

# UNIT-VI

# PRECIPITATION TITRATION

B.KIRUTHIGA  
LECTURER

DEPT OF PHARMACEUTICAL CHEMISTRY



## Precipitation Titration

Analyte is titrated with a standard solution of a precipitating agent in accordance with defined reaction stoichiometry.

Detection of the end point (at completion of the precipitation) is usually by either the appearance of excess titrant or the disappearance of the reactant.

## Formation of insoluble metal-ligand precipitates.

- Argentometric Methods

Titration methods based upon utilizing silver nitrate as a precipitating agent.

- Silver ion is extremely useful in precipitation reactions including:

- Halides ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ )
- Pseudohalides ( $\text{S}^{2-}$ ,  $\text{HS}^-$ ,  $\text{CN}^-$ ,  $\text{SCN}^-$ )



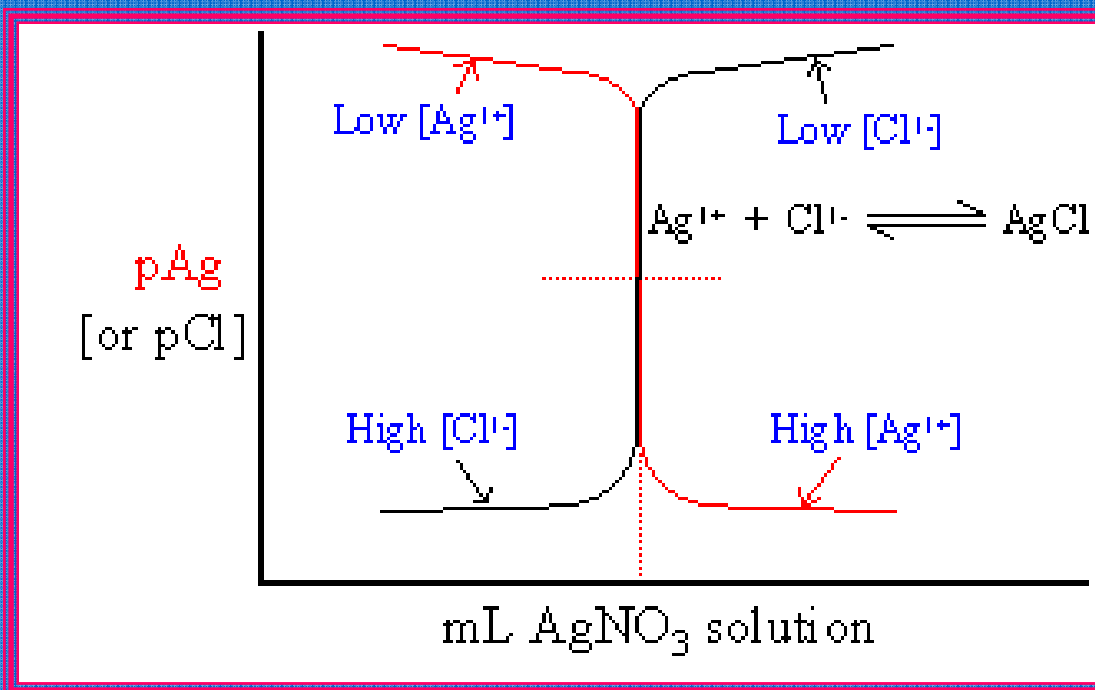
## Requirements

1. The precipitate formation is stoichiometric.
2. To allow the titrant to be added quickly, the equilibrium between the precipitate and its ions in solution must be attained rapidly. A slow attainment of equilibrium will cause overtitration.
3. The precipitate must be of low solubility in the solution. This is indicated by small equilibrium constant ( $K_{sp}$ ).
4. A method to detect the stoichiometric point of the titration must be available. Although a number of indicators are available, in general, the best method for detecting the end point in precipitation titration is by an instrumental technique.

# Titration Curves for Argentometric Methods

- Plots of titration curves are normally sigmoidal curves consisting of pAg (or pAnalyte) versus volume of  $\text{AgNO}_3$  solution added.

Example: Titration of chloride with silver.



The points on the curve can be calculated, given the analyte concentration,  $\text{AgNO}_3$  concentration and the appropriate  $K_{sp}$ .



## Observations About Argentometric Titrations

- High reagent concentrations give sharper, more dramatic equivalence point changes in pAg and better endpoints.



The smaller the  $K_{sp}$ , the more complete the precipitation reaction and the sharper the equivalence region changes.

Both  $K_{sp}$  and the reagent concentrations affect the choice and use of an endpoint indicator.

## Endpoint Indicators for Argentometric Titrations

- Indicators for argentometric titrations are selected to produce a color change at or near the equivalence point.
- Normally the indicator is selected to react with the added titrating agent, not the analyte. If A is the analyte, R the titrating agent and In is the indicator.



