

MONTMORILLONITE EXCHANGE EQUILIBRIA WITH STRONTIUM-SODIUM-CESIUM

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ABSTRACT

The ion exchange isotherms and the free-energy changes of -2278 , -331 , and -4019 cal/mole for the cesium-sodium, strontium-sodium, and cesium-strontium systems respectively were determined for the Bayard, New Mexico montmorillonite. The ion exchange isotherm and the free-energy change of -2035 cal/mole for the cesium-sodium system on the Chambers, Arizona montmorillonite were determined for comparison with the Bayard, New Mexico montmorillonite. A surprising increase in selectivity for cesium and strontium at high cesium and strontium loading was observed in the cesium-sodium and strontium-sodium systems. The selectivity increases were presumed to be related to changes in the c -axis spacings.

INTRODUCTION

Determination of the influence of clay minerals on the behavior of radioactive wastes in soil systems requires a better understanding of the cation exchange characteristics of the clay minerals. The object of this study was to determine several exchange isotherms and associated free-energy changes for a montmorillonite of hydrothermal origin, and to make a comparison of the exchange characteristics of two montmorillonites of different origin.

Studies of the ion exchange isotherms and the determination of the related free-energy changes on clay minerals are limited. The Chambers, Arizona montmorillonite (reference Clay Mineral No. 23 of the American Petroleum Institute) has been studied and the ion exchange isotherms and related free-energy changes were determined by Lewis and Thomas (1963) and by Frysinger and Thomas (1960). The Chambers, Arizona montmorillonite is believed to have originated from volcanic tuff of a basic extrusive which was deposited as ash in a lake basin and altered in place (Kerr *et al.*, 1950b). The montmorillonite chosen for this study was Reference Clay Mineral No. 30a of the American Petroleum Institute, from Bayard, New Mexico. The Bayard, New Mexico montmorillonite is believed to be of hydrothermal origin from solutions penetrating a rhyolitic and andesitic tuff (Kerr *et al.*, 1950b). The exchange isotherm and the free-energy change for the sodium-cesium system on the Chambers, Arizona montmorillonite were redetermined for comparison with previous work by Lewis and Thomas (1963).

METHODS OF INVESTIGATION

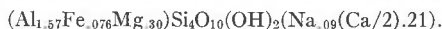
The clay samples used were obtained from the reference clay minerals of Ward's Natural Science Establishment. The chemical compositions

and proposed structural formulas of the Chambers, Arizona and the Bayard, New Mexico montmorillonite are listed by Kerr *et al.* (1950a). A chemical analysis and structural formula for the Bayard, New Mexico montmorillonite used in this study is given in Table 1.

Clay samples were ground to pass a 200-mesh screen and were then treated with a two per cent solution of sodium carbonate for 1 to 2 hours without heating. The sodium carbonate solution was removed and the clay dispersed in distilled water. Particles with an equivalent spherical diameter (e.s.d.) greater than 2μ were allowed to settle from the suspension. The suspension was then run through a centrifuge to remove particles less than 0.1μ e.s.d. The clay particles were divided into two size ranges, 2μ to 1μ and 1μ to 0.1μ e.s.d. by centrifugation. Electron micro-

TABLE 1. CHEMICAL ANALYSIS AND FORMULA OF MONTMORILLONITE FROM BAYARD, NEW MEXICO

SiO ₂	56.00%
Al ₂ O ₃	15.60
Fe ₂ O ₃	1.34
MgO	2.66
CaO	1.29
Na ₂ O	0.66
H ₂ O	21.20
	98.75



graphs of the two size ranges of the Bayard, New Mexico montmorillonites are shown in Figs. 1 and 2. The Chambers, Arizona montmorillonite was fractionated further into a 0.5μ to 0.1μ e.s.d. to correspond with the size fraction used in a previous study by Lewis and Thomas (1963).

