PHARMACEUTICAL ANALYSIS – BP102T

UNIT : II ACID-BASE TITRATIONS AND NON-AQUEOUS TITRATIONS

CLASS:16

TOPIC: NON-AQUEOUS TITRATIONS

NON-AQUEOUS TITRATION:

- Titrations which are performed in non-aqueous solvent i.e solvents other than water.
- Non aqueous titrations, when reactant or products are insoluble in water, react with water or weak acidic or basic cannot be titrated in water due to poor infliction pH at end point in water.
- Most of titrations performed in aqueous media used as solvent but weak acids and weak base don't give sharp end point by using water.
- Commonly used solvents for non-aqueous titrations, acetone, glacial acetic acid, formic acid, ethylenediamine, acetic anhydride, chloroform.
- If analyte is weak acid and titrated with standard base both analyte and water competes each other to give protons to standard base.
- Weak acids are not titrated in aqueous solution as they poorly dissociates.

$$HA + B \rightarrow HB + A^-$$

$$H_2O + B \rightarrow HB + OH^-$$

- For example for titration of weak base, solvent water is replaced by non basic-solvent or acidic solvent and for titration of weak acid, solvent is replaced by non-acidic solvent or basic solvent.

CONCEPT OF NON-AQUEOUS TITRATIONS:

Based on bronsted-lowry theory, Acid a substance which donates protons and a base, a substance which accepts proton.

Bronsted lowry theory states

Acid- dissociates in solution to give proton and form conjugate base.

Base- combines with proton from dissociated acid to produce conjugate acid.

Acid donates proton only when there is a base is present to accept this proton or vice-versa.

$$HB \leftrightarrow H^+ + B^-$$

Acid Proton Conjugate base

$$B + H^+ \leftrightarrow HB^+$$

Base Proton Conjugate acid

Advantages:

- Weak acids and weak bases gives poor end point in aqueous titration but in non-aqueous titration they give good end point.
- Mixture of two or more acids can be analyzed individual acid can give separate end point in different solvents.
- These titrations are simple and accurate.
- Substances which poorly soluble in water but soluble in non-aqueous organic solvents can be determined by non-aqueous titration.
- Speed, precision, accuracy of non-aqueous titration they give good end point and close resembles acidimetry and alkalimetry.

Disadvantages:

- These solvents are expensive.
- Volatile solvents can pollute solvent / environment.
- Ex: Ammonia
- Temperature, moisture and Co2 should be controlled.
- Indicators need to prepare in non-aqueous medium.
- Some solvents are hazardous if mishandled such as ammonia

Selection of solvent:

- Based on solubility and nature of sample
  Ex: if sample is weak acid, basic solvents like DMF or Pyridine are used.
- Should not be any side reaction between sample or titrant and the solvent.
- Solvent shouldn't affect sharpness of end point during titration.
- Titrant and solute should readily miscible with solvent.
- Solvent should have high dielectric constant.
- Weak acids require basic solvents such as ethylenediamine or formamide

- Weak base is titrated in acidic solvents such as anhydrous acetic acid, glycols.

The non-aqueous solvents should be non -toxic and should be available in liquid form.

The organic non-aqueous solvents should have appropriate dielectric constant and easily undergoionization

Role of solvents:

$HCl + H_2O$ ---------- → strong acid ↑

$HCl + CH_3COOH$ ----------→ weak acid↓

$CH_3COOH + H_2O$ ---------- → weak acid↓

$CH_3COOH + NH_3$ ---------- → strong acid ↑

The solvent has an important role which influences the acidic properties of certain compounds. Water as a solvent increase acidity for HCl whereas Acetic acid decreases the acidity of HCl as asolvent. Water as a solvent decreases acidity of acetic acid while ammonia as a solvent increasesacidity of acetic acid

Types of solvents:

1.Aprotic solvents

2.Protic solvents

3.Protpohilic solvents

4.Amphiprotic/ Amphoteric solvents

Aprotic solvents:

These solvents are chemically inert having low dielectric constant and will notgo easy for ionization and doesn't donate or accept protons therefore they don't have acidic or basic in nature.

Examples: benzene, chlorobenzene, acetonitrile, carbon tetra chloride, toluene, chloroform

Protogenic solvents:

These solvents are undergo easy ionization having more dielectric constant.

These solvents which readily donate protons and are acidic in nature.

All acids are acting as protogenic solvents

Examples:Sulphuric acid, hydrogen fluoride

Protophilic solvents:

protophilic solvents are basic in nature and having tendency to attract protons from strong acids and as well as weak acids.

Examples: liq.Ammonia , pyridine, dimethyl formaldehyde, acetone and ether

Amphiprotic / amphoteric solvents:

these solvents having both characteristic features of protophilic and protogenic solvents.

These are the solvents which are able to donate as well as accept protons.

Examples: H2O, alcohol,

acetic acid $HClO_4 \leftrightarrow H^+ + ClO4^-$

$CH_3COOH \leftrightarrow H^+ + CH3COO^-$

$CH_3COOH + HClO_4 \leftrightarrow CH_3COOH_2^+ + ClO4^-$

Effects of solvents:

In aqueous titrations, two types of effects of solvents are seen:

1.Leveling effect

2.Differentiating effect

Leveling effect:

Weak acids and bases are normally used in the presence of strong protophilic i.e pyridine , liquid ammonia and strong protogenic solvents i.e hydrogen fluoride, sulphuric acid because their strengths are enhanced by these solvents.

Weak acid act like strong acid in the presence of strong protophilic solvents as well as weak base act as strong base in the presence of strong protogenic solvents.

This effect is called leveling effect and solvents are called leveling solvents.

Differentiating effect:

Non-aqueous solvent like glacial acetic acid, the dissociation of different acids varies i.e dissociation of perchloric acid is more as compared to hydrochloric acid.

In glacial acetic acid, perchloric acid acts as strong acid as compared to hydrochloric acid.

This effect of differentiating between the strength of acids is called differentiating effect and the solvents like glacial acetic acid etc and these are called differentiating solvents.