

# Concentration Units

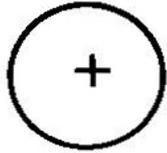
- # Salts & other solutes dissolved in water must be specified with respect to their concentration
- # Oceanographers generally agree on proper units
- # However you will still see every possible unit under the sun being used
- # ppm, ppb, ppt, M, mM,  $\mu$ M, nM, mg/L,  $\mu$ g/L, ng/L, pg/L, nmol/kg

# Important Points

(see handout posted for last class)

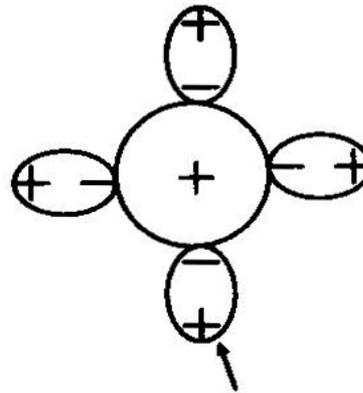
- # Use SI units whenever possible
- # Chemical Oceanographers should use mol/kg with a prefix due to compressibility
- # You must know whether the unit refers to solvent alone or solution as a whole (i.e., molarity vs. molality; ppm as mg/L or mg/kg)

**CONTINUUM MODEL**



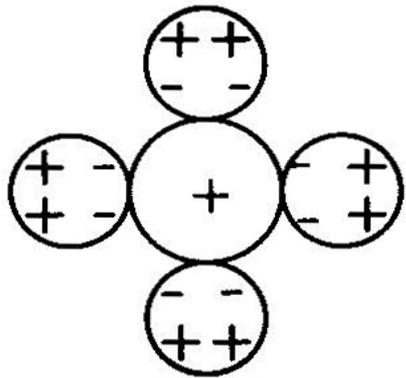
Continuous  
Dielectric  
Medium

**ION-DIPOLE MODEL**



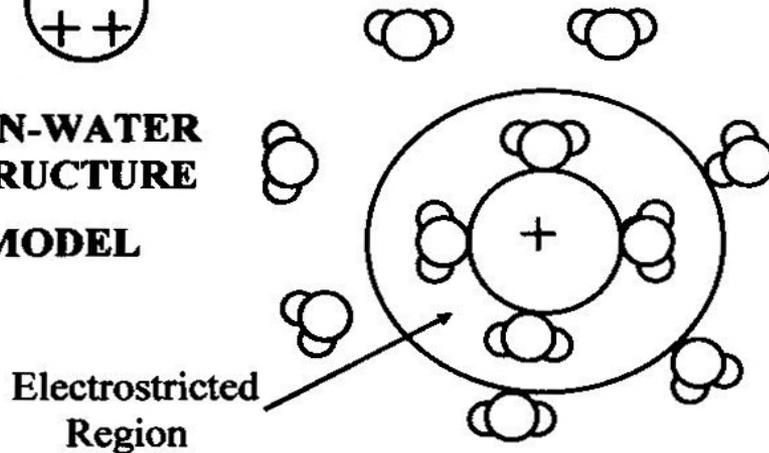
Water Dipoles

**ION-QUADRUPOLE MODEL**



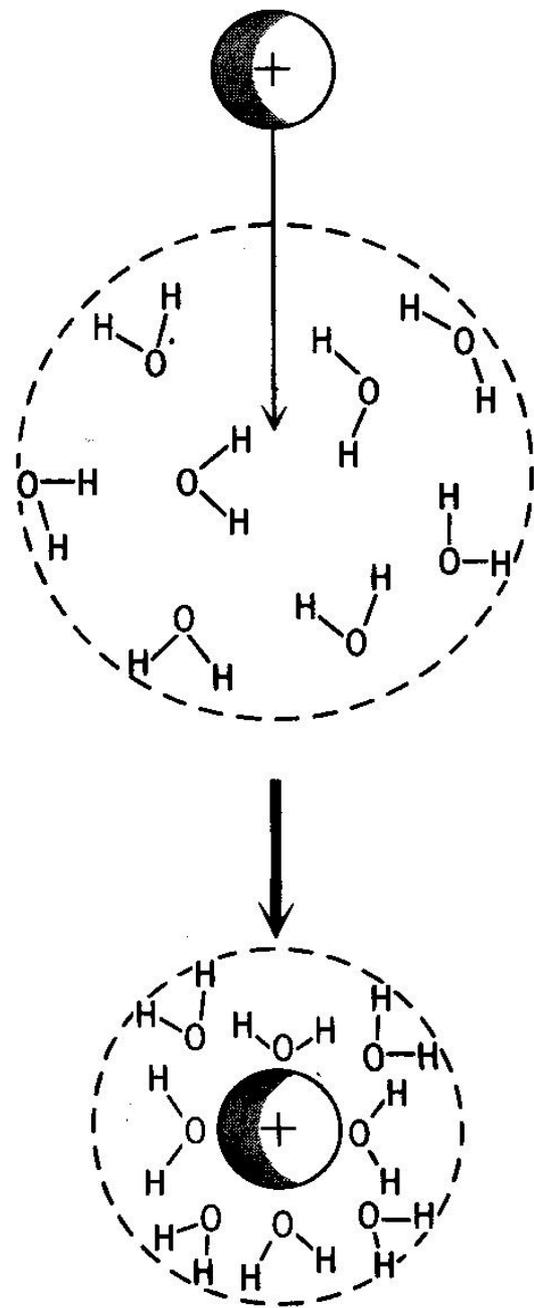
Water Quadrupoles

**ION-WATER STRUCTURE MODEL**



Discussing  
Structure  
Changes in H<sub>2</sub>O  
as Solutes are  
Added

Millero Fig 4.13  
Models to Explain  
Ion-Water  
Interactions p 135



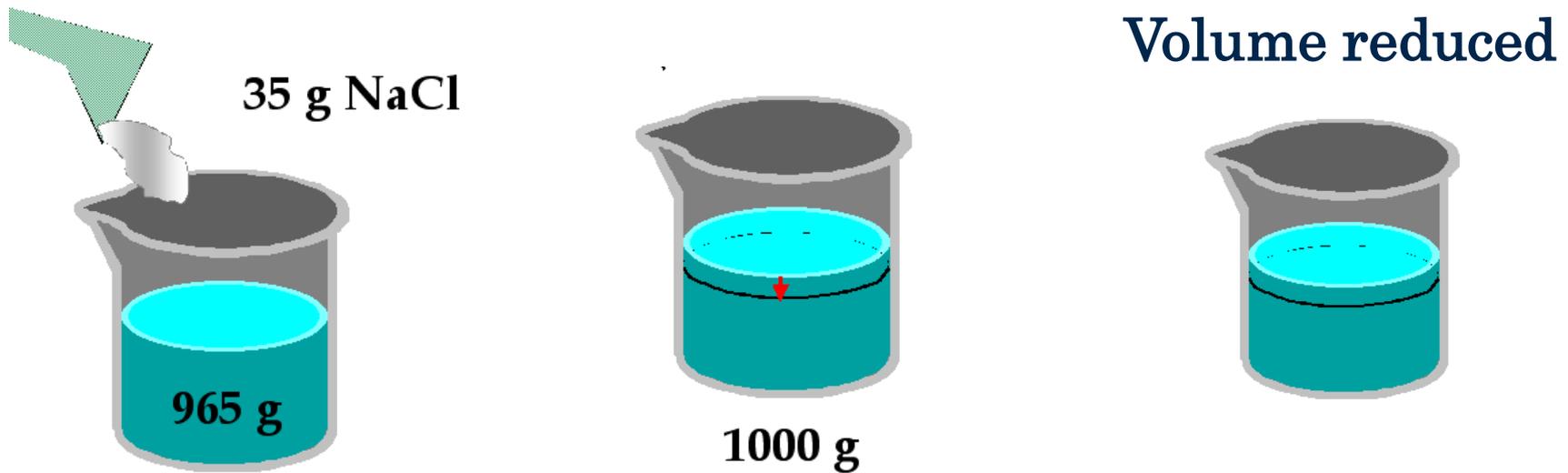
Electrostriction occurs as an ion orients or reorders water molecules causing them to be arranged tightly around the charge center

Libes (1992)

# Electrostriction

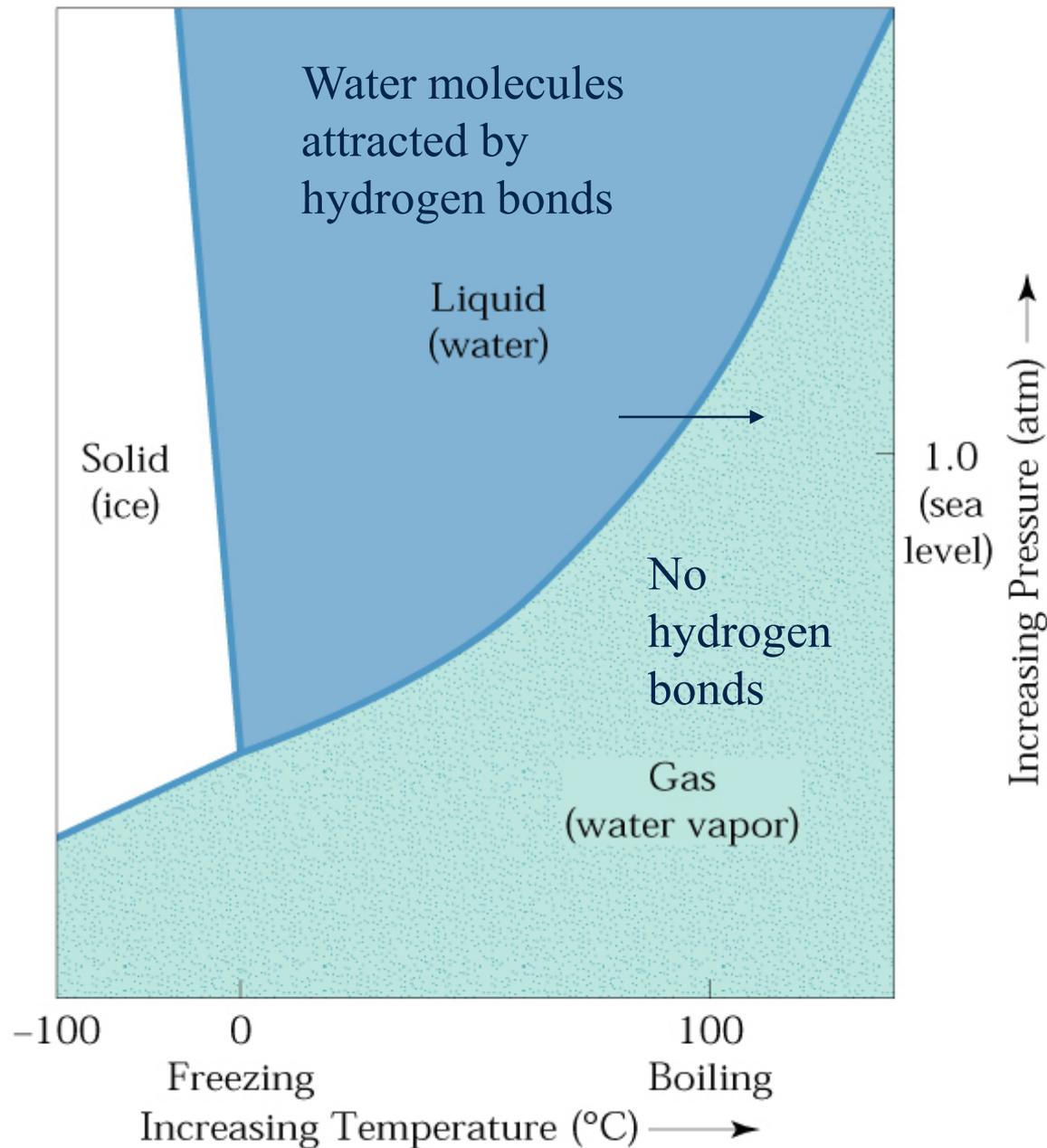
- occurs when adding salt to H<sub>2</sub>O

