

Solution of Electrolyte

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Introduction

- Electrolytes are substances that form ions in solutions, conduct the electric current.
- Electrolytes may be subdivided further into strong electrolytes (hydrochloric acid, sodium sulphate) and weak electrolytes (ephedrine, phenobarbital).
- Strong electrolytes are substances that are completely ionized when they are dissolved in water. They conduct electrical currents very efficiently. The classes of strong electrolytes include: (a) soluble salts e.g. BaCl_2 , (b) strong acids e.g. HCl , HNO_3 , H_2SO_4 , (c) strong bases e.g. NaOH , KOH
- Weak electrolytes are substances that exhibit a small degree of ionization in water. That is, they produce relatively few ions when dissolved in water. Their solutions produce a small current. The most common weak electrolytes are weak acids (e.g. acetic acid) and weak bases (ammonium hydroxide – NH_4OH).

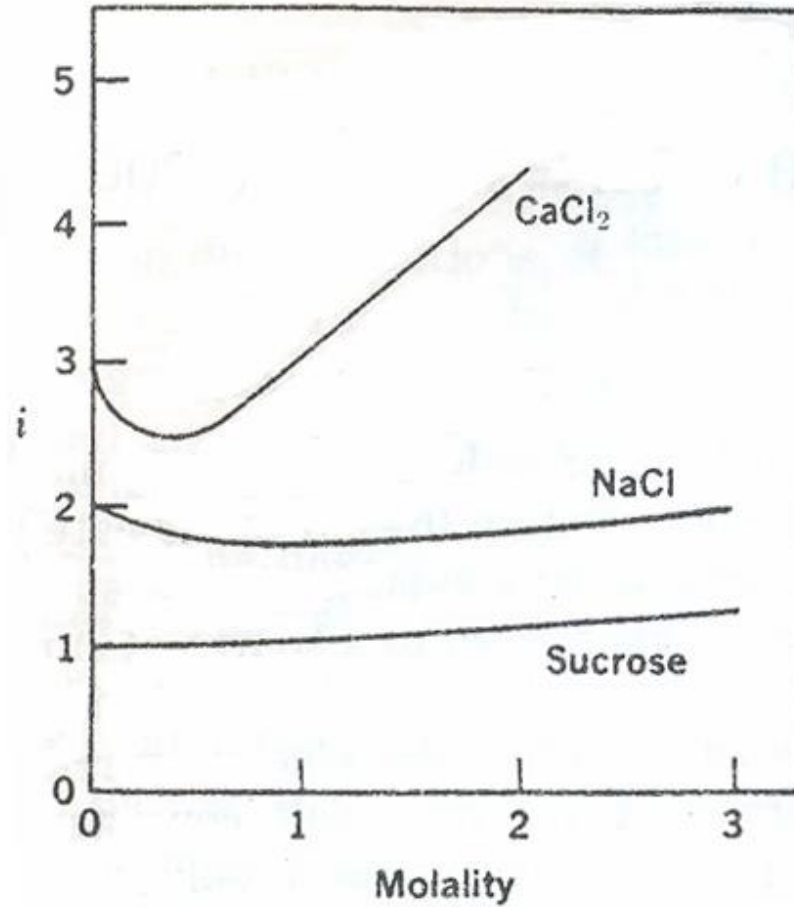
Colligative Properties of Electrolytic Solutions and Concentrated Solutions of Nonelectrolytes

- Van't Hoff observed that the osmotic pressure of dilute solutions of nonelectrolytes could be expressed satisfactorily by the equation $\pi = RTc$, in which R is the gas constant and T is the absolute temperature, and c is the concentration in moles per liter.
- Van't Hoff found, however, that solutions of electrolytes gave osmotic pressure approximately two, three, and more times larger than expected from this equation, depending on the electrolyte investigated.

Colligative Properties of Electrolytic Solutions and Concentrated Solutions of Nonelectrolytes

- The i factor is plotted against the molal concentration of both electrolytes and nonelectrolytes in the following figure.
- For nonelectrolytes, i is seen to approach **unity**, and for strong electrolytes, it tends towards a value equal to the **number of ions formed upon dissociation** e.g. i approaches the value of **2** for solutes such as NaCl and CaSO₄, **3** for K₂SO₄ and CaCl₂, and **4** for FeCl₃.

Colligative Properties of Electrolytic Solutions and Concentrated Solutions of Nonelectrolytes



Van't Hoff i factor of representative compounds

Colligative Properties of Electrolytic Solutions and Concentrated Solutions of Nonelectrolytes

- The van't Hoff factor can also be expressed as the ratio of any colligative property of a real solution to that of an ideal solution, since i represents the number of times greater that the colligative effect is for a real solution (electrolyte or nonelectrolyte) than for an ideal solution.

$$\Delta p = 0.018 i p_1^\circ m$$

$$\pi = iRTm$$

$$\Delta T_f = iK_f m$$

$$\Delta T_b = iK_b m$$

Colligative Properties of Electrolytic Solutions and Concentrated Solutions of Nonelectrolytes

Example: What's the osmotic pressure of a 2.0 m solution of sodium chloride at 20°C?

