

Diffusion of ions in sea water and in deep-sea sediments

YUAN-HUI LI†

Eidgenössische Technische Hochschule (EAWAG) Dübendorf, Switzerland

and

SANDRA GREGORY

Woods Hole Oceanographic Institute, Woods Hole, Mass. 02543 U.S.A.

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Abstract—The tracer-diffusion coefficient of ions in water, D_j^0 , and in sea water, D_j^* , differ by no more than zero to 8 per cent. When sea water diffuses into a dilute solution of water, in order to maintain the electro-neutrality, the average diffusion coefficients of major cations become greater but of major anions smaller than their respective D_j^* or D_j^0 values. The tracer diffusion coefficients of ions in deep-sea sediments, $D_{j,\text{sed.}}$, can be related to D_j^* by

$$D_{j,\text{sed.}} = D_j^* \cdot \alpha / \theta^2,$$

where θ is the tortuosity of the bulk sediment and α a constant close to one.

INTRODUCTION

AS DEFINED by CRANK (1956), "diffusion is the process by which matter is transported from one part of a system to another as a result of random molecular motions". In a two-compartment system filled with the same solution except that one compartment contains a tracer amount of a radioactive isotope of a given ion (Fig. 1a), the radioactive ion will diffuse into the other compartment following Fick's first law, i.e.

$$F_j = -D_j \frac{dC_j}{dx}, \quad (1)$$

where F_j = the flux of radioactive ion j per unit area per unit time,

$\frac{dC_j}{dx}$ = concentration gradient of radioactive ion j ,

D_j = tracer-diffusion coefficient of radioactive ion in electrolyte solution.

In the special case, when a radioactive isotope of a given ion is diffusing in a single-salt solution of that same ion, e.g. Na^{22} in NaCl solution, the tracer-diffusion coefficient of the radioactive ion can be called the 'self-diffusion' coefficient of that ion. Numerically, the tracer- and self-diffusion coefficients are the same at infinite dilution, and can be calculated from the Nernst expression (ROBINSON and STOKES, 1959, p. 317):

$$D_j^0 = \frac{RT\lambda_j}{|Z_j|F^2}, \quad (2)$$

† Present address: Institute of Oceanography, National Taiwan University, P.O. Box 6013 Taipei, Taiwan.

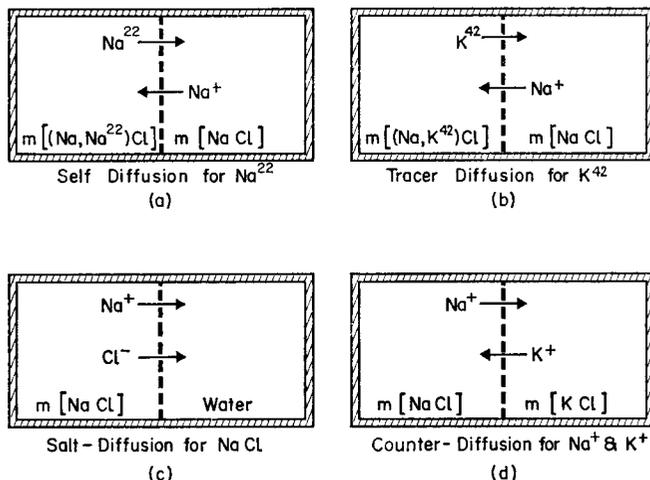


Fig. 1. Diffusion cells with different modes of diffusion.

where: D_j^0 = the limiting tracer- or self-diffusion coefficient of ion j ,
 λ_j^0 = the limiting equivalent conductivity of ion j ,
 $|Z_j|$ = the absolute value of the charge of ion j ,
 R = gas constant,
 T = absolute temperature,
 F = Faraday constant.

Table 1 lists values of D_j^0 calculated from the given λ_j^0 values in Landolt-Bornstein (Vol. 7, 1960). For comparison, D_j^0 values at 25°C are also plotted against ionic potential, $|Z_j|/r_j$, in Fig. 2, where γ_j is the crystal ionic radius of ion j , [γ_j values of monatomic ions are obtained from *Handbook of Chemistry and Physics* (1972) and those of polyatomic ions from MILLERO (1971)]. In general, the higher the ionic potential, the thicker the hydration layer of the water molecules around the ion, therefore, the slower the ionic diffusion. Also, at the same ionic potential, cations diffuse faster than anions.

