PAPER

8

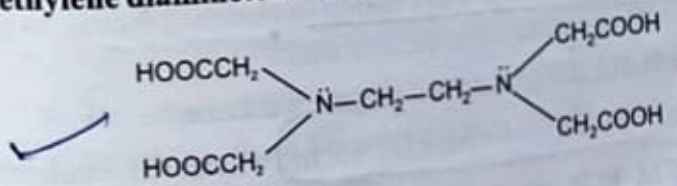
INORGANIC CHEMISTRY

Experiment 11

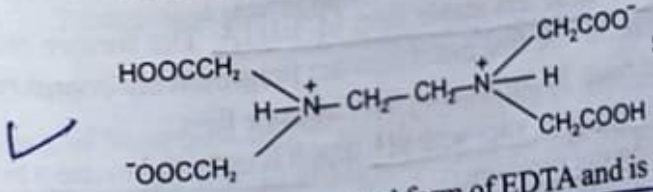
COMPLEXOMETRIC TITRATIONS

Discussion: Complexometric titration is a form of volumetric analysis in which the formation of a coloured complex is used to indicate the end point of a titration. A metal ion indicator capable of producing colour change is usually used to detect the end-point of the titrations. These titrations are particularly useful for the determination of metal ion or mixture of different metal ions in the solution.

EDTA (ethylene diaminetetraacetic acid) is an excellent complexing agent used in complexometric titration.



Structure (I) : H_4Y



Structure (II) : H_2Y^{2-}
(Zwitter ion form)

The structure (I) is the unreacted form of EDTA and is a tetrabasic acid. The four electron rich acetate groups together with the two nitrogen lone pairs makes it a **hexadentate ligand** which will form complexes with octahedral geometry.

For simplicity EDTA is given the formula H_4Y. It being a weak acid dissociates stepwise.

$$H_4Y \rightleftharpoons H^+ + H_3Y^- \quad : \quad pK_1 = 2.0$$

$$H_3Y^- \rightleftharpoons H^+ + H_2Y^{2-} \quad : \quad pK_2 = 2.7$$

$$H_2Y^{2-} \rightleftharpoons H^+ + HY^{3-} \quad : \quad pK_3 = 6.2$$

$$HY_3^- \rightleftharpoons H^+ + Y^{4-} \quad : \quad pK_4 = 10.3$$

Sl.No.	Burette Reading		Volume of EDTA used (mL)
	Initial	Final	
1.			
2.			
3.			

Volume of EDTA used = V_{EDTA} = ——— mL

$$M_{EDTA} \times V_{EDTA} = M_{std.\ ZnSO_4} \times V_{std.\ ZnSO_4}$$

$$M_{EDTA} = \text{——— M}$$

3. **Titration of EDTA vs. Given $ZnSO_4$ Solution:**

Burette : EDTA.

Conical flask : 10 mL given $ZnSO_4$ + 20 mL H_2O + 2mL buffer

Indicator : Erichrome Black-T.

Colour change : Red to Blue.

Sl.No.	Burette Reading		Volume of EDTA used (mL)
	Initial	Final	
1.			
2.			
3.			

Volume of EDTA used = V_{EDTA} = _____ mL

$$M_{EDTA} \times V_{EDTA} = M_{ZnSO_4} \times V_{ZnSO_4}$$

$$M_{ZnSO_4} = \text{\_\_\_\_\_ M}$$

Strength of given $ZnSO_4$ solution = M_{ZnSO_4} × molecular weight of $ZnSO_4$

$$= \left(M_{ZnSO_4} \times 287.56\right) \text{ g/L}$$

Strength of Zn(II) in given $ZnSO_4$ solution = M_{ZnSO_4} × atomic weight of Zn

$$= \left(M_{ZnSO_4} \times 65.3\right) \times 65.3 \text{ g/L}$$

Result: The strength of Zn(II) in the given $ZnSO_4$ solution is _____ g/L.

Experiment 11(c)

Aim: To estimate the amount of M/100 $BaSO_4$ using M/100 EDTA in complexometric titration using methylthymol blue as an indicator by direct tiration. Prepare standard $ZnSO_4$ solution to standardise EDTA.

Theory: [Same as in experiment 11(a).

