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CATIONIC DIFFUSION IN CLAY MINERALS:II. ORIENTATION EFFECTS*

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Abstract—The effect of orientation of vermiculite particles on the diffusion of Na ion was measured by a tracer technique. The diffusion measurements were made on pellets prepared by pressing freeze-dried vermiculite in a cylindrical die and the diffusion coefficient evaluated by a thin-film boundary condition of Fick's law. Because flakes of vermiculite were highly oriented under the pressing force, it was possible to prepare different angles of specimen orientation with respect to the surface where diffusion was initiated. Mathematical relationships of orientation angle, axial ratio of the platelets, and apparent diffusion coefficient were developed. The experimental results on the diffusion of Na ion in K-vermiculite of clay size gave apparent diffusion coefficients of $2{\cdot}21 \times 10^{-7}\,\mathrm{cm^2\,sec^{-1}}$ when the diffusion flux was parallel with the clay platelets and $0{\cdot}45 \times 10^{-7}\,\mathrm{cm^2\,sec^{-1}}$ when the flux was perpendicular to the clay platelets. For the diffusion of Na ion into Na-vermiculite, apparent diffusion coefficients were obtained of $1{\cdot}18 \times 10^{-8}\,\mathrm{cm^2\,sec^{-1}}$ when the diffusion flux was parallel with the clay platelets, and $0{\cdot}18 \times 10^{-8}\,\mathrm{cm^2\,sec^{-1}}$ when the flux was perpendicular to the platelets. For K-vermiculite, the change in apparent diffusion coefficient is a simple one of particle geometry. The Na-vermiculite system exhibited more complicated behavior.

INTRODUCTION

Both isotropy and anisotropy for the diffusion process have been found in noncubic materials (Shewmon, 1963, p. 36). Clay minerals generally have a pronounced platy or fibrous structure. Walker (1959) showed that the cationic movement was isotropic within the plane of the silicate layers of vermiculite flakes. The question may be raised as to whether the diffusion coefficient will be constant or variable along different axes in these minerals. Recently the authors have demonstrated homogeneous and heterogeneous cationic diffusion in clay systems. Homogeneous diffusion is characterized by a single pathway of cationic movement as in clay systems where only external surfaces are present. Heterogeneous diffusion results from at least two pathways of cationic movement as in swelling clay minerals where both external and internal surfaces are available. These studies were conducted with highly oriented specimens of clay minerals in which the flux was at right angles to the clay platelets and thus parallel to the *c* axis.

Most experimentally observed diffusion coefficients are apparent values, in which three main factors are involved, namely, tortuosity effects, interactions of the diffusing ions with the clay minerals, and nature of the ion itself. In a highly oriented clay system, physical tortuosity effects could be studied by determination of apparent diffusion coefficients at various angles of orientation with respect to the direction of diffusion flux. From these results, diffusion coefficients which may reflect only the properties of the diffusing species and the matrix through which movement occurs, could be evaluated. With this objective in mind, the following study was made of effects of clay mineral orientation on the cationic diffusion.

EXPERIMENTAL METHODS

A Montana vermiculite supplied by Ward's Natural Science Establishment, Inc., was used in this study. Salt-free homoionic Na- and K-saturated vermiculite were prepared the same way as described in a previous paper (Lai and Mortland, 1967). Two different particle sizes, 2–5 μ and $< 2\,\mu$ of K-vermiculite were separated by ordinary decantation procedures, and Na-vermiculite with $< 2\,\mu$ particle size only.

In order to obtain highly oriented specimens, the suspension of homoionic vermiculite was freeze dried, and was pressed in a cylindrical die under 1000 psi pressure to make a pellet as described by Cloos and Mortland (1964). The result of this

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method of pellet preparation was to create highly oriented systems in which the *c* axis of the clay particles was parallel to the axis of the cylindrical vermiculite pellet. The highly oriented condition of the clay could easily be observed under the microscope and was made evident by a platy structure similar to a shale. Since a measurement of apparent diffusion coefficients at various angles of orientation with respect to the direction of diffusion flux was the objective of this study, the specimen was cut and mounted as follows:

The pellet was affixed with paraffin to a plexiglas rod with a surface of angle ψ as shown in Fig. 1. The dashed lines show the orientation of vermiculite flakes. The final diffusion specimen was cut into ABCD as shown in Fig. 1. AB is the surface on which the diffusion was initiated in direction y in Fig. 1 and which was formed by carefully slicing with a microtome. θ is the angle of vermiculite platelets oriented with respect to the diffusion flux and has the value of $90° - \psi$. The diffusion studies at various angles of θ were performed. Pellets of kaolinite and bentonite were also tried, but were not rigid enough to be cut into various angles as described with vermiculite. Because of this experimental difficulty, only vermiculite was used in this study.

