows:

##### Static system

$$1/k_{os} \cong 1/k_r + 1/k_i + 1/k_f \quad [10]$$

##### Stirred system

$$1/k_{oi} \cong 1/k_r + 1/k_i \quad [11]$$

##### Vortex batch system

$$1/k_{ov} \cong 1/k_r \quad [12]$$

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

We suggest that 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 previous work (Ogwada and Sparks, 1986b). Due to agitation in the stirred system, the influence of the film diffusion resistance that was prevalent in the static system is greatly reduced by uniform mixing and rapid mass transfer across the hydrodynamic film (Ogwada and Sparks, 1986a,

Table 2. Rate coefficients for film diffusion, intraparticle diffusion, and chemical reaction rate processes for K<sup>+</sup> adsorption under static conditions.

Adsorbent	Temperature	Rate coefficients		
		k <sub>f</sub>	k <sub>i</sub>	k <sub>r</sub>
	K		min <sup>-1</sup>	
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

b). Therefore, the stirred system is assigned only the reaction and intraparticle resistance relations. We have also assumed that in 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 we have assumed that the observed rate coefficient approximates that of the reaction step in the static system and we have therefore assigned only one resistance relation in this system. This seems justified based on previous studies (Ogwada and Sparks, 1986a, b).

Accordingly, the parameters for Eq. [10] can be calculated as follows:

$$1/k_f \cong 1/k_{os} - (1/k_r + 1/k_i) \quad [13]$$

or

$$1/k_f \cong 1/k_{os} - 1/k_{oi} \quad [14]$$

and

$$1/k_i \cong 1/k_{oi} - 1/k_r \quad [15]$$

or

$$1/k_i \cong 1/k_{oi} - 1/k_{ov}. \quad [16]$$

As mentioned above,  $1/k_{os}$ ,  $1/k_{oi}$ , 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 Eq. [14] and [16].

In summary, we have developed a model and assumed that the adsorption of ions from solution by soil particles occurs in a series rather than a parallel-reaction mode. Thus, mass transfer processes 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 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.

#### 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 Univ. of Missouri Source Clays Depository and fractionated before analysis using standard techniques (Jackson, 1964). The cation exchange capacity (CEC) of the kaolinite and vermiculite as determined by Mg-Ca exchange, was 1.2 and 207 cmol (1/2 Mg<sup>2+</sup>) kg<sup>-1</sup>, respectively (Jardine and Sparks, 1984). Basic physicochemical and mineralogical properties of the Chester soil were reported earlier (Ogwada and Sparks, 1986b). Prior

**Table 3. Correlation coefficient (*r*) and SE of estimate of various systems studied using the parabolic diffusion equation.**

	<i>r</i>	SE
Kaolinite	0.9603	4.017
Chester loam	0.9791	2.872
Vermiculite	0.9909	1.249

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<sup>+</sup> adsorption on the clay minerals and Chester soil under static conditions were quantified from observed rate coefficients (Eq. [13]–[16]) using the static, stirred, and vortex techniques given earlier (Ogwada and Sparks, 1986b). The rate coefficients were determined at 283, 298, and 313 K, and energies of activation for K<sup>+</sup> adsorption ( $E_{aa}$ ) were determined using the Arrhenius equation.

We also investigated the quantitative relationship between the rate of mixing or agitation and the rate coefficients. 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 stirred and vortex mixed samples were measured using a stroboscopic light (Strobatac Type 1531).

## RESULTS AND DISCUSSION

### Effect of Mixing Rates on Specific Surface and Rate Coefficients

Specific surface for the Chester soil was relatively constant (53.6 m<sup>2</sup> g<sup>-1</sup>) under stirred conditions for mixing rates of 0 to 478 rpm, but increased abruptly at higher mixing rates (Table 1). The  $k_a$  values increased in the 0 to 370 rpm mixing range, leveled off between 370 to 478 rpm, and then abruptly increased when the mixing rate reached 640 rpm.

Since the specific surface 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 greater reduction of film diffusion as the rate-limiting step. Intraparticle diffusion is therefore likely the rate-limiting step at mixing rates > 370 rpm since the  $k_a$  values remain constant from 370 to 478 rpm. The increase in the  $k_a$  values observed at mixing rates ≥ 640 rpm is related to increased specific surface of the soil (Table 1) rather than being the rate-limiting step. Increased surface could result from abrasion of the colloidal particles by the magnetic stirring rod at the high stirring rates. The leveling off of the  $k_a$  values at mixing rates in the 370- to 478-rpm range influenced our choice of a mixing rate of 435 rpm under stirred conditions (Ogwada and Sparks, 1986b).

