Exchange Adsorption of Strontium on Clay Minerals

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By J. S. WAHLBERG, J. H. BAKER, R. W. VERNON, *and* R. S. DEWAR

ION EXCHANGE ON MINERAL MATERIALS

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CONTENTS

ILLUSTRATIONS

TABLE

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ABSTRACT

A study was made of the ion exchange adsorption of strontium from calcium, magnesium, sodium, or potassium solutions by the clay minerals kaolinite, montmorillonite, and illite. The calcium, magnesium, sodium, and potassium concentrations were varied from $10^{-1}N$ to $10^{-5}N$ while the strontium concentrations were varied from $10^{-1}N$ to approximately $10^{-10}N$. The exchange of strontium by the clay minerals tested was adequately defined by the mass-action equilibrium equation. The adsorption of strontium was greatest from sodium solutions and least from calcium solutions.

INTRODUCTION

As the use of nuclear energy and radioisotopes increases, the chance for contamination of water supplies increases. When these fission products are released into a water supply, it is vital to know in detail the results of the various interactions between these radioactive materials and the environment. One reaction that will be significant in the decontamination of water supplies is the ion exchange reaction. Clay minerals are one of the natural materials that have the capacity to exchange sorbed ions with those ions in solution. The ability to make quantitative predictions of the extent of adsorption of strontium and cesium (which are the most biologically hazardous of the long-lived fission products) by clay minerals—that is, the decontamination of the liquid phase—is of great significance in assessing hazard in the event of accidental release.

Although this study will be useful in making general predictions of the movement of radioisotopes in natural waters, additional variables will have to be evaluated before truly quantitative predictions can be made. Some of these variables requiring additional study are the relative significance, for example, of the clay minerals in contrast to organic matter, oxides, and other minerals; the degree of reversibility

of the sorption reactions; the rate of the sorption reaction; Eh effects; and the degree of mixing of bed and suspended sediments

SCOPE OF INVESTIGATION

The reactions between cations adsorbed by clay minerals and cations in solution have been the subject of many investigations (Vanselow, 1932; Nishita and others, 1956; Øien and others, 1959; Tabikh and others, 1960; Tamura, 1962). Studies of radioion adsorption were undertaken in a systematic investigation to obtain data applicable to the prediction of concentrations of fission products in the liquid phase of streams.

The present study reports distribution coefficients for the adsorption of strontium by clay minerals from aqueous solutions. Previously, Wahlberg and Fishman (1962) reported distribution coefficients for cesium for similar clays and competing cations. To reduce the number of variables in this study, amorphous aluminum and iron oxides and readily acid-soluble minerals were removed from the clay prior to measuring the strontium distribution coefficients. This paper deals with the distribution of strontium between clay minerals and solutions containing the main cations (magnesium, calcium, sodium and potassium) in natural waters.

Many equations have been used to describe cation exchange equilibria by clays, most of which can be grouped in three different classes: those that are based on the mass-action equation, those that are derived from the Donnan theory (Erickson, 1952), and those from the double-layer theory (Lagerwerff and Bolt, 1959). Theoretically, the double-layer theory should describe the exchange of cations by clay minerals better than the other equations because both the mass-action and the Donnan equations must assume that the exchanger consists of a continuous phase with a homogeneous volume charge. The double-layer theory more closely represents the clay-water system in that it assumes the exchanger to be a discontinuous phase with a surface charge. One complicating factor in the use of the double-layer theory to predict the exchange of cations by clay minerals is that the degree of interaction of the clay particles as well as the specificity of a particular cation for the clay is difficult, if not impossible, to determine. These items are normally ignored in double-layer calculations; thus, if there is any great degree of interaction between clay particles or of specificity of cations for the clay, the double-layer theory will not mathematically describe the exchange of cations by clay minerals.

Unpublished studies conducted in this laboratory have shown that the mass-action equation describes the exchange of cations by clay minerals adequately. Generally, the agreement is better for mont-

morillonite than for the other clays studied because the montmorillonite particles are so small that there is little difference in assuming the charge distribution to be homogeneous or to reside only on the surface of the clay.

American Petroleum Institute reference clays kaolinite No. 4, kaolinite No. 7, illite No. 35, and montmorillonite No. 21 were used in this study.

EXPERIMENTAL TECHNIQUES

To reduce the number variables in the systems studied, the clays were treated to remove the amorphous aluminum and iron oxides and readily acid-soluble minerals. The treatment consisted of suspending them in a hot mixture of $1N$ sodium chloride plus $1N$ hydrochloric acid, centrifuging the suspension, and testing the supernatant liquid for aluminum. These three steps were continued until the supernatant solution gave no test for aluminum with ammonium hydroxide. The clays were then suspended in $2N$ solutions of magnesium, calcium, potassium, or sodium chloride; the suspensions were centrifuged; and the supernatant liquids were discarded. The salt washings of the clay were continued until the pH of successive supernatants became constant. Distilled-water washings were then begun and continued until, after mixing and centrifuging, the supernatant contained no detectable chloride. Although this treatment does decompose some small amount of clay, slight clay decomposition is probably preferable to the more complex system which would exist without this treatment. The washed clays were then suspended in distilled water, and the suspension was allowed to settle overnight. The particles (approx. $<1.0\bar{\mu}$) remaining in suspension after an overnight settling period were siphoned off, and a final suspension containing approximately 20 mg per ml (milligram per milliliter) of clay was prepared by dilution with distilled water.

Distribution coefficients for the various clays were determined by pipetting 10 ml of the prepared clay suspensions into cellulose casings previously tied at one end and then tying the other end to seal the clay suspension in the casing. A suspension was placed in a polyethylene bottle; and 10 ml of solution of known concentration of stable strontium, the salt (as the chloride) of the cation with which the clay was saturated, and tracer quantities of strontium-85 were pipetted into the polyethylene bottle. The bottle was capped, and the mixture was shaken for 4 days, after which the fraction of strontium left in solution was determined by comparing the count rate of 1 ml of the clear liquid outside of the cellulose casing with that of the original solution.

RESULTS AND DISCUSSION

The distribution coefficients were calculated from a modified equation given by Tompkins and Mayer (1947),

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

where

K_d=the distribution coefficient in ml per g (milliliters per gram),
$1-f_s$=the fraction of strontium left in solution,
f_s=the fraction of strontium adsorbed,
V=the volume of the solution in milliliters,
M=the mass of the clay in grams at 105°C.

Equation 1 can be transformed to show the relation between the K_d, the amount of strontium adsorbed per unit weight of clay, and the final strontium concentration. Since, by definition,

$$f_s=\frac{(SrX_2)}{(^*Sr^{++})}\cdot\frac{M}{V}$$

and

$$(1-f_s)=\frac{(Sr^{++})}{(^*Sr^{++})},$$

then

$$K_d=\frac{(SrX_2)}{(Sr^{++})}, \tag{2}$$

where

(SrX_2)=the amount of strontium adsorbed by the clay in meq per g (milliequivalent per gram),
$(^*Sr^{++})$=the starting normality of strontium assuming homogeneous mixture of the original solution and the water in the cellulose casing and in the clay suspension, and
(Sr^{++})=the normality of strontium in the equilibrium solution.

The strontium exchange was studied for two classes of exchange—that is, the exchange where the competing cations are of the same valence (homovalent) and the exchange where the competing cations are of different valence (heterovalent). For homovalent exchange the following reaction applies:

$$CaX_2+Sr^{++}\rightleftarrows SrX_2+Ca^{++}.$$

The mass-action equilibrium constant for this reaction is:

$$K_c=\frac{(SrX_2)(Ca^{++})}{(Sr^{++})(CaX_2)}.$$

Since

$$K_d = \frac{(SrX_2)}{(Sr^{++})},$$

then

$$K_c = K_d \frac{(Ca^{++})}{(CaX_2)}, \tag{3}$$

where

(CaX_2) = amount of calcium adsorbed by the clay in meq per g,
(Ca^{++}) = normality of calcium in the equilibrium solution, and
K_c = mass-action equilibrium constant.

Concentrations rather than activities have been used throughout; thus, K_c is not a true thermodynamic mass-action equilibria constant; however, owing to the many uncertainties in prediction of the exchange adsorption of radiocations in natural water, the use of activities rather than concentrations is probably an unnecessary and cumbersome refinement.

In the calculation of the equilibrium constants, normality was used as the unit of concentration, instead of the more commonly used unit of molarity. The quantity of an exchangeable cation on a clay was given in milliequivalents per gram; thus, to maintain the same units it is necessary to use normality for the solution concentration. The equilibrium constant is the same whether millimoles per gram of the clay and molarity are used or milliequivalents per gram of clay and normality of the ions in solution are used as the units of concentration.

