

Diffusion of sea water ions—I. Diffusion of sea water into a dilute solution

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Abstract—Derivations of VINOGRAD and MCBAIN (1941) were applied to explain ionic diffusion out of sea water and into dilute solution. Models so constructed were found to be compatible with experimental data obtained from Cl^- , K^+ , Mg^{2+} and Ca^{2+} diffusion studies. The present investigation suggests that ionic interaction—resulting from the electroneutrality requirement—may extensively modify fluxes of diffusing ions and may also affect the relative distribution of both migrating and non-migrating ions. It is suggested that a change in the ratio ion/Cl in interstitial waters of marine sediments does not necessarily imply that the ion is involved in a chemical reaction or that it migrates.

INTRODUCTION

MUCH attention has been paid in recent years to the role of diffusion of ions and molecules in the geochemical processes of mass transport between sediment and overlying sea water. GOLDBERG and KOIDE (1963) have proposed a diffusion model for migration of uranium from marine sediments. BERNER (1964) proposed a model for explaining sulfate profiles in pore water of anoxic marine sediments (KAPLAN, *et al.*, 1963); LYNN and BONATTI (1965) and MICHARD (1971) have proposed diffusion models for migration of manganese in pore water of marine sediments.

Recent analyses of interstitial waters from deep-sea cores (INITIAL REPORTS OF THE DEEP SEA DRILLING PROJECT, 1969–1972) reveal large compositional variations which may be responsible for large-scale mass transport between oceans and sediments. However, accurate estimation of fluxes due to these concentration gradients can not be made at present as many questions related to the process of diffusion in marine sediments are poorly understood. In particular, there is no experimental data on diffusion in a complex electrolyte mixture such as sea water and there are still many unknowns regarding the roles of exchange between ions and sediments.

Although the theory of diffusion in mixed electrolyte has been studied by a number of investigators (ONSAGER and FUOSS, 1932; MILLER, 1967a, b) there are virtually no reported experimental studies of diffusion systems that contain more than two electrolytes. Theoretical and experimental studies of diffusion in aqueous solution of two salts (e.g. MILLER, 1959; DUNLOP, 1964; LANE and KIRKALDY, 1966; MILLER, 1967a) have demonstrated the complex nature of the diffusion process in these systems due to cross-coupling between the fluxes. Further complications are encountered when the mixture contains weak electrolytes (WENDT, 1965; MORENO *et al.*, 1970) due to the presence of associated species whose concentration—at each point—are dependent on the concentration of other ions. Experimental results in a mixture of weak electrolytes (Na_2SO_4 – H_2SO_4 – H_2O) were found to agree poorly with theoretical predictions (WENDT, 1965).

The present study represents an attempt to investigate experimentally ionic diffusion in sea water, checking the validity of model calculations against results of

controlled experiments. A simple case (diffusion of sea water into dilute solution) was initially chosen to reduce, as much as possible, second-order effects such as the relaxation and electrophoretic effects (ONSAGER and FUOSS, 1932; HARNED and OWEN, 1958).

THEORETICAL CONSIDERATIONS

The flux of a dissolved species (i) in an isothermal solution at rest, can be approximated by (VINOGRAD and MCBAIN, 1941; ROBINSON and STOKES, 1970):

$$J_i = U_i \left(RT \frac{\partial C_i}{\partial X} + Z_i C_i F \frac{\partial E}{\partial X} \right) \quad (1)$$

where:

- R = gas constant (8.31 J/deg-mole)
- F = Faraday's number (96,500 C/eq)
- T = absolute temperature
- Z = valence
- C = concentration (mole/cm³)
- U = mobility at infinite dilution (cm²-mole/J-sec)
- E = electrical potential (V)
- X = linear distance (cm)
- J = flux (mole/cm²-sec).

This equation assumes that the variation of the activity coefficient along the diffusion path is small and neglects the electrophoretic and relaxation effects (ONSAGER and FUOSS, 1932). The latter phenomena have a marked effect on the conductivity of concentrated electrolytes but have a relatively small effect on diffusion. This is attributed (ROBINSON and STOKES, 1970; p. 290) to the fact that, unlike the case of conductivity, ions of diffusing electrolytes move in the same direction so that their relative motion is much smaller.

