COMPLEXATION TITRATION

-they are those in which a complexing agent is used to estimate polyvalent ions

-A complexing agent is an electron donating ion or molecule(ligands), capable of forming one or more covalent or co-ordinate bonds with metal ion and has property different than metal ion

-It is also k/a chelatometry or EDTA titration and these can be considered to be highly accurate titration which can be helpfulin determination of metal ion at conc^{n} of millimol level

- if a single bond is formed b/w complexing agent and metal , then it is called ligands

- if a complexing agent can form more than one bond with polyvalent ion, then it is considered as polydentate& clled as chelating agent.

-if complex formed is soluble in form then it is sequestering agent.

Ligands

The molecular or ionic species which gets directly attached to central metal atom during the formation of complex is called as ligands.

- Ligands attached to central atom through coordinate bond and therefore any atoms,ions or molecule which have tendency to donate a pair of electron to the central metal atom can work as ligands.

Classification of ligands

I Classification on the basis on no of donar atom

i) Monodentate ligands – the ligand which possess only donar atom & can form only one coordinated bond to central metal atom or ion

Aqua H_2O – donar atom (O)

Ammine NH_3 ” (N)

Carbonyl CO ” (O)

Cyano ” (C or N)

ii) Bidentate ligand – the ligand which possess two donar atom & form two co-ordinate

Bond with metal atom or ion.

Eg oscalato COO^{2} donor atom (O & O)

COO

Glycine $NH_2CH_2COO^-$ doanr atom (N&O)

iii) Tridentate ligand- the ligand which possess three donor atom and can form three co-ordinate bond with metal atom or ion

iv) Tetradentate ligand- the ligand which possess 4 donor atom and can form four co-ordinate bond with metal atom or ion

v) Pentadentate ligand- the ligand which contain five donor atom.

vi) Hexadentate ligand – the ligand which contains six donor atom

vii) Bridging ligands – the monodentate ligands which can simultaneously attach themselves to more than one metal ion

Nature of ligands

Ligands or lewis base because they act as e^- donor and hence greater the basic strength of ligands, grater is the stability of complex.

Eg CN^- is more basic than NH_3 therefore cyanocomplexes of a metal ion are more stable than its amine complex

Complexation indicator

M+In

Indicator used in complexometric titration are coloured compound which form coloured chelates with metal ions producing visible colour change & hence are also k/a metalochromic indicator

- These indicator are weak complexing agent that gives different coluors in their complex and uncomplexed form.

- If complexometric rxn are to be achieved successfully ,the metal titrant complex must be more stable than metal indicator complex,so that a sharp cpolour change is obtained.
- Let a metal be denoted by M, indicator by In & Chelate by EDTA
- At the beginning of the reaction the medium contains metal indicator complex (M In) & excess of metal ion(M)
- When EDTA titrant is added to the system competitive rxn takes place b/w free metal ion and EDTA
- Since metal indicator complex is weaker than metal EDTA complex , the metal EDTA is added during the course of titration forms the metal EDTA complex & at the end point, EDTA removes the last traces of metal from the indicator & the indicator changes from the complexed colour to its metal free colour
- If we plot p^m(negative logarithm of metal ion $conc^n$) vs volume of titrant we will find that at the end pt the metal ion $conc^n$ decreases which shows that traces of metal ion has been removed by EDTA

Stability constant of P^m indicator

P^m is a negative logarithm of metal ion concentration.

The value of P^m can be derived from stability constant

According to law of maa action & chemical equ…..

Then , apply negative log ob both side

If a solution is made such that [X=MX] then

Where, k^1= dissociation constant

This means that in a solution containing equal activities of metal complex and free chelating agent, the concentration of metal ion will remain roughly constant

Since chelating agent are also bases the eequl……? in metal buffer solution is often affected by the change in ph

Factors affecting the end point of titration

1) Stability of complex formed
   The greater the stability constant for complex larger is the change of free metal concentration at the equivalence point & more clear could be the end point .
2) The no of steps involved in complex formation
   Fewer the no of steps required in the formation of complex greater will be the break in titration curve at equivalent point & clear would be the end point
3) Effect of ph
   During the complexation titration , the ph must be constant by a use of buffer solution because H+ ions plays an important role in complexation.Most ligands are basic and binds to H+ ions throughout a wide range of ph .some of these H+ ions are frequently displaced from ligands by metal during chelate formation

- Thus stability of metal complex is ph dependent

- Lower the ph of solution less would be the stability of complex because more H+ ion are available to compete with the metal ion for the ligands.

Characteristics of indicator

It is affected by ph

It is used in small concentration (10^{-8}-10^{-6} molar)

It should formed 1:1 complex with the metal ion which must be weaker than metal EDTA complex.

It should be stable and should not react with the solution

The coulour of the indicator and metal complex should be sufficiently different in order to get clear end point and should not compete with EDTA.

It should be chemically stable throughout the titration

Eg eriochrome black T or solochrome black T , calmagite ,murexide ,arsenaza T.

EDTA (Ethylene diamine tetraacetic acid)

It is most widely used analytical chelator used in analysis

Chemaiclay it is 2-(2-(Biscarboxymethylamino ethylcarboxymethyl aminoacetic acid)

It is also known as H_4 EDTA ,editic acid Gluma cleanser , trilon

- EDTA is a tetraprotic acid & can exist & can exist in variety of protonated form represented by

Any or all of these forms may react with given metal to yield a metal EDTA complex and each reaction would be represented with different K.

