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SODIUM–LITHIUM EXCHANGE EQUILIBRIA ON VERMICULITE AT 25° AND 50°C*

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Abstract—Sodium–lithium exchange equilibria between dilute aqueous chloride solutions and 0·2–62 μ Transvaal, South African vermiculite were studied at 25° and 50°C using a dialysis technique. The K content of the vermiculite was reduced to < 1% of the exchange capacity of 2·14 me/g by exhaustive extraction using Na-tetraphenylboron. The thermodynamic equilibrium constants and in turn the standard free energies and heats of exchange were evaluated from the equilibrium selectivity coefficients at the two temperatures. The standard entropy of exchange, $\Delta S°$, was calculated according to the relationship $\Delta G° = \Delta H° - T\Delta S°$. Similar results were obtained for Na → Li and Li → Na exchange at 25°C, thus confirming the reversibility of the reaction.

Sodium preference increased with Na saturation of the vermiculite and equilibrium selectivity coefficients ranged from 6·0 to 22·0 at 25°C. In comparison, selectivity coefficients for Na–Li exchange on montmorillonite ranged from 1·0 to 2·0 and became smaller with increasing Na saturation. The standard free energy and heat of exchange on vermiculite at 25°C were −1444 and −5525 cal mole^{-1}, respectively, resulting in a $\Delta S°$ value of −13·7 e.u. This relatively large entropy change is probably due to differences in ion hydration in the solution and surface phases.

INTRODUCTION

RESULTS of cation exchange equilibria studies with vermiculite reported by Wild and Keay (1964) differ from those generally found for montmorillonite in the four following ways:

A. *Selectivity sequences*

(1) *Montmorillonite.* Almost without exception, the affinity of the clay for the cations decreases with increasing ionic hydrated radii with the order of preference being $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ and $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$ for mono- and di-valent cations, respectively (Cloos *et al.*, 1965; Eliason, 1966; Gast, 1969; Jenny, 1932). The affinity differences, or selectivity coefficients, are usually greater for mono–mono-valent- than di–di-valent-exchange reflecting the greater range of hydrated radii of the monovalent cations.

(2) *Vermiculite.* The selectivity sequence for divalent cations is the reverse of that for montmorillonite or $Mg^{2+} > Ca^{2+} \approx Sr^{2+} \approx Ba^{2+}$. Wild and Keay (1964) relate this to a relatively constant number of water molecules per cation in the interlamellar space of vermiculite which causes the distance between the two silicate surfaces to increase with the diameter of the cation or $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$. Therefore, the attractive forces between the negatively charged silicate sheets and the cations decrease in the order $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$; i.e. the same as that observed for the affinity series.

B *Heats of exchange*

(1) *Montmorillonite.* Observed heats of exchange for uptake of the preferred cation on montmorillonite are generally exothermic (Gast *et al.*, 1969; Laudelout *et al.*, 1968; Martin and Laudelout, 1963), resulting in a decrease in selectivity with increasing temperature. This is consistent with general adsorption theory (Brunauer, 1945). Since the free energy of adsorption, $\Delta G°$, must be negative for spontaneous adsorption to occur and since there is a decrease in the entropy of the adsorbed species (i.e. they lose one degree of freedom), it follows from the relationship $\Delta G° = \Delta H° - T\Delta S°$ that $\Delta H°$ must be negative (i.e. exothermic) and adsorption decreases with increasing temperature. Only if there are other positive entropy contributions associated with the exchange reaction can the heat of exchange for uptake of the preferred cation be endothermic.

(2) *Vermiculite.* Wild and Keay (1964) observed

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exothermic heats of exchange for uptake of the preferred cation for di–di-valent exchange. However, in the exchange of Na^+ with Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}, where the divalent cations were preferred over Na, the preference increases with increasing temperature; i.e. the heat of exchange is endothermic for uptake of the preferred cation. They associate this endothermic heat of reaction with the process of concentrating the divalent cations in interlamellar spaces since the heat of dilution for the reverse process is endothermic.

C. *Entropies of exchange*

(1) *Montmorillonite.* Spontaneous ion exchange reactions on montmorillonite are nearly always accompanied by a relatively small negative entropy change in the order of −1 to −2 e.u. (Gast *et al.*, 1969; Martin and Laudelout, 1963) with some values as great as −4 to −5 e.u. (Laudelout *et al.*, 1968). While these entropy contributions may have a significant effect on the net free energy change due to the temperature factor in the term, $T\Delta S°$, they are small compared to hydration entropy differences for the exchange cations (Robinson and Stokes, 1955). These small entropy changes are probably due to slight changes in ion hydration but this is difficult to prove.

