SPECTROPHOTOMETRIC STUDIES OF COMPLEXING BEHAVIOR OF SOME ORGANIC LIGANDS WITH SELECTIVE METAL IONS

A

DISSERTATION

SUBMITTED TO THE

QUAID-i-AZAM UNIVERSITY

IN

PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE

DEGREE OF

MASTER OF PHILOSOPHY

IN

ANALYTICAL/INORGANIC CHEMISTRY

BY

MUHAMMAD AHMAD

DEPARTMENT OF CHEMISTRY

QUAID-I-AZAM UNIVERSITY

ISLAMABAD

2000

DECLARATION

This is to certify that the dissertation submitted by **Mr. Muhammad Ahmad** is accepted in its present form by the Department of Chemistry, Quaid-i-Azam University, Islamabad as satisfying the dissertation requirement for the degree of Master of Philosophy in chemistry (Analytical/Inorganic Chemistry).

1. Supervisor
   Dr. M.A. RAUF
   AssociateProfessor
   Department of Chemistry
   Quaid-i-Azam University
   Islamabad.

Athar Yaseen Khan

2. Chairman
   Dr. A.Y.Khan
   Department of Chemistry
   Quaid-i-Azam University
   Islamabad.

3. External Examiner

To

BHAI JAAN

to whom I owe so much

CONTENTS

CHAPTER-4 RESULTS AND DISCUSSION

ACKNOWLEDGEMENT

Scientific investigation can be very exacting. One has to accept that the journey, beginning with the choice of a topic and ending with a thesis, is to be completed largely through a with-drawl from cosy things in life. Such a tryst, voluntarily made with solitude, is not easy to bear. A researcher is lucky if he has access to sympathetic and concerned help from the more learned members of his profession, enjoys the solidarity of his peers, the love of his friends and dear-ones, and possesses some amount of personal eccentricity and perseverance. All these factors contribute to the final out come.

I find myself in debt in many directions, and a bit surprised at my own elements of constancy. Thanks are due first of all to my supervisor, **Dr. M.A. Rauf** , whose guidance has been crucial in the completion of this research and **Dr. A. Y. Khan**, chairman department of chemistry Q. A. U. Islamabad, for providing me Lab. Facilities.

My mother has always believed in what ever I have done. Such faith one can summon only from a mother. However sweet memories of my late father have always been other source of warmth and tremendous moral support. With the help of these, lonely research has been less excruciating. I am truly indebted to them.

I wish to express my deepest appreciation to my chum, Mr. Abdul Jabbar, who has at various stages supported my research and was always willing to help in his full capacity. My gratitude goes to Miss. Sadaf Yaqoob who helped in materializing the manuscript. Thanks to my younger brothers Afzaal & Saeed who remained very cordial to me and a source of joy to soothe my tired mind in carrying out my research.

Finally I am thank full to my friends, specially Mr.Shoaib Ali and Mr.Sajid Manzoor at Q.A.U. for their co-operation and chare-full company during my research work.

(MUHAMMAD AHMAD)

ABSTRACT

The present work deals with the specrophotometric complexation studies of VO(II), Mn(II), Fe(III), Pb(II) and Bi(III) with ortho phenanthroline(o-Phen.) as primary and Eosin as secondary ligand. The spectra of these complexes were recorded under optimized pH conditions. The wavelength of maximun absorbance for these complexes were 550nm, 560nm,555nm,558nm and 552nm respectively. The stoichiometries of these complexes were determined by applying Job's method. It was found that Metal:o-phen.:Eosin ratios were 1:1:1, 1:2:1, 1:1:1, 1:2:1 and 1:2:1 respectively for these complexes.. The molar absorption coefficient for these complexes were 1.73×10^4L.mol^{-1}.cm^{-1}1.95×10^4L.mol^{-1}.cm^{-1}, 2.8×10^4L.mol^{-1}.cm^{-1}, 2.05×10^4L.mol^{-1}.cm^{-1}, and 1.92×10^4L.mol^{-1}.cm^{-1}. The stability constants were also determined and log of stability constants were 5.94, 5.77, 6.11, 6.93 and 6.93 respectively. The effect of time and temperature on these complexes was also studied. The effect of diverse ions on the intensity of these complexes was also investigated and the percentage decrease or increase in intensity along with the limiting concentration of these ions was determined. Calibration graphs were plotted to find out the range up to which these complexes obey the Beer's Law, a straight line was observed over the range 3-12 ppm, 0.4-2 ppm, 0.5-2 ppm, 0.5-2 ppm, and 0.4-4 ppm for these complexes respectively.

CHAPTER-1

INTRODUCTION

CHAPTER -1

INTRODUCTION

In reaction with organic reagents, metal ions are generally transformed into coloured complexes or mixed complexes[1].The formation of stable metal complexes requires the presence of the acidic or basic analytical functional groups in the molecules of the reagent, preferably on those positions which allow the formation of five or six membered chelate ring. The most important group of reactions to be considered are those in which complexes are formed between hydrated metal ions and organic molecule or ions, usually through co-ordination of one or more atoms of oxygen, nitrogen or sulphur. Such complex formation is important in analytical chemistry in two ways. Firstly it may produce a species that has more useful characteristics for identification or estimation; and secondly, the concentration of the particular cation can be reduced to a level below those at which they interfere in reaction designed to separate, or other wise characterize, other molecules or ion.

Metal ions in aqueous solution complex themselves because they orient the water molecule immediately surrounding the leading, especially in the transition and higher valent metal ions, to form complexes such as $[Al(H_2O)_6]^{+3}$ and $[Cr(H_2O)_6]^{+3}$. This is a consequence of the dipole moment of the water molecules, leading to the special orientation of the ionic charge on the metal ions. So, complex formation in the solution is a replacement process in which one or more solvent molecules surrounding anions are replaced by other ions of molecule, to give species which usually have very different physical and chemical properties. Rates of exchange of water bounded to metal ions show wide variation, ranging from exchange time of very much less than milliseconds to a half-life measured in days. The species with which a metal ion reacts to form a complex is known as ligand. In most of the cases, formation and dissociation of complex proceeds rapidly by a succession of equilibrium reaction. Because of these stepwise equilibrium, a series of complexes may co-exist in the solution.

The metal cations which absorbs weakly or not at all in the visible spectral region can be changed into strongly coloured compounds by means of complexing agents. Strongly coloured here means that absorption bands, characteristic of the complex have an extension coefficient greater than10^4L.mol^{-1}cm^{-1}.Some complexing agents have proven to be extremely suitable, and these include dithiazone,8-Hydroxy quinoline, 2.2-Pyridoyl and 1,10-Phenanthroline. The colour reaction depends upon the chosen reagent, and oxidation number of the metal ion and in many cases, also upon the pH value of the solution and the most important, the stability constant of the complex. This is extremely important because weaker complexes can be converted to more stable ones by recomplexing with other metal ions and therefore, they can no longer react with first reagent.

Some dyes also act as ligands. Azo dyes are representative of the organic compounds which chelates with metal ions[2]. Frequently, we can trace the effectiveness of the dyes back to the formation of anion association complex between a metal ion already complexed with one or several dye molecules. This complex can be extracted from the aqueous solution with organic solvent and measured photometrically.

Rhodamine-B was the first basic dye to be used for this extraction spectrophotometry. It forms an ion pair with [$SbCl_6$] in acidic solution (6N HCl) at a ratio of 1:1 and this complex was extracted with benzene[3,4].Further examples are the ion association of the methyl violet with fluorotantalate[5], of dodecamolybdato phosphoric acid with Safranin[6] or crystal violet[7] and tetrafluoroborate with methylene blue[8] or monomethyl thionin[9].These ions associate with the acidic or basic dyes, generally have very high molar absorption coefficient since several molecules can be present in the complex. On account of the demand for greater sensitivity and resulting in the lowering in the detection limit up to ppb level, numerous investigations of extraction spectroscopy have been carried out in recent years.

It has been found that if fluorescein compounds are present as counter anions with a metal complex, the molar absorption coefficient is increased and UV-Visible spectrophotometer and spectrofluorimeter can study this association complex. Considerable work has been done on the formation of association complexes(Ternary or Mixed Ligand Complexes) using fluorescein compounds as counter anions. The analytical applications of ternary complexes of some transition and rare earth elements have been investigated[10-13].

Beiley[10] developed a sensitive spectrofluorimetric method for determination of copper(II) in the range 1-6×10^{-7}g, utilizing the ternary complex system. He used 2,9-dimethyl o-Phenanthrolein as a primary ligand and Rose Bengal Extra as a secondary ligand. The complex was extracted in chloroform, diluted with the ammonical acetone and its fluorescence was measured at 570nm with excitation at 560nm.The complex was stable for many days.

Dagnell[14] used the spectrophotometric technique for the determination of the palladium(II) ion in both aqueous and organic phase. The method was based upon the ternary complex formation with pyridine, and Rose Bengal. The molar absorptivities were 5×10^{4} L $mol^{-1}cm^{-1}$(aqueous) and 1.25×10^{5} L $mol^{-1}cm^{-1}$(organic) in the presence of one thousands folds EDTA as masking agent. Under these conditions there was negligible interference with pyridine Rose Bengal system for most of cations. Both colour reactions took place within fifteen minutes and complexes were stable for long periods.

Idriss[15] studied the reaction of Selenium(IV) with alizarin maroon(AZM) as a primary ligand and eosin as secondary ligand spectrophotometrically. The solution spectrum of mixed ligand complex formed was characterized by an absorption band with maximum absorbance at 560nm within the pH range of 6.5-7.2. The pink

$Se(AZM)_2$-$(Eosin)_2$ association complex conformed to Beer's Law over the concentration range of 0.16 to 2μgmL^{-1} of selenium with molar absorption coefficient value of 2.5×10^4L.mol^{-1}.cm^{-1}.

Mercury forms ternary complex with 1,10-Phenanthrolein as primary and eosin as secondary ligand[16]. The reaction occurs at pH 4.5. Ternary complex formed was indicated by the appearance of absorption spectra with maximum absorbance at 552nm. The interaction between mercury and the reagent produced a bathochromic shift. The stoichiometry of the complex was $[Hg(o\text{-}Phen)_2]E$ where E represents the divalent eosin anion. The formation constant of the complex was 4.7×10^3.Effects of different anions and cations were also studied. The validity of the method was checked by analyzing factory effluent containing mercury by standard addition method and good agreement was observed with the other techniques.

Mori[17] who developed a spectrophotometric method for the determination of monocycline by using gallium and eosin further extended the application of the ternary complexes. Monocycline is a derivative of tetracycline (TC) and this group of compounds is a bacteriosatic antibiotic. The colour reaction of eosin as a dye, gallium as the metal ion and monocycline as a TC derivative was studied. Under optimum conditions, monocycline was determined in the range of 1-40μg /10mL in solution and maximum absorbance was observed at 545nm.The molar absorption coefficient of the complex was1.1×10^5 L.mol^{-1}.cm^{-1}. The molar ratio of gallium to eosin was 1:3 evaluated by Job's method. The reaction was completed within ten minutes and the complex was stable for two hours. Additionally this method was applied for the determination of the monocycline in a pharmaceutical preparation and results were found comparable to the other methods.

It is apparent from the preceding discussion that ternary complexes of eosin can be studied by spectrophotometric and spectrofluoremetric methods. Due to high molar absorption coefficient, detection limit of complexing metal is increased and trace metal analyses can be carried out successfully.

The present work aims at the study of complexation of o-Phenanthroline (o-Phen.) as a primary ligand and eosin as a secondary ligand with metal ions namely VO^{+2}, Mn^{+2}, Fe^{+3}, Pb^{+2} and Bi^{+3}. Formation of the complex is indicated by the appearance of absorption spectra in the visible region. Attempt was made to optimize the conditions of the complexation with respect to metal, primary and secondary ligand concentrations, pH of the solution, stability of the complex and effect of interfering ions on the complex. The data was used to find out metal to ligand ratio, concentration of the complex formed and stability constants of the complexes formed. The range up to which Beer's law was obeyed by the complexes for the metal ions, was also investigated.

CHAPTER-2

THEORETICAL BACKGROUND

CHAPTER-2

THEORETICAL BACKGROUND

A complex is a compound that contains a central atom or ion, usually a metal, surrounded by a cluster of ions or molecules. The complex tends to retain its identity even in solution although partial dissociation may occur. The surrounding ions and molecules are called ligands. If a ligand occupy only one co-ordination position, it is called as monodentate like ammonia, while ligands like acetylacetone and ethylene diamine which can occupy two co-ordinating position of the metal atom are called as bidentate and compounds formed are referred to as chelate compounds. Multidentate ligands like ethylene diamine tetra acetate(EDTA) are also well known. In general, metal ion tends to achieve the highest co-ordination number. The transition metal ions of first series are rather small and highest co-ordination number is normally six. For second and third transition metals, co-ordination number is six to eight. If the ligands are bulky, co-ordination number may be low.

In complex formation, each molecule or atom donates a pair of electrons to the empty orbital of central atom thus forming a co-ordinate covalent bond. Total charge on the complex ion is a resultant of charge on metal ion and co-ordinate groups. Thus, ligands surrounding the central atom are arranged in definite patterns in space. The compound with co-ordination number four, has three principal symmetries e.g. tetrahedral (Td), C_4V and C_2V. Those with co-ordination number six have octahedral (Oh) symmetry.

Three theories have been put forward to describe the nature of bonding in metal complexes.

1. Valance bond theory (V.B.T.)considers the metal ligand bond to be covalent in nature. It further explains the structure and magnetic properties of metal complexes[18].
2. The electrostatic crystal field theory (C.F.T.) assumes the metal ligand bond to be ionic and explains the colour and magnetic properties of metal complexes[19].

3. The molecular orbital theory (M.O.T.)accepts the importance of both ionic and covalent bonds, though it does not specifically mention either[20].

2.1 Factors Affecting Complex Stability:

The nature of metal ion and the nature of ligand influence the stability of metal complexes in many way:

2.1.1 Nature of metal ion.

a) Size and Charge of Metal ions

Under the influence of electrostatic force, smaller the size and the larger the charge on a metal ion, more stable the complex will be. So the stability order for the metal ions with increasing charge would be:

$Pt^{+4} > Fe^{+3} > Fe^{+2} > Cu^{+2}$

Whereas in accordance with lrvin rule[21,22], the stability order for the same charge value is

$Mn^{+2} < Fe^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} < Zn^{+2}$

The stability order increases from Mn^{+2} to Cu^{+2} due to regular increase in atomic radii but there is an abrupt decrease in stability at Zn^{+2} due to sudden increase in atomic radius of Zn^{+2}. Finally one can say that stability follows a large charge to radius ratio of a metal ion.

b) Class 'a' and Class 'b' Metal ions

The more electropositive metals like alkali earth metals and the transition metals belong to class 'a'. They form their most stable complexes with neutral ligands containing N,O and S. The less electropositive metals like Pt, Pd, Hg, Pb and Rh etc. are in class 'b' metals. They are characterized by the presence of extra electrons beyond inert gas core and prefer the ligands in which donor atom is one of the heavier element in the N, O, F families[23]. It is believed that the stability of class b metal complexes results from an important covalent contribution to metal ligand bond and from of electron density from metal to ligand via pi(π) bonding.

c) ***Crystal field Effects:***

The conversion of the five degenerate d-orbitls of free metal ion into groups of d- orbitals having different energies on complexation is called crystal field splitting and energy difference between the two levels is called crystal field stabilization energy (CFSE). The CFSE plays an important role in transition metal complexes. The size of crystal field splitting is strongly affected by the oxidation state of metal ion and the type of d electrons present. The crystal field splitting will be higher for higher oxidation states of the metal ions e.g. the complex $[Co(NH_3)_6]^{+3}$ is a low spin whereas $[Co(NH_3)_6]^{+2}$ is a high spin complex. The CFSE is larger for Co^{+3} because the approach of ligand to a small, higher charged metal ion is more close, resulting in strong interaction with its d orbitals.

2.1.2 Nature of the Ligand.

a) *Strength of ligand*

Greater the base strength of ligand, more the tendency it has to form a stable complex. The ligand that bind H^+ firmly, also form stable complexes with metal ions e.g. F^{-1} forms more stable complexes than Cl^{-1}, Br^{-1}, or I^{-1}.

b) *Chelate Effect*

If a ligand contains more than one-donor atoms, then it can co-ordinate to more than one position on the metal ion, resulting in a ring formation. This ring formation is called chelation, which enhances the stability of the complex. This gain in stability, due to chelation is called chelate effect. Extra stability of chelate complexes is confirmed by the relatively higher values of formation and their resistance to substitution.

Treatment of the ammonia complexes with ethylene diamine results in the displacement of ammonia.

$$[Cu(NH_3)_4]^{+2} + 2en \rightarrow [Cu(en)_2]^{+2} + 4NH_3$$

The metal nitrogen bond in ethylene diamine complex is not different in character from that of ammonia complex. The enthalpy change (ΔH), in the formation of $[M(NH_3)_4]^{+2}$ in principle, should be the same[24-25] as that in the form of $[M(en)_2]^{+2}$ but the stabilities of these complexes are different. The increase in stability of $[Cu(en)_2]^{+2}$ can be explained on the basis of entropy changes accompanied in going from reactants in the above system. Reactants (three particle system) have low entropy as compared to product (five particle system). This increase in entropy is responsible for increase in stability of $[Cu(en)_2]^{+2}$. In this example of bidentate ligand complex, the entropy term result in forty percent of the free energy change whereas in monodentate ligand complexes the entropy is often lower and can be neglected.

The chelate effect varies with the size of ring formed on co-ordinates. Five membered ring complexes are considered to be most stable ones. As the ring member increases,the stability rapidly falls. For example in $[Cu(en)_2]^{+2}$, if ethylene diamine is replaced by 1,3-propanediamine, which froms a six membered ring complex; 3.9 K cal/mole of free energy of formation is lost, resulting in decrease of stability. Seven and eight membered ring chelates are not stable[26]. Less than five membered chelate complexes are not common. In these complexes, stability decreases because of ring strain which makes enthalpy more positive. Ring strain is even observed in five and six membered rings. Here, the ring strain is due to the fact that both acceptor atoms like linear arrangements[27], and only a very long chain can form strain free bridge between two co-ordination positions, so silver and mercury complexes are usually not stabilized by chelate effect.

c) ***Steric hindrance:***

The stability of a complex is effected by steric strain in multidentate ligands.When bulky groups are present on the metal ion they repel each other thus destabilizing the system e.g. ethylene diamine form more stable complexes than its tetramethyl derivative. As due to the electron donation by the nitrogen atoms, the metal brings methyl groups close enough.

2.2 The Ligands

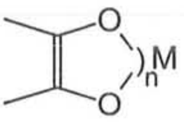
The species with which metal ion reacts to form a complex is called ligand. The most important requirement of the molecule to act as a ligand is the presence of at least one lone pair of electrons which must be easily available to metal atom for the formation of co-ordinate covalent bond. Ligand may be neutral or anionic in nature. In reactions with organic ligands, metal ions are generally transformed into coloured complexes.

2.2.1 Types of Ligands

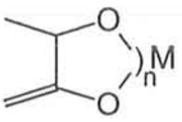
Ligands here are categorized according to their donor atoms. Generally oxygen(O), Nitrogen(N) and sulphur(S) atoms acts as donor atoms. Following are the important families of ligands:

a) *Ligand with donor atoms O, O*

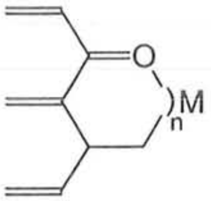
Some examples of organic reagents of this types are, Tiron, pyrocetecol violet, derivatives of Alizarine, Fluorone and dye stuff e.g. Eriochrome cyanin R. These ligands form coloured chelates with transition metals like Iron(II), Iron(III), Titanium(II) ,and Vanadium(IV) etc. to give mainly the following structures:



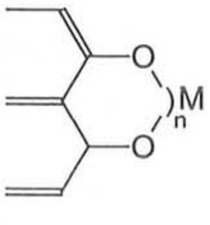
(a)



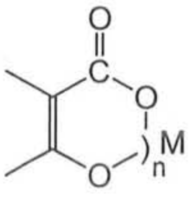
(b)



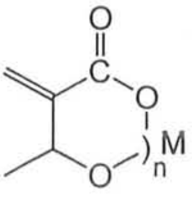
(c)



(d)



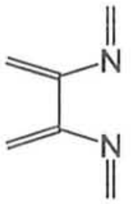
(e)



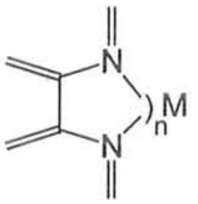
(f)

b) ***Ligand with donor atoms N, N and N, O***

These ligands are often employed as metallochromic reagents. Aromatic nitrogen bases , such as 1, 10 Phenanthrolein, 2, 2-bipyridyl and their derivatives, which possess the functional group (n), are mainly used for the determination of Fe(II) and Cu(II) with these metals. They gives red or yellow cationic complexes[28-31] of the structure(m).



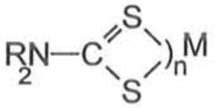
(n)



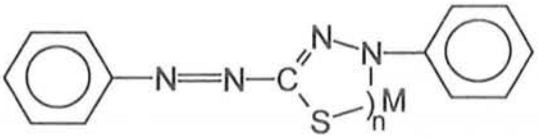
(m)

c) ***Ligand with donor atoms S,S or S, N***

These ligands containing thionic or thiolic groups are examplified by dithiocarbamates, dithiazone, dithiol, with very heavy metals which can yield insoluble sulphides. The complexes of dithiocarbamate[32] can be presented by the general formula(A) and structure of the dithiazonates[33] is given the formula(B).



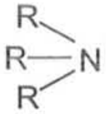
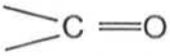
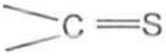
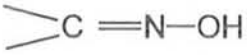
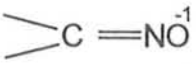
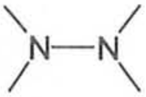
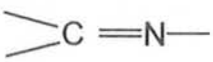
(A)



(B)

The main types of reactive groups are given in table 2.1 with chelating agents with which they occur.

TABLE 2.1

Group	*Examples*
	a, a′, Bipyridine, 4-Hydroxybenzothiazole, 8-Hydroxyquinoline PAN, o-Phenanthroline, Picolinic Acid, Quinalic Acid.
$—O^{-1}$	Acetylacetone, Alizarine, Chloroanilic Acid, Cupferon, Eriochrome Black-T,8-HydroxyquinolineMorin,Murexide, Nitroso-R-Salt, PAN Pyrocatecol, Rhodazonic Acid, Tiron
$—S—$	4-Chloro, 1,2 dimarceptobenzene, diphenyl Thiocarbazone diThiole, Mercepto Benzothiazole, Rubenic Acid, Thiohalide.
$—CO_2^{-1}$	Aliuminon, Anthranilic Acid, EDTA, Glycine, Mandelic Acid Quinaidic Acid, Salicylic Acid.
$—CS_2^{-1}$	Sodium diethyl dithiocarbamate, Zinc dibenzyl dithiocarbamate.
	Acetylacetone, Alizarine, Aluminon, chloro Anilinic Acid, Kojic Acid, Morin, Rhodizonic Acid.
	Thiourea
	Dimethyl Glyoxime, a-furildioxim, Salicyladoxim.
$—N=O$	Cupfurom, a- nitroso-b-naphthol, nitroso-R-salt.
	a-benzoinoxime, dimethyl Glyoxime, a-furildioxime, Nioxime.
	Diphenyl Carbazone, diphenyl Thiocarbazone.
$—N=N—$	Diphenyl Carbazone, diphenyl thio Carbazazone, Eriochrome Black-T, PAN,SPADNS.
	Glyoxal-bis(2-hydroxyanil), Mureoxide.

—OH	a-benzoinoxime, Mandelic Acid.
—NH_2	Anthranilic Acid, ethylene diamine, Glycine, tri amino tri ethy Amine, tri ethylene tetra Amine.
>NH	Thionalide, tri ethylene tetra amine.
>N	Thionalide, tri ethylene tetra amine.
—AsO_3	Arsonic Acids.

2.2.2 Complexing behavior of the Ligands

The formation of stable metal complexes requires the presence of the acidic or basic analytical functional groups in the molecule of the ligand preferably in the positions, which allow the formation of five or six member chelate ring.

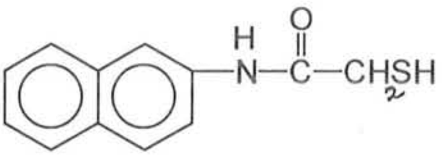
The organic reagents (Ligands) used in chemical analysis are those carbon containing substances which, by some sort of interaction, enables other ions or molecules to be detected or determined. Such organic reagents find many important applications in analytical chemistry of inorganic species[34-37].

The complex forming ability of a ligand is limited by the requirement that the atoms bounded to the metal ion with the complex must be able to donate a pair of electrons to a central metal ion. In practice, this almost restricts the choice to N, O, and S atoms. Nitrogen may be present as *primary, secondary* or *tertiary* amines, nitro, nitroso, azo, diazo, nitrile or acid amide group. Oxygen may co-ordinate as phenolate, carboxylate ion(neutral), alcoholic, ether or as carbonyls of ketones, aldehydes and carboxyl groups. Similarly sulphur may form a bond in ionized thiol and thiocarboxylate anions, thioethers, thioketones and through disulphide groups.

The functional groups differ in their relative complexing ability with different metal ions. e.g. The difference between stability constants of the ethylenediamine complexes of Cu(II) and Zn(II) is much greater than for the corresponding oxalato complexes but these differences are of degree rather than of kind so that reagents are rarely specific.

The transition metal ion forms more stable complexes with ligands containing polarizable positions such as amino groups and heterocyclic nitrogen atoms. There is some overlap in properties between the ions and to the right of transition metal series and earliest of these with filled d orbital, so that ethylenediamine also forms strong complexes with zinc, cadmium and mercury.

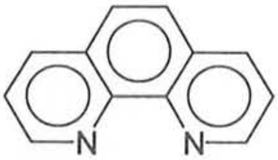
The metals having filled d-orbitals also prefers highly polarizable ligands, especially if the ligand has suitable vacant orbitals to which some of the d electrons can be 'back donated'. This condition favours the sulphur containing ligands(C).



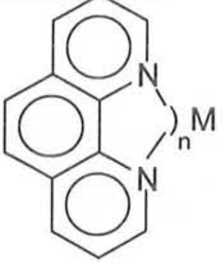
(C)

It must be emphasized, however that these conditions indicates, the broader line the preferred types of ligands for particular class of metal ions , they are by no means exclusive. Instead, all ligands might be expected to interact with all metal ions, to an extent that depends largely upon the nature of the donor groups on the ligands.

In the present work ternary complexes of eosin are prepared by using o-Phenanthroline(o-Phen) as primary ligand. o-Phen is a good complexing agent. It forms complexes with many metal ions. Quantitative analysis of Fe(II) in the metal ore is conducted by using o-Phen as complexing agent[38]. It has heterocyclic condensed ring structure(D) forming complex with metal ions (E) by two nitrogen atoms in a position to act as bidentate ligand and forming a five membered ring with metal ion.

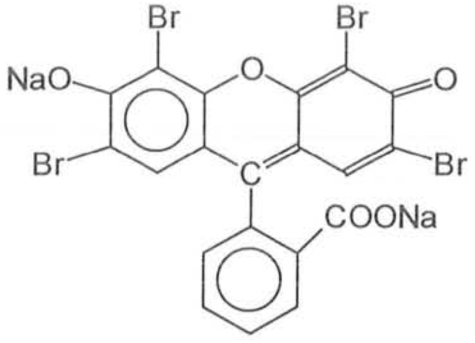


(D)



(E)

Eosin is used as a secondary ligand. It is a disodium salt of 2,4,5,7-tetrabromofluorescein (F) and can be prepared by the bromination of fluorescein in aqueous sodium hydroxide[39]. It is a water-soluble dye and its dilute solution gives green fluorescene. It dyes wool and silk giving yellowish red fluorescen.



(F)

Eosin itself is used as fluorescent indicator for the titration of opaque, highly turbid and deeply coloured solutions[40]. It also has ability to form a complex as counter anions with cationic metal complexes[11-13]. These are coloured complexes with high molar absorption coefficient ($\approx 10^5$L $mol^{-1}cm^{-1}$) in the visible region. So this complex can be studied spectrophotometrically[16] and due to fluorescent nature spectrofluorimetrically[10].

2.3 Types of Ultravoilet and Visible Spectra of Complexes

Three types of transitions which give rise to ultravoilet and visible spectra in metal complexes can be described, although in any particular case it may not be possible to distinguish clearly between them. They are ;

a) Excitations within the transition metal ion, generally associated within states of a d and n configuration, and refer to as d-d transition. Similarly, in rare earth f-f transition can occur.

b) Excitations within the ligand .

c) Charge transfer transitions, involving the transfer of an electron from being mainly on the metal to being mainly on the ligand or vice versa.

a) d-d Transitions

The d-d transitions produce bands in the visible, near ultraviolet, or near infra red regions, with molar extinction coefficients ranging from about 0.1 to 100 L $mol^{-1}cm^{-1}$ and are responsible for the colours of the transition metal complex ions. Although they are the best understood spectra of metal complexes[41], their intensities are too low for them to have much analytical applications. They have their origin in transitions of electrons between filled d-orbital in empty or only half filled d-orbital which differ in energy because of the orientation of the ligand about the central metal ion. Replacement of water molecule in the coordination shell of a metal ion by molecule of an other ligand alters the ligand field strength, also moves the d-d transition band to the longer or shorter wavelengths, depending on whether the new crystal field stabilization energy is smaller or greater than water. This explains why the spectrochemical series which places ligands in order of increasing field strength for one central metal ion, can be used with confidence to predict the direction and relative amounts of wavelength shifts, when complexes containing other ligands are compared with aquo ions.

b) Electronic Excitation with in the ligand

The absorption of ultraviolet or visible radiation by some species M can be considered to be a two step process, the first step of which involves excitation as shown by the equation

$$M + h\nu \rightarrow M^*$$

Where M* represents the atomic or molecular particle in the electronically excited state resulting from absorption of a photon (hν). The life time of the excited state is short (10^{-8} to 10^{-9} s), its existence being terminated by several relaxation processes[42]. Three types of electronic transitions in the ions of absorbing species are involved, namely pi(π), sigma (σ) or non-bonding(n) electrons.

The double bond in an organic molecule contains two types of molecular orbital : a sigma orbital corresponding to one pair of the bonding electrons; and a pi (π) molecular orbital associated with the other pair. Pi (π) orbital are formed by the parallel overlap of atomic p orbital.

In addition to sigma (σ) and pi (π) electrons, many organic compounds contains non-bonding electrons. These unshared electrons are designated by the symbol n.

c) Charge transfer

They arise when the absorption of radiation causes an electronic transition between two orbital in such a manner that the electron in one of the orbital is more heavily concentrated on one atom and in the other it is mainly located on a different atom. Three general types of charge transfer transitions, which give rise to absorption in the ultraviolet and visible regions, have been suggested.

(1) Electrons from the sigma bonding orbitals may be excited to empty t_2g or eg anti bonding orbitals. In both cases there is a net transfer of charge from the ligand to metal. The important properties are the oxidizing character of the central metal ion and the

existence of a partially filled electron shell. The reaction is essentially a photochemical oxidation-reduction process.

(2) Electrons in filled pi orbitals that are localized mainly on the ligand may be excited into the anti-bonding orbitals formed by combining ligand orbitals with the s, p or d-orbital on the metal. This transition again involves transfer from ligand to metal.

(3) Electron from bonding sigma orbital may be excited into vacant orbitals which are localized largely on the ligands. Charge transfer spectra of purely organic molecular complexes are also well known; such spectra can also arise in inorganic solvents containing non metallic inorganic species.

2.4 The Physical basis of colour

Visible light represents a very small part of the electromagnetic spectrum, and corresponds to radiations roughly within the wavelength range of 380-780nm. Sun light covers this range and extends into the ultraviolet region (380 nm), but its composition varies with the season, time of day and climatic conditions. The light from artificial light source is normally white, it varies widely according to the type of lamp. There is a deficiency of blue light in the emission of a tungsten lamp and of red in that of simple discharge lamps. Correction is possible by using filters to absorb the excess of red or blue, but this results in great loss of efficiency. In mercury vapour lamps, the red deficiency can be largely overcome by introducing fluorescent powders within the discharge tube which absorb very short wavelengths and emit light of greater wavelength, so that a good approximation to daylight results. The human eye is able to assess colours with some allowance for the deficiencies of artificial light. So that a white object is recognized as such even when seen in yellowish light.

The absorption of light by coloured substances is due to electronic transitions between different orbitals within the molecule, and the wavelengths absorbed are determined by energy differences between the orbitals. Every dye or pigment therefore, exhibits a pattern of absorption arising from its chemical structure, and this may be represented by an absorption spectrum consisting of a graph in which the degree of the absorption is plotted as ordinate against wavelength (or frequency) as abscissa. This graph is characteristic of a colouring matter, and may be used for identification purposes. Since at a given wavelength the radiation transmitted is the difference between the incident radiation and that absorbed, the curve can be used equally well as a measure of absorption. Absorption spectra are normally determined from samples in solution. Dyed fibers and pigments in paints or other media absorb light in a characteristic pattern, and the unabsorbed light is mainly reflected rather than transmitted; in such cases, however, the physical form of the particles of colouring matter and substrate effect the nature of the reflected light.

The absorption spectrum of a dye may be complex, and the purity of the colour observed depends on the shape of the curve. Bright colours are the result of the narrow absorption bands with sharp peaks, and dullness is associated with broader bands lacking sharpness. Non-spectral colours such as brown are associated with absorption spread evenly over a wide wavelength range, and black is the result of absorption through the visible spectrum.

Many substances absorb radiation of wavelengths above and below the visible range, and the fact that such absorption does not give rise to a coloured appearance is due to the limited sensitivity of the eye rather than to any difference in principle. It is doubtful whether any significant improvement in vision would result from an extension of this sensitivity since radiations in the infra-red and ultraviolet regions are strongly absorbed by many materials.

In every day life coloured materials are often described in loose terms, and at this point it will be well to set out the terms used by colour chemists. The characteristics of a coloured surface may be defined in respect of hue, brightness and strength. Its hue is determined by the predominant wavelength or wavelengths of the reflected light, described as yellow, red, blue, etc. Within each band, hue varies with wavelength, moving towards that of the next band in each direction; thus a blue colour becomes greenish as the wavelength is increased or reddish as it is decreased. It is said that about 150 different hues can be distinguished within the spectrum. Brightness may be regarded as a negative characteristic, as much as it depends on absence of reflected light other than of the hue concerned. Strength is inversely proportional to amount of white light reflected by the surface and serving as a diluent. Although the spectral hues move from violet to red as the wavelength rises from 400-750 nm, colour chemistry is concerned in practice, with reflected or transmitted light, and the effective spectral range therefore, consists of the complementary hues beginning with yellow and ending with green. Hues are said to increase in depth as they move from yellow towards green; thus blue is deeper than red, red than orange and orange than yellow. Any change in a dye molecule causing the hue to move towards green is said to produce a bathochromic effect, and the reverse is called hypsochromic effect. The is to be distinguished from a hyperchromic effect, which is an increase in the intensity of the absorption, that is, in the extinction coefficient of the absorption band, the reverse is a hypochromic effect.

2.5 Instrumental Techniques

Instrumental techniques applied on a system depend upon the characteristics of that system. The ternary complexes of eosin exhibit two important phenomena. *First* is the absorption of the light in visible region, *secondly* they are fluorescent in nature. On the bases of these physical properties two techniques can be employed to study these complexes.

a) Spectrophotometry.

b) Spectrofluorimetry.

a) Spectrophotometry

Spectrophotometry involves the measurement of absorption of radient energy by a chemical species as a function of wavelength of radiation or its measurement at a given wavelength. Spectrophotometric methods are generally rapid and adaptable for the determination of small concentrations of the species. It has also been used to study the complexing behavior of the metal ions[43,44].

UV-Visible spectrophotometer is an instrument that can measure the amount of ultraviolet and visible radiation absorbed by a solution at a given wavelength. The major components of spectrophotometer are source, monochromator, cell and detector.

Source: The most common source of radiation in spectrophotometer is tungsten lamp(350nm-750nm) in visible region. For ultraviolet region, deuterium discharge lamp(185nm-400nm) is preferred due to its stability.

Monochromator: Radiation passing through a entrance slit, enters the monochromator. The key element of the monochromator is the dispersion device. Mostly prism and grating are used as monochromators.

Sample Cell: After leaving monochromator through an exit-slit, radiation in a narrow band strikes on absorbing liquid sample in a cell. It is a rectangular device with 1cm width, preferably composed of quartz material, which is transparent from 180nm to 1000nm.

Detector: The unabsorbed part of the radiation, after passing through the sample cell, impinges on the detector. It converts the radiation energy to electrical current or voltage, which can easily be measured. A photomultiplier tube, is generally used as a detector.

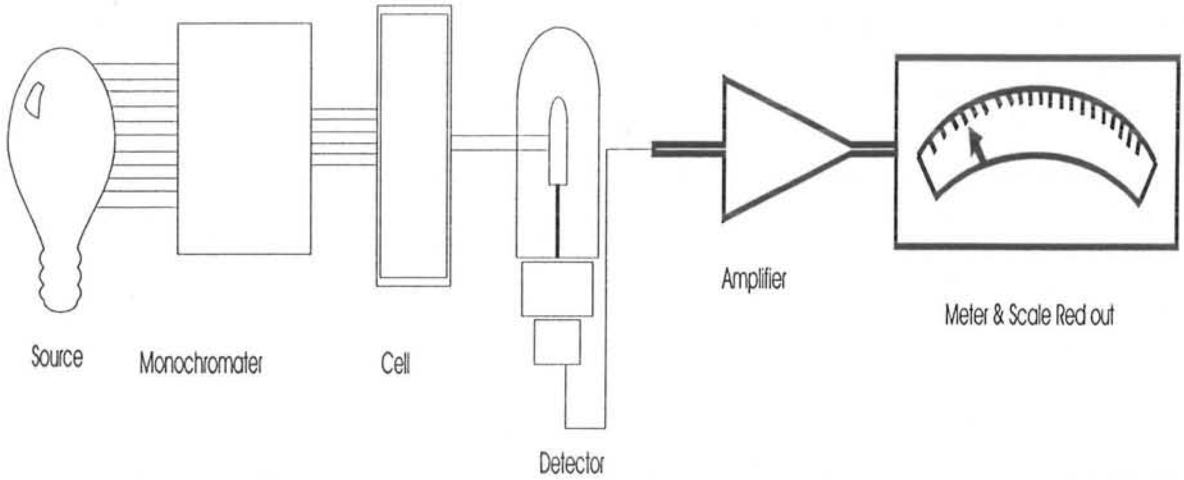


Fig.2.1 Schematic diagram of UV-Visible spectrophotometer.

b) Spectrofluorimetry

Spectrofluorimetry is concerned with the measurement of the intensity of the fluorescence emitted by a species that has absorbed incident radiation. The fluorescence is emitted in all directions and is of longer wavelength than absorbed radiation. Excitation radiation in fluorescence is usually ultraviolet radiation, occasionally visible radiation is also used.

