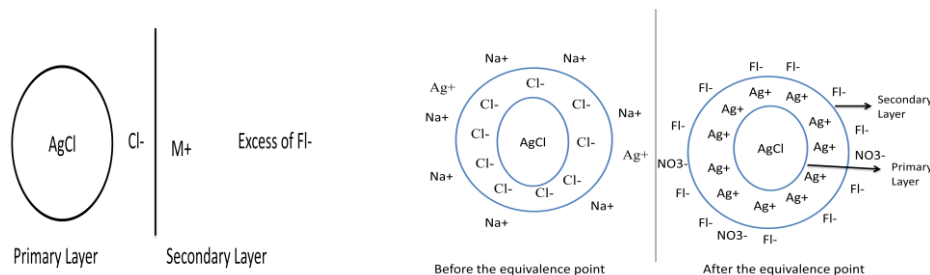


ARGENTOMETRIC/ PRECIPITATION TITRATIONS

Describe the principle involved in titration by Fajans Method.

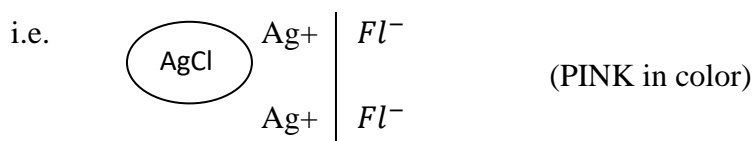
Ans. Adsorption of colored organic compounds on the surface of a precipitate may induce electronic shift in molecule that alters its color. This phenomenon is used to detect the end point of precipitation titration of Ag^+ salts. The mechanism was shown by K. Fajan's. Organic compounds are used as adsorption indicators.

In titration of Cl^- with Ag^+ before equivalence point colloidal particles of AgCl are negatively charged because of adsorption of Cl^- ions from solution.



Before the equivalence point adsorbed Cl^- forms primary layer which makes colloidal particles to be negatively charged. These attract positively charged ions from the solution to form a more loosely held secondary layer. After the equivalence point excess of Ag^+ ions (positively charged) displace negatively charged Cl^- ions from primary layer & particles become positively charged. Anions in the solution are attracted to form the secondary layer.

- A precipitate tends to adsorb most readily those ions that form an insoluble compound with one of the ions in the lattice. Therefore, Ag^+ ions or Cl^- will be more readily absorbed by AgCl precipitate than say NO_3^- or Na^+ ions.
- Fluorescein which is a weak organic acid represented by HFl when added to flask, the anions Fl^- is not adsorbed by colloidal AgCl as long as Cl^- ions are in excess. But once the Ag^+ are in excess, Fl^- ions are attracted to surface of positively charged ions particles.



The resulting aggregate is pink in color & color change is so intense that it serves as visual indicator.

What are the conditions that govern the choice of suitable adsorption indicator.

Ans. Following are the conditions that govern the choice of suitable adsorption indicator:

1. The precipitate should separate in **colloidal condition**. Large quantities of neutral salts, multivalent ions are **avoided** due to their **coagulating effect**. Solution should not be too dilute because amount of precipitate formed will be small & color change is not sharp.
2. Ions of **indicator** must be of **opposite charge** to the ion of **precipitating agent**.

3. Indicator ion should be strongly **adsorbed** immediately **after the equivalence point**.

But **not too strongly** adsorbed by precipitate.

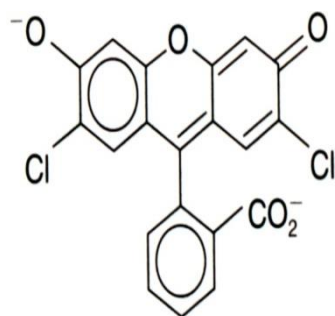
Eg. Eosin (Tetrabromo fluorescein) added to Cl^- --- Ag^+ titration. The adsorption of indicator ion may be a primary process & takes place before equivalence point is reached.

Fluorescein can be used in pH range of 7 to 10.

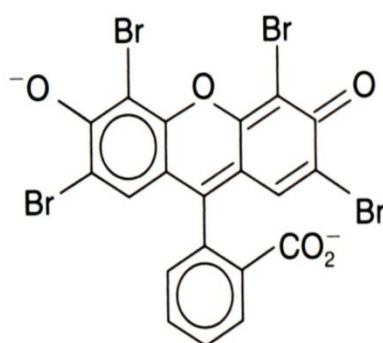
Dichloro Fluorescein can be used in pH range of 4 to 10.

Disadvantage:

- AgX (silver halide) are sensitive to action of light by a layer of adsorbed dyestuff (indicator). Therefore, titration should be carried out with a minimum exposure to sunlight.
- Only 2×10^{-4} to 3×10^{-3} ml of dye/ mol of AgX is added.
- Preparation of Fluorescein indicator: Dissolve 0.2 g fluorescein in 100 ml of 70% ethanol. Or Sodium fluoresceinate in 100 ml of Water.



Dichlorofluorescein



Tetrabromofluorescein (eosin)