12-5 Auxiliary Complexing Agents:

Sometimes it is necessary to add an additional complexing agent to increase the solubility of the analyte at a particular pH.

To permit many metals to be titrated in alkaline solutions with EDTA, we use an auxiliary complexing agent.

This is a ligand that binds the metal strongly enough to prevent the hydroxide from precipitating, but weakly enough to give up the metal when EDTA is added.

$$M + xL \overset{\beta_x}{\rightleftharpoons} ML_x$$

$$ML_x + EDTA \overset{k'_{f\,aux}}{\rightleftharpoons} MY^{n-4}$$

β_x must be less than $k'_{f\,aux}$

Example for auxiliary complexing agent.

Ammonia, Triethanolamine, and citrate.

Metal-Ligand Equilibria

Consider a metal ion that forms two complexes with the auxiliary complexing ligand L:

$$M + L \rightleftharpoons ML$$

$$\beta_1 = \frac{[ML]}{[M][L]} \longrightarrow (1)$$

$$M + 2L \rightleftharpoons ML_2$$

$$\beta_2 = \frac{[ML_2]}{[M][L]^2} \longrightarrow (2)$$

β_i is the equilibrium constants are called overall or cumulative formation constants.

The fraction of metal ion in the uncomplexed state, M, can be expressed as

$$\alpha_M = \frac{[M]}{M_{tot}} \longrightarrow (3)$$

where C_M refers to the total concentration of all forms of M (= M, ML, & ML_2)

$$\therefore M_{tot} = [M] + [ML] + [ML_2]$$

From the equation ① and ②

$$[ML] = \beta_1 [M][L]$$

$$[ML_2] = \beta_2 [M][L]^2$$

$$\therefore M_{tot} = [M] + \beta_1 [M][L] + \beta_2 [M][L]^2$$

$$= [M]\left\{1 + \beta_1 [L] + \beta_2 [L]^2\right\} \longrightarrow ④$$

Substituting ④ in ③

$$\alpha_M = \frac{[M]}{[M]\left\{1 + \beta_1 [L] + \beta_2 [L]^2\right\}}$$

$$= \frac{1}{1 + \beta_1 [L] + \beta_2 [L]^2}$$

11-6

Metal ion Indicators :

End-Point detection methods:

(i) Metal ion indicators.

(ii) Mercury electrode.

(iii) Ion-selective electrode.

(iv) Glass (pH) electrode.

Metal ion Indicators :-

Metal ion indicators are compounds whose color changes when they bind to a metal ion.

Indicators must bind metal less strongly than EDTA.

Eg. Reaction of Mg^{2+} with EDTA, using Eriochrome black T as the indicator.

$$\underset{\text{(Red)}}{Mg\,In} + \underset{\text{(colourless)}}{EDTA} \longrightarrow \underset{\text{(colourless)}}{Mg\,EDTA} + \underset{\text{(Blue)}}{In}$$

At the start of the experiment, a small amount of indicator (In) is added to the colorless solution of Mg^{2+} to form a red complex.

As EDTA is added, it reacts first with free, colorless Mg^{2+}. When free Mg^{2+} is used up, the last EDTA added before the equivalence point displaces indicator from the red $MgIn$ complex.

The change from the red $MgIn$ to blue unbound In signals the end point of the titration.

Most metal ion indicators are also called acid-base indicators, with pK_a values listed in Table 13-3 in the Book.

11-7 EDTA Titration Techniques:-

Direct Titration:-

* The analyte is titrated with standard EDTA.
* The analyte is buffered to a pH at which the conditional formation constant for the metal-EDTA complex is large and the colour of the free indicator is distinctly different from that of the metal-indicator complex.
* An auxiliary complexing agent — for example, ammonia, tartrate, citrate, or triethanolamine — may be employed to prevent the metal ion from precipitating in the absence of EDTA.

Back titration:-

* A known excess of EDTA is added to the analyte.
* Then excess EDTA is then titrated with a standard solution of a second metal ion.
* The metal ion used in the back titration must not displace the analyte metal ion from its EDTA.

Example for Direct titration:

The direct titration of Pb^{2+} is carried out in Ammonia buffer at pH 10 in the presence of tartrate, which complexes the metal ion and does not allow $Pb(OH)_2$ to precipitate.

The lead-tartrate complex must be less stable than the lead-EDTA complex, or the titration would not be feasible.

* Must use this technique when the analyte precipitates in the absence of EDTA or if the reaction with EDTA is too slow, or if the analyte blocks the indicator.

Displacement titration :-

* If there is no suitable indicator for a metal, treat the analyte with excess $Mg(EDTA)^{2-}$ to displace Mg^{2+}. Then titrate the displaced Mg^{2+} with standard EDTA.

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

* Can titrate Hg^{2+} using this procedure.

* The formation constant of MY^{n-4} must be > the formation constant of MgY^{2-}. Otherwise, the displacement won't happen.

* There is no suitable indicator for Ag^+, however, Ag^+ will displace Ni^{2+} from the tetracyano-nickelate (II) ion:

$$2Ag^+ + Ni(CN)_4^{2-} \longrightarrow 2Ag(CN)_2^- + Ni^{2+}$$

The liberated Ni^{2+} can be titrated with EDTA to find out how much Ag^+ was added.

Indirect Titration :-

* Anions that precipitate with certain metal ions can be analyted with EDTA by indirect titration.

Eg. SO_4^{2-} can be analysed by precipitation with excess Ba^{2+} at pH-1.

The $BaSO_4(s)$ is washed then boiled with excess EDTA at pH 10 to bring Ba^{2+} back into solution as $Ba(EDTA)^{2-}$. The excess EDTA is back-titrated with Mg^{2+}.

Anions such as CO_3^{2-}, CrO_4^{2-}, S^{2-}, and SO_4^{2-} can be determined by indirect titration with EDTA.

Masking :-

* A masking agent is a reagent that protects some component of the analyte from reaction with EDTA.

* Masking is used to prevent only element from interfering in the analysis of another element.

* Masking is not restricted to EDTA titrations.

Eg.

Al^{3+} in a mixture of Mg^{2+} and Al^{3+} can be measured by first masking the Al^{3+} with F^-, thereby leaving only the Mg^{2+} to react with EDTA.

Demasking :

Demasking releases metal ion from a masking agent.

Eg. * Cyanide complexes can be demasked with formaldehyde.

$$M(CN)_m^{n-m} + m\,H_2CO + m\,H^+ \longrightarrow m\,H_2C(OH)(CN) + M^{n+}$$

formaldehyde

Eg. * Thiourea masks Cu^{2+} by reducing it to Cu^+ and complexing the Cu^+.

Copper can be liberated from the thiourea complex as Cu^{2+} by oxidation with H_2O_2.