EFFECT OF AL$^{3+}$ AND H$^+$ UPON THE SIMULTANEOUS DIFFUSION OF $^{85}$Sr AND $^{86}$Rb IN KAOLINITE CLAY*

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Abstract – The effect of varying concentrations of Al$^{3+}$ and H$^+$ upon the simultaneous diffusion of $^{85}$Sr and $^{86}$Rb was measured in salt-free aliquots of clay having different Al: H ratios. The Sr and Rb saturation of the CEC was held constant while the exchangeable Al and H were varied from Al$^{3+}$ : H$^+$ to Al$^{2+}$ : H$_3$. Aliquots of each clay-treatment were dually tagged with $^{85}$Sr and $^{86}$Rb. Self-diffusion of Sr and Rb was measured at 4, 24, 48, and 75°C. Radioassay of $^{85}$Sr and $^{86}$Rb was made with an automatic gamma-detection system equipped with a 400 channel analyzer and card punch unit. The self-diffusion equation was programmed for the 7040 computer to permit the simultaneous calculation of $^{85}$Sr and $^{86}$Rb self-diffusion coefficients. Rb diffusion was not significantly altered as the Al$^{3+}$ concentration was increased from 12 to 52 per cent. The diffusion of Sr was significantly increased as Al$^{3+}$ increased from 12 to 52 per cent. The faster diffusing Rb ion had a greater energy of activation than Sr (4.8 to 3.6 kcal/mole), however the Arrhenius frequency factor for Rb (a measure of the probability of ion exchange) was much greater for Rb than Sr (28.8 and 0.4 x 10$^{-4}$, respectively). Altering the Rb and Sr saturation and the complementary ions resulted in changes in the diffusivity, the energy of activation, and the frequency factor for these ions, but not always in the same direction or to the same degree.

INTRODUCTION

The aluminum ion is present in soils in a number of chemical forms including exchangeable, fixed, aluminum-clay complexes involving hydroxy-Al-polymers, and aluminum-iron-phosphate complexes intimately associated with the clay surfaces. Marshall (1964) and Jackson (1963) have pointed specifically to the effect of the aluminum ion upon the exchange properties of clays, its relation to the acidic properties of clays, and its role in the many processes associated with soil genesis; particularly aluminum-oxygen bonding in soil minerals as it affects clay structure and interlayer formation, ion exchange, and soil aggregation. Jenny (1961) has described the alternating cycle of emphasis placed upon hydrogen and aluminum ions during the past 50 years; and in so doing has cited the importance of these two ions in soil chemistry and mineralogy. The reversion of freshly prepared H-clays into H: Al-clays has been demonstrated by a number of investigators, including Coleman et al. (1961).

More recently, it has been shown that the aluminum ion may occur in the exchangeable form, or as fixed aluminum, as hydroxy-aluminum interlayers, or as Fe-Al phosphate complexes (Thomas 1960; Rich 1960; Ragland 1960). Ion exchange-equilibria studies, using clay and soil systems with known Al:K and Al:Ca ratios have been reported by Nye et al. (1961).

The data contained in these publications show that the aluminum ion may directly or indirectly affect many soil properties including the cation exchange capacity, ion fixation, buffering capacity, potentiometric and conductance characteristics, ion distribution coefficients, as well as aluminum interlayer formations and their subsequent effect on the surface properties of clay.

While these investigators have presented evidence of the existence of these aluminum-clay complexes and their result and effect on soil properties and exchange-equilibria, none have related the presence of variable concentrations and chemical forms of aluminum in soil or clay systems specifically to ion diffusion. Investigations in the area of ion diffusion have been largely concerned with self diffusion in soil systems with varied concentrations of ions (Graham-Bryce, 1965); the relation of ion diffusion to the absorption of ions by...
plants and diffusion of ions in clay-mineral systems (Barber, 1962); diffusion of Sr in resin membranes (Lopez-Gonzales and Jenny, 1959); ion diffusion as related to the energy of activation of ions diffusing in clay systems, Gast (1961, 1962), Low (1958), and Lai and Mortland (1962); and finally, the thermodynamics of ion exchange on colloidal materials has been intensively studied by Thomas (1965, 1967).

