

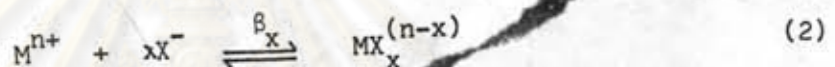


## CHAPTER II

### THEORY

#### 2.1 The Complex Formation Constants

The complex formation constants have been determined based on the complex equilibria, represented by



The thermodynamic complex formation constants can be expressed by equation 3 as

$$\beta_x = \frac{[MX_x^{(n-x)}] \cdot \gamma}{[M^{n+}] [X^-]^x} \quad (3)$$

or

$$\beta_x = \beta_x^c \cdot \gamma$$

where  $\beta_x^c$  is the concentration constant. Thus the determination of  $\beta_x$  requires either effective elimination or evaluation of the activity coefficient terms, which involves the following techniques.

##### 2.1.1 Constant Ionic Medium

In this method, the equilibrium are studied in solution containing relatively large concentration of "neutral" or inert electrolytes to assure the condition of constant ionic strength of the system. It is also assumed these this added ions do

not form complexes with the reacting species and the activity coefficients of ionic species remain constant. The species concentrations are then calculated from the experimental measurements, giving the concentration constants which are valid at a particular ionic strength. The disadvantages of this method are threefold,

(i) The results can be compared only with the data which have been obtained at the same ionic strength and in the same medium (Unfortunately, different workers usually use different ionic strengths).

(ii) Too little is known about the variation of activity coefficients at constant ionic strength to permit reliable estimates of uncertainties from this source. But this is probably the least objection, since if the ions are present in sufficiently small amounts relative to the background electrolyte, their activity coefficients will be constant within experimental errors.

(iii) The so called " free " ions in the electrolyte will be associated to a greater or lesser extent with the ions of the " neutral " electrolyte, especially if the concentration of the latter is high in order to keep the ionic strength constant.

#### 2.1.2 Thermodynamic Constants

It is clearly desirable to determine the thermodynamic complex formation constants so that all systems are directly comparable, and for this purpose the activity coefficient in eq.(3) must be evaluated or eliminated. This can be done in two ways :

(i) Calculate activity coefficients from the extended forms of the Debye-Hueckel equation. (see detail in chapter V)

(ii) Determine  $\beta^C$ 's at various concentrations of salt and extrapolate to infinite dilution at which the activity coefficients become unity.

The second method is usually used to study a system at a series of moderately low and constant ionic strengths.

## 2.2 The Activity Coefficients.

### 2.2.1 The Model of Electrolyte Solution.

The modern theory of electrolytic solutions, the basic propositions of which were formulated by Debye-Hueckel in 1923. The principle type of motion in solutions is translational. The sphere surrounding the central ion does not always contain the same ions. There is continuous interchange between the ions contained in the sphere and other ions. Such a statistical sphere around the central ion is called the "ionic atmosphere" or "ionic cloud". All the ions in solution are equal in all respects; each of which is surrounded by an ionic atmosphere. At the same time each central ion makes part of the ionic atmosphere of some other ion (Fig. 2.1). It is the existence of the ionic atmosphere that, according to Debye-Hueckel, distinguishes real electrolytic solutions from ideal ones.

### 2.2.2 Ion-ion Interaction and Activity Coefficients.

For a hypothetical system of ideal (noninteracting) particles, the chemical potential is given by





Figure 2.1 The Debye-Hueckel model of the ionic atmosphere

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

$$\mu_i \text{ (ideal)} = \mu_i^\circ + RT \ln(m_i) \quad (4)$$

In this expression,  $m_i$  is the concentration of the solute in molal units, and  $\mu_i^\circ$  is its chemical potential in the standard state, i.e., when  $m_i$  assumes a standard or normalized value of unity

$$\mu_i = \mu_i^\circ \quad \text{when } m_i = 1$$

For a real system of interacting particles, the chemical potential is been expressed in the form

$$\mu_i \text{ (real)} = \mu_i^\circ + RT \ln(m_i \gamma_i) \quad (5)$$

$m_i \gamma_i$  is the effective concentration which is known as the activity  $a_i$  of the species  $i$ , where

$$a_i = m_i \gamma_i$$

and the correction factor  $\gamma_i$  is the activity coefficient.

The chemical potential change in going from the standard state to the final state can be written as

$$\mu_i \text{ (real)} = \mu_i^\circ + RT \ln(m_i) + RT \ln(\gamma_i) \quad (6)$$

It is obvious that, when eq.4 is subtracted from eq.6, the difference is the chemical potential change, arising from

interactions between the solute particles, i.e.,

$$\mu_i(\text{real}) - \mu_i(\text{ideal}) = \Delta\mu_{i-I}$$

and, therefore,

$$\Delta\mu_{i-I} = RT \ln(\gamma_i) \quad (7)$$

Thus, the activity coefficient is a measure of the chemical potential change arising from the ion-ion interactions.