(2) *Vermiculite.* Wild and Keay (1964) reported positive entropy changes for both mono–di- and di–di-valent cation exchange on vermiculite. The values were relatively small for di–di-valent exchange (< 2 e.u.) making $T\Delta S°$ the same order of magnitude as $\Delta H°$. However, the $T\Delta S°$ values for mono–di-valent exchange were in the range of 5000–6000 cal per equivalent. It is this large positive value of $T\Delta S°$ which gives the negative value for $\Delta G°$ in spite of the endothermic heats of reaction. That is, the preference of the vermiculite for divalent ions is caused by the greater entropy of the divalent ion-vermiculite system. This gain in entropy may result partly from an increase in configurational entropy when monovalent cations are replaced by half the number of divalent cations, or from changes in cation hydration on passing between the solid and solution phases. Changes in cation hydration between the adsorbed and non-absorbed phases may be especially important in the case of vermiculite.

D. *Variation in the selectivity coefficient with composition*

(1) *Montmorillonite.* The selectivity coefficient generally decreases with increasing saturation of the preferred cation on montmorillonite (Eliason, 1968; Gast, 1969; Lewis and Thomas, 1963) with the values varying as much as a factor of 3–5. As Howery and Thomas (1965) have pointed out, this variation may be explained on the basis of nonideal mixing and/or by a variation in the binding energies of the exchange sites, and it is difficult to resolve which factor is actually responsible.

(2) *Vermiculite.* Results of Wild and Keay (1964) show that the selectivity coefficient increases with increased loading of the vermiculite with the preferred ion. Although they recognize that this is opposite to that found for exchange resins, as it is for montmorillonite, they offer no explanation for this observation. It cannot be explained on the basis of variable exchange sites with the preferred ion being held by the most energetic sites, for this reasoning leads to a decrease rather than an increase in selectivity.

In light of the contrasting results reported for vermiculite and montmorillonite, the hypothesis that comparable differences would hold for mono–mono-valent exchange warranted investigation. Since the alkali metal cations have a much wider range of ion sizes, and hence hydration energies, than the alkaline earth cations, we might expect to find even greater differences. This is obviously the case for Cs, Rb, and K since they interact so strongly with vermiculite that they collapse the lattice. Under these conditions the ions are essentially "fixed" against exchange with other ions and it is impossible to obtain a reversible equilibrium in a reasonable period of time. Since reversibility is required for a straightforward discussion of selectivity and the thermodynamic quantities for the ion exchange process, this study was limited to Li–Na exchange for the monovalent cations. Specifically, Li → Na exchange equilibria properties of a K-depleted sample of Transvaal, South African vermiculite were determined and the results compared with those of similar studies using montmorillonite and kaolinite.

MATERIALS AND METHODS

Vermiculite preparation

Vermiculite flakes were handpicked from a specimen of Transvaal, South African vermiculite, obtained from Ward's Natural Mineral Establishment. The 0·2–62 μ fraction was separated and converted to the Na form by tetraphenylboron extraction as described previously (Klobe and Gast, 1970). Chemical and X-ray analyses of the original material showed it to be a typical hydrobiotite having interstratified 10 Å biotite and 14 Å vermiculite spacings. The average total me/g of (Na + K) per g of K-extracted material was found to be 2·14 me/g, which is comparable to the value of 2·16 me/g found by Barshad (1954). Hence, the material used in this study was a fully expanded vermiculite which was nearly 100% Na-saturated,

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having $< 1\%$ of the exchange capacity saturated with K. Isotopic dilution showed that all of the Na on the vermiculite was isotopically exchangeable with ^{22}Na within a period of a few hours.

A sample of Na-saturated vermiculite was converted to the Li form by transferring it into cellulose acetate dialysis tubing and washing repeatedly in LiCl. The pH of the LiCl was adjusted to 9·0 using LiOH to prevent hydrolysis. Concentration of the equilibrium LiCl solution was reduced to 0·01N by placing the dialysis tubing containing the Li vermiculite in the required volume of distilled water. Chemical analyses of the Li vermiculite showed it to be Na-free and Li-saturated.

