PRINCIPLES OF ESTIMATION BASED ON COMPLEXOMETRY

The volumetric analysis, which involves the estimation of metal ions through the complex formation with a strong multidentate chelating ligand using suitable metal ion indicator, is known as Complexometry. This is also known as complexometric titration.

Conditions necessary in Complexometric titrations:

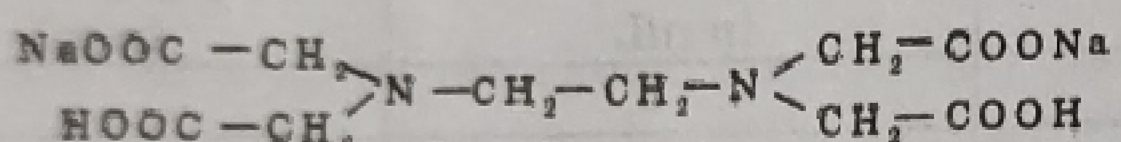
(i). The value of stability constant should be high.

(ii). During complexation the coordination number of the metal ions must be satisfied simultaneously to form water-soluble species.

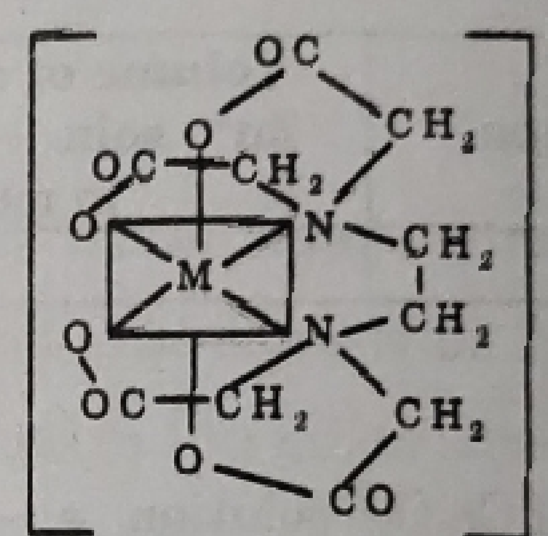
(iii). The rate of the reaction should be fast.

(iv). The end point of the titration should be sharp and suitable indicator must be available for this purpose.

Ethylenediaminetetraacetic acid (EDTA) is commercially available in the form of its water soluble disodium salt, $Na_2H_2EDTA.2H_2O$ (F.W. = 372.24, also called EDTA). It is a hexadentate ligand and forms 1:1 stable complexes with many metal ions.



Na_2H_2EDTA



$[M(EDTA)]^{(n-4)-}$

General Principle:

The metal ions may be quantitatively estimated complexometrically either by direct titration with a standard solution of EDTA or by back titration of the excess EDTA solution of known strength with a standard solution of metal ion.

Na_2H_2EDTA is cannot be used as a primary standard, as it may absorb some moisture. Zinc acetate dihydrate, $Zn(OOCCH_3)_2.2H_2O$ (F.W. = 219.5) is commonly used as the primary standard to standardise EDTA solution. Aqueous solution of zinc acetate is alkaline due to hydrolysis of acetate ion and zinc hydroxide (solubility product: Ks ~10^{-15}) is precipitated. To obtain a clear solution, zinc acetate is dissolved in 1-2% NH_4Cl solution, which is sufficiently acidic to prevent the precipitation of zinc hydroxide.

Since H_2EDTA^{2-} forms 1:1 stable complexes with many metal ions (e.g., M^{2+}):

$$M^{2+} + H_2EDTA^{2-} \rightleftharpoons M(EDTA)^{2-} + 2H^+ \quad \text{.............(i)}$$

$$\therefore [EDTA] \equiv [M^{n+}]$$

Or, 1000mL of (M) EDTA solution ≡ 1 mole M^{2+}

Optimum pH values for EDTA titrations of some common metal ions are:

M^{n+}	Fe^{3+}	Zn^{2+}	Mg^{2+}	Ca^{2+}
Optimum pH	2	9-10	10-12	10-12

End point of complexometric EDTA titrations may be determined using suitable indicators (called metal ion indicators) which form intensely coloured complexes with the metal ions at the optimum pH values, provided (a) the colour of the free indicator (In) is distinctly different from the colour of the metal-indicator complex (M-In), (b) the reaction between the indicator and the metal ion is rapid and reversible and (c) the apparent stability constant of M-In complex is lower than that of the M(EDTA) complex, so that the displacement reaction (ii) is quantitatively shifted to the right in the neighbourhood of the equivalence point.