The equilibrium constant for the homovalent exchange was obtained from the adsorption of strontium at the carrier-free strontium concentration (approx $10^{-10}N$). At this very low strontium concentration the (SrX_2) term will be nearly zero, and the (CaX_2) term in equation 3 will then be, within errors of measurement, equal to the cation exchange capacity of the clays. Thus, at the carrier-free strontium concentration the equilibrium constant can be obtained from the distribution coefficient, calcium concentration in the solution, and the cation exchange capacity for the clay. This procedure was followed at all of the calcium concentrations studied, and an average equilibrium constant was obtained by averaging the equilibrium constants calculated for the various calcium concentrations. This average equilibrium constant was then used with the mass-action equation to calculate the K_d value at all the strontium and calcium concentrations studied. Figures 2, 4, 6, and 8 show the results of this calculation. The curves are the values of K_d predicted from the average equilibrium constant, whereas the points are the actual experimentally determined values. Figures 1, 3, 5, and 7 illustrate the results of the magnesium-strontium experiment.

766-983—65——2

For heterovalent exchange (sodium or potassium with strontium) the system has been complicated owing to the presence of $10^{-3}N$ hydrogen. The hydrogen was added inadvertently because the strontium-85 used in this experiment contained more hydrochloric acid than previous shipments. To explain this system it will be necessary to consider three reactions and the resultant mass-action equilibria-constant equations:

$$2NaX+Sr^{++}\rightleftarrows SrX_2+2Na^+$$

results in

$$K_{c_1}=\frac{(SrX_2)}{(Sr^{++})}\frac{(Na^+)^2}{(NaX)^2}=K_{d_1}\frac{(Na^+)^2}{(NaX)^2}, \tag{4}$$

$$NaX+H^+\rightleftarrows HX+Na^+$$

results in

$$K_{c_2}=\frac{(HX)(Na^+)}{(H^+)(NaX)}, \tag{5}$$

and

$$2HX+Sr^{++}\rightleftarrows SrX+2H^+$$

results in

$$K_{c_3}=\frac{(SrX_2)}{(Sr^{++})}\frac{(H^+)^2}{(HX)^2}=K_{d_3}\frac{(H^+)^2}{(HX)^2}. \tag{6}$$

The K_d' for the system might seem to be the sum of $K_{d_1}+K_{d_3}$. However, in order for equation 5 to be correct, K_{c_3}/K_{c_1} must equal K_{c_2}. Hence, K_{d_1} equals K_{d_3}; and since they are in the same solution, they are not only numerically equal but are the same terms. Hence,

$$K_d'=K_{d_1}=K_{d_3}=K_{c_1}\frac{(NaX)^2}{(Na)^2}=K_{c_3}\frac{(HX)^2}{(H^+)^2}.$$

The equations for K_d are the same if hydrogen is present or absent, the only difference being that when the hydrogen is present the sodium or potassium plus strontium on the clay is not equal to the cation exchange capacity for the clay.

In the calculations the only reaction that is taken into account as a result of the presence of the hydrogen is $NaX+H^+\rightleftarrows HX+Na^+$. Actually, there would have been some aluminum and iron dissolved from the clay, and these ions would also react with the sodium or potassium clays. The quantity of aluminum or iron dissolved was probably small; thus a large error would not be introduced by the

assumption inherent in the calculations that one aluminum or ferric ion is equivalent to the three hydrogen ions that were consumed in the solubilization of the aluminum or ferric ions.

Equations 4 and 5 can be used to calculate the K_d value for any salt concentration if the equilibrium constants K_1 and K_2 are known. The equilibrium constants were evaluated from the results of the adsorption of tracer level (approx $10^{-10}N$) strontium. This evaluation can be done because at the high salt concentration (sodium or potassium) the effect of the hydrogen would be small. Therefore, at the high salt concentration the sodium or potassium on the clay will nearly equal the cation exchange capacity for the clay, and the approximate equilibria constant for the sodium- or potassium-strontium exchange can be evaluated. The experimentally determined K_d can then be used to evaluate the concentration of sodium on the clay at any sodium concentration. Since the sodium plus hydrogen on the clay is equal to the exchange capacity of the clay, equation 5 may be solved to determine the apparent equilibrium constant between hydrogen and sodium. This calculation was done for the exchange of sodium or potassium and the values of the equilibrium constants reported in table 1. Figures 9–16 give a comparison of calculated and experimental K_d values for the sodium- or potassium-hydrogen-strontium exchange; the curves represent the values of K_d that were calculated by the mass-action equations and the equilibrium constants (reported in table 1), whereas the points are the experimentally determined values of K_d.

Table 1 shows the equilibrium constants for the various clays and solutions. As would be expected from the similar ionic sizes of strontium, magnesium, and clacium (Kunin, 1958, p. 26–29), the exchange affinities are close to unity. The equilibrium constant for strontium-magnesium exchange is greater than that for strontium-calcium exchange and is also what would be expected from the hydrated ionic radii (Mg>Ca>Sr).

As would be expected from the difference in valency, the adsorption of strontium is greater from sodium and potassium solutions than from the magnesium and calcium solutions of equal normality. The extent of the exchange of strontium with sodium clay is much greater than with potassium clay. The difference in the replaceability of strontium for sodium compared with that for potassium is greater than would be expected from ion sizes alone.

Figures 1–16 illustrate that the data can be represented adequately by the mass-action equation.

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

[----, not determined]

	K_{M-Sr}[1]	K_{M-H}[2]	Cation exchange capacity (meq per g)[3]
Potassium montmorillonite No. 21[4]	0.2	1.0	1.07
Sodium montmorillonite No. 21	1.1	10.0	1.07
Magnesium montmorillonite No. 21	1.1	--------	1.07
Calcium montmorillonite No. 21	1.1	--------	1.07
Potassium illite No. 35	1.0	14.0	.28
Sodium illite No. 35	3.0	10.0	.28
Magnesium illite No. 35	1.5	--------	.145
Calcium illite No. 35	1.1	--------	.145
Potassium kaolinite No. 4	1.5	2.7	.133
Sodium kaolinite No. 4	4.2	8.3	.190
Magnesium kaolinite No. 4	1.0	--------	.246
Calcium kaolinite No. 4	.9	--------	.246
Potassium kaolinite No. 7	1.5	23.0	.056
Sodium kaolinite No. 7	9.0	30.0	.056
Magnesium kaolinite No. 7	1.8	--------	.043
Calcium kaolinite No. 7	1.2	--------	.043

[1] Equilibrium constant for the reaction $MX_2+Sr^{++}\rightleftarrows SrX_2+M^{++}$.
[2] K for the raction $MX+H^{+}\rightleftarrows HX+M^{+}$.
[3] Cation exchange capacity determined by cesium method (Beetem and others, 1962).
[4] American Petroleum Institute reference clay number.

An inspection of figures 1–16 shows that the greatest difference between experimental results and those calculated from the mean equilibrium constant occurs at the highest strontium concentration. This situation arises because, for simplicity, concentrations rather than activities were used in the calculations of K_d, and the difference between activities and concentrations increases with increasing salt concentrations. The second and probably most important reason for the difference in calculated and experimental distribution coefficients is that at high strontium concentrations the fraction of strontium adsorbed by the clay will be much less than at lower strontium concentrations. As the fraction adsorbed is obtained by difference between the concentration of the standard and the sample, the error in determining the percentage adsorbed becomes greater as the fraction adsorbed becomes less. For the same reason the calculation of K_d also becomes less accurate when the strontium adsorption approaches 100 percent (low salt concentration). Thus, the greatest precision in K_d determination is obtained when the amount of strontium adsorbed is about 50 percent.

CONCLUSIONS

The exchange of strontium with calcium-, magnesium-, sodium-, or potassium-saturated clay minerals is described adequately by the mass-action equation. For the systems studied, the equilibrium constant for calcium or magnesium and strontium exchange was nearly unity and did not vary with exchange capacity; therefore, no large error would be introduced if an equilibrium constant of unity is assumed for the calcium or magnesium exchange with strontium. In general, for sodium or potassium exchange with strontium, the equilibrium constant increased as the cation exchange capacity decreased (table 1).

Another conclusion to be drawn from figures 1–16 is that when the concentration of strontium is below $10^{-4}N$, the K_d value for the exchange of strontium is constant. If the concentration of stable plus radioactive strontium is below $10^{-4}N$, the presence of stable strontium will have no effect on the adsorption of the radioactive strontium by sediments. As most natural waters contain less than $10^{-4}N$ strontium, the adsorption of radiostrontium will be unaffected by the presence of stable strontium.

