ANALYTICAL CHEMISTRY

Complexometric Titrations

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Chapter Description

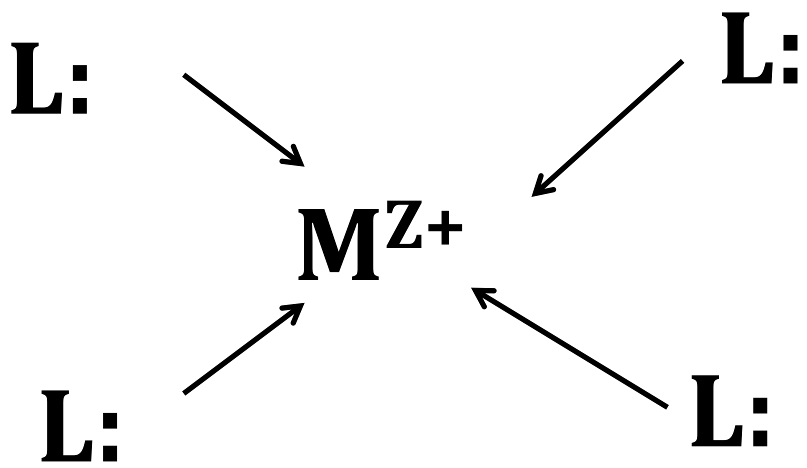
- Expected Outcomes
  - Discuss the formation and stability of metal-ligand complexes
  - Compute the stability and instability constants for the metal complexes
  - Explain the principle of complexometric titrations
  - List and explain different methods of detecting the end point in complexometric titrations

Contents

- Complexometric Titration
- Complexation Equilibria
- Titration Curves
- Organic Complexing Agents
- Aminocarboxylic Acid Titrations
- Indicators for EDTA Titrations
- Application

COMPLEXOMETRIC TITRATION

Definition: Titration method based on complex formation due to reaction between metal ions (cation) and complexing agent (ligand)



Ligand (the donor species or complexing agents) is the groups bound to the central ion in the complex.

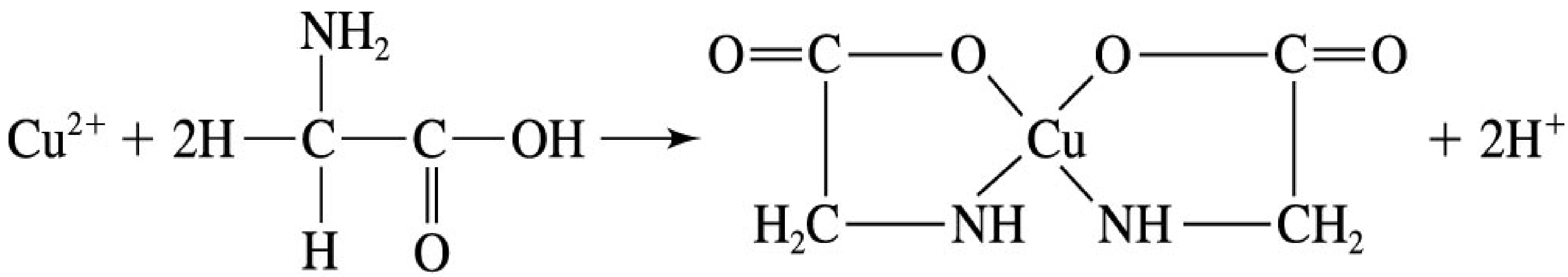
Example of ligand: H_2O, NH_3, Cl^-, Br^-, EDTA

A *Chelate* is produced when ligands are attached to the central ion at two or more coordinating sites to form a five- or six-member heterocyclic ring.

Chelating agent: the organic ligands that involved in the coordination

Most widely used chelating agent = EDTA

A ligand that is attached to central ion at only one point is called unidentate, whereas ligands that have two ore more coordinating sites are called polydentate.



