

The infinite dilution diffusion coefficient for $\text{Al}(\text{OH})_4^-$ at 25°C^1

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Abstract—The infinite dilution diffusion coefficient for $\text{Al}(\text{OH})_4^-$, necessary to calculate fluxes of dissolved Al between sediments and overlying waters, was determined at 25°C . Measurements were made using the diaphragm-cell method by diffusing $\text{Al}(\text{OH})_4^-$ spiked KBr solutions against KCl over a range of ionic strengths. The mean of 9 separate measurements gives $1.04 \pm .02 \times 10^{-5} \text{ cm}^2/\text{s}$ as the infinite dilution diffusion coefficient for $\text{Al}(\text{OH})_4^-$ at 25°C .

INTRODUCTION

IN ORDER TO understand the behavior of any chemical species in the oceans it is necessary to accurately calculate relevant mass fluxes between the various oceanic reservoirs. Recently, several investigators have attempted to estimate fluxes of dissolved Al between marine sediments and the overlying waters using measured concentration gradients (STOFFYN-EGLI, 1982; STOFFYN and MACKENZIE, 1982). One difficulty with these calculations is that appropriate diffusion coefficients for dissolved Al species are unknown. In the pH range of most marine waters and sediments, $\text{Al}(\text{OH})_4^-$ should be the predominant dissolved Al species. For example, at pH 8 $\text{Al}(\text{OH})_4^-$ accounts for $\geq 94\%$ of the sum of Al^{+3} and the hydrated Al species (calculated from data of HEMINGWAY *et al.*, 1978 and MAY *et al.*, 1979).

The purpose of this study was to determine the diffusion coefficient of $\text{Al}(\text{OH})_4^-$ at infinite dilution and 25°C . Once modified using appropriate viscosity, temperature and sediment tortuosity corrections (*e.g.*, LI and GREGORY, 1974; LERMAN, 1979; BERNER, 1980; ULLMAN and ALLER, 1982), this diffusion coefficient should be applicable for calculations of gradient predicted fluxes of dissolved Al between sediments and overlying waters.

METHODS

Diffusion coefficient measurements were made by a modification of the diaphragm-cell method discussed by STOKES (1950) and ROBINSON and STOKES (1959). In this method, a solution with a known concentration of the ion of interest is added to one compartment (compartment 1) of a cell which is separated from a second compartment (compartment 2) by a porous membrane. Compartment 2 is filled with a solution containing a much lower concentration of the ion. Once the geometry of the diaphragm-cell has been calibrated using an ion with known diffusion coefficients, the mean diffusion coefficient of the ion of interest over the range of concentrations in the cell can be calculated from the measured flux through the cell membrane as a function of time.

The design of the diaphragm-cell apparatus used here is modified slightly from that described by ALLER (1983). The

chief modification is that use of a standard membrane between cells rather than various natural materials made the use of rubber gaskets around the membrane described in that study unnecessary and a higher precision in the geometry of the membrane was possible between runs. The plastic clamp holding the membrane was also made $\frac{1}{16}$ " rather than $\frac{1}{8}$ " thick to further improve stirring and reproduction of the boundary layer. In this study, measurements were made by diffusing Al-spiked KBr solutions (compartment 1) through a $0.4 \mu\text{m}$ pore-size nucleopore membrane filter (the cell membrane) into KCl solutions (compartment 2) at the same ionic strength. Reasons for using these particular solutions are explained below. A certified 1000 mg/l Al standard was used to prepare KBr solutions with known Br^- and Al concentrations. The Al spiked KBr and unspiked KCl ($\text{Al} \approx 0$ relative to compartment 1) solutions were brought to pH 13 with KOH prior to use. At this pH virtually all of the dissolved Al is present as $\text{Al}(\text{OH})_4^-$. The KCl concentration in compartment 2 was adjusted to balance KCl present in compartment 1 (due to HCl used to preserve the certified Al standard and the added KOH) and insure constancy in ionic strength across the cell membrane (see discussion).