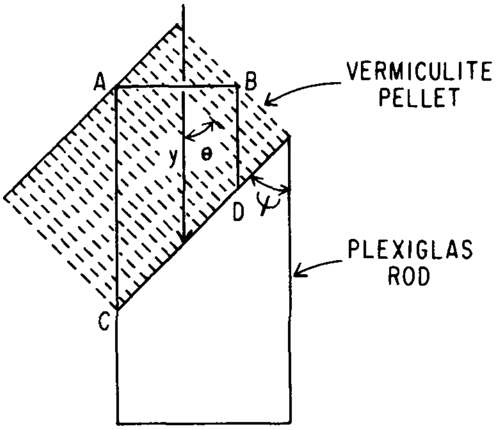

Fig. 1. Schematic drawing of a vermiculite pellet mounted on a plexiglas rod designed to give a plane of angle θ of orientation with respect to the diffusion flux.

Carrier-free ^{22}Na was used as diffusing ion. A tracer technique based on a thin-film boundary condition of Fick's law with application to consolidated media (Lai and Mortland, 1967) was used in this study. The experiments were carried out in duplicate under 81·0 per cent relative humidity at 20 ± 0·05°C as described in the previous report (Lai and Mortland, 1967). The apparent diffusion coefficients reported are the average between duplicates.

DISCUSSION OF RESULTS

Theoretical considerations

Cationic diffusion in the clay minerals with very low moisture content is suggested to be a movement along the surface. Fig. 2 shows diffusion pathways on the surface of a platelet seen edgewise and oriented at an angle θ with respect to the diffusion flux in the y direction. As shown in Fig. 2, BD is the width (w) of the particle, AB the height (h), and ϕ the angle between diagonal BC and width BD. When only the geometry factor is considered, the following mathematical manipulations are easily seen from Fig. 2:

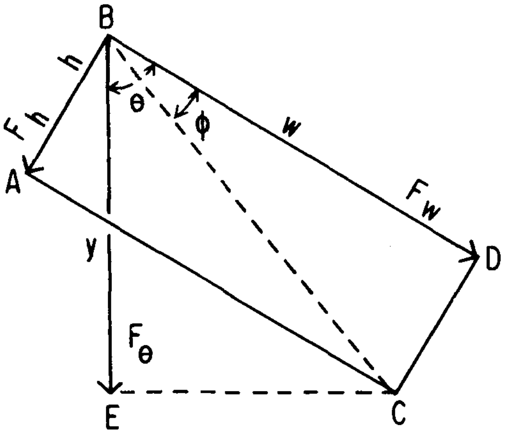

Fig. 2. Model used for analysis of diffusion pathways on the surface of a platy particle seen edgewise and oriented at an angle θ with respect to the diffusion flux.

$$BC = (w^2 + h^2)^{1/2} \quad (1)$$

$$y = BE = BC \cos(\theta - \phi) \quad (2)$$

or

$$y = (w^2 + h^2)^{1/2} \cos(\theta - \phi). \quad (3)$$

Since the mean square displacement (ΔP^2) at time t is (Jost, 1960, p. 25)

$$\Delta P^2 = 2Dt. \quad (4)$$

When the diffusion time t is constant, Equation (4) may be written as

$$D = k\Delta P^2 \quad (5)$$

where k is a constant. If y in Fig. 2 is a displacement at a certain diffusion time t, as $y^2 = \Delta P^2$ the following equation is obtained:

$$D = k\,(w^2 + h^2)\cos^2(\theta - \phi). \qquad (6)$$

For a definite particle size, w and h are constant, Equation (6) may be shown as

$$D = k'\cos^2(\theta - \phi) \qquad (7)$$

where k′ is another constant representing $k(w^2 + h^2)$ of Equation (6). If plots of D vs. $\cos^2(\theta - \phi)$ are made, a straight line should result.