An additional equation is furnished by the electroneutrality requirement:

$$\sum_i Z_i J_i = 0 \quad (2)$$

which can be combined with a set of equations (1) to solve for the values of J_i .

The present analysis is carried out under the assumption that all the ions are free. This assumption, along with the approximations of equation (1) makes possible the solution of equations (1) and (2) for sea water, as they permit the use of infinite dilution mobilities. These mobilities can be calculated from published data of limiting equivalence conductance (λ°) using the relation:

$$U_i = \frac{\lambda_i^\circ}{|Z_i| F^2} \quad (3)$$

where U_i , Z_i and F are defined as above and λ° is expressed in mho cm²/eq.

EXPERIMENTAL

The diffusion experiment (Fig. 1) was designed around a porous glass diaphragm through which sea water ions were allowed to diffuse into a dilute solution. The diffusion cell was made

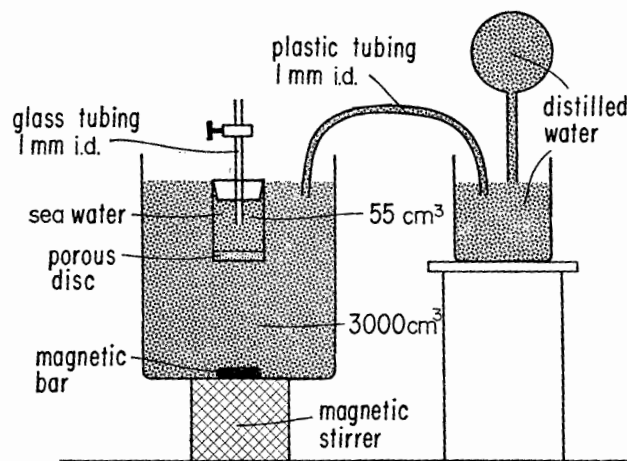


Fig. 1. Schematic representation of the diffusion experiment.

by cutting a commercially-available filter tube (Lab Glass, Inc. No. LG-7160), composed of a porous glass disc (40 mm o.d., 5 mm thick, porosity: 10–15 μ) fused inside a 4 cm i.d. glass tubing. The cell was plugged with a rubber stopper through which a 1 mm glass tube with a Teflon stopcock was inserted. The capacity of the cell was approximately 55 ml, and the volume of the outer solution was 3000 ml. Sea water was placed inside the cell, rather than outside, in order to enhance streaming due to gravitational forces (ROBINSON and STOKES, 1970). This procedure is necessary to avoid the formation of thick stagnant layers at the two surfaces of the diaphragm. The cell was filled by immersing it in a beaker containing artificial sea water (KESTER *et al.*, 1967), plugging it with the stopper and closing the stopcock after eliminating all air bubbles from inside the cell. The cell was then carefully removed from the beaker, thoroughly washed by distilled water, and placed into the large beaker containing distilled water. The water lost by evaporation from the outside compartment was replenished by a siphon arrangement (Fig. 1).

All experiments were carried out at room temperature which was registered to be in the range 22–24°C. The diffusion process was monitored by sampling approximately 1–2 cm³ of the outside solution at various time intervals. The samples were taken immediately after the outside solution was homogenized by turning on the magnetic stirrer for 10 sec. The total amount of salt removed from the system by this procedure was very small and did not amount to more than 1 per cent of the dissolved salt. The samples were collected in plastic vials which were stored in a water-saturated atmosphere to prevent evaporation. A typical experiment was run for about 3 days.

The collected samples were analyzed for Cl⁻, Mg²⁺, Ca²⁺, K⁺ and Na⁺. Chlorinity was measured by a coulometric titrator (Fiske Model 404), and all cations were analyzed by an atomic absorption spectrometer (Perkin-Elmer 303), following the techniques described by PRESLEY (1969). Inaccuracy of analyses is estimated to be $\pm 1\%$ for Cl⁻, $\pm 2\%$ for Mg²⁺ and Ca²⁺ and $\pm 3\%$ for K⁺. The Na⁺ results are not reported here as they were badly scattered due to poor instrumental precision and probably also due to exchange with the glass walls of the outer vessel.

