Activity coefficients of a simplified seawater electrolyte at varying salinity (5–40) and temperature (0 and 25 °C) using Monte Carlo simulations

This is an author produced version of a paper published in:

Marine Chemistry (ISSN: 0304-4203)

Citation for the published paper:

http://dx.doi.org/10.1016/j.marchem.2015.02.006

Downloaded from: http://gup.ub.gu.se/publication/214853

Notice: This paper has been peer reviewed but does not include the final publisher proof-corrections or pagination. When citing this work, please refer to the original publication.

(article starts on next page)
Activity coefficients of a simplified seawater electrolyte at varying salinity (5–40) and temperature (0 and 25°C) using Monte Carlo simulations

Adam Ulfsbo*, Zareen Abbas, David R. Turner

Department of Chemistry and Molecular Biology, University of Gothenburg, SE-412 96 Gothenburg, Sweden

*Corresponding author: ulfsbo@chem.gu.se (Adam Ulfsbo)
Phone: +46 31 786 9053
Abstract
Mean salt activity coefficients of a simplified seawater electrolyte (Na⁺, Mg²⁺, Ca²⁺, Cl⁻, SO₄²⁻, HCO₃⁻, CO₃²⁻) at varying salinity (5-40) and temperature (0-25 °C) were estimated by Monte Carlo (MC) simulations, and compared with Pitzer calculations. The MC simulations used experimentally determined dielectric constants of water at different temperatures, and optimal agreement with the experimental data and the Pitzer calculations was achieved by adjusting the ionic radii. The results, together with a previous study of the carbon dioxide system in sodium chloride solution by the authors, suggest that a complete Monte Carlo description of seawater activity coefficients may be achievable using the charged hard sphere approach with a very limited number of fitted parameters (effective ionic radii), in contrast to the large number of fitted parameters required for a Pitzer model.

1. Introduction
Calculations of chemical potentials and modelling of chemical speciation in seawater currently use either Pitzer equations or an ion pairing approach. Pitzer equations are based on an ion interaction approach, where strong interactions are treated as ion pair formation but weaker interactions are treated as ion-ion interactions that contribute to the respective ions’ activity coefficients (Figure 1). The Pitzer equations are based on an extension of the Debye-Hückel equation using a virial equation approach, where the interactions between pairs and triplets of ions and molecules are described by empirical parameters (Pitzer, 1991). A Pitzer model is therefore dependent on a wealth of experimental data that underlie the database of Pitzer parameters. Pitzer modelling of the major components of seawater (seawater electrolyte) is well established, and is being applied to trace metals as the relevant experimental data become available.

Ion pairing approaches describe even weak ionic interactions as complex formation. Activity coefficients are either treated using a simpler representation (e.g., Dickson and Whitfield, 1981), or are avoided by treating stoichiometric (concentration based) stability constants as functions of salinity (ionic strength) (e.g., Turner et al., 1981). An example of an ion-pairing model adapted to a specific purpose is the CO2SYS programme (Lewis and Wallace, 1998) used for calculations of the carbon dioxide system in seawater, which uses experimentally determined stoichiometric
constants based on total concentrations, e.g., for carbonate \([\text{CO}_3^2\text{]}_T = [\text{CO}_3^2\text{]} + [\text{MgCO}_3^0\text{]} + [\text{CaCO}_3^0\text{}].\) These ion pairing approaches are also dependent on a wealth of experimental data.

Although Pitzer models and ion-pairing models rely on databases and/or fitting functions that summarise a large volume of experimental data, their computational requirements are modest. In contrast, Monte Carlo (MC) simulation requires extensive computing resources but little experimental data. Lund et al. (2003) pioneered the application of MC modelling to the seawater electrolyte, although their calculations were limited to 25 °C. Since applications in marine chemistry require models covering a realistic range of salinities and temperatures, we are assessing the performance of MC simulations in ionic media relevant to seawater. We have previously reported simulations of the activity coefficients of single and mixed salts of the carbonate system in sodium chloride solution between 0 and 1 m and 0 to 25 °C (Abbas et al., 2013). In order to obtain results consistent with Pitzer modelling, it was necessary to allow some ion sizes to vary as a function of temperature. This was interpreted as representing changes in hydration that affect the “effective” ionic size – hydration is not explicitly represented in the hard sphere based MC approach. The resulting dissociation constants of carbonic acid in sodium chloride showed excellent agreement with experimental values (Millero et al., 2007).

