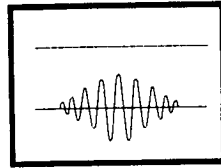


CHAPTER-V



UV SPECTROPHOTOMETRIC STUDY OF SOME BINARY COMPLEXES

Introduction

In many substances, which are colourless, electronic excitation may occur because of the absorption of radiation in UV region. The transitions of closely spaced vibrational and rotational levels are superimposed on electronic transitions.

Transitions are even influenced by the presence of neighbouring molecules and therefore the UV spectra like the visible spectra consists of one or more broad peaks, the wavelength region being 200-400nm¹.

The halide complexes of metals are the main inorganic substances absorbing UV radiation. Tellurium is determined as its iodide complex $[\text{TeI}_6]^{2-}$ by measurements at 335nm. Tetravalent tellurium is allowed to react with HCl and KI and the absorbance of the mixture is measured in 20 minutes. Bismuth and Selenium do interfere in the analysis and hence are removed before the analysis is done, the presence of Iron(II) and Cu(II) should be carefully avoided as they tend to liberate free iodine during the reaction.

The thiocyanate complex of metal ions are also very important. The maximum absorbance λ_{max} for cobalt and uranium thiocyanate complexes are 312 and 375 nm respectively.

Many inorganic substances are determined in ultraviolet region by preparing their complexes with organic ligands.

Some Lanthanides have been simultaneously determined with the help of recording spectrophotometer. In the whole visible and UV region, several characteristic and intense absorption bands for Lanthanides at various wavelengths have been observed. Therefore, multiple analysis is possible to select such wavelength where absorption overlapping is minimum¹⁻⁷.

The composition of complex species in a solution and its stability constant can be determined spectrophotometrically^{8,9,10}. One greatest advantage of this method is that the quantitative measurements can be made without effecting the equilibrium being studied.

Iron(II) complex with non absorbing ligands is made by observing the effect of the ligand on the colour of Iron(II) phenanthroline complex. If the data on phenanthroline complex is available, data on the composition and stability constant of the non absorbing species can be known.

Proposed Spectrophotometric Methods

Some methods have been proposed for the spectrophotometric study of complex formation in solution. Some of them are discussed here :

1. Mole ratio Method :

This method was first employed by Yoe and Jones⁸ to determine the stoichiometry of metal to ligand in a complex. A series of solution

are prepared in which the concentration of one of the elements (usually of metal ion) is kept constant and that of the other (ligand) is varied.

Absorbance of each of the solution of the series is measured at λ_{\max} . A plot is made between absorbance and the mole ratio of the reagents.

This curve is expected to be a straight line from the origin to the point where equivalent amount of the constituents are present, the curves then becomes horizontal because one of the constituent is wholly consumed and its further addition will produce no more of the absorbing complex. If the added constituent is itself an absorbing one, the line after the equivalence point will show a positive slope but would be of smaller magnitude than that prior to equivalence.

