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Ca-K EXCHANGE REACTION AND INTERSTRATIFICATION IN MONTMORILLONITE

ATSUYUKI INOUE AND HIDEO MINATO

Department of Earth Science and Astronomy, College of General Education
University of Tokyo, Komaba, Meguro-ku, Tokyo 153, Japan

Abstract—Cation-exchange equilibrium for Ca-K-montmorillonite was studied at 35°, 50°, and 90°C and at three total normalities of the equilibrium solution (0.1, 0.05, and 0.01 N). Changes of the standard free energy for the exchange from K-montmorillonite to Ca-montmorillonite were determined to be −53, −270, and −393 cal/eq at 35°, 50°, and 90°C, respectively. Changes of the standard enthalpy and entropy were 1.7 kcal/eq and 5.6 cal/eq/degree at 35°C, respectively. The sign of the change of the standard free energy was found to be determined mainly by the entropy change, in particular, by the hydration entropy of the cations.

The calculation of the excess functions indicates that the mixing model of Ca-K-montmorillonite approximates that of a regular solution. Montmorillonite having potassium equivalent ion fraction of 0.1 to 0.7 consists of a random interstratification of Ca-montmorillonite (15.6 Å) and K-montmorillonite (12.6 Å).

Key Words—Enthalpy, Entropy, Free energy, Interstratification, Ion exchange, Montmorillonite.

INTRODUCTION

The cation-exchange properties of montmorillonite have been of interest to mineralogists, geologists, and soil scientists because of the abundance of this mineral in sedimentary rocks and soil. The interlayer cations of natural montmorillonite are mainly Na, Ca, K, and Mg ions. The properties of montmorillonite containing K ions are of special interest to clay mineralogists and geologists because of the influence of potassium on the aggradation of clay minerals during diagenesis. A number of works have been concerned with the thermodynamic aspects of the Ca-K exchange reaction (Hutcheon, 1966; Deist and Talibudeen, 1967a, 1967b; Laudelout *et al.*, 1968; Talibudeen, 1971); but, for the most part, the mixing properties of Ca and K ions in montmorillonite remain to be studied.

On the other hand, Mering and Glaeser (1953) showed that demixing of the cations in Ca-Na-montmorillonite probably took place during the exchange reaction. The interstratification phenomenon in the intermediate range of cationic composition has been reported for various cation pairs: Ca-Na (McAtee, 1956), Ca-K (Chaussidon, 1963), and Cu-Na (McBride, 1976).

To shed light on the formation of illite from montmorillonite through illite/montmorillonite interstratified minerals, the present study of the exchange equilibria and of the mixing properties of Ca and K ions in montmorillonite has been undertaken.

THEORETICAL CONSIDERATIONS

The equilibrium constant for the exchange reaction,

$$2\text{K-clay} + \text{Ca}^{2+} = \text{Ca-clay} + 2\text{K}^{+} \qquad (1)$$

is defined by

$$\ln K = \ln K_c + \ln f_{Ca} - \ln f_K^2 \qquad (2)$$

where f is the activity coefficient for the ion in the clay when its concentration is expressed as an equivalent ion fraction and K_c is the selectivity coefficient defined by

$$K_c = \frac{(Ca^{2+})_c[K^+]_a^2\gamma_K^2}{(K^+)_c^2[Ca^{2+}]_a\gamma_{Ca}} \qquad (3)$$

The parentheses refer to the equivalent ion fraction, the brackets to their molarities in the equilibrium solution, γ to the activity coefficients of the specified ions in the solution, subscript c to the crystal, and subscript a to the solution. Each equivalent ion fraction in the solution is defined by

$$\left.\begin{aligned} (Ca^{2+})_a &= 2[Ca^{2+}]_a/C_0 \\ (K^+)_a &= [K^+]_a/C_0 \\ (Ca^{2+}) + (K^+) &= 1 \\ 2[Ca^{2+}]_a + [K^+]_a &= C_0 \end{aligned}\right\} \qquad (4)$$

where C_0 is the total normality in the solution. It follows from Eq. (3) and (4) that

$$\begin{aligned} K_c &= \left[\frac{(Ca^{2+})_c(K^+)_a^2\gamma_K^2}{(K^+)_c^2(Ca^{2+})_a\gamma_{Ca}}\right]2C_0 \\ &= \left[\frac{\{1-(K^+)_c\}(K^+)_a^2\gamma_K^2}{(K^+)_c^2\{1-(K^+)_a\}\gamma_{Ca}}\right]2C_0 \end{aligned} \qquad (5)$$

Gaines and Thomas (1953) indicated that the activity coefficients of f_{Ca} and f_K were obtained from the following relations

$$\begin{aligned} \ln f_{Ca} &= -N_k(1+\ln K_c) + \int_0^{N_k} \ln K_c\, dN_k \\ \ln f_K^2 &= (1-N_k)(1+\ln K_c) - \int_{N_k}^{1} \ln K_c\, dN_k \end{aligned} \qquad (6)$$

where $N_k = [K^+]_c/\{[K^+]_c + 2[Ca^{2+}]_c\}$. The equilibrium constant is obtained by Eq. (2) and (6);

