6.2.4   Conductometric Titrations

The principle of conductometric titration is based on the fact that during the titration, one of the ions is replaced by the other and invariably these two ions differ in the ionic conductivity with the result that conductivity of the solution varies during the course of titration. The equivalence point may be located graphically by plotting the change in conductance as a function of the volume of titrant added.

In order to reduce the influence of errors in the conductometric titration to a minimum, the angle between the two branches of the titration curve should be as small as possible (see Fig. 6.2). If the angle is very obtuse, a small error in the conductance data can cause a large deviation. The following approximate rules will be found useful.

*   The smaller the conductivity of the ion which replaces the reacting ion, the more accurate will be the result. Thus it is preferable to titrate a silver salt with lithium chloride rather than with HCl. Generally, cations should be titrated with lithium salts and anions with acetates as these ions have low conductivity (Table 4.2 of Unit 4).

*   The larger the conductivity of the anion of the reagent which reacts with the cation to be determined, or vice versa, the more acute is the angle of titration curve.

*   The titration of a slightly ionized salt does not give good results, since the conductivity increases continuously from the commencement. Hence, the salt present in the cell should be virtually completely dissociated; for a similar reason; the added reagent should also be as strong electrolyte.

*   Throughout a titration the volume of the solution is always increasing, unless the conductance is corrected for this effect, non linear titration curves result. The correction can be accomplished by multiplying the observed conductance either by total volume ($V+V'$) or by the factor ($V+V'$)/V, where V is the initial volume of solution and V' is the total volume of the reagent added. The correction presupposes that the conductivity is a linear function of dilution, this is true only to a first approximation.

*   In the interest of keeping V small, the reagent for the conductometric titration is ordinarily several times more concentrated than the solution being titrated (at least 10-20 times). A micro burette may then be used for the volumetric measurement.

The main advantages to the conductometric titration are its applicability to very dilute, and coloured solutions and to system that involve relative incomplete reactions. For example, which neither a potentiometric, nor indicator method can be used for the neutralization titration of phenol ($K_a = 10^{-10}$) a conductometric endpoint can be successfully applied.

Application: Acid-base titration, especially at trace levels. Relative precision better than 1% at all levels. There are also few disadvantages with this technique. As you know the conductance is a non-specific property, concentration of other electrolyte can be troublesome.

The electrical conductance of a solution is a measure of its currents carrying capacity and therefore determined by the total ionic strength. It is a non-specific property and for this reason direct conductance measurement are of little use unless the solution contains only the electrolyte to be determined or the concentrations of other ionic species in the solution are known. Conductometric titrations, in which the species in the solution are converted to non-ionic for by neutralization, precipitation, etc. are of more value.

Some Typical Conductometric Titration Curves are:

1. **Strong Acid with a Strong Base, e.g. HCl with NaOH:** Before NaOH is added, the conductance is high due to the presence of highly mobile hydrogen ions. When the base is added, the conductance falls due to the replacement of hydrogen ions by the added cation as H^+ ions react with OH^- ions to form undissociated water. This decrease in the conductance continues till the equivalence point. At the equivalence point, the solution contains only NaCl. After the equivalence point, the conductance increases due to the large conductivity of OH^- ions (Fig. 6.2).
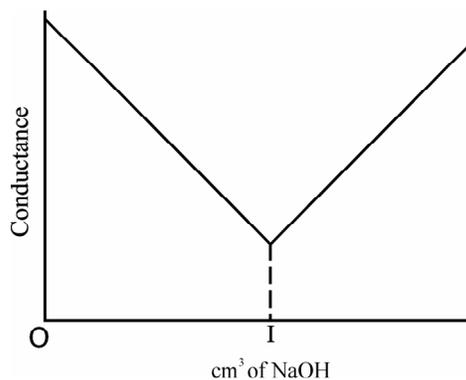

