T.Y.B.SC. (SEM-V) C-503-UNIT-4-CHAPTER-7 COMPLEXOMETRIC TITRATION

Abstract

Complexometric titration (sometimes chelatometry) is a form of volumetric analysis in which the formation of a colored complex is used to indicate the end point of a titration. Complexometric titrations are particularly useful for the determination of a mixture of different metal ions in solution. An indicator capable of producing an unambiguous color change is usually used to detect the end-point of the titration.

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UNIT-4 COMPLEXOMETRIC TITRATIONS

Structure

11.1 INTRODUCTION

In the previous unit you have learnt about the principles and analytical estimations based on redox titration. In this unit you would learn about another very important type of titrimetric method based on complexation equilibrium. In this method, the metal ion to be determined is made to react quantitatively with a suitable reagent and is converted into a complex ion. The equivalence point of the titration is determined by using metal ion indicators or spectrometric or electrometric methods.

In this unit we begin with a brief review of the basic concepts of coordination compounds and the nature and characteristics of the metal-ligand complex equilibria. The basic principle of complexometric titrations and related issues will be illustrated by taking an important complexometric reagent called ethylenediamminetetraacetic acid, EDTA. We would conclude the unit with some important analytical applications of complexometric titrations.

Objectives

After studying this unit, you should be able to:

- define the terms associated with metal-ligand complexes,
- discuss the formation and stability of metal-ligand complexes,
- compute the stability and instability constants for the metal complexes from the given data,
- explain the principle of complexometric titrations,
- describe the theory of metallochromic indicators,
- enlist and explain different methods of detecting the end point in complexometric titrations,

- define and explain the terms like masking, demasking in the context of complexometric determinations,
- suggest strategies for determination of metal ions in a mixture, and
- enlist important analytical applications of complexometric titrations.

11.2 REVIEW OF COORDINATION COMPOUNDS

You would recall from your earlier studies that a number of metals especially the transition elements form a large number of complex compounds in which the metal atoms are bound to a number of anions or neutral molecules. The binding species are referred to as the ligands and the complexes so obtained are called **coordination compounds**. The basic ideas about the structure of these compounds were proposed by a Swiss chemist Alfred Werner. Let us recall some important terms and concepts which you would have learnt in your earlier classes.

11.2.1 Metal-Ligand Complexes

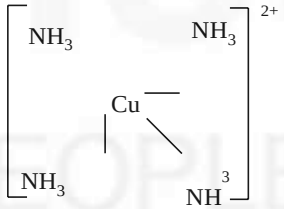
As in this unit we are going to learn about complexometric titrations, it becomes pertinent to recall the meaning and significance of associated common terminology. We begin with the term, complex.

Complex

It is a little difficult to give a comprehensive definition of the term complex. It may however, be sufficient to state that a **complex** or a **coordination compound** is formed when one or more charged or neutral species having lone pair of electrons form a coordinate bond with the metal (generally as positively charged ion). For example, four molecules of ammonia react with aqueous solution of copper (II) ions to give a deep blue coloured complex, named as tetraamminecopper (II) ion.

$$Cu^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4^{2+}];$$

(Tetraamminecopper II ion)



(Structure of tetraamminecopper II ion)

Similarly, carbon monoxide forms complex with metals like iron in the zero oxidation state to form what is called a **metal carbonyl**. You may note that the metals as well as the complexing agent both are neutral in case of metal carbonyls.

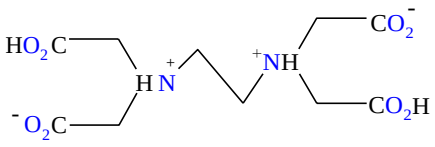
$$Fe(s) + 5CO(g) \rightarrow Fe(CO)_5$$

Ligands

The charged or neutral species with lone pair of electrons that form the coordinate bond with the metal (atom or ion) to form the complex are called **ligands**. These may be simple ions such as Cl^-, small molecules such as H_2O or NH_3, larger molecules such as $H_2NCH_2CH_2NH_2$ (ethylenediamine) or even very large macromolecules, like proteins etc. Further, a ligand that can form only one coordinate bond with the metal atom/ion is called a **unidentate ligand**. Similarly, the one forming two such bonds is called a **didentate** and the one forming more than two bonds is generally referred to as a **polydentate ligand**. However, the terms like, tridentate tetradentate etc. for the ligand forming 3 and 4 coordinate bonds respectively are also used. The number of bonds formed by the ligands is called as their **denticity**. For example one of very

commonly used ligand called ethylenediamminetetraacetic acid, EDTA, is a hexadentate ligand as it forms six bonds with the metal ion.

The structure of the EDTA and its metal complex are given Fig. 11.1. You would learn in details about the complex formation involving EDTA and the related issues and analytical applications in the subsequent sections.

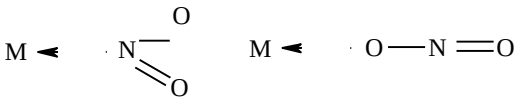


EDTA
Ethylenediaminetetraacetic acid

(a) **(b)**

Fig. 11.1: (a) Structure of EDTA and (b) its metal complex

You would recall that, sometimes, the ligand is capable of forming the bond through two different atoms. Such ligands are called **ambidentate ligands**. For example, NO_2 can coordinate either through nitrogen or through oxygen atom to a central metal atom/ion.

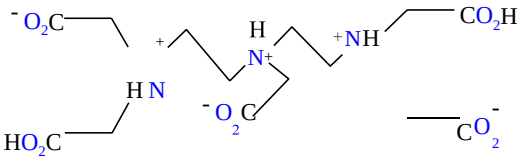


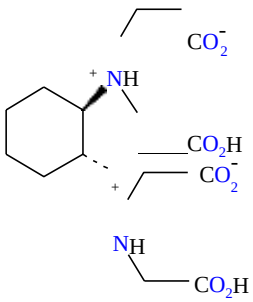
Similarly, the thiocyanate ion can form bonds through S or N atoms.

Chelates

When a polydentate ligand simultaneously forms more than one bond with the same metal atom/ion, it forms a ring type structure called **chelate**. The complexing agent is called a **chelating agent**. EDTA is a good example of a chelating agent. In EDTA a pair of unshared electrons capable of complexing with a metal ion is located on each of the two nitrogen atoms and each of the four ionised carboxyl groups. You may see the chelate or ring formation in the metal-EDTA complex given above. There is no fundamental difference between coordination compound and a chelate compound except that in a chelate compound, ring influences the stability of the complex formed. Thus, a chelate **can be described as a heterocyclic ring structure in which a metal atom/ion is a member of the ring.** The stability of a chelate is usually much greater than that of corresponding unidentate metal complex. The structures of some commonly used polydentate ligands are given in Fig. 11.2.

The word chelate is derived from the Greek word χηλή, chelè meaning claw.



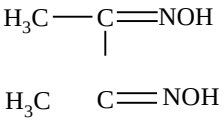


DTPA
Diethylenetriaminepentaacetic acid

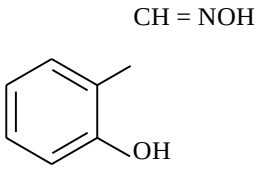
DCTA
***trans*- 1,2-Diaminocyclohexane-tetraacetic acid**

Fig. 11.2: Structures of some commonly used polydentate ligands

The solubility of metal chelates in water can be attributed to the presence of hydrophilic groups such as COOH, SO_3H, NH_2 and OH. If the chelating agent contains acidic as well as basic groups, the complex formed is soluble over a wide range of pH. In the absence of these groups, the solubilities of the chelating agent and the metal chelate are low. However, such chelates may be soluble in organic solvents. The chelating agents that form water-soluble complexes with bi- or polyvalent metal ions are called **sequestering agents.** These squeeze out the metal from the solution; in fact the metal remains in solution, but it fails to give normal ionic reactions as it exists in the form of a complex. Thus a sequestering agent may be defined **as a substance that apparently removes a metal ion from a solution by forming a complex ion that does not have the chemical reactions of the metal ion that is removed.** For example, ethylenediaminetetraacetic acid is a typical sequestering agent. It reacts with most polyvalent metal ions to form water soluble complexes which cannot be extracted from aqueous solutions with organic solvents. On the other hand the complexes of dimethylglyoxime and salicylaldoxime are insoluble in water, but dissolve in organic solvents. You should be clear about the fact that chelating agents generally are good sequestering agents but all chelating agents do not behave the same way. For example the ring forming ligands like, dimethylglyoxime and salicylaldoxime are just chelating agents as these form insoluble complexes.



