SHREE H. N. SHUKLA INSTITUTE OF PHARMACEUTICAL EDUCATION AND RESEARCH

B.PHARM

(SEMESTER –I)

SUBJECT NAME: PHARMACEUTICAL ANALYSIS -I

SUBJECT CODE: BP102TP

UNIT 5(a): CONDUCTOMETRY

Content

Conductometry- Introduction, Conductivity cell, Conductometric titrations, applications.

INTRODUCTION

Determination of conductance of an electrolyte solution by conductometer is called conductometry.

Solutions of electrolytes conduct electric current by migration of ions under the influence of electric field. Here the electrical current is developed due to migration of positively charged ions towards cathode and negatively charged ions towards anode.

Like a metallic conductor, the electrolyte solutions obey Ohm's law. The reciprocal of resistance called as conductance and it is expressed in unit known as mhos or ohms.

The amount of current carried through the electrolyte solution depends upon the relative concentration of electrolyte and mobility of ions in the medium i.e the two factors affecting conductance are speed of ions and their concentration.

Principle of Conductometry:

- In conductometry the electrodes are in contact with electrolyte solution; when potential is applied the current flow through the solution.

- Figure 1 shows movement of ions in solution under influence of applied electrical field between two electrodes i.e. cathode and anode.

- The ions migrates in response to this field, positively charged ions (cations) are attracted by cathode (electrode with - ve charge) and vice versa.
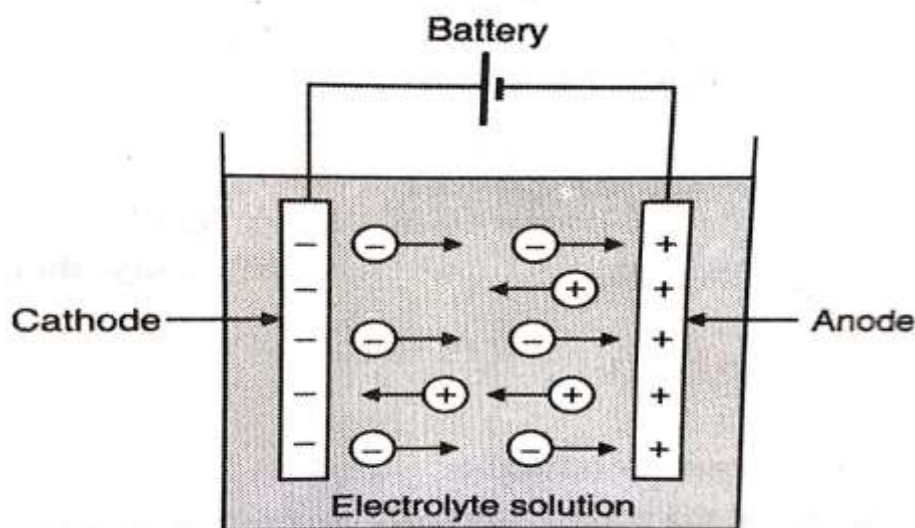
Conductance:

- Reciprocal of the resistance is known as conductance. Conductance is mathematically expressed as:

$$G = \frac{1}{R}$$

- According to Ohms law strength of current (I, amperes) flowing through conducting medium is directly proportional to the potential difference (E, volts) applied across the conductor and inversely proportional to resistance of the conductor (R), mathematically the law is expressed as,

$$I = \frac{E}{R}$$

Specific Resistance:

- Resistance of a conductor is directly proportional to its length (l) and inversely proportional to area of cross section (a) of electrodes

$$R \propto \frac{l}{a} \quad \text{or} \quad R \propto \frac{l}{a}, \rho = R\frac{a}{l} \quad \text{where } \rho \text{ is a constant called specific resistance or resistivity.}$$

Unit: of specific resistance is ohms-cm.