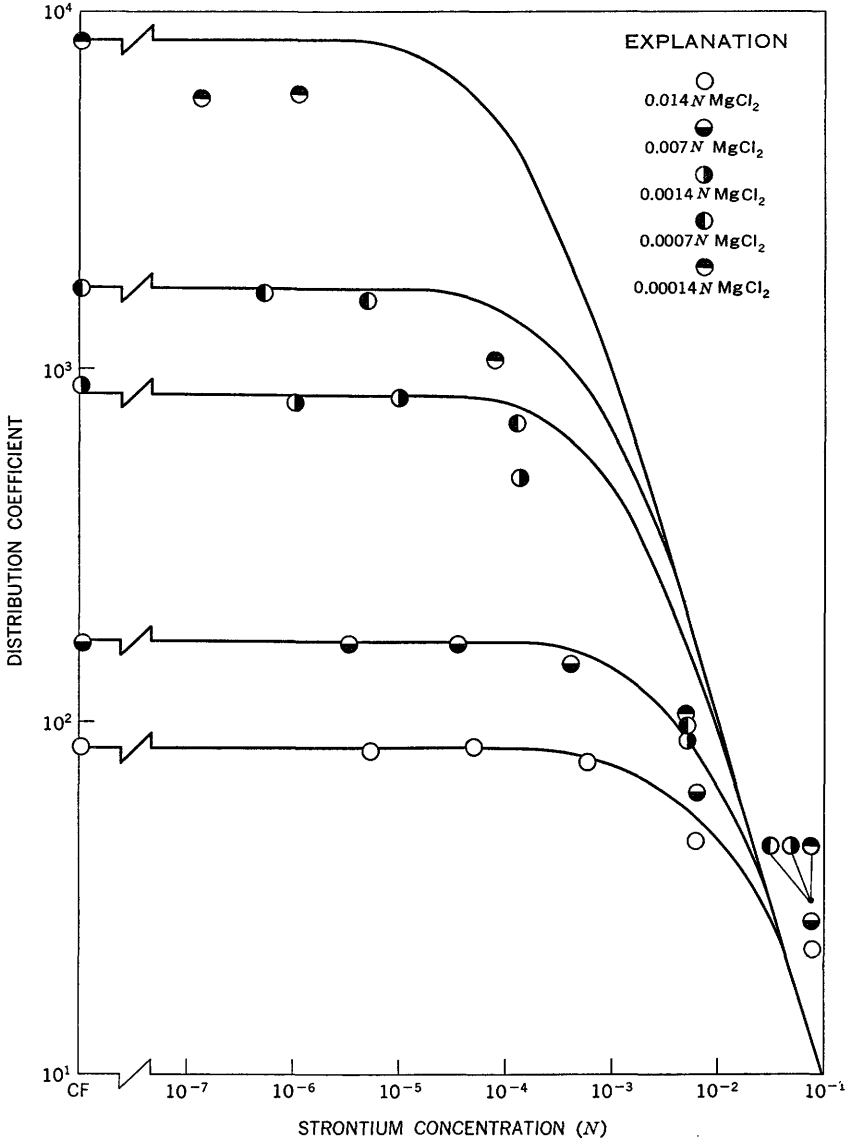

FIGURE 1.—Adsorption of strontium on magnesium montmorillonite No. 21.

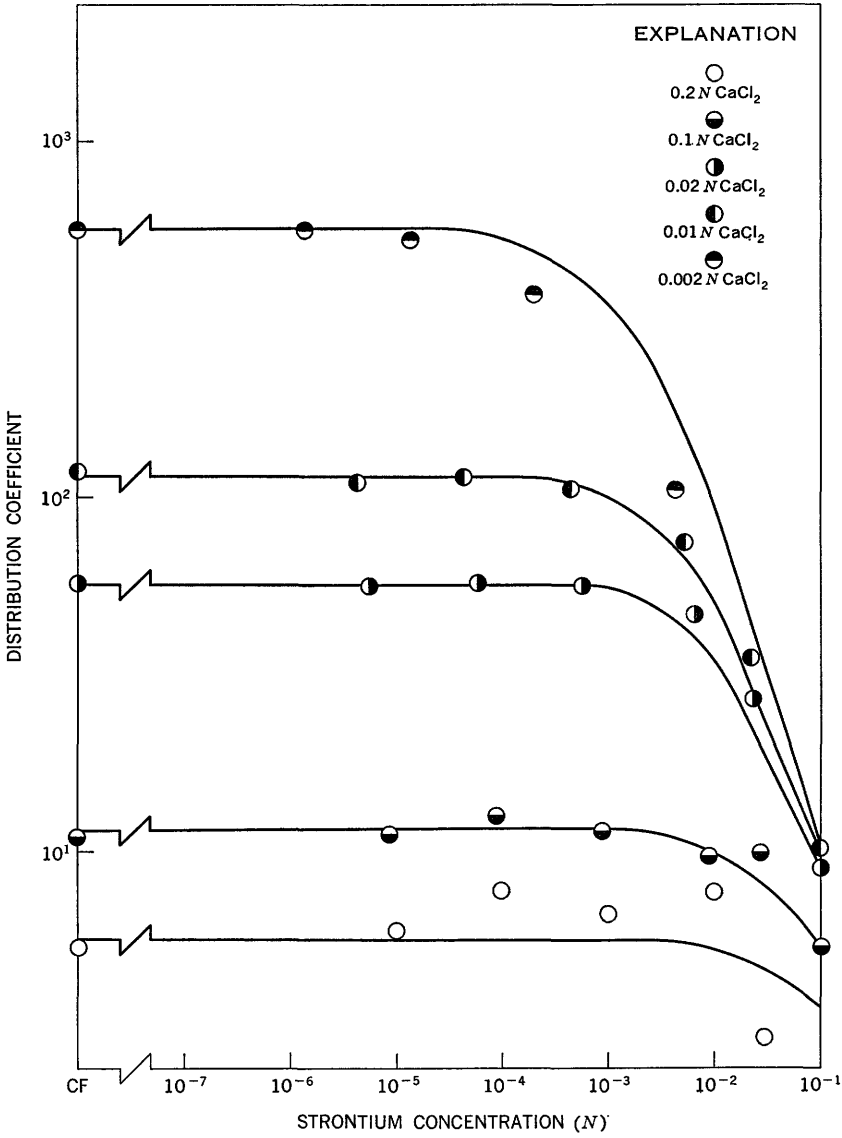

FIGURE 2.—Adsorption of strontium on calcium montmorillonite No. 21;

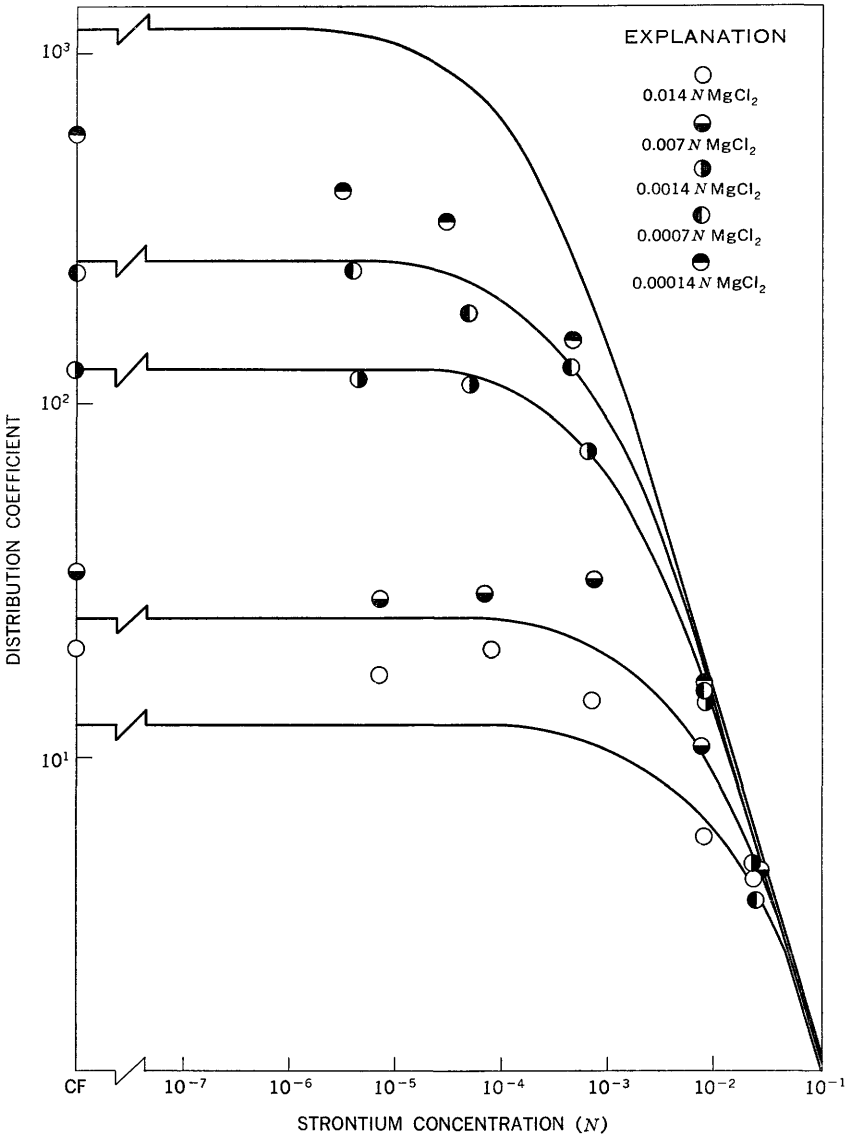

FIGURE 3.—Adsorption of strontium on magnesium illite No. 35.