$$\ln K = -1 + \int_0^1 \ln K_c\, dN_k \qquad (7)$$

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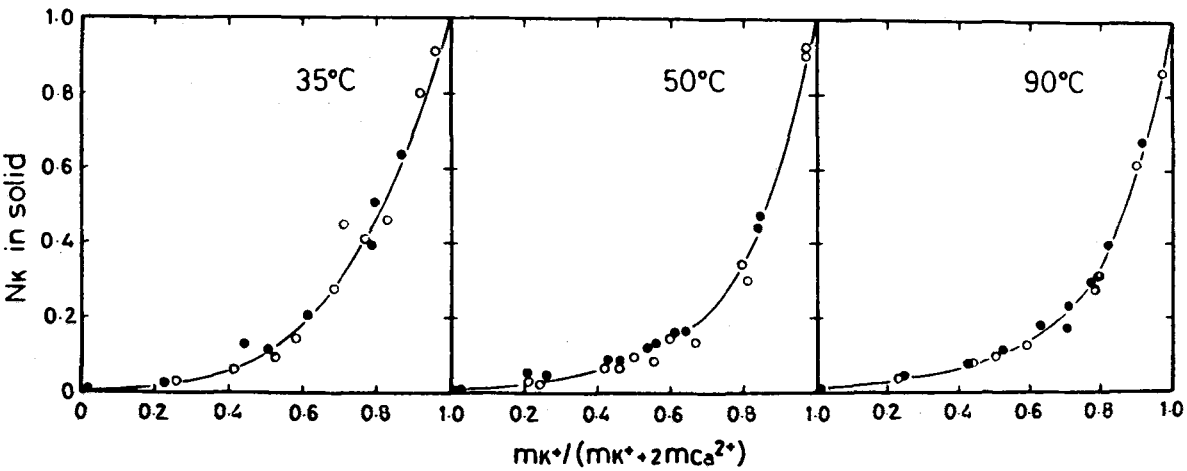


Figure 1. Exchange isotherms obtained with wet clays at 35°, 50°, and 90°C, and a total normality of 0.1 N. Solid and open circles refer to K- and Ca-montmorillonite as starting materials, respectively.

In these relations a constant exchange capacity and negligibly small adsorption of anion are assumed. Further, the activity term of the solvent is neglected because of its very small magnitude (Gaines and Thomas, 1955).

EXPERIMENTAL

The montmorillonite used in this study is a hydrothermal alteration product from Miocene volcanic ash from Aterazawa in Yamagata Pref., Japan. Its chemical composition is given in Table 1. Homoionic clays were prepared by washing with one normal solutions of K and Ca chloride. The cation-exchange capacities (CEC) with K and Ca are 114 and 119 meq/100 g, respectively. Specimens of wet and dried clays were employed as starting materials. The drying temperature was in the range 80°–300°C, below the thermal decomposition temperature of montmorillonite.

About 0.1 g of each homoionic clay was shaken at constant temperature for two days in a polyethylene tube with 50 ml of a Ca-K mixed chloride solution at various ratios of the two salts, but at the same total normality for an experiment. Exchange isotherms were determined at three temperatures (35°, 50°, and 90°C) and at three fixed total normalities (0.1, 0.05, and 0.01 N).

Suspensions in equilibrium were separated, and the contents of Ca and K in both clay and solution were determined by atomic absorption and emission spectroscopy. The equilibrated clays were investigated by means of X-ray powder diffraction at 60% relative humidity, and thermogravimetric analysis was carried out at a heating rate of 2°C/min on sample brought to constant weight at 60% relative humidity.

The experimental values of the selectivity coefficient at each temperature were fitted to a polynomial equation by the least squares method.

RESULTS AND DISCUSSION

Exchange isotherms and the fixation of K ions

The exchange isotherms for homoionic clays at three temperatures and at three fixed total normalities are shown in Figures 1–3. Dilution of the solution and elevation of the ambient temperature resulted in a greater preference for Ca ions. As seen in Figures 2 and 3, the exchange isotherms exhibit a marked hysteresis when the preheated clays were used as starting materials. The degree of hysteresis was independent of the drying temperature in the range 80°–300°C. The isotherms obtained from wet homoionic clays did not exhibit hysteresis (Figure 1). The hysteresis is probably due to the fixation of K ions by montmorillonite, which is facilitated by heating the montmorillonite initially saturated with K ions.

The amount of the K-fixation is defined in the present work as follows; at a certain equivalent ion fraction of solution, it corresponds to N_k on the isotherm (curve a) of the montmorillonite initially saturated with K ions at various fractions minus N^0_k on the isotherm (curve b) of Ca-montmorillonite as seen in Figure 4(b). The relation between the initial K fraction of the starting clay and the amount of K-fixation at various K equivalent fractions of solution is shown in Figure 4. The curves were roughly divided into two parts:

$$(1) \qquad 0 < N_k < 0.6$$

The amount of fixation increases from 0 to 30% of the total CEC.

$$(2) \qquad 0.6 < N_k$$

The amount of fixation is nearly constant with a maximum of 30% of the total CEC. These data suggest that montmorillonite which contains less than 0.4 of N_{Ca} has

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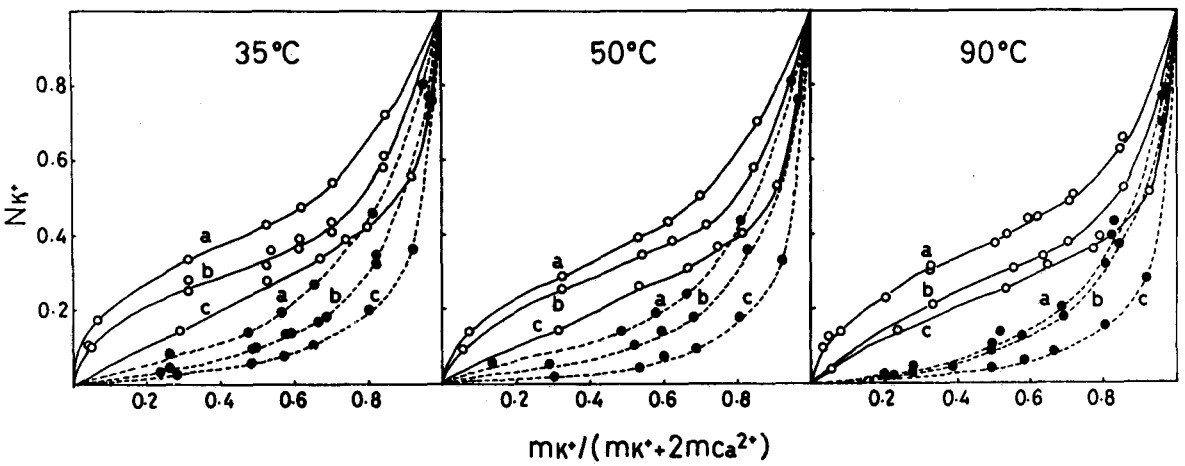


