Complexometric Titration II

Indicators

- ***Indicator*** is a dye which is capable of acting as a chelating agent to give a dye-metal complex.
- The latter is different in colour from the dye itself and also ***has a low stability constant than the chelate-metal complex***.
- The colour of the solution, therefore, remains that of the dye complex until the end point, when an equivalent amount of sodium EDTA has been added.
- As soon as there is the slightest excess of EDTA, the metal-dye complex decomposes to produce free dye; this is accomplished by a change in colour.

❖Metal indicators must comply with the following requirements:

- Metal-indicator complex *must be less stable than the metal-EDTA complex*.
- Binding between metal and indicator *must not be too weak*. It has to avoid EDTA replacing at the beginning of the titration.
- In general, the metal-indicator complex *should be 10 to 100 times* less stable than the metal-titrant complex.
- Colour of the indicator and the metal complexed indicator *must be sufficiently different*.

EDTA Titration Techniques

Direct Titration

Many metals can be determined by direct titrations with EDTA.

Weak metal complexes such as Ca^{2+} , Zn^{2+} and Mg^{2+} should be titrated in basic solution using EBT, Calmagite, or Arsenazo I as the indicator.

- Example
- **Direct determination of Zn^{2+} with EDTA**
- - The complex of ***Zn^{2+}*** with ***EDTA*** is more stable than its complex with ***EBT*** ind.
- **Zn^{2+} + H Ind.$^{2-}$ $\longrightarrow$ Zn Ind.$^{-}$ + H^{+}**
- **Zn Ind.$^{-}$ + H_2Y^{2-} $\longrightarrow$ *ZnY^{2-} + H Ind.$^{2-}$ + H^{+}***

wine red **Blue**

EDTA Titration Techniques

. *Back Titration (indirect)*

- It can be performed for the determination of several metal ions can not be titrated directly but form stable EDTA complexes.

The procedure, a known amount of EDTA is added to the analyte sample solution and the excess is back titrated with a standard solution of "weak" metal ion, Mg^{2+}.

The weak metal ion will not displace the analyte from its EDTA complex.

· ***It is used in the following cases: (when can be used?)***

A. Insoluble substances **e.g.** ***$BaSO_4$, $Ca(C_2O_4)_2$, $PbSO_4$, $Mg_3(PO_4)_2$ … etc.*** Usually soluble in hot ***EDTA.***

B. The reaction between ***M^{n+} & EDTA*** is slow (incomplete) **e.g. Fe^{3+} , Al^{3+} , Cr^{3+} , Th^{4} , … etc.**

C. The ***M^{n+}*** is pptd. at the pH suitable for titration e.g. ***$Al(OH)_3$.***

EDTA Titration Techniques

- *Displacement Titration (what is the conditions??)*

A. The technique **only works** <u>when the unknown metal has tighter binding to EDTA than the Zn^{2+} or Mg^{2+}</u>.

B. Metal ions with <u>no satisfactory indicator</u>.

- MgY^{2-} or ZnY^{2-} complex is added to the solution of unknown metal ion composition.
- · The unknown metal displaces the Mg^{2+} or Zn^{2+}, which is then back titrated.

- $M^{n+} + MgY^{n-2} \longrightarrow MY^{n-4} + Mg^{2+}$

- K_f' for $MY^{n-2} > K_f'$ for MgY^{n-2}

K_f' is constant of complex formation

Titration of Mixtures

- ***EDTA*** is **not a selective reagent** (it chelates with most metal ions)
- Selectivity of ***EDTA*** can be increased by one of the following procedures:
  a) Control of pH of the medium
  b) Adjustment of oxidation number of metal ion
  c) Masking and demasking agent