Specific Conductance:

- Specific conductance (k) of any conductor is reciprocal of specific resistance and mathematically expressed as:

$$k = \frac{1}{\rho} \quad\quad\quad \text{Unit: ohms}^{-1}\text{ cm}^{-1}$$

Equivalent Conductance (λ_v):

- It is defined as the conductance of one gram equivalent of electrolyte contained between two sufficiently large electrodes at 1 cm apart. Where V is the volume in cubic cm containing 1 gm equivalent of electrolyte dissolved in it.
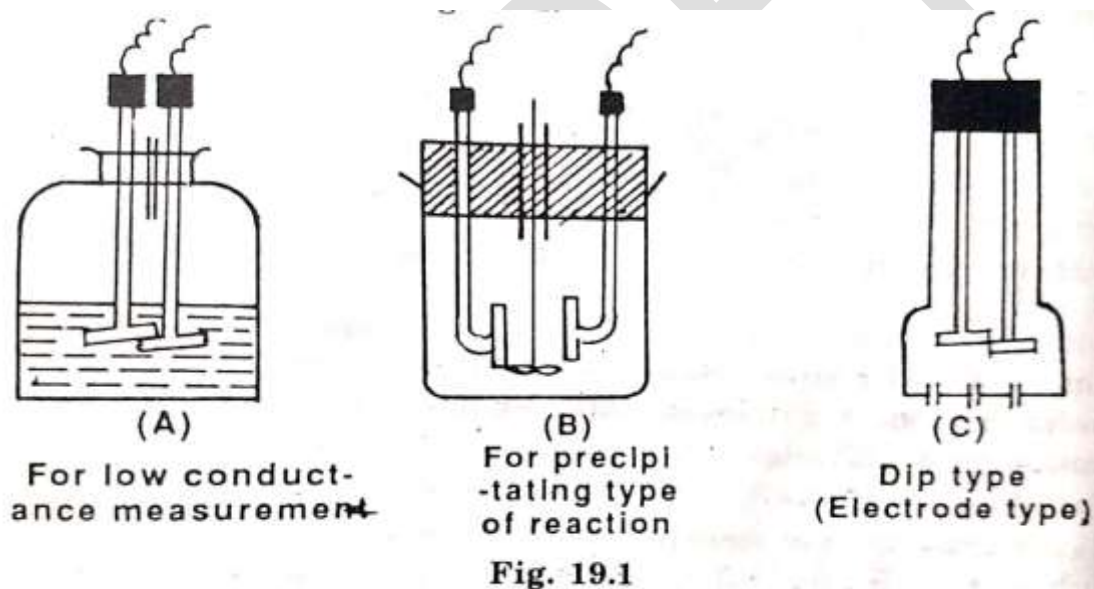
Molecular conductance (µv):

It is defined as the conductance of one gram mole of electrolyte contained between two sufficiently large electrodes at 1 cm apart.

CONDUCTANCE MEASUREMENT

INSTRUMENTATION

- For measurement of conductance of electrolytic solution, conductivity cell and conductometer are needed. After connecting conductivity cell to the instrument measurement can be made.

CONDUCTIVITY CELL:

- Conductivity cells of various types are available. For precision measurements a number of factors are taken into consideration. Two pole of conductivity cells are shown in the Figure 1, 2 & 3.

- Conductance cells are usually made of highly resistant glass, such as pyrex or of quartz and are fitted with platinum electrodes.

- The electrodes usually consist of platinum plates coated with platinum black in order to reduce the polarization effects and are sealed into glass tubes which pass through an ebonite cover so that the distance between the electrode is not altered during experiment.

- The electrodes of conductivity cell may be connected to circuit by means of mercury placed in the tubes. Three types of two pole conductivity cell arrangements are shown in given figures.

(A) For low conduct-ance measurement

(B) For precipi-tating type of reaction

(C) Dip type (Electrode type)

Fig. 19.1

- In the **A type** a wide mouth bottle with bark cork having holes for passing two platinum wires of 1 sq cm size is used.

- In **B type** the electrodes are firmly fixed in the perspex lid which is provided with opening for the stirrer and the tip of the burette. The stirrer may be replaced by magnetic stirrer. This type of cell is more suitable for precipitate giving reactions since the face of electrode plates are vertical and parallel.