Glycine

COMPLEXATION EQUILIBRIA

A metal ion, M reacts with a ligand, L and forming a complex, ML in complexation reaction.

$$M + L \rightleftharpoons ML$$

Complexation reactions occur in a stepwise fashion followed by additional reactions:

$$ML + L \rightleftharpoons ML_2$$

$$ML_2 + L \rightleftharpoons ML_3$$

$$\vdots \qquad\qquad \vdots$$

$$ML_{n-1} + L \rightleftharpoons ML_n$$

$$M + L \rightleftharpoons ML \qquad \beta_1 = \frac{[ML]}{[M][L]} = K_1$$

$$M + 2L \rightleftharpoons ML_2 \qquad \beta_2 = \frac{[ML_2]}{[M][L]^2} = K_1K_2$$

$$M + 3L \rightleftharpoons ML_3 \qquad \beta_3 = \frac{[ML_3]}{[M][L]^3} = K_1K_2K_3$$

$$\vdots \qquad\qquad \vdots$$

$$M + nL \rightleftharpoons ML_n \qquad \beta_n = \frac{[ML_n]}{[M][L]^n} = K_1K_2\ldots K_n$$

β_n → **Formation constant**

- Alpha value = the fraction of the total concentration existing in the form

$$\alpha_M = \frac{1}{1+\beta_1[L]+\beta_2[L]^2+\beta_3[L]^3+\ldots+\beta_n[L]^n}$$

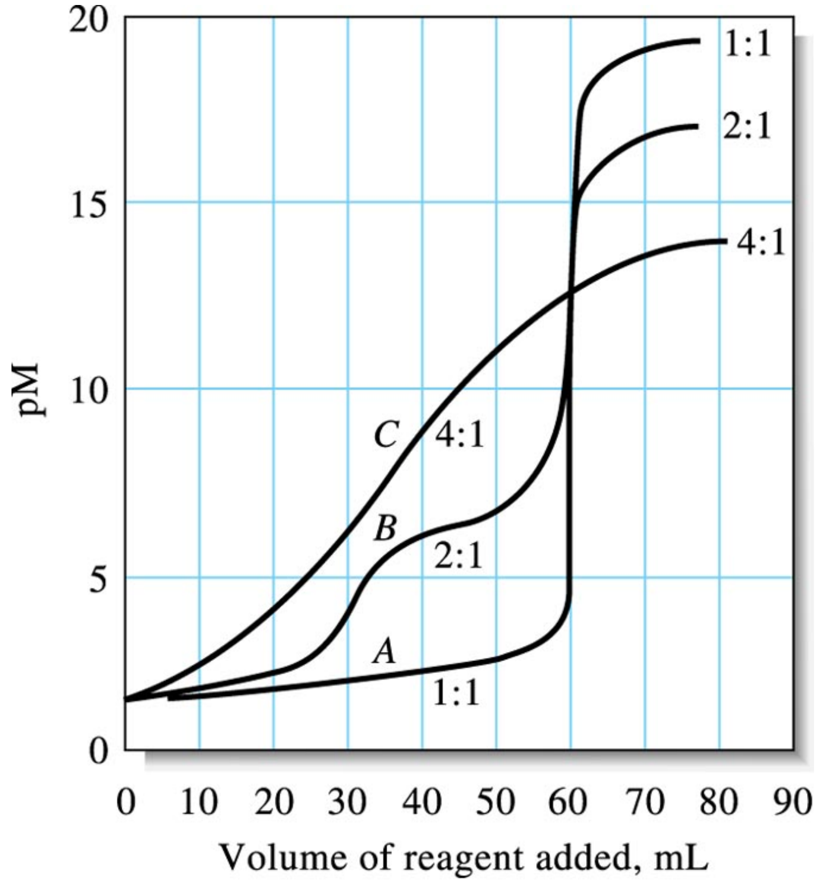
$$\alpha_{ML} = \frac{\beta_1[1]}{1+\beta_1[L]+\beta_2[L]^2+\beta_3[L]^3+\ldots+\beta_n[L]^n}$$

$$\alpha_{ML_2} = \frac{\beta_2[1]^2}{1+\beta_1[L]+\beta_2[L]^2+\beta_3[L]^3+\ldots+\beta_n[L]^n}$$

$$\alpha_{ML_n} = \frac{\beta_n[1]^n}{1+\beta_1[L]+\beta_2[L]^2+\beta_3[L]^3+\ldots+\beta_n[L]^n}$$

