Comparison of Distribution Coefficients for Strontium Exchange From Solutions Containing One and Two Competing Cations

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U.S. DEPARTMENT OF THE INTERIOR
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By J. S. WAHLBERG *and* R. S. DEWAR

ION EXCHANGE ON MINERAL MATERIALS

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ABSTRACT

The ion exchange adsorption of tracer-level strontium by the clay minerals kaolinite and montmorillonite from solutions containing two competing cations was investigated. The exchange of strontium in these systems was successfully predicted from the results of the exchange adsorption of strontium from one competing cation solutions.

INTRODUCTION

Previous studies in this laboratory have dealt with the exchange of radioisotopes with single competing cations on single clays (Wahlberg and Fishman, 1962; Wahlberg and others, 1965). Data obtained in these studies will be useful if they enable prediction of the movement of specific radioisotopes in streams and soils in the presence of several competing cations. The present investigation was performed to evaluate the effect of two competing cations on the exchange of strontium by clay minerals. The study chosen was the exchange of approximately $10^{-10}N$ strontium-85 by kaolinite and montmorillonite from the following chloride solutions: sodium-potassium, sodium-calcium, sodium-magnesium, potassium-calcium, magnesium-calcium, and magnesium-potassium. The clays were left in contact with the solutions for a period of 4 days to insure equilibrium conditions.

The distribution coefficient, K_d (Tompkins and Mayer, 1947), expresses the distribution of an ion between solution and solid phases. If f_s represents the fraction of a substance present that is sorbed by the clay and $(1-f_s)$ represents the fraction remaining in solution, then

$$K_d=\frac{f_s}{(1-f_s)}\cdot\frac{V}{M}, \tag{1}$$

where V is the solution volume in milliliters and M is the mass of the clay in grams. For a particular clay-solution system, the K_d remains approximately constant as the V/M ratio varies; however, as V/M changes, the fraction adsorbed will vary. The constancy of K_d with varying V/M ratios means that if a system is sufficiently defined with regard to salt concentrations and types of earth materials present to assign a distribution coefficient to the system, then by determining either the fraction of radiocation adsorbed or the V/M ratio, the other parameter may be calculated.

Although distribution coefficients are useful for the prediction of radiocation exchange, they apply only at the specific salt concentration at which they were determined. To enable predictions of distribution coefficients at various concentrations, it is necessary to know the relationship between the distribution coefficient and the salt concentrations. To a first approximation, this relationship is given by the mass-action equation. Therefore we chose to use the mass-action equation to correlate the results of the one and two competing cation systems.

To determine the relation between the salt concentration and distribution coefficient, one must consider the exchange reactions involved. For the reactions

$$2\mathrm{NaX}+\mathrm{Sr}^{++}\rightleftarrows\mathrm{SrX}_2+2\mathrm{Na}^+ \tag{2}$$

and

$$\mathrm{CaX}_2+\mathrm{Sr}^{++}\rightleftarrows\mathrm{SrX}_2+\mathrm{Ca}^{++}, \tag{3}$$

the mass-action equilibrium constants are given by the following equations:

$$K_1=\frac{(\mathrm{SrX}_2)(\mathrm{Na}^+)^2}{(\mathrm{Sr}^{++})(\mathrm{NaX})^2}, \tag{4}$$

$$K_2=\frac{(\mathrm{SrX}_2)(\mathrm{Ca}^{++})}{(\mathrm{Sr}^{++})(\mathrm{CaX}_2)}, \tag{5}$$

and, since

$$K_d=\frac{f_s}{(1-f_s)}\cdot\frac{V}{M}=\frac{(\mathrm{SrX}_2)}{(\mathrm{Sr}^{++})}, \tag{6}$$

then

$$K_1=K_d\,\frac{(\mathrm{Na}^+)^2}{(\mathrm{NaX})^2} \tag{7}$$

and

$$K_2=K_d\,\frac{(\mathrm{Ca}^{++})}{(\mathrm{CaX}_2)}, \tag{8}$$

where:

(SrX_2) = quantity of strontium adsorbed on the clay in meq per g (milliequivalent per gram),
(CaX_2) = quantity of calcium adsorbed on the clay in meq per g,
(NaX) = quantity of sodium adsorbed on the clay in meq per g,
(Sr^{++}) = normality of strontium in the equilibrium solution,
(Ca^{++}) = normality of calcium in the equilibrium solution,
(Na^{+}) = normality of sodium in the equilibrium solution, and
K_1, K_2 = mass-action equilibrium constants.

