Electrolyte solution

Presented by the Pharmacist
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Outline

1. Van't Hoff factor (i)

2. Ion pairing

3. Colligative Properties of Electrolyte Solutions

4. Degree of dissociation

5. Ionic strength

6. The L value

Objectives

1. Understand the important properties of solutions of electrolytes.

2. Compare and contrast the colligative properties of electrolytic solutions and concentrated solutions of nonelectrolytes.

3. Apply the theory of strong electrolytes; for example, calculate degree of dissociation, activity coefficients, and so on.

4. Calculate ionic strength.

Van't Hoff Factor(i)

- Van't Hoff corrects for the fact that the number of particles you thrown into solution is not always the number of particles that determine the magnitude of the property.

- The relationship between the moles of solute dissolved and the moles of particles in solution is usually expressed as:

$$\textbf{\textit{Van't Hoff factor (i)}} = \frac{\text{actual number of particles in solution after dissociation}}{\text{number of formula units initially dissolved in solution}}$$

Ion Pairing

- At a given instant a small percentage of the sodium and chloride ions are paired and thus count as a single particle.
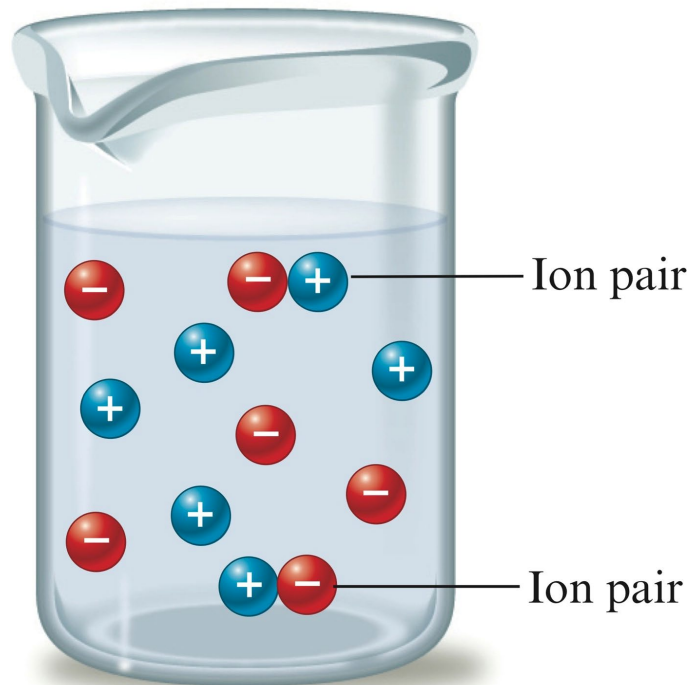
Ion pair

Ion pair

Examples

- The expected value for i can be determined for a salt by noting the number of ions per formula unit (assuming complete dissociation and that ion pairing does not occur).

  - NaCl $i = 2$
  - KNO_3 $i = 2$
  - Na_3PO_4 $i = 4$

Ion Pairing

- Ion pairing is most important in concentrated solutions.

- As the solution becomes more dilute, the ions are farther apart and less ion pairing occurs.

- Ion pairing occurs to some extent in all electrolyte solutions.

TABLE 12.3

The van't Hoff Factor of 0.0500 M Electrolyte Solutions at 25°C		
Electrolyte	i (Measured)	i (Calculated)
Sucrose*	1.0	1.0
HCl	1.9	2.0
NaCl	1.9	2.0
$MgSO_4$	1.3	2.0
$MgCl_2$	2.7	3.0
$FeCl_3$	3.4	4.0

Colligative Properties of Electrolyte Solutions

$\pi = M\ R\ T$

it was found that the π for electrolytes is approximately 2,3, and more times larger than expected from this equation.

So for electrolyte solution the equation will be

$\pi = i\ M\ R\ T$

i = correction factor (Van'ts Hoff factor)

so for the other colligative properties

$$\Delta Tb = i\, Kb\, m \qquad \Delta Tf = i\, Kf\, m$$

$$\Delta P = i\, P_1{}^{\circ}\, m$$

At what temperature will a 5.4 molal solution of NaCl freeze? Kf= 1.86

$\Delta T_f = i\, K_f\, m$

$\Delta T_f = 2 \times 1.86 \times 5.4$

$\Delta T_f = 20.1\ C^o$

FP = 0 – 20.1 = -20.1 C^o

Degree of dissociation :

To differentiate between the strong and weak electrolytes by the fraction of the moles ionized which is the degree of dissociation $\propto$

$$\propto = \frac{A_c}{A_0}$$

A_c = equivalent conductance at conc. (c)

A_o = equivalent conductance at infinite dilution.

