Title: TITRIMETRIC METHODS OF ANALYSIS

Unit Title: Complexometric Titration

Sub-Units:

8.1 Complexometric Titration

Objectives: By the end of the lesson students should be able to:

i) Define coordination compound and give examples of ligands
ii) State the features that make complex stable for titrimetric analysis

8.0 Main Content

8.1 Complexometric reactions and titrations

A coordination compound is a complex consisting of a central positive metal ion and a number of neutral molecules or anions that are chemically associated through ionic or covalent bonds. Complexes such as \([\text{Fe(CN)}_6]^{3-}\) are referred to as “essentially covalent” or “inner sphere” complexes, while those such as \([\text{FeF}_6]^{3-}\) can be described as “essentially ionic” or of the “outer orbital” type. The central atom is the electron acceptor (acid) and the ligand is the electron donor (base). It is for this reason that complexometric titration curves (e.g. for the titration of \(\text{Ag}^+\) with \(\text{CN}^-\) to form the complex \(\text{Ag(CN)}_2^2^-\)) are similar in shape to acid-base titration curves.

Some complexes (aqua & ammonia) undergo very fast substitution reaction-labile complex e.g. \([\text{Zn(H}_2\text{O)}_4]^{2+} + 4\text{NH}_3 \leftrightarrow [\text{Zn(NH}_3)_4]^{2+} + 4\text{H}_2\text{O}\) while others such as \(\text{Co}^{3+}\) and \(\text{Cr}^{3+}\) do not undergo substitution, thus referred to as inert.

Ligands that are attached to the central ion in only one orientation are called unidentate ligands, and they are mostly inorganic molecules or ions such as \(\text{H}_2\text{O}, \text{NH}_3, \text{OH}^-, \text{CN}^-, \text{NO}_2^-, \text{SCN}^-, \text{CH}_3\text{COO}^-\), halides etc. Ligands that have two or more coordinating sites is called a multidentate ligand e.g. ethylenediamine, diethylemtriamine and ethylenediamine tetraacetic acid, EDTA. Some organic ligands form stable complexes containing rings and are called chelates. Examples of such that are very commonly used in titrimetric analysis are EDTA, nitrolitriacetic acid, NTA\([\text{N(CH}_2\text{COOH)}_3]\), 1.10-phenanthroline and dimethylglyoxime (DMG).

The stability of the complexes is one of the key features that facilitate their use in titrimetric analysis. The factor that influences the stability of the complexes are:

i. The basicity of the ligand, which increases the stability
ii. The nature of the ligand (covalently or ionically bonded); and
iii. The nature of the central metal ion (strong electrostatic bonds give rise to more stable complexes).
iv. The number and size of any chelate rings, as well as
v. Resonance
vi. Steric effects may also influence the stability of a complex.
Many ligands are used as titrants in the development of quantitative analysis. In general, these methods are called complexometric titrations. If the ligand used as titrant is a chelating agent, the method is referred to as a chelometric titrations. The key factors or points for successfully performing a complexometric titrations are:

i. Choice of suitable chelating titrant, which reacts selectively with the analyte and forms a stable complex with a well-defined stoichiometry.

ii. Control of the experimental parameters such as pH and competing for ligand in order to optimize the titration and so as to achieve as high an analytical precision as possible, and

iii. Selection of a suitable method for determining the titration end point in order to ensure reproducibility and accuracy of the results.

8.2 Chelates : EDTA, the ultimate, titrating agent for metals

The titrants or titrating agent that is most widely used are the multidentate because they form complexes with higher stability constants. The most efficient ligands are those that form 1:1 molar ratio (metal:ligand) complex, because during the titration the equivalent point is well defined. Simple complexing agents such as NH\textsubscript{3} are rarely used as titrating agent because a sharp end point corresponding to a stoichiometric complex is generally difficult to achieve. This is because the stepwise formation constants are frequently close together and are not very large, and a single stoichiometric cannot be observed. Also, at any point of the titration curve there is a mixture of all possible species Zn\textsuperscript{2+} [Zn(NH\textsubscript{3})\textsubscript{2}]\textsuperscript{2+}[Zn(NH\textsubscript{3})\textsubscript{3}]\textsuperscript{3+} & [Zn(NH\textsubscript{3})\textsubscript{4}]\textsuperscript{2+} in the solution.

The most generally useful titrating agents are aminocarboxylic acids which combine the strong coordinating properties of the basic nitrogen with those of the carboxylic group.

Although there are many multidentate ligands, EDTA is the most successfully reagent for titrating several metals. The advantages of EDTA over other multidentate ligands are as follows:

1. The stoichiometry of the complex is 1:1.
2. Selectively can be controlled by changing the pH of the solution.
3. Na\textsubscript{2}H\textsubscript{2}Y.2H\textsubscript{2}O, a reagent of high solubility, is considered as a good primary standard.
4. There are reliable methods for determining the end point, either by metallochromic indicators or by instrumental methods (electrochemical or photometric).
5. The metal-EDTA complexes are very soluble in water.