Mathematically the following relation between the three angles which any straight line makes with the coordinate axes is known

$$\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1 \qquad (8)$$

where α, β, and γ are the angles which the given line makes with the axes X, Y, and Z respectively. If the true diffusion coefficients are the same in all the axes but the apparent diffusion coefficients are dissimilar in the different directions due to geometry factors, then the equation is

$$D_{\alpha\beta\gamma} = D_\alpha\cos^2\alpha + D_\beta\cos^2\beta + D_\gamma\cos^2\gamma \qquad (9)$$

where $D_{\alpha\beta\gamma}$ is the total resulting coefficient, and D_α, D_β, and D_γ are the component diffusion coefficients along the three corresponding axes. If the diffusion is in a plane which is expressed with the ordinary cartesian coordinate system, then in Equation (9), $\gamma = 90°$, $\alpha + \beta = 90°$, say $\beta = 90° - \alpha$, and Equation (9) may be written as

$$D_{\alpha\beta} = D_\alpha\cos^2\alpha + D_\beta\sin^2\alpha. \qquad (10)$$

This general equation can be applied to the condition as shown in Fig. 2. Suppose F_θ is the resulting diffusion flux along BE with apparent diffusion coefficient D_θ, the component fluxes F_w along BD(w) with D_w and F_h along BA(h) with D_h, respectively; and suppose F_w is larger than F_h. It is seen that D_θ is equivalent to $D_{\alpha\beta}$, D_w to D_α, D_h to D_β, and θ to α, respectively; and thus Equation (10) becomes

$$D_\theta = D_w\cos^2\theta + D_h\sin^2\theta. \qquad (11)$$

This equation also described the relationship that exists between the diffusion coefficients parallel and perpendicular to the c-axis of the lattice of noncubic metal crystals (Shewman, 1963, p. 36).

Effect of orientation on diffusion

Figure 3 shows the apparent diffusion coefficients of Na ions into K-vermiculite pellets at 20° ± 0·05° C under 81·0 per cent relative humidity at various angles of θ. It shows that the apparent diffusion coefficients vary non-linearly with $\cos^2\theta$. If the vermiculite flakes are perfectly oriented as shown in Fig. 1, the angle θ in Figs. 1 and 2 should be the same. According to Equation (7) the apparent diffusion coefficients vary linearly with $\cos^2(\theta - \phi)$. D and θ in Equation (7) were experimentally found, and ϕ could be found by trial-and-error method to fulfill Equation (7). For 2–5 μ K-vermiculite used in this study the ϕ was found to be 10°, and that of < 2 μ was 6° the resulting straight lines as shown in Fig. 3. The angle of ϕ can be used to calculate the axial ratio (width : height) of the platelet from which the "true" diffusion coefficient can be evaluated. This will be discussed later in this paper.

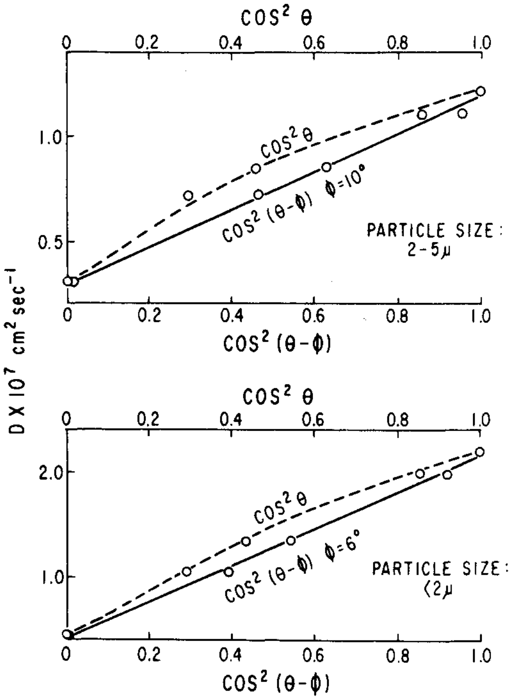

Fig. 3. Relationship of $\cos^2\theta$ and $\cos^2(\theta - \phi)$ with the diffusion coefficient of Na ion in K-vermiculite oriented at various angle of θ with respect to the diffusion flux and equilibrated at 81·0 per cent relative humidity (20°C). The moisture contents of 2–5 μ and < 2 μ particles of K-vermiculite were 3·9 and 3·6 per cent by weight respectively (105°C).

If the angle θ in Figs. 1 and 2 is the same as mentioned in the above section, from Equation (11) the values of D_w and D_h can be calculated from D_θ and θ which are experimentally measurable. Meanwhile, when θ of Fig. 1 is oriented at either 0° or 90° experimentally, these two observed diffusion coefficients are assumed equivalent to D_w and D_h of Equation (11). Table 1 shows both observed

Table 1. Observed diffusion coefficients of Na ion in K-vermiculite oriented at angle $\theta = 90°$ (D_h) and 0° (D_w) with respect to the diffusion flux and calculated results at various intermediate values of θ

$\theta°$	$D_\theta \times 10^7$ (cm^2 sec^{-1})	$D_h \times 10^7$ (cm^2 sec^{-1})	$D_w \times 10^7$ (cm^2 sec^{-1})
		Particle size: 2–5 μ	
0			1·22*
90		0·31*	
22·0	1·11*	0·53†	1·20†
47·5	0·84*	0·37†	1·23†
57·0	0·73*	0·35†	1·42†
		Particle size: < 2 μ	
0			2·21*
90		0·45*	
22·5	1·97*	0·69†	2·19†
48·5	1·35*	0·43†	2·52†
57·0	1·05*	0·56†	2·21†

*Experimentally observed values.

