A Nonsteady State Method for Determining Diffusion Coefficients in Porous Media

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A series of experiments was run to test the feasibility of determining diffusion rates in a porous medium using a nonsteady state method. The experimental procedure is based on a mathematical model of Crank (1970) and involves diffusion from a porous sheet of finite thickness into a finite homogeneous volume. By measuring the composition of the homogeneous volume as a function of time it is possible to calculate integral diffusion coefficients of salts in the porous medium.

INTRODUCTION

Migration of dissolved aqueous species in a porous medium can occur in response to the presence of concentration or activity gradients. In theory the net rate of migration due to this cause can be either determined directly by experimental measurement or predicted indirectly from values of diffusion coefficients in free solution and a knowledge of the physical and chemical properties of the medium. Physical properties of a porous medium which can affect migration or diffusion rates include porosity, tortuosity, degree of pore saturation, and the presence of dead-end pore spaces. In addition, the medium may behave as a semipermeable membrane or in other ways interact electrically or chemically with the pore solutions [Mokady and Low, 1968].

In some porous sediments, where bulk fluid flow and mechanical dispersion are negligible, net diffusion coefficients for dissolved salts can be estimated from the diffusion coefficient in free solution and the sediment porosity and tortuosity (equations (9) and (10)) [Manheim, 1970]. If the porous medium is electrically nonconductive, tortuosity can be calculated from porosity and the formation factor (equation (10)), which is the measured ratio of the specific resistances of the saturated porous medium and the interstitial solution [Archie, 1942; Klinkenberg, 1951; Bear, 1972]. The quantitative importance of variables other than porosity and tortuosity on net diffusion or mass transport rates is often difficult to evaluate. One possible approach in evaluating other variables is to determine the difference between mass transport coefficients measured directly by experiment and coefficients calculated from known values of porosity and tortuosity. This paper describes a simple nonsteady state technique for the direct experimental determination of net diffusion or mass transport coefficients in porous media.

THEORY

Crank [1970] derived an analytical solution for the non-steady state diffusion from a homogeneous solution of limited volume into a plane sheet of finite thickness. This mathematical model was used as a guide to design an experiment to evaluate diffusion in a porous medium. In the experiment, however, diffusion of salt is in the reverse direction, from the plane sheet (region A in Figure 1) into the homogeneous solution (region B).

The initial and boundary conditions for the diffusion model are given by equations (1)-(4):

$$C = C_0 \qquad 0 \le x \le s \qquad t = 0 \qquad (1)$$

$$C = 0 \qquad s < x \le (s + a) \qquad t = 0 \qquad (2)$$

$$a(\partial C/\partial t) = -D(\partial C/\partial x) \qquad x = s \qquad t > 0 \qquad (3)$$

$$(\partial C/\partial x) = 0 \qquad s \le x \le (s + a) \qquad t > 0 \qquad (4)$$

where C is the concentration (g cm^{-3}) of a component at time t (s) and distance x (cm), D is the diffusion coefficient (cm^2 s^{-1}), and s and a are dimensional parameters defined in Figure 1. The coefficient D is related to the flux J (g cm^{-2} s^{-1}) of the component across s by

$$J = -D(\partial C/\partial x) \qquad (5)$$

where J is measured per unit area of pore solution.

Following Crank's [1948, 1970] analytical solution, the diffusion of salt from region A into homogeneous region B can be described as follows:

$$M_t/M_\infty = (1 + b)[1 - \exp(T/b^2) \operatorname{erfc}(T^{1/2}/b)] \qquad (6)$$

where $T = Dt/s^2 \le 1$.

In equation (6), M_t is the amount in grams of the component which has diffused into region B at time t, M_∞ is the amount which will have diffused at infinite time, and b is the equilibrium ratio of the amount of the component in region B to region A at infinite time. For an inert porous medium, b is simply the volume ratio of fluid in region B to region A. Equation (6) is applicable when $T \le 1$. If $T > 1$, the analytical solution of Wilson [1948] should be used.

Of the variables in (6), b, s, and M_∞ are fixed by the geometry of the diffusion cell (Figure 1). By measuring M_t and t, therefore, it is possible to determine D.

