The Speciation of Metals in Natural Waters

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Abstract

The equilibria and rates of reactions of trace metals in natural waters are affected by their speciation or the form of the metal in the solution phase. Many workers have shown, for example, that biological uptake (Anderson and Morel 1982), the toxicity (Sunda and Ferguson 1983) as well as the solubility (Millero et al. 1995; Liu and Millero 1999) is affected by the speciation. For example, Fe(II) and Mn(II) are biologically available for marine organisms, while Fe(III) and Mn(IV) are normally not available. The speciation of metals also affects the rates of oxidation (Millero 1985, 1994; Sharma et al. 1989; Vazquez et al. 1989) and reduction (Millero 1994; Millero et al. 1991) of metals in natural waters.

The ionic interactions of metals are controlled by interactions with inorganic (Cl^-, OH^-, CO_3^{2-}, etc.) and organic ligands (e.g., Fulvic and Humic acids). The speciation of metals is also affected by the oxidation potential (Eh) and the pH in the solution. In this paper we have developed a Pitzer Model (Pitzer 1973, 1991) that can be used to determine the speciation of trace metals in seawater and other natural waters. It is based upon the Miami Pitzer Model (Millero and Pierrot 1998) that has been shown to predict reliable activity coefficients for the major components of seawater. The computer code (Pierrot 2002) for these calculations is described in detail, in this paper. It has been used in an earlier paper (Millero and Pierrot 2002) and more recently used to examine the effect of pH on the speciation of metals in seawater (Millero et al. 2009).

Introduction

The fundamentals of the model can be demonstrated by examining the speciation of a metal (M_i) with the major ionic components of seawater ($X_j = Cl^-$, SO_4^{2-}, CO_3^{2-} etc.). The equilibrium reactions can be described by

$$M_i + k\, X_j \leftrightarrow M_i\left(X_j\right)_k \tag{1}$$

The thermodynamic equilibrium constant for the formation of this complex in pure water $(K_{M_i(X_j)_k})$ is given by

$$K_{M_i(X_j)_k} = \frac{a_{M_i(X_j)_k}}{a_{M_i}\left(a_{X_j}\right)^k} \tag{2}$$

where $a_{M_i(X_j)_k}, a_{M_i}$ and a_{X_j} are the activities of $M_i\left(X_j\right)_k, M_i$ and X_j, respectively. The activity of a species M is related to its concentration [M] and its activity coefficient γ_M by

$$a_M = [M]\,\gamma_M \tag{3}$$

The substitution into equation (2) gives

$$K_{M_i(X_j)_k} = \frac{\left[M_i(X_j)_k\right]}{[M_i]\,[X_j]^k}\ \frac{\gamma_{M_i(X_j)_k}}{\gamma_{M_i}\left(\gamma_{X_j}\right)^k} \tag{4}$$

The stoichiometric equilibrium constant $(K^*_{M_i(X_j)_k})$ in terms of the concentrations in the medium is equal to

$$K^*_{M_i(X_j)_k} = \frac{\left[M_i(X_j)_k\right]}{[M_i]\,[X_j]^k} = K_{M_i(X_j)_k}\ \frac{\gamma_{M_i}\left(\gamma_{X_j}\right)^k}{\gamma_{M_i(X_j)_k}} \tag{5}$$

The total concentration of a ligand (X_j) which complexes with different metals (M_i) can be written as:

$$\left[X_j\right]_T = \left[X_j\right]_F + \sum_i \sum_k \left[M_i(X_j)_k\right] = \left[X_j\right]_F + \sum_i \sum_k k K^*_{M_i(X_j)_k} [M_i]_F [X_j]_F^k \tag{6}$$

where the subscripts T and F refer to the total and free concentrations, respectively. The fraction of the free metal, α_{Mi}, can be calculated from a similar equation:

$$\alpha_{M_i} = [M_i]_F \Big/ [M_i]_T = \frac{1}{1+\sum_j \sum_k K^*_{M_i(X_j)_k} [X_j]^k_F} \tag{7}$$

These two equations (6 and 7) can be used iteratively to calculate the speciation of ions in solution (see description of calculations below). Once the free concentrations of ligands and metals are known, the fraction of any complex $\alpha_{M_i(X_j)_k}$ is calculated from:

$$\alpha_{M_i(X_j)_k} = \left[M_i(X_j)_k\right] \Big/ [M_i]_T = \alpha_{M_i} K^*_{M_i(X_j)_k} [X_j]^k_F \tag{8}$$

To determine the speciation of a metal in electrolyte solution, one requires an estimate of the activity coefficients of all the components of the solution as well as the values in pure water.

To understand the speciation of metals in seawater it is necessary to have a model that accounts for the interactions of the metals with the major components of seawater and the organic ligands that form strong complexes with the metals. In this paper, we outline the methods that can be used to examine the speciation of metals with the major inorganic anions in seawater (OH⁻, HCO_3^-, CO_3^{2-}, SO_4^{2-}, F⁻, Cl⁻, Br⁻, $B(OH)_4^-$) that can form complexes with monovalent, divalent, and trivalent metals in seawater and other natural waters. This inorganic model is based on the Pitzer Equations (Pitzer 1973, 1975, 1991) which can be used to estimate the activity coefficients of ions in a mixed electrolyte solution over a wide range of composition, temperature and pressure.

Models for natural multicomponent electrolytes have been developed by a number of chemists over the years (Harvie and Weare 1980; Harvie et al. 1984; Felmy and Weare 1986; Møller 1988; Greenberg and Moller 1989; Clegg and Whitfield 1995). This method of examining the ionic interactions in multicomponent electrolytes is more reliable than using the ion-pairing models used in earlier studies (Garrels and Thompson 1962; Turner et al. 1981; Millero and Schreiber 1982; Byrne et al. 1988; Millero and Hawke 1992).

The activity coefficients of ions in the past have been estimated using various extensions of the Debye-Hückel equations (Kielland 1937; Davies 1962). More reliable estimates of the activity coefficients can be made using the specific interaction models that use parameters derived from experimental measurements (Pitzer 1973; Millero and Pierrot 1998) using the Pitzer equations.

The Pitzer Ionic Interaction Model

The ion-interaction model of Pitzer (Pitzer 1991) extends the ionic strength range of the Bates-Guggenheim convention by incorporating both long and short-range interactions of ions in solution. The long-range interactions are given by a Debye-Hückel term and the short-range interactions can be divided into interactions between dissimilar ions of like charges (Na^+-Mg^{2+}) and opposite charges (Cl^- - SO_4^{2-}). The activity coefficient of a single ion (cation M, anion X) in solution can be determined from

$$ln(\gamma_M) = Z_M^2\left(f^\gamma + \sum_c \sum_a m_c m_a B'_{ca} + \sum_c \sum_{c'} m_c m_{c'}\,^E\theta'_{cc'} + \sum_a \sum_{a'} m_a m_{a'}\,^E\theta'_{aa'}\right) + \sum_a m_a(2B_{Ma} + EC_{Ma}) + \sum_c m_c(2\theta_{Mc} + \sum_a m_a \psi_{Mca}) + |Z_M|\sum_c \sum_a m_c m_a C_{ca} + \sum_a \sum_{a'} \psi_{Maa'} + \sum_c m_c\left(2\,^E\theta_{Mc}\right) \quad (9)$$

$$ln(\gamma_X) = Z_X^2\left(f^\gamma + \sum_c \sum_a m_c m_a B'_{ca} + \sum_c \sum_{c'} m_c m_{c'} {}^E\theta'_{cc'} + \sum_a \sum_{a'} m_a m_{a'} {}^E\theta'_{aa'}\right) +$$
$$\sum_c m_c (2B_{Xc} + EC_{Xc}) + \sum_a m_a (2\theta_{Xa} + \sum_c m_c \psi_{Xac}) + |Z_X| \sum_c \sum_a m_c m_a C_{ca} +$$
$$\sum_c \sum_{c'} \psi_{Xcc'} + \sum_a \tag{10}$$

where Z_M and Z_X are the charge on the ion and E is the equivalent molality $(E = \sum_i |Z_i| m_i)$.

