

MODULE -I

CHAPTER 1 - INTRODUCTION TO ELECTROCHEMICAL SYSTEMS

LEARNING OBJECTIVES

After reading this chapter, you will be able to identify

- (i) the various facets of Electrochemistry
- (ii) the interdisciplinary nature of Electrochemistry
- (iii) the unique status of Electrochemistry
- (iv) the importance of concepts of Electrochemistry in other fields

The field of Electrochemistry has witnessed rapid progress during the past few decades, especially because of its growing importance in other engineering disciplines as well as all branches of science. It is hence no wonder that any modern text book on electrochemistry will hardly cater to everyone, irrespective of the branch of specialization.

As Table 1 indicates, a text book covering all aspects of Electrochemistry is rendered almost impossible. Hence in this entire module, a few topics of Table 1 will be discussed in detail and other topics will be mentioned in passing.

Ionics

The incorporation of interionic interactions in a solvent medium is customarily designated as ionics in Electrochemistry. The various sub-topics covered in the ionics are Debye - Huckel limiting law and extensions, Conductivity of electrolyte solutions and its applications.

Thermodynamics of electrochemical systems

The construction of electrochemical cells and applications of Nernst equation will be indicated with examples. The liquid junction potentials in concentration cells as well as Donnan membrane equilibrium will be analyzed.

Electrodictics

The kinetics of electrochemical reactions encompasses the classical Butler Volmer equations and various special cases such as Ohm's law and Tafel equations. These lead to a complete analysis of corrosion, electro deposition and electrochemical energy storage devices.

Electroanalytical Chemistry

The polarographic and amperometric techniques play a crucial role in recent developments of biosensors. These along with the differential pulse voltammetry will be discussed.

Energy storage devices

The relevance of ionics and electrodictics as regards the study of batteries, fuel cells and supercapcitors will be indicated. A few common fuel cells will be discussed in detail.

Steady state and transient electrochemical techniques

There exist a variety of electrochemical experimental techniques and the choice of the technique depends upon the needs; however, a common feature underlying all the electrochemical experiments is that the desired relation involves two of the four variables viz current, potential, time, concentration. While the steady state experiments pertain to the system behavior as $t \rightarrow \infty$, the transient experiments provide the dynamical behavior.

WORKED OUT EXAMPLES

1. How does the information on inter – ionic interactions help in the construction of electrochemical cells?

In Nernst equation for cell reactions, the activities of the reactants and products occur explicitly and hence their accurate values are required for estimating electrode potentials.

2. What is the importance of Faraday's laws in kinetics of electrochemical reactions?

Faraday's law provides the maximum amount for a species that can be deposited or dissolved for a chosen charge while a study of the kinetics of electrochemical reactions gives the actual amount and faradic efficiency of the process.

3. Which electrochemical experiments can be employed for qualitative and quantitative analysis?

Polarography was the first electroanalytical technique for qualitative and quantitative analysis of inorganic as well as organic compounds; subsequently several other techniques such as amperometry, differential pulse voltammetry etc are being employed extensively during the past few decades.

4. Distinguish between galvanic and electrolytic cells

In Galvanic cells, chemical energy is converted into electrical energy. Batteries, fuel cells etc are examples of Galvanic cells. Several industrial electrochemical

processes make use of electrolysis where electrical energy is used as an input to produce desired products. Kolbe synthesis, Hall – Heroult processes are two examples of industrially important electrochemical processes.

EXERCISES

1. Why do reference electrodes become un-avoidable in electrochemical measurements?
2. Distinguish between metallic and electrolytic conductances.
3. Which thermodynamic properties can be estimated from the experimental data on electrochemical cells?

SUMMARY

An overview of Electrochemical Science and Technology has been provided. The thermodynamics of electrolytes comprises analysis of ion-ion interactions in a dipolar solvent and Debye-Hückel theory provides a method of computing the activity coefficients. The construction of electrochemical cells leads to the prediction of the feasibility of chemical reactions. The study of electrode kinetics has been demonstrated to be important in various energy storage devices. Different types of electrochemical experiments have been indicated.

CHAPTER 2 - THERMODYNAMICS OF ELECTROLYTE SOLUTIONS – ACTIVITY COEFFICIENTS AND IONIC STRENGTHS

LEARNING OBJECTIVES

After reading this chapter, you will be able to

- (i) comprehend the concept of activity coefficients and ionic strengths of electrolytes
 - (ii) estimate the mean ionic activity coefficients of electrolytes
- and
- (iii) relate the mean ionic activity coefficients to individual ionic contributions

MEAN IONIC ACTIVITIES AND MEAN IONIC ACTIVITY COEFFICIENTS

In the case of concentrated solutions, the properties of ionic species are affected on account of its interactions with other ions sterically and electrostatically. Hence the molar concentration is often an unsuitable parameter. Therefore, what is required is a parameter, related to the number density of ions, but which expresses more realistically the interactions between ions. This parameter is known as activity (a_i) and is related to concentration by γ_i the simple relationship $a_i = \gamma_i c_i$ and γ_i is known as the activity coefficient which has different forms depending upon the manner in which concentration is expressed viz molarity (M) or molality (m) or mole fraction (x). The chemical potential of the electrolyte can be written in any of the following forms:

$$\mu_i = \mu_{i_c}^\circ + RT \ln c_i \gamma_c \quad (\text{molarity scale}) \quad (1)$$

$$\mu_i = \mu_{i_m}^\circ + RT \ln m_i \gamma_m \quad (\text{molality scale}) \quad (2)$$

$$\mu_i = \mu_{i_x}^\circ + RT \ln x_i \gamma_x \quad (\text{mole fraction scale}) \quad (3)$$

where the term within 'ln' is a_i , the ionic activity.

As is well known, any property of a specific type of ion cannot be experimentally measured. It is therefore only possible to employ activity or activity coefficient of an electrolyte which takes into account both anions and cations.

The following notations are required

γ_{\pm} = mean ionic activity coefficient

a_{\pm} = Mean ionic activity

m_{\pm} = Mean molality

m_+ = Molality of cations

m_- = Molality of anions

ν_+ = Stoichiometric number of cations

ν_- = Stoichiometric number of anions

ν = Total Stoichiometric number = $\nu_+ + \nu_-$

The mean ionic parameters are as follows

$$\gamma_{\pm}^{\nu} = \gamma_+^{\nu_+} \gamma_-^{\nu_-} \quad (4)$$

$$a_{\pm}^{\nu} = (a_+^{\nu_+} a_-^{\nu_-}) \quad (5)$$

$$m_{\pm}^{\nu} = m_+^{\nu_+} \cdot m_-^{\nu_-} \quad (6)$$

These equations indicate that $\gamma_{\pm} a_{\pm}$ and m_{\pm} are geometric means of the individual ionic quantities.

In terms of the molality of the electrolyte,

$$m_+ = v_+ m \text{ and } m_- = v_- m$$

Hence the mean ionic molality m_{\pm} is,

$$m_{\pm}^v = (v_+ m)^{v_+} (v_- m)^{v_-}$$

$$\text{or } m_{\pm} = (v_+^{v_+} v_-^{v_-})^{\frac{1}{v}} m$$

We shall demonstrate how the above equations arise by considering the chemical potentials of the electrolytes.