- # Add 35 g of NaCl to 965 g H<sub>2</sub>O = 1000g total
- # Density - NaCl 2.165 g/cm<sup>3</sup>; H<sub>2</sub>O 0.9997 g/cm<sup>3</sup>
- # Volumes = 16.2 cm<sup>3</sup> + 967.9 cm<sup>3</sup> = 984.1 cm<sup>3</sup>
- # Actual Volume = 977.3 cm<sup>3</sup>



# Colligative Properties

- # Physicochemical Properties that vary with number of species in solution not their chemical nature
- # Vapor Pressure Lowering
- # Boiling Point Elevation ( $\Delta T_b$ )
- # Freezing Point Depression ( $\Delta T_f$ )
- # Osmotic Pressure ( $\pi$ )



Explanation of Colligative Properties Based on Changes in Phase Equilibria

## Simple Phase Diagram of Water (Wiley 1999)

# Vapor Pressure Lowering

Magnitude of vapor pressure (v.p.) lowering can be expressed in terms of solute mole fraction

$\Delta P/P^0 = X$     where  $X =$  mole fraction (i.e.,  
ratio of moles  
solute to total moles

$P^0 =$  v.p. of pure solvent

$\Delta P =$  change in v.p.

# Boiling Point Elevation

Boiling point (b.p.) of solution changes

$$\Delta T_b = v K_b m \quad \text{where } m = \text{molality}$$

$K_b$  = constant for solvent

0.512 °C/m for H<sub>2</sub>O

Ions/molecule  $\longrightarrow$   $v$  = van't Hoff factor

$\Delta T_b$  = change in b.p.