The clay fractions were sodium-based with a sodium chloride solution, and were washed with distilled water until chlorine-free. The volume was reduced by centrifugation and the clay was then dried under vacuum at 25 C., using the freeze-drying system shown schematically in Fig. 3. The samples were frozen before setting them in the freeze-drying system. The 1μ to 0.1μ e.s.d. particle size was used for equilibrium studies on the Bayard, New Mexico montmorillonite, and the 0.5μ to 0.1μ e.s.d. particle size was used for the Chambers, Arizona montmorillonite study.

Equilibrium measurements were made using both a batch and a column technique. In the batch equilibrium technique 0.2 g of clay was equilibrated with 10 ml of solution traced with the appropriate radio-



FIG. 2. Electron Micrograph of the 2μ to 1μ equivalent spherical diameter fraction of the Bayard, New Mexico montmorillonite.

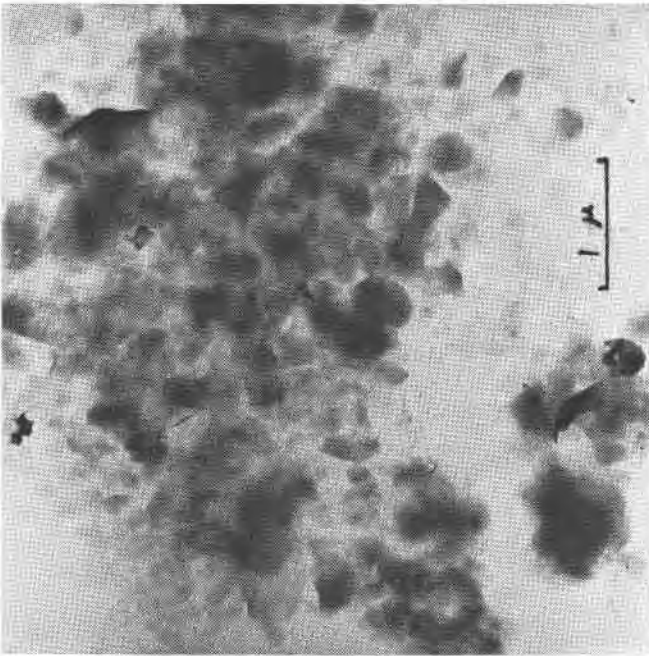


FIG. 1. Electron Micrograph of the 1μ to 0.1μ equivalent spherical diameter fraction of the Bayard, New Mexico montmorillonite.

active isotope. The removal of radioactivity from the solution by the clay was computed by measuring the amount of radioactivity remaining in the equilibrium solution. The batch technique was used only for the strontium-sodium with the Bayard, New Mexico montmorillonite because of inherent difficulties in separating the clay from the equilibrium solution. The column technique was found to be faster and more reliable. The columns were 11 mm outside diameter glass tubes with a fritted-glass disc at one end, and they were packed from bottom to top with glass wool, 1 cm paper pulp, 0.1 gram clay blended with 0.3 grams paper pulp and glass wool. Columns similar to the ones used in this study were described by Lewis and Thomas (1963). The columns fit into Lusteroid counting tubes of a Packard Auto-Gamma Spectrometer with a 3" NaI(Tl) well scintillation crystal. A standard and a blank was run with each clay column. The standard contained 2 ml of the equilibrium solu-

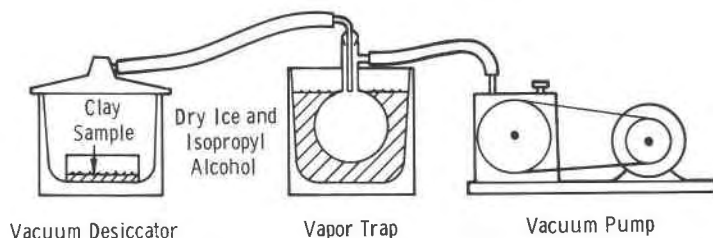


FIG. 3. Freeze-drying apparatus.

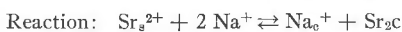
tion being studied, and was equal in volume and counting characteristics to the clay column. The validity of volume-for-volume counting allowed direct counting comparisons between standards and clay columns. The blank was brought to equilibrium with the solution being used in the clay column. The blank and the clay column then were washed with ethyl alcohol to displace solution in the void spaces, and were counted. The counts on the blank were subtracted from the counts on the clay column.

