

THE INCREMENTAL CONCENTRATION CELL AND ITS APPLICATION
FOR STUDYING IONIC DIFFUSION IN SEAWATER

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ABSTRACT

A novel configuration of a concentration cell was used to measure liquid junction potentials generated between seawater and modified seawater. The potentials were found to be compatible with a seawater diffusion model which assumes that ionic mobilities in seawater are close to the limiting mobilities, and that speciation follows the model of Garrels and Thompson (1962). The study suggests that the mobility of sulfate complexes is low and that electrical gradients and ionic association may modify diffusion fluxes in interstitial waters of marine sediments.

INTRODUCTION

Studies on interstitial waters of marine sediments revealed that the ionic composition of the pore waters may differ from the composition of the overlying waters (Presley, 1969; Initial Reports of the Deep Sea Drilling Project, 1969-1972). It is therefore probable, that the concentration gradients at the sediment-seawater interface, would result in a diffusional mass transport between oceans and sediments. Geochemical calculations which consider mass-balances of elements in the oceans must take into consideration the possible contribution of these fluxes to the overall inflow and outflow of seawater ions. Unfortunately, accurate estimates of diffusion fluxes on the ocean floor cannot be presently made, as many problems related to the diffusion process in marine sediments are poorly understood. In particular, there is insufficient experimental data on diffusion in a complex electrolyte system such as seawater, and the role of ion-sediment exchange in the diffusion of seawater ions has not yet been investigated.

In a recent study, Ben-Yaakov (1972) investigated the process of ionic diffusion from seawater into a dilute

solution. It was found that the electrical coupling between the ions extensively modifies the diffusion fluxes. It was concluded, therefore, that this electrical coupling must be taken into consideration when modelling ionic diffusion in marine sediments. The present study represents an attempt to investigate another aspect of ionic diffusion; the role of ion complexing. It is generally accepted that most of the ions in seawater exist as ion-pairs (or complexes), which must be considered in explaining processes in seawater. Garrels and Thompson (1962) have proposed a thermodynamic model for the distribution of these species, and subsequent investigations have shown (Berner, 1971) that this model agrees with a number of independent tests. If the model of Garrels and Thompson (1962) is accepted, then one must conclude that the driving forces of ionic diffusion in seawater are not the concentration gradients of seawater ions, but rather, the individual gradients of the free and complexed species.

Experimental investigation of ionic diffusion in seawater is cumbersome for at least two reasons. First, diffusion processes are slow (a typical value for a diffusion coefficient is 10^{-5} cm²/sec. or about 0.9 cm²/day) and if the experiments are to be repeated for all seawater ions, many weeks and probably months of investigation would be involved. Second, each experimental run would require high precision analyses of all seawater ions in order to detect small concentration changes--which is a difficult and a highly time-consuming task. Application of radioactive tracer techniques for studying ionic diffusion in seawater can greatly simplify the investigation. However, diffusion of tracer ions in electrolyte solutions cannot be equated with the diffusion of the bulk ions (Robinson and Stokes, 1970). It is highly questionable, therefore, whether tracer diffusion studies of seawater ions would shed light on the process of bulk ionic diffusion in seawater.

It is generally accepted (MacInnes, 1961) that the liquid junction potential (or the potential of a concentration cell with transference) is a function--among other things--of the mobility of the ions in the junction. This dependency has been used in the past to estimate the magnitude of the liquid junction potential (Guggenheim, 1930) and to minimize the junction potential of salt bridges (MacInnes, 1961). The present study attempted to apply the dependency between ionic mobility and the liquid junction potential in the reverse direction. That is, liquid junctions were generated and their potential measured for the purpose of estimating ionic mobilities in seawater.