# Freezing Point Depression

Freezing point (m.p.) of solution changes

$$\Delta T_f = - \nu K_f m \quad \text{where } m = \text{molality}$$

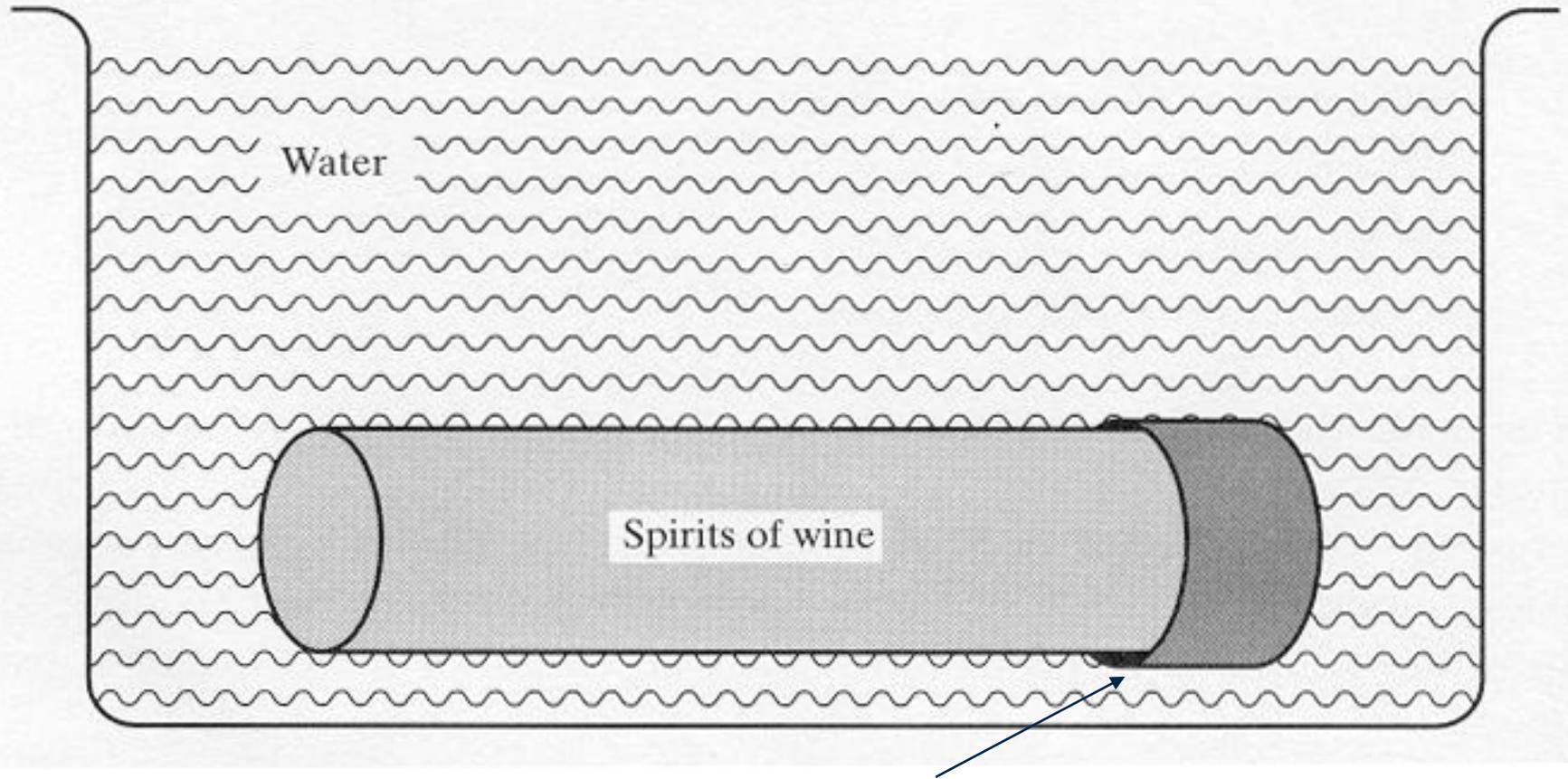
$K_f$  = constant for solvent

1.86 = °C/m for H<sub>2</sub>O

$\nu$  = van't Hoff factor

$\Delta T_f$  = change in m.p.

# Osmotic Pressure ( $\pi$ )



Nollet (1748) used pig bladder membrane (Pilson, 1998)

# Osmotic Pressure ( $\pi$ )

From the Gas Law ( $PV = nRT$ )

$$\pi V = v R T$$

where  $T$  = absolute temp.

$R$  = gas constant

$v$  = van't Hoff factor

$V$  = volume

$\pi$  = osmotic pressure

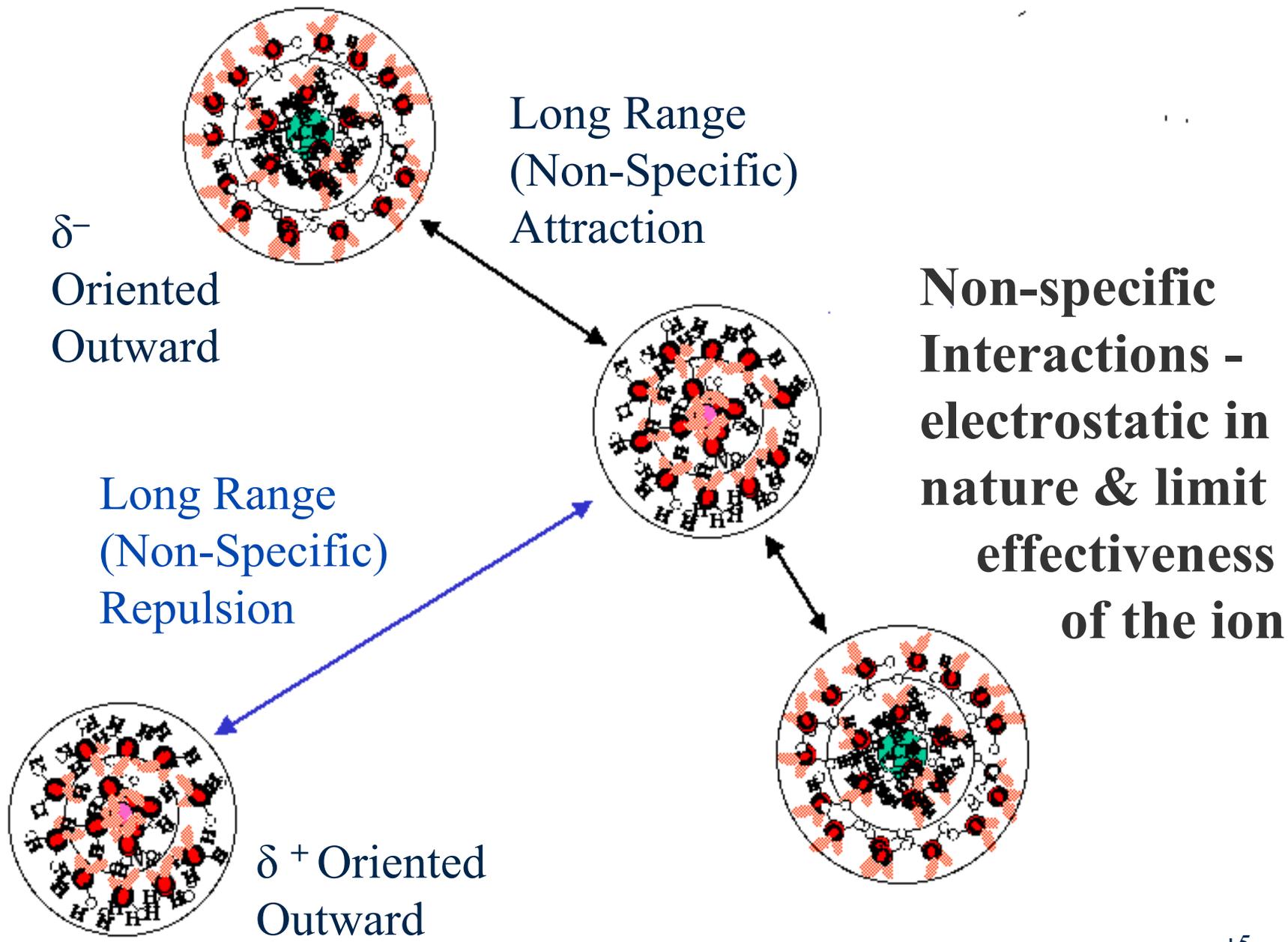
# Important Properties

- # Electrostriction influences density, water structure & mobility of ions in solution
- # It also results in pressure effects for solubility
- # Freezing Point Depression lowers freezing point of natural waters especially seawater
- # Vapor Pressure Lowering reduces evaporation
- # Osmotic Pressure strongly influences diffusion across biological membranes