Procedure:

1. **Preparation of Buffer Solution of NH_3-NH_4Cl (pH= 10):** It is prepared by adding 142 mL concentrated NH_3 solution to 17.5 g NH_4Cl and diluting to 250 mL using distilled water.
2. **Preparation of Standard $ZnSO_4$ Solution in 100 mL Standard Flask:** Prepare standard M/100 $ZnSO_4$ solution using distilled water by transference method.
3. **Titration of EDTA vs. Standard $ZnSO_4$ Solution (Standardisation of EDTA Solution):** Rinse and fill the burette with EDTA solution. Pipette out 10 mL of standard $ZnSO_4$ solution in a conical flask and add 20 mL of water to it. Further add 2 mL of buffer ($NH_3 - NH_4Cl$, pH = 10) and 2-3 drops of Erichrome Black-T as an indicator to it. Titrate the solution against EDTA solution until the colour changes from red to blue. Repeat the titration to obtain three concordant readings.
4. **Titration of EDTA vs. Given $BaSO_4$ Solution:** Rinse and fill the burette with EDTA solution. Pipette out 10 mL of given BaSO4 solution in a conical flask and add 20 mL of water to it. Further add 2 mL of 1M NaOH and 2–3 drops of methyl thymol blue as an indicator to it. Titrate the solution against EDTA solution until the colour changes from blue to grey. Repeat the titration to obtain three concordant readings.

Observation and Calculation:

1. **Preparation of Standard $ZnSO_4$ Solution in 100 mL Standard Flask:**

Molecular weight of $ZnSO_4$ = 287.56 g

Mass of $BaSO_4$ required to prepare (M/100) solution in 100 mL flask = 0.4314 g

Mass of empty weighing bottle = w_1 = _____ g

Mass of bottle + $ZnSO_4$ = w_2 = _____ g

Mass of bottle after transferred = w_3 = _____ g

Mass of $ZnSO_4$ actually transferred = $w_2 - w_3 = w$ _____ g

$$M_{\text{std. } ZnSO_4} = \frac{w}{287.56} \times 10 \text{ _____ M}$$

2. **Titration of EDTA vs. Standard $ZnSO_4$ Solution:**

Burette : EDTA.

Conical flask : 10 mL standard $ZnSO_4$ + 20 mL H_2O + 2 mL buffer.

Indicator : Erichrome Black-T.

Colour change : Red to Blue.

Sl.No.	Burette Reading		Volume of EDTA used (mL)
	Initial	Final	
1.			
2.			
3.			

Volume of EDTA used = V_{EDTA} = _____ mL

$$M_{EDTA} \times V_{EDTA} = M_{\text{std. } ZnSO_4} \times V_{\text{std. } ZnSO_4}$$

M_{EDTA} = _____ M

3. **Titration of EDTA vs. Given $BaSO_4$ Solution:**

Burette : EDTA.

Conical flask : 10 mL given $BaSO_4$ + 20 mL H_2O + 2 mL 1 M NaOH.

Indicator : Methyl thymol blue.

Colour change : Blue to grey.

Sl.No.	Burette Reading		Volume of EDTA used (mL)
	Initial	Final	
1.			
2.			
3.			

Volume of EDTA used = V_{EDTA} = _____ mL

$M_{EDTA} \times V_{EDTA} = M_{BaSO_4} \times V_{BaSO_4}$

M_{BaSO_4} = _____ M

Strength of given $BaSO_4$ solution = M_{BaSO_4} × molecular weight of $BaSO_4$

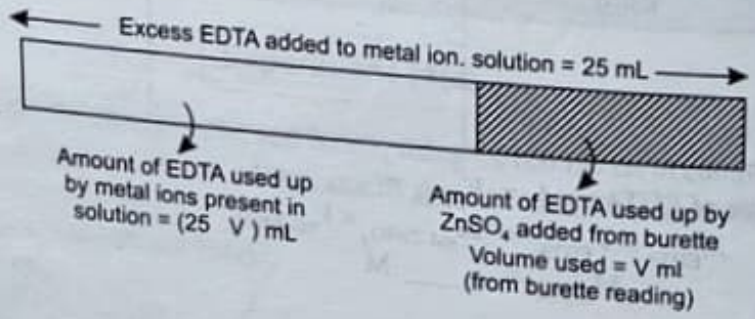
= (M_{BaSO_4} × 233) g/L

Result: The strength of given $BaSO_4$ solution is _____ g/L.