Dimethylglyoxime



Salicylaldoxime

EDTA forms chelates with practically most of the metal ions and this fact is exploited in the complexometric determination of these ions using EDTA. Such titrations are called **complexometric** or **chilometric** or **EDTA titrations.**

Under favourable conditions, more than one metal ion may be present in the complex. In case two metal ions are present, the complex is called a **binuclear complex** and if there are more than two metal ions the complex is referred to as a **polynuclear complex**. The formation of binuclear and polynuclear complexes is favoured by the formation of complex using high concentration of the metal ion. For example, Zn^{2+} and Cl^- ions react to form a binuclear complex, $[Zn_2Cl_6]^{2-}$.

11.2.2 Metal-ligand Equilibrium

The formation of complex between metal and the ligand is an equilibrium process and is characterised by equilibrium constant. An understanding of the formation and dissociation of complexes is essential as it can be used to predict the optimum experimental conditions in methods of analysis based on complexation. In addition, the knowledge of accurate values of these constants can be exploited to explain the behaviour of new chemical systems that are affected by complex formation. Let us take the reaction between Cd^{2+} ion and NH_3. This is a typical complexation reaction and can be represented as given below.

$$Cd^{2+}(aq) + 4NH_3(aq) \quad [Cd(NH_3)_4]^{2+}(aq) \qquad \ldots (11.1)$$

The equilibrium constant for the formation of complex as given in Eq.11.1 is called **formation constant,** K_f, and can be written as follows.

$$K = \left[Cd(NH_3)^{2+}\right] = 5.5 \times 10^7$$

$$f \quad \overline{\left[Cd^{2+}\right]\left[NH_3\right]^4}^4$$

The reverse of reaction 11.1 is characterised by another constant, appropriately called **dissociation constant**, K_d as it corresponds to a dissociation reaction. Numerically the dissociation constant is the reciprocal of K_f.

$$K_d = \frac{1}{K_f} = \frac{[Cd^{2+}][NH_3]^4}{[Cd(NH_3)_4]^{2+}}$$

Generally the complexation reactions occur in a series of steps. The reaction between Cd^{2+} and NH_3 given above also occurs in the same way and involves four successive steps as follows.

$$Cd^{2+}(aq) + NH_3(aq) \rightleftharpoons [Cd(NH_3)]^{2+}(aq)$$

$$[Cd(NH_3)]^{2+}(aq) + NH_3(aq) \rightleftharpoons [Cd(NH_3)_2]^{2+}(aq)$$

$$[Cd(NH_3)_2]^{2+}(aq) + NH_3(aq) \rightleftharpoons [Cd(NH_3)_3]^{2+}(aq)$$

$$[Cd(NH_3)_3]^{2+}(aq) + NH_3(aq) \rightleftharpoons [Cd(NH_3)_4]^{2+}(aq)$$

As all the steps involve equilibrium reactions, it becomes somewhat difficult to ascertain which of the series of reactions is described by the formation constant defined above. In order to resolve this apparent ambiguity, two types of formation constants have been defined. According to the first type, the individual steps are characterised by what are called **stepwise formation constants**. These are designated as K_i for the *i*th step and characterise the successive addition of a ligand to the metal-ligand complex formed in the previous step. Accordingly, the equilibrium constants for four steps shown above are called as, K_1, K_2, K_3, and K_4 respectively. On the other hand, the **overall** or **cumulative formation constants** refer to the reaction upto a certain stage of complex formation. These are designated as β_i and characterise the addition of *i* ligands to the free metal ion. The overall equilibrium constant for the reaction given in Eq. (11.1) will be called as β_4 as it involves bonding of 4 ligands and (NH_3) to the metal ion. This can be shown as given below.

It has been assumed here that neither any insoluble product nor any polynuclear species is formed in the case of complex formation.

$$\beta_4 = K_1 \times K_2 \times K_3 \times K_4$$

In general, we can write it in the following manner

$$\beta_i = K_1 \times K_2 \times \ldots \times K_i$$

As you are aware, the solubility of certain solids or precipitates formed in a reaction increases due to the formation of complex ions. In such cases the characteristic equilibrium constant expression are obtained by combining relevant K_{sp} and K_f expressions. Let us take the example of the precipitate of AgCl. The solubility of AgCl increases in the presence of excess chloride due to the formation of the complex $AgCl_2^-$ ions. The reaction can be written as follows.

$$AgCl(s) + Cl^-(aq) \quad AgCl_2^-(aq) \qquad \ldots.(11.2)$$

The reaction can be separated into the three reactions with known equilibrium constant values. The first of these is the dissolution reaction of AgCl, characterised by its K_{sp} value

$$AgCl(s) \quad Ag^+(aq) + Cl^-(aq); \quad K_{sp} = [Ag^+][Cl^-]$$

The other two reactions are the stepwise formation of $AgCl_2^-$, from Ag^+ ions as given below, the respective equilibrium constants for the reactions being K_1 and K_2..

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(aq) \quad ; \quad K_1 = \frac{AgCl}{[Ag^+][Cl^-]}$$

$$AgCl(aq) + Cl^-(aq) \rightleftharpoons AgCl_2^-(aq) \; ; \quad K_2 = \frac{[AgCl_2^-]}{[AgCl][Cl^-]}$$

The equilibrium constant for reaction given as (11.2) would therefore be equal to $K_{sp}*K_1*K_2$.

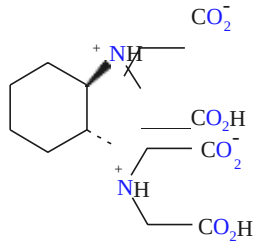
11.2.3 Factors Affecting Stability of Metal-Ligand Complexes

Some of the metal-ligand complexes are quite stable; however we cannot say the same for all the complexes. The stability of complexes is influenced by a number of factors related to the ligand and metal ions. Some of these are as follows.

1. **Nature of the metal ion**: The nature of metal ion determines the type of bonding with the ligand donor atom; more the electrostatic character of the bond stable the complex. Therefore, small ions with high charges lead to stronger complexes.
2. **Nature of the ligand**: The nature of bond formed between the ligand and metal ion also influence the stability. Moreso, the ligands forming chelates impart extra stability. For example the complex of nickel with the hexadentate ligand, penten, is more than 10^{10} times stronger than the one formed by ammonia.
3. **Basicity of the ligand**: The stability of a series of complexes can be correlated to the ability of the ligand to accept a proton; greater the basicity of the ligand greater the stability the complex.
4. **Size of chelate ring**: As mentioned above, the formation of chelates by the ligands makes the complex stable. The formation of five- or six-membered rings provides the maximum stability.
5. **Number of metal chelate rings**: **T**he stability of the complex is directly related to the number of chelate rings formed between the ligand and metal ion. Greater the number of such rings, greater is the stability.
6. **Resonance effects**: The formation of five- or six-membered rings can be explained in terms the conjugative effects which affect the stability of the complex also.
7. **Steric effects**: The steric effects refer to the sizes of the ligands, their spatial arrangement and the distances between the coordination sites. These also play an important role in the stability of the complexes.

SAQ 1

Define denticity of a ligand. Compute the denticity of the following ligand at a pH of more than 10.



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SAQ 2

Show that for the complexation of Cd^{2+} and NH_3, $\beta_4 = K_1 \times K_2 \times K_3 \times K_4$.