Determination of selectivity coefficients

Selectivity coefficients were determined by equilibrating 10 ml of an approximate 1·0% vermiculite suspension, saturated with either Na or Li, in 90 ml of solution containing both cations as chlorides with an appropriate ratio and a total concentration of 0·01N. The chloride solution was labeled with ^{22}Na. Equilibrium was ascertained by radio-assay of the external solution and found to occur within one week. The Na composition of the solution and vermiculite phases at equilibrium were determined by isotopic dilution and a knowledge of the total amount of Na in the system. The Li composition of the two phases was determined from analysis of the external solution using atomic absorption techniques. Selectivity coefficients were determined for Li–Na exchange at 17 different surface compositions and temperatures of 25° and 50°C. Reversibility of the exchange reaction was established by determining selectivity coefficients for Na to Li exchange at 25°C for ten surface compositions.

Evaluation of thermodynamic quantities

Applying mass action theory for the exchange of two monovalent cations A^+ and B^+ according to the reaction

$$B-\text{clay}+A^+-\text{soln} \rightleftharpoons A-\text{clay}+B^+-\text{soln} \quad (1)$$

The thermodynamic equilibrium constant $\bar{K}_B{}^A$ is given by

$$\bar{K}_B{}^A = \frac{(A)\bar{f}_A(B)\gamma_B}{(B)\bar{f}_B(A)\gamma_A} \quad (2)$$

where A and B are the concentrations of the two cations and $\bar{f}$ and γ are activity coefficients of the ions in the surface and solution phase, respectively. The barred quantities refer to the surface phase in all cases. Since the ratios of solution phase activity coefficients in dilute solutions of 1:1 strong electrolytes are essentially one, equation (2) can be written

$$\bar{K}_B{}^A = K_c\frac{\bar{f}_A}{\bar{f}_B} \quad (3)$$

where K_c, the experimentally determined equilibrium selectivity coefficient, is given by

$$K_c = \frac{(\bar{A})(B)}{(\bar{B})(A)}. \quad (4)$$

The thermodynamic equilibrium constant and surface phase activity coefficients may be related to the experimentally determined selectivity coefficient by equations (5–7) if appropriate standard states are used along with the Gibbs-Duhem equation (Gaines and Thomas, 1953; Howery and Thomas, 1965)

$$\ln \bar{K}_B{}^A = \int_0^1 \ln K_c d\bar{X}_B \quad (5)$$

$$\ln \bar{f}_A = -\bar{X}_B \ln K_c + \int_0^{\bar{X}_B} \ln K_c \, d\, \bar{X}_B \quad (6)$$

$$\ln \bar{f}_B = \bar{X}_A \ln K_c - \int_{\bar{X}_B}^1 \ln K_c \, d\, \bar{X}_B \quad (7)$$

where $\bar{X}_A$ and $\bar{X}_B$ are the mole fractions of cations A and B on the clay, respectively. The standard free energy of exchange, $\Delta G°$, for the reaction in equation (1) is in turn related to $\bar{K}_B{}^A$ by the expression

$$\Delta G° = -RT \ln \bar{K}_B{}^A. \quad (8)$$

The standard heat of exchange, $\Delta H°$, can be determined from the temperature dependence of the thermodynamic equilibrium constant using the van't Hoff relationship

$$\frac{(\partial \ln \bar{K}_B{}^A)}{(\partial 1/T)} = -\Delta H°/R \quad (9)$$

and the standard entropy of exchange, $\Delta S°$, can in turn be calculated using the relationship

$$\Delta G° = \Delta H° - T\Delta S°. \quad (10)$$

If the surface behaves as an ideal solid in that there are no significant interactions between ions on neighboring sites, and if all exchange sites are alike, the surface phase activity coefficients for equi-charge exchange have the constant value of unity and the selectivity coefficient is a constant

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value equal to the thermodynamic equilibrium constant for all surface compositions. In such ideal systems, the free energy of mixing, ΔG_m^I, is given by the relationship (Howery and Thomas, 1965)

$$\Delta G_m^I = RT(\bar{X}_A \ln \bar{X}_A + \bar{X}_B \ln \bar{X}_B). \quad (11)$$

