PATHWAYS OF CATIONIC DIFFUSION IN CLAY MINERALS

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ABSTRACT

PATHWAYS OF CATIONIC DIFFUSION IN CLAY MINERALS

by Tung-Ming Lai

In order to study the pathways of cationic diffusion in clay minerals, models of homogeneous and heterogeneous cationic diffusion systems were applied to these minerals and the effects of mineral orientation on diffusion were determined.

The diffusion of Na and Cs ions in expanded Na-vermiculite, which has both internal and external surfaces available for cationic diffusion, decreased with increasing diffusion time, a characteristic of heterogeneous systems. Diffusion of those ions remained essentially constant in collapsed K-vermiculite which has only external surface available for diffusion and can thus be described as homogeneous. The property of homogeneity was further confirmed with cationic diffusion in the vermiculite whose exchange sites were clogged by p-phenylenediamine cation, and in Na- and K-kaolinite which have external surfaces only; while the heterogeneous property was observed to Na- and K-bentonite which have both external and internal surfaces.

The diffusion of Na ion in Na-vermiculite was related to a model originally derived for mathematical analysis of grain boundary problems. The evaluation of diffusion coefficients of external surface (D_e) and of interlayer surface (D_i) was made, and D_e of Na ion in Na-vermiculite was found to be about 5 times larger than that of D_i.

Pellet specimens were prepared by pressing freeze-dried vermiculite in a cylindrical die, with the result that the flakes of vermiculite were highly oriented with the c axis of the minerals parallel with the axis of the cylindrical pellet. It was possible to prepare different angles of specimen orientation with respect to the surface where diffusion was initiated, and the orientation effects were studied. Mathematical relationships of orientation angles, axial ratio of the platelets, and diffusion coefficient were developed. The experimental results on the diffusion of Na ion in vermiculite were shown to obey the proposed mathematical equations in the case of homogeneous system (K-vermiculite), but not in the case of heterogeneous system (Na-vermiculite).

Based on the orientation effects, an effective area factor was utilized in attempts to calculate the "true" diffusion coefficient.

The importance of considering the homo- and heterogeneity of the system in the study of cationic diffusion in clay minerals is suggested.

PATHWAYS OF CATIONIC DIFFUSION IN CLAY MINERALS

By

Tung-Ming Lai

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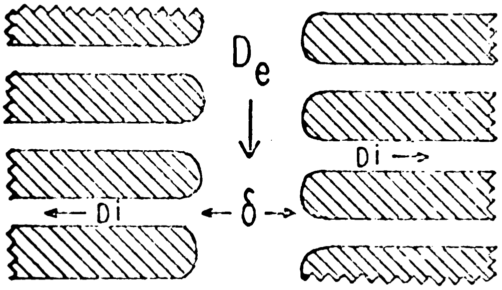
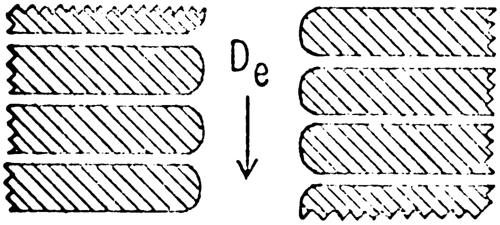
I. INTRODUCTION

Cationic diffusion has been of interest in basic studies of cation exchange and nutrient supply in soils in recent years. However, the mechanism of this process in soils is still not completely established. Diffusion is primarily a random movement of particles. The diffusion in solids has been treated with the mathematics of the random-walk problem in relating diffusion coefficient to the jump frequencies and jump distances of the diffusing atoms (72). As far as the pathways of cationic diffusion in clay minerals are concerned, it has been suggested that cationic diffusion in salt free systems results from movement from exchange site to exchange site on the mineral surface (38,78).

The surface of clay minerals can be subdivided into external and internal surfaces as far as the structure and ion exchange processes are concerned. Ion exchange can occur only on external surface of non-swelling clay minerals. For expanded 2:1 clay minerals exchangeable ions are bonded both on external and interlayer surfaces. Since in salt free systems cations diffuse from one exchange site to another, it is likely that there are at least two diffusion pathways in expanded 2:1 clay minerals: on the external surface and through the interlayer surface as shown in A Fig. 1. For 1:1 clays or collapsed 2:1 minerals, only the external surface is available for cationic diffusion (B, Fig. 1).



A. Heterogeneous system



B. Homogeneous system

Figure 1. Heterogeneous and homogeneous diffusion systems.

Because of the different properties of external and interlayer surfaces, the magnitude of the external diffusion coefficient (D_e) may differ from that of the interlayer diffusion coefficient (D_i). Accordingly, the clay system with both internal and external surfaces as shown in Fig. 1A is heterogeneous as far as the diffusion is concerned, and the type of clay where only external surface is available in Fig. 1B, is considered a homogeneous system.

Furthermore, both isotropy and anisotropy for the diffusion process have been found in noncubic materials (72). Clay minerals generally have a pronounced platy or fibrous structure. Walker (78) 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.

Most experimentally observed diffusion coefficients are apparent values, in which three main factors are involved, namely, tortuosity of pathways, 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.

The investigation was designed to study the pathways of cationic diffusion in clay minerals with the following objectives in mind: (1) to test the hypothesis of homogeneous and heterogeneous diffusion systems, and (2) to study the effects of clay mineral orientation on diffusion.

II. LITERATURE REVIEW

Measurement of Diffusion Coefficients

For the determination of diffusion coefficients one ordinarily utilizes Fick's law of diffusion. An excellent summary of earlier works on the diffusion in and through solids has been given by Barrer (4). In Jost's book (34) the diffusion theories are fairly well integrated. There are varieties of boundary conditions of Fick's second law, and Crank's book (15) is invaluable for the solution of the differential equations of the diffusion type. Shewman's (72) and Girifalco's (28) volumes give a modern treatment of the diffusion in solids.

The development of accurate methods for the measurement of ion diffusion coefficients in soils has received attention for more than a decade. Various methods have been developed at different laboratories to meet the requirements of different boundary conditions of Fick's law. In 1957, Bloksma (6) published a procedure measuring the self-diffusion coefficients of sodium and iodide ions in bentonite and kaolinite pastes by means of layer analysis and use of radioisotopes in a diffusion apparatus. With this apparatus Fletcher and Slabaugh (26) were able to determine the self-diffusion of Ca ion in a Wyoming bentonite gel. Attempting to obtain more accurate data with Bloksma's method, Gast (27) applied Longsworth's zero-time correction equation (46) to this method. However, he found some anomalous results in measurement of cationic diffusivity in bentonite pastes.

In Bloksma's method a layer of soil or clay mineral containing radioactive tracer of the ion under investigation is placed in contact with a similar layer without tracer, and then allowing diffusion to proceed for a certain definite period of time. After measuring radioactivity in the layers, the apparent diffusion coefficient is evaluated on the basis of Fick's law. In order to solve some technical problems in the measurement, Schofield and Graham-Bryce (71) and Graham-Bryce (30) used a thin permeable ion-exchange membrane (Permaplex supplied by the Permutit Co., Ltd.), which was previously prepared in equilibrium with half the initial tracer concentration in the radioactive section, to separate the two layers and after a given time the diffusion of Rb, I, or P ions in the soil was determined. Instead of a membrane, a thin, coarse, nylon-mesh cloth was placed between the layers to facilitate a later separation of the samples at the interface as reported by Olsen et al. (59) in the measurement of self-diffusion of P in soils. However, Lewis and Quirk (44) found that, in the measurement of diffusion of P in soils, no membrane was needed to separate the two layers although a number of membranes were tried and discarded. For the purpose of avoiding the separation procedure in the determination of radioactivity distribution in the layers, Evans and Barber (22) took several autoradiographs at approximately 1-week intervals during the course of the experiments to follow the movement of ^{86}Rb in the samples. Enlarged densitometer tracings were made across the boundary between labeled and unlabeled samples on the autoradiographs and the diffusion coefficient was calculated. On the other hand, Brown et al. (11) applied a quick-freezing technique in order to section the layers into 50μ segments with a refrigerated microtome, after radioisotopes diffused from the labeled layer of soil- or clay mineral-water system to the unlabeled system. The radioactivity of the 50μ sections was determined and the diffusion coefficient was then evaluated. With the same principle of a one-dimensional closed finite diffusion system, but with some difference in the technique of measuring concentration of diffusing ions, Klute and Letey (35) described a method measuring the self-diffusion coefficient of ^{86}RbCl in glass beads. Porter et al. (66) measured chloride diffusion in soils.

In an earlier paper Thomas (73) developed another type of method to measure the self-diffusion coefficients of ions in agar gels. In his method, coefficients of ions traceable by γ-ray can be deduced from determinations of the total activity of a "short rod" of the material from which the diffusion takes place through a thin membrane into a rapidly stirred bath at zero activity. After some modifications were made (1), this method was used to measure the self-diffusion of the Na ion in a montmorillonite suspension by Cremers and Thomas (16).

A thin-film boundary condition of Fick's law which is often used in the study of diffusion in solids, was applied by Lai and Mortland (38) for measuring diffusion coefficients in clay plugs. After depositing a thin film of radioactive tracer on the surface of the plug, thin sections were removed after a given time and radioactivity measurements made on the portion of the plug remaining. The coefficient was evaluated by a graphical method from the solution of Fick's law at this special boundary condition.

Using Amberlite ion exchange paper as a sink maintaining zero concentration of the diffusate at the soil surface, Vaidyanathan and Nye (74) developed another kind of method measuring ionic diffusion in soild. The method was based on the principle that the quantity of ions diffusing from the soil of semi-infinite thickness was directly proportional to the square root of the diffusion time until about half the counter-ions originally on the resin were changed. Values of average diffusion coefficients were calculated using this porportionality constant and the concentration of total exchangeable ions.

With a single piece of vermiculite flake of thickness about 0.1 mm and lateral dimensions of 1 to 2 mm, Walker (78) was able to measure the diffusion of Sr ion in Mg-vermiculite with an optical method by determining the rate of the moving boundary.

Transient and steady-state systems are the two main types used to measure diffusion coefficients in soils and clays. All of the previously mentioned methods are considered as transient systems. In 1954, Husted and Low (33) determined the steady-state counterdiffusion of K-H, K-NH_4, K-Na, and K-Li ions systems through bentonite gels. Their counterdiffusion assembly was mainly constructed with a diffusion chamber containing the bentonite gel and two flow chambers connecting to both ends of the diffusion chamber. The flow rate of the flowates in both chambers were the same, and the concentrations of the flowates were determined. Later on, Dutt and Low (21) constructed another diffusion cell from which solutions of different salt concentrations could be brought into contact with opposite ends of a clay-water paste confined at both ends by means of Millipore filters in a plastic compartment, and diffusion coefficients for the steady-state diffusion of LiCl and NaCl in bentonite-water paste were determined. Very recently, Mokady and Low (52) designed a more complicated diffusion apparatus with the objective that the simultaneous diffusion of water, NaCl and its component ions through Na-bentonite could be made. Olsen et al. (59) also measured the steady-state self-diffusion of P in soils by means of a diffusion cell with the soil sample in the central compartment confined with two porous steel plates on both ends of the sample.

According to the Nernst-Einstein equation, the ionic diffusion coefficient may be calculated from the mobility which may be measured electrically or electro-chemically.