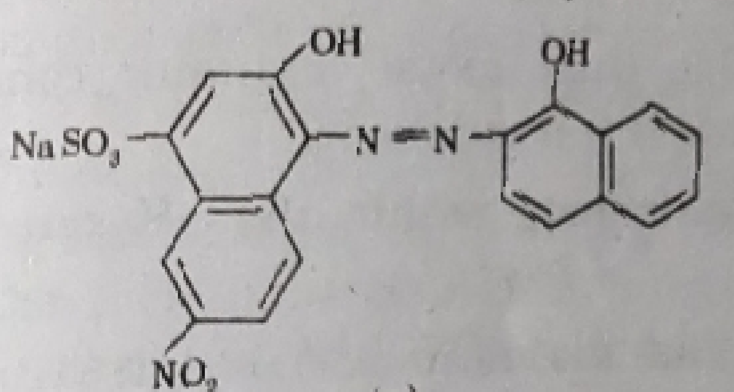
$$MIn^{-} + H_2EDTA^{2-} \rightleftharpoons M(EDTA)^{2-} + H_2In^{-} \quad ....(ii)$$

Principle of detection of end point using metal ion indicator in complexometric EDTA titrations:

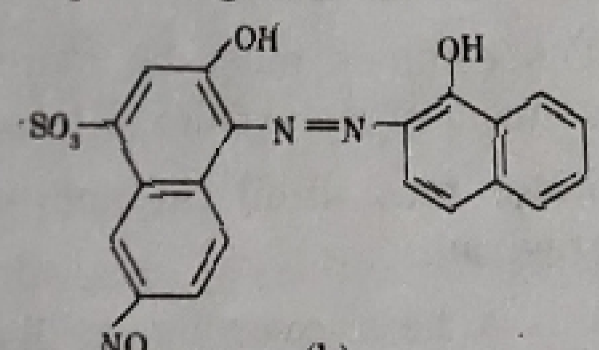
Eriochrome black T is a metal ion indicator. It is also known as Solochrome Black T. The chemical name of this indicator is sodium-1-[(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulphonate. At pH < 5.5, EBT (NaH_2In) solution is red due to H_2In^-; between pH 7 and 11, it is blue due to HIn^{2-}. At pH > 11.5, it is yellowish-orange due to In^{3-}:

$$\underset{\text{Red}}{\underset{(b)}{H_2In^-}} \xrightleftharpoons{\text{pH } 5.3 - 7.3} \underset{\text{Blue}}{\underset{(c)}{HIn^{2-}}} \xrightleftharpoons{\text{pH } 10.5 - 12.5} \underset{\text{Yellowish orange}}{\underset{(d)}{In^{3-}}}$$

The structure of EBT (a) and that (b, c, d) at different pH are given below:

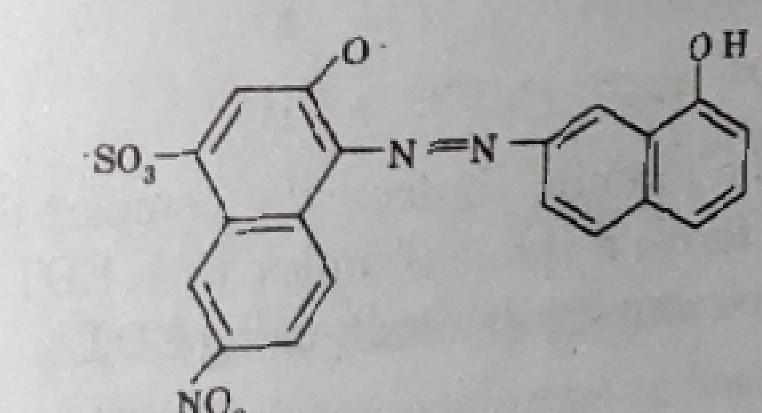


(a)



