Experiment

Verification of the Beer-Lambert's law and determination of ferric ion (Fe^{3+}) concentration of solution by colorimetry

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Date: …… **Temperature: 30 °C**

Objective

Verification of the Beer-Lambert's law and determination of ferric ion (Fe^{3+}) concentration of solution by colorimetry.

Requirements:

(a) Apparatus and Glassware: Colorimeter with cuvettes, Beakers, Volumetric Flask, Pipette.

(b) Chemicals:

- 100 ppm Fe^{3+} solution
- 4 M HNO_3
- 20 % KSCN

1. Principle

***Beer-Lambert's law*:** When a beam of monochromatic radiation of a suitable frequency passes through a transparent homogeneous medium (for quantitative analysis mainly concerned with solutions), it is absorbed by the medium. As a result, the intensity of the light when it finally emerges from the medium is considerably reduced. The decrease of the intensity of a beam of monochromatic radiation depends on the path-length (thickness), *l*, and the concentration, *c*, of the absorbing medium. This is *Beer-Lambert's law* and the absorbance (formally called as optical density), *A*, of the solution is expressed by the following equation:

$$A = \log\left(\frac{I_0}{I_t}\right) = \varepsilon c l \qquad \text{or} \qquad \varepsilon = \frac{A}{cl}$$

where, I_0, is the intensity of the incident beam and, I_t, is the intensity of the transmitted beam. The quantity ε is called the molar absorption coefficient (molar extinction coefficient or molar absorptivity). The ε depends on the frequency of the incident radiation and is greatest where the absorption is most intense. Its dimensions are 1/(concentration × length), and it is normally convenient to express it in liters per mole per centimeter (L mol^{-1} cm^{-1}). Alternative unit is square centimeter per mole (cm^2 mol^{-1}).

According to the above equation, the absorbance of the solution in a container (a cell) of a fixed path-length is directly proportional to the concentration. Thus a graph between absorbance versus concentration should be linear and passing through origin. The solution

giving such a behavior is said to obey *Beer-Lambert's law*. Dilute solutions obey the law over a sufficient concentration range, but the upper limit varies from system to system. At higher concentration, deviations are observed which are owing to the changes taking place in the Deviations are usually found when the colored solute ionizes, dissociates, or associates in the solution and may also occur when monochromatic light is not used.

***Determination of* Fe^{3+} *Concentration*:** Fe^{3+} reacts with thiocyanate (–SCN) to give a series of intensely red-colored compounds, which remain in true solution; Fe^{2+} does not react. Depending upon the –SCN concentration, a series of complexes can be obtained; these complexes are red and can be formulated as $[Fe(SCN)_n]^{3-n}$, where n = 1,……,6. At low –SCN concentration the predominant colored species is $[Fe(SCN)]^{2+}$ {$Fe^{3+} + SCN^- \rightarrow [Fe(SCN)]^{2+}$ }, at 0.1*M* –SCN concentration it is largely $[Fe(SCN)_2]^+$, and at very high –SCN concentration, it is $[Fe(SCN)_6]^{3-}$. In the colorimetric determination a large excess of –SCN should be used, since this increases the intensity and also the stability of the color. Strong acids (HCl or HNO_3 concentration 0.05–0.5*M*) should be present to suppress the hydrolysis:

$$Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+$$

2. Solution preparation

$$1 \text{ ppm} = \frac{1\ \mu g}{1\ mL} = \frac{10^{-6} g}{1\ mL} = \frac{1000 \times 10^{-6} g}{1000 \times 1\ mL} = \frac{10^{-3}\ g}{1000\ mL} = \frac{1\ mg}{1000\ mL}$$

$$\therefore 1000 \text{ ppm} = \frac{1000\ mg}{1000\ mL} = \frac{1\ g}{1000\ mL} = 1\ g\ L^{-1}$$

2.1. 100 ppm Fe^{3+} solution in 1000 mL

$\because$ 55.847 g Fe^{3+} present in – 482.190 g of $NH_4Fe(SO_4)_2 \cdot 12H_2O$

Ferric Ammonium Sulfate Dodecahydrate (FAS)

$$\therefore 0.100 \text{ g } Fe^{3+} \text{ present in } -\frac{482.190}{55.847} \times 0.100 = 0.864 \text{ g of FAS}$$

Dissolve 0.864 g of FAS and 10 mL of concentrated HCl in 1000 mL volumetric flask with distilled water and make upto the mark with distilled water.

2.2. Preparation of 10 ppm Fe^{3+} solution in 250 mL from 100 ppm Fe^{3+} solution

$$N_1V_1 \text{ (100 ppm)} = N_2V_2 \text{ (10 ppm)}$$

$$100 \times V_1 = 10 \times 250$$

$$V_1 = 25 \text{ mL}$$

Take 25 mL of 100 ppm Fe^{3+} solution in 250 mL volumetric flask and make upto the mark with distilled water.

2.3. Preparation of 9 ppm Fe^{3+} solution in 20 mL from 10 ppm Fe^{3+} solution

$$N_1V_1 \text{ (10 ppm)} = N_2V_2 \text{ (9 ppm)}$$

$$10 \times V_1 = 9 \times 20$$

$$V_1 = 18 \text{ mL}$$

Take 18 mL of 10 ppm Fe^{3+} solution in a beaker and add 2 mL of distilled water. Similarly, prepare 8, 7, 6, 5, 4, 3, 2, and 1 ppm solution from 10 ppm Fe^{3+} solution.

