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Activity coefficients in sea water using Monte Carlo simulations

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Abstract

A new approach to the estimation of activity coefficients in sea water has been established using statistical mechanics. The distribution of particles (ions and nonelectrolytes) are simulated with a Monte Carlo method combined with a particle insertion technique that allows calculation of the activity coefficients. The simulations are based on the primitive model of electrolytes and accounts for both short- and long-ranged forces, but does not suffer from the approximations used in the classical theory. Excellent agreement have been found with experimental data and calculations based on the Pitzer model.

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Keywords: Activity coefficients; Sea water; Monte Carlo simulation; Statistical mechanics; Pitzer model; Stoichiometric equilibrium constants

1. Introduction

Activity coefficients in sea water are of great importance in marine chemistry as they are needed to estimate stoichiometric equilibrium constants for phenomena such as mineral solubilities, dissociation constants, complex formation, etc. Due to the high ionic strength of saline waters, the classical Debye–Hückel theory fails and more accurate approaches are required. A well-established method of obtaining activity coefficients in strong electrolyte solutions is the ion interaction model of Pitzer (1973). This model accounts for long-range forces by a classical Debye–Hückel term while short-range forces are included via semiempirical parameters. More recently, the mean

spherical approximation (MSA) has been used successfully to describe the dissociation constants of glycine in sea water (Vilarino and Sastre de Vicente, 1999). MSA theory is also based on the Debye–Hückel theory, but accounts for short-range forces by including particle sizes. Today, however, increased computing power is readily available and simulation methods based on statistical thermodynamics can be applied. The model presented here, like the Debye–Hückel theory, is based on the primitive model of electrolytes but does not suffer from the well-known approximations of Debye–Hückel or MSA. In contrast to Debye–Hückel's ionic sphere assumption, the distribution of particles is simulated with the Monte Carlo method of Metropolis et al. (1953), where all interionic particle interactions are taken into account explicitly. The only adjustable parameter for each particle is its effective hard-sphere radius which greatly simplifies the database required for a successful activity coefficient calculation. Earlier applications

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of the present model have yielded good results for complex systems (Svensson et al., 1992) and since the existing methods rely on empirical findings and approximate equations, we have found it natural to attempt to apply this more accurate method to sea water solutions.

2. Theory and methodology

The simulations are based on a dielectric continuum model where particles (ions and nonelectrolytes) are treated as hard spheres with radii, σ_i , and valencies, z_i , while the nature of the solvent is described solely by the temperature-dependent dielectric constant ϵ_r . The energy of a particle i interacting with another particle j is described using Coulomb's law subject to the following conditions,

$$u(r_{ij}) = \begin{cases} \frac{z_i z_j e^2}{4\pi\epsilon\epsilon_r r_{ij}} & r_{ij} \geq \sigma_i + \sigma_j \text{ (long range)} \\ +\infty & r_{ij} < \sigma_i + \sigma_j \text{ (short range)} \end{cases} \quad (1)$$

where ϵ is the dielectric permittivity of vacuum and e is the elementary charge. Eq. (1) is also known as the primitive model of electrolytes. A canonical ensemble is constructed using a cubic box with periodic boundary conditions and length, L , containing $c_i L^3 N_A$ particles of species i matching the composition of an electrolyte solution with molar concentration c_i . The distribution of particles is simulated using the Metropolis Monte Carlo method (Allen and Tildesley, 1989), where configurations are produced by moving a single particle to a new random position and calculating the total energy U by summing all particle interactions. A new configuration is accepted if the energy is reduced. If the energy is increased, the new state is accepted if $\xi < \exp(-\beta\Delta U)$, where $\beta = 1/kT$ and ξ is a random number between 0 and 1. If a state is rejected, the old state is included in the ensemble instead.

