

# DIVISION S-2—SOIL CHEMISTRY

## Cation-Exchange Kinetics on Montmorillonite Using Pressure-Jump Relaxation

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### ABSTRACT

Batch and flow methods are usually not suitable for measuring kinetics of ion-exchange reactions on soils and soil constituents. These reactions are usually very fast. Thus, a rapid kinetic method must be employed. A pressure-jump relaxation technique was used in this study to investigate the kinetics of Ca-Na and Ca-K exchange on montmorillonite. Single relaxations were observed in both systems. Forward ( $k_1$ ) and backward ( $k_{-1}$ ) rate constants for the cation-exchange reactions were determined and were greater for Ca-Na exchange ( $k_1 = 953 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ ,  $k_{-1} = 643 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ ) than those for Ca-K exchange ( $k_1 = 385 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ ,  $k_{-1} = 432 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ ). The values of the exchange equilibrium constant obtained kinetically were in good agreement with those obtained statically. The exchange isotherms from the static studies showed a preference of K over Ca on montmorillonite, but no preference was observed in the Ca-Na exchange system.

A VOLUMINOUS AMOUNT of research has been conducted on cation exchange on soils and soil constituents. Since the early work of Way (1850), who studied  $\text{NH}_4$ -Ca exchange on soils, it has been generally assumed that exchange processes on soils and soil colloids are rapid, often instantaneous. This may explain in part why most studies on cation exchange have dealt with equilibrium aspects, and only recently have studies appeared on the kinetics and mechanisms of exchange phenomena (Sparks, 1989). Another reason that the kinetics of cation exchange have not been extensively investigated is the lack of appropriate techniques to measure rapid reaction rates. With most batch and flow techniques, one cannot measure the kinetics of chemical reactions that are faster than about 15 s (Sparks, 1989). Moreover, traditional batch and flow methods primarily measure transport-controlled reactions and, thus, apparent rate parameters are determined. Consequently, chemical kinetics are not determined.

Cation-exchange reactions on some clay minerals are particularly rapid, usually occurring within minutes or seconds. Malcom and Kennedy (1969), using a specific ion electrode technique, found that >70% of Ba-K exchange on kaolinite, illite, and montmorillonite occurred in 3 s. Sparks and Jardine (1984), using a continuous flow method, found that adsorption of K on kaolinite and montmorillonite was completed in 40 and 120 min, respectively. With the technique of Sparks and Jardine (1984), a combination of chemical exchange and diffusion phenomena were being measured.

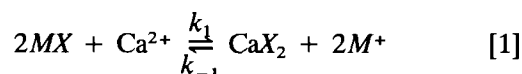
Pressure-jump relaxation is a useful technique for

measuring rapid reaction rates on soil constituents (Sparks, 1989; Sparks and Zhang, 1991). This technique is based on the principle that chemical equilibrium is pressure dependent. The pressure pulse created by an autoclave perturbs a system from equilibrium by a small amount, and then the system decays back to the original equilibrium. The time required for the decay process (from the nonequilibrium to equilibrium state) is referred to as the *relaxation time* ( $\tau$ ), which is related to the specific rates of the elementary reactions involved. With the pressure-jump method, one can measure the chemical kinetics of reactions in millisecond or microsecond time scales. Pressure-jump, as well as other chemical relaxation techniques, have been used to study cation adsorption-desorption kinetics (Hachiya et al., 1979; Negishi et al., 1984; Hayes and Leckie, 1986) and, recently, to investigate anion adsorption-desorption on goethite (Zhang and Sparks, 1989, 1990a, b). In most of these studies, reactions on the oxide-water interface were investigated. No one has used pressure-jump relaxation to study cation-exchange kinetics on clay surfaces. Accordingly, the objective of this study was to investigate the rates of Ca-Na and Ca-K exchange on montmorillonite using pressure-jump relaxation, and to compare the equilibrium constants calculated via kinetics with those determined using a traditional thermodynamic approach.