# Ion-Ion Interactions

- # Many types – non-specific, bonding, contact, solvent shared, solvent separated
- # Non-specific i.e., long range interactions and the concepts of ionic strength, activity & activity coefficient
- # Specific interactions e.g. complexation, ion pairing (strong or weak)
- # Millero cartoons

<http://fig.cox.miami.edu/~lfarmer/MSC215/MSC215.HTM>



# Non-specific Interaction

- # Electrostatic in nature
- # Limits effectiveness of ion in solution
- # Use concept of **activity** to quantify effect

(activity = effective concentration, accounts for non-ideal behavior)

$$\mathbf{a}_i = [\mathbf{i}]_F \gamma_F(\mathbf{i}) \quad \text{where } a_i = \text{activity of ion } i$$

$[\mathbf{i}]_F = \text{free ion conc. (m)}$   
 $\gamma_F(\mathbf{i}) = \text{activity coefficient}$

In short  $\mathbf{a} = [\mathbf{i}] \gamma$  of ion  $i$

# Activity of Individual Ion Influenced by Other Ions

## # Ionic Strength of solution

$$I = 0.5 \sum Z^2 m$$

where I = ionic strength

Z = charge on ion

m = molal conc.

(molarity or molinity

can also be used)

$$a = [i] \gamma$$

# Activity Coefficient ( $\gamma$ )

# Debye-Huckel Theory is starting point

(Primarily for very low ionic strength)

$$\ln \gamma_{\pm} = - A Z^2 I^{0.5} \quad \text{original D.H.}$$

or

$$\ln \gamma_{\pm} = - S_f I^{0.5} / (1 + A_f a I^{0.5}) \quad \text{extended}$$

Where  $\gamma_{\pm}$  is the mean ion activity coefficient

$S_f$ ,  $A$  &  $A_f$  are constants related to temperature

$I$  is ionic strength &  $a$  is the ion size parameter in  $\text{\AA}$

$Z$  is the charge on the ion

# Activity Coefficient ( $\gamma$ )

## # Guntelberg Approximation

$$\ln \gamma_{\pm} = - A Z^2 [I^{0.5}/(1 + I^{0.5})]$$

Where  $\gamma_{\pm}$  is the mean ion activity coefficient

A is a constant

I is ionic strength

Z is the charge on the ion

Useful for  
 $I \geq 0.1$

# Activity Coefficient ( $\gamma$ )

## # Davies Equation

$$\ln \gamma_{\pm} = - A Z^2 [I^{0.5}/(1 + I^{0.5}) - 0.2 I]$$

Where  $\gamma_{\pm}$  is the mean ion activity coefficient

A is a constant (= 1.17)

I is ionic strength

Z is the charge on the ion

Useful for  
 $I \sim 0.5$

# Activity Coefficient ( $\gamma$ )

## # Bronsted-Guggenheim

$$\ln \gamma_{\pm} = \ln \gamma_{\text{DH}} + \sum_j B_{ij}[j] + \sum_j \sum_k C_{ijk}[j][k] + \dots$$