Spectrofluorometer is used to obtain a fluorescence spectrum, just as absorption spectrum is obtained by spectrophotometer. In spectrofluorometer, Mercury or Xenon arc lamps are used as source of radiation. Most of the exciting radiations passes through the sample cell without being absorbed. The absorbed radiation causes the sample to fluoresce in all directions, but the detector only measures the emission that passes through the slit through secondary fluorescence grating.

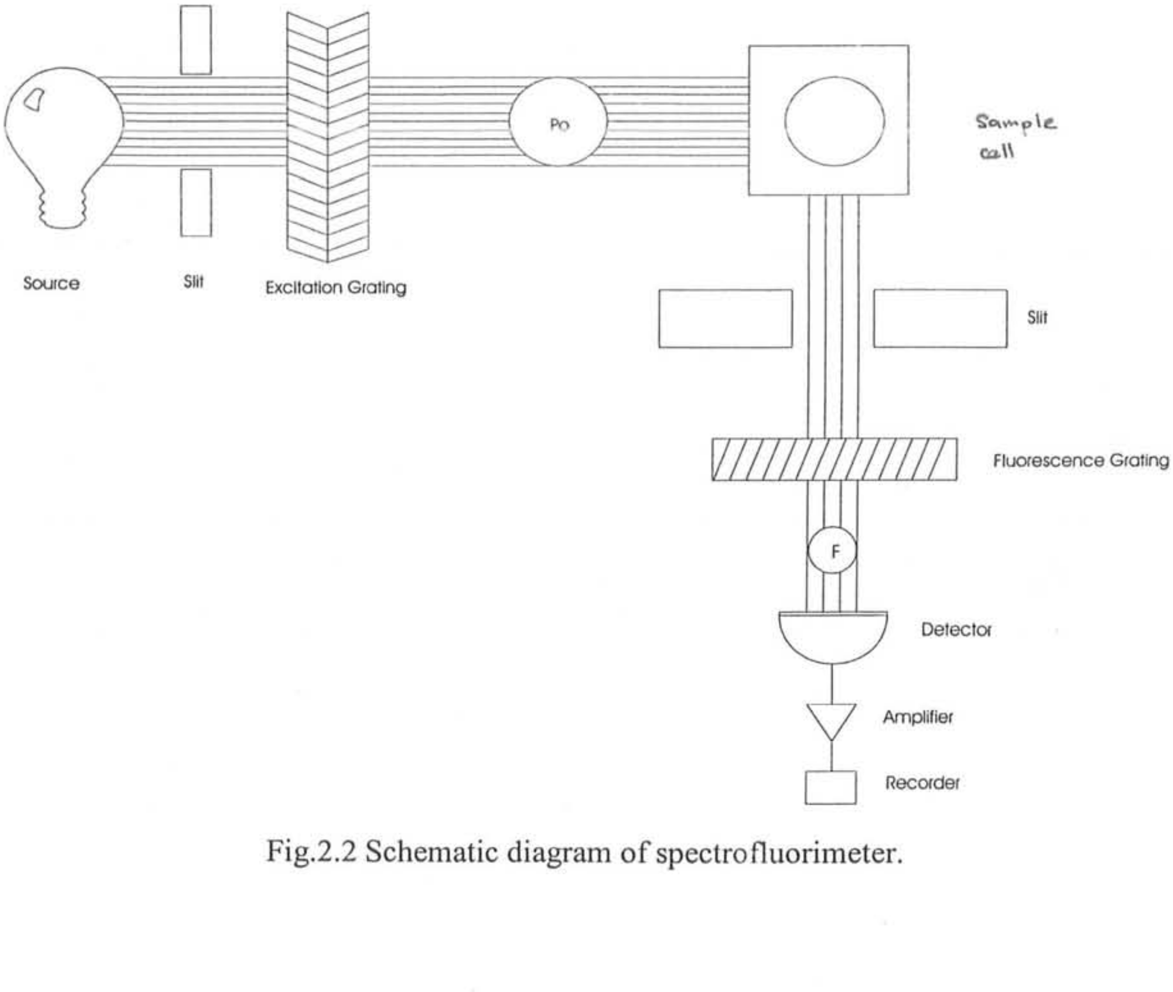


Fig.2.2 Schematic diagram of spectrofluorimeter.

CHAPTER-3
EXPERIMENTAL

CHAPTER-3

EXPERIMENTAL

3.1 Apparatus

SHIMADZU UV-120 spectrophotometer with 10mm matched quartz cell was used for absorption measurements of the solutions.

For pH studies of the solutions, Horiba pH meter was utilized.

Reagents

All the reagents were of analytical grade unless stated otherwise.

S.No.	*Name*	*Formula*	*Source*
1.	o- Phenanthroline	$C_{10}H_{10}O_2.H_2O$	BDH
2.	Eosin Yellow	$C_{20}H_6O_5Br_4Na_2$	BDH
3.	Vanadyl Sulphate	$VOSO_4.H_2O$	BDH
4.	Manganese Nitrate	$Mn(NO_3)_2.4H_2O$	E.Merck
5.	Ferric Nitrate	$Fe(NO_3)_3.9H_2O$	J.T.Baker
6.	Bismuth Nitrate	$Bi(NO_3)_3.5H_2O$	Fluka
7.	Lead Nitrate	$Pb(NO_3)_2$	BDH

3.2 Preparation of the Solutions

1) 1.5×10^{-3}M Eosin –Y

0.104g of eosin-Y was dissolved in 100mL of distilled water to produce a 1.5×10^{-3}M solution of Eosin Y.

2) 1.5×10^{-3}M o-Phenethroline

In order to prepare 1.5×10^{-3}M o-Phenethroline solution, 0.27g were dissolved in 1000mL of distilled water.

3) 1.5×10^{-3}M Vanadyl Sulphate

1.5×10^{-3}M solution of vanadyl sulphate was prepared by dissolving 0.2715g in 1000mL of distilled water.

4) 1.5×10^{-3}M Manganese Nitrate

An exactly weighed amount of 0.38g of manganese nitrate was dissolved in 1000mL of distilled water to prepare a 1.5×10^{-3}M manganese nitrate solution.

5) 1.5×10^{-3}M Ferric Nitrate

Dissolving 0.0606g in 100mL of distilled water produced a 1.5×10^{-3}M solution of ferric nitrate.

6) 1.5×10^{-3}M Bismuth Nitrate

The desired concentration of bismuth nitrate solution was prepared by dissolving 0.59g of bismuth nitrate in 1000mL of distilled water.

One drop of concentrated HNO_3 was added for complete dissolution.

7) 1.5×10^{-3}M Lead Nitrate

Dissolving 0.052g in 100mL of distilled water produced a 1.5×10^{-3}M solution of Ferric Nitrate.

8) 0.1%Gum acacia

0.1g of gum acacia was added in 100mL of warm distilled water. Fresh solution was prepared daily. It was added to the test and blank solutions before the addition of eosin to avoid the precipitation.

9) Solution of ions

Solution of diverse ions used for interference studies were prepared by dissolving the calculated amounts of each compound in distilled water in order to have 1-10 mg mL^{-1} of particular ion.

3.3 Buffer Solutions

Buffer solutions of different compositions were prepared from pH 1-10 as suggested in the literature[45-46]. Table 3.1 shows the preparation of the buffers with different composition.

TABLE 3.1

pH	*Buffer Composition*
1.0	25mL of 0.2M Pot. Chloride + 67mL of 0.2M Hydrochloric Acid.
2.0	25mL of 0.2M Pot. Chloride + 6.5mL of 0.2M Hydrochloric Acid..
3.0	198mL of 0.1M Acetic Acid + 12mL of 0.1M Sod. Acetate.
4.0	185mL of 0.1M Acetic Acid + 15mL of 0.1M Sod. Acetate.
4.5	164mL of 0.1M Acetic Acid + 36mL of 0.1M Sod. Acetate.
5.0	59mL of 0.1M Acetic Acid + 141mL of 0.1M Sod. Acetate.
5.5	19mL of 0.1M Acetic Acid + 181mL of 0.1M Sod. Acetate.
6.0	13mL of 0.1M Acetic Acid + 195mL of 0.1M Sod. Acetate.
7.0	50mL of 0.1M Pot. hydrogen phosphate + 29.1mL of 0.1M Sod. Hydroxide.
8.0	50mL of 0.1M Pot. hydrogen phosphate + 48.1mL of 0.1M Sod. Hydroxide.
9.0	50mL of 0.1M Pot. hydrogen phosphate + 60mL of 0.1M Sod. Hydroxide.
10	50mL of 0.025M Borax + 18.3mL of 0.1M Sod. Hydroxide.
11	50mL of 0.025M Sod. Bicarbonate + 22.7mL of 0.1M Sod. Hydroxide.
12	50mLof 0.025M di sod.hydrogephosphate +18.3mL of 0.1M Sod. Hydroxide.
13	25mL of 0.2M Pot.Chloride + 66mL of 0.2M Sod. Hydroxide.

*Pot.=Potassium

*Sod.=Sodium

3.4 Preparation of Metal Complexes with o-Phenanthroline and Eosin

1) Preparation of VO(II)-Complex

2.5mL of 1.5×10^{-3}M solution of VO^{+2} was taken in 100mL volumetric flask and 20mL of buffer solution of pH 6, 5mL of 1.5×10^{-3}M o-Phenanthroline and 5mL of 0.1% gum acia solution were added to it. The contents were mixed well and 5mL of the 1.5×10^{-3}M eosin solution was added and was again mixed thoroughly and diluted to 100mL. The reagent blank was prepared in the same way except the metal ion.

2) Preparation of Mn(II)-Complex

2.5mL of 1.5×10^{-3}M solution of Mn^{+2} was taken in 100mL of volumetric flask and 20mL of buffer solution of pH 5.5, 5mL of 1.5×10^{-3}M o-Phenanthroline and 5mL of 0.1% gum acia solution were added to it. The contents were mixed well and 5mL of the 1.5×10^{-3}M eosin solution was added and was again mixed thoroughly and diluted to 100mL. The reagent blank was prepared in the same way except the metal ion.

3) Preparation of Fe(III)-Complex

2.5mL of 1.5×10^{-3}M solution of Fe^{+3} was taken in 100mL of volumetric flask and 20mL of buffer solution of pH 5.5, 5mL of 1.5×10^{-3}M o-Phenanthroline and 5mL of 0.1% gum acia solution were added to it. The contents were mixed well and 5mL of the 1.5×10^{-3}M eosin solution was added and was again mixed thoroughly and diluted to 100mL. The reagent blank was prepared in the same way except the metal ion.

4) Preparation of Pb(II)-Complex

2.5mL of 1.5×10^{-3}M solution of Pb^{+2} was taken in 100mL of volumetric flask and 20mL of buffer solution of pH 4.5, 5mL of 1.5×10^{-3}M o-Phenanthroline and 5mL of 0.1% gum acia solution were added to it. The contents were mixed well and 5ml of the 1.5×10^{-3}M eosin solution was added and was again mixed thoroughly and diluted to 100mL. The reagent blank was prepared in the same way except the metal ion.

5) Preparation of Bi(III)-Complex

2.5mL of 1.5×10^{-3}M solution of Bi^{+3} was taken in 100mL of volumetric flask and 20mL of buffer solution of pH 5, 5mL of 1.5×10^{-3}M o-Phenanthroline and 5mL of 0.1% gum acia solution were added to it. The contents were mixed well and 5mL of the 1.5×10^{-3}M eosin solution was added and was again mixed thoroughly and diluted to 100mL. The reagent blank was prepared in the same way except the metal ion.

3.5 Absorption Spectrum of Eosin

Absorption spectrum of aqueous solution of pure eosin was recorded and is shown in Fig.(1.1)

3.6 Absorption Spectrum of Reagent blank

Absorption spectrum of eosin with o-Phenethroline was recorded by mixing equimolar amounts of both species and is shown in Fig. (1.4)

3.7 Effect of pH on the spectrum of eosin and reagent blank

The absorption spectra of the eosin and reagent blank were recorded at different pH to observe its effect Fig.(1.3,1.6).

3.8 Absorption Spectra of Metal ions

Absorption spectra of three metal ions(VO^{+2}, Mn^{+2} and Fe^{+3}) were studied in aqueous medium and are shown in Fig.(2.1,3.1,4.1)

Bi^{+3} and Pb^{+2} have no spectra in visible region.

3.9 Absorption Spectra of Metal Complexes

Absorption spectra of metal complexes were recorded by adjusting their pH in buffer solutions against the reagent blank and is shown in Fig.(2.2,3.2,4.2,5.2,6.2)

3.10 Optimization of pH

By using the buffer solutions of different compositions the pH of the complexes were optimized. Fig.(2.3,3.3,4.3,5.3,6.3)

3.11 Determination of Stoichiometry of the Complexes

Stoichiometry of the complexes was studied by *Job's method*[47-49]. First the relationship of mole fractions of metal *versus* o-Phenenthroline was studied by taking the eosin in excess and then metal *versus* eosin by taking o-Phenenthroline in excess. All these measurements were conducted against the reagent blank.

Fig.(2.4,3.4,4.4,5.4,6.4 & 2.5,3.5,4.5,5.5,6.5)

3.12 Time dependence studies

Time dependent studies of the complexes were conducted under optimum conditions of pH and mole fractions.

Figures(2.6,3.6,4.6,5.6,6.6)

3.13 Effect of Temperature

Effect of varying temperature was also studied on these complexes under optimum conditions of time, pH and mole fractions.

Fig.(2.7,3.7,4.7,5.7,6.7)

3.14 Diverse ion Effect

The effect of diverse ions on the complexes was also taken into account. Equimolar diverse ions were added to the solution with the metal and complex was developed. The interference of the diverse ion was studied by comparing the absorbance of the complex with and without diverse ion at λ_{max} of the complex. Limiting concentration of the diverse ions was determined by varying the concentration of these ions.

Fig.(2.8,3.8,4.8,5.8,6.8 & 2.9,3.9,4.9,5.9,6.9)

The limiting concentration and percentage effect in absorbance is shown in the Tables (4.1-4.10)

3.15 Determination of stability constant

By applying the continuous variation method, concentration, molar absorption coefficient and stability constants of the investigated complexes have been determined[50-55].

3.16 Calibration graphs

Adherence to Beer's law was checked by plotting calibration graphs, by varying the concentration of the metal ions and keeping the o-Phenanthroline and eosin in excess. The range was found up to which Beer's law was obeyed for each complex.

Fig. (2.10,3.10,4.10,5.10,6.10)

CHAPTER-4

RESULTS AND DISCUSSION

CHAPTER-4

RESULTS AND DISCUSSION

4.1 Eosin-Y

Eosin-Y is a disodium salt of 2,4,5,7 tetrabromo fluorescein (F). It is a water soluble dye and its dilute solution gives green fluorescence. It has chromophoric system with auxochromic groups. The absorption spectrum of eosin showed a maximum absorbance at 515nm in the aqueous medium (Fig.1.1). The pH of the solution had a pronounced effect on the intensity of the absorption band but the position of the absorption band remains unchanged (Fig.1.3). Absorbance of the solution of eosin increased up to pH 4 and beyond it, becomes almost constant (fig.1.2). It is probably due to presence of doubly charged eosinate anion above pH 4[56]. Due to this effect of pH, every measurement was recorded against a reagent blank, having pH very close to the sample solution.

There is no significant change in the absorption spectrum of eosin in the presence of o- Phen~~e~~anthroline (Fig.1.4), indicating that there is no direct effect of o-Phenanthroline on the absorption spectrum of eosin. The visible spectrum of a mixture containing eosin and metal ions under investigation exhibited no absorption when the solution was scanned *versus* eosin. It shows that there is no complexation between metal ion and eosin.

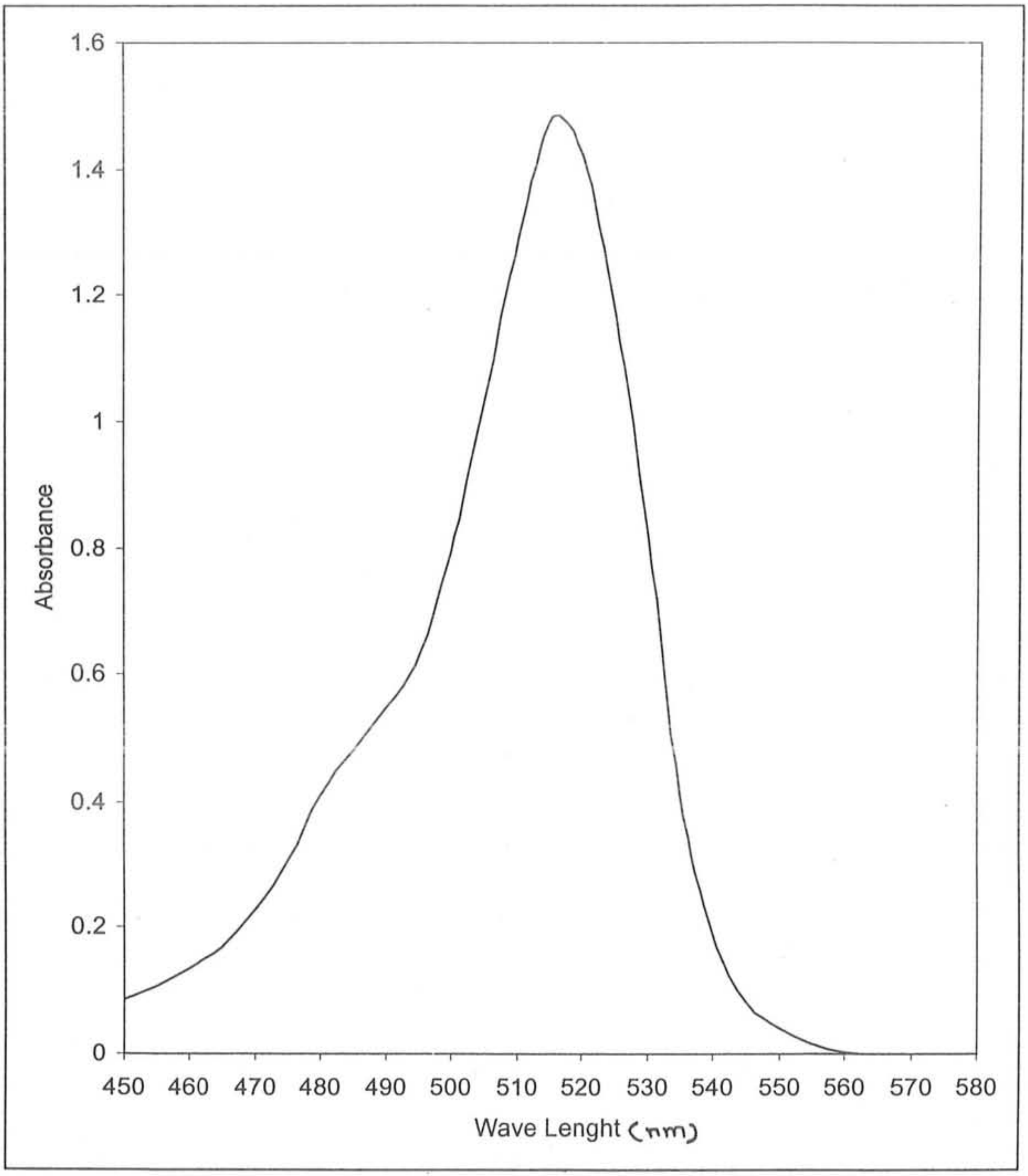


Fig.1.1Absorption spectrum of eosin in aqueous medium.

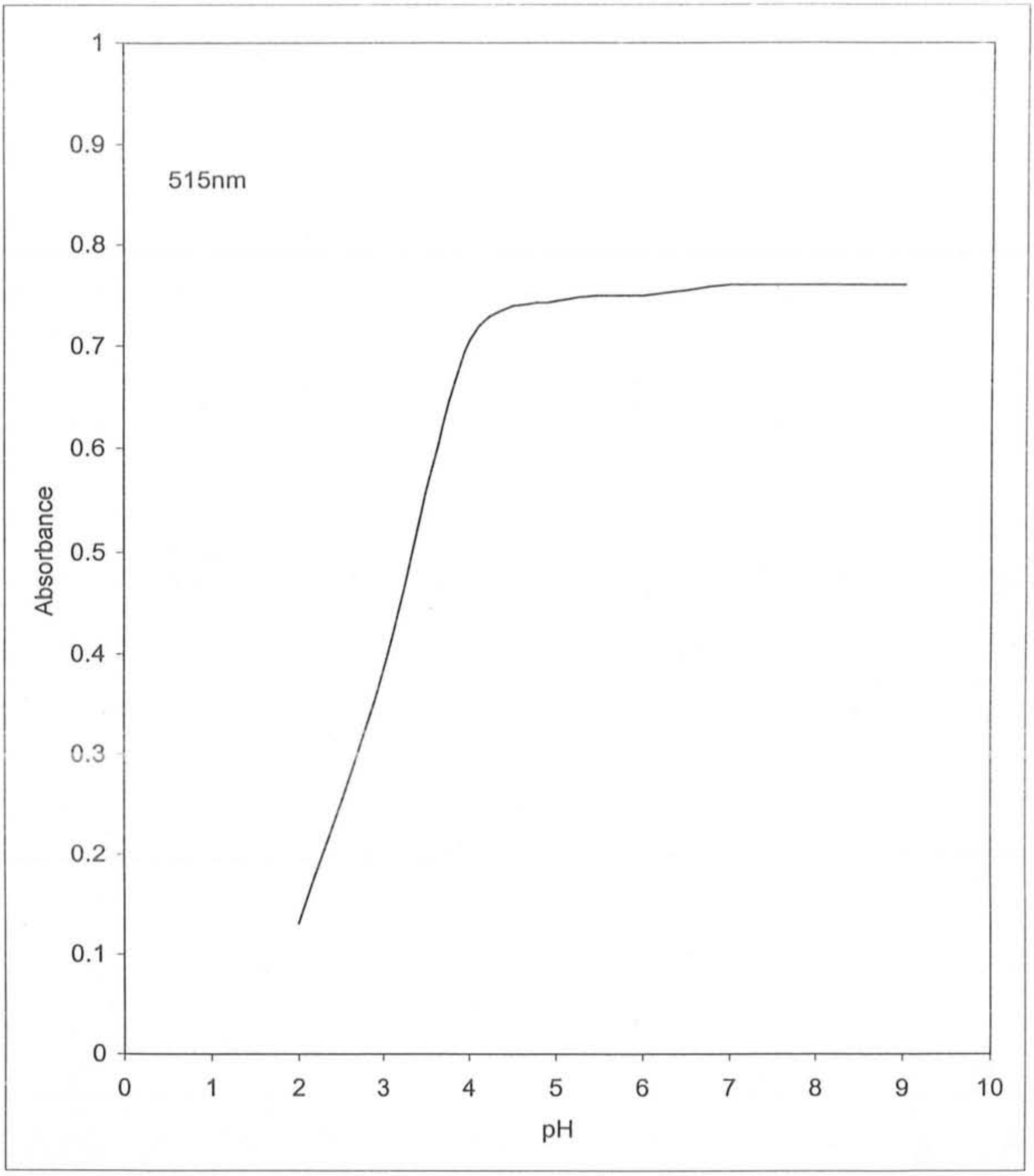


Fig.1.2 Effect of pH on eosin.

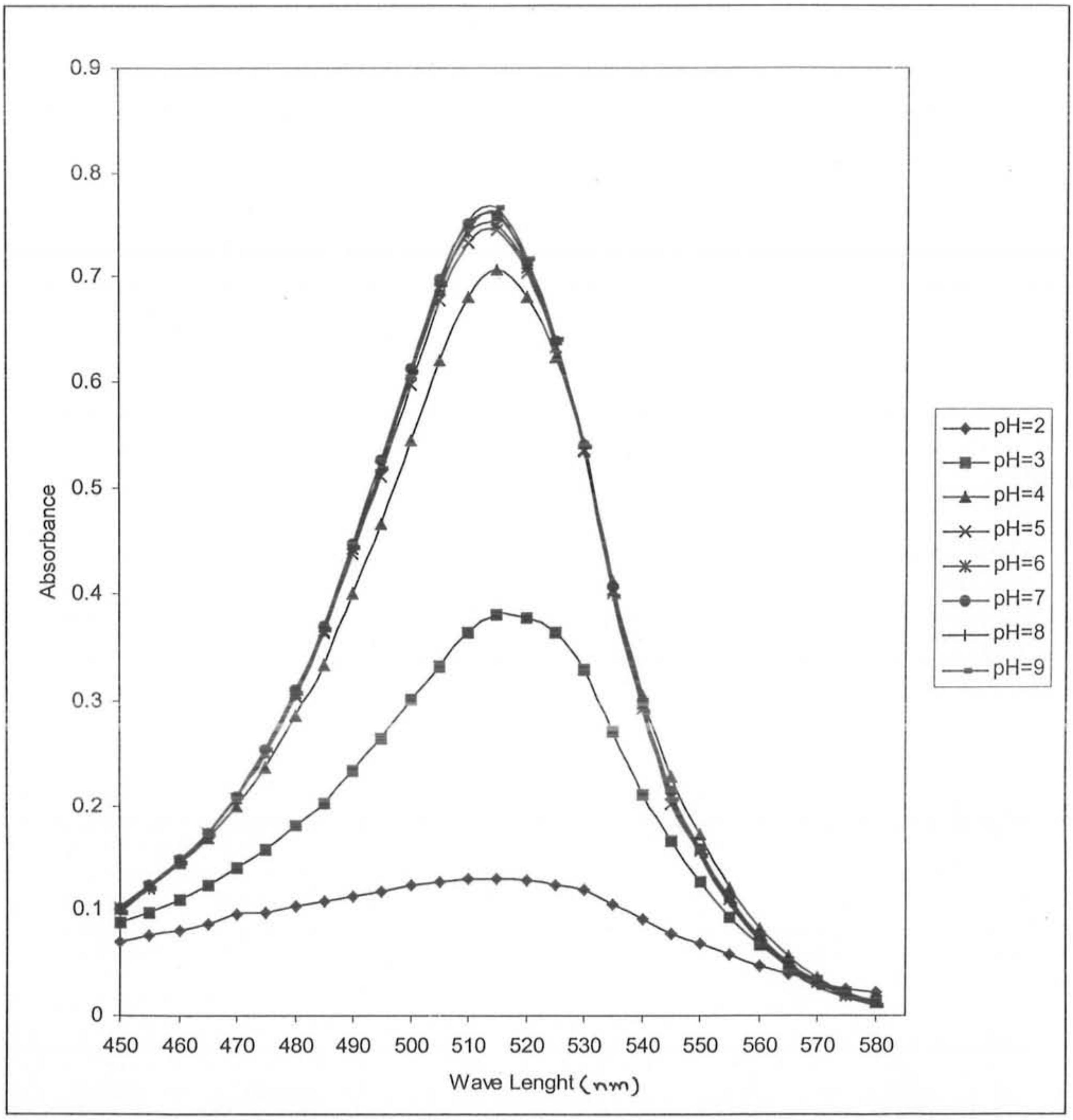


Fig.1.3 Effect of pH absorption spectrum of eosin.

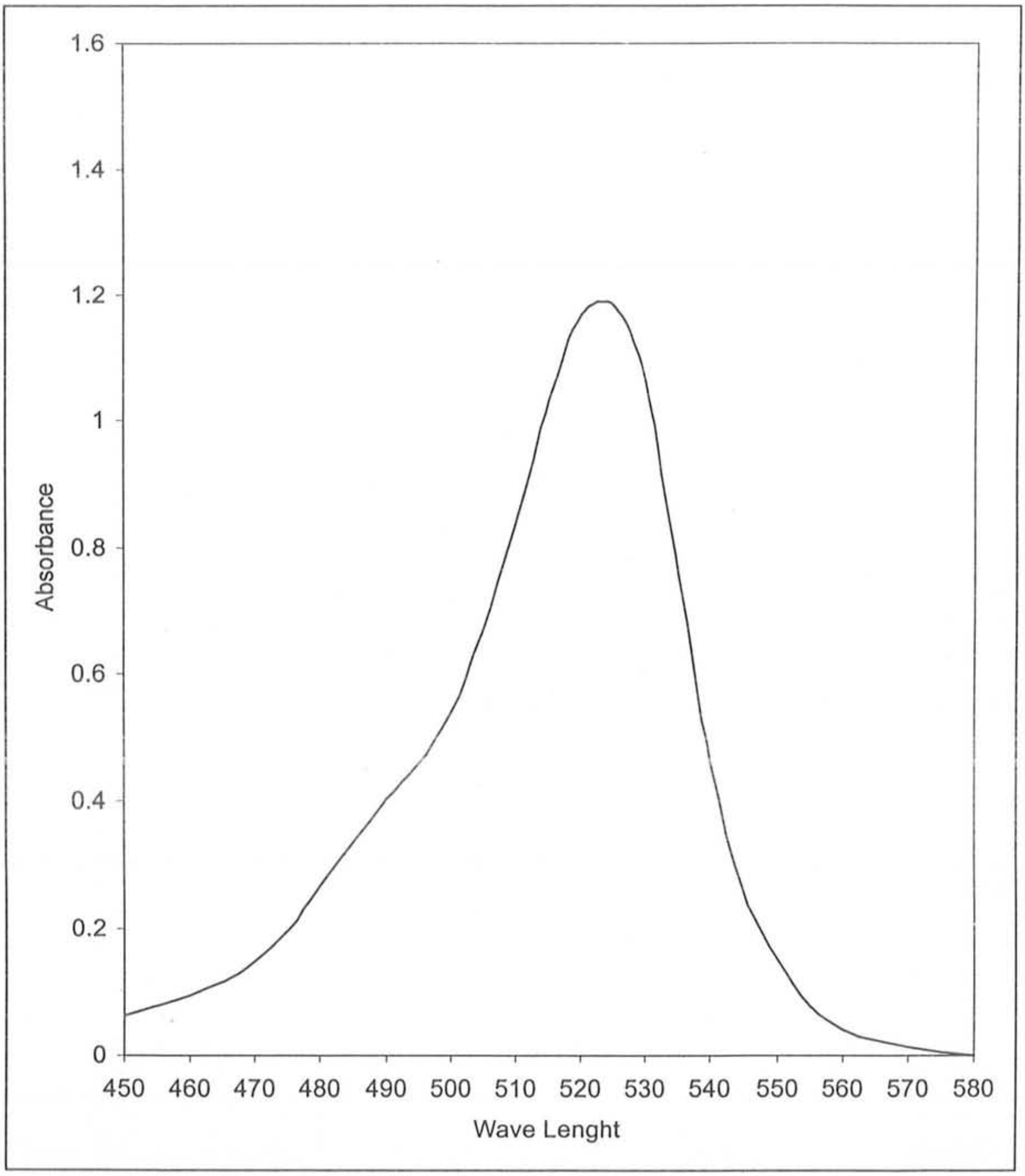


Fig.1.4 Absorption spectrum of eosin with o-Phenanthroline in aqueous medium.

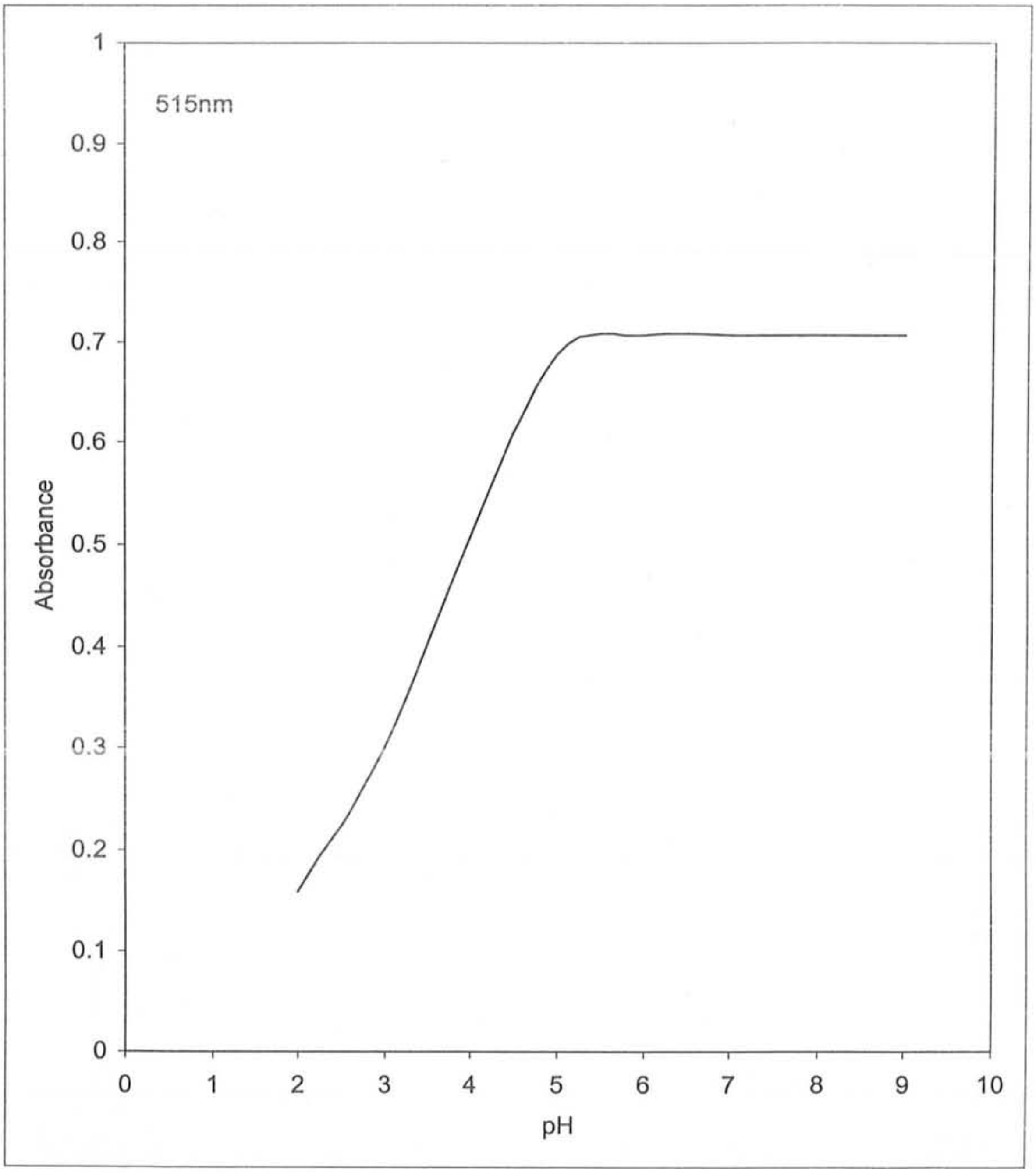


Fig.1.5 Effect of pH on reagent blank .

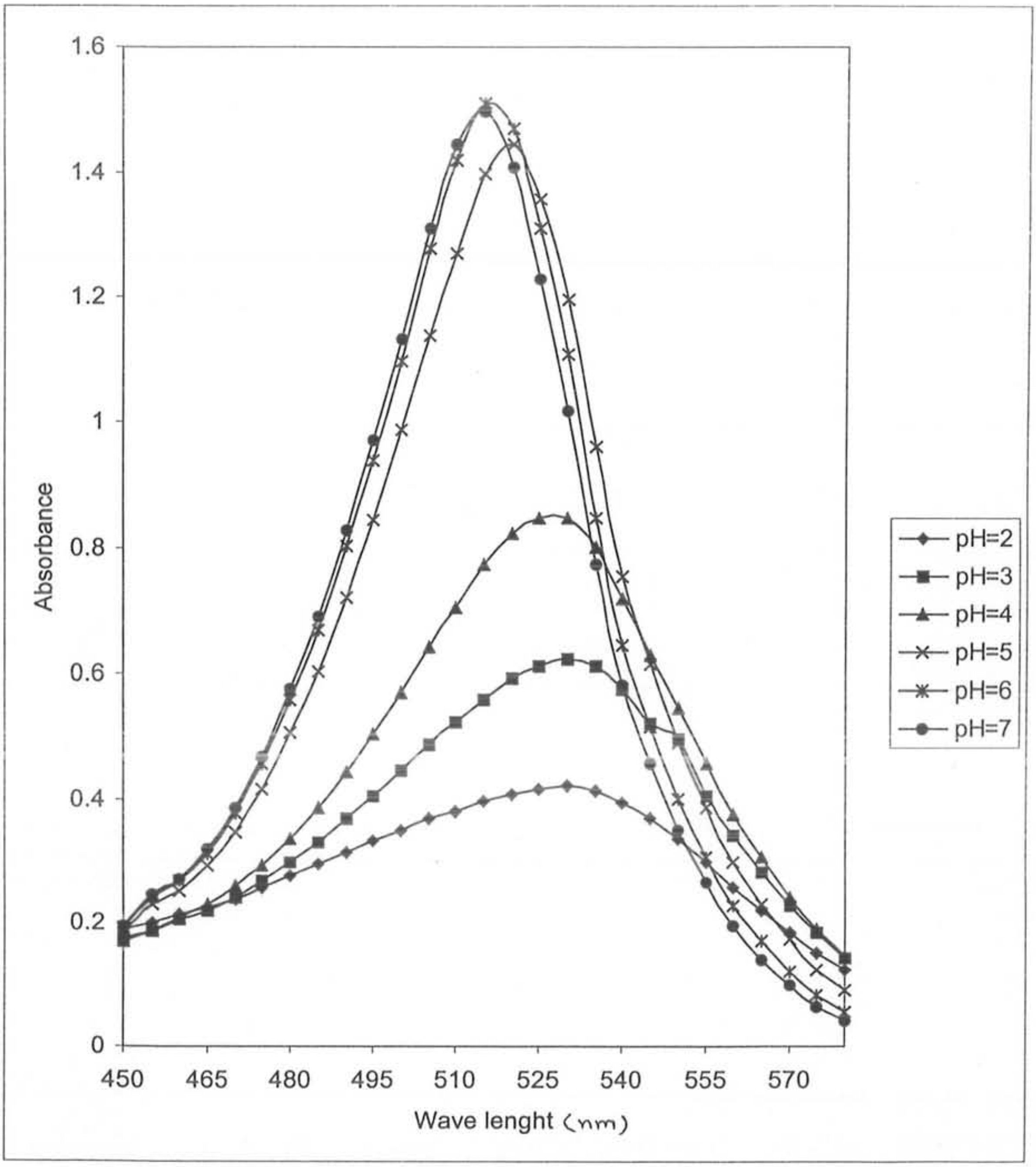


Fig.1.6 Effect of pH on absorption spectrum of reagent blank.

