EXPERIMENT NO. : 1

Aim: To determine the strength of HCl solution by conductometric titration with NaOH solution

Theory:

Conductometry is a measurement of electrolytic conductivity to monitor a progress of chemical reaction. Conductometry has notable application in analytical chemistry, where conductometric titration is a standard technique.

Electrolytic conductivity is a measure of the ability of a solution to carry electric current. Electric solutions conduct electric current by the migration of ions under the influence of electric field. According to Ohm's Law, the current strength (I) flowing through a conductor is directly proportional to the potential difference (E) and inversely proportional to the resistance (R) of the conductor.

i.e. I = E/R or, R = E/I

Where the resistance (R) is the hindrance provided by the solution. The resistance of any conductor varies directly with the length and inversely with its area of cross-section.

$$R = \rho \times (l/a)$$

Where, ρ is the specific resistance and it is the resistance of a unit length of conductor of unit cross-section. (l/a)is called cell constant.

The reciprocal of specific resistance is called specific conductance or conductivity.

Specific conductance (κ) = $1/\rho = (l/a)$ x (1/R) with unit ohm^{-1} cm^{-1}

Conductance of electrolyte depends upon i) number of free ions, ii) charges on the free ions and iii) mobility of the ions on the substitution of one ion by another of different mobility (speed of ions). So, conductometric method can be used to determine the end point of ionic titrations like i) acidimetric titration, ii) precipitation titration, iii) titration involving the formation of complex ion.

Hence there is a net change in conductance of a solution during titration. When a strong acid (e.g. HCl) is titrated against a strong base (e.g. NaOH), the neutralization reaction is the replacement of H^+ ions by an equal number of Na^+ ions, according to the equation:

$$(H^+ + Cl^-) + (Na^+ + OH^-) = Na^+ + Cl^- + H_2O$$

Initially the conductance of a solution of HCl remains very high due to the presence of highly mobile H^+ ions. But with addition of NaOH, the conductance gradually decreases along a straight line. Since H^+ ions combine with OH^- ions to form undissociated water, the faster moving H^+ ions are replaced by relatively slower moving Na^+ ions in aqueous solution. In this way, when all the H^+ ions have been removed, the conductance will reach its lowest limit. Further addition of NaOH will cause the solution to have an excess of the fast moving OH^- ions with the result that its conductance increases linearly with the addition of excess NaOH.

Therefore the nature of the plot (conductance of the solution versus volume of base added) will be as given below:

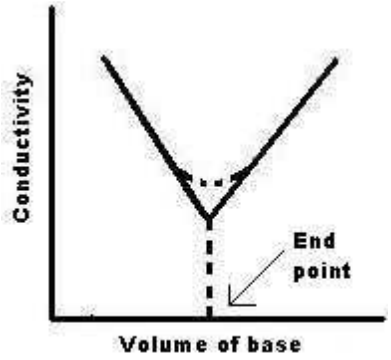


Fig.1 Conductometric titration of a strong acid (HCl) vs. a strong base (NaOH)

Materials:

Apparatus: Conductometer, conductivity cell, beaker, pipette, burette, conical flask.

Chemicals: Hydrochloric acid (HCl), sodium hydroxide (NaOH), conductivity water.

Procedure:

1. HCl solution of unknown strength {approx. (1/200) N} is provided.

2. Standardized 0.1 (N) NaOH solution is provided.

Strength of NaOH should be at-least 10 times higher than that of HCl, to avoid any volume effect on conductometric measurement.

3. Calibration of the instrument done at room temperature.
4. Conductometric Titration:

i) Rinse the conductivity cell a number of times with conductivity water or double distilled water.

ii) Pipette out 150 mL of approx. (N/200)HCl in a beaker and dip the conductivity cell in it, so that the cell should dip completely in solution.

iv) Rinse the burette with NaOH solution and fill with it.

v) Add small amount of NaOH solution (0.5 ml) from burette, stir it, give time to settle down and measure the conductance after each addition.

vi) Go on adding NaOH (at an interval of 0.5 ml) and measure conductivity value. Initially, conductivity will decrease, then it will show a rise. This indicates the attainment of end point.

v) Take at least five readings beyond the end point.