However, if there are significant interactions between neighboring ions the values of $\bar{f}_A$, $\bar{f}_B$ will not have a value of unity as evidenced by the variation in the selectivity coefficient with composition of the surface phase. The free energy of mixing in such nonideal systems, ΔG_m^{II}, is given by the relationship

$$\Delta G_m^{II} = RT(\bar{X}_A \ln \bar{X}_A \bar{f}_A + \bar{X}_B \ln \bar{X}_B \bar{f}_B) \quad (12)$$

and the excess free energy of mixing, ΔG_m^X, is defined by

$$\Delta G_m^X = \Delta G_m^{II} - \Delta G_m^I = RT(\bar{X}_A \ln \bar{f}_A + \bar{X}_B \ln \bar{f}_B). \quad (13)$$

If sufficient data are available for calculation of $\bar{f}_A$ and $\bar{f}_B$ for a complete range of surface composition, the excess free energy of mixing, ΔG_m^X, can be evaluated. In addition, if exchange isotherms are determined for two or more temperatures, the heat of mixing can be calculated from the temperature coefficients of $\bar{f}_A$ and $\bar{f}_B$ using the expression (Howery and Thomas, 1965)

$$\Delta H_m^X = -RT^2 \left[X_A \left(\frac{\partial \ln \bar{f}_A}{\partial T} \right) + \bar{X}_B \left(\frac{\partial \ln \bar{f}_B}{\partial T} \right) \right]. \quad (14)$$

Finally, knowing ΔG_m^X and ΔH_m^X the excess entropy of mixing, ΔS_m^X, can be calculated from the relationship

$$\Delta G_m^X = \Delta H_m^X - T\Delta S_m^X. \quad (15)$$

RESULTS AND DISCUSSION

Values of the experimentally determined selectivity coefficients, K_c, for Li → Na exchange on vermiculite at five surface compositions or mole fractions of Na on the vermiculite, $\bar{X}_{Na}$, are given in Table 1, along with comparable values of K_c for Li → Na exchange on Wyoming bentonite, Chambers montmorillonite and kaolinite (Gast, 1970). The plot of $\ln K_c$ vs. $\bar{X}_{Na}$ for Li → Na exchange on vermiculite at 25° and 50°C, including all data points, is given in Fig. 1. Values for Na → Li exchange at 25°C are also indicated, demonstrating reversibility of the exchange reaction.

The integration indicated in equation (5) for evaluating $\ln \bar{K}_B^A$ was performed by using a planimeter to measure the areas under the curves in Fig. 1. The standard free energies, heats, and entropies of exchange were then calculated using equations (8–10) and are given in Table 2. Again, values for Wyoming bentonite and Chambers montmorillonite are included for comparative purposes.

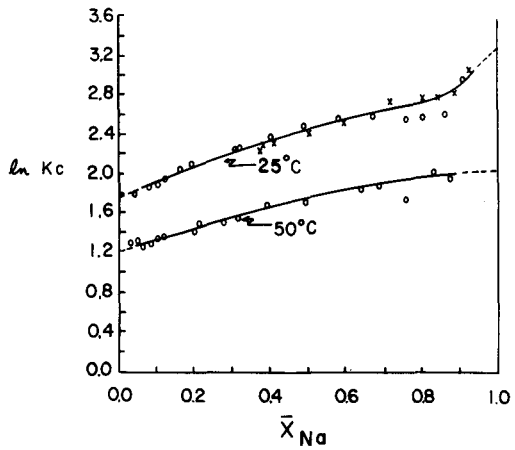


Fig. 1. Natural logarithms of equilibrium selectivity coefficients, $\ln K_c$, vs. mole fraction of Na, $\bar{X}_{Na}$, for Li → Na exchange on Transvaal, South African vermiculite at 25° and 50°C. ○ = Li → Na exchange; × = Na → Li exchange.

The experimental results will be discussed in terms of the four criteria used in the Introduction for comparing previously published ion exchange equilibria data for montmorillonite and vermiculite; namely; (A) selectivity sequences or ion preference, (B) heats of exchange, (C) entropies of exchange, and (D) variation in selectivity coefficients with surface composition of the exchanger.

