

DIFFUSION OF SEAWATER IONS. PART II. THE ROLE OF ACTIVITY COEFFICIENTS AND ION PAIRING

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ABSTRACT

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A theoretical evaluation of basic thermodynamic relationships reveals that variation of activity coefficients, ion pairing and electrical interactions must be considered when modelling ionic diffusion in seawater. The contributions of ion-pair formation and change in activity coefficient along the diffusion path were studied experimentally by conducting diffusion experiments in which solutions of KCl, NaCl, MgCl₂, Li₂SO₄, K₂SO₄, Na₂SO₄ and MgSO₄, at an ionic strength of 0.7, were allowed to diffuse into distilled water. The study reveals that the thermodynamic factor, required to correct for changes in the activity coefficient along the diffusion path, is significant for all the salts studied. Agreement between a simple diffusion model, which does not include ion pairing, and observed data was good for completely dissociated salts, but poor for salts which are known to form ion pairs at the concentration levels studied. The diffusion of MgSO₄, 0.425 of which is associated at $I = 0.7$, was successfully modelled by assuming that the diffusion coefficient of the MgSO₄⁰ ion pair is different from the diffusion coefficient of the dissociated salt. The diffusion coefficient of this ion pair is estimated to be $1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 30°C, as compared to $0.49 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for the dissociated salt. It is suggested that the high mobility of this ion pair could cause magnesium enrichment in pore water of sulfate depleted sediments.

INTRODUCTION

In a previous study, Ben-Yaakov (1972) investigated experimentally the diffusion of seawater ions. It was found that a simple model can predict satisfactorily the diffusion of Cl⁻, K⁺, Mg²⁺ and Ca²⁺ from seawater into a dilute solution. The model took into account ionic interaction due to the electroneutrality requirement but assumed that all seawater ions were free (completely dissociated salts) and that infinite dilution mobilities were applicable to the case under study. However, diffusion studies on single salts conducted previously by many investigators (Harned and Owen, 1958; Robinson and Stokes, 1959) have shown that, (a), mobilities at higher concentration differ, in general, from mobilities at infinite dilution, and (b), ion

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pairing (or ion association) may have a significant effect on the rate of diffusion since migration is carried out, in part, by the ion pairs. It was thus evident that more research was required to test the validity of the results and conclusions of the original study (Ben-Yaakov, 1972) before they could be applied to other seawater ions.

In a subsequent study, Ben-Yaakov (1973) attempted to study the role of ion pairing in diffusion by measuring changes in liquid-junction potential between seawater and incrementally modified seawater. It was found that the agreement between the model-calculated potential shifts and the experimentally determined ones improved markedly if the model assumed speciation according to the model of Garrels and Thompson (1962). The model applied infinite dilution mobilities but assumed that some of the ions migrated in the form of ion-pair aggregates. Being an indirect method, the experiment could not provide numerical values for the mobilities or diffusion coefficients of the ion pairs. It indicated, however, that the numerical values of these mobilities could differ markedly from the mobilities of the individual ions which form the ion pairs. Ion pairing could thus be important in modelling the diffusion of SO_4^{2-} , 60% of which is associated with other ions in seawater (Garrels and Thompson, 1962; Berner, 1971; Whitfield, 1974).

The study of Li and Gregory (1974) seems also to support the conjecture that the diffusion rate of sulfate in seawater is slower than the rate predicted by a simple model. Li and Gregory conducted trace and bulk diffusion experiments. In the latter, seawater ions were allowed to diffuse from seawater into distilled water and the apparent diffusion coefficients were calculated from the experimentally determined ionic fluxes. Careful examination of the results of Li and Gregory (1974) reveals that the behavior of the sulfate ions is different from that of the other ions. As discussed by Ben-Yaakov (1972) and Li and Gregory (1974), the diffusion rates of ions must comply with the electroneutrality requirement. The rate-adjusting mechanism is modelled by assuming a potential gradient (or electric field) in solution along the diffusion path. The electric field enhances the migration rate of ions of one polarity and slows down the diffusion rate of the opposite polarity ions so as to maintain zero charge-transfer. If deviation from single-ion infinite-dilution mobilities is only due to the electric field, the ratio of the apparent diffusion coefficient to the tracer diffusion coefficient should be only a function of the magnitude of the field and the valency of the ion. Indeed, these ratios calculated from the data of Li and Gregory (Table I) seem to be consistent with the simple model for most ions. Whereas the diffusion coefficient of Cl^- is lower by about 10–15% compared with its tracer diffusion coefficient, the diffusion coefficient of K^+ and Na^+ is higher by about the same proportion. Furthermore, the diffusion coefficient of the doubly charged cation Ca^{2+} is higher by about 30% than the respective tracer diffusion coefficient, about twice the change observed from the univalent cations. However, the calculated ratio for

TABLE I

Comparison between bulk and tracer diffusion coefficients for seawater ions, as calculated from the results of Li and Gregory (1974)