RESULTS AND DISCUSSION

Results of the KCl diffusion experiments, conducted for the purpose of cell calibration, and the sea water experiments are given in Tables 1 and 2, respectively. The 1 M KCl experiment was used to estimate the cell's constant (the diaphragm's thickness-to-area ratio) by assuming a linear concentration gradient in the diaphragm and homogeneous solutions on the two sides of the porous disc (VINOGRAD and

Table 1. Concentration of outside solution during KCl diffusion experiments

0.7 M KCl		1.0 M KCl	
Time (hr)	Cl ⁻ (mmole/l)	Time (hr)	Cl ⁻ (mmole/l)
5.33	0.41	5.00	0.64
22.75	1.13	21.50	1.70
25.25	1.29	24.50	1.84
27.25	1.31	26.50	2.06
30.09	1.55	29.50	2.14
47.00	2.16	46.50	3.46
48.33	2.23	48.00	3.49
75.00	3.20	75.75	4.81

Table 2. Composition of outside solution during sea water diffusion experiments

Experiment	Time (hr)	K ⁺ (μmole/l)	Ca ²⁺ (μmole/l)	Mg ²⁺ (μmole/l)	Cl ⁻ (m-mole/l)
3	8.0	5.5	4.5	19.7	0.40
	24.0	17.2	11.2	49.2	0.79
	27.0	19.1	12.8	54.5	0.87
	29.0	20.3	13.5	59.2	1.01
	30.0	20.5	13.9	59.2	1.03
	31.0	21.1	14.1	62.9	1.01
	50.0	34.7	22.1	94.2	1.49
	53.2	36.3	23.2	104.0	1.58
	74.3	49.2	29.8	131.5	2.07
4	8.0	5.4	4.2	19.0	0.34
	24.0	17.1	11.3	47.0	0.79
	26.0	18.5	12.3	50.5	0.92
	29.0	19.7	13.5	55.5	0.94
	31.0	20.8	13.7	58.5	1.03
	48.0	32.8	20.8	84.7	1.53
	51.0	35.1	20.2	91.0	1.39
	53.0	35.3	21.3	94.0	1.61
	56.0	37.4	21.6	96.5	1.77
	62.0	41.2	24.5	109.5	1.86
	83.7	54.8	29.8	135.5	2.23
	99.0	62.6	34.3	157.0	2.66
	103.5	65.5	36.3	160.7	2.68
	125.2	76.6	42.7	189.2	2.94

McBAIN, 1941). Combining equations (1) and (2), one can approximate the diffusion rate (S , mole/sec) of an ion (j) by:

$$S_j' = U_j RT \left(\frac{C_j' - C_j''}{W/A} - Z_j C_j' \frac{\sum_i U_i Z_i \frac{C_i' - C_i''}{W/A}}{\sum_i U_i Z_i^2 C_i'} \right) \quad (4)$$

Where the prime and double prime denote concentrations inside and outside the cell, respectively, A is the effective area of the diaphragm, W is its width and W/A is the cell constant.

A set of (i) equations of the form of equation (4) can be solved numerically by assuming that the potential gradient $(\partial E/\partial X)'$ is constant during a small time increment, Δt . Using this assumption, one can first calculate the potential gradient and then calculate the diffusion rate for each ion. The concentration of the ions inside and outside the cell as a function of time, can be obtained by subtracting at the end of each time increment the amounts $S_i\Delta t$, from inside, and adding this amount to the outside solution.

The cell constant of the present experimental set-up was calculated by the above arithmetical method in a trial-and-error procedure and was found to be $1:2.85 \text{ cm}^{-1}$.

The numerical values for these calculations were as follows: λ_{Cl^-} and λ_{K^+} 76.35 $73.5 \text{ mho cm}^2/\text{equiv.}$, respectively (ROBINSON and STOKES, 1970) and $\Delta t = 360 \text{ sec}$. The calculations were carried out on a small digital computer (PDP-8/L) with a precision of 6 digits and a mantissa range of ± 512 (FOCAL). Fig. 2a demonstrates the fitness that has been obtained for a cell constant value of $1:2.85 \text{ cm}^{-1}$.