On the basis of the observed effects of the aluminum and hydrogen ions upon chemical properties of soils it appears logical that the diffusion of ions also may be affected by the concentration in which these two ions are present in the soil system. This investigation had as its objective to extend the present knowledge of the role of the aluminum and hydrogen ion in soil chemistry by making quantitative measurements of the simultaneous diffusion of $^{85}$Sr and $^{86}$Rb in kaolinite clay containing varied saturations of Sr or Rb with the aluminum or hydrogen ion varying reciprocally as the complementary ion on the exchange complex. The $^{85}$Sr and $^{86}$Rb isotopes were used as substitutes for Ca and K respectively; each behaves similarly to their counter-part in soil chemistry and in addition, these isotopes possess excellent radiation properties for tracer experiments.

**EXPERIMENTAL**

**Clay preparation**

Standard kaolinite clay (No. 5-Lamar Pit, Bath, South Carolina; Wards Natural Science) was used in this study. Four monoionic clay systems were prepared by passing the clay through a 300 mesh sieve followed by repeated washing of the aliquots of clay with a 1 N chloride solution of either Rb, Sr, H or Al. Free salts or acid was removed by sequential washes with water and ethanol until chlorides were not detectable to silver nitrate. Because of the rapid alteration of H-clay to an Al-H-clay the aliquots of H-clay were processed as for Ca and K respectively; each behaves similarly to their counter-part in soil chemistry and in addition, these isotopes possess excellent radiation properties for tracer experiments.

**Experimental**

**Clay preparation**

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**Simultaneous diffusion of Sr and Rb**

Simultaneous diffusion of Sr and Rb was made through the use of the $^{85}$Sr and $^{86}$Rb isotopes. $^{85}$Sr decays by $\gamma$-ray emission with a maximum energy of 0.51 MeV, its half-life is 64 days. $^{86}$Rb has a half-life of 18.7 days and decays by both beta particle and $\gamma$-ray emission; 80 per cent through beta particle radiation (1.71 MeV) and 20 per cent by $\gamma$-ray emission with a maximum energy of 1.08 MeV. The characteristic $\gamma$-ray energies from these respective isotopes (0.51 and 1.08 MeV) enabled the simultaneous detection of the concentration of these isotopes by means of a NaI(Tl) scintillation crystal and a multi-channel analyzer. A dual tag of 70 and 0.90 microcuries of $^{86}$Rb and $^{85}$Sr, respectively, was added to each 50-gram aliquot of prepared clay. This resulted in a final activity after the diffusion period of about 3000 cpm per 100 mg clay. The clays were mixed thoroughly over a period of 2 days to assure a homogeneous system.

**Diffusion techniques**

The simultaneous diffusion of Sr and Rb was repeated for temperatures of 4, 24, 48, and 75°C. A precision oven was used to control the 24, 48, and 75°C temperatures of the clay during the diffusion period. Diffusion at the 4°C was made possible by the use of a small refrigerator. The temperature variation was $\pm 1^\circ C$. The samples were maintained in a saturated atmosphere in order to give additional assurance that the saturated clay would not lose moisture at the elevated temperatures during the diffusion period. The self-diffusion of Sr and Rb was carried out with only slight modifications in the quick-freeze technique previously reported (Brown et al., 1964). The non-radioactive and dually tagged clay were contained in paired lucite cells (2.0 x 1.9 cm) for diffusion of $^{85}$Sr and $^{86}$Rb, following the diffusion period the dual core was frozen in liquid air in 15-20 sec; the lucite cell removed, and the frozen
core mounted in a refrigerated microtome with the non-radioactive core next to the cutting blade. The first 80 slices (50 μ thick) were saved for Sr, Rb, and Al analysis. The remainder of the core (3.0 cm) was partitioned evenly into 40 samples (15 slices, each 50 μ thick); the samples were collected in consecutively numbered and tared radiation counting bottles containing about 2 ml of ethanol. The samples were dried at 70°C, assayed for 85Sr and 86Rb gamma radiation by the detection unit described below. The net weight of clay was obtained and all radiation normalized to cpm/mg of oven-dry clay.