### MATERIALS AND METHODS

#### Theoretical Considerations

For the Ca-Na and Ca-K exchange reaction,



where  $M = \text{Na or K}$ ,  $X = \text{montmorillonite}$ , the thermodynamic exchange equilibrium constant  $K$  is given by

$$K = \frac{\{M\}^2\{\text{CaX}_2\}}{\{MX\}^2\{\text{Ca}\}} = \frac{f_{\text{Ca}}N_{\text{Ca}}\gamma_{\text{M}}^2m_{\text{M}}^2}{f_{\text{M}}^2N_{\text{M}}^2\gamma_{\text{Ca}}m_{\text{Ca}}} = \frac{f_{\text{Ca}}k_v}{f_{\text{M}}^2} \quad [2]$$

where

- $\{ \}$  = denotes activity
- $f$  = activity coefficient of the cation on the exchanger phase
- $N$  = mole fraction of the cation on the exchanger phase
- $\gamma$  = activity coefficient of the cation in the solution phase
- $m$  = molality of the cation in the solution phase
- $k_v$  = Vanselow selectivity coefficient

(Babcock, 1963; Sposito, 1981; Jardine and Sparks, 1984). Applying the Gibbs-Duhem equation to this system and combining with Eq. [2], one obtains the following, using a mole

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Published in Soil Sci. Soc. Am. J. 57:42-46 (1993).

fraction of unity as the standard state for adsorbed ions (Argersinger et al., 1950):

$$\ln K = \int_0^1 \ln k_v d\bar{E}_{Ca} \quad [3]$$

where  $\bar{E}_{Ca}$  is the equivalent fraction of Ca on the exchanger phase, which is,

$$\bar{E}_{Ca} = \frac{2N_{Ca}}{2N_{Ca} + N_M} \quad [4]$$

The exchange equilibrium constant  $K$  can be determined statically by numerical integration if one plots  $\ln k_v$  as a function of  $\bar{E}_{Ca}$  and determines the area under the curve using the trapezoidal rule.

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 can be defined as

$$\begin{aligned} r &= -\frac{d[MX]}{2dt} = -\frac{d[Ca]}{dt} = \frac{d[CaX_2]}{dt} = \frac{d[M]}{2dt} \\ &= -k_1[MX]^2[Ca] + k_{-1}[CaX_2][M]^2 \end{aligned} \quad [5]$$

where  $[ ]$  denotes concentration. At equilibrium,  $r = 0$ , and Eq. [5] becomes

$$r = -k_1[\overline{MX}]^2[\overline{Ca}] + k_{-1}[\overline{CaX_2}][\overline{M}]^2 = 0 \quad [6]$$

where the overbar denotes the equilibrium concentration. Relating this to the law of mass action, one finds,

$$\frac{[\overline{CaX_2}][\overline{M}]^2}{[\overline{MX}]^2[\overline{Ca}]} = \frac{k_1}{k_{-1}} = K' \quad [7]$$

where  $K'$  is the apparent equilibrium constant derived kinetically. Following a small perturbation, e.g., a pressure-jump, equilibrium concentrations are shifted by a small amount,  $x$ . According to the law of mass conservation, the time-dependent concentrations are,

$$\begin{aligned} [MX] &= [\overline{MX}] + 2x \\ [Ca] &= [\overline{Ca}] + x \\ [CaX_2] &= [\overline{CaX_2}] - x \\ [M] &= [\overline{M}] - 2x \end{aligned} \quad [8]$$

Substituting these into Eq. [5], combining with Eq. [6], and assuming that only a small perturbation occurred, any higher order of  $x$  becomes negligibly small. Therefore, one obtains

$$\begin{aligned} \frac{dx}{dt} &= -\{k_1([\overline{MX}]^2 + 4[\overline{MX}][\overline{Ca}]) \\ &\quad + k_{-1}([\overline{M}]^2 + 4[\overline{CaX_2}][\overline{M}])\}x \end{aligned} \quad [9]$$

