

CONDUCTOMETRY- ARTICLE REVIEW

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Abstract:

Conductometry is based on the principle of determination of change in conductivity that is the movement of cations towards the cathode and the movement of anions towards the anode. The electric conductance in accordance with Ohms law which states that the strength of current I passing through the conductor is directly proportional to potential difference and inversely to resistance. The movement of the ions mainly depends on the concentration of the ions. It is a method of quantitative analysis used to identify the concentration of a given analyte in a mixture Conductometric titration(ALPHA -06) involves the continuous addition of a reactant to a reaction mixture. The electrolytic conductivity is associated with the changing concentrations of the two most highly conducting ions-the hydrogen and hydroxyl ions. Conductometry is used to analyze ionic species and monitor a chemical reaction by studying the electrolytic conductivity of the reacting species. It is suitable for coloured solutions. It is used to check the alkalinity of the fresh water, to check water pollution in lakes and rivers ,to determine the purity of solution. The End point was determined accurately and errors were minimized as the end point was graphically determined, The temperature was maintained constant throughout the titration.

Keywords: Electrical conductivity, Ohms law, Conductometric titration, Qualitative analysis, End point

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INTRODUCTION:

Conductometric is based on the measurement of the electrical conductivity of the solutiondue tothe mobility of cations and anions towards respective electrodes. The electrical conductivity is entirely due to the movement of ions. The ability of any ion to transport charge depends on themobility of the ion. The mobility of an ion is affected by factors such as:

- □ Number of ions
- \Box Charge of ions
- \Box Size of ions
- □ Temperature

Conductometry is used to analyze ionic species and to monitor a chemical reaction by studying the electrolytic conductivity of the reacting species or the resultant products. It has notable applications in analytical chemistry. Conductivity measurement can be performed directly by using a conductivity meter or by performing conductometric titration.

Conductometric analysis of electrolytes is a long- me practice.

This is a method of analysis based on measuring electrolytic conductance. Conductance: is the ability of the medium to carry the electric current. Electric current passes through metallic conductor, e.g. wires of iron on copper in the formof electron flow. But conduction of electricity through an electrolyte solution involves migration of Positively charged cations towards the cathode and negatively charged anions

towards the anode.

i.e. current is carried by all ions present in solution.

It depends on the total number of ions present in the solution

Conductance (G) is the reciprocal of the electric resistance R: G=1/R

Conductance unit is 2-1 (also called Siemens, S). (G= conductance resistance) .

DEFINITION:

Conductometry is the measurement of the electrical conductivity, of an electrolyte solution, during the course of a chemical reaction, and the determination of the quantity, of a material present in the solution, by the measurement of its effect on the electrical conductivity of the mixture/solution.

Conductometry means measuring the conductivity of ionic solutions caused by mobility if ionstowards respective electrodes in presence of an electric field.

- Conductivity is measured by using conductometer. Units of conductivity is mhos.
- Conductometry is generally measured by using a wheat stone bridge circuit and a conductivity cell made of platinum.

R=V/i

$$C=1/R$$

V-Potential difference in volts

C- current in amperes

PRINCIPLE:

The main principle involved in this method is that the movement of the ions creates the electrical conductivity. The movement of the ions is main

$^{+}B^{-} + C^{+}D \rightarrow AD + CB$

where A+B- is the solution of strong electrolyte; C+D- is the solution of the reagent. Here the ionic concentration of A+ is determined by reacting the electrolyte solution with the reagent solution so that A+ ions are replaced by the C+ ions. This replacement of the ions with the other ions shows the conductance increase or decrease. This is done mainly by the replacement of the hydrogen ion with other cation.

DEFINITION AND RELATIONS

1.Ohms law:

According to this law, the strength of current (I) flowing through a conductor is directly proportional to the potential difference (E) applied across the conductor and inversely proportional to the resistance (R) of the conductor.

I = E/R

2.Conductance:

It implies the ease with which the current flows through conductor, thus the conductance is reciprocal to resistance.

C = I/R

3.Specific resistance: (ρ) is the resistance offered by a substance of 1cm length and 1sq.cm surface area $R = \rho l/a$

Where, ρ is the specific resistance or resistivity; 1 is the length; a is the cross-sectional area of the homogenous material.

