

MULTIPLE-ION DIFFUSION—I. TECHNIQUES FOR MEASURING AND CALCULATING APPARENT SELF-DIFFUSION COEFFICIENTS IN HETEROIONIC SYSTEMS*

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Abstract—This investigation was designed to integrate the quick-freeze technique for ion diffusion with two computer programs to permit the simultaneous measurement and calculation of the diffusivity of a variable number of ions in heteroionic soil system. Kaolinite clay was prepared so as to have the following percentage saturations of the CEC, Sr²⁺65, Mg²⁺15, Rb⁺10, Na⁺5 and H⁺5. A quadruplicate radioisotope tag consisting of ⁸⁵Sr, ²⁸Mg, ⁸⁶Rb, and ²²Na was used to measure the diffusivity of each ion. The complex spectra were resolved by use of Schonfeld's revised Alpha-M computer program. A probit-transformation procedure was formulated into a computer program to enable the calculation of each diffusion coefficient. These programs are described and illustrated with the diffusivity of ⁸⁶Rb in kaolinite clay.

INTRODUCTION

NUMEROUS methods have been used to measure and calculate the apparent self-diffusion coefficient of ions in soil and clay systems (Barber, 1962; Brown, 1964, 1968; Gast, 1962; Graham-Bryce, 1963; Lai, 1961; Husted, 1954; Kemper, 1960; Lopez-Gonzales, 1959; Phillips, 1964 and Schonfeld, 1960). For the most part these investigations have been concerned with measuring the diffusion coefficient of one ion at a time in homoionic systems. Progress in ion-diffusion research lies in the development of methods which will permit the study of ion diffusivity in soil systems whose physicochemical characteristics can be made to approximate those existing under field conditions. Such investigations demand a combination of techniques which will permit the simultaneous measurement of the diffusivity of a variable number of ions present in a heteroionic system. The measurement and calculation of the diffusivity of single ions in homoionic systems as reported by Brown and Phillips (1964) and Phillips and Brown (1964) was modified to measure the simultaneous diffusion of two ions (Sr and Rb) in a heteroionic system (Brown *et al.* 1968). The method included the use of the

two gamma-ray emitting isotopes, ⁸⁵Sr and ⁸⁶Rb as a dual tag and two computer programs; one for resolving the gamma spectrum of ⁸⁵Sr and ⁸⁶Rb and the other for the subsequent calculation of the self-diffusion coefficient for each ion.

The objective of this investigation was to integrate the quick-freeze technique for measuring ion-diffusion with two improved computer programs so as to permit the simultaneous measurement and calculation of the diffusivity of a variable number of ions in heteroionic systems.

Diffusion techniques

Aliquots of kaolinite clay were prepared in a homoionic form with respect to Sr, Mg, Rb, Na and H; from these, a heteroionic system was prepared to give the following percentage saturations of the CEC—Sr, 65; Mg, 15; Rb, 10; Na, 5; and H, 5. The procedure used to prepare the clay was essentially the same as that previously reported, (Brown *et al.*, 1968). Gamma-ray emitting isotopes ⁸⁵Sr, ²⁸Mg, ⁸⁶Rb, ²²Na were used as tracers in the quick-freeze diffusion technique. Radioassay was carried out by means of a 3-in. NaI(Tl) detector, a 400 channel analyzer and a card punch. The composite radiation data (⁸⁵Sr, ²⁸Mg, ⁸⁶Rb, ²²Na) were automatically punched on cards acceptable as computer input. Two computer programs were used, (a) the Alpha-M γ -spectrum resolving program of Schonfeld (1967) was adopted to resolve the complex spectra to its component parts (⁸⁵Sr,

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^{28}Mg , ^{86}Rb and ^{22}Na); (b) the computer program used previously (Brown *et al.*, 1968) for calculating diffusion coefficients was replaced with a probit-transformation calculation since it was more readily adaptable to computer programming and provided a greater degree of precision. It also permitted the simultaneous calculation of a variable number of diffusion coefficients common to heteroionic soil systems.

