

DIVISION S-2—SOIL CHEMISTRY

Determination of Rate Coefficients for Potassium–Calcium Exchange on Vermiculite using a Stirred-Flow Chamber

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ABSTRACT

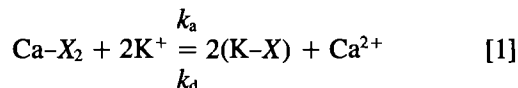
A stirred-flow technique has been widely used to study the rate of ion adsorption on clays and soils. However, no mathematical analysis of chemical kinetics combined with mass transport has been used to derive rate coefficients for ion exchange phenomena. Accordingly, the objectives of this study were to: (i) develop a mathematical model of the kinetics of an elementary cation-exchange reaction combined with transport processes in a stirred-flow chamber and (ii) determine rate coefficients based on this model for K–Ca exchange on a vermiculite. The kinetics of exchange were described by a second-order mechanistic rate law from which the equilibrium exchange equation was derived. The second-order mechanistic rate law combined with an equation of mass balance describing transport were solved numerically. The equilibrium K–Ca exchange data were described by the Gaines and Thomas approach with a thermodynamic exchange equilibrium constant $K_{ex} = 754.6 \text{ L mol}^{-1}$. The values of the apparent adsorption rate coefficient (k_a) ranged from 84 to 185 $\text{L}^2 \text{ mol}^{-2} \text{ min}^{-1}$, as influent rate increased from 0.3 to 2.0 mL min^{-1} . The calculated K–Ca exchange half-life ($t_{1/2}$) ranged from 0.5 to 1.5 min, in agreement with published data based on batch methods.

AN ARRAY of techniques can be employed to measure the rates of soil chemical reactions (Sparks, 1989). These techniques can be categorized into chemical relaxation techniques that monitor reactions rates on millisecond time scales and batch and flow methods that can be used to measure slower reactions ($>15 \text{ s}$). The stirred-flow technique that was developed by Carski and Sparks (1985) is a combination batch and flow method, and it has been extensively used to measure adsorption-desorption reactions on soils and soil components. Seyfried et al. (1989) showed that perfect mixing, i.e., the concentration of the adsorptive in the chamber equals the effluent concentration occurring in the stirred-flow chamber. Bar-Tal et al. (1990) used a stopped-flow test to determine if time-dependent reactions could be measured with the stirred-flow method and employed varying influent concentrations and flow rates to elucidate kinetic models. Eick et al. (1990), using the tests of Bar-Tal et al. (1990), showed that K–Ca exchange on montmorillonite was too rapid to be measured with the stirred-flow

technique, while exchange on vermiculite was kinetically controlled and could be measured.

A number of kinetic models have been used to describe time-dependent soil chemical reactions; a simple first-order equation has been the most widely used model. However, this model is most appropriate for reactions from equilibrium where reverse reactions are not occurring. Sivasubramaniam and Talibudeen (1972) noted that the assumption of a first-order reaction for K desorption is valid as long as the concentration of the displaced K is negligible relative to that of the extracting ion. They also showed that K absorption on soil deviated from a linear first-order reaction when the ratio of K to Al exceeded a certain value. Moreover, a simple first-order model is not appropriate to describe reactions where both chemical kinetics and mass transport processes occur simultaneously and cannot be easily separated. Such conditions are usually the case when one is measuring reaction rates in soils and soil components. In such systems, the best model would be one that combines both chemical kinetics and mass transport. Bar-Tal et al. (1990), using a stirred-flow technique, showed that an instantaneous equilibrium ion exchange reaction combined with mass transport could be integrated analytically such that a pseudo-first-order model was obtained.