Equations 7 and 8 will be applicable in the presence of any number of competing cations. This application can be shown by considering strontium exchange with the two competing cations, sodium and calcium. The sum of reactions 2 and 3 is

$$2NaX+CaX_2+2Sr^{++}\rightleftarrows 2SrX_2+Ca^{++}+2Na^{+}. \qquad (9)$$

The mass-action equilibrium constant, K_t, for reaction 9 is

$$K_t=K_1K_2=\frac{(SrX_2)^2(Ca^{++})(Na^{+})^2}{(Sr^{++})^2(CaX_2)(NaX)^2}.$$

Since

$$K_d=\frac{SrX}{Sr^{++}},$$

then

$$K_d^2=K_1K_2\frac{(CaX_2)(NaX)^2}{(Ca^{++})(Na^{+})^2}.$$

Substituting equations 4 and 5 alternately into equation 8, we see that

$$K_d=K_1\frac{(NaX)^2}{(Na^{+})^2}=K_2\frac{(CaX_2)}{(Ca^{++})}.$$

EXPERIMENTAL TECHNIQUES

The clays were washed with a mixture of 1*N* hydrochloric acid and 1*N* sodium chloride solution until the solution gave a negative test for aluminum with ammonium hydroxide. The clay was then washed with a 2*N* sodium, potassium, calcium, or magnesium chloride solution. This washing was continued until the pH of the salt solution was unchanged during contact with the clay. The clay was then washed with water until the wash solution gave a negative test for the chloride ion with silver nitrate. The clay particles larger than 1 micron in diameter were separated by sedimentation and discarded. The suspension of particles 1 micron and smaller was diluted with water to a concentration of approximately 20 mg per ml (milligrams per milliliter).

The exchange of tracer-level strontium with exchangeable cations was determined on American Petroleum Institute reference clays montmorillonite No. 21 and kaolinite No. 7. The extent of the exchange reaction was determined by a dialysis technique and gamma scintillation counting of the strontium-85 in the clear dialyzate. Ten milliliters of the prepared clay suspension (approx 200 mg) was sealed in a cellulose casing and placed in a 1-ounce polyethylene bottle to which had been added 10 ml of one of the two competing cation solutions. These solutions (as the chloride) contained tracer-level strontium-85 and potassium-calcium, magnesium-calcium, magnesium-potassium, sodium-potassium, sodium-calcium, or sodium-magnesium that were 0.1, 0.05, 0.01, or 0.005N with respect to the individual cations. These mixtures of ions and clay were shaken for 4 days. The fraction of strontium-85 sorbed by the clay was determined by comparing the gamma-scintillation-count rate of a 1-ml aliquot of the clear dialyzate and an equal volume of the bulk solution.

DISCUSSION OF RESULTS

The purpose of this study was to determine if the results of the exchange adsorption of strontium by clay minerals from a two competing cation solution could be calculated from the results of a single competing cation experiment (table 1). The mass-action equation was chosen to define the results of the two competing cation experiment because it was found that the results of the single competing cation experiment were described, at least to a first approximation, by the mass-action equation.

TABLE 1.—*Mass-action equilibrium constants and cation exchange capacities of the clays studied*

Clay	K(Sr)[1]	Cation exchange capacity (meq per g)[2]
Potassium montmorillonite No. 21	0.2	1.1
Sodium montmorillonite No. 21	1.1	1.1
Magnesium montmorillonite No. 21	1.1	1.1
Calcium montmorillonite No. 21	1.1	1.1
Potassium kaolinite No. 7	1.5	.056
Sodium kaolinite No. 7	9.0	.056
Magnesium kaolinite No. 7	1.8	.043
Calcium kaolinite No. 7	1.2	.043

---

[1] Equilibrium constants for the reactions $MX_2+Sr^{++}\rightleftarrows SrX_2+M^{++}$ or $2MX+Sr^{++}\rightleftarrows SrX_2+2M^{+}$ utilizing tracer-level strontium in the presence of a single competing cation. The cation concentrations used in these calculations are expressed in normalities; thus, for monovalent-divalent exchange, the numerical value of K(Sr) will be 100 times less than those values of K(Sr) in the literature where the cation concentrations are expressed as meq per 100 ml.