Observation:

1. Temperature of the experiment:
2. Table 2: Conductometric titration:

Observation	Volume of HCl taken (V_1) (ml)	Total volume of drops of NaOH solution added (ml)	Conductance (mS) S is Ohm^{-1}
1	150	0	4.32
2		0.5	4.13
3		1	4
4		1.5	3.88
5		2	3.75
6		2.5	3.6
7		3	3.48
8		3.5	3.35
9		4	3.2
10		4.5	3.12

11		5	3
12		5.5	2.87
13		6	2.7
14		6.5	2.6
15		7	2.45
16		7.5	2.3
17		8	2.4
18		8.5	2.55
19		9	2.7
20		9.5	2.83
21		10	3
22		10.5	3.2
23		11	3.37
24		11.5	3.55
25		12	3.72
26		12.5	3.95
27		13	4.2

Plot a graph between conductance and volume of titrant (NaOH solution). Two intersecting lines will be obtained (as given in the Figure 1) and the points of intersection of these lines represent the equivalent point (volume of NaOH required for neutralization).

Let, V_2 be the volume of NaOH at the equivalent point (from graph) and the strength of acid is S_1 and strength of NaOH solution is $S_2 = 0.1(N)$.

Then, $V_1 \text{ X } S_1 = V_2 \text{ X } S_2$

Conclusion: The strength of the acid (S_1) is _____ (N)

Discussions:

i) Normally, the coloured solution which cannot be titrated with volumetric method using indicator can be titrated by the conductometric method.

ii) The conductometric titration method can be used in case of weak acid vs. weak base and also in case of very dilute solutions.

iii) Near the end point, no special case is necessary as it is determined graphically.

Precautions:

i) Electrical connection should be made carefully.

ii) Temperature during the experiment should be kept constant as conductance depends on temperature.

iii) Stirring should be done after each addition of titrant.

iv)To avoid the dilution effect, the concentration of the titrant should be10 times more than that of the solution to be titrated.

Questions:

1. Unit of resistance (in terms of basic units)
2. What do you mean by specific conductance, equivalent conductance, molar conductance? Their units and interrelations. On which parameters do these depend?
3. What is cell constant of a conductometric cell?
4. What are the advantages, disadvantages and applications of conductometric titrations.
5. What do you mean by primary standard and secondary standard in titration?
6. Is aqueous NaOH a primary standard? If not how it can be standardized by conductometric titration method?
7. What do you mean by molarity, molality, normality? Their interrelation.
8. How one can prepare 0.1 (N) solution of Oxalic acid, KMnO4 and K2Cr2O7 for redox titration?

EXPERIMENT NO.: 2

Verification of Beer-Lambert Law and determination of amount of iron present in a supplied solution spectrophotometrically

Theory:

When light of particular wavelength passes through a transparent medium, intensity of the transmitted light of the same wavelength generally decreases, as the medium absorbs some amount of light.

Absorbance (*A*) is defined as

$$A = \log_{10} \frac{I_0}{I}$$

where, I_0 is the intensity of the incident light and I is that of the transmitted light of same wavelength.

Absorbance is proportional to the concentration of the light absorbing medium (sample) (*c*), as well as path length (*l*), which is equal to the width of the cuvette (in which the sample solution is taken).

Thus we can write:

$$A = \varepsilon\, c\, l$$

where, ε is a proportionality constant, known as molar absorption coefficient, or molar absorptivity, with unit of L mol^{-1} cm^{-1}.

This equation is known as Beer-Lambert law.

Iron present in aqueous samples can be determined spectrophotometrically by complexation with a suitable complexing agent. The absorbance of the metal-ligand complex is usually measured in the visible region and is related to metal ion concentration.

Colorimetric determination of iron can be done using several known complexing agents. Among the routinely used is 1,10-phenanthroline (phen) which reacts with Fe^{2+} to form an orange-red complex in the pH range from 2-9. Therefore, the first step involves the reduction of any Fe^{3+} present to Fe^{2+} using hydroxylamine hydrochloride.

The procedure depends on the construction of a calibration curve from standard Fe^{2+}, followed by measurement of the unknown Fe^{2+} concentration from the curve.

The first step of an analytical spectrophotometric procedure for quantitative determination of analytes is to find the wavelength at which the analyte complex has maximum absorption (it

will be around **510 nm**). At this wavelength, the molar absorptivity is a maximum and precision is greater. This allows for more precise and sensitive determination. The absorption spectra of the iron-phencolored complex solutions with known ferrous ion concentrations are to be determined first. With those data, we will have to construct the calibration curve. A linear calibration curve will prove the Beer-Lambert law.