Higher ordered kinetic equations are often required when two or more reactants affect the reaction rate. Consider the reversible binary K–Ca exchange reaction:



where X is the charged surface, and k_a and k_d are adsorption and desorption rate coefficients, respectively. If one assumes that the cation-exchange reaction in Eq. [1] is an elementary reaction and diffusion is not the limiting factor, then the reaction rate, r , can be defined as follows (Tang and Sparks, 1993):

$$r = dC_K/2dt = -k_d [\text{K-X}]^2 C_{Ca} + k_a [\text{Ca-X}] C_K^2 \quad [2]$$

where C and $[\]$ denote concentration in the solution and exchanger phases, respectively, t is the time, and C_K and C_{Ca} are the K and Ca concentrations in the chamber solution, respectively. Recently Eq. [2] has been employed in a study of cation-exchange kinetics on montmorillonite using pressure-jump relaxation (Tang and Sparks, 1993). This equation has not been used in analysis of data obtained with the stirred-flow technique that requires a mathematical expression for the mass transport (Bar-Tal et al., 1990).

The objectives of this study were to: (i) develop a

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mathematical model of the kinetics of an elementary cation-exchange reaction combined with transport processes in a stirred-flow chamber and (ii) determine rate coefficients based on this model for K-Ca exchange on a vermiculite.

MATERIALS AND METHODS

Theoretical Considerations

At equilibrium, $r = 0$, and after rearranging Eq. [2], one finds the following:

$$C_{Ca} [K-X]^2 / ([Ca-X] C_K^2) = k_a/k_d = K' \quad [3]$$

where K' is the apparent equilibrium exchange constant derived kinetically. From Eq. [1], one can directly derive the thermodynamic exchange equilibrium constant, K_{ex} :

$$\{Ca\} \{K-X\}^2 / (\{Ca-X\} \{K\}^2) = K_{ex} \quad [4]$$

where $\{ \}$ denotes activity.

Using the Gaines and Thomas (1953) convention to describe K-Ca exchange and to calculate thermodynamic parameters, such as K and Ca K_{ex} and the exchanger-phase ion activity coefficients, for K and Ca , respectively,

$$K_{ex} = f_K^2 E_K^2 \gamma_{Ca} C_{Ca} / (f_{Ca} E_{Ca} \gamma_K^2 C_K^2) = K_C (f_K^2 / f_{Ca}) \quad [5]$$

where E is the equivalent fraction of K^+ and Ca^{+2} on the exchanger phase, f is the activity coefficient of the cation on the exchanger phase, γ is the activity coefficient of the cation in the solution, and K_C is the Gaines-Thomas selectivity coefficient. The activity coefficients of the solution ions were calculated using the Davies equation. Since the activity coefficient of the cation on the exchanger phase cannot be measured or calculated directly, K_{ex} is calculated by applying the Gibbs-Duhem equation in combination with Eq. [5] to obtain the following:

$$\ln K_{ex} = \int_0^{E_K} \ln K_C dE_K \quad [6]$$

The f_K and f_{Ca} values can be calculated as follows:

$$\ln f_{Ca} = E_K (\ln K_C - 1) - \int_0^{E_K} \ln K_C dE_K \quad [7a]$$

$$2 \ln f_K = (1 - E_K) (1 - \ln K_C) + \int_{E_K}^1 \ln K_C dE_K \quad [7b]$$

Similar thermodynamic analysis could be obtained by using the Vanselow convention (1932), since the two models are comparable and can be used to derive K_{ex} (Ogwada and Sparks, 1986a). In Eq. [2] and [3], concentration values are used, while in Eq. [4] and [5], activity values for the solution and exchanger phases are used. If the solution and the exchanger are not ideal solutions, then K' will be a coefficient that varies with the exchanger-phase composition like K_C , rather than a constant like K_{ex} . From Eq. [3], if K' varies, k_a and k_d also vary. Therefore, Eq. [2] was modified to include the following activities:

$$d[C_K]/dt = k_d f_K^2 E_K^2 a_{Ca} - k_a f_{Ca} E_{Ca} a_K^2 \quad [8]$$

where a is the activity of the cation in the solution. Bar-Tal et al. (1990) showed that transport processes must be included to properly analyze data obtained with the stirred-flow chamber so that kinetic rate coefficients could be obtained. The change in effluent concentration from the stirred-flow chamber is expressed by an equation of mass balance (Denbigh, 1944):