Ion	Diffusion coefficients ($10^{-6} \text{ cm}^2 \text{ s}^{-1}$)				
	K^+	Na^+	Ca^{2+}	Cl^-	SO_4^{2-}
Tracer diffusion (D_j)	17.9 ± 0.5	13.5 ± 0.5	7.5 ± 0.5	18.6 ± 0.5	9.8 ± 0.5
Seawater into distilled water (D)	20.7 ± 0.5	16.4 ± 0.5	9.8 ± 0.3	16.5 ± 0.5	4.6 ± 0.4
Ratio (D/D_j)	1.16 ± 0.04	1.21 ± 0.06	1.31 ± 0.08	0.89 ± 0.04	0.47 ± 0.05

sulfate does not follow the prediction of the simple model. If the deviation from the tracer diffusion coefficient was only due to the electric field, the corresponding ratio for sulfate should have been about 70% and not 50%, as experimentally determined. Although this deviation from the expected value could reflect an experimental error, as SO_4^{2-} concentration was determined indirectly by charge balance, it is not inconsistent with the observation of Ben-Yaakov (1973) concerning the possible role of ion pairing on the diffusion of sulfate. It seems evident that our understanding of the mechanism of diffusion is insufficient for accurately modelling the diffusion of seawater ions. A better understanding of the diffusion process should help us to validate and improve the quantitative estimates of mass transport between oceans and sediments.

In the present study we attempted to investigate the role of ion pairing and activity coefficients on the diffusion of seawater ions. The experiments were conducted with single seawater-salts, rather than with seawater, so as to avoid the necessity of applying too many assumptions in the theoretical treatment and model calculations.

THEORETICAL CONSIDERATIONS

The flux of a dissolved species (i) in an isothermal solution at rest is related to the chemical and electrical gradients in solution by (Harned and Owen, 1958; Robinson and Stokes, 1959):

$$J_i = C_i U_i (-\text{grad } \mu_i + z_i F E) \quad (1)$$

where: J = flux ($\text{mol cm}^{-2} \text{ s}^{-1}$), C = concentration (mol cm^{-3}), U = mobility at infinite dilution ($\text{cm}^2 \text{ mol}^{-1} \text{ J}^{-1} \text{ s}^{-1}$), μ = chemical potential ($\mu_0 + RT \ln a$), a = activity, z = valence, F = Faraday's number ($96,500 \text{ coulomb eq}^{-1}$), R = gas constant ($8.3 \text{ J deg}^{-1} \text{ mol}^{-1}$), E = electrical field (V cm^{-1}), and "grad" denotes the gradient operand ($\partial/\partial x + \partial/\partial y + \partial/\partial z$).

This rigorous relationship takes into account the forces due to the gradients of the chemical and electrical potentials but neglects the electrophoretic and

relaxation effects (Onsager and Fuoss, 1932) which should cause only a minor disturbance of the fluxes in diffusion (Harned and Owen, 1958; Robinson and Stokes, 1959). Considering a one-dimensional case and expressing the chemical potential as a function of activity, one obtains:

$$J_i = C_i U_i \left(-RT \frac{\partial \ln a_i}{\partial x} + z_i F E \right) \quad (2)$$

or:

$$J_i = -RT U_i \left(\frac{\partial C_i}{\partial x} + C_i \frac{\partial \ln y_i}{\partial x} - \frac{z_i C_i F}{RT} E \right) \quad (3)$$

where y_i is the activity coefficient on the molar scale.

An additional equation is furnished by the electroneutrality requirement:

$$\sum_i z_i J_i = 0 \quad (4)$$

Combining eq. 4 with a set of (i) equations and solving for the electric field

$$E = \frac{RT}{F} \left[\frac{\sum_i U_i z_i \left(\frac{\partial C_i}{\partial x} + C_i \frac{\partial \ln y_i}{\partial x} \right)}{\sum_i z_i^2 C_i U_i} \right] \quad (5)$$

The explicit relationship (5) can now replace E in eq.1 which can be solved for the fluxes if the mobilities, concentrations, concentration gradients and activity gradients are known. However, numerical solution for seawater diffusion is non-trivial in most cases because of the lack of information on speciation, mobilities of ion pairs, and the gradient of the activity coefficients along the diffusion path. Nonetheless, this treatment could be used to draw some general conclusions concerning deviations from ideality, i.e. from the relation

$$J_i = -D_i^0 \partial C_i / \partial x \quad (6)$$

where $D_i^0 = U_i RT$. The general eq.3 can also be reduced to the form of Fick's law

$$J_i = -D_i \partial C_i / \partial x \quad (7)$$

if

$$D_i = U_i RT \left[1 + \frac{\partial \ln y_i / \partial x}{\partial \ln C_i / \partial x} - \frac{z_i F C_i E}{RT \partial \ln C_i / \partial x} \right] \quad (8)$$

Hence, the term in the square brackets expresses the deviation from ideality due to the change in the electrical potential and in the activity coefficient along the diffusion path. Specific cases of diffusion of seawater ions are considered next.