From the definition of relaxation time,  $\tau$  (Bernasconi, 1976),

$$\frac{dx}{dt} = -\frac{1}{\tau}x \quad [10]$$

the reciprocal relaxation time can be written as

$$\begin{aligned} \tau^{-1} &= k_1([\overline{MX}]^2 + 4[\overline{MX}][\overline{Ca}]) \\ &\quad + k_{-1}([\overline{M}]^2 + 4[\overline{CaX_2}][\overline{M}]) \end{aligned} \quad [11]$$

Rearranging Eq. [11], one obtains

$$\frac{\tau^{-1}}{[\overline{M}]^2 + 4[\overline{CaX_2}][\overline{M}]} = k_1 \frac{[\overline{MX}]^2 + 4[\overline{MX}][\overline{Ca}]}{[\overline{M}]^2 + 4[\overline{CaX_2}][\overline{M}]} + k_{-1} \quad [12]$$

By plotting Eq. [12], the mechanism proposed in Eq. [1] can be tested. If the mechanism is correct, a plot of Eq. [12] gives a straight line with a slope of  $k_1$  and an intercept of  $k_{-1}$ . The apparent equilibrium constant  $K'$  can be determined kinetically, using Eq. [7].

## Experimental Procedures

### Sample Preparation

Wyoming montmorillonite, SWy-1 (Source Clays Repository, Clay Minerals Society, Univ. of Missouri) was used in this study. Homoionic Na- and K-montmorillonite were prepared using the following procedures. One hundred grams of clay were dispersed in 4 L of deionized water overnight, and the <2- $\mu$ m fraction was separated by centrifugation. This suspension was equilibrated with 1.5 M NaCl or KCl solution. Then, 180 mL of 0.05 M HCl solution was added to remove the trace amount of  $CaCO_3$  from the clay. The suspension was heated to 313 K in a water bath to accelerate the reaction. Thereafter, the suspension was centrifuged and the supernatant was decanted. The clay was mixed with 1.5 M Cl salt solutions again, and the supernatant was decanted following centrifugation. This process was repeated three times. The clay was then dialyzed in deionized water to remove excess salt. The dialysis process was terminated when a conductivity test showed that the concentration of salt in the water was <10<sup>-4</sup> M. The final pH values for Na- and K-montmorillonite were 6.75 and 6.82, respectively. The clay was then freeze-dried.

### Static Studies

The Na- or K-saturated montmorillonite, in duplicate, was equilibrated with a set of  $CaCl_2$ -NaCl or  $CaCl_2$ -KCl solutions with an equivalent fraction of 0 to 1 and a constant ionic strength of 0.01 M. The solid concentration was 10.2 g L<sup>-1</sup>. The clay suspensions were shaken on a reciprocating shaker at 296 K for 2 h, at which point equilibrium was attained. The suspension was then centrifuged using a refrigerated super-speed centrifuge (Sorvall RC-5B, Du Pont Instruments, Wilmington, DE) at 7649  $\times$  g for 20 min, and the K, Ca, Na, and Mg concentrations in the supernatant were determined using a Perkin-Elmer 5000 atomic absorption spectrophotometer (Perkin-Elmer Co., Norwalk, CT). The pH of the suspension for both Na-Ca and K-Ca clay systems was between 6.78 and 6.82. There was no significant change in the suspension pH after equilibrium. The purpose of measuring Mg and K concentrations in the Ca-Na clay system or Mg and Na concentrations in the Ca-K clay system was to assess if dissolution of the montmorillonite occurred. The clay was then washed with 80% ethanol three times to remove excess electrolytes. Exchangeable cations were extracted from the clay by shaking with 1.0 M  $NH_4OAc$ , centrifuging, and collecting the supernatant. This process was repeated three times. Exchangeable K, Ca, Na, and Mg in the supernatant were analyzed as before.