For cations without λ_j^0 data, λ_j^0 at 25°C still can be estimated from an empirical formula given by NIGRINI (1970):

$$\lambda_j^0 = 10.56 + 90.72 \log Z_j + 42.95 \gamma_j/Z_j. \quad (3)$$

SIMPSON and CARR (1958) have shown that the temperature dependence of viscosity and self-diffusion of water in the temperature range of 0–100°C can be adequately described by Stokes-Einstein relation, i.e.

$$\left(\frac{D^0 \eta^0}{T}\right)_{T_1} = \left(\frac{D^0 \eta^0}{T}\right)_{T_2}, \quad (4)$$

where η^0 is viscosity of water, and T the absolute temperature. Since the temperature dependence of viscosity of water is well known (DORSEY, 1940), one can predict the temperature dependence of self-diffusion coefficient of water, for example

$$\left(\frac{D_{25^\circ\text{C}}^0}{D_{0^\circ\text{C}}^0}\right)_{\text{water}} = \frac{\eta_{10^\circ\text{C}}^0}{\eta_{25^\circ\text{C}}^0} \times \frac{298.15}{273.15} = 2.19.$$

Table 1. Tracer and self-diffusion coefficients of ions at infinite dilution

Cation	D_j^0 (10^{-6} cm ² /sec)			Anion	D_j^0 (10^{-6} cm ² /sec)		
	0°C	18°C	25°C		0°C	18°C	25°C
H ⁺	56.1	81.7	93.1	OH ⁻	25.6	44.9	52.7
Li ⁺	4.72	8.69	10.3	F ⁻	—	12.1	14.6
Na ⁺	6.27	11.3	13.3	Cl ⁻	10.1	17.1	20.3
K ⁺	9.86	16.7	19.6	Br ⁻	10.5	17.6	20.1
Rb ⁺	10.6	17.6	20.6	I ⁻	10.3	17.2	20.0
Cs ⁺	10.6	17.7	20.7	IO ₃ ⁻	5.05	8.79	10.6
NH ₄ ⁺	9.80	16.8	19.8	HS ⁻	9.75	14.8	17.3
Ag ⁺	8.50	14.0	16.6	S ²⁻	—	6.95	—
Tl ⁺	10.6	17.0	20.1	HSO ₄ ⁻	—	—	13.3
Cu(OH) ⁺	—	—	8.30	SO ₄ ²⁻	5.00	8.90	10.7
Zn(OH) ⁺	—	—	8.54	SeO ₄ ²⁻	4.14	8.45	9.46
Be ²⁺	—	3.64	5.85	NO ₂ ⁻	—	15.3	19.1
Mg ²⁺	3.56	5.94	7.05	NO ₃ ⁻	9.78	16.1	19.0
Ca ²⁺	3.73	6.73	7.93	HCO ₃ ⁻	—	—	11.8
Sr ²⁺	3.72	6.70	7.94	CO ₃ ²⁻	4.39	7.80	9.55
Ba ²⁺	4.04	7.13	8.48	H ₂ PO ₄ ⁻	—	7.15	8.46
Ra ²⁺	4.02	7.45	8.89	HPO ₄ ²⁻	—	—	7.34
Mn ²⁺	3.05	5.75	6.88	HP ₄ ³⁻	—	—	6.12
Fe ²⁺	3.41	5.82	7.19	H ₂ AsO ₄ ⁻	—	—	9.05
Co ²⁺	3.41	5.72	6.99	H ₂ SbO ₄ ⁻	—	—	8.25
Ni ²⁺	3.11	5.81	6.79	CrO ₄ ²⁻	5.12	9.36	11.2
Cu ²⁺	3.41	5.88	7.33	MoO ₄ ²⁻	—	—	9.91
Zn ²⁺	3.35	6.13	7.15	WO ₄ ²⁻	4.27	7.67	9.23
Cd ²⁺	3.41	6.03	7.17				
Pb ²⁺	4.56	7.95	9.45				
UO ₂ ²⁺	—	—	4.26				
Sc ³⁺	—	—	5.74				
Y ³⁺	2.60	—	5.50				
La ³⁺	2.76	5.14	6.17				
Yb ³⁺	—	—	5.82				
Cr ³⁺	—	3.90	5.94				
Fe ³⁺	—	5.28	6.07				
Al ³⁺	2.36	3.46	5.59				
Th ⁴⁺	—	1.53	—				

For ions diffusing slower than the fluoride ion (see Fig. 2), Stokes–Einstein relation also holds fairly well in the temperature range relevant to the ocean, e.g.

$$\frac{D_{j,25^\circ\text{C}}^0}{D_{j,0^\circ\text{C}}^0} = 2.19 \pm 0.07$$

as calculated from Table 1.