Gamma spectrum resolution

In measuring the simultaneous diffusion of ^{85}Sr and ^{86}Rb the resolving of the complex γ -ray spectrum of Sr and Rb was carried out by including a Compton scattering coefficient for Rb in the computer program to arrive at the net ^{85}Sr radiation (Brown *et al.*, 1968). While this method was satisfactory for dual tagging experiments, the approach was not practical where more than two γ -ray spectra must be resolved. For this reason, the revised Alpha-M computer program (Schonfeld, 1967) for resolving γ spectra was made a part of the multiple-diffusion procedure. The Alpha-M program represents an improved computer program for determining radioisotope concentration. It utilizes successive iterations in the least-squares scheme for resolving the γ -ray spectra; in so doing, it permits a more precise estimate of the activity of the isotope, particularly for samples in which the activity is less than 10 counts per channel. The program is highly flexible, it will accommodate and resolve up to 80 isotopes in a mixture, it permits a correction for gain and threshold shifts in the analyzer, loss of counts by isotopic decay, counting time, and sample volume; the data may be expressed either as a fraction of a standard concentration or in total counts per unit of time. Estimates of the standard error for each isotope concentration and a listing of all suspicious channels are given for each spectrum.

The Alpha-M program input sequence consists

of (a) the Alpha-M program and computer control cards, (b) library of standard isotopes, i.e. channel by channel spectral data of the individual isotopes contained on cards, including control cards, and (c) the spectral data of the samples on cards along with control and option cards, including spectral identification, background, half-life, counting time, etc. The precision of the Alpha-M program was measured by resolving several complex γ spectra consisting of combinations of 6 radioisotopes of known activity (^{85}Sr , ^{86}Rb , ^{22}Na , ^{59}Fe , ^{54}Mn , and ^{65}Zn). The results are given in Table 1. These data show about the same magnitude of precision as those reported by Schonfeld (1967) for the resolution of the two-component mixture, ^{60}Co and ^{137}Cs . The program has proved to be adequate for resolving the four-component system (^{85}Sr , ^{86}Rb , ^{28}Mg and ^{22}Na) which is now being used in diffusion experiments. The adaptability of Alpha-M to nutrient uptake studies involving multiple radioisotope tags such as ^{54}Mn , ^{59}Fe , ^{65}Zn , ^{42}K , and ^{28}Mg is worthy of serious consideration.

Calculation of the diffusion coefficient by probit-transformation

In previous publications Phillips and Brown, (1964) and Brown *et al.*, (1968) the diffusion coefficient D was estimated from the formula

$$D = \pi h^2 F^2 / t \quad (1)$$

where $2h$ is the total length of the diffusion cell consisting of two half-cells of length h and F is the fraction of the radioactive ions which have diffused across the interface in a specified time t . Two difficulties have become apparent in subsequent repeated use of this estimator. From a theoretical viewpoint, the presence of h in the formula presents an ambiguity. Though in a mathematical sense, the limiting process which leads to Equation (1) is valid, intuitively one would suppose that the esti-

Table 1. Resolution of complex γ spectra by the Alpha-M computer program

Combination of radioisotope standards*	Activity found in sample; expressed as a fraction of the standard					
	^{85}Sr	^{86}Rb	^{59}Fe	^{54}Mn	^{22}Na	^{65}Zn
^{85}Sr , ^{86}Rb , ^{22}Na , ^{54}Mn , ^{59}Fe , ^{65}Zn	1.02	0.94	0.99	1.07	0.95	0.92
^{85}Sr , ^{86}Rb , ^{54}Mn	0.99	0.91	0.00	1.00		0.01
^{85}Sr , ^{54}Mn	0.98	0.01	0.01	1.01		0.00
^{86}Rb , ^{65}Zn	0.01	0.93	0.00	0.06		0.93
^{85}Sr	0.99	0.00	0.00	0.01		0.01

*Activity of standards (cp2m): Sr 68,675; Rb 28,949; Mn 18,213; Fe 48,631; Zn 109,390; Na 19,641.

mate of D ought not to depend on the size of the cell so long as t is kept small enough to insure that ions at the extreme outer end of the source have negligible probability of completing the migration. Statistically, use of this estimator requires that an estimate of F be obtained from some form of numerical integration of a function defined only pointwise by observations subject to the randomness inherent in making scintillation counts. The potential magnitude of the error involved is difficult to assess, but appears to be considerable. Attempts to improve this method for computer calculation resulted in the adaptation of the probit-transformation method to the self-diffusion equation.