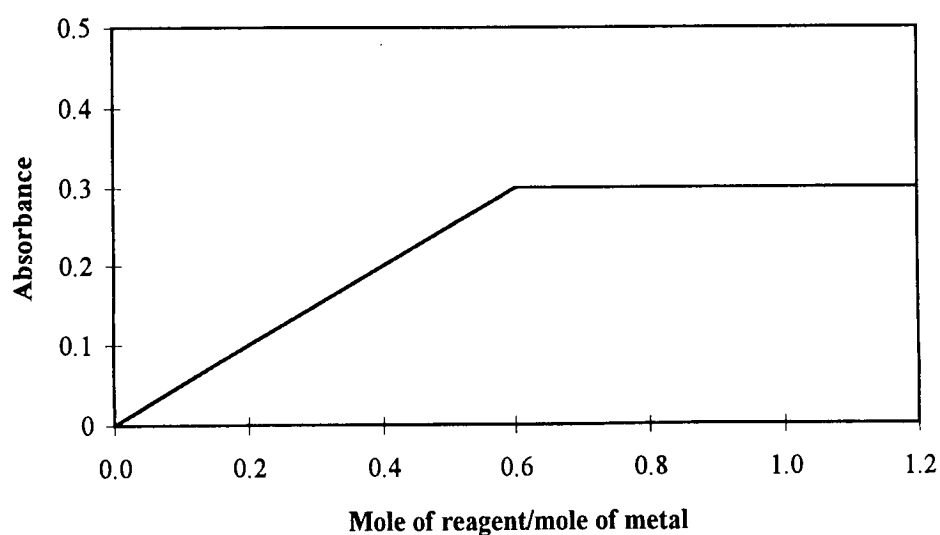


Fig. 5.1

The point of intersection of these two lines provides metal : ligand ratio of the complex species.

2. Job's method of continuous variation :

This method was first employed by Job and later modified by Vosbough and Cooper⁹. A series of solutions of varying mole fractions of the two constituents are prepared where as their sum is kept constant.

The absorbance of each solution is measured at λ_{max} .

The difference between the measured absorbance and the absorbance calculated for the mixed constituents on the assumptions of no reaction between them is plotted against the mole fraction of one of the constituents.

Volume fraction of the metal can be represented as V_m/V_m+V_L where V_m , V_L are the volumes of metal and ligand respectively.

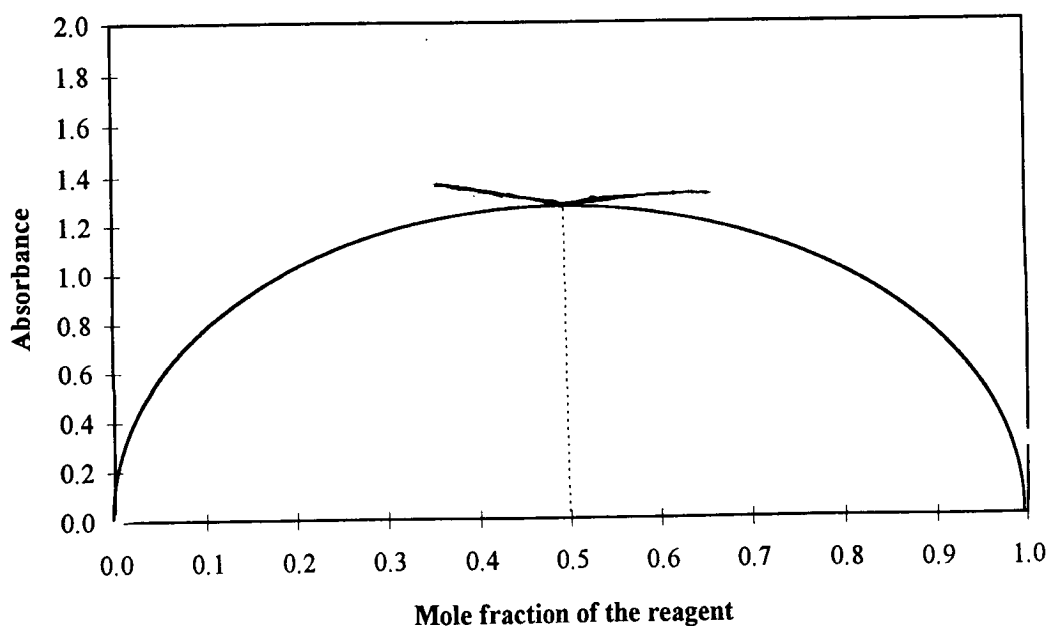


Fig. 5.2

The figure shows maximum at a concentration V_m/V_L ratio which corresponds to the ratio of metal to ligand in the complex.

Determination of the dissociation constant however requires the use of non equimolar solution $P \neq 1$ of the two reactants.

From the knowledge of values of m and n it is possible to calculate the value of K , the dissociation constant.

For 1:1 complex, $m = 1$, $n = 1$.

$$K = \frac{[C \cdot \{(P+1)x - 1\}^2]}{(P-1) \cdot (1-2x)}$$

Similar equations can be derived for 1:2, 2:3, 1:3 etc. complexes.