The Debye-Hückel term (f^γ) is given by

$$f^\gamma = -A_\phi \left[\frac{\sqrt{I}}{1+1.2\sqrt{I}} + \frac{2}{1.2} ln(1 + 1.2\sqrt{I})\right] \tag{11}$$

where A_ϕ is the Debye-Hückel slope (Pitzer 1991) given by the equation:

$$A_\phi = 3.3690153 \; 10^{-1} - 6.3210043 \; 10^{-4} \; T + \frac{9.14252359}{T} - 1.35143986 \; 10^{-2} \ln(T) +$$
$$\frac{2.26089488 \; 10^{-3}}{T-263} + 1.921185973 \; 10^{-6} \; T^2 + \frac{4.52586161 \; 10^{-1}}{680-T} \tag{12}$$

The second (B_{Ma}) and third (C_{Ma}) virial terms for the interaction between ions of dissimilar charge are given by

$$B_{Ma} = \beta_{Ma}^{(0)} + \beta_{Ma}^{(1)} g(\alpha_1 \; \sqrt{I}) + \beta_{Ma}^{(2)} g(\alpha_2 \; \sqrt{I}) \tag{13}$$

$$g'(x) = \frac{-2\left[1 - \left(1 + x - \frac{x^2}{2}\right)exp(-x)\right]}{I \cdot x^2} \tag{14}$$

The derivative of B'_{Ma} is given by

$$B'_{Ma} = \beta_{Ma}^{(1)} g'(\alpha_1 \; \sqrt{I}) + \beta_{Ma}^{(2)} g'(\alpha_2 \; \sqrt{I}) \tag{15}$$

$$g'(x) = \frac{-2[1 - (1 + x + x^2)exp(-x)]}{x^2} \tag{16}$$

For 1-1 and 2-1 electrolytes, $\beta_{Ma}^{(2)} = 0$ and $\alpha_1 = 2.0 \, kg^{1/2}mol^{-1/2}$. For 2-2 electrolytes, $\beta_{Ma}^{(2)} \neq 0$, $\alpha_1 = 1.4 \, kg^{1/2} \, mol^{-1/2}$ and $\alpha_2 = 12 \, kg^{1/2} \, mol^{-1/2}$ The C_{Ma} term is given by

$$C_{Ma} = \frac{C_{Ma}^{\phi}}{2|Z_M Z_a|^{1/2}} \tag{17}$$

Equation (9 and 10) are the original form of the ion-interaction model (Pitzer 1991). Further extensions of the Pitzer model, with additional virial coefficients, were also proposed (Pitzer et al. 1999). These extended models have allowed for accurate representations of osmotic and activity coefficients over the full solubility range of many electrolytes (Archer 1991; Rard and Clegg 1997; Pitzer et al. 1999), but sources for extended parameters are limited (Rard and Wijesinghe 2003).

The higher order terms for the short-range ion interactions in equation (9) are defined for both binary Na-Mg (θ_{Mc}) and triplet Na-Mg-Cl (ψ_{Mca}) interactions. In a mixed electrolyte, the binary mixing parameter is equal to the sum of the interaction parameters between two ions of like charge (θ_{Mc}) and the electrostatic mixing effects of the two ions in solution $\left({}^E\theta_{Mc} \right)$. The electrostatic mixing terms $\left({}^E\theta, \, {}^E\theta' \right)$ account for interactions from mixing unsymmetrical ions of the same charge; equations for these terms are given by Pitzer (1991). The triplet interaction parameter, ψ_{Mca}, represents the interactions between two ions of similar charge with a single ion of opposite charge. For the binary and triplet interaction parameters, the subscript M refers to the cation for which the activity coefficient is determined; a and c refer to the remaining anions and cations in solution. Equation (9) can be written to find the activity coefficient of an anion, denoted as X, and is discussed elsewhere (Pitzer 1991; Campbell et al. 1993; Millero and Pierrot 1998).

The Pitzer equation for neutral solutes N (CO_2, $B(OH)_3$ and H_2S) is given by (Pitzer, 1991)

$$\ln \gamma_N = 2 \sum_n \lambda_{Nn} m_n + 2 \sum_c \lambda_{Nc} m_c + 2 \sum_{Na} \lambda_{Na} m_a + 3 \sum_n \mu_{Nnn} m_n^2$$

$$+ 6 \sum'\sum'_{n<n'} m_a m_a \mu_{Nnn'} + 6 \sum_n' m_N m_n \mu_{NNn} + 6 \sum_n \sum_c m_n m_c \mu_{Nnc}$$

$$+ 6 \sum_n \sum_a m_n m_a \mu_{Nna} + \sum_c \sum_a m_c m_a \zeta_{Nca}$$

$$+ \sum\sum_{c<c'} m_c m_c \eta_{Ncc'} + \sum\sum_{a<a'} m_a m_a \eta_{Naa'} \qquad (18)$$

where n and N are neutral species, c and a are cations and anions. The terms λ_{Nj}, μ_{Njk}, ζ_{Nca}, and η_{Nii} are parameters that must be determined from experimental measurements. In the double summations $c < c'$, $a < a'$, and $n < n'$ indicate that the individual neutral solutes (n), cations (c), and anions (a) are counted only once. The primed summation is used to indicate that n or n′ is not equal to N. The ζ_{Nca} and $\eta_{Nii'}$ parameters are related to triplet interactions (Felmy and Weare, 1986; Pitzer, 1991)

$$\zeta_{Nca} = 6 \mu_{Nca} + 3(|Z_a|/Z_c) \mu_{ncc} + 3(Z_c/|Z_a|) \mu_{naa} \qquad (19)$$

$$\eta_{Ncc'} = 6 \mu_{Nii'} - 3(|Z_i|/Z_{i'}) \mu_{nii'} - 3(Z_i/|Z_{i'}|) \mu_{naa} \qquad (20)$$

where Z_i is the charge on the ion. For sparingly soluble neutral solutes these equations can be simplified to

$$\ln \gamma_N = 2 \sum_c \lambda_{Nc} m_c + 2 \sum_{Na} \lambda_{Na} m_a + \sum_c \sum_a m_c m_a \zeta_{Nca}$$

$$+ \sum\sum_{c<c'} m_c m_c \eta_{Ncc'} + \sum\sum_{a<a'} m_a m_a \eta_{Naa'} \qquad (21)$$

The User Interface

The program is written in Microsoft Excel VBA (Visual Basic for Applications). The workbook called "Miami_Interactions_Model_2016.xlsm" contains only one worksheet. The parameters are entered in the cells on the left of the worksheet and all the results are output in the cells to the right of the worksheet.