For ions diffusing faster than the fluoride ion, D_j^0 follows the following equation rather than equation (4).

$$(D_j^0 \times \eta^0)_{T_1} = (D_j^0 \times \eta^0)_{T_2}, \text{ e.g. } \frac{D_{j,25^\circ\text{C}}^0}{D_{j,0^\circ\text{C}}^0} = \frac{\eta_{0^\circ\text{C}}^0}{\eta_{25^\circ\text{C}}^0} = 2.01 \pm 0.05. \quad (5)$$

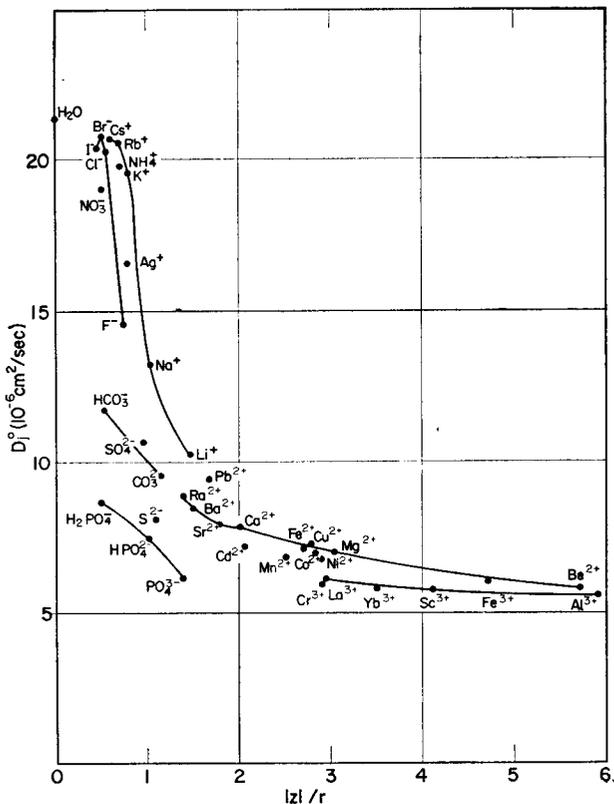


Fig. 2. The tracer- or self-diffusion coefficients at infinite dilution as a function of ionic potential at 25°C.

D_j^0 at higher temperature ranging between 60° and 300°C can be estimated again by equation (2) using NIGRINI's (1970) formula for λ_j^0 , i.e.

$$\lambda_{j,T}^0 = a(T, Z) + b(T, Z) \lambda_{j,25^\circ\text{C}}^0, \quad (6)$$

where the coefficients $a(T, Z)$ and $b(T, Z)$ as function of temperature and charge are given in NIGRINI's (1970) paper.

There are a fair amount of measurements on the tracer- and self-diffusion coefficients of ions in single-salt solution as best summarized in Landolt-Bornstein (Vol. 5, 1969). In general, at a constant temperature the change of the D_j 's of H_2O and Cl^- in NaCl , CaCl_2 and LiCl solutions is closely related to the change of viscosity of the solution (SALVINIEN and BRUN, 1964), i.e.

$$\frac{D_j}{D_j^0} \approx \frac{\eta^0}{\eta}. \quad (7)$$

But for the cations Na^+ and Ca^{2+} , the D_j change is smaller than the viscosity change predicts. This can be explained by realizing that a cation with small crystal ionic radius has a larger hydration layer but that the hydration layer decreases with increasing salt concentration, thus increasing the diffusivity of ion slightly.

There has been only one direct measurement of the diffusion coefficient in sea water (WOLLAST and GARRELS, 1971, for H_4SiO_4), but one can roughly predict D_j in sea water from the viscosity of sea water, for example,

$$\eta^0/\eta_{\text{sea water}(35S\%)} = 0.92 \text{ at } 25^\circ\text{C and } 0.95 \text{ at } 0^\circ\text{C},$$

so D_j in sea water is at most only about 8 per cent smaller than D_j^0 . The present work proves that this is the case.

