STUDIES ON THE FORMATION OF ANIONIC COMPLEXES IN THE PRESENCE OF HIGH CONCENTRATIONS OF ANIONS IN AQUEOUS SOLUTION

By

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TO MY PARENTS

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LIST OF ABBREVIATIONS

DMF	= N, N Dimethyl formamide
en	= Ethylenediamine
HOAc	= Acetic acid
phen	= Ortho phenanthroline
dipy	= 2, 2' dipyridine
gly	= glycinate ion
OX	= oxalate ion
EDTA	= ethylenediamine tetra acetate ion
MLT	= malonate ion
acac	= acetylacetonate ion
L	= ligand
ϵ	= molar extinction coefficient

INTRODUCTION

The solution chemistry of transition metal ions is quite complex. Free metal ions do not exist in aqueous solution but are always present as aquo complexes of the type $M(H_2O)_x^{n+}$, where n = 2-6 and n denotes the oxidation state of the metal ion. These aquo complexes can easily be crystallized out from their solutions. Most of these complexes are colored and absorb at specific wave lengths in the visible region of the electro magnetic radiations. The absorption of light by transition metal complexes have been the subject of numerous investigations extented over a period of nearly eighty years. The first trustworthy quantitative data is that furnished in 1892 on the solutions of chlorides, sulphates and nitrates of copper. Since then the UV and visible spectra of inorganic ions are known and used for a long time. It is fairly recently that much progress has been made in an understanding of the basis of the absorption bands which are being observed. The spectra is essentially due to interaction between a set of attached groups (ligands) and the atomic orbitals of the central metal ion. The free ion of any transition metal has partially filled degenerate d-orbitals which come under the direct attack of electronic fields of the ligands, brought upto it from various prefered directions. The result is a crystal field splitting of the five degenerate d-orbitals in a manner which depends on the strength of the ligand field and the symmetry of the complex. The absorption spectra of a complex ion in the visible region usually arises from the electronic jumps between these seperate d-orbitals. As is often been the case, the theory which was primarily being developed

to account for the spectra has been found helpful in explaining the chemistry as well.

It has been known that the ligands could be arranged in order of their increasing crystal field effects upon the spectra of the complex. Thus in the spectrochemical series

$I^- < Br^- < SCN^- < Cl^- < NO_3^- < F^- < OH^- < CH_3COO^- < H_2O < NCS^- <$ glycine $< NH_3 < SO_3^{--} < NO_2^- < CN^-$

the ligands are arranged in such an order that on moving from left to right, the effect of the first (long wave) absorption maximum is to move it to shorter wave length (this is towards higher energy and implies an increase in Δ on going from left to right.) Where a d-d transition for an aquo ion lies in the near Infra Red, as in the case of $Cu(H_2O)_2^{2+}$, replacement of water by ammonia leads to a shift in the visible and an intesification of color to blue as in $Cu(NH_3)_4^{2+}$. The CN^- group achieves large shift and hence a variety of colors are produced.

In solutions an equilibrium exists between the complex ion and its component species. Thus if $[Co(H_2O)_6]\ Cl_2$ is dissolved in excess of DMF the nature of equilibrium will be

$$[Co(H_2O)_6^{2+}] + 6DMF = [Co(DMF)_6^{2+}] + 6H_2O_6$$

$$\beta_6 = K_{eq} = \frac{[Co(DMF)_6^{2+}]\,[H_2O]}{[Co(H_2O)_6^{2+}]\,[DMF]^6}$$

$$\text{or} \quad k_{eq} = \frac{[Co(DMF)_6^{2+}]\,[H_2O]^6}{[Co(H_2O)_6^{2+}]} \quad \text{since DMF is in large excess.}$$

This equilibrium could be shifted on either side by changing

the concentration of either DMF or H_2O in the system. The equilibrium constant is known as the stability constant and provides information about the stability and concentration of a complex species in the solution. Usually the complex ion are formed in steps depending upon the concentration of the ligands. Thus the above mentioned equilibrium is only obtained at very high concentration of DMF. If the concentration of DMF is gradually increased the stepwise equilibriums observed are

$$[Co(H_2O)_6^{2+}] + DMF = [Co(H_2O)_5\ DMF^{2+}] + H_2O \quad k_1$$

$$[Co(H_2O)_5 . DMF^{2+}] + DMF = [Co(H_2O)_4\ (DMF)_2^{2+}] + H_2O \quad k_2$$

$$[Co(H_2O)_4 .(DMF)_2^{2+}] + DMF = [Co(H_2O)_3\ (DMF)_2^{2+}] + H_2O \quad k_3$$

$$[Co(H_2O)_3 .(DMF)_3^{2+}] + DMF = [Co(H_2O)_2\ (DMF)_4^{2+}] + H_2O \quad k_4$$

$$[Co(H_2O)_2 .(DMF)_4^{2+}] + DMF = [Co(H_2O)\ (DMF)_5^{2+}] + H_2O \quad k_5$$

$$[Co(H_2O)\ .(DMF)_5^{2+}] + DMF = [Co(DMF)_6] + H_2O \quad k_6$$

k_1, k_2, k_3, k_4 etc. are known as stepwise stability constants.

It can be shown that the overall stability constants are related to the stepwise stability constants as

$$\beta_1 = k_1$$
$$\beta_2 = k_1 . k_2$$
$$\beta_3 = k_1 . k_2 . k_3$$
$$\beta_4 = k_1 . k_2 . k_3 . k_4$$
$$\beta_n = k_1 . k_2 . k_3 ..... k_n$$

The stability constants are important quantities and could

be used for the estimation of nature of complex species present in a solution at equilibrium.

It is evident from this consideration that the concentration of the reacting ligands are also very important. Thus it is possible to shift the equilibrium in any desired direction by increasing or decreasing concentration of ligands in the system.