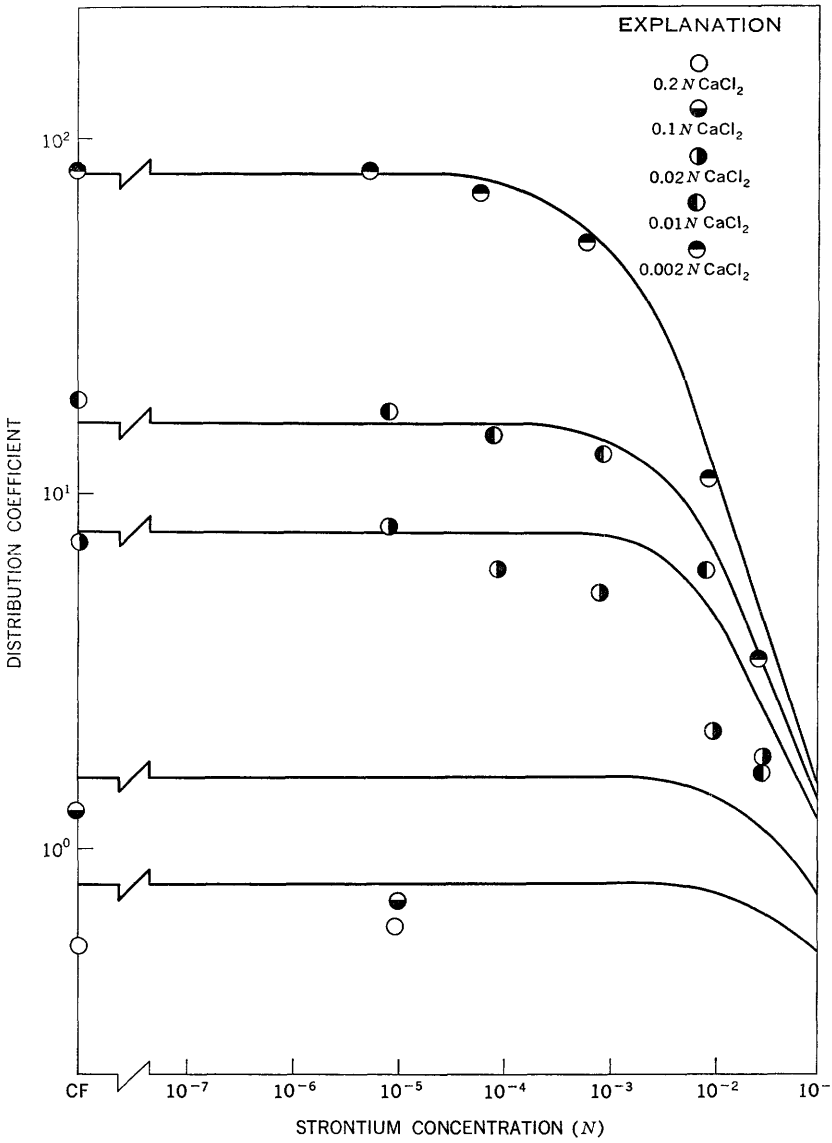

FIGURE 4.—Adsorption of strontium on calcium illite No. 35.

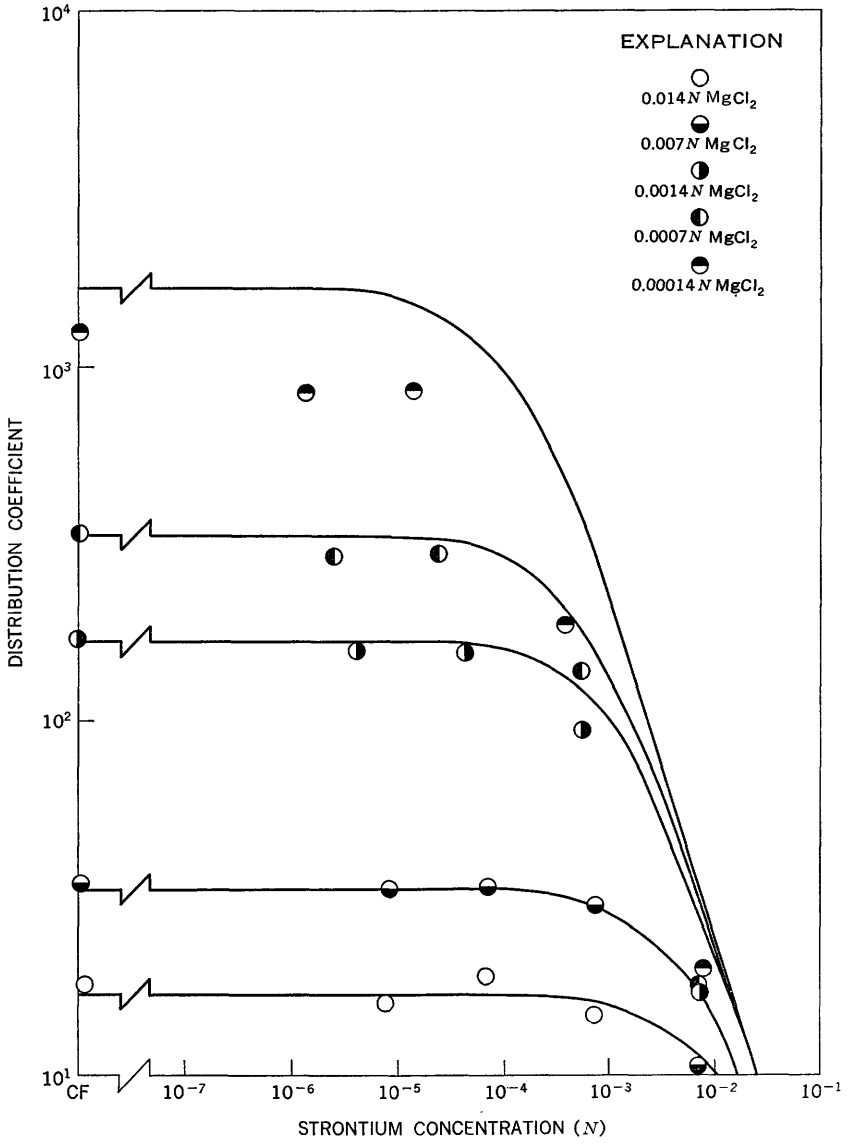

FIGURE 5.—Adsorption of strontium on magnesium kaolinite No. 4.