EXPERIMENTAL PROCEDURE

The apparatus constructed to test the applicability of (6) consisted of a vertical column of porous epoxy-cemented sand (region A) filled with an initially homogeneous salt solution and an open plexiglas cylinder (region B) mounted on top of the column and filled initially with distilled water. The artificial sandstone used in region A was made by cementing together a well-sorted quartz sand of an average grain diameter of 0.2 mm with epoxy glue. Two columns were constructed,

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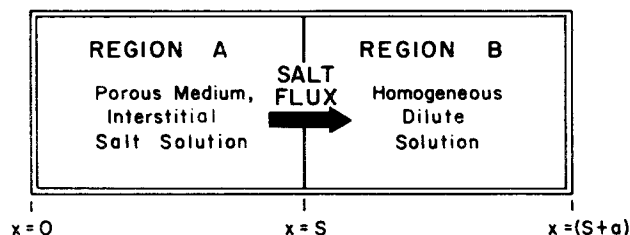
Fig. 1.   Diagrammatic representation of diffusion cell used in experiments.

each having a length of 93.5 cm. Column 1 had a cross-sectional area of 35.4 cm² and a pore volume of 970 cm³. Column 2 had a cross-sectional area of 35.0 cm² and a pore volume of 958 cm³. The sides of each column were covered by epoxy cement to contain the interstitial fluids.

Values for porosity ϕ and formation factor F of the cemented sand were determined on samples prior to the experimental runs and later on cores cut from the columns at the conclusion of the experiments. Porosities were determined on the basis of weight differences between dry and water-saturated samples of known volume. Porosities remained at a constant volume of 0.293 throughout the experiment. The formation factor was determined by comparing the specific resistance of sand samples saturated with a 1-molal NaCl solution with the specific resistance of a free 1-molal NaCl solution. Values of F in the direction of diffusion averaged 11.44 at the start of the experiments but had decreased to 8.87 at the conclusion of the experiments. The permeability of the cemented sand was 8.97 darcies in the direction of diffusion.

In the course of an experimental run, each of the two columns was saturated with fluid and purged of gas by passing the salt solution to be studied through it at a pressure of 1.5 atm. Twenty-eight pore volumes (27 l) of salt solution were passed through to insure internal homogeneity. After complete saturation of the column by the salt solution, the plexiglas cylinder was mounted over the exposed upper end of each column. The whole apparatus was enclosed in a water bath maintained at 35°C. The introduction of 700 ml of distilled water into the cylinder marked the beginning of the experiment and the diffusion of salt from the column up into the cylinder. The solution in the cylinder was kept homogeneous by bubbling it with nitrogen. A total of thirteen 1.0-ml samples was taken from each cylinder over a period of 11 days. The volume of region B was thus reduced by less than 2%. The samples were analyzed by standard atomic absorption techniques to a relative precision of 1%.

RESULTS

A series of experiments was run in which the initial solution in region A was a 1-molal aqueous solution of either NaCl or CaCl₂. Results are shown in Figure 2. The circles and triangles indicate measured variations in composition of the homogeneous solution with time. The solid lines represent trends in composition calculated for different volumes of D in (6). The agreement between observed and calculated compositions for specific values of D are excellent at $t > 3 \times 10^5$ s. At smaller t the rate of diffusion in a given experiment is usually lower than that predicted by later behavior of the salt. This may reflect the fact that the diffusion coefficient D measured by the experiment is an integral value and is a function, in part, of the magnitude of the difference in composition of the fluids in regions A and B at $t = 0$. The accuracy of the experiments was not sufficient to calculate differential diffusion coefficients

[Longsworth, 1945; Crank and Park, 1949], which would define D for a salt solution of specific composition [Robinson and Stokes, 1970, p. 515].

Measured values for the integral diffusion coefficients of NaCl and CaCl₂ in the epoxy-cemented sand are listed in Table 1. For a given experimental run the diffusion coefficients determined for columns 1 and 2 agree within approximately 10%. There was, however, an increase of approximately 30% in the diffusion coefficients for NaCl in each column from the second experimental run to the third. This same trend was also noted in subsequent experiments [Stoessell, 1974].

From measurements of the physical properties of the columns before and after the experiments we believe that extensive contact with the interstitial salt solutions degraded the epoxy cement. Although porosity was not significantly changed, there was a 22% decrease in the formation factor. It is possible that this decrease reflects an elimination of dead-end pore space and a reduction in tortuosity. Consistent with our experimental observations, this decrease in tortuosity would have the effect of increasing diffusion rates.

COMPARISON OF MEASURED AND CALCULATED DIFFUSION COEFFICIENTS

For some nonconductive porous media, where bulk fluid flow and mechanical dispersion are negligible, values of diffusion coefficients can be calculated from values of the diffusion coefficient in free solution $D°$, porosity, and tortuosity. Values of D in (3) are defined for a flux J parallel to x. Let D^* be the diffusion coefficient defined for the flux J^* parallel to the true, tortuous diffusion path m. If flux is measured per unit area of pore solution,

$$J^* = -D^*(\partial C/\partial m) \qquad (7)$$

If β is the average angle between the tortuous path and the x axis, then

$$J = J^* \cos \beta \qquad (8)$$

where $\cos \beta$ is simply (dx/dm) [Klute, 1959]. Defining tortuosity as $L = dm/dx$, we have from (5), (7), and (8),

$$D = D^*/L^2 \qquad (9)$$

If tortuosity is the only property of the medium affecting diffusion rates, then $D^* = D°$, the diffusion coefficient in free solution. For an electrically nonconductive medium, values of L in (9) can be determined from the formation factor F and porosity ϕ by [Bear, 1972, p. 114]:

$$L = F \cdot \phi \qquad (10)$$

It should be noted that if the flux J had been defined relative to a unit area of porous medium rather than to a unit area of pore fluid, both (8) and (9) would require porosity terms.

