Activity of Electrolytes

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For T. Y. B.Sc (Sem - VI)

Ionic Strength

- The ionic strength of a solution is a measure of the concentration of ions in that solution. Ionic compounds, when dissolved in water, dissociate into ions.
- The total electrolyte concentration in solution will affect important properties such as the dissociation or the solubility of different salts.
- One of the main characteristics of a solution with dissolved ions is the ionic strength.
- The ionic strength, I, of a solution is a function of the concentration of all ions present in that solution.

$$I = \frac{1}{2}\sum_{i=1}^{n} c_i z_i^2$$

- Here, c_i and z_i are the molar concentration and the charge of ion **i**. The sum is taken over all ions in the solution. Due to the square of z_i, multivalent ions contribute strongly to the ionic strength. For a 1:1 electrolyte such as sodium chloride, the ionic strength is equal to the concentration, but for MgSO4 the ionic strength is four times higher. Generally multivalent ions contribute strongly to the ionic strength.
- For example the ionic strength of a mixed 0.050 M in Na_2SO_4 and 0.020 M in KCl solution is:

  I = 1/2 × [(Concentration of Na_2SO_4 in M × No. of Sodium ions × (Charge of Sodium)^2) + (Concentration of Na_2SO_4 in M × No. of SO_4 ions × (Charge of SO_4)^2) + (Concentration of KCl × No. of Potassium ions × (Charge of Potassium)^2) + Concentration of KCl in M × No. of Chloride ions × (Charge of Chloride)^2)]

  $I = 1/2 \times [(0.050\ \mathrm{M} \times 2 \times (+1)^2) + (0.050\ \mathrm{M} \times 1 \times (-2)^2) + (0.020\ \mathrm{M} \times 1 \times (+1)^2) + 0.020\ \mathrm{M} \times 1 \times (-1)^2)] = 0.17\ \mathrm{M}$

- The ionic strength of a $CaCl_2$ solution is calculated as follows:

$$\begin{aligned} I &= \frac{1}{2}\left\{z_{Ca}^2\,[Ca^{+2}] + z_{Cl}^2\,[Cl^-]\right\} \\ &= \frac{1}{2}\left\{z_{Ca}^2\,[CaCl_2] + z_{Cl}^2\,2\,[CaCl_2]\right\} \\ &= \frac{1}{2}\left\{2^2\,[CaCl_2] + (-1)^2\,2\,[CaCl_2]\right\} \\ &= 3\,[CaCl_2] \end{aligned}$$

- Here, rectangular brackets [..] symbolize molar concentrations. Please note the stoichiometric factor 2 of Cl- in the second line.
- Based on this equation, a 0.5 molar $CaCl_2$ solution has an ionic strength of $I = 3 \times 0.5$ M = 1.5 M.
- Example: calculate ionic strength of resulting solution of mixing of 50 mL of 0.2 M KNO_3, 20 mL of 0.1 M K_2SO_4, and 30 mL of 0.05 M $Cu(NO_3)_2$ solution.

Total volume = 50 mL + 20 mL + 30 mL = 100 mL

New concentration of each electrolyte will be as follows

For $KNO_3 = N_2 = N_1V_1/V_2 = 50 \text{ x } 0.2/100 = 0.1$ M KNO_3 in 100 mL

For $K_2SO_4 = N_2 = N_1V_1/V_2 = 20 \text{ x } 0.1/100 = 0.02$ M K_2SO_4 in 100 mL

For $Cu(NO_3)_2 = N_2 = N_1V_1/V_2 = 30 \text{ x } 0.05/100 = 0.015$ M $Cu(NO_3)_2$ in 100 mL

μ or I for KNO_3 $I = \frac{1}{2}\sum_{i=1}^{n} c_i z_i^2$ $=\frac{1}{2}[\{(0.1) \text{ x } (+1)^2\} + \{(0.1) \text{ x } (-1)^2\}]$

$= \frac{1}{2}(0.1 + 0.1) = 0.1$ M

μ or I for K_2SO_4 $I = \frac{1}{2}\sum_{i=1}^{n} c_i z_i^2$ $= \frac{1}{2}[\{(2 \text{ x } 0.02) \text{ x } (+1)^2\} + \{(0.02) \text{ x } (-2)^2\}]$