TITRATION CURVES FOR COMPLEXOMETRIC TITRATIONS

Polidentate ligands react more complete with cations compared to ligands with a lesser number of donor groups and tend to form 1:1 complexes. These ligands are more satisfacory.



TITRATIONS WITH INORGANIC COMPLEXING AGENTS

The equivalence point of complexation reaction is determined by an indicator or an appropriate instrumental method.

TABLE 17-1

Typical Inorganic Complex–Forming Titrations

Titrant	Analyte	Remarks
$Hg(NO_3)_2$	Br^-, Cl^-, SCN^-, CN^-, thiourea	Products are neutral Hg(II) complexes; various indicators used
$AgNO_3$	CN^-	Product is $Ag(CN)_2^-$; indicator is I^-; titrate to first turbidity of AgI
$NiSO_4$	CN^-	Product is $Ni(CN)_4^{2-}$; indicator is I^-; titrate to first turbidity of AgI
KCN	Cu^{2+}, Hg^{2+}, Ni^{2+}	Products are $Cu(CN)_4^{2-}$, $Hg(CN)_2$, and $Ni(CN)_4^{2-}$; various indicators used

ORGANIC COMPLEXING AGENTS

Organic complexing agents: inherent sensitivity and potential selectivity in reacting with metal ions.

- Particularly useful in:
  - (i) Precipitating metals
  - (ii) Binding metals to prevent interferences – forming stable complexes : MASKING AGENT
  - (iii) Extracting metal from one solvent to another
  - (iv) Forming complexes that absorb light for spectrophotometric or electrochemical determination and molecular fllourescence spectrometry
  - (v) The most useful = form chelate complexes with metal ions

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$$n\text{HX(org)} + \text{M}^{n+}\text{(aq)} \rightleftharpoons \text{MX}_n\text{(org)} + n\text{H}^+\text{(aq)}$$

Many organic reagents are useful in converting metal ions into form that can be readily extracted from water into an immiscible organic phase.

Extraction are widely used to separate metals of interest from potential interfering ions and to achieve a concentrating effect, extracting into a phase of smaller volume is chosen.

Extractions are applicable to much smaller amounts of metals than precipitations, and they avoid problems associated with coprecipitation.