A. *Ion preference*

Values of both the selectivity coefficients, K_c (Table 1) and the standard free energies of exchange, $\Delta G°$ (Table 2), show that Na is preferred over Li on vermiculite and that the preference is much greater than for the other clays. The preference of Na over Li is to be expected in the case of montmorillonite and kaolinite since, (1) the radii of the fully hydrated ions determine the distance of closest approach of the cation to the negatively charged silicate surface, (2) Na has the smaller hydrated radius, and (3) electrostatic considerations predict that the ion positioned nearest the surface will be preferred. However, it is less obvious that this should be the case in vermiculite which undergoes limited swelling. X-ray results

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Table 1. Experimentally determined equilibrium selectivity coefficients, K_c, vs. mole fraction of Na on the clay, $\bar{X}_{Na}$, for the exchange of Li with Na on four minerals at 25°C

$\bar{X}_{Na}$	Vermiculite	Wyoming bentonite*	Chambers montmorillonite*	Kaolinite*
0·03	6·3		1·4	
0·20	8·3	1·2	1·3	2·0
0·50	12·1	1·0	1·3	1·7
0·80	13·5	1·0	1·2	1·3
0·92	22·2	1·0	1·0	1·3

*Values from Gast (1970).

Table 2. Standard free energies, enthalpies, and entropies of exchange at 25°C for Li → Na exchange on Transvaal, South African vermiculite, Wyoming bentonite, and Chambers montmorillonite

	ΔG° (cal mole^{-1})	ΔH° (cal mole^{-1})	ΔS° (e.u.)
Vermiculite	−1444	−5525	−13·7
Wyoming bentonite*	−48	−150	−0·5
Chambers montmorillonite*	−80	−111	−0·1

*Values from Gast (1970).

(Table 3) show that the c-axis spacings for fully hydrated homionic Li- and Na-vermiculite are 14·6 and 14·9 Å, respectively. As van Olphen (1965) has pointed out, the c-axis spacing for the analogous micaceous mineral, talc, which does not contain interlayer cations, is 9·2 Å. The interlayer spacings for fully hydrated Li- and Na-vermiculite are then 5·4 and 5·7 Å respectively, with reference to the spacing of talc. The crystalline radii of Li and Na ions are 0·78 and 0·98 Å, respectively. If we assume that Li ions are positioned midway between the vermiculite sheets, as X-ray analysis has shown to be the case for Na ions (Bradley and Weiss, 1963), then the distance between the ions and the silicate surface is $[5{\cdot}4 \div (2 \times 0{\cdot}78)/2] = 1{\cdot}92$ Å for Li and $[5{\cdot}7 \div (2 \times 0{\cdot}98)/2] = 1{\cdot}87$ Å for Na. This latter value would be even less (1·82 Å) with a 14·8 Å c-axis spacing for Na-vermiculite as reported by van Olphen (1965). On this basis, we would expect Na to be preferred over Li even though the c-axis spacing for Li-vermiculite is smaller. In addition, the preference for Na would be enhanced by the greater polarizability of Na (0·196 Å^3) compared to 0·079 Å^3 for Li (Cloos *et al.*, 1965).

Table 3. Basal spacings in Å, of hydrated 0·2–62 μ Transvaal, South African vermiculite with varying degrees of saturation with Na and Li

Order	Per cent Na saturation 0	4	50	96	100
1	14·58	14·68	14·83	14·80	14·90
2	14·59	14·64	14·76	14·86	14·90
3	14·60	14·61	14·76		14·89
4	14·60	14·64	14·76	14·88	14·90
5	14·61	14·65	14·75	14·90	

B. *Heat of exchange*

The observed standard heat of exchange, ΔH° for Li → Na exchange is exothermic which is in agreement with results generally observed for uptake of the preferred ion on montmorillonite and for di-di-valent cation exchange on vermiculite (Wild and Keay, 1964). The value of −5525 cal mole^{-1} is much larger than that found for Li–Na exchange on montmorillonite, however. This is probably the result of a much greater decrease in electrostatic free energy on replacement of Li by Na on vermiculite, due to the higher charge density and greater charge deficit in the tetrahedral vs. octahedral layer of vermiculite compared to that of montmorillonite.

C. *Entropies of exchange*

The standard entropy of exchange, ΔS°, calculated from the values of ΔG° and ΔH° according to equation (10) is −13·7 e.u. This value is much greater than those observed for Li → Na exchange

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on the other clays and is in contrast to the positive entropy changes reported by Wild and Keay (1964) for both mono–di- and di–di-valent cation exchange on vermiculite.