The effect of pressure on diffusion has been investigated by CUDDEBACK *et al.* (1953 a and b) and BENEDEK and PURCELL (1954). The reliability of the data by CUDDEBACK *et al.* (1953) is still doubtful, but BENEDEK and PURCELL (1954) showed that the self-diffusion coefficient of water is again closely correlated to the viscosity of water up to pressure 10^4 atmosphere, i.e.

$$\frac{D_P^0}{D_1^0} \approx \frac{\eta_1^0}{\eta_P^0}. \quad (8)$$

For ions, one may assume

$$\frac{D_{j,P}}{D_{j,1}} \approx \frac{\eta_{\text{sol},1}}{\eta_{\text{sol},P}}. \quad (9)$$

Of course, as pressure increases, the hydration layer of the ion may partially collapse, so ions with large hydration layer at atmospheric pressure may tend to diffuse faster than predicted from the equation (9). According to HORNE and JOHNSON (1965), the relative viscosity of sea water (35S‰), η_P/η_1 , at 0.84°C decreases from one to 0.965 as pressure increases from 1 atm to about 600 atm. Then, further increments of pressure will increase the η_P/η_1 ratio; while η_P/η_1 increases with increasing temperature in all pressure range. Also, HORNE and FRYSENGER (1963) showed that the relative specific conductance of sea water (35S‰), K_P/K_1 , at 0.93°C increases with increasing pressure, for example, at 600 atm, $K_P/K_1 \approx 1.08$. Therefore, from both viscosity and conductivity data, one can conclude that the pressure effect on D_j is relatively small (at most 8 per cent) in the ocean.

So far we have been dealing with a system with only a small concentration gradient of radioactive isotope tracer and element-wise there is no real concentration gradient of ions in the system. But in a system which shows a real concentration gradient of ions, the rate of diffusion of a given cation has to be the same as that of a co-diffusing anion (Fig. 1c) or as that of a counter-diffusing cation (Fig. 1d), in order to maintain the electro-neutrality condition everywhere in the system. If the concentration gradients of the diffusing cation and anion have the same magnitude, which is the case for salt-diffusion (Fig. 1c) and for the counter-diffusion of exchangeable ions (Fig. 1d), it has been shown for dilute solutions that (JOST, 1952; VAN SCHAİK *et al.*, 1966):

$$D_{12} = (|Z_1|C_1 + |Z_2|C_2)D_1D_2/(|Z_1|C_1D_1 + |Z_2|C_2D_2), \quad (10)$$

where D_{12} is the salt diffusion or counter-diffusion coefficient. D_1 and D_2 are the tracer- or self-diffusion coefficients of the respective ions, Z_1 and Z_2 are the charge of the respective ions, and C_1 and C_2 are the concentrations of the respective ions expressed as normality.

Similarly, at infinite dilution,

$$D_{12}^0 = \frac{(|Z_1| + |Z_2|)D_1^0 D_2^0}{|Z_1|D_1^0 + |Z_2|D_2^0}, \quad (11)$$

an expression due to Nernst (ROBINSON and STOKES, 1959). In case of an electrolyte solution containing more than three ionic components, the situation becomes much more complicated, but as shown by NEWMAN (1967), any given ion of very dilute concentration in a multi-components electrolyte solution (like sea water) diffuses almost independently of other ions, e.g. salt diffusion coefficient of LiCl in sea water, D_{LiCl} , equal to D_{Li^+} . But for the salt-diffusion of major ions of sea water the fast diffusing ions should be slowed down by slow diffusing ions or vice versa in order to maintain electroneutrality. The extent of the interaction among major ions of sea water during the salt diffusion is investigated in the present work.