Tracer diffusion

Tracer diffusion, by definition, is the diffusion of a species (i) present in a vanishingly small concentration in a solution containing much higher concentrations of other ions. In this case, the magnitude of the electric field eq.5 reduces to zero if the major ions are evenly distributed in solution. The major ions will also maintain a constant ionic strength and the correction term due to variation of the activity coefficient will be negligibly small. Under these conditions the tracer diffusion coefficient should approach the ideal diffusion coefficient D_i^0 . The treatment is thus straightforward for a tracer present in a free form solution. However, if the tracer forms ion pairs with other ions in solution, the possibility of migration of both the free and associated components should be considered. Unfortunately, this problem has not yet been investigated and so the question concerning the possible contribution of ion association in tracer diffusion is still unanswered. It should be noted in this connection that the so-called "tracer diffusion" experiments of Li and Gregory (1974) are in effect "self diffusion" experiments and hence the diffusion coefficients derived are self-diffusion coefficients. This is because the radioactive tracer was placed in seawater which already contained appreciable amounts of the same ion, although a different isotope. It is expected (Robinson and Stokes, 1959) that the radioisotope will readily exchange with the stable isotope and hence the term self diffusion.

Bulk diffusion

It is evident that both the electric field required to maintain electro-neutrality and the activity coefficient gradients should affect the fluxes of ions diffusing from seawater into a dilute solution. It is also to be expected that ion association will modify the diffusion rates. Unfortunately, numerical evaluation of these processes awaits further investigation. We lack, in particular, an experimental verification of a complete model for a mixed electrolyte and numerical data on the mobilities of ion pairs.

Diffusion of a single salt

Some aspects of the problems concerning the role of activity coefficient gradients and ion association in diffusion could be studied by investigating the diffusion of single salts. Diffusion experiments with a poorly dissociated salt, for example magnesium sulfate, should enable the verification of the applicability of the model to high ionic strength solutions and estimation of the mobility of the ion pair MgSO_4^0 at the ionic strength of seawater. The data compiled from this and similar studies should eventually lead to a model of the diffusion of a complex electrolyte mixture such as seawater.

It has been shown (Robinson and Stokes, 1959) that the diffusion

coefficient of a salt, completely dissociated into two ions, can be reduced to the form

$$D_{12} = \frac{U_1 U_2 |z_1 z_2|}{U_1 |z_1| + U_2 |z_2|} RT \left(1 + \frac{d \ln y_{\pm}}{d \ln C} \right) \quad (9)$$

where y_{\pm} is the mean salt activity coefficient, and subscripts (1) and (2) denote the two free ions. The term in parentheses is usually referred to as the "thermodynamic correction factor". Using the relationship between mobility and limiting equivalent conductance (λ^0)

$$U_i = \frac{\lambda_i^0}{|z_i| F^2} \quad (10)$$

gives

$$D_{12} = \frac{RT}{F^2} \cdot \frac{|z_1| + |z_2|}{|z_1 z_2|} \cdot \frac{\lambda_1^0 \cdot \lambda_2^0}{\lambda_1^0 + \lambda_2^0} \left(1 + \frac{d \ln y_{\pm}}{d \ln C} \right) \quad (11)$$

If the salt is partially associated and only a fraction α is dissociated, the apparent diffusion coefficient of the total salt, D_s , will be

$$D_s = \alpha D_{12} + (1 - \alpha) D_m \quad (12)$$

where D_m denotes the diffusion coefficient of the ion pair (assumed to be neutral). It is thus evident that single salt diffusion experiments could provide invaluable information on the diffusion coefficients of the ion pairs postulated for seawater. The ionic strengths of the single salt solutions used during this study were made equal to that of seawater to simulate, as much as possible, the thermodynamic condition of seawater.

EXPERIMENTAL

The experimental set-up and techniques were similar to those used by Ben-Yaakov (1972). The diffusion apparatus is illustrated schematically in Fig. 1.

A Phoenixia-Brand no. 4, 10-20 μ porosity, 3 mm thick sintered glass crucible, served as the diffusion cell. The cell had an internal diameter of 40 mm and a height of 80 mm. It was fitted with a rubber stopper through which a capillary glass tube with a Pyrex stopcock was inserted. The usable volume of the cell was filled with the electrolytic solution to enhance mixing by gravitation to avoid formation of stagnant layers at the diaphragm-solution boundaries (Ben-Yaakov, 1972). The cell was filled with the appropriate electrolytic solution, the solution was allowed to completely saturate the porous diaphragm and the rubber plug was inserted into the cell. Excess fluid, plus any air bubbles, was allowed to escape through the open stopcock, which was immediately closed thereafter. The exterior side of the cell was then carefully washed with distilled water, dried with clean tissue and immersed in a 1000-ml Pyrex beaker containing approximately