Experiment 11(d)

Aim: To estimate the amount of Al(III) ions in given M/100 $AlCl_3$ using M/100 EDTA in complexometric titration using Erichrome Black-T as an indicator by back titration. Prepare standard $ZnSO_4$ solution.

Theory: **Back Titration:** There are many metals ions (like Al^{3+}) whose concentration cannot be determined directly by titrating against EDTA solution. The reason being that they may get precipitated from the solution or may form inert complexes or sometimes a suitable metal indicator is not available. Thus to determine the concentration of these metal ions, an excess of EDTA solution is added to the solution of metal ions and the resulting solution is buffered to the desired pH. Some portion of the EDTA gets complexed with Al^{3+} ions in the solution and the rest of the EDTA is back titrated with a standard metal ion solution (like $ZnSO_4$ or $ZnCl_2$ or $MgCl_2$ or $MgSO_4$) taken in the burette. The end point is determined by using the metal indicator which responds to the Zn^{2+} or Mg^{2+} ions introduced in the back titration.



Procedure:

1. **Preparation of $ZnSO_4$ Solution in 100 mL Standard Flask:** Prepare standard M/100 $ZnSO_4$ solution using distilled water by transference method.
2. **Titration of Standard $ZnSO_4$ vs. $AlCl_3$ Solution:** Pipette out 10 mL of $AlCl_3$ solution (*i.e.*, Al^{3+} ions) in a conical flask. To this add 25 mL of EDTA solution and 2 mL of buffer (*aq* NH_3, pH = 7-8). Boil the solution for a few minutes to ensure complete complexation of the Al^{3+} ions. Cool the solution to room temperature and again add 2 mL of buffer (*aq* NH_3, pH = 7-8) and 2–3 drops of Erichrome Black-T as indicator. Titrate the solution quickly with standard $ZnSO_4$ solution taken in the burette until the color changes from blue to red. Repeat the titration to obtain three concordant readings. This volume corresponds to the excess EDTA in the solution which remains uncomplexed by Al^{3+} ions and thus gets uncomplexed with the Zn^{2+} added from the burette.

Observation and Calculation:

1. **Preparation of Standard $ZnSO_4$ Solution in 100 mL Standard Flask:**

Molecular weight of $ZnSO_4$ = 287.56 g

Mass of $ZnSO_4$ required to prepare (M/100) solution in 100 mL flask = 0.4314 g

Mass of empty weighing bottle = w_1 = _____ g

Mass of bottle + $ZnSO_4$ = w_2 = _____ g

Mass of bottle after transference = w_3 = _____ g

Mass of $ZnSO_4$ actually transferred = $w_2 - w_3$ = _____ g

$$M_{\text{std. } ZnSO_4} = \frac{w}{287.56} \times 10 = \text{\_\_\_\_\_ M}$$

2. **Titration of Standard $ZnSO_4$ vs. $AlCl_3$ Solution:**

Burette : Standard $ZnSO_4$.

Conical flask : 10 mL $AlCl_3$ solution + 20 mL EDTA + 4 mL buffer.

Indicator : Erichrome Black-T.

Colour change : Blue to red.

Sl.No.	Burette Reading		Volume of $ZnSO_4$ used (mL)
	Initial	Final	
1.			
2.			
3.			

Volume of $ZnSO_4$ used = V_{ZnSO_4} = _____ mL

Initial amount of EDTA taken = 25 mL

Amount of EDTA used by $ZnSO_4$ = (V_{ZnSO_4}) mL

$\therefore$ Amount of ED TA used by Al^{3+} ion = $V_{Al^{3+}} = (25 - V_{ZnSO_4})$ mL

$$M_{Al^{3+}} \times V_{Al^{3+}} = M_{ZnSO_4} \times V_{ZnSO_4}$$

$$M_{Al\,3+} \times \left(25 - V_{ZnSO_4}\right) = M_{ZnSO_4} \times V_{ZnSO_4\,(\text{Burette reading})}$$

$$M_{Al^{3+}} = \_\_\_\_\_ \text{ M}$$

Strength of Al (III) ions in given solution of $AlCl_3 = M_{Al^{3+}} \times$ atomic weight of Al

$$= \left(M_{Al^{3+}} \times 27\right) \text{ g/L}$$

Result: The strength of Al (III) ions in the given $AlCl_3$ solution is _____ g/L.

