

The Fluorine Complexation Degree in Seawater

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Received March 3, 2009

Abstract—Ionometric measurements of the complexation degree of fluorides in seawater of 5–35‰ salinity at 25°C were carried out using two procedures for the standardization of the measuring electrochemical circuits. It was shown that, if we determine the degree of the fluorine complexation in seawater using the measured values of the total coefficients of the activity, the fraction of free ions is much dependent on the value used of the activity coefficient of the free ions calculated by means of one of the versions of either the second or third approximation of the Debye–Hückel electrostatic theory of strong electrolyte solutions. With the more correct measurement of the fluorine complexation degree in seawater on the basis of the comparison of the EMF values in pure KCl–KF solutions and in mixtures of these solutions and seawater at equal ionic power and fluoride concentrations, a close correlation was revealed for the free ion fraction in three series of experiments at fluorine contents of 0.2, 0.3, and 0.4 mM (the concentration of the fluorine in seawater of 35‰ salinity amounts to 0.421 ± 0.014 mM.)

DOI: 10.1134/S0001437011010164

INTRODUCTION

According to the available calculated estimates [7, 9, 10, 13], about half (50–53%) of the fluorine in seawater is bound into complexes and exists mainly as MgF^+ ion pairs. Because the fraction of free ions of the i solution component i (α_i) is related to the activity (a_i), the total concentration ($[\Sigma i]$), and the concentration of free ions ($[i]$) according to the known equation

$$a_i = [\Sigma i]\gamma_i^* = [\Sigma i]\alpha_i\gamma_i = [i]\gamma_i, \quad (1)$$

where γ_i^* and γ_i are the total coefficient of activity and the coefficient of activity of the free ions i , respectively, and only the a_i and $[\Sigma i]$ values are directly measurable, to determine the complexation degree ($\beta_i = 1 - \alpha_i$), one must first estimate the γ_i value. This is possible only on the basis of the usage of some nonthermodynamic assumptions and theoretical modeling notions. For example, to estimate the γ_{F^-} values, one may apply the electrostatic theory of the activity coefficients for nonassociated electrolytes by Debye–Hückel. One also may, assuming a reasonably negligible degree of the F^- ion complexation in the solution of a background electrolyte of the same ion power as that in seawater, consider the occurrence of a part of the F^- ions in seawater in the form of complex compounds as a cause of various a_{F^-} values.

This study is aimed to experimentally determine the degree of fluorine complexation in seawater using the measured values of the fluoride activities and to

reveal the degree of concordance of the results obtained using different ways to convert the activity value into the concentration of free fluorine ions.

The experiments used an electrochemical circuit consisting of a fluoride ion-selective electrode and a silver–chloride reference electrode in a saturated KCl solution. The circuit was standardized in the former case using a vastly diluted KF solution (4×10^{-5} – 4×10^{-4} M) and, in the latter case, using mixed KCl–KF solutions with a low fluoride concentration (2 – 4×10^{-4} M) and a total molar ionic force of $I = 0.715$ conforming to that in normal seawater. In the first series of the experiments, the activity of the fluorides was measured in seawater of 5–35‰ salinity and 1×10^{-4} M total fluorine concentration. In the second series, normal seawater of 2 – 4×10^{-4} M total fluorine concentration was used. The temperature of the solution during the measurements was equal to 25°C.

The activity of fluorides is related to the electromotive force (EMF) of the measuring electrochemical circuit (E) by the following equation:

$$E = E_0 + E_D - k \log a_{\text{F}^-}, \quad (2)$$

where E_0 is the EMF of the measuring circuit at $a_{\text{F}^-} = 1$; E_D is the diffusion potential, and k is the angular coefficient calculated from the experimental data as the inclination angle of the EMF's linear dependence on the $\log a_{\text{F}^-}$ value. The value of the diffusion potential is not measurable exactly [3, 4], and its variations

for dilute solutions in seawater contacting with saturated KCl solutions may be as high as several mV [8], which conforms to an error of the determination of the fluorine ion activity of $\sim 10\%$ (4% per 1 mV).