The tracer diffusion coefficient for the radioactive tracer of a given ion in the interstitial solution of sediment, $D_{j,\text{sed}}$, can be related to that in the bulk solution, namely,

$$D_{j,\text{sed}} = D_j \alpha / \theta^2, \quad (12)$$

where α is the ratio of viscosity of the bulk solution to the average viscosity of interstitial solution, and tortuosity θ is the average ratio of the actual tortuous diffusion path of ions around the sediment particles over the straight distance of that path interval. α is a function of both the porosity of the sediment and the salt concentration of the interstitial solution. α is usually less than one, but for deep-sea sediments with high porosity (70 ~ 80 per cent) and high salt concentration in the interstitial water, α may very well approach one. The direct determination of $D_{j,\text{sed}}$ is complicated by the fact that radioactive tracers often exchange with ions absorbed on the surface of sediment particles so what one really measures is the apparent tracer diffusion coefficient of the radioactive tracer in the sediment-solution system, $D'_{j,\text{sed}}$, which can be related to $D_{j,\text{sed}}$ by (CRANK, 1956)

$$D'_{j,\text{sed}} = \frac{D_{j,\text{sed}}}{1 + K_j} = \frac{D_j^* \alpha}{\theta^2(1 + K_j)}, \quad (13)$$

where K_j , the distribution coefficient, is the ratio of absorbed radionuclide in a unit volume of sediment over radionuclide in a unit volume of solution which is in contact with the sediment.

The K_j of many radionuclides in a sea water and deep-sea sediments system has been extensively investigated by DUURSMA and BOSCH (1970) and DUURSMA and GROSS (1971).

The $D'_{j,\text{sed}}$ and K_j of major ions of sea water in sea water-Pacific red-clay system were studied in the present work which proves the validity of the equations (12, 13).

EXPERIMENTAL METHODS

The experimental techniques for measuring the diffusion coefficient of ions in both sea water and red clay are essentially the same. The apparatus basically consists of only two identical lucite cylinder cells (Fig. 1). Both cells were sealed at one end and were filled up with the same diffusion medium (e.g. sea water agar gels or red clay), with the exception that

one was spiked homogeneously with a radioactive tracer of a given ion (e.g. Na^{22} , K^{42} , Ca^{45} , S^{35} , Cl^{36} , etc.). Then the open ends of two cells were joined together (making sure no bubbles remained in between). After a measured length of time, t , the two cells were separated and the radioactivity in each cell was counted separately. The tracer diffusion coefficient, D_j , of ion j , in a chosen diffusion medium was calculated by the following equation; (for derivation, see PHILLIPS and BROWN, 1964):

$$D_j = \pi f^2 x^2 / t, \quad (14)$$

where f = the fraction of radioactive tracer diffused from one cell to another,

x = the length of one cell.

But, equation (14) is applicable only under the boundary condition that during the course of the experiment, one extreme end of the two joined cells should always keep the same initial concentration of radioactive tracer and the other extreme end, zero concentration. So, if the experiment was run too long, the above condition would break down. CRANK (1956, pp. 11-13), has shown that, in order to maintain the above boundary condition, f should be always equal to or less than 0.15 or one should always keep the following relationship:

$$\frac{x}{\sqrt{(4D_j \cdot t)}} \geq 2. \quad (15)$$

Since the length of the cell is fixed, one can estimate roughly the maximum time span for a run from the equation (15) if an approximate magnitude of D_j is known.

Experiment 1, the tracer diffusion in sea water. Each diffusion cell has a dimension of 4 cm in length and 0.6 cm in diameter. To minimize any non-diffusional movement of diffusion medium e.g. thermal convection, mechanical vibration etc., sea water agar gels with different agar-agar concentration were used as diffusion medium instead of plain sea water. D_j 's in three different sea water agar gels (agar-agar concentration of 1/3, 2/3 and 1 per cent by weight) were determined first. D_j in pure sea water was then obtained by extrapolation to zero agar-agar concentration (NAKAYAMA and JACKSON, 1963). For a radiometric counting, the whole sea water agar gel was directly scraped into an aluminum planchet (2 cm dia.) and was homogenized. After the water was dried out, the planchet was ready for the counting.

Experiment 2, diffusion of sea water into distilled water. The experimental procedure is exactly the same as in the first experiment. The only differences are that (1) one cell was filled with sea water-agar gel and the other cell with plain water-agar gel with the same agar-agar concentration, (2) the fractions of individual major cations diffused from one cell to another were calculated by measuring cation concentrations in sea water-agar gel before and after the experiment by the atomic absorption technique, chloride ion by AgNO_3 -titration and SO_4^{2-} by the charge balance calculation. In this second experiment, the diffusion coefficients of major ions as calculated from equation (14) are sort of averages over a certain range of salinity, so they are not exactly constants but still give a sense of relative diffusivity of major ions under the restriction of electroneutrality.