The equilibriums were reached at 25° C. and total normalities of the solutions were constant at 0.05 N. The tracers used were Na²²1.28 Mev gamma, Sr⁸⁵0.51 Mev gamma, and Cs¹³⁴0.60 Mev gamma. Sodium chloride, strontium chloride and cesium chloride salts were used in the solutions. The clay was equilibrated with the solutions for varying periods of time to determine that the clay had reached equilibrium with the solutions.

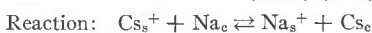
The cation exchange capacity for the Bayard, New Mexico montmorillonite was found to be 1.17 meq/g. The capacity was determined using sodium, strontium and cesium as the cation. Any difference in capacity

due to the cation used was less than the experimental error of the capacity determinations. The cation exchange capacity of the Chambers, Arizona montmorillonite was found to be 1.11 meq/g. Cation exchange capacities are based on the dry weight of the sodium-based clay at 25° C. None of the complicated effects known as "ion fixation" were observed during this study, and all reactions were found to be reversible.

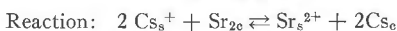
The equilibrium coefficients were calculated using the following definition and conventions of Gaines and Thomas (1953):



$$Kc' = 2 (\text{Co}) \frac{(\text{Sr}_{\text{efc}})(\text{Na}_{\text{efs}})^2}{(\text{Na}_{\text{efc}})^2(\text{Sr}_{\text{efs}})}$$



$$Kc' = \frac{(\text{Cs}_{\text{efc}})(\text{Na}_{\text{efs}})}{(\text{Na}_{\text{efc}})(\text{Cs}_{\text{efs}})}$$



$$Kc' = \frac{1}{2(\text{Co})} \frac{(\text{Cs}_{\text{efc}})^2(\text{Sr}_{\text{efs}})}{(\text{Sr}_{\text{efc}})(\text{Cs}_{\text{efs}})^2}$$

Subscript c = clay

Subscript s = solution

Co = Total normality of equilibrium solution (0.05N)

Subscript efc = Equivalent fraction on clay

Subscript efs = Equivalent fraction in solution

Mean activity coefficient corrections were very small due to the dilute equilibrium solutions used (0.05N), and were neglected during this study.

The equilibrium constants were calculated using the formula of Gaines and Thomas (1953),

$$\ln K = (Y - X) + \int_0^1 \ln Kc' \cdot dN_B$$

where Y is the valence of the ion on the clay and X is the valence of the ion replacing Y. Gibbs free-energy changes were calculated from the equilibrium constants by the relationship $\Delta F^\circ = -RT \ln K$ which for 25° C. simplifies to $\Delta F^\circ = -592.504 \ln K$.

RESULTS AND DISCUSSION

The exchange isotherms for the strontium-sodium, cesium-sodium and cesium-strontium systems plotted in Figs. 4, 5 and 6, respectively show that both montmorillonites have a preference for cesium over sodium, and that a preference for strontium over sodium and cesium over strontium is shown by the Bayard, New Mexico montmorillonite.

The values of the Gibbs free-energy changes for the reactions studied on the montmorillonites are presented in Table 2.

The accuracy of the equilibrium results can be checked by balancing

the Gibbs free-energy changes determined for three related reactions. Using the equation

$$2 \Delta F^\circ(\text{Na}_c \rightarrow \text{Cs}_c) - \Delta F^\circ(2\text{Na}_c \rightarrow \text{Sr}_{2c}) = \Delta F^\circ(\text{Sr}_{2c} \rightarrow 2\text{Cs}_c)$$

the free-energy change in the strontium-cesium system was predicted to be -4225 cal/mole, and the actual measured value was -4019 cal/mole. The free-energy of -2035 cal/mole determined for the Chambers,