Thermodynamics of Equilibria in electrolytes

Consider the dissociation of a salt represented as $M_{v_+} A_{v_-}$ viz.

$$\mu_{M^+} = v_+ (\mu_+^0 + RT \ln a_+) \quad (7)$$

$$\mu_{A^-} = v_- (\mu_-^0 + RT \ln a_-) \quad (8)$$

If μ_2 is chemical potential of the undissociated electrolyte and μ_2^0 is its chemical potential in the standard state, $\mu_2 = \mu_2^0 + RT \ln a_2$. Hence

$$\mu_2^0 = v_+ \mu_+^0 + v_- \mu_-^0 \quad (9)$$

i.e.

$$\mu_2 = v_+ (\mu_+^0 + RT \ln a_+) + v_- (\mu_-^0 + RT \ln a_-) = \mu_2^0 + RT \ln a_2$$

$$\text{or } \ln a_2 = \nu_+ \ln a_+ + \nu_- \ln a_-$$

$$\text{or } a_2 = a_+^{\nu_+} a_-^{\nu_-} \quad (10)$$

The activity of the electrolyte a_2 is given in terms of the individual ionic activities.

If the stoichiometric number is represented as ν , then $\nu = \nu_+ + \nu_-$; the activity of the electrolyte, $a_2 = (a_+^{\nu_+}) \cdot (a_-^{\nu_-}) = a_{\pm}^{(\nu_+ + \nu_-)} = a_{\pm}^{\nu}$,

Thus,

$$a_{\pm} = a_2^{1/\nu} = (a_+^{\nu_+} \cdot a_-^{\nu_-})^{1/\nu} \quad (11)$$

The activity of each ion can be expressed in terms of its activity coefficient and molal concentration. For example, $a_+ = m_+ \gamma_+$ and $a_- = m_- \gamma_-$.

$$\therefore a_2 = (m_+ \gamma_+)^{\nu_+} \cdot (m_- \gamma_-)^{\nu_-}$$

$$\text{and } a_{\pm} = (\gamma_+^{\nu_+} \cdot \gamma_-^{\nu_-})^{1/\nu} \quad (12)$$

If 'm' is the molality of the electrolyte, then $m_+ = \nu_+ m$ and $m_- = \nu_- m$

$$\therefore a_2 = (\nu_+ m \gamma_+)^{\nu_+} (\nu_- m \gamma_-)^{\nu_-}$$

$$\text{or } a_2 = (\nu_+^{\nu_+} \cdot \nu_-^{\nu_-}) (m \gamma_{\pm})^{\nu_+ + \nu_-} \quad (13)$$

$$m_{\pm} = (m_+^{\nu_+} \cdot m_-^{\nu_-})^{1/\nu} = (\nu_+^{\nu_+} \cdot \nu_-^{\nu_-})^{1/\nu} m \quad (14)$$

since $m_+ = \gamma_+ m$ and $m_- = \gamma_- m$. In general, the mean concentration c_{\pm} is

$$c_{\pm} = (c_+^{\nu_+} \cdot c_-^{\nu_-})^{1/\nu} \quad (15)$$

We rewrite the above equation for clarity:

$$a_{\pm} = \gamma_{\pm} m_{\pm} \quad (16)$$

$$a_{\pm} = (a_+^{v_+} a_-^{v_-})^{1/v} = a_{\pm}^{1/v} \quad (17)$$

$$\gamma_{\pm} = (\gamma_+^{v_+} \gamma_-^{v_-})^{1/v} \quad (18)$$

$$m_{\pm} = (m_+^{v_+} m_-^{v_-})^{1/v} = m (v_+^{v_+} v_-^{v_-})^{1/v} \quad (19)$$

TABLE 1: Mean ionic activity and activity coefficients of various electrolytes

Electrolyte	γ_{\pm}	$a_{\pm} = (c_{\pm} \cdot \gamma_{\pm})^v$
NaCl	$(\gamma_+ \gamma_-)^{1/2}$	$c^2 \gamma_{\pm}^2$
Na ₂ SO ₄	$(\gamma_+^2 \gamma_-)^{1/3}$	$4 c^3 \gamma_{\pm}^3$
CaCl ₂	$(\gamma_+ \gamma_-^2)^{1/3}$	$4 c^3 \gamma_{\pm}^3$
LaCl ₃	$(\gamma_+ \gamma_-^3)^{1/4}$	$27 c^4 \gamma_{\pm}^4$
Al ₂ (SO ₄) ₂	$(\gamma_+^2 \gamma_-^3)^{1/5}$	$108 c^5 \gamma_{\pm}^5$

Determination of Activity Coefficients

A number of diverse experimental methods have been employed for estimating the activity coefficients of solutes (electrolytes) in a chosen solvent. Among them, the following methods deserve mention:

1. depression of freezing point
2. elevation of boiling point
3. lowering of vapor pressure
4. measuring cell potentials

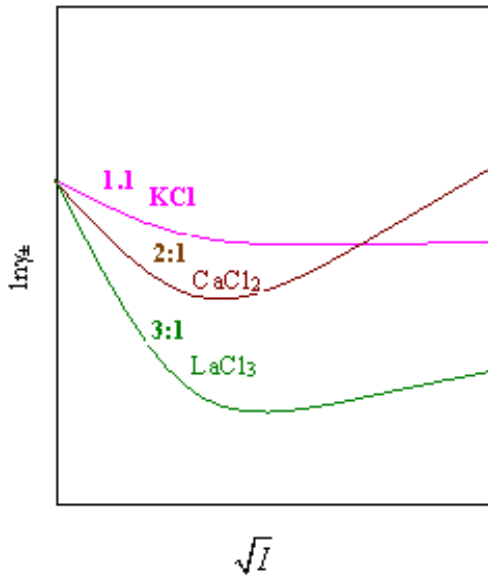


Fig 1: Schematic variation of $\log \gamma_{\pm}$ with square root of the ionic strength for different electrolytes

Fig 1 provides the dependence of the mean ionic activity coefficient on the ionic strength.

The semi-quantitative interpretation of Fig 1 lies in the classical Debye – Hückel theory of electrolytes according to which $\log \gamma_{\pm}$ is in \sqrt{I} where I denotes the ionic strength.

Thermodynamic interpretation of the activity

The excess Gibbs free energy of a system is defined as

$$G^E(T,P,x_i) = G^{\text{actual}}(T,P,x_i) - G^{\text{ideal}}(T,P,x_i)$$

where the first term on the r.h.s is the actual Gibbs free energy while the second term denotes the Gibbs free energy of the ideal system. The excess chemical potential μ_i^{excess} also follows from the above as

$$\mu_i^{\text{excess}} = \left(\frac{\partial G^E}{\partial n_i} \right)_{T,P,n_j(j \neq i)} \quad (20)$$

The excess chemical potential is indicative of the deviation from ideality. Hence

μ_i^{excess} can be written as

$$\mu_i^{\text{excess}} = RT \ln \gamma_i$$

Thus

$$\ln \gamma_i = \frac{1}{RT} \left(\frac{\partial G^E}{\partial n_i} \right)_{T,P,n_j(j \neq i)} \quad (21)$$

Ionic Strength: In this context, it is customary to define a quantity called ‘ionic strength’ as

$$I = \frac{1}{2} \sum_{i=1}^n c_i z_i^2 \quad (22)$$

where c_i is the concentration of ions in the molar scale. The summation includes all the ions present in the electrolytes. This quantity was originally defined by Lewis and Randall in 1921 and has since been extensively employed in the theory of electrolyte solutions. Let one may think that the above equation applies to only strong electrolytes, we hasten to add that the concept of ionic strength holds good

even for weak electrolytes such as acetic acid, formic acid etc. In the latter, we need to include the degree of dissociation while writing the molar concentrations.