$$J C_{Kin} = J C_{Kout} + V_c dC_K/dt + M CEC dE_K/dt \quad [9]$$

where C_{Kin} and C_{Kout} are K concentrations of the influent and effluent solutions, respectively, J is the flow rate, V_c is the solution volume in the chamber, CEC is the cation-exchange capacity, and M is the mass of the adsorbent. Assuming a well-mixed system implies that $C_k = C_{kout}$; therefore, in the subsequent equations, C_{Kout} will be substituted by C_k . Skopp and McCallister (1986) presented an analytical solution for Eq. [9] using limited rate laws including first-order, Langmuir, and empirical fractional-order equations. Bar-Tal et al. (1990) used numerical solution of nonlinear ordinary differential equations to solve Eq. [9] combined with different nonlinear empirical kinetic equations. In our study, the mechanistic exchange model (Eq. [8]) combined with the above transport process (Eq. [9]) was solved numerically by an iteration method and the rate coefficients were fitted by the NLIN procedure (SAS Institute, 1988).

Equilibrium Study

For the calculation of K_{ex} (Eq. [6]), a numerical integration can be used by plotting $\ln K_C$ as a function of E_K and determining the area under the curve using the trapezoidal rule. But the solution of Eq. [7a] and [7b] requires quantitative information on the relationship between K_C and E_K and integration of $\ln K_C$ in the range of 0 to E_K and E_K to 1. Therefore, the data obtained from the equilibrium exchange study were used to fit an empirical polynomial to the natural logarithms of K_C :

$$\ln K_C = a_0 + a_1 E_K + a_2 E_K^2 \dots + a_n E_K^n \quad [10]$$

where A_0, \dots, A_n are the best-fitted empirical coefficients. A stepwise procedure (SAS Institute, 1988) was used to fit the coefficients of a_0 , a_1 , and a_2 for a second-order polynomial, after which the activity coefficients, f_K and f_{Ca} , for any value of E_K could be calculated using Eq. [7a] and [7b].

Kinetic Study

The NLIN procedure of SAS (SAS Institute, 1988) was used to find the best fit of k_a to the numerical solution of Eq. [8] in combination with Eq. [9] (Appendix 1). The solution for k_a involved the calculation of f_K and f_{Ca} by means of Eq. [7a] and [7b]. When the predicted and observed results were compared, the concentration in the chamber was calculated as the mean value between two short time increments according to Schnabel and Richie (1987) and Eick et al. (1990). The desorption rate coefficient, k_d , was calculated as the ratio between k_a and K_{ex} , both k_a and k_d could be fitted by the NLIN procedure, but the correlation between them was very close to 1.0; therefore, the obtained coefficients were insignificant.

An additional mass balance equation was used for stopped-flow and batch experiments; Eq. [9] was replaced with the following:

$$V_c dC_K/dt = M CEC dE_K/dt \quad [11]$$

Experimental Procedures

Equilibrium Potassium-Calcium Exchange Isotherm Determination

A vermiculite clay from Santa Ollala, Spain, was used in this study. Prior to the experiments, the clay was fractionated, using a gravimetric method (Jackson, 1969), to an equivalent diameter of 1 to 2 μm . The CEC of the vermiculite, as

determined by saturation with NaOAc and extraction with a 0.5 M MgOAc, was 172 cmol_c kg⁻¹.

Triplicate 1-g samples of the clays were equilibrated with 0.5 M solutions having a large range of K/Ca ratios. Following leaching three times with 30 mL of the 0.5 M solutions in the centrifuge, the clay was leached three more times with 30 mL of 0.01 M solutions of the same ionic ratio. A constant temperature of 294 ± 1 K was maintained throughout the experiment. The supernatant of the final 0.01 M leaching step was analyzed for Ca by atomic absorption spectrophotometry and for K by flame photometry.