[2] Exchange capacity determined by cesium method (Beetem and others, 1962); reported on an oven-dry basis.

TABLE 2.—*Comparison of experimental and predicted distribution coefficients for magnesium montmorillonite No. 21*

[Exp., experimental; calc., calculated]

Magnesium (*N*)	Calcium (*N*)							
	0.1		0.05		0.01		0.005	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
0.1	5.8	5.8	8.5	8.0	10	11	10	11
.05	6.8	7.6	10	12	19	21	20	22
.01	10	9.5	17	17	56	56	77	77
.005	11	10	18	20	76	76	110	120
	Sodium (*N*)							
0.1	8.5	8.8	8.7	10	11	12	10	12
.05	18	16	18	20	22	23	22	24
.01	46	36	73	60	110	110	110	110
.005	60	43	100	72	190	160	210	190
	Potassium (*N*)							
0.1	7.0	5.6	7.6	7.6	11	11	11	11
.05	14	9.0	17	14	22	21	18	22
.01	20	14	43	30	84	85	96	97
.005	22	17	54	42	140	140	180	170

TABLE 3.—*Comparison of experimental and predicted distribution coefficients for potassium montmorillonite No. 21*

[Exp., experimental; calc., calculated]

Potassium (*N*)	Calcium (*N*)							
	0.1		0.05		0.01		0.005	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
0.1	11	5.8	9.5	9.2	20	17	22	20
.05	9.1	8.5	15	15	41	45	58	58
.01	11	11	25	24	160	160	390	440
.005	13	11	26	25	210	220	740	800

Theoretically, the mass-action equation should not describe the cation exchange reaction by clay minerals nearly as well as the double-layer theory because the mass-action equation assumes that the exchanger (clay) has a homogeneous charge distribution and that the exchange takes place throughout the whole volume of the clay. The double-layer theory (Lagerwerff and Bolt, 1959) presents a truer picture of the clay in that the charges are assumed to be distributed at the surface of the clay.

In practice the mass-action equation should be nearly as reliable as the double-layer theory for many predictions because some of the terms necessary in the double-layer theory (for accurate description of the exchange) are difficult to determine. The mass-action and

TABLE 4.—*Comparison of experimental and predicted distribution coefficients for sodium montmorillonite No. 21*

[Exp., experimental; calc., calculated]

Sodium (*N*)	Calcium (*N*)							
	0.1		0.05		0.01		0.005	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
0.1	11	9	18	17	65	58	90	80
.05	11	10	29	20	120	100	210	200
.01	13	13	25	28	230	230	1100	1000
.005	12	13	26	28	260	260	1900	1600
	Potassium (*N*)							
0.1	13	12	28	21	81	60	100	85
.05	19	16	48	38	220	190	320	300
.01	28	20	96	56	1300	700	2900	2100
.005	31	21	110	90	2000	1800	5500	7000

TABLE 5.—*Comparison of experimental and predicted distribution coefficients for magnesium kaolinite No. 7*

[------, not determined; exp., experimental; calc., calculated]

Magnesium (*N*)	Calcium (*N*)					
	0.05		0.01		0.005	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
0.05	0.5	0.6	1.1	1.2	1.4	1.3
.01	------	.9	2.9	3.0	5.4	4.2
.005	.7	1.0	4.8	4.0	5.1	6.1
	Sodium (*N*)					
0.05	0.2	0.9	1.3	1.4	2.0	1.5
.01	4.8	2.5	6.8	6.1	7.6	6.8
.005	6.0	3.4	11	12	13	14
	Potassium (*N*)					
0.05	------	0.5	------	1.2	1.6	1.3
.01	0.5	.8	3.2	4.6	3.9	6.0
.005	1.5	.8	5.5	5.2	9.6	8.2

double-layer theories predict the same results for homovalent exchange, and for sufficiently small clay particles (montmorillonite) the difference between assuming the charge to reside on the surface or throughout the volume of the clay is not great. A comparison of the calculated and experimental distribution coefficients for montmorillonite and kaolinite show that the agreement between experimental and calculated distribution coefficients (tables 2–7) are on the whole better for montmorillonite (small particle size) than for kaolinite (larger particle size).