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11.3 PRINCIPLES OF COMPLEXOMETRIC TITRATIONS

A complexometric titration is the one in which the reaction between the analyte and titrant involves the formation of a complex. The earliest titrimetric applications involving metal-ligand complexation were developed by Justus Liebig. These pertained to the determination of cyanide and chloride ions using, Ag^+ and Hg^{2+} ions respectively as titrants; the complexes formed being $Ag(CN)_2$ and $HgCl_2$. The utility of complexation titrations improved after the introduction of amino carboxylic acids as multidentate ligands capable of forming stable 1:1 complexes with metal ions. Ethylenediaminetetraacetic acid, EDTA is probably the most widely used of these ligands. The earliest use of EDTA as a titrant could be achieved when metallochromic dyes were available as visual indicators for the end point determination.

In a typical complexometric titration a solution of a complexing agent is added to the analyte solution. This leads to the formation of a stoichiometric complex that is soluble and stays undissociated. Such a quantitative reaction forms the basis of quantitative complexometric determinations. The key steps in designing a typical complexometric determination are

- choosing a suitable complexing agent
- choosing a suitable method of detecting the end point
- choosing the experimental conditions that provides an optimum titration

Complexometric titrations have the advantages of complex formation and at the same time suffer from the limitations of titrimetric methods. For example, although the complex formed is undissociated, it does not suffer from co-precipitation errors as in the case of precipitation titrations. The fact that a complexing agent coordinates with only certain metal ions i.e., it shows selectivity is an added feature of the complex formation. However, on the flip side, the stoichiometry of the complex is not well defined as in a redox, neutralization, or precipitation titration. Further, if the complexing titrant is an organic compound, we need to be careful about the solubility properties of the complex. As mentioned earlier, EDTA is probably the most versatile and exploited titrant in complexometric titrations. Let us learn about the EDTA in detail.

11.3.1 EDTA: An Important Chelating Agent

EDTA is available in pure form but cannot be easily used as a primary standard. The solutions of EDTA are prepared from its soluble disodium salt, $Na_2H_2Y.2H_2O$. The disodium salt is generally preferred as it is non-hygroscopic, water soluble and a very stable sequestering agent. However, it must be dried at 80^o C for several days to obtain the precise composition of the dihydrate. In any case, standardisation of EDTA against a solution of the metal ion to be determined helps to eliminate any errors in endpoint

determination. Alternatively, the standardisation can be accomplished by titrating against a solution made from the primary standard $CaCO_3$.

Though EDTA has been extensively exploited for quantitative determinations of the metal ions it cannot be used for the direct analysis of anions or neutral ligands. In such cases, standard solutions of Ag^+ or Hg^{2+} are used as the titrants. The aqueous solutions of Ag^+ and Hg^{2+} are prepared from $AgNO_3$ and $Hg(NO_3)_2$, respectively. As both of these are secondary standards these need to be standardised. The standardisation is achieved by titrating the reagent against a primary standard like NaCl.

11.3.2 Equilibria Involved in EDTA Titrations

Ethylenediaminetetraacetic acid, or EDTA, is an aminocarboxylic acid that is a versatile titrant which can be used for the analysis of virtually all metal ions. It is a Lewis acid, having six binding sites (four ionised carboxylate groups and two lone pairs on the amino groups), providing six pairs of electrons. In typical analytical determinations completely deprotonated molecule of EDTA forms up to six coordination bonds with a single metal ion. It is accomplished by donation of the lone pairs of electrons to empty orbitals existing on the metal ion.

The resulting product of this reaction is a metal-chelate complex in which EDTA forms a cage-like structure around the metal ion. The actual number of coordination sites depends on the size of the metal ion; however, all metal–EDTA complexes have a 1:1 stoichiometry, irrespective of the valency of the ion as shown below.

$$M^{2+} + [H_2Y]^{2-} \rightleftharpoons [MY]^{2-} + 2H^+$$

$$M^{3+} + [H_2Y]^{2-} \rightleftharpoons [MY]^{-} + 2H^+$$

$$M^{4+} + [H_2Y]^{2-} \rightleftharpoons [MY] + 2H^+$$

The generalised reaction between the metal ion and the EDTA can be described as given below.

$$Y^{4-} + M^{n+} \quad MY^{n-4}$$

Where, Y^{4-} is a shorthand notation for the fully dissociated molecule of EDTA. The formation constant for the complex will be given as following.

$$K_f = \frac{[MY^{n-4}]}{[M^{n+}][Y^{4-}]}$$

For example, the formation of a metal-EDTA complex with Cd^{2+} can be represented as

$$Cd^{2+}(aq) + Y^{4-}(aq) \quad CdY^{2-}(aq)$$

The equilibrium constant (better called as formation constant) for the reaction is given as follows and has a value of 2.9×10^{16} implying that the complex is quite stable and the reaction goes far to the right.

$$K_f = \frac{[CdY^{2-}]}{[Cd^{2+}][Y^{4-}]}$$

The formation constant for the complexes formed by EDTA with different metal ions are compiled in Table 11.1.

Table 11.1: The formation constants of metal-EDTA complexes

Ion	log K_f	Ion	log K_f	Ion	log K_f
Li^+	2.79	Mn^{3+}	25.3 (25° C)	Ce^{3+}	15.98
Na^+	1.66	Fe^{3+}	25.1	Pr^{3+}	16.40
K^+	0.8	Co^{3+}	41.4 (25° C)	Nd^{3+}	16.61
Be^{2+}	9.2	Zr^{4+}	29.5	Pm^{3+}	17.0
Mg^{2+}	8.79	Hf^{4+}	29.5 (μ = 0.2)	Sm^{3+}	17.14
Ca^{2+}	10.69	VO^{2+}	18.8	Eu^{3+}	17.35
Sr^{2+}	8.73	VO_2^+	15.55	Gd^{3+}	17.37
Ba^{2+}	7.86	Ag^+	7.32	Tb^{3+}	17.93
Ra^{2+}	7.1	Tl^+	6.54	Dy^{3+}	18.30
Sc^{3+}	23.1	Pd^{2+}	18.5 (25° C, μ = 0.2)	Ho^{3+}	18.62
La^{3+}	15.50	Zn^{2+}	16.50	Tm^{3+}	19.32
V^{2+}	12.7	Cd^{2+}	16.46	Yb^{3+}	19.51
Cr^{2+}	13.6	Hg^{2+}	21.7	Lu^{3+}	19.83
Mn^{2+}	13.87	Sn^{2+}	18.3 (μ = 0)	Am^{3+}	17.8 (25° C)
Fe^{2+}	14.32	Pb^{2+}	18.04	Cm^{3+}	18.1 (25° C)
Co^{2+}	16.31	Al^{3+}	16.3	Bk^{3+}	18.5 (25° C)
Ni^{2+}	18.62	Ga^{3+}	20.3	Cf^{3+}	18.7 (25° C)
Cu^{2+}	18.81	In^{3+}	25.0	Th^{4+}	23.2
Ti^{3+}	21.3 (25°)	Tl^{3+}	37.8 (μ = 1.0)	U^{4+}	25.8
V^{3+}	26.0	Bi^{3+}	27.8	Np^{4+}	24.6 (25°, μ =1.0)
Cr^{3+}	23.4				

11.3.3 EDTA Titrations and pH

Ethylenediamminetetraacetic acid is a weak acid. It is a hexaprotic (H_6Y^{2+}) acid with successive pK_a values as given in the margins. Of the six values, the first four values correspond to the carboxyl protons, while the remaining two are for the ammonium protons. The equilibrium constant equation can be written as below.