Reactions:

$n\ Fe^{+2} + m\ phen = Fe_n(phen)_m^{2+}$

$4\ Fe^{3+} + 2\ NH_2OH.HCl \rightarrow 4\ Fe^{2+} + N_2O + 4\ H^+ + H_2O$

Ferric ion Hydroxylamine Hydrochloride Ferrous Iron Nitrous Oxide

Apparatus:

1. A spectrophotometer
2. Sample cells or cuvettes

Chemicals and reagents:

1. Stock phenanthroline solution: *(M_r= 180.21)* Dissolve 2.50 g in 100 mL of ethanol and complete to 1.0 L with dist. water. Store the solution in an amber bottle.
2. 0.5 M Hydroxylamine hydrochloride:
3. Standard 0.1 mM Fe^{+2} solution: Prepared by dissolving 0.0392 g of reagent-grade $Fe(NH_4)_2(SO_4)_2$ x 6 H_2O (ferrous ammonium sulfate hexahydrate, *M_r =392.14)* in water in a 1-L volumetric flask containing 1 mL of H_2SO_4 98% (w/w).

Procedure:

1. Accurately transfer 0 (blank),1,2,3,4 and 5 mL of standard Fe^{2+} solution (solution 3) into separate 100 mL volumetric flask.
2. To each solution in step 1 add 2 mL of hydroxylamine hydrochloride solution.
3. Add 1 mL phenanthroline solution to each volumetric flask.
4. Complete to mark with distilled water and shake well.
5. Allow 10 minutes for colour development.
6. Place the blank in the absorption cells provided and make the absorbance value zero (transmittance 100%) reading at 510 nm.
8. Remove one blank cell and place one colored sample in cell and put in its proper place and take the absorbance reading at 510 nm.
9. Measure absorbance of each solution at the λ_{max} **= 510nm** and draw the calibration curve (Absorbance vs actual concentration of Fe^{2+}) to verify L- B law.

With unknown supplied sample:

11. Take the supplied solution in 100 ml volumetric flask, repeat the step 2-5. Measure the absorbance at 510 nm

12. From the calibration curve determine the concentration of Fe^{2+} .

Calculations and discussions:

TABLE:1

Flask no.	Vol. Of 10^{-4} M Mohr Salt solun taken (mL)	Actual conc of Fe^{2+} solution in 100 mL solun. (use $V_1S_1=V_2S_2$ calculation)	OD at λ_{max}
1	1		0.010
2	2		0.022
3	3		0.033
4	4		0.043
5	5		0.054

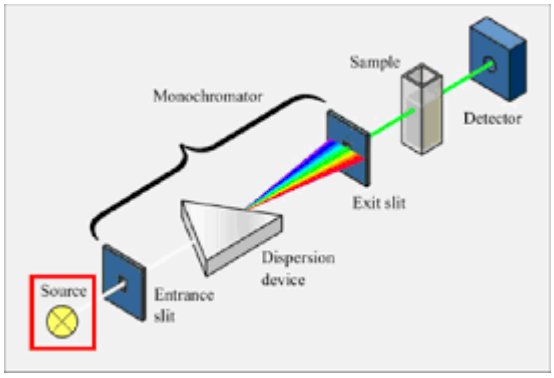
(OD values are corrected for instrumental artifacts)

Prepare a plot of absorbance versus actual concentration of the known solutions (i.e. concn of each five number of Fe^{2+} solutions prepared in step 1). Draw the best fitting straight line through the points – this is called the Beer-Lambert Law plot.