The clay samples were then washed with 60 to 95% ethanol solution until free of electrolytes, as determined by conductivity measurements. Exchangeable K and Ca were extracted from the clay samples with three 30-mL batches of 0.5 M MgOAc solution with K and Ca in the displaced solutions analyzed as before. Magnesium acetate was used rather than NH₄OAc to avoid the release of fixed K⁺ from the vermiculite.

Kinetic Studies

The stirred-flow chamber, first described by Carski and Sparks (1985) and later modified by Seyfried et al. (1989), and the procedure established by Eick et al. (1990) were followed with these modifications: An amount of 0.20 ± 0.01 g of dried clay was loaded into the reaction chamber and a volume of 6.5 ± 0.05 mL of 0.005 M CaCl₂ was added. A peristaltic pump was used to maintain various flow rates ranging from 0.5 to 4 mL min⁻¹ of 0.01 M KCl. The total concentration of Cl⁻ in the chamber, C_T, was kept constant throughout each run. Time zero was defined as the moment of entry of the first drop of effluent into the first tube of the fraction collector. Potassium and Ca in the effluent was analyzed as before. All experiments were performed in duplicate.

RESULTS AND DISCUSSION

Equilibrium Study

The entire range of K/Ca solution equivalent fraction ratios and E_K ranged from 0 to 0.90 of the total CEC (Table 1). The calculated K_c was not constant as E_K varied, indicating that the clay surface was not an ideal solid solution. When ln K_c was plotted as a function of E_K (Fig. 1), the selectivity coefficient increased as E_K increased from 0 to 0.5 and then decreased with a further increase in E_K. These observations can be related to different K adsorption sites on the clay, which could cause selectivity alterations during the exchange reaction (Goulding, 1983; Ogwada and Sparks, 1986a). A second-order polynomial can describe the change in ln K_c as a function of E_K (Eq. [10]), with the following values for the coefficients: a₀ = 3.223, a₁ = 12.245, a₂ = -11.149,

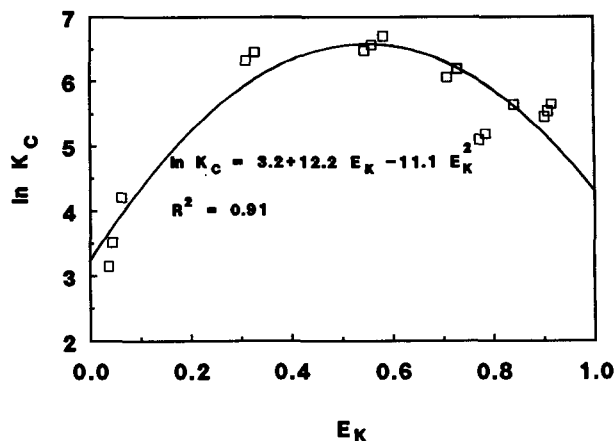


Fig. 1. Relationship between ln(K_c) for K-Ca exchange and the equivalent fraction of K⁺ on the exchanger phase, E_K, on a vermiculite (K_c is the Gaines-Thomas selectivity coefficient). The curve is the following second-order polynomial fitted by the STEPWISE procedure (SAS Institute, 1988): ln K_c = 3.22 + 12.245E_K - 11.149E_K² (R² = 0.91).

and R² = 0.91. Solution of Eq. [6] with [10] gave the value of K_{ex} as 754.6 L mol⁻¹.

Kinetic Study

Bar-Tal et al. (1990) suggested a simple but necessary set of tests for determining whether a reaction monitored by the stirred-flow technique is instantaneous or kinetically controlled. The first test involves stopping the flow for a certain period of time. The assumption of this test is that, under nonequilibrium conditions, stopping the flow for a time sufficient for 50% of the reaction to be completed would enable the system to attain equilibrium, which should result in a drop in effluent concentration (Seyfried et al., 1989). If the reaction is instantaneous, no such drop in the effluent concentration would be observed (Bar-Tal et al., 1990). The results of stopping the flow for 60 min (from 5 min after the start of the run) and then restarting it demonstrated clearly that a kinetic process controls the change in effluent concentration (Fig. 2).