Cremers and Laudelout (17) calculated the diffusion coefficients from the results of conductivity of Na, K, Rb, and Cs ions in bentonite ahd kaolinite with the correction for formation factors. They found that their calculated values agreed quite well with the results of Lai and Mortland (37, 38) obtained by a tracer technique based on Fick's law. Mokady and Low (51) determined the transference number of LiCl or NaCl in the montmorillonite pastes from the emf's of the cell using Beckman electrodes with which Li and Na activities were measured. The diffusion coefficients of LiCl and NaCl in two kinds of bentonite-water systems were then calculated from the results of transference number.

Nature of Cationic Diffusion

The cationic diffusion in soil or clay systems differs from that in water, mainly because of interactions of diffusing ions with the media and tortuosity effects. Walker (78) has suggested that cations diffuse along exchange sites of vermiculite. By means of ^{22}Na and ^{35}S double-labelled Na_2SO_4 tracer techniques, Lai and Mortland (38) demonstrated that Na ion migrated along the negatively charged matrix of the bentonite gel and SO_4 ion moved through the middle of the "channel" of the matrix. In the same paper, an analogy of cationic diffusion in clay minerals to de Boer's "hopping" mechanism of gas adsorption (20) has been proposed by them. Recently, Cremers and Laudelout (17) also adapted the same idea in their studies on surface mobilities of cations in clays. On the other hand, the idea of "jump" distance and jump frequency have been well established in the mechanism of diffusion in solids (72). Based on the results of the effect of salt concentrations on cationic diffusion in soils, Graham-Bryce (29) has also suggested that cations diffuse in the exchange phase of soils. Furthermore, Cremers and Thomas (16) developed a procedure to evaluate the surface diffusion coefficient of Na ion in bentonite gel for the observed apparent coefficient. They presumed that the surface diffusion coefficient depended directly on the fraction of ions counted as belonging to the surface, and this fraction was defined in terms of the base exchange capacity of the suspended mineral. Nye (57) proposed to separate the diffusion of exchangeable ions in soil along the liquid pathway from the solid path in which the movement is associated with the surface of the solid by using mathematical equations.

Almost all of the values of apparent ionic diffusion coefficients in soil and clay systems measured were smaller than that of the same ion in water. As far as the relative order of diffusion rate of various ions is concerned, Husted and Low (33) found that the counterdiffusion rate of K ion through bentonite gels in steady-state depended on the diffusion rate of the counterdiffusing ions which were in the order NH_4 > Na > Li, which is the same as that for those ions in solution. With a transient system, Lai and Mortland (37) also found that as far as the ion species used to saturate the bentonite gels are concerned, the diffusion rate of Na, Rb, Cs, Ca, and SO_4 ions in bentonite systems varied with various kinds of homoionic clays, and that these 5 ions followed the same order, namely, K-clay > Na-clay > Li-clay. However, as far as the diffusion rate of diffusing ions themselves is concerned, in the 3 homoionic systems (K-, Na-, and Li-bentonite) their rates were in the relative order SO_4 > Na > Rb > Ca > Cs which differs from that in the order Cs > Rb > Na > SO_4 > Ca in water. The difference in the relative order of the rate of diffusing ions between the clay and water systems suggested an important influence of the clay structure on the diffusion of ions. With vermiculite, it was also found that the relative diffusion rate of Na ion was larger than that of Cs ion in both Na- and Cs-clays (37).

To evaluate the tortuosity effects, there is a well-written volume on the earlier works, which is reviewed by Carman (12). For modern treatment on this subject, one may refer to Meredith and Tobias's paper (49). Some mathematical equations have been worked out to solve the tortuosity problems in unconsolidated systems (18,40,50). Cremers and Thomas (16) applied a "formation factor" equation in the study of self-diffusion of Na ion in montmorillonite gel, and Cremers and Laudelout (17) used the same equation in measuring surface mobilities of several cations in bentonite gels.

Some workers used anions, such as chloride (35,66) and iodide (6), and urea (6) to evaluate the tortuosity effects on the basis of the assumption that those anions and urea may not react with clays. However, Mokady and Low (53) found that the average activity coefficient of Cl ion was larger than unity during the steady-state diffusion of NaCl through Na-bentonites. In fact, Lai and Mortland (37) demonstrated that the diffusion of SO_4 ion in Na-bentonite gel at low clay contents (less than 9% by weight) was even higher than that in water. As far as urea is concerned, based on the infrared absorption studies Mortland (55) has observed the formation of urea complexes with montmorillonte and its exchangeable cations.

Low (47) has suggested that the viscosity of water increases towards the clay mineral surfaces, and thus the greater viscosity in the vicinity of clay surfaces is also one of the factors influencing cationic diffusion in clay (55). Also, Chaussidon (13) suggested that at very low moisture content, the structure of water is a very important factor affecting cationic mobility in soils and clays.

Effect of Soil Properties on Ionic Diffusion

From the previous section on review of the nature of cationic diffusion in soil and clay systems, the effects of clay structure and kinds of exchangeable ions on ionic diffusion in soils are obvious (36,37,62). In addition to these, the effects of some other soil properties on ionic diffusion have been studied.

The effect of moisture contents on ionic diffusion has been demonstrated by several workers. Their results showed that the diffusion of Na(38), Rb (31,61,65), Sr (36,67), and Cl (66) ions in soils and clays increased with increasing moisture contents. The quantitative relationship between moisture content and ionic diffusion still has not been established. Graham-Bryce (31) found a rapid rise in Rb ion diffusion taking place between 5 and 10% moisture contents in a soil, that may correspond with the establishment of a continuous aqueous diffusion system.

The number of exchange sites present per unit volume should affect the diffusion rate. Increasing the clay content will increase the number of exchange sites, thereby increasing the frequency of exchanges an ion makes in a given distance. This should result in a decrease in the diffusion coefficient. Changes in tortuosity of the diffusion path also could change with clay concentration. These could account for the observations of Lai and Mortland (38) who found that the diffusion coefficients of Na, Cs, and Ca ions in bentonite gels decreased with increasing clay contents. Evans and Barber (22) used agar as a medium to dilute a soil and a kaolinite, and noted that the diffusion of Rb decreased with increasing percentage of soil and clay. On the other hand, when the "true" diffusion coefficient of P in soils was evaluated by a factor obtained by chloride diffusion, Olsen and Watanabe (60) found that the "true" coefficient increased with increasing clay contents.

When the clay content reaches a certain point and the jump from particle to particle becomes the rate-limiting process, then the diffusion could increase with increasing clay content. In fact, Graham-Bryce (32) and Phillips and Brown (63,64) found that the cationic diffusion coefficients increased with increasing bulk density. Their work is based on the results of "hopping distance" as reported by Lai and Mortland (37,38) in which the "hopping distance" between clay particles became smaller as the clay content increased.

Humus has a high ion exchange capacity, and thus the results of Prokhorov (67) and Prokhorov and Frid (68) that the diffusion of Sr-90 in quartz sand and soils decreased with increasing humus content are understandable.

For cationic diffusion relating to the ion exchange properties in soils, it is easy to understand the results of the effects of cation exchange capacity and surface area on the diffusion coefficients of Rb and Sr ions in kaolinite and soils as reported by Evans and Barber (22) and Prokhorov (67).

The diffusion coefficients of Rb ion in different types of soils were determined by Evans and Barber (22) and Graham-Bryce (31,32). Both results indicated the variation of the coefficients in the different soils. The correlation of these coefficients with soil properties, such as pH, cation exchange capacity, exchangeable K, clay content and moisture content was tested by Graham-Bryce (32), but no simple relationship was found. This is not surprising because the diffusion coefficient is controlled by both electro-chemical and geometrical factors for which there can be no simple parameter.

Ionic Diffusion Relating to Other Processes in the Soil

The extensive work on ionic diffusion by Boyd and his co-workers (8,9) has thrown light on the mechanisms of ion exchange in resins. The results obtained by Mortland and Ellis (56) have indicated that the release of fixed K from vermiculite is a diffusion-controlled process. Walker (78) has also shown that the Sr-Mg exchange reaction in vermiculite is a diffusion process. Since then, the concept of the diffusion of cations plays an important role in cation exchange and has been accepted in the field of soil chemistry (5). For example, a study of kinetics of Cs sorption by clay minerals was conducted by Sawhney (70) who found that the Cs sorbed by Ca-montmorillonite reached equilibrium quickly and, in contrast to that, Ca-vermiculite continued to sorb Cs and the equilibrium was not attained even after 500 hours. He explained that whereas Cs diffuses into Ca-vermiculite interlayers, which is a slow process, it does not diffuse into Ca-montmorillonite interlayers.

The double layer theory as related to ionic diffusion has been applied by Lai and Mortland (37) in order to explain the effects of exchangeable cations on the diffusion of Na and Cs ions in the bentonite gels. Furthermore, based on the diffusion studies, the fractions of the exchangeable cations in the diffuse layer were estimated by van Schaik, Kemper, and Olsen (75). They calculated that approximately 70% of exchangeable Na ion and 25% of Ca ion were mobile, and participated in ionic diffusion in a bentonite system.

In a practical sense, the movement of some nutrient ions in soils is to be considered as being controlled by the diffusion process, and rather extensive studies on the nutrient uptake relating to the ionic diffusion in soils have been made.

In 1954 Bray (10) proposed the nutrient mobility concept in which he separated the nutrients into two groups based on mobility in the soil: mobile nutrients such as NO_3, Cl, and SO_4 ions, and relatively immobile nutrients such as P, K, Ca, and Mg ions. He drew a picture of a "hypothetical" narrow root surface sorption zone for supply of relatively immobile nutrients in the soil. Several years later after Bray's publication Walker and Barber (79) were able to show by radioautography with ^{32}P and ^{86}Rb that there was "actually" such a zone present in the soil. Furthermore, Lai, Fang, and Shieh (39) measured the root surface sorption zone of Rb ion in two soils and calculated the distribution of Rb ion in the absorption zone from which it was shown to follow Fick's law of diffusion.

At the low concentration of P ion usually observed in the soil, diffusion is the main process of transport to the plant roots as reported by several investigators (2,7,45,58).

Olsen and Watanabe (60) studied the relationship between the diffusion and uptake of P by corn seedlings, and showed that the observed results were close to the calculated ones based on their proposed diffusion equation. Lewis and Quirk (43) conducted a pot experiment with wheat to correlate the plant growth with the diffusion coefficient of P. The optimum coefficient of P for wheat growth in that particular soil was 5×10^{-9} cm^2 sec^{-1}.

Barber and his associates (23,65,76) have published several papers on the diffusion and uptake of Rb. They found that diffusion coefficient of Rb ion in soils correlated very well with the uptake by plants. For practical purposes, Barber et al. (3) suggested that diffusion should be one of the main processes to be considered in the development of soil tests for available nutrients.