This paper builds on our previous work (Abbas et al., 2013), and focuses on covering a relevant temperature range (0-25 °C) for the estimation of mean activity coefficients of the major chloride, sulphate, and carbonate salts in a simplified seawater electrolyte (salinity 5-40) by MC simulation. Since there are no direct measurements of these mean salt activity coefficients, we have compared the results from the MC simulations with calculations using Pitzer equations, which are based on experimental measurements in single salts and binary mixtures, and thus represent the best available estimations of the mean salt activity coefficients in the seawater electrolyte. This work constitutes a step further towards developing Monte Carlo simulation methodology for the complete seawater ionic medium over relevant ranges of salinity and temperature.

Mean activity coefficients for the seawater salts NaCl, MgCl₂, CaCl₂, Na₂SO₄, MgSO₄, CaSO₄, NaHCO₃, Na₂CO₃, MgCO₃, and CaCO₃ at different temperatures were obtained from MC simulations by using the experimentally determined temperature dependent dielectric constant of
water. Best fits between the activity coefficients calculated by MC and Pitzer were obtained by adjusting the radii of the ions.

2. Theory and methods

2.1 Monte Carlo simulations

The MC simulation used in this study follows that of Abbas et al. (2013). It was developed by Svensson and Woodward and has been described in detail elsewhere (Svensson and Woodward, 1988). Briefly, the MC simulations were performed by the standard Metropolis algorithm (Metropolis et al., 1953) and a canonical ensemble was constructed by using a cubic box with periodic boundary conditions. Unrestricted primitive model (UPM) of a salt solution was used in the simulations. In the UPM, cations and anions are considered as charged hard spheres of different sizes and solvent is represented by a continuum having a specific dielectric constant. In order to model a particular ionic solution or mixture, the dielectric constant as a function of temperature and the radii of the various ions and molecules are required. In order to attain a required concentration of electrolyte within a fixed box length, the number of particles was varied. Various concentrations can also be obtained by keeping the number of ions fixed and varying the box length (Abbas et al., 2009). A simplified seawater electrolyte, containing 0.450 molal (m) Na⁺, 0.5 m Cl⁻, 0.03 m SO₄²⁻, 0.05 m Mg²⁺, 0.01 m Ca²⁺, 0.002 m CO₃²⁻, and 0.002 m HCO₃⁻ ions, corresponding to salinity 35 at 25 °C, was simulated. MC simulations were performed by using a cubic box length of 202 containing 2234 Na⁺, 2502 Cl⁻, 149 SO₄²⁻, 248 Mg²⁺, 50 Ca²⁺, 10 CO₃²⁻, and 10 HCO₃⁻ ions. Simulations at other salinities were achieved by changing the particle number of ions proportionally. The step size used in MC moves was 42 for monovalent ions and 11 for divalent ions. The dielectric constant values of water (εω) used at 0, 5, 10, 15, 20, and 25 °C are shown in Table 1. The osmotic coefficients were calculated by virial route as described in detail in the original article by Svensson and Woodward (1988). Long simulations, i.e., 2 million configurations were performed for equilibration and thereafter 95 million MC configurations, were performed to generate the thermodynamic data. The maximum spread in the calculated activity and osmotic coefficients was less than 0.5%. An example of typical data of activity coefficients as obtained by MC simulations for salinities 5 and 35 at 25 °C are given in Table S1 (Appendix B). The theoretical data was converted from molar to molal scale as described by Abbas et al. (2013).
2.2 Pitzer equations

The Pitzer model (Pitzer, 1991) is one of the most widely used specific interaction models to account for non-ideal behaviour of electrolytes due to ionic interactions, such as in the seawater ionic medium (Harvie et al., 1984; Millero and Pierrot, 1998). It treats strong electrolytes as completely dissociated, and the properties of the solutions are described in terms of interactions between free ions, in contrast to the ion-pairing model (Dickson and Whitfield, 1981).

The Pitzer model is based on an extension of the Debye-Hückel theory using a virial equation approach. The general form of the Pitzer equations for estimating the activity coefficients ions in the absence of neutral species is given by

$$\ln \gamma_i = f^\gamma + \sum_{ij} m_i m_j B_{ij} + \sum_{ijk} m_i m_j m_k C_{ijk}$$

where $f^\gamma$ is a Debye-Hückel term that accounts for long-range interactions, $B_{ij}$ is a coefficient related to binary interactions of all the components (plus-minus, plus-plus and minus-minus), and $C_{ijk}$ is related to ternary interactions of all the components (plus-minus-plus, plus-minus-minus and minus-plus-plus). These interaction coefficients include semi-empirical Pitzer parameters which are linear combinations of ion and solvent specific parameters. Detailed descriptions of Pitzer equations are given in the literature (Clegg and Whitfield, 1991; Pitzer, 1991; Millero and Pierrot, 1998) and will not be repeated here.