Even though mixing rates were several orders of magnitude higher with vortex mixing than with stirring (Table 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 we could obtain with the vortex mixer was 2240 rpm. Both the specific surface and the  $k_a$  values remained constant at the 2240 to 2318 rpm mixing range. Thus, intraparticle diffusion was assumed to no longer be

**Table 4. Energies of activation of rate-limiting steps for K<sup>+</sup> adsorption under static conditions.**

System	Rate-limiting steps		
	Film diffusion	Intraparticle diffusion	Reaction
	kJ mol <sup>-1</sup>		
Kaolinite	4.31	1.07	30.51
Chester loam	4.57	6.50	32.58
Vermiculite	4.25	6.51	33.55

rate-limiting, and the  $k_a$  values obtained at the 2240 to 2318 rpm mixing rates approximated those of the reaction rate step.

The latter assumption is supported by earlier research (Ogwada and Sparks, 1986a), which showed that a kinetic approach is valid for calculation of thermodynamic parameters *only* if diffusion effects are dramatically reduced. These conditions were met *only* if the vortex technique was used.

### Rate-limiting Steps for Kaolinite

The data in Table 2 suggest that the rate controlling process for K<sup>+</sup> 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 to 0.037 min<sup>-1</sup> while intraparticle diffusion rate coefficients ( $k_i$ ) ranged from 15.06 to 15.74 min<sup>-1</sup>. Apparently, intraparticle diffusion has only a minor effect on the rate of K<sup>+</sup> adsorption.

The K<sup>+</sup> adsorption data for kaolinite, the Chester loam, and vermiculite were applied to the parabolic diffusion law equation, and measurements of the correlation coefficient (*r*) and standard error of the estimate (SE) calculated (Table 3). The parabolic diffusion law did not describe K<sup>+</sup> adsorption on kaolinite well as evidenced by lower *r* values and higher SE values than were observed for the Chester loam and particularly for vermiculite. This poor conformity further indicates that the rate-limiting process for K<sup>+</sup> adsorption on kaolinite is not intraparticle diffusion (Boyd et al., 1947; Sparks, 1985). This is precisely the conclusion derived from the data in Table 2. The insignificance of intraparticle diffusion in the kaolinite we studied 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 to 10% vermiculite, mica, and smectite clay minerals were present in the kaolins they studied—presumably interstratified with kaolinite layers. Thus, depending on the source, the  $k_i$  values for kaolinite may not always be as high as we obtained in our study.

The energies of activation for K<sup>+</sup> 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<sup>-1</sup>, respectively, while the  $E_{aa}$  for the reaction step was about 31 kJ mol<sup>-1</sup>. The low  $E_{aa}$  values for film and intraparticle diffusion are characteristic of those values quoted for diffusion processes (Mort-

land and Ellis, 1959; Kuo and Lotse, 1974; Jardine and Sparks, 1984). Since the chemical reaction process is more sensitive to temperature changes than the diffusional processes, one would expect relatively higher  $E_{aa}$  values for the former process (Table 4).

### 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 2). This is evidenced by significant differences between  $k_f$  and  $k_i$  values (Table 2). The estimated  $k_i$  values were on the avg, 8.7 times higher than the  $k_f$  values, indicating that film diffusion was the rate-determining step. The mineralogical composition of the <2- $\mu$ m clay fraction of the Chester soil was predominantly kaolinite with smaller quantities of quartz, chloritized 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 3).

The  $E_{aa}$  values of the two diffusional steps for the Chester loam were low but slightly higher than those for kaolinite (Table 4). The  $E_{aa}$  values for the reaction step for Chester loam were about 33 kJ mol<sup>-1</sup>. This was five times as high as the  $E_{aa}$  value for intraparticle diffusion, and seven times that of film diffusion.

### Rate-limiting Steps for Vermiculite

There was no significant difference between the  $k_i$  and  $k_f$  values for K adsorption on vermiculite (Table 2). This suggests that both film diffusion and intraparticle diffusion were rate-limiting steps. Ion adsorption is often 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<sup>+</sup> adsorption on vermiculite well (Table 3), indicating that intraparticle diffusion may have been the predominant rate-limiting step. This equation has been found by some researchers to describe the kinetics of K exchange on vermiculite (Chute and Quirk, 1966; Jardine and Sparks, 1984).

As with kaolinite and the 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. 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<sup>+</sup> adsorption to occur in interlayers rather than on particle surfaces (Jardine and Sparks, 1984).

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