III. EXPERIMENTAL METHODS

Preparation of Sample

Vermiculite. The vermiculite used in this work was from Libby, Montana and supplied by Ward's Natural Science Establishment, Inc., Rochester, New York. Because the Montana vermiculite contained some micaceous material, the clay fraction (< 2μ) was continuously leached with 2N NaCl solution until the X-ray diffraction pattern showed the disappearance of the 10A spacing (it required about 40 liters of 2N NaCl solution for 100 g clay with continuous leaching for one week). After most of the excess NaCl was washed out with water by a centrifugation procedure, the suspension of Na-vermiculite was passed through the following sequence of Amberlite synthetic resin (supplied by Rohm & Haas Company, Philadelphia, Pennsylvania) columns: OH-IR-45 ⟶ H-IRC-50 ⟶ Na-IRC-50 (OH-IR-45 is a weak amine type anion exchange resin in hydroxy form, H-IRC-50 a weakly carboxylic acid type cation exchange resin in hydrogen form, and Na-IRC-50 that in sodium salt form). This product was a salt-free, Na-saturated vermiculite. The homoionic K-vermiculite was prepared the same way except using K-IRC-50 column instead of Na-resin in the final columning process. For the study of effects of orientation, the 2-5μ particles of K-vermiculite were also separated by ordinary decantation procedures.

Kaolinite and Bentonite. These clays were American Petroleum Institute Clay Mineral Standards Project No. 49 reference clay minerals H-5 and H-25 (also supplied by Ward's Natural Science Establishment, Inc.) respectively. The homoionic clay samples were prepared by washing the $< 2\mu$ fraction with NaCl or KCl solutions and rendering them salt-free.

Preparation of Diffusion Specimen

In order to obtain diffusion specimens oriented as shown in Fig. 1, the clay suspension was freeze dried, and was pressed in a cylindrical die under 1,000 pounds per square inch pressure to make a pellet as described by Cloos and Mortland (14). The result of this 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 clay pellet. The highly oriented condition of the clay resulted in a platy structure easily observed under the microscope as shown in Plate 1.

In order to study orientation effects, it was necessary that measurement be made of apparent diffusion coefficients at various angles of orientation with respect to the direction of diffusion flux. The vermiculite pellet 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. 2. The dashed lines show the orientation of vermiculite flakes. The

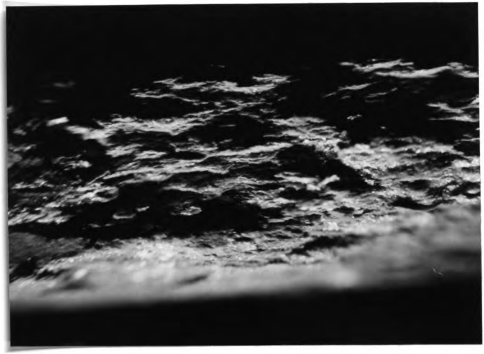


Plate 1. Microscope photograph of longitudinal section of K-vermiculite pellet (x25).

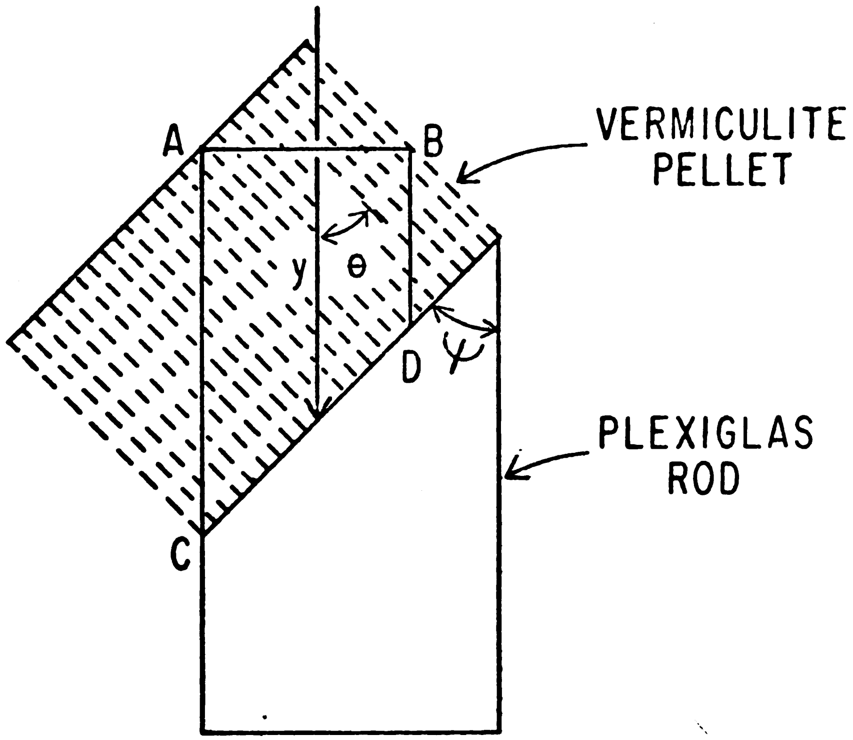


Figure 2. Schematic drawing of a vermiculite pellet mounted on a plexiglas rod designed to give a plane of angle θ of orientation with respect to the diffusion flux.

final diffusion specimen was cut into ABDC as shown in Fig. 2. AB is the surface on which the diffusion was initiated in direction y in Fig. 2 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 $90^0 - \psi$. 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 the orientation studies.

Diffusion Measurement

Fundamentally the same radioactive tracer technique developed by Lai and Mortland (38) was used for measuring apparent diffusion coefficients. Their method was based on the following equation of a thin-film boundary condition of Fick's law of diffusion:

$$C_x = \frac{Q}{\sqrt{(\pi Dt)}} \exp\,(-x^2/4Dt) \qquad (1)$$

Where C_x is the concentration of the diffusing substance at time t at distance x from the initial boundary, Q is the quantity of the substance deposited as a uniform and thin layer on the surface and allowed to diffuse into a semi-infinite medium, and D is the diffusion coefficient. They(38) developed a special experimental technique utilizing the equation [1]. After depositing a thin film of radioactive tracer on the surface of the clay plug, thin slices were removed after a given time and radioactivity measurements made on the remaining portion of the plug. The coefficient was evaluated by a graphical method from the solution of Fick's law at this boundary condition (38). For its application to solid pellet specimens and to measure the coefficients within short diffusion times, some modifications were made.

A micrometer system was used instead of the hypodermic syringe which was used in the original method (38) for the purpose in cutting thin slices from the clay pellets. With this technique a very thin slice accurate to 0.02 mm could be made, and the diffusion time cut down to several hours with the coefficient as low as 10^{-8} cm^2 sec^{-1}.

Theoretically, the diffusion coefficient is evaluated from the slope of ln C_x versus x^2, according to equation [1] this slope has the value of $x^2/4Dt$. If an accurate value of the slope of ln C_x versus x^2 is to be obtained, it is necessary to have several slices from the pellet specimen. These slices should vary over a concentration range of an order of magnitude (72). This means that slices should be taken to a depth of $x^2/4Dt \simeq 2.3$ or $x \simeq 3\sqrt{(Dt)}$. The minimum slice depth which can be taken in this experimental technique is 0.02 mm or 2×10^{-3} cm, so that for 10 slices, which are needed for this procedure, the minimum value of x will be about 2×10^{-2} cm. If D is

10^{-8} cm^2 sec^{-1}, then it should be possible to make an accurate determination of D after a diffusion time $t \simeq (2 \times 10^{-2}/3 \times 10^{-4})^2 \simeq 10^4$ sec $\simeq$ 2.5 hr. In practice, it required several minutes to take the diffusion specimen from the constant temperature bath where the diffusion proceeded and to put it under the NaI(Tl) crystal for radioactivity measurements. To minimize the percentage error of this time interval in the total diffusion time, it was preferable to work at diffusion times no shorter than 4 hours.

The moisture content of sample, conditions for making pellet, and diffusion temperature were controlled. After the freeze dried sample was equilibrated in a desiccator containing saturated $(NH_4)_2SO_4$ solution (81.0% relative humidity at 20°C), 500 mg of sample was weighed and a pellet made in the stainless steel die. The pellet was stored again in the same conditions for at least one day before the diffusion measurement was made, and identical conditions were maintained during diffusion experiments.

To insure that the diffusing source conformed to the thin-film boundary condition of Fick's law, the ^{134}Cs-IR-120 (strongly acidic type Amberlite cation exchange resin absorbed with ^{134}Cs ion), and ^{134}Cs-IRC-50 (weakly acidic type resin absorbed with ^{134}Cs ion) resin loaded papers (supplied by H. Reeve Angel, Clifton, New Jersey), and 3μ pore size cellulose ester type Millipore filter (supplied by Millipore Corporation, Bedford, Massachusetts) soaked with very high specific acitivity ^{134}CsCl (22.7 μC/mg), were compared as radioactive sources. The following results were obtained.

Radioactive Source	Observed Diffusion Coefficient of Cs ion in K-vermiculite at $20^{0}C$ ($cm^2\ sec^{-1} \times 10^{10}$)	
	Experiment 1	Experiment 2
^{134}Cs-IRC-50 paper	1.69	1.83
^{134}Cs-IR-120 paper	1.86	1.66
^{134}CsCl-Millipore filter	1.84	1.98

It shows that these 3 different diffusion sources give practically the same results. All experimental results were in obedience to Fick's law as tested by the original Lai and Mortland method (38). Because of better mechanical strength and easy handling, the Millipore filter was used throughout this investigation.

The carrier-free ^{22}Na and ^{134}Cs of very high specific activity in chloride form were used as diffusing ions. About 0.5 μC of radioactive material was used for each measurement. A Millipore filter was cut into small discs the same size of the clay pellet (about 1 cm in diameter), then soaked in radioactive solution and dried. This was used as the radioactive diffusing source. After the radioactive Millipore disc was equilibrated under the same condition as that of the clay pellet, it was kept firmly in contact with the surface of the clay by a coil spring during the process of diffusion. After the preselected diffusing time, the Millipore disc was taken off, and the radioactivity of the pellet at different distances from the surface was measured with a single channel pulse height analyzer.

The diffusion experiments were conducted in duplicate, and the apparent diffusion coefficients reported are the average between duplicates. In certain figures (Figs. 4, 5, 6, and 7) the average of duplicates are the centers of the circles appearing in the graphs, and the deviation between duplicates is represented by the diameter of the circles.

IV. HOMOGENEOUS AND HETEROGENCEOUS SYSTEMS

Theoretical Background

A grain boundary exists between crystal lattices in polycrystalline forms of some metals. The grain boundary diffusion (D_b) and lattice diffusion (D_ℓ) are well established (28,72). This kind of diffusion has been put on a quantitative basis by Fisher (25). His work was followed by other workers proposing modification (41).

Fisher's model was based on an intuitive picture of grain boundary diffusion which is diffusion along a thin layer of high diffusivity substance sandwiched between a large volume of low diffusivity material. When D_b/D_ℓ is large enough, he assumed that diffusion outside the grain boundary slab was primarily normal to the slab at larger penetrations. After material has diffused into the solid through the surface, the concentration of diffusing material (c) is measured at various distances (y) below the surface. According to Fisher's solution a plot of log c versus y then should give a straight line of slope

$$- \frac{\sqrt{2}}{\sqrt[4]{(\pi D_\ell t)}\ \sqrt{(\delta D_b/D_\ell)}} \qquad (2)$$

where D_ℓ = lattice diffusion coefficient

D_b = grain boundary diffusion coefficient

t = diffusion time

δ = thickness of the grain boundary slab.