The curve fitted by the NLIN procedure using the numerical solution of Eq. [9] (or of Eq. [11] while flow was stopped) with Eq. [8], satisfactorily described the observed results, including the drop in the concentration while the flow was stopped (Fig. 2). The values of k_a and k_d were 123.7 L² mol⁻² min⁻¹ and 0.164 min⁻¹, respectively.

Table 1. Exchangeable K and Ca on a vermiculite as a function of the solution composition in a batch equilibrium experiment; suspension of 0.4 g clay with 30 cm⁻³ of 0.01 M Cl⁻ solutions.†

C _K	C _{Ca}	S _K	S _{Ca}	E _K	E _{Ca}	K _c
mmol _c L ⁻¹		cmol kg ⁻¹		L mol ⁻¹		
0.5	9.5	8 ± 1.8	164 ± 1.8	0.05 ± 0.01	0.95 ± 0.01	41 ± 19
1.1	8.9	55 ± 1.4	116 ± 1.4	0.32 ± 0.01	0.68 ± 0.01	610 ± 37
2.0	8.0	97 ± 2.7	75 ± 2.7	0.56 ± 0.02	0.44 ± 0.02	725 ± 66
3.6	6.4	124 ± 1.7	48 ± 1.7	0.72 ± 0.01	0.28 ± 0.01	469 ± 28
5.8	4.2	138 ± 5.3	34 ± 5.3	0.80 ± 0.03	0.20 ± 0.03	208 ± 52
7.2	2.8	157 ± 1.0	15 ± 1.0	0.91 ± 0.01	0.09 ± 0.01	257 ± 20

† C_K = K concentration in the chamber solution; C_{Ca} = Ca concentration in the chamber solution; S_K and S_{Ca} = adsorbed K and Ca, respectively; E_K and E_{Ca} = equivalent fraction of K⁺ and Ca²⁺ on the exchanger phase, respectively; K_c = the Gaines-Thomas selectivity coefficient.

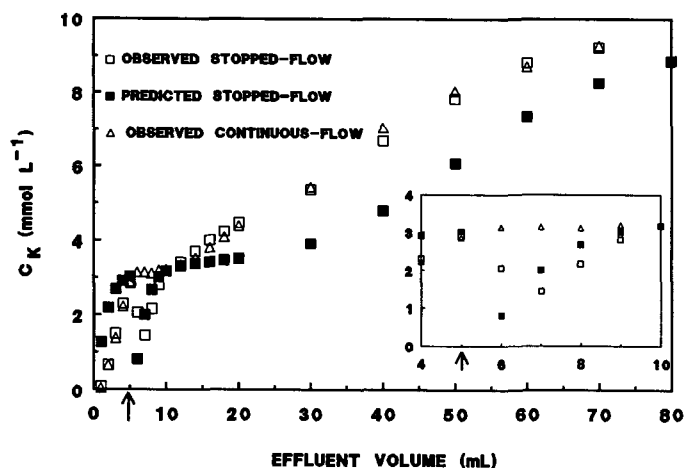


Fig. 2. The effect of stopping the flow on the effluent concentration as a function of effluent volume; the arrow indicates when flow was stopped for 60 min; the predicted points are the numerical solution of the transport equation (Eq. [9]) combined with the kinetic equation (Eq. [8]) containing rate coefficients estimated by the NLIN procedure (SAS Institute, 1988), which are given in Table 2 (C_K is K concentration in the chamber solution).

Use of more than one flow rate provides another way to distinguish experimentally between equilibrium and nonequilibrium conditions (Bar-Tal et al., 1990). Figure 3 shows the results obtained with various flow rates: 0.33, 1, and 2 mL min⁻¹. Curves of the observed effluent concentrations vs. effluent volume (Fig. 3a) for the different flow rates did not overlap, as would be observed for an instantaneous reaction (Bar-Tal et al., 1990, Fig. 2). These results are in agreement with those obtained from the same test, using Llano vermiculite (Eick et al., 1990). The curves of C_K as a function of time fitted by the NLIN procedure for the different flow rates, using the numerical solution of Eq. [9] with Eq. [8], are presented in Fig. 3b. The effect of the flow rate on C_K is predicted satisfactorily. However, for each flow rate, the model overestimated C_K in the first minutes after flow began and underestimated C_K when C_K approached its maximum value, 10 mM.