pK_a values of EDTA

pK_1 = 0.0
pK_2 = 1.5
pK_3 = 2.0
pK_4 = 2.66
pK_5 = 6.16
pK_6 = 10.24

$H_4Y + H_2O \rightleftharpoons H_3O^+ + H_3Y^-$	$K_1 = 1.00 \times 10^{-2} = \frac{[H_2O^+][H_3Y^-]}{[H_4Y]}$
$H_3Y^- + H_2O \rightleftharpoons H_3O^+ + H_2Y^{2-}$	$K_2 = 2.16 \times 10^{-3} = \frac{[H_3O^+][H_2Y^{2-}]}{[H_3Y^-]}$
$H_2Y^{2-} + H_2O \rightleftharpoons H_3O^+ + HY^{3-}$	$K_3 = 6.92 \times 10^{-7} = \frac{[H_3O^+][HY^{3-}]}{[H_2Y^{2-}]}$
$HY^{3-} + H_2O \rightleftharpoons H_3O^+ + Y^{4-}$	$K_4 = 5.50 \times 10^{-11} = \frac{[H_3O^+][Y^{4-}]}{[HY^{3-}]}$

The Y^{4-} form of EDTA is the predominate form at pH values greater than 10.17 and are the only significant form for pH greater than 12. Now since EDTA exists in different forms at a given pH, the principle of mass balance requires that the total concentration of EDTA should be equal to the sum of the concentrations of all the forms of EDTA, viz.,

$$C_{EDTA} = [H_6Y^{2+}] + [H_5Y^+] + [H_4Y] + [H_3Y^-] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}]$$

This implies that the generalised formation constant defined in Eq. (11.1) is not a true formation constant because in the denominator it reflects only one form of EDTA viz., Y^{4-}. Thus, to get a clearer picture of the formation constant we define a parameter ($\alpha_{Y^{4-}}$) to be the fraction of EDTA present as Y^{4-}.

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{[H_6Y^{2+}] + [H_5Y^+] + [H_4Y] + [H_3Y^-] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}]}$$

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{[EDTA]}$$

The value of $\alpha_{Y^{4-}}$ depends on the concentration of H_3O^+ and the acid dissociation constants for EDTA. The expressions for $\alpha_{Y^{4-}}$ can be shown to be in the following manner.

$$\alpha_{Y^{4-}} = \frac{K_{a_1}K_{a_2}K_{a_3}K_{a_4}}{[H_3O^+]^4 + K_{a_1}[H_3O^+]^3 + K_{a_1}K_{a_2}[H_3O^+]^2 + K_{a_1}K_{a_2}K_{a_3}[H_3O^+] + K_{a_1}K_{a_2}K_{a_3}K_{a_4}}$$

The α values for other species are given in terms of the following expressions.

$$\alpha_{HY^{3-}} = \frac{[HY^{3-}]}{[Y']} = \frac{K_{a_1}K_{a_2}K_{a_3}[H_3O^+]^3}{D}$$

$$\alpha_{H_2Y^{2-}} = \frac{[H_2Y^{2-}]}{[Y']} = \frac{K_{a_1}K_{a_2}[H_3O^+]^2}{D}$$

$$\alpha_{H_3Y^-} = \frac{[H_3Y^-]}{[Y']} = \frac{K_{a_1}[H_3O^+]^3}{D}$$

$= \frac{a_1 \quad 3}{D}$

$$\alpha_{H_4Y} = \frac{[H\ O^+\quad]^4}{[Y']} = \frac{\quad^3}{D}$$

where,

$$D = [H_3O^+]^4 + K_{a_1}[H_3O^+]^3 + K_a\ K_a\ [H_3O^+]^2 + K_a\ K_a\ K_a\ [H_3O^+] + K_a\ K_a\ K_a\ K_a$$

The distribution of different species of EDTA as a function of pH is given in Fig. 11.3.

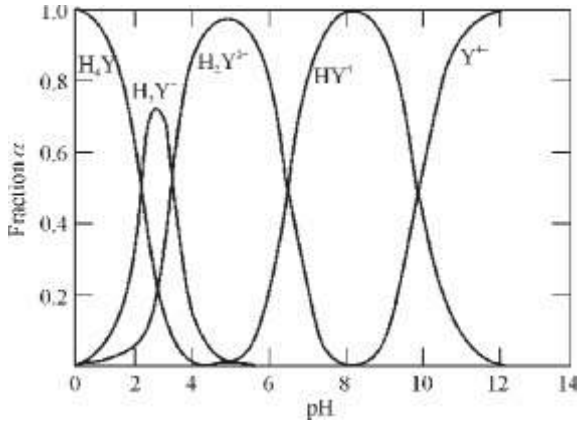

Fig. 11.3: Fractional distribution of different species in the solution of EDTA at different pH values

Fig. 11.3 reveals that in the acidic pH range the species, Y^{4-} is present at very low concentrations whereas it becomes the predominant species at pH of the order of 12.

Substituting the value of $\alpha_{Y^{4-}}$ in the formation constant expression, we get

$$K_f = \frac{[MY^{n-4}]}{[M^{n+}]\alpha_{Y^{4-}} C_{EDTA}}$$

Since at a given pH, the value of $\alpha_{Y^{4-}}$ is a constant it can be combined with the formation constant, we get the following.

$$K_f \times \alpha_{Y^{4-}} = K_f' = \frac{[MY^{n-4}]}{[M^{n+}] C_{EDTA}}$$

The new constant, K_f' is called **apparent** or **conditional stability constant**. As the $\alpha_{Y^{4-}}$ value becomes smaller and smaller with a decrease in the pH, the conditional formation constant also becomes smaller. This in turn means that the metal EDTA complex becomes lesser and lesser stable at low pH. Therefore it becomes pertinent to perform EDTA titrations at suitable pH values using appropriate buffer systems. The values of $\alpha_{Y^{4-}}$ for EDTA at different pH values are given in Table 11.2.

Table 11.2: The $\alpha_{Y^{4-}}$ values for EDTA at different pH values

pH	$\alpha_{Y^{4-}}$	pH	$\alpha_{Y^{4-}}$
0	1.3×10^{-23}	7	5.0×10^{-4}
1	1.9×10^{-18}	8	5.6×10^{-3}
2	3.3×10^{-14}	9	5.4×10^{-2}
3	2.6×10^{-11}	10	0.36
4	3.8×10^{-9}	11	0.85

5	3.7×10^{-7}	12	0.98
6	2.3×10^{-5}	13	1.00

Let us take an example to understand the importance of conditional stability constants.

Example 11.1

Compute the concentration of free Ca^{2+} ions in a 0.10 M solution of CaY^{2-} at a pH=6.0 and at pH=10.0. Use the data given in Table 11.1 and Table 11.2.

$$Ca^{2+} + EDTA \quad CaY^{2-} \qquad K_f' = \alpha_{Y^{4-}} K_f$$

	Ca^{2+}	+	EDTA	CaY^{2-}
$Conc_i$	0		0	0.1
$Conc_f$	x		x	$0.1-x$

$$K_f' = \frac{[CaY^{2-}]}{[Ca^{2+}][EDTA]} = \frac{0.1-x}{x^2}$$

Substituting the values and solving the equations we get the following.
At pH = 10

$$x = [Ca^{2+}] = 2.4 \times 10^{-6} \text{ M}$$

At pH = 6

$$x = [Ca^{2+}] = 3.0 \times 10^{-4} \text{ M}$$

This implies that the complex is less stable at pH = 6.0

11.3.4 Effect of Other Complexing Agents

In addition to pH, the presence of other complexing species also affects the formation constant of metal-EDTA complex, which in turn have effect on the complexometric titration. In case another complexing agent is present in the solution then the value of $[M^{n+}]$ in the formation constant expression gets altered. For example, in NH_4Cl / NH_3 buffer the ligand NH_3 is present which may form several stable M^{n+}–NH_3 complexes. For example, in the titration of Zn with EDTA in presence of ammonia buffer the metal ion forms four different ammonia complexes as given below

$$Zn^{2+} + NH_3 \rightleftharpoons Zn(NH_3)^{2+} \qquad K_{f_1} = \frac{[Zn(NH_3)^{2+}]}{[Zn^{2+}][NH_3]}$$

$$Zn(NH_3)^{2+} + NH_3 \rightleftharpoons Zn(NH_3)_2^{2+} \qquad K_{f_2} = \frac{[Zn(NH_3)_2^{2+}]}{[Zn(NH_3)^{2+}][NH_3]}$$

$$Zn(NH_3)_2^{2+} + NH_3 \rightleftharpoons Zn(NH_3)_3^{2+} \qquad K_{f_3} = \frac{[Zn(NH_3)_3^{2+}]}{[Zn(NH_3)_2^{2+}][NH_3]}$$

$$Zn(NH_3)_3^{2+} + NH_3 \rightleftharpoons Zn(NH_3)_4^{2+} \qquad K_{f_4} = \frac{[Zn(NH_3)_4^{2+}]}{[Zn(NH_3)_3^{2+}][NH_3]}$$

