

**Conclusion:** The conc. of the given solution is ... (M)

**Additional parameter:**

From equation (3),

$$O.D. = \epsilon cl$$

$$\therefore \epsilon = \frac{O.D.}{cl} = \frac{O.D.}{c} \quad (\text{when path length, } l, \text{ of the absorbing medium} = 1 \text{ cm})$$

$\therefore$  the slope of either of the graphs gives  $\epsilon$ , the molar absorption coefficient.

## Experiment 2

To determine the composition and stability constant of Fe (III)—salicylic acid complex colorimetrically by Job's method of continuous variation.

**Theory:** Iron (III) forms a number of coloured complexes with some phenolic compounds, like salicylic acid. Job's method provides an easy way to determine the stoichiometry of such complexes.

The principle of this method is that, if the metal ions and the ligand are taken in equal molarity and mixed in varied proportions, the maximum amount of the complex will be formed at equilibrium, when the proportion of the reactants correspond to the empirical formula of the complex. At this stage the absorption will be maximum also.

Let the empirical formula of the complex be  $A_m B_n$ , which is formed as



Let the molarity of  $A$  and  $B$  be  $x$ . According to the principle mentioned above, if  $m$  parts of  $A$  and  $n$  parts of  $B$  are mixed, then amount of  $A_m B_n$  will be maximum at equilibrium. And in this condition, the absorption will be maximum at a selected wavelength.

pH plays an important role for the stability of the complex. In this case, the optimum pH-range is 2.6-2.8. This is achieved by using a 0.002M HCl solution. Otherwise the complex may hydrolyse.

The stability constant ( $K$ ) of the complex is given by

$$K = \frac{[\text{Fe (III)-salicylic acid}]_{\text{complex}}}{[\text{Fe (III)}]_{\text{unreacted}} [\text{salicylic acid}]_{\text{unreacted}}} \quad (2)$$

For this purpose, a fixed amount of S.A. is complexed with different amount of Fe (III). From the graph of O.D. vs. [Fe (III)], the slope =  $\epsilon$ , i.e., the molar absorptivity is found out.

Now from the equation,

$$O.D. = \epsilon cl = \epsilon c \quad (l = 1 \text{ cm}),$$

$$c = \frac{O.D.}{\epsilon} \quad (3)$$

i.e., concentration of Fe (III) in each solution is determined. This concn. corresponds to the concn. of the complex (numerator). Let the original concn. of Fe (III) in the composition determining concn. (i.e. for maximum absorbance) be  $a$ .

$$\text{Then } [\text{Fe (III)}]_{\text{unreacted}} = (a - c).$$

$$\text{Since iron : S.A. is } 1 : 1, \therefore [\text{S.A.}]_{\text{unreacted}} = (a - c).$$

$$\therefore K = \frac{c}{(a - c)(a - c)} \quad (4)$$

**Equipments:** Colorimeter, 100 ml volumetric flasks, 10 ml graduated pipette, 500 ml beaker, ten 15/20 ml test tubes (preferably stoppered).



**Materials:** Ferric-ammonium sulphate  $[\text{Fe}_2(\text{SO}_4)_3, (\text{NH}_4)_2\text{SO}_4, 24\text{H}_2\text{O}]$ , salicylic acid, HCl.

### Procedure

1. Prepare 400 ml 0.002M HCl solution. (Calculate required volume of conc. HCl, taking its molarity 11.3).
  2. Prepare 100 ml 0.002 M ferric-ammonium sulphate solution in 0.002M HCl solution.  
Dissolve exactly 0.1927g ferric-alum in 20-25 ml 0.002 M HCl solution in a 100 ml volumetric flask. After complete dissolution add 10 ml water, shake well and then make up the volume with 0.002 M HCl. (If larger amount of salt is taken, dilute properly with 0.002 M HCl).
  3. Prepare 100 ml 0.002 M salicylic acid in 0.002M HCl solution.  
Dissolve exactly 0.0276 g salicylic acid in 10 ml water in a 100 ml volumetric flask. After complete dissolution, make up the volume with 0.002 M HCl solution. (If some larger amount of SA is taken, dilute properly with 0.002 M HCl).
- [N.B. In (2) the salt is dissolved in HCl. Water is added in equal amount in both (2) and (3), to keep the same molarity. Generally S.A. does not dissolve in HCl. So it is first dissolved in minimum amount of water, so that the required pH-range is maintained.]
4. Label nine test tubes 1-9 and prepare the solution as in table 3.
  5. Take test tube no. 4 or 6 and determine its O.D. using different filters (wave lengths) from 420-660 nm at about 40 nm intervals.
  6. Plot O.D. vs  $\lambda$  and find  $\lambda_{\text{max}}$ .
  7. Set the spectrophotometer at the  $\lambda_{\text{max}}$  and take O.D. readings of all the solutions.
  8. Plot O.D. vs. volume of salicylic acid and find the maximum absorbance. Find the ratio of vol. of Fe (III) and S.A. for this solution and determine the composition of the complex.  
Let the original concn. of Fe (III) in this solution be  $a$ .
  9. Prepare a saturated solution of S.A. in 0.002M HCl.
  10. **For determination of stability constant** (equilibrium constant) mark another five stoppered test tubes I-V and prepare solutions as per table 6 and take O.D. readings of the solutions.
  11. Plot O.D. vs. concn. of Fe (III) solutions. The slope gives the molar absorptivity,  $\epsilon$ .
  12. Find concn. of  $[\text{Fe (III)}]_{\text{complex}}$ ,  $c = \frac{\text{O.D.}}{\epsilon}$ .
  13. Find concn. of unreacted Fe (III) and S.A.
  14. Calculate stability constant as per equation (4).