Experiment 3, tracer-diffusion in Pacific red clay. The cell dimension is 2 cm in length and 1.9 cm in diameter. Two cells were filled with wet Pacific red clay (water content of about 50 ± 1 per cent by weight) but one cell was spiked with radioactive tracer. In order to facilitate a clean cut separation of two cells later, a filter paper was put between two cells when they were joined together. After the separation, the clay in each cell was homogenized. About 0.2 g of clay was put directly into the planchet. The clay was evenly spread by adding some distilled water and heated at 100°C to dryness before the radiometric counting.

Experiment 4, determination of the distribution coefficient, K_j , of ions in sea water-red clay mixture. Two grams of wet red clay with known water content were mixed with 2 g of sea water with a known amount of radioactive tracer. The mixture was shaken for about one day (i.e. about the same length of time as the experiment 3). The sea water was then separated from clay by centrifuging. K_j can be calculated by the following equation:

$$K_j = [2R_b - R_a(2 + 2f)]\rho_s / [2(1 - f)R_a\rho_w],$$

where: R_b and R_a = radioactivity per unit mass of sea water before and after mixing with wet red clay, respectively,

f = weight fraction of sea water in wet red clay,

ρ_w = density of sea water,

ρ_s = density of dry red clay particles.

The density of dry red clay is about 2.0 ± 0.1 . No appreciable absorption of radioactive tracers on Pyrex-glass container were observed.

RESULTS AND DISCUSSIONS

The tracer diffusion coefficients of major ions in sea water, D_j^* , obtained from the experiment 1 are given in the Table below in unit of 10^{-6} cm²/sec. and are also plotted in Fig. 3.

	K ⁺	Na ⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻
$5 \pm 0.3^\circ\text{C}$	11.4	8.0	5.0	11.5	5.8
$23.7 \pm 0.4^\circ\text{C}$	17.9	13.4	7.5	18.6	9.8

(10^{-6} cm²/sec)

The uncertainty in D_j^* , is about $\pm 0.5 \times 10^{-6}$ cm²/sec and originated mostly by the counting statistics and by the least square fitting of the raw data. The dotted lines in Fig. 3 represent the self-diffusion coefficient of ions in water, D_j^0 , and the solid lines, the predicted D_j^* , from the equation (7) i.e. $D_j^* = D_j^0 \cdot \eta^0/\eta^*$. The observed D_j^* of K⁺, Cl⁻ and SO₄²⁻ agree fairly well with the predicted values,

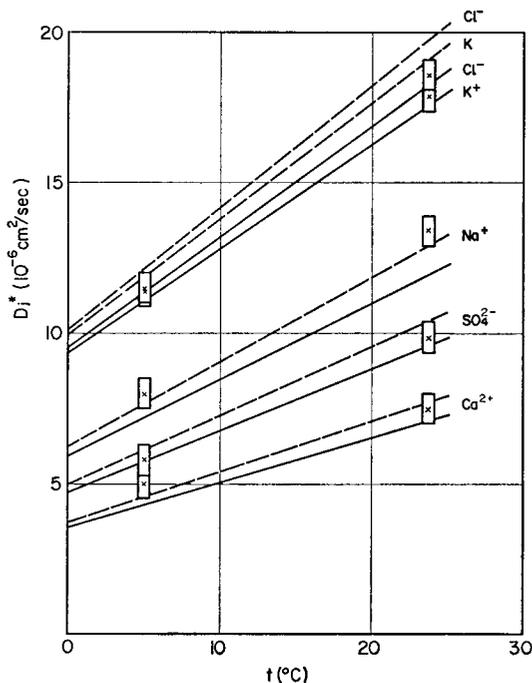


Fig. 3. The tracer-diffusion coefficients of ions in sea water as a function of temperature [dotted lines = D_j^0 , solid lines = D_j^* predicted from equation (7)].

