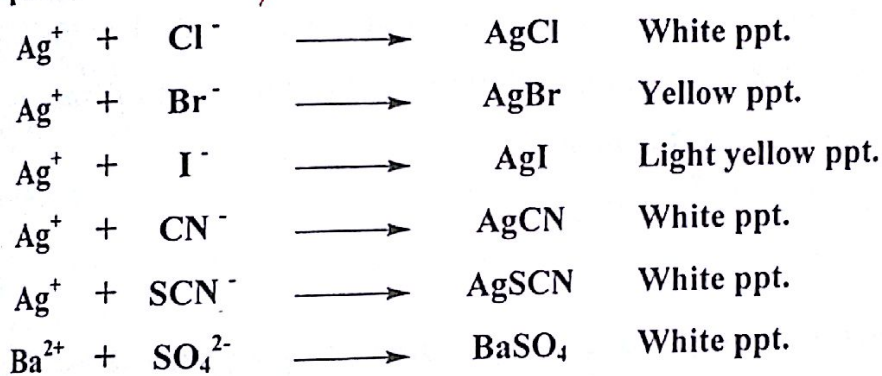# Chapter Nine

Precipitation Titration Curves

9 Precipitation Titration Curves.

Precipitation titrations are reactions /which in ? one of the products is ⅄
slightly soluble salt called Precipitate. Silver nitrate solution is always used
as a precipitating agent. Although this titration is an old method, it is still ·
used for/the determination of such ions as chloride, bromide, iodide, cyanide ⅄
and thiocyanate. Other precipitating agents are limited because of the lack
of necessary indicators to locate the equivalence point. An example of other ⅄
precipitating agent/is barium ion for/the determination of sulphate. ⅄

$$Ag^+ + Cl^- \longrightarrow AgCl \quad \text{White ppt.}$$

$$Ag^+ + Br^- \longrightarrow AgBr \quad \text{Yellow ppt.}$$

$$Ag^+ + I^- \longrightarrow AgI \quad \text{Light yellow ppt.}$$

$$Ag^+ + CN^- \longrightarrow AgCN \quad \text{White ppt.}$$

$$Ag^+ + SCN^- \longrightarrow AgSCN \quad \text{White ppt.}$$

$$Ba^{2+} + SO_4^{2-} \longrightarrow BaSO_4 \quad \text{White ppt.}$$

9.1 Titration curves for precipitation reactions:

Titration curves are important in deducing the properties of an
indicator for the special or certain titration as well as the titration errors
which are likely to be encountered.

When does the precipitate occur?

It occurs when the ionic product of the precipitate exceeds or becomes
larger than the value of solubility product constant (K_{sp}).

$$A^+ + B^- \longrightarrow AB$$

Ionic product $= [A^+][B^-]$

When $[A^+][B^-]$ is less than K_{sp}, the solution is unsaturated and there is no precipitation. When $[A^+][B^-] = K_{sp}$, the solution is saturated, but still there is no precipitation. When $[A^+][B^-]$ is larger then K_{sp}, the solution becomes supersaturated and a precipitation is occurred.

As shown in the preceeding chapters, that acid-base titration curves are the plot of pH values against volume of titrant. Therefore, the pH is the factor that is changed during the titration.

Here, in precipitation titration, the function of the concentration of the ion under test (pI) is changed through the titration. pI as well as pAg are plot against the volume of the added titrant.
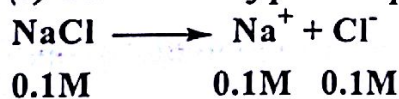
Example: Derive the titration curve of the titration of 25ml of 0.1 M NaCl with 0.1 M AgNO₃ solution. Compare this curve with titration curve of 0.1 M NaI with 0.1 M AgNO₃ solution.
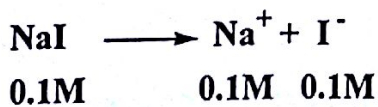$$K_{sp_{AgCl}} = 1.2 \times 10^{-10}, \quad K_{sp_{AgI}} = 1 \times 10^{-16}$$

The solution:

In this titration pCl and pI in addition to pAg are calculated during the titration.

