

Ionic Strength and Ionic Activity

In seawater single ions are not dissolved in pure water, but seawater itself contains high concentrations of ions. The parameter used to characterize aqueous solutions with different amounts of oppositely charged electric charges (ions) is ionic strength, I . It is defined as half the summation of the concentrations multiplied by the respective squared ionic charge (z).

$$I = \frac{1}{2} \sum c_i \cdot z_i^2$$

The sum encompasses all ions present in the medium so that, for a NaCl solution, we have

$$I = \frac{1}{2} ([Na^+] + [Cl^-])$$

Although NaCl is the salt most responsible for the salinity of water, the properties of seawater and a pure NaCl solution with the same concentration are different. For the standard seawater composition used here the ionic strength is approximately 0.7, which corresponds to a salinity of around 35 (grams of salts per kg of water) :

Cl	= 0.54586	' Cl-	Mol/kg (solution)
Na	= 0.46906	' Na+	Mol/kg (solution)
Mg	= 0.05282	' Mg++	Mol/kg (solution)
Ca	= 0.01028	' Ca++	Mol/kg (solution)
SO4	= 0.02824	' SO4--	Mol/kg (solution)
K	= 0.01021	' K+	Mol/kg (solution)
Br	= 0.00084	' Br-	Mol/kg (solution)
Sr	= 0.00009	' Sr++	Mol/kg (solution)
F	= 0.00007	' F-	Mol/kg (solution)
B	= 0.00042	' B(OH) ₃ + B(OH) ₄ -	Mol/kg (solution)

The ionic strength of seawater may be calculated from salinity (DOE, 1994)

$$I = \frac{19.924}{1000 - 1.005 \cdot S}$$

The behaviour of an ion dissolved in water depends on the electrical interaction with the other ions present in solution. Therefore the chemical 'activity' of an ion dissolved in fresh water and in seawater is quite different.

The activity of a chemical species, denoted by $\{A\}$, is strictly related to its concentration by the activity coefficient $\gamma(A)$:

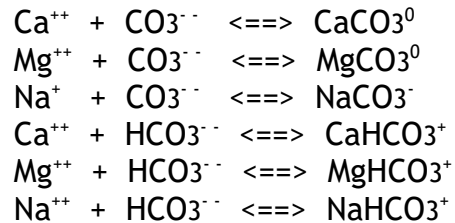
$$\{A\} = \gamma(A) \cdot [A]$$

For infinite dilution, the activity coefficient is 1, but it decreases as the solution becomes more concentrated. If you consider a simple electrolyte, deviation from ideal behaviour can be described through the effect of (relatively) long-range electrostatic interactions. For those interactions, approximations can be derived to describe the dependence of activity coefficients $\gamma(i)$ on ionic strength I .

Seawater has however a higher ionic strength which is, in turn, due to the presence of different electrolyte charges: the combination of these two facts leads to the formation of 'ion pairing' and complex formation in the electrolyte mixture.

As an example, bivalent charged carbonate ions may associate to positively charged Mg^{++} or Na^+ ions forming aliovalent ion pairs such as $NaCO_3^-$ or $MgCO_3^0$

According to Skirrow (1975), the most important ion pairing equilibria in seawater are:



Therefore electrostatic interaction of the CO_3^{--} ions with opposite charges in solution isn't the only factor that decreases the activity of the ion. The ion pairing greatly impairs the same activity, as the carbonate ion in seawater is not 'free', being combined in neutral or lower charged (aliovalent) species in solution.

If no ion-pairing would occur, the free activity coefficient γ of an ion in simple electrolyte solutions varies with ionic strength I according to the Debye-Hückel limiting law

$$\log(\gamma) = -Az^2\sqrt{I} \quad \text{valid for } I < 0.005$$

or to the Davies equation

$$\log(\gamma) = -Az^2\left(\frac{\sqrt{I}}{\sqrt{I}+1} - 0.2 \cdot I\right) \quad \text{valid for } I < 0.5$$

with $A = 1.82 \cdot 10^{-6} \cdot (\epsilon T)^{-1.5}$, where $\epsilon \approx 79$ is the dielectric constant of water, and T is the absolute temperature in K. At 25°, A is about 0.5 for water; z indicates the charge of the ion and I the ionic strength of the solution.

As the ionic strength of seawater is approximately 0.7, which is only slightly higher than the limit of the Davies equation, it should be used in a reasonable way. However, this equation and the Debye-Hückel limiting law no longer apply since they only hold for dilute solutions and simple electrolytes (as opposed to concentrated solutions and electrolyte mixtures of unlike charges) (Zeebe 2001).

The problem will be tackled by using empirical formulas for the equilibrium constants, which employ concentrations, and without the need to calculate activities.

The same approach will be used for the temperature, pressure and salinity dependence of these constants.

The fitting of experimental data has been carried out by DOE 1994, Millero 1995, Weiss 1974 et al. A comprehensive review of such data can be found in Zeebe 2001, Appendix A.