To obtain activity coefficients, the particle insertion method of Widom (1963) is used. This method states that a nonperturbing particle, α , inserted at a random position, \mathbf{r} , will have the activity coefficient γ given by,

$$\ln \gamma = -\ln \langle \exp[-\beta \Delta U_\alpha(\mathbf{r})] \rangle_0 \quad (2)$$

The exponential term enclosed in brackets is the ensemble average of the energy change, ΔU_α , of adding the particle. Eq. (2) is derived in a statistical mechanical framework (Mcquarrie, 1976) and is based on the fundamental definition of the chemical potential, μ_α :

$$\mu_\alpha = \left(\frac{\partial A}{\partial n_\alpha} \right)_{V,T,N} \quad (3)$$

Here, ∂A is the change in the Helmholtz free energy when changing the composition of α . The temperature, the volume and the composition of other species are kept constant.

However, the original Widom method becomes less accurate when dealing with ionic systems, since the addition of a charged particle will violate electroneutrality in the cell. To get around this problem, we have used the modified Widom technique proposed by Svensson and Woodward (1988), where charge scaling is introduced so as to reestablish electroneutrality. This method has shown good results for both uniform and nonuniform electrolyte solutions (Svensson et al., 1991).

2.1. Hard-sphere radii

The only parameters needed to describe a particle in the model are its valency and hard-sphere radius. The latter property includes the hydration shell encapsulating the particle, but should in this context be regarded as an empirical parameter as real solvated ions are neither hard nor spherical. Qualitatively, the hydration is related to the ionic charge density; a small, highly charged positive ion will attract more solvent molecules than a large ion of low charge. Thus, the radius of K^+ is expected to be smaller than that of Na^+ . In the simulations, the radii determine the distance of closest approach between two ions, which is why the *sum* of radii is the important parameter. Particles of same charge are, due to electrostatics, distributed far apart and in such cases their distance of closest approach becomes less crucial. In lack of a stringent procedure describing ions in terms of hard spheres, we have chosen to determine the hard radii by applying mean activity coefficient data from single electrolyte solutions.

A Monte Carlo simulation is performed for the single electrolyte and the hard-sphere radii are

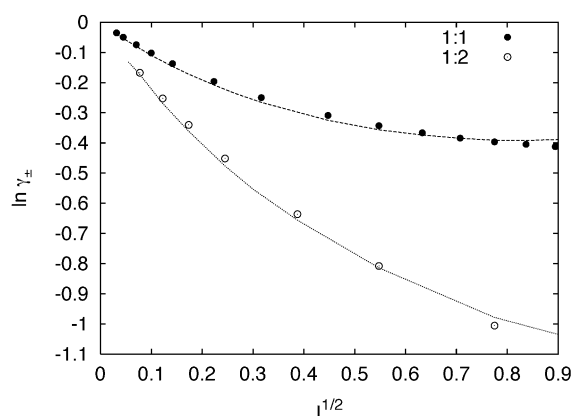


Fig. 1. Calculated (lines) and measured (points) activity coefficients for 1:1 (NaCl) and 1:2 (Na₂SO₄) electrolytes as a function of ionic strength. Experimental data from Robinson and Stokes (1959) and Vanýsek (1995).

adjusted to yield mean activity coefficients equal to experimental determined values. Figs. 1 and 2 represent examples of calculations on 1:1, 1:2 and 2:2 electrolytes and as shown, excellent agreement has been found for all types of electrolytes. In particular, we note good agreement for MgSO₄, despite the fact that we have made no explicit assumption regarding ion association. It is often assumed that MgSO₄ forms ion pairs at low concentration and the Pitzer model

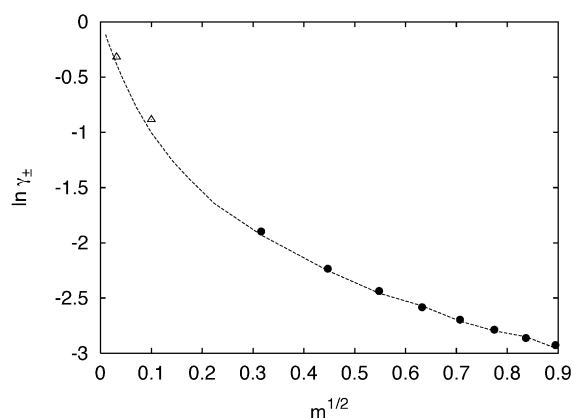


Fig. 2. Calculated (lines) and measured (circles) activity coefficients for a 2:2 electrolyte (MgSO₄) as a function of concentration. Triangles: values calculated using the ion interaction model (Archer and Rard, 1998). Experimental data from Robinson and Stokes (1959).