THEORETICAL CONSIDERATIONS

The liquid junction potential (E_j) generated between two electrolytes is related to the activity of the ions in solution by the differential equation (MacInnes, 1961):

$$dE_j = \frac{RT}{F} \sum \frac{t_i}{z_i} d\mu_i \quad (1)$$

where R is the gas constant, T absolute temperature, F Faraday's constant, t_i , μ_i and z_i are the transference number, chemical potential and valence of a charged species (i), respectively, and the summation is over all charged species. The transference number, defined as the proportion of total charge carried by a given species (i), is related to the mobilities (U) and concentration (C , expressed in equivalents per liter) of the charged species by:

$$t_i = \frac{U_i C_i}{\sum U_i C_i} \quad (2)$$

By combining equations (1) and (2) one obtains the relationship:

$$dE_j = \frac{RT}{F} \sum \frac{U_i C_i / z_i}{\sum U_i C_i} d\mu_i \quad (3)$$

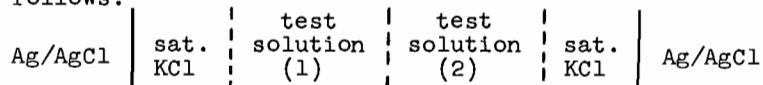
The magnitude of the potential of a given liquid junction can be calculated by integrating equation (3) along the junction under consideration. An analytical solution of this integration was derived by Henderson (MacInnes, 1961) for the mixture boundary junction which is of interest here. This junction is defined as a boundary in which each layer is a linear mixture of the two end solutions. Under these conditions and for the special cases where the activity coefficients and mobilities are constant along the integration path, Henderson's equation is applicable. The equation relates the total liquid potential to the concentration of the charged species of the two end solutions (designated by prime and double prime):

$$E_j = \frac{RT}{F} \frac{\sum \left(\frac{U_i}{z_i}\right) (C_i' - C_i'')}{\sum U_i (C_i'' - C_i')} \ln \frac{\sum U_i C_i''}{\sum U_i C_i'} \quad (4)$$

It should be noted that the integrated value of the junction potential depends only on the concentrations and mobilities of the charged species in the two boundary solutions.

The first basic requirements (mixture boundary) of Henderson's derivation can be easily met experimentally by allowing one electrolyte to leak into the other. If the leaking rate is made larger than the diffusion rate then migration due to diffusion can be neglected and the junction can be considered to be of the mixture boundary type --for all practical purposes. The requirement of constant mobility along the junction can also be approximated because the mobilities change only slightly with concentration (Robinson and Stokes, 1970). However, the requirement of constant activity coefficients cannot be met in the general case, because the two boundary electrolytes would have different compositions. This study attempted to overcome this difficulty by applying a novel experimental technique, the incremental concentration cell, in which the measured potentials are due to small perturbation in the test solution and the activity coefficients are kept approximately constant.

The incremental concentration cell is constructed as follows:



Initially, test solution (1) and (2) are identical (artificial seawater in the present experiments), but during the course of an experiment, a relatively small amount of salt is added to test solution (2). This perturbation will result in a shift in the potentials of the liquid junction solution (1)/solution (2) and solution (2)/saturated KCl and the sum of these shifts is measured by the two reference electrodes.

The incremental addition of salt to solution (2) will not affect the potential of the reference electrodes or that of the junction solution--(1)/KCl. Therefore, these potentials need not be considered when calculating the incremental change in the cell's potential. The initial potential between the two test solutions is of course zero, because they are identical. The potential, generated after the addition of salt to solution (2), can be calculated by Henderson's equation since the mobilities and activity coefficient would not vary markedly along the junction if only a small amount of salt is

added. It is assumed of course, that the junction is of the boundary mixture type.