To make the indicator change color, excess R must be added. Obviously, the smaller the excess added to cause the color change, the smaller the endpoint error.

This means that the indicator should give large color changes at very low concentrations.



# End Point Determination in Precipitation Titrations

Titrations with  $\text{Ag}^+$  are called argentometric titrations.

For argentometric titrations, three classical methods based on color indicators can be used for end point detection:

- Mohr titration – formation of colored precipitate at the end point.
- Volhard titration – formation of a soluble, colored complex at the end point.
- Fajans titration – adsorption of a colored indicator on the precipitate at the end point.







- The concentration of titrant rises sharply near the equivalence point, and the solubility of  $\text{Ag}_2\text{CrO}_4$  is exceeded.
- The titrations are performed only in neutral or slightly basic medium to prevent silver hydroxide formation (at  $\text{pH} > 10$ ).



- Or the formation of chromic acid at  $\text{pH} < 7$ .



$[\text{CrO}_4^{2-}]$  become lower, more  $\text{Ag}^+$  to be added to reach end point, which cause error.

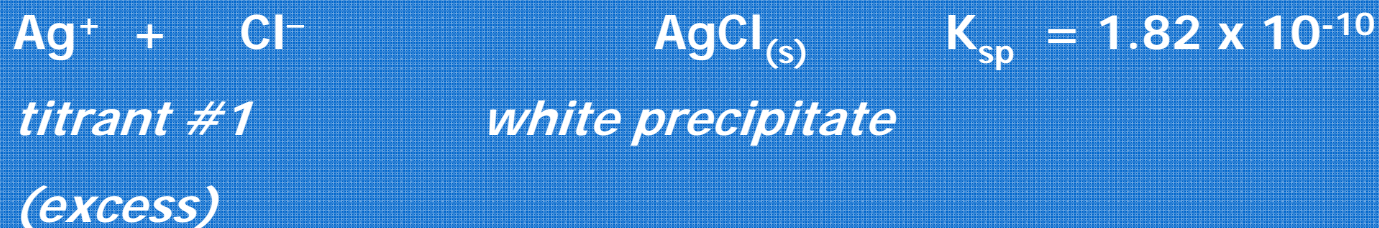
**Suitable pH??**



## Volhard METHOD

Determination of Cl. For titration of silver ion with thiocyanate ( $\text{SCN}^-$ ) and iron(III) as an indicator. First published in 1874.

Reactions:





- The endpoint is routinely used for halide determinations where a known excess of silver ion is added to precipitate the halide ion, and the excess silver ion is back titrated using the thiocyanate/iron(III) as the indicator.
- The silver chloride precipitate is filtered, and the excess silver ion is titrated with thiocyanate producing a white precipitate of AgSCN.
- Once the silver is consumed, the excess thiocyanate reacts with the iron(III) ion producing a red  $\text{FeSCN}^{2+}$  complex. Thus, the appearance of the red color at the endpoint.

The red  $\text{FeSCN}^{2+}$  complex color is detectable at  $6.4 \times 10^{-6}$  M concentrations and above.

The titration is usually done in acidic pH medium to prevent precipitation of iron hydroxides,  $\text{Fe}(\text{OH})_3$ .



- The AgCl precipitate must be separated from the thiocyanate to prevent the reaction:



- Since AgSCN is less soluble than AgCl, equilibrium will shift to the right causing a negative error for the chloride analysis.

To eliminate this error, AgCl must be filtered or add nitrobenzene before titrating with thiocyanate; nitrobenzene will form an oily layer on the surface of the AgCl precipitate, thus preventing its reaction with thiocyanate.



## Fajans Method (Adsorption Indicators)

- Adsorption indicators are organic compounds that tend to be adsorbed onto the surface of the solid precipitate in a precipitation titration.
- Adsorption indicators work best when:
  - They do not precipitate out silver ion when the indicators are at low concentration.
  - They bind to the precipitate only when excess silver ion is present to produce color.

### Example of Adsorption Indicators: Fluorescein

- A polycyclic compound that ionizes in solution to yield yellow-green fluoresceinate ions.

Fluoresceinate adsorbs to silver ions on the surface of a precipitate when excess silver ion is present, producing a reddish-colored surface.