Temperature dependence of the ionic activity

The chemical potential of a solute in the molality scale is

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad (23)$$

$$\frac{\mu_i}{T} = \frac{\mu_i^\circ}{T} + RT \ln a_i$$

However, $\frac{\partial(\mu_i/T)}{\partial T} = -\frac{H_m}{T^2}$ according to Clausius – Clapyron equation

where H_m denotes the partial molar enthalpy

$$\text{Hence, } R \left(\frac{\ln a_i}{\partial T} \right)_P = -\frac{H_m}{T^2} + \frac{H_m^\circ}{T^2}$$

$$\text{ie. } \left(\frac{\ln a_i}{\partial T} \right)_P = \frac{(H_m^\circ - H_m)}{RT^2} \quad (24)$$

where H_m° refer to the partial molar enthalpy in the standard state

Table 2: Mean Ionic activity coefficient of HCl at different molalities

Molality of HCl	γ_{\pm}
0.0005	0.98
0.0904	0.01
0.830	0.05
0.757	0.5
0.809	1.0

we note from the Table that the activity coefficient tends to unity for very dilute solutions.

TABLE 2: The dependence of the mean ionic activity coefficient on molality

m	γ_{\pm}	
	0.05	0.1
KCl	0.815	0.769
H ₂ SO ₄	0.34	0.265
CuSO ₄	0.21	0.16
La(NO ₃) ₃	0.39	0.33
In ₂ (SO ₄) ₃	0.054	0.035
Ca(NO ₃) ₂	0.54	0.48
MgSO ₄	0.22	0.18

TABLE 3: Ionic strengths of 1M salt solutions for different M_{v+} A_{v-} electrolytes

Salt	Type	Ionic Strength
NaCl	1:1	$\frac{1}{2} (1+1) = 1$
K ₂ SO ₄	1:2	$\frac{1}{2} (4+2) = 3$
MgSO ₄	2:2	$\frac{1}{2} (4+4) = 4$

K_3PO_4	1:3	$\frac{1}{2} (9+3) = 6$
$K_4[Fe(CN)_6]$	1:4	$\frac{1}{2} (16+4) = 10$
$La_3(PO_4)_3$	3:3	$\frac{1}{2} (9+9) = 9$

WORKED OUT EXAMPLES

1. Write the expressions for mean ionic activity for 1:1 and 1:2 electrolytes.

(a) 1:1 Electrolyte

$$v_+ = 1; v_- = 1 \therefore v = 2$$

$$m_{\pm} = (v_+^{v_+} \cdot v_-^{v_-})^{1/v} m = m$$

$$\text{or } m_{\pm} = m$$

$$a = (a_{\pm})^v = (v_+^{v_+} \cdot v_-^{v_-}) (m\gamma_{\pm})^{v_+ + v_-}$$

$$\text{or } a = a_{\pm}^2 = (m\gamma_{\pm})^2$$

$$\text{or } a_{\pm} = m\gamma_{\pm}$$

(b) 1:2 Electrolyte

$$v_+ = 2; v_- = 1 \therefore v = 3$$

$$\therefore m_{\pm} = (v_+^{v_+} \cdot v_-^{v_-})^{1/v} m = 4^{1/3} m$$

$$\text{or } m_{\pm} = 1.587 m$$

$$a = (a_{\pm})^3 = (2^2 \cdot 1^1) (m\gamma_{\pm})^3 = 4(m\gamma_{\pm})^3$$

$$\therefore a_{\pm} = (m\gamma_{\pm}) 4^{1/3}$$

2. Calculate (i) mean molality and (ii) ionic strength of 0.05 molar solution of $Mg(NO_3)_2$.

$$(i) m_{\pm} = m(v_+^{v_+} + v_-^{v_-})^{1/v}$$

$$v = v_+ + v_- = 3$$

$$= 0.05 (2^2 \cdot 1)^{1/3}$$

$$= 0.0794$$

$$(ii) \text{ Ionic strength, } I = \frac{1}{2} \sum c_i z_i^2 = \frac{1}{2} [0.05 \times 4 \times 0.05 \times 1] = 0.125$$

3. Write the expressions for γ_{\pm} , m_{\pm} and a_2 for a general $v_+ : v_-$ electrolyte.

$$\text{Mean ionic activity coefficient} = \gamma_{\pm} = (\gamma_+^{v_+} \gamma_-^{v_-})^{1/v} \quad (18)$$

$$\text{Mean molality } m_{\pm} = m(v_+^{v_+} v_-^{v_-})^{1/v} \quad (19)$$

$$\text{Activity of the electrolyte } a_2 = a_{\pm}^v \quad (17)$$

4. What is the ionic strength of the solution containing 1 mol dm⁻³ H₂SO₄, 0.1 mol dm⁻³ Al₂(SO₄)₃ and 0.2 mol dm⁻³ K₂SO₄?

$$\begin{aligned} I &= \frac{1}{2} \sum c_i z_i^2 \\ &= \frac{1}{2} \left[c_{\text{H}^+} z_{\text{H}^+}^2 + c_{\text{SO}_4^{2-}} z_{\text{SO}_4^{2-}}^2 + c_{\text{Al}^{3+}} z_{\text{Al}^{3+}}^2 + c_{\text{Na}^+} z_{\text{Na}^+}^2 \right] \\ &= \frac{1}{2} [2 \times 1 + 1 \times 4 + 0.2 \times 9 + 0.3 \times 4 + 0.4 \times 1 + 0.2 \times 4] = 5.1 \end{aligned}$$

5. The mean ionic activity coefficient of 1 mol are H₂SO₄ is 0.265. Estimate the activity of H₂SO₄.

$$a_2 = a_+^{v_+} a_-^{v_-}$$

$$m_{\pm} = m \left(v_{+}^{v_{+}} v_{-}^{v_{-}} \right)^{1/v}$$

$$= 0.1 (1 \times 4)^{1/3}$$

$$= 0.1587$$

$$a_{\pm} = m_{\pm} \gamma_{\pm}$$

$$= 0.265 \times 0.1587$$

$$= 0.0420$$

$$a_2 = (a_{\pm})^v$$

$$a_2 = 0.0420 \times (0.042)^2$$

$$= 7.42 \times 10^{-5}$$

6. Write the activity coefficients for (a) 1:1 (b) 3:1 (c) 3:2 electrolytes in terms of the individual ionic activities.

$$\text{For } A_{v_{+}} B_{v_{-}} = v_{+} A^{z_{+}} + v_{-} B^{z_{-}}$$

$$a_2 = (a_{+})^{v_{+}} (a_{-})^{v_{-}}$$

Hence

$$\text{(a) 1:1 electrolytes: } a_2 = (a_{+}) (a_{-})$$

$$\text{(b) 3:1 electrolytes : } a_2 = (a_{+})^3 (a_{-})$$

$$\text{(c) 3:2 electrolytes : } a_2 = (a_{+})^3 (a_{-})^2$$

7. Write the general expression for the osmotic coefficient in the Debye – Hückel approximation.

$$1 - \phi = 3A_{D-H} |Z_{+} Z_{-}| \sqrt{I}$$

where ϕ is the osmotic coefficient and A_{D-H} refers to the constant in the Debye – Hückel limiting law.

8. Estimate the ionic strength of a solution containing HCl (molarity 0.005) as well as CaCl₂ (molarity 0.002) at 298 K.

$$I = \frac{1}{2} (0.005 \times 1^2 + 0.002 \times 2^2 + 0.004 \times 1^2) = 0.011 \text{ molar}$$

9. Write the physical significance of the activity coefficients.

The activity coefficient arises as the proportionality constant between ionic activity and concentration viz.

$$a = \gamma_{\text{molal}} m \text{ (molality scale, } m \text{ in mol kg}^{-1}\text{)}$$

$$a = \gamma_{\text{molar}} M \text{ (molarity scale, } m \text{ in mol dm}^{-3}\text{)}$$

If $\gamma \rightarrow 1$ the activity and molality /molarity become identical.