†Calculated values from simultaneous equations based on Equation (11).

values of D_h and D_w at 90° and 0° respectively and calculated results at various intermediate values of θ. It is apparent that the calculated values are very close to the observed values for both D_w and D_h, with both 2–5 μ and < 2 μ particles of K-vermiculite.

Orientation effects in heterogeneous system

Models of homogeneous and heterogeneous cationic diffusion systems applied to clay minerals have been worked out by the authors (Lai and Mortland, 1967). For 1 : 1 clay minerals which have external surfaces only, and 2 : 1 minerals which are collapsed or whose exchange sites are clogged with non-exchangeable cations where the diffusing cation cannot move into the interlayer space, there is only one diffusion coefficient and they may be considered as homogeneous systems. The expanded 2 : 1 clay minerals which have both external and internal surface available for cationic movement are heterogeneous systems. The authors have also suggested that cationic diffusion studies in clay minerals must consider the nature of the systems and whether or not they have homogeneous or heterogeneous properties. Both Equations (7) and (11) are derived on the basis that there is external surface diffusion only, thus this system should be homogeneous. The K-vermiculite has the homogeneous property as reported in the previous paper (Lai and Mortland, 1967). From Fig. 3 and Table 1 it is apparent that this homogeneous system follows Equations (7) and (11). It is of interest to see the application of these two equations to a heterogeneous diffusion system. As reported in the previous paper, the Na-vermiculite shows heterogeneous behavior (Lai and Mortland, 1967). The effect of orientation on the diffusion of Na ion in clay size Na-vermiculite was measured the same way as that of K-vermiculite. Figure 4 shows the results which the apparent self-diffusion coefficients of Na ion in vermiculite versus $\cos^2\theta$ is plotted. When Fig. 4 is compared with Fig. 3, the differences are apparent.

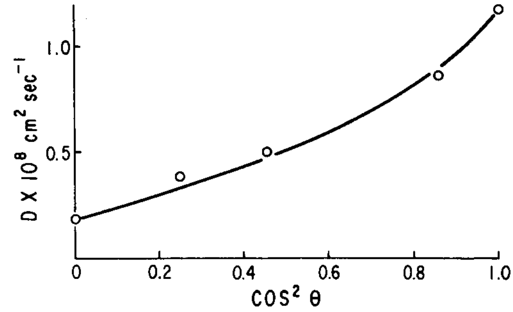

Fig. 4. Relationship of $\cos^2\theta$ with the diffusion coefficient of Na ion in Na-vermiculite oriented at various angles of θ with respect to the diffusion flux and equilibrated at 81·0 per cent relative humidity (20°C). The moisture content of Na-vermiculite was 18·1 per cent by weight (105°C).

In Fig. 3 with K-vermiculite, the D vs. $\cos^2\theta$ has a convex curvature, so that a D versus $\cos^2(\theta-\phi)$ resulting in a straight line as described in Equation (7) can be found. With Na-vermiculite as shown in Fig. 4 it is a concave curve from which the angle ϕ cannot be obtained as in K-vermiculite. It appears that the Equation (7) cannot be directly applied to the heterogeneous Na-vermiculite system as in the case of homogeneous K-vermiculite.

Equation (11) was also used to calculate D_h and D_w from different values of D_θ to compare the observed D_h and D_w in Na-vermiculite as in K-vermiculite. The results are shown in Table 2. When Table 2 is compared with Table 1, it is seen that for the Na-vermiculite system, the calculated results at various angles of θ are not in as good agreement with the observed data at 0° and 90° as in the K-vermiculite systems.

Evaluation of true diffusion coefficient

Cationic diffusion in clay minerals at very low moisture contents is mainly controlled by the nature of the diffusing cation, electrochemical interactions of this cation with the clay mineral, and the tortuosity factor. The first two effects may be considered as the factors affecting the "true" diffusion coefficient in a particular clay mineral

Table 2. Observed diffusion coefficients of Na ion in Na-vermiculite oriented at angle $\theta = 90°$ (D_h) and 0° (D_w) with respect to the diffusion flux and calculated results at various intermediate values of θ

θ^0	$D_\theta \times 10^8$ ($cm^2 sec^{-1}$)	$D_h \times 10^8$ ($cm^2 sec^{-1}$)	$D_w \times 10^8$ ($cm^2 sec^{-1}$)
0			1·18*
90		0·18*	
22·0	0·86*	0·26†	0·79†
47·5	0·50*	0·19†	0·97†
60·0	0·39*	0·09†	0·99†

*Experimentally observed values.