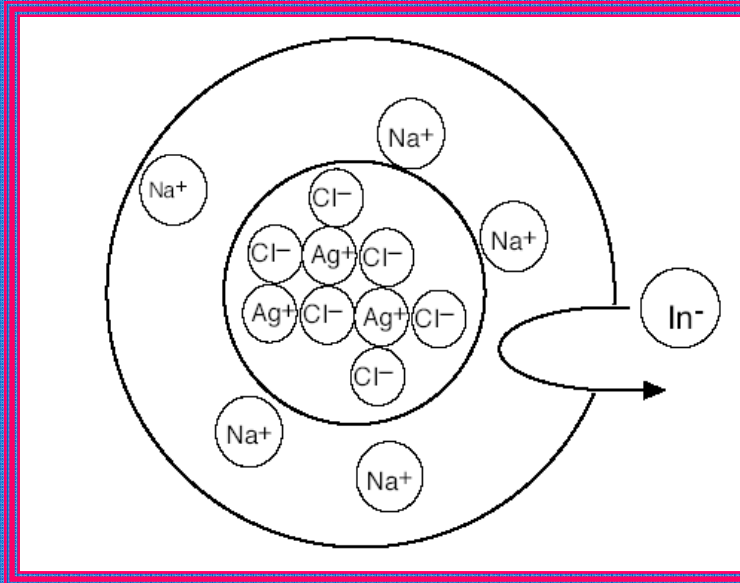
- Only the ionized fluoresceinate produces the red color.
- Titration of NaCl with AgNO<sub>3</sub>



- During the titration, colloids are formed.
  - Before the equivalence point, the surface of the precipitant particles will be negatively charged due to the adsorption of excess Cl<sup>-</sup> the surface of the particles. A diffuse positive counter-ion layer will surround the particles.
  - The primary adsorption layer is negatively charged and the anionic indicator is repelled.



- Before the end point ( $\text{Cl}^-$  in excess).



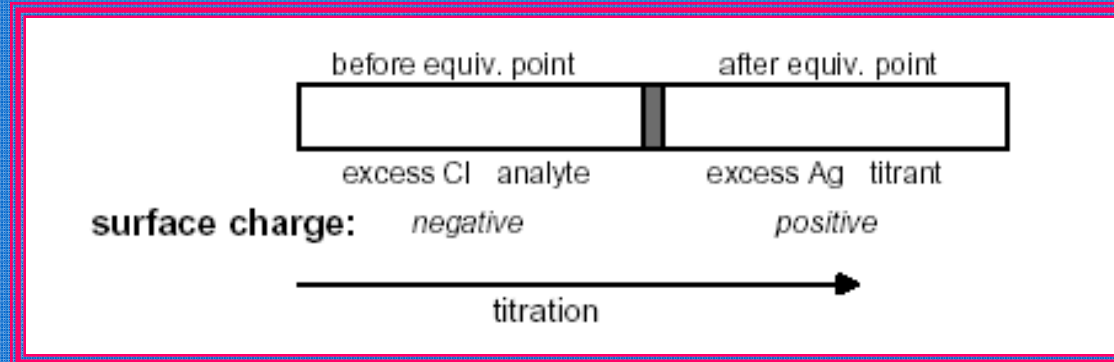
$(\text{AgCl}) \cdot \text{Cl}^-$   
1° Layer

$\text{M}^+$   
2° Layer

When the equivalence point is reached, there is no longer an excess of analyte  $\text{Cl}^-$ , and the surface of the colloidal particles are largely neutral.

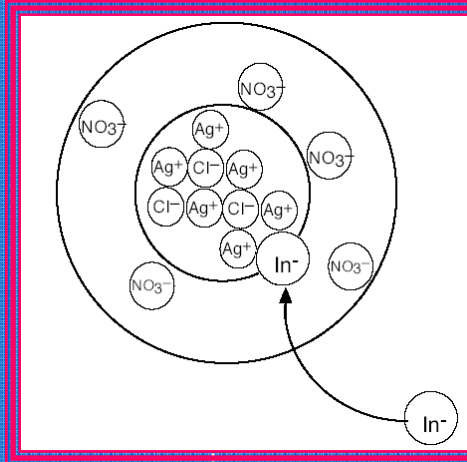


- After the equivalence point, there will be an excess of titrant  $\text{Ag}^+$ , some of these will adsorb to the  $\text{AgCl}$  particles, which will now be surrounded by a diffuse *negative* counterion layer.
- Now, negatively charged fluorescein can penetrate the counter ion layer and adsorb onto the  $\text{AgCl}$  lattice due to its affinity to  $\text{Ag}^+$ .





After the end point  
( $\text{Ag}^+$  in excess).



1° Layer



2° Layer

- The fluorescein concentration is too small to form an  $\text{AgIn}$  precipitate in solution. The formed complex has a red color.
- Conditions that favor the formation of colloids:
  - Fast addition of reagents.
  - Add dextrin to retard coagulation.
  - pH control is important to generate the dye anion in solution.
  - Avoid light, since  $\text{Ag}$ -dye complex is light sensitive and decomposes after a while.



THANK YOU