### Kinetic Studies

The Na- or K-saturated montmorillonite was equilibrated with  $CaCl_2$ -NaCl or  $CaCl_2$ -KCl solutions on a reciprocating

shaker at 296 K for 2 h. The suspension was divided into two portions. One portion of the suspension was analyzed kinetically by pressure-jump relaxation immediately after shaking. The other portion of the suspension was centrifuged, and the supernatant analyzed for Ca, Na, K, and Mg concentrations as before.

Relaxation times ( $\tau$  values) were measured for both the Ca-Na and Ca-K montmorillonite suspensions at five different Ca concentrations, a constant ionic strength of 0.01 M, and a constant temperature of 296 K, using a Dia-Log pressure-jump apparatus (Dia-RPC, Dia-log Co., distributed by Inrad Interactive Radiation Inc., Northvale, NJ) with a conductivity detector (DIA-RPM, Dia-log CO.). The solid concentration was 10.2 g L<sup>-1</sup>. To ascertain that the observed relaxations were caused by cation-exchange reactions on the montmorillonite surface, the following were also examined by pressure-jump relaxation: Na-clay, K-clay, and Ca-clay suspensions, and the supernatant solutions of the Ca-Na and Ca-K clay systems.

During the pressure-jump relaxation measurement, 13.5 MPa of pressure was generated by an autoclave on two conductivity cells, one sample cell containing the cations and clay suspension, and one reference cell containing the supernatant of the sample suspension. Then the pressure was released within 70  $\mu$ s by bursting a brass membrane of 0.05-mm thickness. The reaction system relaxed from the nonequilibrium state back to the original equilibrium state. A digitizer was triggered and the change in conductivity of the suspension during the relaxation process was measured. Since the reference cell compensated for the physical effects, i.e., temperature and mechanical disturbances, the change in the conductivity was only due to the change in concentration of the ions involved in the exchange reaction. The signals were then converted and sent to a microcomputer for analysis. The results of the relaxation could be read from the computer printout and displayed on an oscilloscope. More details about the pressure-jump relaxation apparatus are provided in Zhang and Sparks (1989).

## RESULTS AND DISCUSSION

### Static Studies

The dissolution of montmorillonite during the exchange studies was insignificant. The concentrations of

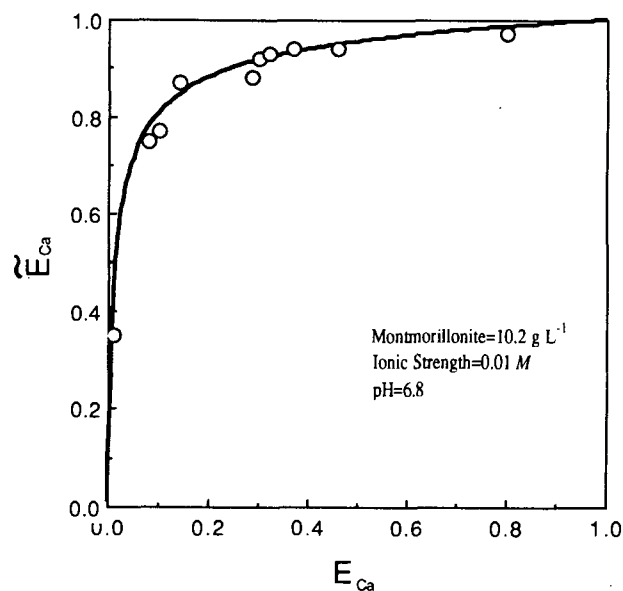


Fig. 1. Isotherm for Ca-Na exchange on montmorillonite, where  $E_{Ca}$  and  $E_{Ca}$  represent the equivalent fractions of Ca on the solution and exchanger phases, respectively. The solid line represents the theoretical nonpreference curve and the points are experimental.

