جامعة الانبار

كلية **: الصيدلة**

قسم : **الكيمياء الصيدلانية**

اسم المادة باللغة العربية**: الكيمياء التحليلية**

اسم المادة باللغة الإنكليزية: **Analytical Chemistry**

المرحلة: **الاولى**

التدريسي: **نغم خيري كريم**

عنوان المحاضرة باللغة العربية: تسحيحات تكوين المعقدات

عنوان المحاضرة باللغة الإنكليزية : **Complex -Formation Titration**

8.1 Introduction

Most metal ions react with electron-pair donors to form coordination compounds or complexes. The donor species, or ***ligand***, must have at least one pair of unshared electrons available for bond formation. Water, ammonia, and halide ions are common inorganic ligands. In fact, most metal ions in aqueous solution actually exist as aquo complexes. Copper(II) in aqueous solution, for example, is readily complexed by water molecules to form species such as $Cu(H_2O)_4^{2+}$. We often simplify such complexes in chemical equations by writing the metal ion as if it were uncomplexed Cu^{2+}. Remember that such ions are actually aquo complexes in aqueous solution.

The number of covalent bonds that a cation tends to form with electron donors is its ***coordination number***. Typical values for coordination number are 2, 4, and 6. The species formed as a result of coordination can be electrically positive, neutral, or negative. For example, copper(II), which has a coordination number of 4, forms a cationic ammine complex, $Cu(NH_3)_4^{2+}$; a neutral complex with glycine, $Cu(NH_2CH_2COO)_2$; and an anionic complex with chloride ion, $CuCl_4^{2-}$.

Titrimetric methods based on complex formation, sometimes called ***complexometric*** methods, have been used for more than a century. The truly remarkable growth in their analytical application, based on a particular class of coordination compounds called ***chelates***. A chelate is produced when a metal ion coordinates with two or more donor groups of a single ligand to form a five- or six-member heterocyclic ring. The copper complex of glycine mentioned is an example. Here, the copper bonds to both the oxygen of the carboxyl group and the nitrogen of the amine group.

A ligand that has a single donor group, such as ammonia, is called ***unidentate*** (single-toothed), whereas one such as glycine, which has two groups available for covalent bonding, is called ***bidentate***. Tridentate, tetradentate, pentadentate, and hexadentate chelating agents are also known.

Another important type of complex is formed between metal ions and cyclic organic compounds, known as ***macrocycles***. These molecules contain nine or more atoms in the cycle and include at least three heteroatoms, usually oxygen, nitrogen, or sulfur.

8.2 Complexation Equilibria

Complexation reactions involve a metal ion M reacting with a ligand L to form a complex ML, as shown in the equation:

$$M + L \rightleftharpoons ML \qquad \text{……….1)}$$

Where the charges on the ions are omitted so as to be general. Complexation reactions occur in a stepwise fashion; the reaction in equation 1 is often followed by additional reactions:

$$ML + L \rightleftharpoons ML_2 \qquad \text{……….2)}$$

$$ML_2 + L \rightleftharpoons ML_3 \qquad \text{……….3)}$$

$$ML_{n-1} + L \rightleftharpoons ML_n \qquad \text{……….4)}$$

Unidentate ligands invariably add in a series of steps, as shown here. With multidentate ligands, the maximum coordination number of the cation may be satisfied with only one ligand or a few added ligands. For example, Cu(II), with a maximum coordination number of 4, can form complexes with ammonia that have formulas $Cu(NH_3)^{2+}$, $Cu(NH_3)_2^{2+}$, $Cu(NH_3)_3^{2+}$, and $Cu(NH_3)_4^{2+}$. With the bidentate ligand glycine (gly), the only complexes that form are $Cu(gly)^{2+}$ and $Cu(gly)_2^{2+}$.

The equilibrium constants for complex formation reactions are generally written as formation constants. Thus, each of the reactions 1 through 4 is associated with a stepwise formation constant K_1 through K_4. For example, $K_1 = [ML]/[M][L]$, $K_2 = [ML_2]/[ML][L]$, and so on. We can also write the equilibria as the sum of individual steps. These have overall formation constants designated by the symbol β_n. Thus,

$$M + L \rightleftharpoons ML \qquad \beta_1 = \frac{[ML]}{[M][L]} = K_1 \quad \ldots\ldots\ldots\ldots 5)$$

$$M + 2L \rightleftharpoons ML_2 \qquad \beta_2 = \frac{[ML_2]}{[M][L]^2} = K_1\, K_2 \quad \ldots\ldots\ldots 6)$$

$$M + 3L \rightleftharpoons ML_3 \qquad \beta_3 = \frac{[ML_3]}{[M][L]^3} = K_1\, K_2\, K_3 \ \ldots\ldots 7)$$

$$M + nL \rightleftharpoons ML_n \qquad \beta_n = \frac{[ML_n]}{[M][L]^n} = K_1\, K_2 \ldots\ldots K_n \ldots 8)$$

Except for the first step, the overall formation constants are products of the stepwise formation constants for the individual steps leading to the product.