Unit of measurement is ohm cm.

4. Specific conductivity: (kv)

is the conductivity offered by a substance of 1cm length and 1sq.cm surface area Unit of measurement is mhos cm⁻¹

5. Equivalent conductivity:

 (λv) is the conductivity of a solution containing equivalent weight of the solute between electrodes 1cm apart and 1sq cm surface area Unit of measurement is mhos cm⁻¹ **6.Molecular** conductance:

This may be defined as "the conductance of a solution containing 1gm mole of electrolyte when placed between two sufficiently large electrodes placed 1cm

apart" \square It is denoted by µvand is measured in mhos **RELATION**

Relation between specific conductance and equivalent conductance: \cdot Consider a rectangular metallic vessel with opposite sides exactly 1cm apart. \cdot If 1 c.c. of the solution is now placed in this vessel the area of the opposite faces of the cube covered by the solution will be 1sq.cm

If 1 c.c. of the solution is placed in the above vessel containing 1gm equivalent of the electrolyte, then the measured conductance will be equal to the equivalent conductance.

 $\lambda = k$

• Now dilute this 1 c.c. of the solution to 10 c.c. by adding 9 c.c. of pure solvent. The equivalent conductance however will be 10 times as specific conductance.

 $\lambda = k \ge 10$

· If the solution containing 1gm equivalent of the electrolyte is dissolved in V c.c. of the solution then

 $\lambda = k \ge V$

Hence equivalent conductance(λ) = specific conductance(k) x volume of solution in c.c. containing 1gm equivalent of the electrolyte(V).

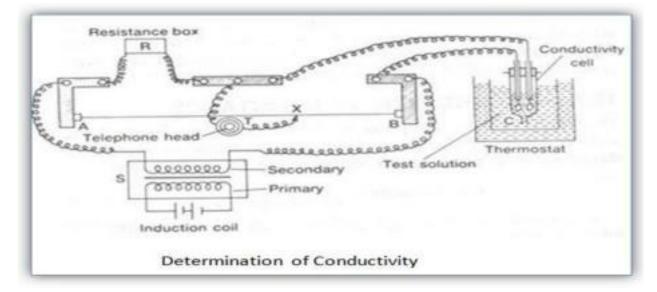
 \cdot The relation which exists between molecular conductance and specific conductance is quite similar to the relation between equivalent conductance and specific conductance. Thus,

 $\mu v = k \times V$

• Molecular conductance = specific conductance × volume of solution in c.c. containing 1gm mole of the electrolyte.

MEASUREMENT OF CONDUCTANCE

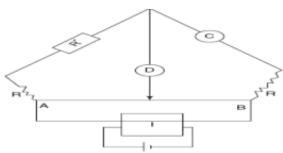
It has already been seen that the measurement of conductance is a measurement of resistance, the Wheatstone bridge method can, therefore, be used for its measurement.



The following are the different bridges used for the measurement of the conductance:

• Kohlrausch bridge: It consists of a meter bridge wire AB with a fixed resistance R on both the ends. To increase the length of the wire, it is connected to the resistance box R*, conductance cellC and the head phone D and a small induction coilI. All these are operated by the battery.

Headphone is used for the detection of the conductance difference.



• Direct reading conductance bridges: head phone replace by magic eye which is an electronic device

METHOD OF MEASUREMENT

The solution whose conductance is to be measured is taken in the conductivity cell. It is known that conductance varies with temperature. It is therefore, necessary to keep the temperature of the solution constant throughout the experiment.

This is achieved by placing the conductivity cell in the thermostat.

The cell is connected to a resistance box R on one side and to a long thin wire AB stretched along a scale on the other side.

Now some known resistance R is taken out of the resistance box.

An alternating current is passed through the solution with the help of an induction coil. the sliding contact d is moved on the wire AB so that minimum or no sound is heard in the head phone.

that knowing R, Ad and Bd, the resistance of the solution can be calculated. Since conductivity of the solution = 1

Resistance of the solution

Therefore, knowing resistance of the solution, the conductivity of the solution can be calculated.