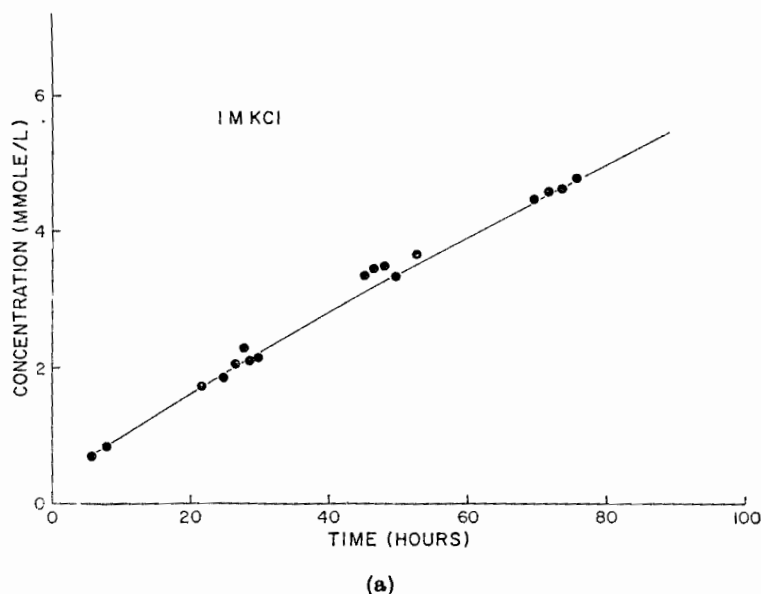
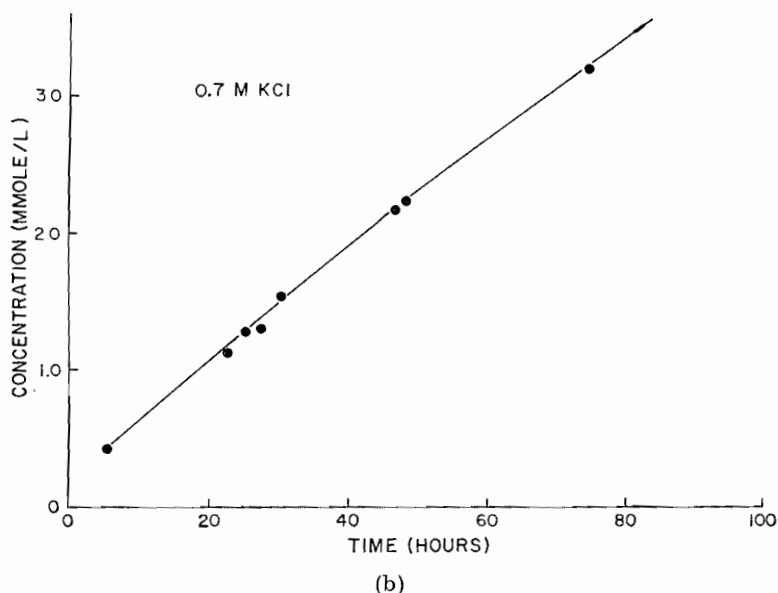


Fig. 2. Concentration of outside solution during 1 M (a) and 0.7 M (b) KCl diffusion experiments. The solid line represents the results of model calculations in which the cell's constant was set at $1:2.85 \text{ cm}^{-1}$.

The calculation was repeated for the diffusion experiment with 0.7 M KCl solution using the value of the cell estimated from the 1 M KCl experiment. Figure 2b compares the calculated (solid line) with the experimental values. It is evident from this figure that the present numerical calculation procedure is adequate for describing the diffusion system to within the experimental accuracy.