10. Calculate γ_{\pm} an aqueous 1.0 m acetic acid a weak monobasic acid whose dissociation constant is 1.75×10^{-5} .

$$K_{dis} = \frac{(a_{H^+})(a_{CH_3COO^-})}{a_{CH_3COOH}} = \frac{(m_{H^+} m_{CH_3COO^-})}{m_{CH_3COOH}} \frac{\gamma_{\pm}^2}{\gamma_{CH_3COOH}}$$

Since γ_{CH_3COOH} can be assumed as unity and $\gamma_{\pm} \ll 1$ can be assumed as unity.

$$K_{dis} = \frac{(m_{H^+} m_{CH_3COO^-}) \gamma_{\pm}^2}{\gamma_{CH_3COOH}} = \frac{\alpha^2 c}{1 - \alpha} = 1.75 \times 10^{-5}$$

$$\alpha = 0.0042$$

EXERCISES

1. Calculate the mean molality of 0.2 m $Al_2(SO_4)_3$.
2. Estimate γ_{\pm} for 0.001 M solution of Na_2SO_4 at 25°C.
3. Determine the approximate cationic and anionic activities for 0.1M $CaCl_2$ at 298K
if $\gamma_+ = 0.078$ and $\gamma_- = 0.33$
4. For 0.002 m $CaCl_2$ solution, calculate $\gamma_{Ca^{2+}}$ and γ_{Cl^-} .
5. The mean ionic activity coefficient $\gamma_{\pm} = 0.265$ for 0.1 M H_2SO_4 . Calculate the activity of H_2SO_4 .
6. The solubility of TlBr in H_2O at 25°C is 1.4×10^{-5} M while the solubility is 2×10^{-2} M in 0.1M KNO_3 . Calculate γ_{\pm} of TlBr.
7. Calculate the activity of the electrolyte and the mean activity of the ions in 0.1 molal solutions of (a) KCl ; (b) H_2SO_4 , (c) $CuSO_4$ (d) $La(NO_3)_3$ and (e) $In_2(SO_4)_3$
8. Calculate the mean ionic molality, m_{\pm} in 0.05 molal solutions of $Ca(NO_3)_3$, $NaOH$ and $MgSO_4$. What is the ionic strength of each of the above solutions?
9. Write the expression for activities of $NaCl$, $CaCl_2$, $CuSO_4$, $LaCl$ in terms of molality.
10. Calculate the ionic strength of 0.01 M acetic acid if the dissociation constant of the acid is 1.8×10^{-5} .
11. Write the expression for the chemical potential of a weak electrolyte.
12. Write the expression for the activity of an ionic species in terms of the appropriate Gibbs free energies.

SUMMARY

The estimation of activity coefficients and ionic strength for diverse types of electrolytes has been illustrated. The importance of the concept of activity coefficients has been pointed out.

CHAPTER 3: DEBYE – HÜCKEL THEORY AND ITS EXTENSIONS

LEARNING OBJECTIVES

After reading this chapter, you will be able to

- (i) derive the Debye – Hückel limiting law for mean ionic activity coefficients
- (ii) analyse the limitations of the Debye – Hückel theory

and

- (iii) calculate the activity coefficients for dilute electrolyte solutions

The theory of electrolyte solutions has a chequered history in so far as it is considered as an ‘impossible’ problem to solve. The difficulties encountered in

developing equilibrium theory of electrolyte solutions so as to compute thermodynamic quantities such as Gibbs free energy, enthalpy, entropy etc are many and among them, mention may be made of the following: (i) diverse coulombic interactions (ion-ion, ion-dipole, dipole-dipole etc);(ii) specific short range interactions;(iii) influence of dielectric properties of the solvent and (iv) need to handle the system as a many body problem etc.

In this context, the most illuminating analysis is provided by the Debye–Hückel theory which despite its simplicity has stood the test of time and has served as a touch stone for more improved modern versions. For this reason, an elaborate analysis of the Debye–Hückel limiting law is provided below.

Assumptions

- (i) Solvent- treated as a dielectric continuum and no explicit incorporation of permanent and induced dipole moments
- (ii) Complete dissociation of ions at all concentrations
- (iii) Ions- assumed as point charges
- (iv) Validity of Boltzmann distribution for ions and thermal energy assumed to be much larger than electrostatic interaction of ions with the electric field.
- (v) The dielectric constant of the solution is assumed to be equal to that of the solvent and assumed to be independent of the electric field.
- (vi) System is assumed to be spherically symmetric.

Mathematical details

Solving linearized version of the Poisson-Boltzmann equation assuming spherical symmetry

Outcome

Theoretical prediction of

(i) Mean ionic activity coefficients

(ii) Osmotic pressure and

(iii) Thermodynamic quantities such as ΔG , ΔH and ΔS .

Limitations

Valid only for dilute solutions up to 0.001 M; not applicable (i) if ion-pairs are formed (ii) for higher concentrations and (iii) non 1:1 electrolytes at moderate concentrations.

Derivation

It is customary to start with the general Poisson equation given by

$$\nabla^2 \phi(r) = -\frac{4\pi\rho(r)}{\epsilon} \quad (1)$$

ϕ - mean electrostatic potential

ρ – net charge density

ϵ - dielectric constant of the medium

If ρ equals zero, we obtain the Laplace equation. ∇^2 is known as the Laplacian operator and can be represented through various coordinate systems such as cylindrical, polar, spherical etc. Although the system is electrically neutral, we are considering a region comprising unequal number of cations and anions which in turn gives rise to a net charge density and hence a non-zero electrostatic potential.

Eqn (1) as given above pertains to the Gaussian units, since a factor of 4π appears. The representation of the Poisson equation in the SI unit is provided in the Appendix A.

The total number of ions per unit volume is $n = n_+ + n_-$, the subscripts indicating the cations and anions. Assuming a spherical symmetry, wherein the distance from a chosen central ion 'r' is the only variable, equation (1) can be written as

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \phi}{\partial r} \right) = -\frac{4\pi\rho}{\varepsilon} \quad (2)$$

$$\rho = ze(n_+ - n_-) \quad (3)$$

where for the sake of brevity, the electrolyte is assumed to be z:z. Assuming the classical Boltzmann distribution law,

$$n_+ = ne^{-ze\phi/kT} \quad (4)$$

$$n_- = ne^{+ze\phi/kT} \quad (5)$$

Note that the exponential term has a sign opposite to the central ion. n_+ denotes the number density of cations in a volume element dV

Thus, the Poisson equation now becomes

$$\nabla^2 \phi = -\frac{4\pi}{\varepsilon} ne \left[e^{-ze\phi/kT} - e^{+ze\phi/kT} \right] \quad (6)$$

The above eqn is now more appropriately designated as the Poisson-Boltzmann equation.