TABLE 6.—*Comparison of experimental and predicted distribution coefficients for potassium kaolinite No. 7*

[Exp., experimental; calc., calculated]

Potassium (*N*)	Sodium (*N*)					
	0.05		0.01		0.005	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
0.05	1.6	0.9	3.8	1.6	3.6	1.8
.01	7.9	4	23	23	29	34
.005	11	6.1	44	57	60	100

TABLE 7.—*Comparison of experimental and predicted distribution coefficients for calcium kaolinite No. 7*

[Exp., experimental; calc., calculated]

Calcium (*N*)	Potassium (*N*)					
	0.05		0.01		0.005	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
0.05	0.7	0.4	1.2	0.8	1.9	0.9
.01	.5	.8	4.4	3.2	4.7	3.9
.005	1.9	1.2	6.5	5.8	9.4	7.0
	Sodium (*N*)					
0.05	0.6	0.7	1.3	0.9	0.9	0.9
.01	2.3	2.4	5.5	4.2	6.3	4.6
.005	6.2	2.8	9.5	7.8	11	8.8

The relatively good agreement between calculated and experimental results (tables 2–7 and figures 1–4) indicate that to a first approximation the mass-action equation may be used to predict the exchange of strontium by clay minerals from the two competing cation solutions. It should be noted that in figures 1–4 the points shown represent the experimentally determined distribution coefficients for the adsorption of strontium from the various solutions. The curves themselves are drawn through points (not shown) calculated from the mass-action equilibrium constants and exchange capacities given in table 1. The curves extend over a greater range (0.0001 to 1.0*N*) than do the experimental points (0.005*N* to 0.1*N*); hence, the curves below 0.005*N* and above 0.1*N* are not to be taken as extrapolations. The curves were calculated from the values of the equilibrium constants and exchange capacities given in table 1 and were plotted to concentrations greater than 0.1*N* to show the convergence of the curves at higher salt concentrations.

CONCLUSIONS

The mass-action equation, to a first approximation, can be used to correlate the results of the single competing cation and strontium exchange with those obtained from a two competing cation and strontium exchange. The results of this experiment show that the distribution coefficients calculated with the mass-action equation agree more closely with the experimental distribution coefficients for materials with high exchange capacities (montmorillonite) than for those with lower exchange capacities (kaolinite). This difference is probably due to the inherent error of the mass-action equation in assuming the clay to be a single-phase system wherein the ions may exchange at both the surface and interior of the crystallite.

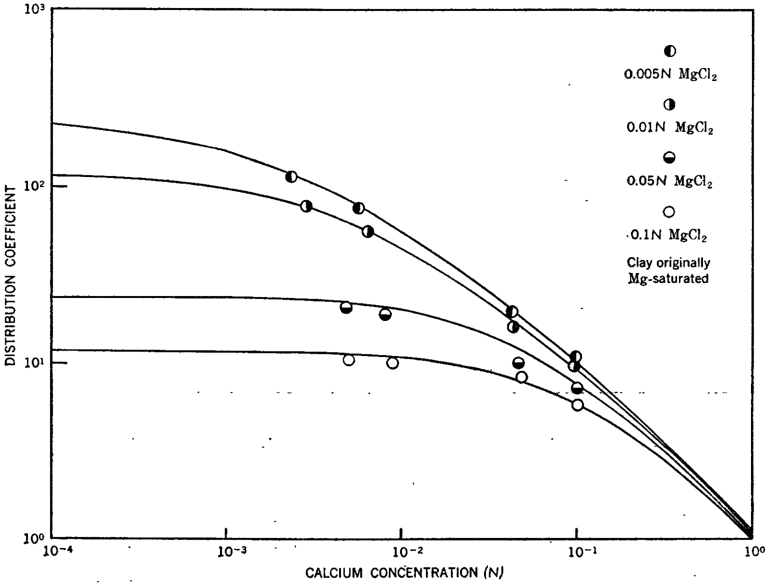

FIGURE 1.—Adsorption of strontium on magnesium-calcium montmorillonite No. 21.