The incremental change in the potential of the junction seawater (2)/KCl can be expressed as:

$$E = \int_2^{\text{KCl}} \frac{RT}{F} \sum \frac{\bar{t}_i}{Z_i} d(\ln \gamma_i \cdot m_i) - \int_2^{\text{KCl}} \frac{RT}{F} \sum \frac{t_i}{Z_i} d(\ln \gamma_i \cdot m_i) \quad (5)$$

where γ_i and m_i are activity coefficient and concentration of charged species (1), respectively, and the bar designates conditions after the salt is added. The last equation can be rewritten to the form:

$$E = \int_2^{\text{KCl}} \frac{RT}{F} \sum \frac{\bar{t}_i}{Z_i} d(\ln m_i) - \int_2^{\text{KCl}} \frac{RT}{F} \sum \frac{t_i}{Z_i} d(\ln m_i) + \int_2^{\text{KCl}} \frac{RT}{F} \sum \frac{\bar{t}_i - t_i}{Z_i} d(\ln \gamma_i) \quad (6)$$

Henderson integration is applicable to the first two integrals if the mobilities are assumed to stay constant along the integration path. The contribution of the third integral is small because $(\bar{t}_i - t_i)$ is small and the dependence of $\ln \gamma_i$ on concentration is also small. Hence, the shift in the potential of the junction solution--(2)/KCl can be estimated by the difference between the two first integrals in the last equation. It can be concluded, therefore, that the total potential shift, which is the sum of potential shifts of this junction and of the junction between the two test solutions previously, could be closely calculated by Henderson's integration of the liquid junction potential.

The calculation can be made in three steps: (1) calculation of the liquid junction potential between the unmodified solution and saturated KCl, (2) calculation of the liquid junction potential between the modified test solution and saturated KCl and (3) calculation of the liquid junction potential between the unmodified and modified solution. The total potential shift (E_c) is given by:

$$E_c = E_3 + E_2 - E_1 \quad (7)$$

where 1,2,3 correspond to the three computation steps.

EXPERIMENTAL

The configuration of the incremental concentration cell used in this study is shown schematically in Figure 1. The two working junctions were constructed by pressing nylon wicks between rubber stoppers and glass tubes. The leak rate through the junctions was adjusted to about 1 ml/week. The assembly was put in a temperature regulated bath and the experiments were run at a temperature of $25 \pm 0.1^\circ\text{C}$. All the experiments were conducted with artificial seawater (Kester *et al.*, 1967) of $35 \pm 0.2\%$ salinity.

The output potential of the cell was signal-conditioned by an electrometer type operational amplifier (Philbrick SP2A), measured digitally and also recorded by a strip chart recorder (1 mv full scale). Each experimental run was commenced by replacing the seawater in the beaker (250 ml) and establishing a base line for the measured potential. The absolute value of this potential was not measured as it is of no interest here. After the potential had stabilized (drift rate of less than $20 \mu\text{v}$ per hour), a small amount of a salt (0.04 or 0.08 equiv/l) was added to the beaker and the magnetic stirrer was turned on, until the salt completely dissolved. The cell was then left to thermally equilibrate until the potential stabilized again. The potential values reported here are the total shift between this stable value and the initial base line.

RESULTS AND DISCUSSION

The measured values of the potential shifts (E_m) due to the incremental addition of various salts are summarized in Table 1. Each reported value is an average of 2-3 repeated runs which were found to reproduce to within $\pm 10 \mu\text{v}$. The overall uncertainty band of the potential measurement is estimated to be $\pm 25 \mu\text{v}$. Experiments were conducted at two incremental additions 0.04 eq/l and 0.08 eq/l. However, the higher level could not be used with bicarbonate salts due to CaCO_3 precipitation whereas two of the salts (KCl and MgSO_4) produced too low a reading for the 0.04 eq/l additions.

The preceding theoretical discussion suggests that the shifts in the liquid junction potentials can be calculated by Henderson's integration (equation 4) of the liquid junction potential provided that the concentration of all charged species and their mobilities are known. Since this information was not known a priori, the liquid junction potential was calculated for different models of ionic speciation and mobilities. In the first calculation (Model A) it was assumed that all seawater ions are free and that their mobilities in seawater are identical to their mobilities in infinite dilute solution (Ben-Yaakov, 1972). The calculated values for NaCl, KCl and CaCl₂ agree with the measured ones (Table 1) to within the experimental accuracy. However, the calculated values of the liquid junction potentials shifts due to the addition of the bicarbonate and sulfate salts are not consistent with the measured values. These results probably indicate that the basic assumption concerning the value of ionic mobilities is correct, but that ion pairing (Garrels and Thompson, 1962) must be taken into account which explains why the assumption of free ions has not produced the desired results.