**Fig. 6.2: Conductometric titration of a strong acid (HCl) vs. a strong base
(NaOH)**

2. **Weak Acid with a Strong Base, e.g. acetic acid with NaOH:** Initially the conductance is low due to the feeble ionization of acetic acid. On the addition of base, there is decrease in conductance not only due to the replacement of H^+ by Na^+ but also suppresses the dissociation of acetic acid due to common ion acetate. But very soon, the conductance increases on adding NaOH as NaOH neutralizes the un-dissociated CH_3COOH to CH_3COONa which is the strong electrolyte. This increase in conductance continues raise up to the equivalence point. The graph near the equivalence point is curved due the hydrolysis of salt CH_3COONa. Beyond the equivalence point, conductance increases more rapidly with the addition of NaOH due to the highly conducting OH^- ions   (Fig. 6.3).
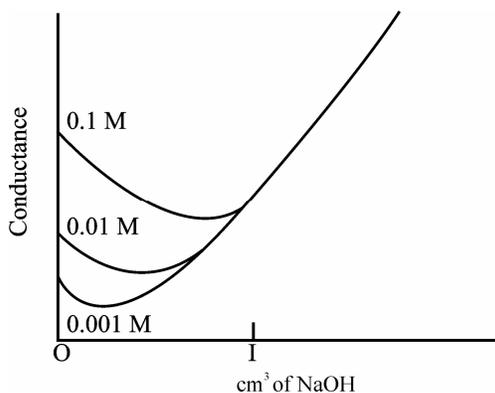

**Fig. 6.3: Conductometric titration of a weak acid (acetic acid) vs. a strong base
(NaOH)**

3. **Strong Acid with a Weak Base, e.g. sulphuric acid with dilute ammonia**: Initially the conductance is high and then it decreases due to the replacement of H^+. But after the endpoint has been reached the graph becomes almost horizontal, since the excess aqueous ammonia is not appreciably ionised in the presence of ammonium sulphate (Fig. 6.4).
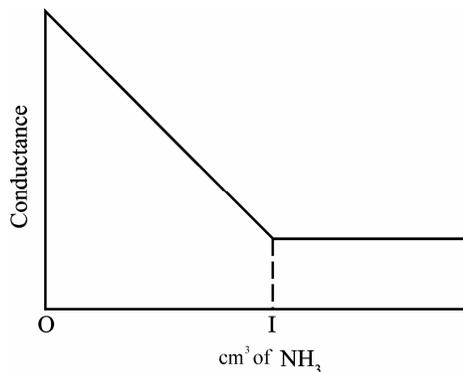
Fig. 6.4: Conductometric titration of a strong acid (H_2SO_4) vs. a weak base (NH_4OH)

4. **Weak Acid with a Weak Base**: The nature of curve before the equivalence point is similar to the curve obtained by titrating weak acid against strong base. After the equivalence point, conductance virtually remains same as the weak base which is being added is feebly ionized and, therefore, is not much conducting (Fig. 6.5).
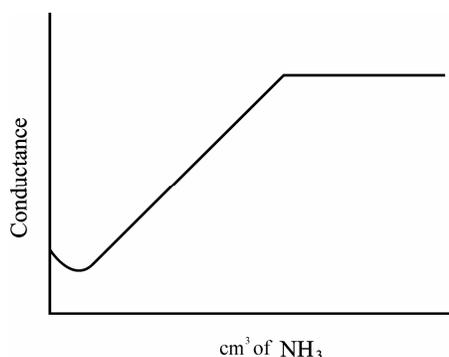

Fig. 6.5: Conductometric titration of a weak acid (acetic acid) vs. a weak base (NH_4OH)

5. **Mixture of a Strong Acid and a Weak Acid vs. a Strong Base or a Weak Base**: In this curve there are two break points. The first break point corresponds to the neutralization of strong acid. When the strong acid has been completely neutralized only then the weak acid starts neutralizing. The second break point corresponds to the neutralization of weak acid and after that the conductance increases due to the excess of OH^- ions in case of a strong base as the titrant. However, when the titrant is a weak base, it remains almost constant after the end point similar to Fig. 6.5 (Fig. 6.6).
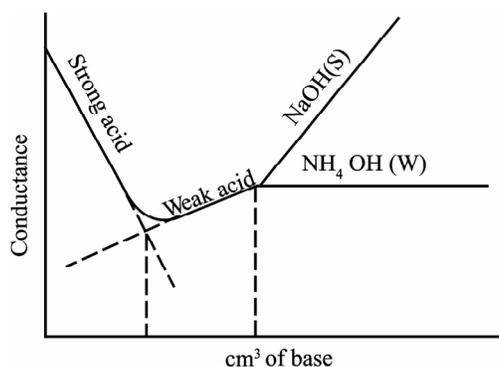