4.2 Complexation of VO^{+2} with o-Phenanthroline and Eosin

Vanadium in oxidation state +4 is d^1 system. Chemistry of VO^{+2} is dominated by oxygen compounds. Selbin[57,58] has concluded that VO^{+2} is a most stable di atomic ion. In aqueous medium it exists as hydrated ion $[VO(H_2O)_5]^{+2}$ with blue colour. It is amphoteric in nature and is readily soluble in both acidic and basic medium. Vanadyl may form five or six co-ordinated complexes. In few cases of certain Schiff bases complexes, the structure is distorted trigonal bipyramidal[59]. In majority of the cases, the ligands are bi or polydentate[60], where as simple complex species have also been characterized[61,62].

The absorption spectrum of the vanadyl ion in aqueous medium shows an absorption band at 780nm (Fig.2.1). The spectrum of reaction mixture of vanadyl, o-Phenethroline and eosin *versus* reagent blank shows an apparent decrease in absorption at 510nm and exhibits a new band at 550nm (Fig. 2.2). The appearance of the new band at 550nm indicates the formation of the metal complex with o-Phenanthroline. and eosin. The pH of the complex was optimized by using buffer solutions at different pH. Maximum complexation was obtained at pH 6 (Fig.2.3).

The stoichiometry of the complex has been determined by applying continuous variation method (*Job's Method*).The mole fractions of the two components were varied continuously, keeping their combined concentration constant, and by taking the third component in large excess for all the solutions in the series. The molar ratio of the vanadyl, o-Phenethroline and eosin was found to be 1:1:1 as shown in the figures (2.4,2.5).Thus composition of the complex was found to be [VO(o-Phen)]E, where E represents the divalent eosin anion.

In the formation of this complex, the primary ligand(o-Phen.), on entring the co-ordination sphere of VO^{+2}, forms co-ordinate covalent bond by its two nitrogens, but their complex ion still bears overall +2 charge on the co-ordination sphere, and it is free to associate with secondary ligand(Eosin) to form a ternary complex. This ternary complex exhibits an absorption band at 550nm.

Concentration, molar absorptivity and stability constants of the complex

By applying continuous variation method, the concentration, molar absorptivity and stability of the complex have been determined[50-55].

Concentration: It is essential to know the exact concentration of the complex formed, the exact concentration of the metal ion combined with the ligand and exact concentration of the ligand combined with the metal ion to form the complex.

In Figure (2.5) the extrapolated value(A_{ext}) at the piont of crossection, on the continuous variation plot corresponds to the total absorbance of the complex, if the complex formation has been completed. Actually complex is dissociative in nature and absorbance reading is therefore somewhat lower.

The concentration of the complex has been determined from the following equation:

$$A/A_{ext} = MX/C$$

Where C is the total analytical concentration.

From the continuous variation curve (Fig.2.5) values of A, A_{ext} and C were obtained.

$A = 1.15$

$A_{ext}=1.3$

$C = 7.5\times10^{-5}M$

MX = Concentration of the complex

Now by putting these values in above equation, concentration of the complex can be calculated.

$$\begin{aligned} MX &= A\times C/A_{ext} \\ &= 1.15\times7.5\times10^{-5}/1.30 \\ &= 6.63\times10^{-5}M \end{aligned}$$

Molar Absorption Coefficient: The molar absorption coefficient of the complex can be calculated by using the following equation:

$A = \varepsilon CL$

ε is a constant at same wavelength , called molar absorption coefficient and has a units of $L.mole^{-1}.cm^{-1}$.The use of this symbol specifically requires that the concentration is expressed in units of molarity and sample path length in centimeters.

A = Absorption of the complex at 550nm.

C = Concentration of the complex.

L = Path length

Concentration of the complex have been calculated already

$C = 6.63\times10^{-5}M$

$L = 1cm$

By applying the above equation

$$\varepsilon = A/CL$$

$$=1.15/1\times6.63\times10^{-5}$$

$$=1.73\times10^{4}L.mole^{-1}cm^{-1}$$

Stability Constant: The magnitude of the stability constant of the complexes formed in aqueous solutions by particular metal ions with specific ligands is important in analytical chemistry. So, these values should be different up to certain limits, for other metals with same ligand, because they provide the indications of the levels at which interference by such species is likely to be encountered in the analytical methods.

The equation of the complex formation is:

$$[VO(o\text{-}Phen.)]^{+2} + E^{+2} \leftrightarrow [VO(o\text{-}Phen.)]E$$

$$K = [VO(o\text{-}Phen.)]E_{eq} / [VO(o\text{-}Phen.)]_{eq}[E]_{eq}$$

K = Equilibrium Constant

The equilibrium concentration of the metal ion and ligand can be determined as follows

$[VO(o\text{-}Phen.)]_{eq} = [VO(o\text{-}Phen.)] - [VO(o\text{-}Phen.)]E_{eq}$

$= 7.5\times10^{-5} - 6.63\times10^{-5}$

$= 8.7\times10^{-6}M$

Now equilibrium concentration of the secondary ligand can be calculated as

$[E]_{eq} = [E] - [VO(o\text{-}Phen.)]E_{eq}$

$= 7.5\times10^{-5} - 6.63\times10^{-5}$

$= 8.7\times10^{-6}M$

By putting these values in the equilibrium equation

$K = 6.63\times10^{-5} / (8.7\times10^{-6})(8.7\times10^{-6})$

$K = 8.76\times10^{5}$

$\text{Log } K = 5.94$

It is apparent form the stability constant that complex is very unstable.

Effect of Time

Effect of time on the stability of the complexes has been investigated. The complex formation is immediately started after the mixing of the reagents and it is completed in half-hour. After two hours the complex started decomposing as indicated by a decrease in the absorption value at λ_{max}. It is evident form the observation that reaction proceeds through moderate speed and complex is unstable. So optimum time for complex formation is one hour (Fig.2.6)

Effect of Temperature

The rise of temperature further destabilizes the complex. This complex was very sensitive to temperature, and was stable only up to 30°C and beyond 30°C decomposition was started (Fig.2.7). The optimum temperature for complexation was 25°C. This further confirms the unstable nature of the complex.

This complex is unstable because it formed only due to association of cationic complex and divalent eosin anion.

Effect of cations and anions

In spectrophotometric determinations, the concentrations of the interfering metal ions must be very low, if the complex formation by interfering ions results in the formation of a species which absorbs at the same wavelength at which complex to be analyzed absorbs. A masking agent is used, which complexes with the interfering ion and reduces their concentration. Masking agent should not effect the species of interest and its complex with interfering ion must have absorption band outside the spectral region in which the measurements are made.

The effect of various cations Cr^{+3}, Ca^{+2}, Mg^{+2}, Sr^{+2}, Ni^{+2}, Co^{+2},Cu^{+2}, Al^{+3}, K^{+1}, Ba^{+2} (Fig.2.8) and anions Cl^{-1}, Br^{-1}, I^{-1}, NO^{-1}_3, IO^{-1}_3, SO^{-2}_4 and CN^{-1} (Fig.2.9) has been studied on the complexation of the vanadyl complex. The limiting concentration and percentage decrease in absorbance is shown in the Tables (1.3,1.4).

It is observed that Ni^{+2}, Co^{+2},Cu^{+2} and Al^{+3}effects the complex by increasing the absorbance at λ_{max} of the complex. It is probably due to the formation of complexes of respective foreign ions, which have absorption band overlapping the absorption band of vanadyl complex with high molar absorption coefficient. Cr^{+3} effects by decreasing the absorbance, inhibiting the vanadyl complex formation. Ca^{+2}, Mg^{+2}, Sr^{+2} K^{+1},and Ba^{+2} show no significant effect.

The Cl^{-1}, Br^{-1}, I^{-1} and NO^{-1}_3 don't effect the complex when present in equimolar amounts, but IO^{-1}_3, SO^{-2}_4 decreases the absorbance. The CN^{-1} has the most striking effect on the complex, even when present in small amounts.

Calibration graphs

The Beer's law was obeyed over a range 3-12 ppm for VO^{+2} by the vanadyl complex system. Primary and secondary ligands were used in excess. Fig.(2.10)

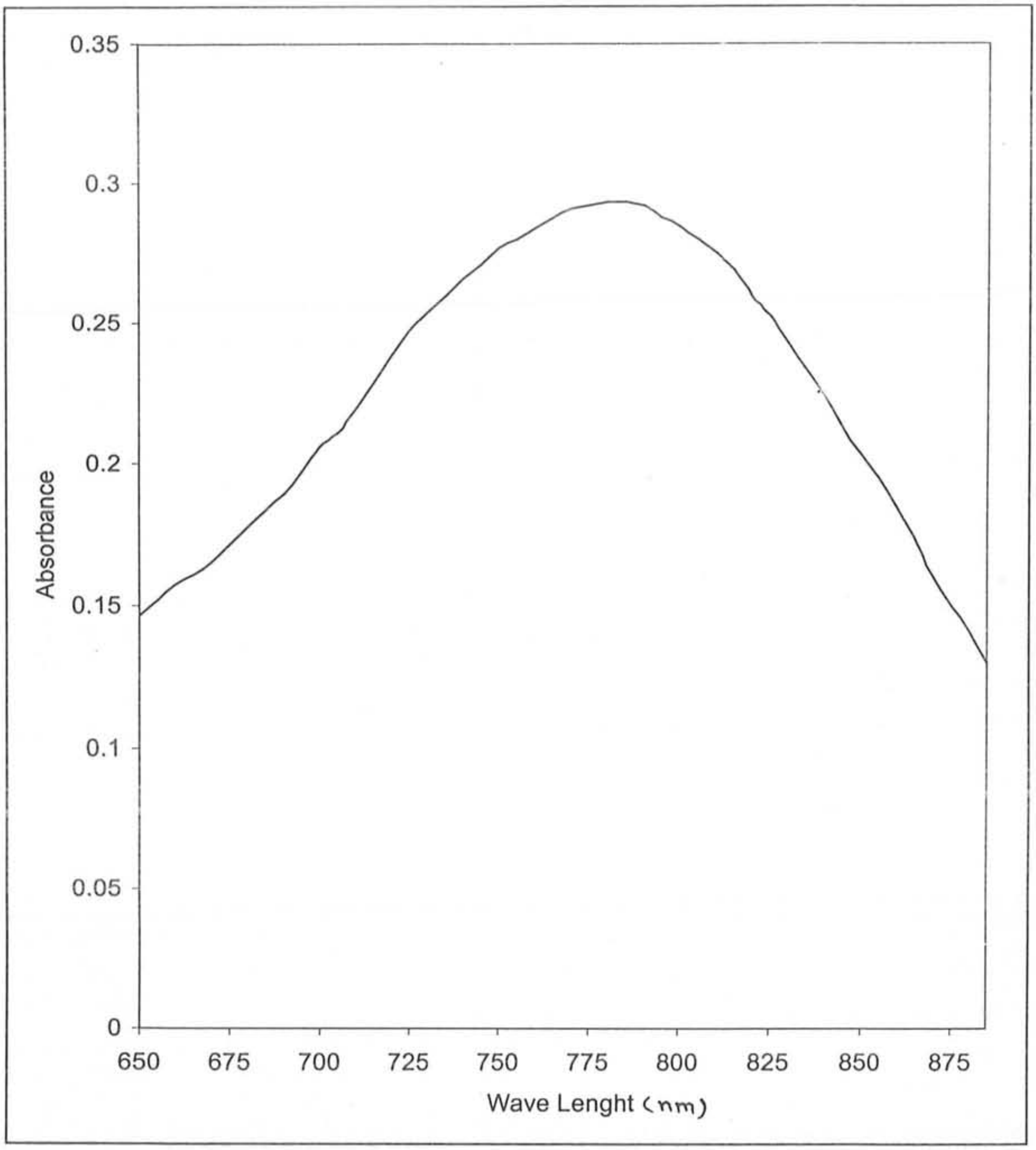


Fig.2.1 Absorption spectrum of VO(II) in aqueous medium.

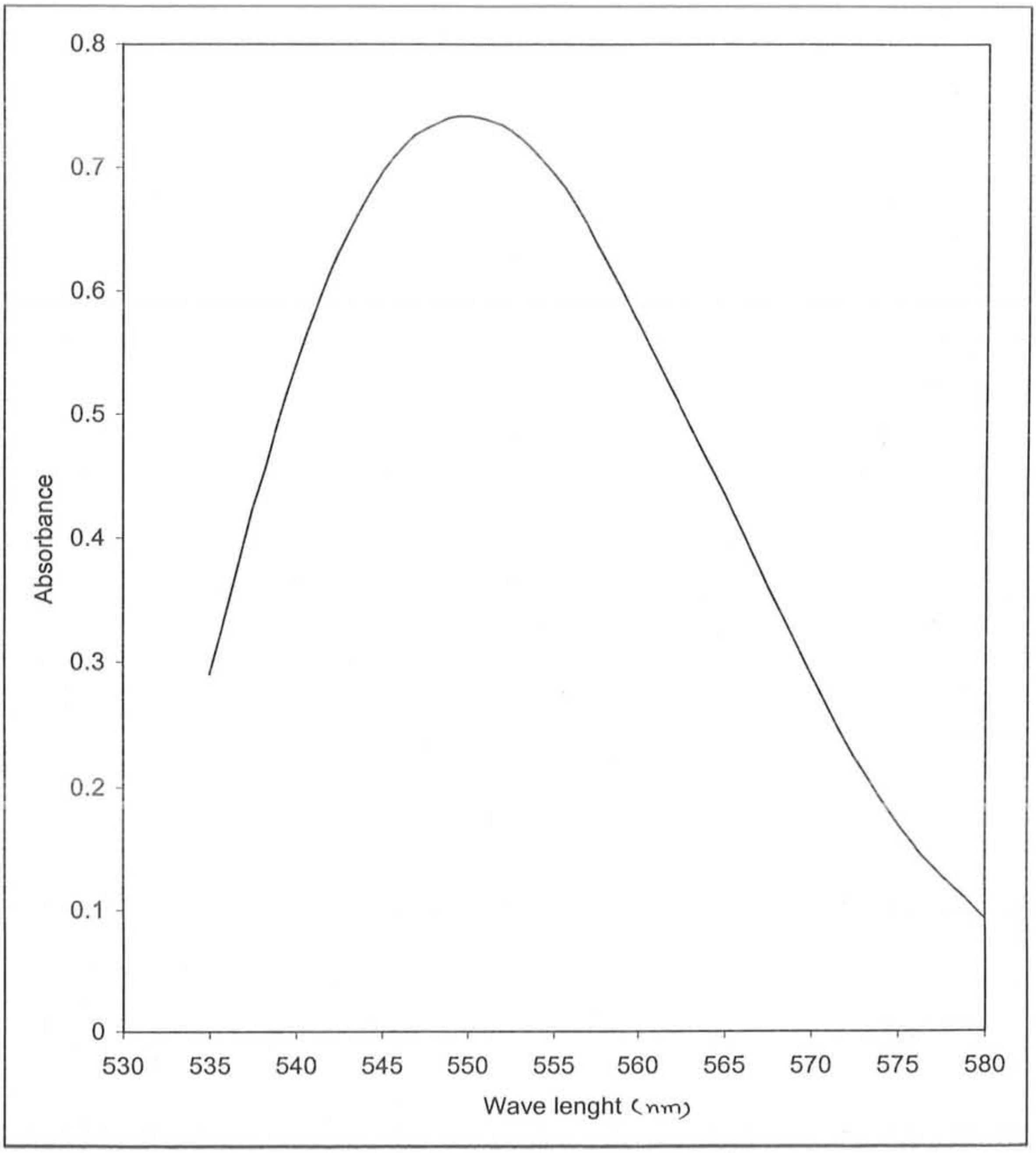


Fig.2.2 Absorption spectrum of VO(II)-complex.

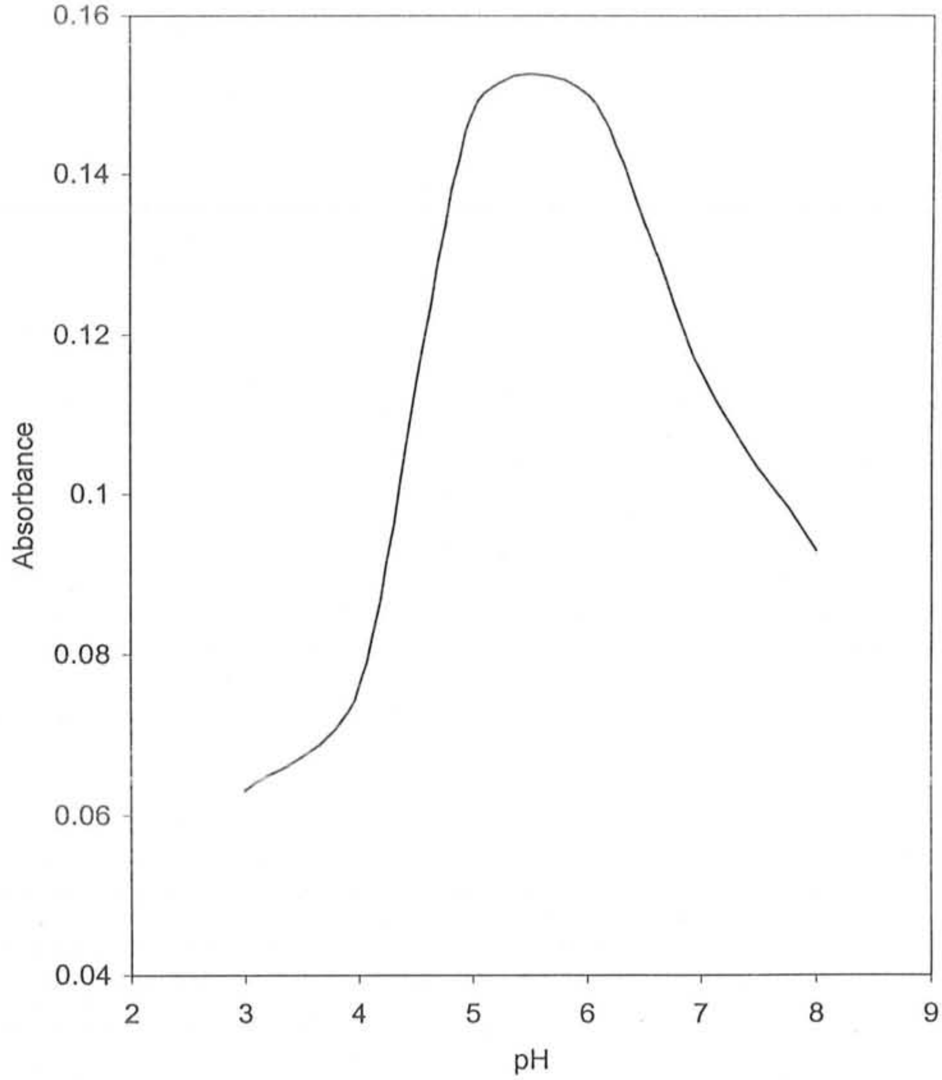


Fig.2.3 Effect of pH on VO(II)-complexation.

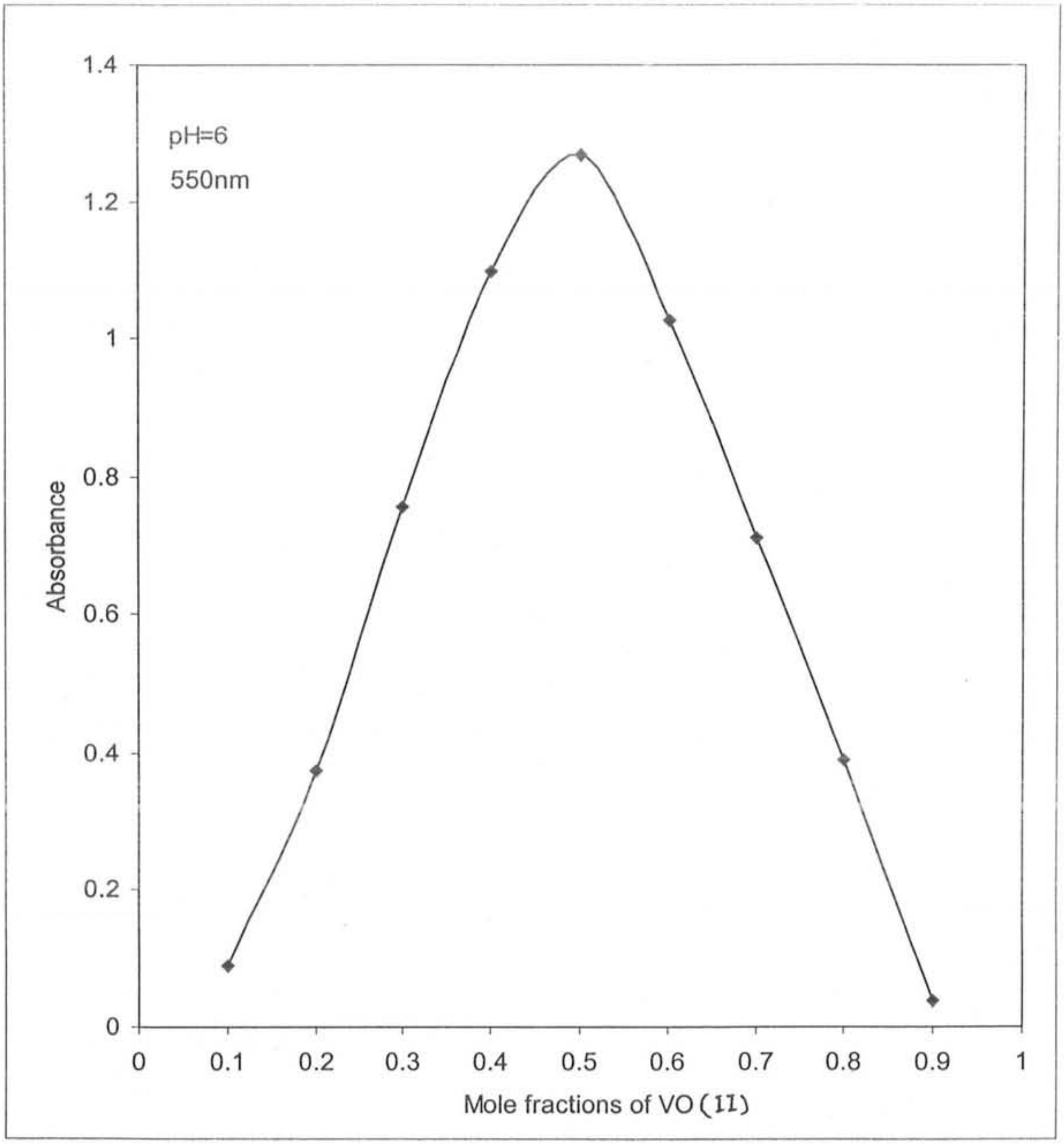


Fig.2.4 Stoichiometric study of VO(II)-complex (VO vs o-Phenanthroline)

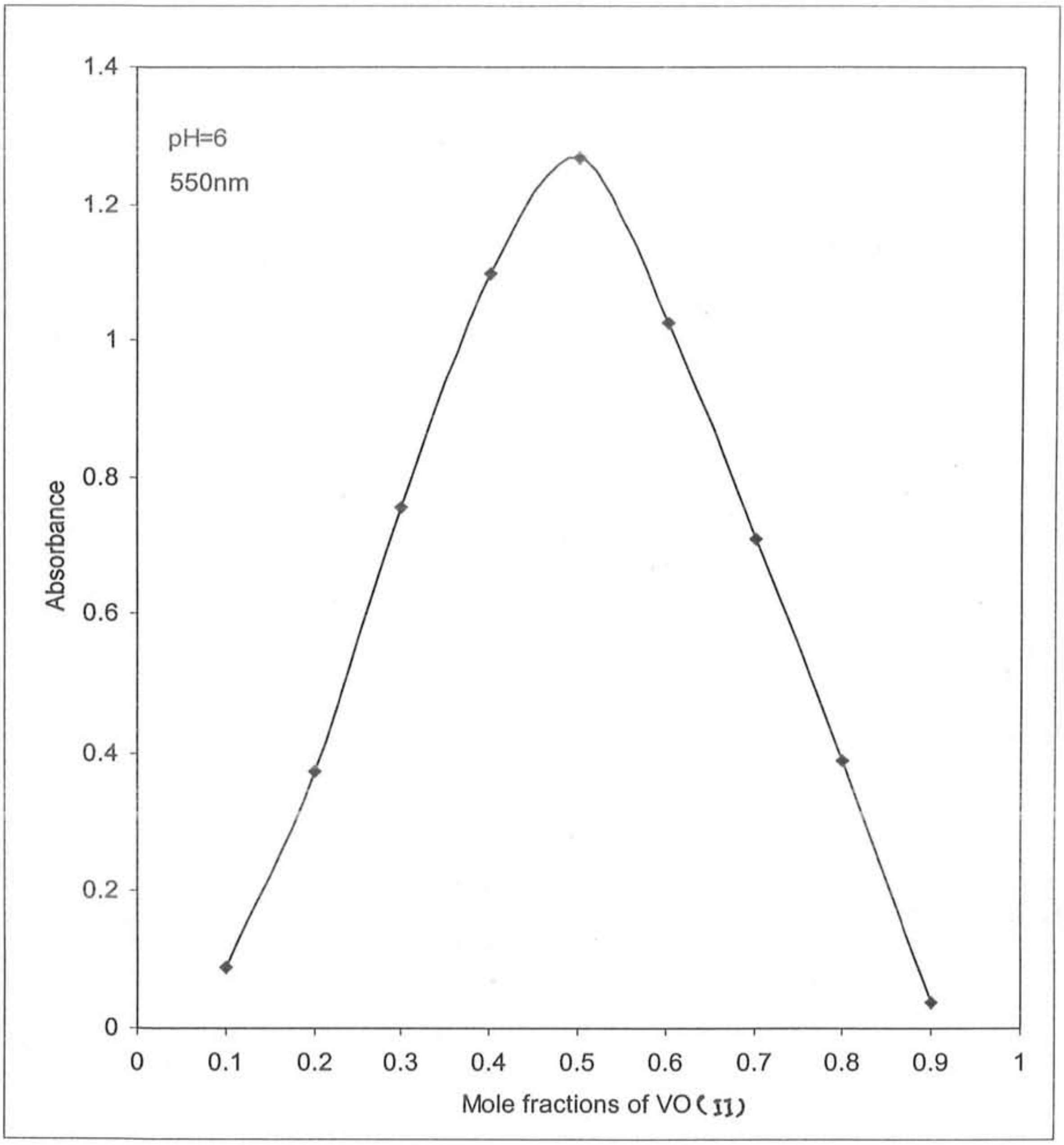


Fig. 2.5 Stoichiometric study of VO(II)-Complex (VO vs Eosin)

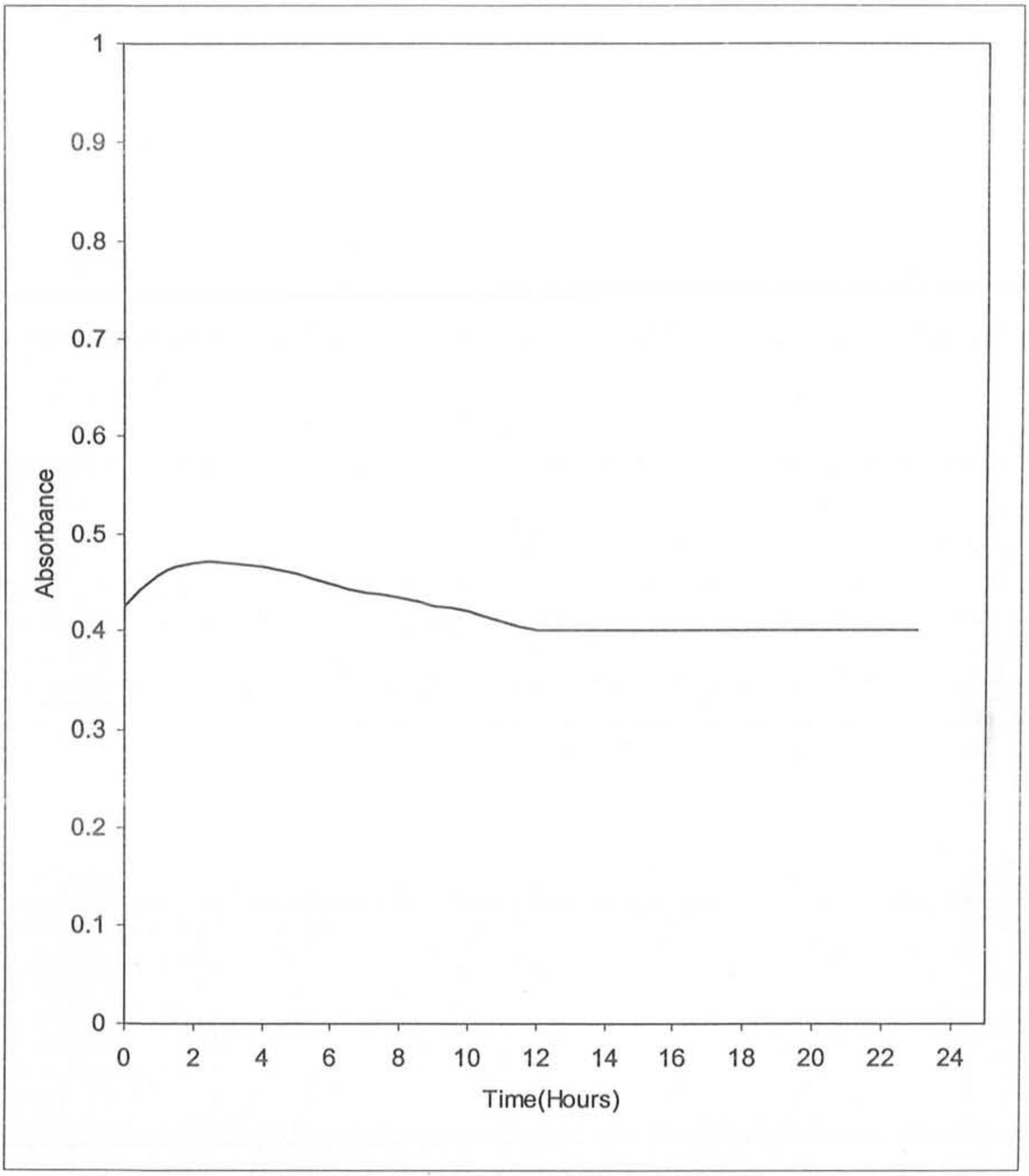


Fig.2.6 Effect of time on VO(II)-complexation.

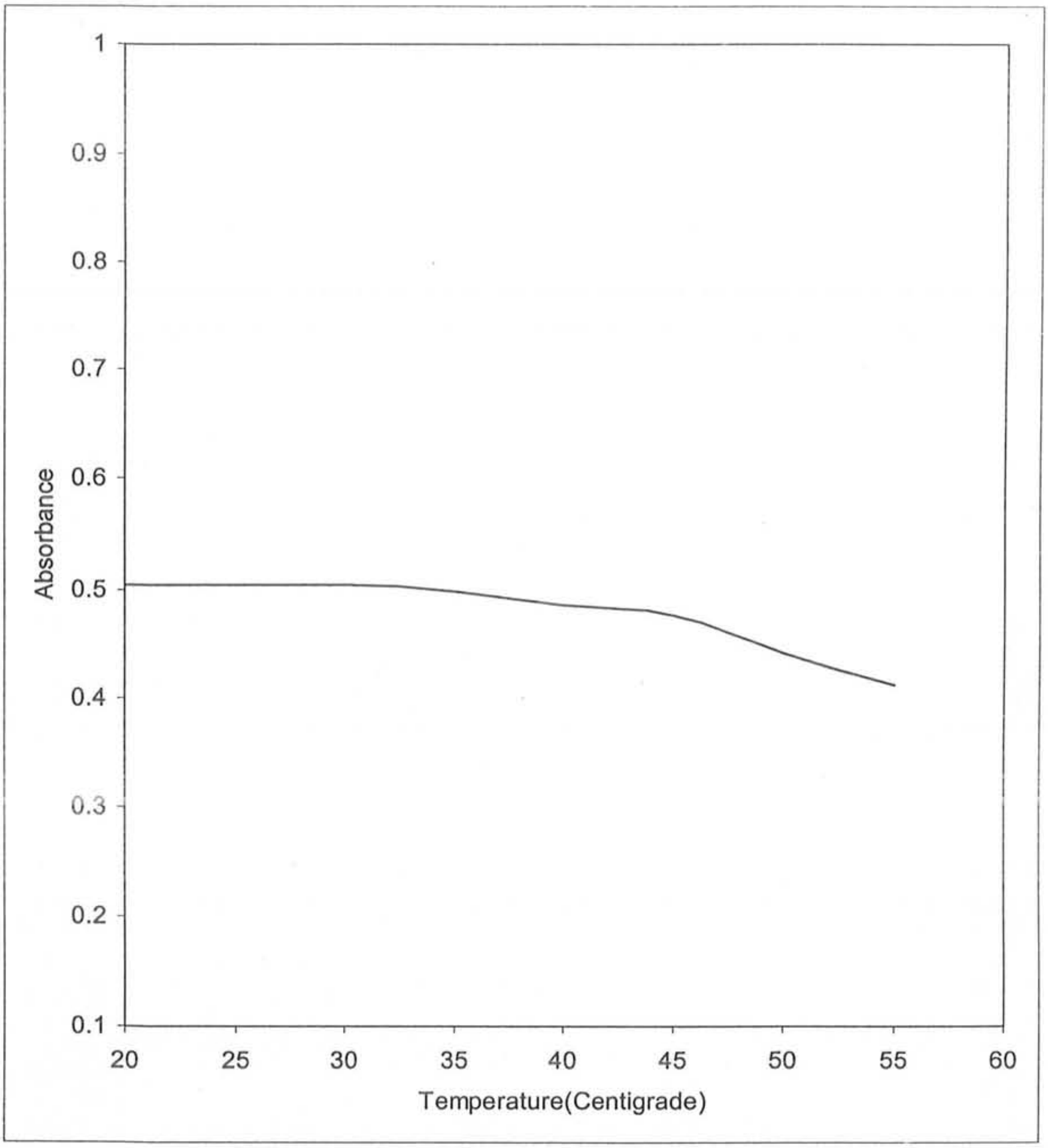


Fig. 2.7 Effect of temperature on VO(II)-complexation.

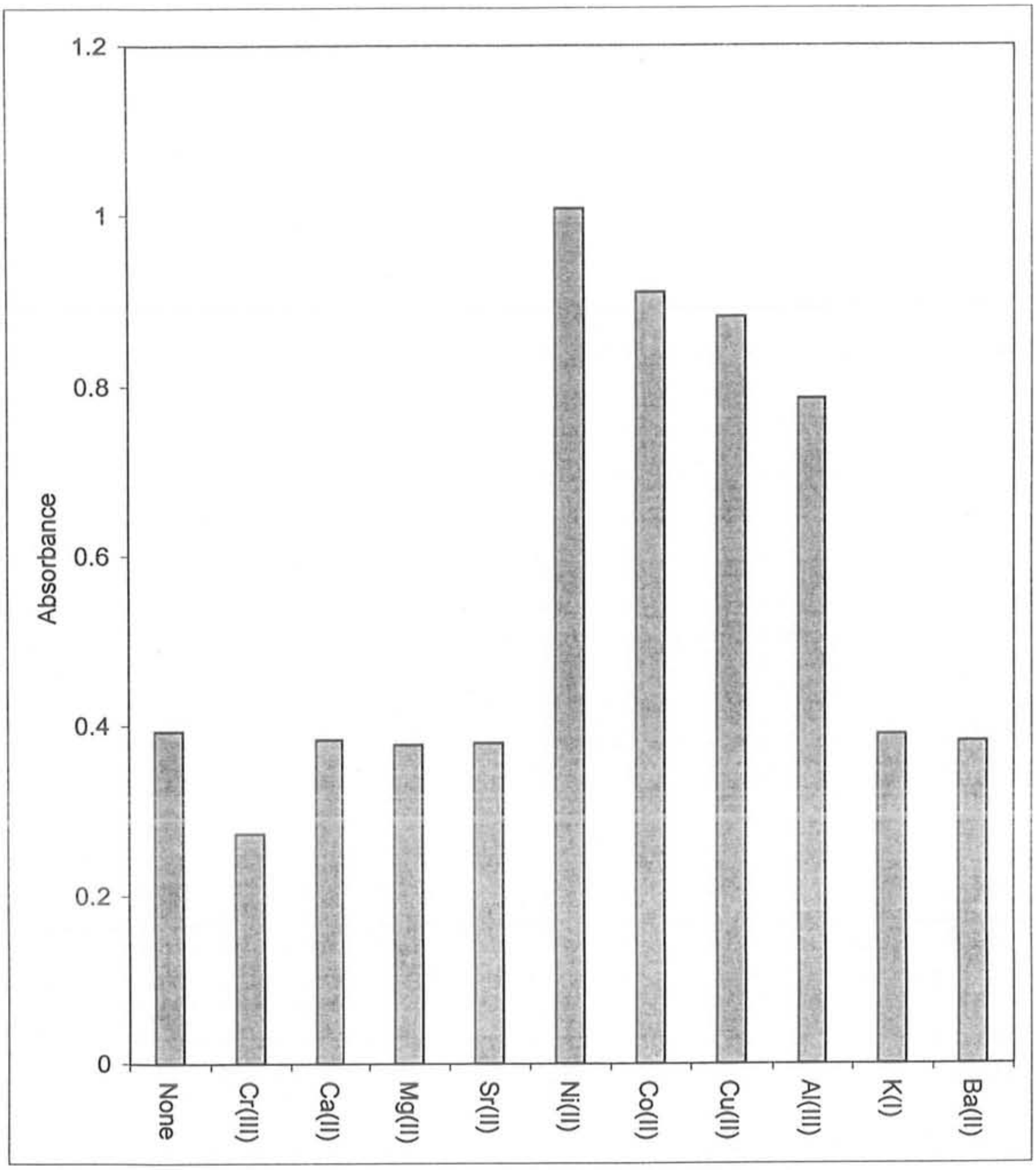


Fig.2.8.. Effect of different cations on VO(II)-complexation.

