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Sodium-Calcium, Calcium-Potassium, and Potassium-Sodium Exchange Equilibria on a Montmorillonitic Soil

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We carried out experiments on Na-Ca, Ca-K, and K-Na exchange equilibria on a montmorillonitic soil to obtain ionic composition data of both exchanger and aqueous phases. In this experiment we used a chloride background ionic medium instead of a perchlorate ionic medium because the amounts of Ca adsorbed from the CaCl_2 and $\text{Ca}(\text{ClO}_4)_2$ solutions were nearly the same.

The total adsorbed cationic charge (TC) for the Na-Ca exchange system was about 0.32 eq/kg and the value did not vary with the proportion of the adsorbed ions. On the other hand, the TC value for exchange systems involving K was about 0.3 eq/kg, indicating that about 0.02 eq/kg of K was not exchangeable to 1 M NH_4OAc that was used for extracting the adsorbed cations.

The natural logarithms of thermodynamic equilibrium constants were 0.717, 2.764, and -1.550 for $\text{Na} \rightarrow \text{Ca}$, $\text{Ca} \rightarrow \text{K}$, and $\text{K} \rightarrow \text{Na}$ exchange reactions, respectively. There was only a small thermodynamic inconsistency among these values irrespective of the reduction in TC. The relationship between the excess Gibbs energy of mixing of the exchange reaction and mol fractions of the cations on the exchanger for each exchange system met a condition imposed by a subregular solution model.

Key Words: cation exchange, montmorillonitic soil, solution model, thermodynamics.

The prediction of the ionic composition of a soil solution which is at equilibrium with an exchanger phase has been a main problem in soil chemistry. In the early 1950's Argersinger et al. (1950), Gaines and Thomas (1953), and Högfeldt (1952) derived a set of general thermodynamic equations which relate the exchanger phase activity coefficients to the experimentally measurable selectivity coefficient. These equations made it possible to predict the ionic composition of an exchanger phase from the ionic composition in aqueous phase once a single cation exchange isotherm for the exchanger was given.

But the practical significance of these equations for prediction of the ionic composition in actual soil systems is limited because the applicability of these equations is restricted to binary ion exchange reactions. This restriction in the thermodynamics of ion exchange was removed by Chu and Sposito (1981) who extended these general thermodynamic relations so

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that activity coefficients in ternary cation exchange systems could be computed from relevant experimental data. For the computation of activity coefficients following their relations, however, a large amount of experimental data on a ternary system are required and they are, in this sense, not practical.

The actual prediction of the exchanger phase ionic composition from a solution phase ionic composition or the reverse prediction in ternary cation exchange systems were achieved by the application of solution models to the exchanger phase (Elprince and Babcock 1975; Wiedenfield and Hoosner 1978; Elprince et al. 1980). In these solution models the model parameters required to compute the exchanger phase activity coefficients in a ternary ion exchange system are solely calculated from experimental data on three cyclic binary exchange reactions. Elprince and Babcock (1975) and Wiedenfield and Hoosner (1978) applied Wilson's model (Wilson 1964) to Na^+ - Rb^+ - Cs^+ exchange on a montmorillonite, Na^+ - K^+ - Cs^+ exchange on an attapulgite, and Na^+ - Mg^{2+} - Ca^{2+} exchange on a montmorillonitic soil, but neither of these investigators provided the data on actual ternary exchange equilibria to examine the accuracy of the model predictions. Elprince et al. (1980) applied the subregular solution model (Currie and Curtis 1976) to NH_4^+ - Ba^{2+} - La^{3+} exchange on a montmorillonite and compared the model predictions with the actual experimental data, which indicated that the subregular solution model gave quite satisfactory predictions. To date, however, only a few studies on the application of solution models to ternary ion exchange equilibria on soils and clays have been published and, therefore, an additional study is necessary to evaluate the validity of the models. The present study was undertaken to obtain ionic composition data on the cyclic binary cation exchange equilibria involving Na^+ , K^+ , and Ca^{2+} on a montmorillonitic soil and examine the applicability of the subregular solution model.

SOIL SAMPLE

A soil sample collected from the B horizon of a montmorillonitic Red Yellow soil in Nagano Prefecture, Japan was used. The soil sample contained 0.8% of organic carbon and 26% clay on an oven-dry basis. The dominant clay mineral species was montmorillonite accompanied by minor amounts of vermiculite and illite.