The user inputs the temperature and either the salinity or individual concentrations for main seawater ions. Valid ranges are 0 to 40 $^{\circ}$C for temperature and 0 to 45 for salinity.

As an option, the user can then slightly vary the medium composition by entering different pH, TCO_2, total CO_2, H_2S or PO_4, and divalent or trivalent concentrations to investigate the effects these parameters would have on activity coefficients and speciation (Millero et al. 2009). If no values are entered in these optional fields, the pH will be assumed to be 8.1 (on the free scale), the total CO_2 will be calculated from the seawater composition and the total H_2S and PO_4 as well as all the divalent and trivalent concentrations will be assumed to be 0 (see Figure 1). When the input information is entered properly on the sheet, the user clicks on "Click Here When READY". The program will then start the calculations and output the results. A typical output is shown in Figure 2.

For each cation and anion handled by the program, the activity coefficient is calculated in stages of increasing complexity (see below). The activity coefficients of some neutral species and the stoichiometric dissociation constants of a few acids are also displayed (see Figure 2).

Finally, after an iterative procedure which, in turn, first calculates the free concentration of each ligand from an initial concentration of complexing ions and then calculates the fraction of each complex from the new ligand concentrations until the ligand concentrations converge, the program outputs the activity coefficient of each complex species, its thermodynamic and stoichiometric dissociation constant (log K and log K*) and the speciation of each complexing

metal (reported as a fraction of the total molality of the metal in question). A sample of the output is shown in Figure 3.

The time necessary to perform all the calculations is in the order of a few seconds, and depends mostly on the iterative process used to calculate the metals' speciation.

Calculations Sequence

A flow chart diagram of the calculations is shown in Figure 4. The activity coefficient of any ion is calculated in stages. The first stage is the part common to all ions, namely the Debye-Hückel term and the medium terms (B_{Ma}) and (C_{Ma}). The second stage includes the binary interaction parameters $(\beta^{0)},\beta^{1)},C^{\phi}...)$ of major ions (with a non-negligible concentration) of unlike charges. The next stage of the calculations includes higher order parameters relating to short range binary and tertiary interactions between ions of the same charge (Θ and ψ). The final stage includes the unsymmetrical terms which account for the electrostatic effect of mixing unsymmetrical ions of the same charge ($^E\Theta$ and $^E\Theta'$).

The osmotic coefficient (ϕ) is calculated with the same three levels using the equation

$$\phi - 1 = |Z_M Z_X|\, f^{\phi} + m(2\nu_M \nu_X/\nu)\, B^{\phi}_{MX} + m^2\, [2(\nu_M \nu_X)^{3/2}/\nu]\, C^{\phi}_{MX} \qquad (22)$$

$$\ln \gamma = |Z_M Z_X|\, f^{\gamma} + m\,(2\nu_M \nu_X/\nu)\; B^{\gamma}_{MX} + m^2\,(2\nu_M \nu_X)^{3/2}/\nu]\, C^{\gamma}_{MX} \qquad (23)$$

where

$$f^{\phi} = (1/2)[f' - f/I] \qquad (24)$$

$$f^{\gamma} = (1/2)\, f' \qquad (25)$$

and

$$B^\phi_{MX} = \lambda_{MX} + I\lambda'_{MX} + (\nu_M/2\nu_X)(\lambda_{MM} + I\lambda'_{MM}) + (\nu_X/2\nu_M)(\lambda_{XX} + I\lambda'_{XX}) \tag{26}$$

$$B^\gamma_{MX} = 2\lambda_{MX} + I\lambda'_{MX} + (\nu_M/2\nu_X)(2\lambda_{MM} + I\lambda'_{MM}) + (\nu_X/2\nu_M)(2\lambda_{XX} + I\lambda'_{XX}) \tag{27}$$

$$C^\phi_{MX} = [3/(\nu_M\nu_X)^{1/2}][\nu_M\mu_{MMX} + \nu_X\mu_{MXX}) \tag{28}$$

$$C^\gamma_{MX} = (3/2)\,C^\phi_{MX} \tag{29}$$

Pitzer examined a number of forms for f^ϕ and B^ϕ for various electrolytes. He found that the equations

$$f^\phi = -A^\phi I^{1/2}/(1 + b\,I^{1/2}) \tag{30}$$

$$B^\phi_{MX} = \beta^0_{MX} - \beta^1_{MX}\exp(-\alpha I^{1/2}) \tag{31}$$

gave the best results where $b = 1.2$ and $\alpha = 2.0$ for 1-1, 2-1, and 3-1 electrolytes. For 2-2 electrolytes the value of B^ϕ_{MX} is given by

$$B^\phi_{MX} = \beta^0_{MX} + \beta^1_{MX}\exp(-\alpha_1 I^{1/2}) + \beta^2_{MX}\exp(-\alpha_2 I^{1/2}) \tag{32}$$

where $\alpha_1 = 1.4$ and $\alpha_2 = 12.0$. The limiting slopes for the equations are given by

$$f^{GX} = -A_\phi\,(4I/1.2)\,\ln(1 + 1.2\,I^{1/2}) \tag{33}$$

$$f^\phi = -A_\phi\,I^{1/2}/(1 + 1.2\,I^{1/2}) \tag{34}$$

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$$f^{\gamma} = -A_{\phi} [I^{1/2}/(1 + 1.2\,I^{1/2}) + (2/1.2) \ln (1 + 1.2\,I^{1/2})] \tag{35}$$

and the *B* and *C* coefficients are given by

$$B^{GX}_{MX} = \beta^0_{MX} + (2\beta^1_{MX}/4I) [1 - \exp(-2I^{1/2}) (1 + 2\,I^{1/2})] \tag{36}$$

$$B^{\phi}_{MX} = \beta^0_{MX} + \beta^1_{MX} \exp(-2I^{1/2}) \tag{37}$$

$$B^{\gamma}_{MX} = 2\beta^0_{MX} + (2\beta^1_{MX}/4I) [1 - \exp(-2I^{1/2})(1 + 2I^{1/2} - 2I)] \tag{38}$$

$$C^{GX}_{MX} = C^{\phi}_{MX}/2 \tag{39}$$

$$C^{\gamma}_{MX} = (3/2)\,C^{\phi}_{MX} \tag{40}$$

The limitation slope A_{ϕ} is given by

$$A_{\phi} = (1/3) (2\pi N_0 \rho_{o0}/1000)^{1/2} (e^2/DkT)^{3/2} \tag{41}$$

At 25 ℃ the value of A_{ϕ} is 0.392. Values of A_{ϕ} at temperatures from 0 to 350 ℃ can be

estimated at other temperatures from (Møller 1988)

$$A_{\phi} = 0.336901532 - 6.32100430 \times 10^{-4}\,T + 9.14252359/T - 1.35143986 \times 10^{-2}\,\ln T$$

$$+ 2.26089488 \times 10^{-3}/(T - 263) + 1.92118597 \times 10^{-6}\,T^2 + 45.2586464/(680 - T) \tag{42}$$

At this stage, the program performs the ion pairing correction to a few activity coefficients (Millero and Pierrot 1998), after which the activity coefficients for all ions and neutral species are output on the spreadsheet.