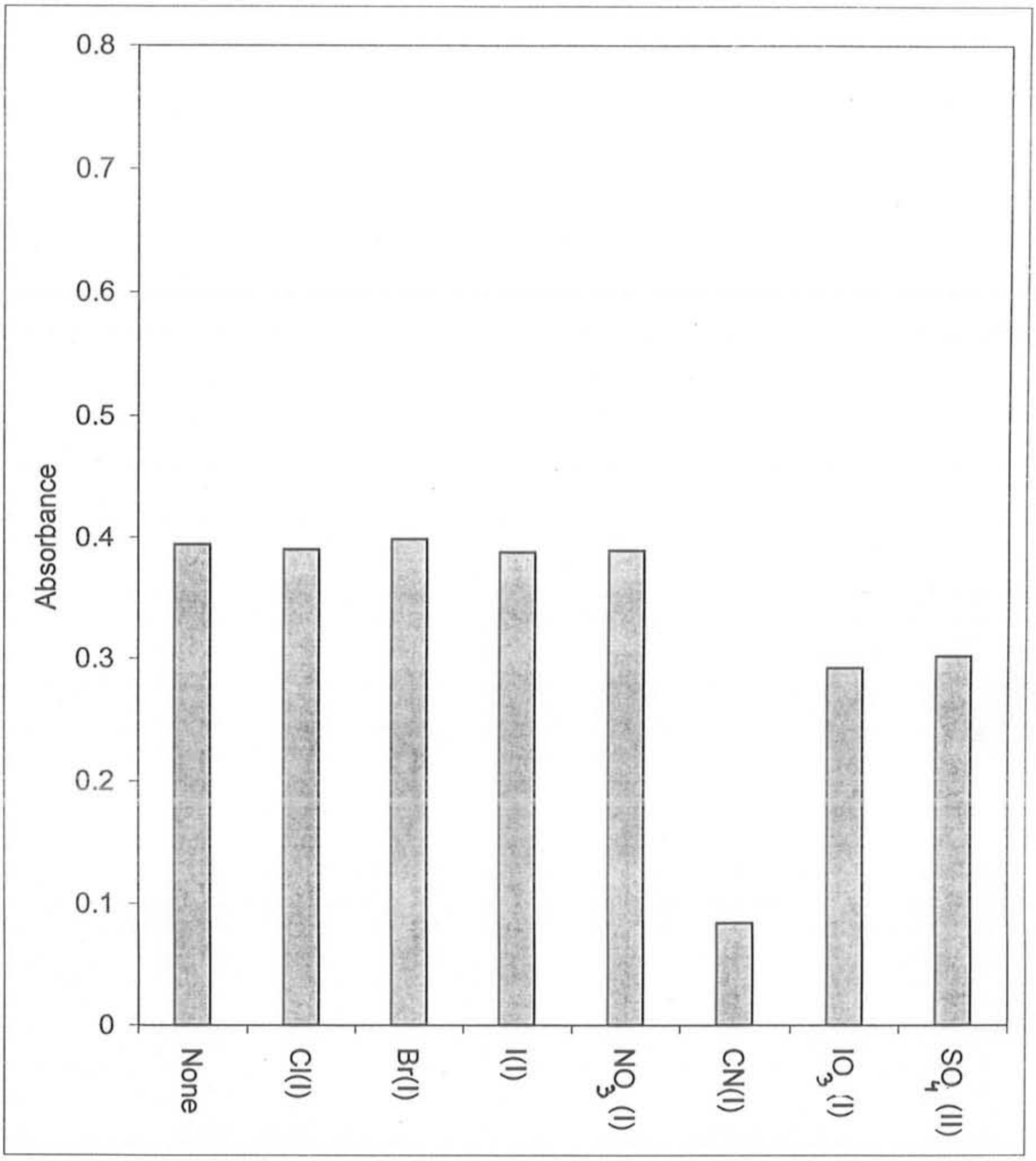


Fig. 2.9 Effect of different anions on VO(II)-complexation.

TABLE 4.1

Effect of different cations on VO(II)-complexation

Cations	*Limiting conc.(M)*	*% Effect on intensity*
Cr^{+3}	1.3×10^{-6}	-7
Ca^{+2}	3.7×10^{-4}	-2
Mg^{+2}	7.2×10^{-4}	-2
Sr^{+2}	1.3×10^{-4}	-3
Ni^{+2}	1.5×10^{-7}	+9
Co^{+2}	2.5×10^{-7}	+8
Cu^{+2}	2.9×10^{-7}	+7
Al^{+3}	8.5×10^{-7}	+5
K^{+1}	3.7×10^{-6}	-1
Ba^{+2}	1.3×10^{-6}	-2

*All the cations were added as their nitrate salts.

TABLE 4.2

Effect of different anions on VO(II)-complexation

Anions	*Limiting conc.(M)*	*% Effect on intensity*
Cl^{-1}	3.7×10^{-2}	-2
Br^{-1}	3.7×10^{-2}	-3
I^{-1}	3.7×10^{-3}	-4
NO_3^{-1}	3.7×10^{-1}	-1
IO_3^{-1}	3.7×10^{-5}	-4
SO_4^{-2}	3.7×10^{-5}	-8
CN^{-1}	1.3×10^{-7}	-6

*All the anions were added as their potassium salts.

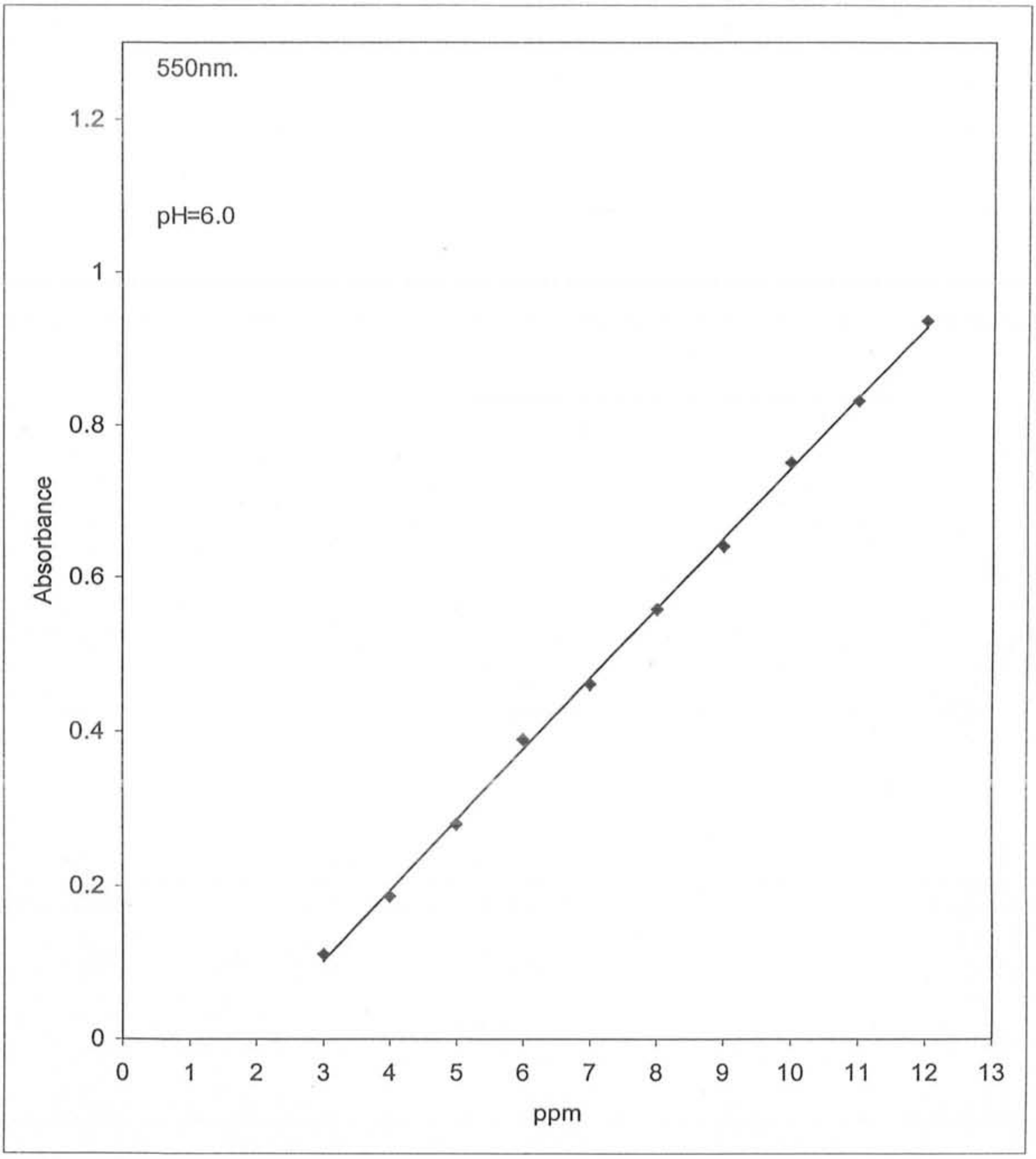


Fig.2.10 Adherence to Beer's law for VO(II)-complex.

4.3 Complexation of Mn^{+2} with o-Phenanthroline and Eosin

Manganese in oxidation state +2 is a d^5 system. This divalent state is the most stable state. In neutral or acidic solutions, there is a very pale pink hexaaquo ion $[Mn(H_2O)_6]^{+2}$, which is resistant to oxidation. The equilibrium constant for complex formation in aqueous solution is low as compared to iron(II) and copper(II), because Mn^{+2} is the largest of these and it has no ligand field stabilization energy in its high spin complexes, which are in majority. In octahedral fields, tranisitions are spin forbidden as well as parity forbidden, thus giving extremely pale colour of compounds. In tetrahedral environment, the transitions are spin forbidden and are no longer parity forbidden, thus colour is hundred times stronger , giving pale yellow green colour.

The absorption spectrum of the Mn^{+2} ion in aqueous medium shows very weak absorption band in ultraviolet region (Fig.3.1). The spectrum of reaction mixture of manganese, o-Phenathroline and eosin *versus* reagent blank shows an apparent decrease in absorption at 510nm and exhibits a new band at 560nm (Fig. 3.2). The appearance of the new band at 560nm indicates the formation of the metal complex with o-Phenathroline and eosin. Using buffer solutions at different pH optimized the pH of the complex. Maximum complexation was obtained at pH 5.5 (Fig. 3.3).

The stoichiometry of the complex has been determined by applying continuous variation method (*Job's Method*).The mole fractions of the two components were varied continuously, keeping their combined concentrations constant, and by taking the third component in large excess for all the solutions in the series. The molar ratio of the manganese, o-Phenethroline and eosin was found to be 1:2:1 as shown in the Fig. (3.4,3.5).The composition of the complex was found to be $[Mn(o\text{-}Phen)_2]E$.

In the formation of the complex, the primary ligand(o-Phen.), on entering the co-ordination sphere of Mn^{+2}, forms co-ordinate covalent bond by its two nitrogens, but their complex ion still bears over all +2 charge on the co-ordination sphere, and it is free to associate with secondary ligand (Eosin) to form a ternary complex. This ternary complex exhibits an absorption band at 560nm.

Concentration, molar absorptivity and stability constants of the complex

By applying continuous variation method, the concentration, molar absorptivity and stability of the complex have been determined[50-55].

Concentration: In Figure (3.5) the extrapolated value(A_{ext}) at the piont of crossection, on the continuous variation plot corresponds to the total absorbance of the complex, if the complex formation has been completed. Actually, the complex is dissociative in nature and absorbance value is therefore somewhat lower.

The concentration of the complex has been determined from the following equation:

$$A/A_{ext} = MX/C$$

Where C is the total analytical concentration.

From the continuous variation curve (Fig.3.5) values of A, A_{ext} and C were obtained.

$A = 1.25$

$A_{ext}=1.45$

$C = 7.5\times10^{-5}M$

MX = Concentration of the complex

Now by putting these values in above equation concentration of the complex was calculated:

$$MX = A\times C/A_{ext}$$

$$= 1.25\times7.5\times10^{-5}/1.45$$

$$= 6.46\times10^{-5}M$$

Molar Absorption Coefficient: The molar absorption coefficient of the complex can be calculated by using the following equation:

$A = \varepsilon CL$

ε is a constant at same wavelength , called molar absorption coefficient and has the units of $L.mole^{-1}.cm^{-1}$.The use of this symbol specifically requires that the concentration is expressed in units of molarity and sample path length in centimeters.

A = Absorption of the complex at 560nm.

C = Concentration of the complex.

L = Path length

Concentration of the complex have been calculated already

$C = 6.46\times10^{-5}M$

$L = 1cm$

By applying the above equation

$$\varepsilon = A/CL$$

$$=1.25/1\times6.63\times10^{-5}$$

$$=1.95\times10^{4}L.mole^{-1}cm^{-1}$$

Stability Constant: Stability of a complex is very important.

The equation of the complex formation is following:

$$[Mn(o\text{-}Phen.)_2]^{+2}+E^{+2} \quad \leftrightarrow \quad [Mn(o\text{-}Phen.)_2]E$$

$$K = [Mn(o\text{-}Phen.)_2]E_{eq} / [Mn(o\text{-}Phen.)_2]_{eq}[E]_{eq}$$

K = Equilibrium Constant

The equilibrium concentration of the metal ion and ligand can be determined as follows

$$[Mn(o\text{-}Phen.)_2]_{eq} = [Mn(o\text{-}Phen.)_2]\text{-} [Mn(o\text{-}Phen.)_2]E_{eq}$$

$$= 7.5\times10^{-5} - 6.46\times10^{-5}M$$

$$= 1.04\times10^{-5}M$$

Now equilibrium concentration of the secondary ligand can be calculated as

$$[E]_{eq} = [E]\text{-} [Mn(o\text{-}Phen.)_2]E_{eq}$$

$$= 7.5\times10^{-5}\text{-}6.46\times10^{-5}M$$

$$= 1.04\times10^{-5}M$$

By putting these values in the equilibrium equation

$$K = 6.46\times10^{-5} / (1.04\times10^{-5})\,(1.04\times10^{-5})$$

$$K = 5.97\times10^{5}$$

$$\text{Log } K = 5.77$$

It is apparent form the stability constant that the complex is not very stable.

Effect of Time

Effect of time on the complexes has been investigated. The complex formation is immediately started after the mixing of the reagents and it is completed in half-hour. After one hour the decomposition of the complex was started, indicated by the decrease in the absorption at λ_{max}. The optimum time for complex formation is half hour

(Fig.3.6)

Effect of Temperature

This complex was very sensitive to temperature, as decomposition was started above 20 °C (Fig.3.7). The optimum temperature for complexation is 20°C. This further confirms the unstable nature of the complex.

Effect of cations and anions

The effect of various cations Cr^{+3}, Ca^{+2}, Mg^{+2}, Sr^{+2}, Ni^{+2}, Co^{+2},Cu^{+2}, Al^{+3}, K^{+1}, Ba^{+2} (Fig.3.8) and anions Cl^{-1}, Br^{-1}, I^{-1}, $NO^{-1}{}_{3}$, $IO^{-1}{}_{3}$, $SO^{-2}{}_{4}$ and CN^{-1} (Fig.3.9) has been studied on the complexation of the manganese complex. The limiting concentration and percentage decrease in absorbance is shown in the Tables (1.5,1.6).

It was observed that Ni^{+2}, Co^{+2},Cu^{+2} and Al^{+3}effects the complex by increasing the absorbance at λ_{max} of the complex. It is probably due to the formation of complexes of respective foreign ions, which have absorption band overlapping the absorption band of manganese complex with high molar absorption coefficient. Cr^{+3} effects by decreasing the absorbance, inhibiting the manganese complex formation. Ca^{+2}, Mg^{+2}, Sr^{+2} K^{+1},and Ba^{+2} show no significant effect.

The Cl^{-1}, Br^{-1}, I^{-1} and NO^{-1}_3 shows minute effects on the complex when present in equimolar amounts, but IO^{-1}_3, SO^{-2}_4 decreases the absorbance. The CN^{-1} has the most striking effect on the complex, even when present in small amounts.

Calibration graphs

The system follows Beer's law over the range 0.4-2 ppm for Mn^{+2}. Primary and secondary ligands were used in excess.Fig.(3.10)

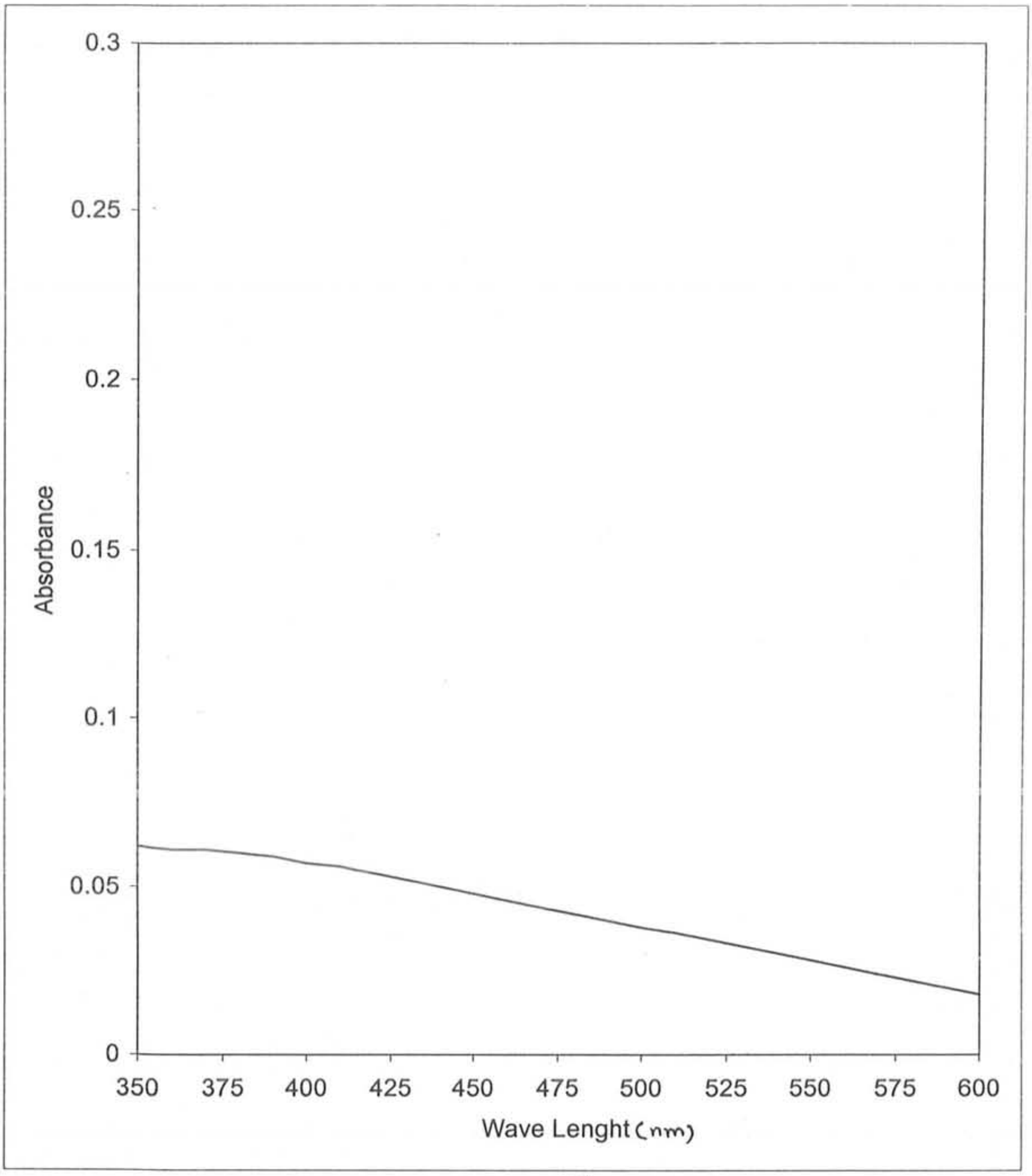


Fig.3.1 Absorption spectrum of Mn^{+2} in aqueous medium.

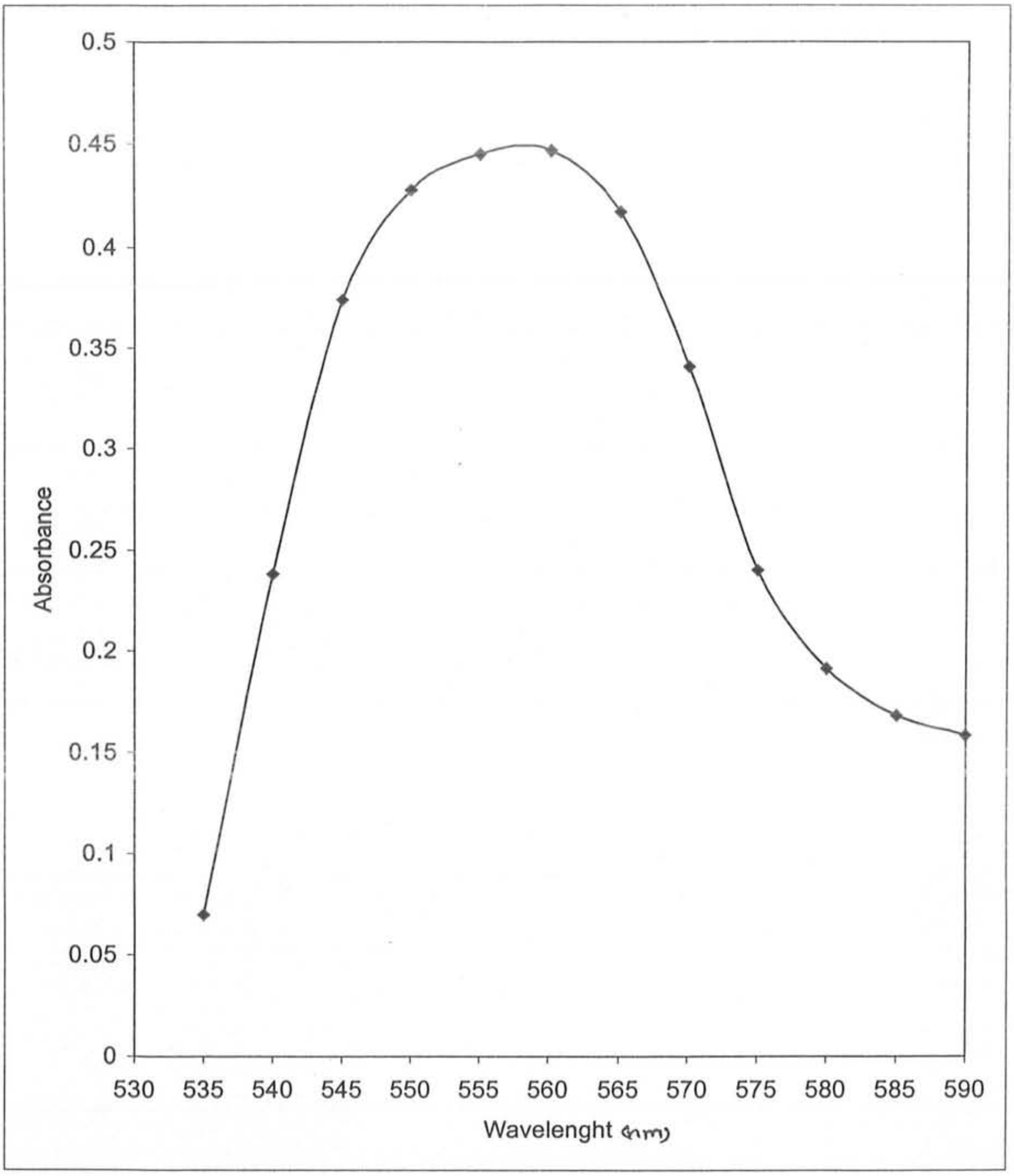


Fig.2.2 Absorption spectrum of Mn(II)-complex.

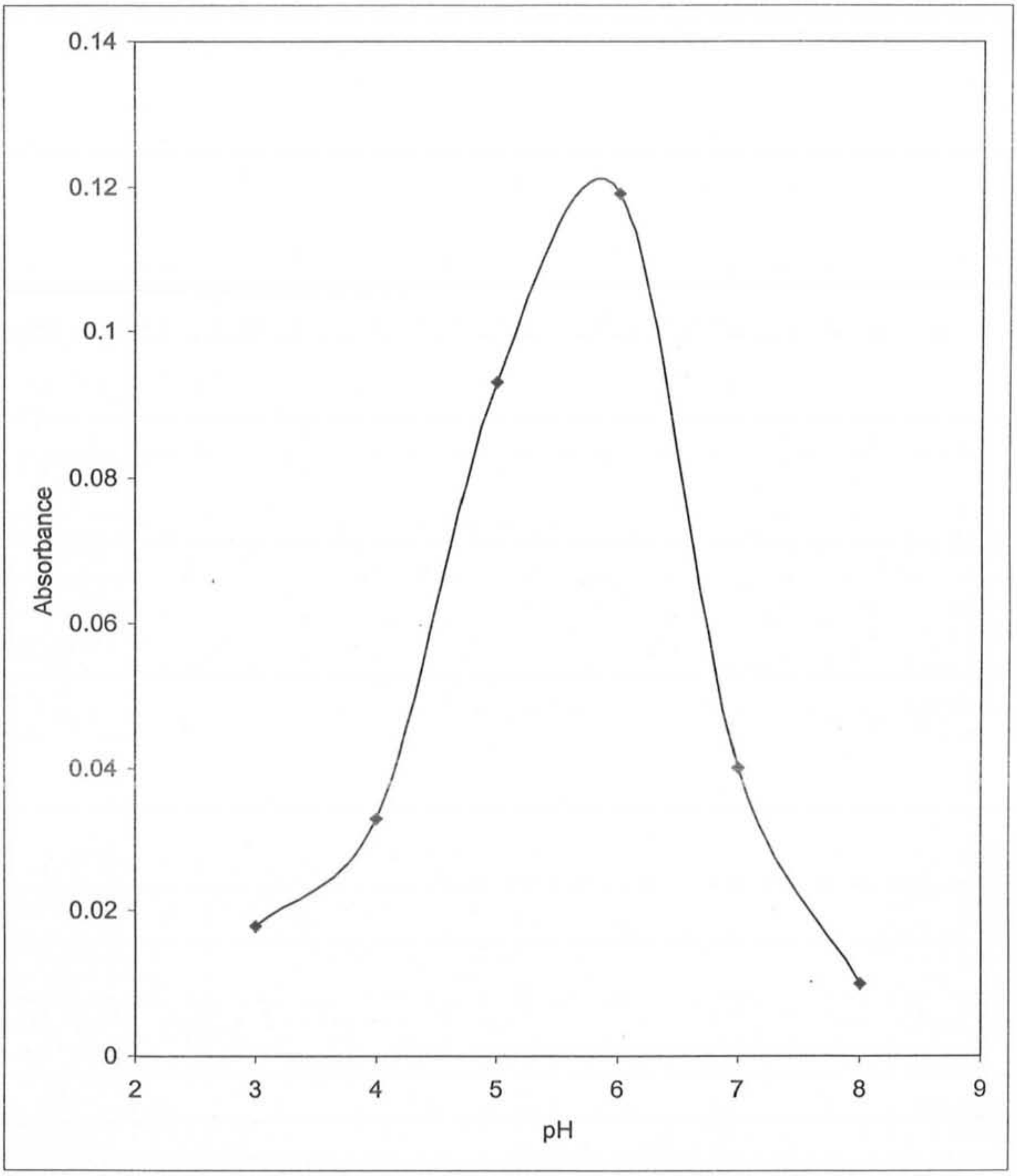


Fig.2.3 Effect of pH on Mn(II)-complexation.

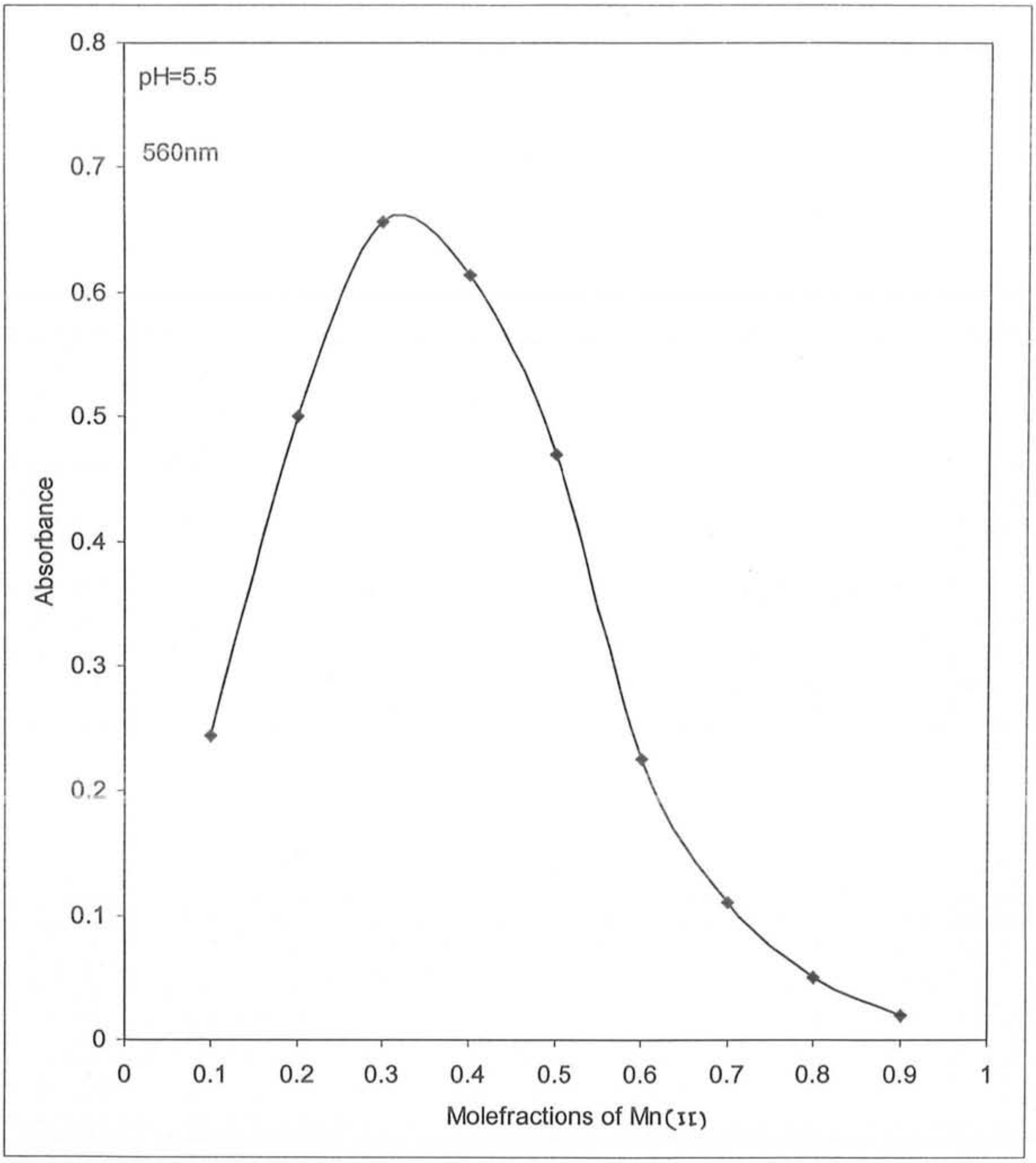


Fig.3.4 Stoichiometric study of Mn(II)-complex (Mn vs o-phenanthroline)

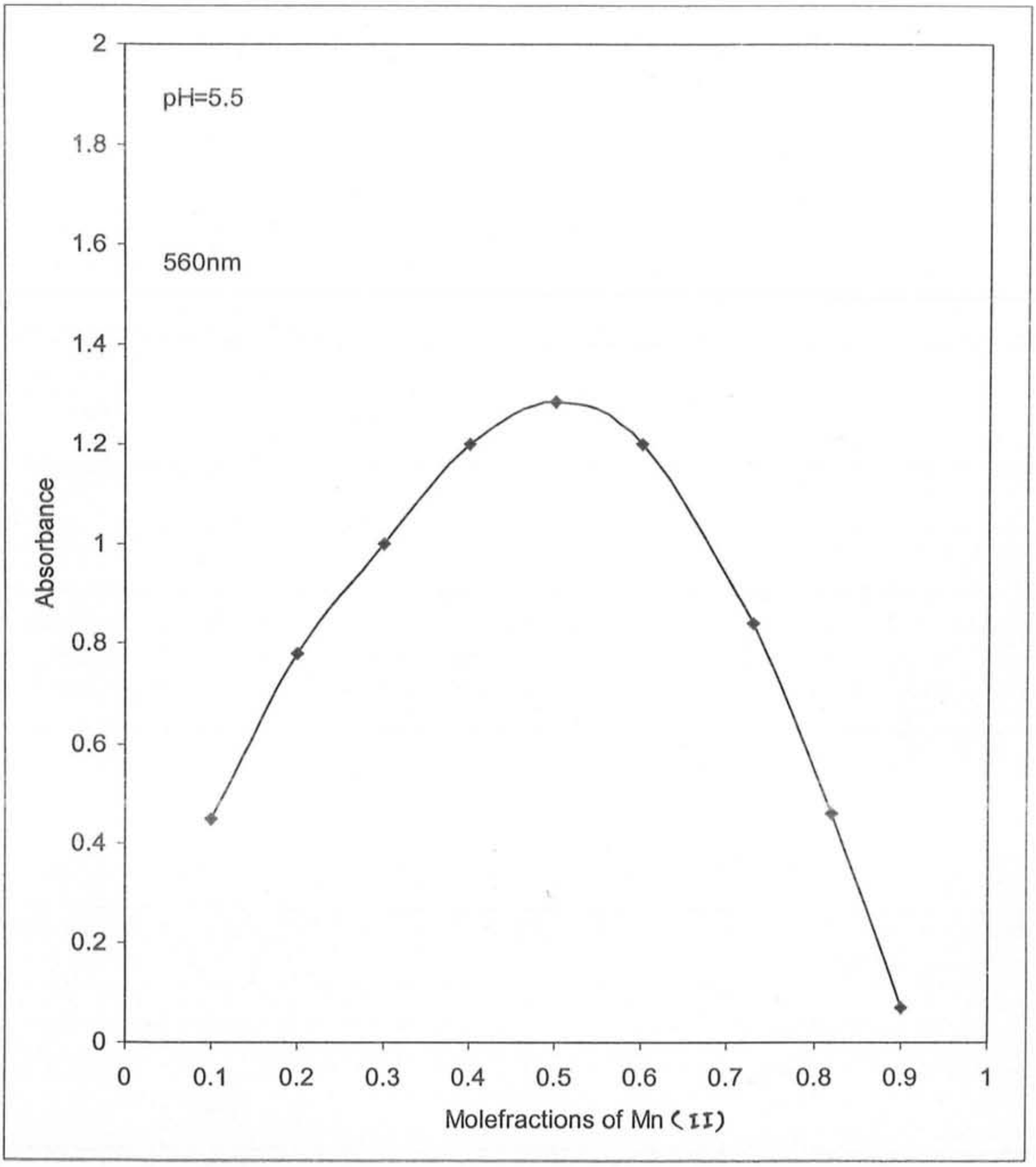


Fig.3.5 Stoichiometric study of Mn(II)-complex (Mn vs eosin)

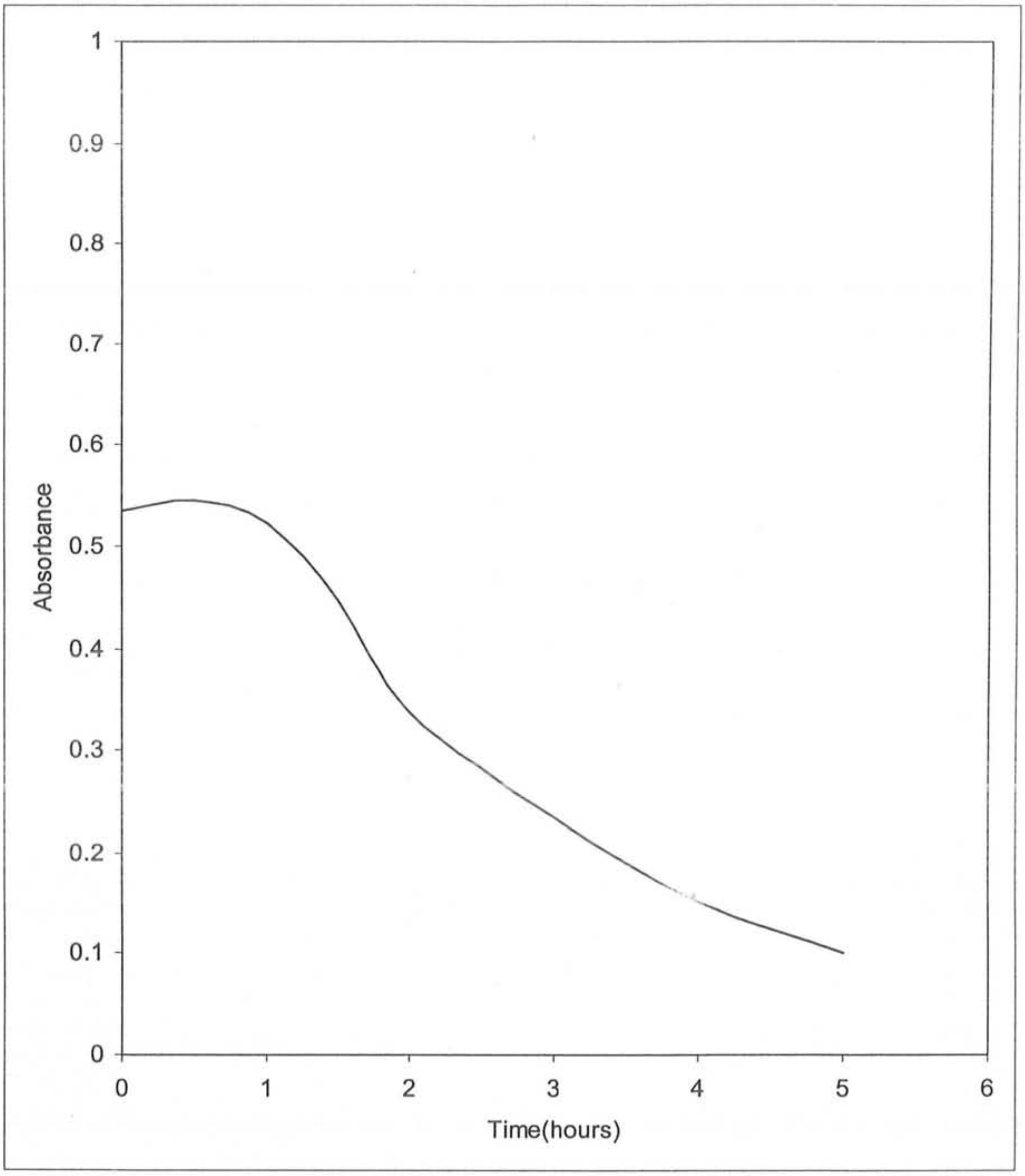


Fig.3.6 Effect of Time on Mn(II)-complexation.

