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Monte Carlo simulation of the dissociation constants of CO₂ in 0 to 1 molal
sodium chloride between 0 and 25°C

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Abstract

Stoichiometric dissociation constants of the carbon dioxide system in NaCl solution between 0 and 1 molal and 0 to 25°C were estimated by Monte Carlo (MC) simulations, and compared with Pitzer calculations and experimental measurements. The MC simulations used experimentally determined dielectric constants of water at different temperatures, and optimal agreement with the experimental data and Pitzer calculations was achieved by adjusting the ionic radii. This simple procedure resulted in effective ionic radii which were further used to simulate the activity coefficients of salt mixtures. The first and second stoichiometric dissociation constants of carbonic acid in NaCl solution (pK_1^* and pK_2^*) were estimated from the MC-derived activity coefficients of mixed salts in NaCl. The MC results are in good agreement with the experimental data as well as with the Pitzer calculations. This study shows that Monte Carlo simulations in the temperature and ionic strength range relevant to seawater can provide pK values of the same quality as Pitzer calculations, and constitutes the first step in developing a temperature-dependent MC model for seawater. While MC calculations require greater computing resources, the number of parameters derived by fitting to thermodynamic data is substantially smaller than for Pitzer calculations.

Key Words: Monte Carlo, MC, simulations, Pitzer, sea water, CO₂, dissociation constants, pK_1^* , pK_2^* , activity coefficients.

Introduction

One of the cornerstones of marine chemistry is the study of the thermodynamics of the seawater ionic medium. This ionic medium consists of 11 dissolved components (Clegg and Whitfield, 1991), which together with pH provide the basis for thermodynamic modelling. The earliest approaches to modelling the thermodynamics of the seawater ionic medium used the ion-pairing approach, beginning with the pioneering work of Garrels and Thompson

(1962). This approach assumes that the activity coefficients of dissolved ions and molecules are a function of ionic strength, and that specific interactions between ions of opposite charge are treated as complex formation reactions. Extended Debye-Hückel equations are used to describe the dependence of activity coefficients on ionic strength (Dickson and Whitfield, 1981; Millero and Schreiber, 1982; Turner et al., 1981). The number of complexes formed increases rapidly with the number of components modelled, with the result that much experimental data is needed to generate a reliable model. Even when such data are available, the limitations of the extended Debye-Hückel equations limit the accuracy of ion-pairing models.

An alternative approach, which has been widely applied to the carbon dioxide system and other weak acids, is the development of equations that allow the conditional stability constants (concentration products) to be calculated from salinity and temperature (Dickson et al., 2007). In order to generate reliable equations, accurate measurements of the concentration products are required over the relevant salinity and temperature ranges.

The current state of the art for modelling of seawater thermodynamics is based on Pitzer equations (Clegg and Whitfield, 1991; Millero and Pierrot, 1998). These are extended Debye-Hückel equations whose form is based on a virial expansion, and where the interactions between pairs and triplets of ions and molecules are described by empirical parameters.

The common feature of these approaches to chemical speciation modelling is that they require a great deal of thermodynamic data, since they include a large number of parameters whose values must be determined experimentally. In this paper we explore an alternative approach, Monte Carlo (MC) modelling, which demands very little experimental data. All that is needed is the dependence of water's dielectric constant on temperature, and the hard sphere radii of the ions and molecules to be modelled. Monte Carlo modelling does, however,

require extensive computing resources. Lund et al. (2003) have previously shown that Monte Carlo modelling can be applied to the seawater ionic medium, but did not test the applicability of their model in the full temperature range of 0 to 25 °C, an essential requirement for seawater modelling. In this work we have focused on covering a relevant temperature range (0 °C to 25 °C) for the carbon dioxide system in sodium chloride solution (0 to 1 molal). This is the first step towards developing Monte Carlo simulations for seawater at different temperatures.

Theoretical methods

Monte Carlo simulations

The MC simulation method used in this study was developed by Svensson and Woodward and has been described in detail elsewhere (Svensson and Woodward, 1988). Here we shall summarize the main features of this method. 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. The interaction between charged hard spheres is described by a coulombic potential as shown in Figure 1. The interaction energy (μ_{ij}) between two ions becomes infinite when ions are at a distance of closest approach because the ions are considered as rigid hard spheres which do not overlap. At distances greater than their closest approach the interaction between ions is given by Coulomb potential. To obtain activity coefficients a modified Widom particle insertion method was used (Svensson and Woodward, 1988). The Widom method (Widom, 1963) states that a non-

perturbing particle α inserted at a random position r will have the activity coefficient γ given by

$$\ln \gamma = -\ln \langle \exp[-\beta \Delta U_\alpha(r)] \rangle_0 \quad (1)$$