The program then calculates stoichiometric association constants (K*) for all the complexes from thermodynamic values at 25°C found in the literature. Finally, using an iterative process, the speciation of each metal complex is calculated. First, the concentration of each ligand is initiated as the total concentration calculated from the seawater composition. Carbonate and phosphate species, as well as proton and bisulfide initial concentrations are calculated from the TCO_2, PO_4, pH and H_2S values entered by the user. Next, the free concentration of each ligand which gives its correct total concentration (equation 6) is found. It is then used to calculate the free fraction of each metal (equation 7) from which the free concentration of metal is obtained and used in the next iteration of calculating the free ligand concentration (equation 6). The process is repeated until the free concentrations of both ligands and metals converge. Once convergence of all ligands and metals is obtained, the fraction of each complex can be calculated from equation 8. It is noteworthy to mention that the equations are a lot simpler when the concentration of the metals is zero. In that case, the ligand concentrations converge a lot faster and the speciation of the metals can still be calculated (equation 8).

Pitzer Parameters Used in the Model

The cations and anions that are covered by the model are given in **Table 1**. The model includes most monovalent, divalent and trivalent metals and anions in seawater. A number of neutral solutes are also included. The Pitzer parameters used for the major components are those from the Miami Pitzer Model (Millero and Pierrot 1998). References for some of the other Pitzer Parameters for the divalent and trivalent cations used are given in **Table 2.** The parameters

used to estimate the activity coefficients of divalent ion pairs are given in **Table 3**. The parameters for the trivalent ion pairs have been calculated according to their charge as suggested by Millero (1992) using the following equations for +1 and +2 charged ions:

$$\beta_{MX}^{(0)}(+1) = \frac{(0.62-0.0523)}{1.201} \quad and \quad \beta_{MX}^{(0)}(+2) = \frac{(1.11-0.0523)}{1.201} \tag{43}$$

Finally, the association constants for the divalent and trivalent ion pairs in water at 25°C are given in **Table 4** and **Table 5**. The temperature range of validity for these constants was extended, when possible using enthalpy and heat capacity data (**Table 6** and **Table 7**).

Present and Future of the Program

As stated previously, the program calculates values of the activity coefficients and stability constants in water and seawater for all various complexes of a series of divalent and trivalent metals. It also outputs the speciation of these metals for the composition selected by the user. As a check, a few activity coefficients and dissociation constants for acids are given in **Table 9** and **Table 10**. The results of our model should be useful in examining the competition of the formation of inorganic and organic complexes of metals in seawater (Millero and Pierrot 2002) and the effects of changing the environment can have on speciation (Millero et al. 2009). Most of the ions that the program can handle, along with their interaction parameters and stability constants, are stored in the program as arrays. It is therefore relatively easy to add new ligands, acids or metals to expand the Miami Pitzer Model. However, since one needs to modify the code itself to do so, we do not feel that this is a realistic option for the users. The model could be improved by replacing estimated parameters by measured ones when they become available. Since a number of the Pitzer coefficients for metals have been estimated, studies of the formation of metal complexes with inorganic ligands are needed to improve the speciation of

metals complexing with inorganic and organic ligands in seawater (Gledhill and Buck 2012; Town and Filella 2000). Recent molal volume and compressibility measurements have been made on a number of components of seawater, which can be incorporated in our model to make reasonable estimates of the effect of pressure on the speciation in seawater (Millero and Huang 2011, 2013; Millero 2014; Millero and Sharp 2013; Rodriguez et al. 2013). The program is available online at http://dx.doi.org/10.17604/M6MW2G.

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Table 1. The cations and anions considered in the Miami Trace Metal Model.

Neutral Solutes	NH_3, $B(OH)_3$, H_3PO_4, H_2S, SO_2, CO_2
Monovalent Cations	H^+, Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Hg^+, Cu^+
Divalent Cations	Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Be^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, UO_2^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}
Trivalent Cations	Y^{3+}, Al^{3+}, Ga^{3+}, In^{3+}, La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Fe^{3+}
	Pm^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, Lu^{3+}
Monovalent Anions	F^-, Cl^-, Br^-, I^-, OH^-, HCO_3^-, $B(OH)_4^-$, ClO_3^-, ClO_4^-, BrO_3^-, CNS^-
	NO_2^-, NO_3^-, HSO_4^-, HS^-, HSO_3^-, $H_2PO_4^-$, $H_2AsO_4^-$, $C_2H_3OH^-$
Divalent Anions	SO_4^{2-}, CO_3^{2-}, SO_3^{2-}, HPO_4^{2-}, $HAsO_4^{2-}$
Trivalent Anions	PO_4^{3-}, AsO_4^{3-}

Table 2. References of single electrolyte Pitzer parameters ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, C^{ϕ}) used in this study for the divalent and trivalent ions at 25°C.

Cation	Cl^-	SO_4^{2-}	Br^-
Ba^{2+}	1, 2, 3		1, 2
Mn^{2+}	1, 3	4	equal to Co^{2+}
Fe^{2+}	1		equal to Co^{2+}
Co^{2+}	1, 3	4	1
Ni^{2+}	1, 3	4	equal to Co^{2+}
Cu^{2+}	1, 2	2, 4	equal to Zn^{2+}
Zn^{2+}	1	2, 4	1
UO_2^{2+}	1	4	equal to Zn^{2+}
Be^{2+}		4	
Cd^{2+}	5	2, 4	
Pb^{2+}	5	equal to Cd^{2+}	
Al^{3+}	1		
Ga^{3+}	1(=$GaClO_4$)		
In^{3+}	1		
Other Trivalent^{3+}	6, 7		

(**1**) Pitzer and Mayorga (1973) (**2**) Silvester and Pitzer (1978) (**3**) Criss and Millero (1996) (**4**) Pitzer and Mayorga (1974) (**5**) Kim et al. (1988) (**6**) Pitzer et al. (1978) (**7**) Criss and Millero (1999).

Table 3. Interaction parameters of divalent ion pairs used in this study.