The soil sample was air-dried and crushed with a wooden pestle to pass through a 105- μm sieve.

EXPERIMENTAL METHODS

For the Na^+ - Ca^{2+} exchange experiment, a 0.5 g portion of the soil sample was placed in a tared 10-cm³ glass centrifuge tube with a fitted stopper. To this tube 9 cm³ of 1 eq/dm³ NaCl was added, mixed vigorously, centrifuged, and the clear supernatant was decanted. This cycle was repeated another 4 times to saturate the soil sample with Na. After the third renewal of the solution the tube was allowed to stand overnight to secure complete saturation.

After the final decantation in the saturating step 9 cm³ of a mixed NaCl/ CaCl_2 solution with a total cation concentration of 0.05 eq/dm³ was added, mixed vigorously, centrifuged, and the supernatant was decanted. This equilibration procedure was repeated another 4 times with one overnight equilibration as in the saturation step. The final supernatant solution was collected and the pH, and Na and Ca concentration were determined. After the

final decantation the tube was weighed to estimate the volume of the entrained solution and then the adsorbed cations were extracted with 1 M NH_4OAc . The cation concentration in the extract and the equilibrium solution was determined by atomic absorption spectroscopy.

The experiment was carried out in duplicate in a room maintained at 25°C.

The amounts of the adsorbed cations were calculated using the following equation:

$$\Gamma_i = (C_{i,\text{ext}} V_{\text{ext}} - C_{i,\text{ent}} V_{\text{ent}}) / w, \quad (1)$$

where Γ , C , V , and w stand for cation adsorption (mol/kg), concentration (mol/dm³), volume (dm³), and weight of the soil sample (kg), respectively. The subscripts i , ext, and ent refer to the adsorbed species (this case Na and Ca), extract, and entrained solution, respectively.

$\text{Na}^+\text{-K}^+$ and $\text{K}^+\text{-Ca}^{2+}$ exchange experiments were carried out in essentially the same way using relevant salt solutions. Ions used for initial saturation were K^+ and Na^+ for $\text{Ca}^{2+}\text{-K}^+$ and $\text{K}^+\text{-Na}^+$ exchange experiments, respectively.

Throughout the present experiment chloride salts were used instead of perchlorate salts. The use of the latter was recommended by Sposito et al. (1983) in order to avoid the spurious increase in cation exchange capacity (CEC) due to the preferential adsorption of CaCl^+ . This decision was made after a preliminary experiment in which Ca adsorptions from 0.05 eq/dm³ CaCl_2 and $\text{Ca}(\text{ClO}_4)_2$ solutions were measured following the method described above.

RESULTS AND DISCUSSION

Effect of background ionic medium

Recently Sposito et al. (1983) explained the apparent increase in the cation exchange capacity (CEC) with increasing Ca saturation that was observed for cation exchange equilibria on a montmorillonite in a chloride background ionic medium in terms of the preferential adsorption of CaCl^+ . In an example given by Sposito et al. (1983) the apparent CEC of a montmorillonite sample at Ca-saturation was about 1.0 eq/kg in perchlorate background medium and about 1.2 eq/kg in a chloride background ionic medium. The measured Ca adsorption by the present montmorillonitic soil sample was, however, 0.1611 ± 0.0011 mol/kg in the perchlorate background medium and 0.1620 ± 0.0012 mol/kg in the chloride background medium and there was no significant difference between these values, suggesting that the contribution of CaCl^+ adsorption was negligible. Similar results were reported by Suarez and Zahow (1989). Based on this observation chloride salts were used in the present study.

Thermodynamic equilibrium constants

Equilibrium ionic composition data of both aqueous solution and exchanger phases are listed in Tables 1, 2, and 3. Fifth column of the tables shows the values of the total normality (TN) of the equilibrium aqueous solutions while the 6th column shows the values of the total adsorbed cationic charge (TC). In the $\text{Na}^+\text{-Ca}^{2+}$ exchange equilibrium, the TC values remained fairly constant at around 0.32 eq/kg whereas in the $\text{Ca}^{2+}\text{-K}^+$ and $\text{K}^+\text{-Na}^+$ exchange equilibria the TC values were appreciably lower except when the soil was saturated with Na^+ in the $\text{Na}^+\text{-K}^+$ exchange equilibrium experiment. The reduction of the TC value was probably caused by the fixation of K^+ in the interlayer spaces of the montmorillonite and/or vermiculite contained in the soil sample, which was discussed at length by Talibudeen

Table 1. Composition data for Na-Ca exchange system.

