DIVISION S-2—SOIL CHEMISTRY

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

Asher Bar-Tal,* Matthew J. Eick, Sala Feigenbaum, Donald L. Sparks, and Svetlana Fishman

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 \( K_{equ} = 754.6 \text{ L mole}^{-1} \text{ mol}^{-1} \). The values of the apparent adsorption rate coefficient \( k_a \) ranged from 84 to 185 \( \text{L mole}^{-1} \text{ min}^{-1} \), as influent rate increased from 0.3 to 2.0 \( \text{mL min}^{-1} \). 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 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. Scefried 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 onmontmorillonite 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:

\[
\text{K}^+ + \text{Ca}^{2+} \text{Ca-X}_2 + 2\text{K}^+ = 2(\text{K-X}) + \text{Ca}^{2+}
\]

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):

\[
r = \frac{dC_k}{dt} = -k_d \left[\text{K-X}\right]^2 C_{Ca} + k_a \left[\text{Ca-X}\right]C_k
\]

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 onmontmorillonite 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
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:

\[
C_{a} (K-X)^{2}/([Ca-X]C_{k}) = k_{a}/k_{d} = K'
\]  

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

\[
\{Ca\} \left[ K-X \right]^{2}/\{Ca-X\} \left[ K \right]^{2} = K_{ex}
\]

where \{ \} denotes activity.

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

\[
K_{ex} = \frac{f_{k}E_{k} \gamma_{Ca} C_{Ca} / (f_{Ca}E_{Ca} \gamma_{Ca} C_{Ca})}{K_{C}} = K_{C} (f_{k}/f_{Ca})
\]

where \( E \) is the equivalent fraction of \( K^{+} \) and \( Ca^{2+} \) on the exchange phase, \( f \) is the activity coefficient of the cation on the exchanger phase, \( \gamma \) 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 exchange 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:

\[
\ln K_{ex} = \int_{0}^{E_{k}} \ln K_{C} dE_{k}
\]

The \( f_{k} \) and \( F_{Ca} \) values can be calculated as follows:

\[
\ln f_{k} = E_{k} / \int_{0}^{E_{k}} \ln K_{C} dE_{k}
\]

\[
2 \ln f_{k} = (1 - E_{k}) (1 - K_{C}) + \int_{0}^{1} \ln K_{C} dE_{k}
\]

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 exchange phases are used. If the solution and the exchanger are not ideal solutions, then \( K' \) will be a coefficient that varies. Therefore, Eq. [2] was modified to include the following activities:

\[
d[C_{k}] / dt = k_{a} f_{k} E_{k} C_{Ca} - k_{d} f_{Ca} E_{Ca} a_{k}
\]

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):

\[
J C_{K_{in}} = J C_{K_{out}} + V_{c} dC_{k} / dt + M C E C dE_{k} / dt
\]

where \( C_{K_{in}} \) and \( C_{K_{out}} \) 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 \( C_{i} = C_{i_{0}} \), therefore, in the subsequent equations, \( C_{K_{out}} \) will be substituted by \( C_{i} \). 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 \( K_{ex} \) 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 \( K_{C} \):

\[
\ln K_{C} = a_{0} + a_{1} E_{k} + a_{2} E_{k}^{2} + \ldots + a_{n} E_{k}^{n}
\]

where \( A_{0}, \ldots, A_{n} \) 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 \( K_{ex} \) 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 desertion rate coefficient, \( k_{a} \), was calculated as the ratio between \( k_{a} \) and \( K_{ex} \); both \( k_{a} \) and \( K_{ex} \) 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:

\[
V_{c} dC_{k} / dt = M C E C dE_{k} / dt
\]

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 \( \mu \)m. The CEC of the vermiculite, as
determined by saturation with NaOAc and extraction with a 0.5 M MgOAc, was 172 cmol 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 CaCl\(_2\) 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 0.9 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 lnK\(_c\) as a function of E\(_K\) (Eq. [10]), with the following values for the coefficients:

\[
a_0 = 3.223, a_1 = 12.245, a_2 = -11.149
\]

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\]

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 during the exchange reaction (Goulding, 1983; Ogwada and Sparks, 1986a). A second-order polynomial can describe the change in lnK\(_c\) as a function of E\(_K\) (Eq. [10]), with the following values for the coefficients:

\[
a_0 = 3.223, a_1 = 12.245, a_2 = -11.149
\]

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.\(^8\)

<table>
<thead>
<tr>
<th>C(_K)</th>
<th>C(_Ca)</th>
<th>S(_K)</th>
<th>S(_Ca)</th>
<th>E(_K)</th>
<th>E(_Ca)</th>
<th>K(_c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>9.5</td>
<td>8 ± 1.8</td>
<td>164 ± 1.8</td>
<td>0.05 ± 0.01</td>
<td>0.95 ± 0.01</td>
<td>41 ± 19</td>
</tr>
<tr>
<td>1.1</td>
<td>8.9</td>
<td>55 ± 1.4</td>
<td>116 ± 1.4</td>
<td>0.32 ± 0.01</td>
<td>0.68 ± 0.01</td>
<td>610 ± 37</td>
</tr>
<tr>
<td>2.0</td>
<td>8.0</td>
<td>97 ± 2.7</td>
<td>75 ± 2.7</td>
<td>0.56 ± 0.02</td>
<td>0.44 ± 0.02</td>
<td>725 ± 66</td>
</tr>
<tr>
<td>3.6</td>
<td>6.4</td>
<td>124 ± 1.7</td>
<td>48 ± 1.7</td>
<td>0.72 ± 0.01</td>
<td>0.28 ± 0.01</td>
<td>469 ± 28</td>
</tr>
<tr>
<td>5.8</td>
<td>4.2</td>
<td>138 ± 5.3</td>
<td>34 ± 5.3</td>
<td>0.80 ± 0.03</td>
<td>0.20 ± 0.03</td>
<td>208 ± 52</td>
</tr>
<tr>
<td>7.2</td>
<td>2.8</td>
<td>157 ± 1.0</td>
<td>15 ± 1.0</td>
<td>0.91 ± 0.01</td>
<td>0.09 ± 0.01</td>
<td>257 ± 20</td>
</tr>
</tbody>
</table>