Ion pairing was taken into account in the second set of calculations by including in Henderson's integration (equation 4) all charged species according to the model of Garrels and Thompson (1962). The concentration of the free and associated species, of both original and spiked seawater, was calculated by an iteration method (Ben-Yaakov and Goldhaber, 1972), assuming activity coefficients and dissociation constants according to Berner (1971). Apart from a knowledge of the concentration of all charged species in solution, application of Henderson's equation also requires a knowledge of the mobilities of the charged species. The study of Ben-Yaakov (1972) as well as the calculation of Model A, described above, suggest that the mobilities of the free ions in seawater are close to mobilities at infinite dilution. However, as no data are available for the mobilities of complexed species (such as NaSO₄⁻, CaHCO₃⁺), an assumption had to be made regarding the value of these mobilities. The simplest assumption that can be made, is that the mobility of charged ion pairs is close to the mobility of the free anion. This is deemed to be a reasonable assumption because the degree of hydration of an ion pair is probably smaller than that of each ion in its free state due to partial cancellation of the electrical fields. It is likely, therefore, that the mobility of the ion pair is limited by its effective volume which should be close to that of the anions (SO₄⁻, HCO₃⁻).

The assumption of speciation according to the model of Garrels and Thompson (1962) and mobilities of ion pairs equal to the mobilities of the respective anions (Model B) improved the agreements between the calculated and measured potentials for the bicarbonate salts (Table 1). However, the calculated potential shifts due to the addition of the sulfate salts were still in poor agreement with the measured ones. These results probably indicate that the mobility of the charged sulfate complexes are not equal to the mobility of the sulfate ion. It was found that the agreement between the calculated and measured potentials improves if the mobilities of the charged sulfate species are assumed to be much smaller than the mobility of the free sulfate ion. In fact, the best agreement was obtained when the mobilities of the charged sulfate species was assumed to be nil (Model C). The overall agreement between the calculated potential shifts according to Model C (Table 1 and Fig. 2) is very good, considering the approximate nature of the Garrels and Thompson model (Thompson and Ross, 1966).

The agreement between the calculated potential shift according to Model C, and the measured one, suggests that the assumption regarding the low mobility of the charged sulfate complexes may be valid. The low mobility may be attributed to a large effective cross-section of the sulfate complexes which increases the drag. This would imply that the two ions forming the ion pair are not in close proximity to one another and that a number of hydration molecules are involved in this ionic interaction. This implication is in accord with the study of Eigen (1957) on general and specific ionic interaction in solution. He concluded, from sound absorption spectra of electrolytes in aqueous solution, that because the interacting ions are at a relatively larger distance (6-8 Å), sulfate ion pairs involve a number of hydration molecules.

According to the model of Garrels and Thompson (1962) approximately 60% of the sulfate ions in seawater are complexed. As the results of the present study suggest, the mobility of the sulfate complexes is low, the effective diffusion coefficient of total sulfate in seawater is probably lower by about 60% than the diffusion coefficient of the free sulfate ion. However, the actual diffusion flux of a given ion in seawater is not only a function of the concentration gradient of that ion, but also a function of the concentrations, concentration gradient and mobilities of all seawater ions (Ben-Yaakov, 1972). Therefore, it is impossible to assign a single diffusion coefficient to a given ion and the actual

diffusion flux of each ion can be evaluated for each case only after taking into account electrical cross-coupling between the ions (Ben-Yaakov, 1972).