If EDTA forms a stronger complex with M^{n+} ion than ammonia then it will displace NH_3 from the metal-NH_3 complex. However, the presence of NH_3 decreases the

stability of the M^{n+}-EDTA complex. Therefore the presence of another complexing ligand like ammonia does affect the metal-EDTA equilibria. Similar to the case of EDTA at different pH values, here too the relative concentrations of the metal ion (zinc) can be expressed in terms of a parameter given below.

$$\alpha_{Zn^{2+}} = \frac{[Zn^{2+}]}{[Zn']}$$

where [Zn'] is the total concentration of zinc ions when no EDTA has been added,

$$[Zn'] = [Zn^{2+}] + [Zn(NH_3)^{2+}] + [Zn(NH_3)_2^{2+}] + [Zn(NH_3)_3^{2+}] + [Zn(NH_3)_4^{2+}]$$

The value of $\alpha_{Zn^{2+}}$ depends only on the concentration of NH_3 and the formation constants for the zinc-ammonia complexes. In general the parameter $\alpha_{M^{n+}}$ may be defined as the ratio of the concentration of the free metal ion to the all the forms of metal/ metal complexes present before the addition of EDTA.

11.3.5 Metal-EDTA Titration Curves

In the previous unit you have learnt about computing the titration curve for a redox titration wherein we computed the solution potential at different stages of the titration. We shall take up a similar exercise here also in the context of a complexometric titration. It is interesting to note that the computation is somewhat similar to the acid-base titration curve about which you learnt in the previous block. You would recall that in acid base titrations we measure the pH of the solution. In case of complexometric determination of metal ions we compute **pM**; the negative log of the free metal ion concentration present in the solution at different stages of the titration. The plot is similar to the one obtained in acid base titration. The schematic plot showing the titration curve of a metal EDTA titration is given in Fig.11.4.

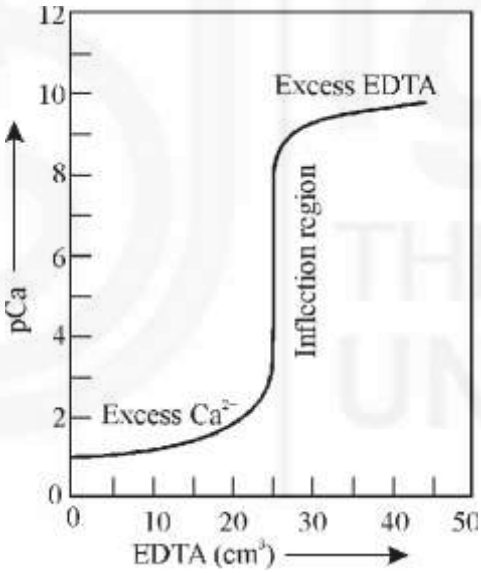

Fig. 11.4: A schematic diagram showing the titration curve of a metal EDTA titration

The schematic titration curve shown in Fig 11.4 has three distinct regions, the initial region where there is an excess of the metal ion the inflection region corresponding to the equivalence or end point and the third region where there is an excess of the titrant EDTA. The jump or the rise in the pM value around the equivalence point depends on many factors like the stabilities of the metal indicator and metal EDTA complexes besides pH. As discussed earlier, the value of $\alpha_{Y^{4-}}$ depends a great deal on the pH of the solution accordingly the titration curve also gets altered. The effect of pH on the titration curve of a metal-EDTA titration is shown in Fig.11.5.

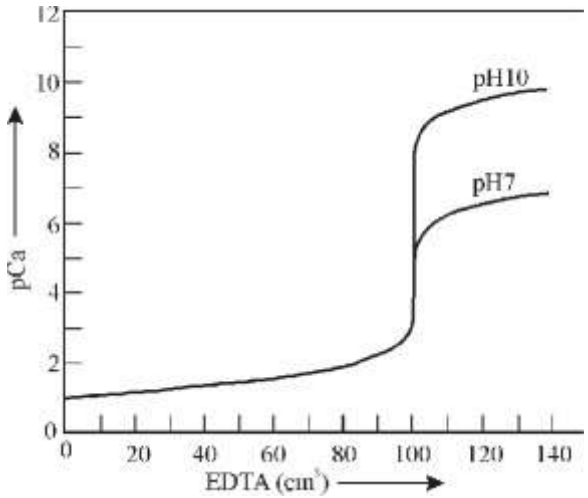

Fig.11.5: Effect of pH on the metal-EDTA titration curve

SAQ 3

Silver forms a 1:1complex with ethylenediamine having a formation constant of 5.0×10^4. Calculate the concentration of silver ions in equilibrium in a solution containing 0.1M each of the complex and the ligand.

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11.4 DETERMINATION OF EQUIVALENCE POINT

The equivalence point of a complexation titration occurs when stoichiometrically equivalent amounts of analyte and titrant have reacted. For titrations involving metal ions and EDTA, the equivalence point occurs when the concentrations of the metal ion and EDTA are equal. The accuracy of the end point depends on the relative strength of the metal–indicator and metal-titrant complex. If the metal-indicator complex is too strong, the color change occurs after the equivalence point. If it is too weak, the end point is observed before reaching the equivalence point.

As the concentration of metal ion decreases abruptly at the end point, in principle, any method, which can determine this disappearance of free metal ions, can be used to detect equivalence point in complexometric titrations. This is usually detected with a metallochromic indicator wherein the end point is determined by change in the colour of a metal ion indicator that responds to change in metal ion concentration. In addition, we may resort to instrumental determination of the equivalence point. Spectrophotometric, potentiometric and conductometric methods are commonly employed instrumental methods. Let us learn about the different methods of determination of the end point of complexometric titrations.

11.4.1 Metallochromic Indicators

The most practical and versatile method is the visual end point detection by using metallochromic indicators. Metallochromic indicators or metal ion indicators are the compounds that are capable of forming a complex with the metal ion being determined. In favourable conditions the metal-indicator complex formed has an intense color which is distinctly different from the uncomplexed indicator. The metal-indicator has

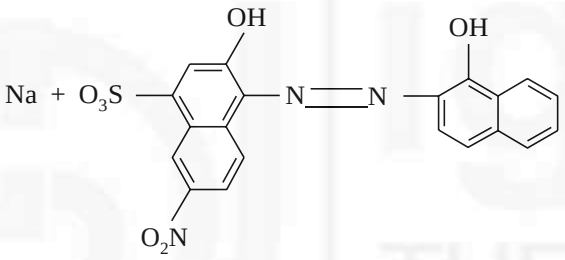
a low stability constant than the chelate-metal complex. Therefore, in the course of the titration the colour of the solution remains that of the metal-indicator complex until the end point, when an equivalent amount of the titrant has been added. At the equivalence point the titrant decomposes metal-dye complex to produce free dye which is manifested by a change in the colour. It is important that the stability constant for the metal-indicator complex is lower than the metal-titrant complex and has an optimum value. If it is too large, the sample will be over titrated, and if it is too small, an under titration is possible. Let us try to visualise the changes occurring during the course of complexometric titration involving metallochromic indicator.

As the indicator is added in very small amount generally no titration error is observed.