Fisher's solution is limited to certain simple cases, which Whipple (81) extended and published in his solution with fewer limitations. With his more complex solution, the grain boundary concentration contours can be calculated at different conditions. Fig. 3 is adapted from Whipple and shows concentration contours changing with β, and

$$\beta = \frac{D_b \delta}{2\, D_\ell \sqrt{D_\ell t}} \tag{3}$$

It is seen that with small values for β, the preferential penetration down the grain boundary is small. Contrariwise, great preferential penetration down the grain boundary exists when values for β are large. Therefore, the degree of discrimination of grain boundary from lattice diffusion can be varied with the variation of β. From equation [3], it follows that with varying either D_b/D_ℓ ratio or diffusion time (t), the magnitude of β should be changed. Experimentally, it has been demonstrated that the contribution of grain boundary diffusion or lattice diffusion to the observed apparent diffusion (including both D_b and D_ℓ) in polycrystalline zinc, varied with different diffusion temperatures (77). With polycrystalline cadmium it was also found that the observed diffusion coefficients decreased with increasing diffusion time (48).

Although Fisher's and Whipple's solutions were originally derived for solving grain boundary problems, basically it can be applied to the problem of heterogeneous diffusion

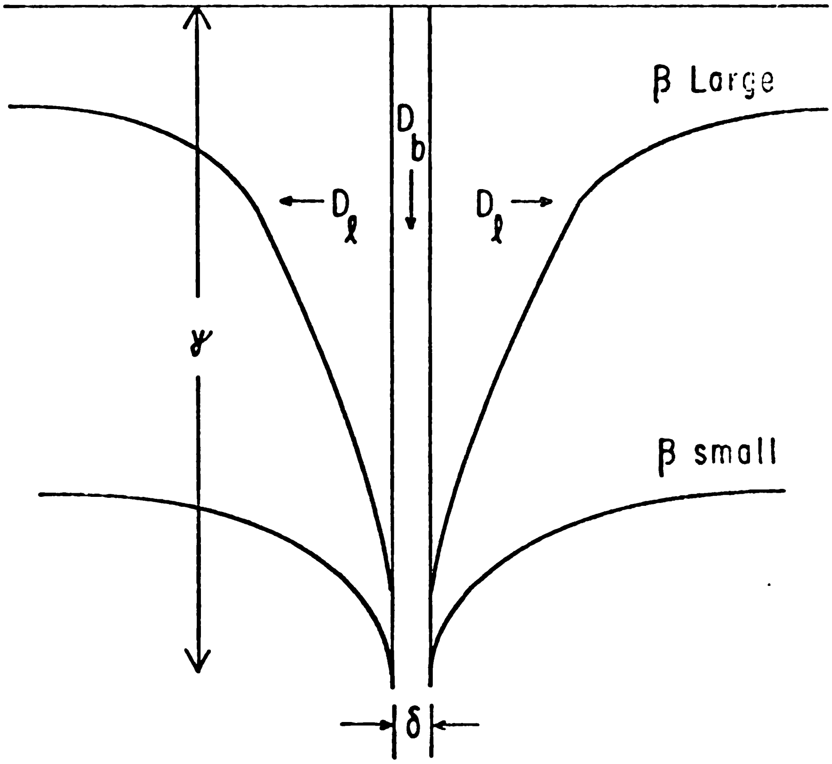


Figure 3. Model used for grain boundary diffusion analysis.

systems with high-diffusivity pathways. Consequently, it is possible to distinguish the high-diffusivity path diffusion from lattice diffusion in heterogeneous systems by varying diffusion time according to equation [3].

Homogeneous and Heterogeneous Systems

Figure 4 shows the apparent diffusion coefficients of Na ions into Na- and K-vermiculite pellets at 20°C under 81.0% relative humidity. The moisture content was 18.1% by weight for Na-vermiculite, and 3.6% for K-vermiculite (105°C).

It shows very clearly that the apparent diffusion coefficients of Na ion in Na-vermiculite decrease with increasing diffusion time, while remaining essentially constant in K-vermiculite. From X-ray diffraction results, the 15A spacing of Na-vermiculite indicates an expansion that will allow the Na ion to move into its interlayer regions. The 10A spacing of K-vermiculite means a collapsed structure, with the result that only external surface is available for cationic diffusion. If one compares the results in Fig. 4 with the self-diffusion of cadmium by Mahmoud and Kamel (48), it is easy to see the following analogies: (1) the change of the apparent diffusion coefficient with diffusion time for Na-vermiculite and polycrystalline Cd, and (2) the uniformity of diffusion coefficient with time for both K-vermiculite and monocrystalline Cd. In the former both grain boundary and lattice diffusion occur, in the latter only

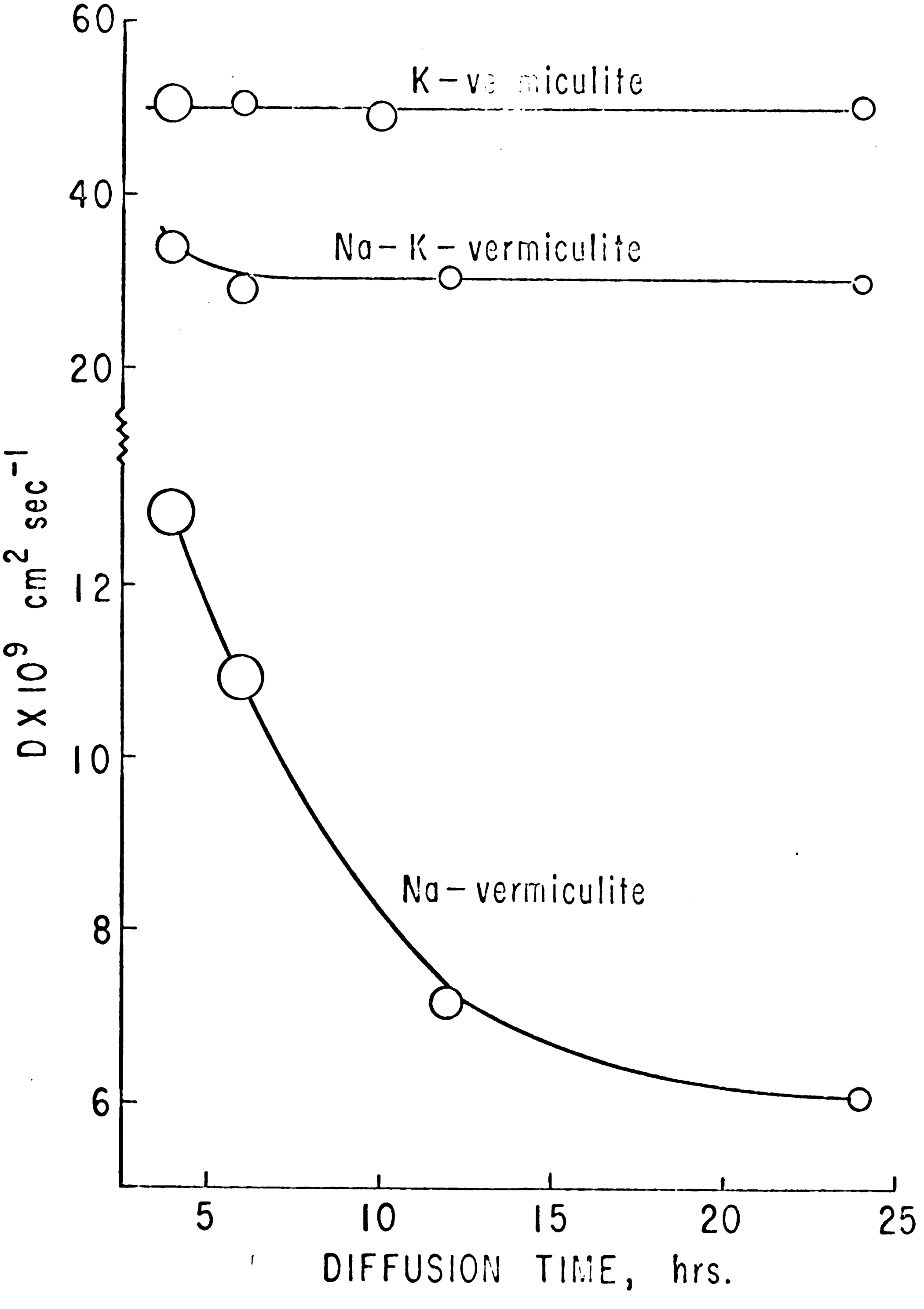


Figure 4. Relationship of diffusion time with the diffusion coefficient of Na ion in vermiculite on samples equilibrated at 81.0% relative humidity (20°C). The moisture contents of K-, Na-K-, and Na-vermiculite were 3.6, 6.8, and 18.1% by weight respectively (105°C).

lattice diffusion for monocrystalline Cd and only grain boundary diffusion for K-vermiculite. It seems obvious that both Na-vermiculite and polycrystalline Cd are heterogeneous diffusion systems with at least two coefficients, D_e and D_i in Na-clay and D_b and D_ℓ in polycrystalline Cd respectively; and homogeneous systems describe the cases of K-vermiculite and monocrystalline Cd with only one diffusion coefficient. Theoretically, it has been pointed out that the value of β (equation [3]) is inversely proportional to time t. When time is short, β, is large, the diffusion in the high-diffusivity path (D_b in equation [3]) predominates in the over-all process. When time becomes longer, the opposite is true. Therefore, the observed diffusion coefficient in heterogeneous systems decreases with increasing time. Under the experimental conditions in this study, the diffusion coefficients obtained were observed values, and thus only apparent coefficients. It can be observed, however, that Na-vermiculite conforms to effects expected of a heterogeneous diffusion system and K-vermiculite to homogeneous diffusion. It is also apparent that the external surface diffusion coefficient is larger than interlayer diffusion coefficient.

The results of diffusion of Cs ions in Na- and K-vermiculite as shown in Fig. 5 also demonstrate the different behavior of diffusion in these two systems. For Cs ion diffusion, the expanded Na-clay is still a heterogeneous system, and that of the collapsed K-system, homogeneous.