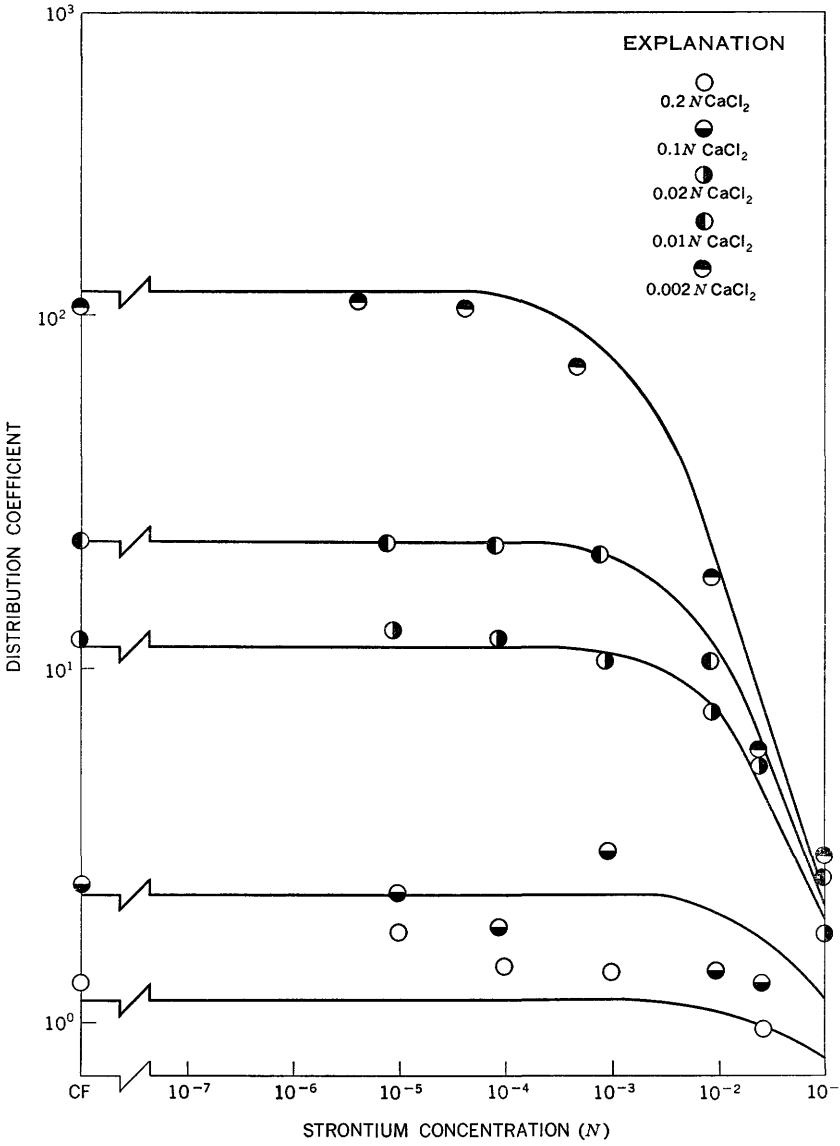

FIGURE 6.—Adsorption of strontium on calcium kaolinite No. 4.

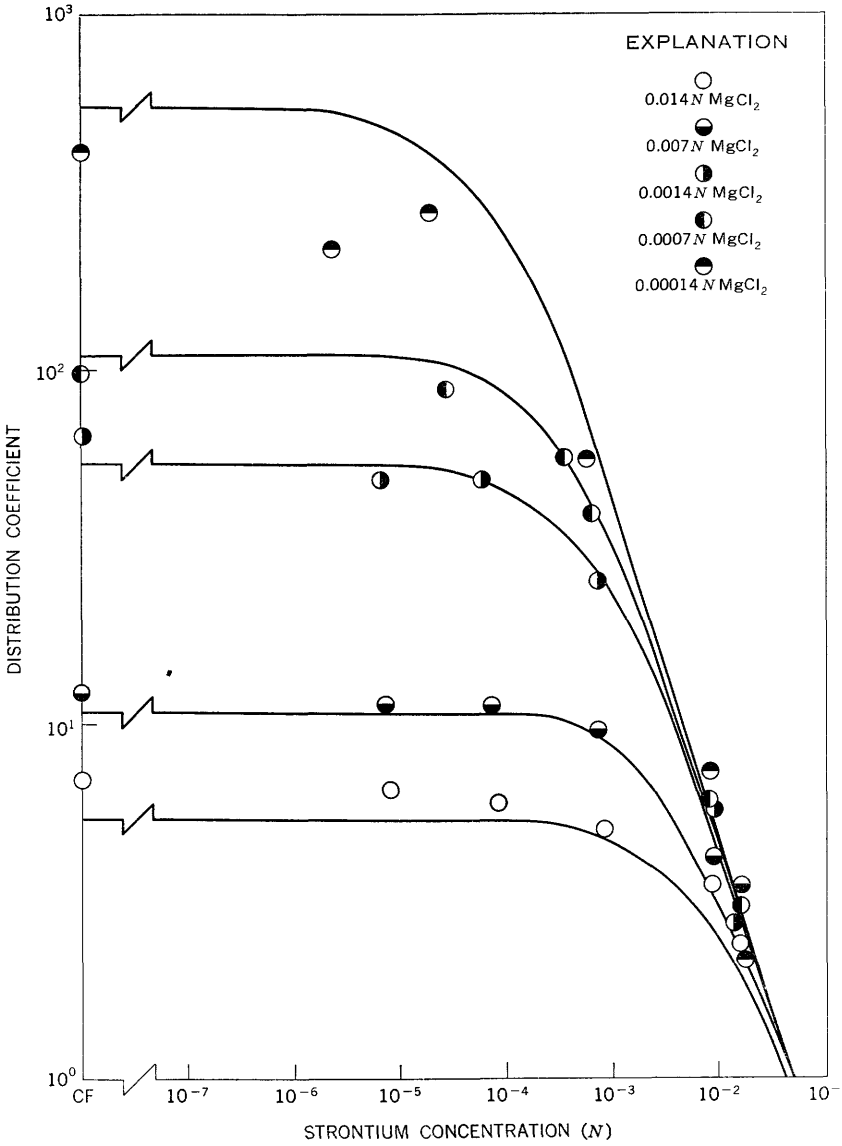

FIGURE 7.—Adsorption of strontium on magnesium kaolinite No. 7.

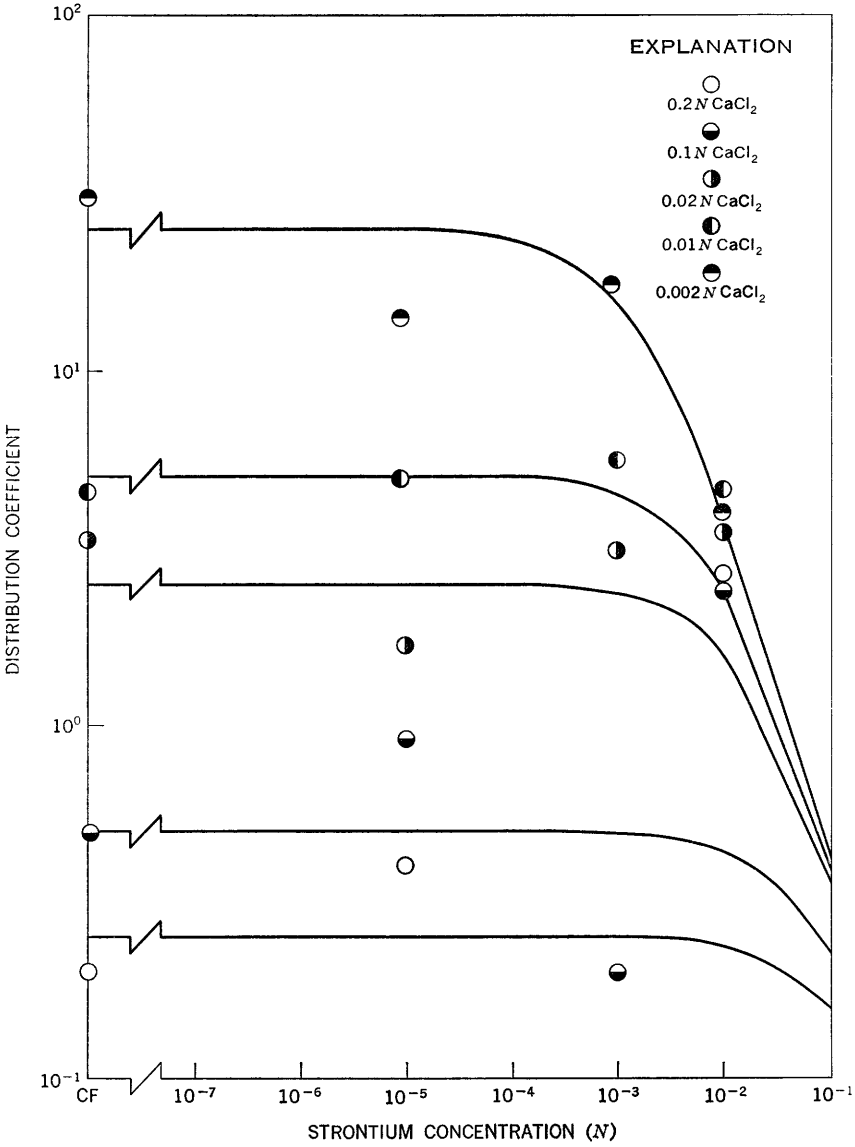

FIGURE 8.—Adsorption of strontium on calcium, kaolinite No. 7.