Here β is $1/k_B T$, k_B is the Boltzmann constant and T is temperature in kelvin. The exponential term enclosed in the brackets is the ensemble average of the energy change, ΔU_α , of adding the particle. This method provides a direct calculation of chemical potential. However, the original Widom method becomes less accurate when dealing with the ionic systems of finite sizes, since the addition of a charged particle will violate electroneutrality in the cell. This effect can be reduced considerably by using very large systems, but such simulations require enormous computation times. Svensson and Woodward (1988) proposed a simple charge rescaling method to re-establish electroneutrality in the computation cell. This method has shown good results for symmetrical as well as for asymmetrical electrolytes and very good agreement with Grand Canonical Monte Carlo (GCMC) simulations (Valleau et al., 1980). Note that in GCMC simulations the problem of violation of electroneutrality in the cell does not exist because only electroneutral systems are considered. This MC simulation method has recently been used to calculate the activity and osmotic coefficients of large number of salts (Abbas et al., 2009). The major advantage of the MC method used in this study is that single ion activity coefficients are directly obtained by this particle insertion method.

In order to attain a required concentration of electrolyte in the cubic box the side length was varied at fixed number of total particles. In the MC simulations reported here, large systems, i.e. 1000 ions for 1:1 and 900 ions for 1:2 electrolytes were used. Long simulations, i.e. chains of 95 million MC configurations, were performed to generate the thermodynamic data.

Method of data analysis

In experimental work the properties of solutions are usually studied at constant pressure and at specified molal concentration. These conditions correspond to the Lewis-Randall (LR) representation. Theory on the other hand normally provides properties of solutions in the McMillan-Mayer (MM) representation. In the MM representation the chemical potential of the solvent is kept constant and molar concentrations are used. In order to compare the theoretical predictions with the experimental data the theoretical data has to be converted to molal scale or vice versa (Robinson and Stokes, 1970). The conversion of theoretical data from molar to molal scale was performed according to Equation (2)

$$\gamma_{\pm} = \frac{\rho_s - 0.001cW}{\rho_0} \gamma_{\pm} \quad (2)$$

where

ρ_0 = density of solvent (water) at 25 °C in g cm⁻³,

γ_{\pm} = mean ionic activity coefficient in the molar (mol L⁻¹) concentration,

γ_{\pm} = mean ionic activity coefficient in the molal (mol kg⁻¹) concentration,

W = molecular weight of the solute,

c = molar concentration of solution,

ρ_s = density of solution at 25 °C in g cm⁻³,

ρ_s can be calculated by using the following formula:

$$\rho_s = \rho_0 + \alpha c - \beta c^{3/2} \quad (3)$$

The values of the constants α and β are given by Novotny and Sohnel (1988). For NaHCO₃ salt solution density values were obtained from Lobo and Quaresma (1989).

A rigorous method of converting between the MM and LR systems requires knowledge of the partial molar volumes of ions. However, this is not necessary at concentrations below 2 molal (Haynes and Newman, 1998). The experimental data for ionic activity coefficients at different temperatures were taken from different sources; HCl (Hamer and Wu, 1972; Robinson and Harned, 1941), NaCl (Hamer and Wu, 1972; Pitzer et al., 1984), NaHCO₃ (Goldberg, 1981; Peiper and Pitzer, 1982) and Na₂CO₃ (Peiper and Pitzer, 1982).

Activity Coefficient Calculations and Fitting Procedure

Ionic radii are required in order to calculate the activity and osmotic coefficients by MC simulations. In the present approach we generally considered that large weakly charged ions such as Cl⁻ and HCO₃⁻ will have radii in solution equal to their crystallographic values, whereas small or highly charged ions such as H₃O⁺, Na⁺ and CO₃²⁻ will acquire radii in solution larger than their crystallographic values due to hydration. The CO₂ molecule was considered as a neutral spherical molecule. The hypothesis that highly charged ions are strongly hydrated whereas large weakly charged ions are unhydrated is well supported by recent experimental and simulation studies. For example dielectric relaxation spectroscopy studies (Buchner, 2008) revealed that effective hydration numbers of Cl⁻, K⁺, Na⁺ and CO₃²⁻ are 0, 0, 4.5 and 13, respectively. Such hydration patterns are also seen by other techniques as well as by Molecular Dynamics (MD) simulations (Ohtaki and Radnai, 1993). In the literature there is very little information about the hydration of HCO₃⁻. In a recent study (Dopieralski et al., 2011) it was found that HCO₃⁻ ion has hydration number 5.5 at infinite dilution. Moreover simulations indicated that water around this ion is not tightly bound. There is a general consensus that the CO₂ molecule in water exhibits properties of a typical hydrophobic solute. For example quantum based MD simulations have shown that the CO₂ molecule in water intensifies the H-bonding among the surrounding water molecules (Kumar et al., 2009). Such a cage formation is very typical for the solvation of hydrophobic solutes.