Gamma-ray detection system

The simultaneous measurement of the gamma radiation from multiple-tagged systems was carried out by means of an automatic gamma counting unit (Nuclear-Chicago, Model 1085) modified to include a 400 multichannel analyzer (RIDL, Model 34–27). The analyzer was electronically tied through a parallel-to-serial converter to an IBM (026) card punch modified electronically to print and punch-out the radiation data stored in the analyzer on standard IBM data-processing cards. Accessories included a digital pulse height stabilizer and a display oscilloscope. The stabilizer maintained the desired channel-energy calibration of the analyzer (1 MeV/channel). The 3 in. x 3 in. NaI (Tl) well-type crystal, accommodating a 1 in. x 3 in. sample bottle, had a resolution of 9 per cent for 137Cs and an efficiency of 27 per cent. The unit permits either a manual or automatic radioassay of samples with the usual preset counting time, automatic erase of the stored data in the analyzer after each sample, and a region of interest selector permitting the selection of a limited range of channels. Only 200 of the 400 channels were used for the detection of 85Sr and 86Rb. The photopeaks of 85Sr and 86Rb were stored in channels 51 and 108, respectively, as shown by the spectra of these isotopes given in Fig. 1.

The radiation data for each sample were transferred to the data card in this sequence; sample identification the first 5 places on the card, followed by the first number of the 10 channels to be included on the card (i.e., 010), followed by the radiation count (up to 6 digits) for each of the 10 successive channels. The accumulated radiation count for each channel was printed as well as punched on the card which enabled a visual check of the data. The unit was adjusted to detect either

![Gamma-ray spectrum for 86Rb and 85Sr and a mixture of these two isotopes. Spectra were obtained with the gamma-ray detection unit described in text.](image-url)
or both $^{85}$Sr (0.51 MeV) and $^{86}$Rb (1.08 MeV) for successive clay samples from the diffusion experiment; each sample was counted for 2 min with the data stored in channels 45-119 and subsequently transferred to the IBM cards. The $^{86}$Sr photo peak was stored in channels 45 through 64, while the $^{85}$Rb photo peak was included in channels 100 through 119 (Fig. 1). Since each diffusion core had 40 samples, a total of 320 cards was used per core. The Compton-scattering coefficient for Rb was evaluated for a broad range of $^{86}$Rb:$^{85}$Sr activities; 0:10, 0:500, 0:1000; to 50:10, 50:500, and 50:1000. The contribution of $^{86}$Rb to the count in the $^{85}$Sr photo peak (channels 45-64) was equal to 0:51 of the net count for Rb photo peak (channels 100-119). Thus, the net $^{85}$Sr count was obtained by subtracting $^{85}$Sr background plus the product of the net Rb count (channels 100-119) and 0:51 from the gross $^{85}$Sr count. A comparison of the known activity of a series of $^{85}$Sr standards alone and in the presence of $^{86}$Rb indicated that the calculated net $^{85}$Sr count varied no more than 4 per cent.

Computer program

The adaptation of the self-diffusion equation (Fick's second law) for use with the quick-freeze technique has been previously reported (Phillips and Brown, 1964). The equation was arranged in a Fortran source-deck to accept the net radiation data of $^{85}$Sr and $^{86}$Rb and the subsequent calculation of the apparent self-diffusion coefficients of either or both of these ions by the 7040 computer. The data cards were preceded by the 5 library cards; card 1: the header card containing: (a) instruction to calculate the self-diffusion coefficient for either Rb, Sr, or Rb and Sr simultaneously; (b) the diffusing time; (c) the diffusing distance; (d) the Sr and/or Rb background to be subtracted; (e) the Rb Compton coefficient (0:51); and (f) sample identification information; cards 2, 3, 4, and 5: sample-weight data for normalizing all net counting data to counts of Sr or Rb per mg of clay. The option of plotting the experimental ion distribution curve for the diffusing ions and fitting it to the theoretical self-diffusion curve was also included (Fig. 2).