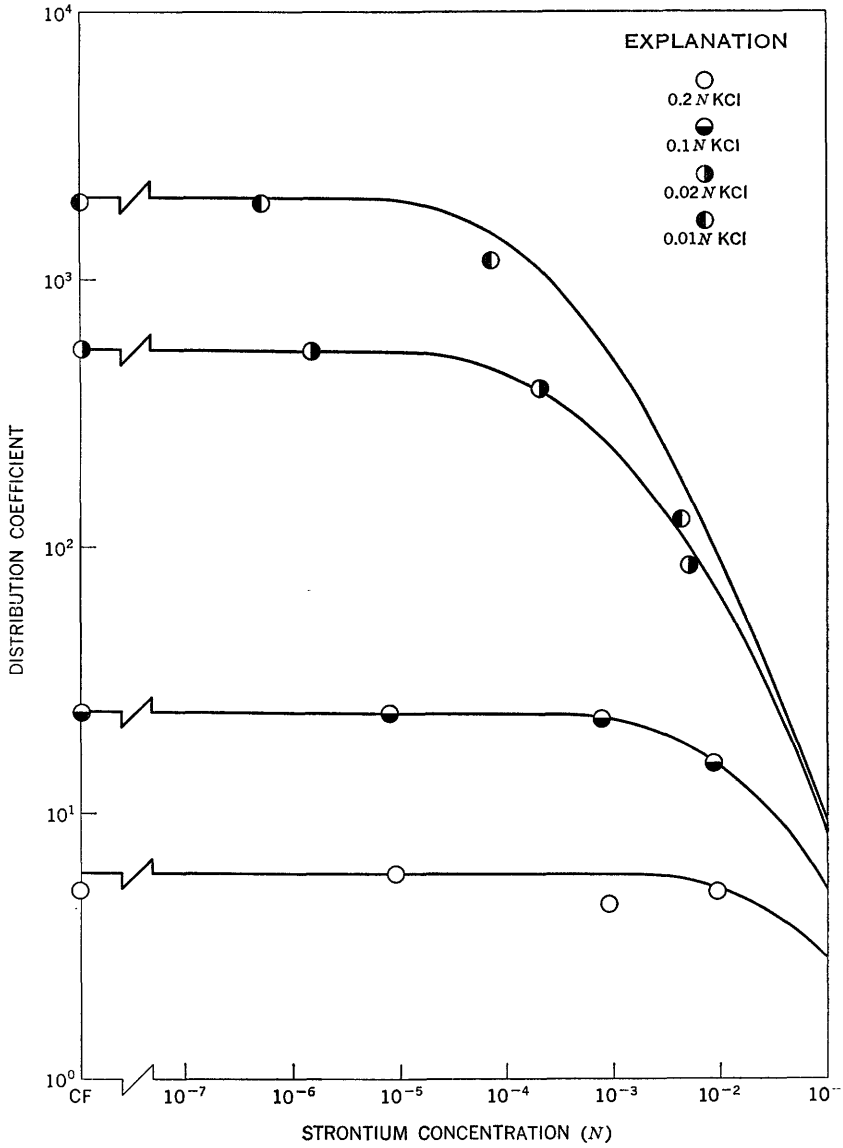

FIGURE 9.—Adsorption of strontium on potassium montmorillonite No. 21.

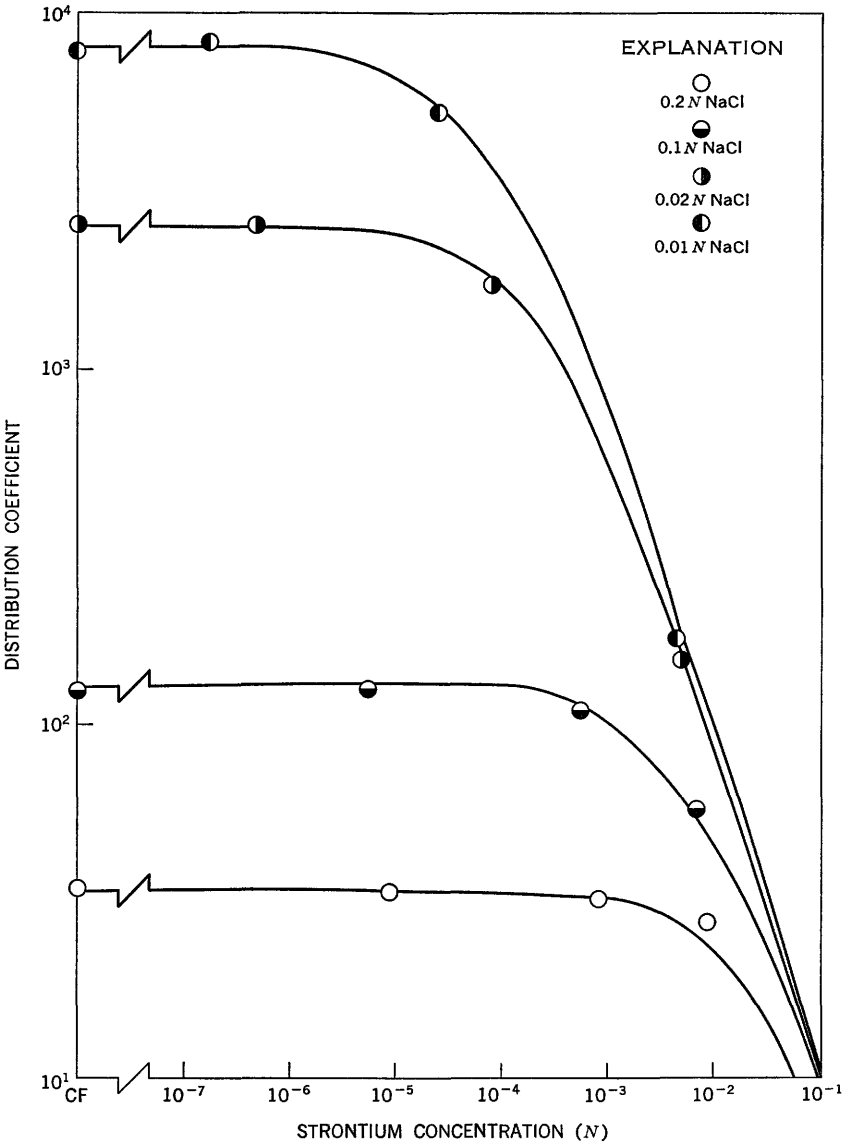

FIGURE 10.—Adsorption of strontium on sodium montmorillonite No. 21.

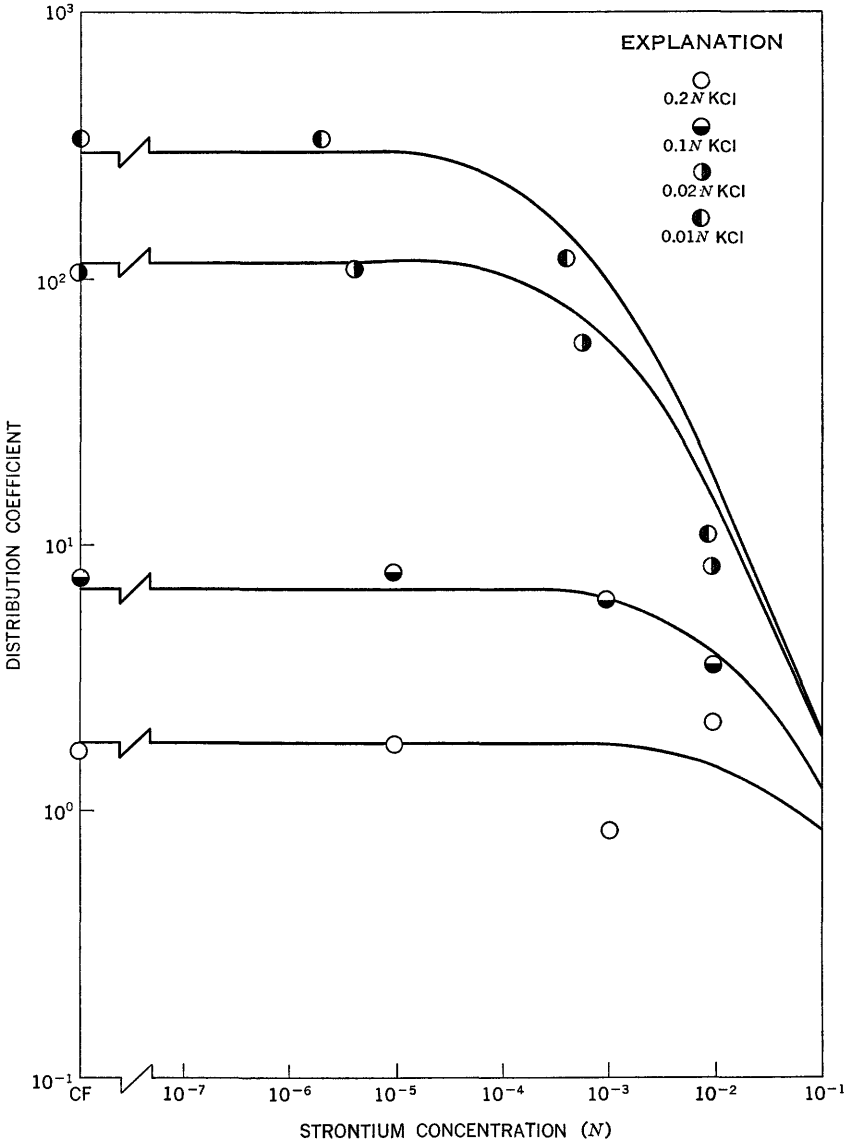

FIGURE 11.—Adsorption of strontium on potassium illite No. 35.