For 1:2 complex.

$$K = \frac{C^2 P [(P+2)(x-2)]^3}{(P-1)^2 \cdot (2-3x)}$$

where in the above equation

C - Molar concentration of metal ion

P - Ratio of molar concentration of ligand to that of metal

X - Volume fraction of ligand where the maximum amount of complex is formed.

In few cases Likussar and Boltz has successfully applied this method to determine the conditional stability constant using following equation

$$\log K'f = 0.3750 - 3 \log K + \log Y_{\max} - 4 \log (1 - Y_{\max})$$

3. Slope ratio method

This method has often proved useful in the identification of weak complexes. This is employed only when one complex is formed¹⁰.

The complex formation reaction can be forced to complete in the excess of only one of the reagents and the Beer's law is still obeyed for the following reactions



If L is present in excess, then

$[M_mL_l] = F_m M_m L_l$ and as per Beer's law

$$A_m = \epsilon \cdot b \cdot M_m L_l = \epsilon b \cdot F_m / m$$

A plot between A and F_M would be linear. If, the concentration of M is much greater than that of L then

$$M_m L_l = F_L / l$$

and

$$A_L = \epsilon b M_m L_l = \epsilon b F_L / l$$

Under these conditions the values of the slopes (A/F_m) and A/F_L of the straight lines can be determined. The ratio of L and M combination can be calculated from the ratio of the slopes.

$$\frac{A_m / F_m}{A_l / F_l} = \frac{S_m}{S_l} = \frac{b / m}{b / l} = \frac{l}{m}$$

S_m and S_l represents the slopes of the two lines.

In the present work Job's method of continuous variation has been used for the study of the composition and formation constants of the complexes under study.

Experimental

Absorption spectra in UV and visible ranges are observed because of the absorptions due to electronic vibrations. Substances, depending upon their electronic structures, usually show characteristic absorption at one or more wavelengths in the UV and visible regions. It is therefore necessary to study the variation of optical density with wavelength of the system under investigation and to choose one or more suitable wave lengths for the experimental purpose.

Selection of wave length

Lanthanides are known to show strong absorption bands in the UV region. This necessitates the use of comparatively dilute solutions for spectral studies of Lanthanide complex¹¹.

For the present study the metal ion (Tb(III), Dy(III), Er(III) and Sm(III)) solution and ligand solution were mixed in definite molar ratio in which they combine to form the complex. Optical densities at various wavelengths (220 to 350 nm) were measured and the observed values were plotted against the corresponding wave lengths (nm). Suitable wavelengths were chosen for actual experimental studies. A

Systronics (India) digital pH meter model 335 and Systronics (India) UV visible spectrophotometer model-118 were used for pH measurements and absorbance studies, respectively.

All reagents were of analytical grade. Aquous solutions of metal and ligand were prepared by usual methods. A series of solutions with varying concentration of metal and ligand were prepared and their absorbance were measured.

Composition of complex was determined by Job's method of continuous variation using equimolar solutions of metal and ligand. Determination of stability constant however requires the use of nonequimolar solution of the two reactant.

For the determination of stability constant of the complex solution of different molarity of metal and ligand have been used to make standard series of solutions. pH of the test solutions was adjusted with dilute hydrochloric acid and solution of sodium hydroxide solutions.

Results and Discussion

Spectrophotometric study of complex formation of Tb(III) with PAR, PAN, Methylene blue and 1, 10 Phenanthroline :

The literature records a λ_{\max} value of Tb(III) solution at 378 nm. All the measurements have been carried out at this wavelength. By applying Job's method of continuous variation (Fig. 5.3), the

composition of complexes under study in solution was found to be 1:1 in each case and the stability constant values at pH 3.10 ± 0.1 have been calculated and listed as under -

$$[\text{Tb}(\text{PAR})]^{3+} \log \beta_1 = 3.48$$

$$[\text{Tb}(\text{PAN})]^{3+} \log \beta_1 = 4.12$$

$$[\text{Tb}(\text{MB})]^{3+} \log \beta_1 = 4.44$$

$$[\text{Tb}(1,10 \text{ phen})]^{3+} \log \beta_1 = 4.87$$

Spectrophotometric data are presented in Table 5.1, 5.2, 5.3 and 5.4 respectively.