- The **C or Dip type**: In a wide bore corning glass tube is fixed copper wires, the tip of which have two platinum plates of 1 sq. cm in size fixed at 1 cm apart. The terminals of copper wire are taken out for connections. The position of wire is fixed in glass tube by rosin. The two inside faces of platinum electrode of cell are plated with platinum black. This reduces polarization effect and allows absorption of ion on its surface.
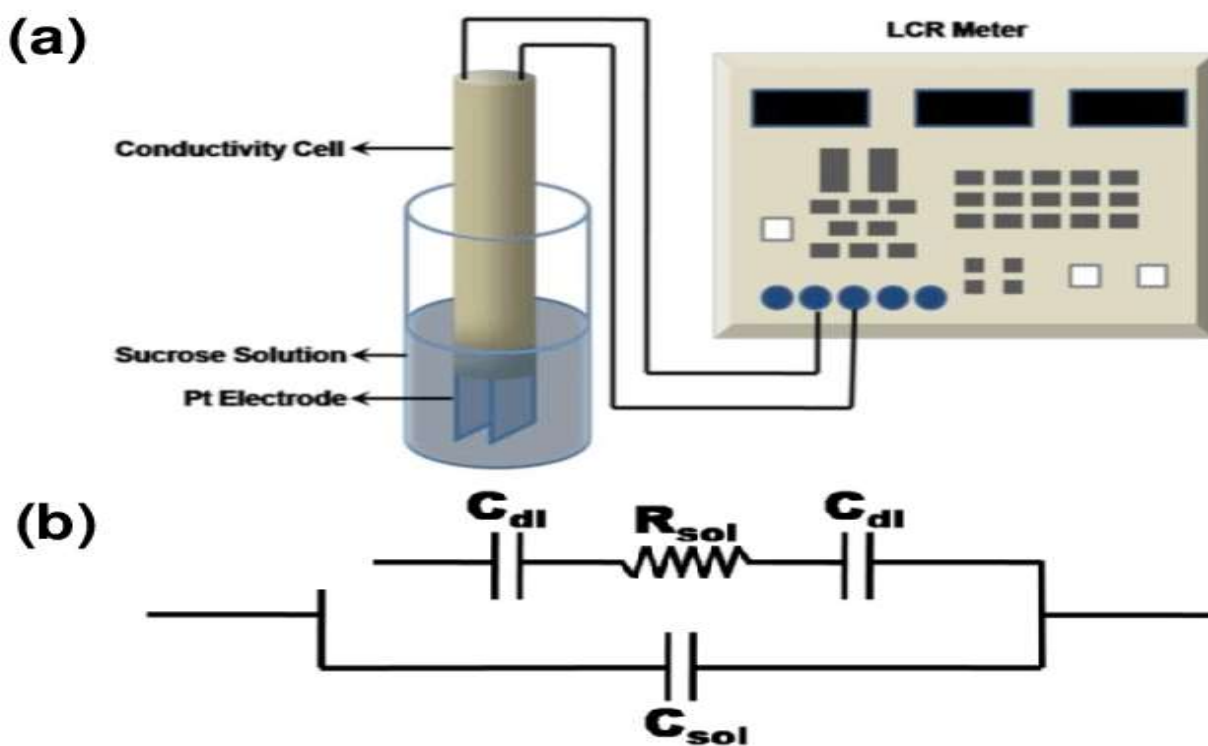
- The electrodes are generally made up of two parallel sheets of platinum foil which do not bend readily.

- The relative positions of these electrodes are fixed by sealing the connected tubes into the side of conductivity cell.

- When smooth platinum electrodes are used polarization of electrodes may occur, though alternating current is employed. This can be removed by coating the electrodes with finely divided platinum black.

- The platinisation is carried out by dipping the electrodes in a solution containing 2 to 3% of chloroplatinic acid and 0.02 to 0.03 gm of lead acetate in the cell.

- The current is passed through this solution for 15-20 min. Here electrolysis of chloroplatinic acid takes place and the electrodes get blackened because of the coating of finely divided platinum.

- These electrodes are then washed repeatedly with distilled water and finally conductivity water. When the cell is not in use it should be kept dipped in conductivity water.

CONDUCTIVITY WATER:

- Conductivity of solution of any electrolyte is very sensitive to presence of impurities. It is therefore necessary that water used in a measurements of conductance should be of high degree of purity.

