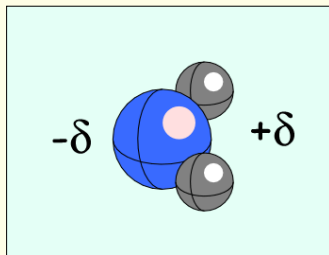


## Physical Chemistry of Aqueous Solutions

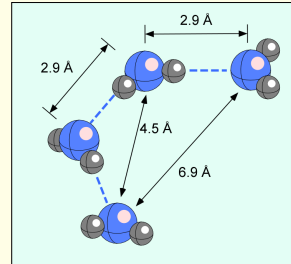
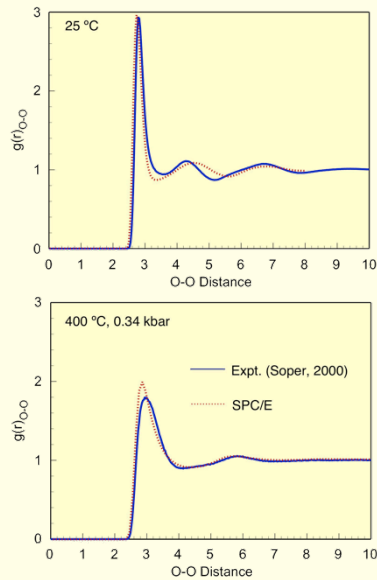
Advanced Aqueous Geochemistry  
DM Sherman, University of Bristol

### The Water Molecule

The O-H bond is “polar covalent”; from the difference in electronegativity, the OH bond is 39 % ionic. This gives the water molecule a large **dipole moment**.



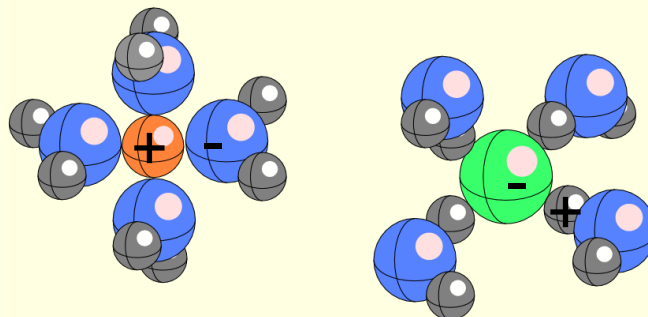
## Hydrogen Bonding



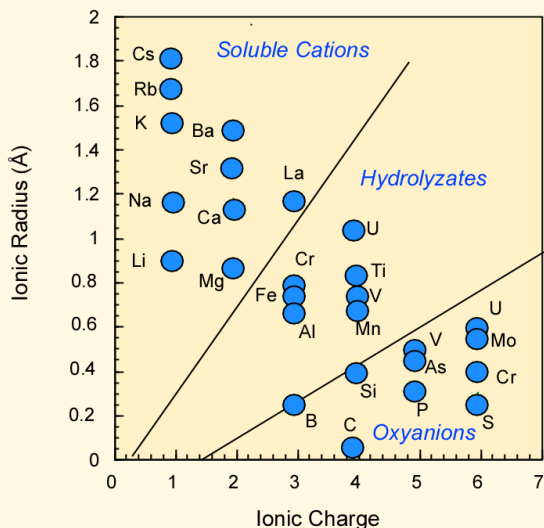
Water molecules are attracted to each other via the **hydrogen bond** (dipole-dipole interaction)

## Ion Hydration

The dipole moment of the water molecule means that water molecules will be attracted to ions in solution. This is why ionic compounds will dissolve in water.



## Ionic Potential and Ion Hydration

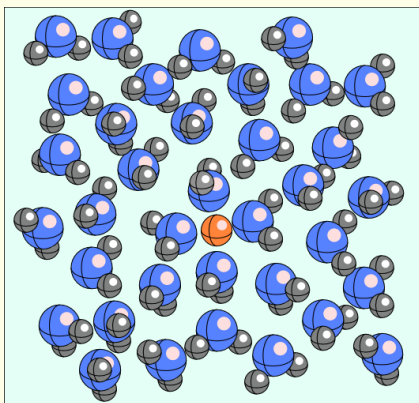


Large cations with low charge will be weakly hydrated.

Small cations with high charge will form oxyanions (or oxycations).

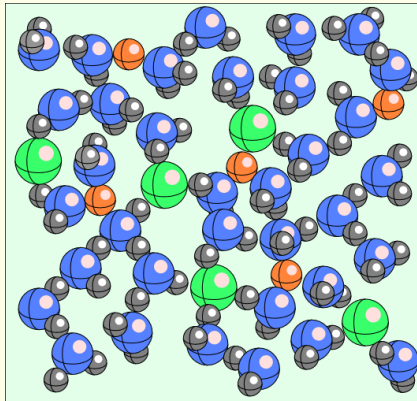
## Ion-Ion Interactions

In very dilute aqueous solutions, the ions do not interact with each other. Moreover, the presence of the ions has no effect on the bulk structure of water.