TABLE 17-2

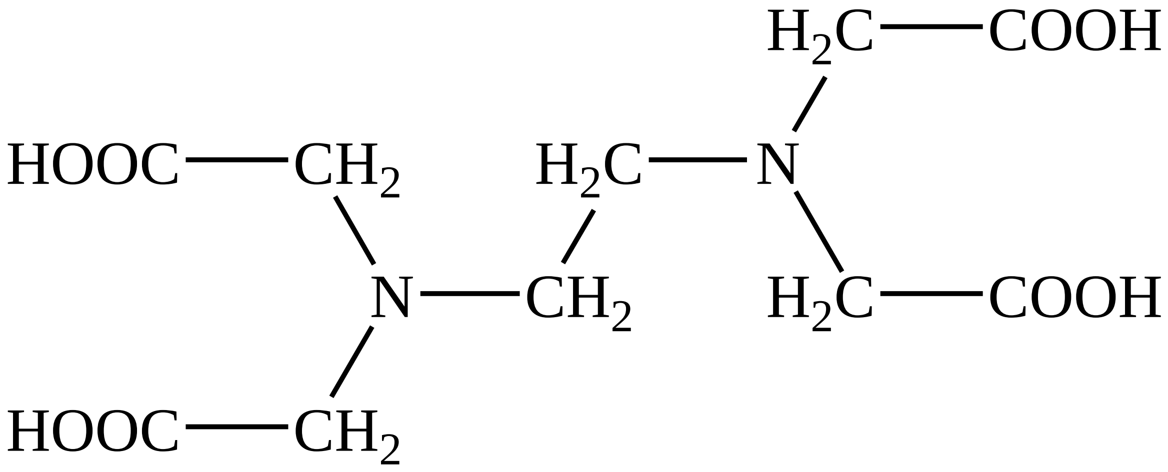
Organic Reagents for Extracting Metals

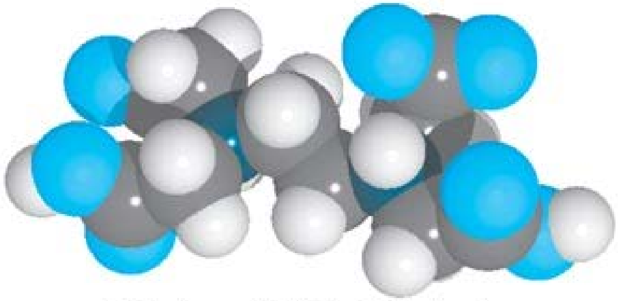
Reagent	Metal Ions Extracted	Solvents
8-Hydroxyquinoline	Zn^{2+}, Cu^{2+}, Ni^{2+}, Al^{3+}, many others	Water → Chloroform ($CHCl_3$)
Diphenylthiocarbazone (dithizone)	Cd^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}, many others	Water → $CHCl_3$, or CCl_4
Acetylacetone	Fe^{3+}, Cu^{2+}, Zn^{2+}, U(VI), many others	Water → $CHCl_3$, CCl_4, or C_6H_6
Ammonium pyrrolidine dithiocarbamate	Transition metals	Water → Methyl isobutyl ketone
Tenoyltrifluoroacetone	Ca^{2+}, Sr^{2+}, La^{3+}, Pr^{3+}, other rare earths	Water → Benzene
Dibenzo-18-crown-6	Alkali metals, some alkaline earths	Water → Benzene

AMINOCARBOXYLIC ACID TITRATIONS

EDTA (ethylenediaminetetraacetic acid)

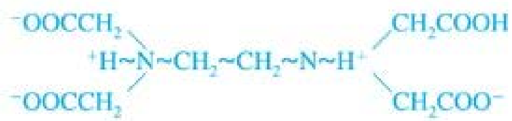
The EDTA is a hexadentate ligand comprising four oxygen and two nitrogen donor atoms.



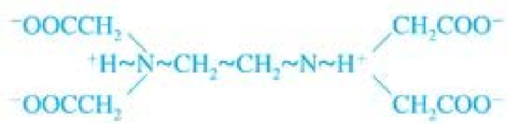


Molecular model of the H_4Y zwitterion.