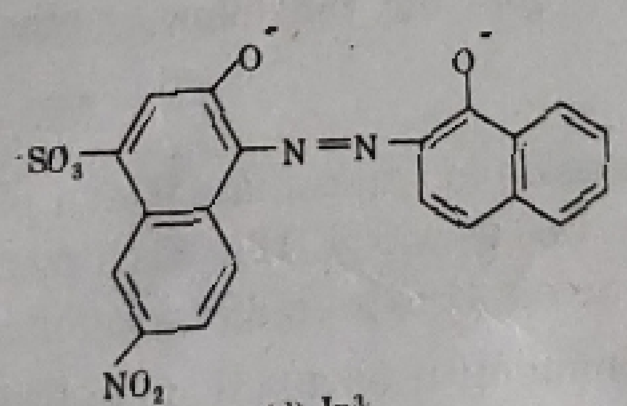
(b)

At pH <5.5, it is red (H_2In^-)



(c), HIn^{2-}

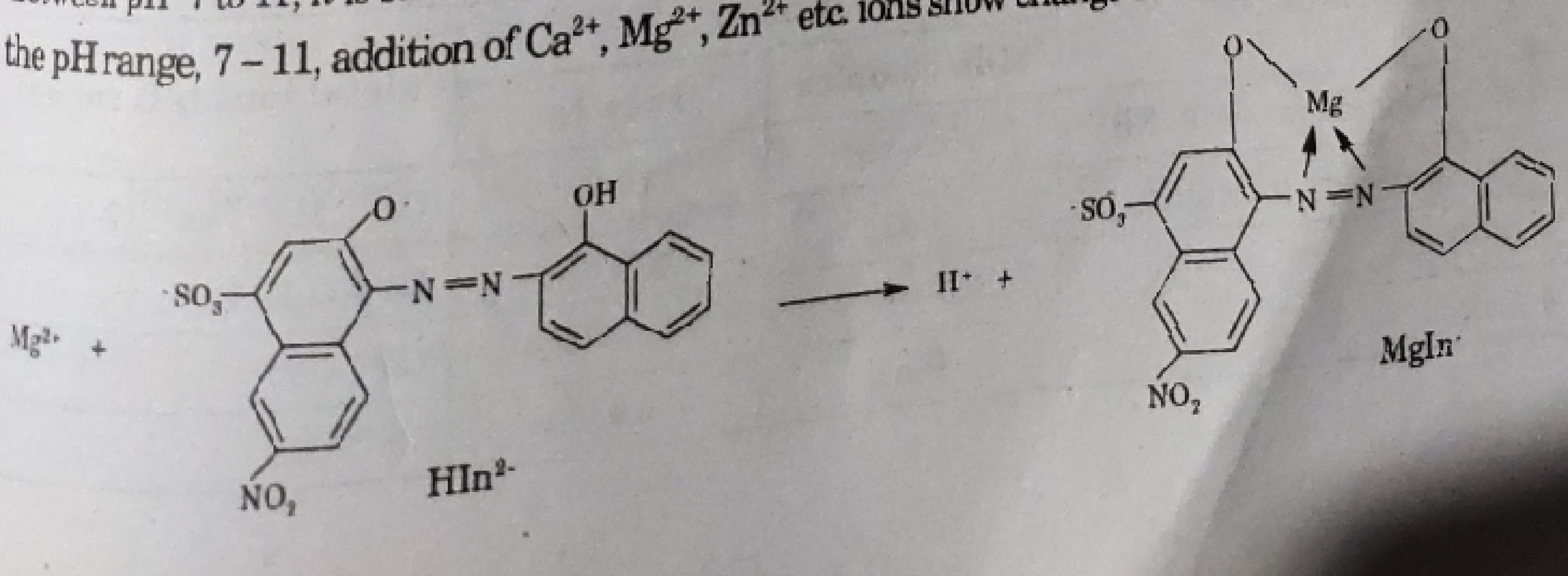
Between pH 7 to 11, it is blue (HIn^{2-})