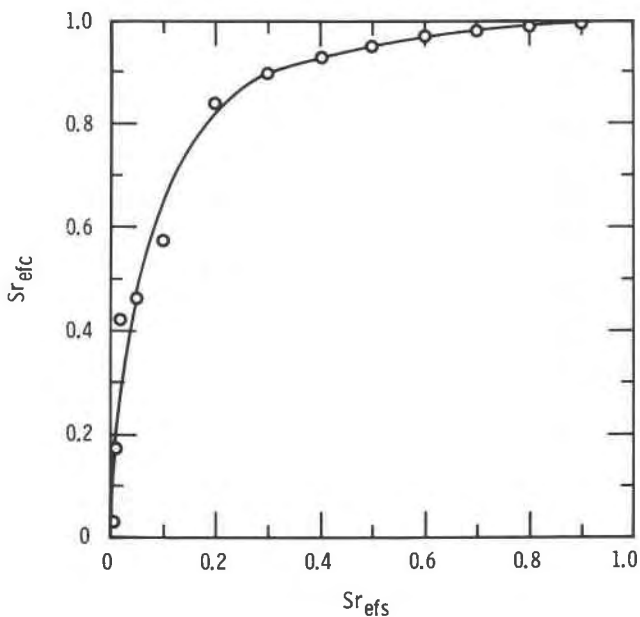


FIG. 4. The 25° C. isotherm for the reaction $\text{Sr}_e^{2+} + 2\text{Na}_c \rightleftharpoons 2\text{Na}_e^+ + \text{Sr}_{2c}$ on the Bayard, New Mexico montmorillonite. Total equilibrium solution normality was constant at 0.05.

Subscript efc = Equivalent fraction on clay

Subscript efs = Equivalent fraction in solution

Arizona montmorillonite also is in good agreement with the free-energy of -2152 cal/mole reported by Lewis and Thomas (1963).

The results of the equilibrium studies with the Kc' and $\ln Kc'$ values calculated are tabulated in Tables 3–6. The $\ln Kc'$ values of the equilibrium reactions of the Bayard, New Mexico montmorillonite are plotted in Fig. 7. The $\ln Kc'$ values and the $\ln Kc'$ curve presented by Lewis and Thomas (1963) for the sodium-cesium system are shown in Fig. 8. The sodium-cesium system of the Bayard, New Mexico montmorillonite shows a surprising increase in the selectivity for cesium above 90 per cent

cesium loading. The selectivity for strontium was found to increase over the entire range of strontium loading in the sodium-strontium system on the Bayard, New Mexico montmorillonite. Over the range from 0 to 40 per cent strontium loading the montmorillonite was sodium selective. Above 40 per cent it became strontium selective, with a marked increase in strontium selectivity above 90 per cent strontium loading. In the

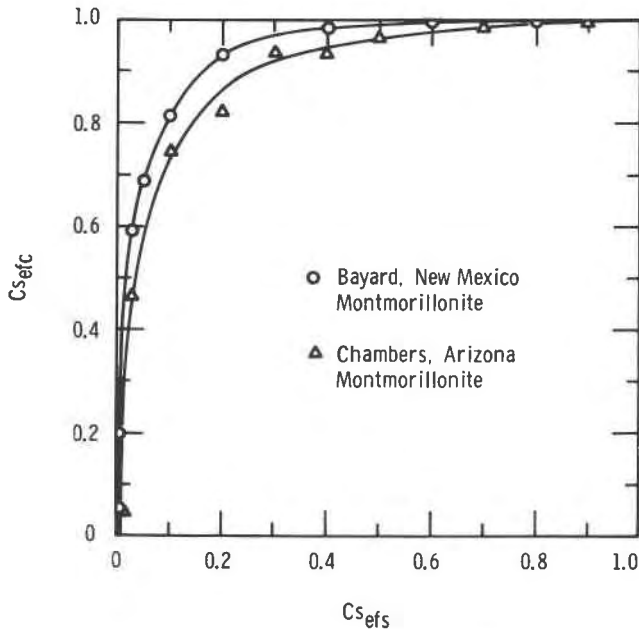


FIG. 5. The 25°C isotherm for the reaction $Cs_s^+ + Na_c \rightleftharpoons Na_s^+ + Cs_e$ on the Bayard, New Mexico and Chambers, Arizona montmorillonites. Total equilibrium solution normality was constant at 0.05.