General Procedure Involved in Conductometry

For the conductometric titration of an acid with a base, the general process is as follows:

• 10 ml of the acid must be diluted with approximately

100 ml of distilled water (so that the changes in the conductance brought on by the addition of the base become small). • A burette must now be filled with the base and the initial volume must be noted.

• In this step, a conductivity cell must be inserted into the diluted acid solution in a way that both the electrodes are completely immersed.

• Now, the conductivity cell can be connected to a digital conductometer in order to obtain an initial reading.

• The base must now be added drop wise into the acid solution. The volume of base added must be noted along with the corresponding change in the conductance.

• Asharp increase in the conductance of the solution implies that the endpoint has been reached. However, a few more readings must be taken after the endpoint of the titration. • These observed values must now be plotted graphically. The equivalence point can be obtained from the point of intersection between the two lines.

The strength of the acid can now be calculated via the formula S2 = (V1S1)/10; where S2 is the strength of the acid, V1 is the volume of base added (as per the equivalence point on the conductometric titration graph), and S1 is the strength of the base (already known). Here, the volume of the acid (V2) is equal to 10 ml.

Theory The theory behind this type of titration states that the end-point corresponding to the titration process can be determined by means of conductivity measurement.

The theory behind this type of titration states that the end-point corresponding to the titration process can be determined by means of conductivity measurement.

For a neutralization reaction

between an acid and a base, the addition of the base would lower the conductivity of the solution initially. This is because the H+ ions would be replaced by the cationic part of the base. After the equivalence point is reached, the concentration of the ionic entities will increase. This, in turn, increases the conductance of the solution. Therefore, two straight lines with opposite slopes will be obtained when the conductance values are plotted graphically. The point where these two lines intersect is the equivalence point.

Types of Conductometric Titrations

The following are the types of different

IAJPS 2024, 11 (02), 398-406

E.Nagadeepthi et al

Conductometric Titrations.

- 1. Acid- base or neutralization titrations
- 2. Replacement or displacement titrations
- 3. Red ox tit-rations
- 4. Precipitation titrations
- 5. Complexometric titrations
- 6. Non-aqueoustitrations

1.Acid-Base or Neutralization Titrations

When the base is added to HCL solution, the conductance fails due to the formation of an undissociated h1O molecule.

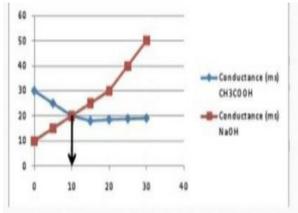
After the equivalence point, the conductance increases due to large conductivity of OH- ions. 1.

Weak Acid + Strong Base

Eg: Ch₂COOH vs 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 Ch₂COOH to Ch₂COONa which is the strong electrolyte.

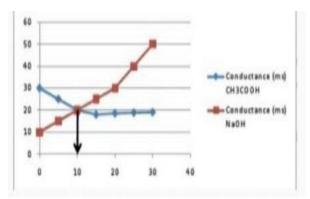
This increase in conductance continues to rise up to the equivalence point. The graph near the equivalence point is curved due the hydrolysis of salt Ch_2COONa . Beyond the equivalence point, conductance increases more rapidly with the addition of NaOH due to the highly conducting OH – ions.



2. Strong Acid + Weak Base

Before the end point, the fall in conductance is due to H+ is replaced by $NH_{4}+$ and conductance becomes constant due to common ion effects (NH_4Cl decreases ionization of NH_4OH).

Eg: HCl vs NH4OH



3. Strong Acid + Strong Base Eg: NaOH vs HCl

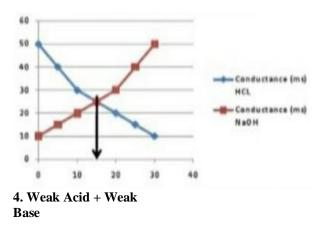
Before NaOH is added, the conductance is high due to the presence of highly mobile hydrogen ions.

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 continuestill the equivalence point. At the equivalence point, thesolution contains only NaCl.