Experiment 11(e)

Aim: To estimate the amount of Ca(II) in given M/100 $CaCO_3$ solution using M/100 EDTA in complexometric titration using Erichrome Black-T as indicator by Substitution displacement titration. Prepare standard $ZnSO_4$ to standarised EDTA and M/10 Mg – EDTA complex solution.

Theory: **Substitution Titration/Displacement Titration:** The complex formed between Ca^{2+} ion and Erichrome Black-T is not very stable (the formation constant of Ca – In is only about one-fourth of that of Mg).

Stability: Ca – In < Mg – In (In = indicator).

Ca – EDTA > Mg – EDTA,

As a consequence, significant conversion of Ca – In(red) to HIn^{2-} (blue) occurs well before equivalence *i.e.*, the colour change occurs prematurely in the titration of Ca^{2+} with EDTA because Ca^{2+} ions has a large tendency to form Ca – EDTA complex. Thus, with Ca^{2+} ions alone no sharp end point can be obtained and the transition from red to blue is not observed. Thus, when Ca^{2+} ions are titrated with EDTA, a relatively stable Ca complex is formed.

$$Ca^{2+} + \underset{(EDTA)}{H_2Y^{2-}} \rightleftharpoons \underset{\substack{(Complex)\\(more\ stable)}}{CaY^{2-}} + 2H^+$$

Whereas with Mg^{2+} ions, a somewhat less stable complex is formed.

$$Mg^{2+} + \underset{(EDTA)}{H_2Y^{2-}} \rightleftharpoons \underset{\substack{(Complex)\\(less\ stable)}}{MgY^{2-}} + 2H^+$$

Also the order of stability is

$$Ca — EDTA > Mg — EDTA > Mg — In > Ca — In$$

- Ca^{2+} ions can be determined by displacement/substitution titration. The displacement or substitution titration may be used for metal ions (*e.g.*, Ca^{2+}) which do not react (or react unsatisfactorily) with metal indicator or for metal ions which form EDTA complexes that are more stable than those of other metals such as Mg and Zn. Thus, this technique is useful where no satisfactory indicator is available for the metal ion being determined. The metal cation (Ca^{2+}) to be determined be treated with Mg – EDTA when the following reaction takes place.

$$Ca^{2+} + MgY^{2-} \rightleftharpoons CaY^{2-} + Mg^{2+}$$
(less stable) (more stable)

The amount of Mg^{2+} ions set free is equivalent to the cations (Ca^{2+}) present and can be titrated with a standard solution of EDTA and suitable metal indicator (*i.e.*, Erichrome Black-T).

$$Mg^{2+} + HIn^{2-} \rightleftharpoons MgIn^{-} + H^{+}$$
(Indicator) (Red)

$$MgIn^{-} + H_2Y^{2-} \rightleftharpoons MgY^{2-} + HIn^{2-} + H^{+}$$
(Red) (Blue)

Procedure:

1. **Preparation of Buffer Solution of NH_3-NH_4Cl (pH= 10):** It is prepared by adding 142 mL concentrated NH_3 solution to 17.5 g NH_4Cl and diluting to 250 mL using distilled water.
2. **Preparation of Standard $ZnSO_4$ Solution in 100 mL Standard Flask:** Prepare standard M/100 $ZnSO_4$ solution using distilled water by transference method.
3. **Titration of EDTA vs. Standard $ZnSO_4$ Solution (Standardisation of EDTA Solution):** Rinse and fill the burette with EDTA solution. Pipette out 10 mL of standard $ZnSO_4$ solution in a conical flask and add 20 mL of water to it. Further add 2 mL of basic buffer ($NH_3 - NH_4Cl$, pH = 10) and 2–3 drops of Erichrome Black-T as an indicator to it. Titrate the solution against EDTA solution until the colour changes from red to blue. Repeat the titration to obtain three concordant readings.
4. **Titration of EDTA vs. $CaCO_3$ Solution:** Pipette out 10 mL of $CaCO_3$ solution in a conical flask and add 20 mL of deionised H_2O to it. Then add 2 mL buffer ($NH_3 - NH_4Cl$, pH = 10) and 2 mL of (M/10) Mg—EDTA complex (Mg—EDTA complex is prepared by mixing equal volumes of 0.2 M EDTA solution and 0.2 M $MgSO_4$ solution). Then add 2–3 drops of Erichrome Black-T as an indicator to it. Titrate the solution against EDTA solution until the color changes from red to blue. Repeat the titration to obtain three concordant readings.