Concentration (M)		Adsorption (eq/kg)		TN	TC
[Na]	[Ca]	Na	Ca	(eq/dm ³)	(eq/kg)
0.0500	<0.0001	0.322	n.d. ^a	0.0500	0.322
0.0485	0.00075	0.199	0.060	0.0505	0.319
0.0465	0.00200	0.126	0.096	0.0500	0.318
0.0450	0.00250	0.106	0.107	0.0500	0.320
0.0430	0.00350	0.082	0.118	0.0500	0.318
0.0410	0.00450	0.069	0.127	0.0500	0.323
0.0390	0.00550	0.060	0.133	0.0500	0.326
0.0370	0.00650	0.054	0.136	0.0500	0.326
0.0350	0.00750	0.043	0.141	0.0500	0.325
0.0300	0.01000	0.034	0.145	0.0500	0.324
<0.0001	0.02500	n.d. ^a	0.157	0.0500	0.314

^a Not determined.**Table 2.** Composition data for Ca-K exchange system.

Concentration (M)		Adsorption (eq/kg)		TN	TC
[K]	[Ca]	K	Ca	(eq/dm ³)	(eq/kg)
0.0500	<0.0001	0.304	n.d. ^a	0.0500	0.304
0.0485	0.0010	0.260	0.020	0.0505	0.300
0.0465	0.0020	0.236	0.030	0.0505	0.296
0.0450	0.0025	0.231	0.033	0.0500	0.297
0.0430	0.0035	0.227	0.040	0.0500	0.307
0.0410	0.0045	0.206	0.046	0.0500	0.298
0.0390	0.0055	0.195	0.050	0.0500	0.295
0.0370	0.0065	0.189	0.055	0.0500	0.299
0.0350	0.0075	0.188	0.059	0.0500	0.306
0.0300	0.0100	0.160	0.067	0.0500	0.294
0.0150	0.0175	0.107	0.094	0.0500	0.295
<0.0001	0.0250	n.d. ^a	0.145	0.0500	0.290

^a Not determined.

(1981).

Figure 1 shows the exchange isotherms for the three binary exchange equilibria. The dotted lines in these figures represent the nonpreference exchange isotherms which can be expected when the Vanselow selectivity coefficient takes the value of unity (Sposito 1981). As easily seen from the figures the soil slightly prefers Ca²⁺ over Na⁺ and strongly prefers K⁺ over Ca²⁺ and Na⁺.

To determine the thermodynamic equilibrium constants, the Vanselow selectivity coefficient (K_v) was calculated according to the following equation and plotted in Fig. 2:

$$K_v = N_j^{z_i}(M_i)^{z_j} / N_i^{z_j}(M_j)^{z_i}, \quad (2)$$

where N is the mol fraction of the adsorbed ion, (M) is the activity of an ion in aqueous phase, and z is the valence of a cation. Subscripts i and j refers to cations i and j . Single ion activity coefficient in aqueous solutions was calculated using Davies equation (Sposito 1981). Data points in Fig. 2 indicate that the natural logarithm of the selectivity coefficient varied linearly with the equivalent fraction of a cation on the exchanger and the data were fit by regression analysis to straight lines. Regression coefficients from the statistical analyses

Table 3. Composition data for K-Na exchange system.

Concentration (M)		Adsorption (eq/kg)		TN	TC
[Na]	[K]	Na	K	(eq/dm ³)	(eq/kg)
0.0500	<0.0001	0.330	n.d. ^a	0.0500	0.330
0.0485	0.0015	0.264	0.040	0.0500	0.304
0.0465	0.0035	0.220	0.077	0.0500	0.297
0.0450	0.0050	0.192	0.099	0.0500	0.291
0.0430	0.0070	0.166	0.128	0.0500	0.294
0.0410	0.0090	0.143	0.147	0.0500	0.290
0.0390	0.0110	0.125	0.162	0.0500	0.287
0.0370	0.0130	0.113	0.191	0.0500	0.304
0.0350	0.0150	0.091	0.193	0.0500	0.284
0.0300	0.0200	0.072	0.225	0.0500	0.297
0.1500	0.0350	0.027	0.268	0.0500	0.295
<0.0001	0.0500	n.d. ^a	0.309	0.0500	0.309

^a Not determined.