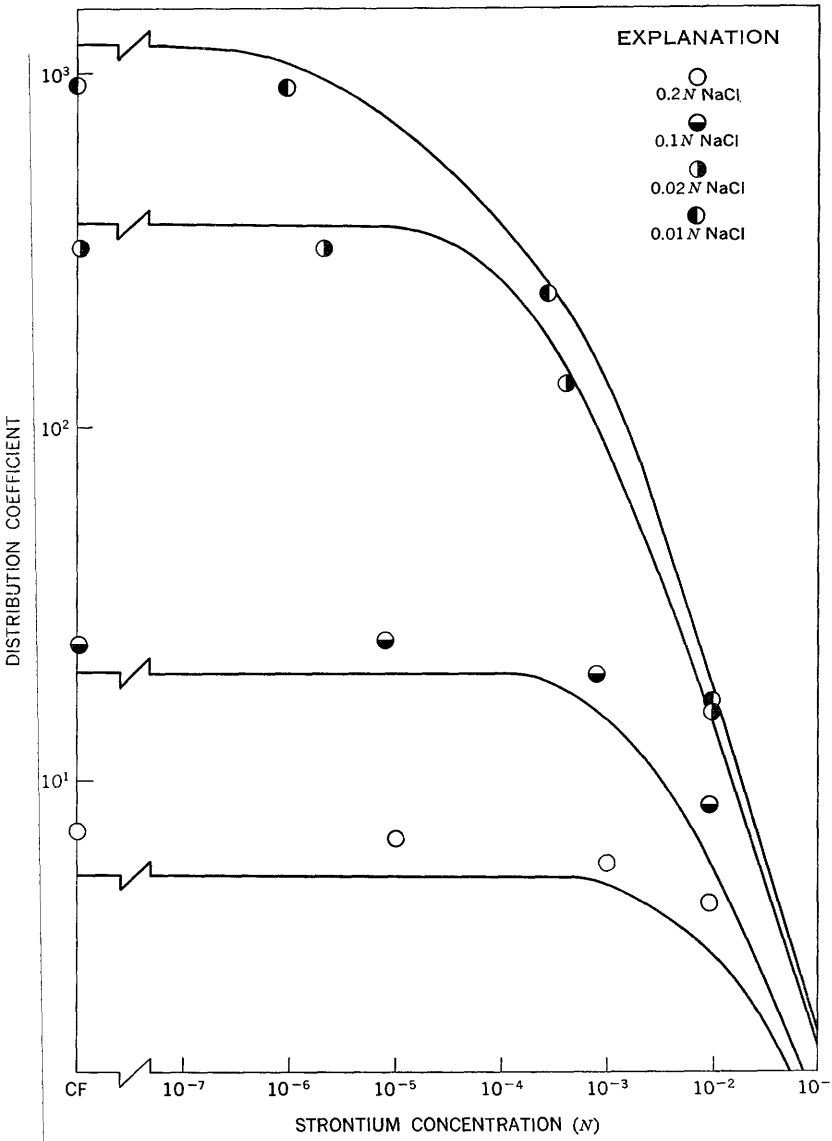

FIGURE 12.—Adsorption of strontium on sodium illite No. 35.

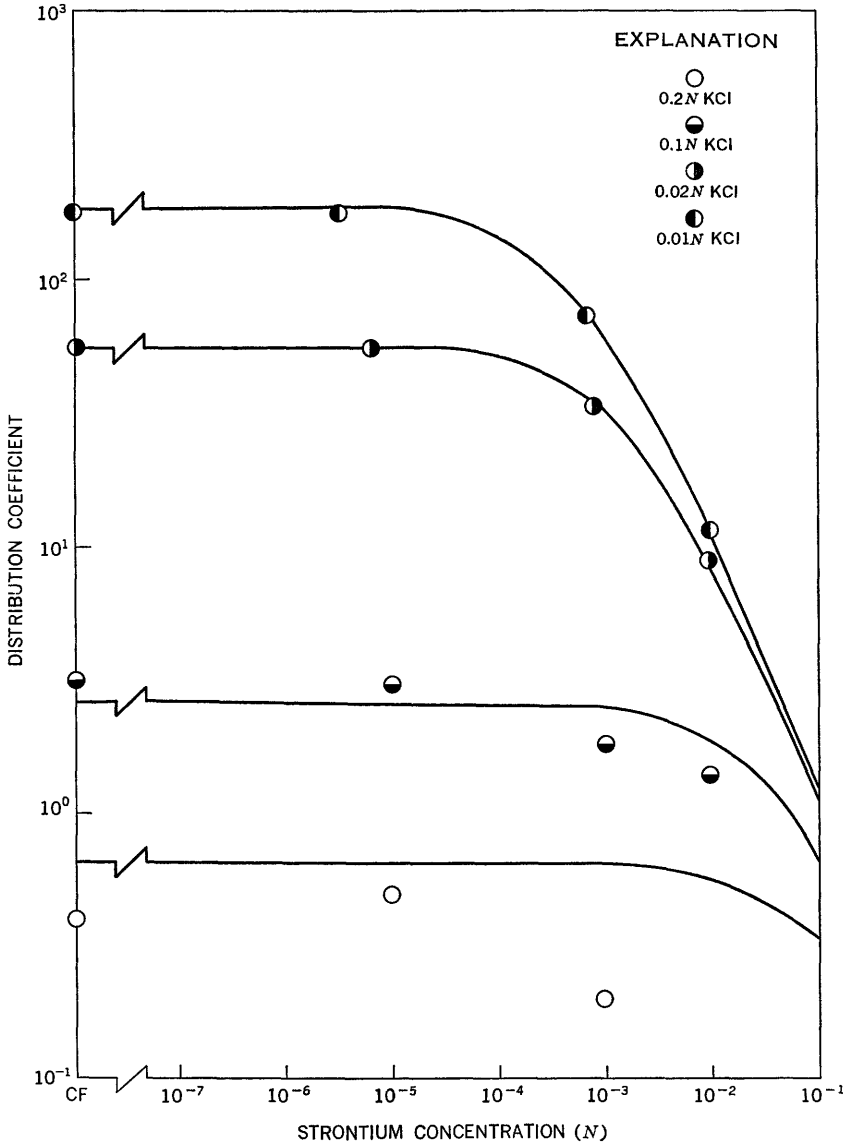

FIGURE 13.—Adsorption of strontium on potassium kaolinite No. 4.