- For purpose ordinary distilled water is not suitable due to dissolved CO_2 and traces of laboratory gases.

- Thus absolutely pure water, known as conductance water is used. It can be prepared by distilling ordinary distilled water containing an acidified solution of $KMnO_4$, through an alkaline solution of $KMNO_4$, and condensing the vapours by a tin condenser in a flask of glass provided with a soda lime guard tube.

CONDUCTIVITY METER
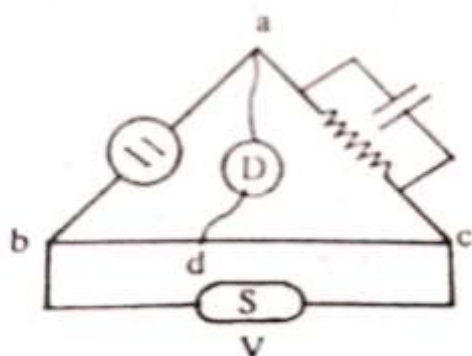
The conductance measurements are made by using conductivity bridge. The conductivity meters are made by using wheatstone bridge circuit. In this cell placed in one arm of the wheatstone bridge circuit **ab** and resistance R constitutes the arm **ac** The arms **bd** and **dc** are in the form of calibrated slide wire resistor. The balance point of **d** is a sliding contact which shows no signal to detector D.

- This detector is either a galvanometer, earphone, oscilloscope, magic-eye or now-a-days calibrated digital display.

- A source of alternating current (V) with a frequency of 50 - 60 Hz or a mains operated oscillator giving a current with frequency up to 3000 Hz is used in the circuit by connecting b and c.

- Conductivity meters have a range switch (selector range) to select appropriate standard resistances (or standard conductances), a calibrate switch (calibrate) with which the instrument is calibrated to a desired value of conductance. A number of conductivity meters are commercially available.

- To measure the conductance of electrolyte solution, conductivity cell is dipped into it and terminals connected to test terminals of Conductivity Bridge. The selector switch is set to the appropriate conductance range and reading is recorded from the galvanometer read out meter.

CONDUCTOMETRIC TITRATIONS

One of the most important application of conductometry is the conductometric titrations. Various types of acid-base titrations, replacement titrations, precipitation and complex formation reaction involving titrations are possible.

PRINCIPLE

- It is known that at infinite dilutions or in very dilute solutions, ions act independent of each other and they contribute to the conductance of the solution.

- Both cations and anions have varying degree of ionic mobilities (or conductance values). Thus, when a solution of one electrolyte is added (as a titrant) to the solution of another electrolyte the overall conductance after addition) will depend whether a reaction occurs or not.

- If no chemical reaction occurs between the electrolyte solution and another added to it, the overall conductance of the solution will increase.

- All ions will contribute to the conductance of the solution for example addition of sodium nitrate solution to the sodium chloride solution.

- However, when a chemical reaction occurs, replacement or substitution of ions take place and depending upon the ionic conductance of replacing and replaced ions conductance will either increase or decrease.

- E.g. when a solution of sodium hydroxide is added to the hydrochloric acid solution replacement of H^+ ion of high mobility with that of Na^+ with low mobility takes place and conductance is found to decrease.

- The principle of conductometric titration is based upon the substitution of ions of one mobility (conductance) by the ions of another mobility. Thus

$$A^+ B^- + C^+ D^- = A^+ D^- + C^+ B^-$$
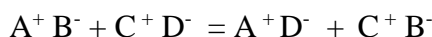
- The conductance will increase or decrease depending upon whether the mobility of C+ ion is greater or lesser than that of ion A.

- In conductometric titrations, titrant is added in small volume and conductivity measured. The points thus obtained after the addition of each increment of titrant is plotted to give a graph which consists of two straight lines intersecting at the equivalence point.

- Naturally, accuracy of the methods is greater when the angle of intersecting line is more acute.