In this work, for the solution containing seven common components of seawater (Na$^+$, Mg$^{2+}$, Ca$^{2+}$, Cl$^-$, SO$_4^{2-}$, HCO$_3^-$, and CO$_3^{2-}$) one needs to know 50 binary, temperature dependent, parameters and 20 ternary parameters, as well as temperature dependent stability constants for CaCO$_3$ and MgCO$_3$. The addition of the other major and minor seawater components (K$^+$, Sr$^{2+}$, Br$^-$, and F$^-$) requires more parameters, but they do not contribute much to the background medium term of the Pitzer equation (Millero and Pierrot, 1998).

2.3 Model parameterization

The Pitzer parameters used in this work are based on the modified MIAMI Ionic Interaction Model (Waters and Millero, 2013), which is an update of the previous MIAMI model (Campbell et al., 1993; Millero and Roy, 1997; Millero and Pierrot, 1998) and is currently the principal chemical speciation model of seawater. The model is applicable primarily to major ions in seawater (from 0 to 50 °C, and 0 to 40 salinity) containing the species H$^+$, Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$,
Sr$^{2+}$, Cl$^-$, Br$^-$, OH$^-$, HCO$_3^-$, B(OH)$_4^-$, HSO$_4^-$, SO$_4^{2-}$, CO$_3^{2-}$, CO$_2$, B(OH)$_3$, and H$_2$O. In addition to this model and the seawater model of Clegg and Whitfield (1995), there are also Pitzer models not written predominantly for thermodynamic modelling of the seawater ionic medium. Two examples are FREZCHEM (Marion, 2002; Marion et al., 2008) and PHREEQC (Parkhurst and Appelo, 2013), where the latter is mainly based on the Harvie et al. (1984) (HMW) model (Plummer et al., 1988).

For this work, Pitzer equations have been included in the in-house calculation programme GIVAKT, which uses the iterative optimization algorithm developed for HALTAFALL (Ingri et al., 1967), implemented in Excel Visual Basic. GIVAKT uses the same 5-term equation for the temperature dependence as PHREEQC and the HMW model, which requires some refitting of temperature dependences for the limited temperature range of interest here (Abbas et al., 2013). The 5-term equation for parameter $P$ at temperature $T/K$ is given by:

$$P(T) = p_1 + p_2 \left(\frac{1}{T} - \frac{1}{T_r}\right) + p_3 \ln\left(\frac{T}{T_r}\right) + p_4 (T - T_r) + p_5 (T^2 - T_r^2)$$

(2)

where $T_r$ is the reference temperature 298.15 K. In cases where the coefficients cannot be converted to the form of Equation (2) by linear transformation, multiple linear regression was used over the relatively limited temperature range 0 – 50 °C. Parameters calculated at 1 °C intervals from the original source equations were refitted to Equation (2) by multiple linear regression against the appropriate functions of $T/100$ and $T_r/100$ to ensure that the $x$ variables were of the same order of magnitude. The residuals were less than 1% with the exception of parameter values very close to zero. The MIAMI model includes the formulation of Clegg et al. (1994) for the H – HSO$_4$ and H – SO$_4$ binary interactions. This includes more complex formulations for the parameters’ dependence on temperature and ionic strength which were developed to fit activity coefficients in up to 6 mol kg$^{-1}$ sulphuric acid in water. We have refitted these parameters to the simpler PHREEQC formulation for the much lower (sulphate) concentration range encountered in seawater (Appendix A).

It is difficult to determine the error in the calculated activity coefficient contributed by a single parameter in Pitzer equations. A method for estimating such an error is to compare models using different values for a given parameter; however, such a comparison offers no statistically relevant information on the error. For comparison with our current implementation of the modified
MIAMI model in GIVAKT, we include calculations using PHREEQC with its default Pitzer database. The mean activity coefficients of the chloride and sulphate salts in seawater as a function of salinity at 25 and 0 °C estimated by the two Pitzer models, are shown in Figure 2. Excellent agreement is seen at 25 °C, with some divergences for sulphate and salts at 0 °C and higher salinities. This reflects well the quality and coverage of the available experimental data: while these salts are all well studied at 25 °C, experimental data at low temperatures are much less extensive.