In aqueous solutions species like $[FeCl(H_2O)_5]^{+2}$, $[Fe(CNS)(H_2O)_5]^{+2}$ are obtained[1]. The complexes are highly colored and are formed in solution by increasing the concentration of chloride or thiocyanate ions. The orange red colored product, primarily $[Fe(SCN)(H_2O)_5]^{+2}$ in solution containing ferric ions and thiocyanate ions have been used for the colorimetric estimation of Iron in dilute solutions. A deep yellow colored species was obtained when ferric chloride was dissolved in 12M HCl solution. The $[FeCl_4^-]$ is considered to be responsible for the deep color[2]. Similar chlorocomplexes of nickel (II), cobalt (II), copper (II) have been obtained by dissolving respective metal halides in in hydrochloric acid of different concentrations[3,4]. These chloro complex anions are of different stability. The differences in stability have been utilized for the seperation of these metal ions by anion exchange resins[5].

Most of the studies on the formation of metal halide anionic complexes were done by dissolving the metal ions in hydrogen halides, which also introduced hydrogen ions in the system. Increased concentration of hydrogen ions could shift the equilibrium on either side and even completly destroy the complex species. The effects due to hydrogen ions could lead to erroneous stability constants and spectra of the complex.

It is surprising to note that very few studies were done by controlling the pH (i.e. hydrogen ion concentration) of the solutions in the systems. The spectra of some metal halides in dilute aquous solutions are markedly effected by increasing the concentration of halide ions. The change in spectra is considered as due to the formation of species lide

$[Pb(H_2O)_3Cl]^+$, $[Pb(H_2O)_2Cl_2]$, $[Pb(H_2O)Cl_3]^-$ or $[PbCl_4]^{--}$.

From the change in the absorption spectra with change in the concentration of halide ions, the concentrations of $[Pb(X)]^+$ or $[Pb(H_2O)_3X]^+$ have been obtained.

It may be noted that as the number of ligands of the same kind around a central atom increase, the absorption bands moves to longer wave length. Thus as the concentration of chloride ions is increased, the color of solution of copper ions, first blue on account of slight absorption in the red and green from a d-d transition band of $[Cu(H_2O)_4]^{+2}$, gives way to green as replacement of water by chloride progressively moves the absorption band in the visible region of the spectrum. This shift is completed i.e. no more change in the absorption band occurs when all the water molecules are replaced by chloride ions, thus forming a complex ion of the formula $[CuCl_4]^{--}$.

This phenomenon has been observed in a number of cases. This effect of shifting of absorption band has attracted quite an attention from scientists. Considerable work has been done in this field, yet some aspects have still been looked over. Mostly systems in acidic medium have been studied. It was, therefore, thought to work out systems in which the pH of the medium is not changed

during complex formation. The anionic concentration should be increased by the addition of neutral salts so that the phenomenon is observed independent of the hydrogen ion concentration.

A number of systems containing first row transition metal ions such as cobalt (II), nickel (II), copper (II), chromium (III) etc. were studied in solution containing high concentrations of anionic ligands such as NO_2^-, NO_3^-, SO_4^{--}, $S_2O_3^{--}$, SO_3^{--} etc. Some of these anions formed complexes with the metal ions thus producing strong absorption bands in the visible region of the spectrum where as in some other systems no change in the absorption spectra were observed. In a few systems, the metal ions were either oxidized or reduced by the anions thus producing some side reactions.

The electrical conductance of solutions containing metal ions depends upon the nature of ions present in the solution. When the nature of species in solution changes, the electrical conductance of such solutions must also be effected. Specially when a number of anions combine to form anionic complexes, there should be some change in the electrical conductance of the system. Unfortunately no data an electrical conductances was availabe for halide complexes formed in solutions of 12M HCl. Thus it was considered appropriate to study the electrical conductance of these systems and try to correlate the changes in electrical conductances with the stoichometry of the resulting metal complexes. Thus the observed change in the absorption spectra and electrical conductance were utilized in obtaining the composition and nature of the complexes formed in solution.

HISTORICAL REVIEW

Metal salts like metal halides were supposed to be ordinary salts like alkali halides forming simple covalent or ionic bonds. This idea was rejected when French[6] in 1924 proved that organic and inorganic salts of copper are coordinate compounds. He found that all curpric ions are coordinated to anions in this salt. Some organic salts are stable while others decompose by water yielding a hydrated curpric ion, which, however, is also a coordination compound.

Early theory of coordination was furnished by Werner[7] who gave the idea of coordination sphere. In 1926 Deniges[8] obtained the spectra of cobalt (II) salts (halides and sulphates) in presence of excess of concentrated, Hydrobromic acid in the orange region (700-640 nm) of the spectrum. The spectra of the cobalt (II) ion in combination with Hydrobromic acid was found to be twice as intense as that obtained in concentrated Hydrochloric acid solution. On the contrary greenish solution was found to be less intense than blue color of Hydrochloric acid solution. When cobalt (II) salts were dissolved in 10M Hydrogen Iodide solution the greenish coloration reached a maximum. No reasonable explaination could be given to this phenomenon.

In 1929 Sachindra Nath[9] studied a system of $CuSO_4 - Na_2SO_3$ in absence of air. He found an increase in the extinction coefficient with increase in the sulphite ion concentration. This phenomenon was ascribed to the formation of an unstable complex with the formula $[Cu(SO_4)\ SO_3^{--}]$.

Valliant[10] in 1930 reported a change in the absorption

spectra of solutions of $CaCl_2$, $Co(NO_3)_2$, and $CoSO_4$ in the presence of $ZnCl_2$ and or $ZnSO_4$ in aquous solutions. These changes in spectra were atributed to the substitution of one anion by another in the coordination sphere of the transition metal ion and change in the concentration of various ions present in the system.

Brode[11] determined the absorption spectra for cobalt (II), Bromide, Iodide and Chloride in solutions of their corresponding halogen acids in 1931. Samuel[12] in the same year observed the UV and Visible spectra of complex salts of Iron (II), cobalt (II), nickel (II) and palladium (II) with halide ions. He observed that when ammonia molecules were progressively replaced by $\bar{N}O_2$, $\bar{C}l$ or $\bar{C}N$ groups a turnery point was observed in the absorption curve which ultimately developed into a secondary absorption maximum and then converted into principle band. He had correlated his observations for the formation of complexes of these anionic ligands. A similar type of work was done by Johnson et al[13] in 1933. These workers studied the coordination complexes of chromium (III). The characteristic band due to chromium (III) in the red part of the spectrum, moved further into red when three ethelenediammine molecules were successively replaced by $\bar{\bar{C}}_2O_4$ in the complex ion $[Cr(en)_3]^{+3}$. A similar shift was observed in $[Cr(H_2O)_6]^{+3}$ and $[Cr(H_2O)_4\ SO_4]^{+}$ complex ions. It was then thought by Bombadas[14] in 1933 that anions attached to the ionic sphere of the complex do no effect the absorption spectrum in the visible region when the cations are colored and anions are colorless.