Table 1
Best fit of sum radii (i.e. cation+anion) in single-electrolyte solutions

	NaCl	KCl	CaCl ₂	MgCl ₂	Na ₂ SO ₄	HCl	NH ₄ Cl
($\sigma_+ + \sigma_-$) (Å)	3.5	3.2	4.5	4.7	3.4	4.2	3.2

has required additional parameters in order to properly describe this effect.

By the above procedure, we have examined the major and some of the minor sea water components in the range $I=0.1-0.8$, which yielded the sum radii shown in Table 1.

Based on the assumption that anions are only weakly hydrated (Simonin et al., 1996), the radius of the chloride ion is set equal to its crystallographic radius which allows the calculation of the single-ion hard-sphere radii as shown in Table 2. These values are comparable to those used in the MSA calculations by Vilarino and Sastre de Vicente (1999) and simulations with their radii yield similar results.

To find hard-sphere radii of nonelectrolytes, a similar route is followed, where experimentally determined Setchenow constants (Setchenow, 1889; Lee, 1997), k_s , are used as the source of activity coefficients:

$$\ln \gamma_i = k_s m \quad (4)$$

where γ_i is the activity coefficient of the nonelectrolyte i in an electrolyte solution of molality m . A simulation of a sodium chloride solution is performed and the hard-sphere radius of a neutral Widom particle is adjusted until the right Setchenow parameter is obtained. The results for a number of gases are shown in Table 3, where s represents the standard error.

2.2. The sea water model

Many recipes of sea water are available (Bidwell and Spotte, 1985). Here, we have chosen the

Table 2
Hard-sphere radii of individual ions in sea water

	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	NH ₄ ⁺	H ⁺
σ (Å)	1.8	1.5	3.0	2.8	1.7	1.6	1.5	2.5

composition given by Platford and Dafoe (1965) ($[\text{Na}^+] = 0.482 \text{ m}$, $[\text{K}^+] = 0.009 \text{ m}$, $[\text{Mg}^{2+}] = 0.055 \text{ m}$, $[\text{Ca}^{2+}] = 0.011 \text{ m}$, $[\text{Cl}^-] = 0.564 \text{ m}$ and $[\text{SO}_4^{2-}] = 0.029 \text{ m}$ at 35) in order to be able to directly compare with their experimental values (Platford, 1965b; Platford and Dafoe, 1965). As our model consists of a fixed volume, the molar activity coefficients, γ , thus obtained need to be converted to the more commonly used molal scale (Clegg and Whitfield, 1991)

$$\gamma = y \left(\frac{d - \sum_i c_i M_i}{d_0} \right) \quad (5)$$

where d and d_0 are the densities of sea water and of pure water, respectively. M_i is the molecular weight of species i . The effect of inserting a minor species is determined solely by the interactions with the six major ions. In a typical sea water simulation using a box length of 90, around 480 particles are present ($S = 35 \text{‰}$). This is illustrated in Fig. 3. The partial concentrations, $c_i = N_i/V$, can be described only to a certain degree of precision as only integer values of particle numbers, N_i , are allowed. However, the effect on the calculated activity coefficients is very small—around 0.2%. Increasing the box size and, thus, the number of particles greatly affects the computation time as the number of interaction terms calculated according to Eq. (1) is equal to

$$\sum_{j=1}^{N-1} (N-j) \propto N^2 \quad (6)$$

The run time of a simulation of 480 particles is around half an hour on a standard personal computer

Table 3
Setchenow constants in sodium chloride solution at 298 K

	σ (Å)	k_s^{litt}	k_s^{calc}	Ref.
O ₂	2.2	0.312	0.319	Millero, 2000
N ₂ O	1.9	0.245	0.248	Millero, 2000
CO ₂	1.7	0.201	0.209	Millero, 2000
H ₂ S	1.4	0.155	0.158	Millero, 2000
NH ₃	0.8	0.076	0.072	Sing et al., 1999
s			5×10^{-3}	

The calculated values are obtained by simulating with the given hard-sphere radii.