TYPES OF CONCTOMETRIC TITRATION

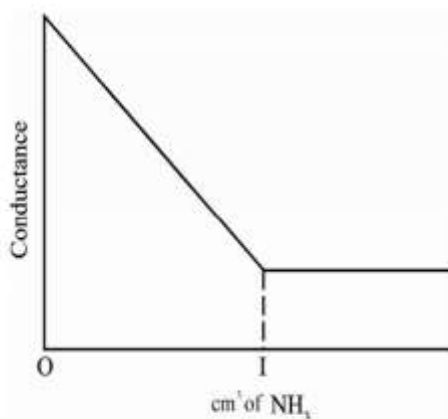## 1. Strong acid with Strong Base

In the titration of hydrochloric acid with sodium hydroxide, initial fall in conductance is due to replacement of hydrogen ions of high ionic mobility (350) with slow mobility sodium (50) ions. After the endpoint conductance rises due to excess of hydroxyl ions (199) being added. The shape of graph as shown in figure is obtained.
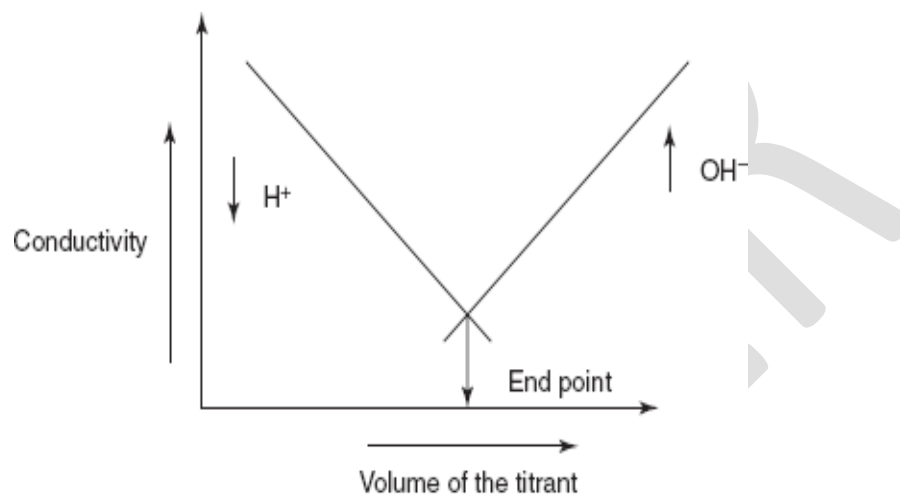
2. Strong acid with Weak Base

The titration of strong acid like hydrochloric or sulphuric with dilute ammonia solution gives the graph as shown in figure. Conductance.

The progressive fall in conductance is due to the disappearance of hydrogen ions of high ionic mobility during neutralization. After the end the graph becomes almost horizontal because ionization of ammonia is prevented in the presence of ammonium chloride or ammonium sulphate formed during neutralization reaction.


Conductometric titration of a strong acid (H_2SO_4) vs. a weak base (NH_4OH)

3. Weak acid with Strong Base

In the titration of weak acid like acetic acid or boric acid with strong base like NaOH, the shape of graph will depend upon the conc. and dissociation constant of the acid.

Thus in the neutralization of acetic acid initial conductance is due to ionization of small amount of acetic acid.

The progressive salt formation increases conductance which in turn repress ionization of acetic acid. These two opposing influences show fall followed by rise conductance. After the neutralization a break occurs showing rise in conductance due to hydroxyl ions a shape of graph shown in figure will be observed.