The computer calculation gave reproducible values with only an occasional re-run of a sample required. The standard deviation for the apparent self-diffusion coefficient of Rb was $6.46 \pm 0.40 \times 10^{-7}$ cm$^2$/sec with a coefficient of variation of 5.6 per cent; while for Sr, these values were $2.60 \pm 0.18 \times 10^{-7}$ cm$^2$/sec and 6.8 per cent, respectively.

The activation energies for the self-diffusion of Rb and Sr were calculated using the method described by Lopez-Gonzales and Jenny (1959), the final equation being:

$$\ln A.S.D. = \ln A - \frac{E_a}{RT}$$

where $\ln A.S.D.$ is the natural logarithm of the apparent self-diffusion coefficient; $E_a$ is the energy

![Fig. 2. Ion distribution curves for the simultaneous self-diffusion of $^{86}$Rb and $^{85}$Sr in kaolinite clay: circles represent the experimental distribution and the solid lines the theoretical distribution.](image-url)
of activation expressed in cal/mole, \( R \) is the universal gas constant (1-987 cal/mole \( \times T \)), and \( \ln A \) is the natural logarithm of the y-intercept. A graph plotting \( \ln \text{A.S.D.} \) vs. the reciprocal of the absolute temperature resulted in a straight line relationship, thus enabling the determination of \( \ln A \) in Equation (1). The Arrhenius frequency factor \( (A) \) \( (A \text{ in Equation (1)}) \) of Sr and Rb was calculated for each treatment. As applied to clay systems, \( A \) defines the probability of ion interaction; it includes the frequency of oscillations which an ion undergoes at a given exchange site. It represents a relative measure of the probability of ion exchange; an increase in the probability, all other things being equal, should result in an increase in the diffusion rate. Statistical analysis of the data was completed to evaluate the effects of temperature, Rb and Sr concentration, and the Al:H ratios on the self-diffusion of \(^{86}\text{Rb}\) and \(^{85}\text{Sr}\).

**RESULTS**

The diffusion data reported is defined in terms of the apparent self-diffusion coefficient and as such does not attempt to separate out the various tortuosity factors as has been reported by some investigators (Porter *et al.*, 1960; Olsen and Watanabe, 1963). The justification for this usage has been previously reported (Phillips and Brown, 1964). The reader is also reminded that the frame of reference of the data is with respect to the entire soil medium and not just the soil solution.

**Apparent self-diffusion of \(^{86}\text{Sr}\) and \(^{86}\text{Rb}\)**

Changes in the diffusivity of Rb and Sr as a function of ion concentration, complementary ions, and temperature are shown in Figs. 3(a) and 3(b). The \( "r" \) values for Rb diffusion ranged from 0.98 to 0.99, while the \( "r" \) values for Sr varied from 0.91 to 0.97. The apparent self-diffusion coefficients for \(^{86}\text{Rb}\) and \(^{85}\text{Sr}\) were significantly different (at the 1 per cent level) between temperatures (4, 24, 48, and 75°C). Increasing the exchangeable Al\(^{3+}\) at the expense of exchangeable H\(^+\) did not significantly change the diffusion of Rb at any temperature; the mean value for the Al:H treatments was 10.05 \( \times 10^{-7} \text{ cm}^2/\text{sec} \). Sr diffusion was increased significantly (1 per cent level) as the Al:H ratio was changed from Al\(_{12}:\text{H}_{34}\) to Al\(_{52}:\text{H}_1\); the increase being from 1.99 to 3.03 \( \times 10^{-7} \text{ cm}^2/\text{sec} \) at 24°C.

