

### ✓ 9.20 DEBYE-HUCKEL LIMITING LAW

One of the most significant contributions to our understanding of the behavior of electrolyte solutions is the Debye-Huckel limiting law. Debye and Huckel (1923) derived an equation which offers quantitative calculation of mean activity coefficients of strong electrolytes. The values obtained theoretically were in good agreement with the experimental values as long as the concentrations are kept low. The equation which they derived is known as Limiting Law equation. The name signifies that its application is limited to dilute solutions of strong electrolytes only. This limiting law is based on the following assumptions:

- (i) Electrolytes are completely dissociated into ions in solution.
- (ii) The solutions are dilute, with a concentration of 0.01m or lower.
- (iii) The interactions between ions of solute are electrostatic in character. Electrostatic forces are strictly long rang interactions.
- (iv) The ions in the solution are subject to random thermal motion which disrupts the orientation of oppositely charged species caused by the interionic attractions.
- (v) Each ion is regarded as point charge and is surrounded by ions of opposite charge, forming an ionic atmosphere.
- (vi) The dielectric constant of an electrolyte solution is uniform and independent of the actual concentration of the dissolved solute.

The energy associated with the ionic atmosphere is electrical in origin. It therefore, must be a function of charge density and the potential produced by the ionic atmosphere. According to Debye-Huckel theory the energy of ionic interaction is electrostatic in origin and may be defined as the energy of charging a central ion in the electric field of an ionic cloud.

The energy of a charged body, that is the work expended in the process of charging, is half the product of its charge and potential. Hence for an ion of charge  $+Z_i e$  the energy it possesses by virtue of its ionic atmosphere is given as

$$E_i = \frac{1}{2} (\text{charge}) (\text{potential})$$

$$E_i = \frac{1}{2} (Z_i e) \left( \frac{-Z_i e k}{D} \right)$$

$$E_i = - \frac{Z_i^2 e^2 k}{2D}$$

The corresponding energy for a 1 g ion is obtained on multiplying by the Avogadro number,  $N$ , so that

$$E_i = - \frac{N Z_i^2 e^2 K}{2D} \quad (9.74)$$

According to the definition of chemical potential the chemical potential of a particular ion in an ideal solution is given by

$$\mu_i = \mu_i^0 + RT \ln x_i \quad (9.75)$$

When  $x_i$  is mole fraction in the given solution. For a non-ideal solution one can write

$$\begin{aligned} \mu_i &= \mu_i^0 + RT \ln a_i \\ \mu_i &= \mu_i^0 + RT \ln \alpha x_i + RT \ln \gamma_i \quad (\because a_i = \gamma_i x_i) \end{aligned} \quad (9.76)$$

Where  $a_i$  is the activity and  $\gamma_i$  the activity coefficient of ionic species. The difference between Eqs (9.75) and (9.76) is  $RT \ln \gamma_i$  which is equal to the difference in free energy change accompanying the addition or removal of 1g ion of the given species from a large volume of real and ideal solution respectively. This difference of free energy may be regarded as, equivalent to the electrical energy of the ion due to its atmosphere; that is to say, the departure from ideal behavior is ascribed entirely to interionic forces. Hence Eq. (9.74) became as.

$$\begin{aligned} RT \ln \gamma_i &= -\frac{NZ_i^2 \epsilon^2 k}{2D} \\ \ln \gamma_i &= -\frac{NZ_i^2 \epsilon^2 k}{2DRT} \end{aligned} \quad (9.77)$$

From Eq. (9.38), we know

$$\begin{aligned} k &= \left( \frac{4\pi \epsilon^2 \sum n_i Z_i^2}{DkT} \right)^{1/2} \\ \text{or } k &= \frac{2\epsilon(\pi)^{1/2} (\sum n_i Z_i^2)^{1/2}}{(DkT)^{1/2}} \end{aligned}$$