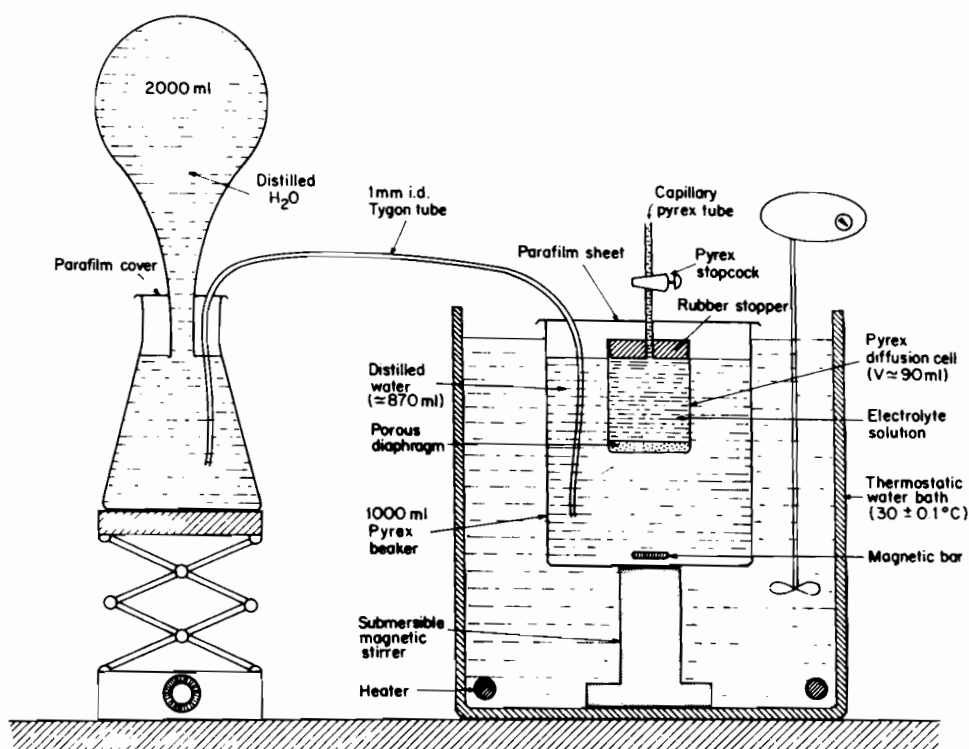


Fig.1. The apparatus used in the diffusion experiments.

870 ml of distilled water. The exact volumes of the outer and inner solutions were determined at the end of each experiment. The beaker was covered with a sheet of Parafilm to minimize external contamination and the water lost by evaporation was continuously replenished by the siphon arrangement illustrated in Fig.1.

The diffusion system was suspended in a thermostatic water bath above a submersible magnetic stirrer and kept at $30 (\pm 0.1)^\circ\text{C}$. The outer solution was stirred continuously by a 5 mm long, 1.5 mm thick Teflon-coated magnetic bar.

Diffusion was monitored by sampling $1 (\pm 0.01)$ ml of the outer solution at selected time intervals. The samples were directly transferred into 50-ml volumetric flasks to which 1 ml of an 8% KCl aqueous ionization buffer solution was added, and the solution was diluted to volume with distilled water. For K^+ diffusion experiments, a NaCl ionization buffer was applied.

Li, Na, K and Mg were analyzed by atomic absorption spectrometry. The analytical error is within $\pm 1\%$ of the reported values for Mg and Li and within $\pm 2\%$ of the K and Na data.

MODEL CALCULATION

Calculation of single salt diffusion coefficients, D_{12}^0 and D_c

Single salt diffusion coefficients were calculated via eq.11. The respective limiting equivalent conductivities for 30°C were obtained by non-linear (Lagrangian) interpolation of Robinson and Stokes (1959, appendix 6.2) data. The thermodynamic correction factors $(1 + d \ln \gamma_{\pm} / d \ln c)$ for the different salts were calculated by plotting $\ln \gamma_{\pm}$ vs. $\ln m$ (data from Robinson and Stokes, 1959, app. 8.10) and estimating the tangent at $I = 0.35$ (Fig.2). This concentration corresponds to the mid-point of the diaphragm assuming a linear concentration gradient across it. For the salts

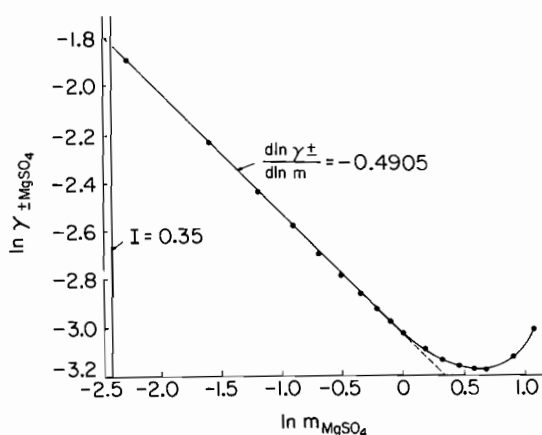


Fig.2. A graphical representation of the relationship between $\ln \gamma_{\pm}$ and $\ln m$ used for the estimation of the thermodynamic correction factors $\left(1 + \frac{d \ln \gamma_{\pm}}{d \ln C}\right)$.

under study the derivative of $\ln \gamma_{\pm} = f(\ln c)$ is nearly constant within the investigated concentration range. Also, the error introduced by taking the derivative on the molal, rather than on the molar scale, is very small compared with the error in estimating the activity coefficient itself (Butler, 1964).