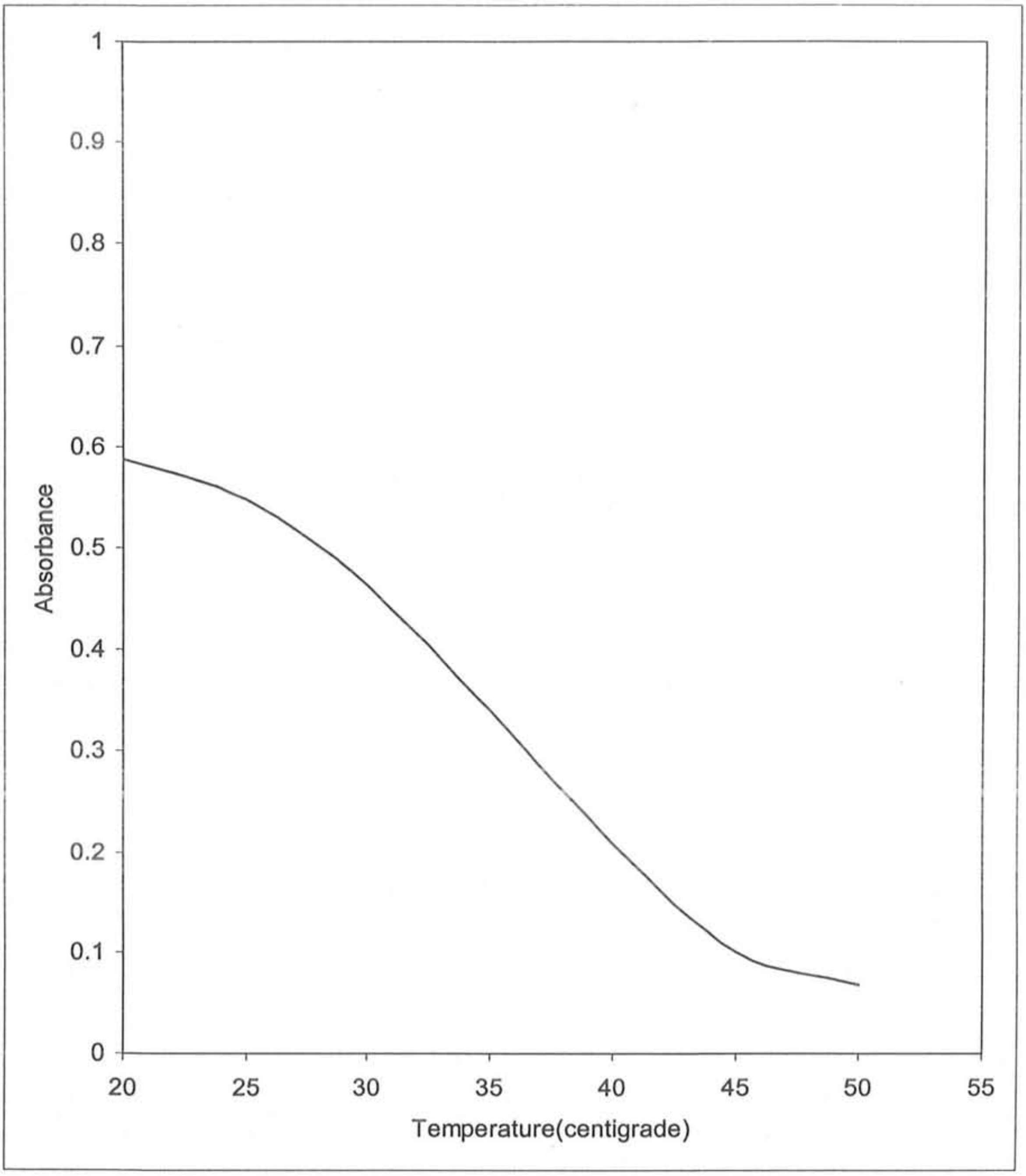


Fig.3.7 Effect of Temperature on Mn(II)-complexation.

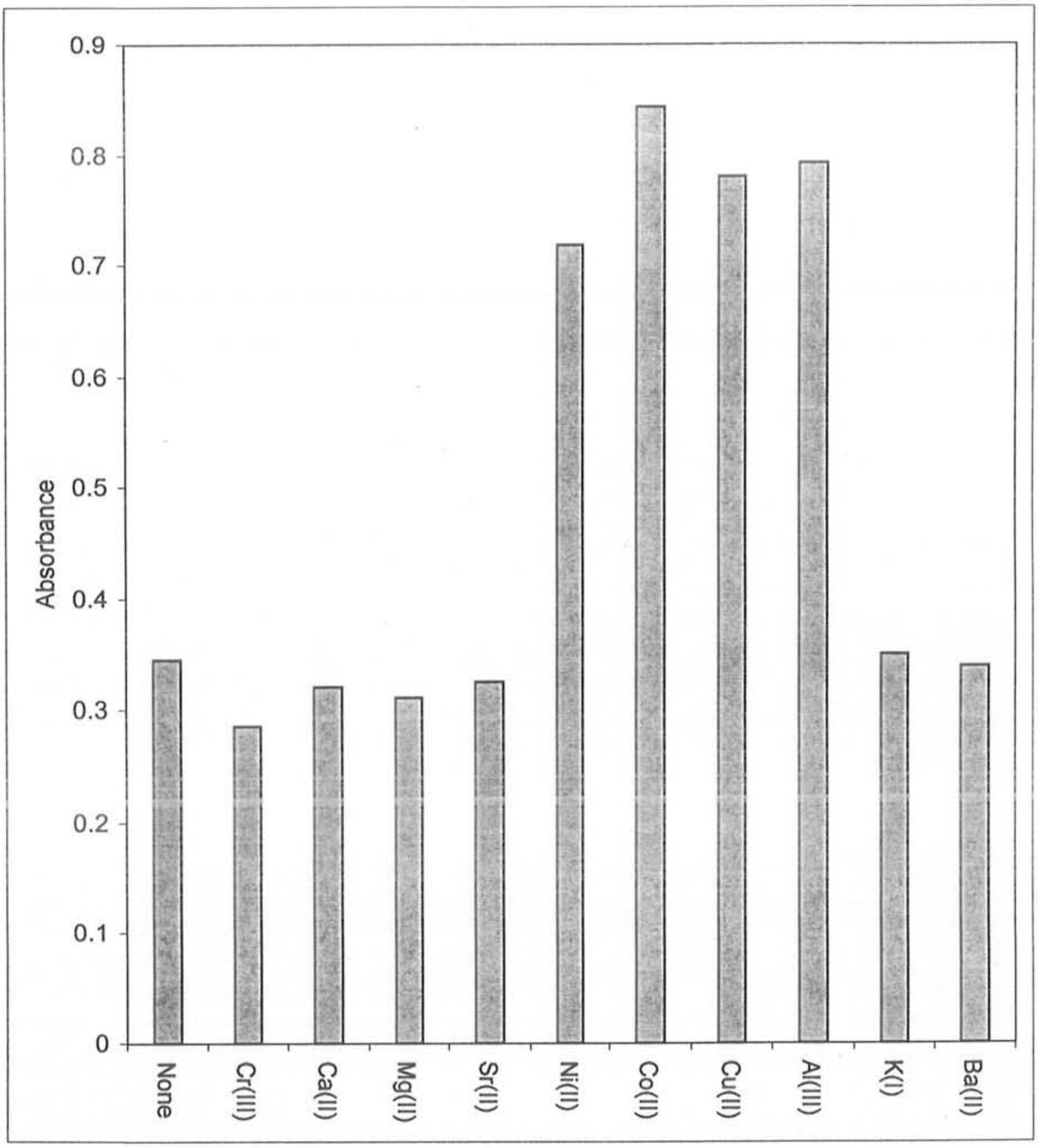


Fig.3.8 Effect of different cations on Mn(II)-complexation.

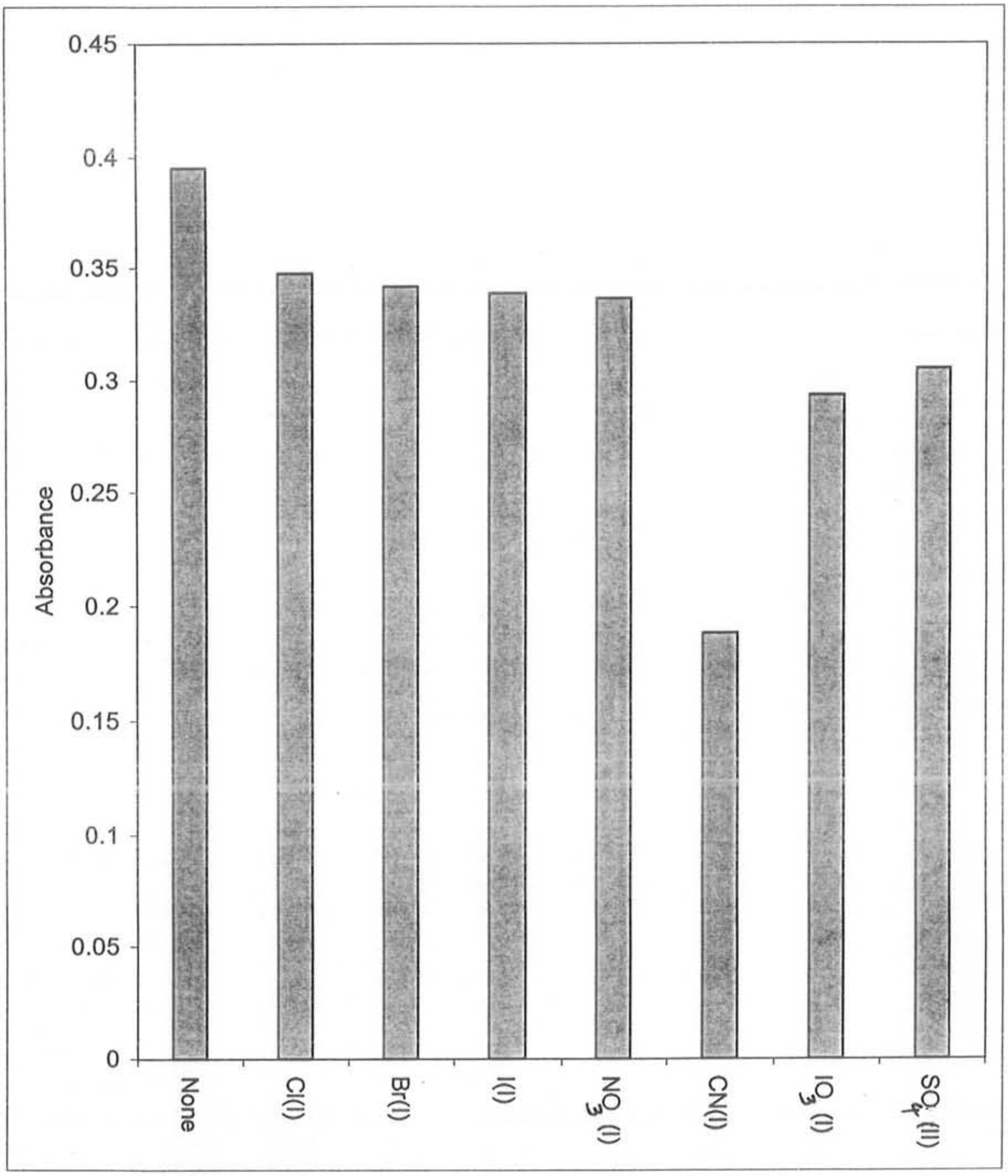


Fig. 3.9 Effect of different anions on Mn(II)-complexation.

TABLE 4.3

Effect of different cations on Mn(II)-complexation

Cations	*Limiting conc.(M)*	*% Effect on intensity*
Cr^{+3}	1.3×10^{-6}	-5
Ca^{+2}	3.7×10^{-4}	-3
Mg^{+2}	7.2×10^{-4}	-2
Sr^{+2}	1.3×10^{-4}	-5
Ni^{+2}	3.7×10^{-7}	+8
Co^{+2}	3.7×10^{-7}	+15
Cu^{+2}	3.7×10^{-7}	+8
Al^{+3}	3.7×10^{-7}	+9
K^{+1}	3.7×10^{-4}	-2
Ba^{+2}	1.3×10^{-4}	-7

*All the cations were added as their nitrate salts.

TABLE 4.4

Effect of different anions on Mn(II)-complexation

Anions	*Limiting conc.(M)*	*% Effect on intensity*
Cl^{-1}	3.7×10^{-2}	-4
Br^{-1}	3.7×10^{-2}	-3
I^{-1}	3.7×10^{-3}	-3
NO_3^{-1}	3.7×10^{-1}	-1
IO_3^{-1}	3.7×10^{-5}	-7
SO_4^{-2}	3.7×10^{-5}	-8
CN^{-1}	1.3×10^{-7}	-10

*All the anions were added as their potassium salts.

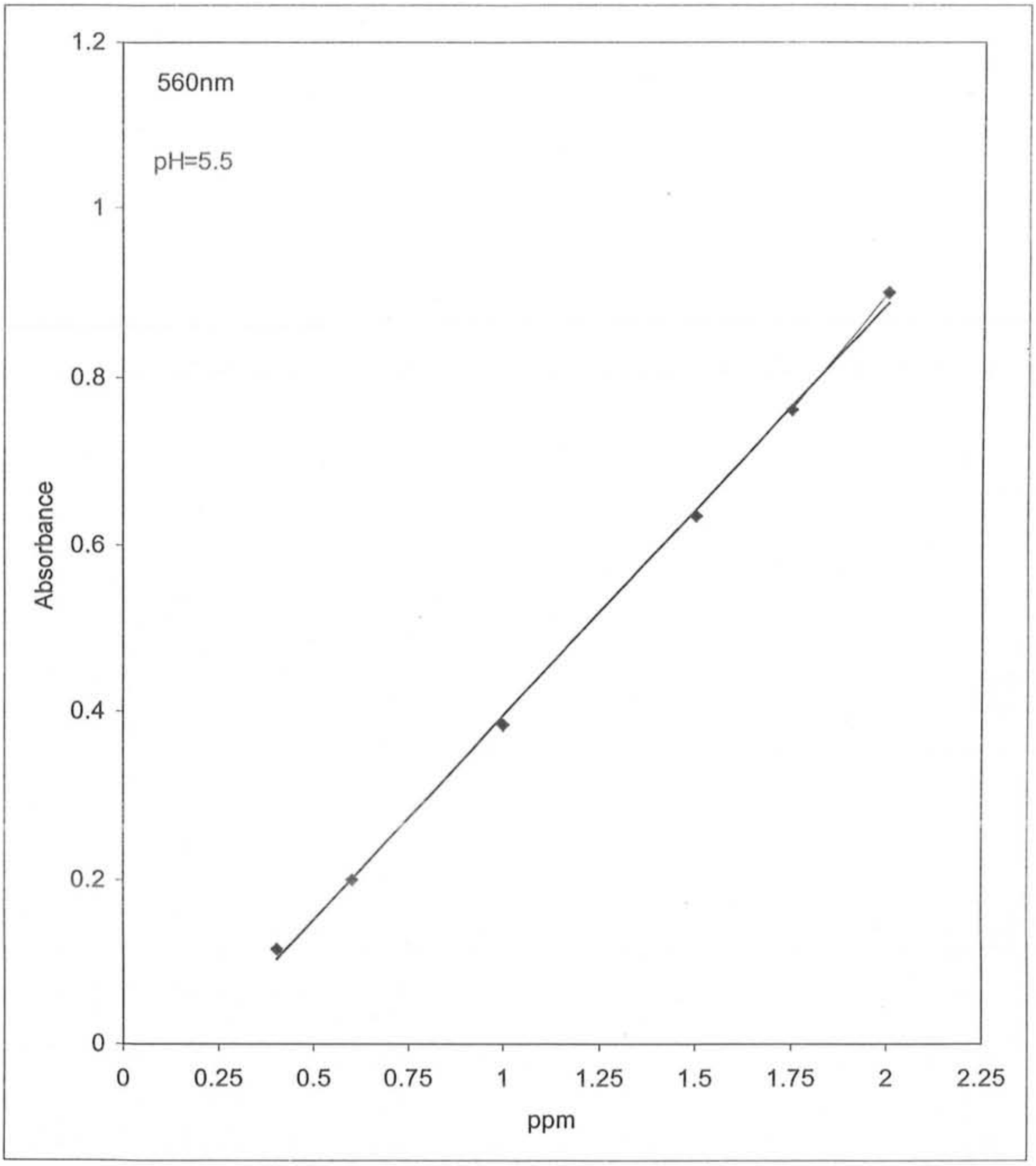


Fig.3.10 Adherence to Beer's law for Mn(II)-complex

4.4 Complexation of Fe^{+3} with o-Phenanthroline and Eosin

Ferric ion is a d^5 system. One of the most conspicuous feature of Fe^{+3} in aqueous solution is its tendency to hydrolyze or to form complex. The hydrolysis of pale purple ion $[Fe(H_2O)_6]^{+3}$ in non complexing media is complicated and condition dependent[63,64].On long standing it is converted to deep yellow colour forming an anionic complex $[Fe(OH)_6]^{-3}$.In the presence of complexing anions such as Cl^{-1}, the hydrolysis of Fe^{+3} is more complicated giving chloro, aqua and hydroxy species as well as $[FeCl]^{-1}$ at high chloride ion concentration[65].The affinity of Fe^{+3} for amine is very low. No simple amine complex exists in aqueous solution; addition of aqueous ammonia only precipitates the hydrous oxide. Chelating amines e.g. EDTA, form complexes, among which the seven co-ordinated complex$[Fe(EDTA)H_2O]^{-3}$. Only ligands like bipyridin and phenathroline , which produce ligand fields strong enough to cause spin paring for fairly stable complexes.

The absorption spectrum of the Fe^{+3} ion in aqueous medium shows very strong absorption band in ultraviolet region (Fig.4.1). The spectrum of reaction mixture of Fe(III), o-Phenethroline and eosin *versus* reagent blank shows an apparent decrease in absorption at 510nm and exhibits a new band at 555nm (Fig.4.2). The appearance of the new band at 555nm indicates the formation of the metal complex with o-Phen. and eosin. Using buffer solutions of different pH optimized the pH of the complex. Maximum complexation was obtained at pH 5.5 (Fig. 4.3).

The stoichiometry of the complex has been determined by applying continuous variation method (*Job's Method*).The mole fractions of the two components were varied continuously, keeping their combined concentrations constant, and by taking the third component in large excess for all the solutions in the series. The molar ratio of the Iron(III), o-Phenanthroline and eosin was found to be 1:1:1 as shown in the Fig. (4.4,4.5).Thus composition of the complex was found to be $[Fe(o\text{-}Phen)_2]E$.

In the formation of this complex, the primary ligand(o-Phen.), on entering the co-ordination sphere of Fe^{+3}, forms co-ordinate covalent bond by its two nitrogens, but their complex ion still bears overall +3 charge on the co-ordination sphere, and it is free to associate with secondary ligand (Eosin) to form a ternary complex. This ternary complex exhibits an absorption band at 555nm.

Concentration, molar absorptivity and stability constants of the complex

By applying continuous variation method, the concentration, molar absorptivity and stability of the complex have been determined[50-55].

Concentration: In Figure (4.5) the extrapolated value(A_{ext}) at the piont of crossection, on the continuous variation plot corresponds to the total absorbance of the complex, if the complex formation has been completed. Actually, the complex is dissociative in nature and absorbance value is therefore somewhat less.

The concentration of the complex has been determined from the following equation:

$$A/A_{ext} = MX/C$$

Where C is the total analytical concentration.

From the continuous variation curve (Fig.4.5) values of A, A_{ext} and C were obtained.

$A = 1.87$

$A_{ext}=2.07$

$C = 7.5\times10^{-5}M$

MX = Concentration of the complex

Now by putting these values in above equation concentration of the complex can be calculated.

$$MX = A\times C/A_{ext}$$

$$= 1.87\times7.5\times10^{-5}/2.07$$

$$= 6.78\times10^{-5}M$$

Molar Absorption Coefficient: The molar absorption coefficient of the complex can be calculated by using the following equation:

$A = \varepsilon CL$

ε is a constant at same wavelength , called molar absorption coefficient and has a units of L.mole^{-1}.cm^{-1}.The use of this symbol specifically requires that the concentration is expressed in units of molarity and sample path length in centimeters.

A = Absorption of the complex at 560nm.

C = Concentration of the complex.

L = Path length

Concentration of the complex have been calculated already

$C = 6.78\times10^{-5}M$

$L = 1cm$

By applying the above equation

$$\varepsilon = A/CL$$

$$=1.87/1\times6.78\times10^{-5}$$

$$=2.8\times10^{4}L.mole^{-1}cm^{-1}$$

Stability Constant: Stability of a complex is very important.

The equation of the complex formation is following:

$$[Fe(o\text{-}Phen.)]^{+3} + E^{+2} \quad \leftrightarrow \quad [Fe(o\text{-}Phen.)]E$$

$$K = [Fe(o\text{-}Phen.)]E_{eq} / [Fe(o\text{-}Phen.)]_{eq}[E]_{eq}$$

K = Equilibrium Constant

The equilibrium concentration of the metal ion and ligand can be determined as follows

$$[Fe(o\text{-}Phen.)]_{eq} = [Fe(o\text{-}Phen.)] - [Fe(o\text{-}Phen.)]E_{eq}$$

$$= 7.5\times10^{-5} - 6.78\times10^{-5}M$$

$$= 7.2\times10^{-6}M$$

Now equilibrium concentration of the secondary ligand can be calculated as

$$[E]_{eq} = [E] - [Fe(o\text{-}Phen.)]E_{eq}$$

$$= 7.5\times10^{-5} - 6.78\times10^{-5}$$

$$= 7.2\times10^{-6}M$$

By putting these values in the equilibrium equation

$$K = 6.78\times10^{-5} / (7.2\times10^{-6})\,(7.2\times10^{-6})$$

$$K = 1.31\times10^{6}$$

$$\text{Log } K = 6.11$$

Effect of Time

The complex formation started immediately after the mixing of the reagents and it was completed in half-hour. The complex remained stable for more than 24 hours. The optimum time for complex formation was half-hours (Fig.4.6)

Effect of Temperature

This complex is stable up to 40 °C (Fig.4.7). The optimum temperature for complexation is upto 35°C. This complex is relatively stable. This stability of the complex is probably due to strong association of the primary ligand (o-Phenanthroline) with Fe^{+3}, resulting in the formation of stable cationic complex which associates with the eosin anion.

Effect of cations and anions

The effect of various cations Cr^{+3}, Ca^{+2}, Mg^{+2}, Sr^{+2}, Ni^{+2}, Co^{+2},Cu^{+2}, Al^{+3}, K^{+1}, Ba^{+2} (Fig.4.8) and anions Cl^{-1}, Br^{-1}, I^{-1}, NO^{-1}_3, IO^{-1}_3, SO^{-2}_4 andCN^{-1} (Fig.4.9) has been studied on the complexation of the manganese complex. The limiting concentration and percentage decrease in absorbance is shown in the Tables (1.7,1.8).

It is observed that Cr^{+3}, Ni^{+2}, Co^{+2},Cu^{+2} and Al^{+3}effects the complex by decreasing the absorbance at λ_{max} of the complex. Ca^{+2}, Mg^{+2}, Sr^{+2} K^{+1},and Ba^{+2} show no significant effect. This complex is less effected by the cations, showing preference of the ligand for Fe(III) as compared to other metal ions.

The Cl^{-1}, Br^{-1}, I^{-1} and NO^{-1}_3 shows no effects on the complexation when present in equimolar amounts, but effect is pronounced when concentration is raised. The anions IO^{-1}_3, SO^{-2}_4 decreases the absorbance when present in equimolar amounts. The CN^{-1} has most striking effect on the complex, even when it is present in small amounts.

Calibration graphs

The system follows Beer's law over the range 0.3-2 ppm for Fe^{+3}. Primary and secondary ligands were used in excess. Fig.(4.10)

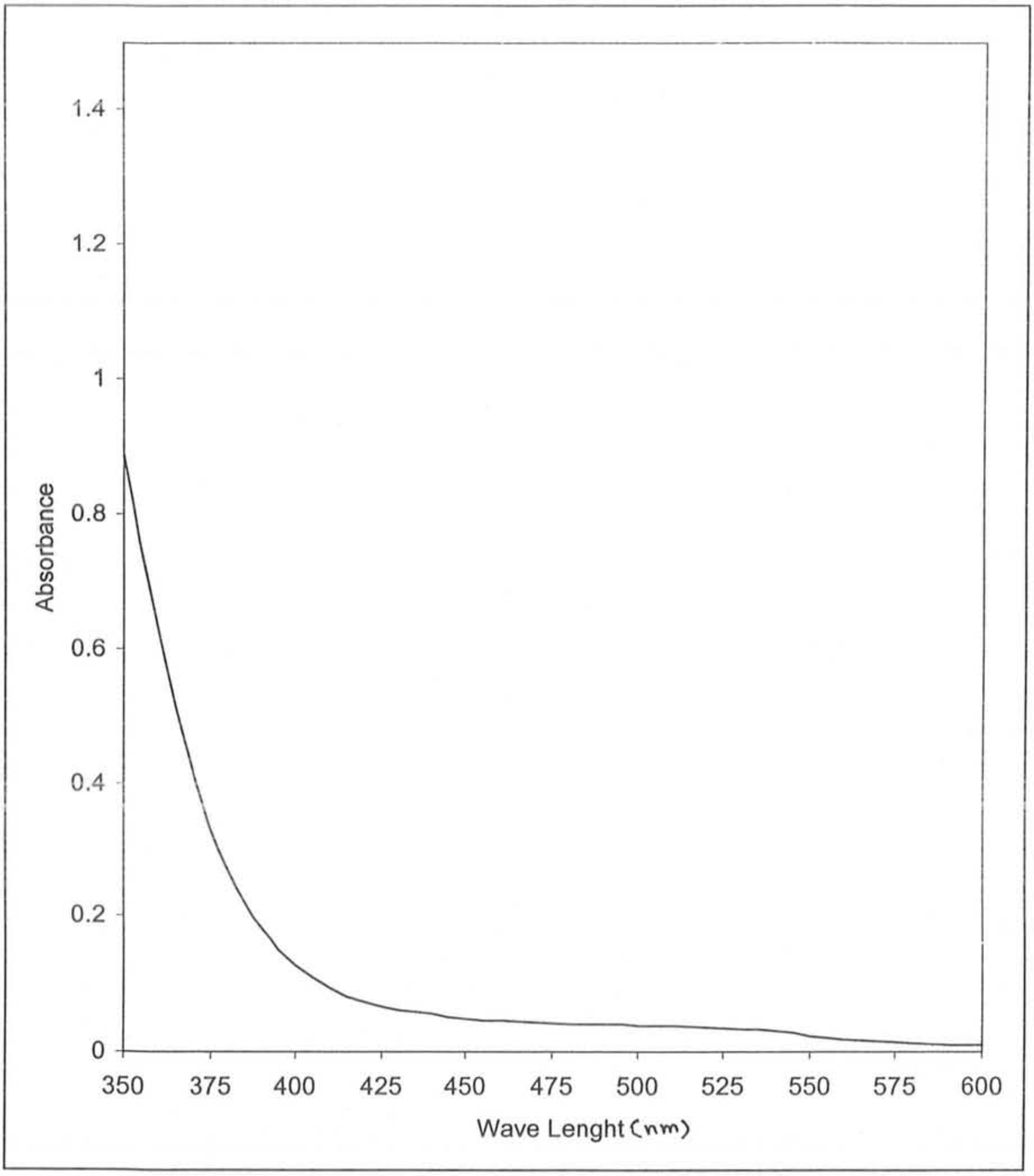


Fig.4.1 Absorption spectrum of Fe(III) in aqueous solution.

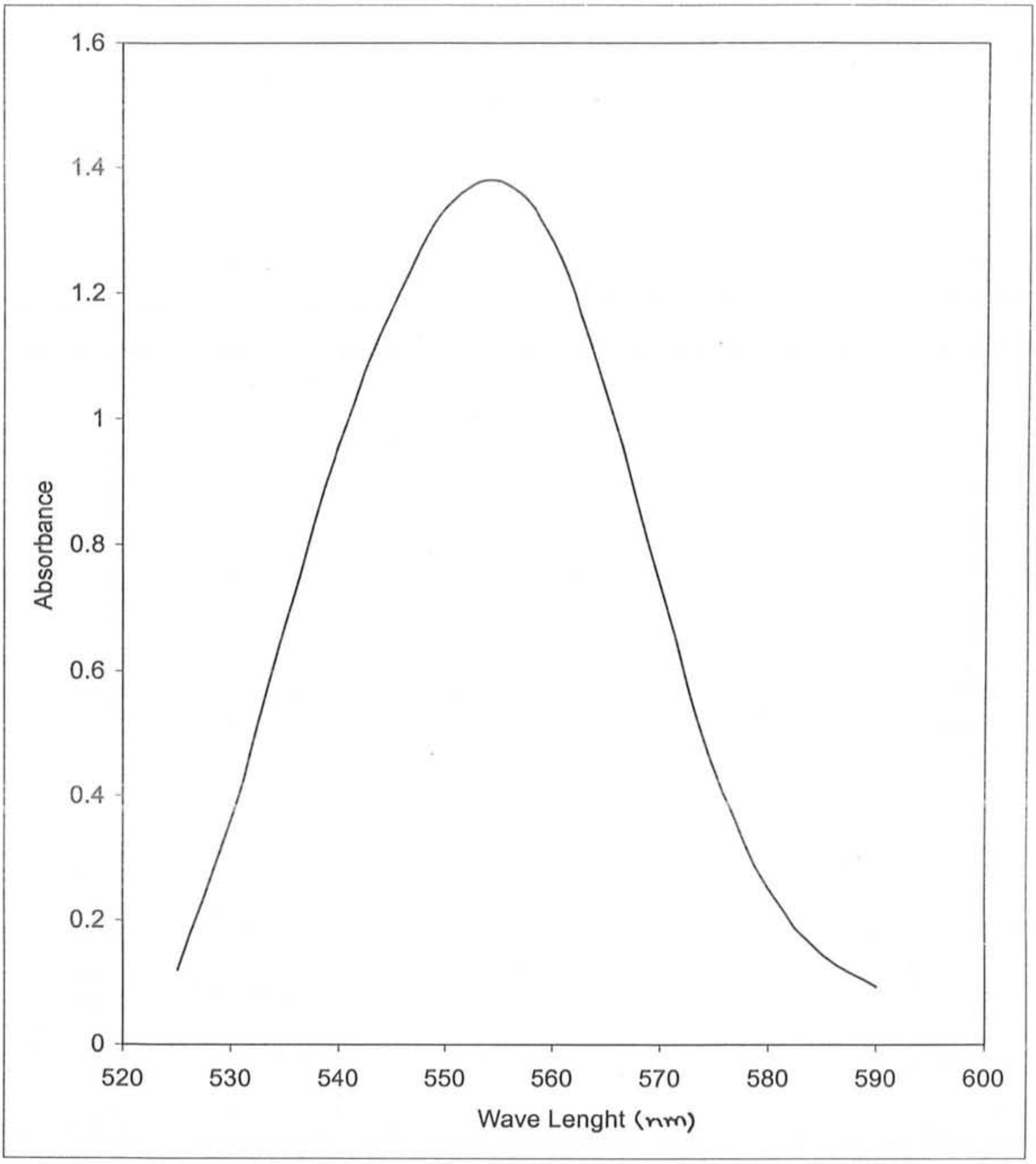


Fig.4.2 Absorption spectrum of Fe(III)-complex.

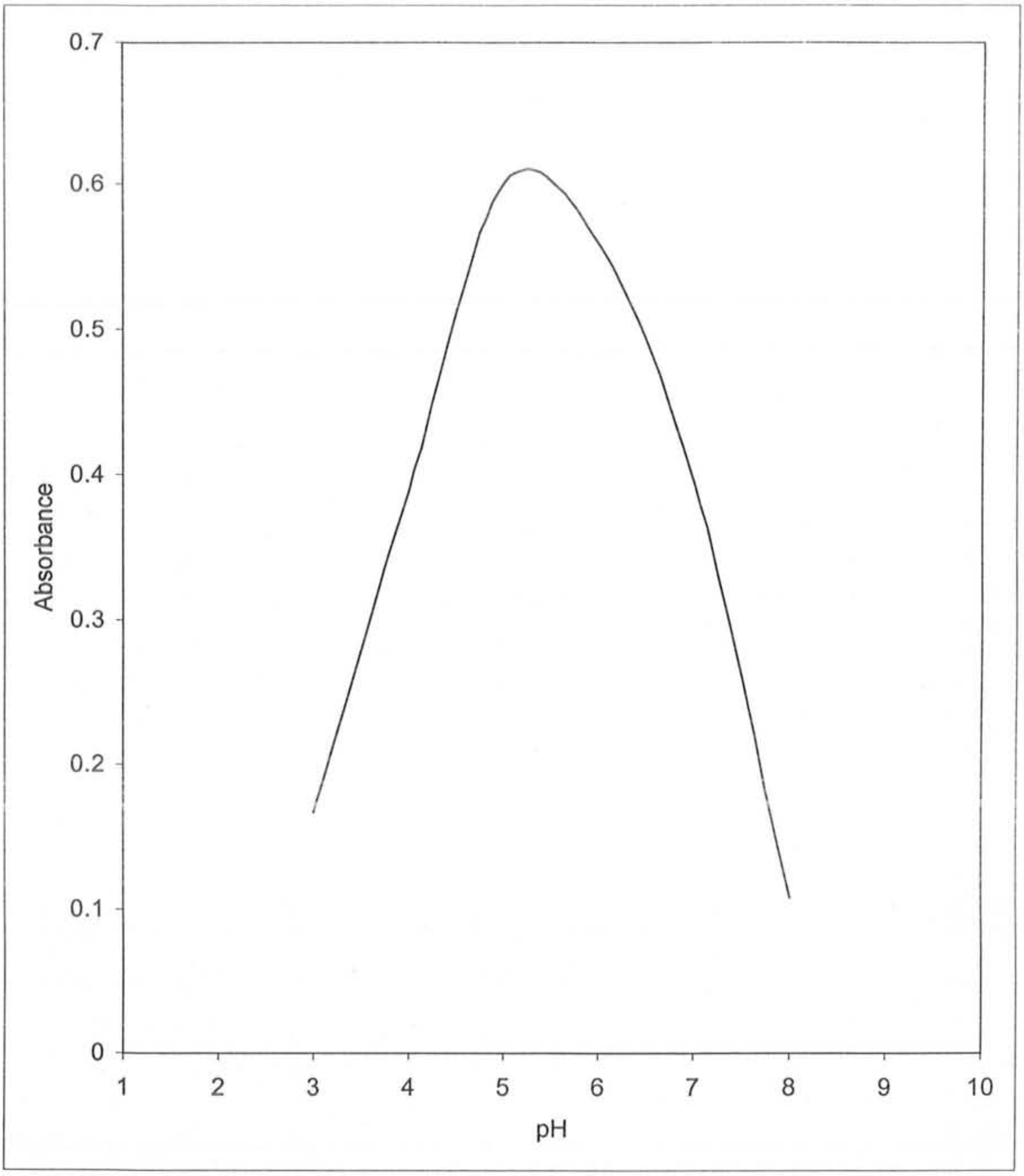


Fig.4.3 Effect of pH on Fe(III)-complexation.