The present experiment has been performed at lower pH because at this pH a soluble 1:1 metal azo dye complex is formed which could be easily studied using spectrophotometric method¹²⁻¹⁸. However at higher pH i.e. 6.5 ± 0.1 and higher concentration of reagents precipitation takes place on standing.

It may be stated here that minor differences in the wave length of maximum absorption for the metal ion is due to the chosen experimental conditions.

Spectrophotometric study of complex formation of Dy(III) with PAR, PAN, Methylene blue and 1,10 phenanthroline :

The literature reveals that lanthanides combine with 1-10 phenanthroline to form complex compounds with different ratios. For the present study when different proportions of metal and reagent

solutions were mixed and their light absorbing properties were studied, it was found that at 320 nm wave length maximum absorption takes place.

In this study thus the experiment was carried out at 320 nm absorption by metal ion. By applying Job's method of continuous variation (Fig. 5.3) at pH 3.10 ± 0.1 , composition and stability constants of complexes have been calculated as under :

$$[\text{Dy}(\text{PAR})]^{3+} \log \beta_1 \text{ 1:1} = 4.50$$

$$[\text{Dy}(\text{PAN})]^{3+} \log \beta_1 \text{ 1:1} = 4.05$$

$$[\text{Dy}(\text{MB})]^{3+} \log \beta_1 \text{ 1:1} = 4.15$$

$$[\text{Dy}(1,10 \text{ phen})]^{3+} \log \beta_1 \text{ 1:1} = 5.28$$

Spectrophotometric data are presented in Table 5.5, 5.6, 5.7 and 5.8 respectively.

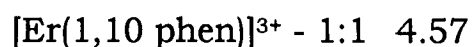
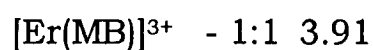
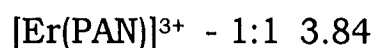
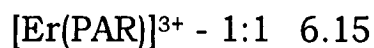
The present exercise has been performed at lower pH because at this pH a soluble 1:1 metal azo dye complex is formed which could be easily studied using spectrophotometric method. However at higher pH i.e. 6.5 ± 0.1 and higher concentration of reagents precipitation takes place on standing.

It may be stated here that minor differences in the wave length of maximum absorption for the metal ion is due to the chosen experimental conditions.

Spectrophotometric study of complex formation of Er(III) with PAR, PAN, Methylene blue and 1, 10 phenanthroline :

T. Moeller and Co-workers have studied Er(III)-5, 7 dichloro 8-hydroxy quinoline/complex by UV spectrophotometric techniques¹⁹. Recently Gerald et al. have reported crown ether complexation by Er(III)²⁰. The literature reports a λ_{\max} value for Er(III) solution at 260 nm.^{11,21} Job's method of continuous variation was applied at 260 nm to study metal- ligand complex formation equilibria (Fig. 5.3).

The metal ligand ratio and stability constants at pH 3.10 ± 0.1 were found to be ;



Data related to this observation is presented in Table Number 5.9, 5.10, 5.11 and 5.12.

This exercise has been performed at lower pH because at this pH a soluble 1:1 metal azo dye complex is formed which could be easily studied using spectrophotometric method. However at higher pH i.e. 6.5 ± 0.1 and higher concentration of reagents precipitation takes place on standing.

It may be stated here that minor differences in the wave length of maximum absorption for the metal ion is due to the chosen experimental conditions.