8.3 Titrations with Inorganic Complexing Agents

Complexation reactions have many uses in analytical chemistry, but their classical application is in ***complexometric titrations***. Here, a metal ion reacts with a suitable ligand to form a complex, and the equivalence point is determined by an indicator or an appropriate instrumental method. The formation of soluble inorganic complexes is not widely used for titrations, but the formation of precipitates, particularly with silver nitrate as the titrant, is the basis for many important determinations.

The progress of a complexometric titration is generally illustrated by the titration curve, which is usually a plot of pM = -log [M] as a function of the volume of titrant added. Most often, in complexometric titration the ligand is the titrant and the metal ion the analyte, although occasionally the reverse is true. Most simple inorganic ligands are unidentate, which can lead to low complex stability and indistinct titration end points. As titrants, multidentate ligands, particularly those having four or six donor groups, have two advantageous over their unidentate counterparts. First, they generally react more completely with cations and thus provide sharper end points. Second, they ordinarily react with metal ions in a single-step process, whereas complex formation with unidentate ligands involves two or more intermediate species.

The advantage of a single-step reaction is illustrated by the titration curves shown in Figure 8-1. Each of the titrations involves a reaction that has an overall equilibrium constant of 10^{20}. Curve *A* is derived for a reaction in which a metal ion M having a coordination number of 4 reacts with a tetradentate ligand D to form the complex of MD. (We have again omitted the charges on the two reactants for convenience). Curve *B* is for the reaction of M with a hypothetical bidentate ligand B to give MB_2 in two steps. The formation constant for the first step is 10^{12} and for the second 10^8. Curve *C* involves a unidentate ligand A that forms MA_4 in four steps with successive formation constant of 10^8, 10^6, 10^4, and 10^2. These curves demonstrate that a much sharper end point is obtained with a reaction that takes place in a single step. For this reason, multidentate ligands are ordinarily preferred for complexometric titration.

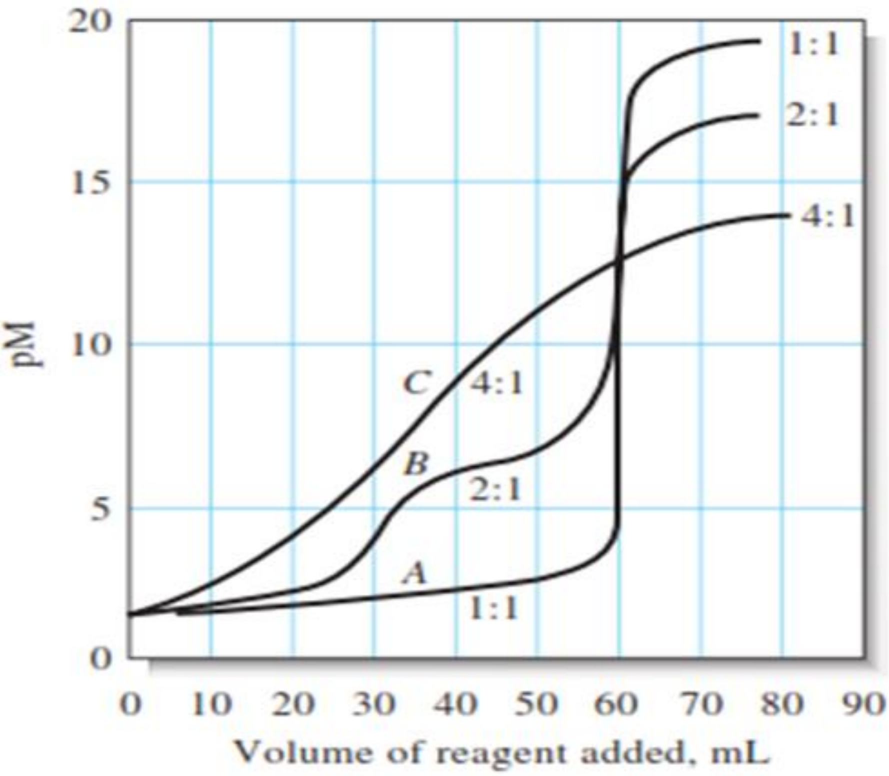

Figure 8-1 Titration Curves for Complexometric Titrations. Titration of 60.0 mL of a solution that is 0.020 M in metal M with (A) a 0.020 M solution of the tetradentate ligand D to give MD as the product; (B) a 0.040 M solution of the bidentate ligand B to give MB_2; and (C) a 0.080 M solution of the unidentate ligand A to give MA_4. The overall formation constant for each product is 10^{20}.

The most widely used complexometric titration employing a unidentate ligand is the titration of cyanide with silver nitrate. This method involves the formation of the soluble $Ag(CN)_2^-$. Other titrant are $Hg(NO_3)_2$ for analyte Br^-, Cl^-, SCN^-, CN^-, thiourea, and $NiSO_4$ for CN^-, and KCN for Cu^{2+}, Hg^{2+}, Ni^{2+}.