Figure 2. Exchange isotherms obtained with materials dried at 80°C. Solid and open circles refer to Ca- and K-montmorillonite as starting materials, respectively. a: total normality of 0.1 N; b: total normality of 0.05 N; c: total normality of 0.01 N.

the same physical properties as end member K-montmorillonite.

Figure 5 indicates that the selectivity coefficients for the montmorillonite initially saturated with K ions at various fractions vary with N_k. When the initial $N_k > 0.5$, K_c is nearly the same for the various pretreatments and the untreated materials, though preheating causes K-fixation.

Thermodynamic analysis

The value of ln K_c was calculated using data from isotherms having no hysteresis as shown in Figure 1.

The activity coefficient of the cations in solution, Eq. (5), was evaluated at 35°, 50°, and 90°C using the Guggenheim-Glueckauf equation (Glueckauf, 1949) of $\gamma_K^2/\gamma_{Ca} = (\gamma_{KCl})^4/(\gamma_{CaCl_2})^3$. Neglecting a concentration dependence term, the activity coefficient was obtained from the following relation;

$$\log \gamma = -A_\gamma |Z_+ Z_-| \frac{\sqrt{I}}{1+\sqrt{I}} \qquad (8)$$

Table 1. Chemical composition of the original montmorillonite.

	Wt %	Number of cations[1]
SiO_2	57.08	4.02
Al_2O_3	19.63	1.63
Fe_2O_3	2.25	0.12
MnO	0.02	—
MgO	0.67	0.07
CaO	0.33	0.02
Na_2O	3.52	0.48
K_2O	0.07	0.01
Ig. loss	16.81	
Total	100.38	

[1] Calculated on the basis of 11 oxygens.

where A_γ is given by

$$A_\gamma = \left(\frac{2\pi N d_0}{2.303}\right)^{1/2} \left(\frac{e^2}{DkT}\right)^{3/2} \qquad (9)$$

where D is the dielectric constant, d_0 is the density of the pure solvent, and I is the ionic strength ($= 0.5 \Sigma M_i Z_i^2$). The value of A_γ at each temperature was tabulated by Cobble (1964). If the activity coefficient in solution is neglected, a greater error results in the calculation of the thermodynamic functions of heterovalent ion pairs.

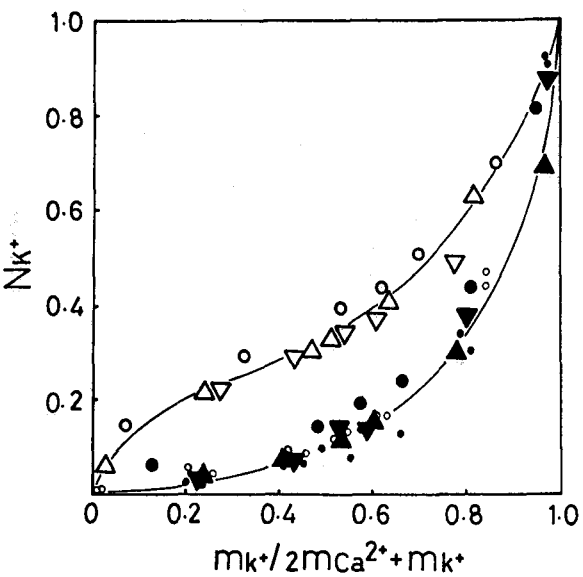


Figure 3. Exchange isotherms obtained with materials treated by various means. ●○: wet materials; ●○: materials dried at 80°C; ▲△: materials dried at 200°C; ▼▽: materials dried at 300°C. Solid and open designs refer to Ca- and K-montmorillonite, respectively.

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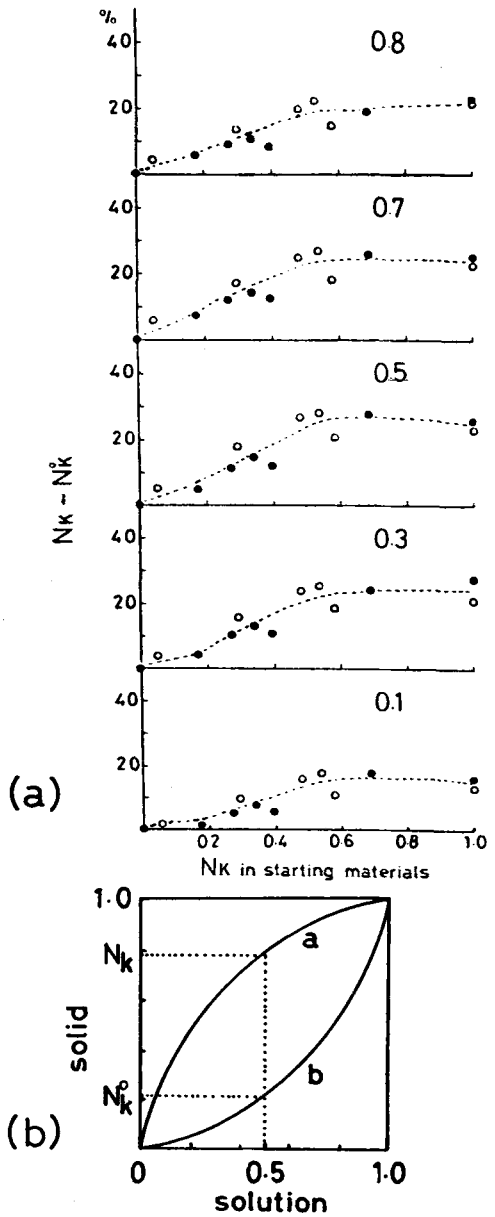