### Results and Calculations

**Table 1:** Preparation of 100 ml exact 0.002 M Ferric-ammonium sulphate solution in 0.002 M HCl  
weight required = 0.1927 g.

**Table 2:** Preparation of 100 ml exact 0.002 M salicylic acid solution in 0.002 M HCl.

Weight required = 0.0276 g

(You may first prepare 0.02 M and then dilute to 0.002 by adding 0.002 M HCl quantitatively).

**Table 3: Preparation of solutions for determination of composition of complex**

Test tube No.	Vol. of $\text{Fe}^{3+}$ (0.002M) (ml)	Vol. of S.A. (0.002 M) (ml)	Total vol. (ml)
1	9	1	10
2	8	2	10
3	7	3	10
4	6	4	10
5	5	5	10
6	4	6	10
7	3	7	10
8	2	8	10
9	1	9	10

**Table 4: Determination of  $\lambda_{\text{max}}$  (taking test tube no. 4 or 6)**

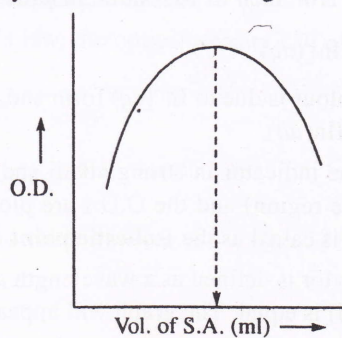
$\lambda$ (nm)	O.D.
420	...
460	...
500	...
...	...
...	...

The nature of the graph will be as in experiment 1.

**Table 5: Determination of the composition of the complex**

Test tube no.	O.D. at $\lambda_{\text{max}} = \dots$ nm
1	...
2	...
...	...
8	...
9	...

The plot of O.D. vs vol. of salicylic acid is shown in Fig. 5.5.

**Fig. 5.5**



From the plot, the vol. ratio of Fe (III) and S.A. at maximum absorbance = ...:...

∴ empirical formula of the complex is ...

Original concn. of Fe (III) in this solution ... (M)

**Table 6:** Preparation of solutions for determination of stability constant and O.D. readings at  $\lambda_{\max} = \dots$  nm

Test tube no.	Vol. of 0.002 M $\text{Fe}^{3+}$ soln. (ml)	Vol. of 0.002M S.A. soln. (ml)	Vol. of 0.002 M HCl soln. (ml)	Total vol. (ml)	Conc. of $\text{Fe}^{3+}$ (M)	O.D.
I	1	5	4	10	...	...
II	2	5	3	10	...	...
III	3	5	2	10	...	...
IV	4	5	1	10	...	...
V	5	5	0	10	...	...

The plot of O.D. vs. concn. of Fe (III) is shown in Fig. 5.6.

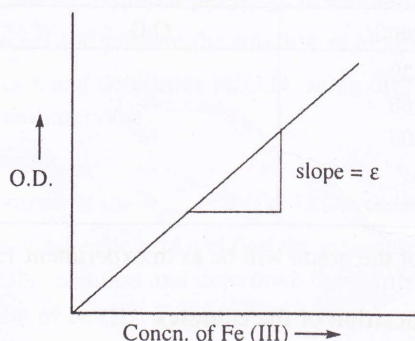


Fig. 5.6

### Experiment 3

*Determination of—(a) Isobestic point of bromocresol green indicator, and (b) Indicator constant of the indicator.*

**Theory:** An acid-base indicator is a weak acid or base which exhibits two distinct colours in dissociated and undissociated forms of the molecule.

If the indicator be represented as  $\text{HIn}$ , then its ionisation in aqueous solution may be shown as



In strong alkaline solution, the colour is due to  $\text{In}^-(aq)$  form and in strong acid medium, the colour is due to the undissociated form of  $\text{HIn}(aq)$ .

When two different spectra of the indicator in strong alkali and in strong acid medium is studied using long range of filters (in visible region) and the O.D.s are plotted against wavelengths, the two curves will cut at a point. This point is called as the **isobestic point** of the indicator.

Hence isobestic point of an indicator is defined as a wavelength at which the absorbance of the two forms (dissociated and undissociated) is equal. The graph will appear as shown in Fig. 5.7.