The correlation between i and α

$\quad$ i = 1+ α(v-1)

$$\alpha = \frac{i-1}{v-1} \qquad \text{v : is the no. of ions}$$

Example:

The freezing point of a 0.10 m solution of acetic acid is -0.188 C°. Calculate the degree of ionization of acetic acid at this conc. Acetic acid dissociates into two ions. Kf= 1.86

Ionic strength :

Relate the interionic attraction for solution of strong electrolytes and for solutions of weak electrolytes together with salts and other electrolytes, such as exist in buffer systems.

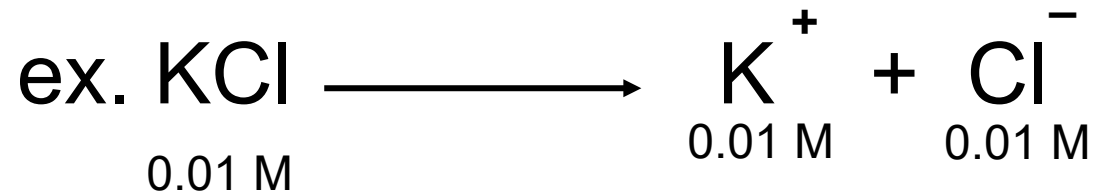$$\mu = \frac{1}{2} (c_1 z_1^2 + c_2 z_2^2 + \ldots\ldots c_i z_i^2)$$

$$\mu = \frac{1}{2} \sum_{1}^{i} c_i z_i^2$$
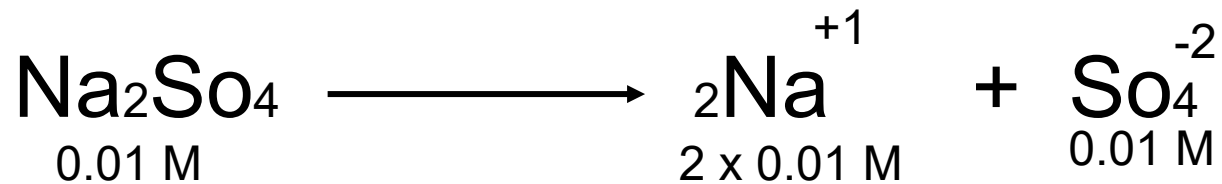
C is the molar conc. of ions

Z is the valence

we divided by 2 because +v and –v ion pairs contribute to the total electrostatic interaction, whereas we are interested in the contribution of each ion separately

So μ represents the contribution to the electrostatic forces of the ions of all types.

ex. KCl $\longrightarrow$ K$^+$ + Cl$^-$

0.01 M   0.01 M   0.01 M

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

$Na_2So_4 \longrightarrow 2Na^{+1} + So_4^{-2}$

0.01 M   2 x 0.01 M   0.01 M

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

$$= 0.03$$

μ total = μ KCl + μ Na$_2$So$_4$ (for solution of them)

Example:

What is the ionic strength of (a) 0.01 M KCl, (b) 0.01M $BaSO_4$,(c) 0.01 M Na_2SO_4

(d) what is the ionic strength of a solution

containing all three electrolytes .

Example:

A buffer contains 0.3 mole of K_2HPO_4 and 0.1 mole of KH_2PO_4 per liter of solution. Calculate the ionic strength of the solution.

The L value:

$\Delta Tf = i\ Kf\ m$

used for the colligative properties of nonelectrolyte and electrolyte solutions.

in dilute solution it can be modified slightly by

$\Delta Tf = L\ c$ $L = i\ Kf$

c = M molar conc.

At a conc.of a drug that is isotonic with body fluids

L = i Kf = L iso = 1.9 for non electrolytes

= 2.0 for weak electrolytes

= 3.4 for univalent electrolytes

Reference

MARTIN'S PHYSICAL PHARMACY AND PHARMACEUTICAL SCIENCES