3. Results and discussion
In this work we have focused on covering a relevant temperature range (0 to 25 °C) for the estimation of activity coefficients of major electrolytes in seawater (salinity 5-40), including NaCl, MgCl2, CaCl2, Na2SO4, MgSO4, CaSO4, NaHCO3, Na2CO3, MgCO3, and CaCO3. MC simulations were performed at different temperatures using experimental values of the dielectric constant of water and specific cation and anion radii. As noted above, the only adjustable parameters are the ionic radii. We do not attempt to compare the activity coefficients of individual ions, since these cannot be defined unequivocally but are dependent on a conventional division of mean salt activity coefficients, where the Pitzer and MC approaches follow different conventions. All comparisons will therefore be restricted to mean activity coefficients of salts, and also osmotic coefficients, which are independent of conventions. All results are available online as supplementary data (Appendix B).

3.1 Activity coefficients of chloride salts
Mean activity coefficients of NaCl in the simplified seawater electrolyte as a function of salinity at different temperatures estimated by MC and Pitzer are shown in Figure 3. Generally, there was a good agreement between the two models, with a slight tendency towards overestimation by MC at intermediate salinities. The temperature dependence was most apparent at salinities greater than 20 with decreasing activity at decreasing temperature. In all MC simulations, the ionic radius of Cl– was kept constant to its crystallographic value, while the Na+ radius was adjusted at different temperatures (Table 1). These radii are significantly larger than the Na+ crystal radius (0.102 nm), and are interpreted as representing the effective ionic radius of hydrated Na+, since hydration is not treated explicitly in the MC approach used here.
Mean activity coefficients of the 1:2 electrolytes MgCl$_2$ and CaCl$_2$ in the simplified seawater electrolyte as a function of salinity at different temperatures are shown in Figure 4. Excellent agreement was found between MC and Pitzer over the entire salinity and temperature range. At low temperatures, however, there was a small deviation in CaCl$_2$ at higher salinities. For both salts the temperature dependence was opposite to that of NaCl, where MgCl$_2$ showed stronger temperature dependence than CaCl$_2$. These differences indicate dissimilarities in the temperature coefficients of the relevant ionic interactions, since the strength of the long-range Debye-Hückel term decreases with decreasing temperature. The observed sequence Na$^+$, Ca$^{2+}$, Mg$^{2+}$ reflects an increase in the ionic charge : radius ratio.

3.2 Activity coefficients of sulphate salts

Initially we used the crystallographic radius of SO$_4^{2-}$ (0.240 nm) in the MC simulations, which resulted in a large deviation for all sulphate salts. However, for the chloride salts the MC simulations were in good agreement. With the temperature dependent radius of Na$^+$ from optimisation of the NaCl simulations, the radius of SO$_4^{2-}$ was adjusted and the best fit resulted in a much smaller radius (0.130 nm) than the crystallographic value (Table 1). It should be noted that in these simulations the radius of Na$^+$ is temperature dependent as its temperature dependent value was found from the pure single salt NaCl, as shown in our previous work (Abbas et al., 2013) and in Table 1. Although the best fitted radius of SO$_4^{2-}$ is without any physical propriety, the best fitted radii obtained by our approach should be considered as optimised distances between the cation and anion for each specific salt. It is well known by both experimental and theoretical studies that sulphate salt solutions consist of ion pairs along with dissociated ions even at low concentrations (Buchner et al., 1999). Such ion pairing effects lower the mean ionic activity coefficients compared with dissociated salt solutions. In the primitive model, as used in the MC simulations, ions are considered as non-overlapping charged hard spheres dissolved in a structureless solvent, where the ion pairing effects have to be taken into account by decreasing the cation-anion distance. This is also due to the assumption that the hard sphere ions never overlap in the MC simulations, even at high concentrations. In reality ions are soft polarizable species and hydration layers may also overlap at increasing salt concentrations. In the MC simulations these effect are indirectly included by adjusting the distance between anion and cation. In order to model the strong interaction between cation and anion, the SO$_4^{2-}$ radius needed to be decreased since the radii of Na$^+$, Mg$^{2+}$, and Ca$^{2+}$ were kept constant in the MC simulations.
Similar sized radii have also been used by others. For example, Lund et al. (2003) used a radius of 0.160 nm that was estimated from best fit of sum radii of single salts to experimental data, setting the radius of Cl− fixed to its crystallographic value. These values are comparable to those used in the mean spherical approximation (MSA) calculations (0.149 nm) by Vilarino and Sastre de Vicente (1999). MSA is based on the integral equations theory of electrolyte solutions but the interaction of an ion with the ionic medium is described in a linear approximation. MSA used in the study as mentioned above was also based on the primitive model of electrolyte, i.e., the ions are considered as charged hard spheres of different sizes and the solvent as a structureless continuum. The difference between the sulphate radius optimized by MC and MSA can be due to the fact that in MSA a concentration dependent dielectric constant of salt solution was used whereas in the MC a fixed dielectric constant at each temperature was used. In a previous study (Abbas et al., 2007), it was shown that inclusion of concentration dependent dielectric constant leads to larger fitted ionic radii compared with the case of fixed dielectric constant.