(a) Calculation of pCl and pI before addition of AgNO₃ solution.

$$NaCl \longrightarrow Na^+ + Cl^-$$

0.1M   0.1M   0.1M

$$pCl = -\log [Cl^-] = -\log 0.1 = 1$$

$$NaI \longrightarrow Na^+ + I^-$$

0.1M   0.1M   0.1M

$$pI = -\log [I^-] = -\log 0.1 = 1$$

(b) After addition 15 ml of AgNO₃ solution.

$$\underset{AgNO_3}{(0.1 \times 15)} = \underset{NaCl}{(0.1 \times V)}$$

$$\underset{AgNO_3}{(0.1 \times 15)} = \underset{NaI}{(0.1 \times V)}$$

$$V_{NaCl} = \frac{0.1 \times 15}{0.1} = 15 \text{ ml reacting volume of NaCl.}$$

Unreacting volume of NaCl = 25-15 = 10 ml.

Total volume = 15+25 = 40 ml.

$$(10 \times 0.1) = 40 \times M_{NaCl}$$

$$M_{NaCl} = \frac{10 \times 0.1}{40} = 0.025 \text{M}.$$

$$NaCl \longrightarrow Na^+ + Cl^-$$

0.025M   0.025M   0.025M

pCl = -log [Cl⁻] = -log 0.025 = 1.6

$Ksp_{AgCl} = [Ag^+][Cl^-] = 1.2 \times 10^{-10}$

$$\mp \log Ksp = \mp \log[Ag^+] \mp \log[Cl^-] = \mp \log 1.2 \times 10^{-10}$$

pKsp = pAg + pCl = -(-10+0.08) = 9.92

pAg = pKsp - pCl = 9.92-1.6 = 8.32

Following the same calculation with NaI

∴ pI = 1.6

pKsp = pAg + pI = -log 1.0×10^{-16} = -(-16) = 16

∴pAg = 16- pI = 16-1.6 = 14.4

The same scheme of calculation is followed for any addition of volume
of AgNO₃ solution till before the equivalence point.

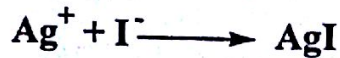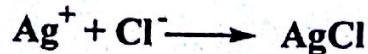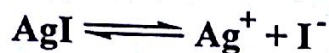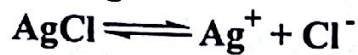*(c) After addition 25ml of 0.1M AgNO₃ solution.*

$$(V \times M)_{AgNO_3} = (V \times M)_{NaCl}$$

$$(25 \times 0.1)_{AgNO_3} = (25 \times 0.1)_{NaCl}$$

$$(25 \times 0.1)_{AgNO_3} = (25 \times 0.1)_{NaI}$$

All NaCl and NaI solutions are converted into AgCl and AgI
precipitates. It means that the Cl⁻ and I⁻ are completely altered to their
slightly soluble precipitates:

$$Ag^+ + Cl^- \longrightarrow AgCl$$

$$Ag^+ + I^- \longrightarrow AgI$$

Cl^- and I^- ions in the solutions are coming from the ionisation of AgCl and AgI:

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$

$$AgI \rightleftharpoons Ag^+ + I^-$$

$\therefore$ This stage is the equivalence point. $\therefore [Ag^+][Cl^-] = 1.2 \times 10^{-10}$

$$[Ag^+] = [Cl^-] = (1.2 \times 10-10)^{\frac{1}{2}} = 1.1 \times 10^{-5}$$

$$\mp \log[Ag^+] = \mp[Cl^-] = \mp\log 1.1 \times 10^{-5}$$

$\therefore pAg = pCl = -(-5+0.04) = 4.96$.   Also, $[Ag^+][I^-] = 1 \times 10^{-16}$

$$[Ag^+] = [I^-] = (1 \times 10^{-16})^{\frac{1}{2}} = 10^{-8}$$

$$\mp \log[Ag^+] = \mp\log[Cl^-] = \mp\log 10^{-8}$$

$$pAg = pI = 8$$

(d) After addition 30ml of AgNO₃ solution.

$$\underset{AgNO_3}{(25 \times 0.1)} = \underset{NaCl}{(25 \times 0.1)}$$

$$\underset{AgNO_3}{(25 \times 0.1)} = \underset{NaI}{(25 \times 0.1)}$$

The End point has been exceeded and the excess of added AgNO₃ solution = 30 - 25 = 5ml.

$$5 \times 0.1 = 55 \times M_{AgNO_3}$$

$$M_{AgNO_3} = \frac{5 \times 0.1}{55} = 9.1 \times 10^{-3} M$$

$$pAg = -\log[Ag^+] = -\log 9.1 \times 10^{-3} = 2.04$$

$pCl = 9.92 - 2.04 = 7.88$, and $pI = 16 - 2.04 = 13.96$.