According to the Debye-Hueckel theory (10), the chemical potential change has been shown to be given by

$$\Delta\mu_{i-I} = \frac{-N_A (Z_i e)^2 \chi}{2D(1 + \chi a)} \quad (8)$$

Hence, combining eq.7 and eq.8 leads to

$$RT \ln(\gamma_i) = \frac{-N_A (Z_i e)^2 \chi}{2D(1 + \chi a)} \quad (9)$$

$$\ln(\gamma_i) = \frac{-N_A (Z_i e)^2 \chi}{2DRT (1 + \chi a)}$$

This individual ionic activity coefficient can be transformed into a mean ionic activity coefficient,

On the basis of the expression 11 for  $\chi$ , eq.10 becomes

$$\ln \gamma_{\pm} = \frac{-N_A (Z_+Z_-) e^2 \cdot BI^{1/2}}{2 DKT} \cdot \frac{1}{1 + \chi a}$$

$$\log \gamma_{\pm} = \frac{-1}{2.303} \frac{N_A e^2 B(Z_+Z_-) I^{1/2}}{2DKT} \cdot \frac{1}{1 + \chi a} \quad (13)$$

For a greater compactness, a constant is defined by

$$A = \frac{1}{2.303} \frac{N_A e^2 \cdot B}{2DKT}$$

and eq. 13 is then re-written as

$$\log \gamma_{\pm} = \frac{-A (Z_+Z_-) I^{1/2}}{1 + \chi a} \cdot 1$$

Using  $\chi = BI^{1/2}$ , the final expression becomes

$$\log \gamma_{\pm} = \frac{-A (Z_+Z_-) I^{1/2}}{1 + BaI^{1/2}} \quad (14)$$

The derivation of eq.14 is such that the numerator of the right hand side,  $-A [Z_+Z_-] I^{1/2}$ , gives the effect of the long range coulombic force, while the denominator  $(1 + BaI^{1/2})$  shows how these are modified by the short range interactions between ions.



$$\ln(\gamma_{\pm}) = \frac{-N_A (Z_+ Z_-) e^2}{2DRT} \frac{\chi}{(1 + \chi a)} \quad (10)$$

Now, by substituting  $\chi$  from eq.11

$$\chi = \frac{(4\pi e^2 \sum z_i^2 n_i^2)^{1/2}}{(DRT)^{1/2}} \quad (11)$$

$\chi$  can be expressed in a different form. Since

$$\sum n_i z_i e^2 = \frac{\sum N_A e^2 c_i z_i^2}{\sum 1000}$$

The term  $1/2 \sum c_i z_i^2$  had been empirically introduced by Lewis as a quantity which is important for the treatment of ionic solution. Since it quantifies the charge in an electrolyte solution, it was known as the ionic strength and is given the symbol  $I$ .

Thus,  $\chi$  can be expressed as

$$\chi = \frac{(8\pi N_A e^2)^{1/2} I^{1/2}}{(1000 DRT)^{1/2}}$$

or as

$$\chi = B I^{1/2} \quad (12)$$

where

$$B = \frac{(8\pi N_A e^2)^{1/2}}{(1000 DRT)^{1/2}}$$



### 2.2.3 Semi-Empirical Formula for Calculating Activity Coefficients.

The activity coefficients in an eq.14 gives an adequate representation of the activity coefficients of normally dissociated salts of 1:1 and 2:1 valence types in sufficiently dilute solutions in terms of the single arbitrary parameter  $a$ , and the ionic strength,  $I$  of a solution. Equation 14., however, predicts an activity coefficient which is always a decreasing function of the concentration, whereas experimentally a minimum usually occurs, followed by, a more or less, rapid rise of the activity coefficient at high concentration. Hueckel explained this effect in terms of the change in dielectric constant of the solvent near the ions, which led to a second arbitrary constant  $D$  in the equation

$$\log \gamma_{\pm} = \frac{-A (Z_+Z_-) I^{1/2}}{1 + BaI^{1/2}} + DI \quad (15)$$

This equation has been of great practical value, and has been extensively employed for the extrapolation of standard potentials and the representation of activity coefficient data. Its theoretical foundations have, however, been frequently criticized. Furthermore, it usually fails to give a reasonably accurate representation of the observed activity coefficients at ionic strengths much greater than unity. To overcome this, further arbitrary terms  $I^2$  and even higher powers are sometimes introduced (11).