Mean activity coefficients of the 2:2 electrolytes MgSO4 and CaSO4 in the simplified seawater electrolyte as a function of salinity at different temperatures are shown in Figure 5. There was an excellent agreement between the models at low to intermediate salinities, although with some deviations towards higher salinities at low temperatures. Compared to the activity coefficients of MgSO4, there was a stronger salinity and temperature dependence of the activity coefficients of CaSO4 with respect to the Pitzer model. Neither the Pitzer model nor the MC simulations require an explicit treatment of ion-pairing between Mg2+ and SO42− or Ca2+ and SO42−, although ion pairing models include relatively strong interactions with log10K > 2 in both cases (Dickson and Whitfield, 1981). However, both approaches include an implicit recognition of strong interactions. In the Pitzer model, this is shown by the inclusion of the parameter β(2), which is used only in the case of strong +/− interactions, and where the value of β(2) is suggested to have a direct relationship to the corresponding stability constant in an ion pairing model (Pitzer and Mayorga, 1974). In the MC approach, the strong interaction is treated implicitly by the use of an unrealistically small radius for the sulphate ion, as discussed above. Figure 5 shows that these two approaches agree well, with the sulphate radius also providing good MC simulations for sodium sulphate (Figure 1).
3.3 Activity coefficients of carbonate salts

Mean activity coefficients of the 1:1 and 1:2 salts NaHCO$_3$ and Na$_2$CO$_3$ are shown in Figure 6. In our previous work (Abbas et al., 2013), both the Na$^+$ and HCO$_3^-$ radii were kept at their crystallographic values of 0.102 and 0.156 nm, respectively, whereas the Na$^+$ radius was considered hydrated and allowed to vary with temperature (Table 1) and CO$_3^{2-}$ was kept unhydrated at its crystallographic value. In this study, the Na$^+$ radius was consistently considered to be hydrated with temperature dependence according to Table 1. This resulted in best fit radii of HCO$_3^-$ and CO$_3^{2-}$ which were lower than the crystallographic values. Excellent agreement was found for both salts as a function of salinity at higher temperatures. There was a slight tendency of MC overestimating NaHCO$_3$ activity coefficients at higher salinities and lower temperatures, whereas underestimation of Na$_2$CO$_3$ was observed towards higher salinities for all temperatures. As was discussed in the case of the sulphate salts the best fitted radii, smaller than the crystallographic values, should be considered as a way of including strong cation-anion interactions by decreasing the distance between the opposite charged ions. Although the best fit radii of the anions may be without any physical propriety, ion pairing is present in these salts due to the strong attraction between the oppositely charged ions.

Mean activity coefficients of the 2:2 salts MgCO$_3$ and CaCO$_3$ as a function of salinity at different temperatures are shown in Figure 7. In the case of MC, both cations and anions are of the same charge and radii as the corresponding sulphate salts (Table 1). Good agreement is found at higher temperatures, whereas MC underestimates activity coefficients towards higher salinities and lower temperatures compared to Pitzer. However, in the case of CaCO$_3$ at 0 °C there is excellent agreement between MC and the default PHREEQC Pitzer model at higher salinities. The MC results are well within the uncertainty as given by the difference between the different Pitzer models. This reflects well the difficulties in determining the error in the calculated activity coefficients contributed by a single parameter in Pitzer equations, as well as the quality and coverage of the available experimental data, where experimental data at low temperatures are much less extensive.