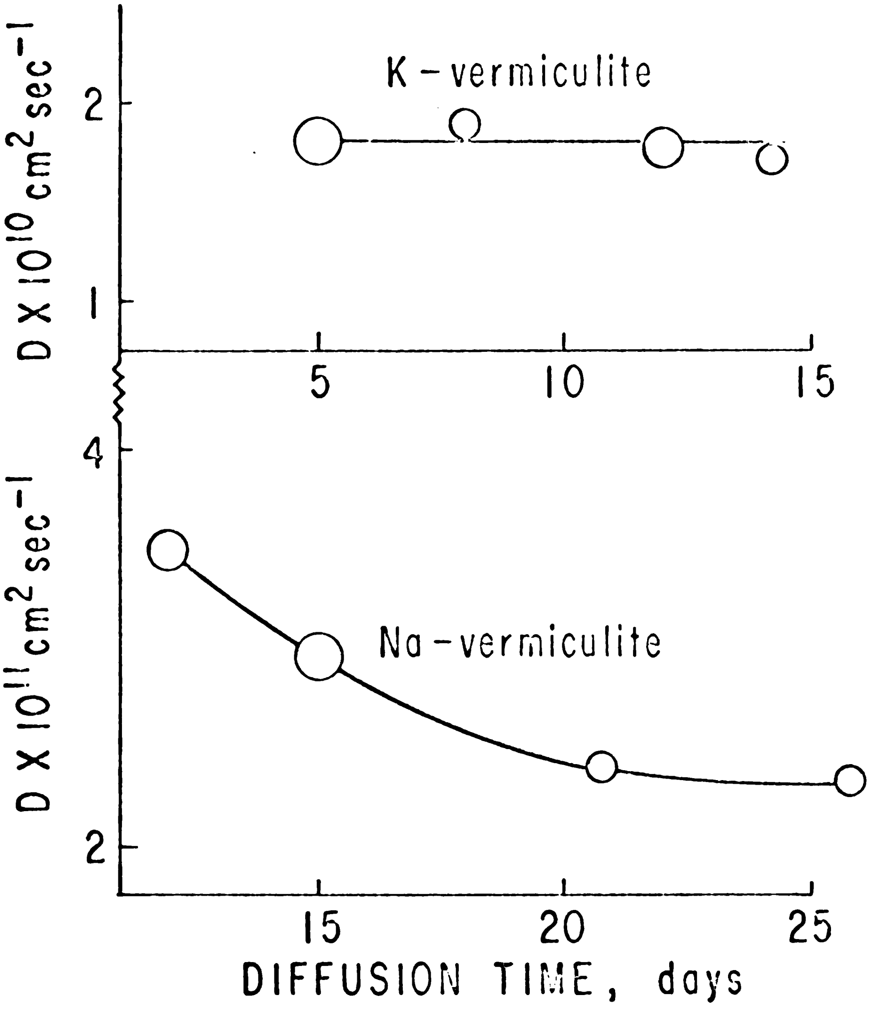


Figure 5. Relationship of diffusion time with the diffusion coefficient of Cs ion in vermiculite on samples equilibrated at 81.0% relative humidity (20°C).

Mortland (54) found some organic salts, such as p-phenylenediamine dihydrochloride, effectively prevented K absorption on vermiculite, even though the vermiculite was expanded. He proposed that the cation exchange sites were 'clogged' with those organic cations which K could not displace, with the result that the K was unable to enter the internal vermiculite surface. If this is true, after the vermiculite is saturated with those organic cations, it should act as a homogeneous diffusion system. Figure 6 indicates that with respect to both Na and Cs ions, the observed diffusion coefficient remains unchanged with diffusion time thus fulfilling the above prediction.

Regardless of Na or K saturation the kaolinite has only external surface. Figure 7 proves that both Na- and K-kaolinite are homogeneous systems with respect to the diffusion of Na ion. There is no change in apparent diffusion coefficient with time. Bentonite will not be completely collapsed by K ion saturation, thus Figure 7 shows the observed diffusion coefficients of Na ion in K-bentonite decreases with increasing time, suggesting that both external and internal surface diffusion occur. The expanded Na-bentonite certainly shows the heterogeneous property.

Graham-Bryce (32) noted that several investigators have found that ionic diffusion in soils decreased with time. Gast (27) also reported some anomalous results in measurement of cationic diffusivity in bentonite pastes. He suggested that multiple rate processes contributed from the diffuse

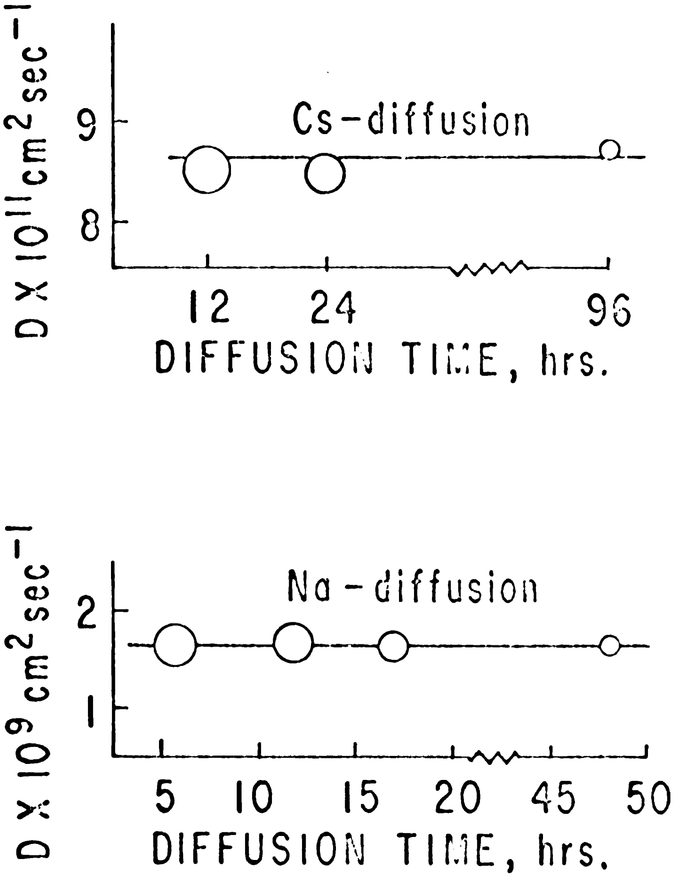


Figure 6. Relationship of diffusion time with the diffusion coefficients of Cs and Na ions in protonated p-phenylenediamine saturated vermiculite on samples equilibrated at 81.0% relative humidity (20°C). The moisture content of the sample was 7.4% by weight.

Figure 7. Relationship of diffusion time with the diffusion coefficient of Na ion in kaolinite and bentonite equilibrated at 81.0% relative humidity (20°C). The moisture contents were 1.3% in K-kaolinite, 1.7% in Na-kaolinite, 6.7% in K-bentonite, and 20.2% in Na-bentonite by weight respectively (105°C).

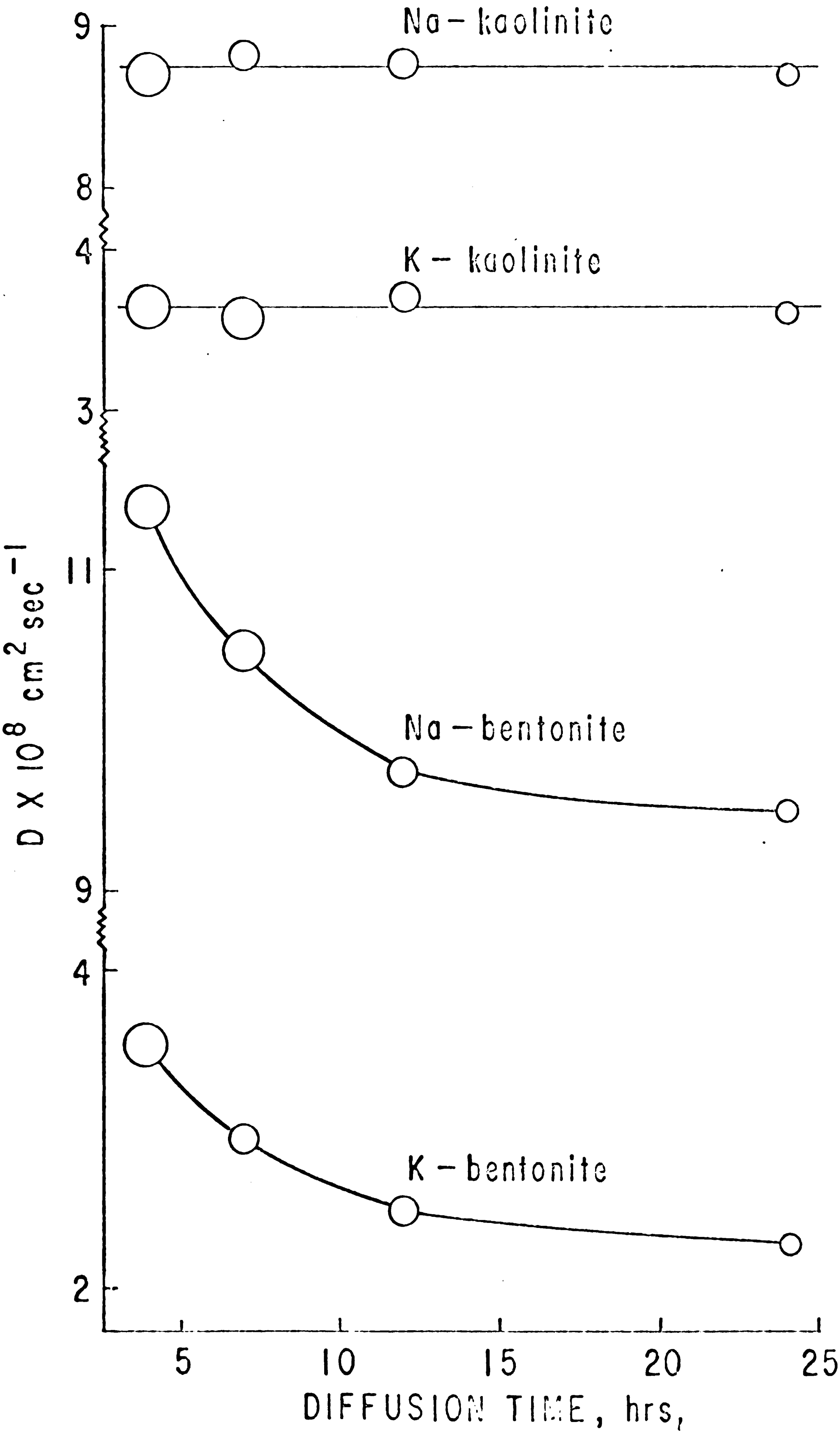

Na- kaolinite
K - kaolinite
Na-bentonite
K - bentonite
D X 10^8 cm^2 sec^{-1}
9
8
4
3
11
9
4
2
5
10
15
20
25
DIFFUSION TIME, hrs,

Figure 7

layer and true solution ions and the Stern layer ions were responsible. Meanwhile he also showed the observed diffusion coefficients of Na, Ba, and Ce decreased with time. It may be that these results can be explained as resulting from heterogeneous systems as described here.

The Diffusion Model

Several alterations of the Fisher model have been published which basically follow his idea. The grain boundary is considered as a "sink" from which the diffusant moves normally to the lattice of the polycrystalline body although in a very thin region near the exposed surface the ordinary lattice diffusion is dominant. At larger penetrations of the polycrystalline material, the lattice diffusion is no longer influenced by the exposed surface and the "boundary sinks" play the crucial role. This is the region of experimental interest in grain boundary diffusion studies. If one compares the clay system of Fig. 1 A with Fisher's original idea, it may be seen that there is a possibility of adapting this model of a heterogeneous diffusion system to clay minerals. Even in the very thin region near the exposed surface, where the proposed mathematical analysis for grain boundary can not be applied, it is possible to adapt in the clay system because the diffusant in the interlayers comes normally from the "sink" of the external surface "channel" as shown in Fig. 1 A. It is impossible to have the cation penetrate directly from the exposed surface through the crystal layer into the interlayer space under ordinary temperature conditions. Furthermore, it is seen in grain boundary diffusion that there is no significant additional penetration along the grain until β (equation [3]) > 1. Since the thickness of δ (equation [3]) of polycrystalline metals is usually very small, of the order of A, the value of D_b/D_ℓ should be large enough so that β is large in order that the grain boundary diffusion can be observed. In the case of clay minerals, δ is equivalent to the thickness of the channel formed by the external surfaces as shown in Fig. 1 A. The value of δ of clay system in ordinary conditions should be much larger than that of polycrystalline metals. With the comparison between the heterogeneous system of clays and polycrystalline metals, it seems reasonable to assume that the value of D_e/D_i in clays should be much less than that of D_b/D_ℓ in metals. Because of the larger value of δ and with the short time, the heterogeneous diffusion in clay systems is observed as shown in Figs. 4, 5, and 7.

