

SELF-DIFFUSION OF EXCHANGEABLE CATIONS IN BENTONITE¹

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ABSTRACT

A special integral form of the solution of Fick's law was applied to study the self-diffusion of Na, Cs, and Ca ions in Wyoming bentonite plugs by means of a radioactive tracer technique. A simple procedure for measuring diffusion coefficients was developed by depositing a thin radioactive tracer film on the surface of clay mineral plugs at controlled temperatures. Thin sections of the clay plugs were removed and radioactivity measurements made on the portion of the plugs remaining. The self-diffusion coefficients of the ions were evaluated by a graphical method from the solution of Fick's law at special boundary conditions. Under oven-dry conditions at 105 °C, diffusion of Na ion in a bentonite film was observed, while in the same experiment, SO_4^{2-} ion did not diffuse. In a clay-water system, however, the anion diffused much more rapidly than the cation. Based on the experimental results of observing Na^{22} - and S^{35} -tagged Na_2SO_4 diffusion, different diffusion paths were proposed using a picture of the clay matrix as a structure with "channels." Diffusion coefficients of exchangeable cations decreased with increasing clay contents. From the results of activation energy and self-diffusion coefficients of Na and Ca ions at various clay-water concentrations, the relative "hopping distances" of diffusing ions were calculated and discussed. It is suggested that in the self-diffusion of exchangeable Na ion in bentonite the ion could be hopping from one individual clay plate to another, and the Ca ion from one "package" of plates to another "package" of plates.

INTRODUCTION

Diffusion is a process by which ions, atoms or molecules move randomly from one position to another. Theoretically this process is involved in various kinds of transport phenomena, and the study of diffusion will lead to an understanding of the microscopic nature of various kinds of particle movement. The extensive work on diffusion by Boyd and co-workers (1947, 1953) has thrown light on the mechanisms of ion exchange in resins. Several workers (Kitchener, 1957, p. 59) have confirmed their work. Recently, the results obtained by Mortland and Ellis (1959) have indicated that the release of fixed K from vermiculite is a diffusion-controlled process.

The study of ion mobilities in ion exchangers is of both theoretical and

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practical interest. Figures for ion mobilities can be derived from diffusion coefficients under certain circumstances. Spiegler and Coryell (1953) have demonstrated the relationship between the diffusion coefficients and ion mobilities in resins. By means of layer analysis Bloksma (1957) measured the self-diffusion coefficients of sodium and iodide ions in clay-water pastes and calculated the mobility of adsorbed ions on montmorillonite and kaolinite. For a better understanding of the nature and rate of diffusion of ions, Husted and Low (1954) have studied the counter-diffusion of K with Li, Na, and NH_4 ions through bentonite plugs.

Diffusion studies may be utilized to elucidate the structure of the system as regards the transport properties concerned. Several equations have been derived to show the relation between the diffusion coefficient and the vibrating frequency of diffusible ions or atoms. These equations also can be used to calculate the distance between equilibrium sites (deBoer, 1953, p. 227; Glasstone, Laidler, and Eyring, 1941, p. 524; Dushman and Langmuir, 1922). Fujii and Thomas (1958) have studied the structure and composition of agar by self-diffusion measurements. The correction between the diffusion coefficient and the cross-linkage of resins has been studied by several workers (Boyd, Soldano, and Bonner, 1954; Despic and Hills, 1956).

A knowledge of diffusion in clay minerals is of importance for interpreting and understanding the rate, behavior, and nature of ion movement in clays. Interdiffusion, by which one species of ion moves in one direction while another moves in opposite direction, is complicated because the two kinds of ions do not have the same behavior. The simplest and most rigorous kind of diffusion study that can be made is that of self-diffusion in which the difference between two interdiffusing substances vanishes. Foreign ions are not introduced into the system for self-diffusion measurements; consequently, the results are more straight forward than those of interdiffusion of dissimilar ions. It may be, therefore, that such studies will reveal more precise information concerning the mechanism of ion transport phenomena in clays than other types of studies. Even for this more simplified case, a number of variables influence the self-diffusion of the exchangeable cations of clays, among which are presumed to be the nature of the clay, properties of the water in proximity to the clay surface as well as those of free water, and distance between successive equilibrium positions of diffusing exchangeable cations.

Radioactive tracer techniques have been introduced for measuring the interdiffusion of isotopes in an approach to self-diffusion. This technique also offers the advantage of measuring a very dilute concentration thus obtaining a determination of the diffusion coefficient without effect by the concentration. However, most diffusion work has been carried out at rather high concentration ranges and with complicated methods or proce-

dures. A simple and accurate method for measuring self-diffusion is needed for extensive studies of this process in clays.

With these ideas in mind, this study has been carried out for the purpose of developing a simple method for measuring self-diffusion coefficients of exchangeable cations in clay-water plugs. A mechanism of ion diffusion in clay-water systems has also been proposed based on the experimental results from the determination of self-diffusion coefficients and activation energies at various clay concentrations.