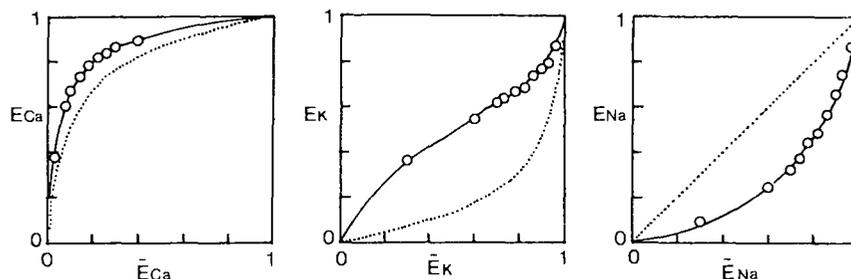


Fig. 1. Exchange isotherms for exchange systems Na-Ca (left), Ca-K (center), and K-Na (right). \bar{E}_j and E_j are equivalent fractions of cation j in an aqueous phase and an exchanger phase, respectively. Dotted lines are nonpreference isotherms. Solid lines were drawn only for eyes' guide.

are listed in Table 4. The thermodynamic equilibrium constants were calculated using these regression equations and the standard relation:

$$\ln K_{\text{ex}} = \int_0^1 \ln K_v dE, \quad (3)$$

where E is the equivalent fraction of a cation on the exchanger. The calculated natural logarithms of the thermodynamic equilibrium constants are 0.717, 2.764, and -1.550 for $\text{Na}^+\text{-Ca}^{2+}$, $\text{Ca}^{2+}\text{-K}^+$, and $\text{K}^+\text{-Na}^+$ exchange reactions, respectively. For the present cyclic exchange reactions the equilibrium constants must satisfy the following relation if the experimental data are thermodynamically consistent and the exchange reactions reversible:

$$\ln K_{\text{ex}}(\text{Na} \rightarrow \text{Ca}) + \ln K_{\text{ex}}(\text{Ca} \rightarrow \text{K}) + 2 \ln K_{\text{ex}}(\text{K} \rightarrow \text{Na}) = 0, \quad (4)$$

where the notation $K_{\text{ex}}(i \rightarrow j)$ indicates that the equilibrium constant was calculated for a reaction in which an exchanger saturated with cation i was converted to that saturated with cation j . Substitution of K_{ex} in Eq. 4 with experimental values yielded a value of 0.381, which corresponds to the inconsistency in the standard free energy change of 0.47 kJ/eq. The possible causes of this inconsistency are the experimental error in the determination of the cations in the aqueous and exchanger phases and the irreversibility of some of the exchange

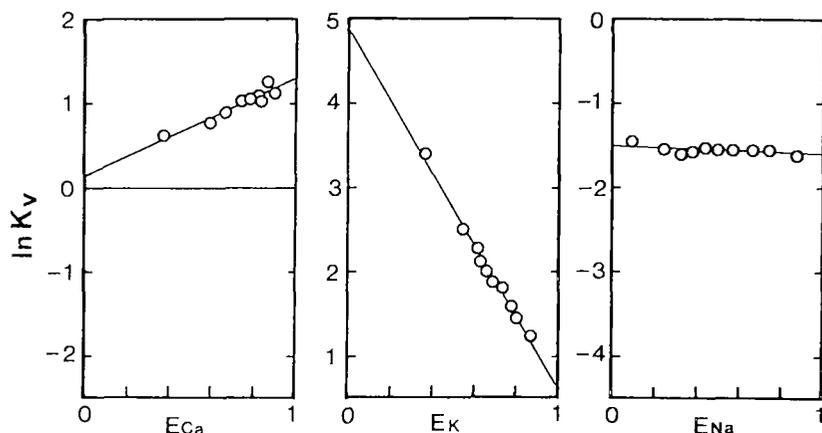


Fig. 2. Relationships between negative logarithm of Vanselow selectivity coefficient and equivalent fraction of the cation in the exchanger phase for Na-Ca (left), Ca-K (center), and K-Na (right) exchange systems. Solid lines are regression lines.

reactions as evidenced by the reduction of TC value in the reactions involving K^+ (Tables 2 and 3). This inconsistency is, however, not more pronounced than the reported values for cyclic cation exchange reactions involving three cations on specimen montmorillonites, which were about 0.6 kJ/eq (Sposito 1981).