Estimation of the diffusion-cell constant

The diffusion cell constant, i.e. the ratio between the effective width and the effective area of the cell's diaphragm (W/A), was estimated from a 1 M KCl diffusion experiment by a trial and error calculation of a constant which yielded the best-fit curve to the experimental data, presented in concentration—time coordinates. Plotting of the curve was performed with the aid of a desk-top Hewlett-Packard model 9821-A computer with a peripheral 9862-A plotter. The concentration in the outer solution (C_t) was calculated from

$$C_t = C_{(t-\Delta t)} + D(\Delta C)_{(t-\Delta t)}(\Delta t)/(V_{\text{out}}W/A) \quad (13)$$

In eq.13 the term (W/A) denotes the cell constant, D is the diffusion coefficient of KCl at 30°C , ΔC is the difference between the molar concentrations across the cell diaphragm at the previous $(t - \Delta t)$ calculation step, Δt is the time increment selected (1 h) and V_{out} is the volume of the outer solution. The cell constant, $W/A = 0.0581 \text{ cm}^{-1}$, was obtained from the thermodynamically corrected diffusion coefficient (eq.11) for 1 M KCl.

Estimation of the observed single-salt diffusion coefficients, D_{obs}

The single-salt observed diffusion coefficients were estimated via eq. 13 by a trial and error procedure to yield the best-fit curve to the experimental data in concentration—time coordinates.

RESULTS AND DISCUSSION

The thermodynamic correction factors evaluated for the salts under study range between approximately 0.9 to 0.5 (Fig.3; Table II). These factors are, in effect, transforming the concentration gradients into the corresponding

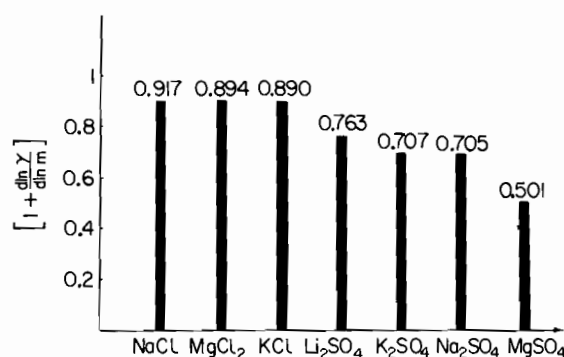


Fig.3. Thermodynamic correction factors for the salts under study. See "Model Calculation" section for outline of the calculation method used to estimate these factors.

chemical potential gradients. As already observed above, the total force on a dissolved constituent is proportional to the electrochemical potential gradient whereas the diffusion coefficient relates the flux to the concentration gradient. The apparent diffusion coefficient for an ion in a given system is therefore not only dependent on the inherent mobility of the ion and the electrical interaction (Ben-Yaakov, 1972) but also on the change in ionic strength along the diffusion path. A variation of the ionic strength will change the activity by affecting the activity coefficient and will thus modify the diffusion coefficients of the migrating species. The magnitude of the thermodynamic correction factors evaluated here clearly demonstrates

TABLE II

Observed and estimated diffusion coefficients. D_{12}^0 = calculated diffusion coefficient without including the thermodynamic correction factor. $D_c = D_{12}^0 \left(1 + \frac{d \ln \gamma}{d \ln m}\right)$.
 D_{ob} = observed diffusion coefficients. All values are for 30°C

Salt (I = 0.7)	$\left(1 + \frac{d \ln \gamma}{d \ln m}\right)$	D_{12}^0 ($10^{-5} \text{ cm}^2 \text{ s}^{-1}$)	D_c ($10^{-5} \text{ cm}^2 \text{ s}^{-1}$)	D_{ob} ($10^{-5} \text{ cm}^2 \text{ s}^{-1}$)	D_{ob}/D_c
KCl	0.8903	2.23	1.98	—*	—
NaCl	0.9174	1.81	1.66	1.66	1.00
MgCl ₂	0.8936	1.41	1.26	1.26	1.00
Li ₂ SO ₄	0.7630	1.14	0.87	0.92	1.06
K ₂ SO ₄	0.7073	1.72	1.21	1.32	1.09
Na ₂ SO ₄	0.7055	1.39	0.98	1.13	1.15
MgSO ₄	0.5095	0.96	0.49	0.72	1.47

* The KCl solution was used for calibration of the diffusion cell.

their significant influence on the value of the diffusion coefficient. This is particularly true for the sulfate salts for which the values of the thermodynamic factors range between 0.76 and 0.5 (Table II).

The experimental procedure adopted here calls for calibration of the diffusion cell by a salt solution with a known diffusion coefficient. The cell's constant (W/A) is determined during the calibration phase by matching the model calculation to the experimental points, assuming that the diffusion coefficient of the salt is known accurately. In the previous study (Ben-Yaakov, 1972) the cell was calibrated with a 0.7 M KCl solution and the calibration was verified by running a diffusion experiment with NaCl and comparing the experimental points with the model calculation. The agreement between the expected and experimentally observed points was very good despite the fact that the model did not take into account the thermodynamic correction factors. The present evaluation of these factors for KCl and NaCl (Fig.3; Table II) seems to offer a simple explanation to the fact that a good agreement was previously obtained despite the oversimplified diffusion model. This could readily be understood by considering the following:

The cell constant (W/A) was obtained by fitting the simpler model, which did not include the thermodynamic correction factor, to the experimental data points. Hence the (W/A) value so evaluated also included a correction to the fact that the thermodynamic factor was omitted. That is, the (W/A) value was smaller by the amount required to compensate for the omission of the thermodynamic factor for the model. Later, this same adjusted (W/A) factor was used in the model calculation for the NaCl experiment. Since the

values of the thermodynamic correction factor for NaCl and KCl are nearly the same (Table II), the (W/A) factor provided the necessary thermodynamic adjustment for the NaCl model calculation.