EXPERIMENTAL METHODS

Theoretical Considerations

Differential solution of Fick's law of diffusion can be applied to various diffusion systems under a variety of boundary conditions. When a definite quantity Q of substance is deposited as a uniform and infinitely thin layer on the surface and allowed to diffuse into an infinitely thick diffusion medium, this boundary condition can be treated as Fick's law for instantaneous sources, and the following solution will be found (Barrer, 1951, p.45):

$$C_x = \frac{Q}{\sqrt{(\pi D t)}} e^{-x^2/4Dt}, \quad (1)$$

where C_x is the concentration of the diffusing substance at time t and distance x from the initial boundary and D is the diffusion coefficient. When the diffusing time t is constant, eq. (1) may be written as

$$\log C_x = \text{constant} - (0.1086/Dt) x^2. \quad (2)$$

If plots of $\log C_x$ versus x^2 are made, a straight line should result and its slope should be a function of diffusion coefficient D .

The experimental method used in this study was tested to see whether the special boundary conditions as described by eq. (1) were fulfilled. A small drop (less than 10λ) of Na^{22} -tagged NaCl solution was placed on the surface of Na-bentonite plug (the method for preparing clay sample and the detailed procedures will be given below) and allowed to diffuse until time t . The clay plug was cut into slices with a razor blade. The thickness of each slice was measured and the square of the distance calculated from the initial surface of the plug, which is the x^2 in eq. (1) or (2). The radioactivity of each slice was measured and the dry weight determined. The specific radioactivity of the clay was calculated and expressed as counts per minute per mg (CPM/mg), which is equivalent to C_x of eq. (1) or (2). The results are plotted in Fig. 1. The straight line in Fig. 1 established the experimental boundary conditions of diffusion, thus satisfying eq. (1), and the diffusion coefficient D could be evaluated.

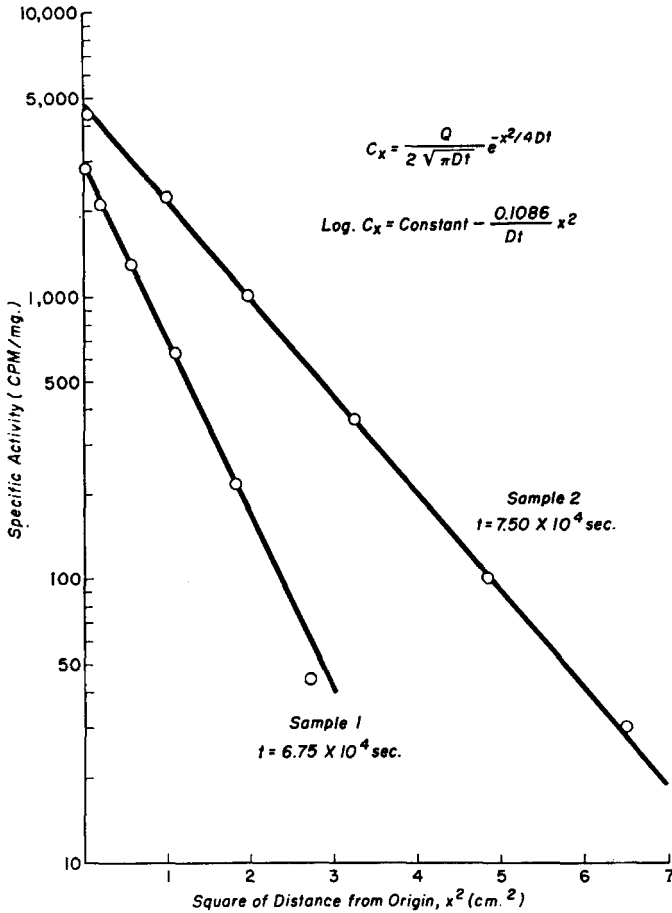


FIGURE 1.—The specific radioactivity of Na-bentonite slices vs. square of distance from the origin at two sampling times.

Preparation of Cation-Saturated Bentonite

Clay fraction ($< 2 \mu$) of Wyoming bentonite was separated by ordinary sedimentation and decantation procedures. The clay suspension was passed through a OH ion saturated anion exchange resin IR 4B column in order to remove all free anions and then passed through a column containing H ion saturated cation exchange resin IR 120. The H-clay was titrated immediately with NaOH (for preparing Na-clay) or $\text{Ca}(\text{OH})_2$ (for Ca-clay) to pH 7.0. The neutralized clay suspension was evaporated by infrared heat until it was in a gel or paste condition. Then a base-saturated and salt free clay plug was ready for diffusion experiments. Cesium-clay was pre-

pared by adding CsCl solution to a clay suspension which was then thrown down by centrifugation. This procedure was repeated four times. Four symmetries of CsCl to one of clay were added the first time. Three, two, and one symmetry values were added at the second, third, and fourth time respectively in order to obtain as complete Cs saturation as possible. Double-distilled water was used to wash out the excess CsCl in the clay until the extract was free from chloride by AgNO₃ test. The clay content of the gel or paste was restricted to certain limits in order to obtain the proper consistency with which to work. If the gels or pastes were too stiff, it was not possible to place them in the hypodermic syringes in which diffusion proceeded, without including air bubbles. If the clay content was too low, a sharp slice of clay gel or paste could not be obtained. The above considerations therefore governed the clay contents of the gels or pastes.