The same scheme of calculation is followed for any addition of volume of AgNO₃ solution after equivalence point.

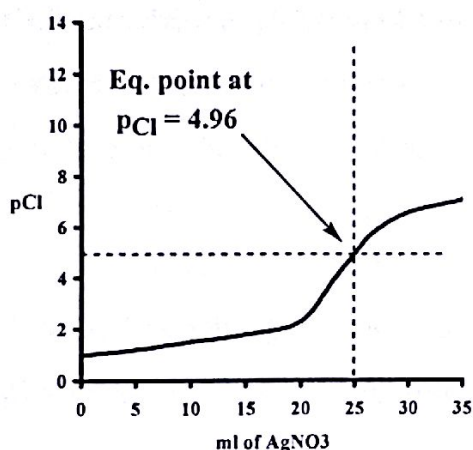Therefore, the following data are obtained for both titrations with AgNO₃ solution.

pCl	1	1.6	4.96	7.88
pAg	0	8.32	4.96	2.04

pI	1	1.6	8	13.96
pAg	0	14.4	8	2.04

A plot of pCl and pI against volume of AgNO₃ solution gives the following titration curves.
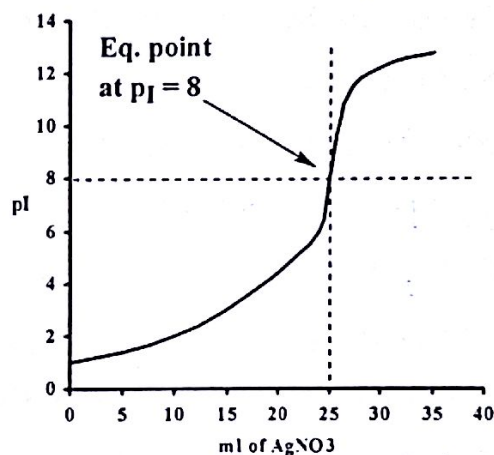
(a)   (b)

Fig(9-1): Titration curves of halides with 0.1M AgNO₃:

(a) For 0.1M NaCl   (b) For 0.1M NaI

It is clear from fig(9-1) that there is sudden change in pCl and pI round the equivalence point. The change is more clear with the titration of NaI since the solubility product constant of AgI is very small(1×10^{-16}) compared with solubility product constant of AgCl (1.2×10^{-10}).
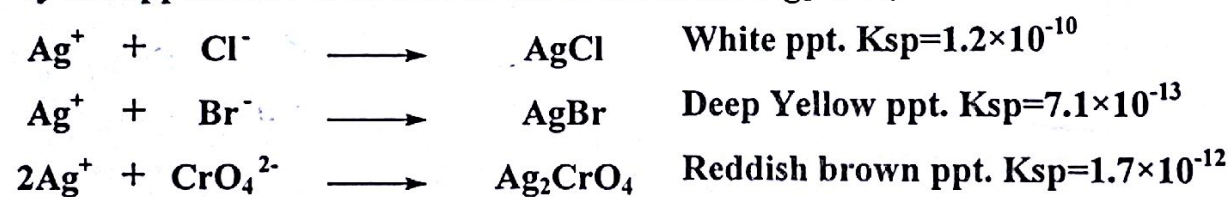
However, as the concentration of the analyte (Cl⁻ or I⁻) and the titrant (AgNO₃) are increased, there will be an enhancement in the equivalence point region change.

On the other hand, if the concentrations are decreased (to become 0.01 or 0.001M) there will be a weak change at/equivalence point region and a large titration error will occur. Therefore, concentrations of the reagents should be taken in consideration before any precipitation titration.

9.2 Methods of detection equivalence points in precipitation titrations.

9.2.1 Method of formation second coloured precipitate(Mohr's method).

The formation of a second precipitate of/distinctive colour is the base for end-point detection with the Mohr's method. The procedure has been widely used to the titration of chloride ion and bromide ion with standard silver nitrate solution. The method is employed also for the standardisation of $AgNO_3$ solution with standard NaCl solution. The end-point is signaled by the appearance of brick-red silver chromate Ag_2CrO_4.

$$Ag^+ + Cl^- \longrightarrow AgCl \quad \text{White ppt. Ksp}=1.2\times10^{-10}$$

$$Ag^+ + Br^- \longrightarrow AgBr \quad \text{Deep Yellow ppt. Ksp}=7.1\times10^{-13}$$

$$2Ag^+ + CrO_4^{2-} \longrightarrow Ag_2CrO_4 \quad \text{Reddish brown ppt. Ksp}=1.7\times10^{-12}$$

In the titration of Cl^- or Br^- with $AgNO_3$ in the presence of K_2CrO_4 as indicator, AgCl or AgBr is firstly precipitated followed by Ag_2CrO_4 at the equivalence point.