Let us denote the metal ion being determined as M, the indicator by I and titrant as T. In the beginning of the titration, the reaction medium contains the metal-indicator complex, MI and the uncomplexed metal ion, M; the metal ion being the major component. As the titrant, T is added to the solution, it complexes with the free metal ions; the MI complex being undisturbed. Once the free metal ions are exhausted, a competitive reaction sets in between the titrant and the indicator for the remaining metal ions. As the metal-indicator complex (MI) is weaker than the metal-titrant complex, the titrant binds the metal ions in preference to the indicator and in the process dissociates the MI complex. At the end point, EDTA removes the last traces of the metal from the indicator and the indicator changes its colour from the complexed colour form to its metal free colour. Let us illustrate it with the help of an example.

In case of an important complexometric determination viz., hardness of water we use eriochrome black T or solochrome black as metal ion indicator. Eriochrome black T is sodium 1-(1-hydroxy-2-napthylazo)-6-nitro-2napthol-4-sulphonate. Its structure is as shown below.

At present, several different indicators are available for each metal ion. It is possible to choose a metallochromic indicator purely on the basis of ease in observing a color change.



Eriochrome black –T

In the beginning of the titration, eriochrome black –T forms a wine red complex with the metal ions subsequent addition of the EDTA is used in complexing the free metal ion. At the end point of the titration, when the available metal ions are fully complexed with EDTA, the colour changes to blue– the colour of the free indicator.

$$MIn^{-} + H_2Y^{2-} \rightarrow MY^{2-} + HIn^{2-}$$

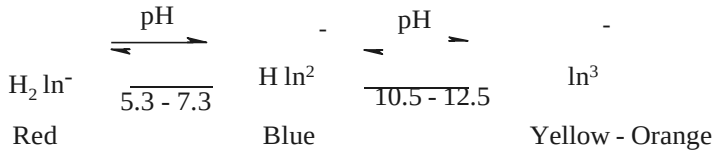
(wine red) (blue)

where H_2Y^{2-} represents disodium salt of EDTA and HIn^{2-} represents eriochrome black T in a buffer solution of pH 10.

While using the metallochromic indicators one must be careful about the pH of the reaction solution. This is so because most visual metallochromic indicators, in addition to being complexing agents, are also acid-base indicators. In other words, they are capable of undergoing a color change with a corresponding change in pH of the solution. For example, calmagite- an indicator for the determination of calcium ions which may be represented as H_3In, undergoes a change in color from the red (H_2In^{-}) to blue (HIn^{2-}) at a pH of about 8.1. The blue of HIn^{2-} changes to the red-orange (In^{3-}) at

a pH of about 12.4. As the color of metal-indicator complexes are red, it can be used as a metallochromic indicator only in the range of pH = 9–11, at which almost all the

indicator is present as HIn^{2-} (blue). It is, therefore, important to maintain the pH of the solution in the course of the complexometric titrations.



The useful pH range for some common metallochromic indicators is compiled in Table 11.3.

Table 11.3: Some common metallochromic indicators and their useful pH range

Indicator	Useful pH range	Useful for
Calmagite	9 – 11	Ba, Ca, Mg, Zn
Eriochrome Balck R	7.5-10.5	Ba, Ca, Mg, Zn
Eriochrome Blue R	8-12	Ca, Mg, Zn, Cu
Murexide	6-13	Ca, Ni, Cu
PAN	2-11	Cd, Cu, Zn
Salicylic acid	2-3	Fe

A number of metallochromic indicators are available. However, for any such indicator to be used for the visual detection of end points in complexometric titration must meet the following requirements.

- The colour reaction must occur at the end point when nearly all the metal ion is complexed with EDTA.
- The indicator must be very sensitive to metal ions (i.e. to pM) so that the colour change occurs as near to equivalence point as possible.
- The colour reaction should be specific or selective.
- The colour contrast between the free and the metal-bound indicator complex should be readily observable.
- The metal-indicator complex must possess sufficient stability else it would not display a sharp colour change. Further, the metal-indicator complex must be less stable than the metal-EDTA complex. This is to ensure that, at the end point, EDTA is able to remove all the metal ions from the metal indicator-complex. It is desirable that the change in equilibrium from the metal indicator complex to the metal-EDTA complex should be sharp and rapid.

11.4.2 Instrumental Methods of End Point Detection

The detection of end point of a complexometric titration with the help of metallochromic indicators is quite effective. Yet, we may have situations wherein either we do not have a suitable indicator or we are not in a position to use it, for example if the metal ion solution is intensely coloured. In such a situation it becomes pertinent to look for alternative means of detecting the end point. Some of the possible alternatives are discussed below.

Spectrophotometric Method

In spectrophotometric determinations we study the interaction of radiation with the analyte and measure the extent of radiation absorbed. You would learn in details about spectrophotometric determinations in the Block-1 of the MCH-003 course. The spectrophotometric method of end point determination in complexometric titrations

are meaningful when there is a drastic change in the absorption spectrum on the formation of a metal complex between the metal ion and the ligand or when one complex is converted to another. In such cases the end point can be detected more accurately and in relatively dilute solutions as compared to the visual methods. For example, in the titration using disodium EDTA an accurate end point can be obtained when the concentration is of the order of 0.001M. Another advantage of the spectrophotometric determination of the end point is that we can determine the end point of a titration involving a coloured ion without using an indicator. Further, the end point in the titrations involving colourless complexes can also be determined by making spectrophotometric measurements in the ultraviolet region.

Potentiometric Method

Potentiometric determination of the end point in complexometric titrations can be used only for those ions for which specific ion electrodes are available. This is so because since there is no change in oxidation state during the titration. Therefore a redox couple and a suitable indicator electrode or an ion selective electrode is a prerequisite for the purpose. It is, however, possible in case of some metal ions to perform the titration with a complexing titrant using an indicator electrode constructed from the same metal. The potential at the indicator electrode in such a situation would be determined by the half reaction.

$$M^{n+} + ne \longrightarrow M$$

the corresponding potential being given by the following Nernst expression.

$$E = E^{0}_{M^{n+}/M} - \frac{0.0592}{n} \log \frac{1}{[M^{n+}]}$$

A saturated calomel electrode is generally used to complete the cell. As the potential at the indicator electrode depends on the concentration of the free ions whose concentration decreases during the titration, the cell potential also changes. In the vicinity of the equivalence point there is an abrupt change in the pM value which in turn produces an abrupt change in the potential. In some cases, however, a mercury electrode can be made sensitive to EDTA ions and can be used for end point determination as explained under amperometric method.

Amperometric Method

Amperometry is an electroanalytical method of analysis in which the information about the analyte can be obtained by measuring the current developed on a microelectrode as a function of applied potential. The mercury electrode used for following the titration consists of a drop of mercury in contact with the solution containing the metal ion and a drop or two of the solution of Hg (II)-chelate. In case of EDTA as the titrant, the half-cell potential is determined by the Hg/HgY^{2-} couple.

The potential of this couple is altered by the changing concentration of M^{2+} ions that are being titrated as these also form complex with EDTA.

$$M^{n+} + HgY^{2} \rightarrow MY^{n-4} + Hg^{2+}$$

It can be shown that the potential at the stoichiometric point is determined primarily by the concentration of metal ion being titrated. The concentration of metal ions changes sharply at the stoichiometric point which in turn changes the electrode potential sharply. In general, abrupt potential changes of the order of about 200-250 mV can be easily and accurately detected; more stable the complex, larger is the potential change for the titration. As this indicates the end point, the amount of titrant added till this stage is equivalent to the amount of metal present. You would

learn about the technique of amperometric titration in details in Unit 9 of the MCH 004 course.

SAQ 4

What are metallochromic indicators? What is the principle of their action?

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11.5 APPLICATIONS OF COMPLEXOMETRIC TITRATIONS

As mentioned earlier, EDTA is a versatile chelating titrant that has been used in innumerable complexometric determinations. The versatility of EDTA can be ascribed to the different ways in which the complexometric titration can be executed. Let us learn about different ways in which we can use EDTA titrations.