It was in 1934 that some reasonable theories were put forward to explain the phenomenon. Kiss and Geszner[3] studied the molar extinction coefficient on the entire visible part of the spectrum for $CoCl_2$, $Co(NO_3)_2$ and $CoSO_4$ in different concentrations of HCl,

HNO_3 and H_2SO_4. The observed changes in colors of the metal chlorides, nitrates and sulphates were thought to be due to stark effect and ion deformation. The color changes observed for cobalt (II) in solution in presence of chlorides and thiosulphate ions were assumed to be due to chromophoric change of constitution. In case of simultaneous changes of absorption spectra, it could not be determined whether changes were due to ion deformation, stark effect or dehydration. These workers also studied the effects of HCl, HNO_3, H_2SO_4 on the absorption spectra of nickel (II) salts such as $NiSO_4$ or $Ni(NO_3)_2$. A slight change in the visible spectra of nickel (II) nitrate ion was observed which was considered to be due to stark effect and deformation of ions. The significant change in the spectrum of nickel (II) ions observed in concentrated solution of chlorides, sulphates and thiosulphates were considered to be due to the formation of complexes. No explaination could be found for the changes of spectra caused simultaneously by the deformation of ions, stark effect or by formation of complexes and dehydration.

Emil katona[4] in 1935 worked on copper (II) complexes of sulphates, nitrates and chlorides and observed that blue color of dilute aqueous cupric salt solution originates from $[Cu(H_2O)_6]^{2+}$ ion. The slight increase in extinction coefficient observed in the absorption spectrum of $Cu(NO_3)_2$ in 7.5M H_2SO_4 solution was explained by this author as due to stark effect and deformation of ions. Stronger effects observed in more concentrated solution were considered to be due to the formation of sulphato or nitrato complex ions. As the extinction coefficient of concentrated H_2SO_4 solution of $CuSO_4$ is much higher than that of a pure aqueous solution, the coordination complexes of sulphate and nitrate ions with copper (II)

must have a deeper blue coloration than the aquous ion. On the contrary a decrease in the extinction coefficient of copper (II) spectrum was observed in 12.5 and 15M H_2SO_4 solution, which was explained to be due to the formation of colorless undissociated anhydrous salt. Presence of free anhydrous copper sulphate is very improbable in concentrated H_2SO_4 but formation of a complex acid $H_2[Cu(SO_4)_2]$ could very well account for these observations. At halogen ion concentration higher than 2M the absorption spectrum shows the existence of complexes of different composition. The change in color observed in the solution of copper halides containing large amounts of halide ion, cannot be explained by the hydrate theory since in water containing H_2SO_4, no color was observed. The complex formation is an endothermic process. In water solutions, the aquo cupric ion is hydrated complex of cupric ions and has a coordination number 6, where as chloro and bromo complex ions have coordination number 4 or containing 2 coordinative water molecules, besides the four halogen ions. The constitution of sulphate and nitrate complexes could not be explained by these workers.

Kiss[15] in 1936, studied the absorption spectrum of copper (II) salts uppon the addition of ammonia in the system. He found that the solution of these salts showed an absorption spectrum characteristic of the ions $[Cu(H_2O)_2(NH_3)_4]^{2+}$. When 2-4M ammonium salts were added to the solution, only a small change in absorption spectrum of copper (II) chloride was observed uppon the addition of ammonia. It was suggested that sulphate ions both in pure water and in ammonical solutions of cupric ions do not form sulphato complexes but take a position in the ionic sphere and ammonia is coordinated with the metal ion.

Mathieu[16] in 1936, studied visible spectra of six coordinated metal complexes and suggested that the absorption depends on the nature of the metal, coordinated groups and should be very sensitive to the change in type of bond between the metal and ligands. He studied that an increase in the atomic masses of ligands produce slight effects, on the absorption, where as if coordinating groups are replaced by other groups of different electron affinity, there is a considerable change in the absorption spectrum. He further suggested that there must be some coordination between chemical lability of the ligand and the displacement of the spectral band.

Another system $CoCl_2$–$MgCl_2$ was studied by Howell and Jackson[17] These workers studied the absorption spectra of $CoCl_2.6H_2O$ in the presence of increasing concentrations of $MgCl_2$. The extinction coefficient at the maximum of four absorption bands at 695, 666, 626 and 621 nm were plotted against concentration of $MgCl_2$. It was observed that the blue complex was not formed until the concentration of $MgCl_2$ was 4M and the amount of blue complex increased with the increasing concentration of $MgCl_2$ in the system. At 4M concentration of $MgCl_2$ the ratio of chloride ions to water molecules was 2:3. These workers suggested the following mechanism for this reaction:

$$[Co(H_2O)_6]^{2+} + Cl^- \rightleftharpoons [Co(H_2O)_4\ Cl_2]$$

$$[Co(H_2O)_4Cl_2] + Cl^- \rightleftharpoons [Co(H_2O)\ Cl_3]$$

These workers also suggested that $[CoCl_4^{--}]$ could not be obtained due to insufficient concentration of chloride ions in the solution.

In 1937 Dirking[18] used Lithium chloride instead of $MgCl_2$ and confirmed the existence of $[CoCl_4^{--}]$ by studying molecular weights,

transport phenomenon and absorption spectra of cobalt (II) chloride, cobalt (II) bromide and cobalt (II) cyanide in a number of solvents such as methanol, ethanol, acetone and methyl cyanide. He concluded that change in color from red to blue in the spectrum was due to the formation of $[CoCl_4]^{--}$ complex ion in the solution. The existence of $H_2[CoCl_4]$, $H_2[CoBr_4]$ and $H_2[Co(CN)_4]$ were also established.