Linearising the exponential terms in the above eqn and assuming $z=1$ viz 1: 1 electrolyte solution for algebraic simplicity,

$$\begin{aligned}
\frac{1}{r} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \phi}{\partial r} \right) &= -\frac{4\pi}{\epsilon} ne \left[1 - \frac{ze\phi}{kT} - 1 - \frac{ze\phi}{kT} \right] \\
&= \frac{4\pi}{\epsilon} ne \left[\frac{2ze\phi}{kT} \right] \\
&= \left(\frac{8\pi ne^2 \phi}{\epsilon kT} \right) = \kappa_D^2 \phi
\end{aligned} \tag{7}$$

where the new quantity κ_D is as follows: $\kappa_D = \left(\frac{8\pi ne^2}{\epsilon kT} \right)^{1/2}$

and in anticipation, κ_D is designated as the inverse Debye length.

$$\frac{1}{r^2} \frac{d}{dr} \left[r^2 \frac{\partial \phi}{\partial r} \right] = \kappa_D^2 \phi \tag{8}$$

Multiplying the above eqn by 'r' everywhere, it follows that

$$\frac{1}{r} \frac{d}{dr} \left[r^2 \frac{\partial \phi}{\partial r} \right] - \kappa_D^2 \phi r = 0$$

By defining a new variable, $\phi = \frac{V}{r}$

$$\frac{1}{r} \frac{d}{dr} \left[r^2 \frac{\partial (V/r)}{\partial r} \right] - \kappa_D^2 \left(\frac{V}{r} \right) r = 0$$

$$\frac{1}{r} \frac{d}{dr} \left[r^2 \left(\frac{r \frac{dV}{dr} - V}{r^2} \right) - \kappa_D^2 V \right] = 0$$

$$\frac{1}{r} \left[r \frac{d^2 V}{dr^2} + \frac{dV}{dr} - \frac{dV}{dr} \right] - \kappa_D^2 V = 0. \text{ Equivalently,}$$

$$\frac{d^2V}{dr^2} - \kappa_D^2 V = 0$$

The above simple second order linear ordinary differential equation has the general solution as

$$V = Ae^{\kappa_D r} + Be^{-\kappa_D r} \quad (9)$$

where A and B are arbitrary constants to be determined by the physical situation. If the distance between two ions tend to infinity, the potential should become zero and hence the arbitrary constant A should be zero.

Since $\phi = \frac{V}{r}$,

$$\phi = \frac{Be^{-\kappa_D r}}{r}. \quad (10)$$

In order to identify the constant B, we expand $e^{-\kappa_D r} \approx 1 - \kappa_D r$. Thus, $\phi(r) = \frac{B(1 - \kappa_D r)}{r}$. For very dilute solution, $\kappa \rightarrow 0$ and hence $\phi(r) \rightarrow \frac{B}{r}$. In this case, the potential at r should be that due to the classical coulomb law i.e $\phi(r) \rightarrow \frac{ze}{\epsilon r}$.

Hence $B = \frac{ze}{\epsilon}$ consequently.

$$\phi(r) = \frac{ze}{\epsilon r} e^{-\kappa_D r} \quad (11)$$

The above is the central result of the Debye-Huckel theory since it gives the electrostatic potential as a function of the distance, in an electrolyte solution whose dielectric constant is ϵ . The parameter κ_D , obviously has the dimension of the inverse length and on account of its origin in the Debye-Huckel formalism, it is called as the inverse Debye length. Since κ_D can also be considered as arising from

an ionic cloud surrounding a central ion, $1/\kappa_D$ is sometimes known as the thickness (or radius) of the ionic atmosphere. If $\kappa_D=0$, i.e if the inverse Debye length becomes zero, the classical coulomb law is recovered. The concentration of the solution appears in κ_D through the number density. We may once again linearize the exponential term of the above eqn in order to deduce some additional insights viz.

If $e^{-\kappa_D r} \simeq 1 - \kappa_D r$

$$\varphi(r) = \frac{ze}{\epsilon r} - \frac{ze\kappa_D}{\epsilon} \quad (12)$$

$\frac{ze}{\epsilon r} \rightarrow$ represents the potential due to the ion itself

$-\frac{ze\kappa_D}{\epsilon} \rightarrow$ represents the potential arising from the presence of the ionic

atmosphere and we rewrite it as φ_{atm} . Eqn (12) is of little use since the potential φ cannot be evaluated experimentally although computer simulations enable the functional dependence of the electrostatic potential. One may also note that the equation (12) is valid only if $\kappa_D r < 1$.

On the other hand, the concept of the mean ionic activity coefficient is of immense use since it serves as a measure of the ionic interactions and is indicative of the deviations from ideal behaviour. Furthermore, thermodynamic properties of electrolyte solutions need to be estimated in order to know the validity of any theoretical treatment. For this purpose, we now deduce the expression for the mean ionic activity coefficient in the following manner:

$$\text{Electrical work} = W_{\text{el}} = \int_0^{ze} \varphi_{\text{atm}} d(ze) = -\int_0^{ze} \frac{ze\kappa_D}{\epsilon} d(ze) = -\frac{\kappa_D (ze)^2}{2\epsilon} \quad (13)$$

The electrochemical potential of an i^{th} ion may be written as

$$\mu_i = \mu_i + kT \ln a_i + W_{el} \quad (14)$$

where a_i is the ionic activity. W_{el} can also be considered as the excess chemical potential on account of deviations from ideal behaviour. Furthermore, the electrical work may also be written in terms of the ionic activity as

$$W_{el} = +kT \ln \gamma_i = -\frac{z_i^2 e^2 \kappa_D}{2\epsilon} \quad (15)$$

Hence

$$\ln \gamma_i = -\frac{z_i^2 e^2 \kappa_D}{2\epsilon kT} \quad (16)$$

The above eqn yields the individual ionic activity coefficient of an electrolyte solution. Specialising the above eqn for cations and anions separately,

$$\ln \gamma_+ = -\frac{z_+^2 e^2 \kappa_D}{2\epsilon kT} \quad (17)$$

$$\ln \gamma_- = -\frac{z_-^2 e^2 \kappa_D}{2\epsilon kT} \quad (18)$$

Unfortunately, the individual ionic activity coefficients are not obtainable experimentally and hence the above two equations are combined so as to deduce the mean ionic activity coefficient γ_{\pm} defined as

$$\gamma_{\pm}^{\nu} = (\gamma_+^{\nu_+} \gamma_-^{\nu_-}) \quad (19)$$

where ν_+ and ν_- denote the stoichiometric numbers of the electrolyte. Further $\nu = \nu_+ + \nu_-$.

For an electrolyte such as CaCl_2 , $\nu_+ = 1$ and $\nu_- = 2$.

From eqns (17) and (18),

$$v \ln \gamma_{\pm} = v_+ \ln \gamma_+ + v_- \ln \gamma_- = -\frac{e^2 \kappa_D}{2\epsilon kT} [v_+ z_+^2 + v_- z_-^2] \quad (20)$$

$$\ln \gamma_{\pm} = \frac{-e^2 \kappa_D}{2\epsilon kT} \left[\frac{v_+ z_+^2 + v_- z_-^2}{v_+ + v_-} \right] \quad (21)$$

It is well known that for any electrolyte, $v_+ z_+ = v_- z_-$.

$$\text{Therefore, } z_+ = \frac{v_- z_-}{v_+} \text{ and } z_- = \frac{v_+ z_+}{v_-}$$

$$\therefore v_+ z_+^2 + v_- z_-^2$$

$$= v_+ \left(\frac{v_- z_-}{v_+} \right) z_+ + v_- \left(\frac{v_+ z_+}{v_-} \right) z_-$$

$$= z_+ z_- (v_+ + v_-)$$

$$\ln \gamma_{\pm} = -\frac{e^2 \kappa_D}{2\epsilon kT} |(z_+ z_-)| \quad (22)$$

$$\kappa_D^2 \text{ was defined as } \frac{8\pi n e^2}{\epsilon kT}$$

n = number of ions per cm^3 ; rewriting n in terms of molar concentration,

$$\kappa_D^2 = \frac{4\pi e^2 N_A \sum c_i z_i^2}{\epsilon kT \times 1000} \quad (23)$$

But the ionic strength of a solution is defined as

$$I = \frac{1}{2} \sum c_i z_i^2$$

and

$$\kappa_D^2 = \frac{8\pi e^2 N_A I}{\varepsilon kT \times 1000}$$

N_A = Avogadro number; e denotes the electronic charge; I = Ionic strength; ε denotes the dielectric constant of the solvent and the factor 1000 in the denominator indicates that the concentration should be in moles per litre while calculating the ionic strength. As shown below, the mean ionic activity coefficient follows as

$$\log_{10} \gamma_{\pm} = -0.51 |z_+ z_-| \sqrt{I}.$$

The above equation is known as the Debye-Hückel limiting law in view of its validity to very dilute solutions. (concentration limit tending to zero). The inverse Debye length is directly proportional to the square root of the ionic strength of the solution. If we substitute various quantities in the above eqn,

$$\kappa_D^2 = \frac{8 \times 3.14 \times (1.6 \times 10^{-19} C)^2 \times (6.023 \times 10^{23}) \text{cm}^{-3} I}{1000 \times 78.4 \times 1.38 \times 10^{-23} \times 300 \text{ VC}} \quad (24)$$