3.4 Osmotic coefficient and overall temperature dependence

The differences in osmotic coefficients calculated by Pitzer equations and MC simulations in the simplified seawater electrolyte are shown in Figure 8. Although the differences are small, there is
a clear, almost monotonic temperature dependence. This is reflected in the corresponding differences between calculations of the mean salt activity coefficients (Table 2), where all except NaCl also show monotonic temperature dependences with the largest effects observed for the sulphate and carbonate salts. This indicates that one or both of the two modelling approaches have shortcomings in their ability to reproduce temperature dependence correctly. Given that the Pitzer parameters are based on experimental data, these shortcomings most likely arise with the MC simulations, where the cation interactions with sulphate and carbonate have been represented by reduced ionic radii. Although of little significance for the results as whole, a minor offset was observed at lower salinities, even at 25 °C. This suggests that ion-pairing with sulphate and carbonate is significant, even at low salinity (ionic strength). Although the temperature dependent dielectric constant of water was used in the MC, the dielectric constant of water also changes with salt concentrations. To accurately simulate the experimental data such effects need to be included in the model and at present there is lack of such experimental data.

4. Conclusions
We have compared the results of Monte Carlo simulations of mean salt activity coefficients in a simplified seawater electrolyte containing the major ions Na⁺, Mg²⁺, Ca²⁺, Cl⁻, SO₄²⁻, and the minor ions HCO₃⁻ and CO₃²⁻ with Pitzer calculations. Good agreement is obtained over the temperature range 0 – 25 °C and salinity range 5 – 40, with somewhat increasing deviations at lower temperatures. The Monte Carlo approach, which treats the ions as hard spheres in a medium of known dielectric constant, is able to accommodate two important effects by adjustment of effective ionic radii away from the known crystal radii. The first is hydration, where the effective ionic radius is increased, resulting in temperature-dependent cation radii. The second effect is strong cation-anion interactions, where the effective anion radius (sulphate and carbonate in this case) is smaller than the crystal radius. These results, together with our previous study of the carbon dioxide system in sodium chloride solution, suggest that a complete Monte Carlo description of seawater activity coefficients may be achievable using the hard sphere approach with a very limited number of fitted parameters (effective ionic radii), in contrast to the large number of fitted parameters required for a Pitzer model. Monte Carlo modelling does, however, require substantial computing resources.
Acknowledgements

The authors acknowledge the financial support from the Swedish Research Council Formas (contract no. 214-2008-1383). The availability of computing resources at the C3SE centre at Chalmers University of Technology is greatly acknowledged.
References


Dickson, A.G. and Whitfield, M., 1981. An ion-association model for estimating acidity constants (at 25°C and 1 atm total pressure) in electrolyte mixtures related to seawater (ionic strength < 1 mol kg \(^{-1}\) H\(_2\)O). Marine Chemistry, 10(4): 315-333, 10.1016/0304-4203(81)90012-8


Vilarino, T. and Sastre de Vicente, M.E., 1999. The mean spherical approximation methodology applied to the acid-base equilibria of glycine in artificial seawater. Physical Chemistry Chemical Physics, 1(10): 2453-2456, 10.1039/A900918C
Appendix A

Refit of Clegg et al. (1994) sulphate parameters

The paper by Clegg et al. (1994) uses extended formulations for $\beta$ and $C$, with a complex $T$ dependence, $\alpha_{\text{H,SO}_4}$ dependent on temperature, and $C$ dependent on ionic strength. These formulations were developed to fit activity coefficients in up to 6 mol kg$^{-1}$ sulphuric acid in water. We have therefore tested whether these parameters can be refitted to the simpler PHREEQC temperature dependence equation for the conditions encountered in seawater (0-50 °C and 0-1 molal).

The values of the $\beta$ and $C$ parameters affect not only the binary interactions ($\text{H}^+ - \text{SO}_4^{2-}$ and $\text{H}^+ - \text{HSO}_4^-$ in this case), but also the summations of $B'$ and $C$ terms that contribute to the non-specific terms in the Pitzer equation for an ion’s activity coefficient. For seawater conditions, these terms will be largest at low pH, i.e., where the hydrogen ion concentration is at a maximum. The maximum contribution of these terms to the values of $\ln \gamma$ in seawater at pH 3 is very small (Table A.1)

Table A1. Maximum contributions of summation terms to calculated $\ln \gamma$ in seawater at pH 3.