Figure 4. (a) The relation between the initial N_k value and the amount of K-fixation in the clay. The upper right values refer to potassium equivalent ion fractions ($m_{K+}/m_{K+} + 2m_{Ca2+}$) in the equilibrium solution at 35°C and 0.05 N. Solid and open circles refer to Ca- and K-montmorillonite, respectively. (b) The amount of K-fixation = $100(N_k - N^0_k)$ at certain equivalent ion fractions in solution. a: isotherm obtained with dried montmorillonite initially saturated with K ions at a certain equivalent ion fraction; b: isotherm obtained with Ca-montmorillonite.

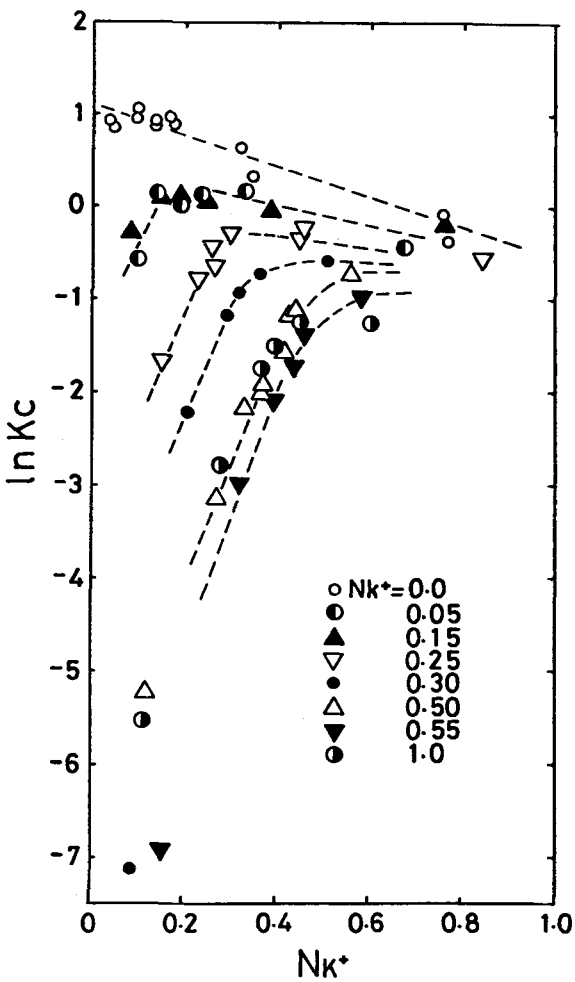


Figure 5. The variation of ln K_c with N_k in the cases of various initial N_k at 35°C and 0.05 N.

The relation between ln K_c and N_k is shown in Figure 6. When the relation at each temperature was fitted by a linear or a quadratic equation, a smaller standard deviation resulted than by using a cubic fit. A linear equation was used for the ln K_c:N_k relationship for the thermodynamic calculations estimating the experimental error. The coefficients of a linear equation are given in Table 2. The equilibrium constant was calculated from Eq. (7). Further, changes of the standard free energy (ΔG_0), enthalpy (ΔH_0), and entropy (ΔS_0) of the exchange reaction were evaluated by the following equations;

$$\Delta G_0 = -RT \ln K \quad (10)$$

$$\Delta H_0 = -R \frac{\partial (\ln K)}{\partial (1/T)} \quad (11)$$

$$\Delta S_0 = \frac{\Delta H_0 - \Delta G_0}{T} \quad (12)$$

The relation for ln K vs. 1/T was assumed to be linear over the range 35°–90°C where ΔH_0 was evaluated. The values of ΔG_0, ΔH_0, and ΔS_0 listed in Table 3 are smaller than those previously reported (Hutcheon, 1966; Laudelout *et al.*, 1968).