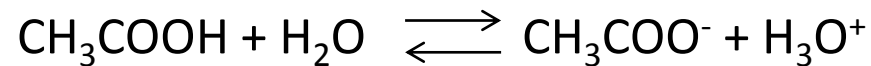
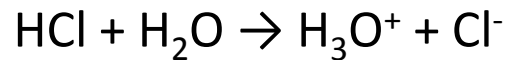
Answer: the i factor for a 2 m solution of sodium chloride as observed in the figure is about 1.9

$$\pi = iRTm$$

$$= 1.9 * 0.082 * 293 * 2 = 91.3 \text{ atm}$$

Arrhenius Theory of Electrolytic Dissociation

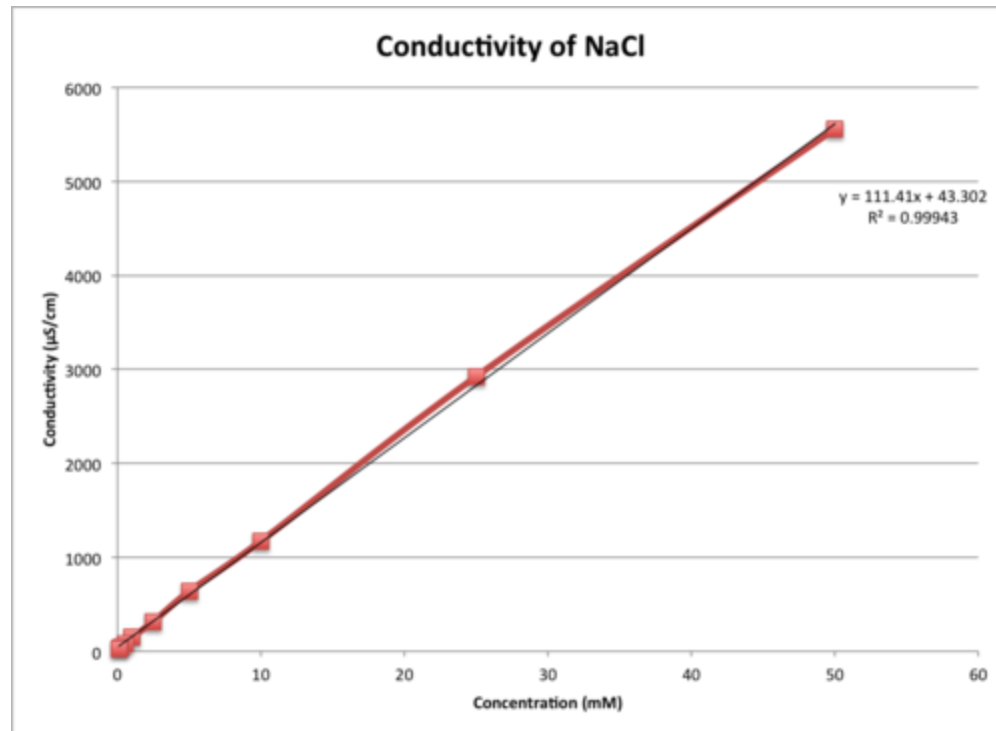
- Arrhenius proposed the now classic theory of dissociation: when electrolytes are dissolved in solution, the solute exists in the form of ions in the solution.



- In fact, Arrhenius did not consider strong electrolytes to be ionized completely except in extremely diluted solutions. He differentiated between strong and weak electrolytes by the fraction of the molecules ionized: the degree of dissociation α .
- A strong electrolyte is one that dissociated into ions to a high degree and a weak electrolyte is one that dissociated into ions to a low degree.

Arrhenius Theory of Electrolytic Dissociation

- Two methods can be used to determine the degree of dissociation:
- First method: the degree of dissociation can be determined from conductance measurements. Equivalent conductance at infinite dilution Λ_0 was a measure of the complete dissociation of the solute into its ions and that Λ_c represented the number of solute particles present as ions at concentration c .



Arrhenius Theory of Electrolytic Dissociation

Hence the fraction of solute molecules ionized, or the degree of dissociation, can be expressed by the equation

in which $\Lambda_c / \Lambda^\circ$ is known as the conductance ratio

Example: The equivalent conductance of acetic acid at 25°C and at infinite dilution is 390.7 mho cm²/Eq. The equivalent conductance of a 5.9*10⁻³ M solution of acetic acid is 14.4 mho cm²/Eq. What's the degree of dissociation of acetic acid at this concentration?

Answer:

$$\alpha = \frac{\Lambda_c}{\Lambda_0}$$

$$= 14.4/390.7$$

$$= 0.037 \text{ or } 3.7\%$$

Arrhenius Theory of Electrolytic Dissociation

- Second method to find α : The van't Hoff factor i can be connected with the degree of dissociation α in the following way:

$$\alpha = \frac{i - 1}{v - 1}$$

where v is the number of ions produced from the electrolyte ionization
e.g. for NaCl $v=2$, for CaCl_2 $v=3$

- The cryoscopic method is used to determine i from the expression

$$i = \frac{\Delta T_f}{k_f m}$$

Arrhenius Theory of Electrolytic Dissociation

Example: Calculate the degree of ionization of 0.1 m acetic acid providing that its freezing point is -0.188°C .