Diffusion Measurement

A radioactive tracer technique was used for measuring self-diffusion coefficients with diffusing time t as a constant, and the concentrations, in this case radioactivity, at various distances x from the initial boundary were measured. The base-saturated and salt-free bentonite gels or pastes were carefully placed in a 2-ml hypodermic syringe from which the tip had been removed. Precautions were taken to exclude air bubbles. A smooth surface of the clay plug was obtained by slicing it along the top edge of the syringe with a razor. A tiny drop (less than 10 λ) of Na²²-, Cs¹³⁴-, or Ca⁴⁵-labeled chloride salt solution was deposited as a thin film on the top of the plug in the syringe. The amounts of radioactive substance added in each experiment were of a magnitude to give the most desirable counting rates. The quantities of radioisotope-tagged salt solution should be high enough to provide high counts with the benefit of a low standard error. However, the counting rate can not be so high that there has to be a correction for the coincidence loss of the counting instrument. On the other hand, the specific activity of the tagged solution should be high enough to keep the concentration of stable salts low enough that diffusion is not affected by salt concentration. For the particular geometry conditions of the counter used in this experiment, the total radioactivity used in each measurement was 1-2 μ c. The amount of stable salt used in the various experiments was 4×10^{-3} meq of NaCl in solution, 2×10^{-6} meq of CsCl in solution, and 1×10^{-3} meq of CaCl₂ in solution, respectively.

The clay pastes or gels, syringes, and radioisotope-labeled solutions were equilibrated in a preset constant temperature chamber at least 2 days before the diffusion experiments were made. After the radioactive solution was deposited, the syringe was covered with a polyethylene sheet in order to prevent evaporation and to keep the water within the clay plugs in a

nonchanging state. After a preselected time, usually 1 or 2 days, the clay plug in the syringe was placed in a vertical position directly under the counter and the radioactivity recorded. This was the activity at zero distance ($x = 0$). The syringe was taken off immediately, and some of the clay gel extruded by forcing it out with the plunger. After recording the extent of the extrusion (x), it was sliced off with a razor blade and the radioactivity of the remaining plug was measured. For every slice of clay plug that was cut off, the corresponding radioactivity of the plug remaining in the syringe was measured. In general for Na or Cs diffusion, six measurements were made, while seven or eight were made in the Ca diffusion experiments. The radioactivity of Na^{22} and Cs^{134} was measured by a scintillation counter with a NaI(Tl) crystal, and Ca^{45} by a thin mica end window Geiger-Mueller counter. The diffusion experiments were conducted in duplicate, the diffusion coefficients reported being the average between duplicates.

Evaluation of Diffusion Coefficients

Theoretically, the diffusion coefficient can be evaluated from the slope of the straight line in Fig. 1. However, the distance x in Fig. 1 was an average value, since the exact value of x could not be measured at that particular experimental condition. Therefore, D , the diffusion coefficient, cannot be obtained very precisely from Fig. 1. Figure 1 shows only that the experimental technique obeys Fick's law at special boundary conditions. In the author's particular experimental technique, the procedure used by Anderson and Richards (1946) for measuring self-diffusion coefficients of lead in lead sulfide and by Jakubovic, Hills and Kitchener (1958) for resins, can be applied for evaluation of D .

In this experimental condition, the total radioactivity of the clay plug was measured at the surface of the plug. A portion of the activity underneath the surface is absorbed by the clay, and this kind of absorption follows the familiar exponential law:

$$I = I_0 e^{-kx}, \quad (3)$$

where I_0 is the measured activity without absorption and I , the activity observed through an absorber of thickness x with absorption coefficient k . Therefore, any radio tracer at a distance x below the surface will contribute an amount of measured total activity from the surface proportional to

$$C_x e^{-xk} dx. \quad (4)$$

Therefore, the total activity recorded at the surface of clay plug will be

$$A_0 = \frac{Q}{\sqrt{(\pi Dt)}} \int_0^{\infty} e^{-(x^2/4Dt + kx)} dx. \quad (5)$$

Similarly, when the surface of plug has been sliced down to a depth x below the original surface, the radioactivity measured at the new surface will be given by

$$A_x = \frac{Q}{\sqrt{(\pi D t)}} \int_0^\infty e^{-(x^2/4 D t + kx)} dx. \tag{6}$$

Put

$$y = \frac{x}{2 \sqrt{(D t)}} + k[\sqrt{(D t)}], \tag{7}$$

and integrating between $y = y_0 = k \sqrt{(D t)}$ and $y = \infty$, the following equation will be obtained:

$$A_0 = Q e^{k^2 D t} (1 - \operatorname{erf} y_0), \tag{8}$$

where $\operatorname{erf}(y)$ is called the error function or probability integral. Eq. (6) can also be written in the same way as

$$A_x = Q e^{k^2 D t} (1 - \operatorname{erf} y). \tag{9}$$

Combining eqs. (8) and (9),

$$\frac{A_x}{A_0} = \frac{1 - \operatorname{erf} y}{1 - \operatorname{erf} y_0}. \tag{10}$$

If $A_x/A_0 \ll 1$, when the measurement of activity of the clay plug is made at any appreciable depth below the original boundary surface, since $\operatorname{erf} y_0 < 1$, eq. (10) can be reduced approximately to

$$\operatorname{erf} y = 1 - \frac{A_x}{A_0}. \tag{11}$$

The values of A_0 and A_x can be obtained from experiments described previously and the value of y can be found from $\operatorname{erf} y$ in any standard probability tables. A plot of y versus x should result in a straight line passing through the origin. The values of y and x found experimentally are plotted in Fig. 2. The fact that straight lines are obtained in Fig. 2 indicates that the experiments follow the given theoretical equations. The diffusion coefficient D can be evaluated from the straight line of slope $1/[2 \sqrt{(D t)}]$, where t is the known diffusing time.