The Ca-preference at the concentration of 0.05 N of

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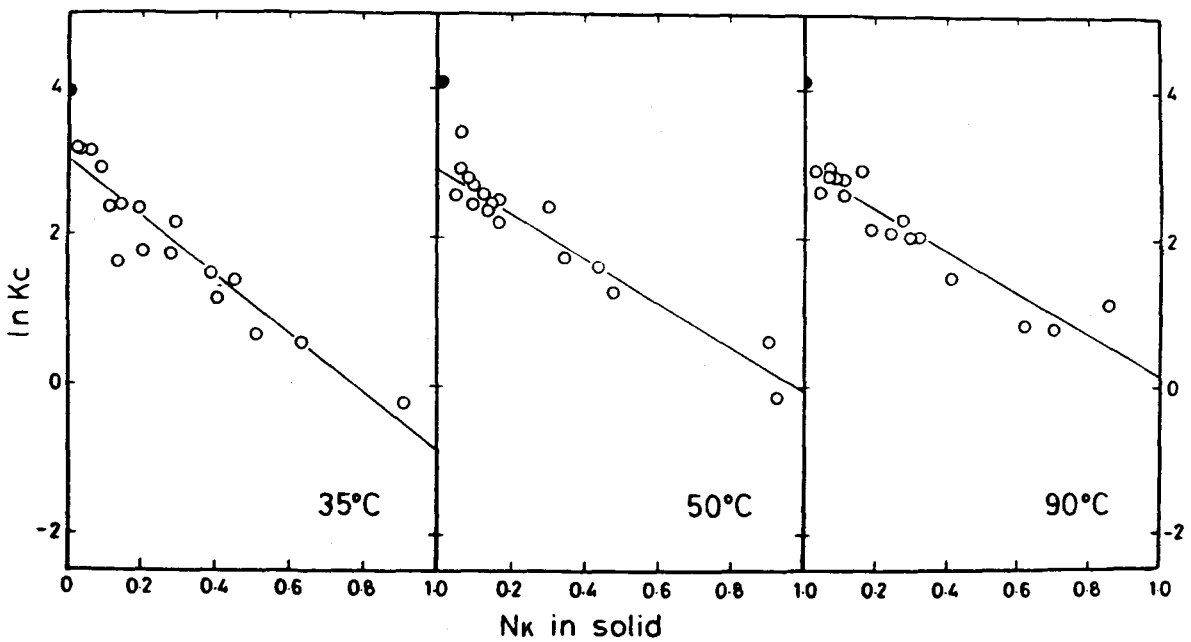


Figure 6. Plots of ln K_c vs. N_K for wet montmorillonite at 35°, 50°, and 90°C, and 0.1 N. The lines are the regression lines at respective temperatures.

solution is caused by a negative ΔG_0 value. However, this Ca-preference does not necessarily mean that the Ca ion is more strongly bound to the clay than is the K ion. The binding strength is normally defined by enthalpy alone. A positive ΔH_0 in Table 3 suggests that the K ion is more strongly bound than the Ca ion. That is, since the interlayer space of Ca-montmorillonite is larger than that of K-montmorillonite, the distance of the Ca ions in the interlayer space from the charged surface is greater than that of the K ions. The adsorbed Ca ion is more hydrated than the adsorbed K ion. From the viewpoint of electrostatic binding energy, therefore, the binding strength of the Ca ion to the charged surface may be weaker than that of the K ion.

The sign of ΔG_0 is determined by ΔH_0 and ΔS_0 [Eq. (12)]. According to the values in Table 3 and the Ca-preference at the lower concentration in the equilibrium solution, the sign of ΔG_0 is determined by ΔS_0 rather than ΔH_0. ΔS_0 is the sum of all entropy changes in the system. For the solid entropy contribution of montmorillonite, if the exchanger is assumed to have only one kind of exchange site, Ca ion must occupy two adjacent sites on the crystal, while K ion occurs randomly. The cation configuration entropy for the K-clay is larger than for the Ca-clay. However, the volume of the Ca-clay is larger than that of the K-clay. The increase in the volume of the exchanger will tend to increase the entropy of the cations. The entropy change of silicate layer scarcely contributes to the entire entropy change through the exchange reaction. Finally the entropy change in the solid is small, whereas the difference between the hydration entropy of Ca and K ions is significant (Hutcheon, 1966; Deist and Talibudeen, 1967b). In the present work, the sign of ΔG_0 is also determined mainly by the difference between the hydration entropy of the cations.

The activity coefficients of the cations on the clay were calculated by Eq. (6). The result is shown in Fig-

Table 2. Regression coefficients (ln $K_c = aN_K + b$).

	a	b	σ^1
35°C	−3.884 ±0.396	3.026 ±0.146	±0.381
50°C	−2.272 ±0.218	2.900 ±0.086	±0.236
90°C	−2.859 ±0.305	2.975 ±0.109	±0.294

[1] Standard deviation of ln K_c.

Table 3. Thermodynamic data for equilibrium constants (ln K), standard free energy (ΔG_0), standard enthalpy (ΔH_0), and standard entropy (ΔS_0).

Temperature	ln K	ΔG_0 (cal/eq)	ΔH_0 (cal/eq)	ΔS_0 (cal/eq/degree)
35°C	0.0858	−52.5	1662.8	5.6
50°C	0.4201	−269.7		
90°C	0.5449	−393.0		

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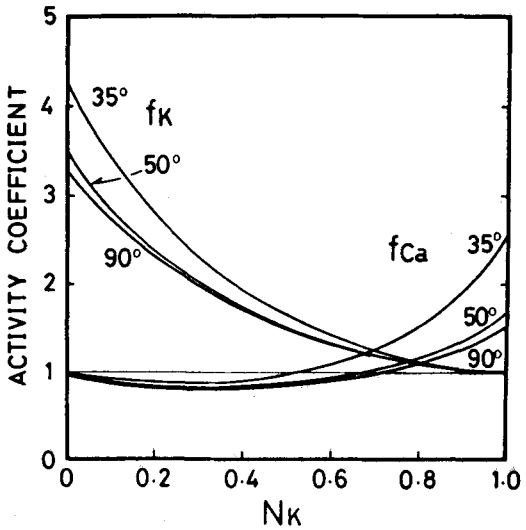


Figure 7. The activity coefficients of adsorbed cations.

ure 7. The activity coefficient of K ion departs positively from the ideal value over the entire compositional range. On the other hand, that of Ca ion shows a positive departure at $N_{Ca} < 0.5$, and a negative departure at $N_{Ca} > 0.5$ from the ideal value of 35°C.