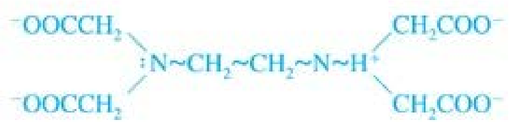
(a) H_4Y



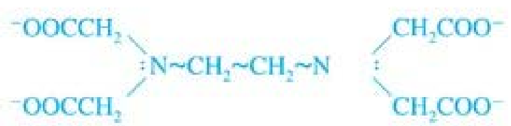
(b) H_3Y^-



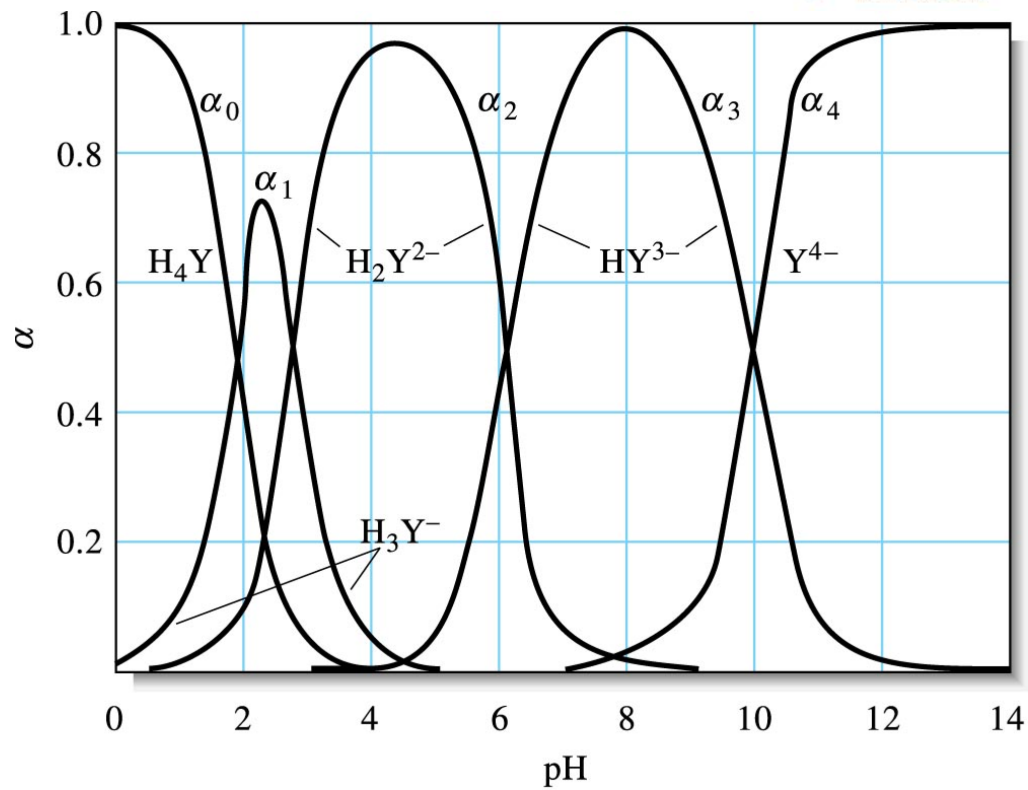
(c) H_2Y^{2-}



(d) HY^{3-}



(e) Y^{4-}



Fraction of EDTA species as a function of pH

EDTA EQUILIBRIA

$$H_4Y \rightleftharpoons H^+ + H_3Y^- \qquad K_{a1} = 1.0 \times 10^{-2} = \frac{[H^+][H_3Y^-]}{[H_4Y]}$$

$$H_3Y^- \rightleftharpoons H^+ + H_2Y^{2-} \qquad K_{a2} = 2.2 \times 10^{-3} = \frac{[H^+][H_2Y^{2-}]}{[H_3Y^-]}$$

$$H_2Y^{2-} \rightleftharpoons H^+ + HY^{3-} \qquad K_{a3} = 6.9 \times 10^{-7} = \frac{[H^+][HY^{3-}]}{[H_2Y^{2-}]}$$

$$HY^{3-} \rightleftharpoons H^+ + Y^{4-} \qquad K_{a4} = 5.5 \times 10^{-11} = \frac{[H^+][Y^{4-}]}{[HY^{3-}]}$$