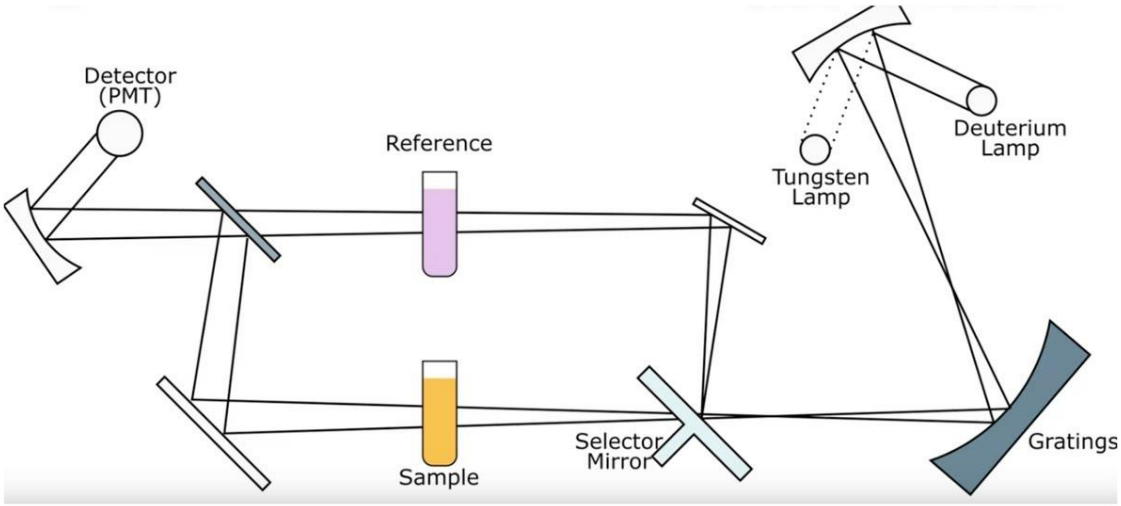
2. Place the best absorbance value of unknown solution onto this plot and determine its concentrations.

Question:

1. Structure of phenanthroline and Fe-Phan complex.
2. Origin of colour in Fe-Phan complex
3. Concept of spectral range
4. Schematic diagram of spectrophotometer.
5. Role of hydroxylamine hydrochloride
6. What is molar extinction coefficient (ε) and on which parameters does it depend?
7. Relation between transmittance and absorbance.
8. If a sample has a percent transmittance of 50%, what is its absorbance?
9. Why the linearity of B-L law breaks down at high concentration of the analyte?