(b) weak acid vs strong base
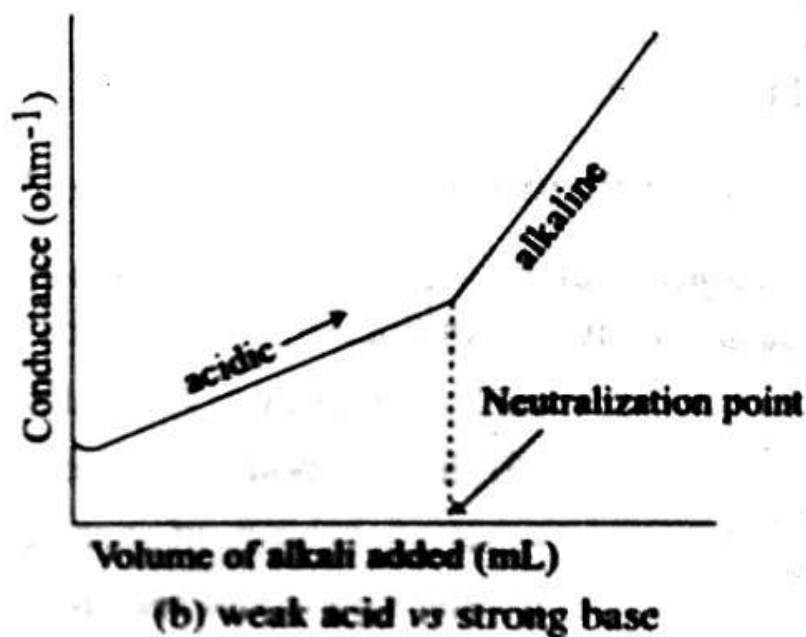
4. Weak acid with Weak Base
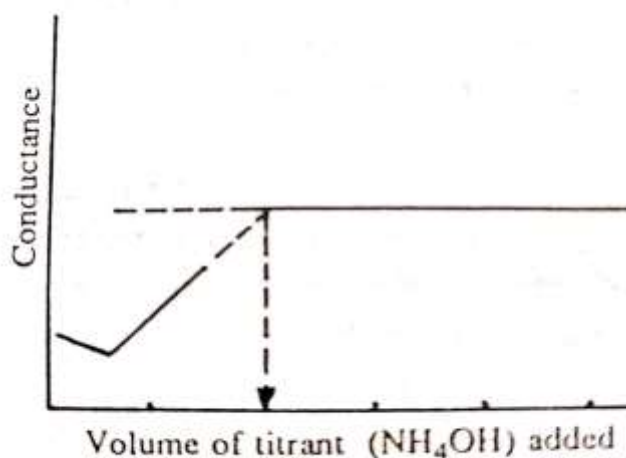
Titration of weak acid like acetic acid or phenol with weak base aqueous ammonia solution shows the graph as depicted in figure.

The neutralization curve up to endpoint of weak acid is similar to that obtained with sodium hydroxide.

Conductance rises due to the salt formation of weak acid. After the equivalence point an excess of aqueous ammonia solution has no effect upon the conductivity because of suppression of ionization of ammonia by the salt formed.

5. Very weak acid with Strong Base

Figure shows the titration curve of very weak acid like boric acid with sodium hydroxide solution. Initially conductance is very small but increases progressively as neutralization proceeds.

This is because of salt formation which accounts for rise in conductance due to hydrolysis. After the equivalence point the sharp rise in conductance is due to excess hydroxide ion added as titrant
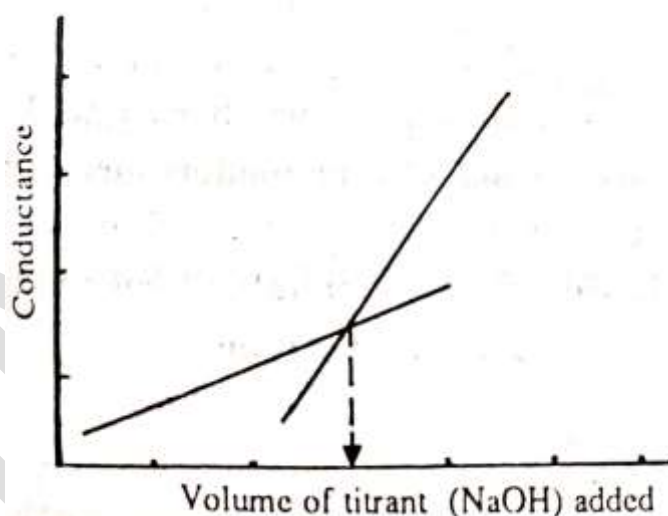

6. Mixture of HCl (strong acid) & CH₃COOH (weak acid) with Strong Base

This is shown in the figure, initially conductance falls due to neutralization of strong acid and then rises as the weak acid is converted into its salt. After the complete neutralization of both acids conductance finally rises more steeply as the excess of alkali (OH⁻) ions are introduced.