In the above, the dielectric constant of water has been employed as 78.4 and $T = 300 \text{ K}$ is assumed. 1 Joule equals one volt-coulomb. Since the inverse Debye length has a dimension of 'length', we make use of the well-known conversion factor $1 \text{ cm} = 1.113 \times 10^{-12} \text{ F}$ (Farad = Coulomb/Volt) thus yielding

$$\kappa_D^2 = \frac{8\pi e^2 N_A I}{\varepsilon kT \times 1000} = \frac{8 \times 3.14 \times (1.609 \times 10^{-19} C)^2 \times 6.023 \times 10^{23} \times I}{78.4 \times 4.14 \times 10^{-21} \text{ VC} \times 1000 \times 1.113 \times 10^{-12} \text{ F}}$$

$$\kappa_D^2 = 1.08556 \times 10^{18} \text{ cm}^{-2} I$$

$$\frac{1}{\kappa_D^2} = \frac{9.211 \times 10^{-16}}{I} \text{ cm}^2$$

$$\frac{1}{\kappa_D} = \frac{3.035 \times 10^{-8}}{\sqrt{I}} \text{ cm} \quad (25)$$

Table 1: Debye Lengths (in nm) of various electrolytes at 298K

c (mol.dm ⁻³)	Change type of the electrolyte				
	1:1	1:2	2:2	1:3	2:3
1	0.30	0.18	0.15	0.12	0.08
10 ⁻¹	0.96	0.56	0.48	0.39	0.25
10 ⁻²	3.04	1.75	1.52	1.24	0.78
10 ⁻³	9.61	5.55	4.80	3.92	2.48
10 ⁻⁴	30.4	17.5	15.2	12.4	7.8
10 ⁻⁵	96.1	55.5	48.0	39.2	24.8

For numerical calculations, the above equation is especially convenient if the solvent is water and temperature is ~ 300 K. The concentration should be in moles per litre in calculating the ionic strength. Since the ionic strength $I = \frac{1}{2} \sum c_i z_i^2$, the eqn for the mean ionic activity coefficient from the D-H limiting law is

$$\log_{10} \gamma_{\pm} = - \frac{|z_+ z_-| (1.609 \times 10^{-19} \text{ C})^2 \times \sqrt{I}}{2 \times 2.303 \times 78.3 \times 4.14 \times 10^{-2} \times VC \times 3.04 \times 10^{-8} \text{ cm}} \quad (26)$$

$$\log_{10} \gamma_{\pm} = -0.51 |z_+ z_-| \sqrt{I} \quad (\text{Debye-Hückel limiting law})$$

The numerical value of 0.51 is designated as ‘A’

Improved versions of the Debye- Hückel limiting law

$$\log_{10} \gamma_{\pm} = -A |z_+ z_-| \sqrt{I} \quad \text{Debye-Hückel limiting law}$$

$$\log_{10} \gamma_{\pm} = \frac{-A|z_+z_-|\sqrt{I}}{1+Ba\sqrt{I}} \quad \text{Debye-Hückel equation}$$

$$\log_{10} \gamma_{\pm} = \frac{-A|z_+z_-|\sqrt{I}}{1+Ba\sqrt{I}} + bI \quad \text{Debye-Hückel extended equation}$$

where B and a are independent of number density but depend upon the temperature and dielectric constant. Table 2 indicates how A and B vary with temperature for aqueous electrolytes

Table 2: Temperature dependence of A and B in the Debye - Hückel theory for aqueous solution

T(K)	A (mol/kg) ^{-1/2}	B [(mol/kg) ^{1/2} Å] ⁻¹
273	1.129	0.3245
288	1.155	0.3269
298	1.175	0.3284
303	1.184	0.3292
333	1.255	0.3343
363	1.345	0.3400

Although the Debye – Hückel theory of electrolyte solutions provides a satisfactory description for extremely dilute electrolyte solutions, it is entirely inadequate for (i) 1:1 electrolyte at concentrations at >10⁻³ M solutions and (iii) polyvalent electrolytes even at <10⁻³ M. There are several methods by which the limitations of the Debye – Hückel limiting law can be overcome, both empirically

and rigorously. Among many excellent treatments, the most impressive version is the well – known Mean Spherical approximation (MSA). The final analysis of MSA is as follows:

$$(\ln \gamma_i)_{MSA} = \frac{-z_i^2 e^2 \Gamma}{\varepsilon k T (1 + \Gamma \sigma)} \quad (27)$$

where σ is the ‘hard sphere’ diameter while Γ is the mean spherical approximation parameter and $\Gamma \rightarrow \frac{\kappa_D}{2}$ for low concentrations. If the hard diameter sphere $\sigma \rightarrow 0$ and $\Gamma \rightarrow \frac{\kappa_D}{2}$, the above equation becomes

$$\ln \gamma_i = \frac{-z_i^2 e^2 \kappa_D}{2kT}$$

which is the Debye – Hückel limiting law (eqn 16). The MSA and its other refined versions ensure that the theory of inter – ionic interactions of electrolyte solutions becomes valid for more concentrated solutions and for polyvalent electrolytes.

Other solvents and other temperatures

The numerical value A is

$$A = 5.77057 \times 10^4 (\varepsilon T)^{-3/2} \text{ m}^{3/2} \cdot \text{mol}^{-1/2} = 1.82481 \times 10^6 (\varepsilon T)^{-3/2} \text{ dm}^{3/2} \cdot \text{mol}^{-1/2}$$

and, for water at 25° C,

$$A = 1.61039 \times 10^{-2} \text{ m}^{3/2} \cdot \text{mol}^{-1/2} = 0.50925 \text{ dm}^{3/2} \cdot \text{mol}^{-1/2}$$

The numerical value B is

$$B = 1.5903 \times 10^{10} (\varepsilon T)^{-1/2} \text{ m}^{1/2} \cdot \text{mol}^{-1/2} = 502.90 (\varepsilon T)^{-1/2} \text{ dm}^{3/2} \cdot \text{mol}^{-1/2} \cdot \text{nm}^{-1}$$

and, for water at 25° C,

$$B = 1.0392 \times 10^8 \text{ m}^{1/2} \cdot \text{mol}^{-1/2} = 3.2864 \text{ dm}^{3/2} \cdot \text{mol}^{-1/2} \cdot \text{nm}^{-1}$$

Fig 1 provides the variation of γ_{\pm} with \sqrt{I} for various electrolytes. It is of interest to note that for non 1:1 electrolyte there exists a minimum value of γ_{\pm} and is indicative of ion association and reflects the failure of the Debye – Hückel limiting law