Subscript *efc* = Equivalent fraction on clay

Subscript *efs* = Equivalent fraction in solution

strontium-cesium system of the Bayard, New Mexico montmorillonite, the initial selectivity for cesium was greater than in the sodium-cesium system, and a decrease in cesium selectivity was noted above 40 per cent cesium loading.

In the sodium-cesium system of the Chambers, Arizona montmorillonite a gradual decrease in selectivity for cesium, followed by a definite increase in cesium selectivity above 90 per cent cesium loading, was observed. The increase in cesium selectivity above 90 per cent cesium loading corresponds to the cesium selectivity change observed in the Bayard,

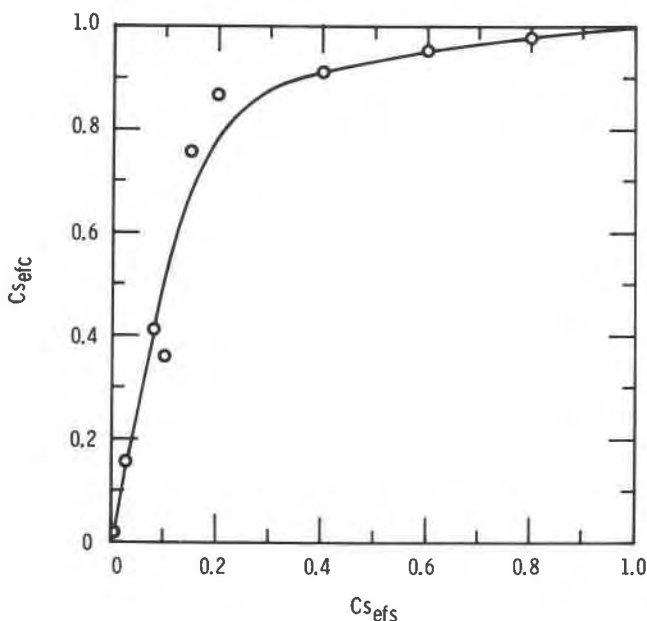


FIG. 6. The 25°C isotherm for the reaction $2Cs_s^+ + Sr_{2c} \rightleftharpoons Sr_s^{2+} + 2Cs_c$ on the Bayard, New Mexico montmorillonite. Total equilibrium solution normality was constant at 0.05.

Subscript efc = Equivalent fraction on clay
 Subscript efs = Equivalent fraction in solution

New Mexico sample, but the increase was not observed by Lewis and Thomas (1963). The cesium selectivity above 90 per cent cesium loading showed a marked decrease in the equilibrium results given by Lewis and Thomas. The difference in the cesium selectivity change reported by Lewis and Thomas, as compared to this study, may be due to differences

TABLE 2. FREE-ENERGIES OF EXCHANGE AT 25°C.
 BAYARD, NEW MEXICO MONTMORILLONITE

Reaction	ΔF° , cal/mole
$Cs_s^+ + Na_{ec} \rightleftharpoons Na_s^+ + Cs_c$	-2278
$Sr_s^{2+} + 2Na_{ec} \rightleftharpoons 2Na_s^+ + Sr_{2c}$	-331
$2Cs_s^+ + Sr_{2c} \rightleftharpoons Sr_s^{2+} + 2Cs_c$	-4019
Chambers, Arizona Montmorillonite	
Reaction	ΔF° , cal/mole
$Cs_s^+ + Na_{ec} \rightleftharpoons Na_s^+ + Cs_c$	-2035

TABLE 3. EQUIVALENT FRACTIONS C_{S_s} , C_{S_e} AND EQUILIBRIUM COEFFICIENTS Kc' , $\ln Kc'$ FOR THE BAYARD, NEW MEXICO MONTMORILLONITE REACTION, $Cs_s^+ + Na_c \rightleftharpoons Na_s^+ + Cs_e$