Mg and K in the Ca-Na clay system, and Mg and Na in the Ca-K clay systems were negligible. The Ca-Na and Ca-K exchange isotherms for montmorillonite are shown in Fig. 1 and 2, respectively.

To determine which cation is preferred over the other in the Ca-K or Ca-Na exchange systems, one can calculate and plot the thermodynamic nonpreference isotherm for constant ionic strength according to the following equation,

$$\bar{E}_{Ca} = 1 - \left\{ 1 + \frac{1}{\Gamma I} \left[ \frac{3}{(1 - E_{Ca})^2} - \frac{4}{(1 - E_{Ca})} + 1 \right] \right\}^{-1/2} \quad [13]$$

where  $I$  = the ionic strength of the solution

$\bar{E}_{Ca}$  = equivalent fraction of Ca on the exchanger phase

$E_{Ca}$  = equivalent fraction of Ca in the solution phase

$$\Gamma = \frac{\gamma_M^2}{\gamma_{Ca}} \quad [14]$$

Equation [13] is based on Sposito (1981, Ch. 5, Eq. [5.30b]). However, 3 and 4 in the equation of Sposito (1981) were misplaced. As shown in Fig. 1, there was no significant preference of Na over Ca on montmorillonite. This agrees with earlier published data for Ca-Na exchange on montmorillonite (Shainberg et al., 1980; Sposito et al., 1983).

Figure 2 shows the isotherm for Ca-K exchange on montmorillonite. The experimentally observed points lie below the theoretical nonpreference curve, indicating a preference of K over Ca. Similar results have been observed by several other researchers, who showed a negative free energy for Ca→K exchange on montmorillonite

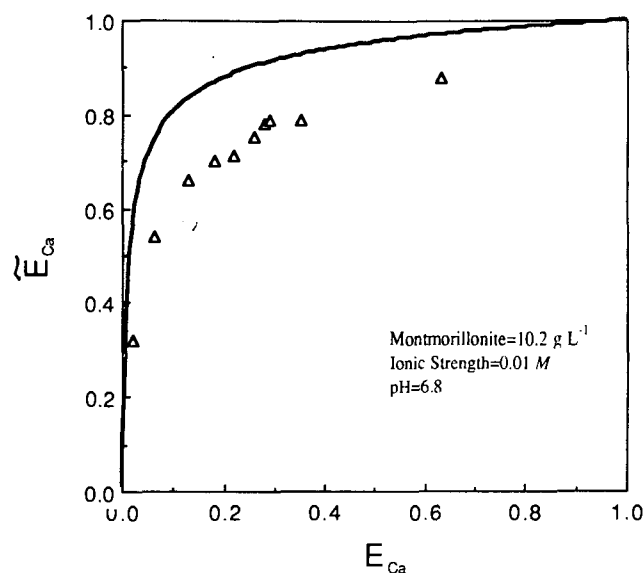


Fig. 2. Isotherm for Ca-K exchange on montmorillonite, where  $E_{Ca}$  and  $E_{Ca}$  represent the equivalent fractions of Ca on the solution and exchanger phases, respectively. The solid line represents the theoretical nonpreference curve and the points are experimental.