The preceding discussion clearly indicates that the diffusion coefficient determined through this study may not be accurate on an absolute scale due to the approximate nature of the model. We have neglected the effect of viscosity on diffusion (Robinson and Stokes, 1959; Li and Gregory, 1974) nor did we take into account the electrophoretic effect (Onsager and Fuoss, 1932). However, a comparison between the calculated diffusion coefficient of KCl used to calibrate the cell and published data seems to support our assumption concerning the validity of the diffusion model presented here. Harned and Owen (1958) compiled experimental data on the diffusion coefficient of KCl over a large concentration range. From these data the diffusion coefficient for 0.7 M KCl was found by interpolation to be $1.87 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 25°C. Applying the model presented here, we calculated the diffusion coefficient of 0.7 M KCl at 25°C to be $1.78 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ which is about 5% lower than the experimentally determined value. We consider this to be a good agreement since we are interested in phenomena and processes which might have a gross effect on the diffusion coefficients.

The magnitude of the thermodynamic correction factors (Table II) seems to suggest that the correction for activity coefficient along the diffusion path might be significant for bulk diffusion of seawater. When seawater ions diffuse from seawater into a dilute solution the ionic strength changes along the diffusion path and therefore the activity coefficient should also vary. On the other hand, in tracer diffusion cases the ionic strength is kept constant and hence the value of the thermodynamic correction factor approaches unity. It is thus evident that diffusion coefficients obtained by a bulk diffusion experiment cannot be compared with diffusion coefficients determined by tracer diffusion experiments.

Goldhaber et al. (1977) evaluated the diffusion coefficient of the sulfate ion in pore water of marine sediment by conducting a set of experiments in which sulfate was allowed to diffuse from sulfate-rich to sulfate-poor sediment. This diffusion case, is, to a first approximation, a tracer diffusion experiment because sulfate is a minor constituent of seawater; it contributes only about 8% to the total ionic strength. The value of the diffusion coefficient estimated through that experiment ($4.0 \pm 0.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) was compared by Goldhaber et al. with the experimental results of Li and Gregory (1974) ($4.6 \pm 0.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$), indicating the good agreement between the two sets of results. However, the quoted results of Li and Gregory were obtained by a bulk diffusion experiment in which seawater was allowed to diffuse into distilled water. This type of experiment is inherently different from the tracer diffusion experiments conducted by Goldhaber et al. It appears that a direct comparison between the values of the two diffusion coefficients is rather meaningless because of the

entirely different conditions of electrical interaction and thermodynamic effects.

The diffusion coefficients, D_{ob} , derived from the present experiments (Table II) are in good agreement with the model estimated values, D_c , for the chloride salts NaCl and MgCl₂ (Fig.4). These salts are almost completely dissociated and the good agreement seems to suggest that the model presented here accurately predicts (within 10%) the diffusion coefficients of single dissociated salts. However, the good agreement between the experimentally determined and calculated values of the diffusion coefficient for the chloride solutions does not in itself exclude the existence of ion pairs in the tested solutions (M. Wedborg, personal communication). Rather, the data suggest either complete dissociation or similarity between the mobility of the dissociated and associated components.

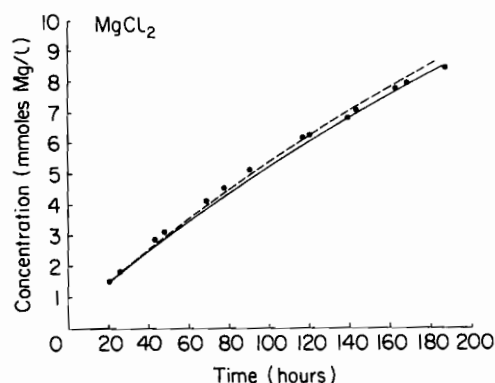


Fig.4. Observed (circles) and estimated (solid line) concentration of outside solution during a MgCl₂ diffusion experiment. The estimate is based on eq.13 as outlined in the "Model Calculation" section.

The deviation between the observed diffusion coefficients, D_{ob} , and the calculated ones, D_c , seems to be related to ion association, or ion pairing. For the sulfate salts (Table II), the agreement is best (within 9%) for Li₂SO₄ (Fig.5), which is probably the most dissociated salt, and worst for MgSO₄ (Fig.6), the most associated one. This observation seems to indicate that the bulk diffusion of the sulfate salts is affected by ion pair formation. It has been suggested (Harned and Hudson, 1951 a, b) that the deviation can be modelled by assuming that the mobility, or diffusion rate of the ion pair, is different from the mobility of the dissociated ions (eq.12 above). This model was applied to the present MgSO₄ data by assuming a dissociation constant for MgSO₄⁰ of $10^{-2.36} \text{ mol l}^{-1}$ and assuming for the activity coefficients of Mg²⁺, SO₄²⁻ and MgSO₄⁰ the values 0.26, 0.17 and 1.13, respectively (Whitfield, 1974). Using these parameters, the dissociation factor α , was calculated to be 0.525 for 0.175 M ($I = 0.7$) MgSO₄. Applying eq.12, the