EDTA is a amphiprotic substance which means that it can donate and accept proton.

The 4 H_2 atom are acidic and because of this formula of EDTA is often written as X_4Y (X_4= 4 acidic H_2 atom & Y- remaining structure)

The lone pair of e- on N atom in EDTA are capable of accepting proton.

EDTA can therefore exist in many different forms depending upon ph of solution.

At very low ph EDTA will be present in its protonated form (H_6Y^{2+})

At very high Ph ,EDTA will be present in its completely deprotonated form Y^{4-}

Eg

Very stable complexis formed b/w metal ions and EDTA in its completely deprotonated form Y^{4-}

In order to get significant portion of EDTA into this form, solution of EDTA used in titration are typically buffered at high Ph

EDTA is mostly purchased as dehydrated salt eg-disodium EDTA

Stability of complex

1) Stability complex

Most of the reaction involved in complexometric titration are achieved by combining metal ions with chelating agent in 1:1 ratio.

Increase in temperature cause slight increase in the ionization of the complex and slight lowering of K

- The presence of electrolyte having no ion in common with the complex decreases K but the presence of ethanol increases 'K' due to separation of of ionization
- The stability constant is an important parameter of a complex.It may be used to express the stability of a complex because it indicates the stability of a complexes form.
- Higher the value of stability constant greater is the thermodynamic stability of the complex in a solution.

2) Effect of ph

At very high ph , EDTA will be present in its completely deprotonated form & a very stable complex can be achieved in this form.

- However as the ph of the solution goes up the value of OH increases & so they tend to precipitate out of the solution as metal hydroxide
- Once the metal has precipitated out it is not in the solution, so it cannot react.
- The effect of hydroxide can be minimized through the use of auxiliary complexing agent eg NH_3,tartarate,citrate,etahnalomine).

3) Charged density on central metal ion

The stability of complex depends upon the charged density on the central metal ion which inturn depends upon charge /radius ratio (higher the magnitude of charge & smaller the size of ion , more will be the charged density & greater is the stability of the complex)

For eg :- magnitude of the charge on CO^{2+} & Cd^{2+} ion is the same but ionic radius of CO^{2+} ion is 69 and Cd^{2+} is 97.

Charge density of CO^{2+} is greater than Cd^{2+} and hence complexes formed by CO^{2+} is more stable than Cd^{2+}.

Types of complexation titration

i) Direct titration
ii) Back titration
iii) Replacement or substitution titration

iv) Alkalimetric titration

Back titration method

Back titration technique must be adopted when the metal to be determined cannot be kept in a solution at the ph needed for complex formation or when there is no suitable indicator for the titration

-If standard solution of EDTA is titrant , it is added in excess and the solution is buffered and back titrated with standard solution of metal ion

- Usually standard solution for back titration is made of $MgSO_4$ or $ZnSO_4$.

Substitution titration

In this method there is replacement of one ion by another .

-The most widely used application is the titration of metal ions with EDTA

- In this case metal ion to be determine can be treated with magnesium complex of EDTA.

- The magnesium complex is less stable than metal EDTA complex & after the displacement occurs , the Mg ions are titrated with standard EDTA solution.

Alkalimetric titration

If one controls the ph of the solution of EDTA the following two reaction with metal ions are important.

The hydrogen ions are titrated & can be titrated with standard base using a potentiometric end point or acid base indicator.

- This type of titration can be used as back titration method to avoid large excess of EDTA.

- The acid liberated can also be determined by iodometric method & iodine liberated is titrated with standard thiosalphate solution

-Alkalimetric method have the disadvantage that the solution of metal to be titrated must be neutralized before titration starts.

Masking and Demasking

Whenever in procedure we require to suppress interfering species in a solution without any physical separation, it is done by using masking agent.

- Cyanide ion is the effective masking agent for the determination of Ca & Mg
Following species of cations interfere with the determination of Ca & Mg

Cd,Cu,Zn ,Ni ,Ag

Demasking
This is the process to revive the metal ions which are suppressed by masking agent so that they can take part in a chemical reaction
Eg methanol ethanoilacid
Chloral hydrate

Need of Masking and Demasking Agent
EDTA as well as its salt complexes with several metal ions & during the estimation of specific ion other ionic impurities are also estimated. This gives false value.

2) Sometimes when two or more ions are estimated in the same mixture each ion has to be selectively titrated

Method
– Addition of precipitants

- Addition of complexing agent

- ph control

1) Addition of precipitants
When interference due to the following ions are encounter, the precipitants are added and collected ,then estimated separately.

Interfering ion	Precipitants
Zn, Cu	Ferrocyanide
Cu ,Co,Pb	Na sulphide,thioacetamide

2) Addition of complexing agent
Addition of complexing agent causes formation of complexes with interfering ions
- These complexes are more stable than EDTA complexes and thus eliminates impurities & titration can be done easily.

Eg Interfering ion	Complexing agent
- Al,Fe,Titanium	Ammonium Flouride

- Hg	K iodide
- Ag, Cu ,Hg,Zn,Cd,Co,Ni	K cyanide in alkaline medium

3) pH control

EDTA complexes with alkaline earth metal are not stable below pH-7 but in this pH range and upto pH-3, complexes with iron, cobalt and thorium are stable and can be selectively titrated with varying pH.