As far as the accuracy of diffusion coefficient measurements is concerned, it may be stated that, first, the longer the diffusing time t , the less the slope of the y versus x straight line and the smaller the percentage error in the measuring distance x . This will tend to give more accurate results. However, it should be noted that, theoretically, the diffusion medium in this case should be infinite. This means that the diffusing time t cannot be so long that the radio tracer reaches the bottom of the clay plugs. Also, it

may be observed that in Fig. 2, the y value near the original boundary surface deviated from the straight line because it could not satisfy the $A_x/A_0 \ll 1$ condition. Theoretically, the use of γ -emitting or β -emitting

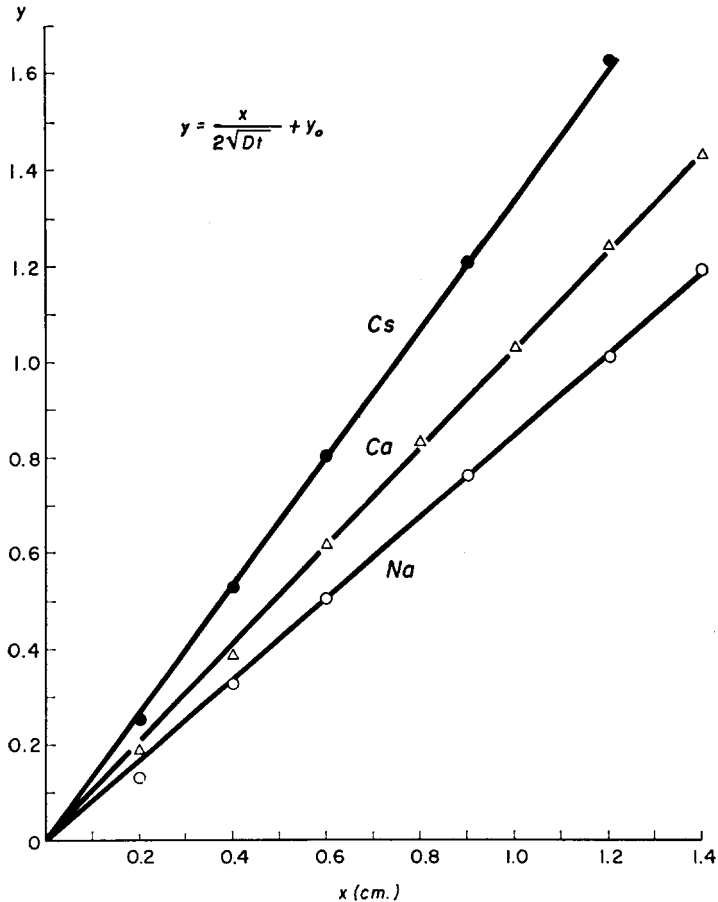


FIGURE 2.—The values of y (from eq. 11) vs. distance from the origin.

isotopes should make no difference in the diffusion measurement with respect to accuracy. However, practically, Ca^{45} is a weak beta emitter and exhibits self-absorption. Therefore, if the same amount of radioisotopes were used employing the same geometry factors and efficiency of counting system, the counting rate of Ca^{45} would be considerably lower than that of Na^{22} or Cs^{134} in the clay plugs. The result is that the standard error is lower in the Na or Cs diffusion measurements.

DISCUSSION OF RESULTS

Diffusion Path

While self-diffusion may be the simplest kind of diffusion and may be a good way to study the mechanism of particle movement, the diffusion medium should be also considered. The diffusion media used in this study were bentonite gels or pastes with high water contents. Equation (1) is the solution of Fick's general equation applied to a solid phase, and the results from Figs. 1 and 2 have shown that diffusion during the experimental conditions followed this equation very well. Therefore, the clay plugs may be considered as semisolids which have some kind of matrix structure with various size "channels." In these systems we may consider the bentonite as the negatively charged matrix with "channels" filled up with exchangeable cations and water. When very small numbers of ions are introduced to this system, there are two possible paths for diffusion: (1) the ions migrate along the surface of the matrix, and (2) the ions move along the middle of the "channel."