Observation and Calculation:

. Preparation of $ZnSO_4$ Solution in 100 mL Standard Flask

Molecular weight of $ZnSO_4$ = 287.56 g

Mass of $ZnSO_4$ required to prepare (M/100) solution in 100 mL flask =0.4314 g

Mass of empty weighing bottle = w_1 = _____ g

Mass of bottle + $ZnSO_4$ = w_2 = _____ g

Mass of bottle after transference = w_3 = _____ g

Mass of $ZnSO_4$ actually transferred = $w_2 - w_3 = w$ = _____ g

$$M_{\text{std. } ZnSO_4} = \frac{w}{287.56} \times 10 \quad \text{_____ M}$$

Titration of EDTA vs. Standard $ZnSO_4$ Solution:

Burette : EDTA

Conical flask : 10 mL standard $ZnSO_4$ + 20 mL H_2O + 2 mL buffer

Indicator : Erichrome Black-T

Colour change : Red to Blue

Sl.No.	Burette Reading		Volume of EDTA used (mL)
	Initial	Final	
1.			
2.			
3.			

Volume of EDTA used = V_{EDTA} = _____ mL

$M_{EDTA} \times V_{EDTA} = M_{std.\ ZnSO_4} \times V_{std.\ ZnSO_4}$

M_{EDTA} = _____ M

3. Titration of EDTA vs. $CaCO_3$ Solution:

Burette : EDTA.

Conical flask : 10 mL $CaCO_3$ solution + 20 mL H_2O + 2 mL Mg—EDTA complex + 2 mL buffer

Indicator : Erichrome Black-T.

Colour change : Red to Blue.

Sl.No.	Burette Reading		Volume of EDTA used (mL)
	Initial	Final	
1.			
2.			
3.			

Volume of EDTA used = V_{EDTA} = _____ mL

$M_{CaCO_3} \times V_{CaCO_3} = M_{EDTA} \times V_{EDTA}$

M_{CaCO_3} = _____ M

Strength of Ca (II) in given solution of $CaCO_3$ = M_{CaCO_3} × atomic mass of Ca

= (M_{CaCO_3} × 20) g/L

Result: The strength of Ca (II) in the given $CaCO_3$ solution is _____ g/L.

Experiment 11(f)

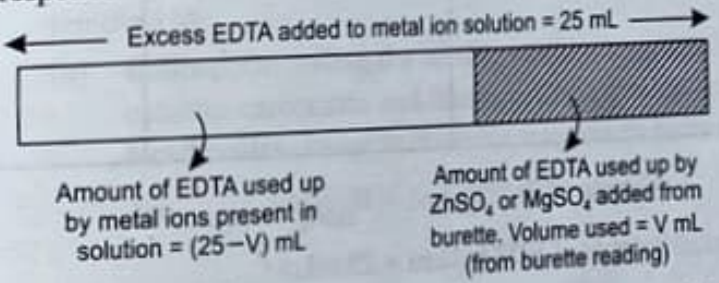
Aim: To estimate the amount of Ca (II) in a sample of drug/milk/food sample/biological sample using (M/100) EDTA in complexometric titration using Erichrome Black-T as indicator by back titration. Prepare standard $ZnSO_4$ solution to standardise EDTA.

Theory: **Back Titration:** There are many metal ions (like Ca^{2+}) whose concentration cannot be determined directly by titrating against EDTA solution. The reason being that they from inert complexes. Like in case of Ca^{2+}, the complex formed between Ca^{2+} ion and Erichrome Black-T is not very stable (the formation constant of Ca—In is very low). As

a consequence, significant conversion of Ca — In (red) to HIn^{2-} (blue) occurs well before equivalence i.e. the color change occurs prematurely in the titration of Ca^{2+} with EDTA because Ca^{2+} ions has a large tendency to form Ca — EDTA complex. Thus, with Ca^{2+} ions alone, no sharp end point can be obtained and the transition from red to blue is not observed. Thus, when Ca^{2+} ions are directly titrated with EDTA, a relatively stable Ca complex is formed.

$$Ca^{2+} + \underset{\text{(EDTA)}}{H_2Y^{2-}} \rightleftharpoons \underset{\text{(Complex)}}{CaY^{2-}} + 2H^+$$

Thus to determine the concentration of Ca^{2+} ions, an excess of EDTA solution is added to the solution of Ca^{2+} ions and the resulting solution is buffered to the desired pH. Some portion of the EDTA gets complexed with Ca^{2+} ions in the solution and the rest of the EDTA is back titrated with a standard metal ion solution (like $ZnSO_4$ or $ZnCl_2$ or $MgCl_2$ or $MgSO_4$) taken in the burette. The end point is determined by using the metal indicator which responds to the Zn^{2+} or Mg^{2+} ions introduced in the back titration.