1. **Direct Titration**: It is the simplest and the most convenient method in which the standard solution of EDTA is slowly added to the metal ion solution till the end point is achieved. It is similar to simple acid-base titrations. For this method to be useful the formation constant must be large and the indicator must provide a very distinct color change as mentioned earlier. Further we need standardized solution of EDTA and sometimes auxiliary complexing agents may be required. Some important elements which could be determined directly by the complexometric titration are Cu, Mn, Ca, Ba, Br, Zn, Cd, Hg, Al, Sn, Pb, Bi, Cr, Mo, Fe, Co, Ni, and Pd, etc. However, the presence of other ions may cause interference and need to be suitably handled.

2. **Back Titration**: In this method, an excess of a standard solution of EDTA is added to the metal solution being determined so as to complex all the metal ions present in the solution. The excess of EDTA left after the complex formation with the metal is back titrated with a standard solution of a second metal ion. This method becomes necessary if the analyte precipitates in the absence of EDTA or reacts too slowly with EDTA, or it blocks the indicator. For example, determination of Mn is done by this method because a direct titration is not possible due to precipitation of $Mn(OH)_2$. The excess EDTA remaining after complexation, is back titrated with a standard Zn solution using Eriochrome black T as indicator. However, one has to ensure the standard metal ion should not displace the analyte ion from their EDTA complex.

3. **Replacement Titration**: When direct or back titrations do not give sharp end points or when there is no suitable indicator for the analyte the metal may be determined by this method. The metal to be analyzed is added to a metal-EDTA complex. The analyte ion (with higher K_f') displaces EDTA from the metal and the metal is subsequently titrated with standard EDTA. For example, in the determination of Mn an excess of Mg EDTA chelate is added to Mn solution. The Mn ions quantitatively displace Mg from Mg-EDTA solution because Mn forms a more stable complex with EDTA.

$$M^{n+} + MgY^{2-} \rightleftharpoons (MY)^{(n-4)+} + Mg^{2+}$$

The freed Mg metal is then directly titrated with a standard solution of EDTA using Eriochrome black T indicator. Ca, Pb and Hg may also be determined by this method.

4. **Indirect Titration**: Certain anions that form precipitate with metal cations and do not react with EDTA can be analyzed indirectly. The anion is first precipitated with a metal cation and the precipitate is washed and boiled with an excess of disodium EDTA solution to form the metal complex.

$$M^{n+} + H_2Y^{2-} \rightleftharpoons (MY)^{(n-4)+} + 2H^+$$

The protons from disodium EDTA are displaced by a heavy metal and titrated with sodium alkali. Therefore, this method is also called **alkalimetric titration**. For example, barbiturates can be determined by this method.

11.5.1 Selectivity in Complexometric Titrations

EDTA is a very unselective reagent because it complexes with a wide variety of metal ions. In such a situation it becomes difficult to determine a given metal ion in presence of another ion. In order to achieve some kind of selectivity we need to exploit the differences in the stabilities of the metal-EDTA complexes, etc. A number of strategies have been evolved to perform selective determination of ions. This in turn increases the applicability of complexometric titrations based on EDTA. Some of the common strategies are as follows.

- Use of masking and demasking agents
- pH control
- Classical separation
- Solvent extraction
- Kinetic masking

Let us learn about these strategies.

Masking and Demasking

Masking may be defined as the process in which a substance without the physical separation of it or its reaction products is so transformed that it does not participate in a reaction. In simple words its reaction is masked. In the act of demasking the ability of the masked substance to participate in the reaction is recovered. This is useful if a sample contains a mixture of two or more metal cations. In one of the ways of masking, the masking agent acts either by precipitation or by formation of complexes that are more stable than the interfering ion-EDTA complex. For example, many heavy metals such as Co, Cu and Pb, can be separated in the form of insoluble sulphides using sodium sulphide. These are filtered, decomposed and titrated with disodium EDTA.

In masking by complex formation such masking agents are employed that form more stable complexes with the interfering metal ions than that with the ion under analysis. The most important aspect is that the masking agent must not form complexes with the metal ion under analysis. Let us take an example of masking agents used.

A mixture of Zn and Mg can be determined by treating the mixture with KCN which would form a complex with Zn ion and the magnesium ions can be titrated with EDTA. The masked Zn ions can be librated or demasked by treating with aldehydes such as formaldehyde and titrated with EDTA. In fact, potassium cyanide reacts with a number of metal ions such as silver, copper, mercury, iron, zinc, cadmium, cobalt and nickel, etc. in alkaline medium to form complexes which are more stable than the corresponding EDTA complexes, so that other ions, such as lead, magnesium, manganese and the alkaline earth metals can be determined in their presence.

The strategy of masking and selective demasking can be used for successive titration of a number of metal ions in a mixture. For example, the components of a mixture containing Mg, Zn, and Cu can be determined as per the following strategy.

1. In the first step an excess of standard EDTA is added to the mixture and the remaining EDTA is back titrated with a standard solution of Mg^{2+} ions using solochrome black as indicator. This provides the sum of the concentrations of all the three metals present.

2. In the second step a portion of the mixture is treated with an excess of KCN so as to mask the Zn and Cu ions in terms of their cyanide complexes. On titration we get the amount of Mg only.

3. In the next phase an excess of chloral hydrate (or a 3:1 solution of formaldehyde and acetic acid) is added to the titrated solution. This liberates the Zn^{2+} from the cyanide complex. The solution is now titrated until the indicator turns blue. This gives the amount of Zn only.

4. Knowing the amounts of magnesium and zinc, the amount of copper can be determined by subtracting the amounts of Mg and copper from the total amount of the metal ions obtained in step 1.

pH control

This method is based upon the differences in stability of the complexes formed between the metal ions and the chelating agent. As you have learnt earlier, the formation of a metal chelate is dependent on the pH of the reaction medium. In weakly acid solution, the chelates of many metals such as alkaline earth metals are completely dissociated, whereas chelates of Bi, Fe^{3+} or Cr are readily formed at this pH. Thus, in acidic solution, Bi can be effectively titrated with a chelating agent in the presence of alkaline earth metals. A mixture of bismuth and lead ions can be successfully titrated by first titrating the bismuth at pH 2 with xylenol orange as indicator, and then adding hexamine to raise the pH to about 5, and titrating the lead.

Classical separation

These are attempted only be applied if they are not tedious; further only those precipitates may be used for separations in which, after being re-dissolved, the cations can be determined complexometrically. Some of the examples are CaC_2O_4, nickel dimethylglyoximate, and CuSCN.

Solvent extraction

Solvent extraction may sometimes be employed for selectivity. In this method a metal ion in the mixture can be converted into a complex that can be extracted by a suitable solvent and then determined by EDTA. For example, Zinc can be separated from copper and lead by adding excess of ammonium thiocyanate solution and extracting the resulting zinc thiocyanate with 4-methylpentan-2-one (isobutyl methyl ketone); the extract is diluted with water and the zinc content determined with EDTA solution.

Kinetic masking

This is a special case in which the complexation of metal ion is too slow to be effective. In other words, the metal ion does not form a complex due to its kinetic inertness. For example, the reaction of chromium (III) with EDTA is quite slow. It is, therefore, possible to titrate other metal ions which react rapidly without interference from Cr (III). Determination of iron (III) and chromium (III) in a mixture is a typical example.

SAQ 5

Suggest a strategy for the complexometric determination of Zn and Mg in a mixture.

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11.6 SUMMARY

Complexometric titrations involve the reaction between the analyte and titrant leading to the formation of a stoichiometric complex that is soluble and stays undissociated. This quantitative reaction forms the basis of extensive applications of complexometric methods. Choosing a suitable complexing agent, selecting a method for the detection of the end point and ascertaining the optimum experimental conditions for the titration are essential steps of a complexometric determination.

Ethylenediaminetetraacetic acid, EDTA, is probably the most widely exploited chelating agent in complexometric determinations. It is a hexadentate ligand that forms 1:1 complexes with most of the metal ions. The complex formation is characterised in terms of an equilibrium constant called formation constant whose reciprocal is referred to as instability constant. As EDTA is a hexaprotic acid it dissociates to varying extent at a given pH. The ionic species and their concentration at a given pH affect the formation constants of different complexes. To account for these we have to use conditional formation constants. In addition to the pH of the medium, the presence of other complexing agents also affects the metal ligand equilibria and need to be considered.