If Ksp_{AgCl} (1.2×10^{-10}) is compared with Ksp Ag_2CrO_4 (1.7×10^{-12}), Ag_2CrO_4 must firstly precipitated, but practically AgCl is firstly precipitated because:

1- CrO_4^{2-} requires $2Ag^+$ concentration which means that it requires high concentration of Ag^+.

2- K_2CrO_4 is added in small concentrations (1ml of 0.02M K_2CrO_4) which becomes about (0.003-0.004M) in the titration system, while Cl^- or Br^- are not less than 0.1M. Therefore, AgCl and AgBr are firstly

176

precipitated followed by Ag_2CrO_4 at the equivalence point. Little extra of $AgNO_3$ solution is added to clarify the end point. In order to know this excess of $AgNO_3$ solution, an indicator blank is operated at the time of the analysis. Here, the silver ion consumption of a chloride-free suspension of $CaCO_3$ is measured in about the same volume of solution and with the same amount of the indicator.

Attention must be paid to the acidity of the medium because the equilibrium $2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$ is replaced to the right as the hydrogen ion concentration is increased. Since silver dichromate is considerably more soluble than the silver chromate, the indicator reaction in acidic solutions requires larger silver ion concentration. If the medium is made strongly alkaline, there is danger that silver oxide will precipitate: $2Ag^+ + 2OH^- \rightleftharpoons 2AgOH_{(S)} \rightleftharpoons Ag_2O + H_2O$.

Thus, the determination of chloride by the Mohr method must be carried out in a medium that is neutral or slightly alkaline (pH 7-9). The convenient way of maintaining the hydrogen ion concentration within this suitable limits the is by the addition of small amounts of sodium carbonate, calcium carbonate or borax to the solution under test.

9.2.2 Methods of forming coloured complex solution(The Volhard method).

The most important application of the Volhard method is for indirect determination of halides. A measured excess of standard silver nitrate solution is added to the halide sample and the excess of silver ion is determined by back-titration with a standard thiocyanate solution. The requirement of a strongly acid environment represents a distinct advantage for the Volhard titration over other methods for halides because such ions

as carbonate, oxalate and arsenate (which form slightly soluble silver salts in neutral media) do not interfere.

Ferric ion is used as indicator in the back titration. Ferric salt is added as $Fe(NO_3)_3$ or as $Fe_2(SO_4)_3$ to give about 0.2M iron(III). Thiocyanate ion (SCN^-) is obtained by addition NH_4SCN or $KSCN$ to give a solution of 0.1M which is standardised with standard $AgNO_3$ solution in the presence of ferric ion indicator.

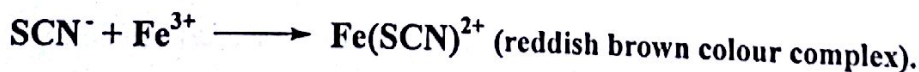Thiocyanate ion reacts with silver ion to form white precipitate of silver thiocyanate.

$$Ag^+ + SCN^- \longrightarrow AgSCN$$

At equivalence point, the added SCN^- reacts with Fe^{3+} ions to form the reddish brown colour of the complex $Fe(SCN)^{2+}$.

$$Fe^{3+} + SCN^- \longrightarrow Fe(SCN)^{2+}$$

Volhard method is used to determine Cl^-, Br^- and iodide in acidic medium of 0.1M HNO_3.