Table 1 shows a comparison of values of D determined by experimental technique and values calculated from (9) and (10). Values of $D°$ for NaCl and CaCl₂ in free solution at 35°C were calculated from differential diffusion coefficients of Bruins [1929] [Stoessell, 1974] and are assumed to be 1.97 × 10⁻⁵ cm² s⁻¹ and 1.51 × 10⁻⁵ cm² s⁻¹, respectively. Values of ϕ and F were determined experimentally, as described earlier. F was assumed to decrease linearly as a function of the number of experimental runs made within each column.
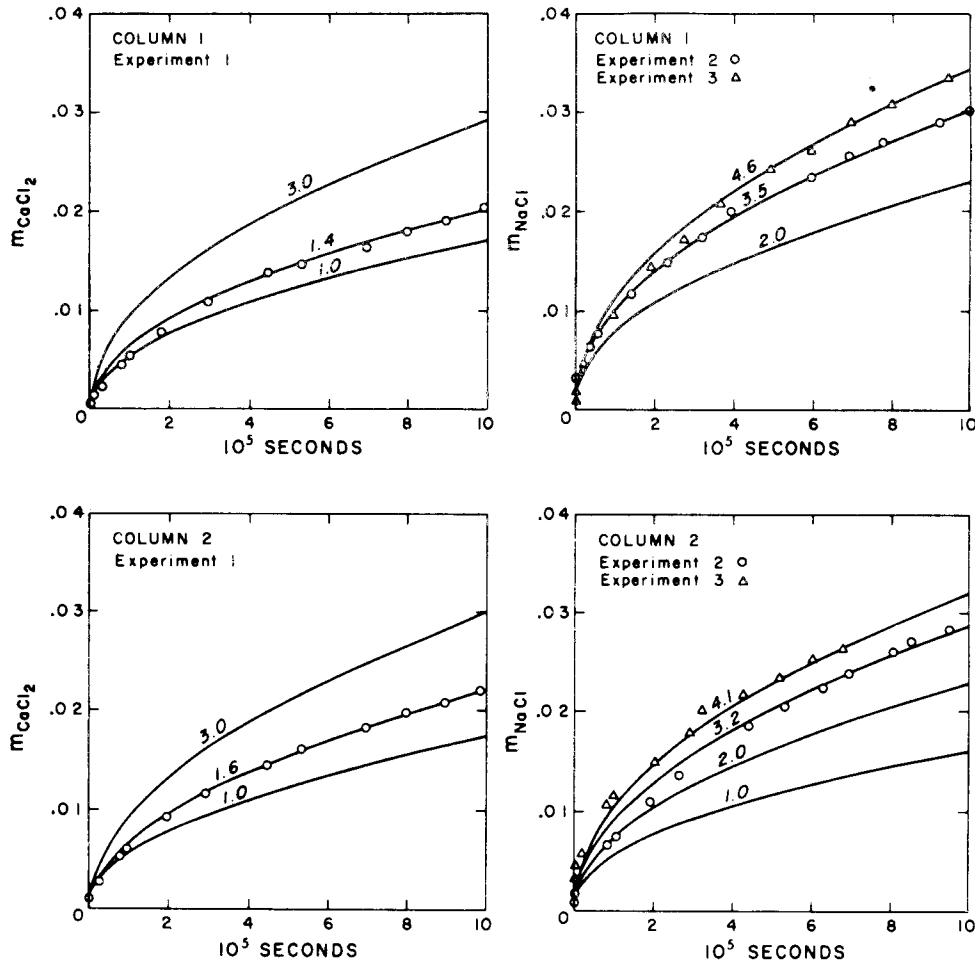
Fig. 2. Variation in composition of region B as a function of time. Circles and triangles are measured values. Solid lines are predicted trends calculated from equation (6) for selected values of the diffusion coefficient D (10^{-6} cm^2 s^{-1}).