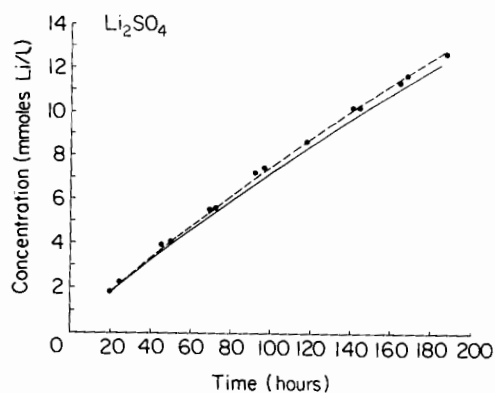


Fig.5. As for Fig.4 but for Li_2SO_4 diffusion.

diffusion coefficient of the MgSO_4 ion pair is calculated to be $0.974 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ as compared to $0.49 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ calculated for the dissociated MgSO_4 (Table II); all values for 30°C . The diffusion coefficient of the magnesium sulfate ion pair as calculated by relationship (12) is specific for the case under study, i.e. diffusion of MgSO_4 into a dilute solution. The diffusion coefficient intrinsically contains the thermodynamic correction factor. By dividing out this factor (0.5095 from Table II) we can obtain the tracer diffusion coefficient for the MgSO_4 ion pair, D_m^0 . Applying this approach we obtain $D_m^0 = 1.91 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. This value is much higher than the self diffusion coefficient of the sulfate ion ($1.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and that of the magnesium ion ($0.80 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$).

The marked increase in the mobility of the MgSO_4 ion pair compared to the mobility of the dissociated salt is attributed (Harned and Owen, 1958;

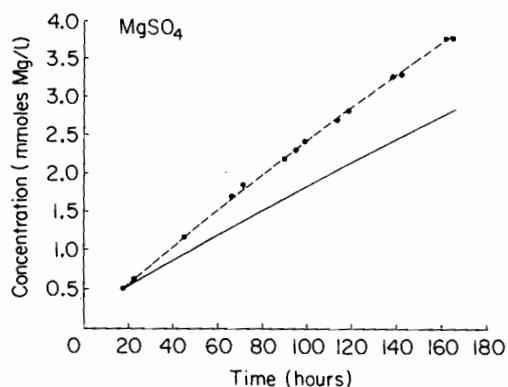


Fig.6. As for Fig.4 but for MgSO_4 diffusion. The large difference between the estimated line and the experimental data is postulated to be a result of the high mobility of the MgSO_4 ion pair.

Robinson and Stokes, 1959) to the loss of hydration water as a result of ion pair formation. Hydration water slows down the mobility of ions by increasing the effective cross section and hence the drag. Being apparently neutral, the MgSO_4 ion pair should have a smaller effective cross section and hence a higher mobility.

The observations of the present study concerning the higher mobility of the magnesium sulfate ion pair are in accord with the data of Harned and Hudson (1951 a, b). They studied the diffusion of MgSO_4 and ZnSO_4 at low concentration by a conductance method. A comparison between our results and the data of Harned and Hudson for MgSO_4 (Table III) reveals the same general behaviour for MgSO_4 — an observed diffusion coefficient which is considerably higher than the calculated one. A direct quantitative comparison between the sets of data cannot be made owing to the different experimental conditions. Nonetheless, both studies clearly indicate that the tracer diffusion coefficient of the ion pair is significantly higher than the diffusion coefficient of the dissociated salt. Our estimate of D_m^0 is much higher than that estimated by Harned and Hudson (1951 b). This much higher value could be a result of underestimation of D_c , perhaps because we did not take into account the electrophoretic effect (Onsager and Fuoss, 1932).

If the increase in ion-pair mobility results from loss of hydration water, it is not unreasonable to assume that the mobility of the ion pair should be higher than the mobility of the sulfate ion. This could be inferred from the probability that the mobility of the latter is largely limited by its size; however, although the ionic radius of the magnesium ion is smaller, its movement is slowed down considerably by the hydration shell resulting from its large hydration number (Harned and Owen, 1958). It is thus postulated that the mobility of the magnesium sulfate ion pair, which is assumed to have partially lost its hydration water, should have about the same value as the mobility of the sulfate ion (Harned and Owen, 1958). The tracer diffusion coefficient is calculated from the limiting equivalent conductance to be about $1.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Our estimate of the tracer diffusion coefficient of the magnesium sulfate ion pair is much higher, for unknown reasons.

Although the results of the present study help to clarify the process of ionic diffusion in seawater, many questions are still left open. In particular, a complete diffusion model for seawater ions which takes into account the effect of ion-pair formation and possible change of activity coefficient along the diffusion path is lacking. Nevertheless some general conclusions concerning ionic diffusion in marine sediments can be drawn from this investigation if the model including migration by ion pairs is accepted.