The titration curve for the metal EDTA titration has three characteristic regions, the initial region where there is an excess of the metal ion the inflection region corresponding to the equivalence or end point and the third region where there is an excess of the titrant EDTA. The jump or the rise in the pM value around the equivalence point depends on many factors like the stabilities of the metal indicator and metal EDTA complexes. The equivalence point of the titration is usually detected with a metallochromic indicator that responds to change in metal ion concentration. The equivalence point is indicated by a change in the colour of the indicator. In addition, we may resort to instrumental methods like spectrophotometric, potentiometric and conductometric methods for the end point determination.

The versatility of EDTA as a chelating titrant has been used in innumerable complexometric determinations. The complexometric titration involving EDTA can be executed in a number of possible ways that leads to its extensive applications. EDTA is a very unselective reagent as it complexes with a wide variety of metal ions. However, it is possible to achieve some kind of selectivity by exploiting the differences in the stabilities of its complexes with different metal ions. Some of the strategies are use of masking and demasking agents, pH control, classical separation, solvent extraction and kinetic masking.

11.7 TERMINAL QUESTIONS

1. Enlist the key steps in designing a typical complexometric determination.

2. EDTA is a versatile complexing agent. What are its limitations?

3. Lead-EDTA chelate having the formula PbY^{2-} has a formation constant of 1.1×10^{14}. Compute the conditional formation constants at a pH = 10.

4. What are the essential requirements for a metallochromic indicator to be used for complexometric titrations? You may use Table 11.2 for the required data.

5. What is the principle of spectrophotometric determination of end point in complexometric titrations?

6. Explain with the help of a suitable example, the masking-demasking method of estimating different ions in a mixture by titrating against EDTA.

11.8 ANSWERS

Self Assessment Questions

1. Denticity of a ligand refers to the number of bonds formed by it with the metal atom/ion in a complex. At a pH of more than 10 the carboxyl groups and the substituted amino functional groups are expected to be ionised. Accordingly the given ligand would have a denticity of six or in other words it would act as a hexadentate ligand.

2. Cd^{2+} ions form a series of complexes with ammonia. The equations for the complex formations and the corresponding stepwise formation constants are as follows.

$Cd^{2+}(aq) + NH_3(aq) \rightleftharpoons Cd(NH_3)^{2+}(aq)$	$K_1 = \frac{[Cd(NH_3)^{2+}]}{[Cd^{2+}][NH_3]}$
$Cd(NH_3)^{2+}(aq) + NH_3(aq) \rightleftharpoons Cd(NH_3)_2^{2+}(aq)$	$K_2 = \frac{[Cd(NH_3)_2^{2+}]}{[Cd(NH_3)^{2+}][NH_3]}$
$Cd(NH_3)_2^{2+}(aq) + NH_3(aq) \rightleftharpoons Cd(NH_3)_3^{2+}(aq)$	$K_3 = \frac{[Cd(NH_3)_3^{2+}]}{[Cd(NH_3)_2^{2+}][NH_3]}$
$Cd(NH_3)_3^{2+}(aq) + NH_3(aq) \rightleftharpoons Cd(NH_3)_4^{2+}(aq)$	$K_4 = \frac{[Cd(NH_3)_4^{2+}]}{[Cd(NH_3)_3^{2+}][NH_3]}$

The expression for β_4 would be $\beta_4 = \frac{[Cd(NH_3)_4^{2+}]}{[Cd^{2+}][NH_3]^4}$

We are to demonstrate $\beta_4 = K_1 \times K_2 \times K_3 \times K_4$

Let us evaluate the R.H.S; $K_1 \times K_2 \times K_3 \times K_4 =$

$$\frac{[Cd(NH_3)^{2+}]}{[Cd^{2+}][NH_3]} \times \frac{[Cd(NH_3)_2^{2+}]}{[Cd(NH_3)^{2+}][NH_3]} \times \frac{[Cd(NH_3)_3^{2+}]}{[Cd(NH_3)_2^{2+}][NH_3]} \times \frac{[Cd(NH_3)_4^{2+}]}{[Cd(NH_3)_3^{2+}][NH_3]}$$

Cancelling the terms in the numerator and denominator, we get the following.

$$= \frac{[Cd(NH_3)_4^{2+}]}{[Cd^{2+}][NH_3]^4} = \beta_4$$

3. $Ag(NH_2CH_2CH_2NH_2)^+ \rightleftharpoons Ag^+ + NH_2CH_2CH_2NH_2$

Initial conc.:	0.1	0	0.1
Equilibrium conc.:	$0.1 - x$	x	$0.1 + x$

$$K_d = \frac{1}{K_f} = \frac{1}{5.0 \times 10^4} = 2 \times 10^{-5} = \frac{x \times (0.1 + x)}{(0.1 - x)}$$

As the K_d value is small we can ignore x in comparison to 0.1, we get the following.

$$= \frac{x \times (0.1)}{(0.1)} = x = 2 \times 10^{-5}$$

4. Metallochromic indicators or metal ion indicators are the compounds that are capable of forming a complex with the metal ion being determined and can be used to determine the end point in the complexometric determination of the metal ions.

   The metal-indicator complex has a lower stability constant than the titrant-metal complex and has an intense color which is distinctly different from the uncomplexed indicator. In the beginning of the titration the indicator forms a complex with the metal ion and the solution bears the metal-indicator complex colour. When the titrant, EDTA is added it complexes with the free metal ion till they are present and thereafter the titrant displaces the indicator from the metal-indicator complex and the colour of solution changes indicating the end point in the titration.

5. A mixture of Zn and Mg can be determined by using back titration and masking. An excess of standard EDTA can be added to the mixture and the remaining EDTA is back titrated with a standard solution of Mg^{2+} ions using solochrome black as indicator. This provides the sum of the concentrations of all the two metals present. Thereafter a portion of the mixture can be treated with an excess of KCN so as to mask the Zn as its cyanide complex and the amount of magnesium can be determined by titration with EDTA.

Terminal Questions

1. The key steps in designing a typical complexometric determination are as follows.
   - choosing a suitable complexing agent
   - choosing a suitable method of detecting the end point
   - choosing the experimental conditions that provide an optimum titration

2. It is true that EDTA is a versatile complexometric agent and has been extensively exploited for quantitative determinations of the metal ions. However, it cannot be used for the direct analysis of anions or neutral ligands.

3. We know that, $K'_f = \alpha_{Y^{4-}} K_f$

   The value of $\alpha_{Y^{4-}}$ at a pH of 10 = 0.36 and the value of $K_f = 1.1 \times 10^{18}$

   $\Rightarrow K'_f = 0.36 \times 1.1 \times 10^{18} = 3.96 \times 10^{17}$

4. In order to be used as a metallochromic indicator in complexometric titrations it should meet the following requirements.

- The colour contrast between the free and the metal-bound indicator complex should be readily observable.
- The colour reaction should be specific or selective.
- The metal-indicator complex must possess sufficient stability and it must be less stable than the metal-EDTA complex.
- The change in equilibrium from the metal indicator complex to the metal-EDTA complex should be sharp and rapid.
- The colour reaction must occur before the end point when nearly all the metal ion is complexed with EDTA.

5. The spectrophotometric method of end point determination in complexometric titrations is based on the change in absorption spectrum on the formation of a complex between the metal ion and the ligand or the conversion of one complex to another.

6. In this method of determination of more than one metal ion in a mixture thereof, generally one of the metal ions is made to react with a suitable reagent called masking agent such that the metal ion is so transformed that it does not participate in the reaction. The other ions are then determined. The masked ion can then be demasked and determined. For example, a mixture of Zn and Mg can be titrated by treating the mixture with KCN which would form a complex with Zn ion and the magnesium ions can be titrated with EDTA. The masked Zn ions can be librated or demasked by treating with aldehydes such as formaldehyde and titrated with EDTA.

SOME USEFUL BOOKS

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