a) Control of pH of the medium

- **First group:** Trivalent & tetravalent cations **e.g.** ***(Bi^{3+} , Fe^{3+} , Th^{4+})*** and ***Hg^{2+}*** titrated (form stable complex) at pH 1-3 using conc. ***HNO_3.***
- **Second group:** Divalent metals **e.g.** ***(Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , pb^{2+}*** and ***Cd^{2+})*** titrated (form stable complex) at pH 4-6 using acetate buffer.
- **Third group:** Alkaline earth metal **e.g.** ***(Ba^{2+} , Sr^{2+} , Ca^{2+})*** and ***Mg^{2+}*** titrated (form stable complex) at pH=10 using ammonia buffer or 8% ***NaOH.***
- **From the mentioned above,** we can titrate ***M^{n+}*** of the first group at pH 1-3 without interference of the second and third groups or at pH 4-6 we can titrate ***M^{n+}*** of the second group without interference of the third group.
- **e.g.** Mixture of ***Bi^{3+} & pb^{2+}:*** First titrating ***Bi^{3+}*** at pH = 2 using xylenol orange as ind., then increased pH to 5 by adding hexamine and titrating ***pb^{2+}.***

b) Adjustment of oxidation number of metal ion

- This solves the interference between M^{n+} of the same group of pH.
- **Examples:**
- Ascorbic acid (vit. C) is reducing agent used in:
- Removal of interference of Fe^{3+} in first group (pH 1-3) ⟶ reduced to Fe^{2+}
- Removal of interference of Hg^{2+} in first group (pH 1-3) ⟶ reduced to Hg^{o} (pptd.).
- Removal of interference of Cu^{2+} in second group (pH 4-6) ⟶ reduced to ***cuprous*** (Cu^{1+}).

- Oxidation of Cr^{3+} $\xrightarrow[H_2O_2]{\text{alkaline}}$ to CrO_4^{2+}

- Fe^{2+} , Hg^{o}, ***Cuprous*** , CrO_4^{2-} do not react with ***EDTA***

c) Masking and demasking agent

- **Masking agents:** Protects some component of analyte from reacting with EDTA. **These reagents** form complexes with interfering ions which **are more stable than complexes formed with ind. & *EDTA*.**

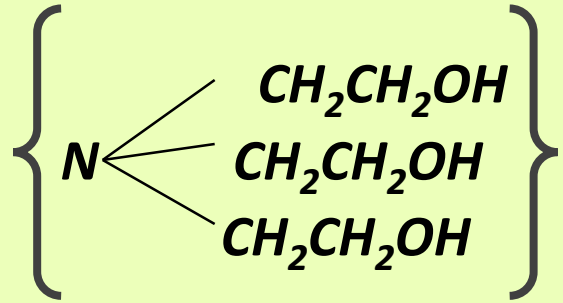
- **Examples of masking agent:** **(give examples of masking agent)**

KCN: It is used as masking agent for Ag^{+} , Cu^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , … etc.

$$M^{+} + 2\,CN^{-} \longrightarrow [M(CN)_2]^{-}$$

$$M^{+} + 4\,CN^{-} \longrightarrow [M(CN)_4]^{2-}$$

Triethanolamine: It is used as masking agent for Fe^{3+} , Al^{3+} and Sn^{2+}



Fluoride (e.g. NH_4F): It is used as masking agent for Fe^{3+} and Al^{3+} to give $[FeF_6]^{3-}$ and $[AlF_6]^{3-}$

Iodide (*KI*): It is used as masking agent for Hg^{2+} to give tetraiodo complex (HgI_4)

- **Demasking agent :** Releasing masking agent from analyte.
- **Example:**
- Example of using masking and demasking agents in complexometry is the analysis of 3 metals, Cu, Cd and Ca. the following method of analysis is followed

Step 1: All metals are titrated

Ca → Ca-EDTA

Cd + EDTA ⇌ Cd-EDTA

Cu → Cu-EDTA

How can we determine a mixture of metals using complexometric titration?

Step 2: Only Ca titrated

[Cu, Cd] + cyanide ion → [Cu-cyanide]complex

[Cd-cyanide]complex

Ca + cyanide ion → no reaction $\xrightarrow{\text{EDTA}}$ *Ca-EDTA*

- *Step 3: Cd and Ca are titrated*
- *[Cd-cyanide]complex + HCHO* $\rightleftharpoons$ *Cd^{2+} (free)*

- *[Cu-cyanide]complex + HCHO* $\longrightarrow$ *no reaction*

demasking agent

Cd

+ EDTA $\rightleftharpoons$ { *Cd-EDTA* ; *Cu-EDTA* }

Cu

Oxidation with H_2O_2 releases Cu^{2+} from [Cu^{+}-Thiourea] complex.