## Ion-Ion Interactions

With increasing concentration, ions start to interact with each other. The chemical potential of an ion will depend upon the concentration of the other ions.



Ion-ion interactions may be *specific* (e.g., **ion-pairs** or **complexes**) or non-specific (long-range coulombic interactions).

## Ion-Ion Interactions

We define the activity (chemical potential) of an aqueous ion (A) relative to the standard state of a *1 molal solution of A with the properties of infinite dilution*.

$$\mu_A = \mu_A^0 + RT \ln \gamma_A [A]$$

Standard state

molal concentration

Activity coefficient

## Ionic Strength

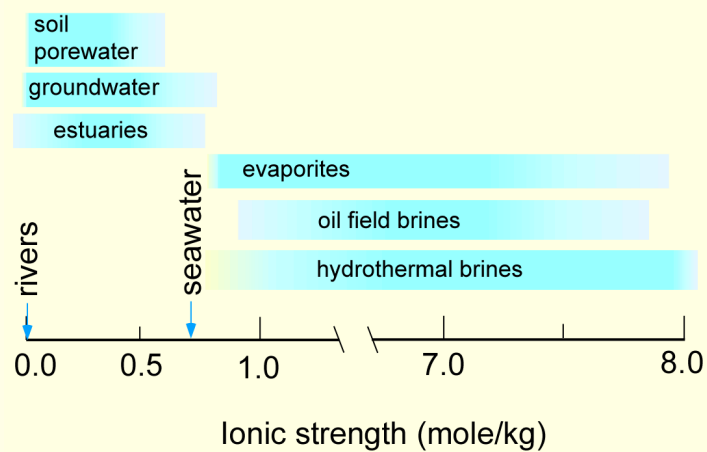
The **ionic strength** of a solution is a measure of the overall concentration of ions in terms of their charge:

$$I = \frac{1}{2} \sum_j m_j z_j^2$$

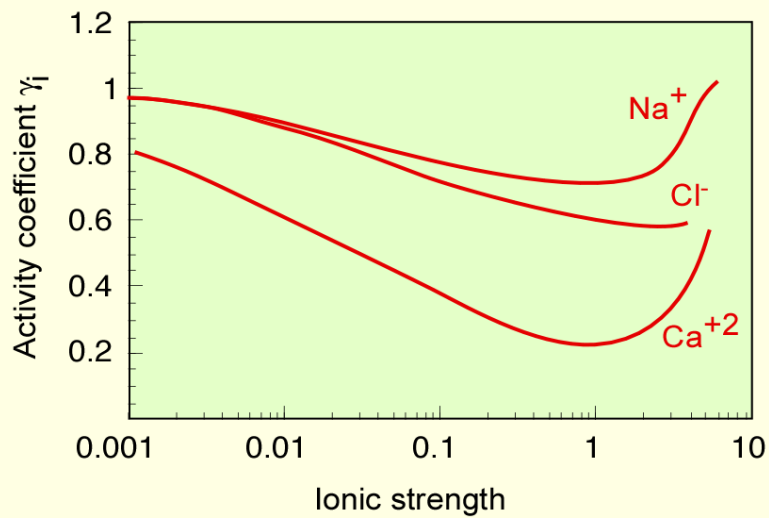
Charge of ion j

Molal concentration of ion j

## Ionic Strength of Natural Waters



## Effect of Ionic Strength on Activity Coefficients



## Debye-Huckel Theory

Debye-Huckel theory provides an estimate of ion activity coefficients:

$$\log(\gamma_j) = -Az_j^2 \sqrt{I}$$

Charge of ion j

Constant

This is only good up to ionic strengths  $< 0.01$  m.

## Assumption of Debye-Huckel Theory

- Ion is a hard charged sphere
- Ion feels electrical field from other ions
- Ions in continuum of dielectric constant which is the solvent
- Used Poisson-Boltzmann equation

## Problems with DH Theory

- Accounts only for the coulombic forces of the ions - neglects electrostatic forces
- Not all electrolytes are strong
- Ions not really spherical and dielectric constant is not constant

*D-H equation does not work in solutions with high ionic strength !*

## Extended Debye-Huckel Theory

More elaborate models take into account the size of the ions:

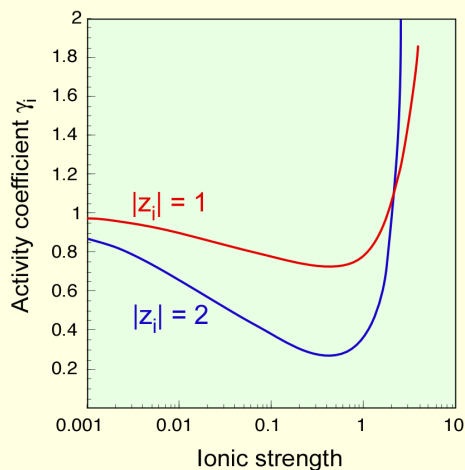
$$\log(\gamma_j) = -Az_j^2 \frac{\sqrt{I}}{1 + BM\sqrt{I}}$$

Charge of ion j

Ion size

This is good up to ionic strengths < 0.1 m.