2.4. 4 M HNO_3 in 100 mL

$$N_1V_1 \text{ (Conc. } HNO_3) = N_2V_2 \text{ (4 M)}$$

$$16 \times V_1 = 4 \times 100$$

$$V_1 = 25 \text{ mL}$$

Take 25 mL of concentrated HNO_3 in 100 mL volumetric flask and make upto the mark with distilled water.

2.5. 20 % KSCN in 100 mL

Dissolve 20.000 g of KSCN in distilled water in 100 mL volumetric flask and make up to the mark with distilled water.

3. Procedure

- Prepare a set of standard solutions of different ppm, *i.e.* 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 ppm of Fe^{3+}.
- Take 20 mL of the different ppm solutions in different beakers and add each of the beaker 3 mL of 20 % KSCN and 2 mL of 4 M HNO_3 solutions.
- Prepare a blank solution, *i.e.* a solution that contains all the components of the mixtures to be analyzed except for Fe^{3+} ions; 20 mL distilled water, 3 mL of 20 % KSCN, and 2 mL of 4 M HNO_3 solutions.
- Measure the absorbance of the above prepared solution in a spectrophotometer (Colorimeter) at 490 nm (Blue-Green filter)
- Determine the concentration of iron in the given unknown solution by comparison with values on a reference curve obtained from different concentrations of the standard Fe^{3+} solutions.

4. Observation Table

S. No.	Concentration of Fe^{3+} in ppm	Absorption
1	1	0.071
2	2	0.149
3	3	0.234
4	4	0.319
5	5	0.407
6	6	0.499
7	7	0.599
8	8	0.684
9	9	0.726
10	10	0.735
11	**Unknown solution**	0.356

5. Calculation

Plot a graph by taking **the concentrations of Fe^{3+} of different ppm solutions along X-axis (abscissa) and corresponding absorbance of different ppm solutions along Y-axis (ordinate)**. Such a plot gives a deviation from straight line as shown in **Fig. 1**.

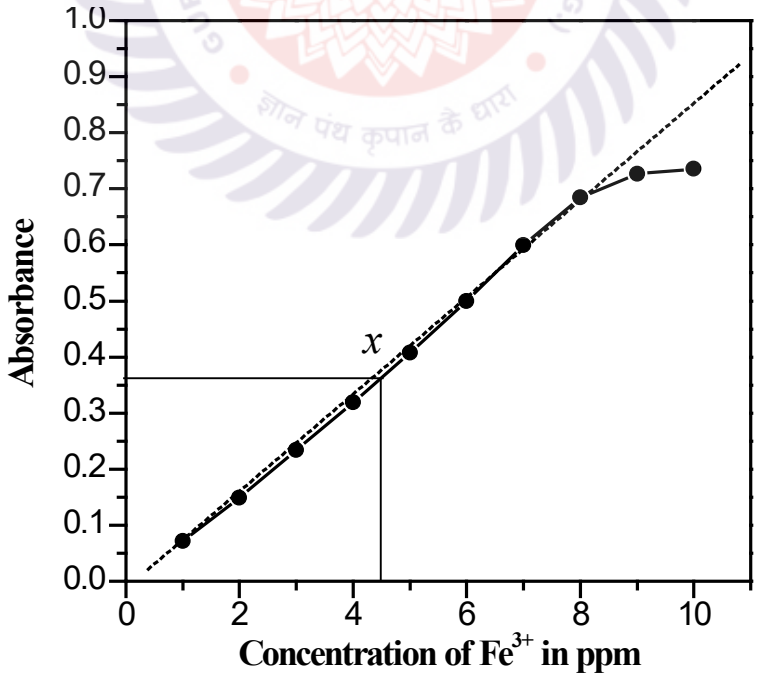

Fig. 1. Plot of absorbance versus concentration of Fe^{3+} ion.

The concentration of the unknown solution can be calculated by marking the point on the deviation line corresponding to its absorbance. **The *x* mark represents the point corresponding to the unknown solution**. A perpendicular drawn from this point on the concentration axis gives the concentration of Fe^{3+} ion in ppm of the unknown solution.

6. Results and Discussion

The concentration of the given unknown solution is obtained to be 4.46 ppm Fe^{3+}.

The linear graph appears for the solutions of Fe^{3+} ions ranging of concentrations from 1 to 8 ppm obeys the *Beer-Lambert's law*. Thereafter, for the higher concentrations deviation is observed from linearity of the curve.

7. Precautions

(i) Strong acids HCl or HNO_3 should be used to suppress the hydrolysis. H_2SO_4 is not recommended, because of sulfate ions have a certain tendency to form complex with Fe^{3+} ions.

(ii) A large excess of –SCN should be used, since this increases the intensity and stability of the color of Fe^{3+} complexes.

8. Further Reading

(i) Read up the theory of *Beer-Lambert's law*.

(ii) How does the colorimeter work?

(iii) *Vogel's Text Book of Quantitative analysis*, Eds: 5th, Longman Scientific and Technical, John Wiley and Sons Inc., New York, 1989.

(iv) *Physical Chemistry*, P. W. Atkins and J. D. Paula, Eds: 7th, Oxford University Press.

(v) *University Practical Chemistry*, P. C. Comboj, Vishal Publishing Co. Jalandhar.