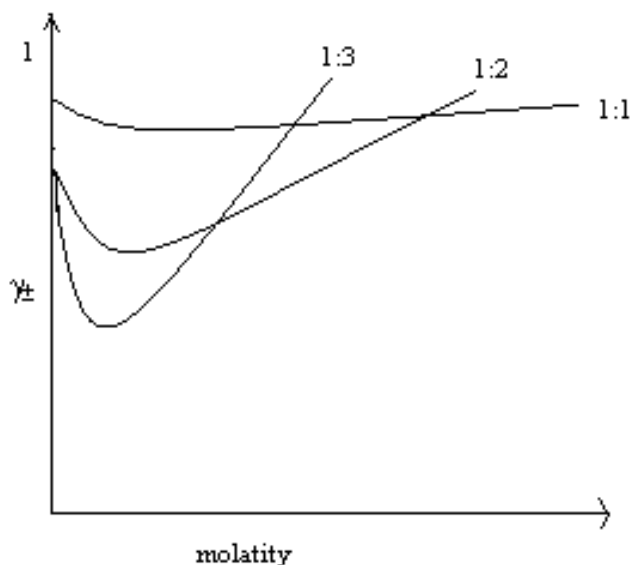
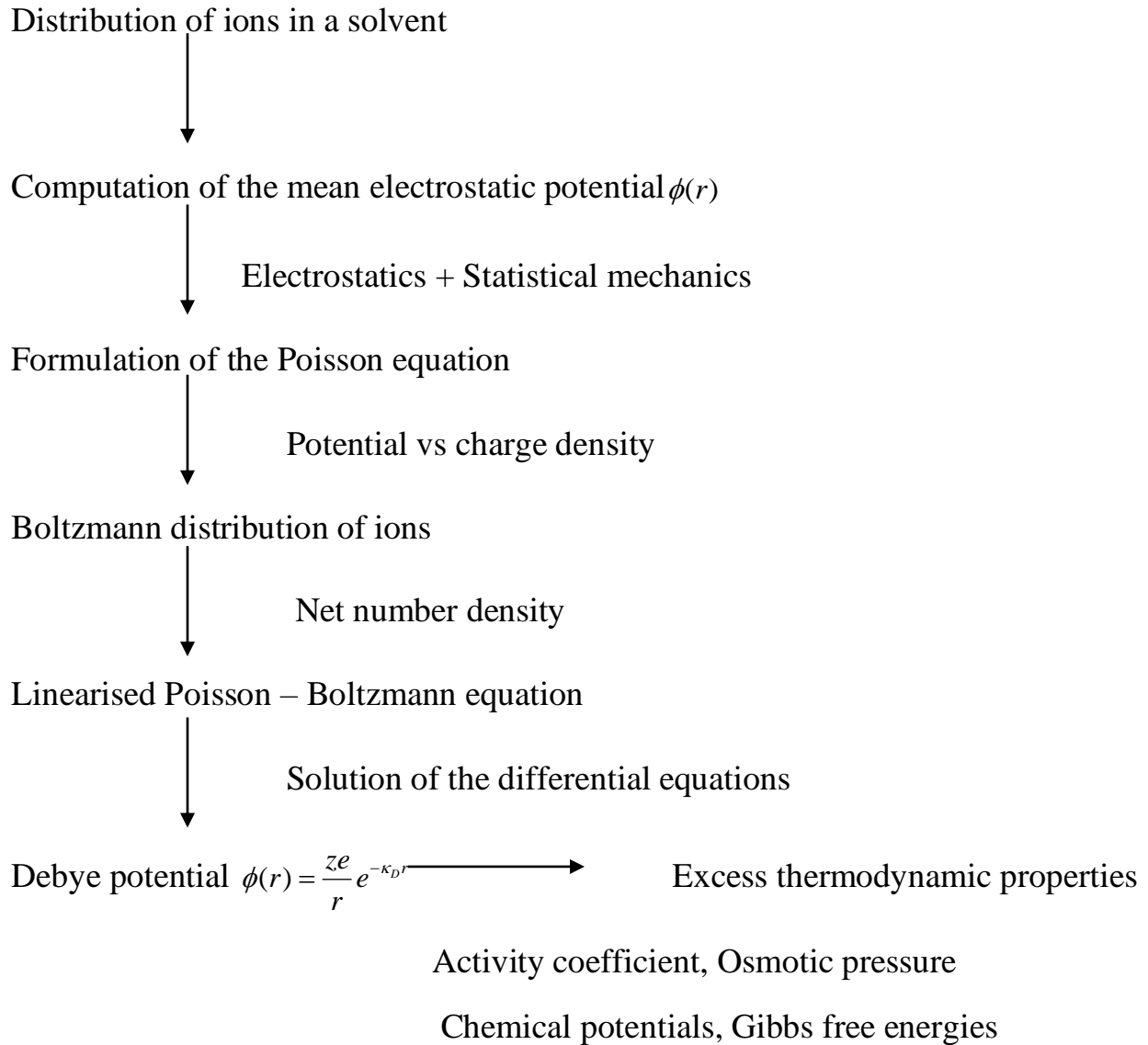


Fig 1: Schematic variation of the mean ionic activity coefficient on molarity of the electrolyte at 298K

Physical Significance of the Debye length

The Debye length sometimes denoted as L_D is $\frac{1}{\kappa_D}$ in the above notation and it plays a central role in condensed matter physics. The Debye length represents the characteristic length within which the influence of the electric field is felt ie. beyond L_D , the electric field does not have any effect on the ionic distributions.

Flow Chart for the Debye – Hückel theory of electrolyte solutions



The Debye – Hückel theory pertains to the primitive model of the electrolyte since the solvent is treated as a continuum while ions are considered as point charges. The next improvement is provided by Restricted primitive model wherein the ions are treated as hard sphere, with the solvent being a dielectric continuum. There are other hierarchical improvements in this context such as Hypernetted Chain (HNC), Generalized Mean Spherical Approximation etc. The net result is that the Debye

length $\frac{1}{\kappa_D}$ is an involved function of the bulk concentration of the electrolyte as well as ion sizes.

WORKED OUT EXAMPLES

1. Calculate the radius of the ionic atmosphere in aqueous NaCl solution of concentration $10^{-3} \text{ mol L}^{-1}$

$$I = \frac{1}{2} \sum c_i z_i^2 = 10^{-3}$$

$$\frac{1}{\kappa_D} = \frac{3.035 \times 10^{-8}}{\sqrt{I}} \text{ cm} = 9.59 \times 10^{-7} \text{ cm}$$

2. Use the Debye-Hückel limiting law to evaluate γ_{\pm} in $10^{-4} \text{ mol lit}^{-1}$ of 2:2 electrolytes at 25°C

$$I = \frac{1}{2} c_i z_i^2 = \frac{1}{2} [10^{-4} \times 4 \times 10^{-4} \times 4] = 4 \times 10^{-4} \text{ mol cm}^{-3}$$

$$\log_{10} \gamma_{\pm} = -0.51 |z_+ z_-| \sqrt{I}$$

$$\log \gamma_{\pm} = -0.51 \times 4 \times \sqrt{4 \times 10^{-4}} \quad \text{and} \quad \gamma_{\pm} = 0.91$$

3. Calculate the Debye length for $8.25 \times 10^{-5} \text{ mol kg}^{-1}$ solution of $\text{Al}_2(\text{SO}_4)_3$.

$$\begin{aligned} I &= \frac{1}{2} \sum c_i z_i^2 \\ &= \frac{1}{2} \left\{ 2 \times 8.25 \times 10^{-5} (3)^2 + 3 \times 8.25 \times 10^{-5} (2)^2 \right\} \\ &= \frac{8.25 \times 10^{-5}}{2} \{18 + 12\} = 15 \times 8.25 \times 10^{-5} \text{ mol kg m}^{-1} \end{aligned}$$

$$= 1.2375 \times 10^{-3} \text{ mol kg m}^{-1} = 1.2375 \text{ mol m}^{-3}$$

$$\kappa_D^2 = \frac{e^2 \times 2I}{\epsilon_0 \epsilon kT}$$

$$= \frac{1.60^2 \times 10^{-38} \times 2 \times (1.2375 \times 10^{-3}) \times 6.023 \times 10^{23}}{78 \times 8.85 \times 10^{-12} \times 4.14 \times 10^{-21}}$$

$$= \frac{1.60^2 \times 2 \times 1.2375 \times 6.023}{78 \times 8.85 \times 4.14}$$

$$\kappa_D^2 = 1.335 \times 10^{19} \text{ met}^{-2}$$

$$1/\kappa_D = 2.736 \times 10^{-10} \text{ met}$$

4. A 50% (v/v) aqueous ethanol (dielectric constant =68) contains 0.001 mol kg⁻¹ each in HBr and CaBr₂. Find the mean activity coefficient (γ_{\pm}) of CaBr₂ in this solution at 300K using the Debye - Hückel limiting law.