The apparent self-diffusion coefficients for Sr and Rb, the energy of activation \( (E_a) \) and the Arrhenius frequency factor \( (A) \) are related to changes in the percentage of exchangeable Al\(^{3+}\) in Fig. 4. In these treatments the percentage saturation by H\(^+\) was decreased from 34 to 1 per cent as Al\(^{3+}\) was increased from 12 to 52 per cent saturation. Since Rb and Sr were held constant (44 and 7.5 per cent) in these treatments, the principal effects are therefore related to the substitution of Al\(^{3+}\) for H\(^+\) as the complementary ion to Rb or Sr. The diffusion values are given for 24°C (D) as well as the mean of the four temperatures (\( \bar{D} \)).

**Fig. 3.** The relationship between the concentration of extractable Al\(^{3+}\) and the apparent self-diffusion coefficient for Rb and Sr in kaolinite clay under temperatures of 4, 24, 48, and 75°C.
The diffusivity of Sr (Fig. 4(a)) increased significantly (1 per cent level) from 1.99 to $3.03 \times 10^{-7}$ cm$^2$/sec at 24°C (3.12 to 4.03 based on the mean of all temperatures) as AI saturation increased from 12 to 52 per cent. For Sr, $E_o$ increased from 2.7 in the presence of 12 per cent AI to 3.0 kcal/mole in the presence of 52 per cent AI; (A) also increased from 0.26 to $4.03 \times 10^{-4}$ as AI saturation increased. The increase in diffusivity of Sr, despite an increasing $E_o$, can be attributed to the increase in (A). The increase in (A) overrode the effect of an increase in $E_o$ and consequently caused an increase in the diffusivity of Sr as AI saturation increases.

The diffusion of Rb (Fig. 4(b)) was not altered by increasing the AI saturation. The mean Rb diffusion coefficients for the Al:H treatments were $5.47 \pm 0.31 \times 10^{-7}$ cm$^2$/sec at 24°C and $10.05 \pm 0.51 \times 10^{-7}$ cm$^2$/sec as the mean of the four temperatures. The $E_o$ for Rb was constant at 5.1 kcal/mole for Al saturations up to 33 per cent, but decreased to 4.9 for the 52 per cent Al treatment; (A) remained constant $3.7 \times 10^{-4}$ for AI saturations up to 33 per cent, but decreased to $25.12 \times 10^{-4}$ as AI increased to 52 per cent. Thus, where Rb saturation was held constant at 7.5 per cent its diffusion remained constant despite changes in the Al:H ratio and decreased in both $E_o$ and (A).

The relationships between the diffusion of Rb and Sr, their activation energy and frequency factor, and their per cent saturation of the clay are given in Fig. 5. The diffusivity of Rb at 7.5 per cent saturation represents the mean of the four Al:H treatments, and the average over the four temperatures. The diffusion coefficient of Rb increased from $10.05$ to $14.08 \times 10^{-7}$ cm$^2$/sec as the saturation increased from 7.5 to 100 per cent. For the 7.5 per cent Rb saturation, the complementary ions were Sr$_{44}$:Al$_{33}$:H$_{18}$ while for the 51 per cent saturation Sr$_{19}$ was the only complementary ion present. Thus, the increased diffusion of Rb was associated not only with an increase in Rb saturation but also with a change in the complementary ions. $E_o$ was 5.1 kcal/mole at 7.5 per cent and 51 per cent Rb saturation and decreased to $4.8 \times 10^{-4}$ kcal/mole at 100 per cent Rb saturation; (A) however, increased from $34.39$ to $41.69 \times 10^{-4}$ as the Rb saturation increased from 7.5 to 51 per cent, but decreased to $28.84 \times 10^{-4}$ at 100 per cent Rb saturation. The increased diffusivity of Rb between 7.5 and 51 per cent is related to the increase in (A) since $E_o$ remained constant; the increase between 51 and 100 per cent saturation was associated with a decrease in both $E_o$ and (A). In this case, $E_o$ offset the effect of the decrease in (A).