Ion pair\Ion	Cl	Na	Mg	Ca
$PbCl^+$	$\beta^{(0)} = 0.15^{(1)}$		$\Theta = -0.37^{(1)}$	$\Theta = -0.37^{(1)}$
$PbCl_2$	$\lambda = -0.22^{(1)}$	$\lambda = -0.28^{(1)}$	$\lambda = -0.4^{(1)}$	$\lambda = -0.4^{(1)}$
$PbCl_3^-$		$\beta^{(0)} = -0.19^{(1)}$	$\beta^{(0)} = 0.3^{(1)}$	$\beta^{(0)} = 0.4^{(1)}$
$CuCO_3$	$\lambda = 0.4^{(2)}$			
$Cu(CO_3)_2^{2-}$	$\beta^{(0)} = 1.22^{(2)}$			
$CuHCO_3^+$	$\beta^{(0)} = 0.6^{(2)}$			
$Cu(OH)^+$	$\beta^{(0)} = 0.2^{(2)}$			
$Cu(OH)_2$	$\lambda = 0.98^{(2)}$			
$FeCO_3$	$\lambda = 0.54^{(2)}$			
$Fe(CO_3)_2^{2-}$	$\beta^{(0)} = 1.04^{(2)}$			

(1) From Millero and Byrne (1984) **(2)** determined from K^*_{MX} of Millero and Hawke (1992).

Table 4. Values for the association constants of ion pairs (logarithm of constants) for some divalent metals in water at 25 $^{\circ}$C. (K, mol kgH$_2$O^{-1}).

Anion	Mg[1]	Ca[1]	Sr[1]	Mn[2]	Fe[2]	Co[2]	Ni[2]	Cu[2]	Zn[2]	Cd[2]	Pb[2]	Anion	UO$_2$[3]	Anion	Cu(I)[4]	Hg	Anion	Be[5]
CO$_3$	2.9	3.2	3.2	4.1	7.17	4.49	5.37	6.73	4.71	4.35	7	CO$_3$	10.4	Cl	3.10	7.2	CO$_3$	7.53
(CO$_3$)$_2$					5.45			10.41	7.25		10.29	(CO$_3$)$_2$	18.1	(Cl)$_2$	5.42	14	OH	8.6
HCO$_3$				1.28	1.47	1.41	1.63	1.82	1.74	1.37	2.05	(CO$_3$)$_3$	20.5	(Cl)$_3$	4.75	15.1	(OH)$_2$	14.34
OH	2.2	1.3		3.4	4.49	4.35	4.13	6	5.03	3.91	6.28	F	5	(Cl)$_4$		15.4	(OH)$_3$	18.74
(OH)$_2$				5.78	7.39	9.99	8.99	11.74	11.09	7.63	10.87	(F)$_2$	9	HS	11.8	21.4	(OH)$_4$	18.57
HS				7.5	6.2	6	6.2	8.7	6.8	8	9.2	(F)$_3$	11.3	(HS)$_2$	17.6	26.6	F	5.61
(HS)$_2$								14.9	14.7	14.6	15.9	(F)$_4$	12.6				(F)$_2$	9.68
SO$_4$	2.21	2.28	2.1	2.26	2.20	3.06	2.29	2.36	2.36	2.45	2.75	OH	8.2					
(SO$_4$)$_2$							3.20		3.63		4.51	OH	8.2					
Cl				0.39	0.32	0.26	0.17	0.53	0.33	1.56	1.48							
(Cl)$_2$										1.88	2.03							
(Cl)$_3$										1.51	1.86							
F	1.83	1.33																

(1) Millero and Schreiber (1982) **(2)** Millero and Hawke (1992) except for HS complexes which were taken from Zhang and Millero (1994) and extrapolated to zero ionic strength **(3)** Choppin (1989) **(4)** Sharma and Millero (1988) **(5)** Turner et al. (1981).

Table 5. Values for the association constants of ion pairs (logarithm of constants) for some trivalent metals in water at 25 ^{o}C. (K, mol kgH$_2$O^{-1}).

Anion	La[1]	Ce[1]	Pr[1]	Nd[1]	Pm[1]	Sm[1]	Eu[1]	Gd[1]	Tb[1]	Dy[1]	Ho[1]	Er[1]	Tm[1]	Yb[1]	Lu[1]	Y[2]	Al[2]	Ga[2]	In[2]	Fe[3][4]
OH	5.1	5.6	5.6	5.67	5.77	5.81	5.83	5.79	5.98	6.04	6.1	6.15	6.19	6.22	6.24	6.3	9.03	11.4	10	11.81
(OH)$_2$																11.59	18.69	22.09	20.17	21.11
(OH)$_3$																15.99	26.99	31.69	29.59	28.96
(OH)$_4$																19.48	32.98	39.38	33.91	34.49
HCO$_3$	2.02	1.95	1.89	1.83	1.79	1.75	1.6	1.72	1.71	1.72	1.73	1.76	1.79	1.84	1.9					
CO$_3$	6.82	6.95	7.03	7.13	7.22	7.3	7.37	7.44	7.5	7.55	7.59	7.63	7.66	7.67	7.7	6.94	8.43	8.79	7.6	
(CO$_3$)$_2$	11.31	11.5	11.65	11.8	11.96	12.11	12.24	12.39	12.52	12.65	12.77	12.88	13	13.08	13.2					
SO$_4$	3.21	3.29	3.27	3.26	3.34	3.28	3.37	3.25	3.2	3.15	3.16	3.15	3.07	3.06	3.01	3.47			3.86	4.27
(SO$_4$)$_2$																5.3			5.43	6.11
(SO$_4$)$_3$																			5.52	
Cl	0.29	0.31	0.32	0.32	0.31	0.3	0.28	0.28	0.27	0.27	0.27	0.28	0.27	0.16	-0.03	0.8		0.89	3.26	1.28
(Cl)$_2$																			6.38	1.16
(Cl)$_3$																			5.83	
F	3.12	3.28	3.48	3.56	3.63	3.58	3.63	3.75	3.85	3.89	3.95	3.98	3.99	4.02	4.05	4.8	7.01	5.28	4.6	6.03
(F)$_2$																8.74	12.73	9.61	8.1	10.66
(F)$_3$																	16.71		10.3	13.66
(F)$_4$																	19.67		11.51	
(F)$_5$																	20.73			
(F)$_6$																	20.46			
H$_2$PO$_4$	2.5	2.43	2.37	2.31	2.27	2.23	2.21	2.2	2.19	2.2	2.21	2.24	2.27	2.32	2.38					
HPO$_4$	4.87	4.98	5.08	5.18	5.27	5.35	5.42	5.49	5.54	5.6	5.64	5.68	5.71	5.73	5.75					
(HPO$_4$)$_2$	8.17	8.34	8.5	8.66	8.81	8.96	9.1	9.24	9.37	9.49	9.62	9.73	9.84	9.95	10.05					

(1) Millero (1992) **(2)** Byrne et al. (1988) for hydrolysis data and Turner et al. (1981) for the other ion pairs. **(3)** Millero and Pierrot (2007) **(4)** Millero et al. (1995).

Table 6. Values of Enthalpies (in kJ. mol^{-1}) for the reaction $M^{2+} + n\ X^- \Leftrightarrow M(X)_n^{(2-n)}$.