The difference between this value and that for montmorillonite is too great to be explained by experimental error, even though the $\Delta H°$ values calculated from selectivity data are subject to rather large uncertainties. As discussed previously (Gast *et al.*, 1969), the uncertainties in $\Delta G°$ are in the range of ± 50–100 cal mole^{-1}, which is equivalent to an uncertainty of 0·08–0·17 in $\ln \bar{K}_B{}^A$ at 25°C. An error of $\pm 0{\cdot}1$ $\ln \bar{K}_B{}^A$ results in an uncertainty of about ± 800 cal mole^{-1}. Since

$$\Delta S° = \frac{\Delta H° - \Delta G°}{T} \qquad (16)$$

the $\Delta S°$ values can be considered accurate to $\pm 2{\cdot}5$–$3{\cdot}0$ e.u.

Changes in the hydration of Li on going from the surface to the solution phase probably account for both the relatively large entropy change and the decrease rather than increase in entropy as reported by Wild and Keay (1964). The X-ray results in Table 3 show that the *c*-axis spacing for Li vermiculite is 0·3 Å less than for the Na vermiculite. Since Li has a larger hydrated size in aqueous solution than Na, this suggests that Li would undergo a significant increase in hydration in the process of passing from the surface to the solution phase resulting in an increased ordering of water and consequently a decrease in entropy.

D. *Variation in selectivity coefficients with surface composition*

The equilibrium selectivity coefficients clearly increase with increased loading of the vermiculite with the preferred ion (Na) as reported by Wild and Keay (1964). As indicated previously, this variation in K_c cannot be explained on the basis of variable exchange sites with the preferred ion being held by the more energetic sites, for this reasoning leads to a decrease rather than an increase in selectivity. Alternately, this deviation from ideal behavior can be attributed to nonideal mixing and the relative contributions of the excess heats and entropies of mixing, $\Delta H_m{}^X$ and $\Delta S_m{}^X$, to the excess free energy of mixing $\Delta G_m{}^X$. The $\Delta G_m{}^X$ can be calculated according to equations (13–15), using the values of the surface phase activity coefficients $\bar{f}_{Li}$ and $\bar{f}_{Na}$ calculated from the experimental data using equations (6) and (7).

The surface phase activity coefficients calculated from experimental data taken at 25° and 50°C are shown in Fig. 2 plotted as $\ln \bar{f}_{Li}$ and $\ln \bar{f}_{Na}$ vs. $\bar{X}_{Na}$.

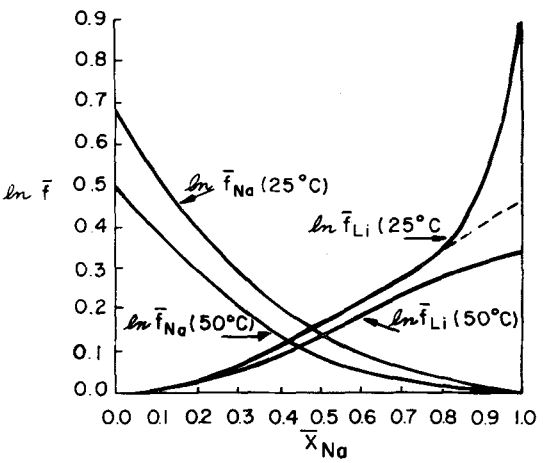


Fig. 2. Natural logarithms of surface phase activity coefficients, $\ln \bar{f}_{Na}$, and $\ln \bar{f}_{Li}$ vs. mole fraction of Na, $\bar{X}_{Na}$, for Li → Na exchange on Transvaal, South African vermiculite at 25° and 50°C.

The values of $\bar{f}_{Li}$ and $\bar{f}_{Na}$ are positive and greater than unity as a result of the increase in $\ln K_c$ with $\bar{X}_{Na}$ (Fig. 1). The similarity in the plots indicates that the two ions behave much alike on the surface. The excess free energies, enthalpies, and entropies of mixing, $\Delta G_m{}^X$, $\Delta H_m{}^X$, and $\Delta S_m{}^X$, are given in Table 4. The ideal free energy and entropy of mixing, $\Delta G_m{}^I$ and $\Delta S_m{}^I$, are included to provide some measure of the significance of the excess quantities. The ideal entropy of mixing is given by

$$\Delta S_m{}^I = \frac{-\Delta G_m{}^I}{T} \qquad (17)$$

since $\Delta H_m{}^I = 0$. The values of $\Delta H_m{}^X$ were calculated for the median temperature of 37·5°C, assuming a linear variation of $\ln \bar{f}_{Li}$ and $\ln \bar{f}_{Na}$ between 25° and 50°C. All other values in Table 4 were calculated for 37·5°C to be consistent.