The effect of Sr saturation and changes in the complementary ions upon the diffusion of Sr are shown in Fig. 5(b). The diffusion of Sr in the Sr$_{100}$ treatment was $2.49 \times 10^{-7}$ cm$^2$/sec at 24°C, and
3.64 × 10⁻⁷ cm²/sec averaged over all four temperatures. The diffusion of Sr was both increased and decreased as its saturation was increased from approximately 45 to 100 per cent depending upon the complementary ion. The presence of Rb alone or Rb, Al and H increased the diffusion of Sr from 3.64 to 4.25 and 3.64 to 4.03 × 10⁻⁷ cm²/sec, for these respective ion combinations. Holding the percentage Sr and Rb constant (44 and 7.5 per cent saturation) and varying the Al : H ratio from 51 : 1 to 12 : 34 decreased the diffusion of Sr from 4.03 to 3.12 × 10⁻⁷ cm²/sec; despite changes in ion saturation, \( E_a \) and (A) both increased as Sr saturation was increased from 44 to 100 per cent. Changes in the complementary ion caused variations in \( E_a \); Sr₁₅,Rb₅₁ was 2.5 kcal/mole as compared to 3.6 for Sr₁₀₀. (A) increased from 0.22 to 1.15 × 10⁻⁴ as Sr saturation was increased from Sr₁₀₀:Rb₅₁ to Sr₁₅,Rb₅₁. Thus the replacement of Rb₅₁, or Al₅₂ with Sr decreased the diffusion coefficient for Sr, and increased \( E_a \) and (A). In this case, \( E_a \) was dominant over (A).

**DISCUSSION**

The relationship between the apparent self-diffusion of ions, their energy of activation, the Arrhenius frequency factor, the distance between equilibrium sites, ion mobility, and activity coefficients have been reported by a number of workers, including Lopez-Gonzales and Jenny (1959), Lai and Mortland (1962), Gast (1962, 1963), Low (1958), and Graham-Bryce (1965). Where ion-diffusion was determined in homoionic systems the relationship between the ion diffusion \( E_a \) and (A) followed an orderly pattern. In most cases, low \( E_a \) values were associated with the faster diffusing ions, while high \( E_a \) values were associated with the slower rate of diffusion. The diffusion rate was also related to the “hopping distance” (distance between equilibrium sites); the shorter the distance the slower the diffusion rate (Lai and Mortland, 1962). Self-diffusion of ions in heterionic systems, such as reported by Lopez-Gonzales and Jenny (1959), and Graham-Bryce (1965), showed the influence of the concentration of the diffusing ion and the effect of its complementary ion upon its diffusion rate and \( E_a \) and (A) values. While heterionic systems may have equal concentrations of each ion (such as Rb⁺, Sr²⁺, H⁺, Al³⁺) in the paired-diffusion cells, the diffusion processes may involve an exchange of unlike ions, i.e. Rb⁺ for H⁺ or Rb⁺ for Sr²⁺, instead of the expected Rb⁺ for Rb⁺ exchange. Changes in the per cent saturation of a given ion not only involves a change in the concentration of the diffusing ion, but an addition or a change in complementary ions which may alter \( E_a \).
and (A), as well as the distance between preferred-equilibrium sites resulting in a measurable effect upon the diffusion rate.

The effect of changes in the per cent saturation and the complementary ions upon the values of $E_a$ and (A) are shown for selected treatments in Table 1. In comparing Rb and Sr diffusion in the homoionic systems (Rb$_{100}$ and Sr$_{100}$), the diffusivity of Rb is greater than Sr, yet its $E_a$ is much larger than that of Sr; attributed, at least in part, to the larger hydrated size of the Rb ion. In this case, the greater probability of exchange of Rb (28.84 compared to 1.15) accounts for Rb diffusing faster than Sr.