†Calculated values from simultaneous equations based on Equation [11].

system. Most experimentally observed diffusion coefficients are apparent values which include the tortuosity effects. For unconsolidated systems some mathematical equations have been worked out to solve the tortuosity problems (Meredith and Tobias, 1962). Cremers and Thomas (1966) applied a "formation factor" equation in the study of self-diffusion of Na ion in a suspension of montmorillonite, and Cremers and Laudelout (1966) used the same equation in measuring surface mobilities of several cations in montmorillonite gels. In consolidated systems cationic movement occurs through tortuous paths and channels which can hardly be classified and described mathematically. Because of the complexity of these geometry factors, only some empirical correlations are available (Meredith and Tobias, 1962).

If a homogeneous diffusion system such as the diffusion of Na ion in K-vermiculite has only one "true" diffusion coefficient, the various apparent coefficients observed at different orientation angles (D_θ, D_w, and D_h) as shown in the previous results must mainly be due to tortuosity effects. The orientation effects could be then applied in evaluating the "true" diffusion coefficient in a particular system. Based on this assumption, the evaluation is proposed in the following section.

Great difficulties exist in the direct measurement of the "true" diffusion coefficient (D_t) of cations on a clay mineral surface. If the formation factor (F) is known, the true coefficient can be calculated from the experimentally observed value (D_o) as $D_t = F\,Do$. Although the formation factor is not available for consolidated media, such as clay pellets in this study, some other value relating to a formation factor may be worked out.

The formation factor is a function of effective area and porosity (Millington and Quirk, 1964). If in a given medium the porosity is constant, the formation factor is related only to the effective area. On the other hand, when the diffusion process is treated macroscopically, the net flow of ions per second over a plane of unit area at a certain point is the product of the diffusion coefficient times the concentration gradient along the direction of flow resulting in the general equation (Wert and Thomson, 1964, p. 65):

$$\frac{1}{A}\frac{dN}{dt} = -D\frac{dC}{dy} \qquad (12)$$

where dN refers to a net flow of ions through area A at a time interval dt, and dC/dy is the concentration gradient. Therefore, it is suggested that the following relationship holds:

$$\frac{D_{tp}}{D_o} = \frac{A_o}{A_e} \qquad (13)$$

where D_{tp} means the "true" diffusion coefficient in a medium with effective area A_e at a given porosity condition, and D_o is the observed apparent coefficient with observed total diffusion area A_o at the same porosity condition. When the angle θ (Fig. 2) is at 0° only the area along the width (w) of the particle, which is parallel to the diffusion flux, contributes to the effective area. On the other hand, the area along the height (h) which is perpendicular to the flux makes no contribution. As the angle θ changed to 90° the opposite is true, the area along the height of the particle is effective, and not that along the width. Therefore, the effective diffusion area of the same particle changes with the variations of angle θ (Fig. 2), and the effective area may be calculated as follows:

θ^0	Effective area
0	$A_e = w \times b$
90	$A_e = h \times b$

where w, h, and b are the width, height, and length of the particle respectively. When θ is either 0° or 90°, the observed total diffusion area may include two portions: one is the area parallel to the diffusion flux and another is that perpendicular to the flux, and the conditions of ionic movement in these two areas may not be the same. When the angle $\theta = 0°$, the flux direction is parallel to the width and when $\theta = 90°$, it is parallel to the height of the particle. In the above conditions the resulting direction of the flux is uni-directional, although basically each ion in the diffusion process moves randomly from one position to another. When ions move in the area perpendicular to the direction of diffusion flow, such as when they move in the area along the height of the particle in case of $\theta = 0°$ and that of width in case of $\theta = 90°$, it is considered as two-directional movement. In this situation, the average diffusion area is half of the physical dimension. The above development related to Barrer's (1941, p. 44) discussion of infinite and semi-infinite systems. Therefore, the observed total diffusion area may be calculated as follows:

$\theta°$	Total diffusion area
0	$A_o = (w + h/2) \times b$
90	$A_o = (h + w/2) \times b$

Suppose R is an effective diffusion area factor which is the ratio of effective area to the observed total diffusion area ($A_e : A_o$), then Equation (13) is written as

$$D_{tp} = 1/R \times D_o. \tag{14}$$

The effective area factor R of the same particle also changes with the variations of angle θ, it follows:

$\theta°$	Effective area factor	
0	$R = \frac{A_e}{A_o} = \frac{w \times b}{(w + h/2) \times b} = \frac{w}{w + h/2}$	(15)
90	$R = \frac{A_e}{A_o} = \frac{h \times b}{(h + w/2) \times b} = \frac{h}{h + w/2}$	(16)

The actual values of w and h of the particle may not be easily determined; however, the ratio of $w:h$ can be obtained from this study. From Equation (7) the angle ϕ of K-vermiculite used in this study was found to be 10° for 2–5 μ, and 6° for $< 2\ \mu$ particles. The width:height ratios were then 5·7 : 1 and 9·5 : 1 respectively. These ratios may not be exactly the physical dimension of the K-vermiculite particles because they are calculated from data obtained from the diffusion process, but may be considered as an "effective diffusion dimension". This may be the reason that these ratios do not agree well with the results reported by Raman and Mortland (1966), in which the ratios were calculated from surface area data obtained from the B.E.T. equation. The width:height ratios obtained in this study may be applied better in evaluation of the effective area factor. When the experimentally obtained $w:h$ ratio is applied to calculate the effective area factor as shown in Equations (15) and (16), the D_{tp} can be then calculated from the experimentally observed diffusion coefficient (D_o) according to Equation (14). The calculated values of D_{tp} and R, the experimentally obtained data of $w:h$ and D_o at angle $\theta = 0°$ and 90°, and also the apparent density of the pellets of both 2–5 μ and $< 2\ \mu$ particles of K-vermiculite, are listed in Table 3. It shows that for both 2–5 μ and $< 2\ \mu$ particles the two calculated values of D_{tp}, from D_o at $\theta = 0°$ and 90°, agree rather well.

Formation factor relates both effective area and porosity. Here only the effective area factor is evaluated. Even though the pellets of two kinds of particle sizes, 2–5 μ and $< 2\ \mu$, of K-vermiculite were prepared the same way by pressing in a die under 1000 psi pressure, the apparent density of the pellet of 2–5 μ particles was smaller than that of $< 2\ \mu$ particles as shown in Table 3. The porosity of these two kinds of specimens should then be different. The effects of porosity on diffusion include the factors of size, shape, and unit number of pores. For consolidated media, no matter which factors (size, shape, and unit number of pores) affect the diffusion, the over-all influence will be the distance between the particles, or in other words, the compactness of the diffusion specimen. When all other conditions are the same, the more compact the specimen, the faster the diffusion rate. This observation was made by Graham-Bryce (1965) and Phillips and Brown (1965) who also found that the cationic diffusion coefficients increased with increasing bulk density. For example, in a given soil, as the bulk density increased from 1·34 to 1·64 g/cc at 21°C, the Rb ion diffusion coefficient increased from $1{\cdot}8 \times 10^{-8}$ to $8{\cdot}1 \times 10^{-8}$cm² sec⁻¹ (Graham-Bryce, 1965). In these two papers, they both attempted to explain the effect of bulk density on diffusion based on the results of "hopping

Table 3. Values of width:height ratio ($w:h$), effective area factor (R), observed (D_o), and "true" diffusion coefficients (D_{tp}) of specimens oriented at angle $\theta = 0°$ and 90° with respect to the diffusion flux of Na ion in two different particle sizes and apparent densities of K-vermiculite pellets

θ^0	$w:h$	R	$D_o \times 10^7$ (cm² sec⁻¹)	$D_{tp} \times 10^7$ (cm² sec⁻¹)
Particle size: 2–5 μ Apparent density: 1·79 g/cc				
0	5·7 : 1	0·919	1·22	1·33
90	5·7 : 1	0·260	0·31	1·19
Particle size: $< 2\ \mu$ Apparent density: 1·87 g/cc				
0	9·5 : 1	0·950	2·21	2·33
90	9·5 : 1	0·174	0·45	2·58

distance" (which has the same physical meaning of jump distance (Shewmon, 1963, p. 51) that is used in the modern terminology in diffusion) as reported by the authors (Lai and Mortland, 1961, 1962). The increase of clay content and bulk density resulted in a shorter average "jump distance" between particles, and the over-all result is the increase of diffusion rate.