Procedure:

1. **Preparation of Buffer Solution of NH_3-NH_4Cl (pH= 10):** It is prepared by adding 142 mL concentrated NH_3 solution to 17.5 g NH_4Cl and diluting to 250 mL using distilled water.
2. **Preparation of Standard $ZnSO_4$ Solution in 100 mL Standard Flask:** Prepare standard M/100 $ZnSO_4$ solution using distilled water by transference method.
3. **Titration of Standard $ZnSO_4$ vs. Given Sample of Milk Containing Ca^{2+} Ions:** Pipette out 10 mL of given sample of milk (*i.e.*, Ca^{2+} ions) in a conical flask. To this add 25 mL of 0.01 M EDTA solution to it and 2 mL of buffer (NH_3 — NH_4Cl, pH = 10). Boil the solution for a few minutes to ensure complete complexation of the Ca^{2+} ions. Cool the solution to room temperature and again add 2 mL of buffer (NH_3 — NH_4Cl, pH = 10) and 2–3 drops of Erichrome Black-T as indicator. Titrate the solution quickly with standard $ZnSO_4$ solution taken in the burette until the color changes from blue to red. Repeat the titration to obtain three concordant readings. This volume corresponds to the excess EDTA in the solution which remains uncomplexed by Ca^{2+} ions and thus gets complexed with the Zn^{2+} added from the burette.

Observation and Calculation:

1. **Preparation of Standard $ZnSO_4$ Solution in 100 mL Standard Flask:**

Molecular weight of $ZnSO_4$ = 287.56 g

Mass of $ZnSO_4$ required to prepare (M/100) solution in 100 mL flask = 0.4314 g

Mass of empty weighing bottle = w_1 = _____ g

Mass of bottle + $ZnSO_4$ = w_2 = _____ g

Mass of bottle after transferrence $= w_3 =$ _____ g

Amount of $ZnSO_4$ actually transferred $= w_3 - w_2 = w =$ _____ g

$$M_{\text{std. } ZnSO_4} = \frac{w}{287.56} \times 10 = \text{———} \text{ M}$$

2. **Titration of Standard $ZnSO_4$ vs. Given Sample of Milk Containing Ca^{2+} Ions:**

Burette : Standard $ZnSO_4$.

Conical flask : 10 mL of given sample of milk + 20 mL EDTA + 4 mL buffer.

Indicator : Erichrome Black-T.

Colour change : Blue to red.

Sl.No.	Burette Reading		Volume of EDTA used (mL)
	Initial	Final	
1.			
2.			
3.			

Volume of $ZnSO_4$ used $= V_{ZnSO_4} =$ _____ mL

Initial amount of EDTA taken = 25 mL

Amount of EDTA used by $ZnSO_4 = V_{ZnSO_4}$ mL

$\therefore$ Amount of EDTA used by Ca^{2+} ion $= V_{Ca^{2+}}(25 - V_{ZnSO_4})$

$$M_{Ca^{2+}} \times V_{Ca^{2+}} = M_{ZnSO_4} \times V_{ZnSO_4}$$

$$M_{Ca^{2+}} \times (25 - V_{ZnSO_4}) = M_{ZnSO_4} \times V_{ZnSO_4 \text{ (Burette reading)}}$$

$$M_{Ca^{2+}} = \text{_____ M}$$

Strength of Ca^{2+} ions in given sample of milk $= M_{Ca^{2+}} \times$ atomic weight of Ca

$= (M_{Ca^{2+}} \times 20)$ g/L

Result: The strength of Ca^{2+} ions in the given sample of milk is _____ g/L.

Experiment 11(g)

Aim: To determine the total, temporary and permanent hardness of given water sample using M/100 EDTA in complexometric titration using Erichrome Black-T as an indicator. Prepare standard M/100 $CaCO_3$ solution and M/10 Mg—EDTA complex solution.

Theory: **Hard and Soft Water:** Depending on the nature of substances disolve in it, natural water is classified as hard and soft.