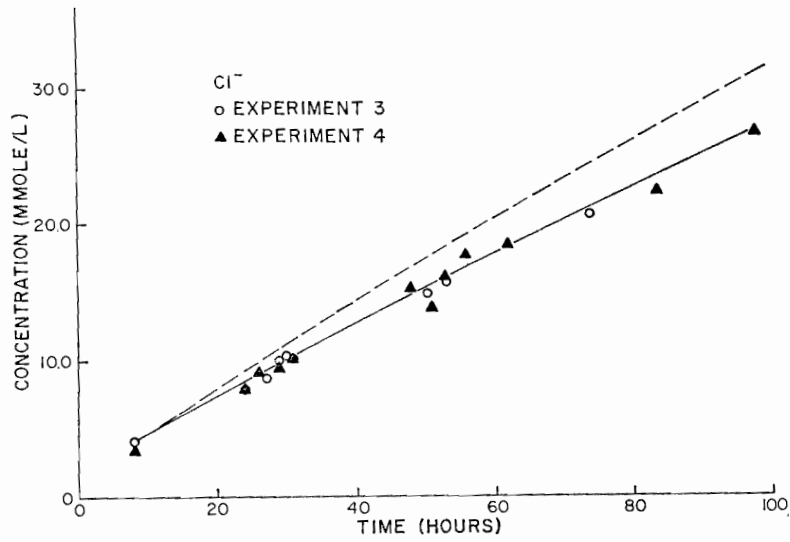


The calculation was repeated for sea water by solving seven equations of the form of equation (3) and using the numerical values given in Table 3. The ionic concentration used as initial condition for the calculation was derived from the analysed results of the first sample taken approximately 8 hr after commencing the experiments. The purpose of this procedure was to reduce the errors that might result from the transient conditions before the onset of a gradient in the diaphragm.

Table 3. Data for model calculation.
(ROBINSON and STOKES, 1970, p. 463)

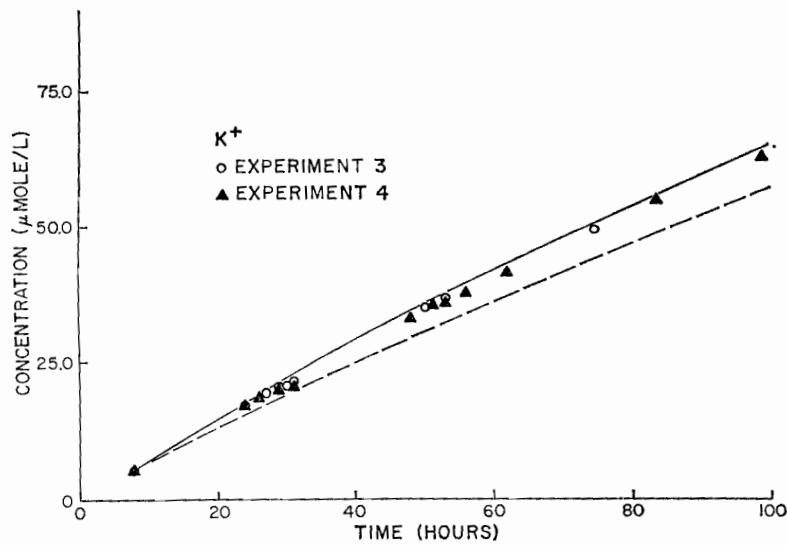
Ion	λ^0 (mho cm ² /equiv)
Na ⁺	50.11
K ⁺	73.52
Mg ²⁺	53.06
Ca ²⁺	59.50
Cl ⁻	76.35
HCO ₃ ⁻	44.50
SO ₄ ²⁻	80.00

The results of the model calculations are compared to the experimental results in Figs. 3a, b, c and d. The solid lines in the figures summarized the results of the calculations, whereas the broken line gives the concentrations of the ions in the outside solution for the hypothetical case in which the ions are free to diffuse by themselves with a constant diffusion coefficient which is equal to their self-diffusion coefficients. It is evident from Figs. 3a, b, c and d that the model calculation, which takes into account charge neutrality, can predict the experimental results. It appears that electrical coupling between ions extensively modifies their fluxes. The