Two end points (a) and (b) for neutralization of strong acid and weak acid are observed respectively.

Titration of mixture of acids with weak base(like ammonia hydroxide) will show the graph similar up to neutralization of both Afterwards conductance remains same due to suppression of ionization of weak base.
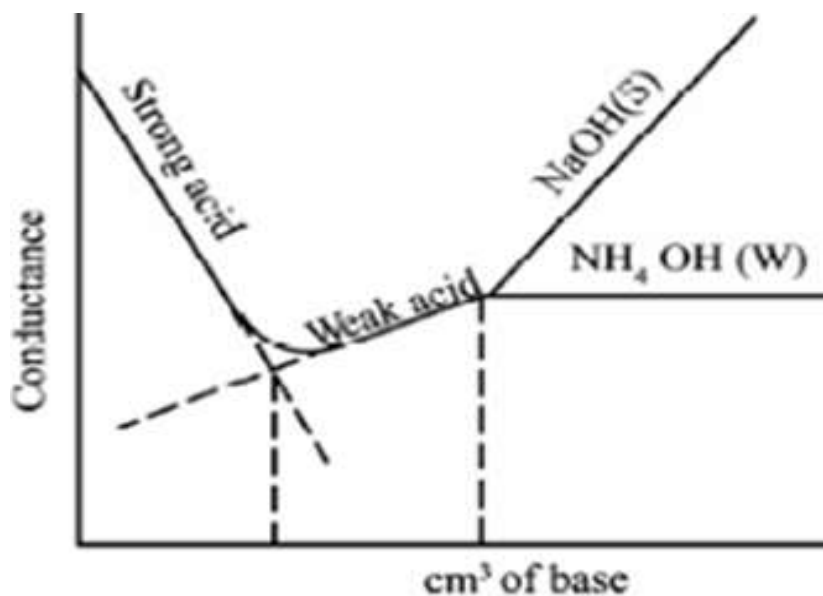
7. Displacement Titrations:

Titration of salt of weak acid (sodium acetate) with strong acid (HCl) and Titration of salt of weak base (ammonium chloride) with strong base (sodium hydroxide) can be followed by conductometer.

The shape of graph for this type of titrations are shown in figure.
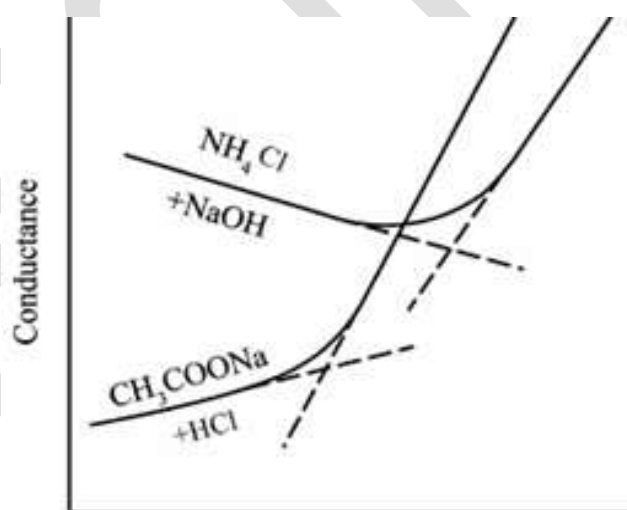
In the sodium acetate (CH_3COONa) titration with HCl, the initial increase in conductivity is due to slightly great ionic mobility of chloride ions (Cl^-) than that of the acetate ion (CH_3COO^-).

Until replacement is complete solution contains sufficient CH_3COONa to suppress the ionization of liberated CH_3COOH.

Near equivalent point the acetic acid is sufficiently ionized to give rise in conductance. Beyond equivalence point the excess of hydrochloric acid accounts for high conductance.

Similarly, in titration of ammonium chloride (NH_4Cl) with sodium hydroxide (NaOH) the initial fall in conductance is due to replacement of ammonium ion (high mobility) by the sodium ion (low mobility). After equivalence point, steep rise in conductance is due to hydroxyl ion (OH^-) of sodium hydroxide (NaOH).