$C_{S_{efs}}$	$C_{S_{efe}}$	Kc'	$\ln Kc'$
0.8	0.998	176.05	5.17
0.6	0.997	235.74	5.46
0.4	0.982	81.80	4.39
0.2	0.932	54.48	4.00
0.1	0.812	38.87	3.66
0.05	0.684	41.09	3.72
0.025	0.592	56.59	4.04
0.005	0.194	47.77	3.87
0.001	0.051	53.73	3.98

TABLE 4. EQUIVALENT FRACTIONS Sr_s , Sr_e AND EQUILIBRIUM COEFFICIENTS Kc' , $\ln Kc'$ FOR THE BAYARD, NEW MEXICO MONTMORILLONITE REACTION, $Sr_s^{2+} + 2Na_c \rightleftharpoons 2Na_s^+ + Sr_{2e}$

Sr_{efs}	Sr_{efe}	Kc'	$\ln Kc'$
0.9	0.995	47.93	3.87
0.8	0.989	42.72	3.75
0.7	0.982	39.36	3.67
0.6	0.972	32.19	3.47
0.5	0.948	17.56	2.87
0.4	0.931	17.61	2.87
0.3	0.897	13.94	2.63
0.2	0.838	10.15	2.32
0.1	0.575	2.59	0.95
0.05	0.462	2.92	1.07
0.02	0.420	0.30	-1.20
0.005	0.174	0.25	-1.38
0.004	0.170	0.37	-1.00
0.001	0.030	0.16	-1.84

TABLE 5. EQUIVALENT FRACTIONS Cs_s , Cs_e AND EQUILIBRIUM COEFFICIENTS Kc' , $\ln Kc'$ FOR THE BAYARD, NEW MEXICO MONTMORILLONITE REACTION, $2Cs_s^+ + Sr_{2e} \rightleftharpoons Sr_s^{2+} + 2Cs_e$

$C_{S_{efe}}$	$C_{S_{efe}}$	Kc'	$\ln Kc'$
0.8	0.977	138	4.86
0.6	0.955	346	5.48
0.4	0.919	391	5.97
0.2	0.869	1,153	7.05
0.15	0.744	818	6.71
0.1	0.360	3,645	8.20
0.08	0.410	8,226	9.02
0.025	0.165	10,180	9.23
0.005	0.017	2,340	7.76

TABLE 6. EQUIVALENT FRACTIONS C_{S_s} , C_{S_e} AND EQUILIBRIUM COEFFICIENTS Kc' FOR THE CHAMBERS, ARIZONA MONTMORILLONITE REACTION, $C_{S_s}^+ + Na_c \rightleftharpoons Na_s^+ + C_{S_e}$

$C_{S_{efs}}$	$C_{S_{efc}}$	Kc'	$\ln Kc'$
0.9	0.998	45.50	3.82
0.7	0.984	26.38	3.27
0.5	0.965	27.25	3.30
0.4	0.934	21.20	3.05
0.3	0.937	34.70	3.55
0.2	0.821	18.32	2.91
0.1	0.743	26.03	3.26
0.025	0.465	33.92	3.52
0.001	0.044	46.30	3.84

in the clay samples, sample preparation methods, equilibrium column techniques, or other unknown differences between the two studies. Lewis and Thomas' treatment of the Chambers, Arizona montmorillonite with sodium hexametaphosphate during sample preparation is a good example of the differences between the two studies.