The mixing properties of Ca and K in montmorillonite

The excess functions. To clarify the mixing properties of Ca and K ion in montmorillonite, excess functions were calculated by the following equations (Howery and Thomas, 1965);

$$\Delta G^{ex} = RT[N_k \ln f_K + \tfrac{1}{2}(1 - N_k)\ln f_{Ca}] \quad (13)$$

$$\Delta H^{ex} = R\left\{N_k \frac{\partial \ln f_K}{\partial (1/T)} + \frac{1 - N_k}{2} \frac{\partial \ln f_{Ca}}{\partial (1/T)}\right\} \quad (14)$$

$$\Delta S^{ex} = \frac{\Delta H^{ex} - \Delta G^{ex}}{T} \quad (15)$$

The excess functions may be usually represented

Table 4. Excess free energy (ΔG^{ex}), enthalpy (ΔH^{ex}), and entropy (ΔS^{ex}) at 35°C.

N_K	ΔG^{ex} (cal/eq)	ΔH^{ex} (cal/eq)	ΔS^{ex} (cal/eq/degree)
0	0	0	0
0.1	53.5	93.1	0.1
0.2	95.1	165.6	0.2
0.3	124.8	217.3	0.3
0.4	142.6	248.3	0.3
0.5	148.6	258.7	0.4
0.6	142.6	248.3	0.3
0.7	124.8	217.3	0.3
0.8	95.1	165.6	0.2
0.9	53.5	93.1	0.1
1.0	0	0	0

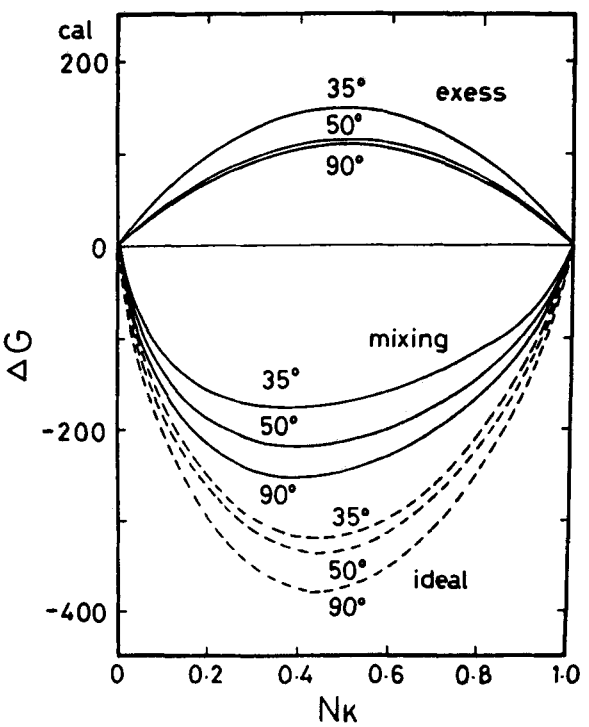


Figure 8. The excess free energy as a function of N_K. "Mixing" and "ideal" refer to actual and ideal mixing free energy, respectively.

by the Margules expansion (Thompson, 1967); for example,

$$\Delta G^{ex} = (A + BN_k + CN_k^2 + DN_k^3 + \cdots)RT.$$

If the selectivity coefficient is expressed by a linear equation of N_k, the excess functions are deduced to be cubic equations of N_k by Eq. (13), (14), and (15). Actually, the third-order term is cancelled in the excess functions, resulting in quadratic equations of N_k. According to Thompson (1967), when excess functions are approximated by quadratic equations of N_k, such solution is referred to as a symmetric regular solution. When excess functions are cubic equations, it is an asymmetric regular solution. Truesdell and Christ (1968) indicated that the K–H exchange reaction in montmorillonite can be treated by regular solution approximation.

Changes of mixing free energy and excess free energy for N_k are shown in Figure 8. Excess enthalpy and entropy calculated by Eq. (14) and (15) are also given in Table 4. If a solution is a regular one, the value of mixing entropy is equal to that of an ideal solution, and the value of excess entropy is then zero over the entire compositional range. The present data, in actual fact, showed only minor variation due to experimental errors. Eventually, the mixing of Ca and K in montmorillonite is approximately that of a regular solution.

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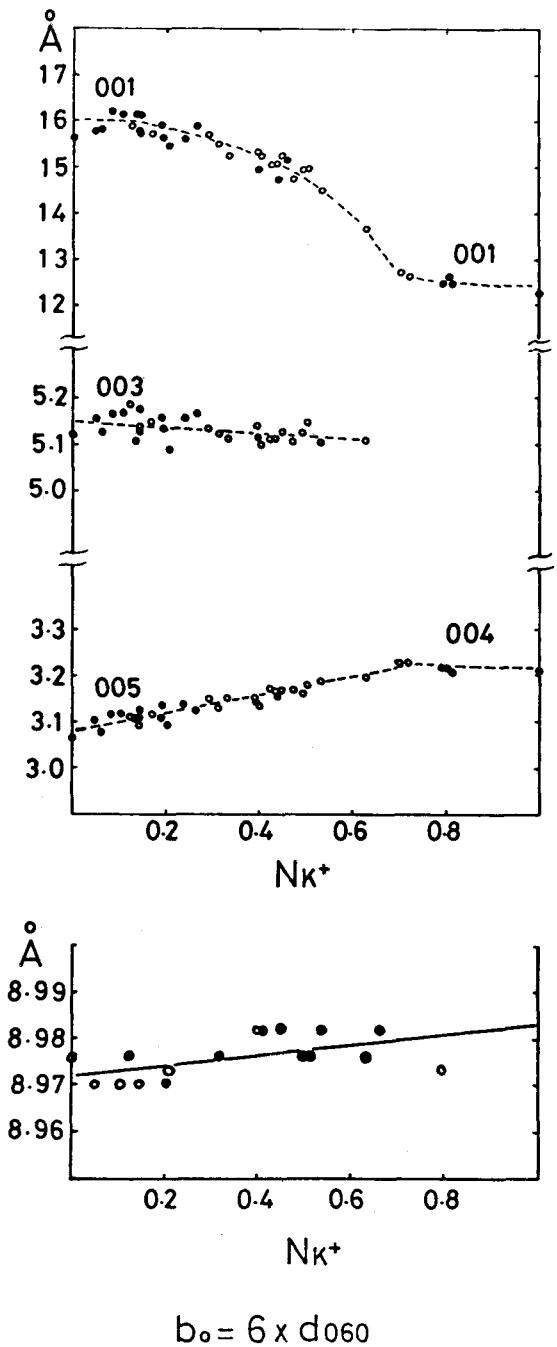