Since the values of $\ln \bar{f}_{Li}$ and $\ln \bar{f}_{Na}$ are positive and decrease with increasing temperature, the values of $\Delta G_m{}^X$ and $\Delta H_m{}^X$ are both positive. The significant $\Delta H_m{}^X$ value indicates that ions near the vermiculite surface are sufficiently close to one another that the binding energies are affected by the nearest neighbors; i.e. the nonideality which causes the variation in $\ln K_c$ with surface composition is due to changes of the energetics as well as entropy changes. This might be expected in light of the high exchange capacity or charge density of the vermiculite.

However, the results (Table 4) show that excess heats of mixing are offset to a large extent by the excess entropies of mixing. The sources of these

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Table 4. Ideal free energies and entropies of mixing, ΔG_m^I and ΔS_m^I, and excess free energies, enthalpies, and entropies of mixing, ΔG_m^X, ΔH_m^X and ΔS_m^X, for Li → Na exchange on 0·2–62 μ South African vermiculite at 37·5°C

$\bar{X}_{Na}$	ΔG_m^I (cal mole^{-1})	ΔS_m^I (e.u.)	ΔG_m^X (cal mole^{-1})	ΔH_m^X (cal mole^{-1})	ΔS_m^X (e.u.)
0	0·0	0·0	0·0	0·0	0·0
0·1	−200·3	0·64	36·8	124·9	0·28
0·2	−308·5	0·99	64·6	218·3	0·50
0·3	−377·5	1·21	83·4	299·2	0·70
0·4	−415·1	1·34	93·8	331·4	0·77
0·5	−427·4	1·38	95·6	348·6	0·81
0·6	−415·1	1·34	90·3	350·9	0·84
0·7	−377·0	1·21	79·4	345·6	0·86
0·8	−308·5	0·99	63·6	332·6	0·87
0·9	−200·3	0·64	40·5	258·2	0·82
1·0	0·0	0·0	0·0	0·0	0·0

excess entropies are difficult to identify. A possible source is the formation of interstratified layers rich in one cation over the other, rather than a uniform distribution of each cation on all surfaces. Such interlayering was found to occur in Cs–Na systems on a sample of this same vermiculite (Klobe and Gast, 1970). The *c*-axis spacings shown in Table 3 for the hydrated vermiculite with increased Na saturation gives some indication that such interstratification occurs in these systems also. However, the small 0·3 Å difference in spacings of homionic Na vs. Li vermiculite makes it difficult to draw any definite conclusions.

SUMMARY AND CONCLUSIONS

Results for Li → Na exchange on vermiculite reported here agree with those generally reported for montmorillonite in that:

(1) Na^+, which has the smaller hydrated radius in aqueous solution, is preferred over Li.

(2) The heat of exchange for uptake of the preferred cation is exothermic; i.e. selectivity decreases with increasing temperature.

(3) There is a decrease in entropy associated with uptake of the preferred cation.

The preference for Na over Li is much greater for vermiculite than montmorillonite, however, and is reflected by a greater heat of exchange. This probably reflects a greater decrease in electrostatic free energy due to both a higher charge density and greater degree of charge substitution in the tetrahedral layer vs. octahedral layer of vermiculite compared to that of montmorillonite. The heat of exchange is partially offset by a relatively large decrease in entropy, probably resulting from differences in ion hydration between the solution and surface phases.

Values of the equilibrium selectivity coefficients increased with increased loading of the vermiculite with the preferred ion, (Na). This is in agreement with the results reported for cation exchange on vermiculite by Wild and Keay (1964) and is attributed to non-ideal mixing with significant contributions from both the excess heats and entropies of mixing.

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Résumé – On a étudie les équilibres d'échange sodium–lithium entre des solutions de chlorures diluées et une vermiculite du Transwaal, Afrique du Sud dans les conditions suivantes: taille des particules: 0,2 à 62 μ, température 25 et 50°C, technique de l'échange, dialyse. La teneur en potassium de la vermiculite a été réduite à moins de 1% de la capacité d'échange – qui est 2,14 me/g – par une extraction exhaustive à l'aide du tétraphénylborate de sodium. Les constantes d'équilibre thermodynamique puis les énergies libres standard et les chaleurs d'échange ont été évaluées à partir des coefficients de sélectivité à l'équilibre aux deux températures. L'entropie standard d'échange, $\Delta S°$, a été calculée par la relation $\Delta G° = \Delta H° - T\Delta S°$. Des résultats similaires ont été obtenus pour les échanges Na → Li et Li → Na, à 25°C, ce qui confirme la réversibilité de la réaction.