Once the diaphragm-cell compartments were filled with appropriate solutions and air bubbles were removed, the cell was placed in an incubator at $25 \pm 0.5^\circ\text{C}$ and an initial sample was taken. Both sides of the cell membranes were vigorously and continuously stirred with plastic coated magnetic bars which were at a distance of $<1 \text{ mm}$ from the surface of the membrane. Samples were taken in compartment 2 for Br^- and Al determinations at 4-5 time intervals. Concentrations remaining in compartment 1 were calculated from mass balance. An independent set of measurements showed that loss of Al to container walls is not significant on the time scale of our experiments and can be ignored in mass balance calculations. The ratio of the diffusion coefficients of $\text{Al}(\text{OH})_4^-$ and Br^- was determined from the slope of $\ln[(C_1^0 - C_1^t)/(C_1^0 - C_2^t)]$ (where \ln = natural logarithm, C = concentration, C^0 = initial concentration and subscripts 1 and 2 refer to compartments 1 and 2, respectively) against time for both ions. The initial sample was omitted from these calculations to insure that fluxes through the cell membrane were at steady-state (ROBINSON and STOKES, 1959; ALLER, 1983). Because this is a steady-state method, the effect of adsorption within the membrane can be ignored even for very high adsorption coefficients (see ALLER, 1983 for a theoretical treatment). Our procedure is similar to that used by WOLLAST and GARRELS (1971) to measure the diffusion coefficient of silica in seawater. In our experiments, the so-called cell constant (which is a function of the diaphragm-cell geometry) was determined simultaneously with the $\text{Al}(\text{OH})_4^-$ diffusion coefficient during each run by measurement of Br^- diffusion.

Concentrations of dissolved Al were determined fluorimetrically by the modified lumogallion method described

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by MACKIN and ALLER (1983). The precision in these measurements was $\sim 5\%$ or better. Dissolved Br^- was determined colorimetrically with a precision of $\sim 3\%$ by the chloramine-T oxidation procedure described by PRESLEY (1971). Dissolved IO_3^- determinations, which are discussed below, were made by the Ce-As catalytic method of BARKLEY and THOMPSON (1960) as modified by ULLMAN (1982). The precision was usually $\sim 3\%$ or better. All of the above measurements were made using standards prepared in the same matrix as samples.

RESULTS AND DISCUSSION

A plot from a typical set of Al and Br^- measurements is shown in Fig. 1. The results of all measurements are summarized in Table 1.

The experimental conditions used in this study were chosen so as to minimize problems in interpretation of the diffusion coefficient measurements for $\text{Al}(\text{OH})_4^-$. In all but one of the runs the ionic strength was constant across the diaphragm-cell membrane. Therefore, gradients in solute activity coefficients need not be included in a theoretical treatment of the diffusion coefficients (ROBINSON and STOKES, 1959; LASAGA, 1979; KATZ and BEN-YAAKOV, 1980). Aqueous solutions of KCl and KBr were used as the diaphragm-cell media because the infinite dilution diffusion coefficients of K^+ , Cl^- , and Br^- are nearly identical. Therefore, cross-coupling terms in the diffusion coefficients for these ions approximately cancel one another (MCDUFF and ELLIS, 1979), and solvent activity gradients across the membrane are minimized. Neglecting ion-pair formation (*e.g.* DYRSSEN and WEDBORG, 1980), the diffusion coefficient for Br^- which can be used in our experiments to find the $\text{Al}(\text{OH})_4^-$ diffusion coefficient is simply the value at infinite dilution. It may be more correct to adjust

Table 1. Summary of results of diffusion coefficient measurements

Ionic Strength		Al or IO_3^- (mM)	Number of runs	$D_{\text{Al}}/D_{\text{Br}}^{**}$	$D_{\text{I}}/D_{\text{Br}}^{***}$
Compartment 1	Compartment 2				
1	1	9.27	2	0.518(+.004)	-
0.5	0.5	4.63	2	0.515(+.022)	-
1	0.5	9.27	1	0.520	-
0.1	0.1	0.927	4	0.516(+.009)	-
0.5	0.5	1.98	2	-	0.526(+.007)

* Initial concentration in compartment 1 (mM = millimolar)

** Ratio of diffusion coefficients of $\text{Al}(\text{OH})_4^-$ and Br^-

(\pm one standard error)

*** Ratio of diffusion coefficients of IO_3^- and Br^-

(\pm one standard error)

individual diffusion coefficients for the viscosity of our solutions (ROBINSON and STOKES, 1959); however, since we measure the ratio of two diffusion coefficients, for which the viscosity effect should be the same, this complication is ignored.