COMPLEXES OF EDTA AND METAL IONS

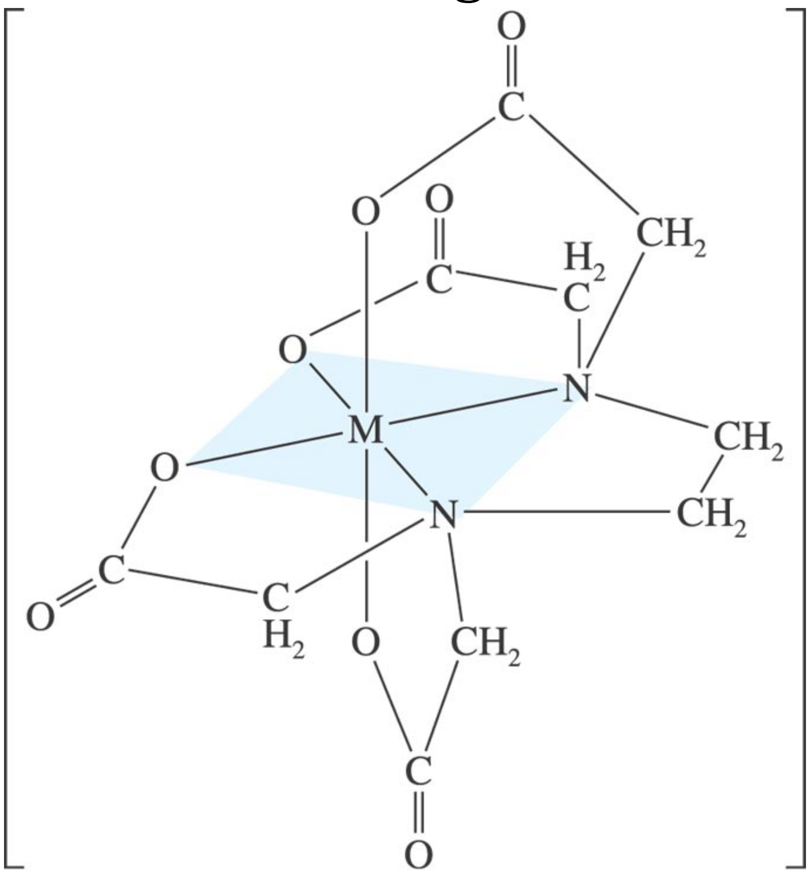
EDTA combines with metal ions in a 1:1 ratio regardless of the charge on the cation.

Example: $Ag^+ + Y^{4-} \rightleftharpoons AgY^{3-}$

$Al^{3+} + Y^{4-} \rightleftharpoons AlY^-$

In general: $M^{n+} + Y^{4-} \rightleftharpoons MY^{(n-4)+}$

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



INDICATORS FOR EDTA TITRATIONS

usually an ORGANIC DYE such as

(i) Fast Sulphon Black (for Cu determination, purple → green)

(ii) Eriochrome Black T (for Ca & Mg, red → blue)

(iii) Calmagite (for Ca & Mg, wine red /purple → blue)

ERIOCHROME BLACK T

$H_2O + H_2In^- \rightleftharpoons HIn^{2-} + H_3O^+$ $K_1 = 5 \times 10^{-7}$

Red — Blue

$H_2O + HIn2^- \rightleftharpoons In^{3-} + H_3O^+$ $K_2 = 2.8 \times 10^{-12}$

Blue — Orange

Approaching the equivalence point, the excess metal ion reacts with indicator to form complexes (red solution). The solution turns blue with the first slight excess of EDTA in the absence of metal ions.