Where  $n_i$  is the number of ions per ml. It may be replaced by  $NC_i/1000$ , where  $C_i$  is the number of gram ions dissolved per liter,  $k$  is the Boltzmann constant,

$$k = \frac{R}{N}$$

$$\begin{aligned} k &= \frac{2\epsilon(\pi)^{1/2} \left( \sum \frac{NC_i}{1000} Z_i^2 \right)^{1/2}}{\left( \frac{DRT}{N} \right)^{1/2}} \\ k &= \frac{2\epsilon \left( \frac{\pi}{1000} \right)^{1/2} (N)^{1/2} (\sum C_i Z_i^2)^{1/2}}{\left( \frac{DRT}{N} \right)^{1/2}} \end{aligned}$$

$$k = \frac{2 \epsilon \left( \frac{\pi}{1000} \right)^{1/2} N \left( \sum C_i Z_i^2 \right)^{1/2}}{(DRT)^{1/2}} \quad (9.68)$$

Substituting this value of  $K$  into Eq. (9.77), we get

$$\ln \gamma_i = \frac{-NZ_i^2 \epsilon^2}{2 DRT} \cdot \frac{2 \epsilon \left( \frac{\pi}{1000} \right)^{1/2} N \left( \sum C_i Z_i^2 \right)^{1/2}}{(DRT)^{1/2}}$$

Multiplying both sides by negative and on rearranging we get

$$-\ln \gamma_i = \frac{N^2 Z_i^2 \epsilon^3}{DRT} \cdot \frac{\left( \frac{\pi}{1000} \right)^{1/2} \left( \sum C_i Z_i^2 \right)^{1/2}}{(DRT)^{1/2}}$$

$$-\log \gamma_i = \frac{N^2 \epsilon^3 \left( \frac{\pi}{1000} \right)^{1/2}}{2.303 R^{3/2}} \cdot \frac{Z_i^2 \left( \sum C_i Z_i^2 \right)^{1/2}}{(DT)^{3/2}} \quad (9.79)$$

The term in the large parentheses consists of several constants, only and may be replaced by  $A'$ .

$$-\log \gamma_i = \frac{A' Z_i^2 \sqrt{\sum C_i Z_i^2}}{(DT)^{3/2}} \quad (9.80)$$

Further, we know that

$$\mu = \frac{1}{2} \sum C_i Z_i^2$$

$$2\mu = \sum C_i Z_i^2 \quad (9.81)$$

Substituting the value of  $\sum C_i Z_i^2$  from Eq. (9.81) into Eq. (9.80) we get

$$-\log \gamma_i = \frac{A' Z_i^2 \sqrt{2\mu}}{(DT)^{3/2}}$$

$$-\log \gamma_i = \frac{A' \sqrt{2} Z_i^2 \sqrt{\mu}}{(DT)^{3/2}}$$

$$-\log \gamma_i = \frac{A'' Z_i^2 \sqrt{\mu}}{(DT)^{3/2}} \quad (9.82)$$

For a given solvent and temperature,  $D$  and  $T$  have definite values which may be inserted into Eq. (9.82) to give

$$\log \gamma_i = -A Z_i^2 \sqrt{\mu} \quad (9.83)$$

By inserting the values of  $N$ ,  $E$ ,  $\pi$ ,  $R$ ,  $D$ , and  $T$ , the value of  $A$  is found to be 0.509 at 25°C, hence

$$-\log \gamma_i = 0.509 Z_i^2 \sqrt{\mu} \quad (9.84)$$

Eqs. (9.83) and (9.84) represent the Debye-Huckel limiting law. This expresses the variation of the activity coefficient of an ion with the ionic strength of the solution. It is expected to hold for dilute solutions of electrolytes as is clear from the fact that the expression for the potential of an ion due to ionic atmosphere was derived assuming dilution being approached. Moreover, from Eq. (9.84). It follows that activity coefficient of an ion should decrease with increasing ionic strength of the solution.

Since the individual activity or activity coefficient, of an ion cannot be determined experimentally, it is not possible to make direct test of Eq. (9.83). However, it is possible to relate the individual ion activities to the measurable mean activities of the ions. If one molecule of a binary electrolyte dissociates into  $V$  ions, of which  $V_+$  are cations and  $V_-$  anions, then the mean activity coefficient is related to individual ionic activity coefficient  $\gamma_+$  and  $\gamma_-$  by

$$\begin{aligned} \gamma_{\pm} &= (\gamma_+^{v_+} \gamma_-^{v_-})^{1/v} \\ \log \gamma_{\pm} &= \frac{1}{v} \log (\gamma_+^{v_+} \gamma_-^{v_-}) \\ &= \frac{1}{v} [\log \gamma_+^{v_+} + \log \gamma_-^{v_-}] \\ &= \frac{1}{v} [V_+ \log \gamma_+ + V_- \log \gamma_-] \end{aligned} \quad (9.58)$$