The process involves the addition of measured excess of silver nitrate solution for complete precipitation of the halides. The excess silver nitrate solution is determined by back-titration of the solution in the presence of the ferric indicator with standard solution of thiocyanate.

$$Cl^- \text{ or } Br^- \text{ or } I^- + Ag^+ \longrightarrow AgCl \text{ or } AgBr \text{ or } AgI$$

$$Ag^+ + SCN^- \longrightarrow AgSCN$$

$$SCN^- + Fe^{3+} \longrightarrow Fe(SCN)^{2+} \text{ (reddish brown colour complex)}.$$

Silver chloride ($AgCl$) in contrast to the other silver halides ($AgBr$ and AgI), is more soluble than silver thiocyanate. As a consequence, the following reaction:

$$AgCl_{(S)} + SCN^- \rightleftharpoons AgSCN_{(S)} + Cl^-$$
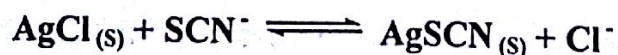
causes the end point in the Volhard determination of chloride to fade; an over consumption of thiocyanate ion and a negative error for the

analysis may result. The magnitude of this error is dependent upon the indicator concentration. About 0.2M of iron(III) ion is the most convenient concentration. Three processes are used to avoid the reaction of AgCl precipitate with thiocyanate ion:

(a) Addition of coagulant at high concentration such as the addition of 5ml of 1M KNO_3 or 1M $NaNO_3$ which increases the ionic strength of the solution. As a result, it enhances the coagulation of AgCl precipitate which lowers the opportunity of its contact with SCN^- ions.

(b) Filtration of AgCl precipitate and after washing the precipitate, the filtrate is back titrated with thiocyanate ion solution after addition 1ml of 0.2M Fe^{3+} indicator. The filtration of AgCl precipitate isolates it from thiocyanate ion.

(c) The most widely employed modification consists of coating silver chloride with nitrobenzene (a viscous liquid) which covers AgCl precipitate and forbids it from contact with thiocyanate ions solution. One millilitre was found sufficient for this purpose which is added and the mixture is stirred before titration with thiocyanate solution.

In case of determination of Br^- and I^-, there is no need to use any of the above processes because AgBr(Ksp=3.5×10^{-13}) and AgI (Ksp=1×10^{-16}) are less soluble than AgSCN (Ksp=7.1×10^{-13}) and AgCl (Ksp=1.2×10^{-10}).

9.2.3 Method of using adsorption indicators (Fajans method)

Adsorption means the masking of a material on the surface on another material while the *absorption* is the transition of material inside another material.

Most of the formed precipitates are impure because of the contamination by copercipitaion. One type of copercipitaion is the adsorption of different ions on the surface of the precipitate particles or

crystals. The adsorption occurs mostly by one of the colloidal precipitates where their particles possess high surface area. Although the colloidal precipitates cause problems to the analyst, but the colloidal phenomenon can be exploited in the precipitation titrations using adsorption indicators to locate the end point. Adsorption occurs near the equivalence point and results not only in a colour change but also a transfer of colour from the solution to the solid.

K. Fajans (1923) is considered the first who demonstrated the possibility of using adsorption indicators to locate the end point in precipitation titrations or reactions.

Adsorption indicators are organic compounds which may be acidic dyes such as in the series of Fluorescein and Eosin which are used as sodium salts, or basic dyes such as in the Rhodamine 6G which are used as halogen salts.

Fluorescein, for example, is used in the determination of chloride by titration its solution with silver nitrate solution. Since fluorescein is weak acid, it is partially ionised into hydrogen ions and fluoresceinate ions. In the beginning of the titration, AgCl is formed and adsorbs chloride ions on its surfaces since it is present in excess and the precipitate has the ability to adsorb its ions. There is no chance for the fluoresceinate to be adsorbed on the AgCl surface because it is repelled by the negative chloride ions (Fig 9-1).
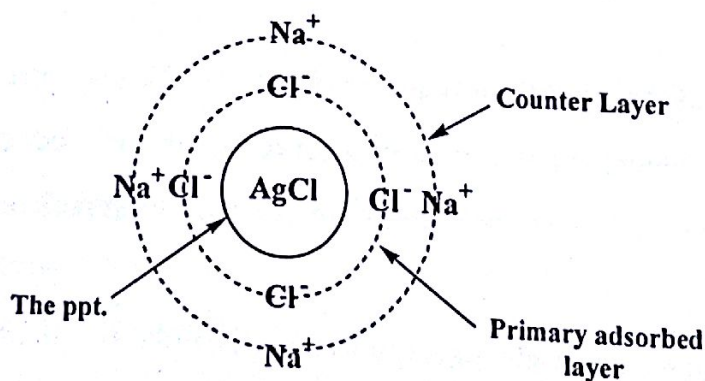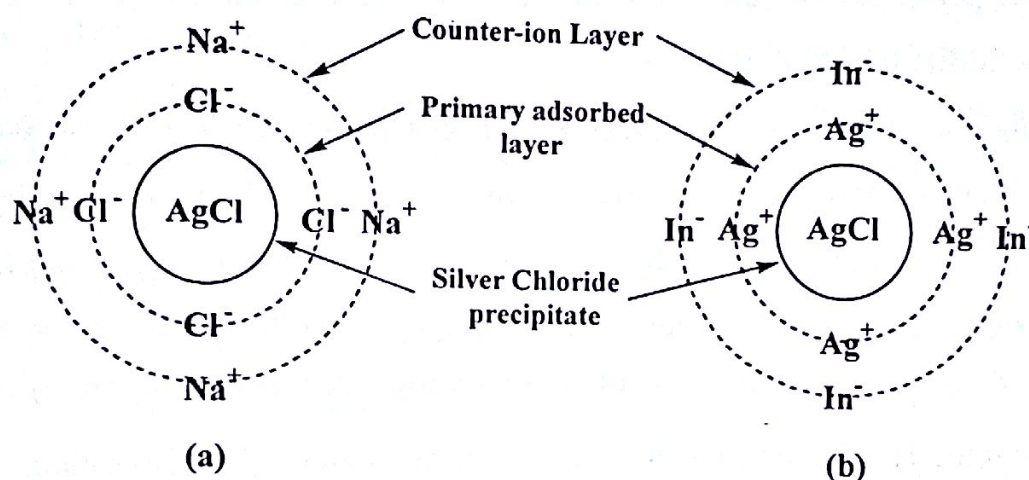