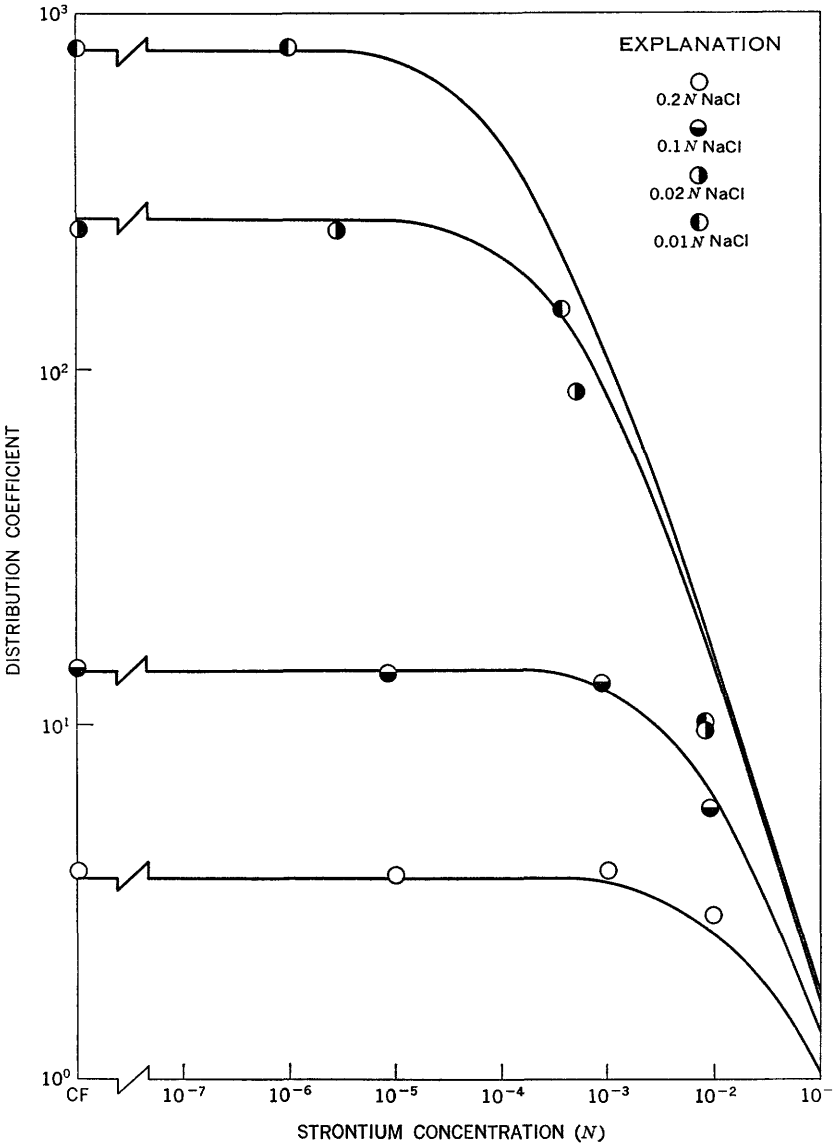

FIGURE 14.—Adsorption of strontium on sodium kaolinite No. 4.

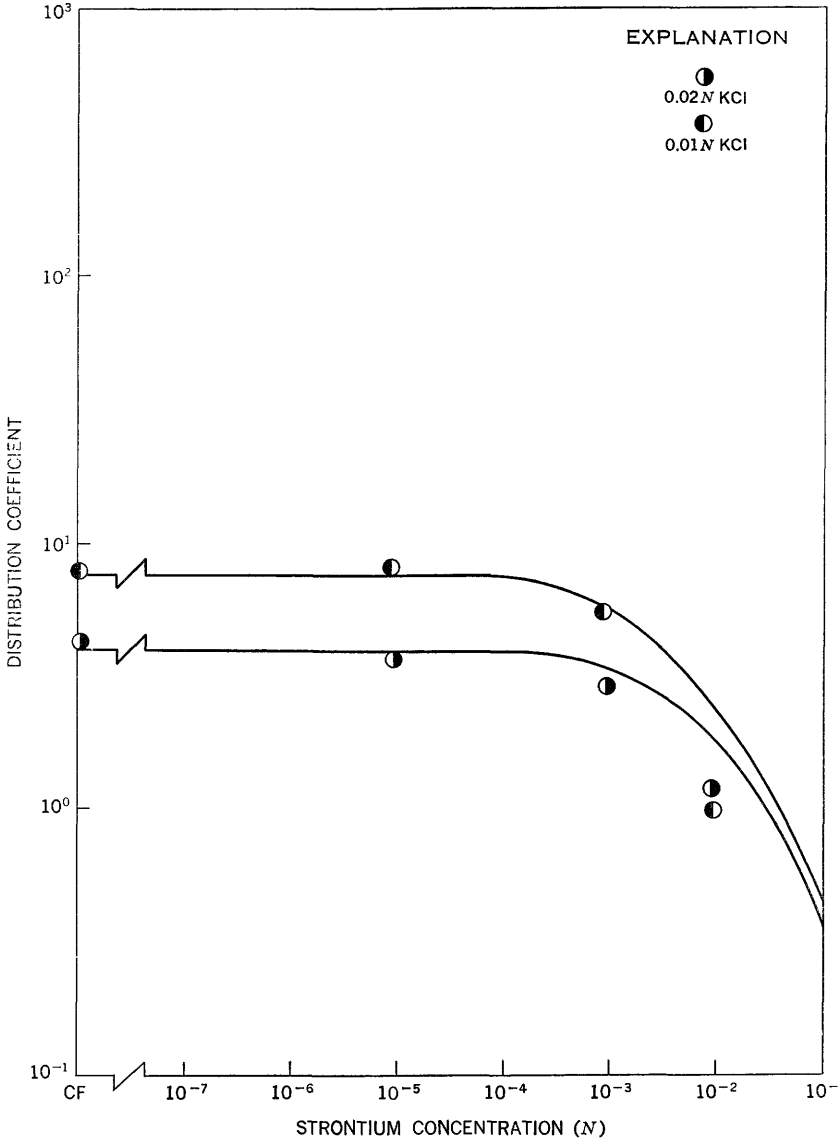

FIGURE 15.—Adsorption of strontium on potassium kaolinite No. 7.

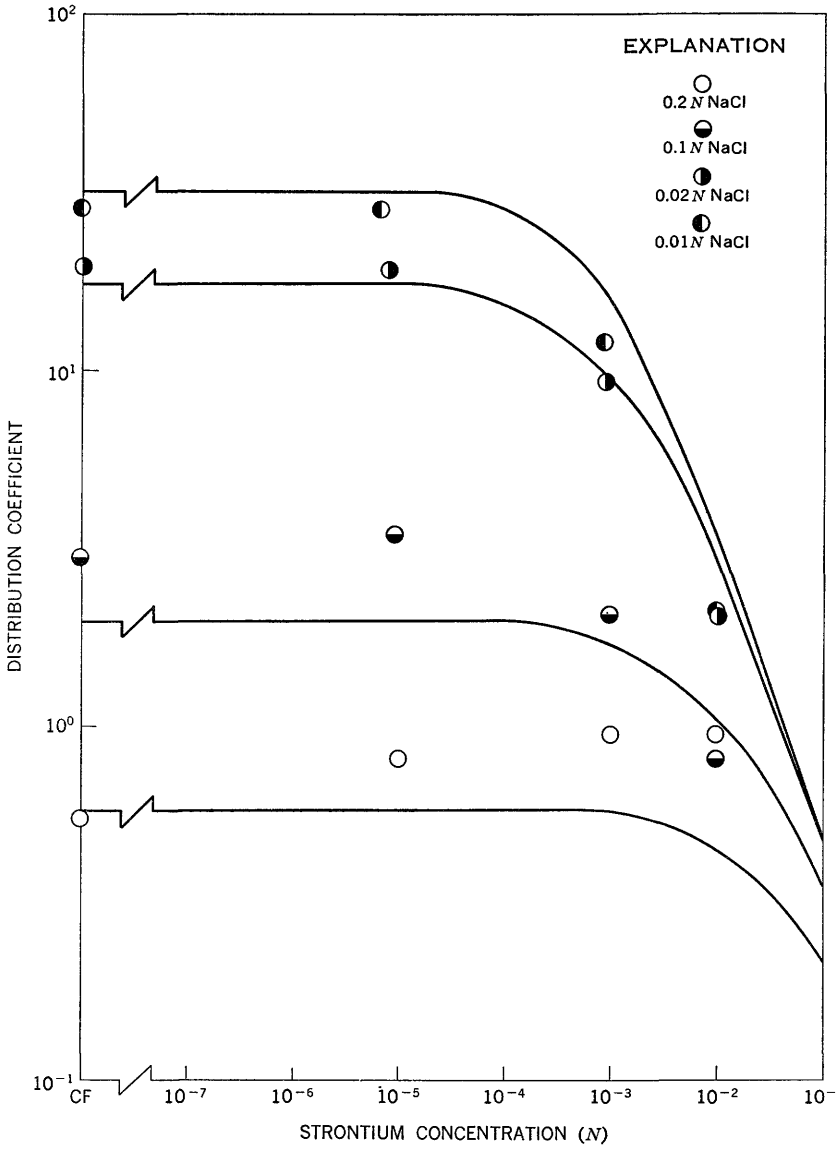

FIGURE 16.—Adsorption of strontium on sodium kaolinite No. 7.

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