Ionic diffusion in marine sediments is far more complicated than the case of diffusion in seawater due to possible solution-sediment reaction. Ion exchange between the pore water and the solid phase of the sediment would modify the ionic fluxes (Van Schaik et al., 1966). However, since the nature of this ion-exchange process and its role in modifying diffusional fluxes are still poorly understood, it is as yet impossible to accurately calculate diffusion fluxes in marine sediments. The present study suggests, however, that the driving forces of the diffusional fluxes in marine sediments are the concentration gradients of both free ions and the complexed ionic species.

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Table 1 - Experimental and theoretical values of the liquid junction potential shifts. See text for details of model calculations.

| Salt | $\Delta \text{salt} = 0.04 \text{ eq/l}$ | | | | | | $\Delta \text{salt} = 0.08 \text{ eq/l}$ | | | | | |
|---------------------------------|--|---------|---------|---------|---------|---------|--|---------|---------|---------|---------|---------|
| | Ec (mv) | | | Em (mv) | | | Ec (mv) | | | Em (mv) | | |
| | Model A | Model B | Model C | Model A | Model B | Model C | Model A | Model B | Model C | Model A | Model B | Model C |
| NaCl | -0.246 | -0.263 | -0.259 | -0.229 | -0.475 | -0.508 | -0.475 | -0.508 | -0.500 | -0.479 | -0.479 | -0.479 |
| KCl | -0.033 | -0.040 | -0.036 | -- | -0.064 | -0.077 | -0.064 | -0.077 | -0.069 | -0.058 | -0.058 | -0.058 |
| CaCl ₂ | -0.431 | -0.449 | -0.458 | -0.446 | -0.832 | -0.867 | -0.832 | -0.867 | -0.882 | -0.847 | -0.847 | -0.847 |
| NaHCO ₃ | 0.047 | 0.101 | 0.109 | 0.129 | -0.091 | 0.188 | -0.091 | 0.188 | 0.204 | -- | -- | -- |
| KHCO ₃ | 0.260 | 0.325 | 0.334 | 0.324 | 0.503 | 0.625 | 0.503 | 0.625 | 0.642 | -- | -- | -- |
| K ₂ SO ₄ | 0.269 | 0.318 | 0.405 | 0.438 | 0.569 | 0.611 | 0.569 | 0.611 | 0.787 | 0.861 | 0.861 | 0.861 |
| MgSO ₄ | -0.129 | -0.116 | -0.046 | -- | -0.249 | -0.207 | -0.249 | -0.207 | 0.087 | 0.025 | 0.025 | 0.025 |
| Na ₂ SO ₄ | 0.086 | 0.096 | 0.184 | 0.220 | 0.166 | 0.184 | 0.166 | 0.184 | 0.364 | 0.474 | 0.474 | 0.474 |

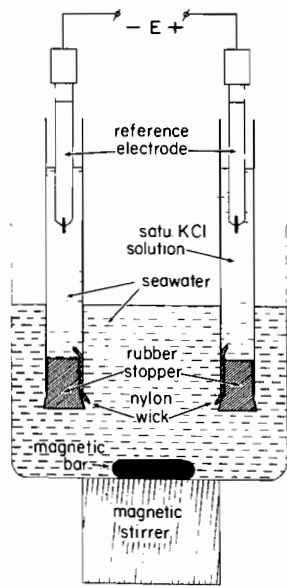


Figure 1: Practical realization of the incremental concentration cell.

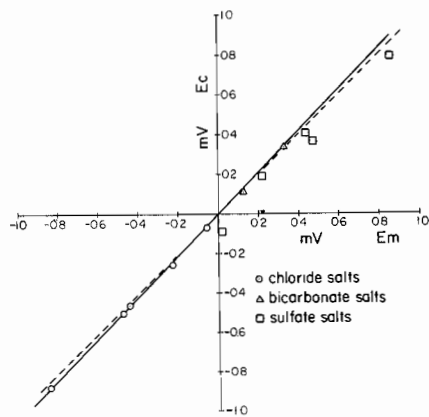


Figure 2: Measured potential shifts (E_m) compared to theoretical values (E_c) calculated by Henderson's equation and assuming ionic speciation according to model C.