$= \frac{1}{2}(0.04 + 0.08) = \frac{1}{2}(0.12) = 0.06$ M

μ or I for $Cu(NO_3)_2$ $I = \frac{1}{2}\sum_{i=1}^{n} c_i z_i^2$ $= \frac{1}{2}[\{(0.015) \text{ x } (+2)^2\} + \{2(0.015) \text{ x } (-1)^2\}]$

$= \frac{1}{2}(0.060 + 0.030) = \frac{1}{2}(0.090) = 0.045$ M

$I_{mix} = 0.1 + 0.06 + 0.045 = 0.205$ M

The ionic strength is an important parameter for the calculation of mean ionic activity co-efficient. The mean ionic activity co-efficient can be calculated using Debye-Huckel Theory.

The Debye-Huckle Theory

- The theory was proposed by Peter Debye and Erich Huckle in 1923.
- In non-electrolyte solutions, the intermolecular forces are mostly comprised of weak Van Der Wall's forces that have $1/r^2$ dependence.
- The properties of electrolyte solutions significantly deviate from the laws used to derive chemical potential of solutions.
- In electrolyte solutions, there are significant electrostatic interactions between solute-solute and solute-solvent molecules.
- This electrostatic interaction is governed by Coulomb's law and has $1/r^2$ dependence.
- The behaviour of electrolyte solution deviates considerable from that ideal solution.
- For that purpose, we utilize the activity of individual component rather than concentration to calculate the deviation from ideal solutions.
- The theory help to calculate mean ionic co-efficient ($\gamma_\pm$).
- This activity coefficient is used in the calculation of the pHs (saturation pH) but it can also be used to determine the minimum concentration of a dissolved element required to be in equilibrium with its solid (salt) element.
- The Debye-Huckle theory or Debye-Huckle limiting law is mainly dependent on following three assumptions.
    1. Electrolytes completely dissociates into ions.
    2. Solutions of electrolytes are very dilute.
    3. Each ion is surrounded by ions of the opposite charge.
- It is theoretical explanation for departures from ideality in solutions of electrolytes and plasmas.
- It is a linearized Poisson–Boltzmann model, which assumes an extremely simplified model of the electrolyte solution but nevertheless gave accurate predictions of mean activity coefficients for ions in dilute solution.
- The Debye-Hückel equation provides a starting point for modern treatments of non-ideality of electrolyte solutions.

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

$$\text{Now, } \frac{-1.824 \times 10^{6}}{(\in T)^{3/2}} = A$$

$$log\gamma_{\pm} = A \left|z_{+}z_{-}\right|\sqrt{I}$$

Where A is empirical parameter.

For Example: Consider a solution of 0.01 M $MgCl_2$ (aq) with an ionic strength of 0.030 M. what is the mean ionic co-efficient?

$$log\gamma_{\pm} = -0.509 \left|2 \times 1\right|\sqrt{0.030}$$
$$log\gamma_{\pm} = -1.018 \times 0.1732$$
$$log\gamma_{\pm} = -0.1763$$
$$\gamma_{\pm} = Antilog\ -0.1763$$
$$\gamma_{\pm} = 0.67$$

Activity and Activity Co-efficient of Solutions

- In case of electrolyte solutions activity and molar concentration are not same due to intermolecular interactions that results into large deviations from the ideal solutions.
- G. N. Lewis introduced the concept of ‘activity’ that can be used in place of molar concentration in case of electrolyte solutions.
- The activity of solution of a substance in given system may be defined as the product of its molar concentration and a certain factor called activity co-efficient.

$a = \gamma c$……………………………………………..[1]

Hence, $\gamma = a/c$……………………………………..[2]

Where γ is known as activity co-efficient. For non-ideal solutions it is just less than unity whilst in case of ideal solutions it is unity.