Of greater importance is the uncertainty related to the calculation of the free ion activity coefficients. For now, to estimate them, the Debye–Hückel theory of either the second

$$\log \gamma_i = -\frac{Az_i^2 \sqrt{I}}{1 + \dot{a}B\sqrt{I}} \quad (3)$$

or third approximation

$$\log \gamma_i = -\frac{Az_i^2 \sqrt{I}}{1 + \dot{a}B\sqrt{I}} + CI, \quad (4)$$

is used, where z_i is the charge of an i ion, A and B are the constants for a given temperature ($A = 0.5115$ and $B = 0.3291$ at 25°C); \dot{a} is the distance of the maximum approach (diameter) of the ions in Angstrom units ($1 \text{ \AA} = 10^{-8} \text{ cm}$), I is the ionic force of the solution, and C is a constant for the given electrolyte concentrations usually obtained in an empiric way [6]. As the third approximation, of common usage are the semi-empirical equations by Davis [6]

$$\log \gamma_i = -\frac{Az_i^2 \sqrt{I}}{1 + \sqrt{I}} + 0.1z_i^2 I \quad (5)$$

and by Meites [5]

$$\log \gamma_i = -\frac{Az_i^2 \sqrt{I}}{1 + 1.5\sqrt{I}} + 0.2z_i^2 I. \quad (6)$$

A common viewpoint concerning the ion sizes in aquatic solutions is lacking. Some authors allow the usage of the crystallographic radii of the ions, while others propose using the sizes of the hydrated ions (but with no available sufficiently reliable ways to calculate them). In view of this, the \dot{a} value is mostly determined by means of fitting by the criterion of the best agreement of the experimental data on the activity coefficients with the values calculated using the analytical equations. Thus, by [12], the \dot{a} parameter for fluorine is within 5.3 \AA at the recommended value of 3.5 \AA . Even a higher $\dot{a} = 8.2 \text{ \AA}$ follows from the hydration model in which the hydrated ion radius is taken to be equal to the sum of its crystallographic radius and the diameter of the hydration water molecule. In view of the fact that the C value is also not defined rigorously in theory, Eqs. (5) and (6) must be considered as the empiric ratios averaged for many electrolytes that coincide in form with the analytical relationship that follows from the Debye–Hückel electrostatic theory for solutions of nonassociated electrolytes.

In very dilute solutions of $I < 0.001$, the contribution of the linear member of Eq. 4 is negligible and the variations of the \dot{a} parameter have almost no effect on the γ_i values. Therefore, in 4×10^{-5} – $4 \times 10^{-4} \text{ M}$ solutions of KF low-associated electrolytes, the second approximation of the Debye–Hückel equation is allowable to be used to calculate the activity coefficients of fluorine ions. Because $[\text{F}^-] \approx [\Sigma \text{F}^-]$, one may assume

$$a_{\text{F}^-} \approx [\Sigma \text{F}^-] \gamma_{\text{F}^-}. \quad (7)$$

By standardizing the measuring circuit using dilute solutions of KF, one may measure the activity of fluorides in seawater to the accuracy of the difference of the diffusion potentials. However, later on, in determining the fraction of free ions by Eq. (1)

$$\alpha_{\text{F}^-} = \frac{a_{\text{F}^-}}{[\Sigma \text{F}^-] \gamma_{\text{F}^-}} \quad (8)$$

the uncertainty of the estimates considerably increases because of the lack of a strict way to calculate the activity coefficients of the free ions at high ionic forces (all the uncertainties related to the selection of the \dot{a}_{F^-} , value are finally reflected in the α_{F^-} value).

For seawater of 35‰ ($I \approx 0.7$), the difference in the values of the activity coefficients of the free ions calculated using the second approximation of the Debye–Hückel equation at different values of the \dot{a} parameter varied from 3.3 to 8.2 \AA and are as high as 20% (Table 1). The calculations using the semi-empirical equations by Davis and Meites result in the γ_{F^-} values in the seawater being equal to 0.687 and 0.892 , respectively, and differ from each other by more than 20%. The average γ_{F^-} value amounts to 0.717 ± 0.110 for the whole range of the calculated values, which conforms to an uncertainty of $\pm 15\%$ for the calculation of the α_{F^-} value.