GENERAL CONCLUSIONS

There are two basic assumptions on the application of Equations (7) and (11) to the cationic diffusion in clay minerals: (1) the system should have external surface diffusion only, and (2) the diffusion specimen should be perfectly oriented. Because of the homogeneity of diffusion property of K-vermiculite, experimental results show the diffusion of Na ion in this system, both 2–5 μ and $<2\ \mu$ particles, conformed with Equations (7) and (11), (Fig. 3 and Table 1). As far as the degree of orientation of the specimens used in this study is concerned, quantitative data could not be obtained. Several techniques for orientation studies of certain crystal planes in rock have been reported, for example Fayed (1966) published an X-ray diffraction method measuring the orientation of the micaceous minerals in slate. However, that technique could not be applied to these pellet specimens. In Table 1 the experimental results show obedience to Equation (11). This, in addition to microscopic examination, suggests that these specimens were very highly oriented.

The observed values of coefficients (D_w and D_h) in K-vermiculite showed considerable difference between specimens oriented at 0° and at 90° with respect to the direction of diffusion flux. The calculated "true" coefficients in a given size particle system agreed very closely however. This seems to be good support of the homogeneous nature of cationic diffusion in K-vermiculite. It also appears very likely that the principle of homogeneous and heterogeneous diffusion systems as suggested by the authors (Lai and Mortland, 1967) could be applied in general. Meanwhile, the diffusion of Na ion in Na-vermiculite, a heterogeneous diffusion system, did not show conformity with Equations (7) and (11). This seems to support the authors' suggestion (Lai and Mortland, 1967) that in cationic diffusion studies in clay minerals, one must consider the nature of the system and whether only external or external and interlamellar diffusion pathways are possible.

REFERENCES

Barrer, R. M. (1941) *Diffusion In and Through Solids:* Cambridge University Press, London, 464 pp.

Cloos, P., and Mortland, M. M. (1964) Apparatus for electrical conductivity measurements of clay plugs in corrosive gases and at low temperatures: *Soil Sci. Soc. Am. Proc.* **28**, 719–720.

Cremers, A. and Laudelout, H. (1966) Surface mobilities of cations in clays: *Soil Sci. Soc. Am. Proc.* **30**, 570–576.

Cremers, A., and Thomas, H. C. (1966) Self-diffusion in suspensions. Sodium in montmorillonite at equilibrium: *J. Phys. Chem.* **70**, 3229–3234.

Fayed, L. A. (1966) X-ray diffraction study of orientation of the micaceous minerals in slate: *Clay Minerals* **6**, 333–340.

Graham-Bryce, I. J. (1965) Diffusion of cations in soils: *Plant Nutrient Supply and Movement,* Intern. Atomic Energy Agency, Vienna, Austria, *Tech. Rep.* No. **48**, 42–56.

Jost, W. (1960) *Diffusion in Solids, Liquids, Gases:* Academic Press, New York, 652 pp.

Lai, T. M., and Mortland, M. M. (1961) Diffusion of ions in bentonite and vermiculite: *Soil Sci. Soc. Am. Proc.* **25**, 353–357.

Lai, T. M., and Mortland, M. M. (1962) Self-diffusion of exchangeable cations in bentonite: *Clays and Clay Minerals*, Pergamon Press, New York, **9**, 229–247.

Lai, T. M., and Mortland, M. M. (1968) Cationic diffusion in clay minerals: I. Homogeneous and heterogeneous systems: (Accepted for publication). *Soil Sci. Soc. Am. Proc.*

Meredith, R. F., and Tobias, C. W. (1962) Conduction in heterogeneous systems: *Advan. Electrochem. Electrochem. Eng.* **2**, 15–47.

Millington, R. J., and Quirk, J. P. (1964) Formation factor and permeability equations: *Nature* **202**, 143–145.

Phillips, R. E., and Brown, D. A. (1965) Ion diffusion—III. The effect of soil compaction on self diffusion of rubidium-86 and strontium-89: *Soil Sci. Soc. Am. Proc.* **29**, 657–661.

Raman, K. V., and Mortland, M. M. (1966) External specific surface area of vermiculite: *Am. Mineralogist* **51**, 1787–1792.

Shewmon, P. G. (1963) *Diffusion in Solids:* McGraw-Hill, New York, 203 pp.

Walker, G. F. (1959) Diffusion of exchangeable cations in vermiculite: *Nature* **184**, 1392–1393.

Wert, C. A., and Thomson, R. M. (1964) *Physics of Solids:* McGraw-Hill, New York, 436 pp.