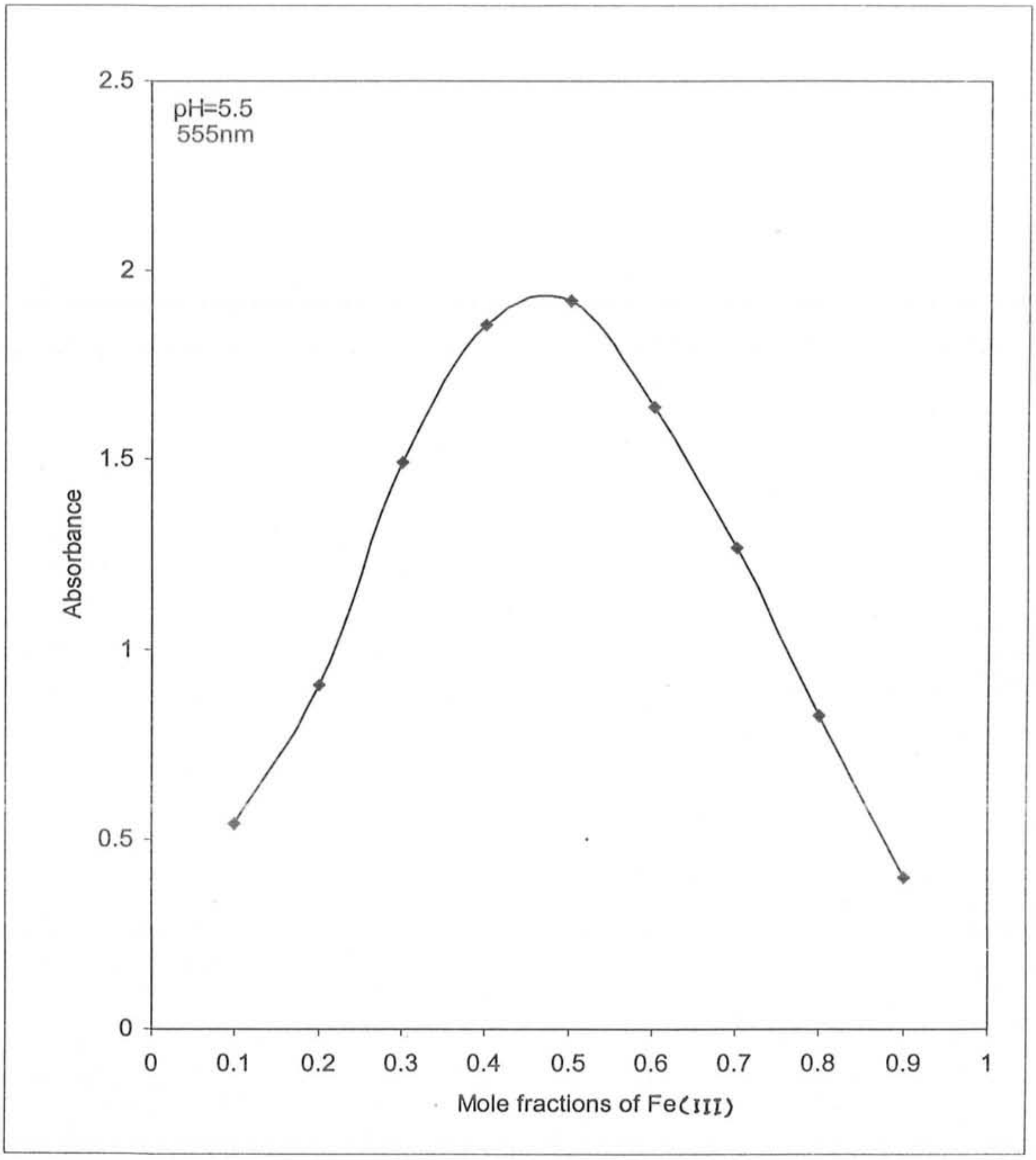


Fig.4.4 Stoichiometric study of Fe(III)-complex(Fe vs o-Phen)

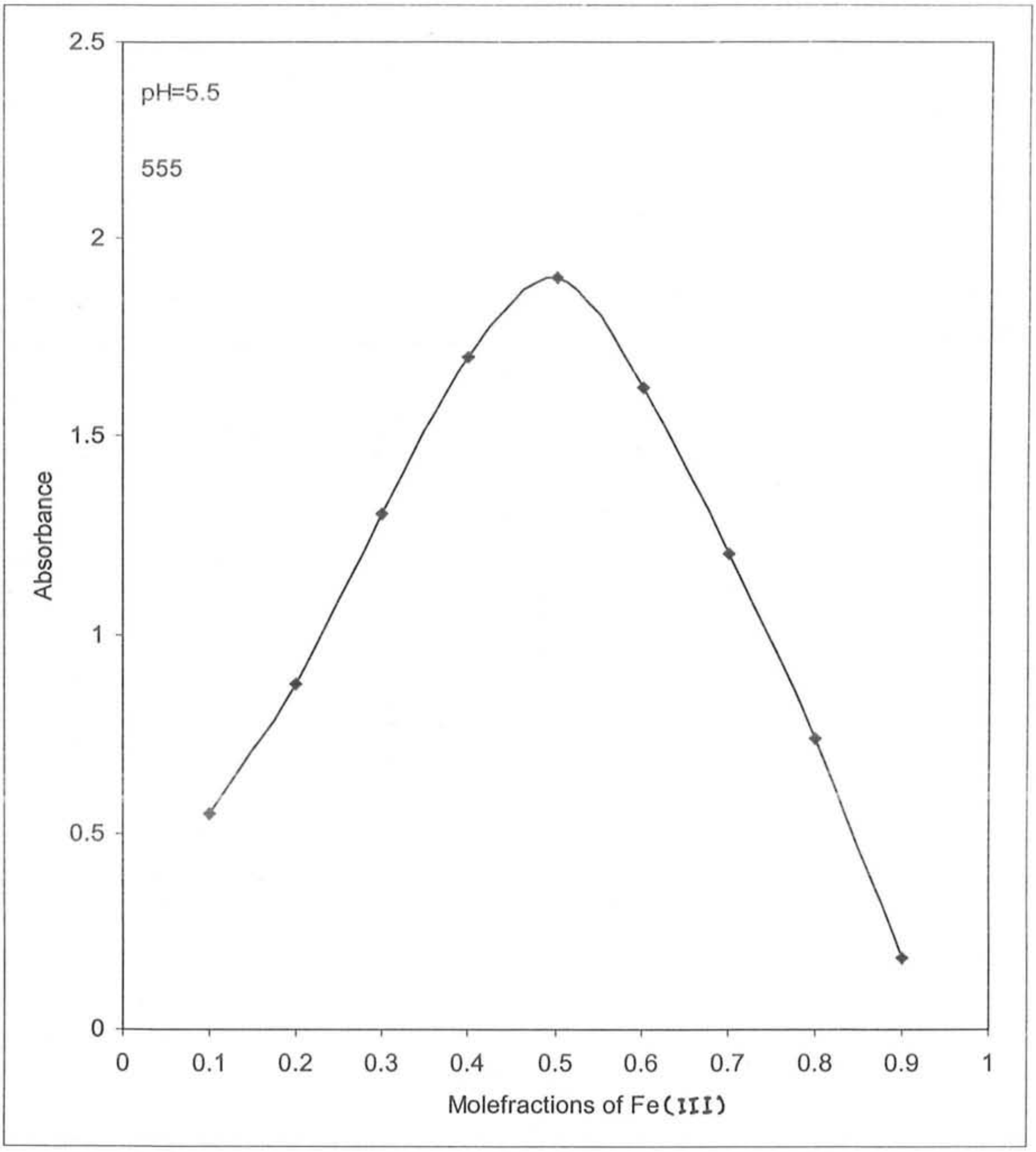


Fig.4.5 Stoichiometric Study of Fe(III)-complex(Fe vs eosin)

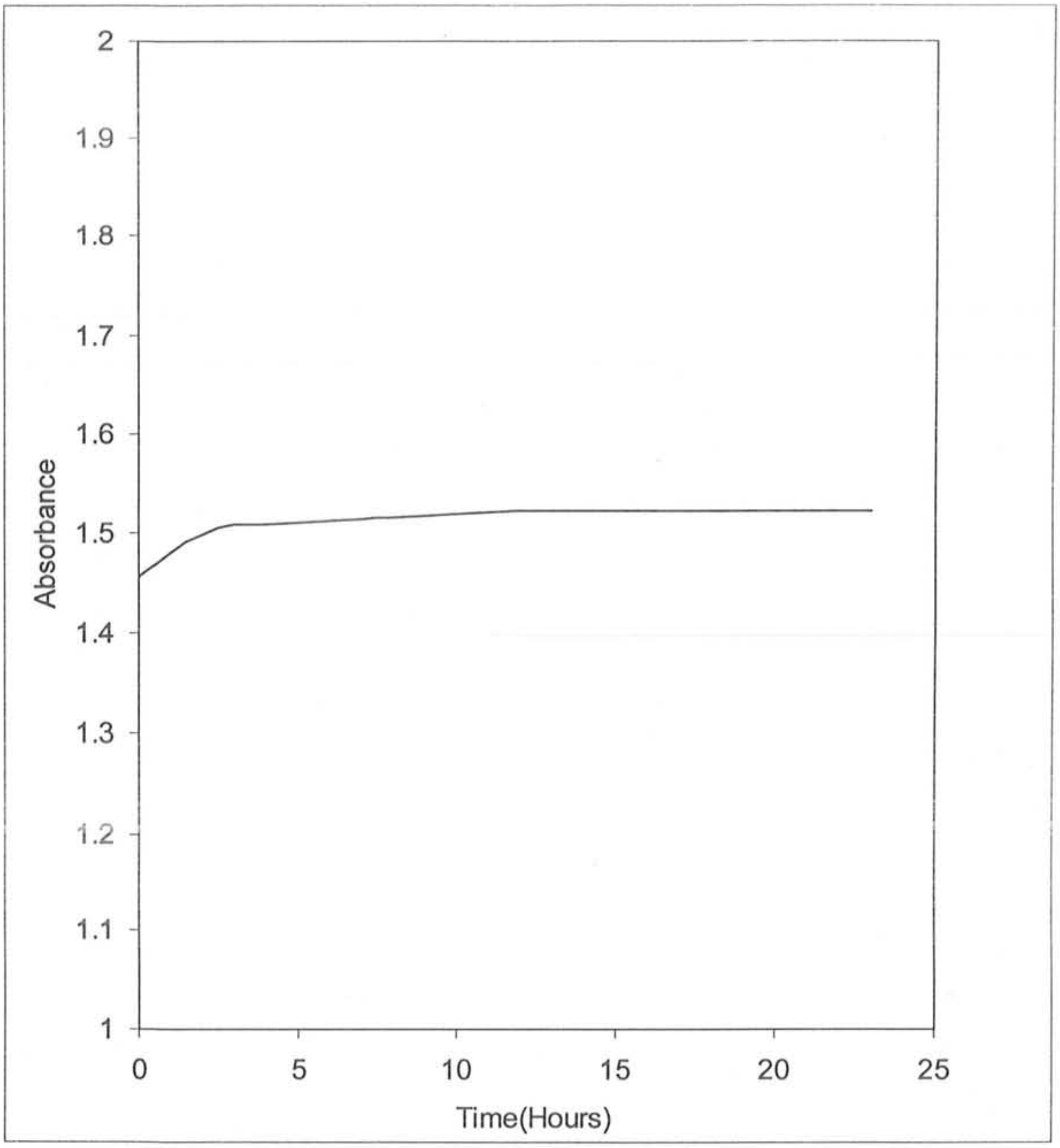


Fig.4.6 Effect of time on Fe(III)-complexation.

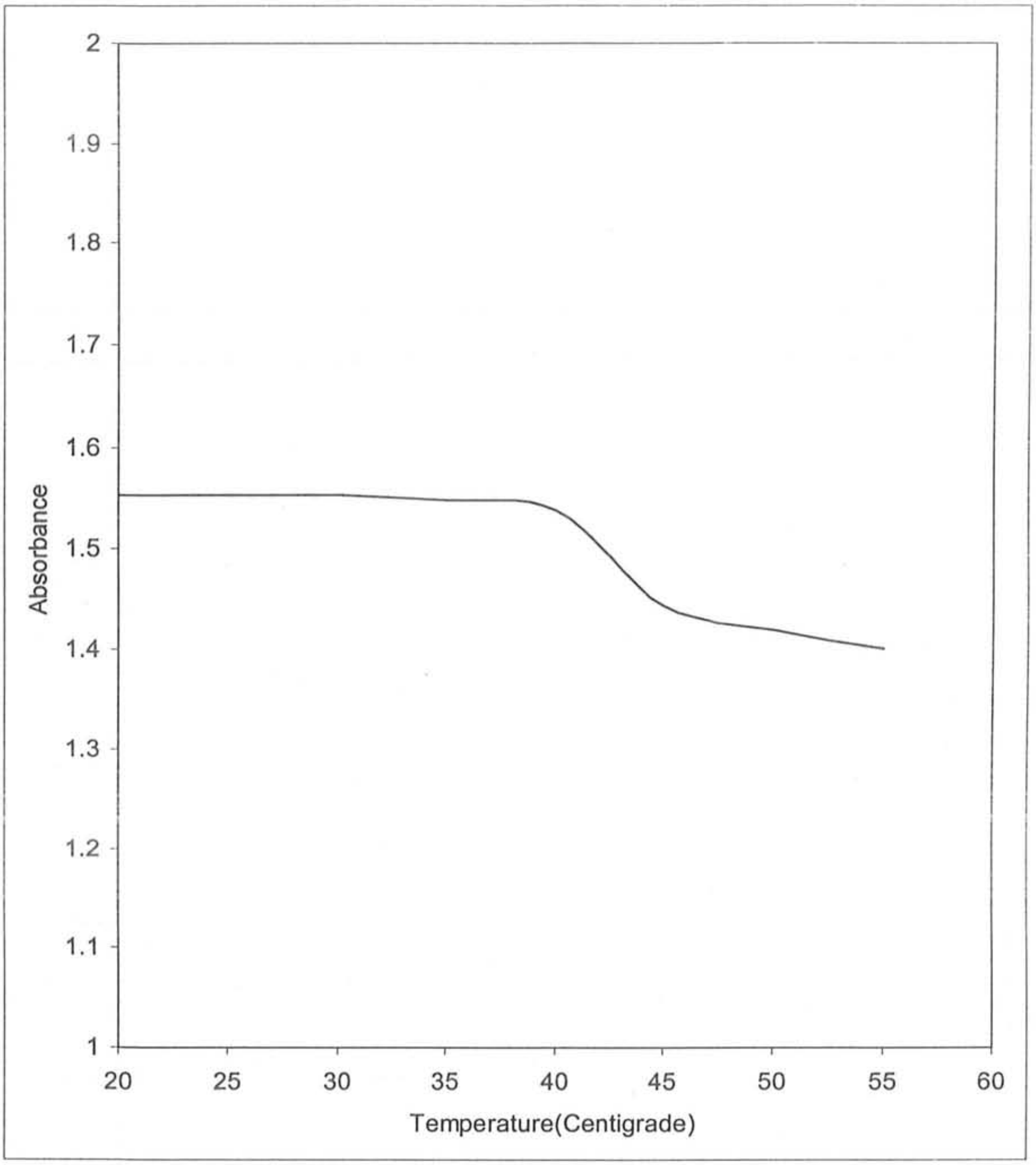


Fig. 4.7 Effect of temperature on Fe(III)-complexation.

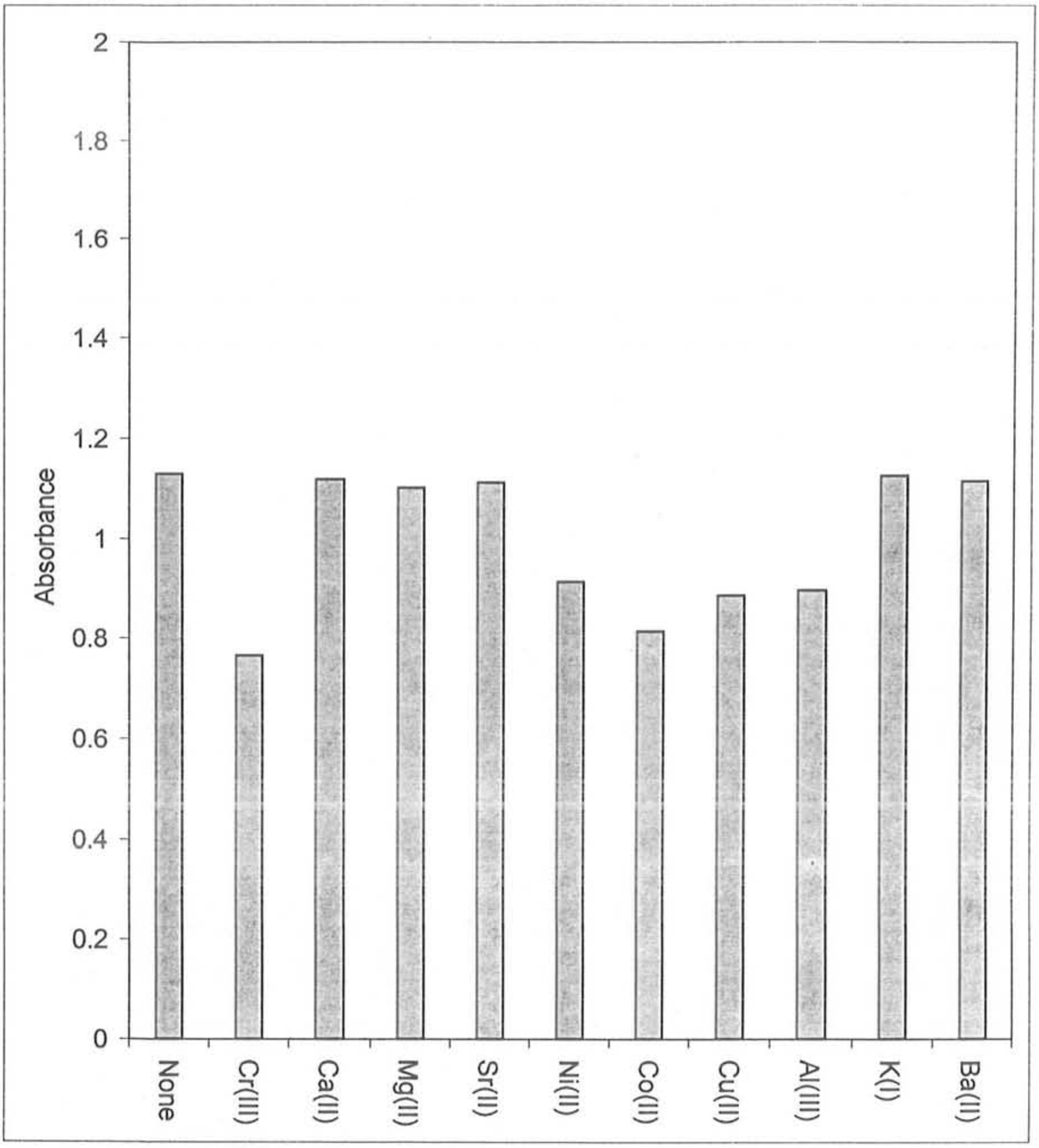


Fig.4.8 Effect of different cations on Fe(III)-complexation.

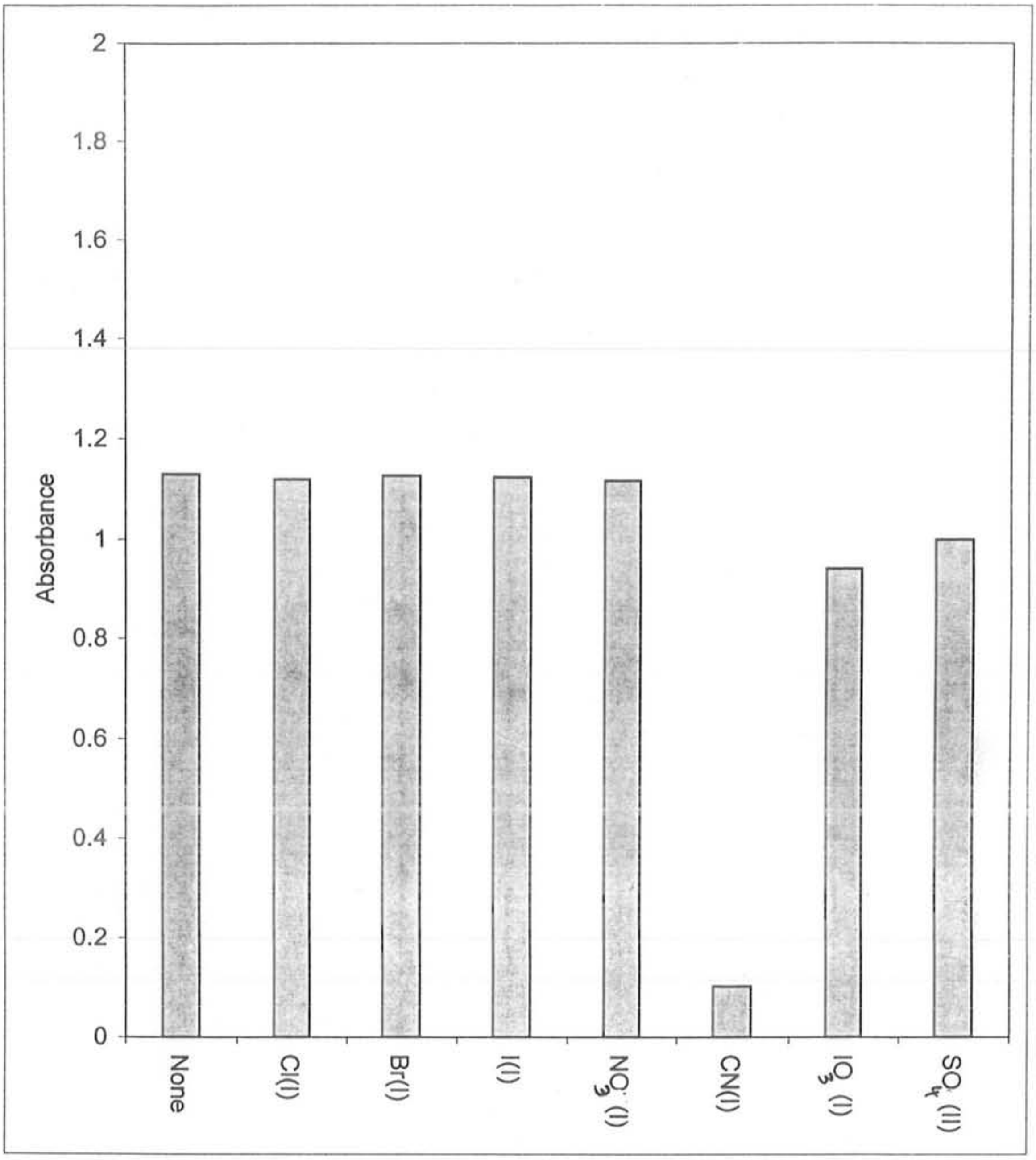


Fig. 4.9 Effect of different anions on Fe(III)-complexation.

TABLE 4.5

Effect of different cations on Fe(III)-complexation

Cations	*Limiting conc.(M)*	*% Effect on intensity*
Cr^{+3}	1.3×10^{-5}	10
Ca^{+2}	3.7×10^{-4}	-3
Mg^{+2}	7.2×10^{-4}	-4
Sr^{+2}	1.3×10^{-4}	-3
Ni^{+2}	3.7×10^{-6}	-9
Co^{+2}	3.7×10^{-6}	-12
Cu^{+2}	3.7×10^{-6}	-7
Al^{+3}	3.7×10^{-6}	-5
K^{+1}	3.7×10^{-4}	-1
Ba^{+2}	1.3×10^{-4}	-2

*All the cations were added as their nitrate salts.

TABLE 4.6

Effect of different anions on Fe(III)-complexation

Anions	*Limiting conc.(M)*	*% Effect on intensity*
Cl^{-1}	3.7×10^{-2}	-5
Br^{-1}	3.7×10^{-2}	-3
I^{-1}	3.7×10^{-3}	-4
NO_3^{-1}	3.7×10^{-1}	-1
IO_3^{-1}	3.7×10^{-5}	-4
SO_4^{-2}	3.7×10^{-5}	-8
CN^{-1}	1.3×10^{-7}-2	-15

*All the anions were added as their potassium salts.

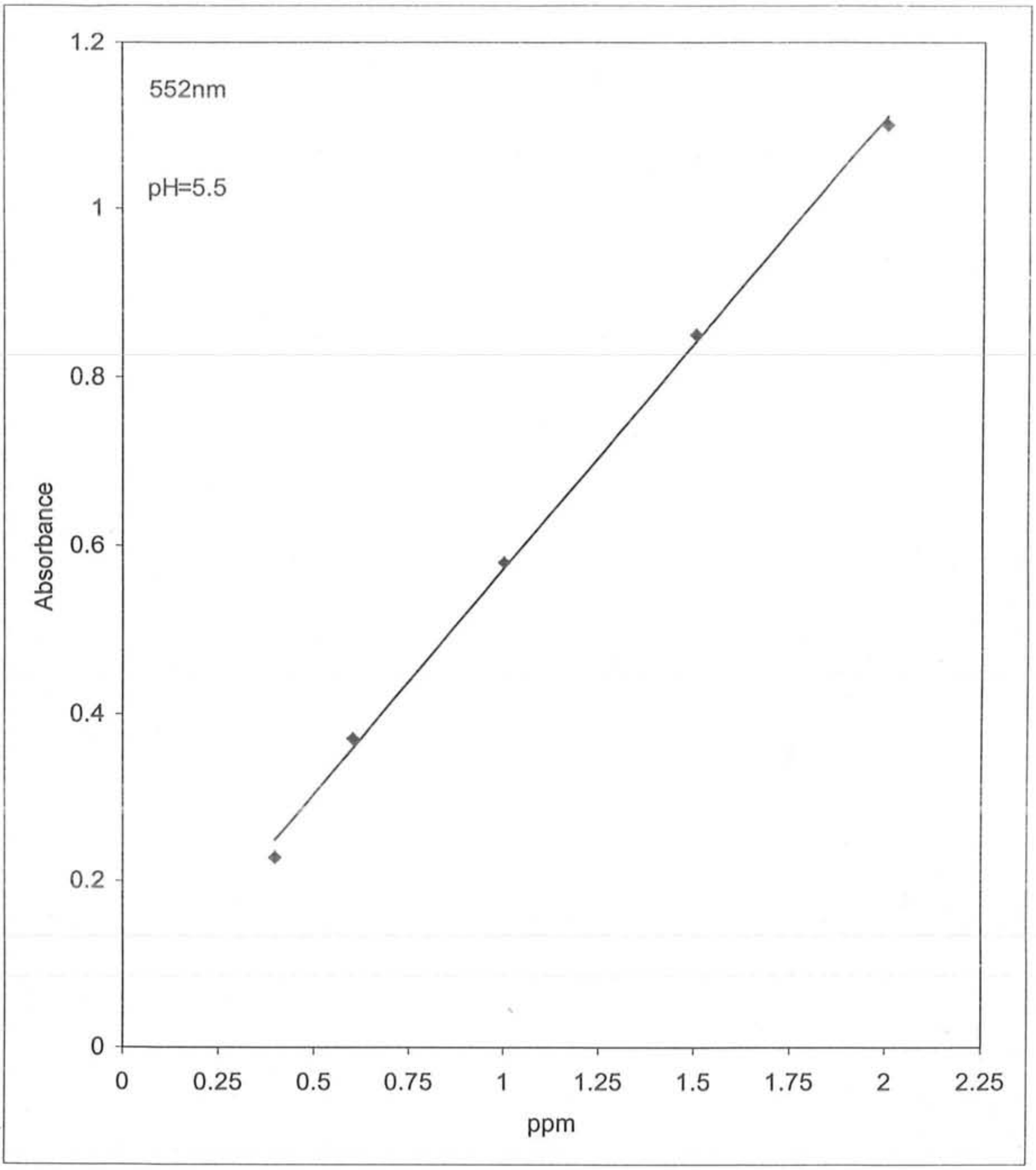


Fig.4.10 Adherence to Beer's law for Fe(III).

4.5 Complexation of Pb^{+2} with o-Phenanthroline and Eosin

The soluble salts of Pb^{+2} gives hydrated ions and these hydrated ions are partially hydrolyzed in water[65]. Lead also forms the numerous complexes that are mostly octahedral, however trigonal bi pyramidal[67,67] and polymeric complexes are also formed.

The absorption spectrum of the Pb^{+2} ion in aqueous medium shows weak absorption band in ultraviolet region. The spectrum of reaction mixture of lead, o-Phenethroline and eosin *versus* reagent blank shows an apparent decrease in absorption at 510nm and exhibits a new band at 558nm (Fig.5.2). The appearance of the new band at 558nm indicates the formation of the metal complex with o-Phen. and eosin. Using buffer solutions of different pH optimized the pH of the complex. Maximum complexation was obtained at pH 4.5 (Fig. 5.3).

The stoichiometry of the complex has been determined by applying continuous variation method (*Job's Method*).The mole fractions of the two components were varied continuously, keeping their combined concentrations constant, and by taking the third component in large excess for all the solutions in the series. The molar ratio of the lead, o-Phenethroline and eosin was found to be 1:1:1 as shown in the Figures (5.4,5.5).Thus composition of the complex was found to be $[Pb(o\text{-}Phen)_2]E$.

In the formation of this complex, the primary ligand(o-Phen.), on entering the co-ordination sphere of Pb^{+2}, forms co-ordinate covalent bond by its two nitrogens, but their complex ion still bears overall +2 charge on the co-ordination sphere, and it is free to associate with secondary ligand (Eosin) to form a ternary complex. This ternary complex exhibits an absorption band at 558nm.

Concentration, molar absorptivity and stability constants of the complex

By applying continuous variation method, the concentration, molar absorptivity and stability of the complex have been determined[50-55].

Concentration: In Figure (5.5) the extrapolated value(A_{ext}) at the piont of crossection, on the continuous variation plot corresponds to the total absorbance of the complex, if the complex formation has been completed. Actually, the complex is dissociative in nature and absorbance value is therefore somewhat less.

The concentration of the complex has been determined from the following equation:

$$A/A_{ext} = MX/C$$

Where C is the total analytical concentration.

From the continuous variation curve (Fig.5.5) values of A, A_{ext} and C were obtained.

$A = 1.481$

$A_{ext}=1.54$

$C = 7.5\times10^{-5}M$

MX = Concentration of the complex

Now by putting these values in above equation concentration of the complex can be calculated.

$$\begin{aligned} MX &= A\times C/A_{ext} \\ &= 1.481\times7.5\times10^{-5}/1.54 \\ &= 7.21\times10^{-5}M \end{aligned}$$

Molar Absorption Coefficient: The molar absorption coefficient of the complex can be calculated by using the following equation:

$A = \varepsilon CL$

ε is a constant at same wavelength , called molar absorption coefficient and has a units of $L.mole^{-1}.cm^{-1}$.The use of this symbol specifically requires that the concentration is expressed in units of molarity and sample path length in centimeters.

A = Absorption of the complex at 558nm.

C = Concentration of the complex.

L = Path length

Concentration of the complex have been calculated already

$C = 7.21\times10^{-5}M$

$L = 1cm$

By applying the above equation

$$\varepsilon = A/CL$$

$$=1.481/1\times7.21\times10^{-5}$$

$$=2.054\times10^{4}L.mole^{-1}cm^{-1}$$

Stability Constant: Stability of a complex is very important.

The equation of the complex formation is following:

$$[Pb(o\text{-}Phen.)]^{+2} + E^{+2} \leftrightarrow [Pb(o\text{-}Phen.)]E$$

$$K = [Pb(o\text{-}Phen.)]E_{eq} / [Pb(o\text{-}Phen.)]_{eq}[E]_{eq}$$

K = Equilibrium Constant

The equilibrium concentration of the metal ion and ligand can be determined as follows

$$[Pb(o\text{-}Phen.)]_{eq} = [Pb(o\text{-}Phen.)]\text{-} [Pb(o\text{-}Phen.)]E_{eq}$$

$$= 7.5\times10^{-5} - 7.21\times10^{-5}M$$

$$= 2.9\times10^{-6}M$$

Now equilibrium concentration of the secondary ligand can be calculated as

$$[E]_{eq} = [E]\text{-} [Pb(o\text{-}Phen.)]E_{eq}$$

$$= 7.5\times10^{-5}\text{-}7.21\times10^{-5}$$

$$= 2.9\times10^{-6}M$$

By putting these values in the equilibrium equation

$$K = 7.21\times10^{-5} / (2.9\times10^{-6})(2.9\times10^{-6})$$

$$K = 8.57\times10^{6}$$

$$Log\ K = 6.93$$

Effect of Time

The complex formation started immediately after the mixing of the reagents and it was completed in half-hour. The complex remained stable for more than 24 hours. The optimum time for complex formation was two hours (Fig.5.6)

Effect of Temperature

This complex is stable up to 30 °C (Fig.5.7). The optimum temperature for complexation is up to 25°C. This complex is relatively stable. Complex is relatively less stable.

Effect of cations and anions

The effect of various cations Cr^{+3}, Ca^{+2}, Mg^{+2}, Sr^{+2}, Ni^{+2}, Co^{+2},Cu^{+2}, Al^{+3}, K^{+1}, Ba^{+2} (Fig.5.8) and anions Cl^{-1}, Br^{-1}, I^{-1}, NO^{-1}_3, IO^{-1}_3, SO^{-2}_4 andCN^{-1} (Fig.5.9) has been studied on the complexation of the lead complex. The limiting concentration and percentage decrease in absorbance is shown in the Tables (1.9,1.10).

It is observed that Cr^{+3}, Ni^{+2}, Co^{+2},Cu^{+2} and Al^{+3}effects the complex by decreasing the absorbance at λ_{max} of the complex. Ca^{+2}, Mg^{+2}, Sr^{+2} K^{+1},and Ba^{+2} show no significant effect. This complex is less effected by the cations, showing preference to the ligand as compared to other metal ions.

The Cl^{-1}, Br^{-1}, I^{-1} and NO^{-1}_3 shows no effect on the complex when present in equimolar amounts, but effect is pronounced when concentration is raised. The anions IO^{-1}_3, SO^{-2}_4 decreases the absorbance when present in equimolar amounts. The CN^{-1} has most striking effect on the complex, even when it is present in small amounts.

Calibration graphs

The system follows Beer's law over the range 0.5-2 ppm for Pb^{+2}. Primary and secondary ligands were used in excess.Fig.(5.10).

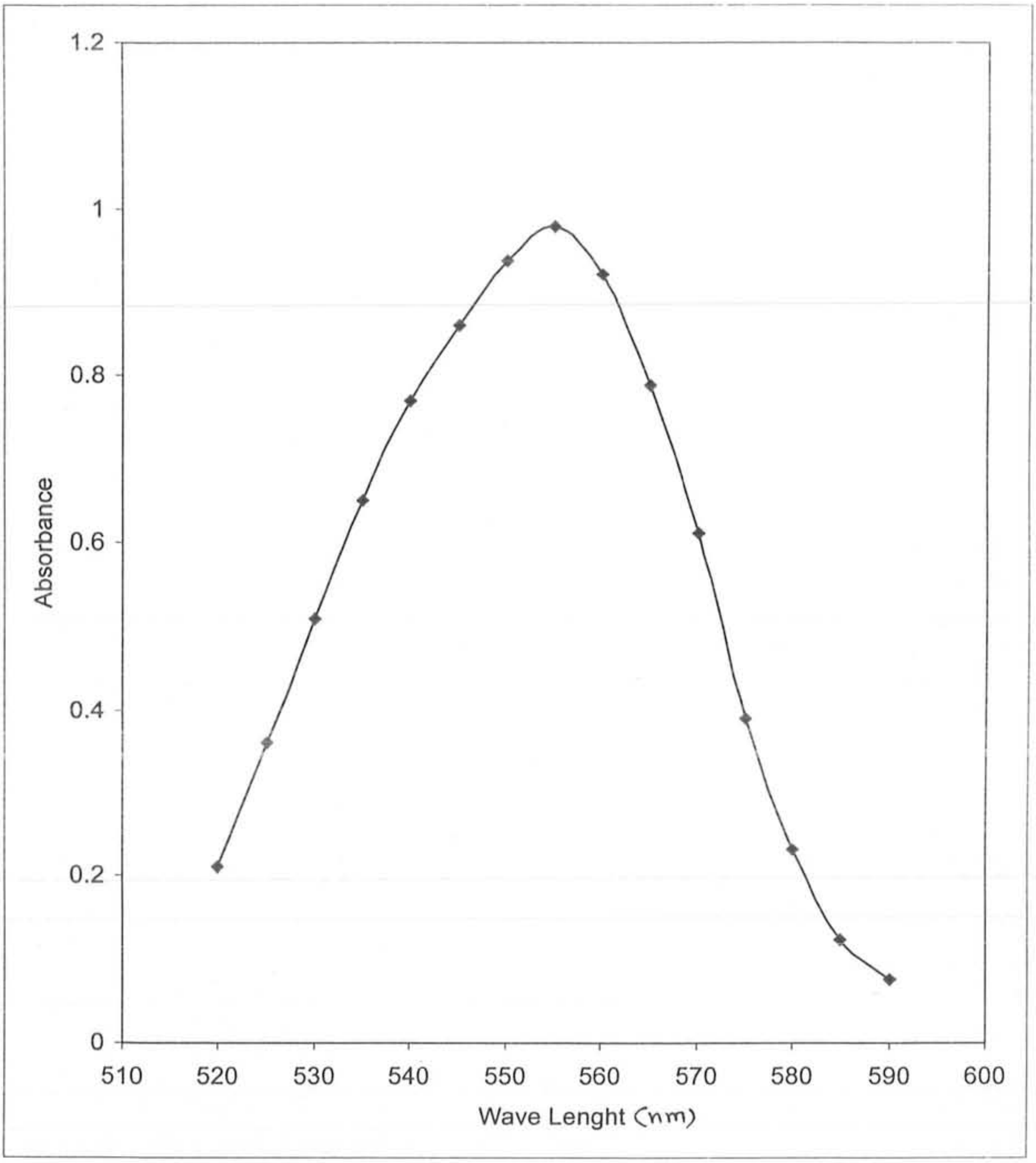


Fig.5.2 Absorption spectrum of Pb(II)-complex.

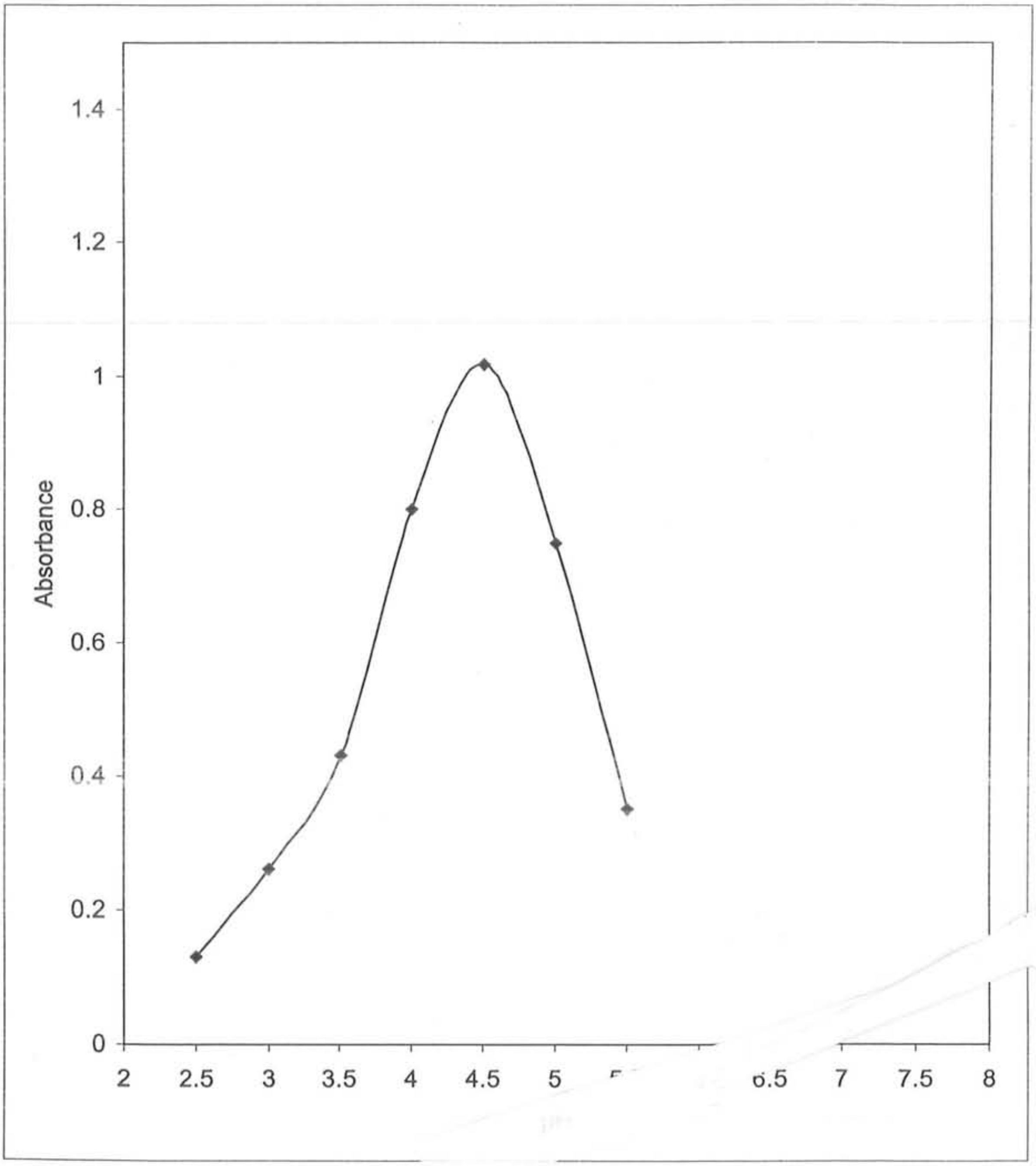


Fig.5.3 Effect of pH on Pb(II)-complexation.