The effect of increased selectivity with increased loading of cesium and strontium on the sodium clay may be due to the difference in the c -axis spacing noted in the x -ray work with the Bayard, New Mexico montmorillonite. Samples of the Bayard, New Mexico montmorillonite based

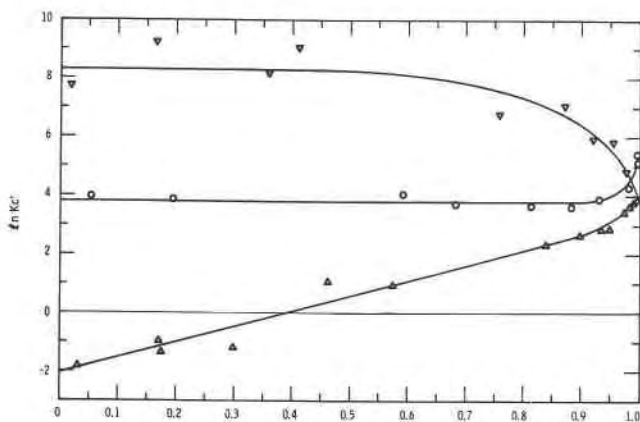
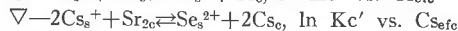
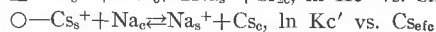
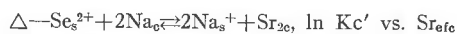


FIG. 7. The stoichiometric equilibrium coefficients on the Bayard, New Mexico Montmorillonite at 25°C:



Subscript efc = equivalent fraction on clay.

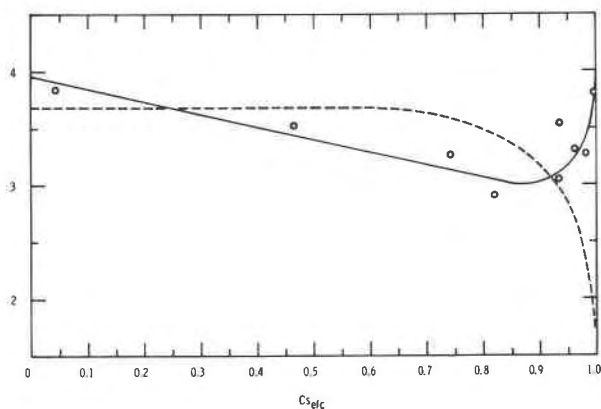
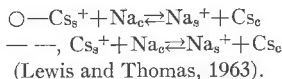


FIG. 8. The stoichiometric equilibrium coefficients on the Chambers, Arizona Montmorillonite at 25°C:



Subscript etc = equivalent fraction on clay.

with sodium, strontium, and cesium were air-dried at 25° C. *X*-ray patterns indicated one molecular interlayer of water in each case. The sodium, strontium, and cesium *x*-ray mounts were equilibrated with a saturated glycol atmosphere at 70° C. and a normal spacing of about 17.7 Å was found. Samples of the sodium, strontium, and cesium-based clay were saturated with 0.05 N chloride solutions of sodium, strontium, and cesium respectively and *x*-ray patterns indicated an interlayer spacing change from the air-dried samples. The strontium-based clay was found to have approximately a 20 Å *c*-axis spacing and the sodium *c*-axis spacing was greater than 40 Å. The cesium-based clay was found to maintain its one molecular interlayer of water or about 12.5 Å. Clay minerals with smaller *c*-axis spacings have been shown to be more selective for cesium by Tamura (1960). The increase in the selectivity for cesium over sodium at 90 per cent cesium loading presumably corresponds to a decrease in the *c*-axis spacing from greater than 40 Å to 12.5 Å. A cesium selectivity increase does not occur until nearly 90 per cent of the sodium has been exchanged, allowing a relatively rapid approach to the 12.5 Å *c*-axis spacing for cesium. The increase in the strontium selectivity over sodium presumably corresponds to a *c*-axis spacing change from greater than 40 Å to 20 Å. The strontium exchange for sodium allows a progressive *c*-axis spacing change from greater than 40 Å to the 20 Å strontium spacing. The *c*-axis spacings of strontium and cesium are close enough (about 20 Å and 12.5 Å, respectively) to result in the "usual"

type of isotherm in a cesium-strontium system where cesium selectivity decreases with increasing fraction of cesium on the clay. Further study of the c-axis spacing in connection with selectivity changes in montmorillonites is planned.

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