\(^8\) 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 Ca\(^+\) on the exchanger phase, respectively; K\(_c\) = the Gaines-Thomas selectivity coefficient.
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, 1.0, and 2.0 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 L$^2$ mol$^{-2}$ min$^{-1}$ with a range of 35.7 to 185.5 L$^2$ mol$^{-2}$ min$^{-1}$. Tang and Sparks (1993) determined a $k_a$ of 25,920 L$^2$ mol$^{-2}$ min$^{-1}$ for K-Ca exchange on montmorillonite using a pressure jump relaxation technique, indicating a much faster reaction rate than for vermiculite in agreement with Eick et al. (1990). The estimated $k_a$ increased from 83.9 to 185.5 L$^2$ 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 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 $K_c$.

<table>
<thead>
<tr>
<th>Flow rate, mL min$^{-1}$</th>
<th>0.33</th>
<th>1.0</th>
<th>1.0t</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_c$, L$^2$ mol$^{-2}$ min$^{-1}$</td>
<td>83.9</td>
<td>134.1</td>
<td>123.7</td>
<td>185.5</td>
</tr>
<tr>
<td>$k_a$, min$^{-1}$</td>
<td>0.11</td>
<td>0.18</td>
<td>0.16</td>
<td>0.25</td>
</tr>
<tr>
<td>Standard error of $k_a$</td>
<td>19.0</td>
<td>34.4</td>
<td>38.0</td>
<td>54.0</td>
</tr>
<tr>
<td>t-test</td>
<td>4.4***</td>
<td>3.9**</td>
<td>3.3***</td>
<td>3.4**</td>
</tr>
<tr>
<td>Standard error of the estimate, mM</td>
<td>0.78</td>
<td>1.05</td>
<td>1.08</td>
<td>1.29</td>
</tr>
</tbody>
</table>

** 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 \( (k_a, \text{K adsorption rate coefficients}) \).

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 \( (C_k = 0.01 \text{M and } C_{Ca} = 0.0 \text{M}) \). 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 \( (k_a, k_b) \), 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 L² mol⁻² min⁻¹ (Fig. 4). These values of \( t_{1/2} \) are in agreement with published results, using batch techniques. Elkhadib and Hern (1988) reported that >50% of exchangeable K on the clay fraction of various soils was displaced within 5 min. Zasoski and Burau (1978) found that the time required for complete K adsorption on colloidal MnO₂ was <2.5 min. In studying the effect of kinetic methodology on K absorption 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.

**REFERENCES**


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Vanselow, A.P. 1932. Equilibria of the base-exchange reactions of
APPENDIX 1

* INPUT;
DATA INFLOW; INFILE IN;
INPUT TIME CKOUT CKIN CT J CEC M VC Keq;
MCEC = M*CEC; JV = J/VC; INFL = JV CKIN;
* NLIN;
PROC NLIN DATA = INFLOW METHOD = DUD;
PARAMETERS K = 100;
* INITIAL CONDITIONS;
CK = O; SK = O;
* NUMERICAL SOLUTION;
dt = 0.1;
t = dt to TIME BY dt;
OUTFL = JV CK;
EK = SK VC/MCEC;

* CALCULATING THE ACTIVITY COEFFICIENTS OF
  THE ADSORBED CATIONS
ln(KC) = a0 + a1EK + a2EK^2;
Integral [ln(KC)] = a0EK + (1/2)a1EK^2 + (1/3)a2EK^3
2ln(fK) = (1 - Ek)[1 - ln(KC)] + ln(KC) - Integral
  [ln(KC)];
ln(fC) = Ek ln(KC - 1) - Integral [ln(KC)];
Ec = 1 - Ek;
fK = exp[2 ln(fK)];
fC = exp[ln(fC)];

* CALCULATING IONIC STRENGTH AND SOLUTION
  ION ACTIVITY COEFFICIENT—DAVIES EQUATION;
  I = 0.5(CK + 4(CT - CK)/2);
  SQI = IS^0.5;
  γk = exp[-0.506[SQI/(1+SQI)] - 0.3I]
  γC = exp[-0.506 × 4[SQI/(1 + SQI)] - 0.3 I]

* KINETICS CALCULATIONS;
Qdes = kCfCγC(1 - Ek)fc;
Qads = (k0/Kc)Ek fCfcγC(Ck/2 - CK/2);

* DIFFERENTIAL EQUATIONS:
SK = SK + (Qads - Qdes)dt;
CK = CK + (Qdes + INFL - Qads - OUTFL)dt;
END;
* COMPARING OBSERVED WITH PREDICTED;
MODEL CKOUT = CK;