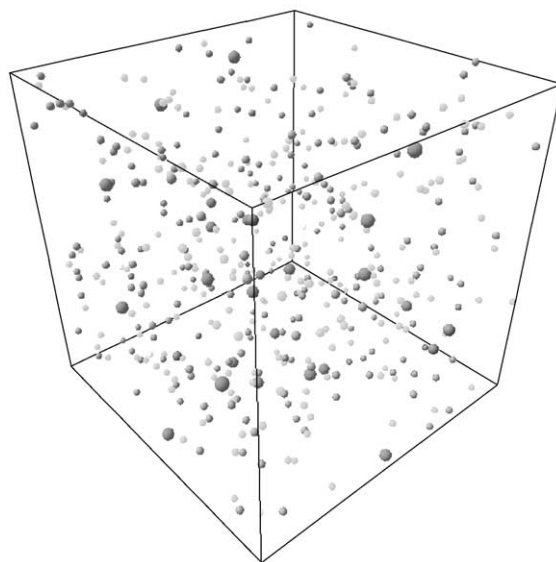


Fig. 3. Snapshot of a Monte Carlo simulation of sea water ($S = 35 \text{‰}$), captured using the GISMOS package (Lejdefors et al., 2000).

and doubling this number would increase the simulation time by a factor four.

3. Results

3.1. Activity coefficients

Our simulations have yielded single ion activities at various salinities, which have been fitted to the expression

$$\ln \gamma_i = aS + bS^{0.5} + cS^{1.5} \quad (7)$$

where S is the salinity in per mille. The parameters a , b and c are listed in Table 4 and are valid in the range $0 \leq S \leq 35 \text{‰}$ at 298 K.

Due to the principle of macroscopic electroneutrality, single-ion activity coefficients cannot be measured experimentally and their determination is always subject to a conventional definition. In our model, however, both electrostatic and hard-sphere contributions are calculated for individual ion activity coefficients. Note that the magnitude of the hard-sphere term is not unique, since our choice of the radius for the chloride ion is somewhat arbitrary. A small modification of the

Table 4

Results of a fit for single-ion activity coefficients (cf. Eq. (7)) at 298 K

	<i>a</i>	<i>b</i>	<i>c</i>	<i>s</i>
Na ⁺	0.0205532	−0.159354	−0.000986596	1×10^{-3}
K ⁺	0.0194030	−0.162823	−0.000979393	8×10^{-4}
Mg ²⁺	0.1071180	−0.664265	−0.006752640	2×10^{-3}
Ca ²⁺	0.1041940	−0.670623	−0.006511840	2×10^{-3}
Cl [−]	0.0205745	−0.157099	−0.000879540	2×10^{-3}
SO ₄ ^{2−}	0.1000860	−0.738175	−0.005971080	3×10^{-3}
NH ₄ ⁺	0.0194030	−0.162823	−0.000979393	8×10^{-4}
H ⁺	0.0232680	−0.151911	−0.000928230	8×10^{-4}

s is the standard error of the fit.

chloride ion radius with a few tenths of an Ångström would not affect mean activity coefficients, but would numerically change the hard-sphere contribution. That is, the two contributions are coupled in that lowering the radius permits closer particle approach and, thus, an increase of the electrostatic term. In Fig. 4, we have partitioned the activity coefficient of the chloride ion into its electrostatic and hard-sphere contributions, respectively.