$MIn^- + HY^{3-} \rightleftharpoons HIn^{2-} + MY^{2-}$

red — blue

CALMAGITE INDICATOR

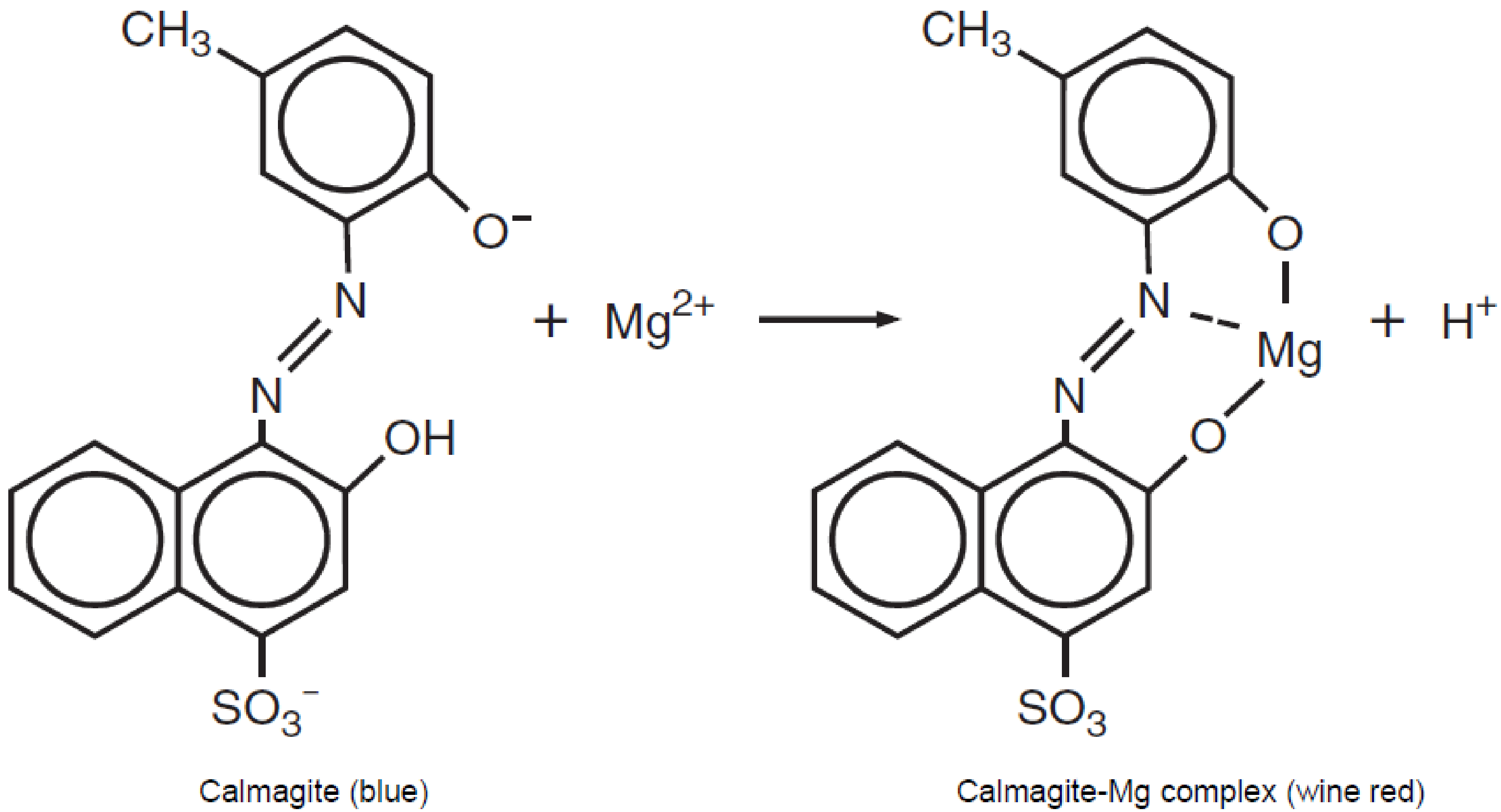
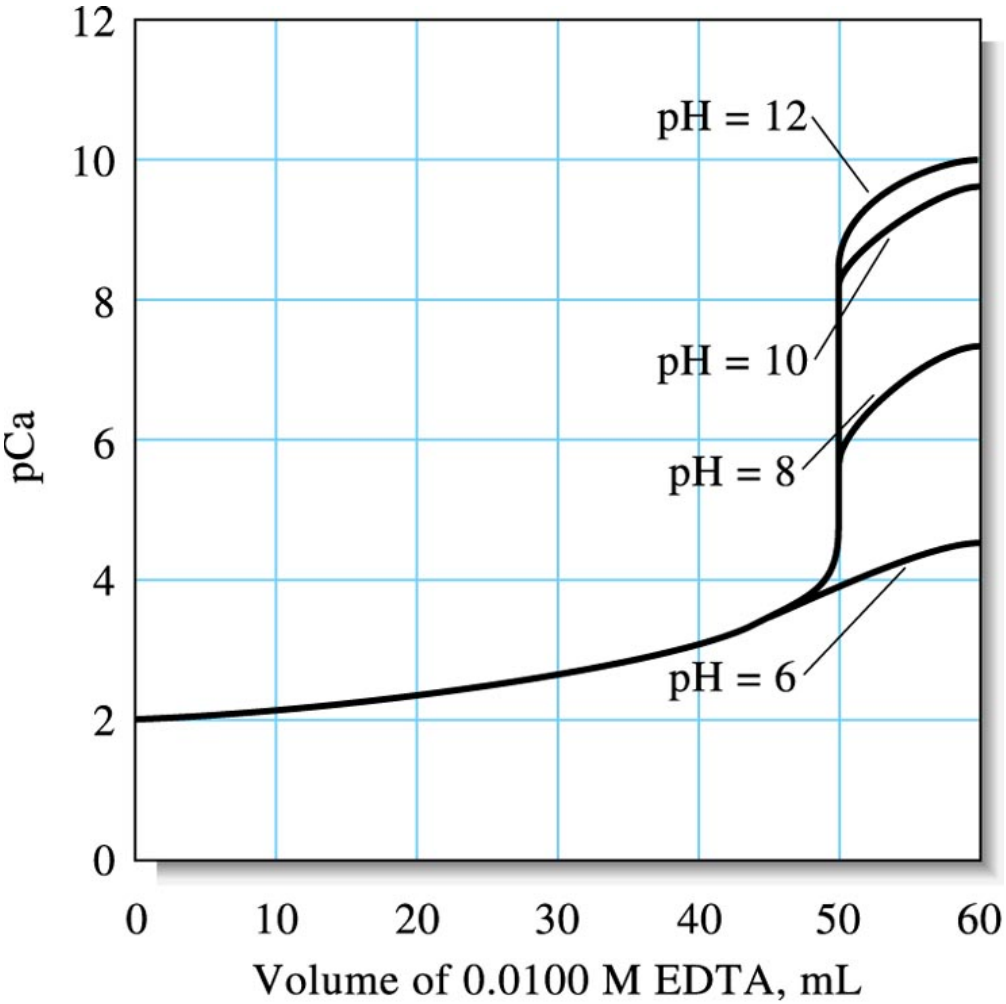