The difficulties in the analytical calculations of the activity coefficients of the free ions in the solutions of the electrolytes of medium and high concentrations promoted a search for other ways to determine the γ_i values. Garrels [2, 11] used the assumption by McInnes

$$\gamma_{\text{KCl}}^2 = \gamma_{\text{K}^+} = \gamma_{\text{Cl}^-} \quad (9)$$

to calculate the γ_i values using the “mean-salt” procedure by which

$$\gamma_{\text{F}^-} = \frac{\gamma_{\pm \text{KF}}^2}{\gamma_{\pm \text{KCl}}}. \quad (10)$$

Table 1. Calculations of the free fluorine ion fraction using the data of ionometry in seawater of 0.1 mM total fluoride concentration using different ways to estimate the activity coefficients of the free ions

Seawater salinity, ‰	Measured activity of the fluorine ions, μM	Calculated value of the free ion fraction α_{F^-} with different procedures of the γ_{F^-} estimation											
		the γ_{F^-} calculation using Eq. (3) by the second approximation of the Debye–Hückel theory					the γ_{F^-} calculation using semiempirical equations for the second approximation of the Debye–Hückel theory				the γ_{F^-} calculation using the mean-salt method (10)		
		$\dot{a} = 3.3 \text{ Å}$		$\dot{a} = 5.3 \text{ Å}$		$\dot{a} = 8.2 \text{ Å}$		by Davis (5)		by Meites (6)			
		γ_{F^-}	α_{F^-}	γ_{F^-}	α_{F^-}	γ_{F^-}	α_{F^-}	γ_{F^-}	α_{F^-}	γ_{F^-}	α_{F^-}		
5	59.3	0.758	0.782	0.787	0.754	0.818	0.725	0.771	0.769	0.813	0.729	0.780	0.760
10	52.6	0.702	0.750	0.744	0.707	0.788	0.668	0.728	0.723	0.800	0.658	0.736	0.715
15	48.9	0.667	0.733	0.719	0.681	0.771	0.635	0.706	0.693	0.806	0.607	0.712	0.687
20	46.3	0.643	0.720	0.702	0.660	0.759	0.610	0.695	0.666	0.820	0.564	0.698	0.663
25	44.5	0.624	0.714	0.689	0.647	0.751	0.593	0.689	0.647	0.840	0.530	0.692	0.644
30	43.2	0.609	0.710	0.678	0.637	0.744	0.581	0.687	0.630	0.864	0.500	0.686	0.630
35	42.0	0.597	0.703	0.670	0.627	0.739	0.568	0.687	0.611	0.892	0.471	0.683	0.614

In 0.7 M solutions, the $\gamma_{\pm KF}$ and $\gamma_{\pm KCl}$ values are equal to 0.654 and 0.626, respectively [6], which results in the value of $\gamma_{F^-} = 0.683$ conforming quite closely to that calculated using the equation by Davis (Table 1).

As seen from the data in Table 1 containing the results of the measurements of the fluoride activity in seawater of 5–35‰ salinity and the calculated values of the fraction of free ions for the different ways of the γ_{F^-} estimation, the range of α_{F^-} values amounts to 7–33% and increases with the salinity growth, which characterizes the reliability of this way to determine the complexation degree of fluorides in seawater.

In the second series of experiments, as standard solutions, we used mixed KCl–KF solutions with 2–4 × 10⁻⁴ M fluoride concentrations and a $I = 0.715$ ionic force (being equal to that in seawater of 35‰ salinity). Because the thermodynamic stability constant of KF⁰ for the ion pairs is not high ($K_{KF^0}^0 = 0.16$) and considerably lower than those of fluoride complexes with sodium, potassium, and magnesium [1], the complexation degree of the fluoride in the 0.7 M KCl–KF solutions is 5% or below and the assumption of the occurrence of free fluorides in these solutions seems to be quite reasonable. The KCl–KF solutions were mixed in various proportions with normal seawater containing equal amounts of fluoride (2 × 10⁻⁴, 3 × 10⁻⁴, or 4 × 10⁻⁴ M), and then their EMF values were measured (Table 2).