Soft Water: Water free from soluble salts of Ca/Mg bicarbonate, chloride, sulphate is called soft water. It readily gives lather with soap.

Hard Water: Water containing solube Ca and Mg salts of bicarbonates, chlorides and sulphates is called hard water. It does not give lather with soap because the sodium stearate present in soap changes to the corresponding Ca/Mg salts which precipitates out. Thus, hard water forms scum/precipitate with soap.

For example, $2C_{17}H_{35}COONa + Ca^{2+}/Mg^{2+} \longrightarrow (C_{17}H_{35}COO)_2\ Ca/Mg \downarrow + 2Na^+$

Because of this scum formation, hard water is unsuitable for laundary washing and dyeing. It is also harmful for steam boilers because over a period of time the inner surface of the boiler gets covered with the **boiler scale** (which is largely $CaSO_4$, $CaCO_3$ and magnesium oxychloride). This boiler scale is a poor heat conductor and thus efficiency is drastically effected and boilers have been put completely out of action by local overheating due to boiler scale. It is therefore necessary to make the water soft before it can be used.

- Hardness of water is of 2 types:

(A) **Temporary Hardness:** It is due to the presence of bicarbonates of Ca or Mg. It can be removed by:

(*a*) **Boiling:** On boiling the soluble calcium bicarbonate changes to insoluble calcium carbonates and hence get precipitated and soluble magnesium bicarbonates change to insoluble magnesium hydroxides.

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

$$Mg(HCO_3)_2 \xrightarrow{\Delta} Mg(OH)_2 \downarrow + 2CO_2 \uparrow$$

(*b*) **Clark's Process:** In this, calculated quantity of lime is added to hard water which causes precipitation of calcium carbonate and magnesium hyroxide which can be filtered off.

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + Mg(OH_2) \downarrow + 2H_2O$$

(B) **Permanent Hardness:** It is due to the presence of soluble Ca/Mg sulphates/ chlorides. It cannot be removed by boiling. It can be removed by.

(*a*) **Treatment with Na_2CO_3 (washing soda):**

$$CaSO_4 + Na_2CO_3 \rightleftharpoons CaCO_3 \downarrow + Na_2SO_4$$

$$MgSO_4 + Na_2CO_3 \rightleftharpoons MgCO_3 \downarrow + 2NaCl$$

Other methods to remove permanent harndness involves ion-exchange method, synthetic resin method and Calgon's method.

Hardness of water is generally due to dissolved Ca and Mg salts and may be determined by complexometric titration. The hardness is expressed in parts of $CaCO_3$ per million of water.

Procedure: 1. **Preparation of Buffer Solution of NH_3-NH_4Cl (pH= 10):** It is prepared by adding 142 mL concentrated NH_3 solution to 17.5 g NH_4Cl and diluting to 250 mL using distilled water.

2. **Preparation of Standard Hard Water (Standard M/100 $CaCO_3$ in 1000 mL Standard Flask):** Take 1 g of $CaCO_3$ and dissolve it in dilute HCl (as $CaCO_3$ is insoluble in water, so first dissolved in dilute HCl) and then evaporate to dryness on

water bath. The residue left is dissolved in distilled water to make one litre solution. Each mL of this solution contains 1 mg of $CaCO_3$.

3. **Titration of EDTA vs. Standard Hard Water (Standardisation of EDTA):** Rinse and fill the burette with EDTA. Pipette out 50 mL of standard hard water in a conical flask. Then add 10 mL buffer (NH_3—NH_4Cl, pH = 10) and 10 mL of Mg — EDTA complex (Mg — EDTA complex is prepared by mixing equal volumes of 0.2 M EDTA solution and 0.2 M $MgSO_4$ solution). Then add 2–3 drop of Erichrome Black-T as an indicator to it. Titrate the solution against EDTA solution until the colour changes from red to blue. Repeat the titration to obtain three concordant readings.
4. **Titration of EDTA vs. Given Sample of Water (Determination of Total Hardness):** Pipette out 50 mL of given sample of water in a conical flask. Then add 10 mL buffer (NH_3 — NH_4Cl, pH = 10) and 10 mL of Mg — EDTA complex. Then add 2–3 drops of Erichrome Black-T as an indicator to it. Titrate the solution against EDTA solution, until the color changes from red to blue. Repeat the titration to obtain three concordant readings.
5. **Titration of EDTA vs. given sample of water (Determination of Permanent hardness):** Take 250 mL of the given sample of water in a 500 mL beaker and boil gently for 20-30 minutes (by boiling, temporary hardness present would be precipitated out as CaCO3 or $MgCO_3$). Cool and filter it directly into a 250 mL standard flask. Also during filtration, do not wash the filter paper. Then dilute the filtrate upto the mark with deionsed water and mix well.