Pearce and Dawson[19] studied the effect of equimolar and equimolal concentrations of NH_4Cl, KCl, NaCl, LiCl, HCl and $CaCl_2$ on the absorption spectra of cobalt (II) chloride. It was observed that the absorption bands widen with increasing concentration of added salts. This widening of the absorption bands was directly proportional to the ionic charge and inversely proportional to the ionic volume of the added cations.

In 1938 Tsuchida[20] studied the absorption spectra and stability of a number of coordination complexes of metal ions such as iron (II), cobalt (II), nickel (II) etc. with a number of anionic ligands such as NO_2^-, NCS^-, NO_3^-, etc. He discovered that metal complexes generally exhibit two selective bands of which one is in visible and other is in the UV region. He also observed some selective bands due to the ligands, ions, molecules coordinated in the complex ion superposing on the coordination band. The origin of color was attributed to the first band. This band was considered to be due to the electron jump in the incompletely filled d-orbitals of the central metal ion and appeared only when the central ion was a transition element. He showed that substitution of ligands proceed in the direction in which the second band is shifted towards the shorter wavelength. The order of

decreasing stability found was $NH_3 < \bar{N}O_2 < \bar{O}NO < H_2O < \bar{N}CS < \bar{O}H < \bar{N}O_3 < \bar{C}l < C\bar{\bar{O}}_3$. Spectra of chromium was also studied[21] and it was found to obey spectro chemical series smilar to that previously reported for cobalt.

Change of color from pink to blue by the addition of HCl to solution of $Co(NO_3)_2$ in alcoholic and aqueous mixtures was studied by Bobtelsky and Spiegler[22] in 1949. It was observed that blue color in water mixture did not appear if the concentration of HCl was below 5M. When alcohol was used as a solvent the blue color appeared even at a very low concentration of HCl. The extinction coefficient observed at the band maxima at 690 and 660 nm showed the maximum ratio of cobalt ion to halide ions as 1:4 indicating that $[Co\ X_4]^{2-}$ ions are formed in presence of excess of halide ions.

Katzin and Gebert[23] in 1950 discussed possible electronic configuration of the resulting cobalt (II) complex when red color was changed to blue in $CoCl_2$ by addition of excess of chlorides ions. The normal pink solution of aquous $CoCl_2$ with absorption band at 510 nm was considered to be due to hexa hydrated cobalt (II) ions. When excess of chloride ions is present in the system the blue color is produced due to the complex ion such as $[CoCl_2\ (H_2O)_2]$, $[CoCl_3\ (H_2O)]^{-}$ or $[CoCl_4]^{\bar{\bar{}}}$. The relative concentrations of each species was thought to depend on the equilibrium between the metal ion, anions or molecules of bases (electron donor) present in the system. The characteristic spectra of each species was also given in this paper. Evidence was also provided that blue complexes have tetrahedral arrangements of ligands around the metal ion.

The absorption spectra of solutions containing complexes of

chromium (III) ions were observed by Elving and Zeneel[24] in 1957. The absorption spectra of hexa aquo, chloropenta aquo and dichlorotetra aquo chiromium (III) ions were observed in the presence of high concentrations of perchloric acid, the position of the band maxima for these ions shifted towards the red side of the spectrum in a regular manner with the increase in number of complexed chloride ions. In the presence of 12M HCl the absorption spectrum obtained was characteristic of a complex species $[Cr(H_2O)_3\ Cl_3]$ found in the solution. The complex does not form to any appreciable extent if the concentration of HCl is below 12 moles/litre. Since this complex was not formed in the presence of 5M concentration of $CaCl_2$, its formation in 12M HCl was considered to be due to the concentration of hydrogen ions present in the system. The mechanism of the formation of $[Cr(H_2O)_3\ Cl_3]$ was also suggested by these authors.

In 1959 Katzin and Lingafelter[25] observed the absorption spectrum at the various stages of complexing of nickel (II) ions with ethylenediamine and showed that the spectra was due to $[Ni(en)(H_2O)_4]^{2+}$ and $[Ni(en)_2\ (H_2O)_2]^{2+}$. The absorption band centered at 400 nm (as well as the others) showed a shift towards lower wavelength and an increase in intensity. The complex $[Ni(en)(H_2O)_4]$ $(NO_3)_2$ was also prepared in solid state and this blue colored complex ion showed the absorption spectrum characteristic of a six coordinated nickel (II) complex. This was also confirmed by x-ray studies by the same workers. The absorption spectra of nickle (II) chloride in molten LiCl/KCl were discussed in terms of ligand field theory by Benson and Harrington[26]. These workers suggested that Ni^{2+} ion was surrounded by 4 chloride ions in a nearly

tetrahedral arrangement.

Webber and Sutcliffe[27] studied, by spectrophotometric method, cobalt (III) ions in presence of perchloric acid and the increasing concentration of $NaHSO_4$. These workers showed that at best one sulphate is present in the coordination sphere of the cobalt (III) ions. The composition of the complex was changed to $Co(SO_4)_2^-$ when studied at 30°C. The change in spectra caused by various amounts of sodium bisulphate were also recorded. It was seen that the principal change in spectrum occured in the UV region which suggested the formation of ion pairs.

The effect of addition of bromide, chloride and thiocyanide to solution of cobalt (II) ions in acetic acid over the temperature range 25-64°C was studied in detail by Proll and Sutcliffe[1] in 1962. These workers postulated the presence of $[CoX]^+$, $[CoX_2]$, $[CoX_3]^-$ and $[CoX_4]^{--}$ species (where X = Cl, Br, SCN ions) from spectrophotometric investigations.

Nordmann[28] studied the effect of increasing concentration of various anions (such as ClO_4^-, Cl^-, NO_3^-) furnished by their alkali metal salts upon the absorption spectrum of chromium (III) salts. $CrCl_3$ in $NaClO_4$, $CrCl_3$ in NaCl and $Cr(NO_3)_3$ in $NaNO_3$ were studied. These solutions were stable after three days and gave the same absorption spectrum for several months. In general two absorption bands were observed in the visible region for these systems. The band positions and relative data is reproduced below:

$CrCl_3$	— $NaClO_4$	system	415 nm , 575 nm
$CrCl_3$	——NaCl	"	415 nm , 585 nm
$Cr(NO_3)_3$	— $NaNO_3$	"	410 nm , 575 nm

These workers also observed the formation of a small amount of $Cr(OH)_3$ in chromium (III) — $NaNO_3$ salt solution.