- The activity co-efficient may be regarded as the measure of extent to which an ion or molecule departs from the ideal behaviour. Since a represents the effective or ideal concentration while c represents calculated or expected concentration.
- Consider a univalent electrolyte of type BA (NaCl, KCl) whose ionisation can be represented as follows.

$$BA \rightleftharpoons B^+ + A^-$$

- The equilibrium constant (k) can be represented as follows.

$$k = \frac{[B^+][A^-]}{[BA]}$$

$$k = \frac{a_+a_-}{a_2}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots[3]$$

Where a_+ is the activity of cation B^+, a_- is the activity of anion A^-, and a_2 is the activity of undissociated electrolyte BA.

- The mean activity of the two ions ($a_\pm$) may be considered as the geometric mean of the activities of the respective ions.

$$a_\pm^{1+1} = a_\pm^2 = a_+^1\, a_-^1$$

$$a_\pm = \sqrt{a_+a_-}$$

$$a_\pm = (ka_2)^{½}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots[4]$$

The separate activity co-efficients for ions are as follows.

$$\gamma_+ = \frac{a_+}{c_+}\ and\ \gamma_- = \frac{a_-}{c_-}$$

The mean activity co-efficient for the two ions can be represented as the geometric mean of the activity co-efficients of the ions.

$$\gamma = \gamma_\pm = \sqrt{\gamma_+\gamma_-}$$

$$= \sqrt{\frac{a_+}{c_+}\frac{a_-}{c_-}} = \frac{a_\pm}{c_\pm}$$

$$\gamma = \gamma_\pm = \frac{\sqrt{ka_2}}{c}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots[5]$$

Where $c_\pm = c$

- In general, for an electrolyte which dissociates into ν+ and ν- we have

$B_{\nu+}A_{\nu-} \rightarrow {}_{\nu+}B^{+} + {}_{\nu-}A^{-}$

- If a+, a- and a_2 represent the activities of the cations, anions and undissociated electrolyte, respectively, then

$ka_2 = a_+^{\nu+} + a_-^{\nu-}$

the mean activity is then given as follows

$$a_\pm^{\nu_+\nu_-} = a_\pm^{\nu} = a_+^{\nu_+}\, a_-^{\nu_-}$$

$$a_\pm = \left(a_+^{\nu_+} a_-^{\nu_-}\right)^{1/(\nu_+ + \nu_-)}$$

$$a_\pm = \left(a_+^{\nu_+} a_-^{\nu_-}\right)^{1/\nu}$$

$$a_\pm = (ka_2)^{1/\nu} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots[6]$$

ν = total number of ions = $\nu_+ + \nu_-$

if the total concentration of the electrolyte is c then the activity co-efficient of the ions are

$$\gamma_+ = \frac{a_+}{\nu_+ c} \; and \; \gamma_- = \frac{a_-}{\nu_- c} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots[7]$$

The mean activity co-efficient of the electrolyte is given by

$$\gamma_\pm = \left(\gamma_+^{\nu_+} \gamma_-^{\nu_-}\right)^{1/\nu}$$

$$\gamma_\pm = \left[\left(\frac{a_+}{\nu_+ c}\right)^{\nu_+} \left(\frac{a_-}{\nu_- c}\right)^{\nu_-}\right]^{1/\nu}$$

$$\gamma_\pm = \left[\left(a_+{}^{\nu_+} a_-{}^{\nu_-}\right)^{1/\nu} / \left(\nu_+ c\right)^{\nu_+} \nu_- c^{\nu_-}\right)^{1/\nu}\right] \text{ from equation no. 7}$$

$$\gamma_\pm = \frac{a_\pm}{c_\pm} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots[8]$$

From equation 6 and 8

$$\gamma_\pm = \frac{(ka_2)^{1/\nu}}{c_\pm}$$

Convenient Standard State

- For gas and vapour, standard state is at very low pressure

$$\lim_{p\to 0} \frac{a}{p} \to 1$$

At very low pressure a/p → 0 hence $\gamma \to 1$.

- For pure solid and liquid, at given temperature and 1 atm pressure if activity is unity then it is standard state.
- For solvent in solution: if mole fraction of solvent is denoted as x_1 then standard state for solvent is as follows.

$$\lim_{x_1\to 1} \gamma = 1$$

- For solute in solution: it has no physical significance.

I have work hard preparing this material……

You also work hard preparing from this material!!!!

Best Luck….