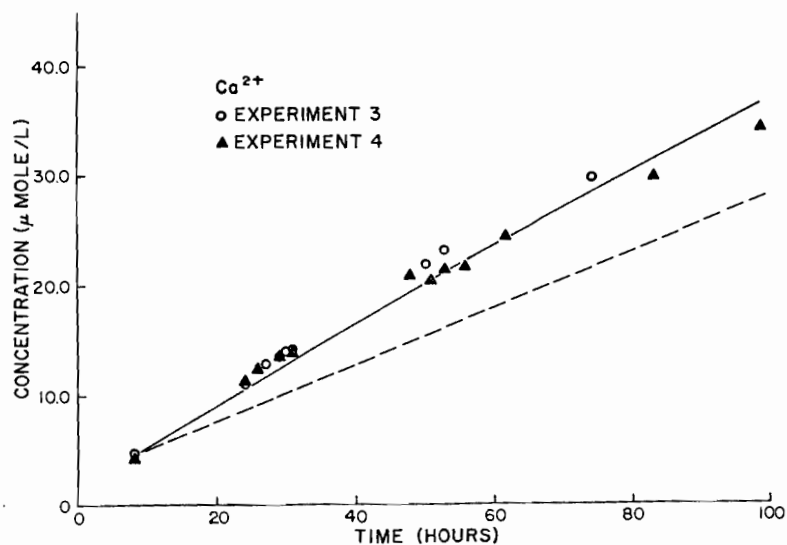


3a

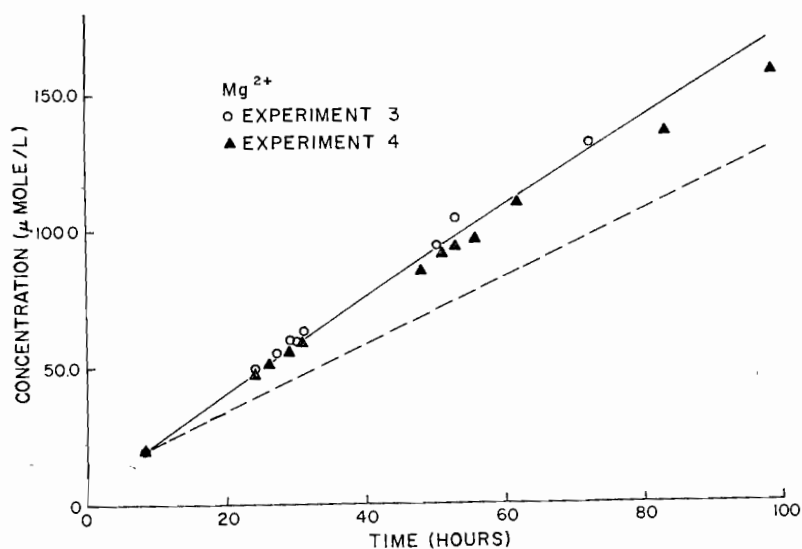
Fig. 3. Concentration of Cl^- (a), K^+ (b), Ca^{2+} (c) and Mg^{2+} (d) in outside solution during sea water diffusion experiment compared to model calculation (solid line). The broken line represents the results of a model calculation which does not include the electroneutrality requirement.



3b



3c



3d

diffusion coefficients of all the cations are larger than the self-diffusion coefficient whereas the diffusion coefficient of the anion (Cl^-) is smaller than its self-diffusion coefficient. This phenomenon fits the concept of a potential gradient which apparently persists along the diffusion path. A potential gradient would increase the flux of ions carrying a charge of one polarity and, at the same time, decrease the flux of oppositely-charged ions. Furthermore, the percentage change in the fluxes (or diffusion coefficients) should be a function of the valence of ions, as the force exerted on a charged particle by an electric field is linearly proportional to the charge held

by the particle. This effect can clearly be detected in the present experimental results. The percentage change in the diffusion coefficients of the univalent ions (as compared to the self-diffusion coefficients) is found to be approximately 20 per cent, while the corresponding change for a bivalent ion is approximately 40 per cent.