8. Precipitation and complex formation titration

Conductometric titration of this type can be satisfactorily performed when:

1. The reaction product is sparingly soluble.

2. Forms stable complex, and

3. The precipitate do not have strong adsorbent properties.

4. Titration of silver nitrate with potassium chloride or sodium sulphate with barium chloride gives the shape of graph as shown in figure.
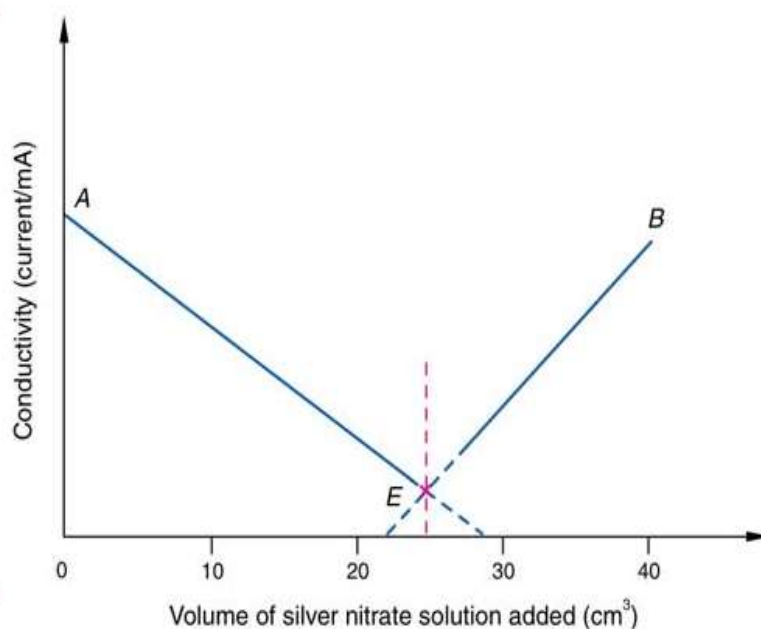
APPLICATIONS OF CONDUCTOMETER IN ANALYSIS

1. Determination of solubility of sparingly soluble material:

The specific conductance (k) of saturated solution of sparingly soluble salt is determined. The equivalent conductance of sparingly soluble salt in saturated solution is considered practically equal to the limiting value of conductance. This can be obtained by summation of limiting conductance of constituent ions.

Thus from measuring specific conductance and limiting conductance of constituent ions of sparingly soluble material, solubility a can be determined.

2. Kinetic Studies:

Kinetic studies of reaction is based upon the measurement of conductivity before, during and at the end of chemical reaction. In any reaction in which ions are produced, consumed or exchanged the course of reaction can be followed. E.g. in alkaline hydrolysis of ethyl acetate.

3. Degree of dissociation of weaker electrolytes:

The degree of dissociation of weaker electrolyte (α) can be found by use of following equation i.e.

$\alpha = \frac{\wedge V}{\wedge \infty}$, where, $\wedge V$ = Equ. Conductance at given at given dilution V

$\wedge_\infty$ = Equ. Conductance at infinite dilution

4. Basicity of organic compounds:

This can be found by using empirical formula given by following formula:

$$B = \frac{\wedge_{1024} - \wedge_{32}}{10.8}$$

Where, $\wedge_{1024} - \wedge_{32}$ = equivalent conductance of the salt at 25 °C and dilution of 1024 litres and 32 litres per gram equivalent respectively. This method is not correct in case of very weak acids whose salts are considerably hydrolysed in solution.

4. Determination of concentration:

The determination is based on determination of the conductivity of the solution of different concentrations.

A series of solutions with known content of electrolyte, is prepared, determine their conductivities and plot the calibration curve of conductivity of solution against concentration of electrolyte.

Then determine the conductivity of unknown solution and find the concentration by using calibration curve.

Direct conductometric analysis is very convenient for routine analysis of solutions containing a single, electrolyte, especially if the solutions are coloured or turbid. The industrial conductometers are widely used for automatic control of solution concentration at chemical plant.