Netzel and Drol[29] in 1963 observed small spectral changes near the maximum of absorption band at 400 nm. when chloride and bromide (concentration $\leqslant$ 0.12M) were present in aqueous solution of $Ni(ClO_4)_2$. The stability constant was calculated for the formation of $[Ni(H_2O)\ Cl]^+$ at ionic strength of 5.7M of chloride ions, assuming that presence of a 1:1 halide complex was responsible for the shift in absorption maximum.

Coleman[5] studied spectrum of cobalt (II) ions entrapped in cation and anion exchangers containing chloride ions to provide information about the nature of complex ion in these media. The chloride ion concentration was varied at fixed cobalt (II) ion concentration by equilibration with gaseous HCl — H_2O mixture. In both cation and anion exchangers the cobalt (II) coordination changed from octahedral to tetrahedral as the chloride ion concentration was increased. The spectra of tetrahedral species observed in anion exchangers was considered to be due to $[CoCl_4]^{--}$ ion.

In 1967 Myers and Willet[30] studied the absorption spectra of $CuCl_2$ in hydrous ethylacetate in the presence of 4M — HCl. These workers concluded that a square planar species, $[CuCl_4]^{--}$ was formed due to high concentration of chloride ions in ethylacetate. Cohen[31] observed the anionic complex formation by copper (II) chloride and nitrate in potassium chloride solutions through their absorption and ESR spectra.

In the recent years the change in absorption spectra of metal ions in presence of halides was studied by changing temperature

and pressure. In 1969 Griffith and coworkers[32], studied the formation of tetrahedral complexes $[NiBr_3\ (solvent)]^-$, $[NiBr_4]^{2-}$, $[NiI_3\ (solvent)]^-$ and $[NiI_4]^{2-}$ in acetone in the presence of bromide and iodides of lithium and ammonium ions. The trihalo species is unaffected by counterion but the extent of formation of tetrahalo complex is dependent upon the size of the counterion. $[Co(OAc)_3]$ reacted with chloride ions in acetic acid to produce a rather unstable species with an intense absorption band at 460 nm. This was observed by Koehl, et al[33]. The same species was produced when solid $Na_3[Co(CO_3)_3] . 3H_2O$ was added to a concentrated solution of HCl in glacial acetic acid. The spectrum and properties were consistent with the formula $[CoCl_4]^{2-}$.

Karelnikov and coworkers[34] have studied the effect of temperature upon the absorption spectra of $[CoCl_4]^{2-}$ in aquous solution in the visible region of spectrum at different temperatures. In 1971 Ludwig and Textor[35] confirmed, the existence of monomeric complex ions such as $[CuCl_3]^-$ and $[CuBr_3]^-$. The spectra of these compounds were interpreted by means of Molecular Orbital Theory. All the theoretically possible complexes with the mixed chloro-bromo ligand systems have been obtained. The three coordination complexes of copper (II) are supposed to be less stable than tetra and hexa coordinated copper (II) complexes. The energy of first allowed electronic transition changes with the average optical ligand electro negativity by a successive exchange of the individual halide ligand.

In 1974 Sawada and Tanaka[36] investigated the equilibrium between $Co(ClO_4)_2$ and LiCl in 0.1M $LiClO_4$ — HOAc solution by potentiometric and spectrophotometric methods. These workers

obtained the three and four coordinated cobalt (II) species as $LiCoCl_3$ and Li_2CoCl_4 and studied the absorption spectra of these compounds.

STATEMENT OF THE PROBLEM

It is evident from the proceeding review of literature that the studies done on the formation of anionic complexes in different concentrations of anions in solutions can be broadly divided into three categories.

i. Studies on the formation of halogen complexes of transition metal halides in the presence of high concentration of hydrogen halides in aqueous solutions. In these studies the effect of hydrogen ions introduced along with halides upon complex formation is not fully explored.

ii. Studies centered on the formation of metal complexes dissolved in molten alkali metal salts. Obviously these complexes are formed at elevated temperatures and the equilibrium becomes more and more complicated at such high temperatures.

iii. A few studies have been done cn the formation of complex ion in solutions containing neutral salts which do not introduce excessive amounts of hydrogen ions. These studies are also limited to the study of effects of halide salts upon transition metal halides. Further more these studies do not produce any quantitative and equirnial results for the formation of complexes of a particular stoichometry. The composition of the complexes is only assumed. It was, therefore, considered appropriate to study the formation of complexes of transition metal salts in solutions of high concentrations of other anions such as NO_3^-, NO_2^-, SO_3^{--}, $S_2O_3^{--}$, SO_4^{--} and similar other anions. Obviously the number and nature of ions is changed

during complex formation. As the conductance of a system depends upon the number and nature of ions, so the change in electrical conductance was considered to provide information about the stoichometry of the complex formed. With these considerations an elaborate investigation was started for complex formation in solutions of large concentrations of anions while maintaining the hydrogen ion concentration of the solution at the same level as in the aqueous solution of transition metal salts. Electrical conductances of these solutions should also provide some information about the composition of the complex ion formed in the solution.

EXPERIMENTAL

a. Absorption of light in the UV and Visible regions:

It is found that the ions which absorb in the visible or UV are those which have electronic structure such that an electronic transition from one energy level to another can be brought about by the absorption of only the relatively small amount of energy represented by a photon in the visible or UV region. These include the ions of transition elements. It is possible to study the composition of a sample by measuring its ability to absorb light. Spectrophotometric techniques particularly in the UV, VIS region have been much used in studying the absorption spectra and kinetics of complexes of transition metals. Spectrophotometer is an instrument which includes provisions for continously varying the wavelength of the light being employed, and is therefore, well adapted for studying the way in which the absorption of the sample varies with wavelength.