In order to clarify this point, Na^{22} and S^{35} in double-labeled Na_2SO_4 was deposited on the surface of a Na-bentonite plug and the diffusion coefficients of Na and SO_4 ions in the clay plug were determined simultaneously. Since Na^{22} is a γ -emitter and S^{35} a weak β -emitter it is not difficult to measure their radioactivity differentially by using a suitable absorber (to stop the S^{35} radiation) with scintillation and Geiger-Mueller counters. The diffusion coefficients of these two ions are shown in Table 1. It is obvious that the diffusion coefficient of the SO_4 ion was considerably greater than that of Na ion. Moreover, when these diffusion coefficients in clay plug are compared with those at the infinite dilution in water (Table 1), one can see that the diffusion coefficient of SO_4 ion in clay gel is very close to that in water while that of Na in clay is almost 3 times less than that of Na in water. Another experiment was conducted with Na^{22} - and S^{35} -tagged Na_2SO_4 which was placed on an oven-dried Na-bentonite

TABLE 1.—DIFFUSION COEFFICIENTS OF SODIUM AND SULFATE IONS IN NA-BENTONITE PLUG AND FILM

Ion	D ($\text{cm}^2 \text{sec}^{-1}$) in Plug at 25 °C	D ($\text{cm}^2 \text{sec}^{-1}$) in Film at 105 °C	D^1 ($\text{cm}^2 \text{sec}^{-1}$) in Water at 25 °C
Na^+ (1)	$5.35 \pm 0.11 \times 10^{-6}$	$7.4 \pm 0.7 \times 10^{-9}$	1.35×10^{-5}
(2)	$4.67 \pm 0.08 \times 10^{-6}$		
SO_4^{2-} (1)	$1.15 \pm 0.03 \times 10^{-5}$	No observable diffusion	1.08×10^{-5}
(2)	$1.27 \pm 0.04 \times 10^{-5}$		

¹ At infinite dilution (Kolthoff and Lingane, 1952, p. 52).

film for diffusion measurements. This film was placed in a 105 °C oven for 26 days after which the diffusion coefficients were determined (Table 1). In this system the diffusion coefficient of Na was $7.4 \times 10^{-9} \text{ cm}^2 \text{ sec}^{-1}$, and the movement of SO_4 ion was too low to calculate a diffusion coefficient. Hence, we may think of the cation Na moving along the surface of the matrix from one exchange site to another while the anion, SO_4 , migrates along the path in the middle of the "channel" without being particularly affected by the charged "channel wall" in the case of the clay-gel experiment. Thus the anions move faster than cations in the clay plugs. In the oven-dried Na-bentonite film, the situation was different; the "channel" was so narrow that the anions could not escape the negatively charged wall effect, thus making it very difficult to get through the "channel." The cation, on the other hand, was able to migrate along the "channel wall" by exchange reactions with the exchangeable cations. The same picture of cations moving from one fixed ionic group to another along a polymer chain while the anions pursue a straight path down the middle of the "channel" has been presented by Schlogl and Stein (1958) for cation exchange resins. Several other workers also have reported that the self-diffusion coefficients of cations were much smaller than those of anions in resins (MacKay and Meares, 1959). Other results have also supported Schlogl and Stein's mechanism (Dux and Steigman, 1958).

Effect of Concentration on Diffusion Coefficients

An external substance is needed as the diffusing source for performing diffusion measurements. Most diffusion experiments reported have been carried out at rather high concentrations of external solution. Despic and Hills (1957) reported that the self-diffusion coefficients of Na in resins depended on the concentration of the external solution. Fick's law as defined says that the diffusion coefficient should be independent of the concentration. The following experiment was conducted for the purpose of finding out the effect of concentration of the diffusing source on the diffusion coefficient measurements.

One milliliter of various concentrations of NaCl solution tagged with the same activity of Na^{22} was placed in a tube with Cenco Cellophane membrane at the bottom to support the solution. The diameter of the tube was the same as that of the syringe used for performing previously described diffusion experiments. Various concentrations of NaCl solution were placed on the Na-clay plug in the syringe. The Na ion could pass easily through the Cellophane membrane into the clay plug. The diffusion coefficients were determined in the usual way and the results are shown in Table 2. It should be noted that the membrane factor was not used in calculating D , so the value of D given in Table 2 is used merely to show the relative

values for purposes of comparison. From Table 2 it is apparent that D decreases with decreasing external concentration of NaCl solution. After the concentration is less than 0.01 N NaCl, the self-diffusion coefficients are constant and independent of concentration. The amount of Na-bentonite used in this experiment was about 0.5 g with a total cation exchange capacity of 0.4 meq, and the total volume of the clay plug about 2 ml. When 1 ml of normal NaCl solution was placed on the clay plug, the containers of the external solution and clay plug having the same diameter, the ratio of number of equivalents of external solution and the clay plug was 1:0.2. With such a large amount of Na ions introduced into the diffusion medium, it is possible that some of Na ions will move through the middle of the

TABLE 2.—SELF-DIFFUSION COEFFICIENTS OF SODIUM ION IN BENTONITE PLUGS AS A FUNCTION OF VARIOUS EXTERNAL CONCENTRATIONS OF SODIUM CHLORIDE AT 25 °C

Normality of NaCl	D^1 (cm ² sec ⁻¹ × 10 ⁶)
1.004	4.82 ± 0.09
0.104	3.48 ± 0.07
0.014	2.28 ± 0.04
0.005	2.30 ± 0.04
0.004	2.25 ± 0.04

¹ These diffusion coefficients are uncorrected for the membrane properties.