   Take 50 mL of the filtrate in a conical flask. Then add 10 mL buffer (NH_3 — NH_4Cl, pH = 10) and 10 mL of Mg — EDTA complex. Then add 2-3 drops of Erichrome Black-T as an indicator to it. Titrate the solution against EDTA solution until the color changes from red to blue. Repeat the titration to obtain three concordant readings.
6. **Determination of Temporary Hardness:** Temporary hardness of given sample of water is calculated by substracting the permanent hardness from the total hardness.

Observation and Calculation:

Let volume of the water taken for each titration = 50 mL

Volume of EDTA used when titrated against standard hard water = V_1 mL.

Volume of EDTA used when titrated against given sample of hard water = V_2 mL.

Volume of EDTA used when titrated against water having permanent hardness = V_3 mL.

(*a*) **Strength of EDTA Solution:**

1 mL of standard hard water contains = 1 mg of $CaCO_3$.

50 mL of standard hard water contains = 50 mg of $CaCO_3$.

Volume of EDTA consumed for 50 mL of standard hard water = V_1 mL.

$\therefore$ V_1 mL of EDTA is used for = 50 mg of $CaCO_3$.

1 mL of EDTA is used for = $\left(\frac{50}{V_1}\right)$ mg of $CaCO_3$

or Strength of EDTA solution = $\left(\frac{50}{V_1}\right)$ mg/mL of EDTA.

(*b*) **Total Hardness:**

Volume of EDTA used for 50 mL of given sample of hard water = (V_2) mL.

Since, 1 mL of EDTA will consume = $\left(\frac{50}{V_1}\right)$ mg of $CaCO_3$

V_2 mL of EDTA will consume = $\left(\frac{50}{V_1} \times V_2\right)$ mg of $CaCO_3$

Hence, 50 mL of given sample of hard water = $\left(\frac{50}{V_1} \times V_2\right)$ mg of $CaCO_3$

1 mL of sample water = $\left(\frac{50 \times V_2}{V_1} \times \frac{1}{50}\right)$ mg of $CaCO_3$

1000 mL of sample water = $\left(\frac{\cancel{50} \times V_2}{V_1} \times \frac{1000}{\cancel{50}}\right)$ mg of $CaCO_3$

$$= \frac{V_2 \times 1000}{V_1} \text{ mg of } CaCO_3$$

$\therefore$ $$\boxed{\text{Total hardness} = \frac{V_2 \times 1000}{V_1} \text{ ppm}}$$

(*c*) **Permanent Hardness:**

Volume of EDTA used for 50 mL of water, containing permanent hardness = V_3 mL.

Since, 1 mL of EDTA consumes = $\left(\frac{50}{V_1}\right)$ mg of $CaCO_3$.

V_3 mL of EDTA consumes = $\left(\frac{50}{V_1} \times V_3\right)$ mg of $CaCO_3$.

Hence, 50 mL of given sample of water contains permament hardness = $\left(\frac{50}{V_1} \times V_3\right)$ mg of $CaCO_3$.

1 mL of given sample of water contains permanent hardness = $\left(\frac{50 \times V_3}{V_1} \times \frac{1}{50}\right)$ mg of $CaCO_3$.

1000 mL of water contains permanent = $\left(\frac{\cancel{50} \times V_3}{V_1} \times \frac{1000}{\cancel{50}}\right)$ mg of $CaCO_3$.

$$= \left(\frac{V_3 \times 1000}{V_1}\right) \text{ mg}$$

$$\boxed{\text{Permanent hardness} = \frac{V_3}{V_1} \times 1000 \text{ ppm}}$$

(*d*) **Temporary Hardness** = Total hardness – Permanent hardness.

$$= \left(\frac{V_2 \times 1000}{V_1} - \frac{V_3 \times 1000}{V_1}\right) \text{ ppm.}$$

Result:

The given sample of hard water contains

(*a*) Total hardness = _____ ppm

(*b*) Permanent hardness = _____ ppm

(*c*) Temporary hardness = _____ ppm