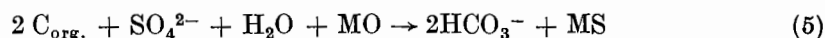
The presence of a potential gradient in the diaphragm was also detected by a direct measurement of the potential difference between the two sides of a diaphragm. The potential was measured with two reference electrodes with a ceramic junction (Corning Model 476029). The potential between the electrodes was first measured in sea water and in a dilute solution (0.01 M KCl) and the shift was found to be less than 1.5 mV. Next, the potential across the diaphragm was measured by inserting one electrode through the stopper of the cell and placing the other electrode in the outside solution. The potential across the membrane was measured to be 36.8 mV (corrected for initial difference between the electrodes). This measured value does not represent the accurate potential across the diaphragm, because it also includes the difference between the two liquid junction potentials. However, the internal solution of the two electrodes was 4 M KCl and one would expect that the magnitude of the liquid junction potential would be small (MACINNES, 1961), and was estimated by Henderson's equation (MACINNES, 1961) to be less than 1 mV for the two junctions.

Henderson's equation is based on the assumption that the junction consists of solutions which are linear mixtures of the boundary solutions. As this assumption is compatible with our assumption that the concentration gradients in the diaphragm are linear, we may use the Henderson equation for estimating the potential across the diaphragm. This value was calculated to be 39.3 mV which is in good agreement with the measured value (36.8 mV).

DIFFUSION IN MARINE SEDIMENTS

Ionic diffusion in marine sediments will be modified by chemical reactions between ions and sediment (VAN SCHAİK *et al.*, 1966) and to a lesser degree, by the relaxation and electrophoretic effect (ONSAGER and FUOSS, 1932). It is evident, therefore, that the present model may not be sufficient for accurately describing the diffusion process in this case. Nonetheless, it is of interest to examine qualitatively the possible effects of the electrical coupling between ions during diffusion in marine sediments. This will be studied here by considering the case of ionic diffusion in anoxic marine sediments.

Oxidation of organic matter by sulfate-reducing bacteria (ZOBELL and RITTENBERG, 1948) can be represented schematically as:



This model assumes that the sulfide is precipitated as metal sulfide (MS) and that the produced CO_2 is in the form of bicarbonate at the pH of the pore water. The metal is assumed to enter the system as a metal oxide (MO). The overall effect of this process is to consume sulfate and produce bicarbonate, causing sulfate to diffuse into the sediment and bicarbonate to diffuse out. These ionic fluxes must be coupled, because the electrical charge carried by the two migrating ions must be equal to maintain charge neutrality in the sediment. Hence:

$$J_{\text{SO}_4}^{2-} = 2 \cdot J_{\text{HCO}_3^-} \quad (6)$$

The electric field, required to maintain this condition, would cause a transient migration of all the other ions until each ion will build up a concentration gradient which is sufficient in magnitude to cancel out the electrical force due to the potential gradient. Once this equilibrium is reached, the condition will be stationary and only sulfate and bicarbonate will migrate. These conditions are exemplified in Fig. 4, which depicts the results obtained by applying the present model to the case of diffusion in anoxic marine sediments.