La préférence pour le sodium augmente avec le taux de saturation en Na de la vermiculite, et les coefficients de sélectivité à 25°C vont de 6,0 à 22,0. Par comparaison, les coefficients de sélectivité pour l'échange Na–Li sur la montmorillonite vont de 1,0 à 2,0 et diminuent quand la saturation en Na augmente. L'énergie libre standard et la chaleur d'échange avec la vermiculite sont respectivement de – 1444 et – 5525 cal mole^{-1}, ce qui entraine un $\Delta S°$ de – 13,7 u.e. Cette variation d'entropie relativememt importante est probablement due aux différences existant pour l'hydratation ionique entre la phase solution et la phase superficielle.

Kurzreferat – Natrium–Lithium Austauschgleichgewichte zwischen verdünnten wässrigen Chloridlösungen und 0,2 bis 62 μ Transvaal, südafrinkanischen Vermiculit wurden bei 25 und 50°C unter Verwendung einer Dialysentechnik studiert. Der K Gehalt des Vermiculit wurde unter Verwendung von Na-tetraphenylbor durch erschöpfende Extrahierung auf weniger als 1% der Austauschleistung von 2,14 me/g reduziert. Die thermodynamischen Gleichgewichtskonstanten, sowie die normalen freien Energien und Austauschwärmen wurden aus den Gleichgewichts-Selektivitätskoeffizienten bei den zwei Temperaturen bewertet. Die normale Austauschentropie S° wurde gemäss der Beziehung $D° = H° - T S°$ berechnet. Ähnliche Ergebnisse wurden erhalten für Na → Li und Li → Na Austausch bei 25°C, wodurch die Reversibilität der Reaktion bestätigt wird.

Bevorzugung für Natrium nahm zu mit der Na-Sättigung des Vermiculits und die Gleichgewichts-Selektivitätskoeffizienten erstreckten sich von 6,0 bis 22,0 bei 25°C. Vergleichsweise erstreckten sich die Selektivitätskoeffizientan für Na–Li Austausch an Montmorillonit von 1,0 bis 2,0 und wurden kleiner mit zunchmender Na-Sättigung. Die normale freie Energie und Austauschwärme an Vermiculit bei 25°C waren – 1444 bzw. – 5525 cal mol^{-1}, was einen $\Delta S°$ Wert von – 13,7 e.u. ergibt. Diese verhältnismässig grosse Entrepieanderung ist wahrscheinlich eine Folge von unterschiedlicher Ion-Hydratisiertung in der Lösungsphase und an der Oberfläche.

Резюме — Натриево-литиевое обменное равновесие между разбавленными хлоридными растворами и фракцией 0,2–62 мк вермикулита из Трансвааля были изучены с использованием техники диализа. Содержание K в вермикулите было снижено до <1% обменной емкости или 2,14 мг/г тщательной экстракцией с помощью Na-тетрафенилбора. Константы термодинамического равновесия, а затем стандартные свободные энергии и теплоты обмена были определены по коэффициентам равновесной селективности для двух температур. Стандартная энтропия обмена $\Delta S°$ была вычислена по равенству $\Delta G° = \Delta H° - T\Delta S°$. Сходные результаты были получены для обмена Na → Li и Li → Na при 25°, подтверждая обратимость реакции.

Избирательность для Na возрастала с насыщением им вермикулита, коэффициенты равновесной селективности колебались от 6 до 22,0 при 25°. В сравнении с ними коэффициенты селективности для обмена Na–Li на монтмориллоните составляли от 1,0 до 2,0 и уменьшались

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с возрастанием насыщения натрием. Стандартная свободная энергия и теплота обмена на вермикулите при 25° были равны соответственно — 1444 и — 5225 кал/моль$^{-1}$, а $\Delta S°$ — 13,7. Такое относительно большое изменение энтропии, вероятно, вызвано различиями в гидратации ионов в растворе и поверхностных фазах.

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