“channel.” The diffusion rate will then be faster than that at lower concentrations of external solutions where a small percentage of the total Na added can move through the “channels.” When the concentration of external solution reaches a certain point, there is no diffusion of Na ion through the middle path of the “channel,” and then the diffusion coefficient of Na ion will be independent of the external concentration. Also the high salt concentration undoubtedly affected the structure of the clay fabric, which in turn would affect diffusion. In these experiments the critical concentration of the external solution was 0.01 N, where the ratio of equivalents of the diffusing source and diffusing medium was about 1:20. Another important point indicated by these results is that if the higher external concentrations are plotted versus the self-diffusion coefficients, and extrapolated to the origin, the diffusion coefficient which is then obtained at infinite dilution will be different from that which is actually observed at the low clay concentration end of the curve. In the region where the diffusion coefficient is independent of concentration it may be assumed

that the anion added with the isotope was not acting as an agent in the diffusion of the cation and that movement was largely by exchange from one site to another.

Effect of Clay Content on Diffusion Coefficients

The diffusion medium in this study was a clay-water system. Once the clay content changes, the average size of the "channels" and the water content also change. The relationships of bentonite contents with the self-diffusion coefficients of Na, Cs, and Ca ions are shown in Table 3. All

TABLE 3.—SELF DIFFUSION COEFFICIENTS IN BENTONITE PLUGS WITH VARIOUS CLAY CONTENTS AT 25 °C

Ion	Bentonite Content (percent)	D (cm ² sec ⁻¹)	$D/W^1 \times 10^8$
Na ⁺	7.8	$6.15 \pm 0.12 \times 10^{-6}$	66.7
	8.9	$5.70 \pm 0.11 \times 10^{-6}$	62.6
	12.9	$4.47 \pm 0.09 \times 10^{-6}$	51.3
	15.2	$3.60 \pm 0.07 \times 10^{-6}$	42.4
Cs ⁺	9.8	$7.25 \pm 0.14 \times 10^{-7}$	8.0
	12.0	$5.81 \pm 0.11 \times 10^{-7}$	6.6
	14.6	$4.62 \pm 0.09 \times 10^{-7}$	5.4
	16.6	$4.00 \pm 0.08 \times 10^{-7}$	4.8
Ca ²⁺	17.9	$2.36 \pm 0.07 \times 10^{-6}$	28.7
	23.9	$1.95 \pm 0.06 \times 10^{-6}$	25.6
	28.0	$1.75 \pm 0.05 \times 10^{-6}$	24.3

¹ Percent water in system on a weight basis.

diffusion coefficients decreased with increasing clay contents in the concentration ranges used in this work, *i.e.* the range on a dry weight basis was Na-clay 8.9–15.2 percent; Cs-clay, 9.8–16.6 percent; and Ca-clay, 17.9–28.0 percent, respectively. Water was in the "channels" of the diffusion system. If the change of clay contents with the change in diffusion coefficients was due only to change in quantities of water, the ratio between diffusion coefficient (D) and corresponding water content (W) should be constant. The ratio D/W was calculated and is shown in Table 3. It can be seen that the ratio D/W decreased as clay contents increased, which suggests that some other factors must affect diffusion of exchangeable cations when the clay contents are changed. This point will be discussed later.

Activation Energy

The diffusion coefficients depend on temperature in accordance with the relation

$$D = A e^{-E/RT}, \quad (12)$$

in which E is the activation energy, A the activation constant, T the absolute temperature, and R the gas constant. The self-diffusion coefficients of Na and Cs ions were determined at 5, 15, 25, and 35 °C. A plot of diffusion coefficient (D) versus the reciprocal of absolute temperature ($1/T$) is shown in Fig. 3. The curves indicate that the activation energy of diffusion in this experiment was independent of temperature in the range from 5 to 35 °C, and that the activation energy can be evaluated from the slopes. The activation energies of self-diffusion of Na and Ca ions at different clay contents were calculated, and the results are given in Table 4. The