## Davies Equation



The Davies equation is the most useful for geochemistry.

$$\log(\gamma_j) = -Az_j^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right)$$

This is good up to ionic strengths < 0.5 m.



## Ionic speciation

As much as possible, we try to explicitly account for the specific ion interactions by calculating the **ionic speciation**:

Cations form **complexes** and **ion-pairs** with ligands such as  $\text{Cl}^-$  and  $\text{HCO}_3^-$ .

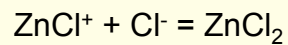
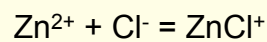
Cations hydrolyze with water to form hydroxy complexes such as  $\text{M}(\text{OH})^+$ .

## Example: Ion speciation in Seawater

Species	Molality	Species	Molality
$\text{Na}^+$	$4.8 \times 10^{-1}$	$\text{Ca}^{2+}$	$9.6 \times 10^{-3}$
$\text{NaSO}_4^-$	$6.0 \times 10^{-3}$	$\text{CaSO}_4$	$1.1 \times 10^{-3}$
$\text{NaHCO}_3$	$1.7 \times 10^{-4}$	$\text{CaHCO}_3^-$	$4.6 \times 10^{-5}$
$\text{K}^+$	$1.0 \times 10^{-2}$	$\text{Mg}^{2+}$	$4.8 \times 10^{-2}$
$\text{Cl}^-$	$5.7 \times 10^{-1}$	$\text{MgSO}_4$	$7.4 \times 10^{-3}$
$\text{SO}_4^{2-}$	$1.5 \times 10^{-2}$	$\text{MgHCO}_3^-$	$2.2 \times 10^{-4}$
$\text{HCO}_3^-$	$1.5 \times 10^{-3}$		

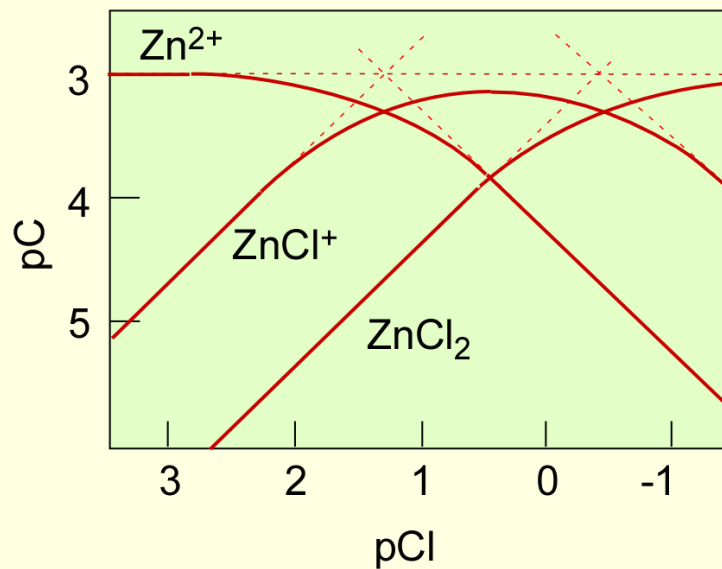
## Ion Complexation

Ligands such as  $\text{Cl}^-$ ,  $\text{HS}^-$ ,  $\text{OH}^-$ ,  $\text{HCO}_3^-$  and the conjugate bases of organic acids (e.g., acetate,  $\text{CH}_3\text{COO}^-$ ) can complex with metals in solution:



These reactions may enhance the solubility of metals by lowering the activities (or concentrations) of free metals.

## Ion Complexation (Cont.)



### Example: Zn speciation in Seawater

Species	Molality	Activity
Zn <sup>2+</sup>	$1.0 \times 10^{-8}$	$2.0 \times 10^{-9}$
ZnCl <sup>+</sup>	$2.5 \times 10^{-9}$	$1.86 \times 10^{-9}$
ZnSO <sub>4</sub>	$1.0 \times 10^{-9}$	$1.2 \times 10^{-9}$
ZnCl <sub>2</sub>	$5.9 \times 10^{-10}$	$6.9 \times 10^{-10}$

Note: only 66% of Zn is free Zn<sup>2+</sup>.

### Summary

- Understand the origin of ion solvation.
- Activities of ions are relative to a standard state of “1 molal solution with properties of infinite dilution”.
- Ionic Strength
- Davies equation good up to  $I < 0.5$  m.