After the equivalence point, the conductance increases due to the large conductivity of OH- ions Fall in conductance due to replacement of high conductivity hydrogen ions by poor conductivity sodium ions.

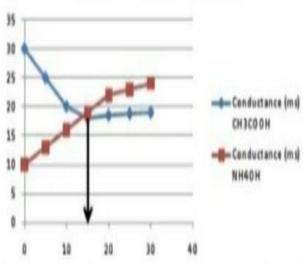
Rise of conductance is due to increase of hydroxyl ions.



The nature of the 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 the same as the weak base which is being added is feebly ionized and, therefore, is not much conducting. **Eg:** CH_3COOH vs NH_4OH

E.Nagadeepthi et al

Increase in conductance due to excess of CH₃COOH. Constant conductance due to suppression of NH₄OH by CH₃COOH



2. Replacement or Displacement Titrations

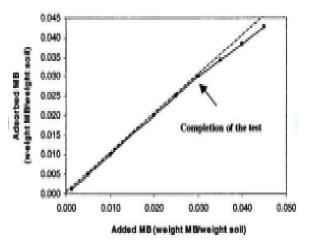
When a salt of a weak acid is titrated with a strong acid, the anion of the weak acid is replaced bythat of the strong acid and weak acid itself is liberated in the undissociated form.

Salts of strong acid and weak base vs strong base.

E.g.: NH₄Cl vs NaOH

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. Salts of strong base and weak acid vs strong acid

e.g.: CH₃COONa vs HCl



3. Redox Titrations conductometric titration is used for the titration

involving redox reaction. In redox titration, besides

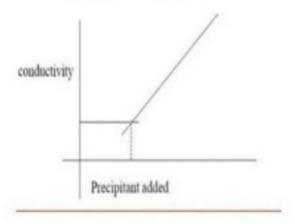
active reactant there is a presence of large excess of electrolytes e.g. acids and the change in conductance during titration is often low, and the location of the end point becomes difficult.

In this titration, there will be reduction in the number of hydrogen ions. The conductivity will reduce as the number of H+ ions are decreased.

4.Precipitation Titrations

e.g.: KCl vs AgNO3

When silver nitrate is added, the first part there is no increase in conductivity as there is only replacement of Cl- ions with NO₃- ions. After the end point, conductivity increases because of increase in the concentration of silver as well as nitrate ions.



5.Complexometric Titrations

e.g.: KCl vs Hg (ClO4)2

Complexometric titrations are particularly applicable to determine the metal ions in the sample solution. An interesting complex formation reaction is the determination of mercury by cyanide ion. Mercury(II) nitrate a solution as nitrate exists almost as a free ion. It may be titrated with potassium cyanide solution.

Before the equivalence point, one Hg (II) is replaced by 2 K+ ion conductance that varies only slightly. After end point there is an addition of K+ and CN

ions and conductivity increase sharply and the end point is readily determined from the

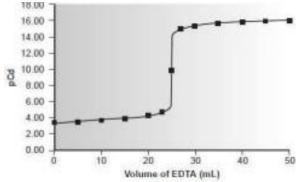
6. Non-Aqueous Titrations

Non-aqueous titrations can also be measured using conductometry.

Ex: a) Titration of weak bases vs. perchloric acid in

dioxane-formic acid.

b) Titration of weak organic acids in methanol vs. tetramethylammonium hydroxide in methanol benzene.



Instrumentation of Conductometer

The instrument used for the measurement of conductance is known as conductometer. It consists of,

- Current source
- Conductivity cells
- Electrodes.
- 1. Current Source
- Mechanical high frequency AC generator by Washburn.
- ◆Vreeland oscillator by Taylor and Acree
- ♦ Vacuum tube oscillator by Hall and Adams.
- ◆ When electrical potential is applied across electrode two process occurs:
- 1. Electrons accumulate near the electrodes.
- 2. Transfer of charge through the interference.
- Electrodes become polarized leading to high cell resistance.

2 Conductivity Cells

- Made of Pyrex or quartz and are fitted with two platinum electrodes
- Should be placed in vessel containing water to maintain constant temperature *Types:*
- 1.Wide mouthed cell
- 2.Cell for reactions producing precipitation
- 3. Dip type cells

1. Wide Mouthed Cell

Wide mouthed fitted with an ebonite cover which has provisions for platinum electrodes and burettes.

