Ionic strength

•For <u>weak electrolytes solutions</u> and <u>non-electrolytes</u> the ionic concentration terms and activities are usually identical.

•For <u>strong electrolytes</u> and for solutions of <u>weak electrolytes together with salts</u> and other electrolytes (as in <u>buffers</u>), it is important to use activities instead of concentrations.

•**Ionic strength (μ)** is used to relate interionic attractions and activity coefficients.

•It represents the contribution to the electrostatic forces of the ions of all types, depend on the total number of ionic charges.

(c) $Na_2 SO_4$:

$$\mu = \frac{1}{2}[(0.02 \times 1^2) + (0.01 \times 2^2)]$$

$$= 0.030$$

(d) The ionic strength of a 0.010 M solution of salicylic acid is 0.003 as calculated from a knowledge of the ionization of the acid at this concentration (using the equation $[H_3O^+] = \sqrt{K_a c}$). Unionized salicylic acid does not contribute to the ionic strength. The ionic strength of the mixture of electrolytes is the sum of the ionic strength of the individual salts. Thus,

$$\mu_{total} = \mu_{KCl} + \mu_{BaSO_4} + \mu_{Na_2SO_4} + \mu_{HSal}$$

$$= 0.010 + 0.040 + 0.030 + 0.003$$

$$= 0.083$$

Debye and Hückel theory

Based on three assumptions of how ions act in solution:
1. Strong electrolytes completely dissociate into ions in solution.
2. Solutions of Electrolytes are very dilute, on the order of 0.01 M.
3. Each ion is surrounded by ions of the opposite charge, on average.

$$\log \gamma_i = -A z_i^2 \sqrt{\mu}$$

A= for water at 25°C, is a factor that depends only on the temperature and the dielectric constant of the medium, is approximately 0.51

TABLE 6–2
VALUES OF A FOR SOLVENTS AT 25°C~

Solvent	A_{calc}
Acetone	3.76
Ethanol	2.96
Water	0.509

Osmotic Coefficient

➤As the solution becomes <u>more dilute</u>, **i** approaches **v** (= valence), the number of ion into which an electrolyte dissociate, and at infinite dilution, i = v or i/v =1.

➤The ratio **i/v** is designated as **g** and is known as the **practical osmotic coefficient** when expressed on a molal basis.

➤In case of weak electrolyte, it provides a measure of the degree of dissociation.

$$\Delta T_f = g v K_f m$$

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Osmolality

Osmotic coefficient and osmolarity

- Osmotic pressure unit is atmospheres and in clinical practice is expressed by Osmols or milliosmols (mOsm)
- 1Osmol= 1mole of substance in1kg water
- Osmolality = total no. of particles in 1 kg of water
- Osmolarity = total no. of particles I 1L of water
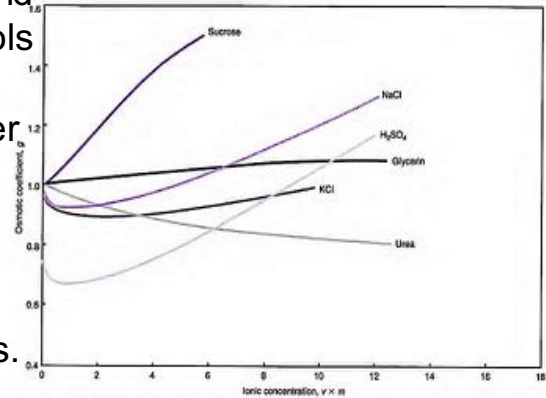- It is effected by the interionic interactions.

Fig. 6-6. Osmotic coefficient, g, for some common solutes. (From G. Scatchard, W. Hamer, and S. Wood, J. Am. Chem. Soc. 60, 3061, 1938. With permission.)

Milliosmolality (mOsm/kg) $= i \cdot mm$

where i is approximately the number of ions formed per molecule and mm is the millimolal concentration.

EXAMPLE 6–16

Calculating Milliosmolality

What is the milliosmolality of a 0.120 m solution of potassium bromide? What is its osmotic pressure in atmospheres?

For a 120 millimolal solution of KBr:

Milliosmolality $= 1.86 \times 120 = 223$ mOsm/kg

A 1-osmolal solution raises the boiling point 0.52°C, lowers the freezing point 1.86°C, and produces an osmotic pressure of 24.4 atm at 25°C. Therefore, a 0.223-Osm/kg solution yields an osmotic pressure of $24.4 \times 0.223 = 5.44$ atm.

Examples 6-17, 6-18 and 6-19 are important

Osmolarity = (Measured osmolality)
     $\times$ (Solution density in g/mL)
     − Anhydrous solute concentration in g/mL)

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Thanks for your attention