The values of k_a fitted by the NLIN procedure are presented in Table 2. Stopping the flow had no effect on the value of the apparent rate coefficients. The average estimated k_a was 112.6 L² mol⁻² min⁻¹ with a range of 35.7 to 185.5 L² mol⁻² min⁻¹. Tang and Sparks (1993) determined a k_a of 25 920 L² mol⁻² min⁻¹ for K-Ca exchange on montmorillonite using a pressure jump relaxation technique, indicating a much faster reaction rate for montmorillonite than for vermiculite in agreement with Eick et al. (1990). The estimated k_a increased from 83.9 to 185.5 L² mol⁻² min⁻¹ as the flow rate increased from 0.33 to 2.0 mL min⁻¹. The observed effect of the flow rate on the estimated k_a and the deviations of the predicted curves from the observed data indicate that an apparent rate coefficient was being measured, rather than an actual rate constant for K-Ca exchange on the clay (Sparks, 1989). The increase in k_a as a function of flow rate in the range of 0.33 to 2.0 mL min⁻¹ is probably due to a diffusion effect. These results indicate that if one aims to apply the rate coefficients for simulation of ion

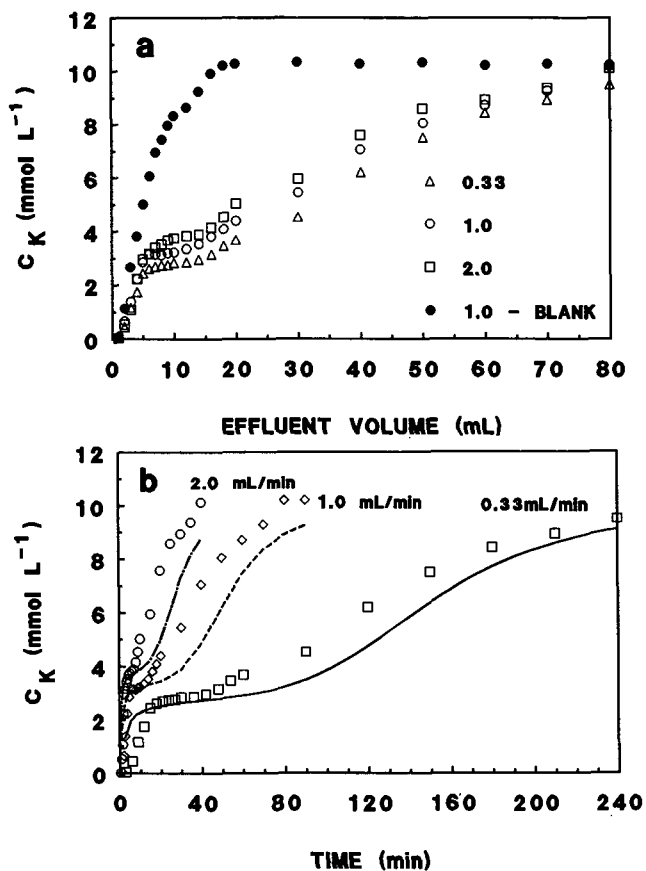


Fig. 3. The effect of flow rate on the effluent concentration as a function of (a) the effluent volume and (b) time; the curves are the numerical solutions of the transport equation (Eq. [9]) combined with the kinetic equation (Eq. [8]), with rate coefficients estimated by the NLIN procedure (SAS Institute, 1988), which are given in Table 2 (C_K is K concentration in the chamber solution).

transport in field, the study with a stirred-flow chamber should employ a flow rate similar to that in the field.