Figure 9. The relation between N_k and crystallographic parameters. Solid and open circles refer to Ca- and K-montmorillonite as starting materials, respectively. In the b-axis parameter, each point was an average of eight measurements. The specimens were X-rayed at 60% relative humidity.

That is to say, if K and Ca ions happen to occupy adjacent sites, an extra energy is induced. In the present work, the extra energy is endothermic, and the cations tend to repel each other.

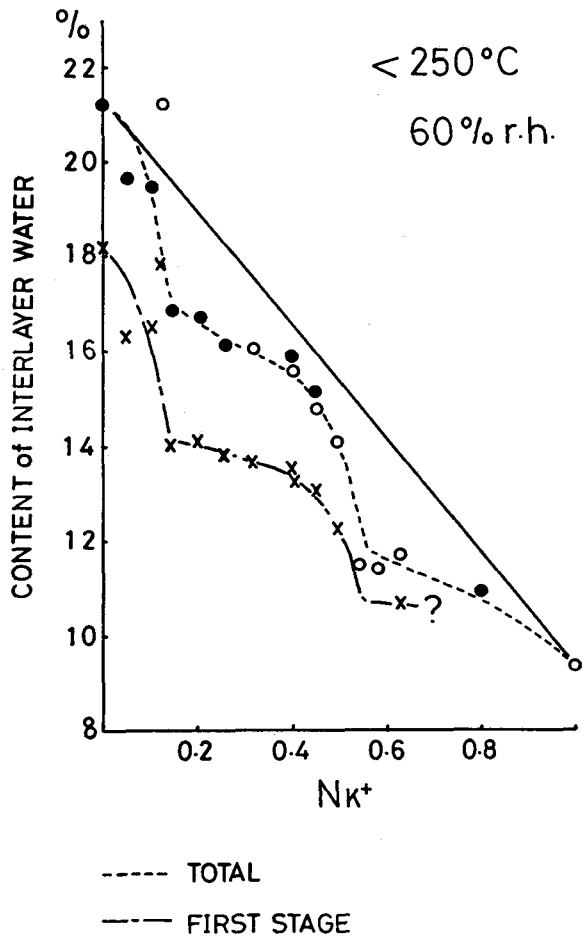


Figure 10. Plots of interlayer water content vs. N_k. Solid line refers to mechanical mixtures. × = dehydrated water in first stage; ●○ = total dehydrated water. Solid and open circles refer to Ca- and K-montmorillonite as starting materials, respectively.

Other properties in the mixing of Ca and K. The relation between the b-axis parameter and cationic composition is shown in Figure 9. The b-axis parameter of montmorillonite changed slightly from 8.972 Å to 8.983 Å by regression analysis over the entire compositional range. On the other hand, the c-axis spacing changed markedly. The d(001) spacings of Ca- and K-montmorillonites are 15.6 Å and 12.6 Å at 60% relative humidity, respectively. Compared with the reflections of mechanical mixtures of Ca- and K-montmorillonite, Ca-K exchanged montmorillonite can be distinguished by the differences of the position of the reflections and of the peak shape. As shown in Figure 9, the greater the value of N_k, the smaller the value of the d(003) spacing. When N_k exceeds 0.6, the corresponding reflection cannot be detected. The d(001) and d(004) spacings change little in the range of $0.7 < N_k < 1.0$, but when $N_k < 0.7$, the d(001) spacing increases to 15.6 Å. On the other hand,

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the d(004) spacing of the K-montmorillonite decreases to a value corresponding to the d(005) spacing of Ca-montmorillonite. With montmorillonite of $0 < N_k < 0.1$ and $0.7 < N_k < 1.0$, basal reflections were approximately integral. In the range of $0.1 < N_k < 0.7$, however, the integrality of the basal reflections was not conserved. MacEwan *et al.* (1961) indicated that integrality is not generally conserved when random interstratification occurs. Therefore, it is interpreted that montmorillonite with $0.1 < N_k < 0.7$ consists of a random interstratification of K-montmorillonite (12.6 Å) and Ca-montmorillonite (15.6 Å).

Superlattices, that is, regular interstratifications, will tend to be formed (Guggenheim, 1952). Sato (1965) discussed the interstratification from the viewpoint of interaction energy between unit layers. According to Sato's diagram (see Figure 1, 1965), the random interstratification in the present work probably represents partial random interstratification with a tendency towards segregation.

The relationship between the cationic composition of the clay and its interlayer water content is shown in Figure 10. There was a dehydration stage in K-montmorillonite below 250°C, whereas two dehydration stages can be noted in Ca-montmorillonite. The amount of first dehydration is referred to as the first stage, and the net amount of two dehydration stages as the total amount. The total water contents of Ca-K exchanged montmorillonite were always less than those of mechanical mixtures, in the intermediate composition range. In addition, interlayer water content seems to change stepwise with N_k as seen in Figure 10.