Comparing the diffusion of Rb in homoionic systems with that in heteroionic systems, decreasing Rb saturation from 100 to 51 per cent by adding Sr$_{49}$ as the complementary ion resulted in a decreased diffusivity of Rb and an increase in both $E_a$ and (A). The increase in $E_a$ overcame the tendency for an increase in diffusion due to the increase in (A). In this same treatment the diffusion of Sr was increased by increasing the Rb concentration while $E_a$ and (A) were reduced; hence the reduction in $E_a$ overcame the effect of a decreased probability of exchange resulting in an increased diffusion of Sr. For the heteroionic systems with H$^+$, change in the magnitude of (A) (0.45 for the Al$_{52}$:H$_1$ treatment as compared to 0.26 for Al$_{12}$:H$_{34}$ treatment) accounts for the two diffusion rates of 4.03 and 3.12 x 10$^{-7}$ cm$^2$/sec for Sr in these two treatments.

Lai and Mortland (1962) in relating "hopping distances" to diffusion rates and $E_a$ values indicated a degree of uncertainty was associated with the calculated distances, due primarily to the assumed value of 10$^{-13}$ sec as the "halting" time for the ions at a given site. For this reason the "hopping distances" were not calculated for these diffusion data. It appears, however, in heteroionic systems that the distance between preferred-equilibrium sites may not be consistently related in the same way to the diffusion rate. For example, in Fig. 5(a), the diffusion of Rb increases as Rb saturation increases from 7.5 to 100 per cent, which means that the diffusion rate of Rb is increasing while at the same time the distance between Rb sites is becoming shorter, reaching a minimum at 100 per cent Rb saturation. On the other hand, increasing Sr saturation from 45 to 100 per cent (in the presence of Al$^{3+}$ or Rb$^+$) (Fig. 5(b)) which should give rise to a shorter distance between equilibrium sites resulted in decreased diffusivity of Sr.

Table 1. Changes in the apparent self-diffusion coefficient, energy of activation and the Arrhenius frequency factor of Rb and Sr diffusing in homoionic and heteroionic clay systems

<table>
<thead>
<tr>
<th>Homoeionic systems</th>
<th>Heteroionic systems with Sr : Rb : Al : H</th>
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<tbody>
<tr>
<td></td>
<td>Rb$_{100}$</td>
</tr>
<tr>
<td>Rb</td>
<td>Sr</td>
</tr>
<tr>
<td>A.S.D.†</td>
<td>14·81</td>
</tr>
<tr>
<td>$E_a$‡</td>
<td>4·778</td>
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<tr>
<td>(A)§</td>
<td>28·84</td>
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</table>

*Increase or decrease is relative to values for homoionic systems; Rb$_{100}$ and Sr$_{100}$.
†Apparent self-diffusion coefficient (×10$^7$ cm$^2$/sec); mean of four temperatures. Coefficient of variation for Rb; 5·6 per cent, Sr; 6·8 per cent.
‡Energy of activation in cal/mole.
§Arrhenius frequency factor (×10$^4$).

SUMMARY

A radioassay program was presented for the simultaneous measurement of multiple ion diffusion in soils and clays. The apparatus included a y-ray detection unit with a NaI(Tl) detector, multichannel analyzer and card punch unit. The radiation data and the parameters of the self-diffusion equation were programmed for calculation of the Rb and Sr coefficients with the 7040 computer. The program can be extended to include the simultaneous measurement of a large number of ions.
important in soils and clay systems. The self-diffusion coefficients for Rb and Sr were 9.62 ± 0.21 and 2.49 ± 0.15 × 10^{-7} cm²/sec at 24°C. The energy of activation for Rb was larger than for Sr, however the Arrhenius frequency factor was much greater for Rb than Sr. Equal concentrations of Rb and Sr resulted in a decreased diffusivity of Rb and an increase in Sr diffusivity. Maintaining the Rb and Sr saturation constant at 7.5% per cent and 44% per cent, respectively, and changing the Al:H ratio from Al₁₂:H₃₄ to Al₁₅:H₃ did not alter Rb diffusivity; however, Sr diffusion was increased from 1.99 to 3.03 × 10^{-7} cm²/sec (24°C) as Al³⁺ was increased. The energy of activation and the Arrhenius frequency factor were altered by changes in ion saturation and in the complementary ions, but not always in the same direction or degree in relation to changes in the diffusion coefficient. Since the mechanism controlling the rate of ion diffusion may not be the same for different combinations of diffusing ions, an evaluation of the activation energy and frequency factor gives a better understanding to the observed changes in the diffusivity of ions.