In 1960 Levine and MacCallum (42) published their modification of Fisher's model mainly introducing a suitable empirical function to describe the loss of diffusant from the high diffusivity "sinks" into the lattice of the polycrystalline body. It was based on the observation that, in the penetration range most commonly covered in polycrystalline diffusion experiments, the log of the average concentration varied as the 6/5 power of penetration depth. A few years later Le Claire (41) rearranged Levine and MacCallum's solution in order to put it in more practical form. If D_e and D_i of clay systems are equivalent to D_b and D_ℓ of polycrystalline metals respectively, the following equation is adapted from Le Claire's report (41)

$$D_e\delta = \left(\frac{d \log c}{dy^{6/5}}\right)^{-5/3} \left(\frac{4D_i}{t}\right)^{1/2} \left(\frac{d \log c}{d(\eta\beta^{-1/2})^{6/5}}\right)^{5/3} \qquad (4)$$

where D_e = external diffusion coefficient

D_i = interlayer diffusion coefficient

c = concentration of diffusing ion

y = penetration depth

t = diffusion time

δ = thickness of the channel formed by the external surfaces of clay particles

$\eta = y/(D_i t)^{1/2}$

$\beta = (D_e\delta)/[2D_i(D_i t)^{1/2}]$

According to equation [4], the log of average concentration varies linearly with the 6/5 power of penetration depth y, in contrast with the linear correlation with y^2 in ordinary homogeneous systems at a thin-film boundary condition of Fick's law. For the purpose of verifying heterogeneous diffusion of Na in Na-vermiculite with Levine and MacCallum's equation, the pellet was sectioned with a microtome at the accuracy of 5μ, and the specific radioactivity of ^{22}Na of each slice was measured after a given time t was allowed for diffusion. Figure 8 shows results of comparing the plot

Figure 8. Specific activity of ^{22}Na versus penetration distance (y) for the diffusion of Na ion in Na-vermiculite at 4 and 24 hours.

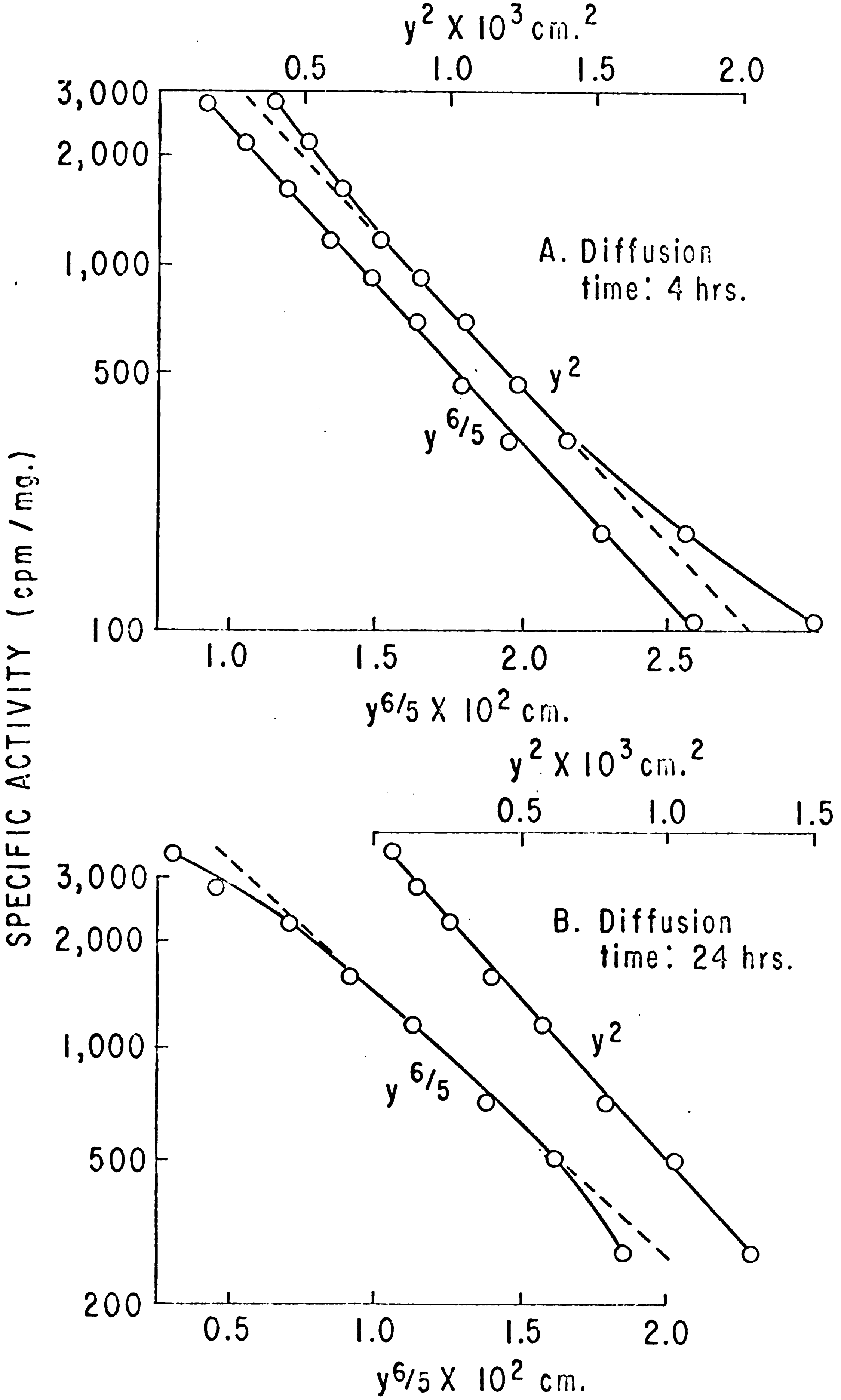

SPECIFIC ACTIVITY (cpm / mg.)
$y^2 \times 10^3$ cm.^{2}
0.5
1.0
1.5
2.0
3,000
2,000
1,000
500
100
A. Diffusion time: 4 hrs.
y^2
$y^{6/5}$
1.0
1.5
2.0
2.5
$y^{6/5} \times 10^2$ cm.
$y^2 \times 10^3$ cm.^{2}
0.5
1.0
1.5
3,000
2,000
1,000
500
200
B. Diffusion time: 24 hrs.
y^2
$y^{6/5}$
0.5
1.0
1.5
2.0
$y^{6/5} \times 10^2$ cm.

Figure 8

of log of specific activity of ^{22}Na versus $y^{6/5}$ and y^2 at a diffusion time of 4 hours. The linearity of log c versus $y^{6/5}$ reveals the possibility of Levine and MacCallum's modified model applying to clay systems. By the time of 24 hours for the diffusion of Na ion in Na-vermiculite under these experimental conditions, β becomes so small that the ordinary homogeneous diffusion plays the dominant role. Therefore, experimental results as plotted in Fig. 8 indicate that at 24 hours diffusion time, log c varies linearly with y^2, not $y^{6/5}$. Results obtained at 10 hours diffusion time indicated lack of complete linearity for both $y^{6/5}$ and y^2.

If any two values of D_e, D_i, and δ are known, the third value can be calculated from equation [4], because $d\log c/dy^{6/5}$ is the slope of a plot of $\log c \sim y^{6/5}$ at a certain time t. To the author's knowledge none of the 3 values for clay systems are available. However, given a certain clay system under uniform conditions the 3 values, D_e, D_i, and δ should be constant. In addition Le Claire (41) has reported that for practical purposes, when β is large (2-10), $d\log c/d(\eta\beta^{-1/2})^{6/5}$ approaches a constant value of 0.78. Then, if β is in the range of 2-10, equation [4] is written as follows

$$D_e\delta/D_i^{1/2} = (0.78)^{5/3}\left(\frac{d\log c}{dy^{6/5}}\right)^{-5/3}\left(\frac{4}{t}\right)^{1/2} \qquad (5)$$

Diffusion time is the only factor necessary to change in order to test the constancy of β under the experimental condition in this study. If β is constant, then the value of

$D_e\delta/D_i^{1/2}$ should not change with various diffusion times. Following are the experimental results obtained by finding the slopes of log c $\sim y^{6/5}$ at various diffusion times and then calculated according to equation [5]

Diffusion time, Hr.	$D_e\delta/D_i^{1/2} \times 10^5$
4	1.59 ± .18
6	1.61 ± .05
8	1.80 ± .16

It is seen that for the varying diffusion times above for Na ion diffusing into Na-vermiculite the constancy of D_e, D_i, δ and β are as described in equation [5].

Evaluation of Diffusion Coefficients in the Heterogeneous System

As the observed diffusion of Na ion into Na-vermiculite consists of external and interlayer surface diffusion, the observed apparent coefficient (D_o) is the average contribution from D_e and D_i. It is of interest to attempt to evaluate those two coefficients in the heterogeneous system. In a heterogeneous system the observed flux of diffusant along the concentration gradient is the sum of the flux of the external surface channel and of the interlayer pathway, and for the homogeneous system the observed flux is that of external diffusion only. When the heterogeneous clay system is oriented such that the observed flux is parallel to the external surface channel as shown in Fig. 1 A, it is less than that in the homogeneous situation because of leakage perpendicularly to the interlayer positions. As shown previously D_e is larger than D_i, the flux in the external surface channel should be larger than that in the interlayer space. Therefore, in this particular case the observed flux in the heterogeneous system is the result of movement through the external pathway modified by leakage to the internal pathway. For

$$\text{Flux} = -D \frac{dc}{dy} \qquad (6)$$

where c is the concentration of diffusing ion, y is the penetration depth and D is the diffusion coefficient, since only the absolute value of the flux is of interest in this case, the following equation should be true

$$D_o \frac{dc_o}{dy_o} = D_e \frac{dc_e}{dy_e} - D_i \frac{dc_i}{dy_i} \qquad (7)$$

where the subscripts o, e, and i stand for observed, external, and interlayer respectively. For diffusion of Na ion in Na-vermiculite, values of D_o, dc_o, and dy_o can be obtained experimentally. In order to get the values for the external surface diffusion in the Na-vermiculite system, the author prepared a vermiculite system which is collapsed by K ion yet saturated with Na ion on the exchange sites of the external surface. The purpose of this was to study Na diffusion in Na-vermiculite where internal surface had been eliminated as a diffusion pathway. The Na-K-vermiculite system was prepared by using the K-vermiculite previously described in this study, and then passing the suspension of K-clay through a Na-IRC-50 resin column. After columning, the Na-K-vermiculite suspension was freeze dried immediately. The X-ray pattern of this Na-K-clay showed the spacing of 10.4A with a little broader peak than that of K-system. The behavior of homogeneity in diffusion of Na ion of the Na-K-system was also tested as shown in Fig. 4. It indicates that it is characterized pretty well as a homogeneous diffusion system since the Na ion showed little change in diffusion coefficient with time. An indirect method was utilized to calculate dc_i and dy_i of equation [7] and is described in the following section.