2. Cell for Reactions Producing Precipitation

- ➤ Mainly used for ppt reactions.
- Also, wide mouthed fitted with ebonite cover which has provisions for burette, electrolyte.
- ➤ Stirrers may be Mechanical or magnetic.

3.Dip Type Cells

Nothing much to consider, will be updated shortly. **Electrodes**

The surface is coated with platinum black to avoid polarization effects and increase effective surface area.

- Platinization of electrodes is done by coating solution of 3% chloroplatinic acid and lead acetate on it to get a uniform coating.
- Electrode usage depends on conductivity and concentration.
- If conc is low then electrodes should be largely and closely packed.

Advantages of Conductometric Titrations:

1.Determinations of specific conductivity is not required

- 2.No indicator is necessary
- 3.Suitable for colored or dilute solutions

4.Since end point is determined by graphical means accurate results are obtained with minimum error 5.Used for analysis of turbid suspensions, weak acids, mix of weak and strong acids 6.Temperature need not be known provided it is maintained constant throughout the titration. 7.Colored or dilute solutions or turbid suspensions can be used for titrations.

8. Temperature is maintained constant throughout the titration.

9.End point can be determined accurately and errors are minimized as the end point is being determined graphically.

10.Does not require indicators since change in conductance is measured by conductometer.

- 11.Suitable for colored
- solutions.

12.Since end point is determined by graphically means accurate results are obtained with minimum error.

13.Used for analysis of turbid suspensions, weak acids, weak bases, mix of weak and strong acids. 14.Temperature is maintained constant throughout the titration.

15. This method cab be used with much diluted solutions.

16.Be seen by eye.

17.Determination of specific conductivity is not required.18.Suitable for colored or dilute solutions, 18.Used for analysis of turbid suspensions, weak acids, weik bases, mix of weak & strong acids. 20.Temperature need not be known provided it is maintained constant throughout the titration.

Disadvantages of Conductometric Titrations:

1.Only a few specific redox titrations can be done with the help of this process. This is because the conductivity of the solution is masked by relatively high hydronium ion concentration.

2. The accuracy of conductometric titration is low when the concentrations of the electrolyte are high, making the titration process unsatisfactory.

3.Conductometric titration technique, only a few specific redox titrations can be carried out. 4.It

shows less accurate results when the total electrolytic concentration is high in the solution.

5.Increased level of salts in solution masks the conductivity changes, in such cases it does notgive accurate results.

6.Application of conductometric titrations to redox systems is limited because, high concentrations of hydronium ions in the solution tends to mask the changes in conductance

7.By conductometric titration technique, only a few specific redox titrations can be carried out.

8.It shows less accurate results when the total electrolytic concentration is high in solution. Itmakes it less satisfactory.

9.In certain cases, the accuracy of conductometric titration is low when the concentrations of the electrolyte are high, making the titration process unsatisfactory.

10.Interference of high conc. of other electrolytes

APPLICATIONS

Degree of dissociation of weaker electrolytes:

The degree of dissociation of weak electrolyte is given by

 $\alpha = \lambda v / \lambda \infty$

Where

 λv = equivalent conductance at a given dilution

V $\lambda \infty$ = equivalent conductance at an infinite dilution λv can be found experimentally.

Hence the degree of ionization of weak electrolyte can be calculated.

- Determination of soap in oil
- Determination of accelerators in rubber
- Determination of total soap in latex
- Specific conductance of water
- Check water solubility in rivers and lakes
- Alkalinity of fresh water
- ✤ Salinity of sea water

Deuterium ion concentration in water- deuterium mixture

- Food microbiology for tracing micro-organisms
- Tracing antibiotics
- Estimation ash content in sugar juices

Purity of distilled and deionized water can determine

Solubility of sparingly soluble salts like AgCl, can be detected

- ✤ estimation of vanillin in vanilla flavor
- Determination of atmospheric SO2
- Basicity of organic acids
- ✤ Ionic product of water
- Degree of hydrolysis

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