Answer: Acetic acid dissociates into two ions, so $v = 2$.

To calculate i :

$$i = \frac{\Delta T_f}{k_f m}$$

$$= 0.188 / (1.86 * 0.1) = 1.011$$

It is possible now to calculate the degree of ionization:

$$\alpha = \frac{i - 1}{v - 1}$$

$$= (1.011 - 1) / (2 - 1) = 0.011 \text{ or } 1.1\%$$

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Arrhenius Theory of Electrolytic Dissociation

- The Arrhenius theory is now accepted for describing the behavior only of weak electrolytes. The degree of dissociation of a weak electrolyte can be calculated satisfactorily from the conductance ratio or obtained from the van't Hoff factor i .
- As for strong electrolytes, they dissociate completely in dilute and moderately concentrated solution.
- Moreover, a discrepancy exists between α calculated from i ratio and α calculated from the conductivity ratio for strong electrolyte solutions at concentrations greater than about 0.5 M.
- Thus degree of dissociation according to Arrhenius theory does not account for behavior of strong electrolyte. Instead, it is more convenient to consider a strong electrolyte as completely ionized and to introduce a factor that expresses the deviation of the solute from 100% ionization. The activity and activity coefficient are used for this purpose.

Activity and Activity Coefficient

- The large number of oppositely charged ions in solutions of strong electrolytes influence one another through interionic attractive forces.
- For solution of nonelectrolytes, regardless of concentration, the number of ions is small and the interionic attractive forces are insignificant.
- As for strong electrolytes, ions can associate at high concentrations into groups known as ion pairs. Thus the values of the freezing point depression and the other colligative properties are less than expected for solutions of unhindered ions. Consequently, a strong electrolyte may be completely ionized, yet incompletely dissociated into free ions.
- You may think of the solution as having an “effective concentration” or, as it is called, an activity. This concept was first introduced by Lewis and Randall.

Activity and Activity Coefficient

- The activity (a), in general, is less than the actual or stoichiometric concentration of the solute (m), not because the strong electrolytes are partly ionized, but rather because some of the ions are effectively “taken out of play” by the electrostatic forces of interaction.
- At infinite dilution in which the ions are so widely separated that they do not interact with one another, the activity a of an ion is equal to its concentration:

$$a = m.$$

- As the concentration of the solution is increased, the ratio becomes less than unity because the effective concentration or activity of ions becomes less than the molal concentration. This ratio is known as the practical activity coefficient (γ), thus:

$$a = \gamma m$$

Activity and Activity Coefficient

- A cation and an anion in an aqueous solution may each have a different ionic activity.
- The activity of an electrolyte is defined by its mean ionic activity a_{\pm}

$$a_{\pm} = (a_+^m a_-^n)^{1/(m+n)}$$

- where a_+ is the activity of the cation, and a_- is the activity of the anion, the exponents m and n give the stoichiometric number of given ions that are in solution.
- Thus an NaCl solution has a mean ionic activity of $a_{\pm} = (a_{\text{Na}^+} a_{\text{Cl}^-})^{1/2}$
- Whereas an FeCl_3 solution has a mean ionic activity of $a_{\pm} = (a_{\text{Fe}^{+3}} a_{\text{Cl}^-}^3)^{1/4}$
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Ionic strength

EXAMPLE 6-11

Calculating Ionic Strength

What is the ionic strength of (a) 0.010 M KCl, (b) 0.010 M BaSO₄, and (c) 0.010 M Na₂SO₄, and (d) what is the ionic strength of a solution containing all three electrolytes together with salicylic acid in 0.010 M concentration in aqueous solution?

(a) KCl:

$$\begin{aligned}\mu &= \frac{1}{2}[(0.01 \times 1^2) + (0.01 \times 1^2)] \\ &= 0.010\end{aligned}$$

b) BaSO₄:

$$\begin{aligned}\mu &= \frac{1}{2}[(0.01 \times 2^2) + (0.01 \times 2^2)] \\ &= 0.040\end{aligned}$$

(c) Na_2SO_4 :

$$\begin{aligned}\mu &= \frac{1}{2}[(0.02 \times 1^2) + (0.01 \times 2^2)] \\ &= 0.030\end{aligned}$$

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 $[\text{H}_3\text{O}^+] = \sqrt{K_a c}$). 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,

$$\begin{aligned}\mu_{\text{total}} &= \mu_{\text{KCl}} + \mu_{\text{BaSO}_4} + \mu_{\text{Na}_2\text{SO}_4} + \mu_{\text{HSal}} \\ &= 0.010 + 0.040 + 0.030 + 0.003 \\ &= 0.083\end{aligned}$$