<table>
<thead>
<tr>
<th>Ion pair</th>
<th>$B'$ summation</th>
<th>$C$ summation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}^+ - \text{SO}_4^{2-}$</td>
<td>0.000004</td>
<td>0.000003</td>
</tr>
<tr>
<td>$\text{H}^+ - \text{HSO}_4^-$</td>
<td>0.00000004</td>
<td>0.0000002</td>
</tr>
</tbody>
</table>

The binary interaction contribution to $\ln \gamma$ for $\text{H}^+$, $\text{HSO}_4^-$ and $\text{SO}_4^{2-}$ is, after division by the counterion concentration, $2B + ZC$. The value of $Z$ in seawater is given by $Z = 1.737 I$, where $I$ is the ionic strength. Applying the standard Pitzer formulation, i.e., without the extensions of Clegg et al. (1994), to the $\text{H}^+ - \text{HSO}_4^-$ interaction we have:

\[
2B + ZC = 2\beta^0 + 2\beta^1 g(x) + ZC^{\theta/2} \quad (C = C^{\theta/2} \text{ for a 1:1 interaction}) \tag{A.1}
\]

\[
B + ZC/2 = a_1 + a_2 (1/T - 1/T_r) + a_3 \ln(T/T_r) + a_4 (T - T_r) + a_5 (T^2 - T_r^2)
\]

\[
+ b_1 g(x) + b_2 g(x) (1/T - 1/T_r) + b_3 g(x) \ln(T/T_r) + b_4 g(x) (T - T_r) + b_5 g(x) (T^2 - T_r^2)
\]

\[
+ c_1 (Z/4) + c_2 (Z/4)(1/T - 1/T_r) + c_3 (Z/4) \ln(T/T_r) + c_4 (Z/4)(T - T_r) + c_5 (Z/4)(T^2 - T_r^2)
\]  \tag{A.2}
where the $a$, $b$ and $c$ terms provide the temperature parameters for $\beta^0$, $\beta^1$ and $C^\phi$ respectively: $x$ is equal to $\alpha \sqrt{I}$ with $\alpha$ having the default value 2, and $T_r = 298.15$K. The parameter values were obtained by multiple linear regression, using $T/100$ and $T_r/100$ to ensure that the regression variables are of the same order of size. The treatment of the $\text{H}^+ – \text{SO}_4^{2-}$ is similar, except that here $C = C^\phi/(2 \sqrt{2})$, so that the factor in the last line of the equation becomes $(Z/(4 \sqrt{2}))$. The fitted parameters are shown in Table A.2: the mean square deviations about the regressions are $1.5 \times 10^{-5}$ ($\text{H}^+ - \text{SO}_4^{2-}$) and $1 \times 10^{-7}$ ($\text{H}^+ - \text{HSO}_4^-$).
Appendix B

Supplementary data to this article can be found online at
http://dx.doi.org/10.1016/j.marchem.xxx.xx.xxx.
Tables and table captions

Table 1. Dielectric constant of water ($\varepsilon_w$) at different temperatures and ionic radii of Na$^+$, Mg$^{2+}$, Ca$^{2+}$, Cl$^-$, SO$_4^{2-}$, HCO$_3^-$, and CO$_3^{2-}$.

<table>
<thead>
<tr>
<th>$t$ (°C)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_w$</td>
<td>87.90</td>
<td>85.90</td>
<td>83.95</td>
<td>82.04</td>
<td>80.18</td>
<td>78.36</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
<th>Radius (nm)</th>
<th>0.140</th>
<th>0.150</th>
<th>0.155</th>
<th>0.155</th>
<th>0.160</th>
<th>0.168</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td></td>
<td>0.295</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td></td>
<td>0.274</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td></td>
<td>0.181</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl$^-$</td>
<td></td>
<td>0.130</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td></td>
<td>0.090</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td></td>
<td>0.130</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Absolute standard deviations of the differences between mean activity coefficients, $\Delta \ln \gamma$ (Figure 10) and osmotic coefficients (OC), $\Delta \phi$ (Figure 9) from Pitzer equations (Waters and Millero, 2013) and Monte Carlo simulations over the salinity range 5 to 40. The standard deviations are reported as (SD)E-3.