The individual ion activity coefficients are validated by calculating mean activity coefficients of some common sea water salts. As shown in Table 5, excellent agreement have been found with our model, experimental data and Pitzer calculations.

Here, we see that our method performs equally well as the Pitzer model, despite the fact that the number of adjustable parameters is smaller in the

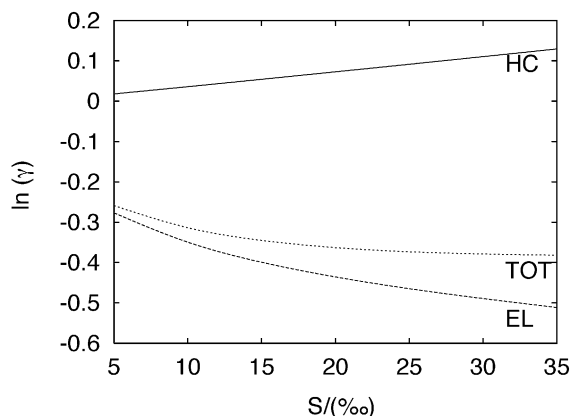


Fig. 4. Hard-core (HC) and electrostatic (EL) contributions to the total activity coefficient (TOT) of the chloride ion.

Table 5

Measured (Platford, 1965; Platford and Dafoe, 1965) and calculated mean activity coefficients in sea water

Salt	<i>T</i> (K)	<i>S</i> (‰)	γ^{Exp}	γ^{Present}	γ^{Pitzer}
Na ₂ SO ₄	298	35	0.374 ± 0.016	0.374	0.364
		25	0.405 ± 0.016	0.399	0.394
		15	0.435 ± 0.016	0.445	0.444
		5	0.620 ± 0.016	0.560	0.564
K ₂ SO ₄	298	35	0.385 ± 0.016	0.381	0.369
		35	0.352 ± 0.018^a	0.360	0.344
NaCl	298	35	0.672 ± 0.007	0.664	0.667
		15	0.730 ± 0.001	0.699	0.709
KCl	298	35	0.645 ± 0.008^a	0.645	0.639
CaSO ₄	298	35	0.136^b	0.152	0.150
<i>s</i>				0.023	0.021

Pitzer calculations are made using the sea water model of Clegg and Whitfield (1995).

^a From Clegg and Whitfield (1991).

^b From Culberson et al. (1978).

simulation approach. However, the calculated values for calcium sulfate show some deviations from the experimental data, which may be due to “ion pair” formation. As divalent oppositely charged ions strongly attract each other, the dielectric continuum becomes less applicable and effectively ϵ is lowered. Currently, no attempts have been made to correct for this effect, but introducing a variable dielectric constant may be a way of getting around the problem. In the framework of the Pitzer model, these matters are frequently dealt with by the inclusion of association constants. In practice, the latter approach could be incorporated into our model but would violate the very foundation of the theory as statistical mechanics describe equilibrium in terms of distributions. Furthermore, inclusion of association constants would add more parameters to an otherwise simple approach.

The activity coefficients calculated for uncharged particles in sea water obeys Setchenow’s rule expressed in terms of the ionic strength, $\ln \gamma = k_s I$. As no electrostatic forces are acting on a neutral particle, the activity coefficient depends only on the hard-sphere radius of the solute and, in Fig. 5, we present the sea water Setchenow constants as a function of this property.

3.2. Equilibrium constants

Also of interest to marine chemistry are stoichiometric equilibrium constants. As an example, we

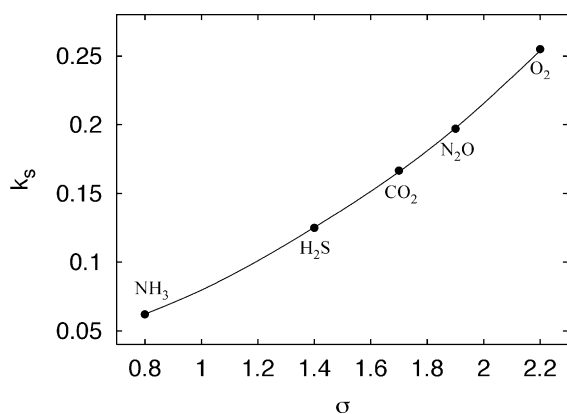
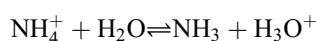