From Table 1 it can be seen that D (experimental) and D (calculated) agree within a factor of 1.1-1.6. Calculated values of D are consistently lower than the experimentally determined values. This could be due in part to mechanical convection and an increased salt flux which may have been induced in the upper part of the columns by the bubbling of nitrogen and circulation of fluid in region B. Correlation between D (experimental) and the mixing rate in region B has not been tested. The discrepancy may also reflect a difference in type between the integral values of D determined by experiment and the differential values of $D°$ compiled by Bruins [1929]. The consistent difference in behavior of columns 1 and 2 with respect to the diffusion of NaCl as evidenced by the ratios of D (measured) to D (calculated) suggests that there may be differences in the internal properties of the columns which influence diffusion rates. If this is so, then porosity and formation factor, as determined by standard techniques, are inadequate to characterize these properties.

CONCLUSIONS

It was found by experiment that the nonsteady state diffusion of dissolved NaCl and CaCl$_2$ out of a finite thickness of porous cemented sand into a dilute homogeneous solution of limited volume can be described by (6). By measuring the composition of the homogeneous solution with time it is possible to calculate a value for the net diffusion coefficient of the salt in the porous medium. An experimental run of 5-10 days was found to be necessary in order to obtain accurate results.

TABLE 1. Comparison of Diffusion Coefficients Determined by Experiment With Diffusion Coefficients Calculated From Equation (9)

Experiment No.	Column	Tortuosity L	Initial Solution Composition, molality	D (experimental), 10^{-6} cm^2 s^{-1}	D (calculated), 10^{-6} cm^2 s^{-1}	Ratio of D (experimental) to D (calculated)
1	1	3.38	1.04 CaCl$_2$	1.4	1.3	1.1
1	2	3.35	1.07 CaCl$_2$	1.6	1.3	1.2
2	1	2.98	1.00 NaCl	3.5	2.2	1.6
2	2	2.96	1.00 NaCl	3.2	2.3	1.4
3	1	2.60	1.00 NaCl	4.6	2.9	1.6
3	2	2.61	1.00 NaCl	4.1	2.9	1.4

An advantage of the method is the simple experimental design, which would lend itself to the study of a variety of geologically realistic sediments and interstitial fluids. For example, diffusion coefficients could be measured in some systems where the formation factor cannot be used to calculate true tortuosity, either because the sediment itself is electrically conductive or because dead-end pore space is significant. In systems where ion exchange is significant, (6) can be used to test whether mass transport can be adequately described by a simple apparent diffusion constant, implying that diffusion is the rate-controlling step. Finally, the system lends itself to the study of net diffusion or mass transport in compositionally complex interstitial solutions [*Stoessell*, 1974].

REFERENCES

Archie, G. E., The electrical resistivity log as an aid in determining some reservoir characteristics, *Petrol. Technol.*, 5(T.P. 1422), 8 pp., 1942.

Bear, J., *Dynamics of Fluids in Porous Media*, pp. 113–114, Elsevier, New York, 1972.

Bruins, H. R., Coefficients of diffusion in liquids, in *International Critical Tables of Numerical Data: Physics, Chemistry and Technology*, vol. 5, edited by E. W. Washburn, pp. 63–76, McGraw-Hill, New York, 1929.

Crank, J., A diffusion problem in which the amount of diffusing substance is finite, 4, Solutions for small values of the time, *Phil. Mag., 39.*, 362, 1948.

Crank, J., *The Mathematics of Diffusion*, 1st ed. (revised), pp. 52–56, Oxford University Press, London, 1970.

Crank, J., and G. S. Park, An evaluation of the diffusion coefficient for chloroform in polystyrene from simple absorption experiments, *Trans. Faraday Soc., 45*, 240, 1949.

Klinkenberg, L. J., Analogy between diffusion and electrical conductivity in porous rocks, *Geol. Soc. Amer. Bull., 62*, 559, 1951.

Klute, C. H., Diffusion of small molecules in semicrystalline polymers, 2, The permeability of unoriented polymer films, *J. Polymer Sci., 41*, 307, 1959.

Longsworth, L. G., The diffusion of electrolytes and macromolecules in solution: A historical survey, *N. Y. Acad. Sci., 46*, 211, 1945.

Manheim, F. T., The diffusion of ions in unconsolidated sediments, *Earth Planet. Sci. Lett., 9*, 307, 1970.

Mokady, R. S., and P. F. Low, Simultaneous transport of water and salt through clays, 1, Transport mechanisms, *Soil Sci., 105*, 112, 1968.

Robinson, R. A., and R. H. Stokes, *Electrolyte Solutions*, 2nd ed. (revised), p. 515, Butterworth, London, 1970.

Stoessell, R. K., *Experimental Study of Multi-Cation Diffusion in an Artificial Quartz Sandstone*, M.S. thesis, 150 pp., La. State Univ., Baton Rouge, 1974.

Wilson, A. H., A diffusion problem in which the amount of diffusing substance is finite, 1, *Phil. Mag., 39*, 48, 1948.