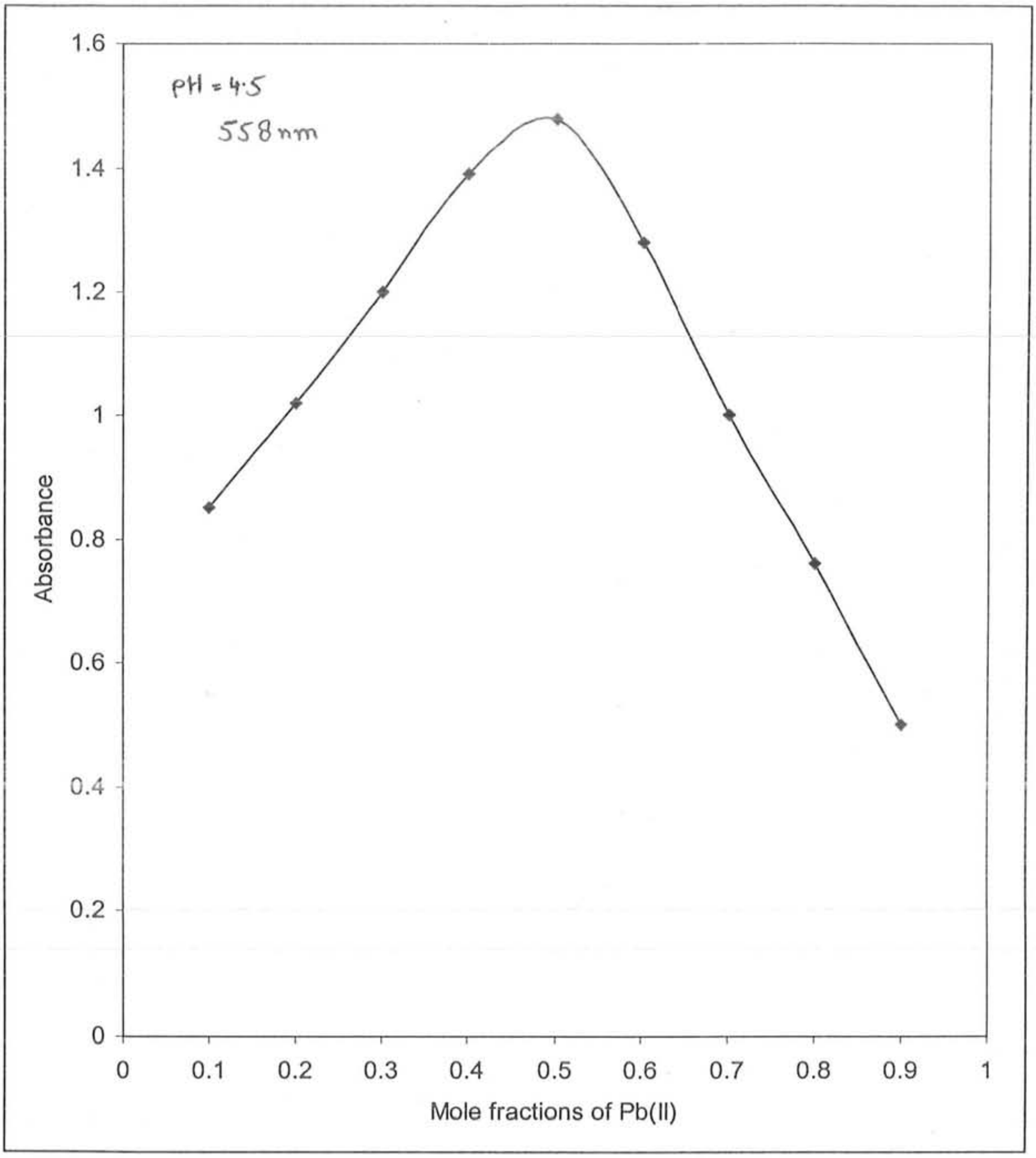


Fig. 5.5 Stoichiometric study of Pb(II)-complex (Pb(II) vs eosin.)

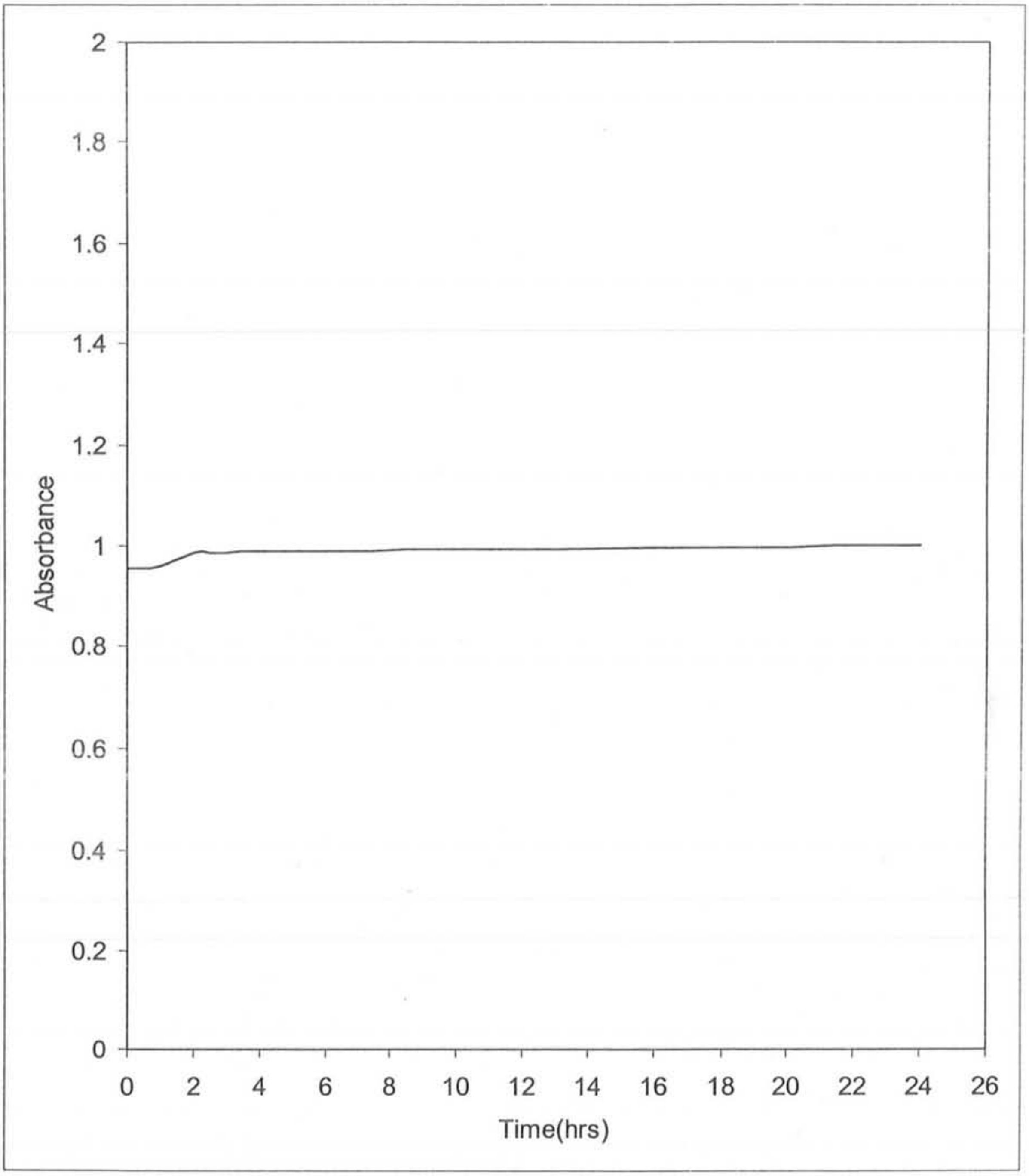


Fig.5.6 Effect of time on Pb(II)-complexation.

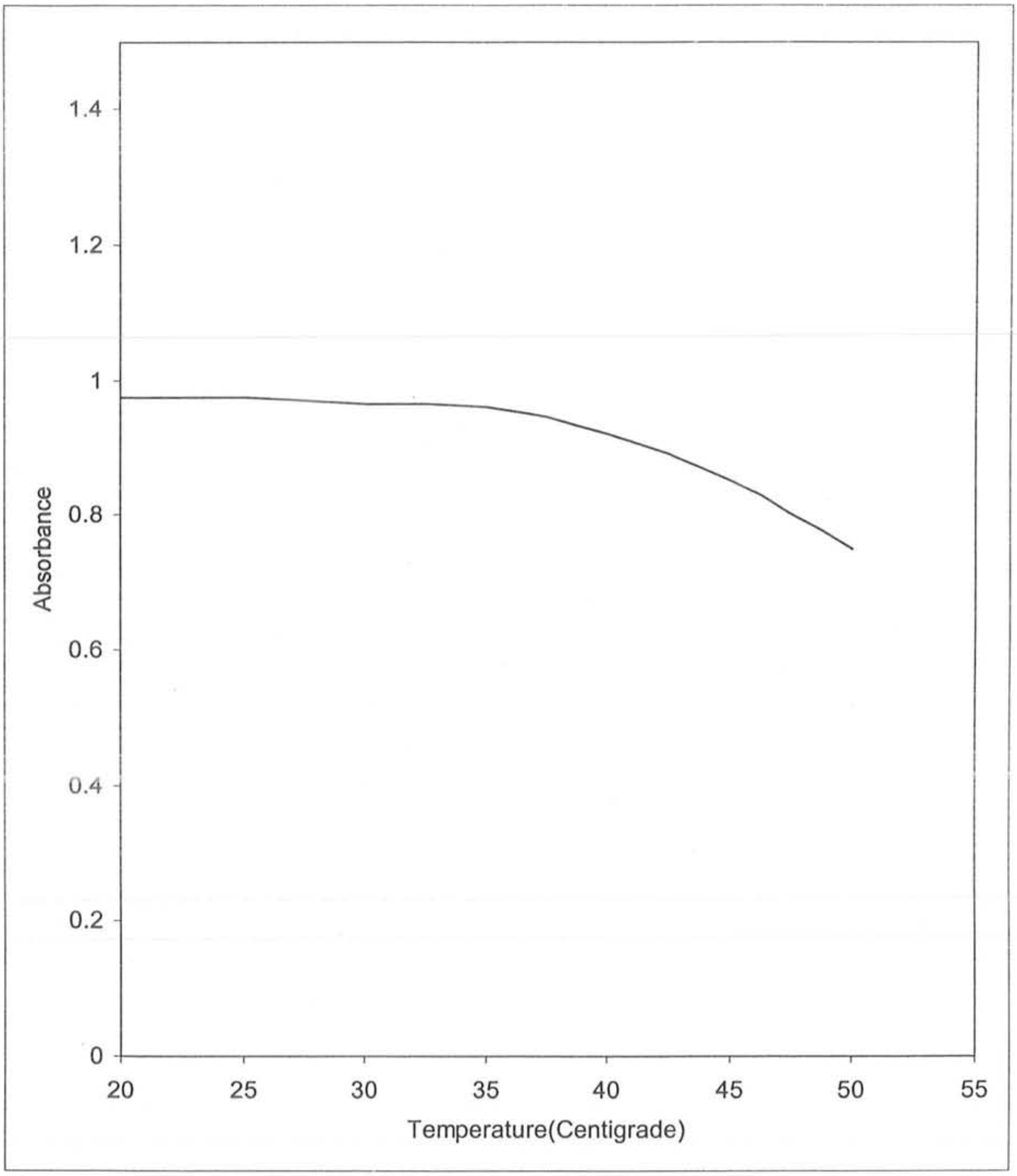


Fig.5.7 Effect of temperature on Pb(II)-complexation.

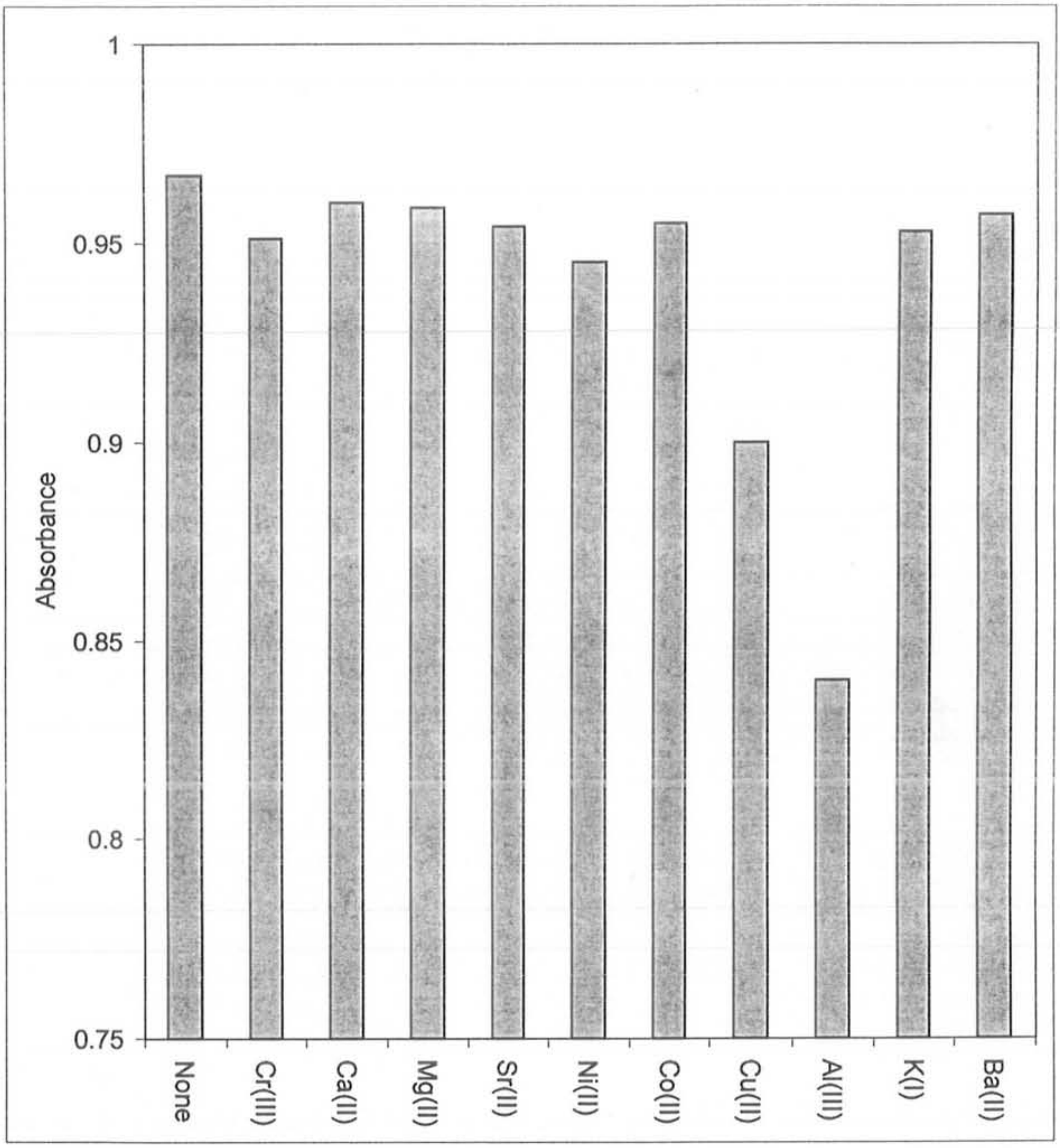


Fig.5.8 Effect of different cations on the Pb(II)-complexation.

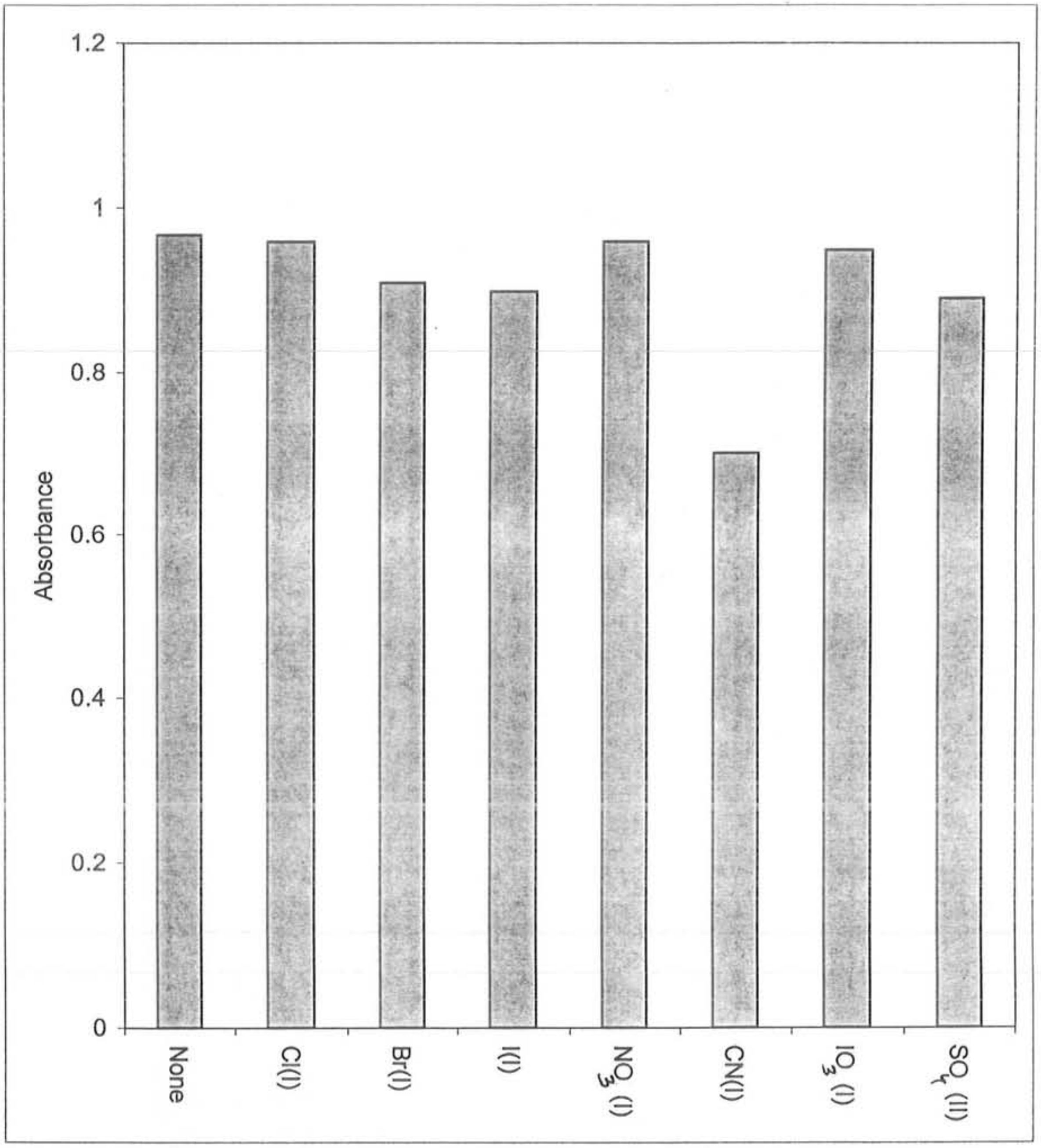


Fig. 5.9 Effect of different anions on the Pb(II)-complexation.

TABLE 4.7

Effect of different cations on Pb(II)-complexation

Cations	*Limiting conc.(M)*	*% Effect on intensity*
Cr^{+3}	1.3×10^{-5}	-12
Ca^{+2}	3.7×10^{-4}	-3
Mg^{+2}	7.2×10^{-4}	-4
Sr^{+2}	1.3×10^{-4}	-3
Ni^{+2}	3.7×10^{-5}	-9
Co^{+2}	3.7×10^{-5}	-10
Cu^{+2}	3.7×10^{-6}	-7
Al^{+3}	3.7×10^{-6}	-5
K^{+1}	3.7×10^{-4}	-1
Ba^{+2}	1.3×10^{-4}	-2

*All the cations were added as their nitrate salts.

TABLE 4.8

Effect of different cations on Pb(II)-complexation

Anions	*Limiting conc.(M)*	*% Effect on intensity*
Cl^{-1}	3.7×10^{-2}	-2
Br^{-1}	3.7×10^{-2}	-3
I^{-1}	3.7×10^{-3}	-4
NO_3^{-1}	3.7×10^{-1}	-1
IO_3^{-1}	3.7×10^{-5}	-4
SO_4^{-2}	3.7×10^{-5}	-8
CN^{-1}	1.3×10^{-7}	-18

*All the anions were added as their potassium salts.

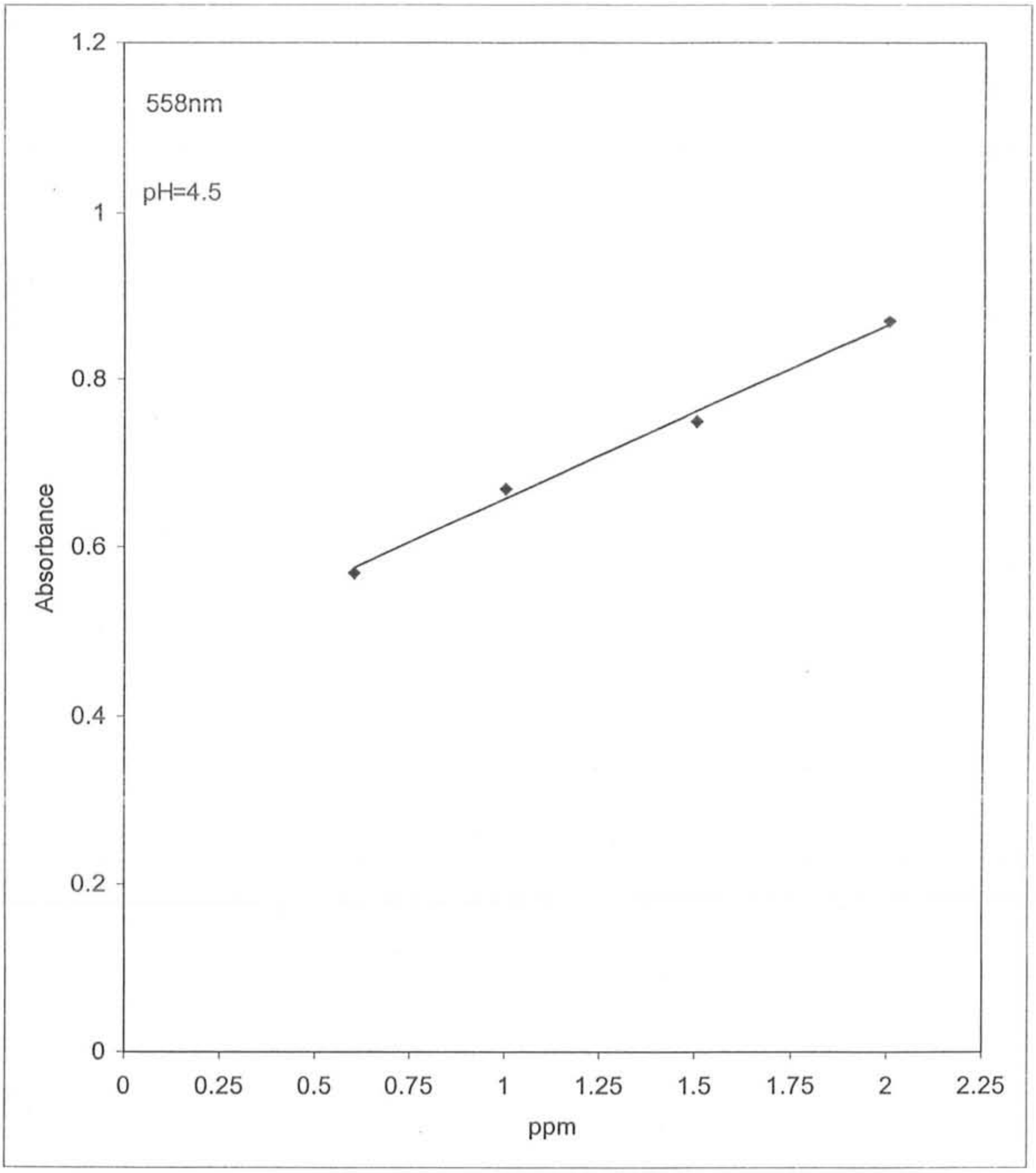


Fig.5.10 Adherence to Beer's law for Pb(II)-complex.

4.6 Complexation of Bi^{+3} with o-Phenanthroline and Eosin

Among all his family members bismuth have true cationic chemistry. Aqueous solutions contains well defined hydrated cations. But there is no evidence of simple$[Bi(H_2O)_n]^{+3}$ aqua ions. Bi^{+3} associates with nitrate ions in aqueous solutions.

The nitrate ion appears to be bidentate, and all members of the set $Bi(NO_3)(H_2O)_n^{+2}$----$Bi(NO_3)^{-1}{}_4$ appear to occure[59].

The absorption spectrum of the Bi^{+3} ion in aqueous medium shows weak absorption band in ultraviolet region. The spectrum of reaction mixture of bismuth, o-Phenethroline and eosin *versus* reagent blank shows an apparent decrease in absorption at 510nm and exhibits a new band at 552nm (Fig.6.2). The appearance of the new band at 552nm indicates the formation of the metal complex with o-Phen. and eosin. Using buffer solutions of different pH optimized the pH of the complex. Maximum complexation was obtained at pH 5 (Fig. 6.3).

The stoichiometry of the complex has been determined by applying continuous variation method (*Job's Method*).The mole fractions of the two components were varied continuously, keeping their combined concentrations constant, and by taking the third component in large excess for all the solutions in the series. The molar ratio of the B(III), o-Phenethroline and eosin was found to be 1:2:1 as shown in the Figures (6.4,6.5).Thus composition of the complex was found to be $[Bi(o\text{-}Phen)_2]E$.

In the formation of this complex, the primary ligand(o-Phen.), on entring the co-ordination sphere of Bi(III), forms co-ordinate covalent bond by its two nitrogens, but their complex ion still bears overall +3 charge on the co-ordination sphere, and it is free to associate with secondary ligand (Eosin) to form a ternary complex. This ternary complex exhibits an absorption band at 552nm.

Concentration, molar absorptivity and stability constants of the complex

By applying continuous variation method, the concentration, molar absorptivity and stability constant of the complex have been determined[50-55].

Concentration: In Figure (6.5) the extrapolated value(A_{ext}) at the piont of crossection, on the continuous variation plot corresponds to the total absorbance of the complex, if the complex formation has been completed. Actually, the complex is dissociative in nature and absorbance value is therefore somewhat lower than actual value.

The concentration of the complex has been determined from the following equation:

$$A/A_{ext} = MX/C$$

Where C is the total analytical concentration.

From the continuous variation curve (Fig.6.5) values of A, A_{ext} and C were obtained.

$A = 1.34$

$A_{ext}=1.44$

$C = 7.5\times10^{-5}M$

MX = Concentration of the complex

Now by putting these values in above equation concentration of the complex can be calculated.

$$MX = A\times C/A_{ext}$$

$$= 1.34\times7.5\times10^{-5}/1.44$$

$$= 6.98\times10^{-5}M$$

Molar Absorption Coefficient: The molar absorption coefficient of the complex can be calculated by using the following equation:

$A = \varepsilon CL$

ε is a constant at same wavelength , called molar absorption coefficient and has a units of $L.mole^{-1}.cm^{-1}$.The use of this symbol specifically requires that the concentration is expressed in units of molarity and sample path length in centimeters.

A = Absorption of the complex at 552nm.

C = Concentration of the complex.

L = Path length

Concentration of the complex have been calculated already

$C = 6.98\times10^{-5}M$

L = 1cm

By applying the above equation

$$\varepsilon = A/CL$$

$$=1.34/1\times6.98\times10^{-5}$$

$$=1.92\times10^{4}L.mole^{-1}cm^{-1}$$

Stability Constant: Stability of a complex is very important.

The equation of the complex formation is following:

$$[Bi(o\text{-}Phen.)]^{+3} + E^{-2} \leftrightarrow [Bi(o\text{-}Phen.)]E$$

$$K = [Bi(o\text{-}Phen.)]E_{eq} / [Bi(o\text{-}Phen.)]_{eq}[E]_{eq}$$

K = Equilibrium Constant

The equilibrium concentration of the metal ion and ligand can be determined as follows

$$[Bi(o\text{-}Phen.)]_{eq} = [Bi(o\text{-}Phen.)] - [Bi(o\text{-}Phen.)]E_{eq}$$

$$= 7.5\times10^{-5} - 6.98\times10^{-5}M$$

$$= 5.2\times10^{-6}M$$

Now equilibrium concentration of the secondary ligand can be calculated as

$$[E]_{eq} = [E] - [Bi(o\text{-}Phen.)]E_{eq}$$

$$= 7.5\times10^{-5} - 6.98\times10^{-5}$$

$$= 5.2\times10^{-6}M$$

By putting these values in the equilibrium equation

$$K = 6.98\times10^{-5} / (5.2\times10^{-6})\ (5.2\times10^{-6})$$

$$K = 2.58\times10^{6}$$

$$\text{Log } K = 6.41$$

Effect of Time

The complex formation started immediately after the mixing of the reagents and it was completed in half-hour. The complex remained stable for more than 24 hours. The optimum time for complex formation was two hours (Fig.6.6)

Effect of Temperature

This complex is stable up to 30 °C (Fig.6.7). The optimum temperature for complexation is up to 25°C. This complex is relatively stable. Complex is relatively less stable.

Effect of cations and anions

The effect of various cations Cr^{+3}, Ca^{+2}, Mg^{+2}, Sr^{+2}, Ni^{+2}, Co^{+2},Cu^{+2}, Al^{+3}, K^{+1}, Ba^{+2} (Fig.5.8) and anions Cl^{-1}, Br^{-1}, I^{-1}, $NO^{-1}{}_3$, $IO^{-1}{}_3$, $SO^{-2}{}_4$ andCN^{-1} (Fig.6.9) has been studied on the complexation of the lead complex. The limiting concentration and percentage decrease in absorbance is shown in the Tables (1.9,1.10).

It is observed that Cr^{+3}, Ni^{+2}, Co^{+2},Cu^{+2} and Al^{+3}effects the complex by decreasing the absorbance at λ_{max} of the complex. Ca^{+2}, Mg^{+2}, Sr^{+2} K^{+1},and Ba^{+2} show no significant effect. This complex is less effected by the cations, showing preference to the ligand as compared to other metal ions.

The Cl^{-1}, Br^{-1}, I^{-1} and $NO^{-1}{}_3$ shows minute effects on the complex when present in equimolar amounts, but effect is pronounced when concentration is raised. The anions $IO^{-1}{}_3$, $SO^{-2}{}_4$ decreases the absorbance when present in equimolar amounts. The CN^{-1} has most striking effect on the complex, even when it is present in small amounts.

Calibration graphs

The system follows Beer's law over the range 0.4-4 ppm for Bi(III). Primary and secondary ligands were used in excess.Fig.(6.10).

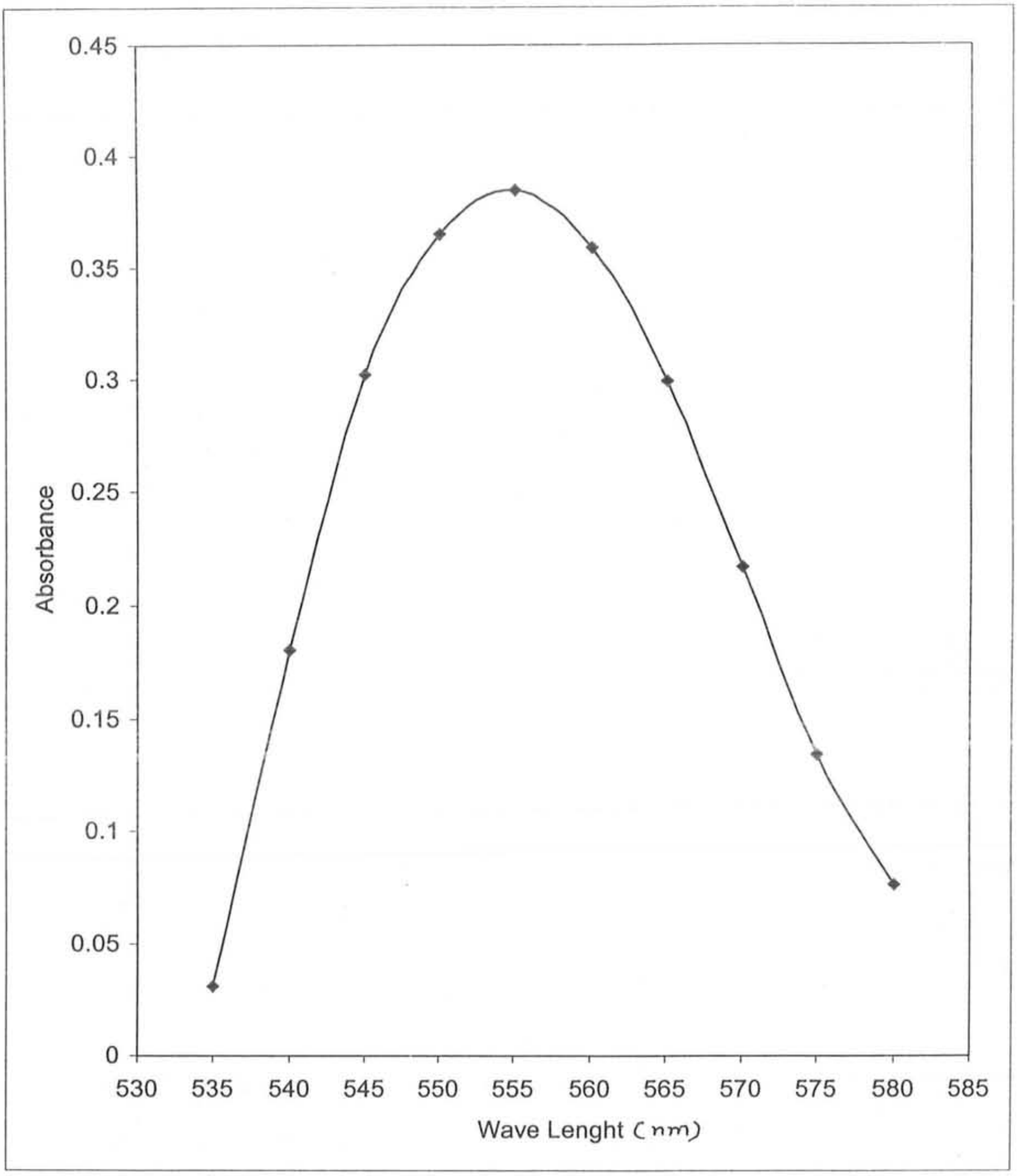


Fig.6.2 Absorption spectrum of Bi(III)-complex.

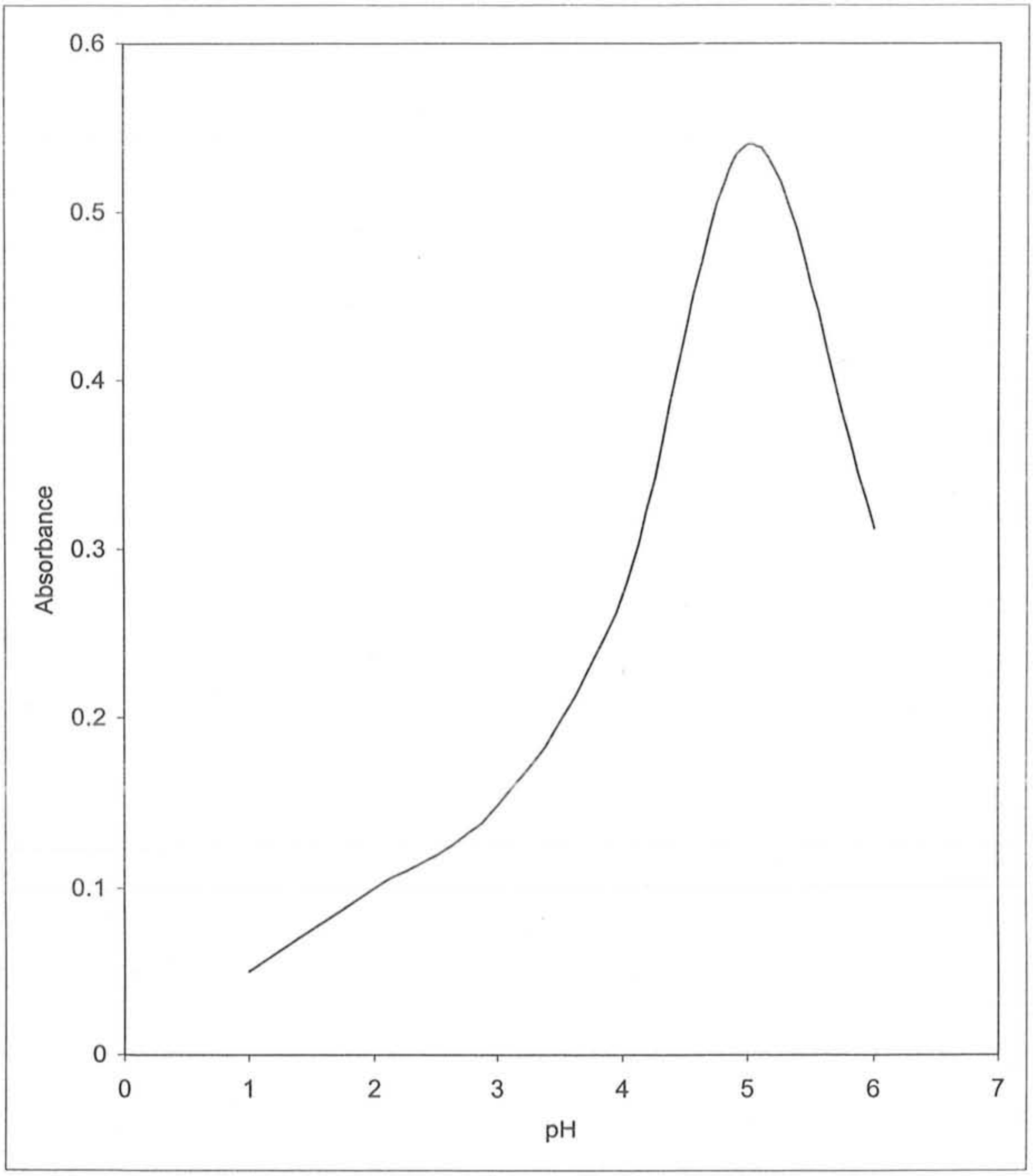


Fig.6.3 Effect of pH on Bi(III)-complexation.