Spectrophotometric study of complex formation of Sm(III) with PAR, PAN, Methylene Blue, and 1, 10 phenanthroline

The literature reports a λ max value for Sm(III) solution at 294nm.¹¹ Job's method of continuous variation was applied to study the metal ligand complexation equilibria. Metal ligand ratio for the studied complexes were found to be 1:1 and stability constants $\log \beta_1$ were calculated to be -

[Sm(PAR)] ³⁺	1:1	3.90
[Sm(PAN)] ³⁺	1:1	5.68
[Sm(MB)] ³⁺	1:1	3.02
[Sm(1,10 phen)] ³⁺	1:1	3.95

Data are presented in the table 5.13, 5.14, 5.15 and 5.16. This exercise has been performed at lower pH because at this pH a soluble 1:1 metal azo dye complex is formed which could be easily studied using spectrophotometric method. However at higher pH i.e. 6.5±0.1 and higher concentration of reagents precipitation takes place on standing.

It may be stated here that minor differences in the wave length of maximum absorption for the metal ion is due to the chosen experimental conditions.

Table 5.1: Spectrophotometric data for Terbium(III) - PAR complex equilibria at 378 nm.

S.No.	M/400 mol dm ⁻³ of metal (ml)	M/600 mol dm ⁻³ of PAR (ml)	Absorbance
1	10	0	0.018
2	9	1	1.152
3	8	2	1.729
4	7	3	1.926
5	6	4	1.621
6	5	5	1.512
7	4	6	1.400
8	3	7	1.000
9	2	8	0.0730
10	1	9	0.421

Table 5.2: Spectrophotometric data for Terbium(III)1-(2-Pyridyl azo) 2-Naphthol complex equilibria at 378nm λ_{max} .

S.No.	M/400 mol dm ⁻³ of metal (ml)	M/600 mol dm ⁻³ of ligand (ml)	Absorbance
1	9	1	0.270
2	8	2	0.401
3	7	3	0.561
4	6	4	0.621
5	5	5	0.931
6	4	6	1.017
7	3	7	1.050
8	2	8	0.850
9	1	9	0.717

**Table 5.3: Spectrophotometric data for Terbium(III) Methylene
Blue complex equilibria at 378 nm λ_{\max} .**

S.No.	M/400 mol dm ⁻³ of metal (ml)	M/600 mol dm ⁻³ of ligand (ml)	Absorbance
1	9	1	0.364
2	8	2	0.453
3	7	3	0.707
4	6	4	0.758
5	5	5	1.081
6	4	6	1.063
7	3	7	1.015
8	2	8	0.233

**Table 5.4: Spectrophotometric data for Terbium(III) 1,10
Phenanthroline complex equilibria at λ_{\max} 378 nm.**

S.No.	M/400 mol dm ⁻³ of metal (ml)	M/600 mol dm ⁻³ of ligand (ml)	Absorbance
1	9	1	0.011
2	8	2	0.016
3	7	3	0.018
4	6	4	0.020
5	5	5	0.022
6	4	6	0.014
7	3	7	0.013
8	2	8	0.012
9	1	9	0.010
10	0	10	0.008

Table 5.5 : Spectrophotometric data for Dysprosium(III) - PAR complex equilibria at 320 nm.

S.No.	M/400 mol dm ⁻³ of metal (ml)	M/600 mol dm ⁻³ of PAR (ml)	Absorbance
1	10	0	1.23
2	9	1	1.28
3	8	2	1.53
4	7	3	1.71
5	6	4	1.920
6	5	5	1.564
7	4	6	1.080
8	3	7	0.864
9	2	8	0.321
10	1	9	0.033

Table 5.6: Spectrophotometric data for Dysprosium(III) - PAN complex equilibria at 320 nm.

S.No.	M/400 mol dm ⁻³ of metal (ml)	M/600 mol dm ⁻³ of PAN (ml)	Absorbance
1	10	0	1.671
2	9	1	1.776
3	8	2	1.812
4	7	3	1.914
5	6	4	1.973
6	5	5	1.845
7	4	6	1.743
8	3	7	1.403
9	2	8	1.200
10	1	9	1.184

Table 5.9 : Spectrophotometric data for Erbium(III) 4-(2-Pyridyl azo) Resorcinol complex equilibria at 260 nm λ_{\max} .