8.2.1 EDTA Equilibria

We can represent EDTA as H\textsubscript{4}Y (a tetraprotic acid), the following equilibria apply to a Na\textsubscript{2}H\textsubscript{2}Y solution:

\[
\begin{align*}
H\textsubscript{4}Y & \rightleftharpoons H^{+} + H\textsubscript{3}Y^{-} & K_1 = 1.00 \times 10^{-2} = \frac{[H\textsubscript{3}Y^{-}]}{[H\textsubscript{4}Y]} \\
H\textsubscript{3}Y^{-} & \rightleftharpoons H^{+} + H\textsubscript{2}Y^{2-} & K_2 = 2.14 \times 10^{-3} = \frac{[H^{+}] [H\textsubscript{2}Y^{2-}]}{[H\textsubscript{3}Y^{-}]} 
\end{align*}
\]
8.3 METAL-EDTA titration curves

A titration is performed by adding the chelating agent to the sample. The titration curve for Ca\(^{2+}\) with EDTA at pH10 is shown below. Before the equivalence points the Ca\(^{2+}\) concentration is nearly equal to the amount of unchelating (unreacted) calcium since the dissociation of the chelate is slight. At equivalent point and beyond, pCa is determined from the dissociation of the chelate at the given pH; using Kf or K’f. The effect of pH on the titration is glaring from the curve for titration at pH7. The more stable the chelate (the larger Kf) the farther to the right will be the equilibrium of the reaction and the larger will be the end-point break. Also, the more the stable the chelate, the lower the pH at which the titration can be performed.

\[
\begin{align*}
H_2Y^{2-} & \leftrightarrow H^+ + HY^3- & K_3 &= 6.92 \times 10^{-7} = \frac{[H^+][HY^3-]}{[H_2Y^{2-}]} \\
HY^3- & \leftrightarrow H^+ + Y^4- & K_4 &= 5.50 \times 10^{-11} = \frac{[H^+][Y^4-]}{[HY^3-]}
\end{align*}
\]

8.4 Detection of the end-point

The detection of end point of a complexometric titration with EDTA can be achieved with metallochromic indicators or by means of instrumental methods (potentiometrically or perometrically or photometrically).

Metallochromic indicators are colored organic dyes that can also function as ligands to form chelates with metallic ions. There are both similarities and differences between metallochromic indicator and protolytic indicators in the way they function:

1. Whereas pH indicator respond to H\(^+\), the metallochromic indicators respond to the pM of different cations such as Mg\(^{2+}\), Ca\(^{2+}\), Cu\(^{2+}\) etc.
2. The chelates exhibit different colours compared to those of the free indicator just as acid-base indicators do during their protolytic reactions. However, metallochromic indicator responds to both to pH and Pm which make their use more complicated.

3. The chelates they form are often intently coloured and can be discriminated at concentration of $10^{-6}$ to $10^{-7}$ m.

Eriochrome Black T and calmagite are two of the most commonly used metallochromic indicators. Eriochrome Black T and calmagite contains three ionizable proton, both are tribasic weak acids and can be represented by $\text{H}_3\text{In}$ with Sulfonic acid group completely dissociated in aqueous solution.

This indicator can be used for the titration of $\text{Mg}^{2+}$ with EDTA. If added to the sample, it forms a red complex with part of $\text{Mg}^{2+}$, the colour of the uncomplexed indicator is blue. As soon as all free $\text{Mg}^{2+}$ is titrated, the EDTA displaces the indicator from the Mg, causing a change in the colour from red to blue:

\[
\begin{align*}
\text{MgIn} + \text{H}_2\text{Y}^{2-} & \rightarrow \text{MgY}^{2-} + \text{HIn}^{2+} + \text{H}^+ \\
\text{Red} & \rightarrow \text{colourless} \\
\text{blue} & \rightarrow \text{colourless}
\end{align*}
\]

The EDTA titration can be used to determine total hardness of water using Eriochrome Black T as indicator. But Eriochrome Black T cannot be used to indicate direct titration of calcium in the absence of magnesium with EDTA, because, the indicators form too weak a complex with Ca to give a sharp end point.

The titration of Ca and Mg with EDTA is done at pH10, using an NH$_3$/NH$_4$Cl buffer.

Calmagite is preferred in complexometric titrations with EDTA because it is more stable in aqueous solutions, Eriochrome Black T is unstable and must be freshly prepared prior to use.

### 8.4.1 Detection of end point by monitoring absorbance

The need to observe end point is a major limitation when using visual indicator to determine end point. This may be difficult in a situation where the solution is already coloured e.g. NH$_3$ is used to adjust the pH of solution containing $\text{Cu}^{2+}$ before its titration with EDTA. The presence of intensely coloured $\text{[Cu(NH}_3)_4]^{2+}$ complex obscures the indicator colours making accurate determination of end point difficult. Other absorbing species may also interfere in the process. This is often a problem when analyzing clinical sample blood or environmental sample such as natural waters.

In a situation whereby one species in a complexometric titration absorbs electromagnetic radiation, the equivalent point can be located by monitoring the absorbance of the analytical solution at a carefully selected wavelength. For example, equivalence point for the titration of $\text{Cu}^{2+}$ with EDTA in the presence of NH$_3$, can be located by monitoring the absorbance at a wavelength of 745 nm, where the $\text{[Cu(NH}_3)_4]^{2+}$complex absorbs strongly.

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\begin{align*}
\text{[Cu(NH}_3)_4]^{2+} + 4\text{Y}^- & \rightarrow \text{CuY}^{2-} + 4\text{NH}_3 \\
\end{align*}
\]
The equivalence point is given by the intersection of the linear segments, which are extrapolated if necessary to correct for any curvature in the titration curve.

**References:**


Harris DC (2013) Exploring Chemical Analysis 5th Ed WH Freman and Company NY