REFERENCES

EFFECT OF AL³⁺ AND H⁺


Résumé – L'effet des concentrations variables de Al³⁺ et de H⁺ sur la diffusion simultanée de Al³⁺ et de H⁺ sur la diffusion simultanée de ⁸⁶Sr et de ⁸⁶Rb a été mesuré sur des parties aliquotes d'argile sans sel, ayant des rapports Al:H différents. La saturation Sr et Rb du CEC a été maintenue constante, tandis que l'on variait Al et H, échangeables, de Al₂₃:H₃₄ à Al₁₅:H₃. Les parties aliquotes de chaque traitement d'argile ont été attachées deux par deux avec ⁸⁶Sr et ⁸⁶Rb. L'auto-diffusion de Sr et de Rb a été mesurée à 4, 24, 48 et 75°C. Le titrage radio de ⁸⁶Sr et de ⁸⁶Rb a été fait par un système automatique de détection aux rayons gamma, muni d'un analyseur 400 voies et d'un appareil à cartes perforées. L'équation d'auto-diffusion a été mise sous forme de programme pour l'ordinateur 7040 qui a calculé simultanément les coefficients d'auto-diffusion de ⁸⁶Sr et de ⁸⁶Rb. La diffusion de Rb n'a pas subi de modification significative, alors que la concentration de Al³⁺ augmentait de 12 à 52 pour cent. Par contre la diffusion plus rapide avait une plus grande énergie d'activation que Sr (4.8-3.6 kcal/mole), toutefois, le facteur de fréquence Arrhenius pour Rb (une mesure de la possibilité de l'échange d'ions) était beaucoup plus grand pour Rb que pour Sr (28.8 et 0.4 × 10⁻⁴, respectivement). La modification de la saturation
de Rb et de Sr et des ions complémentaires a apporté des changements dans la diffusivité, l'énergie d'activation, et la facteur de fréquence pour ces ions, mais pas toujours dans le même sens ou au même degré.


Резюме—Эффект меняющихся концентраций Al³⁺ и H⁺ на одновременную диффузию ⁸⁵Sr и ⁸⁶Rb измерялся в бессолевых аликвотах глины, имеющих различные отношения Al : H. Насыщение СЕС посредством Sr и Rb удерживалось постоянным, в то время как обменные Al и H изменялись с Al₂₄°:H₁ до Al₁₂°:H₃₄. Аликвоты каждой обработки глиной были дважды мечены ⁸⁵Sr и ⁸⁶Rb. Самодиффузия Sr и Rb измерялась при 4, 24, 48 и 75°C. Радиоактивный анализ ⁸⁵Sr и ⁸⁶Rb проводился пользуясь автоматической системой обнаружения гаммовых лучей, оснащённой анализатором на 400 каналов и перфокартовым устройством. Уравнение самодиффузии программировалось для вычислительной машины 7040, чтобы предоставить возможность одновременного вычисления коэффициентов самодиффузии ⁸⁵Sr и ⁸⁶Rb. Диффузия Rb в значительной степени не изменилась, поскольку концентрация Al³⁺ повысила с 12 до 52%. Диффузия Sr значительно увеличилась по мере повышения Al³⁺ с 12 до 52%. Быстрее распространяющийся изотоп Rb обладает большей энергией активации, чем Sr (4,8до 3,6 ккал/моль), однако частотный фактор Аррениуса для Rb (измерение вероятности ионобмена) намного больше для Rb чем для Sr (28,8 и 0,4 × 10⁻⁴ соответственно). Изменения насыщение Rb и Sr и дополнительные ионы повлияло за собой изменений коэффициент диффузии, энергии активации и частотного фактора для этих ионов, но не всегда в том же направлении или в той же степени.