The dissolved Al concentrations used in our experiments were very low in comparison to K^+ , Cl^- and Br^- concentrations (Table 1). Therefore, diffusion of $\text{Al}(\text{OH})_4^-$ should not contribute significantly to cross-coupling terms in the diffusion coefficients of either these ions or the solvent (for a theoretical treatment of cross-coupling see LASAGA, 1979). Cross-coupling as well as ion-pair formation could potentially influence the diffusion coefficients determined for $\text{Al}(\text{OH})_4^-$ (LASAGA, 1979; KATZ and BEN-YAAKOV, 1980). Data in Table 1 show that over a wide range of ionic strength the ratio of the diffusion coefficients of $\text{Al}(\text{OH})_4^-$ and Br^- was nearly constant. Even the run with $I = 1.0$ (I = ionic strength) in compartment 1 and $I = 0.5$ in compartment 2 gave results which did not differ significantly from the mean of the other measurements. These results indicate that, within the error in our measurements, cross-coupling and ion-pair formation do not significantly affect the diffusion of $\text{Al}(\text{OH})_4^-$. Most studies which report large effects in this regard are based on diffusion of a concentrated electrolyte into distilled water. Such studies maximize the effect of ion-pairing on solute transport in part because of solvent activity gradients and solute-solvent cross-coupling.

ALLER (1983) reported slight deviations in the ratios of $\text{NH}_4^+/\text{Br}^-$ and $\text{Si}(\text{OH})_4/\text{Br}^-$ diffusion coefficients, as determined by the method used here, from the theoretical values at infinite dilution. These deviations could be accounted for by repulsion of Br^- during diffusion through the cell membrane due to a slight negative charge on the membrane surface. Since Br^- and $\text{Al}(\text{OH})_4^-$ possess the same charge, the effect of this charge repulsion on the ratio of their diffusion coefficients should be minimal. In order to test this assertion we have made measurements identical to those described previously but with IO_3^- (added as KIO_3) replacing Al in the compartment 1 solutions. IO_3^- is similar to $\text{Al}(\text{OH})_4^-$, being a relatively large, singly charged anion. Also, the reported $\text{IO}_3^-/\text{Br}^-$ diffusion coefficient ratio at infinite dilution is very close to the values for $\text{Al}(\text{OH})_4^-/\text{Br}^-$ determined in our experiments. Therefore, IO_3^- should

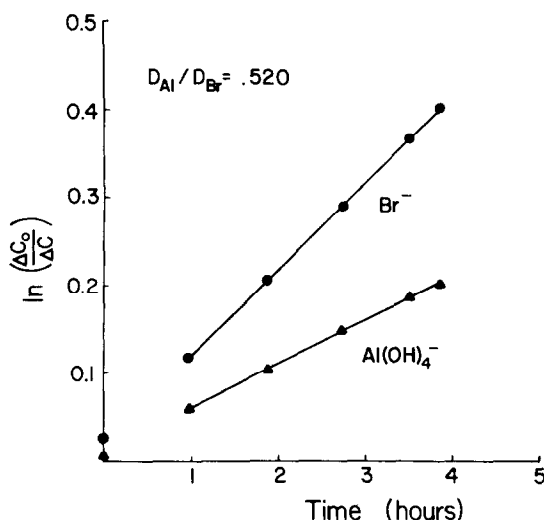


FIG. 1. Example plot used to determine the ratio of diffusion coefficients of $\text{Al}(\text{OH})_4^-$ (D_{Al}) and Br^- (D_{Br}). ΔC_0 = concentration difference between compartments 1 and 2 at the beginning of the run ($C_1^0 - C_2^0$); ΔC = concentration difference at time t ($C_1 - C_2$). Time is relative to $t = 0$ for the first sample.

give a good estimate of the magnitude of the charge repulsion effect on $\text{Al}(\text{OH})_4^-$ diffusion. The agreement between the average of our measured $\text{IO}_3^-/\text{Br}^-$ diffusion coefficient ratios (0.526; Table 1) and the value at infinite dilution (0.527; LI and GREGORY, 1974) is very good, indicating that, within the error in measurements, any charge repulsion effects for IO_3^- , and by inference $\text{Al}(\text{OH})_4^-$, and Br^- must cancel.

Based upon the above discussion, the mean ratio of the $\text{Al}(\text{OH})_4^-/\text{Br}^-$ diffusion coefficients from our measurements and the diffusion coefficient for Br^- at infinite dilution and 25°C should yield a very good estimate of the infinite dilution value for $\text{Al}(\text{OH})_4^-$ at 25°C. Using $D_{\text{Al}}/D_{\text{Br}} = 0.5165$ (mean of 9 measurements) and $2.01 \times 10^{-5} \text{ cm}^2/\text{s}$ as the infinite dilution diffusion coefficient for Br^- at 25°C (LI and GREGORY, 1974), gives $1.04 \pm .02 \times 10^{-5} \text{ cm}^2/\text{s}$ (± 2 standard errors) for $\text{Al}(\text{OH})_4^-$. The accuracy in this diffusion coefficient may be somewhat lower than the stated analytical precision due to the factors discussed previously.

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