N-Methylacetamide (NMA) is a high dielectric constant organic solvent (165 at 40°C, 19) in which many inorganic salts are quite soluble, and in which clay minerals can be suspended as well as in water. After freeze dried Na-vermiculite was dehydrated as much as possible by vacuum pumping, it was suspended in NMA at 40°C (the freezing point of NMA is 30.6°C) over-night. The Na-vermiculite was found to be collapsed as indicated by the spacing of 10.1A, although upon exposure to the atmosphere this system gradually reexpanded as water was absorbed. The radioisotope dilution method was applied to measure the total exchangeable Na ion in Na-vermiculite in water suspension with a value found of 141.4 m.e./100 g (the cation exchange capacity of the same sample measured by ordinary $CaCl_2$ saturation method was 150.0 m.e /100 g). The same technique was used to measure the amount of Na ion of Na-vermiculite in NMA, it was only 16.6 m.e./100 g. For the purpose of comparing chemical behavior of vermiculite in NMA and in water, the absorption of Cs ion by different systems in those two solvents was measured by ^{134}Cs tracer technique. The following results were found.

	Absorption of Cs ion at 40^{0}C m.e./100 g
K-vermiculite in water	26.7
K-vermiculite in NMA	28.6
Na-vermiculite in water	121.5
Na-vermiculite in NMA	29.2

It shows clearly that in K-clay the difference in absorption of Cs ion between these two solvents is very small. The great difference between the two solvents for the Na-system is due to the fact that Na-vermiculite is collapsed in NMA, so that the absorption of Cs ion is limited mainly to external surface, and behaves in a manner similar to the collapsed K-system. The value of 141.4 m.e./100 g is considered as total exchangeable Na ion for Na-vermiculite, and that of 16.6 suggested as the amount of Na ion on the external surface only. The percentage of exchange sites for Na ion in the interlayer space of Na-vermiculite can then be calculated as $[(141.4 - 16.6)/141.4] \times 100 = 88.3\%$.

After the diffusion of Na ion proceeded for 6 hours, specimens of Na-vermiculite and of Na-K-vermiculite were sectioned and specific activity of ^{22}Na was determined as described previously. The values of D_o and D_e were measured from Na- and Na-K-clays respectively, and the values of dc_o, dy_o, dc_e, and dy_e were read from the plots of log c versus penetration depth. The value of dc_i was calculated from dc_o based on the value of 88.3% of interlayer exchange sites in comparison with the total sites of the system. It was assumed that at any point in the system, the diffusing Na was distributed between the external and internal exchange sites in proportion to the relative distribution of external and internal exchange sites. All the experimental and calculated values were then put into equation [7] as follows

$$1.10 \times 10^{-8} \times \frac{85.3}{0.03} = 3.01 \times 10^{-8} \times \frac{45.3}{0.03} - D_i \times \frac{75.3}{0.03} \quad (8)$$

The value found for D_i was 0.57×10^{-8} cm^2 sec^{-1}. For diffusion of Na ion in Na-vermiculite in these experimental conditions, the ratio of D_e/D_i is then 3.01×10^{-8} cm^{2}sec^{-1}/ 0.55×10^{-8} cm^2 sec^{-1} = 5.28.

V. ORIENTATION EFFECTS

Theoretical Considerations

Cationic diffusion in the clay minerals with very low moisture content is suggested to be a movement along the surface. Figure 9 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. 9, 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. 9:

$$BC = (w^2 + h^2)^{1/2} \tag{9}$$

$$y = BE = BC \cos(\theta - \Phi) \tag{10}$$

or

$$y = (w^2 + h^2)^{1/2} \cos(\theta - \Phi) \tag{11}$$

Since the mean square displacement (ΔP^2) of diffusion at time t is (34)

$$\Delta P^2 = 2Dt \tag{12}$$

When the diffusion time t is constant, equation [12] may be written as

$$D = k\Delta P^2 \tag{13}$$

where k is a constant. If y in Fig. 9 is a displacement of diffusion at a certain diffusion time t, as $y^2 = \Delta P^2$ the following equation is obtained:

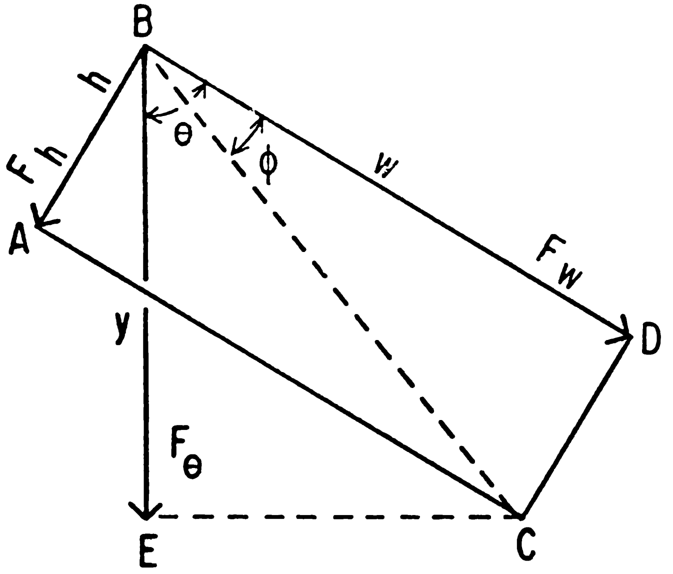


Figure 9. Model used for analysis of diffusion pathways on the surface of a platy particle seen edgewise and oriented at an angle θ with respect to the diffusion flux.

$$D = k(w^2 + h^2) \cos^2 (\theta - \phi) \qquad (14)$$

For a definite particle size, w and h are constant, equation [14] may be shown as

$$D = k' \cos^2 (\theta - \phi) \qquad (15)$$

where k' is another constant representing $k(w^2 + h^2)$ of equation [14] If plots of D versus $\cos^2 (\theta - \phi)$ 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

$$\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1 \qquad (16)$$

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

$$D_{\alpha\beta\gamma} = D_\alpha \cos^2 \alpha + D_\beta \cos^2 \beta + D_\gamma \cos^2 \gamma \qquad (17)$$

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 [17], $\gamma = 90^0$, $\alpha + \beta = 90^0$, say $\beta = 90^0 - \alpha$, and equation [17] may be written as

$$D_{\alpha\beta} = D_\alpha \cos^2 \alpha + D_\beta \sin^2 \alpha \qquad (18)$$

This general equation can be applied to the condition as shown in Fig. 9. 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 [18] becomes

$$D_\theta = D_w \cos^2 \theta + D_h \sin^2 \theta. \qquad (19)$$

This equation also describes the relationship that exists between the diffusion coefficients parallel and perpendicular to the c-axis of the lattice of noncubic metal crystals (72).

Effect of Orientation on Diffusion

Figure 10 shows the apparent diffusion coefficients of Na ions into K-vermiculite pellets at $20^0 \pm 0.05^0$C under 81.0% 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. 2, the angle θ in Figs. 2 and 9 should be the same. According to equation [15] the apparent diffusion coefficients vary linearly with $\cos^2 (\theta - \Phi)$. D and θ in equation [15] were experimentally found, and Φ could be found by trial-and-error method to fulfill equation [15]. For 2 - 5μ K-vermiculite used in this study the Φ was found to be 10^0, and that of < 2μ was 6^0, the resulting straight lines as shown in Fig. 10. The angle Φ can be used to calculate the axial ratio (width:height) of

Figure 10. Relationship of $\cos^2 \theta$ and $\cos^2 (\theta - \phi)$ with the diffusion coefficient of Na ion in K-vermiculite oriented at various angles of θ with respect to the diffusion flux and equilibrated at 81.0% relative humidity (20°C).

The moisture contents of 2-5μ and < 2μ particles of K-vermiculite were 3.9 and 3.6% by weight respectively (105°C).

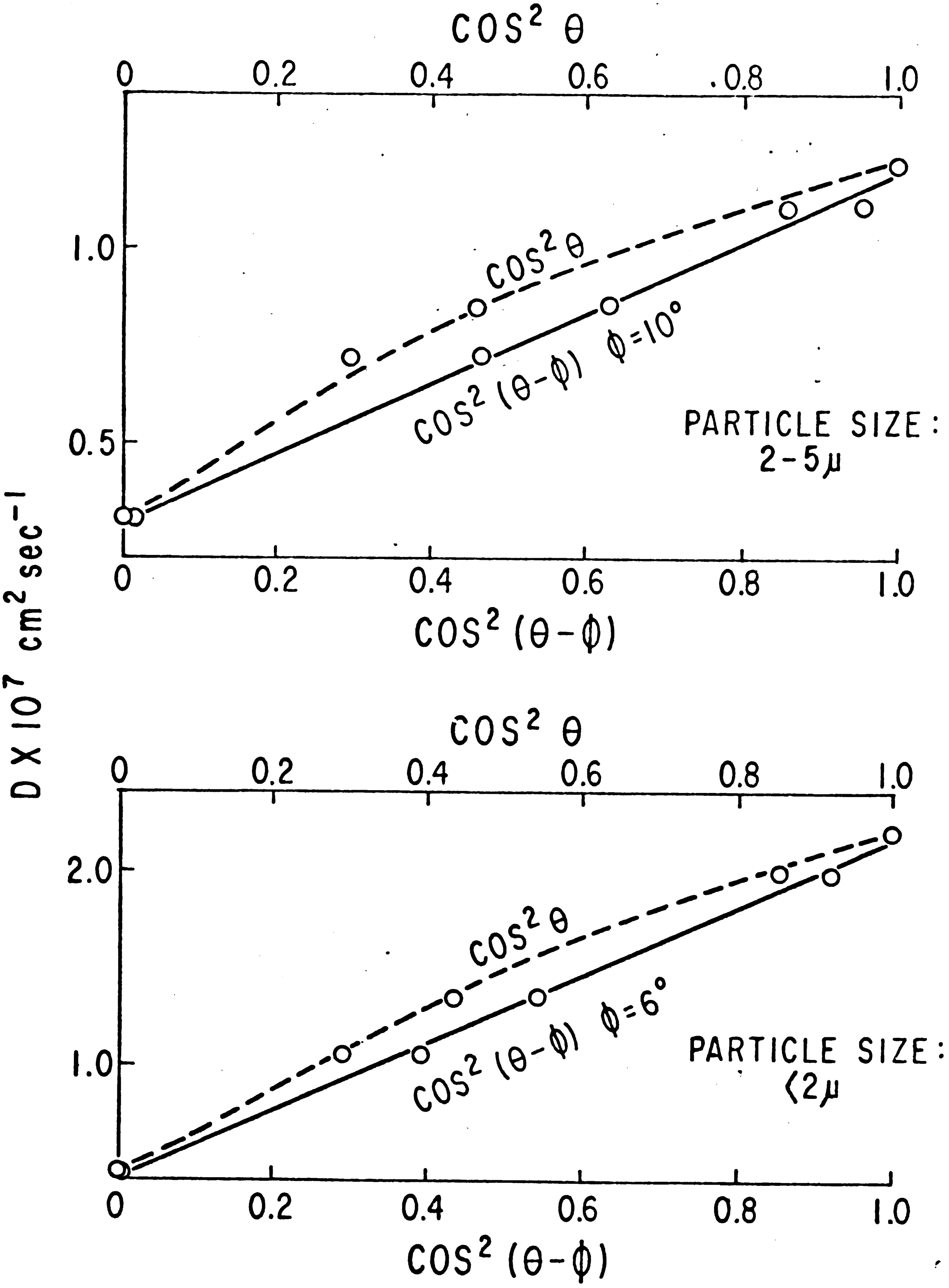

COS² θ
0
0.2
0.4
0.6
0.8
1.0
1.0
0.5
COS² θ
COS² (θ-φ) φ=10°
PARTICLE SIZE: 2-5μ
0
0.2
0.4
0.6
0.8
1.0
COS² (θ-φ)
D X 10⁷ cm² sec⁻¹
COS² θ
0
0.2
0.4
0.6
0.8
1.0
2.0
1.0
COS² θ
COS² (θ-φ) φ=6°
PARTICLE SIZE: <2μ
0
0.2
0.4
0.6
0.8
1.0
COS² (θ-φ)

Figure 10

the platelet from which the "true" diffusion coefficient can be evaluated. This will be discussed later in this study.