The above changes have been found in other systems: Na-Ca (Glaeser and Mering, 1954) and Na-Cu (McBride, 1976). These authors interpreted this to mean that the Ca or Cu ion was not fully hydrated until the cations occupied 30% of the exchange sites. In the Ca-K system, as well as in the Na-Ca and Na-Cu systems, variations of thermodynamic data, basal spacings, and interlayer water content suggest that the Ca ions are not fully hydrated until they occupy about 30% of the exchange sites because of the energy barrier for hydration of cations in the montmorillonite. When Ca ions occupy more than 30% of the exchange sites, they attain an intrinsic hydration state. Eventually, the interstratification in the intermediate composition range may be due to the difference between the hydration states of the cations in the interlayer space.

The interstratification of K-montmorillonite and Ca-montmorillonite may be distinguished from that between illite and Ca-montmorillonite; the former has characteristic spacings of 12.6 Å and 15.6 Å, while the latter has spacings at 10 Å and 15.6 Å. Chaussidon (1963) reported that an interstratification containing a unit layer of 10 Å was made by repeated cycles of humidifying and desiccating Ca-K-montmorillonite. This suggests the possibility that K-montmorillonite/Ca-montmorillonite changes progressively into illite/Ca-montmorillonite. As expected from Figure 2, if K-montmorillonite is dehydrated, the selectivity for K ion in this montmorillonite becomes greater. In nature, elevation of temperature and compaction during diagenetic processes may bring about such dehydration of montmorillonite.

CONCLUSION

In the Ca-K exchange reaction, montmorillonite showed a greater selectivity for the Ca ion. The mixing model of Ca-K-montmorillonite can be approximated as that of a regular solution by thermodynamic analysis.

According to variations of basal spacings and interlayer water content, montmorillonite with $0.1 < N_k < 0.7$ consists of a random interstratification of Ca- and K-montmorillonite; moreover, it may be in the state of a partial random interstratification with a tendency towards segregation. This interstratification is probably due to the difference between the hydration states of the cations in the interlayer space.

When montmorillonite initially saturated with K ions is dehydrated, it exhibits an isotherm that is different from that of Ca-montmorillonite. This is due to the K-fixation in montmorillonite. The amount of this fixation is a function of the initial N_k of the clay. Thus, when montmorillonite is dehydrated, it becomes richer in K ions, a phenomenon which suggests a mechanism of the aggradational formation of illite from montmorillonite during diagenetic processes.

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Резюме—Изучалось катионно-обменное равновесие для Ca-K-монтмориллонита при температурах 35°, 50°, и 90°C и при трех полных нормальностях равновесного раствора (0,1, 0,05, и 0,01 N). Изменения стандартной свободной энергии для обмена от K-монтмориллонита до Ca-монтмориллонита были определены как −53, −270, и −393 кал/эк при 35°, 50°, и 90°C соответственно. Изменения стандартной энтальпии и этропии были соответственно 1,7 ккал/эк и 5,6 кал/эк/градус при 35°C. Было установлено, что знак изменения стандартной свободной энергии определяется в основном изменением энтропии, в особенности гидрационной энтропии катионов.

Подсчет остаточных функций показывает, что модель смешивания Ca-K-монтмориллонита апроксимирует модель обыкновенного раствора. Монтмориллонит, имеющий калиевую эквивалентную ионную фракцию от 0,1 до 0,7, характеризуется нерегулярным переслаиванием Ca-монтмориллонита (15,6 Å) и K-монтмориллонита (12,6 Å).

Resümee—Das Kationenaustausch-Gleichgewicht für Ca-K-Montmorillonit wurde bei 35°, 50°, und 90°C und bei 3 Gesamtnormalitäten der Gleichgewichtslösung (0,1, 0,05, und 0,01 N) untersucht. Die Änderungen der freien Energie beim Austausch von K-Montmorillonit zu Ca-Montmorillonit ergaben Werte von −53, −270, und −399 cal/Äqu bei 35°, 50°, 90°C und bzw. Die Änderungen der Standard-Enthalpie und -Entropie betrugen 1,7 kcal/Äqu bzw. 5,6 cal/Äqu/Grad bei 35°C. Es zeigte sich, daß die Änderung der freien Energie vor allem von der Änderung der Entropie abhängt, insbesondere von der Hydratations-Entropie der Kationen.

Die Berechnung der Überschußenergien läßt erkennen, daß das Mischungsmodell für Ca-K-Montmorillonit dem einer regulären Lösung nahekommt. Montmorillonit mit einem Kalium-Ionenanteil von 0,1 bis 0,7 bestehen aus einer ungeordneten Wechsellagerung von Ca-Montmorillonit (15,6 Å) und K-Montmorillonit (12,6 Å).

Résumé—L'équilibre d'échange de cations pour la montmorillonite Ca-K a été étudié à 35°, 50°, et 90°C et à trois normes totales de la solution d'équilibre (0,1, 0,05, et 0,01 N). Les changements d'énergie libre standard pour l'échange de montmorillonite-K à la montmorillonite-Ca ont été déterminés à −53, −270, et −393 cal/eq à 35°, 50°, et 90°C, respectivement. Les changements de l'enthalpie et de l'entropie standards étaient de 1,7 kcal/eq et 5,6 cal/eq/degré à 35°C, respectivement. On a trouvé que le signe du changement de l'énergie libre standard était déterminé principalement par le changement d'entropie, en particulier, par l'entropie d'hydratation des cations.

Le calcul des fonctions en excès indique que le modèle de mélange de montmorillonite-Ca-K est proche de celui d'une solution régulière. La montmorillonite ayant une fraction d'ion d'équivalent de potassium de 0,1 à 0,7 consiste en une interstratification au hasard de montmorillonite-Ca (15,6 Å) et de montmorillonite-K (12,6 Å).

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