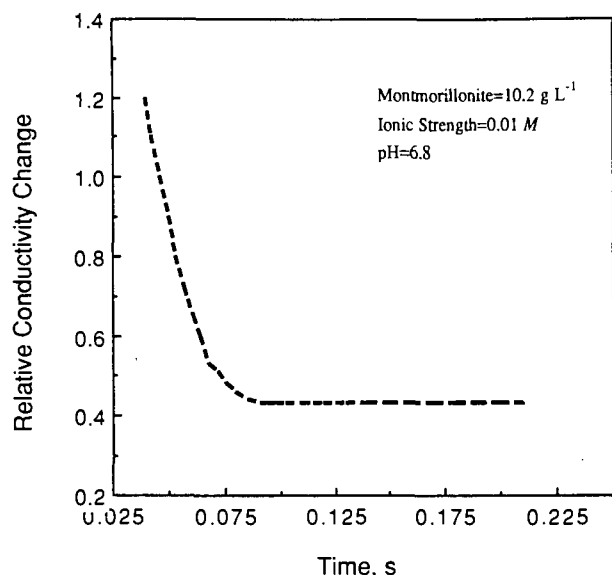


Fig. 3. Typical pressure-jump relaxation curve for Ca-Na exchange on montmorillonite showing relative change in conductivity vs. time.

(Hutcheon, 1966; Jensen, 1973; Talibudeen and Goulding, 1983). The selectivity of K over Ca on montmorillonite has been ascribed to the low hydration number and polarizability of K (Goulding, 1986) and the mica and hydrous mica character of montmorillonite (Talibudeen and Goulding, 1983). The contribution of mica and hydrous mica interlayers was obtained from measurements of the differential enthalpy of K-Ca exchange on montmorillonite by Talibudeen and Goulding (1983). Eberl et al. (1986) found that smectite could fix K and produce illite-smectite mixed-layer structures as it was subjected to wetting and drying cycles. Numerous authors have found a preference for K over Ca on minerals such as vermiculite, illite, and kaolinite. (Jensen, 1973; Udo, 1978; Levy et al., 1988; Thellier and Sposito, 1988). The high selectivity of K on mica and vermiculite is due to its size. Potassium can enter the interlayer of vermiculite, resulting in an interlayer collapse.

### Kinetic Studies

A typical relaxation curve was observed for Ca-Na exchange on montmorillonite with a single relaxation. The direction of the relaxation signals indicated a decrease in the relative change in conductivity of the suspension during relaxation (Fig. 3). The semilog plot of the relaxation curve resulted in a straight line. The observed single relaxation curve indicated that only one reaction mechanism for Ca-Na exchange was operational. Although not shown, a similar single relaxation curve was observed for Ca-K exchange on montmorillonite.

The dependence of  $\tau^{-1}$  on the equilibrium concentration of Ca<sup>2+</sup> for Ca-Na and Ca-K exchange is shown in Fig. 4. The  $\tau^{-1}$  values increased linearly with increasing Ca<sup>2+</sup> concentration in both exchange systems, indicating that the rate at which equilibrium is reached increases with increasing [Ca<sup>2+</sup>] in the system.

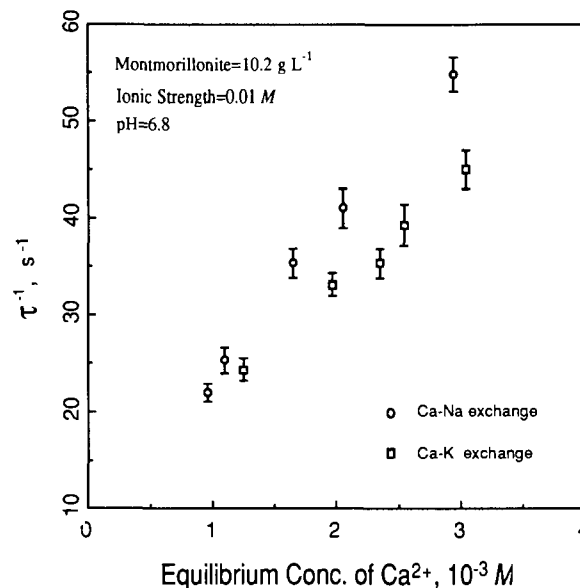


Fig. 4. Relationship between equilibrium Ca<sup>2+</sup> concentration in solution and reciprocal relaxation times ( $\tau^{-1}$ ) for Ca-Na and Ca-K exchange on montmorillonite.