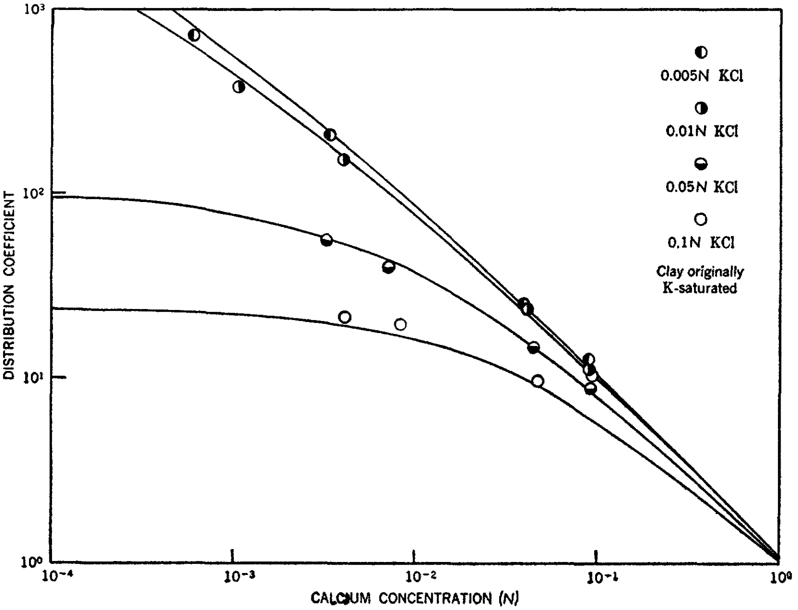

FIGURE 2.—Adsorption of strontium on potassium-calcium montmorillonite No. 21.

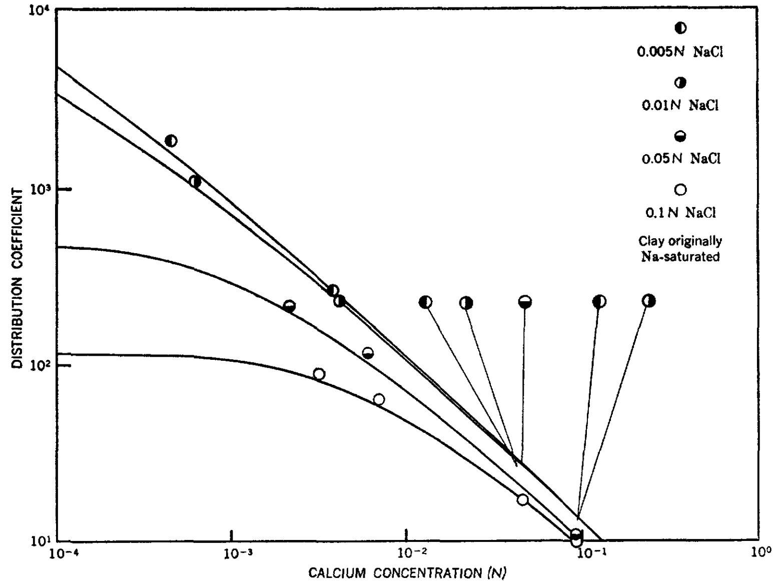

FIGURE 3.—Adsorption of strontium on sodium-calcium montmorillonite No. 21.

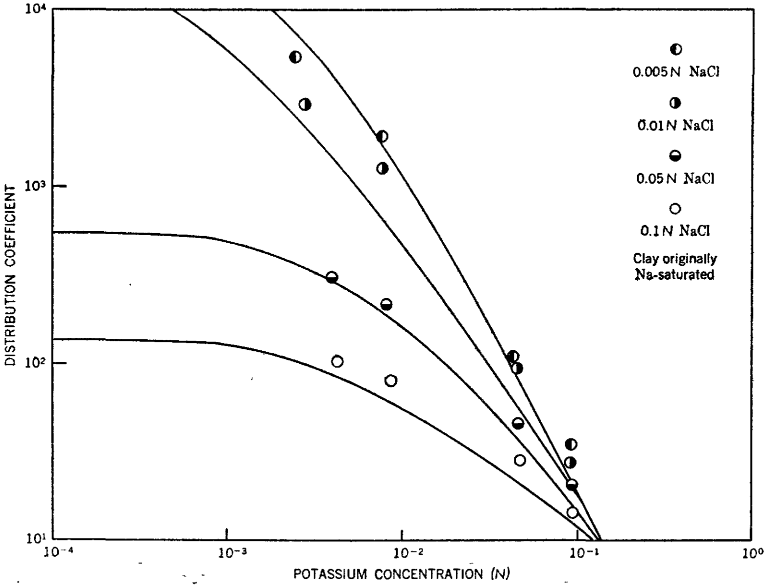

FIGURE 4.—Adsorption of strontium on sodium-potassium montmorillonite No. 21.

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