Salt activity coefficients at different temperatures were obtained by using the experimentally determined temperature-dependent dielectric constant of water. Best fits between the activity coefficients calculated by MC and experimental data or from Pitzer calculations were obtained by adjusting the radius of the hydrating ion. Best fitted radii obtained from single salts were used to simulate the ionic activity coefficients in salt mixtures. Note this fitting scheme generates effective ionic radii which implicitly include the effects of ion hydration.

Pitzer calculations

The Pitzer model (Pitzer, 1991) is one of the most widely used specific interaction models used 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 single-ion activity coefficients is given by

$$\ln \gamma_i = f^{\gamma} + \sum_{ij} m_i m_j B_{ij} + \sum_{ijk} m_i m_j m_k C_{ijk} \quad (4)$$

where f^{γ} 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 empirical Pitzer parameters which are linear combinations of ion and solvent specific parameters. The Pitzer equations used in this work are given in Appendix A.

Pitzer equations have been implemented in different computer codes focusing on thermodynamic modelling of seawater. The Miami models (Millero and Pierrot, 1998; Millero and Roy, 1997) and the FREZCHEM model (Marion and Kargel, 2008) are two of the most prominent Pitzer-based models developed for seawater (Marion et al., 2011). The Pitzer equations are also implemented in other commercial and free computer codes. However, the results are only as good as the underlying set of parameters. Different sets are available and one should note that, for example, substitution of revised parameters can lead to consistency issues, even at 25 °C (Clegg and Whitfield, 1991). One should also note that the Pitzer parameters carry uncertainties, which are often ignored in the practical application of the Pitzer equations (Spitzer et al., 2011).

In general, parameterizations of interaction and mixing parameters of electrolytes have been determined at 25 °C (Harvie et al., 1984; Pitzer, 1991). Several extensions of the 25 °C parameterizations have been made over the years for use in natural systems. Millero and Roy (1997) extended the Pitzer model of the major components of seawater to include the carbonate system in natural waters, valid from 0-6 m and 0-50 °C. Millero and Pierrot (1998) extended the model to include divalent and trivalent metals.

Millero et al. (2007) derived equations for the stoichiometric dissociation constants of carbonic acid in NaCl solution (0-6 m, 0-50 °C) from potentiometric measurements. From these, and together with literature data, they derived Pitzer parameters for the interactions of Na^+ with HCO_3^- and CO_3^{2-} from 0-50 °C and 0-250 °C, and also parameters for neutral interactions of CO_2 in NaCl from 0-50 °C.

In this study, we use the geochemical modelling software PHREEQC (Parkhurst and Appelo, 1999), previously PHRQPITZ (Plummer et al., 1988), developed at the U.S. Geological Survey, for the estimation of activity coefficients of species of the carbon dioxide system in

sodium chloride solution (0-1 m, 0-25 °C). The source and derivation of the parameters used are described in Appendix B.

Stoichiometric dissociation constants of carbonic acid

In this study we calculate the stoichiometric dissociation constants of carbonic acid in sodium chloride (pK_1^* and pK_2^*) based on the free pH scale. The dissociation of dissolved CO_2 in water is described by the equilibria



where K_1 and K_2 are the first and second thermodynamic dissociation constants. Note that very small concentration of H_2CO_3 is not treated explicitly. In an ionic medium, such as seawater or sodium chloride solution, the stoichiometric dissociation constants (indicated by an asterisk) are expressed in terms of concentrations

$$K_1^* = [H^+][HCO_3^-]/[CO_2] \quad (7)$$

$$K_2^* = [H^+][CO_3^{2-}]/[HCO_3^-] \quad (8)$$

which are related to the thermodynamic dissociation constants by

$$K_1^* = K_1 a_{H_2O} \gamma_{CO_2} / \gamma_H \gamma_{HCO_3} \quad (9)$$

$$K_2^* = K_2 \gamma_{HCO_3} / \gamma_H \gamma_{CO_3} \quad (10)$$

where a_{H_2O} is the activity of water and γ_i is the single-ion activity coefficient for species i .

The activity of water is derived from the osmotic coefficient ϕ through

$$\ln a_{H_2O} = -(\sum m_i / m_{H_2O}) \phi \quad (11)$$

where m_{H_2O} is the molality of water. The osmotic coefficient in the MC simulation is calculated through virial route (Svensson and Woodward, 1988).