Résumé— L'effet de l'orientation de particules de vermiculite sur la diffusion d'ion Na a été mesuré par une méthode au tracé. Les mesures de diffusion ont été faites sur des pastilles préparées par compression de vermiculite séchée et congelée dans une matrice cylindrique. Le coefficient de diffusion a été évalué sur la limite d'une couche mince selon les conditions de la loi de Fick. A cause de la projection très forte d'éclats de vermiculite sous l'effet de la force de pression, il a été possible de préparer divers angles d'orientation des spécimens, en raison de la surface de départ de la diffusion. On a ainsi dèveloppé des relations mathématiques de l'angle d'orientation, du rapport axial des plaquettes et du coefficient apparent de diffusion. Les résultats expérimentaux sur la diffusion d'ion Na dans la vermiculite -K de taille argileuse, donnaient des coefficients de diffusion de 2,21 × 10^{-7} cm^2 sec^{-1}, quand le flux de diffusion était parallèle aux plaquettes d'argile et de 0,45 × 10^{-7} cm^2 sec^{-1}, quand le flux était perpendiculaire aux plaquettes d'argile. Quant à la diffusion d'ion Na dans la vermiculite -Na, les coefficients apparents de diffusion obtenus étaient de 1,18 × 10^{-8} cm^2 sec^{-1}, pour un flux de diffusion parallèle aux plaquettes et de 0,18 × 10^{-8} cm^2 sec^{-1} pour le flux perpendiculaire aux plaquettes. Le changement du coefficient apparent de diffusion pour la vermiculite -K est un simple phénomène de géométrie particulaire. Les systèmes de vermiculite -Na ont manifesté un comportement beaucoup plus complex.

Kurzreferat—Die Wirkung der Orientierung von Vermiculitteilchen auf die Diffusion von Natriumionen wurde mit Hilfe einer Tracertechnik gemessen. Die Diffusionsmessungen wurden an Plättchen, die durch Pressen von kühlungsgetrocknetem Vermiculit in einem zylindrischen Presstempel hergestellt worden waren, ausgeführt und der Diffusionskoeffizient wurde durch einen Dünnfilmgrenzzustand des Gesetzes von Fick bestimmt. Der hohe Orientierungsgrad der Vermiculitblättchen unter dem Einfluss der Druckkraft ermöglichte es, verschiedene Winkel der Probenorientierung in Bezug auf die Oberfläche, an der die Diffusion einsetzte, herzustellen. Es wurden mathematische Beziehungen zwischen dem Orientierungswinkel, dem Axialverhältnis der Plättchen und dem Scheinbaren Diffusionskoeffizienten entwickelt. Die Versuchsergebnisse, die bei der Diffusion von Na Ion in K-Vermiculit von Tongrösse erhalten wurden, wiesen scheinbare Diffusionskoeffizienten von 2,21 × 10^{-7} Strömung senkrecht zu den Tonplättchen Werte von 0,45 × 10^{-7} cm^2 sec^{-1} ergaben. Für die Diffusion von Na Ion in Na Vermiculit wurden bei Diffusionsströmung parallel zu den Tonplättchen scheinbare Diffusionskoeffizienten von 1,18 × 10^{-8} cm^2 sec^{-1} erhalten, und bei Diffusionsströmung senkrecht zu den Plättchen Werte von 0,18 × 10^{-8} cm^2 sec^{-1}. Bei K-Vermiculit ist die Änderung des scheinbaren Diffusionskoeffizienten einfach durch die Teilchengeometrie bedingt. Im Falle des Na-Vermiculit Systems liegen die Verhältnisse etwas komplizierter.

Резюме—Эффект ориентации вермикулитовых частиц на диффузию иона Na измеряется по методу меченых атомов. Измерения диффузии проводились на гранулах, приготовляемых прессованием вермикулита, подвергнутого сушке при температуре ниже в цилиндрическом мундштуке, а коэффициент диффузии оценивается по условиям тонкой пленки на границе по закону диффузии Фика. Вследствие того, что хлопья вермикулита были сильно ориентированы под прижимающей силой, можно было приготовить различные углы ориентации образца по отношению к поверхности, на которой инициировалась диффузия. Разрабатывалось математическое соотношение угла ориентации, осевого отношения пластиночек и кажущегося коэффициента диффузии. Экспериментальные результаты на диффузию иона Na в вермикулите-K размера глины дали кажущиеся коэффициенты диффузии в 2,21 x 10^{-7} cm^2 $сек^{-1}$, когда диффузионный поток был параллельным к пластиночкам глины и 0,45 x 10^{-7} cm^2 $сек^{-1}$ когда поток был перпендикулярным к пластиночкам. Для диффузии иона Na в вермикулит-Na получались кажущиеся коэффициенты диффузии 1,18 x 10^{-8} cm^2 $сек^{-1}$, когда диффузионный поток был параллельным с пластиночками глины, а 0,18 x 10^{-8} cm^2 $сек^{-1}$, когда поток был перпендикулярным к пластиночкам. Для вермикулита—K изменение в кажущемся коэффициенте диффузии является просто изменением геометрии частиц. Системы вермикулита—Na показали более сложное поведение.