C 142(Experiment No._____)

NAME:_____ **BATCH:_____**

ROLL NO:_____ **SEM:_____**

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STUDY OF THE COMPOSITION OF FERRIC-SULFOSALICYLIC ACID COMPLEX (JOB'S METHOD OF CONTINUOUS VARIATION)

AIM: To determine stoichiometry of a chemical reaction experimentally using Job's method.

THEORY

The formation constant (β) for the metal (M) – ligand (L) reaction is given by

$$mM + nL \rightleftharpoons M_m L_n$$

$$\beta = \frac{[M_m L_n]}{[M]^m [L]^n} \qquad \text{------ (1)}$$

If **C** be the molar concentration of each of the metal and the ligand, and if we use **v** ml of the solution of ligand and **(10-v)** ml of the solution of the metal so that the total volume of the mixed solution is always 10 mL, the total concentration of metal will be:

$$T_M = [M] + m[M_m L_n] = (10\text{-}v)C$$

or $$[M] = (10\text{-}v)C - m[M_m L_n] \qquad \text{- - - - - (2)}$$

And that of ligand,

$$T_L = [L] + n[M_m L_n] = v\,C$$

or $$[L] = vC - n[M_m L_n] \qquad \text{- - - - - (3)}$$

where [M] and [L] are the uncomplexed metal and ligand ion concentration resepctively.

Hence, $$\beta = [M_m L_n] / \{(10\text{-}v)C - m[M_m L_n]\}^m . \{vC - n[M_m L_n]\}^n$$

or $$[M_m L_n] = \beta . \{(10\text{-}v)C - m[M_m L_n]\}^m . \{vC - n[M_m L_n]\}^n = f(v)$$

Since β, C, n and m are constants.

At a certain volume $v = v_{max}$; $[M_m L_n]$ is maximum i.e.,

$$\{d[M_m L_n] / dv\}_{V = Vmax} = 0$$

From equation (1),

$$ln [M_m L_n] = ln \beta + m\, ln [M] + n\, ln [L]$$

or

$$\frac{d\, ln [MmLn]}{dv} = \frac{m\, d[M]}{[M]dv} + \frac{n\, d[L]}{[L]dv} = 0 \text{ at } v = v_{max}$$

From equation (2 and 3),

$$\frac{m}{[M]}(-C) + \frac{n}{[L]}(C) = 0$$

or $$n[M] = m[L]$$

or $$n\,C(10\text{-}v_{max}) = m\,C\,v_{max}$$ from equation 2 and 3 at $v = v_{max}$

or $$m/n = (10\text{-}v_{max}) / v_{max}$$

During complex formation, any physical property of the solution related to the complex formation continuously changes with the change in the composition of the constituents, and attains an extreme value at $v = v_{max}$. If D_0 and D be the absorbances of the solution before and after complex formation (assuming the additively rule), then

$$D = \varepsilon_M [M] l + \varepsilon_L [L] l + \varepsilon_{ML} [M_m L_n] l$$

$$D_0 = \varepsilon_M T_M l + \varepsilon_L T_L l$$

where ε_M, ε_L and ε_{ML} are the extinction coefficients of the metal, ligand and the complexes, respectively and 'l' is the cell length. That is, $D\text{-}D_0$ will also be maximum at $v = v_{max}$ when both the metal and ligand are colorless, and D = f(v) when the complex is colored. If we plot D against v, we should get a curve with a maximum at $v = v_{max}$, from this graph, we can get the value of m/n and hence the composition of the

complex.

A number of phenolic compounds (for example, sulfosalicylic acid) form colored complexes with Fe^{3+} salts.

$$Fe^{3+} + \text{sulfosalicylic acid} \rightleftharpoons \text{complex (colored)}$$

The stiochiometry of the complex can be determined by Job's method. When equimolar solutions of the two reactants are mixed in varying proportions, the maximum amount of the complex at equilibrium is formed when the proportion of the reactants employed corresponds to the empirical formula of the complex. That is,

$$a\,A + b\,B \rightleftharpoons A_a B_b$$

Maximum number of $A_a B_b$ is present if **a** parts of **x** molar solution of **A** are mixed with **b** parts of **x** molar solution of **B**. If **a/b = 1**, the composition of the complex is **AB**.

MATERIALS REQUIRED: Ferric alum, sulfosalicylic acid, conc. HCl, volumetric flasks, stoppered glass test tubes, pH meter, spectrophotometer with cuvettes, distilled water etc.

PROCEDURE

1. Prepare 0.002 M solutions of Fe^{3+} and sulfosalicylic acid in 100 mL volumetric flasks separately.
2. Mix the solutions of Fe^{3+} and sulfosalicylic acid in test tubes in different proportions as per table (*note: The optimum pH for the stability of the complex is about 2.6-2.8. So, adjust the pH of the solutions of the reactants using N/10 HCl (if necessary)*.
3. Using Spectrophotometer, measure the optical density for a particular solution taken into the cuvette by making blank zero and choose the lambda maximum i.e., a wavelength where the absorbance reaches a maximum value.
4. Measure the optical density using the maximum lambda for each solution.
5. Plot a graph of volume of sulfosalicylic acid solutions against absorbance of each solution.

TABLE

Solution No.	Volume of Fe^{3+} (mL)	Volume of sulfosalicylic acid (mL)	Optical Density
1.	9	1	
2.	8	2	
3.	7	3	
4.	6	4	
5.	5	5	
6.	4	6	
7.	3	7	
8.	2	8	
9.	1	9	

OBSERVATIONS CALCULATIONS AND RESULTS

1. Lambda max = _____ nm
2. Calculate the molar extinction coefficient values and empirical formula for each and compostion of complex.
3. Plot a graph of volume of sulfosalicylic acid solutions against absorbance of each solution.