Light is electromagnetic radiation and may be described in terms of either its wavelength or frequency. Most frequently wavelengths are expressed in microns ($1\mu = 10^{-6}$ m = 0.001 mm.) When refering to UV or visible regions it is expressed in millimicrons or nanometers ($1m\mu = 10^{-9}$ m = 0.001μ = 1nm.) The portion of electromagnetic spectrum used in absorptimetric measurements is arbitrarily divided into the UV, which extends from about 100 – 400 nm; the VIS, which extends from 400 — 760 nm; and the near infrared (NIR), which extends from 760 to about 1500 nm.

Two properties of light are of interest. One is its quality or kind, which is described by its wavelength; the other is its quantity or amount, which is usually refered to as intensity. It is the first of these which governs the extent to which a beam of light is capable of interacting with any particular kind of substance; by measuring the intensities of light transmitted by the sample and comparing this with the light with which the sample was illuminated, we can secure a quantitative measure of the extent of the interaction between the sample and the energy contained in the light beam.

The laws governing the absorption of light by samples were formulated by Beer and Lambert. It relates the intensities of the light beams incident upon and transmitted by a solution of fixed thickness to the concentration of the solution. Mathematically these laws can be written in combined form as given below:

$$\text{Log } \frac{I_o}{I_t} = \epsilon ct$$

Where $\text{Log } \frac{I_o}{I_t}$ is called optical density or absorbance of the medium.

c is concentration expressed in gm mole/litre.

t is the thickness in centimeters.

and ϵ is the molecular extinction coefficient.

The absorption bands observed in the solution spectra of transition metal ions are due to electronic transitions from lower energy d-orbitals to the higher energy d-orbitals. The splitting of 5 degenerate d-orbitals in two or more groups of

orbitals with different energies is caused by the interaction of ligands. These spectra are adequately explained by means of Crystal field and Ligand field theories. A detailed discussion on these theories can be found in stander text books.

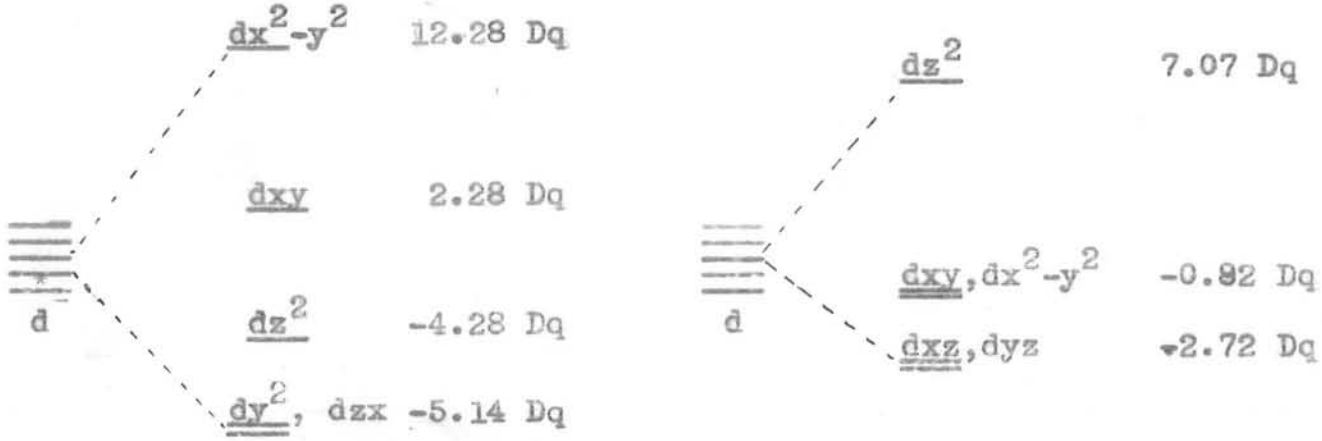
The extent and nature of crystal field splitting of d-orbitals depends upon

i. nature of the ligand.
ii. geometry and symmetry of the coordination compund formed.

Some ligands such as H_2O, halides and oxatate etc. produce little splitting between the groups of d-orbitals of the metal ion while other ligands such as $\bar{C}N$, $\bar{N}O_2$, en etc. produce a large difference of energy between the lower and higher energy orbitals.

The d-orbitals in an octahedral field are split into two sets of orbitals as t_{2g} (triply degenerate) lower in energy and e_g (doubly degenerate) higher in energy orbitals, while in a tetrahedral environment around the metal ion the splitting pattern is same but only the positions of orbitals are inverted.

Similarly the d-orbitals in a square planar complex split into four different energy sets and three sets of a d-orbitals are produced for trigonal bipyramid coordination compounds as shown.



Square planar Trigonal bipyramid

As the splitting of d-orbitals depends upon the symmetry of the coordination compounds, the electronic transitions also vary with the change in geometry or symmetry of the complex ion. Thus if two or three absorption bands are observed in an octahedral complex of a metal ion, the bands may further split by lowering the symmetry or changing geometry of the complex to square planar. Similarly molar extinction coefficient is also effected by the geometry of the complex ion. The more symmetrical molecules like octahedral are usually associated with small extinction coefficient in the range of 6-30 where as square planar complexes are associated with coefficients of the order of 50-100. Similarly tetrahedral complex ions absorb in lower energy range (NIR) and are associated with very high extinction coefficients of the order of several hundreds.

Thus it is possible to obtain some information about the complex formation and their geometry from the study of their absorption spectra.

b. Instrument Used:

The spectra in the course of these investigations were obtained on a Hitachi Model 323 UV-VIS-NIR Recording Spectrophotometer. The instrument is equiped with a Deuterium Lamp for UV and Tungsten Lamp for visible, which are automatically switchedover in the selected wavelength range. It has a wavelength range of 185 to 2500 nm and is a double beam, ratio recording spectrophotometer. The detectors are photomultiplier tubes and PbS cell automatically adjustable. The instrument has bilateral type of slites which are automatically adjustable from 0.005 to 2 mm.