Since MC simulations and Pitzer calculations use different conventions for assigning single ion activities, all comparisons are made using salt activity coefficients. The stoichiometric dissociation constants of carbonic acid in sodium chloride solution were calculated from the appropriate salt activity coefficients and the activity of water derived from both the MC simulations and Pitzer calculations between 0 to 25 °C and 0 to 1 m NaCl according to

$$K_1^* = \frac{K_1 a_{H_2O} \gamma_{CO_2}}{\gamma_{HCl} \gamma_{NaHCO_3}} * \gamma_{NaCl} \quad (12)$$

$$K_2^* = \frac{K_2 \gamma_{NaHCO_3}}{\gamma_{HCl} \gamma_{Na_2CO_3}} * \gamma_{NaCl} \quad (13)$$

The calculated stoichiometric dissociation constants were compared with the measurements of Millero et al. (2007). The activity coefficients and the activity of water from the MC simulations were fitted to third degree polynomials to enable comparison with experimental data at different ionic strengths.

Results and Discussions

In this work we have explored the possibility of using Monte Carlo simulations to estimate the activity coefficients of important seawater salts, such as NaCl, NaHCO₃, Na₂CO₃, and salt mixtures of NaHCO₃, Na₂CO₃ and HCl in NaCl, at temperatures ranging from 0 to 25 °C. The maximum ionic strengths set to 1 molal because this is the most relevant ionic strength range for seawater (salinity 35 ≈ 0.72 m). MC simulations were performed at different temperatures using experimental values of dielectric constant and specific cation and anion radii. The activity coefficients calculated by the MC simulations were fitted to the

experimental data or to the calculated values by using the Pitzer model as implemented in the PHREEQC computer code. The only adjustable parameter is ion radius either of cation or anion depending on the salt type. The activity coefficients of CO₂ in NaCl at different temperatures were also calculated and fitted to the experimental data by adjusting the radius of CO₂. The results for single salts, salt mixtures and CO₂ solubility in seawater are discussed in the following subsections.

Activity coefficients of single salts from 0 to 25 °C

Activity coefficients of NaCl at different temperatures are shown in Figure 2. Experimental data for the temperatures 0, 5-15, and 25 °C are taken from the work of Pitzer et al. (1984), Harned and Cook (1939), and Hamer and Wu (1972), respectively. In MC simulations the only adjustable parameter is the ion radius. In the first MC simulation (MC-1), the radii of Na⁺ and Cl⁻ were kept constant at all temperatures to 0.168 nm (hydrated) (Abbas et al., 2009) and 0.181 nm (crystallographic) (Marcus, 1997), respectively. In the second simulation (MC-2), the radius of Na⁺ was adjusted with respect to temperature, while the radius of Cl⁻ was kept constant to its crystallographic value (Table 1). Experimentally determined dielectric constant values of water at different temperatures (Kay et al., 1969) are given in Table 1. The reasonably good agreement between the MC simulations, Pitzer calculations, and experimental data shows that the MC method is a reliable and transparent method for estimating these activity coefficients. The best fitted ionic radii obtained for Na⁺ (MC-2) ranged from 0.140 to 0.168 nm as temperature increased from 0 to 25 °C (Table 1). In the case when both ion radii were kept constant (MC-1) there was less agreement towards lower temperatures and higher ionic strengths. Since the crystallographic radius of the Na⁺ ion is 0.102 nm (Marcus, 1997), the simulation results indicate that the Na⁺ ion is hydrated in the NaCl solution.

In Figure 3 the activity coefficients of the single salt NaHCO_3 estimated by MC and the Pitzer calculations are compared. Since there are limited experimental data available for this system the discussion focuses on the MC and Pitzer values. For comparison, the experimental data of Goldberg (1981) are included. However, it should be noted that the hydrolysis equilibria of CO_2 were ignored in this author's analysis (Peiper and Pitzer, 1982). The first simulation (MC-3) used the hydrated radius (as in MC-1) of Na^+ together with the crystallographic radius of HCO_3^- of 0.156 nm (Marcus, 1997). In the second simulation (MC-4) the crystallographic radii for both ions were used. As can be seen in Figure 3 the results from the Pitzer calculations are in good agreement with MC-4. However, MC-3 agrees well with experimental data at lower but deviate at higher ionic strengths. The sharp and continuous decrease of activity coefficients of NaHCO_3 at increasing ionic strength as estimated by the Pitzer calculations is a typical indication of stronger cation-anion interaction. Such a strong interaction between Na^+ and HCO_3^- ions is also indicated by a recent quantum based molecular dynamics simulation (Dopieralski et al., 2011). It was shown that hydration number of Na^+ decreases as it approaches close to the HCO_3^- ion. Since ions are considered as charged hard spheres in MC simulations the ion size needs to be decreased in order to provide a stronger cation-anion interaction therefore for NaHCO_3 crystallographic radii provided best fit to the experimental data.