A direct comparison of the values of the apparent rate coefficients obtained in this study with published data based on the flow method is meaningless, because the kinetic model used in this study (Eq. [8]) has not been used in previous studies of K-Ca exchange on clays. Therefore, we simulated a theoretical batch experiment for K-Ca exchange on the same clay using rate coefficients obtained with the stirred-flow technique. Then,

Table 2. Apparent adsorption rate coefficients (k_a) for K-Ca exchange on vermiculite, estimated by the NLIN procedure (SAS Institute, 1988) as affected by flow rates of 0.33, 1.0, and 2.0 mL min⁻¹ and stopping flow. The apparent desorption rate coefficient (k_d) was calculated as the ratio between k_a and K_{eq} .

	Flow rate, mL min ⁻¹			
	0.33	1.0	1.0†	2.0
K_a , L ² mol ⁻² min ⁻¹	83.9	134.1	123.7	185.5
k_d , min ⁻¹	0.11	0.18	0.16	0.25
Standard error of k_a	19.0	34.4	38.0	54.0
<i>t</i> -test	4.4***	3.9**	3.3**	3.4**
Standard error of the estimate, mM	0.78	1.05	1.08	1.29

** , *** Significant at $P = 0.01$ and 0.001 , respectively.

† Stopped flow test.

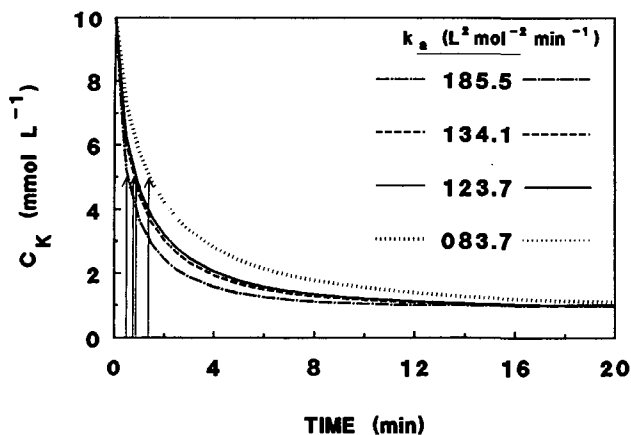


Fig. 4. A simulation of a theoretical batch experiment describing the change of K concentration in the chamber solution, C_K as a function of time, using the mass balance (Eq. [11]) and kinetics (Eq. [8]) equations, containing the rate coefficients given in Table 2. The reaction half-time ($t_{1/2}$, analogous to the half-life used to describe radioactive decay) for the curves are indicated by arrows (k_a = K adsorption rate coefficients).

the reaction half-time ($t_{1/2}$, analogous to the half-life used to describe radioactive decay) in the simulation (Fig. 4) was compared with published data based on batch techniques. The same ratio of solution to clay as in the stirred-flow chamber was used for the simulation of this theoretical experiment (30 mL/1 g). Initial solution concentrations of K and Ca in the simulation were the same as those used in the stirred-flow chamber experiment ($C_K = 0.01 M$ and $C_{Ca} = 0.0 M$). In the simulation of the batch experiment, the time to approach equilibrium ranged from 4 to 15 min, depending on the values of the rate coefficients (k_a and k_d), which were obtained from the stirred-flow chamber experiments. The initial change in the concentration of the simulated solution was very rapid, and the half-time ($t_{1/2}$) of the reaction ranged from 0.5 to 1.5 min as k_a varied from 185.5 to 83.9 $L^2 mol^{-2} min^{-1}$ (Fig. 4). These values of $t_{1/2}$ are in agreement with published results, using batch techniques. Elkhatib and Hern (1988) reported that >50% of exchangeable K on the clay fraction of various soils was displaced within 5 min. Zamoski and Burau (1978) found that the time required for complete K adsorption on colloidal MnO_2 was <2.5 min. In studying the effect of kinetic methodology on K adsorption rate coefficients, Ogwada and Sparks (1986b) found that the $t_{1/2}$ for K adsorption on a Llano vermiculite ranged from 0.32 min with a vortex-batch technique to 5.4 min with a stirred-batch method. Our study yields a $t_{1/2}$ that is in agreement with those measured using batch methods, and it avoids the difficulty of rapid separation of the solid phase from the liquid phase, which is one of the main problems with batch techniques.