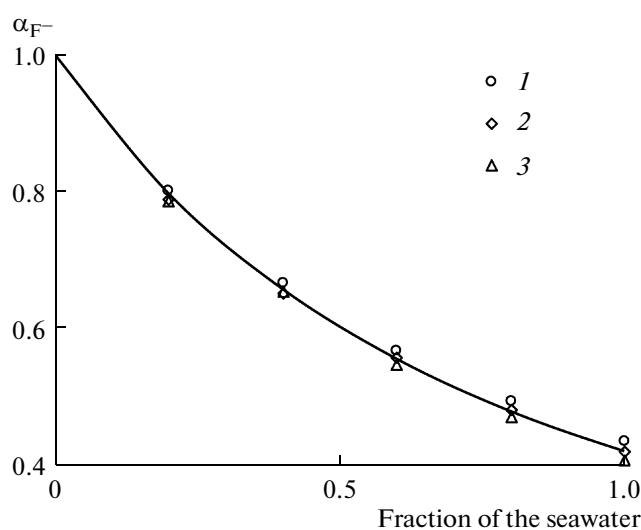
Assuming the absence of the association of the fluorides in the KCl–KF solutions, Eq. (2) for these solu-

tions and their mixtures with seawater should be written, respectively, as

$$E_{KF(KCl)} = E_0 + E_D - k \log([\Sigma F^-] \gamma_{F^-}) \quad (11)$$

Table 2. Calculations of the free fluorine ion fraction according to the data of the ionometry in the mixtures of the KCl–KF solutions and the normal seawater with equal ionic forces and fluoride concentrations

Seawater fraction in the mixture	Total concentration of fluorides in mM [ΣF^-]	E , mV	α_{F^-}
0.2	0.2	-323.6	0.802
0.4	"	-319.1	0.667
0.6	"	-315.2	0.569
0.8	"	-311.7	0.493
1.0	"	-308.7	0.436
0.2	0.3	-333.3	0.789
0.4	"	-328.6	0.651
0.6	"	-324.8	0.557
0.8	"	-321.2	0.481
1.0	"	-317.9	0.420
0.2	0.4	-340.0	0.786
0.4	"	-335.5	0.654
0.6	"	-331.2	0.548
0.8	"	-327.5	0.471
1.0	"	-324.0	0.408



Variations of the fraction of free fluorine ions (α_{F^-}) in the mixtures of KCl–KF solutions and normal seawater with equal ionic forces and fluoride concentrations. 1–3—0.2, 0.3, and 0.4 mM F^- , respectively.

and

$$E_{KF(KCl-SW)} = E_0 + E_D - k \log([\Sigma F^-] \alpha_{F^-} \gamma_{F^-}). \quad (12)$$

Neglecting the difference in the values of the diffusion potentials at the boundaries of the KCl saturated solution and the 0.7 M KCl–KF solutions and seawater, which is confirmed by the E_D calculations by means of the Henderson equation [4], from (11) and (12) follows the expression for the fraction of free fluorine ions in the seawater:

$$\log \alpha_{F^-} = \frac{E_{KF(KCl)} - E_{KF(KCl-SW)}}{k}, \quad (13)$$

where the $k = 56.3$ coefficient conforms to the inclination of the calibrating line (11).

The treatment of the experimental data with Eq. (13) showed that the close agreement of the free ion fractions was observed in the three series of the experiments at fluorine contents of 0.2, 0.3, and 0.4 mM. This fraction decreases nonlinearly from 0.792 ± 0.009 at a 20% seawater content in the mixture to 0.421 ± 0.014 in seawater of 35‰ salinity (figure).

Thus, the two procedures of the ionometric determination of the fluoride's complexation degree in seawater gave pronouncedly different results. The first method used the values of the activity coefficients of

the free ions calculated on the basis of the Debye–Hückel electrostatic theory of strong electrolyte solutions and resulted in a lower degree of the fluoride complexation in the seawater ($\alpha_{F^-} = 0.47–0.70$). The other method gave rise to a higher complexation degree ($\alpha_{F^-} = 0.42$). This value seems to be more preferable because the latter procedure is based upon on the quite real assumption (confirmed by other data) of the negligible association of F^- ions in 0.7 M KCl solutions.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research (project no. 07-05-0804).

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