Activity coefficients of Na_2CO_3 at different temperatures are shown in Figure 4. Experimental data at 25 °C are taken from the work of Goldberg (1981). Since CO_3^{2-} is a doubly charged ion and Na^+ is usually hydrated in its alkali salts it was not obvious which ion should be considered as hydrated or which one unhydrated. In order to resolve this issue several simulations were performed by considering Na^+ or CO_3^{2-} hydrated as well as both ions hydrated. In the Figure 4 two cases are compared i.e., in the first MC simulation (MC-5) the crystallographic radius of Na^+ is used and all hydrating water is bound to the CO_3^{2-} ion

whereas in the second simulation (MC-6) Na^+ is hydrated and CO_3^{2-} is considered as unhydrated. Note that in MC-5 the hydrated size of CO_3^{2-} was not varied at different temperatures whereas in MC-6 Na^+ radius varied with temperature and had the same values as determined in the case of NaCl. At all temperatures both simulations were in good agreement with Pitzer at low and high ionic strengths. However, at intermediate ionic strengths (0.4-0.6m) MC simulations underestimated the Pitzer data.

The crystallographic radii used in MC to obtain good fit to the NaHCO_3 and Na_2CO_3 may seem unrealistic at first sight but we have to keep in mind that in these salts ion pairing is present which is due to the strong attraction between the oppositely charged ions. Such attraction is not included in the potential function used in the MC simulation. Therefore to model the activity coefficients of associated electrolytes by charged hard spheres the distance between the two oppositely charged ions needs to be decreased. Therefore the best fitted radii obtained from the MC simulations should be considered as optimized distance between the two oppositely charged ions. Recently, preferred ion pair formation between like sized ions over unlike-sized ions has been explained by dielectric continuum model (Lund et al., 2010). Ion-specific effects in binary salts of Hofmeister series were explained qualitatively. This model might be interesting for single salts relevant for sea water but it will be challenging to implement for salt mixtures due to the complexity of dielectric behaviour of mixed ionic solutions.

Activity coefficients of mixed salts from 0 to 25 °C

Activity coefficients of 0.002 m NaHCO_3 and Na_2CO_3 in varying concentrations of NaCl up to ionic strength of 1 m from MC simulations and Pitzer calculations are shown in Figures 5 and 6, respectively. The ion radii used in the MC simulations are shown in Table 2. For NaHCO_3 in NaCl (MC-7) the crystal ionic radius was used for Na^+ , while for Na_2CO_3 in

NaCl the variable Na^+ radius from MC-2 was used. In both cases there is good agreement between the MC simulations and the Pitzer calculations. A good agreement between MC and Pitzer in the case of NaHCO_3 in NaCl indicate that Na^+ and HCO_3^- ions remain associated even in the presence of NaCl. However, the case of Na_2CO_3 in NaCl is more complicated. Although we have obtained a good agreement between the MC and Pitzer by considering carbonate as dehydrated and sodium as hydrated ion we cannot be sure which ion is hydrated and which ion is dehydrated. Therefore we should consider this result as the best optimized distance between Na^+ and CO_3^{2-} in NaCl. This point will be elaborated in the section related with the dissociation constants of CO_2 in NaCl.

Ionic activity coefficients of HCl in NaCl are shown in Figure 7. The ionic radius of H^+ was set to 0.230 nm in MC simulations, whereas the radius of Cl^- was equal to its crystallographic value. The NaCl salt radii were same as in the case of pure NaCl (Table 1). At concentrations > 0.2 m the MC data deviate from the experimental data. Note that no further optimization of HCl radii in NaCl was done because its concentration in sea water is very low.

Activity coefficients of CO_2 in NaCl from 0 to 25 °C

The activity coefficients of CO_2 in NaCl at 0, 5, 15 and 25 °C are shown in Figure 8 as estimated by MC simulations and Pitzer calculations. In MC simulations the CO_2 molecules were considered as neutral hard spheres. As no electrostatic interactions are acting on a neutral molecule, the activity coefficient depends only on the hard-sphere radius through the excluded volume effect. The MC simulations data were fitted to Pitzer calculation results by adjusting the radius of CO_2 (Figure 8). As demonstrated in the figure, an excellent fit to the Pitzer calculations was obtained as well as to experimental data from the work of Harned and Davis (1943) at 0 and 25 °C. The best fitted radii of CO_2 at 0, 5, 10, 15, 25 and 25 °C were

