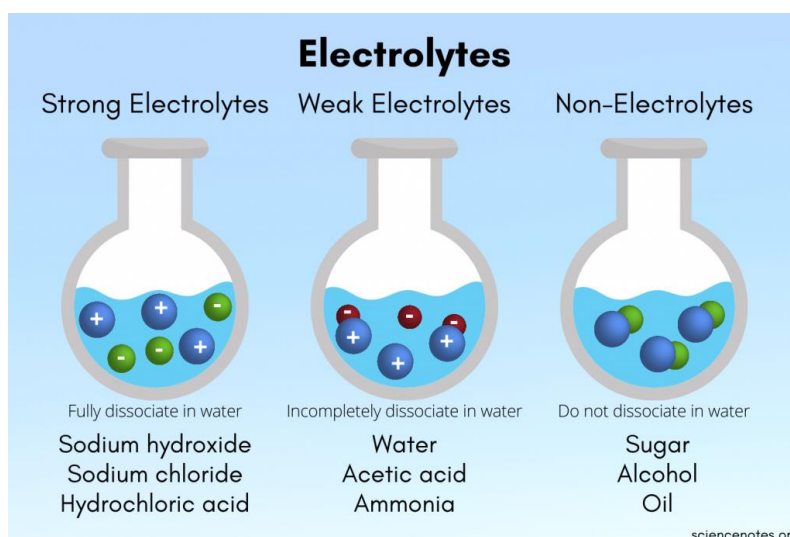**Electrolytes**

Electrolytes are chemicals that break into ions (ionize) when they are dissolved in water. The positively-charged ions are called cations, while the negatively charged ions are called anions. Substances are categorized as strong electrolytes, weak electrolytes, or nonelectrolytes.

1. Strong Electrolytes

Strong electrolytes completely ionize in water. This means 100% of the dissolved chemical breaks into cations and anions. However, it does not mean the chemical completely dissolves in water! For example, some species are only slightly soluble in water, yet are strong electrolytes. This means that not very much dissolves, but all that does dissolve breaks into ions.

Examples: Strong acids, strong bases, and salts are strong electrolytes.

2. Weak Electrolytes

Weak electrolytes partially ionize in water. Pretty much any dissociation into ions between 0% and 100% makes a chemical a weak electrolyte, but in practice, around 1% to 10% of a weak electrolyte breaks into ions.

Examples: Weak acids and weak bases are weak electrolytes. Most nitrogen-containing molecules are weak electrolytes. Water is considered a weak electrolyte by some sources because it partly dissociates into H^+ and OH^- ions, but a nonelectrolyte by other sources because only a very small amount of water dissociates into ions.

3. Nonelectrolytes

If a substance doesn't ionize in water at all, it's a nonelectrolyte.

Examples: Most carbon compounds are nonelectrolytes. Fats, sugars, and alcohols are largely nonelectrolytes.

Activity ionic strength

The properties of electrolyte solutions can significantly deviate from the laws used to derive chemical potential of solutions. In nonelectrolyte solutions, the intermolecular forces are mostly comprised of weak Van der Waals interactions, and for practical purposes this can be considered ideal. In ionic solutions, however, there are significant electrostatic interactions between solute-solvent as well as solute-solute molecules. These electrostatic forces are governed by Coulomb's law. Consequently, the behavior of an electrolyte solution deviates considerably from that an ideal solution. Indeed, this is why we utilize the activity of the individual components and not the concentration to calculate deviations from ideal behavior. In 1923, Peter Debye and Erich Hückel developed a theory that would allow us to calculate the mean ionic activity coefficient of the solution, γ±, and could explain how the behavior of ions in solution contribute to this constant.

Assumptions of Debye-Hückel Theory

The Debye-Hückel theory is based on three assumptions of how ions act in solution:

1. 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.

Debye and Hückel developed the following equation to calculate the mean ionic activity coefficient γ±

$$\log \gamma_{\pm} = -\frac{1.824 \times 10^6}{(\varepsilon T)^{3/2}} \mid z_+ z_- \mid \sqrt{I}$$

where

- • ε is the dielectric constant,

- • $z+$ and $z-$ are the charges of the cation and anion, respectively, and

- • I is the ionic strength of the solution.

The Equation above is known as the **Debye-Hückel Limiting Law**. The ionic strength is calculated by the following relation:

$$I = \frac{1}{2} \sum_i m_i z_i^2$$

where m_i and z_i are the molality and the charge of the ion in the electrolyte. Since most of the electrolyte solutions we study are aqueous ($\varepsilon=78.54$) and have a temperature of 298 K, the Limiting Law in Equation of **Debye-Hückel Limiting Law** reduces to

$$\log \gamma_{\pm} = -0.509 \mid z_+ z_- \mid \sqrt{I}$$

Example Calculate ionic strength, mean ionic activity coefficient $\gamma_{\pm}$, and the mean ionic molality $m_{\pm}$ for a 0.02 *molal* aqueous solution of zinc chloride, $ZnCl_2$.

SOLUTION

Zinc chloride will dissolve as

$$ZnCl_2 \longrightarrow Zn^{2+}(aq) + 2\,Cl^-(aq)$$
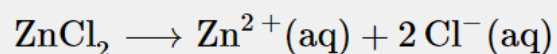
The concentrations of the zinc and chloride ions will then be 0.02 and 0.04 molal, respectively. First calculate the mean ionic molality. The mean ionic molality is defined as the average molality of the two ions (see Electrolyte Solutions)

$$m_{\pm} = (m_+^{\nu+} m_-^{\nu-})^{\frac{1}{\nu}}$$

where ν is the stoichiometric coefficient of the ions, and the total of the coefficients in the exponent. In our case, the mean ionic molality is

$$m_{\pm} = (m_{Zn}^{\nu(Zn)} m_{Cl}^{\nu(Cl)})^{\frac{1}{\nu(Zn)+\nu(Cl)}}$$

$$= [(0.02)^1 (0.04)^2]^{\frac{1}{3}}$$

$$= [(0.02)(0.0016)]^{\frac{1}{3}}$$

$$= 3.17 \times 10^{-2}$$

To calculate the mean ionic activity coefficient, we first need the ionic strength of the solution from Equation below

$$I = \frac{1}{2}[(0.02)(+2)^2 + (0.04)(-1)^2]$$

$$= \frac{1}{2}(0.08 + 0.04) = 0.06$$

Now we can calculate the activity coefficient:

$$\log \gamma_\pm = -0.509 \mid (+2)(-1) \mid \sqrt{0.06}$$

$$= (-0.509)(2)(0.245)$$

$$= -0.250$$

$$\gamma_\pm = 10^{-0.25}$$

$$= 0.1627$$