In order to adapt probit-transformation as a procedure to calculate diffusivity of ions, recall the solution of the diffusion equation (Fick's second law)

$$C(x, t) = C_0/2 \left[1 + \operatorname{erf} \left(\frac{x}{2(Dt)^{1/2}} \right) \right] \quad (2)$$

which expresses the concentration $C(x, t)$ of ions at a distance x cm from the interface after diffusion at a rate D has been allowed to proceed through time t sec. C_0 is the concentration of the ion source at time $t = 0$. If we assume that scintillation counts are proportional to actual ion concentration, then equivalently $C(x, t)$ and C_0 of Equation (2) may refer to scintillation counts per unit rather than actual ion concentration. Dividing through by C_0 and using the definition of the error function, then

$$\frac{C(x, t)}{C_0} = \frac{1}{2} + \frac{1}{(\pi)^{1/2}} \int_{-\infty}^{x/2(Dt)^{1/2}} \exp[-v^2] dv. \quad (3)$$

If we make the transformation $u = 2(Dt)^{1/2}v$, then

$$\begin{aligned} \frac{C(x, t)}{C_0} &= \frac{1}{(2\pi)^{1/2}(2Dt)^{1/2}} \int_{-\infty}^x \\ &\times \exp \left[-1/2 \left(\frac{u}{(2Dt)^{1/2}} \right)^2 \right] du \end{aligned} \quad (4)$$

i.e. the ratio $C(x, t)/C_0$ as a function of x is identical with the cumulative distribution function of a normal distribution with mean 0 and variance $2Dt$. Even though the actual origin $x = 0$ corresponding to the location of the interface may be difficult to specify experimentally, we note that any arbitrary shift of the origin of the form $z = x - a$ results in

$$\begin{aligned} \frac{C(z, t)}{C_0} &= \frac{1}{(2\pi)^{1/2}(2Dt)^{1/2}} \int_{-\infty}^{z-a} \\ &\times \exp \left[-1/2 \left[\frac{u}{(2Dt)^{1/2}} \right]^2 \right] du \end{aligned}$$

$$\begin{aligned} &= \frac{1}{(2\pi)^{1/2}(2Dt)^{1/2}} \int_{-\infty}^x \\ &\times \exp \left[-1/2 \left(\frac{u-a}{(2Dt)^{1/2}} \right)^2 \right] du \end{aligned} \quad (5)$$

i.e. the ratio $C(z, t)/C_0$ plotted as a function of z with arbitrary origin is identical with the cumulative distribution function of the same normal distribution but with mean at a . Hence, if C_1, C_2, \dots, C_n denote n scintillation counts at locations z_1, z_2, \dots, z_n respectively along the axis of the diffusion cell, then we may proceed graphically by plotting C_i/C_0 as a function of z_i on normal probability paper, smoothing a straight line through the points, and estimating D from the slope of the fitted line. In general, if z_α and $z_{1-\alpha}$ are the graphical estimates of the α and $1 - \alpha$ percentiles, then D is estimated by

$$D = (z_{1-\alpha} - z_\alpha)^2 / 8tN_{1-\alpha}^2 \quad (6)$$

where $N_{1-\alpha}$ is the $1 - \alpha$ percentile of the standard normal distribution.

In practice, since the true value of C_0 , the concentration or equivalently the initial scintillation count of the source, is rarely known, we substitute an independent estimate of C_0 , e.g. the average of the last four counts, in the ratios before plotting. Though this results in a slight but equal degree of correlation among the resulting ratios, we feel that the overall effect on D is negligible. This procedure was tested by using data from a multi-ion diffusion experiment in which the diffusivity of ^{85}Sr , ^{28}Mg , ^{86}Rb , and ^{22}Na was measured for the heteroionic kaolinite clay system described above. Only the data for ^{86}Rb has been included in this report. Figure 1 illustrates the graphical procedure when applied to the ^{86}Rb data given in Table 2. From Equation (6) the self-diffusion coefficient for ^{86}Rb is 3.91×10^{-6} cm²/sec.