0.215, 0.205, 0.200, 0.200, 0.190 and 0.185 nm, respectively, as shown in the inset in Figure 8. Note that in these simulations the only adjustable parameter was the CO₂ radius because the Na⁺ and Cl⁻ radii at different temperatures were the same as optimized from the pure NaCl (MC-2, Table 1). The temperature dependent trend is opposite to that seen for ionic solutions, i.e. at lower temperatures there is strong association among the ions and therefore in MC simulations ion sizes have to decrease to capture the correct trend. On the other hand the experimental data of CO₂ activity at different temperature show higher values at lower temperatures. This may be rationalized as at high temperatures the ionic solution has high entropy and therefore the excluded volume effect of CO₂ on the activity coefficient of the whole system, i.e. CO₂ + NaCl, is low. On the other hand at 0 °C, entropy of NaCl solution decreases and the excluded volume effect of CO₂ is enhanced, which eventually leads to higher activity coefficients.

Stoichiometric dissociation constants of CO₂ in NaCl solutions at different temperatures

The activity coefficients of the mixed salts obtained by MC simulations and Pitzer calculations were used to estimate the stoichiometric dissociation constants of carbonic acid in NaCl solution (pK₁^{*} and pK₂^{*}). The radii obtained in simulations MC-2, MC-7, MC-8 and MC-9 (Tables 1 and 2) were used for these calculations. The constants estimated by MC simulations and by Pitzer calculations are compared with the measurements and fitted equations of Millero et al. (2007) in Figure 9. The residuals of pK₁^{*} and pK₂^{*}, i.e. the difference between the experimentally derived constants and those derived from MC simulations and the Pitzer calculations, and also the fitted equations with temperature and molality dependency, are shown in Figure 10. Overall, there is an excellent agreement between constants estimated from the two different models and the experimental data. The resulting residuals show a better fit to experimental data toward lower temperatures and ionic

strengths. The residuals of both MC and Pitzer are on the same order as the residuals between the experimental data and the fitted equations (Table 3).

However, we noted that the residuals of pK_2^* calculated from the MC and Pitzer model were large in the case when the radius of Na^+ was 0.146 nm and of CO_3^{2-} was 0.20 nm as well as in the case of Na^+ 0.102 and CO_3^{2-} 0.244 nm. These results indicate that in MC simulations we cannot treat carbonate as a large hydrated ion and have to consider it as unhydrated. However, we shall keep in mind that the present simulations are based on the simplest model of charged hard spheres which excludes softness of ions. In reality the ions are soft, and in particular negatively charged ions have electron density spread over a large surface and are easily polarizable. Inclusion of polarization in the potential function will be treated in the future

Conclusions

In this study we have shown that Monte Carlo simulations can provide good estimates of the stoichiometric dissociation constants of CO_2 in sodium chloride solutions from 0 to 1 molal and from 0 to 25°C. The only fitted parameters in the MC simulations are 6 ion or molecule radii, of which only 2 are temperature dependent. In contrast, the Pitzer approach requires 20 interaction parameters derived from 58 coefficients for temperature dependence. This difference will grow as the complexity of the medium studied is increased. Due to recent advancements in computer technology computational power is rapidly increasing and it can be expected that in future MC simulations will be readily available. Future work will be focused on increasing the complexity of the medium to enable MC simulations in seawater.

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APPENDIX A. Pitzer equations

The activity coefficients for cations (M), anions (X), and neutral species (N) are given by

$$\ln \gamma_M = z_M^2 f^\gamma + 2 \sum_a m_a (B_{Ma} + E C_{Ma}) + z_M^2 \sum_c \sum_a m_c m_a B'_{ca} + z_M \sum_c \sum_a m_c m_a C_{ca} + \sum_c m_c (2\Theta_{Mc} + \sum_a m_a \Psi_{Mca}) + \sum_a \sum_{a'} m_a m_{a'} \Psi_{aa'M} \quad (A1)$$

$$\ln \gamma_X = z_X^2 f^\gamma + 2 \sum_c m_c (B_{cX} + E C_{cX}) + z_X^2 \sum_c \sum_a m_c m_a B'_{ca} + z_X \sum_c \sum_a m_c m_a C_{ca} + \sum_a m_a (2\Theta_{Xa} + \sum_c m_c \Psi_{Xac}) + \sum_c \sum_{c'} m_c m_{c'} \Psi_{cc'X} \quad (A2)$$

$$\ln \gamma_N = \sum_c m_c (2\lambda_{Na}) + \sum_a m_a (2\lambda_{Nc}) + \sum_c \sum_a m_c m_a \zeta_{Nca} \quad (A3)$$

where z_i is the charge, m_i the molality of cation (c) and anions (a) in the mixed solution, $E = 1/2 \sum m_i z_i$ is the equivalent molality, The limiting law f^γ is given by

$$f^\gamma = -A_\phi [I^{1/2} / (1 + 1.2I^{1/2}) + (2/1.2) \ln(1 + 1.2I^{1/2})] \quad (A4)$$