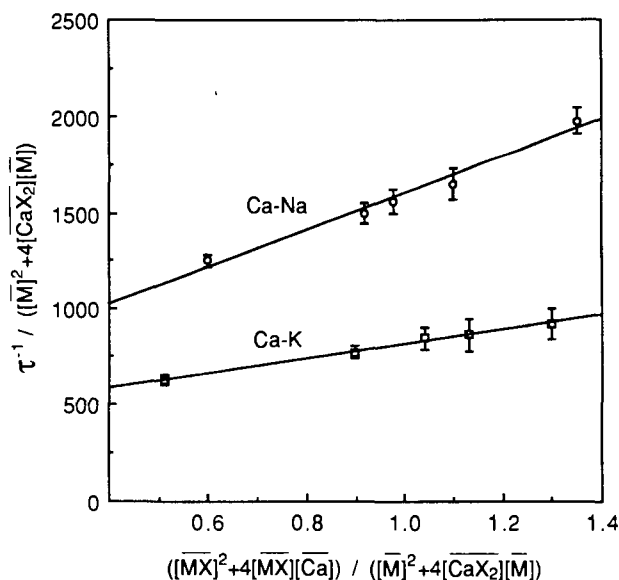


Fig. 5. Plots of  $\tau^{-1}$  (reciprocal relaxation times)/ $([M]^2 + 4[CaX_2][M])$  vs.  $([MX]^2 + 4[MX][Ca]) / ([M]^2 + 4[CaX_2][M])$  where  $M = \text{Na or K}$ , and  $X = \text{montmorillonite}$ , as given in Eq. [12] for Ca-Na and Ca-K exchange on montmorillonite.

Plots of Eq. [12] are shown in Fig. 5. The linearity of the plots confirms that Eq. [1] correctly describes the mechanism for Ca-Na and Ca-K exchange on montmorillonite. The  $k_1$  and  $k_{-1}$  values, obtained from the slope and intercept of the plots in Fig. 5, are listed in Table 1. The rate constants for Ca-Na exchange were greater than those for Ca-K exchange, indicating that Ca-Na exchange was faster than Ca-K exchange. As also shown in Table 1, the apparent exchange equilibrium constants  $K'$  obtained kinetically agree well with the exchange equilibrium constants  $K$  calculated statically.

**Table 1. Forward ( $k_1$ ) and backward ( $k_{-1}$ ) rate and equilibrium ( $K_{eq}$ ) constants determined from kinetic and static studies for Ca-Na and Ca-K exchange on montmorillonite**

Exchange system	$k_1$	$k_{-1}$	$K_{eq}$	
			Kinetic ( $K'$ )	Static ( $K$ )
	$L^2 \text{ mol}^{-2} \text{ s}^{-1}$			
Ca-Na	953	643	1.48	1.20
Ca-K	385	432	0.89	0.85

Comparing Eq. [2] with Eq. [7], one is able to find that the difference between  $K'$  and  $K$  is that  $K'$  was obtained using concentrations while  $K$  was obtained using activities. If an exchange system has low ionic strength and behaves nearly as an ideal exchanger phase, then the activity coefficients for both solution and solid phases should be close to unity. As a result,  $K'$  obtained from Eq. [7] should be very close to  $K$  calculated from Eq. [2] if the kinetic technique used was suitable for the reaction.

The activity coefficients of cations on both solution and solid phases were considered as unity in this study because of the low ionic strength. Therefore,  $K'$  from the kinetic study is comparable with  $K$  from the static study. As shown in Table 1, the value of  $K'$  agrees well with the value of  $K$  for both Ca-Na and Ca-K exchange reactions on montmorillonite. This is an indication that, with pressure-jump relaxation, chemical kinetics is being measured for Ca-Na and Ca-K exchange on montmorillonite since a kinetic approach cannot be employed to calculate apparent equilibrium constants ( $K' = k_1/k_{-1}$ ) if mass transfer is occurring (Ogwada and Sparks, 1986).

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