Debye - Hückel limiting law is $\log_{10} \gamma_{\pm} = -A |z_+ z_-| \sqrt{I}$

where $A = \frac{1.823 \times 10^6}{(\epsilon T)^{3/2}}$

when $\epsilon = 68$, $A = \frac{1.823 \times 10^6}{(68 \times 300)^{3/2}}$ at $T = 300\text{K}$

$$(68 \times 300)^{3/2}$$

$$\text{or } A = \frac{1.823 \times 10^6}{2.914 \times 10^6} = 0.6256$$

$$2.914 \times 10^6$$

$$I = \frac{1}{2} \sum m_i z_i^2 = \frac{1}{2} [0.001 \cdot 1^2 + 0.001 \cdot 1^2 + 0.001 \cdot 2^2 + 0.002 \cdot 1^2]$$

$$\text{or } I = \frac{1}{2} [0.001 + 0.001 + 0.004 + 0.002] = 0.004$$

$$\therefore \log_{10} \gamma_{\pm} = -0.6256 \times 2 \times 1 \times (0.004)^{1/2} = -0.6256 \times 2 \times 0.06324$$

$$\text{or } \log_{10} \gamma_{\pm} = -0.07913$$

$$\gamma_{\pm} = 0.8334$$

5. Calculate the Debye length of the ionic atmosphere for 0.012 N LaCl_3 in nitrobenzene (dielectric constant = 34.8) at 300 K.

$$\text{Debye length, } \frac{1}{\kappa_D} = 2.81 \times 10^{-10} \left(\frac{\varepsilon T}{\sum c_i z_i^2} \right)^{1/2}$$

where ‘ ε ’ is the dielectric constant and c_i is the concentration of the electrolyte in mL^{-1} .

For LaCl_3 , $c = 0.012 \text{ N} = 0.004 \text{ M}$

$$\varepsilon = 34.8 \text{ and } T = 300 \text{ K}$$

$$\sum c_i z_i^2 = (c_{\text{La}^{3+}} \cdot z_{\text{La}^{3+}}^2 + c_{\text{Cl}^-} \cdot z_{\text{Cl}^-}^2)$$

$$= 4 \times 10^{-3} \cdot 3^2 + 3 \times 4 \times 10^{-3} \cdot 1^2$$

$$= 36 \times 10^{-3} + 12 \times 10^{-3} = 48 \times 10^{-3} = 0.048$$

$$\therefore \frac{1}{\kappa_D} = 2.81 \times 10^{-10} \times \left(\frac{34.8 \times 300}{4.8 \times 10^{-2}} \right)^{1/2}$$

$$= 2.81 \times 10^{-10} \times 10^2 \left(\frac{34.8 \times 3}{4.8} \right)^{1/2}$$

$$\text{or } \frac{1}{\kappa_D} = 13.1 \text{ \AA}$$

6. The solubility product of CdSO_4 is $9.2 \times 10^{-11} \text{ M}^2$. Calculate the mean activity coefficient of the Cd and SO_4^{2-} ions in a solution containing 0.05 M each of KNO_3 in KCl , compare the solubility of CdSO_4 in water.

The ionic strength of the solution containing KNO_3 and KCl is

$$I = \frac{1}{2} \sum_i c_i z_i^2 = 0.1 \text{ M}$$

$$\log_{10} \gamma_{\pm} = -A |z_+ z_-| \sqrt{I} = -2^2 \times 0.51 \times \sqrt{0.1} = -0.645$$

$$\text{Hence } \gamma_{\pm} = 0.226$$

K_{sp} in water = $9.2 \times 10^{-11} \text{ M}^2$. Hence the solubility is

$$s = \sqrt{K_{sp}} = 9.6 \times 10^{-6} \text{ M}$$

If the solubility in the solution is s ,

$$K_{sp} = s^2 \gamma_{\pm}^2$$

$$9.2 \times 10^{-11} = s^2 (0.226)^2$$

$$\text{solubility} = 4.25 \times 10^{-5} \text{ M}$$

Thus the solubility increases in the salt solution.

EXERCISES

1. The ionic strength of 0.1 M lanthanum phosphate solution is -----

2. The time taken for the formation of ionic atmosphere in the case of 1.0 M NaCl solution is nearly -----seconds.
3. Which of the following has the largest thickness of the ionic atmosphere?
(A) 1.0 M KCl ; (B) 0.1 M KCl ; (C) 0.01 M KCl and (D) 1.5 M KCl
4. Calculate (i) the activity of the electrolyte and (ii) the mean ionic activity, a_{\pm} of ions in 0.01 molal solutions of (a) Lanthanum nitrate and (b) Indium

sulphate, using the Debye-Huckel limiting law for the mean ionic activity coefficients.

5. Write the equation for the osmotic pressure of 1:1 electrolytes of 0.0001 M concentration under the Debye – Hückel approximation.
6. Use the Debye – Hückel limiting law to estimate γ_{\pm} in 10^{-6} M solution of ZnSO_4 .
7. Write the expression for the mean electrostatic potential (ψ) at a central ion on the basis of Debye–Hückel’s theory.
8. Calculate the Debye length for 0.001 M solution of 2: 2 electrolytes in nitrobenzene at 25°C .
9. Consider the ions of charges Z_i and z_j immersed in a solvent of dielectric constant ϵ . The diameters are σ_i and σ_j respectively. Write the expression for the pairwise interaction u_{ij} for this system.
10. What is the mean distance between ions when their number density is 1×10^{24} ions / cm^3 ?

SUMMARY

The subtle features underlying the Debye–Hückel theory of electrolytes have been outlined. The limitations and merits of the Debye–Hückel theory they have been pointed out. Recent improvements of the Debye – Hückel theory have been indicated.

Appendix A

An important aspect wherein the SI and Gaussian units differ is the placement of the 4π 's in the governing equation. Units wherein the 4π 's have been eliminated

from Maxwell's equations are rationalized units; SI units are an example of rationalized units, since the 4π 's do not appear. Gaussian units are not rationalized and hence '4 π ' appears.

1. 1 statvolt is (approximately) 300 Volts

2. The conversion from SI to Gaussian units can be accomplished by replacing $1/4\pi\epsilon_0$ by $1/\epsilon_r$. Thus Poisson's equation in SI and Gaussian units are as follows.

$$\nabla^2\phi = -\frac{\rho}{\epsilon_r} \text{ (SI)} \qquad \nabla^2\phi = -\frac{4\pi\rho}{\epsilon_r} \text{ (Gaussian)}$$

where ϵ_r is the relative permittivity (or dielectric constant) given by ϵ/ϵ_0 .

In SI units, $\nabla^2\phi = \frac{-\rho}{\epsilon\epsilon_0}$

In Gaussian units, we replace $4\pi\epsilon_0$ by 1. Hence, $\nabla^2\phi = -\frac{4\pi\rho}{\epsilon}$

3. ϵ_0 is the permittivity of vacuum.

SUMMARY

The assumptions underlying Debye Hückel theory are pointed out. Recent improvements pertaining to the theory of electrolyte solutions have been indicated.