A set of two matched quartz cells of one cm. thickness were employed for recording the spectra of solutions. Although silica cells were available, the quartz cells were prefered for the entire operating range of wavelength, from the far - UV through NIR. The scan speed was usually adjusted in the UV, VIS & NIR regions as 26.7, 53.2, 266 nm/min. respectively during all of the investigations.

c. Ions and Conductance:

The electrical conductivity of a solution is dependent upon both the nature and the concentration of every ionic species present in the solution. When a voltage is applied accross two electrodes immersed in a solution of an electrolyte, the dissolved ions will migrate towards the opposite electrodes i.e. the positive ion towards cathode and negative ions towards anode. This migration of ions through the solution constitutes the flow of electric current through the solution and this

current is greater in the more concentrated solution because of the larger number of ions moving through the solution. However, the current which flows through a solution depends not only on the number of ions which can be set in to motion, but also on the rate at which these ions move.

$$\frac{1}{R} = K\,(C_A\,\lambda_A + C_B\,\lambda_B + \ldots\ldots + C_Z\,\lambda_Z)$$

Where K is a constant of proportionality, C_i is the concentration in equivalents per litre of the ith ion in a solution and λ_i is a numerical constant characteristic of thation.

The resistance of a column of solution of uniform cross sectional area A(cm^2) between two electrodes 1 cm. apart is given by

$$R = \rho\left(\frac{l}{A}\right)$$

The proportionality constant ρ, which is called 'specific resistance' is equal to the measured resistance in a cell for which l and A are equal. For solutions of electrolytes dec- reases with increasing temperature i.e. is dependent on concentration and nature of solution.

The quantity l/A is called the 'cell constant.' Since the conductance of a solution is the reciprocal of its resis- tance.

$$\frac{1}{R} = \frac{1}{\rho} \cdot \frac{A}{l} = K\left(\frac{A}{l}\right)$$

Where K is called the 'specific conductance.' The con- ductance itself is expressed in reciprocal ohms or mhos and the specific conductance is expressed in mhos/cm.

The equivalent conductance is the specific conductance of a hypothetical solution which contains 1 gm. equivalent of solute per cm. Expressing the concentration in gram equivalents per 1000 cm. (which differs from its value in gram equivalent per litre by only 0.0027 per cent, an entirely negligible amount), we get expression for equivalent conductance.

$$\Lambda = 1000 \frac{K}{c} = 1000 \frac{1}{A} \frac{1}{R} \cdot \frac{1}{c}$$

The molar conductance is defined by an equation identical with the above except that the concentration is taken in gram mole/1000 cm.

Conductance of solution containing transition metal ions and alkali metal ions were measured on a Griffine conductance bridge model 575-820 supplied by Griffine and George Limitted. It has a dip type cell with platinized platinum electrodes. The cell constant is 1.0 for the electrodes. It was verified by using a number of standard solutions of KCl. The conductance is read directly. The null point is obtained by meter deflection to the left and reading zero or nearly zero i.e. greatest possible deflection to the left. Distilled water was used as a solvent for the measurements. Generally the conductance of three sets of solutions

i. transition metal salts of known concentration.
ii. alkali metal salts of different concentration.
iii. solutions containing both transition metals and alkali metal salts, were measured and compared.

d. Preparation of Solutions:

All chemicals used were of analytical reagent grade and

were used without further purification. Stock solutions of alkali metal salts were prepared by dissolving accurately weighed amount of salts in minimum volume of water and subsequently dilution to known volume in a volumetric flask. The molarities of the prepared solutions were then determined by conventional methods. These stock solutions were then diluted to any described concentrations and calculated amount of transition metal salts were dissolved in these solutions. Usually 25-50 ml. of each solution was prepared. Alkali metal salt solutions were used as blanks in the instrument for recording absorption spectra.

e. Procedure:

Stock solutions of 0.1M $Co(NO_3)_2\ 6H_2O$ was prepared in water. Stock solution of 8M $NaNO_2$ was prepared by dissolving 138 gm. of the salt in 250 ml. of water in a volumetric flask.

In each of 25 ml. flasks one ml. of $Co(NO_3)_2\ 6H_2O$ stock solution was added and then volumes of $NaNO_2$ stock solution was added to get 0.5, 1, 1.5, 1.7, 1.8, 1.9, 2.0, 3.0, 3.5, 5.0 and 7.5M solution of $NaNO_2$ in 25 millilitres. Finally the solutions were diluted to 25 ml. in the volumetric flasks. These solutions were throughly mixed and left in the dark for 24 hours. Then the absorption spectra of each solution was obtained in the UV, VIS and NIR region. The spectra was repeated after 48 hours and then again after 96 hours. No change in spectra was observed. The spectra are reproduced in Fig. 1 and the λ_{max} along with the molar extinction coefficient, calculated on the basis of concentration of the transition metal salt, are reproduced in Table 1. The conduc-

tances of the solutions were also measured after 24 hours. The results are given in Table 1.

This general scheme for preparation of solutions and the spectrophotometric studies were repeated with every system. The results are reproduced on the following pages.

TABLE NO. 1

System: $Co(NO_3)_2.6H_2O$ — $NaNO_2$

Concentration of $Co(NO_3)_2.6H_2O$ = 0.01M

Maximum concentration of $NaNO_2$ obtained = 7.5M

Temperature 298°K

S. No.	Concentration of NO_2	Absorption maximum		Molar conductance of $Co(NO_3)_2.6H_2O$	Molar conductance of $NaNO_2$	Molar conductance of $Co(NO_3)_2.6H_2O$ + $NaNO_2$
		λ_{max}	ϵ			
	(Moles/litre)	(nm)	(litres/mole cm)	($Ohms^{-1}$)	($Ohms^{-1}$)	($Ohms^{-1}$)
1.	0.00	510	6	300	—	300.0
2.	0.50	389	75	300	50.0	56.00
3.	1.00	402	100	300	48.0	50.0
4.	1.50	403	140	300	45.0	43.3
5.	1.70	405	170	300	44.5	42.4
6.	1.80	406	180	300	43.5	41.7
7.	1.90	408	210	300	43.2	41.6
8.	2.00	408	215	300	43.0	41.0
9.	3.00	408	220	300	35.3	34.7
10.	3.50	408	225	300	32.3	31.1
11.	5.00	408	240	300	23.8	23.5
12.	7.50	408	250	300	18.0	17.2
13.	2.00	387	70	300	44.0	45.5