For the term A_ϕ PHREEQC uses the equation

$$A_\phi = 1.400684E6(\rho_w/DT)^{3/2} \quad (A5)$$

where ρ_w is the density of water, D is the static dielectric constant of water (Bradley and Pitzer, 1979) and T is temperature in Kelvin. At 25 °C the A_ϕ term in PHREEQC is defined to be 0.392 for consistency with the Harvie et al. (1984) database. The difference in A_ϕ between PHREEQC and the equation of Møller (Møller, 1988) is of the order of 1E-05 units and has little effect on the resulting activity coefficients.

The term Θ_{ij} is related to binary interactions between ions of the same sign. Where the ionic charges differ (i.e. carbonate and chloride in this work), Θ_{ij} includes terms ${}^E\theta$ and ${}^E\theta'$ to account for unsymmetrical mixing effects (Pitzer, 1991). The term Ψ_{ijk} is related to ternary ionic interactions of two similarly charged ions with an ion of opposite charge. The neutral interactions are described by the parameters λ and ζ . The latter become more important at

higher ionic strengths. The binary and ternary mixing parameters are determined from mixtures of two electrolytes with a common ion. The second and third virial coefficients for 1-1, 1-2 and 1-3 electrolytes are given by

$$B_{MX} = \beta_{MX}^{(0)} + \left(\beta_{MX}^{(1)}/2I\right)[1 - (1 + 2I^{1/2}) \exp(-2I^{1/2})] \quad (\text{A6})$$

$$B'_{MX} = \left(\beta_{MX}^{(1)}/2I^2\right)[-1 + (1 + 2I^{1/2} + 2I) \exp(-2I^{1/2})] \quad (\text{A7})$$

$$C_{MX} = C_{MX}^{\Phi}/(2|z_M z_X|^{1/2}) \quad (\text{A8})$$

where I is the ionic strength. The $\beta^{(0)}$, $\beta^{(1)}$ and C^{Φ} parameters account for binary interactions of the individual components of each electrolyte and are determined experimentally and have been tabulated for many electrolyte systems (Greenberg and Møller, 1989; Harvie et al., 1984; Millero and Hawke, 1992; Millero and Pierrot, 1998; Møller, 1988; Pabalan and Pitzer, 1987; Pitzer, 1991). The number of interaction parameters required for an ionic medium increases with the complexity of the ionic medium (Millero and Pierrot, 1998).

APPENDIX B. Pitzer parameters and stability constants

The Pitzer specific interaction model in PHREEQC (Parkhurst and Appelo, 1999) is described by the constants and parameters in the database *pitzer.dat*. The default Pitzer model is based on the 25 °C model formulation of (Harvie et al., 1984), which uses a 5-term equation for the parameter temperature dependence. The equation for parameter P at temperature T/K is given by

$$P(T) = b_1 + b_2 \left(\frac{1}{T} - \frac{1}{T_R}\right) + b_3 \ln\left(\frac{T}{T_R}\right) + b_4(T - T_R) + b_5(T^2 - T_R^2), \quad T_R = 298.15 \text{ K}. \quad (\text{B1})$$

Binary (+/-) interaction parameters

NaCl and HCl

Pitzer parameters for NaCl from 0-300°C (Møller, 1988) are given by Equation B2 and for HCl from 0 to 250°C (Christov and Møller, 2004) are given by Equation B3:

$$P(T) = a_1 + a_2T + a_3/T + a_4 \ln T + a_5/(T - 263) + a_6T^2 + a_7/(680 - T) + a_8/(T - 227) \quad (\text{B2})$$

$$P(T) = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5/T + a_6 \ln T + a_7/(T - 263) + a_8/(680 - T) \quad (\text{B3})$$

In cases where these coefficients cannot be converted to the form of Equation B1 by linear transformation, multiple linear regression was used over the relatively limited temperature range 0 – 50°C. Parameters calculated at 1°C intervals from Equations B2 and B3 were refitted to Equation B1 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 resulting parameters are shown in Table B1.