S.No.	M/400 mol dm ⁻³ of metal (ml)	M/600 mol dm ⁻³ of ligand (ml)	Absorbance
1	10	0	0.088
2	9	1	0.383
3	8	2	0.599
4	7	3	0.855
5	6	4	1.275
6	5	5	1.500
7	4	6	1.753
8	3	7	1.750
9	2	8	1.741
10	1	9	1.731

Table 5.10 : Spectrophotometric data for Erbium(III) 1-(2-Pyridyl azo) 2-Naphthol complex equilibria at 260 nm λ_{\max} .

S.No.	M/400 mol dm ⁻³ of metal (ml)	M/600 mol dm ⁻³ of ligand (ml)	Absorbance
1	9.5	0.5	0.183
2	9.0	1.0	0.219
3	8.5	1.5	0.275
4	8.0	2.0	0.368
5	7.5	3.5	0.432
6	7.0	3.0	0.529
7	6.0	4.0	0.720
8	5.0	5.0	0.700
9	4.0	6.0	0.653
10	3.0	7.0	0.653
11	2.0	8.0	0.245

**Table 5.11 : Spectrophotometric data for Eribium(III)- Methylene
Blue complex equilibria at 260 nm.**

S.No.	M/400 mol dm ⁻³ of metal (ml)	M/600 mol dm ⁻³ of ligand (ml)	Absorbance
1	10	0	1.43
2	9	1	1.61
3	8	2	1.65
4	7	3	1.68
5	6	4	1.73
6	5	5	1.61
7	4	6	1.58
8	3	7	1.55
9	2	8	1.51

**Table 5.12 : Spectrophotometric data for Eribium(III) - 1, 10
phenanthroline complex equilibria at 260 nm.**

S.No.	M/400 mol dm ⁻³ of metal (ml)	M/600 mol dm ⁻³ of ligand (ml)	Absorbance
1	9	1.0	0.314
2	8.5	1.5	0.473
3	8.0	2.0	0.672
4	7.0	3.0	0.705
5	6.0	4.0	1.270
6	4.0	6.0	1.455
7	3.0	7.0	1.261
8	2.0	8.0	1.213
9	1.0	9.0	1.121

**Table 5.13 : Spectrophotometric data for Sm(III) - 4-(2-Pyridyl
azo) Resorcinol complex equilibria at 310 nm.**

S.No.	M/400 mol dm⁻³ of metal (ml)	M/600 mol dm⁻³ of ligand (ml)	Absorbance
1	9	1	0.832
2	8	2	1.165
3	7	3	1.230
4	6	4	1.508
5	5	5	0.697
6	4	6	0.672
7	3	7	0.667
8	2	8	0.612
9	1	9	0.260

**Table 5.14: Spectrophotometric data for Sm(III) - 1-(2-Pyridyl
azo) 2-Naphthol complex equilibria at 310 nm.**

S.No.	M/400 mol dm⁻³ of metal (ml)	M/600 mol dm⁻³ of ligand (ml)	Absorbance
1	9	1	0.353
2	8	2	0.415
3	7	3	0.403
4	6	4	0.852
5	5	5	1.136
6	4	6	1.471
7	3	7	1.605
8	2	8	1.375
9	1	9	1.371