<table>
<thead>
<tr>
<th>Salt</th>
<th>0 °C</th>
<th>5 °C</th>
<th>10 °C</th>
<th>15 °C</th>
<th>20 °C</th>
<th>25 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>2.3</td>
<td>1.9</td>
<td>2.3</td>
<td>2.3</td>
<td>2.2</td>
<td>1.9</td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td>2.0</td>
<td>2.1</td>
<td>2.3</td>
<td>1.9</td>
<td>1.8</td>
<td>2.2</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>3.6</td>
<td>1.5</td>
<td>1.0</td>
<td>2.2</td>
<td>3.1</td>
<td>2.8</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>6.0</td>
<td>5.7</td>
<td>4.8</td>
<td>4.7</td>
<td>5.4</td>
<td>4.8</td>
</tr>
<tr>
<td>MgSO$_4$</td>
<td>4.6</td>
<td>5.6</td>
<td>4.2</td>
<td>2.6</td>
<td>3.3</td>
<td>2.8</td>
</tr>
<tr>
<td>CaSO$_4$</td>
<td>15.3</td>
<td>9.8</td>
<td>4.0</td>
<td>4.1</td>
<td>3.5</td>
<td>3.1</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>3.2</td>
<td>1.8</td>
<td>1.8</td>
<td>2.5</td>
<td>2.2</td>
<td>2.1</td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td>13.2</td>
<td>13.4</td>
<td>12.7</td>
<td>14.3</td>
<td>15.3</td>
<td>13.4</td>
</tr>
<tr>
<td>MgCO$_3$</td>
<td>20.6</td>
<td>18.3</td>
<td>14.9</td>
<td>14.7</td>
<td>14.5</td>
<td>15.8</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>31.3</td>
<td>22.3</td>
<td>15.6</td>
<td>17.5</td>
<td>18.2</td>
<td>17.6</td>
</tr>
</tbody>
</table>

| OC ($\Delta \phi$) | 3.5 | 4.2 | 3.6 | 3.0 | 2.9 | 4.1 |
Figures and figure captions

**Figure 1.** Schematic diagram of interactions treated as complexes (solid lines) and free ions (dashed or no lines) by the Pitzer model. Stronger complexes are indicated by thicker lines. Modified after the ion-pairing diagram for the main components of seawater by Dyrsen and Wedborg (1974).
Figure 2. Calculated mean activity coefficients of the five major salts in seawater at 25 and 0 °C as a function of salinity. Two different Pitzer models and databases are compared; the modified MIAMI Interaction Model (lines) and PHREEQC (markers). Note that additional modifications have been made to the former, i.e., the model parameterization of Waters and Millero (2013) (see Section 2.3), whereas the default database was used in the latter.
Figure 3. Mean activity coefficients of NaCl and Na$_2$SO$_4$ in seawater from the Pitzer model (solid lines) and Monte Carlo simulations (closed circles) as a function of salinity at 25 and 0 °C. The dashed lines in the 25 °C panel represent the temperature dependence (25, 20, 15, 10, 5, and 0 °C) in descending order. PHREEQC calculations are included at 0 °C for comparison.
Figure 4. Mean activity coefficients of MgCl$_2$ and CaCl$_2$ in seawater from the Pitzer model (solid lines) and Monte Carlo simulations (closed circles) as a function of salinity at 25 and 0 °C. The dashed lines in the 25 °C panel represent the temperature dependence (25, 20, 15, 10, 5, and 0 °C) in descending order. PHREEQC calculations are included at 0 °C for comparison.
Figure 5. Mean activity coefficients of MgSO₄ and CaSO₄ in seawater from the Pitzer model (solid lines) and Monte Carlo simulations (closed circles) as a function of salinity at 25 and 0 °C. The dashed lines in the 25 °C panel represent the temperature dependence (25, 20, 15, 10, 5, and 0 °C) in descending order. PHREEQC calculations are included at 0 °C for comparison.
Figure 6. Mean activity coefficients of NaHCO₃ and Na₂CO₃ in seawater from the Pitzer model (solid lines) and Monte Carlo simulations (closed circles) as a function of salinity at 25 and 0 °C. The dashed lines in the 25 °C panel represent the temperature dependence (25, 20, 15, 10, 5, and 0 °C) in descending order. PHREEQC calculations are included at 0 °C for comparison.
Figure 7. Mean activity coefficients of MgCO$_3$ and CaCO$_3$ in seawater from the Pitzer model (solid lines) and Monte Carlo simulations (closed circles) as a function of salinity at 0 and 25 °C. The dashed lines in the 25 °C panel represent the temperature dependence (25, 20, 15, 10, 5, and 0 °C) in descending order. PHREEQC calculations are included at 0 °C for comparison.
Figure 8. Normalised plot of the difference in osmotic coefficient, $\Delta \phi/(1-\phi)$, between the Pitzer and Monte Carlo models as a function of salinity at different temperatures.