Cation	OH[1]	(OH)$_2$[2]	CO$_3$[3]	SO$_4$[3]	Cl[4]	(Cl)$_2$[4]	(Cl)$_3$[4]
Mg	6.49						
Ca	9.41						
Mn	4.39	7.70	12.55				
Fe	-0.63	-0.29	12.55				
Co	5.23	-10.00	12.55				
Ni	-6.02	-16.82	12.55				
Cu	-5.65	-21.46	12.55	7.95			
Zn	0.21	-17.41	12.55				
Cd	-1.05	-5.36			1.26	3.77	10.04
Pb	-11.09	-20.38	12.55				
Be[5]	-8.16	-23.81					

(**1**) Baes and Mesmer (1981) (**2**) calculated from relationship in Baes and Mesmer (1981) (**3**) Byrne et al. (1988) (**4**) Martell and Smith (1982) (**5**) Enthalpy for Be(OH)$_3$ (= -11.24 kcal mol^{-1}) from Baes and Mesmer (1981) was used.

Table 7. Values of Enthalpies (in kJ. mol^{-1}) and Heat Capacities (in J. mol^{-1} K^{-1}) for the reaction $M^{3+} + n\ OH^- \Leftrightarrow M(OH)_n^{(3-n)}$ (from Baes and Mesmer 1981).

Cation	ΔH (kJ. mol^{-1})				ΔCp (J. mol^{-1} K^{-1})
	n=1	n=2	n=3	n=4	n=1
La	-44.61				276.76
Ce	-46.03				275.25
Pr	-45.78				274.08
Nd	-45.80				273.08
Pm	-45.95				272.18
Sm	-45.90				271.35
Eu	-45.79				270.57
Gd	-45.48				269.90
Tb	-45.96				269.06
Dy	-45.97				268.22
Ho	-45.99				267.44
Er	-45.99				266.72
Tm	-45.97				266.10
Yb	-45.91				265.43
Lu	-45.87				264.99
Y	-46.66	-124.34	-212.14	-310.04	267.39
Al	-49.95	-152.50	-262.49	-374.62	246.02
Ga	-63.32	-171.74	-289.12	-410.92	262.76
In	-58.43	-163.88	-280.24	-382.87	262.76

Table 8. Model species used to estimate the activity coefficients of unknown ion pairs.

Model	Estimated ion pair
$CuCO_3$	$MnSO_4$, $MnCO_3$, $FeSO_4$, $CoSO_4$, $CoCO_3$, $NiSO_4$, $NiCO_3$, $CuSO_4$, $ZnSO_4$, $ZnCO_3$, $CdSO_4$, $CdCO_3$, $PbSO_4$, $PbCO_3$, UO_2SO_4, UO_2CO_3, $BaCO_3$
$Cu(CO_3)_2^{2-}$	$Ni(SO_4)_2^{2-}$, $Cu(SO_4)_2^{2-}$, $Zn(SO_4)_2^{2-}$, $Zn(CO_3)_2^{2-}$, $Pb(SO_4)_2^{2-}$, $Pb(CO_3)_2^{2-}$, $UO_2(SO_4)_2^{2-}$, $UO_2(CO_3)_2^{2-}$
$CuHCO_3^-$	$MnHCO_3^-$, $FeHCO_3^-$, $CoHCO_3^-$, $NiHCO_3^-$, $ZnHCO_3^-CdHCO_3^-$, $PbHCO_3^-$
$CuOH^+$	$SrOH^+$, $MgOH^+$, $CaOH^+$, $BaOH^+$, $MnOH^+$, $FeOH^+$, $CoOH^+$, $NiOH^+$, $ZnOH^+$, $CdOH^+$, $PbOH^+$, UO_2OH^+
$Cu(OH)_2$	$Mn(OH)_2$, $Fe(OH)_2$, $Co(OH)_2$, $Ni(OH)_2$, $Zn(OH)_2$, $Cd(OH)_2$, $Pb(OH)_2$, $UO_2(OH)_2$
$PbCl^+$	$MnCl^+$, $MnHS^+$, $FeCl^+$, $FeHS^+$, $CoCl^+$, $CoHS^+$, $NiCl^+$, $NiHS^+$, $ZnCl^+$, $ZnHS^+$, $CdCl^+$, $CdHS^+$, $CuCl^+$, $CuHS^+$, $HgCl^+$, $HgHS^+$, UO_2Cl^+, UO_2F^+, $PbHS^+$
$PbCl_2$	$Cd(HS)_2$, $CdCl_2$, $Cu(HS)_2$, $Pb(HS)_2$, $Zn(HS)_2$, $Hg(HS)_2$, $HgCl_2$, UO_2F_2
$PbCl_3^-$	$CdCl_3^-$, $HgCl_3^-$, $UO_2F_3^-$
$PbCl_4^{2-}$	$HgCl_4^{2-}$, $UO_2F_4^{2-}$
OH^-	$Be(OH)_3^-$
SO_4^{2-}	$Be(OH)_4^{2-}$

Table 9. Sample output of the Miami Trace Metal Model: activity coefficients of major seawater species at t=25 ^{o}C and S=35 ‰.

	Species	Molality	γ	Free Fraction (%)
Cation	Sr^+	0.00009	0.19278	
	Na^+	0.48610	0.63912	
	K^+	0.01058	0.59572	
	Mg^{2+}	0.05474	0.20324	
	Ca^{2+}	0.01066	0.19745	
Anion	Cl^-	0.56577	0.69216	100.00%
	SO_4^{2-}	0.02927	0.11394	100.00%
	CO_3^{2-}	0.00020	0.04335	43.13%
	HCO_3^-	0.00193	0.59307	100.00%
	Br^-	0.00087	0.71477	
	F^-	0.00007	0.32018	55.83%
	$B(OH)_4^-$	0.00009	0.39865	
Neutral	NH_3		1.01458	
	$B(OH)_3$		1.00744	
	H_3PO_4		1.08290	
	H_2S		1.11414	
	SO_2		1.03751	
	CO_2		1.16187	
	HF		1.01075	

Table 10. Sample output of the Miami Trace Model: dissociation constants of acids in seawater at t = 25 $^\circ$C and S = 35 ‰.

Acid	pK*$_1$	pK*$_2$	pK*$_3$
CO_2	1.546	5.826	8.952
H_2S	6.527		
H_3PO_4	1.600	5.955	8.782
NH_4	9.228		
H_2SO_4	1.009		
H_2O	13.215		
HF	2.551		
H_2SO_3	1.473	6.083	
$B(OH)_3$	8.592		
Acetic	4.284		
Calcite	6.397		
Aragonite	6.220		
H_3AsO_4	1.830	5.748	8.718