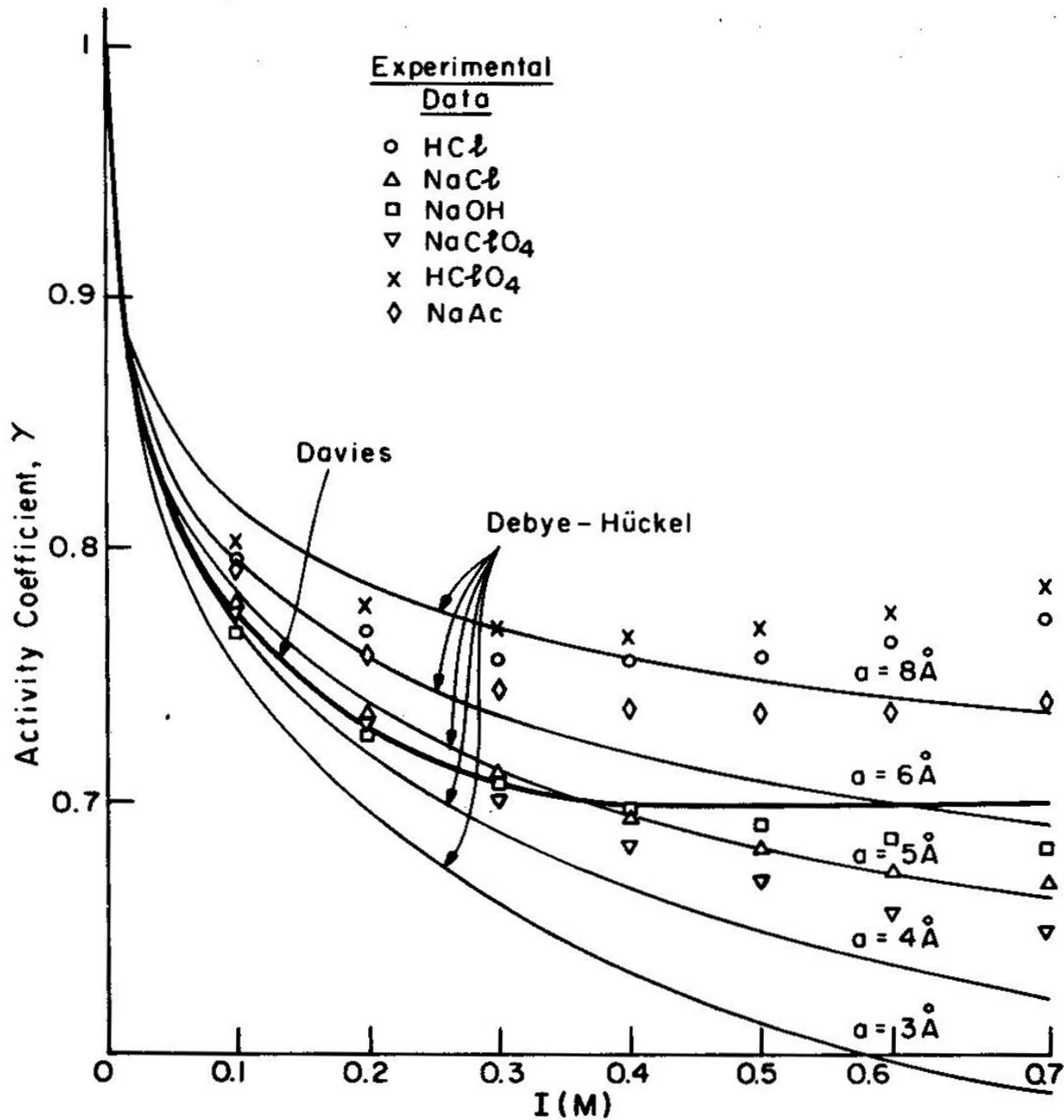
Where  $\gamma_{\pm}$  is the mean ion activity coefficient

$\gamma_{\text{DH}}$  is the  $\gamma$  from Debye-Huckel

$B_{ij}$  is a virial coefficient for ion pairs

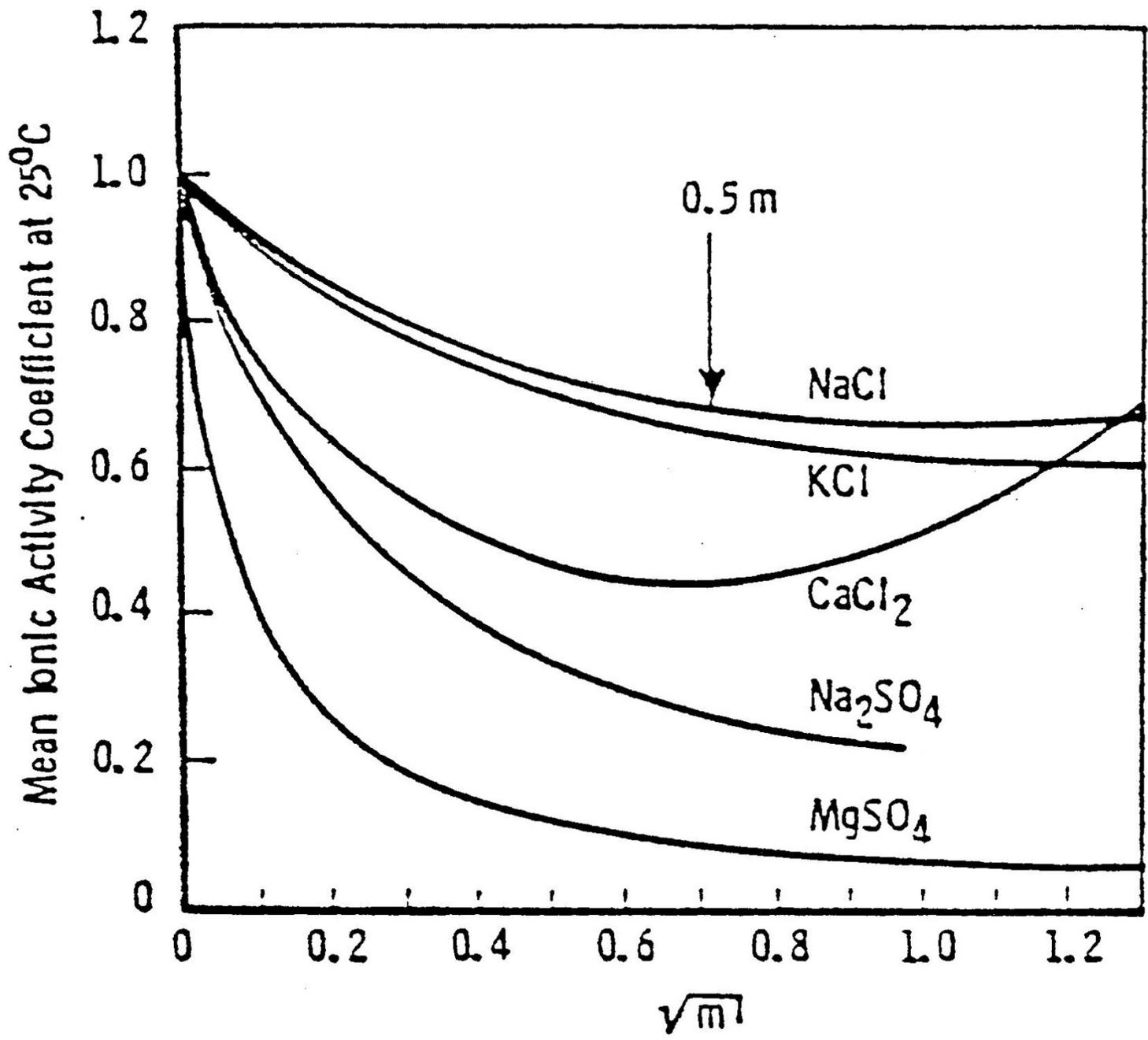
$C_{ijk}$  is a virial coefficient for three ions