Fig (9-1): A schematic diagram illustrating the adsorption of Cl^- ions on AgCl ppt.

When the equivalence point occurs, there will be an excess positive silver ions and are strongly adsorbed to the particles of AgCl precipitate (the precipitate adsorb its ions). Under these conditions, the fluoresceinate ions forms the counter-ion layer. The net result is the appearance of the red colour (or pinkish colour) of silver fluoresceinate on the surface of the precipitate, while the original colour of fluoresceinate ions in the solution is yellowish green (Fig 9-2).

(a)   (b)

Fig(9-2): A schematic diagram illustrating the adsorption of chloride and silver ions on AgCl precipitate and the role of the indicator to locate the end point (a) before the end point. (b) after the end point.

The adsorption is a reversible process, the dye being desorbed upon back-titration with chloride ions.

The successful application of an adsorption requires the following properties:

1- The particles of the precipitate must be of colloidal dimensions so that the quantity of the indicator adsorbed is enhanced to the high specific surface area of the solid. The solution must be not very dilute which gives little precipitate rendering the change in the indicator colour unclear and the equivalence point can not be easily distinguished.

2- The precipitate must strongly adsorbs its own ions. This property is a characteristic of colloidal precipitate.

3- The charge of indicator ion must be an opposite to precipitating agent charge.

4- The indicator should not be adsorbed before the complete precipitation of halide. The adsorption should occur at the equivalence point after complete precipitation of the halide.

5- The pH of the solution must be such as to insure that the ionic form of the indicator predominates.

The use of adsorption indicators is accompanied with some problems. The silver halides are sensitive to light by the adsorbed dye layer. Therefore, the precipitation titrations processes are carried out far from direct light. The concentration of the indicator should not be more than $2 \times 10^{-4} - 3 \times 10^{-3}$ M for each mole of silver halides. A reasonable quantity of the indicator is adsorbed on the precipitate surface to give clear change in the indicator colour.

Titrations involving adsorption indicators are rapid, accurate and reliable.

Their application, however, is limited to a relatively few precipitation reactions in which a colloidal precipitate is rapidly formed.

Most adsorption indicators are weak acids. Their use is thus confined to neutral or slightly acidic solution where the indicator is present predominantly as the anion. Flourescein indicator (Fig 9-3) is used in the determination of chloride. This indicator is very weak organic acid ($Ka=1 \times 10^{-8}$). The most suitable pH range for this indicator is 7-10. Dichloroflourescein is also organic acid but it is stronger than flourescein. It works in weak acidic medium (pH not more 4.4). This indicator can be used in very dilute solutions .

Eosin (Fig 9-3) which is tetra bromoflourescein is an acid more stronger than dichloroflourescein which can be used in acidic medium has a pH range of (1-2) and its colour change can be distinguished clearly in the presence of acetic acid (pH<3).