Table B1. NaCl and HCl interactions: coefficients for Equation B1

Parameter	b_1	b_2	b_3	b_4	b_5
$\beta_{\text{NaCl}}^{(0)}$	0.0753754	-9168.85	-84.6746	0.264859	1.39349E-04
$\beta_{\text{NaCl}}^{(1)}$	0.277027	-21627.4	-204.338	0.645977	-3.40649E-04
C_{NaCl}^{Φ}	1.41282E-03	1518.30	14.1983	-0.0447676	2.36731E-05
$\beta_{\text{HCl}}^{(0)}$	0.176122	42199.0	415.032	-1.36042	7.42416E-04
$\beta_{\text{HCl}}^{(1)}$	0.298850	-171937	-1692.16	5.54635	0.00302463
C_{HCl}^{Φ}	0	0	0	0	0

NaHCO₃ and Na₂CO₃

The Pitzer parameters for these interactions, valid from 0-50 °C (Millero et al., 2007), are given by Equation B4:

$$P(T) = a_0 + a_1(T - T_R) + a_2(T - T_R)^2 \quad (\text{B4})$$

Linear transformation results in the following coefficients for given in Table B2.

Table B2. NaHCO₃ and Na₂CO₃ interactions: coefficients for Equation B1

Parameter	b_1	b_2	b_3	b_4	b_5
$\beta_{\text{NaHCO}_3}^{(0)}$	0.028	0	0	-0.01023	1.80E-05
$\beta_{\text{NaHCO}_3}^{(1)}$	0.044	0	0	0.01273	-1.80E-05
$C_{\text{NaHCO}_3}^{\Phi}$	-0.01243	0	0	0	0
$\beta_{\text{Na}_2\text{CO}_3}^{(0)}$	0.0362	0	0	-0.1663	2.84E-04
$\beta_{\text{Na}_2\text{CO}_3}^{(1)}$	1.51	0	0	0.8	-1.34E-03
$C_{\text{Na}_2\text{CO}_3}^{\Phi}$	0.0052	0	0	0.05496	-9.30E-05

Binary (+/+), (-/-) and triplet interactions

Pitzer parameters for the interactions, $\Theta_{\text{H, Na}}$ (0-97 °C) and $\Psi_{\text{Na, K, Cl}}$ (0-85.7 °C), are given by Equation B5 (Christov and Møller, 2004).

$$P(T) = a_0 + a_1/T \quad (\text{B5})$$

Linear transformation results in the coefficients given in Table B3

Table B3. Binary (+/+) and triplet (+/+/-) interactions: coefficients for Equation B1

Parameter	b_1	b_2	b_3	b_4	b_5
$\Theta_{\text{H, Na}}$	0.03454	-4.0543	0	0	0
$\Psi_{\text{Na, H, Cl}}$	-0.002511	3.59309	0	0	0

No temperature dependence has been derived for the (-/-) and triplet (-/-/+) interaction parameters given in Table B4.

Table B4. Binary (-/-) and triplet (-/-/+) interactions: temperature-independent values

Parameter	b_1	Reference
$\Theta_{\text{Cl, HCO}_3}$	0.0359	(Peiper and Pitzer, 1982)
$\Theta_{\text{Cl, CO}_3}$	-0.053	(Peiper and Pitzer, 1982)
$\Psi_{\text{Cl, HCO}_3, \text{Na}}$	-0.0143	(Peiper and Pitzer, 1982)
$\Psi_{\text{Cl, CO}_3, \text{Na}}$	0.016	(Thurmond and Millero, 1982)

Neutral interaction terms

The Pitzer parameters for neutral interactions of CO₂ in NaCl, valid from 0-50 °C, are given by Equation B6 (Harned and Davis, 1943; Millero et al., 2007)

$$P(T) = a_0 + a_1/T + a_2 \ln T \quad (\text{B6})$$

Linear transformation results in the coefficients given in Table B5

Table B5. Neutral interactions: coefficients for Equation B1

Parameter	b_1	b_2	b_3	b_4	b_5
$\lambda_{\text{Na},\text{CO}_2}$	0.1182	279.63	0.7881	0	0
$\zeta_{\text{CO}_2,\text{Na},\text{Cl}}$	-8.151E-03	-19.7	-0.0596	0	0

Thermodynamic constants of carbonic acid

The ionization of carbonic acid in pure water is described by stepwise dissociation constants given by the equation (Millero et al., 2007)

$$pK_i = A_1 + A_2T + A_3/T + A_4 \ln T + A_5/T^2 \quad (\text{B7})$$

while PHREEQC uses cumulative association constants described by the equation:

$$\log_{10}K(T) = b_1 + b_2(1/T - 1/T_R) + b_3 \log_{10}(T/T_R) + b_4(T - T_R) + b_5(T^2 - T_R^2) \quad (\text{B8})$$

Linear transformation results in the coefficients given in Table A6

Table B6. Thermodynamic constants of carbonic acid in water: coefficients for equation (B7)

	b_1	b_2	b_3	b_4	b_5
$\log_{10}K_2$	-83.2997	0	4821.38	31.60641	0
$\log_{10}K_{12}$	-197.6103	0	10595.05	72.24527	0

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