Mixing property

Elprince et al. (1980) employed the subregular solution model of Currie and Curtis (1978) to express the exchanger phase activity coefficients as a function of exchanger phase composition. In this model the natural logarithm of the activity coefficient is expressed as the Margules expansion of third order. When the subregular solution model is applied to a binary cation exchange system, the following expression for the excess Gibbs molar energy of mixing G^E is obtained (Grover 1977; Elprince et al. 1980)

$$G^E = RTN_iN_j\{\ln f_{ij}^\infty + N_i(\ln f_{ji}^\infty - \ln f_{ij}^\infty)\}, \quad (5)$$

where f_{ij}^∞ is the activity coefficient of cation i when its mol fraction approaches zero on an exchanger containing cations i and j , R is the molar gas constant, and T is the absolute temperature. Therefore a plot of $G^E/(RTN_iN_j)$ vs. N_i should give a straight line if the model assumptions are valid.

For a binary cation exchange reaction G^E is, by definition, given by the following equation

$$G^E = RT(N_i \ln f_i + N_j \ln f_j). \quad (6)$$

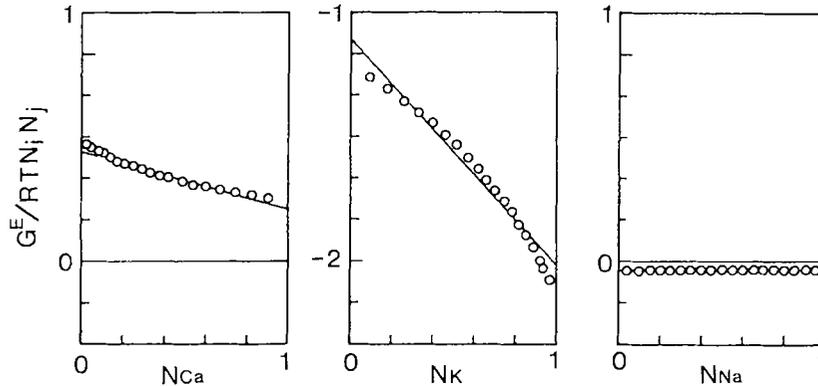
The activity coefficients f_i and f_j are given by the following standard equations (Argersinger et al. 1950; Sposito 1981);

$$z_j \ln f_i = E_j \ln K_v - \int_0^{E_j} \ln K_v dE_j, \quad (7)$$

and

Table 4. Regression coefficients for equations relating $\ln K_v$ to equivalent fraction of an adsorbed cation, $\ln K_v = aE_j + b$.

Exchange system	j	a	b
Na-Ca	Ca	1.157	0.138
Ca-K	K	-4.286	4.907
K-Na	Na	-0.082	-1.509

**Fig. 3.** Relationship between $G^E/RTN_i N_j$ and N_j for exchange systems Na-Ca (left), Ca-K (center), and K-Na (right). N_i and N_j are the mol fractions of the cations i and j . For explanation of G^E , see text. Solid lines are regression lines.

$$z_i \ln f_j = -(1 - E_j) \ln K_v + \int_{E_j}^1 \ln K_v dE_j. \quad (8)$$

Equations 7 and 8 and the regression equations relating $\ln K_v$ to E_j (Table 4) were employed to calculate the exchanger phase activity coefficients for each binary exchange reaction. The calculated values of the activity coefficients, in turn, were used to calculate G^E as a function of the exchanger phase composition according to Eq. 6. And thus $G^E/(RTN_i N_j)$ ($i, j = \text{Na, Ca, K}$) was plotted against N_j in Fig. 3. For each exchange system the graph conformed fairly well to a straight line as could be predicted from the subregular solution model, indicating that the model can be used to predict values of exchanger phase activity coefficients in the $\text{Na}^+ \text{-Ca}^{2+} \text{-K}^+$ ternary cation exchange system.