Fig. 5. Line: Setchenow constants in sea water (0–35‰) as a function of hard-sphere radii of the nonelectrolyte. Points: radii assigned to a number of gasses, cf. Table 3.

calculate the dissociation constant of ammonium in sea water based on the free hydrogen scale,



which can be expressed in terms of molality by the stoichiometric constant,

$$K_a^{\text{st}} = \frac{m_{\text{NH}_3} m_{\text{H}^+}}{m_{\text{NH}_4^+}} = K_a \frac{a_{\text{w}} \gamma_{\text{NH}_4^+}}{\gamma_{\text{H}_3\text{O}^+} + \gamma_{\text{NH}_3}} \quad (8)$$

where K_a is the thermodynamic equilibrium constant as obtained in pure aqueous solution. Using the calculated activity coefficients it is now possible to derive the stoichiometric constant as a function of salinity (Table 6). This has been done earlier by Clegg and Whitfield (1995) using the Pitzer formalism. Experimental data are available from Khoo et al. (1977).

Table 6

The $\text{p}K_a^{\text{st}}$ of ammonia in sea water at 298 K obtained from measurements (Khoo et al., 1977), the Pitzer model (Clegg and Whitfield, 1995) and Monte Carlo simulations

$S/\text{‰}$	Exp.	Pitzer	Present
0	9.245	9.245	9.245
5	9.260	9.259	9.267
15	9.290	9.285	9.301
25	9.320	9.311	9.332
35	9.351	9.337	9.364
s		1.5×10^{-4}	2.5×10^{-4}

Table 7

The activity of water, a_{w} , at 298 K as a function of salinity

$S (\text{‰})$	Exp.	Present	Pitzer
5	0.9973	0.9974	0.9974
10	0.9947	0.9948	0.9948
15	0.9921	0.9921	0.9921
20	0.9895	0.9895	0.9895
25	0.9868	0.9867	0.9868
30	0.9840	0.9839	0.9840
35	0.9813	0.9812	0.9814
s		8.5×10^{-5}	6.5×10^{-5}

Experimental values are taken from Millero and Leung (1976) and the Pitzer calculations are made using the sea water model of Clegg and Whitfield (1995).

3.3. Activity of water

Finally, our simulations yield the osmotic coefficient, ϕ , which can be used to obtain the activity of water, a_{w} , through the relationship

$$\ln a_{\text{w}} = -\phi M_{\text{H}_2\text{O}} \sum m_i \quad (9)$$

As shown in Table 7, excellent agreement is found with experimental data as well as with values obtained using the Pitzer model.

4. Discussion

Activity coefficients obtained using the Monte Carlo simulation scheme are in excellent agreement with experimental data as well as with data calculated using the Pitzer model. This indicates that the primitive model of electrolytes correctly accounts for particle interactions in saline media (up to $S = 35 \text{‰}$). In the case of highly charged ions of opposite sign, the model may need correction due to the fact that the dielectric continuum model becomes inadequate for describing their interaction at short separation. One possible improvement could be achieved by introducing a variable dielectric constant, but currently we are not aware of a well-described theory suitable for this purpose.

The only parameter needed to describe a particle (i.e. its hard-sphere radius) can be obtained from mean activity coefficients of single-electrolyte solutions, which are readily available in the literature. In the present work, we have fitted the hard-sphere radii

using a manual trial-and-error method but by applying a least square method, more precise results may be obtained. Furthermore, as the sea water solution is examined on a microscopic level the model may be expanded to yield other properties. This could, for example, be particle distribution functions used to study inter-ionic distances and, hence, possible ion-pair formation. These advantages combined with the fast increase in computing power of personal computers, make this model a competitive alternative to existing thermodynamic sea water models.

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