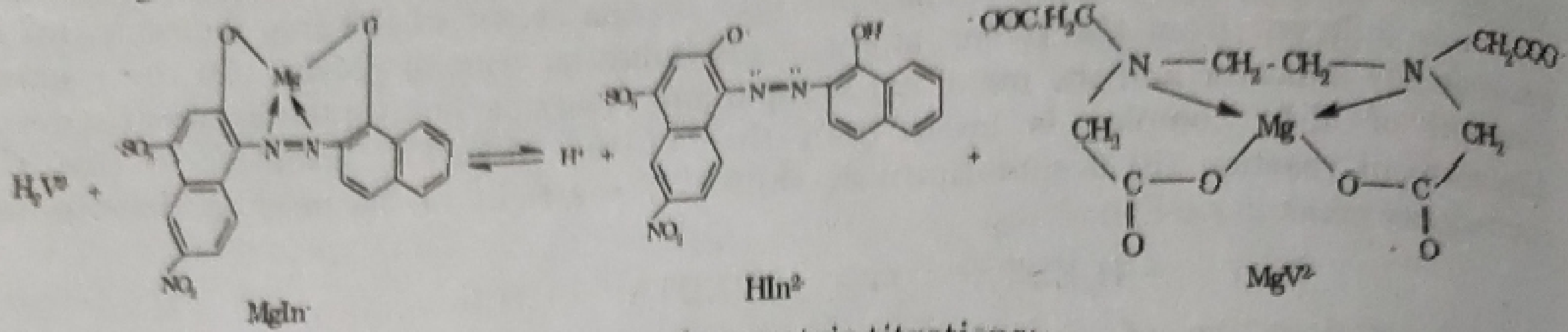
(d), In^{3-}

Above pH 11.5, it is yellow orange (In^{3-})

In the pH range, 7 – 11, addition of Ca^{2+}, Mg^{2+}, Zn^{2+} etc. ions show change of colour from blue to wine red:



EDTA now reacts with above complex changing the colour to deep blue according to the following reaction:



The choice of metal ion indicators in complexometric titrations:

A good metal ion indicator should possess the following characteristics:

(i) Just before the end point, when almost all the metal ions are complexed with EDTA, the solution should be intensely coloured.

(ii) The colour should be specific or at least selective.

(iii) There must be sharp contrast of colour between the free indicator and metal-indicator complex so that the detection of end point becomes easy.

(iv) The indicator must be sensitive to metal ions so that the sharp colour change occurs at the equivalence point.

(v) The metal-indicator complex must possess sufficient stability to obtained sharp colour change at the equivalence point.

(vi) Metal-EDTA complex must be more stable than metal- indicator complex to ensure complete replacement of metal from M-In complex at the end point.

(vii) The indicator must fulfil the above requirements within the pH range at which the titration is carried out.

EDTA is a hexa co-ordinated ligand but disodium salt is tetra co-ordinated. The disodium salt Na_2H_2V ionises in water as $Na_2H_2V \rightleftharpoons 2Na^+ + H_2V^{2-}$ (complex ion).

With Ca^{2+}, Mg^{2+}, Zn^{2+} etc. the following reaction takes place:

$$M^{2+} + H_2V^{2-} \rightleftharpoons [MV]^{2-} + 2H^+$$

The above discussion indicates that definite pH of the medium controls the complex formation with the indicator as well as with EDTA. Each metal ion forms a stable complex with EDTA at a definite pH. Hence it is necessary to use buffer solution in complexometric titration using EDTA.

Some of the commonly used metal ion indicators used in complexometric EDTA titrations are listed below:

Indicator (In)	Colour		Metal ions (pH range)
	M-In complex	Free In	
1. Eriochrome Black – T (EBT)	Wine red	Blue	Ca^{2+}, Mg^{2+}, Zn^{2+} (7–11)
2. Patton-reeders indicator	Red	Pure blue	Ca^{2+} (12-14)
3. Murexide	Red-yellow	Blue-violet	Ca^{2+} (12)
4. Calcon	Pink	Pure blue	Ca^{2+} (12)