The numerical equivalent of the foregoing graphical procedure was formulated for computer application in the following manner: For each ratio (C_i/C_0) , calculate $y_i = \operatorname{probit}(C_i/C_0)$, i.e., the usual probit-transformation used in bioassay (Finney, 1962). Estimate the slope B of the linear regression model $y_i = A + Bz_i + e_i$ as usual by

$$\hat{B} = \sum_{i=1}^n (z_i - \bar{z})y_i / \sum_{i=1}^n (z_i - \bar{z})^2.$$

Then the estimate of D is given by

$$D = (2t\hat{B}^2)^{-1} \quad (7)$$

with estimated standard error given approximately by

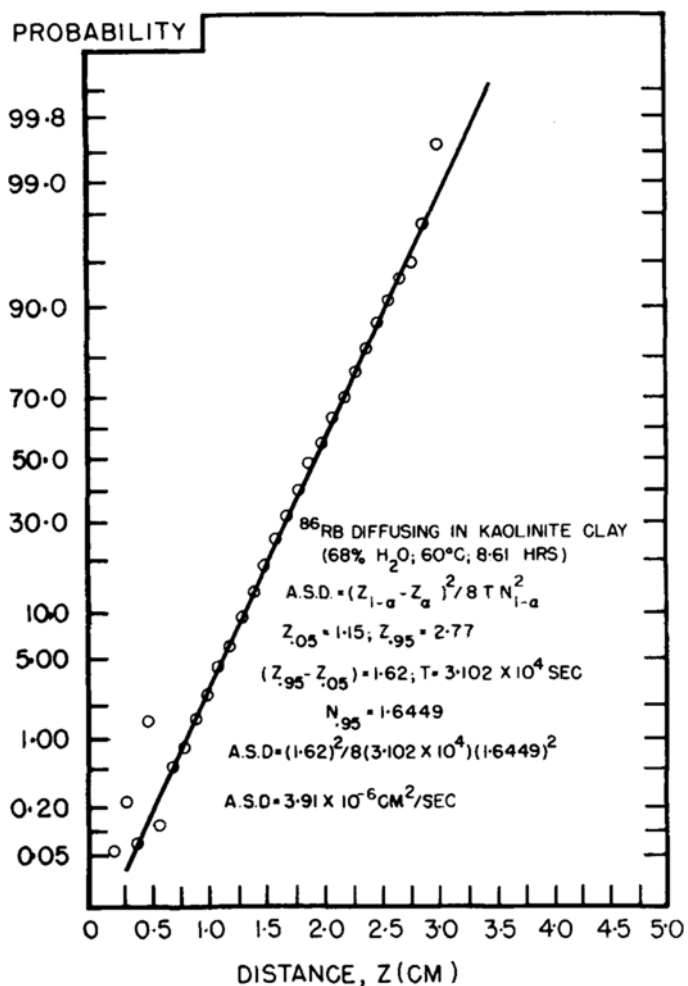


Fig. 1. Probit-transformation plot of data used to calculate the apparent self-diffusion coefficient of Rb in kaolinite clay.

$$s_D = \hat{\sigma} / t \hat{B}^3 \left(\sum_{i=1}^n (z_i - \bar{z}) \right)^{1/2}$$

where
$$\hat{\sigma}^2 = \left[\sum_{i=1}^n (y_i - \bar{y})^2 - \frac{\bar{y}}{\bar{z}} \sum_{i=1}^n (z_i - \bar{z}) y_i \right] / n - 2. \tag{8}$$

In practice, since there is a tendency for a sharp increase in the variance of y at either extremity, we obtain an initial fitted regression $\hat{y} = \hat{A} + \hat{B}z$ and an estimate $\hat{\sigma}^2$ for those points corresponding to $0.10 \leq C_i/C_0 \leq 0.90$, then allow additional points to be included in a subsequent final fit if $|y_i - \hat{y}_i| < 3\hat{\sigma}$. Using this method, the estimated diffusivity

for the ^{86}Rb data shown in Table 2 is $D = 4.04 \times 10^{-6}$ cm²/sec with a standard error of $s_D = 5.74 \times 10^{-8}$.