If the angle θ in Figs. 2 and 9 is the same as mentioned in the above section, from equation [19] 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. 2 is oriented at either 0^o or 90^o experimentally, these two observed diffusion coefficients are assumed equivalent to D_w and D_h of equation [19]. Table 1 shows both observed values of D_h and D_w at 90^o and 0^o 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 2-5μ and < 2μ particles of K-vermiculite.

Orientation Effects in Heterogeneous System

Both equations [15] and [19] 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 shown in Fig. 4. From Fig. 10 and Table 1 it is apparent that this homogeneous system follows equations [15] and [19]. It is of interest to see the application of these two equations to a heterogeneous diffusion system. As indicated in Fig. 4, the Na-vermiculite has shown heterogeneous behavior. The effect of orientation on the diffusion of Na ion in clay size Na-vermiculite was

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

θ	$D_\theta \times 10^7$ ($cm^2\ sec^{-1}$)	$D_h \times 10^7$ ($cm^2\ sec^{-1}$)	$D_w \times 10^7$ ($cm^2\ sec^{-1}$)
Particle size: 2-5μ			
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: < 2μ			
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 [19].

measured the same way as that of K-vermiculite. Figure 11 shows the results which the apparent self-diffusion coefficients of Na ion in vermiculite versus $\cos^2 \theta$ is plotted. When Fig. 11 is compared with Fig. 10, the differences are apparent. In Fig. 10 with K-vermiculite, the D versus $\cos^2 \theta$ has a convex curvature, so that a D versus $\cos^2(\theta - \phi)$ resulting in a straight line as described in equation [15] can be found. With Na-vermiculite as shown in Fig. 11 it is a concave curve from which the angle ϕ cannot be obtained as in K-vermiculite. It appears that the equation [15] cannot be directly applied to the heterogeneous Na-vermiculite system as in the case of homogeneous K-vermiculite.

Equation [19] 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 0^0 and 90^0 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

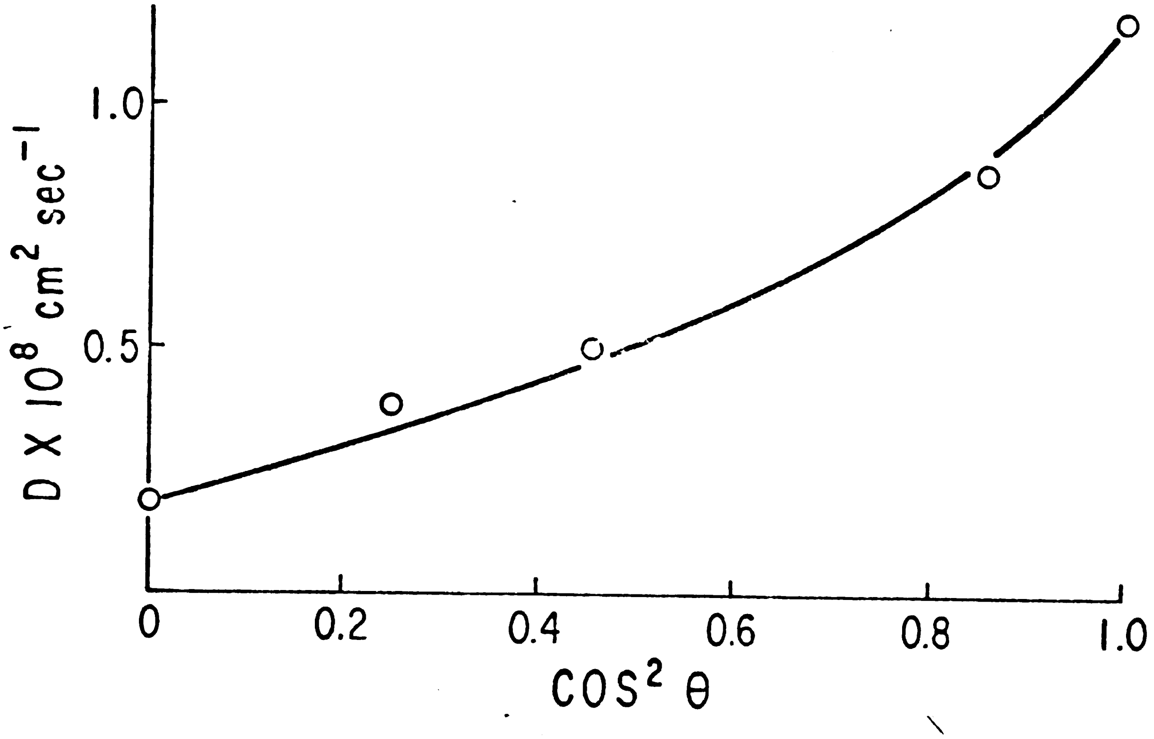


Figure 11. Relationship of $\cos^2\theta$ with the diffusion coefficient of Na ion in Na-vermiculite oriented at various angles of θ with respect to the diffusion flux and equilibrated at 81.0% relative humidity (20°C).

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

θ	$D_\theta \times 10^8$ (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 [19].

two effects may be considered as the factors affecting the "true" diffusion coefficient in a particular clay mineral 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 (12,40,50). Cremers and Thomas (16) applied a "formation factor" equation in the study of self-diffusion of Na ion in a suspension of montmorillonite, and Cremers and Laudelout (17) 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 (49).

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 $D_t = F\ D_o$. 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 (50). If in a given medium the porosity is constant, the formation factor relates 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 (80):

$$\frac{1}{A}\ \frac{dN}{dt} = -D\ \frac{dC}{dy} \tag{20}$$

where dN refers to a net flow of ions through area A at a time interval dt, and dC/dy is the concentration gradient. It shows that the diffusion coefficient is inversely proportional to area, when other conditions are equal. Therefore, it is easily seen that the following relationship holds:

$$\frac{D_{tp}}{D_o} = \frac{A_o}{A_e} \tag{21}$$

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. 9) is at 0^0 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 changes to 90^0 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. 9), 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 0^0 or 90^0, 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 $\theta = 0^0$, the flux direction is parallel to the width and when $\theta = 90^0$, 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 $\theta = 0^0$ and that of width in case of $\theta = 90^0$, it is considered as two-directional movement. In this situation, the average diffusion area is half of the physical dimension. The above development relates to Barrer's (4) discussion of infinite and semi-infinite systems. Therefore, the observed total diffusion area may be calculated as follows:

θ^0	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 [21] is written as

$$D_{tp} = 1/R \times D_o. \tag{22}$$

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

θ^0	Effective area factor	
0	$R = \frac{A_e}{A_o} = \frac{w \times b}{(w + h/2) \times b} = \frac{w}{w + h/2}$	(23)
90	$R = \frac{A_e}{A_o} = \frac{h \times b}{(h + w/2) \times b} = \frac{h}{h + w/2}$	(24)

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 [15] the angle Φ of K-vermiculite used in this study was found to be 10^0 for $2\text{-}5\mu$, and 6^0 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 (69), 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 [23] and [24], the D_{tp} can be then calculated from the experimentally observed diffusion coefficient (D_o) according to equation [22]. The calculated values of D_{tp} and R, the experimentally obtained data of w:h and D_o at angle $\theta = 0^0$ and 90^0, and also the apparent density of the pellets of both 2-5μ and < 2μ particles of K-vermiculite, are listed in Table 3. It shows that for both 2-5μ and < 2μ particles the two calculated values of D_{tp}, from D_o at $\theta = 0^0$ and 90^0, 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, 2-5μ and < 2μ, of K-vermiculite were prepared the same way by pressing in a die under 1,000 pounds per square inch pressure, the apparent density of the pellet of 2-5μ particles was smaller than that of < 2μ particles as shwon in Table 3. The porosity of these two kinds of specimens should then be

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 $\theta = 0^0$ and 90^0 with respect to the diffusion flux of Na ion in two different particle sizes and apparent densities of K-vermiculite pellets.

θ	w:h	R	$D_o \times 10^7$ ($cm^2 sec^{-1}$)	$D_{tp} \times 10^7$ ($cm^2 sec^{-1}$)
Particle size:		2-5μ	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:		< 2μ	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

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 overall 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 (32) and Phillips and Brown (63,64) 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 1.8×10^{-8} to 8.1×10^{-8} cm sec^{-1} (32). In these two papers, they both attempted to explain the effect of bulk density on diffusion based on the basis of "hopping distance" (which has the same physical meaning as jump distance (72), that is used in the modern terminology in diffusion) as reported by Lai and Mortland (37, 38). The increase of clay content and bulk density resulted in a shorter average "jump distance" between particles, and the overall result is the increase of diffusion rate.

VI. CONCLUSIONS

1. This study shows that at least two cationic diffusion pathways are possible in clay minerals at very low moisture content. For 1:1 clay minerals which have external surface only, and collapsed or clogged 2:1 minerals where the cation cannot move into the interlayer space, there is only one pathway and may be considered as a homogeneous system. The expanded 2:1 clay minerals are heterogeneous diffusion systems in which cationic movement can take place along external surfaces and through the interlayer regions of the minerals.

2. In these particular experiments the diffusion coefficient of Na ion on the external surface of Na-vermiculite was about 5 times larger than in the interlayer surface. The much greater magnitude of Na diffusion in the homogeneous system (Na-K-vermiculite) compared with that of Na into the heterogeneous system (Na-vermiculite) is easily explained by the above results.

3. There are two basic assumptions on the application of equations [15] and [19] to the cationic diffusion in clay minerals: (i) the system should have an external surface diffusion pathway only, and (ii) the diffusion specimen should be perfectly oriented. Because of the homogeneity of the diffusion pathway of K-vermiculite, experimental results show that the diffusion of Na ion in these systems, both 2-5μ and $< 2\mu$ particles, conformed with equations [15] and [19].

4. The preparation of the clay pellets resulted in a high degree of orientation of the clay platelets. The observed values of diffusion coefficients of Na ion in K-vermiculite showed considerable difference between specimens oriented at 0^0 and 90^0 with respect to the direction of diffusion flux. The calculated "true" coefficients in a given size particle system agreed very closely however, regardless of direction of diffusion. This supports the homogeneous nature of cationic diffusion in K-vermiculite.

5. The diffusion of Na ion in Na-vermiculite, a heterogeneous diffusion system, did not show conformity with equations [15] and [19]. Based on this and other results from this investigation, it suggests that cationic diffusion studies in clay minerals must consider the nature of the system and whether or not it has homogeneous or heterogeneous properties.

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