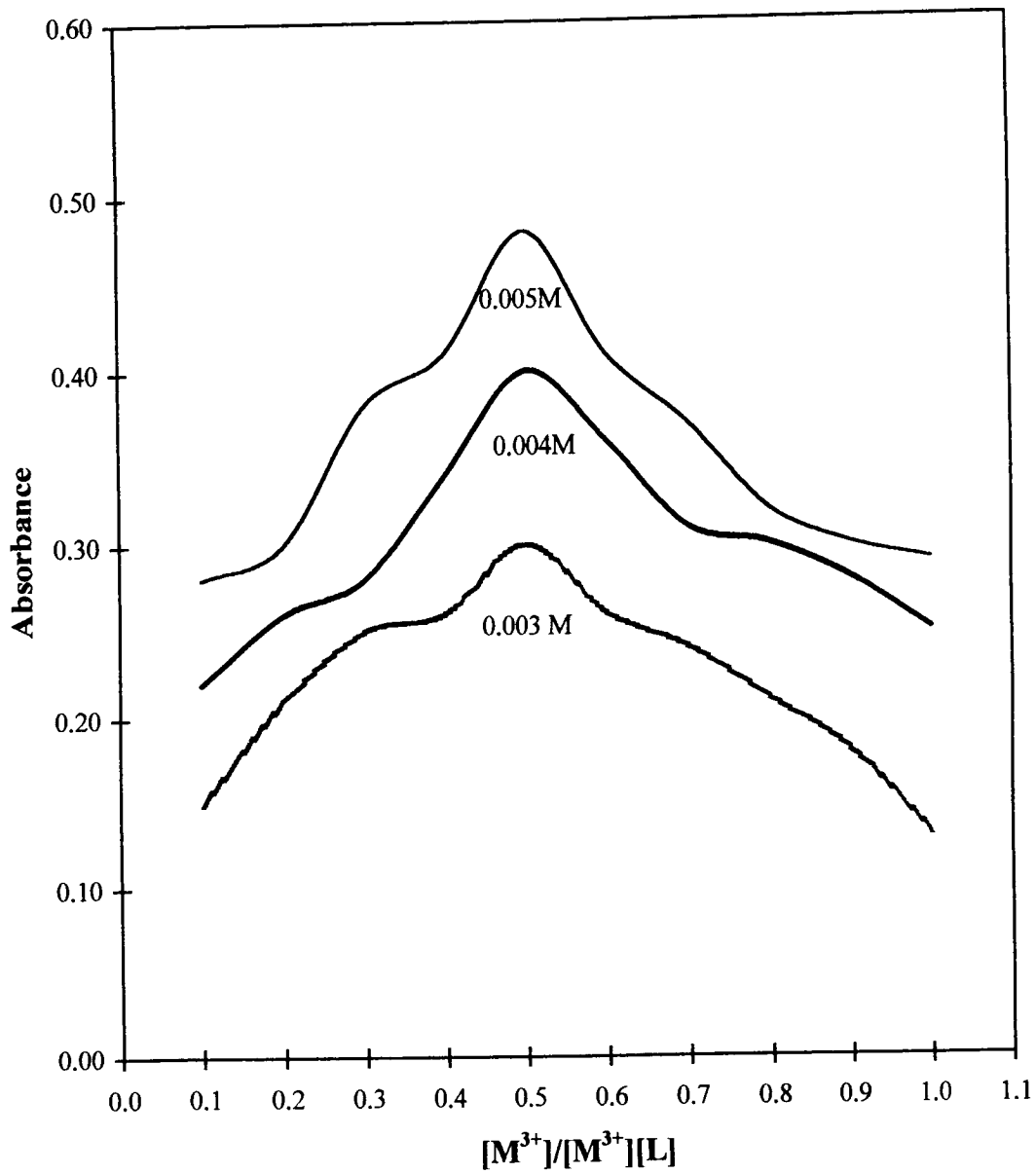
Table 5.15: Spectrophotometric data for Sm(III) - Methylene Blue complex equilibria at 310 nm.

S.No.	M/400 mol dm ⁻³ of metal (ml)	M/600 mol dm ⁻³ of ligand (ml)	Absorbance
1	9	1	0.431
2	8	2	0.570
3	7	3	0.492
4	6	4	0.324
5	5	5	1.739
6	4	6	1.616
7	3	7	0.966
8	2	8	0.722
9	1	9	0.314

Table 5.16 : Spectrophotometric data for Sm(III) - 1, 10 phenanthroline complex equilibria at 310 nm.

S.No.	M/400 mol dm ⁻³ of metal (ml)	M/600 mol dm ⁻³ of ligand (ml)	Absorbance
1	9	1	0.501
2	8	2	0.702
3	7	3	1.235
4	6	4	1.314
5	5	5	1.360
6	4	6	1.450
7	3	7	1.351
8	2	8	1.320
9	1	9	1.201

Fig. 5.03: Job's plot for composition of Dy(III)-PAN complex at 320 nm.



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