About 60% of the sulfate ions are associated with other ions in seawater (Garrels and Thompson, 1962; Berner, 1971; Whitfield, 1974). Some 25% of the sulfate ions are associated with magnesium, 20% with sodium and the rest with calcium and potassium. If the interstitial water of a given layer of a marine sediment is depleted in SO_4^{2-} (as is found in anoxic marine

sediments) the concentration of free and associated sulfate will be lower at that zone compared with the sediment of normal seawater. Thus, when modelling the diffusion of sulfate ions, not only the concentration gradient of the free sulfate but also the concentration gradients of the ion pairs should be considered. One ramification is that associated ions, e.g. a magnesium in the MgSO_4^0 ion pair, will migrate with the diffusing sulfate. This "hitchhiking effect" will pump magnesium into the sulfate-depleted region. There, the ion pair will dissociate, increasing the concentration of free magnesium. This process will set up a concentration gradient for magnesium which will cause back diffusion of magnesium from the sulfate depleted zone. The real picture is even more complex since charge neutrality must be preserved. Hence, the onset of an electrical potential gradient along the diffusion path is expected. It is thus evident that diffusion of the sulfate ion could initiate a chain reaction affecting the concentration profiles of other ions even if they are not involved in any chemical reaction. Although the exact magnitudes of these effects cannot be assessed because of the lack of a complete diffusion model, first order estimates can be obtained from an approximate analysis.

Consider an anoxic marine sediment in which the pore water is depleted in SO_4^{2-} in relation to normal seawater concentration (Berner, 1974). Denoting the total sulfate concentration gradient by $(dc/dx)_{\text{SO}_4^{2-}}$, the concentration gradient of the magnesium sulfate ion pair will be about $0.25 (dc/dx)_{\text{SO}_4^{2-}}$. Because of SO_4^{2-} depletion, the free magnesium concentration will be higher and its concentration gradient equal to $-0.25 (dc/dx)_{\text{SO}_4^{2-}}$. Assuming a steady-state condition, the total flux of magnesium into the sediment must be balanced by the flux of magnesium out of the sediment. Hence,

$$0.25 (dc/dx)_{\text{SO}_4^{2-}} D_{\text{MgSO}_4^0} + (-0.25 (dc/dx)_{\text{SO}_4^{2-}} + \Delta) D_{\text{Mg}^{2+}} = 0 \quad (14)$$

where Δ is the extra concentration gradient of magnesium required to balance out the influx of magnesium by the "hitchhiking effect". Simple algebraic manipulation gives

$$\Delta = -0.25 (dc/dx)_{\text{SO}_4^{2-}} \times [D_{\text{MgSO}_4^0}/D_{\text{Mg}^{2+}} - 1] \quad (15)$$

where the negative sign signifies a higher concentration of magnesium at the SO_4^{2-} depleted zone. Assuming that the magnitude of the diffusion coefficient of MgSO_4^0 is about twice the numerical value of $D_{\text{Mg}^{2+}}$, then

$$\Delta = -0.25 (dc/dx)_{\text{SO}_4^{2-}} \quad (16)$$

The present rough analysis thus predicts the onset of a magnesium concentration gradient which is about one quarter of the concentration gradient of dissolved SO_4^{2-} but of opposite sign, i.e. an enrichment in magnesium concentration in sulfate depleted sediment layers. Deviation from this postulated profile might be an indication of chemical reaction

between magnesium in the interstitial water and the solid phase (McDuff and Gieskes, 1976).

Many investigators (e.g. Siever et al., 1965; Brooks et al., 1968; Drever, 1971; Nissenbaum et al., 1972 and Sholkovitz, 1973) reported a depletion in magnesium in interstitial waters of recent marine sediments and, in particular, in anoxic sediments. The depletion was attributed to incorporation of magnesium into clay minerals (Sholkovitz, 1973) but authigenic formation of high-magnesium calcite was also postulated (Berner et al., 1970) as a possible sink for magnesium. The overall loss of Mg^{2+} to the sediment by burial and diffusion should equal the river input if a steady state ocean is assumed. The present study suggests that the diffusion of Mg^{2+} to the sediment is enhanced when a sulfate concentration gradient is also present. Hence, the actual diffusion flux of Mg^{2+} into an anoxic marine sediment should be larger than the value estimated from a simple diffusion model which does not take into account the role of ion pairing.

Applying the same reasoning as above, depletion of Mg^{2+} in interstitial waters of marine sediments should cause a slight enrichment in SO_4^{2-} concentration in oxic sediments. Earlier investigators who reported a slight increase in SO_4^{2-} concentration in aerobic marine sediments (Shishkina, 1964; Sayles and Mangelsdorf, 1976) attributed this increase to in situ oxidation of pyrite. It is postulated here that this steady-state enrichment could be a result of SO_4^{2-} diffusion into the sediment by the "hitchhiking effect" mentioned above.

Considering our present state of knowledge concerning the mechanism of ionic diffusion in seawater and, in particular, the lack of a complete and rigorous diffusion model, the preceding analysis should be considered only as a possible mechanism for reactions that might take place during ionic diffusion in seawater. Much more research is evidently required before a quantitative assessment of the relative importance of these processes can be made.

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