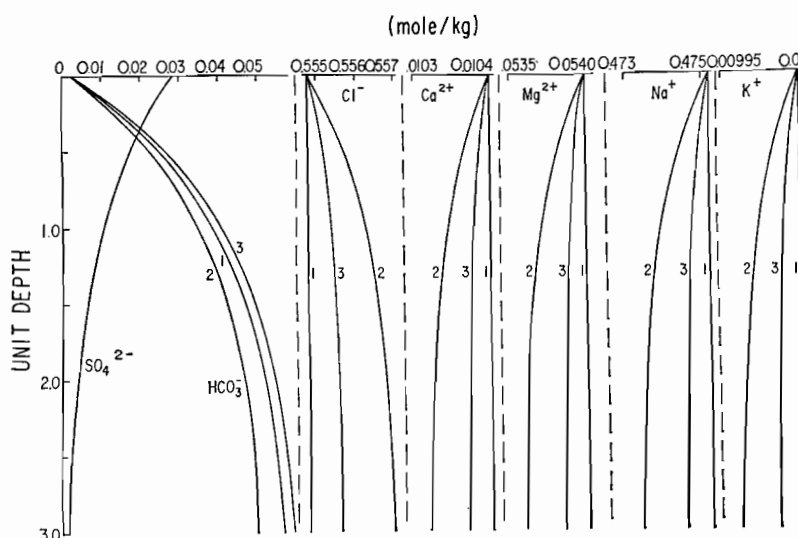


Fig. 4. Model calculation of diffusion in anoxic marine sediments. Case No. 1 was calculated under the assumption that only sulfate and bicarbonate migrate and that they have identical mobilities. Case No. 2 was calculated under the assumption that only sulfate and bicarbonate migrate and their mobilities were derived from Table 3. Case No. 3 is similar to case No. 2 but it includes the contribution of the diffusion of ammonia. One unit depth is defined as the depth at which SO_4^{2-} concentration drops to $1/e$ of its value at the upper boundary.

Results plotted in Fig. 4 were obtained with the following assumptions: (a) the model described by equations (1) and (2) is valid in anoxic marine sediments, (b) steady state has been reached; i.e. the partial derivatives of equation (1) with respect to X is zero, (c) only sulfate and bicarbonate migrate, (d) the concentration of sulfate in the pore water is exponential with depth reaching zero at infinite depth, and (e) the composition at the sediment-water interface is that of average sea water. Seven partial derivatives of equation (1) coupled with equations (2) and (6) were solved numerically for three cases which are labelled in the figure as numbers 1, 2 and 3. Number 1 represents the condition that would be reached if the sulfate and bicarbonate mobilities are identical. In this hypothetical case, the potential gradient vanishes since the electroneutrality requirement is fortuitously fulfilled. In number 2, the mobilities of sulfate and bicarbonate were assumed to be equal to those in dilute solution (Table 3). In this case, electroneutrality is maintained due to a potential gradient in the sediment which would modify fluxes of the two ions. The

calculation of number 3 (Fig. 4) is similar to number 2, except that it includes NH_4^+ ($\lambda^\circ = 73.55 \text{ mho cm}^2/\text{equiv.}$) as an additional migrating ion. Ammonia is produced during decomposition of organic matter (RICHARDS, 1965) and one would expect that this ion would diffuse upward. It was assumed that ammonia production is proportional to C_{org} oxidation according to the average composition of plankton (FLEMING, 1940; REDFIELD *et al.*, 1963).

The overall percentage change in the concentrations of nonmigrating ions—due to electrical coupling—is estimated here to be in the range of 0.5–1 per cent. However, the actual change in the sediments may be quite different due to the other processes mentioned above.

CONCLUSIONS

The results of the present study suggest that the model presented by equation (1) and (2) can closely describe diffusion of sea water into a dilute solution. Both the model calculations and the experimental data show that electrical cross-coupling between ions can markedly modify the diffusion process. It is evident, therefore, that this interaction must be taken into account when analyzing or constructing models for diffusion of sea water ions. This phenomenon, however, may be negligible in specific cases such as diffusion of tracers or when the self-diffusion coefficients of the ions are fortuitously capable of maintaining charge neutrality.

Although the present model was found to be useful in predicting the experimental results, it is still questionable whether it is accurate enough for describing ionic diffusion in marine sediments. In the latter case, one has to take into account the relative motion between the ions (ONSAGER and FUOSS, 1932) and chemical interaction with the sediment (VAN SCHAIK *et al.*, 1966), both of which may modify the ionic fluxes. Further flux modification may result from the fact that some of the sea water ions are complexed and undissociated (GARRELS and THOMPSON, 1962). Hence, the present model calculations of diffusion in interstitial water of anoxic marine sediments may not provide a quantitative assessment of the process, but rather demonstrate its nature.

The study suggests that a diffusion process in marine sediments may change the ionic balance of the pore water due to the possible build-up of a potential gradient in the sediment. This potential gradient will establish a concentration gradient for all the non-diffusing ions, thereby changing the ratio between the ions. It appears, therefore, that a change in the ratio ion/Cl from that found in sea water does not necessarily imply that the ion is involved in a chemical reaction or that the ion is migrating along a concentration gradient.

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