Useful at  
any I

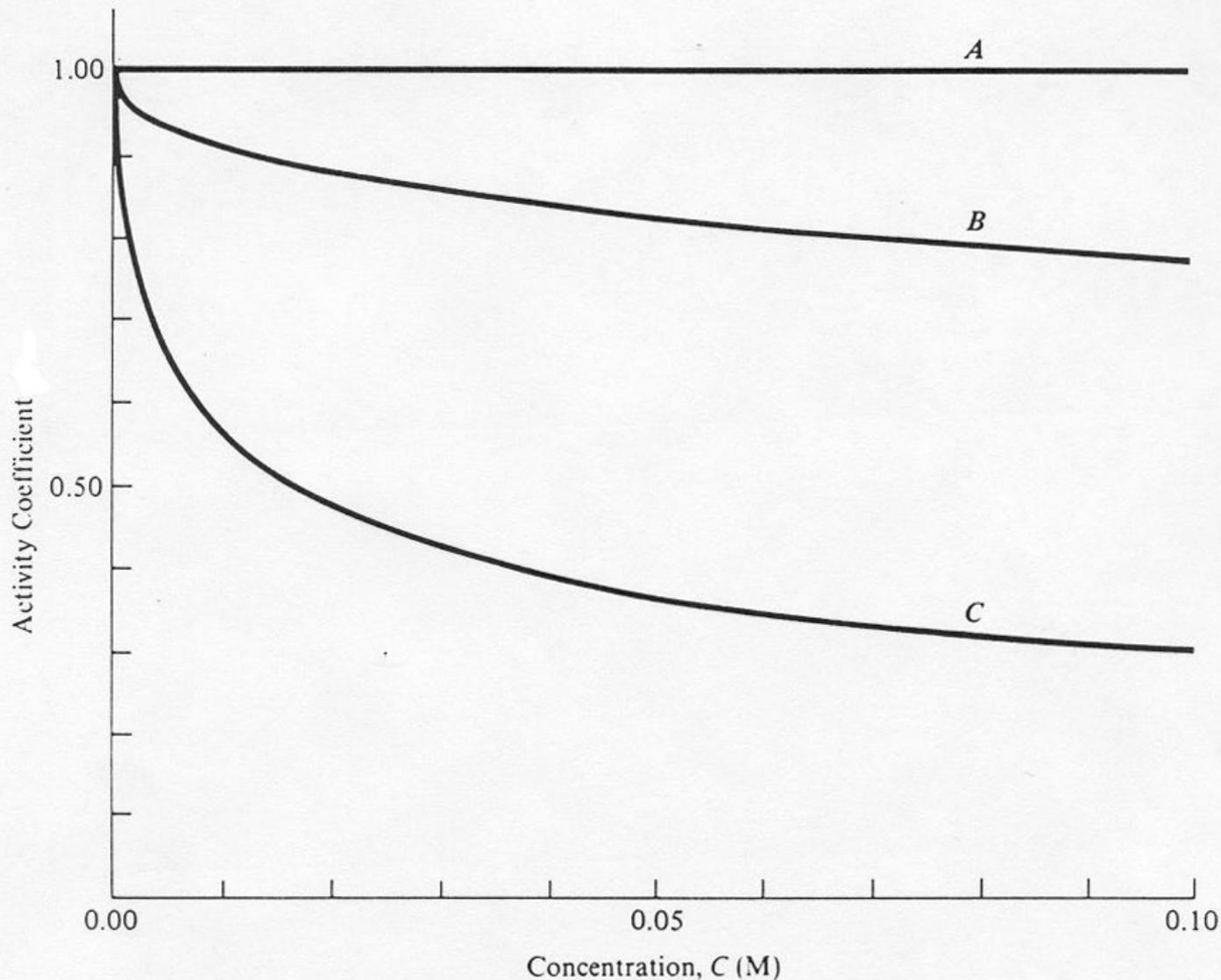


Comparison of  
Davies Equation  
& Extended  
Debye-Huckel  
for monovalent  
Ions