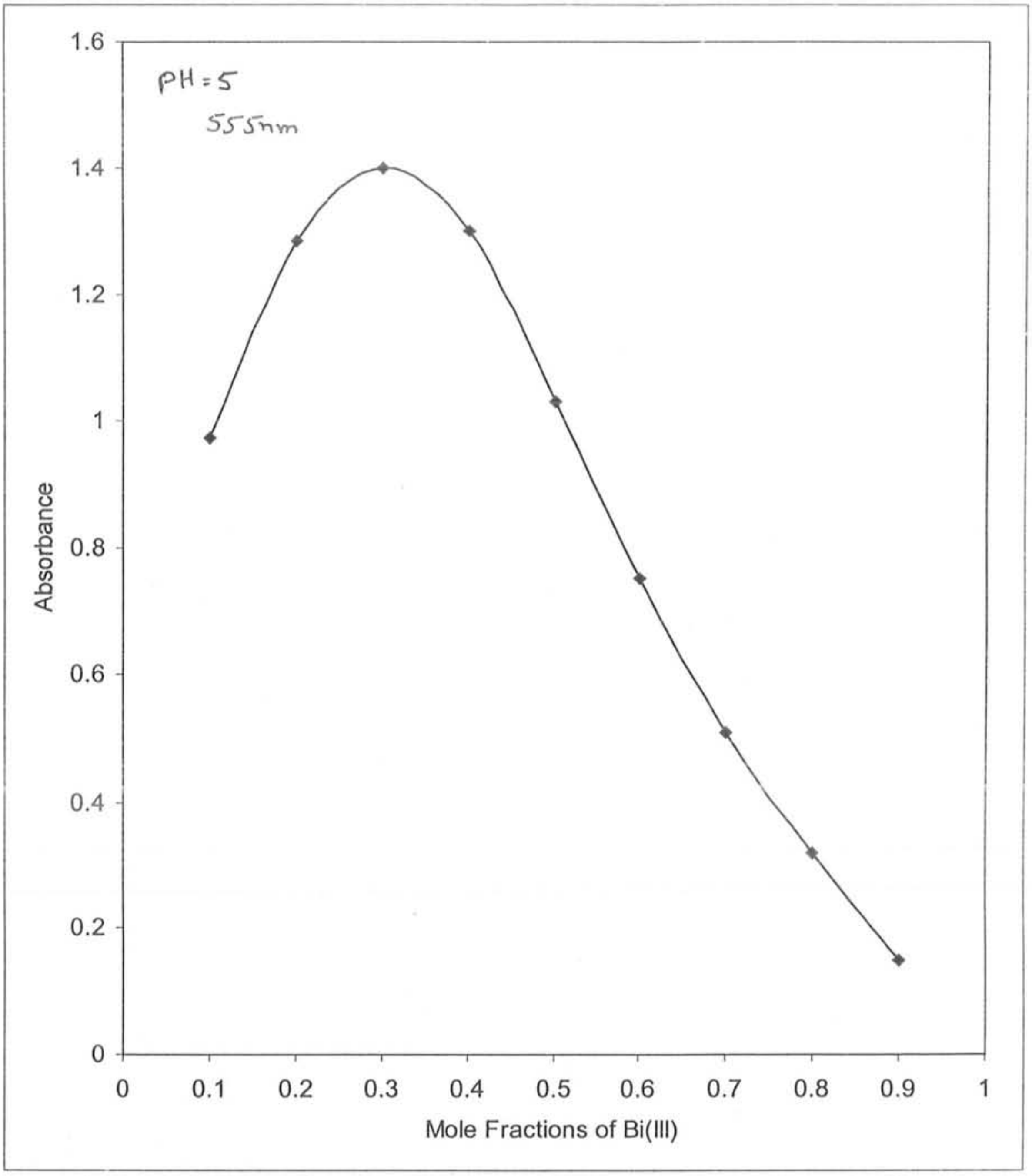


Fig.6.4 Stoichiometric study of Bi(III)-complex (Bi(III) vs o-Phenanthroline)

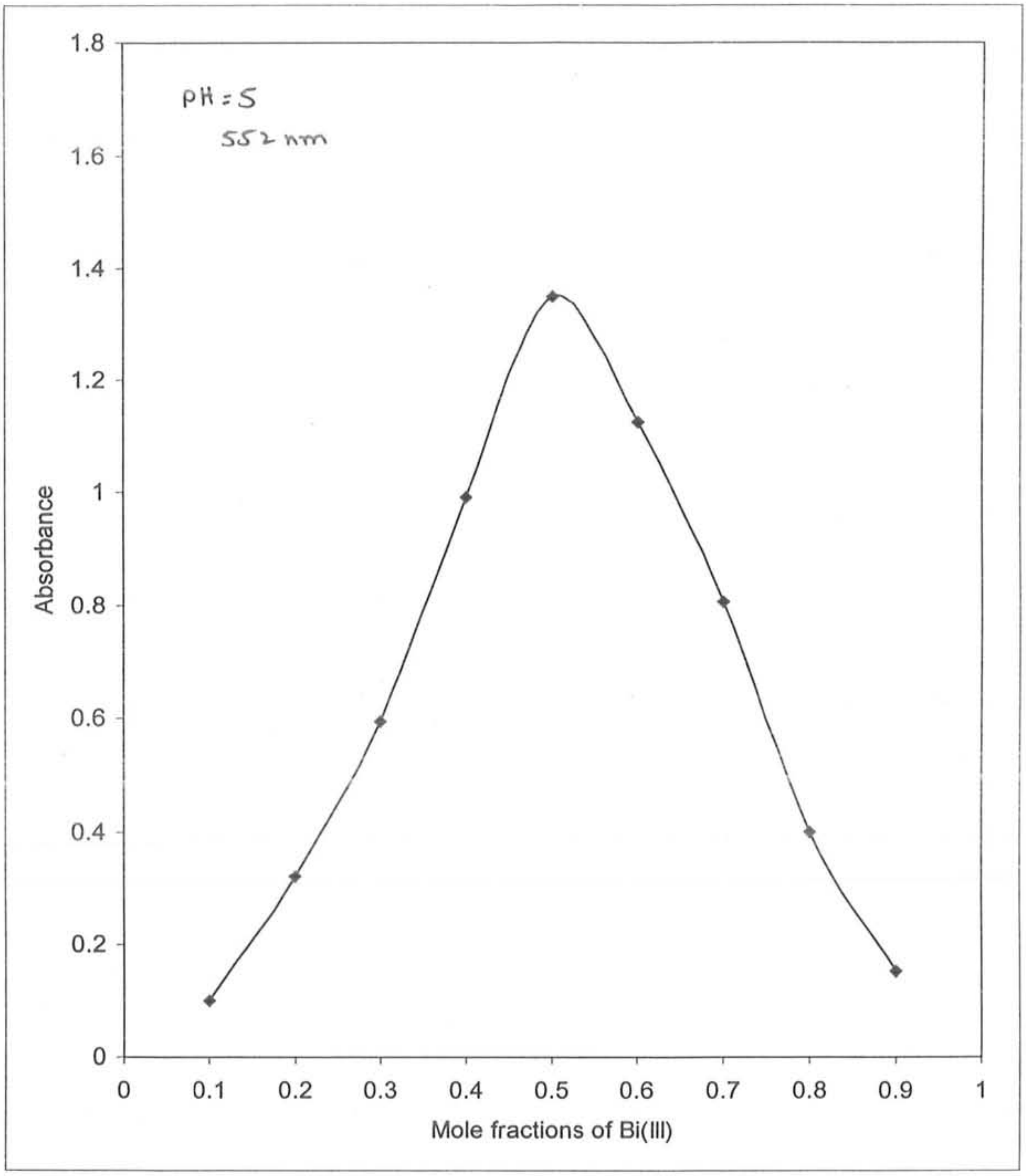


Fig. 6.5 Stoichiometric study of Bi(III)-complex (Bi(III) vs Eosin)

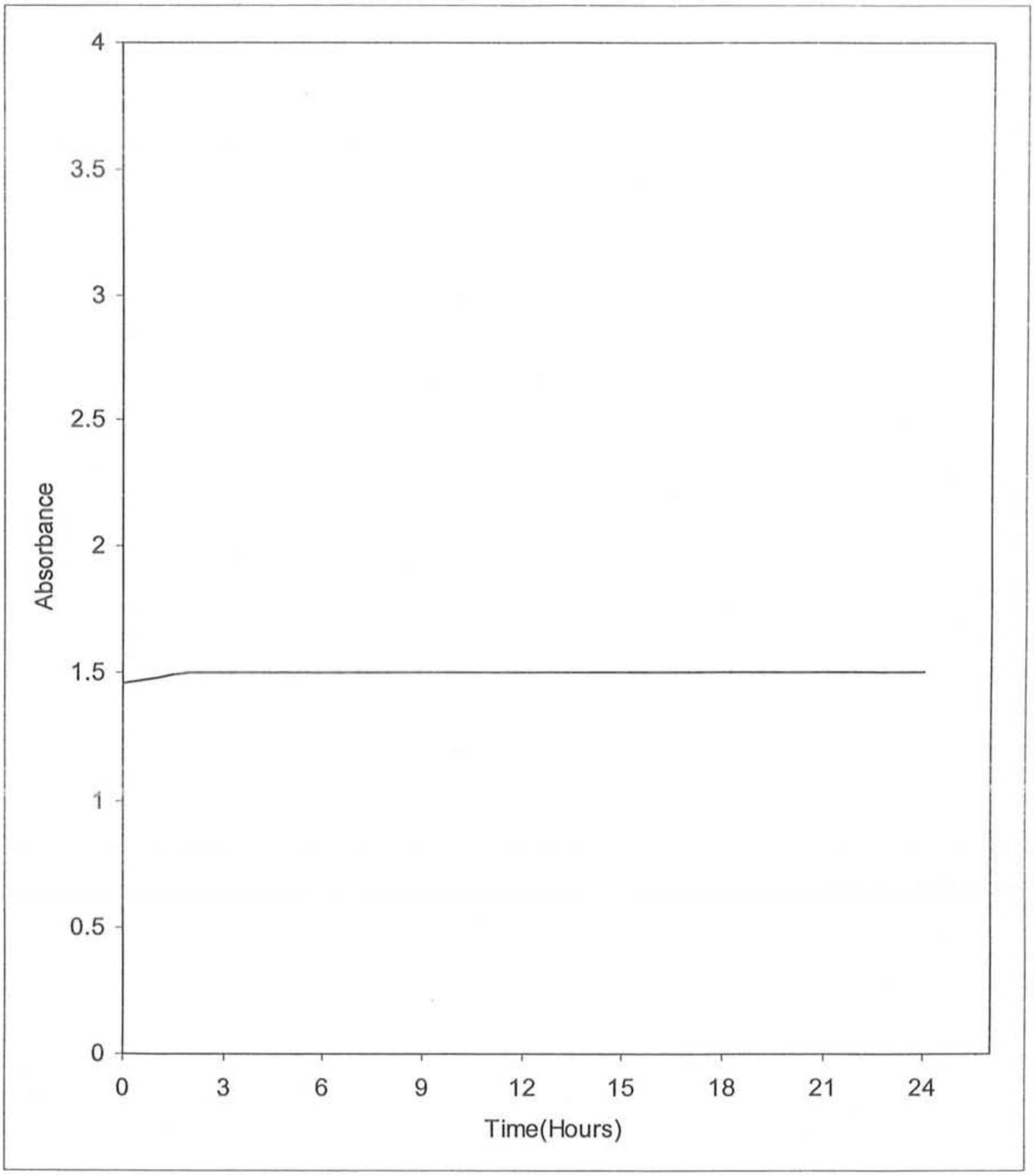


Fig.6.6 Effect of time on Bi(III)-complexation.

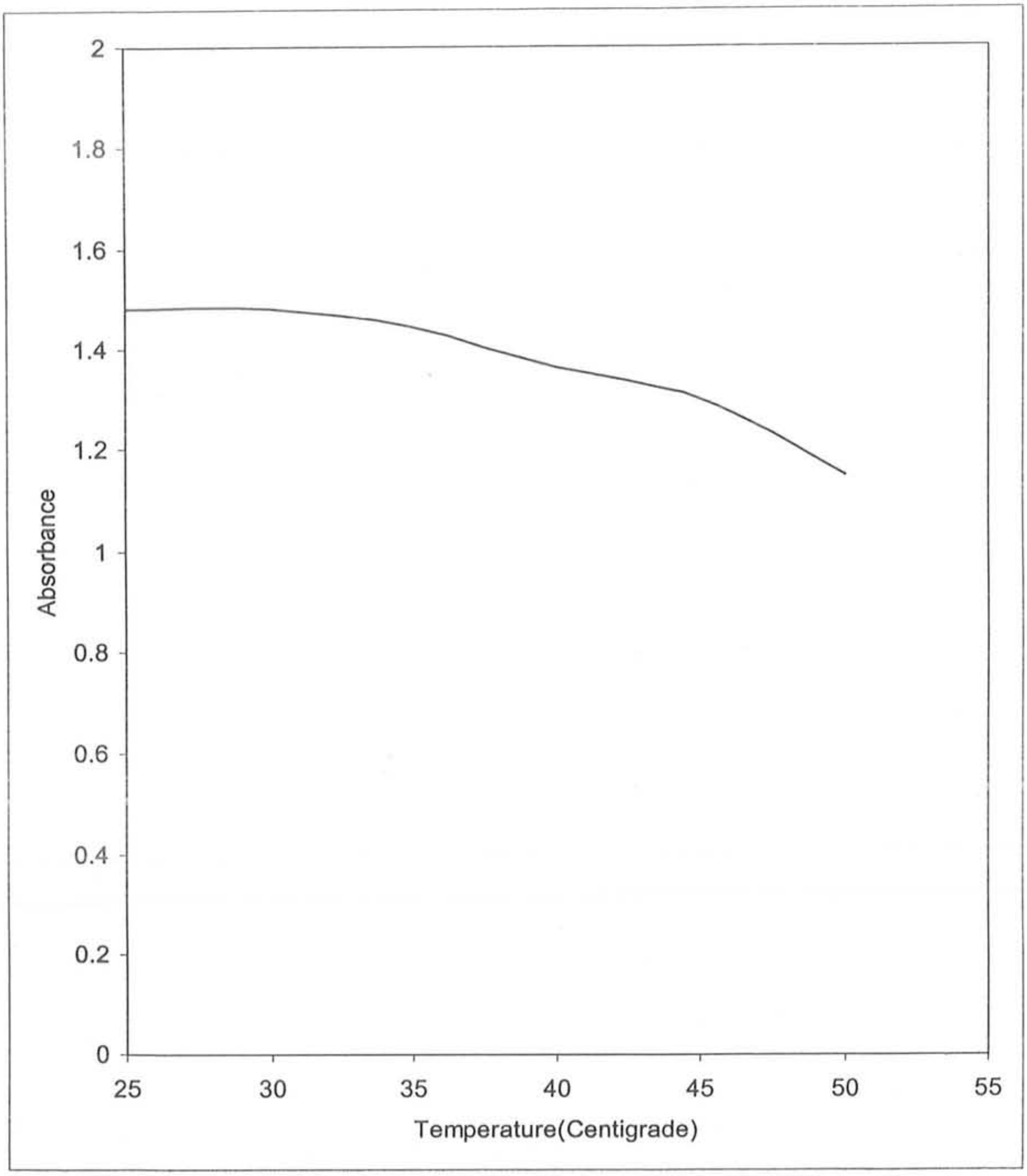


Fig. 6.7 Effect of temperature on Bi(III)-complexation.

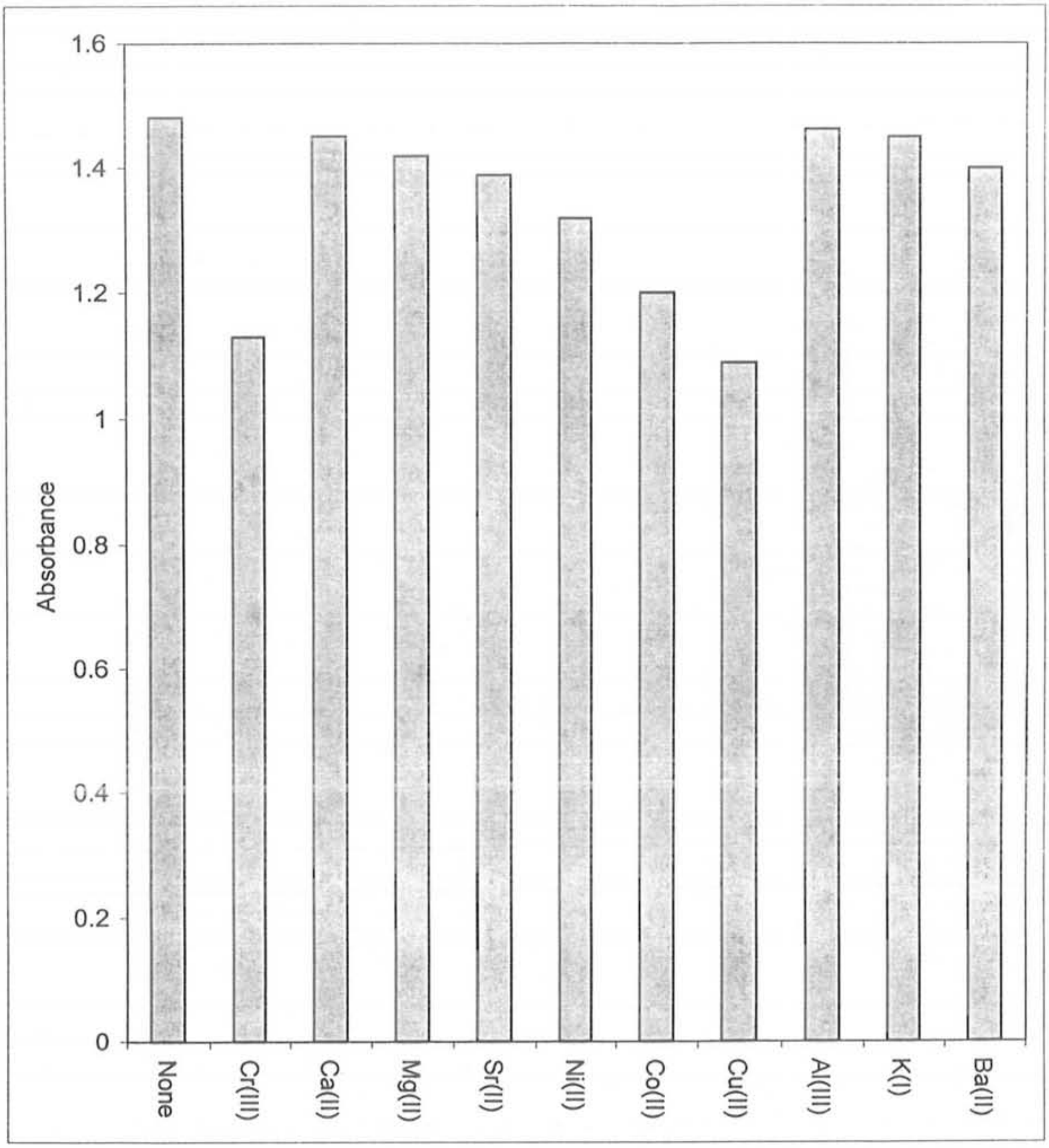


Fig.6.8 Effect of different cations on Bi(III)-complexation.

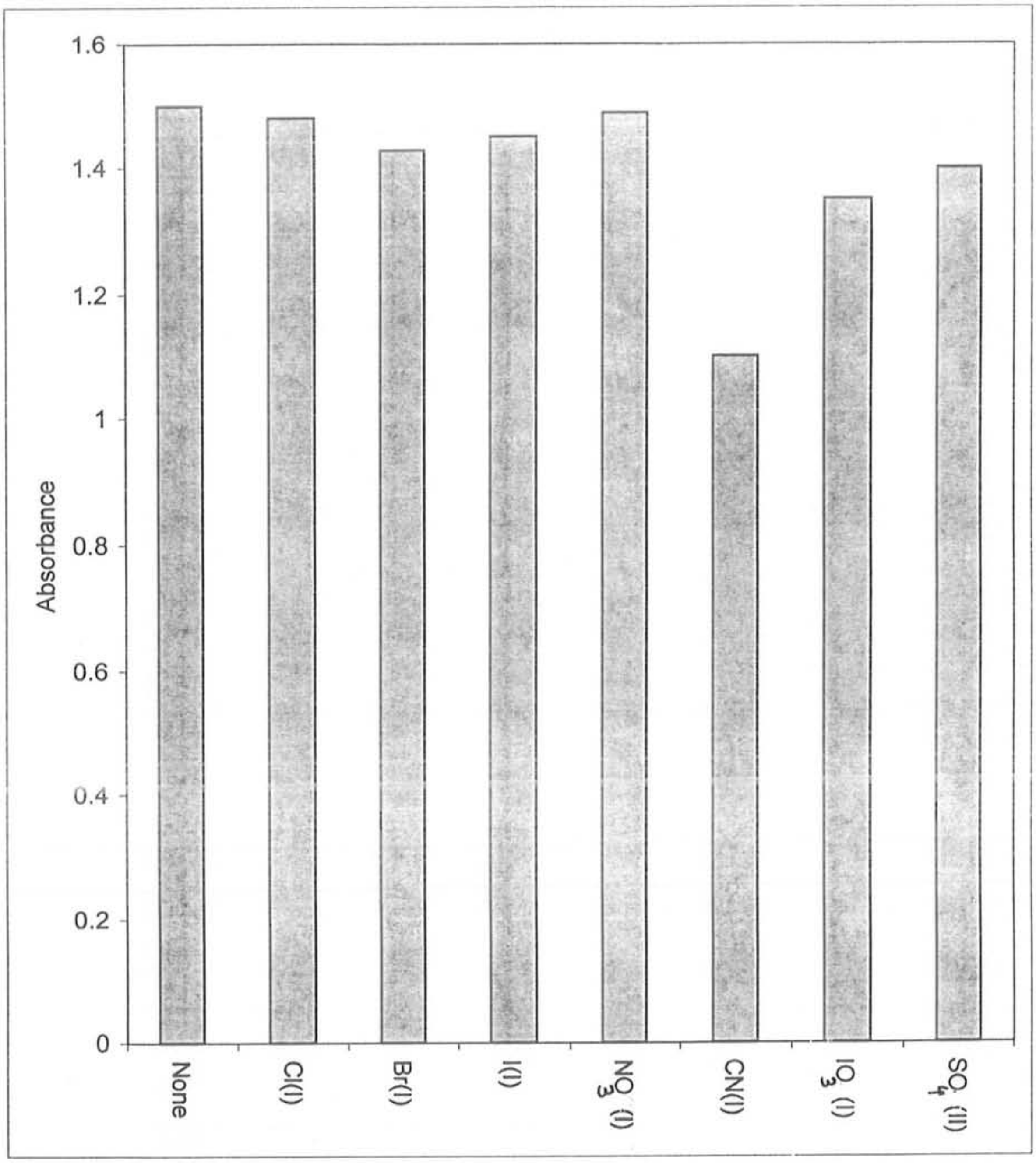


Fig. 6.9 Effect of different anions on Bi(III)-complexation.

TABLE 4.9

Effect of different cations on Bi(III)-complexation

Cations	*Limiting conc.(M)*	*% Effect on intensity*
Cr^{+3}	1.3×10^{-5}	-12
Ca^{+2}	3.7×10^{-4}	-3
Mg^{+2}	7.2×10^{-4}	-4
Sr^{+2}	1.3×10^{-4}	-3
Ni^{+2}	3.7×10^{-5}	-8
Co^{+2}	3.7×10^{-6}	-12
Cu^{+2}	3.7×10^{-6}	-15
Al^{+3}	3.7×10^{-5}	-5
K^{+1}	3.7×10^{-4}	-1
Ba^{+2}	1.3×10^{-4}	-2

*All the cations were added as their nitrate salts.

TABLE 4.10

Effect of different anions on Bi(III)-complexation

Anions	*Limiting conc.(M)*	*% Effect on intensity*
Cl^{-1}	3.7×10^{-2}	-2
Br^{-1}	3.7×10^{-2}	-3
I^{-1}	3.7×10^{-3}	-4
NO_3^{-1}	3.7×10^{-1}	-1
IO_3^{-1}	3.7×10^{-5}	-4
SO_4^{-2}	3.7×10^{-5}	-8
CN^{-1}	1.3×10^{-7}	-6

*All the anions were added as their potassium salts.

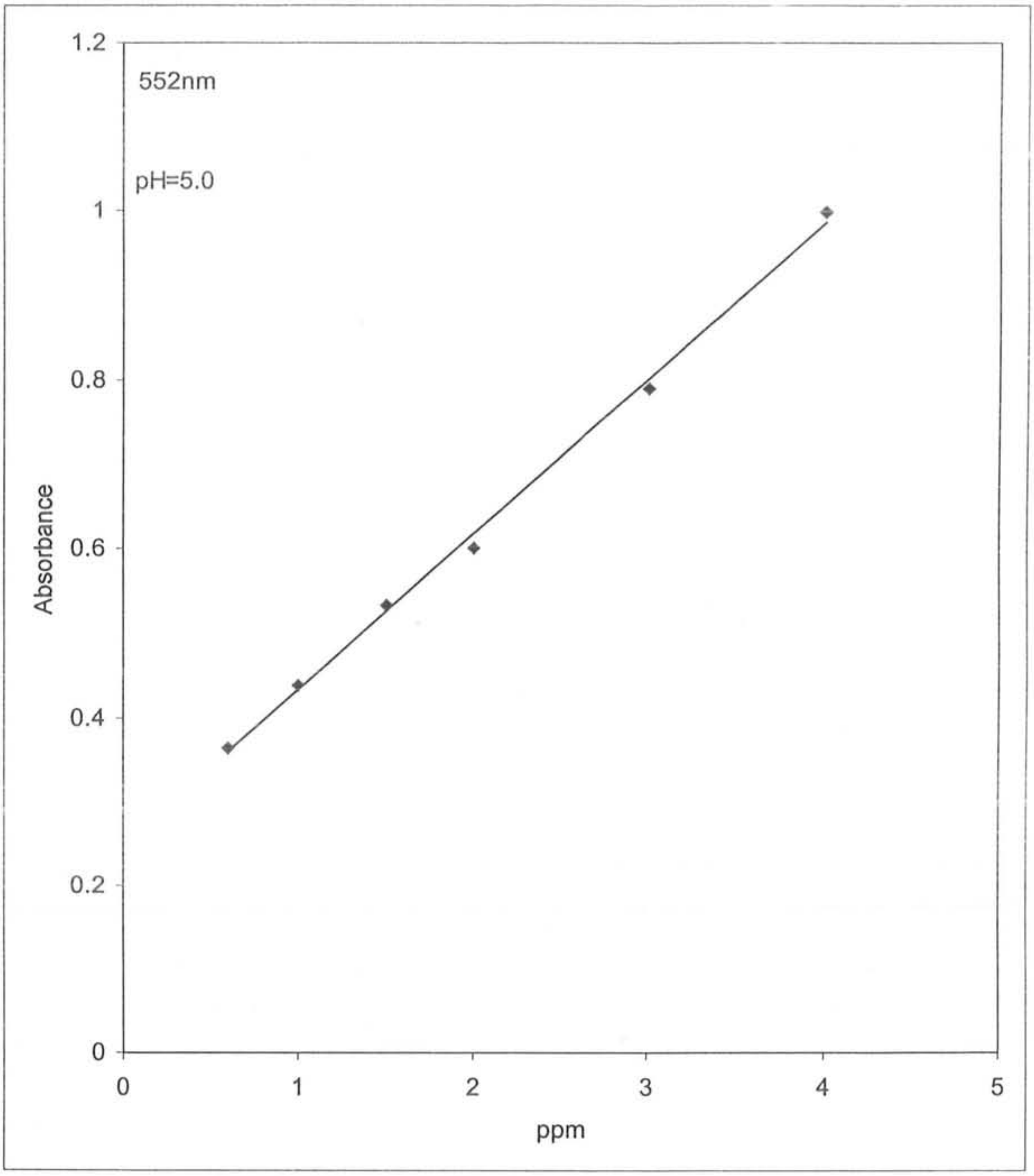


Fig.6.10 Adherence to Beer's law for Bi(III)-complex.

CONCLUSION

CONCLUSION

The complexes of VO(II), Mn(II), Fe(III), Pb(II) and Bi(III) showed their maximum absorbance at 550nm, 560nm,555nm,558nm and 552nm respectively. The maximum complexation was achieved at pH 6.0, 5.5, 5.5, 4.5 and 5.0 respectively.

Stoichiometries of these complexes were investigated by *Job's method* of continuous variation and are given below:

Complexes	***Stoichiometry***		
	Metal	*o-Phen*	*Eosin*
VO(II)-complex	1	1	1
Mn(II)-complex	1	2	1
Fe(III)-complex	1	1	1
Pb(II)-complex	1	2	1
Bi(III)-complex	1	2	1

Log of stability constant of these complexes ranged from 5.77 to 6.93, indicating the dissociative nature of these complexes. Time dependent studies of these complexes showed that Mn(II)-complex was stable only for two hours and VO(II)-complex for five hours where as other complexes were stable above twenty four hours. These complexes are very temperature sensitive. Mn(II)-complex started decomposing even above 20^0C and VO(II)-complex above 30^0C, other complexes were stable above 35^0C. It is evident from the stability constant and time dependent studies that Mn(II)-complex is least stable complex whereas complexes of VO(II), Fe(III), Pb(II) and Bi(III) were relatively stable.

Diverse ion effect showed that K^{+1}, Ca^{+2}, Mg^{+2}, Ba^{+2}, Sr^{+2},Cl^{-1}, Br^{-1}, I^{-1} and NO_3^{-1} have no significant effect on the VO(II), Mn(II), Fe(III), Pb(II) and Bi(III) complexation. In case of VO(II) and Mn(II) complexation, addition of Al^{+3}, Cu^{+2}, Co^{+2}, and Ni^{+2} caused an increase in absorbance where as Cr^{+3}, SO_4^{-2}, IO_3^{-1} and CN^{-1} caused a decrease in absorbance at the wave length of maximum absorbance of these complexes. In case of Fe(III), Pb(II) and Bi(III) complexation, presence of Al^{+3}, Cu^{+2}, Co^{+2}, Ni^{+2} Cr^{+3}, SO_4^{-2}, IO_3^{-1} and CN^{-1} decrease the absorbance. CN^{-1} has a drastic effect on complexation and it even starts to interfer at very low concentration (10^{-7}M).

The complexes obey the Beer's Law over ppm level. For the complexes of Fe(III), and Pb(II) a straight line was observed over the range at 0.5-2 ppm. VO(II), Mn(II),and Bi(III) complexes obey the Beer's law in the range of 3-12 ppm, 0.4-2 ppm and 0.4-4 ppm respectively.

REFERENCES

REFERENCES

1). Babko, A. K., *Talanta*, 1968, **15**, 721.

2). Perkampus,H.H., *UV-VISIBLE Spectroscopy and its Applications*, Springer-Verlag, New York (USA). 1992.

3). Luke, C. L., *Anal. Chem.*, 1953, **25**, 674.

4). White, C. E. and Rose, H. J., *Anal. Chem.*, 1953, **25**, 351.

5). Polucktou,N. S., *Z. Anal. Chim.*, 1958, **13**,396.

6). Dcret, L., *Anal. Chim. Acta*, 1958, **21**, 86.

7). Babko, A. K., *Z. Anal. Chim. Acta*, 1966, **21**, 196.

8). Ducret, L., *Anal. Chim. Acta.*, 1957, **17**. 213.

9). Psztor, L. and Bode, J. D., *Anal. Chem.*,1960, **32**,1530.

10). Bailey, B. N., Dagnall, R.M. and West, T. S., *Talanta*, 1966,**13**,1661.

11). Dagnall, R.M., ElGharmy, M. T. and West, T.S., *Talanta*, 1988, **15**, 1353.

12). ElGharmy, M. T. and Frei, R. W., *Talanta*, 1969, **16**, 253.

13). Idriss, K. A., Awad, A., Seleim, M. M.and Abu-Bakar, M. S., *Anal. Chim. Acta*,1980, **116**, 413.

14). Dagnall , R . M., Ghamry , M . T. and West , T . S., *Talanta* , 1968 , **15** , 1353.

15). Idriss , K . A., Seleim , M . M., Abu-Bakr , M . S . and Saeh , M .S., *Analyst*, 1982 , **12**, 107.

16). Mudakavi , J . R., *Analyst*, 1984 , **109** , 1577.

17). Mori, I., Fujita, Y., Kawabe , H., Fujita , K., Tanaka . T. and Kishimoto , A., *Analyst*, 1986 , **111** , 1409.

18). Pauling , L., *The Native of chemical bond* , 3rd ed. , Cornell Ithica N . Y(USA) 1960.

19). Sharp , A . G., *Inorganic Chemistry* , 2nd ed. ELBS,London,1986.

20). Phillips , C . S . G. and Williams , R . J . P., *Inorganic Chemistry* , Oxford university press, London, 1966.

21). Iruing and Williams , R . J . P., *Nature*, 1948 , **162** , 746.

22). Iruing and Williams , R. J. P, *J . Chem . Soc.*, 1953 , 3192.

23). Caluin , M.and Baidar , J . C ., *Am. Chem . Soc.*, 1948 , **68** , 949.

24). Spike , G . G. and Parry , R . W., *Am . Chem . Soc.*, 1953 , **75** , 2726.

25). Schwarzabach , G . Z., *Inorg . Chem . Soc* ., 1955 ,286.

26). Schwarzabach,G.Z., Senn , H. and Anderegg , G., *Helv . Chem . Acta*, 1957, **40** , 1886.

27). Schwarzabach ,G.Z., *Helv . Chem. Acta*, 1952 , **35** , 2333.

28). Blaus , F., *Monatsh Chem.*,1988 , **19** , 647.

29). Moss , M . L. and Mellon , M . G., *Ind . Eng . Chem. Anal* , 1943 , **15**,116 .

30). Mason , S . F., *Inorganic Chim . Acta Rev*,. 1968 , **2** , 89 .

31). Williams , R . J.P., *J . Chem . Soc.*, 1955 , 137 .

32). Eisenberg , R., *Progr .Inorg . Chem.*, 1970 , **12** , 295 .

33). Jorgensen . C . K., *Inorg . Complexes* , Academic Press , New York(USA), 1963.

34). Sandell , E . B., *Colorimetric determination of traces of Metals* , Interscience, New York (USA), 3 rd Ed, 1959.

35). Feigl , F ., *Spot Test in Inorganic analysis* , Elsevier Publishing Co., Amsterdam, 5th ed., 1958.

36). Feigl , F ., *Chemistry of Specific , Selective and Sensitive Reactions*, Academic Press, New York(USA), 1949.

37). Welcher, F.J, *Organic Analytical Reagents* , Van Nostrand , New York(USA), 1947.

38). Novak , J ., Funke A. and Kleinert , P ., *Z . Anal . Chem*., 1968 ,239 .

39). Paliwal, R.C.,Prasad,A. and Agarwal, S.N., *Dyes And Intermediates,* Small business publication, (Delhi),1950.

40). Wheast.R,*CRC Hand book of Chemistry and Physics*, CRC Press 79th ed.,35 1998.

41). Sandell , E . B ., *Colourimetric determination of traces of metals,* 3rd ed, Interscience Publishers , Inc . New York (USA),1960.

42). Hall , F . L . T .,*Industrial toxicology,* Williams and Wilkins Co ., Baltimore(USA), 1949.

43). Isukahara I., *Anal. Chim.Acta,* 1979 , **92** , 379

44). Stoner, R.E. and Dasier . W., *Anal. Chem.,* 1960 , **32** . 1207 .

45). Bernard, L.O., *Hawk's physiological Chemistry,* 14th ed. MacGraw Hill Book Company, 1211.

46). Weast,R., *Hand Book of Physics and Chemistr*y, The Chemical Rubber Co. 63rd ed. 1982.

47). Moss, M.L. *Chemistry: Preparation of systems for absorptiometric Measurements. Analytical Absorption Spectroscopy*, John Wiley and Sons, Inc New York(USA) 1950.

48). Harvey, A.E. and Manning, D.L., *J.Am.Chem.Soc.,*1950, **72**,4488.

49). Ayres, G.H. and Young, H.F., *Anal. Chem*., 1952, **24**, 165.

50). Martell, A.E. and Caloin, M., *Chemistry of metal Chelate Compounds.* Printice Hall, Inc. Englewood Cliffs, N.J(USA). 1952.

51). Hilderbrand, G.P. and Railley, C.N., *Anal. Chem.,*1954, **29**, 357.

52) Meites, L. and Thoms, H.C., *Advanced Analytical Chemistry.,* McGraw Hill Book Company, Inc., New Yark(USA), 1958.

53). Job,P.,*Ann. Chim*., 1928,**10**,113.

54). Shrif,F.G., and Awad,A.M., *Inorg.Nucl.Chem*.,1962,**24**,79.

55). Foley, T.R. and Anderson, C.R., *J.Am.Chem.Soc.,*1948,**70**,1195.

56). Mchedlov-Petrosyan,N.O.,Adanovich,L.B. and Nikishima, *Zh.Analit.Khim.*, 1980,**35**,1495.

57). Selbin, K.A, *J.Chem. Rev.*, 1965, **65**,153.

58). Dunitz, J.D. and Orgel, L.E., *Adv. Inorg. Radiochem.*, 1960, **2**, 1

59). Cotton and Wilkinson, *Advanced Inorganic Chemistry,* 5th ed. Wiley Interscience.New York (USA).1988.

60). Ortiga,R.B., *Acta Crystallogr.*, 1980. **B36**, 1986.

61). Bukovec, P. and Colic, L., *Acta Crystallogr,* 1980. **B36**, 1925.

62). Garner, C.D.,*J.Chem.Soc Dalton Trans,*1980, 667.

63). Khoe,G.H., *J.Chem.Soc. Dalton Trans*, 1986,1901.

64). Flynn,C.M., *J.Chem.Rev.*,1984,**84**,31.

65). Schlogel,R., and Jones,W.,*J.Chem.Soc.Dalton Trans*, 1984,1283.

66). Sylva,R.N and Brown,P.L., *J.Chem.Soc.Dalton Trans*,1980,1577.

67). G.Ghristou.,*Polyhedron*,1984,**2**,1247.