The computer calculated value of 4.04×10^{-6} cm²/sec was slightly greater than the value (3.91) determined graphically from the data in Fig. 1. Since identical data was used in both calculations, the difference in the values results from the mechanical fit of the line in the graphical calculation as compared to the more precise mathematical fit of the line in the computer calculation. These techniques have proved to be quite adequate in the measurement of the simultaneous diffusion of four ions ^{85}Sr , ^{28}Mg , ^{86}Rb and ^{22}Na . The value of 4.04×10^{-6} cm²/sec represents the diffusivity of Rb in kaolinite clay at 60°C, 68 per cent moisture

Table 2. Sample data for calculating the self-diffusion coefficient of ⁸⁶Rb diffusing in kaolinite clay*

Sample No.	Distance (cm) z	Counts (Mg/Min) C ₀ †	C _i /C ₀	Probit‡
1	0.1	-0.0009	0.0000	
2	0.2	0.1192	0.0006	
3	0.3	0.4330	0.0022	
4	0.4	0.1278	0.0007	
5	0.5	2.7900	0.0143	
6	0.6	0.2104	0.0011	
7	0.7	1.0046	0.0051	
8	0.8	1.6230	0.0083	
9	0.9	3.0667	0.0157	
10	1.0	4.9194	0.0252	
11	1.1	8.4711	0.0433	
12	1.2	11.9530	0.0612	(3.4549)
13	1.3	18.9680	0.0971	3.7015
14	1.4	27.1330	0.1388	3.9144
15	1.5	36.7134	0.1879	4.1142
16	1.6	48.8690	0.2500	4.3257
17	1.7	61.5649	0.3150	4.5183
18	1.8	77.7143	0.3976	4.7405
19	1.9	96.5288	0.4939	4.9847
20	2.0	108.6235	0.5558	5.1403
21	2.1	124.8093	0.6386	5.3548
22	2.2	136.3081	0.6975	5.5171
23	2.3	150.4677	0.7699	5.7385
24	2.4	159.9509	0.8184	5.9094
25	2.5	169.9754	0.8697	6.1251
26	2.6	176.8180	0.9047	6.3040
27	2.7	182.2831	0.9327	6.4961
28	2.8	185.5401	0.9494	(6.6387)
29	2.9	190.5348	0.9749	
30	3.0	194.6197	0.9958	
31	3.1	195.6645	1.0012	
32	3.2	195.5673	1.0007	
33	3.3	195.8993	1.0024	

*CEC 5.0 meq/100 g; percentage saturation of CEC was Sr-65, Mg-15, Rb-10, Na-5 and H-5. Radioisotopic tags used were ⁸⁵Sr, ²⁸Mg, ⁸⁶Rb, and ²²Na.

†Estimated C₀ = 195.4377.

‡Using 3σ limits, only the probits between the parenthesized values were admissible for the numerical estimate of D.

content, and 10 per cent saturation of the CEC. In the same clay the diffusivity of Sr (65 per cent saturation) was 1.91, Mg (15 per cent saturation) was 1.82, and Na (5 per cent saturation) was 1.71; all values being × 10⁻⁶ cm²/sec. Additional data from multi-ion diffusion experiments showing the magnitude of complementary ion effects upon ion diffusivity in heteroionic systems has been completed and prepared for publication as a second paper in a sequence of reports on multiple ion diffusion. The diffusion techniques and computer

programs outlined can be readily used to measure the diffusivity of ions in complex heteroionic systems containing variable combinations of γ-ray emitting isotope tracers such as ⁸⁵Sr (or ⁴⁷Ca), ²⁸Mg, ⁸⁶Rb (or ⁴²K), ²²Na, ⁵⁴Mn, ⁵⁹Fe, and ⁶⁵Zn. The measurement of the simultaneous movement of each ion in a heteroionic soil systems whose physical and chemical properties are representative of field conditions should give data which are more realistic than the ion exchange data obtained by salt-solution extraction procedures.