Eosin is strongly adsorbed by silver halides, therefore, it is not used for the determination of chloride because the Eosinate ion competes the chloride ion on adsorption before the equivalence point. Thus, the indicator colour changes before the equivalence point and gives inexact titration results. Bromide and iodide ions are more adsorbed than Eosinate ion, therefore, there is no serious competition and a clear equivalence point can be obtained even with dilute solutions. The Eosin exhibits a magenta colour when it is adsorbed on precipitate surface.

The former indicators are prepared by dissolving their sodium salts in water or dissolving the indicator itself in 70% ethyl or methyl alcohol.

A few cationic adsorption indicators are known, these are suitable for titrations in strongly acid solutions. For such indicators, adsorption of the indicator and colouration of the precipitate occur in the presence of an excess of the anion of the precipitate.

Rhodamine 6G (Fig 9-3) is an example of the basic organic adsorption indicators, and which is used in the form of hydrochloride (0.05% aqueous solution). It is used for the determination of silver ions by titration its solution with standard potassium bromide solution in the presence of dilute nitric acid (not more than 0.5M). The indicator colour changes at the equivalence point into bluish-violet. The precipitate of AgBr does not adsorb the indicator cation unless the occurrence of the equivalence point.

There are many other organic dyes which can be used as adsorption indicators not only for halides determination but to determine other ions. For example, cyanide can be determined by titration using diphenylcarbazide

as an indicator. The colour of the precipitate becomes pale violet at
equivalence point. Some adsorption indicators are compiled in table (9-1)
with their characteristics and applications.

Table (9-1): Some adsorption indicators

The indicator	Its application	Colour change	Titration conditions
1- flourescein	Cl^- with Ag^+	Yellowish green to pinkish	Neutral or slightly basic
2- Dichloro-flourescein	Cl^-, Br^-, I^- and SCN^- with Ag^+	Yellowish green to red	pH (4.4-7.0)
3- Eosin	Br^-, I^- and SCN^- with Ag^+	Pink to Reddish violet	pH (1-2) acetic acid
4- Rose Bengal	I^- in the presence of Br^- and Cl^- with Ag^+	Red to violet	Addition of $(NH_4)_2CO_3$
5- Diiododimethyl-flourescein	I^- with Ag^+	Reddish orange to Reddish blue	pH (4-7)
6- Chromotrope	Br^- with Ag^+	Pink to greenish gray	0.1M acetic acid
7- Alizarin red	I^- in the presence of Cl^- with Ag^+	Yellow to pink	Neutral
8- Rhodamine 6G	Br^- with Ag^+	Pinkish orange to violet red	0.3M HNO_3
9- Phenosafranine	Cl^- and Br^- with Ag^+	Red to blue	0.3M HNO_3
10- Tartrazine	I^- with Ag^+ or SCN^- and $I^- + Cl^-$ with excess Ag^+	Colourless to green	

Fig (9-3) shows three structures for three common adsorption indicators.
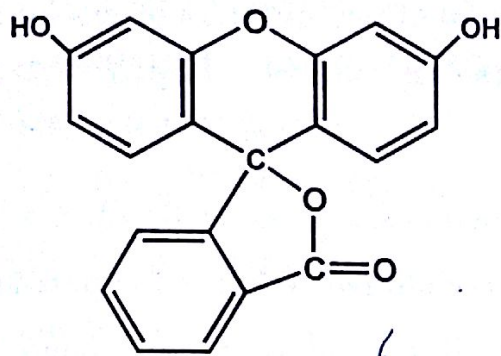
(1) 1-Fluorescein   (2) 2-Eosin

H₃CH₂CN ... NHCH₂CH₃

تبقّد الارقام
من آم الدرس

C—OCH₂CH₃
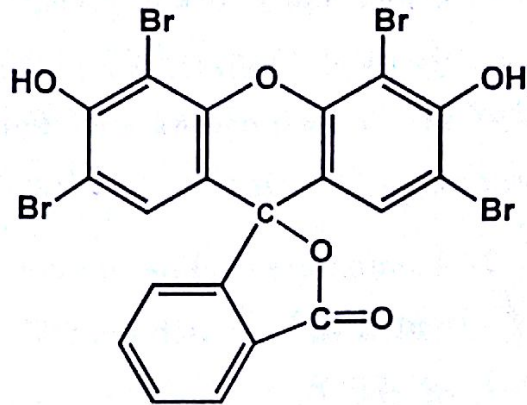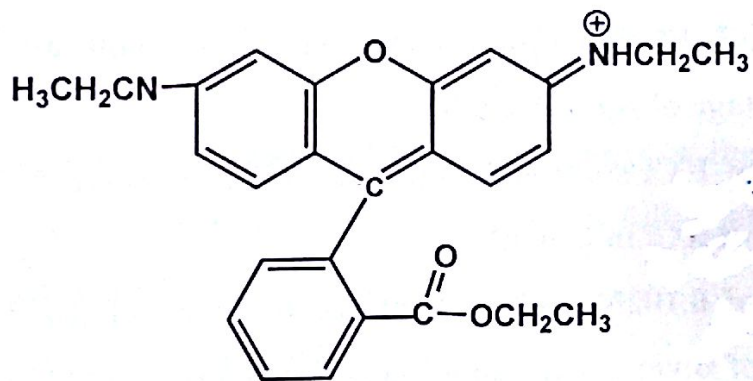
(3) 3-Rhodamine 6G