Morel & Hering 1993



Activity Coefficient vs. Conc., Monovalent & Divalent Systems



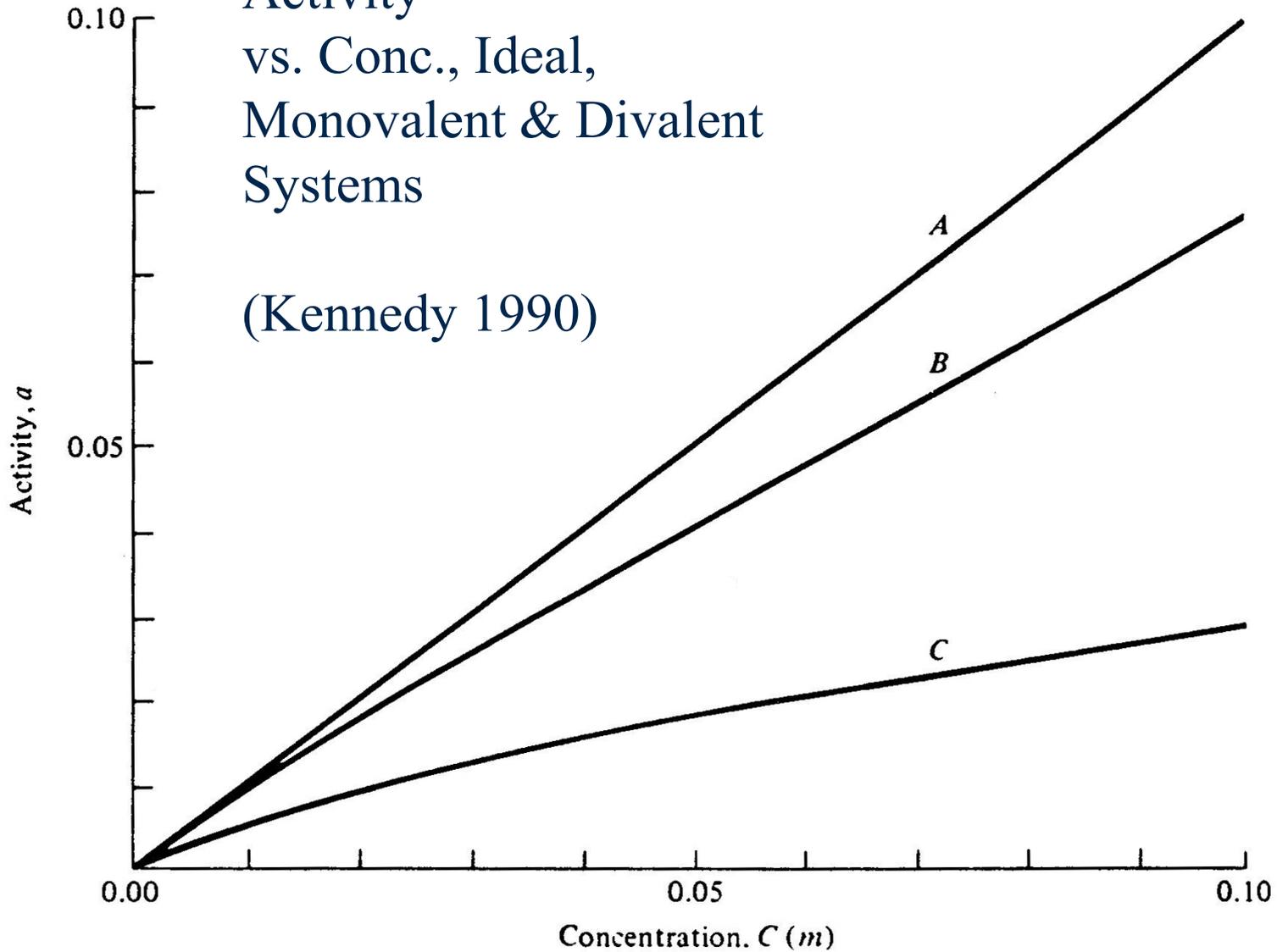
Activity Coefficient vs. Conc., Ideal, Monovalent & Divalent Systems

(Kennedy 1990)

**FIGURE 4-2** Activity coefficient as a function of concentration in the solution: (A) ideal solution for which  $\gamma = 1.00$  at all concentrations; (B) activity coefficient for  $\text{Na}^+$  in NaCl solutions; (C) activity coefficient for  $\text{Ca}^{2+}$  in  $\text{CaCl}_2$  solution.

Activity  
vs. Conc., Ideal,  
Monovalent & Divalent  
Systems

(Kennedy 1990)



**FIGURE 4-1** Activity as a function of concentration: (A) ideal solution for which  $a = C$ ; (B)  $\text{Na}^+$  activity in  $\text{NaCl}$ ; (C)  $\text{Ca}^{2+}$  activity in  $\text{CaCl}_2$ .

# Putting It All Together

# Calculate ionic strength from concentrations of all ions in solution using  $I = 0.5 \sum Z^2 m$

# Use Davies Equation to calculate activity coefficients for all ions of interest ( $Z = 1, 2, 3, 4$ )

$$\ln \gamma_{\pm} = - A Z^2 [I^{0.5}/(1 + I^{0.5}) - 0.2 I]$$

# Calculate activity of the ions of interest using their concentrations and activity coefficients

$$a = [i] \gamma$$

# Example: pH of SW

pH is defined as the negative  
logarithm of the hydrogen ion activity

$$\text{pH} = -\log a_{\text{H}^+}$$

At a typical ionic strength of seawater  $I = 0.7$

From Davies Equation  $\text{H}^+$  activity coefficient

$$\ln \gamma = -A Z^2 [I^{0.5}/(1 + I^{0.5}) - 0.2 I]$$

If  $Z = 1$  &  $A = 1.17$  then  $\ln \gamma = -0.37$  &  $\gamma = 0.69$

## Example: pH (cont.)

If a typical seawater pH is 8.2

Then  $H^+$  activity is  $1 \times 10^{-8.2}$  or  $6.31 \times 10^{-9} M$

From  $a = [i]\gamma$  or  $a_{H^+} = [H^+]\gamma_{H^+}$  & calculated  $\gamma = 0.69$

$$6.31 \times 10^{-9} M = [H^+] \times 0.69$$

$$[H^+] = 9.14 \times 10^{-9} M$$

Activity of  $H^+$  is 31% lower than it's concentration

Effectiveness of  $H^+$  is 31% lower due to crowding

This phenomenon is greater for divalent ions