SUMMARY

Techniques for measuring and calculating the apparent self-diffusion coefficient in a heteroionic clay system were presented. The quick-freeze technique was modified to include four radioisotopes ^{85}Sr , ^{28}Mg , ^{86}Rb , and ^{22}Na as a tracer for Sr, Mg, Rb, and Na. The complex γ -spectra was resolved by use of Schonfeld's revised Alpha-M computer program to arrive at the concentration of each of these four ions. The ion concentration values were subsequently inserted into a probit transformation for computer calculation of each diffusion coefficient.

The method extends the range of ion diffusion research into the area of multi-tagged systems permitting an evaluation of complementary ion effects upon the simultaneous diffusion of a variable number of ions common to soil systems.

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Résumé—Cette étude a pour but d'intégrer la technique de gel rapide pour la diffusion des ions à deux programmes d'ordinateurs en vue de permettre la mesure et le calcul simultanés de la diffusivité d'un nombre variable d'ions dans les systèmes de sols hétéroioniques. L'argile kaolinite a été préparée de telle sorte à avoir les pourcentages de saturation suivants du CEC, $\text{Sr}^{2+}65$, $\text{Mg}^{2+}15$, $\text{Rb}^{+}10$, $\text{Na}^{+}5$ et $\text{H}^{+}5$. Un traceur radioisotope en quatre exemplaires consistant en ^{85}Sr , ^{28}Mg , ^{86}Rb , et ^{22}Na a servi pour mesurer la diffusivité de chaque ion. Les spectres complexes ont été résolus par le programme d'ordinateur Alpha-M révisé de Schonfeld. Une méthode de transformation sévère a été mise en formule et introduite au programme de l'ordinateur pour permettre le calcul de chaque coefficient de diffusion. Ces programmes sont décrits et illustrés avec la diffusivité de ^{86}Rb dans l'argile kaolinite.

Kurzreferat—Diese Untersuchung sollte der Integrierung der Schnellfriertechnik für Ionen-Diffusion mit zwei Computerprogrammen dienen, um gleichzeitige Messung und Berechnung der Diffusivität einer variablen Anzahl von Ionen in heteroionischen Bodensystemen zu gestatten. Kaoliniton wurde so präpariert, daß er die folgenden prozentuellen Sättigungen der Kationenaustauschleistung aufwies: $\text{Sr}^{2+}65$, $\text{Mg}^{2+}15$, $\text{Rb}^{+}10$, $\text{Na}^{+}5$ und $\text{H}^{+}5$. Eine vierfache Radioisotopenmarkierung umfassend ^{85}Sr , ^{28}Mg , ^{86}Rb und ^{22}Na wurde zur Messung der Diffusivität jedes Ions benutzt. Die komplizierten Spektren wurden unter Anwendung des revidierten Alpha-M Computerprogramms von Schonfeld aufgelöst. Es wurde eine Probit-Umwandlungsmethode in einem Computerprogramm verarbeitet, um die Errechnung jedes Diffusions-Koeffizienten zu ermöglichen. Diese Programme sind mit der Diffusivität von ^{86}Rb in Kaolinit-Ton beschrieben und veranschaulicht.

Резюме—Задачей исследования была подготовка техники быстрого замораживания для изучения ионной диффузии с использованием вычислительных машин с тем чтобы одновременно производить измерения и вычисления диффузионного перемещения разнообразных ионов в гетероионных почвенных системах. Каолинитовая глина была приготовлена таким образом, чтобы насыщение ее емкости катионного обмена составляло (в %): $\text{Sr}^{2+}-65$; $\text{Mg}^{2+}-15$; $\text{Rb}^{+}-10$; $\text{Na}^{+}-5$; $\text{H}^{+}-5$. Для измерения диффузионного перемещения ионов использовались

радиоизотопы ^{85}Sr , ^{28}Mg , ^{86}Rb , ^{22}Na . Сложные спектры были расшифрованы с помощью вычислительной машины по заново проверенной Альфа-М программе Шонфелда. Специальные программы для вычислительной машины позволили вычислить каждый коэффициент диффузии. Эти программы охарактеризованы и проиллюстрированы диффузионным распространением ^{86}Rb в каолиновой глине.