General discussion

As discussed in the previous sections the experimental data on the three binary cation exchange reactions were thermodynamically consistent in view of the experimental uncertainty and the mixing property of the exchanger phase met the requirement imposed by the subregular solution model. The next step of the study would be, therefore, to obtain equilibrium ionic composition data for the $\text{Na}^+ \text{-Ca}^{2+} \text{-K}^+$ ternary exchange system and to compare them with subregular solution model predictions. But these data were not obtained in the present study because we thought that there was a problem in our experiment, *i.e.*, the reduction of the TC value in systems involving K^+ (Tables 2 and 3).

The reduction of the TC value in cation exchange reactions involving K^+ has been reported for soils and clay minerals. Deist and Talibudeen (1967), and Talibudeen (1972)

Table 5. Amounts of Ca and K ions extracted successively with NH₄OAc and NaOAc from soil samples saturated with Ca and equilibrated either with 0.05 eq/dm³ CaCl₂ or with 0.05 eq/dm³ KCl.

Equilibrated with	Cations extracted with			
	1 M NH ₄ OAc (eq/kg)		1 M NaOAc (eq/kg)	
	Ca	K	Ca	K
CaCl ₂	0.321 ± 0.003	tr.	tr.	0.0031 ± 0.0008
KCl	0.0044 ± 0.0009	0.292 ± 0.004	tr.	0.0255 ± 0.0037

reported that the TC value decreased considerably with the increase of K⁺ in the K⁺-Ca²⁺ exchange equilibrium on soils. Jensen (1973) reported similar experimental results for a montmorillonite but not for a kaolinite. The reduction of the TC value in these cation exchange systems is probably due to the incomplete recovery of the adsorbed K⁺ or Ca²⁺ by the NH₄OAc extraction (Talibudeen 1981). To confirm this assumption, 10 portions of the soil sample were first saturated with Ca²⁺, five out of 10 were repeatedly equilibrated with a 0.05 eq/dm³ KCl solution, and the remainder equilibrated with a 0.05 eq/kg CaCl₂ solution as described in the experimental method section. The adsorbed cations were first extracted five times with 1 M NH₄OAc and then extracted another five times with 1 M NaOAc. The analytical results are summarized in Table 5. Table 5 shows that the adsorbed Ca²⁺ was extracted by 1 M NH₄OAc nearly completely whereas only 0.29 eq/kg of the adsorbed K⁺ was recovered by the NH₄OAc extraction. The unextracted K⁺ was recovered by NaOAc extraction and only a trace amount of Ca²⁺ was found in that extract. Ca(OAc)₂ and Mg(OAc)₂ solutions were also tested as a second extractant but NaOAc was found to be superior. The fact that the sum of the amounts of K⁺ recovered by the two successive extractions was nearly equal to the amount of Ca²⁺ extracted from the Ca-saturated and Ca-equilibrated soil sample indicates that the reduction of the TC value was caused by the incomplete extraction of the adsorbed K⁺ but not Ca²⁺.

The above experimental results suggest that it is possible to obtain a constant TC value of about 0.32 eq/kg even for exchange systems involving K⁺ if the adsorbed cations are extracted doubly by NH₄OAc and NaOAc. But the fact that neither Ca²⁺ nor NH₄⁺, the latter has an affinity very similar to that of K⁺, could extract the adsorbed K⁺ completely suggests that the unextracted K⁺ was not "exchangeable" at least in the K-Ca exchange system. The compulsory extraction of that K⁺ by Na salts would, therefore, not be suitable for obtaining ionic composition data for the calculation of thermodynamic constants for the K⁺-Ca²⁺ exchange system.

Many sources of experimental error affect the accuracy of the values of the calculated thermodynamic quantities, e.g., determination of extracted cations, loss of soil samples during repeated decantation, extrapolation to obtain limit values of ln K_v etc., including the reduction of the TC value. To ignore the reduction of the TC value of about 0.02 eq/kg might be permissible as far as the accuracy of the thermodynamic equilibrium constant is concerned. However it would lead to a serious relative error in predicting the exchangeable cation composition of a natural soil from a given soil solution composition because the prediction is made under the assumption of a constant value of TC and many natural soils contain only <0.02 eq/kg of exchangeable K⁺.

Further studies on the thermodynamics of cation exchange involving K⁺ as well as on the experimental methods to characterize the exchange equilibria are still needed before the thermodynamics of multicomponent cation exchange can be applied successfully for predict-

ing exchangeable cation status of field soils.

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