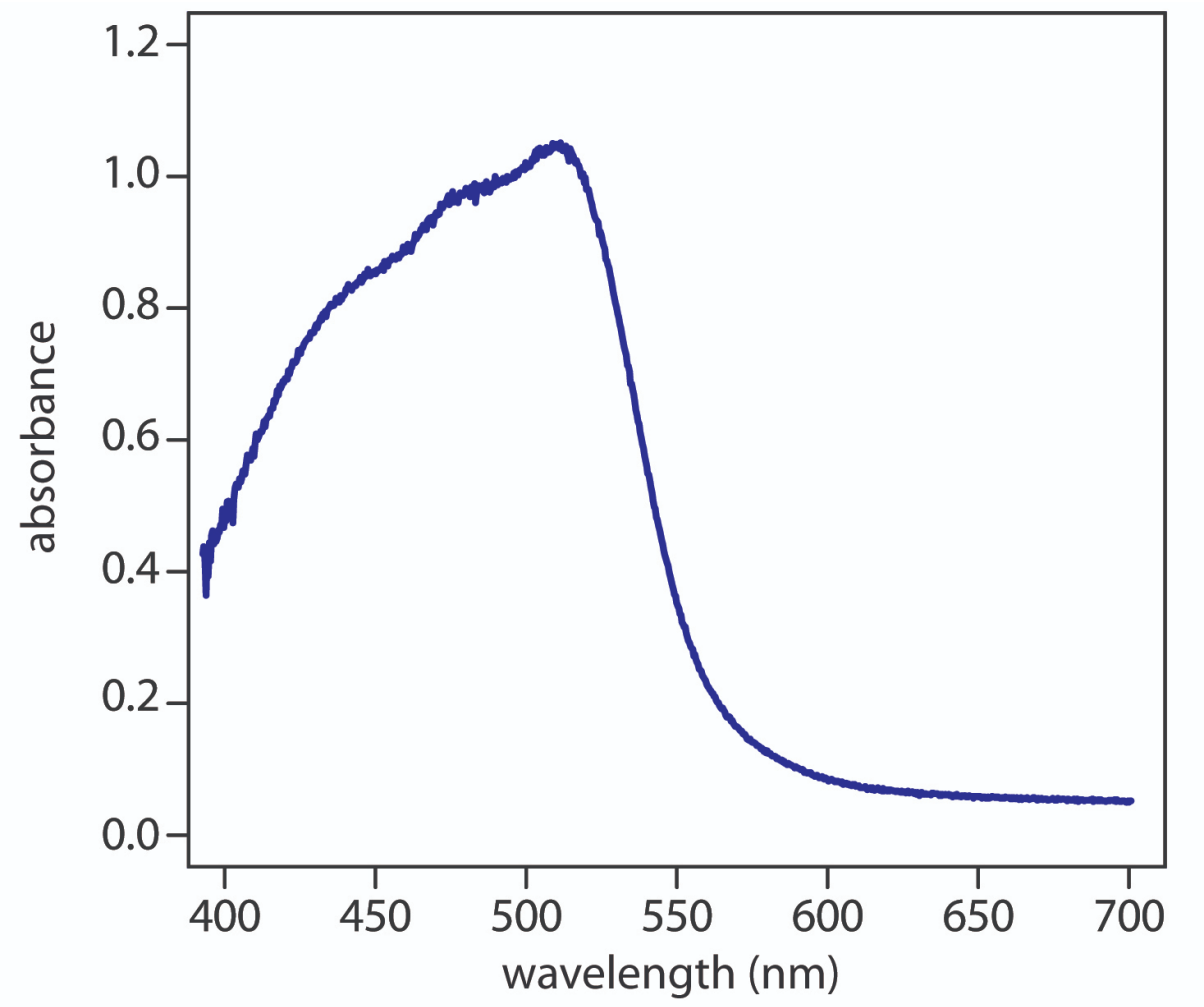
Single Beam Spectrophotometer



Double Beam spectrophotometer
Construction & Working

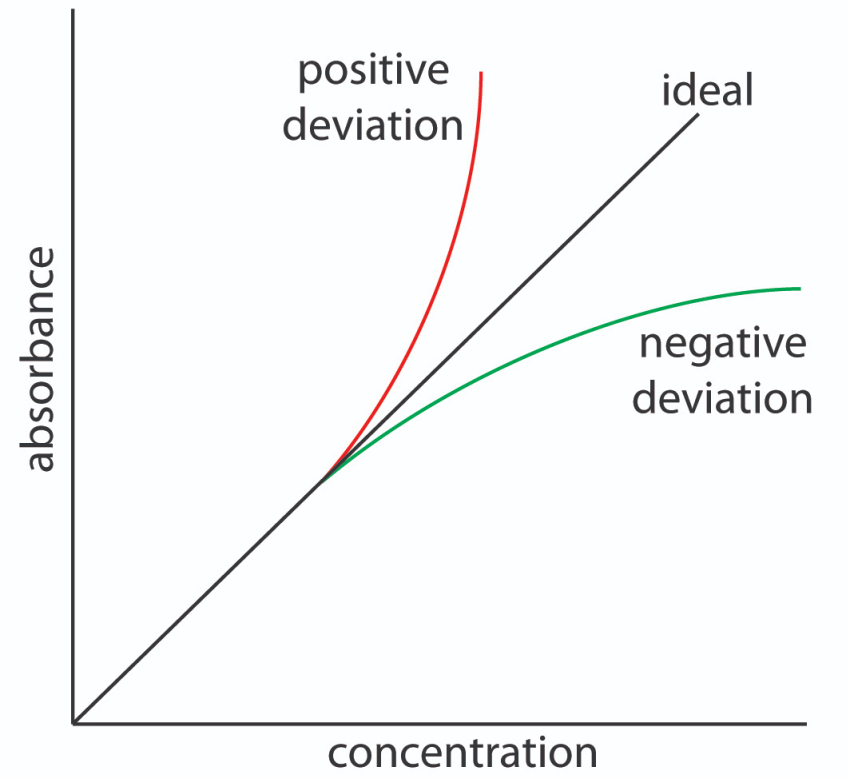
Selection mirror: Beam Splitter

PMT: Photomultiplier tube (light is converted into electrical signal)



UV/Vis spectrum for the metal–ligand complex $Fe(phen)_3^{2+}$, where phen is the ligand *o*-phenanthroline.

Limitation:



Beer's law is a limiting law that is valid only for low concentrations of analyte. There are two contributions to this fundamental limitation to Beer's law.

1. At higher concentrations the individual particles of analyte no longer behave independently of each other. The resulting interaction between particles of analyte may change the analyte's absorptivity.
2. A second contribution is that the analyte's absorptivity depends on the sample's refractive index. Because the refractive index varies with the analyte's concentration, the values of a and ε may change. For sufficiently low concentrations of analyte, the refractive index is essentially constant and the calibration curve is linear.