Fig. 6.6 Conductometric titration of a mixture of a strong acid (HCl) and a weak acid (CH_3COOH) vs. a strong base (NaOH) or a weak base (NH_4OH)

6. **Displacement (or Replacement) Titrations**: When a salt of a weak acid is titrated with a strong acid, the anion of the weak acid is replaced by that of the strong acid and weak acid itself is liberated in the undissociated form. Similarly, in the addition of a strong base to the salt of a weak base, the cation of the weak base is replaced by that of the stronger one and the weak base itself is generated in the undissociated form. If for example, M-HCl is added to 0.1 M solution of sodium acetate, the curve shown in Fig.6.7 is obtained, the acetate ion is replaced by the chloride ion after the endpoint. The initial increase in conductivity is due to the fact that the conductivity of the chloride ion is slightly greater than that of acetate ion. Until the replacement is nearly complete, the solution contains enough sodium acetate to suppress the ionization of the liberated acetic acid, so resulting a negligible increase in the conductivity of the solution. However, near the equivalent point, the acetic acid is sufficiently ionized to affect the conductivity and a rounded portion of the curve is obtained. Beyond the equivalence point, when excess of HCl is present (ionization of acetic acid is very much suppressed) therefore, the conductivity arises rapidly. Care must be taken that to titrate a 0.1 M-salt of a weak acid, the dissociation constant should not be more than 5×10^{-4}, for a 0.01 M -salt solution, $K_a < 5 \times 10^{-5}$ and for a 0.001 M-salt solution, $K_a < 5 \times 10^{-6}$, i.e., the ionization constant of the displace acid or base divided by the original concentration of the salt must not exceed above 5×10^{-3}. Fig. 6.6. Also includes the titration of 0.01 M- ammonium chloride solution versus 0.1 M - sodium hydroxide solution. The decrease in conductivity during the displacement is caused by the displacement of ammonium ion of grater conductivity by sodium ion of smaller conductivity.
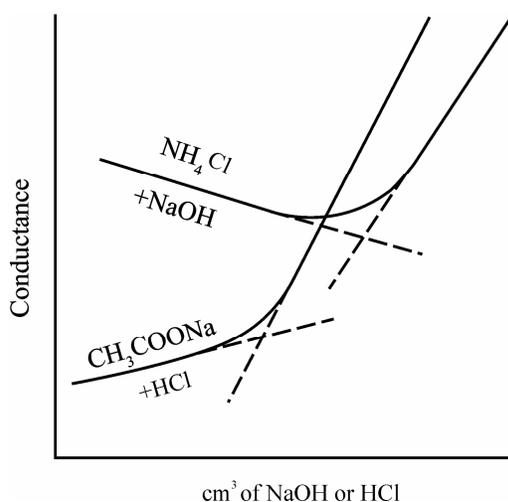

Fig. 6.7: Conductometric titration of a salt of weak acid (sodium acetate) vs. strong acid (HCl); salt of a weak base (NH₄Cl) vs. a strong base (NaOH)

7. **Precipitation Titration and Complex Formation Titration**: A reaction may be made the basis of a conductometric precipitation titration provided the reaction product is sparingly soluble or is a stable complex . The solubility of the precipitate (or the dissociation of the complex) should be less than 5%. The addition of ethanol is sometimes recommended to reduce the solubility in the precipitations. An experimental curve is given in Fig. 6.8 (ammonium sulphate in aqueous-ethanol solution with barium acetate). If the solubility of the precipitate were negligibly small, the conductance at the equivalence point should be given by *AB* and not the observed *AC*. The addition of excess of the reagent depresses the solubility of the precipitate and, if the solubility is not too large, the position of the point B can be determined by continuing the straight portion of the two arms of the curve until they intersect (Fig. 6.8).