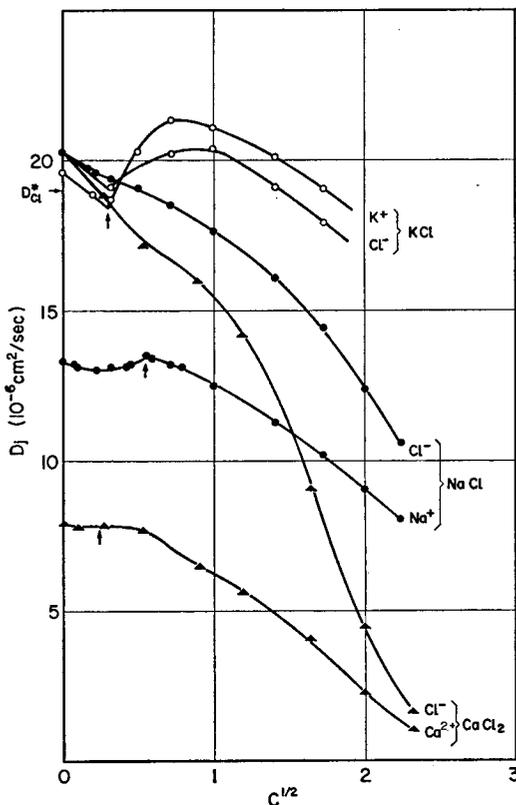


Fig. 4. The tracer-diffusion coefficients of ions in different single or salt solution, as a function of $C^{1/2}$.

but D_{j^*} of Na^+ and Ca^{2+} are very similar to their own D_{j^0} values. It is interesting to notice that D_{Na^+} and $D_{\text{Ca}^{2+}}$ in NaCl and CaCl_2 solutions are again very close to D_{j^0} values at \sqrt{C} where $D_{\text{Cl}^-} = D_{\text{Cl}^-}^*$, as indicated with arrows in Fig. 4 (data from WANG, 1952, 1953). The average diffusion coefficients of major ions of sea water under the restriction of electroneutrality \bar{D}_{j^*} , as obtained from the experiment 2 are: (in unit of $10^{-6} \text{ cm}^2/\text{sec}$).

	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}
$23.7 \pm 0.4^\circ\text{C}$	20.7 ± 0.5	16.4 ± 0.5	9.8 ± 0.3	9.8 ± 0.3	16.5 ± 0.5	(4.6 ± 0.4)

\bar{D}_{j^*} of cations are all greater and of anions smaller than their respective tracer diffusion coefficients in sea water, D_{j^*} , or in water, D_{j^0} , as also shown by BEN-YAAKOV (1972).

The consequence of the different diffusivity of major ions is that any salinity gradient will provide a mechanism for the fractionation or the change of relative abundance of major ions in sea water. BEN-YAAKOV (1972) also illustrated this effect in his diffusion model of the interstitial water of deep-sea sediments. In an

air-sea boundary layer, if there be a high salinity gradient due to evaporation one would expect an enrichment of ions in the order of: $\text{SO}_4^{2-} > \text{Ca}^{2+} \approx \text{Mg}^{2+} > \text{Na}^+ \approx \text{Cl}^- > \text{K}^+$ which is quite different from the enrichment order in marine aerosol and the distillate of sea water i.e. $\text{K}^+ > \text{Ca}^{2+} > \text{SO}_4^{2-} > \text{Mg}^{2+} > \text{Na}^+ \approx \text{Cl}^-$ (BRUYEVICH and KORZH, 1969). The possible mechanism(s) for the enrichment of ions in marine aerosol and in the distillate of sea water were discussed extensively in the 'Working Symposium on Sea-Air Chemistry' (*J. Geophys. Res.* **77** (27), 1972) and beyond the scope of this paper. But, at least, one can conclude that the fractionation by diffusion alone cannot explain the observed enrichment order of ions in marine aerosol and distillate of sea water.

The apparent tracer-diffusion coefficients of ions in red clay, $D'_{j,\text{sed.}}$, obtained from the experiment 3 are given below and plotted in Fig. 5.

	Cl^-	Na^+	SO_4^{2-}	Ca^{2+}	
$5 \pm 0.3^\circ\text{C}$	5.9 ± 0.4	3.5 ± 0.1	3.3 ± 0.2	0.85 ± 0.05	$(10^{-6} \text{ cm}^2/\text{sec})$
$23.7 \pm 0.4^\circ\text{C}$	10.2 ± 0.4	5.8 ± 0.2	5.3 ± 0.2	1.55 ± 0.1	$(10^{-6} \text{ cm}^2/\text{sec})$