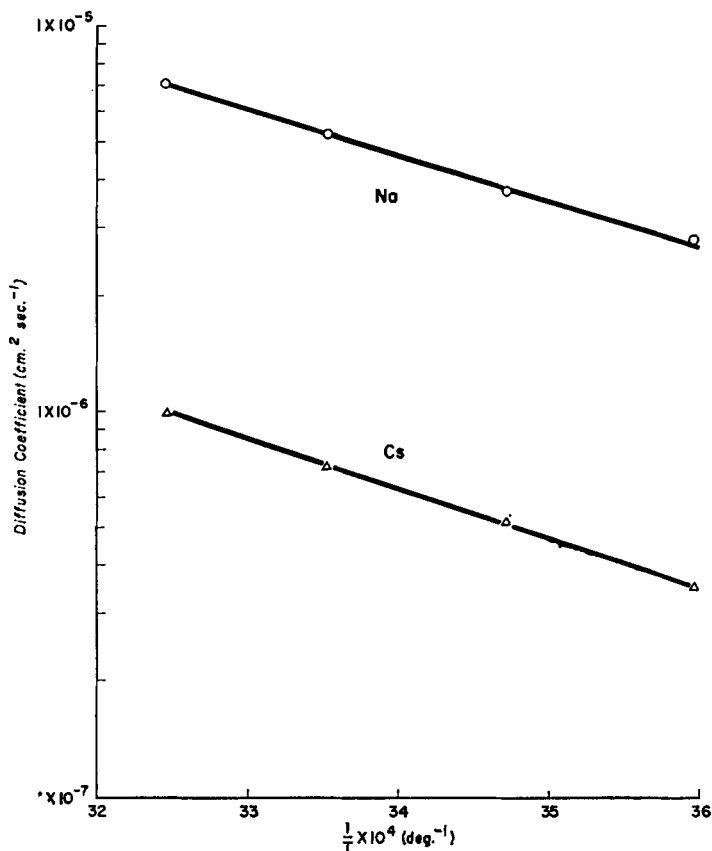


FIGURE 3.—The self-diffusion coefficients of Na and Cs ions in bentonite plugs vs. the reciprocal of absolute temperature.

activation energies of self-diffusion of Na ions were in the range from 3806 ± 114 to 6040 ± 181 cal per mole with the clay content ranging from 8.9 to 15.2 percent. The activation energies of Ca diffusion were in the range 8747 ± 262 to 10856 ± 326 cal per mole with the clay content 17.9–28.0 percent. The activation energy decreased with increasing clay contents and with decreasing diffusion coefficients in both systems of Na and Ca ions. This relationship will be discussed in detail in following sections.

TABLE 4.—ACTIVATION ENERGY AND HOPPING DISTANCE FOR SELF-DIFFUSION OF IONS IN BENTONITE PLUGS

Ion	Bentonite Content (percent)	D ($\text{cm}^2 \text{sec}^{-1} \times 10^6$)	E (cal mole ⁻¹)	a^1 (cm $\times 10^8$)
Na ⁺	8.9	5.70 ± 0.11	6040 ± 181	24.8
	12.9	4.47 ± 0.09	5176 ± 155	10.6
	15.2	3.60 ± 0.07	3806 ± 114	3.0
Ca ²⁺	17.9	2.36 ± 0.07	10856 ± 326	931
	23.9	1.95 ± 0.06	9654 ± 290	307
	28.0	1.75 ± 0.05	8747 ± 262	135

¹ The calculated hopping distance a cannot be considered an absolute value because of the uncertainty of τ_0 .

Hopping Distance of Diffusing Ions

The adsorption equilibrium may be considered a dynamic state. The adsorbed particle (molecule, atom, or ion) vibrates perpendicularly to the adsorbent surface, and each has the probability of exchanging with other particles under a dynamic condition. A picture of gas adsorption has been presented by de Boer (1953, p. 96) who illustrates the dynamic character of adsorption processes. Suppose that an adsorbed molecule at position A vibrates with respect to the surface atoms. After an average time τ_m , it will pick up energy E and hop to another adsorption spot B . It will then vibrate again until once more, after an average halting time τ_m , it will hop again. The halting time is related to energy E and temperature by the equation

$$\tau_m = \tau_0 e^{E/RT}. \quad (13)$$

The constant τ_0 is related to the time of oscillation of surface atoms of the adsorbent. Based on this idea de Boer (1953, p. 226) considered gas diffusion by surface migration as a process by which the molecule hops from one adsorption site to another. According to Kruyer (de Boer, 1953, p. 227),

the relation between diffusion coefficient (D) and distance between adsorption sites (a) for surface migration can be expressed:

$$D = \frac{1}{4} \frac{a^2}{\tau_m}, \quad (14)$$

where a is the hopping distance between adsorption sites and τ_m the time spent at a given site. Combining eqs. (13) and (14) we can write

$$D = \frac{1}{4} a^2 \tau_0^{-1} e^{-E/RT}. \quad (15)$$

It has been suggested that the exchangeable cations will migrate along the exchange sites on the surfaces of clay matrix in the diffusion process. Hence the mechanism of exchangeable cation diffusion through surface migration by hopping from one exchange site to another can be applied to these studies. The self-diffusion coefficient (D) and the activation energy (E) have been calculated; consequently, the hopping distance can be determined by eq. (15).

Based on the statistical theory of rate process the self-diffusion coefficient D is given by (Glasstone, Laidler, and Eyring, 1941, p. 524)

$$D = e d^2 (k T/h) e^{\Delta S^\ddagger/R} e^{-E/RT}, \quad (16)$$

where d is the distance between two successive equilibrium positions of a diffusing molecule, atom, or ion; k , Boltzmann's constant; h , Planck's constant; ΔS^\ddagger , entropy of the activated state; E , activation energy; R , gas constant; and T , absolute temperature. In the same diffusion system the entropy ΔS^\ddagger will be a constant; then the eq. (16) can be reduced to

$$D = K d^2 (k T/h) e^{-E/RT}, \quad (17)$$

where K is a constant including the terms $e^{\Delta S^\ddagger/R}$ and e in (16). Dushman and Langmuir (1922) have given a semi-empirical formula for diffusion in solids:

$$D = b^2 \nu e^{-E/RT}, \quad (18)$$

where b is the distance between planes of diffusing atoms or ions in the direction of diffusion, ν is the vibration frequency of the solid, $\nu = E/Nh$, and N , Avogadro's number, h , Planck's constant, and the other terms have their usual significance. This semi-empirical equation has been applied to many solid diffusion systems and represents the experimental results very well in many instances (Barrer, 1951, p. 300). In comparing eqs. (15), (17), and (18), one will find the diffusion coefficient D is proportional to

$$(\text{diffusing distance})^2 \cdot e^{-E/RT}, \quad (19)$$

and the proportionality constant will be $1/4\tau_0^{-1}$ in eq. (15), $K(kT/h)$ in (16), and ν in (18), and all have the vibration dimension of sec^{-1} . The proportionality constant in these experimental systems is not known. However, Kruyer (de Boer, 1953, p. 234) has found that a constant value

of τ_0 is 10^{-13} sec in most adsorption studies. The hopping distances a were calculated according to eq. (15) using the value of 10^{-13} sec for τ_0 . These results are shown in Table 4. It should be noted that the absolute value of a is uncertain because the value of τ_0 in the authors' experimental systems is uncertain. The a has value, however, for comparing systems. From Table 4 it can be seen that the hopping distances were decreased with increasing clay contents in both Na and Ca diffusion. This may mean that the diffusion rate is limited by the hopping distance between the "edge" of the clay particles since the hopping distance between the exchange sites on the surface of clay particles should not be so affected by changing clay content. Higher clay content would shorten the distance between the "edges" with a resulting decrease in the a value. Another observation is that the a value is approximately an exponential function of the clay content. There may be some relation between the a values and the diffuse double layer of the clay particles.

When the a values of the Na systems are compared with that of Ca, one can see that the value for Ca is much greater than that of Na. It is rather well known that the Na-bentonite swells between platelets as water is added while Ca-bentonite expands to only about 19.5 Å and remains in that condition as more water is added. Therefore, the rate limiting diffusion of exchangeable Na ion in Na-clay could be hopping from one individual platelet to another, and that of Ca ion from "package" of platelets to other "packages." The a values of the Ca system consequently would be larger than those of the Na systems since the average distance between "packages" probably would be greater than the distance between individual platelets. Another explanation for this observation is that the τ_0 for the Na-clay may be quite different from that of the Ca-clay. The entropy of the activated state of Na-clay may differ from that of Ca-clay, thus resulting in quite different values of τ_0 . If this were true, it probably would be permissible to compare the data from the same kind of clay at different concentrations but not between systems containing different exchangeable ions.

CONCLUSIONS

Diffusion in clay-water systems is not a simple process. In addition to interaction between clay and exchangeable ions, the interaction between clay and water also occurs. These two interactions may affect each other. There could be more than one diffusion coefficient in these systems, as Richman and Thomas (1956) pointed out in resin studies. Ion diffusion in clay-water systems may have different energy barriers to overcome for each different diffusion process.

In the diffusion system studied, there were at least two paths for diffusing cations, namely: migration along the exchange sites on the surface

of particles in the clay matrix, and jumping from the exchange site on one particle to the site on another particle. When high concentrations of salts are introduced, there is the third path down the middle of the "channel."

The number of exchange sites present per unit volume should affect the diffusion rate. Increasing the amount of clay present per unit volume will increase the number of exchange sites, thereby increasing the average number 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. This reasoning is confirmed by the data in this study.

In general, low rates of diffusion are accompanied by high activation energies. In considering the viscosity of the medium, it may be assumed that the higher the clay concentration the higher the average viscosity of the water in the system, as indicated by the intensive work of Low (1960). If this is true there will be a higher energy barrier for diffusion, which should result in a higher activation energy. However, other factors besides the viscosity of the medium may be operating. The hopping distance a also may be a factor in the energy barrier. It seems reasonable to suggest that the farther apart the rate-limiting exchange sites may be, the greater the energy barrier and consequently the larger the activation energy must be. If this is valid reasoning, and if hopping from particle to particle or from clay packet to clay packet is the rate limiting exchange reaction, then as clay concentration increases, the closer together clay particles become and the lower the a value or hopping distance. Decrease in a and activation energy with increasing clay content is shown in Table 4. Fujii and Thomas (1958) also found that the activation energy was smaller for the diffusion of Na ion in concentrated agar gels than in the gels that were more dilute. There was a lower self-diffusion coefficient of Na ion in the concentrated gels than in the dilute ones. These observations are in accord with those made in this paper on clay gels. The activation energy for diffusion may be a function of both viscosity of the medium and the hopping distance. In these studies, the viscosity factor may be overshadowed by the distance factors.

The value of the activation energy of self-diffusion of Na ion in the 15.2 percent bentonite plug was very close to that of Na ion in water. The activation energy of self-diffusion of Na ion in certain concentrations of agar gels was lower than that in water (Fujii and Thomas, 1958). It could be that the relationship between the activation energies of self-diffusion and the clay content may not be linear. It is possible that over a certain range of clay contents there is a peak value of over-all activation energies, where a certain diffusion process may predominate. This, however, may change over other ranges of clay concentration where other factors may predominate.

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