The rate of K adsorption, according to the kinetic model used in this study (Eq. [8]), was dependent on both adsorbed and solution ion activities. In previously published works, a first-order reaction, considering only the adsorbed ion concentration, has been used successfully to describe K-Ca exchange on clays and soils (Carski and Sparks, 1985; Jardine and Sparks, 1984;

Ogwada and Sparks, 1986b). The kinetic model used in our study was derived from the same chemical equation as the thermodynamic exchange reaction (Eq. [1]). The Gaines and Thomas convention or the Vanselow model, which are well-accepted models for describing ion exchange on clays, can be used in our approach.

CONCLUSIONS

A mechanistic kinetic model derived from a reversible binary K-Ca exchange reaction can be used to determine rate coefficients for ion exchange on vermiculite. The flow rate affected the obtained rate coefficient. Therefore, for prediction of K transport in soil in the field, the flow rate in the stirred-flow chamber should be similar to that in the field. The exchange rate of K-Ca on vermiculite is not negligible like that on montmorillonite and should be taken into consideration in prediction of K transport in soil.

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APPENDIX 1

* INPUT;
 DATA INFLOW; INFILE IN;
 INPUT TIME C_{Kout} C_{Kin} C_T J CEC M V_C K_{eq} ;
 MCEC = M*CEC; $JV = J/V_C$; $INFL = JV C_{Kin}$;
 * NLIN;
 PROC NLIN DATA = INFLOW METHOD = DUD;
 PARAMETERS $K_a = 100$;
 * INITIAL CONDITIONS;
 $C_K = 0$; $S_K = 0$;
 * NUMERICAL SOLUTION;
 $dt = 0.1$;
 $t = dt$ to TIME BY dt ;
 OUTFL = $JV C_K$;
 $E_K = S_K V_C / MCEC$;

* CALCULATING THE ACTIVITY COEFFICIENTS OF THE ADSORBED CATIONS

$\ln(K_c) = a_0 + a_1 E_K + a_2 E_K^2$;
 Integral $[\ln(K_c)] = a_0 E_K + (1/2)a_1 E_K^2 + (1/3)a_2 E_K^3$;
 $2\ln(f_K) = (1 - E_K)[1 - \ln(K_c)] + \ln(K_{eq}) - \text{Integral} [\ln(K_c)]$;
 $\ln(f_{Ca}) = E_K \ln(K_c - 1) - \text{Integral} [\ln(K_c)]$;
 $E_{Ca} = 1 - E_K$;
 $f_K^2 = \exp[2 \ln(f_K)]$;
 $f_{Ca} = \exp[\ln(f_{Ca})]$;

* CALCULATING IONIC STRENGTH AND SOLUTION ION ACTIVITY COEFFICIENT-DAVIES EQUATION;

$I = 0.5[C_K + 4(C_T - C_K)/2]$;
 $SQI = I^{0.5}$;
 $\gamma_K = \exp[-0.506[SQI/(1+SQI)] - 0.3I]$;
 $\gamma_{Ca} = \exp\{-0.506 \times 4[SQI/(1+SQI)] - 0.3 I\}$

* KINETICS CALCULATIONS;

$Q_{ads} = k_a C_K^2 \gamma_K^2 (1 - E_K) f_{Ca}$;
 $Q_{des} = (k_d / K_{eq}) E_K^2 f_K^2 \gamma_{Ca} (C_T/2 - C_K/2)$;

* DIFFERENTIAL EQUATIONS:

$S_K = S_K + (Q_{ads} - Q_{des})dt$;
 $C_K = C_K + (Q_{des} + INFL - Q_{ads} - OUTFL)dt$;
 END;

* COMPARING OBSERVED WITH PREDICTED;
 MODEL $C_{Kout} = C_K$;