	A	B	C
1	*Instructions*	**Click Here When**	
2		**READY**	
3	1 - Enter the Temperature	*Temperature(oC)*	
4	- - - - - - - - - - - - - >	25.00	
5			
6	2 - Enter Salinity	*Salinity*	
7	- - - - - - - - - - - - - >	35.000	
8			
9		*Molalities*	
10	OR Molalities - - - - - - - - - >	*Sr*	9.4317E-05
11	(Delete Salinity Value)	*Na*	0.4860964
12		*K*	0.01057804
13		*Mg*	0.05474389
14		*Ca*	0.01065784
15			
16		*Cl*	0.56577268
17		*SO$_4$*	0.02926736
18		*CO$_3$*	0.00019952
19		*HCO$_3$*	0.00192625
20		*Br*	0.00087062
21		*F*	6.8924E-05
22		*B(OH)$_4$*	8.7062E-05
23			
24			
25	3 - Adjust Conditions below:		
26			
27			
28	*Parameter*	*Value*	
29	*pH*		
30	*TCO$_2$*		
31	*H$_2$S*		
32	*PO$_4$*		
33			
34	*Divalent*	*Molality*	
35	*Mn*		
36	*Fe*		
37	*Co*		
38	*Ni*		
39	*Cu(II)*		
40	*Zn*		
41	*UO2*		
42	*Be*		
43	*Cd*		
44	*Pb*		
45	*Hg*		
46	*Cu(I)*		
47			
48	*Trivalent*	*Molality*	
49	*La*		
50	*Ce*		
51	*Pr*		
52	*Nd*		
53	*Pm*		
54	*Sm*		
55	*Eu*		
56	*Gd*		
57	*Tb*		
58	*Dy*		
59	*Ho*		
60	*Er*		
61	*Tm*		
62	*Yb*		
63	*Lu*		
64	*Y*		
65	*Al*		
66	*Ga*		
67	*In*		
68	*Fe(III)*		
69			

Figure 1. Input section of the program.

Cation	Molality	γM		Anion	Molality	γX	Free Fraction (%)		Neutral	Molality	γN		Acid	pK*1	pK*2	pK*3
Sr	0.0001	0.1928		Cl	0.5658	0.6922	100.00%		NH3		1.0146		CO2	1.546	5.826	8.952
Na	0.4861	0.6391		SO4	0.0293	0.1139	100.00%		B(OH)3		1.0074		H2S	6.527	N/A	N/A
K	0.0106	0.5957		CO3	0.0002	0.0433	43.13%		H3PO4		1.0829		H3PO4	1.600	5.955	8.782
Mg	0.0547	0.2032		HCO3	0.0019	0.5931	100.00%		H2S		1.1141		NH4	9.228	N/A	N/A
Ca	0.0107	0.1974		Br	0.0009	0.7148			SO2		1.0375		H2SO4	1.009	N/A	N/A
H		0.5531		F	0.0001	0.3202	55.83%		CO2		1.1619		H2O	13.215	N/A	N/A
Li		0.7210		B(OH)4	0.0001	0.3986			HF		1.0108		HF	2.551	N/A	N/A
Rb		0.5950		HSO4		0.7994							H2SO3	1.473	6.083	N/A
Cs		0.5474		HS		0.6840							B(OH)3	8.592	N/A	N/A
NH4		0.6043		OH		0.2743	47.64%						HAc	4.284	N/A	N/A
Ba		0.1671		I		0.7556							Calcite	6.397	N/A	N/A
Mn		0.1876		ClO3		0.6481							Aragonite	6.220	N/A	N/A
Fe(II)		0.2068		ClO4		0.6964							H3AsO4	1.830	5.748	8.718
Co		0.2082		BrO3		0.6092										
Ni		0.2125		CNS		0.7259										
Cu(II)		0.1825		NO2		0.6402										
Zn		0.1947		NO3		0.6275										
UO2		0.2420		H2PO4		0.5334										
Be		0.0771		HPO4		0.0529										
Cd		0.0914		PO4		0.0000										
Pb(II)		0.0297		H2AsO4		0.7955										
MgOH		0.8974		HAsO4		0.0857										
Cu(I)		0.6305		AsO4		0.0002										
La		0.0476		HSO3		0.7358										
Ce		0.0502		SO3		0.1051										
Pr		0.0495		Acetate		0.6503										
Nd		0.0493														
Pm		0.0495														
Sm		0.0501														
Eu		0.0506														
Gd		0.0507														
Tb		0.0510														
Dy		0.0513														
Ho		0.0516														
Er		0.0513														
Tm		0.0512														
Yb		0.0512														
Lu		0.0511														
Y		0.0516														
Al		0.0623														
Ga		0.0949														
In		0.0003														
Fe(III)		0.0617														

Figure 2. Sample output of the program: activity coefficients for all ions and major neutral species, and pK* for some acids.

Left panel:

	Ion Pair	log K	Υ	log K*	Fraction(tr)
	Mn		0.1876		68.1%
	MnOH	3.40	0.6969	2.27	0.0%
	Mn(OH)2	5.78	2.1902	3.59	0.0%
Mn	MnHCO3	1.28	1.3217	0.21	0.2%
	MnCO3	4.10	1.3771	1.87	0.6%
	MnHS	7.50	0.6433	6.80	0.0%
	MnSO4	2.26	0.6433	0.78	12.0%
	MnCl	0.39	0.6433	-0.31	19.1%
	Ion Pair	log K	Υ	log K*	Fraction(tr)
	Fe		0.2068		60.0%
	FeOH	4.49	0.6969	3.40	0.6%
	Fe(OH)2	7.39	2.1902	5.24	0.0%
	FeHCO3	1.47	1.3217	0.44	0.3%
Fe(II)	FeCO3	5.45	1.3002	3.29	13.1%
	Fe(CO3)2	7.17	0.1965	4.47	0.0%
	FeHS	6.20	0.6433	5.54	0.0%
	FeSO4	2.20	0.6433	0.76	10.2%
	FeCl	0.32	0.6433	-0.33	15.8%
	Ion Pair	log K	Υ	log K*	Fraction(tr)
	Co		0.2082		39.9%
	CoOH	4.34	0.6969	3.25	0.3%
	Co(OH)2	9.19	2.1902	7.04	0.0%
	CoHCO3	1.41	1.3217	0.38	0.2%
Co	CoCO3	4.49	1.3771	2.31	0.9%
	CoHS	6.00	0.6433	5.35	0.0%
	CoSO4	3.06	0.6433	1.63	49.5%
	CoCl	0.26	0.6433	-0.39	9.2%
	Ion Pair	log K	Υ	log K*	Fraction(tr)
	Ni		0.2125		62.5%
	NiOH	4.13	0.6969	3.05	0.3%
	Ni(OH)2	8.99	2.1902	6.85	0.0%
	NiHCO3	1.63	1.3217	0.61	0.5%
Ni	NiCO3	5.37	1.3771	3.20	11.0%
	NiHS	6.20	0.6433	5.55	0.0%
	NiSO4	2.29	0.6433	0.87	13.4%
	Ni(SO4)2	3.20	0.6703	0.81	0.3%
	NiCl	0.17	0.6433	-0.47	12.0%
	Ion Pair	log K	Υ	log K*	Fraction(tr)
	Cu		0.1825		15.7%
	CuOH	6.00	0.6485	4.89	4.4%
	Cu(OH)2	11.74	1.6102	9.67	1.0%
	CuHCO3	1.82	1.0198	0.85	0.2%
Cu(II)	CuCO3	6.73	1.2146	4.54	61.8%
	Cu(CO3)2	10.41	0.2341	7.58	7.5%
	CuHS	8.70	0.6433	7.99	0.0%
	Cu(HS)2	14.90	0.6703	14.01	0.0%
	CuSO4	2.36	0.6433	0.87	3.4%
	CuCl	0.53	0.6433	-0.18	5.9%

Right panel:

	Ion Pair	log K	Υ	log K*	Fraction(tr)
	La		0.0476		28.2%
	LaOH	5.10	0.1938	3.93	0.9%
	LaHCO3	2.02	0.1938	1.18	0.8%
	LaCO3	6.82	0.8830	4.19	49.1%
	La(CO3)2	11.31	0.8830	7.32	7.4%
La	LaSO4	3.21	0.8830	1.00	8.2%
	LaCl	0.29	0.1938	-0.48	5.3%
	LaF	3.12	0.1938	2.02	0.1%
	LaH2PO4	2.50	0.1938	1.62	0.0%
	LaHPO4	4.87	0.8830	2.33	0.0%
	La(HPO4)2	8.17	0.8830	4.35	0.0%
	Ion Pair	log K	Υ	log K*	Fraction(tr)
	Ce		0.0502		21.7%
	CeOH	5.60	0.1938	4.45	2.2%
	CeHCO3	1.95	0.1938	1.14	0.6%
	CeCO3	6.95	0.8830	4.34	53.6%
	Ce(CO3)2	11.50	0.8830	7.53	9.3%
Ce	CeSO4	3.29	0.8830	1.10	8.0%
	CeCl	0.31	0.1938	-0.44	4.5%
	CeF	3.28	0.1938	2.20	0.1%
	CeH2PO4	2.43	0.1938	1.57	0.0%
	CeHPO4	4.98	0.8830	2.46	0.0%
	Ce(HPO4)2	8.34	0.8830	4.54	0.0%
	Ion Pair	log K	Υ	log K*	Fraction(tr)
	Pr		0.0495		19.2%
	PrOH	5.60	0.1938	4.45	2.0%
	PrHCO3	1.89	0.1938	1.07	0.4%
	PrCO3	7.03	0.8830	4.42	56.2%
	Pr(CO3)2	11.65	0.8830	7.67	11.4%
Pr	PrSO4	3.27	0.8830	1.08	6.7%
	PrCl	0.32	0.1938	-0.43	4.0%
	PrF	3.48	0.1938	2.39	0.2%
	PrH2PO4	2.37	0.1938	1.50	0.0%
	PrHPO4	5.08	0.8830	2.55	0.0%
	Pr(HPO4)2	8.50	0.8830	4.70	0.0%
	Ion Pair	log K	Υ	log K*	Fraction(tr)
	Nd		0.0493		16.1%
	NdOH	5.67	0.1938	4.51	1.9%
	NdHCO3	1.83	0.1938	1.01	0.3%
	NdCO3	7.13	0.8830	4.51	59.2%
	Nd(CO3)2	11.80	0.8830	7.82	13.5%
Nd	NdSO4	3.26	0.8830	1.06	5.5%
	NdCl	0.32	0.1938	-0.43	3.4%
	NdF	3.56	0.1938	2.47	0.2%
	NdH2PO4	2.31	0.1938	1.44	0.0%
	NdHPO4	5.18	0.8830	2.65	0.0%
	Nd(HPO4)2	8.66	0.8830	4.85	0.0%
	Ion Pair	log K	Υ	log K*	Fraction(tr)
	Pm		0.0495		13.2%

Figure 3. Preview of the output of the speciation calculations for the divalent and trivalent ions.
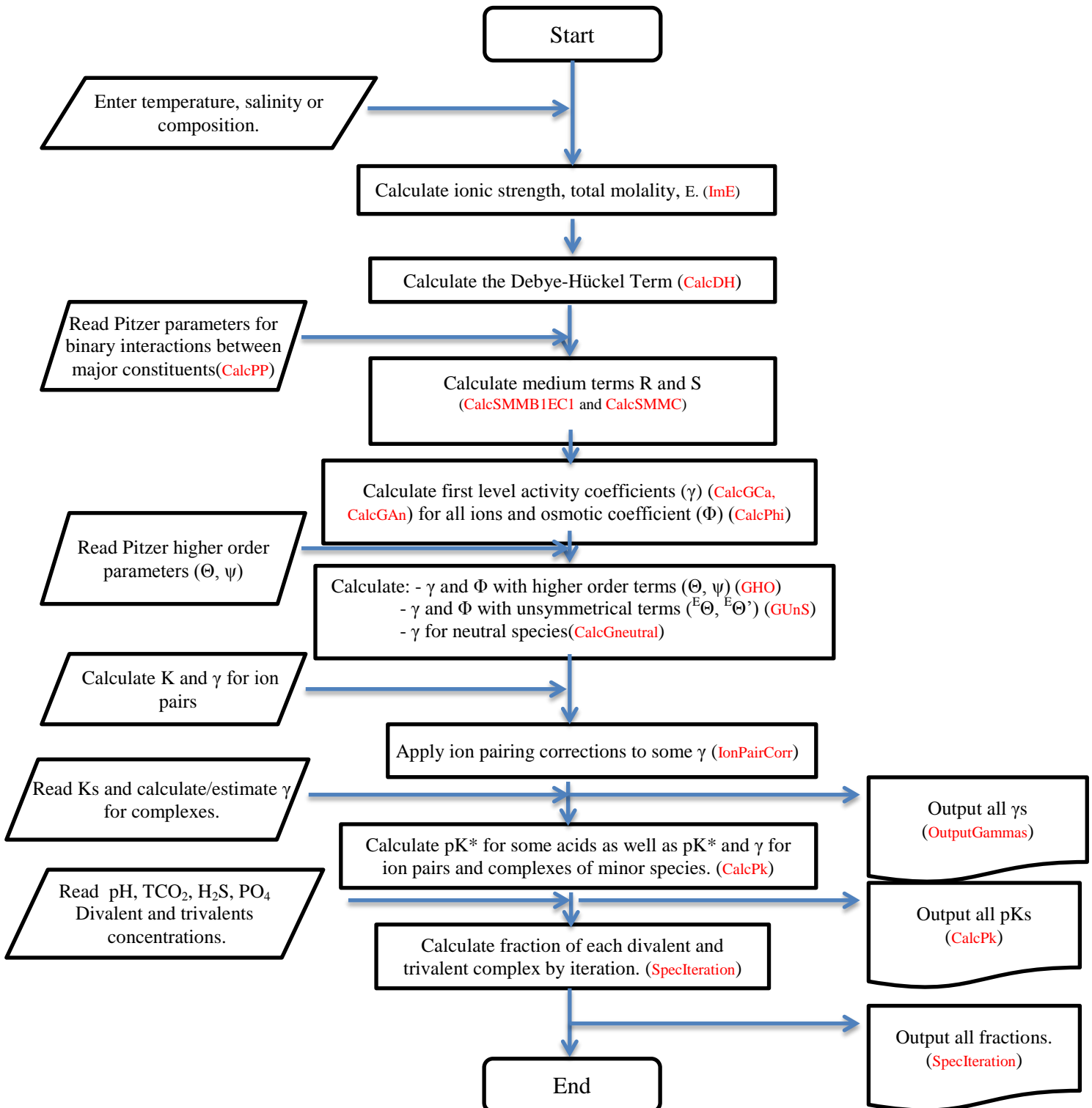
Figure 4. Program Flow Diagram. Text in red gives the name of the subroutines in the code.