Fig (9-3): Three types of adsorption indicators.

9.3 Problems:

1- A solution of silver nitrate is added to mixture of Cl^- and I^- solution. Which ion is firstly precipitated.? What is the concentration of the firstly precipitated ion in the moment of precipitation of the second ion if the concentration of both ions is 0.01M. $Ksp_{AgCl}=1.2\times10^{-10}$, $Ksp_{AgI}=1\times10^{-16}$.

2- Ammonium oxalate solution is added to a mixture of 0.01M Ca^{2+} and 0.01M Ba^{2+}. Which ion is firstly precipitated! What is the percentage of the first ion in the moment of precipitation of the second ion? $KspBaC_2O_4 =1.7\times10^{-7}$, $KspCaC_2O_4=2.6\times10^{-9}$.

3- 0.30 gram of silver alloy is dissolved in nitric acid and titrated with 0.1M NH_4SCN solution which requires 23.80 ml. Calculate the percentage of Ag in the alloy.

4- 25 ml of KCl solution requires 34 ml of 0.105M $AgNO_3$. Calculate the weight of KCl in 250 ml.

5- 40 ml of 0.102M $AgNO_3$ is added to 25 ml of $BaCl_2$ solution. The excess of silver nitrate solution is titrated with 0.098M of thiocyanate which requires 15 ml. Calculate the $BaCl_2$ weight in 250 ml.

6- 0.1g of silver alloy contains 90.2% silver and 9.8% copper. The alloy is dissolved in nitric acid and titrated with KSCN solution which requires 10.2 ml. Calculate the concentration of KSCN solution and the weight of KSCN in litre of solution.

7- A mixture of KCl and KBr weighs 0.30745g requires 30.98 ml of 0.1007M $AgNO_3$ solution. Calculate the percentages of KCl and KBr in the sample.

8- A mixture of $BaCl_2$ and BaI_2 weighs 7.5g contains inactive impurities is dissolved in water and diluted to 250 ml. 25 ml of this solution is titrated with 0.084M $AgNO_3$ solution using bromophenol blue

indicator which requires 41.2 ml to neutralise Cl^- and I^-. 50 ml of the same solution is titrated with 0.084M $AgNO_3$ solution in the presence of Eosin indicator which requires 38.3 ml to neutralise I^- only. Calculate the percentages of $BaCl_2$ and BaI_2 in the sample.

9- Calculate the change in pCl in the titration of 50 ml of 0.1M NaCl with 0.2M $AgNO_3$ after/the addition of the following volumes: (a) 10 ml. (b) 20 ml. (c) 25 ml. (d) 35 ml. $Ksp_{AgCl}=1.2\times10^{-10}$.

10- 40 ml of 0.1M NaBr is titrated with 0.2M $AgNO_3$. Calculate the change of pBr after/the addition of the following volumes of 0.2M $AgNO_3$: (a) 10 ml. (b) 20 ml. (c) 25 ml. $Ksp_{AgBr}=7.1\times10^{-13}$.

11- 30 ml of 0.1M NaI was titrated with 0.2M $AgNO_3$. Calculate the change of pI after/the addition of the following volumes of $AgNO_3$: (a) 10 ml. (b) 15 ml. (c) 25 ml. $Ksp_{AgI}=7.1\times10^{-16}$.

12- 25 ml of $AgNO_3$ was titrated with 0.2M NH_4SCN in the presence of ferric indicator. Calculate pAg and pSCN at the following stages:
a) Before/the addition of SCN^-.
b) After/the addition of 10 ml of SCN^-.
c) At equivalence point.
d) After addition 5 ml after equivalence point. $Ksp_{AgSCN}=7.1\times10^{-13}$.