If the valences of the ions are  $Z_+$  and  $Z_-$  respectively, then by the relationship between the value and the number of ions, i.e.,  $V_+ Z_+ = V_- Z_-$ , it follows that

$$\frac{V_+}{V_-} = \frac{Z_-}{Z_+}$$

$$\log \gamma_{\pm} = \frac{1}{v_+ + v_-} [Z_- \log \gamma_+ + Z_+ \log \gamma_-]$$

$$\log \gamma_{\pm} = \frac{1}{v_+ + v_-} [Z_- (-AZ_+^2 \sqrt{\mu}) + Z_+ (-AZ_-^2 \sqrt{\mu})]$$

$$\log \gamma_{\pm} = -\frac{AZ_+ Z_- \sqrt{\mu} (Z_+ + Z_-)}{Z_- + Z_+}$$

$$\log \gamma_{\pm} = -A Z_+ Z_- \sqrt{\mu} \quad (9.86)$$

Equation (9.86) also represents the Debye-Huckel limiting law for dilute solutions. According to this law the deviation from the ideal behavior in a given solvent is governed by the ionic strength of the medium and valence of the ions of electrolyte, but is independent of their chemical nature.

### Verification of the Debye-Huckel Limiting Law

The mean activity coefficients of various electrolytes can be determined experimentally by a number of methods, e.g. measurement of vapour pressure, freezing point, solubility or electromotive force. In general, it is found that the mean activity coefficient of an electrolyte decreases with increasing concentration, but at higher concentration range it is frequently found that the mean activity coefficient increases with increasing concentration, thus passing through a minimum.

The law can be tested by plotting a graph between  $-\log \gamma_{\pm}$  and  $\sqrt{\mu}$ , at room temperature. All electrolytes should give a straight line passing through the origin. The slope of the line depends on  $Z_+$  and  $Z_-$  values of the given electrolytes. For electrolytes this slope should be  $A$ , for 1-2 or 2-1 type electrolytes  $2A$  for 1-3 or 3-1 electrolytes  $3A$  etc.

**Example 9.7.** Calculate the mean activity coefficient of (i) a 1-1 electrolyte, e.g., NaCl at a molality of 0.01 and of (ii) 1-2 electrolyte, e.g.,  $\text{Na}_2\text{SO}_4$  at a molality of 0.001 in aqueous solution of 25°C.

#### Solution:

- (i) For 1-1 electrolyte, the ionic strength is equal to its molality, hence  $\mu = 0.01$ ,  $Z_+ = Z_- = 1$ , so

$$\log \gamma_{\pm} = -0.509 \times 1 \times 1 \sqrt{0.01}$$

$$\log \gamma_{\pm} = -0.0509$$

$$\gamma_{\pm} = -0.889$$

- (ii) For 0.001 molal 1-2 electrolyte.

$$\mu = \frac{1}{2} (0.002 \times 1^2 + 0.001 \times 2^2)$$

$$\mu = 0.003$$

$$\log \gamma_{\pm} = -0.509 \times 1 \times 2 \sqrt{0.003}$$

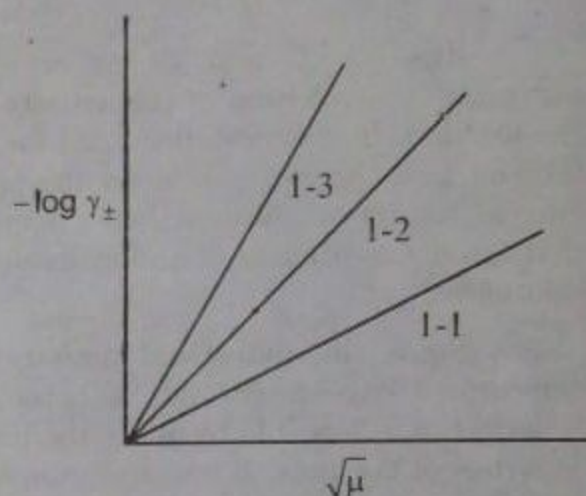


Fig. 9.7. Test of Debye-Huckel limiting law for different electrolytes.