Figure 3 Reaction between magnesium and calmagite indicator

EDTA TITRATION CURVES



Titration between Ca^{2+} with Na_2EDTA at different pH

As the pH increases, the equilibrium shifts to the right.

TITRATION METHODS EMPLOYING EDTA

Direct method

- The solution containing the metal ion to be determined is buffered to the desired pH (e.g. to pH = 10) and titrated directly with the standard EDTA solution.

Potentiometric methods (by using electrodes)

Spectrophotometric methods (measurement of UV/vis absorption)

Back-titration methods

- A known amount of EDTA is added to the analyte sample solution and the excess EDTA is back-titrated with a standard solution of Mg^{2+} or Zn^{2+} solution to an EBT or Calmagite indicators.

Displacement methods

- An unmeasured excess of Mg or Zn complex of EDTA solution is added into the analyte sample solution.
- The liberated Mg^{2+} or Zn^{2+} is then titrated with a standard EDTA solution.

$$MgY^{2-} + M^{2+} \rightleftharpoons MY^{2-} + Mg^{2+}$$

APPLICATION

Determination of water hardness for household and industrial uses

- Hard water contains Ca, Mg and heavy metal ions that form precipitates with soap (but not detergents)
- This results in a waste of soap and the precipitate is a slimy curd that is difficult to remove
- Important because: Heated hard water will form $CaCO_3$ precipitates that will clogs the boilers and pipes.

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