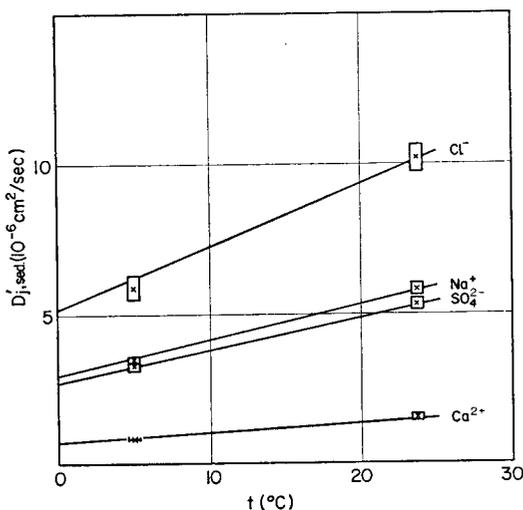


Fig. 5. The apparent diffusion coefficients of ions in red clay as a function of temperature.

The solid lines in Fig. 5 were drawn by using the same temperature dependence of D_j^* in sea water as obtained from Fig. 2. The good fitting of data points with the solid lines shows that the temperature dependence of $D'_{j,\text{sed.}}$ and D_j^* are the same, i.e. $D'_{j,\text{sed.}}/D_j^*$ is independent of temperature. $D'_{j,\text{sed.}}/D_j^*$ as calculated from the best fit values from Figs. 3 and 5 are:

Cl^-	SO_4^{2-}	Na^+	Ca^{2+}
$D'_{j,\text{sed.}}/D_j^* = 0.548 \pm 0.026$	0.552 ± 0.036	0.450 ± 0.023	0.195 ± 0.018

Experiment 4 showed that there is almost no absorption of Cl^{36} and S^{35} (in the form of SO_4^{2-}) on red clay, i.e. K_j for Cl^- and SO_4^{2-} are zero. In other words, $D'_{j,\text{sed.}} = D_{j,\text{sed.}}$ for Cl^- and SO_4^{2-} , and $\alpha/\theta^2 = D_{j,\text{sed.}}/D_j^* = 0.55 \pm 0.04$ for the red clay-sea water system.

Since $\alpha/\theta^2 = 0.55$ and $D'_{j,\text{sed.}}/D_j^*$ values for Na^+ and Ca^{2+} are known, the distribution coefficient, K_j , for the tracers Na^{22} and Ca^{45} can be calculated from the equation (13). The results are $K_{\text{Na}^+} = 0.27 \pm 0.01$ and $K_{\text{Ca}^{2+}} = 1.82 \pm 0.30$ which is in good agreement with the direct measurements i.e. $K_{\text{Na}^+} = 0.3 \pm 0.05$ and $K_{\text{Ca}^{2+}} = 1.4 \pm 0.3$ as obtained from the experiment 4. The agreement suggests that the true tracer diffusion coefficient of ions in deep-sea sediment $D_{j,\text{sed.}}$ is related to that in sea water, D_j^* , by the simple equation:

$$D_{j,\text{sed.}} = D_j^* \alpha/\theta^2.$$

The apparent tracer diffusion coefficient is applicable only when diffusion is accompanied by the absorption of diffusing substance on the sediment. As emphasized by MANHEIM (1970), LERMAN and WEILER (1970), $D'_{j,\text{sed.}}$ should not be confused with $D_{j,\text{sed.}}$ and uncritically applied to any other general diffusion problem.

SUMMARY

(1) The tracer-diffusion coefficient of a given ion in water D_j^0 and in sea water D_j^* differ no more than 0–8 per cent, so for the first approximation, D_j^0 values can be safely used as D_j^* in sea water, (2) the temperature and pressure dependence of D_j and viscosity, η , of solution are closely related. Since pressure effect on η is small, one can assume the same for D_j , (3) under the restriction of electro-neutrality, the average diffusion coefficient \bar{D}_j^* of major cations are greater but of major anion, smaller than their respective D_j^* and D_j^0 . But for ions with very low concentration, $\bar{D}_j^* = D_j^*$, (4) the tracer diffusion coefficient of ions in deep-sea sediment, $D_{j,\text{sed.}}$ and in sea water D_j^* , are related by the simple equation:

$$D_{j,\text{sed.}} = D_j^* \alpha/\theta^2.$$

The factor α/θ^2 of sediment can be determined easily by measuring the tracer diffusion coefficient of Cl^- or SO_4^{2-} in the sediment with the present technique.

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