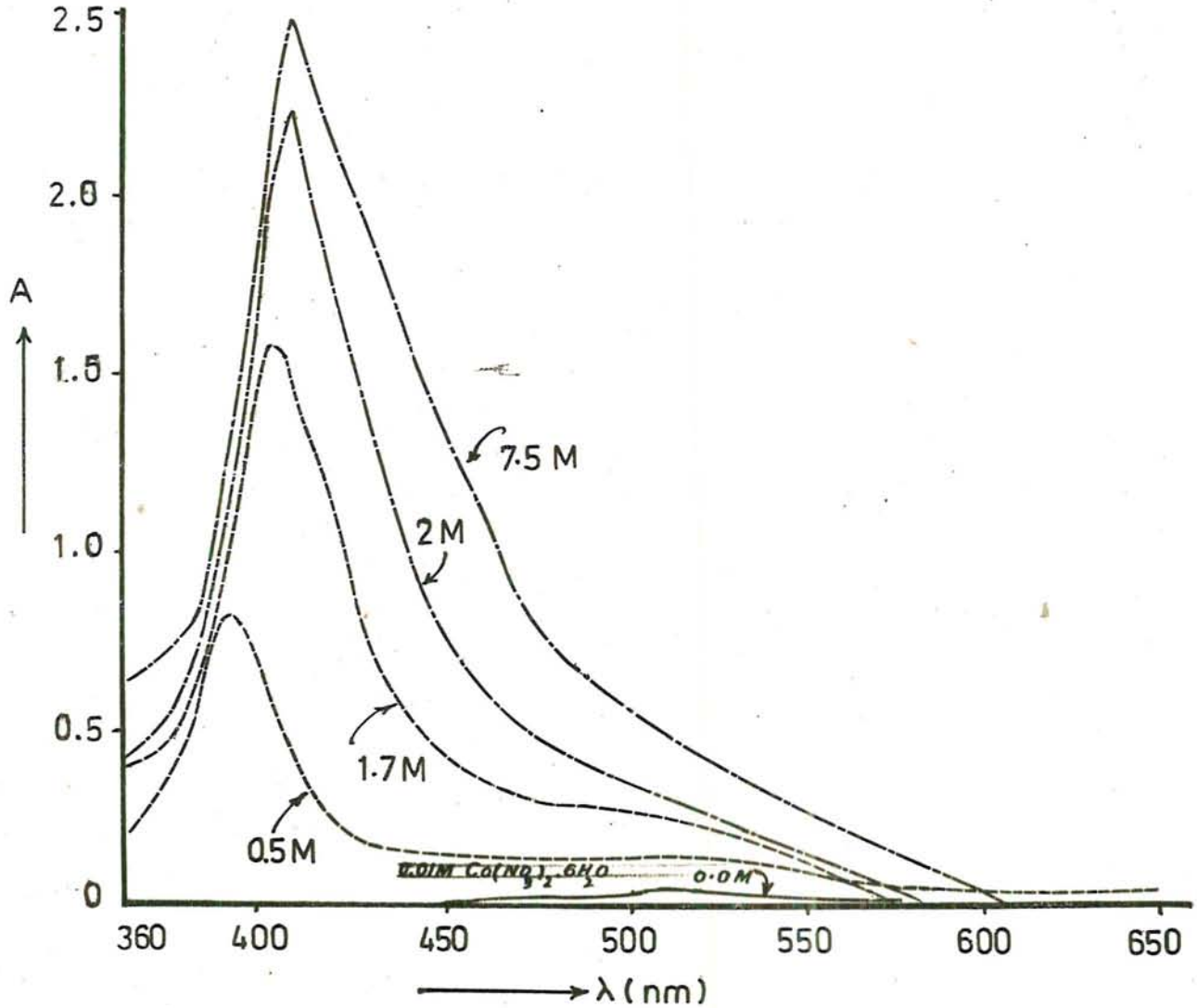


FIG:1. The Spectra of $Co(NO_3)_2 \cdot 6H_2O$ in varying concentrations of $NaNO_2$ at room temperature

TABLE NO. 2

System: $Ni(NO_3)_2 \cdot 6H_2O$ — $NaNO_2$

Concentration of $Ni(NO_3)_2 \cdot 6H_2O$ = 0.05M

Maximum concentration of $NaNO_2$ obtained = 7.5M

Temperature 298°K

S. NO.	Concentration of NO_2^- (Moles/litre)	Absorption maximum λ_{max} (nm)	Absorption maximum ϵ (litres/mole cm)	Molar conductance of $Ni(NO_3)_2 \cdot 6H_2O$ ($Ohms^{-1}$)	Molar conductance of $NaNO_2$ ($Ohms^{-1}$)	Molar conductance of $Ni(NO_3)_2 \cdot 6H_2O + NaNO_2$ ($Ohms^{-1}$)
1.	0.00	700 1175	3.0 5.0	118	—	118
2.	0.50	680 1140	3.00 5.0	118	50.0	56.4
3.	1.00	672 1102	3.5 3.5	118	48.0	52.8
4.	2.00	655 1080	4.0 4.0	118	43.0	47.1
5.	3.00	642 1068	4.3 4.3	118	35.3	38.9
6.	4.00	635 1047	4.7 4.7	118	30.6	33.5
7.	5.00	625 1025	5.2 5.2	118	23.8	24.2
8.	6.00	620 1010	5.8 5.8	118	20.8	21.2
9.	6.50	617 1006	5.8 5.8	118	19.7	20.2
10.	7.00	614 1002	5.9 5.9	118	18.9	19.1
11.	7.10	611 1000	6.0 6.0	118	18.7	18.8
12.	7.20	608 990	6.6 6.6	118	18.5	18.5
13.	7.40	608 990	7.0 7.0	118	18.1	18.1
14.	7.50	608 990	700 7.0	118	18.0	17.9
15.	7.20*	611 1000	5.8 5.8	118	20.0	20.4

*After boiling the solution.

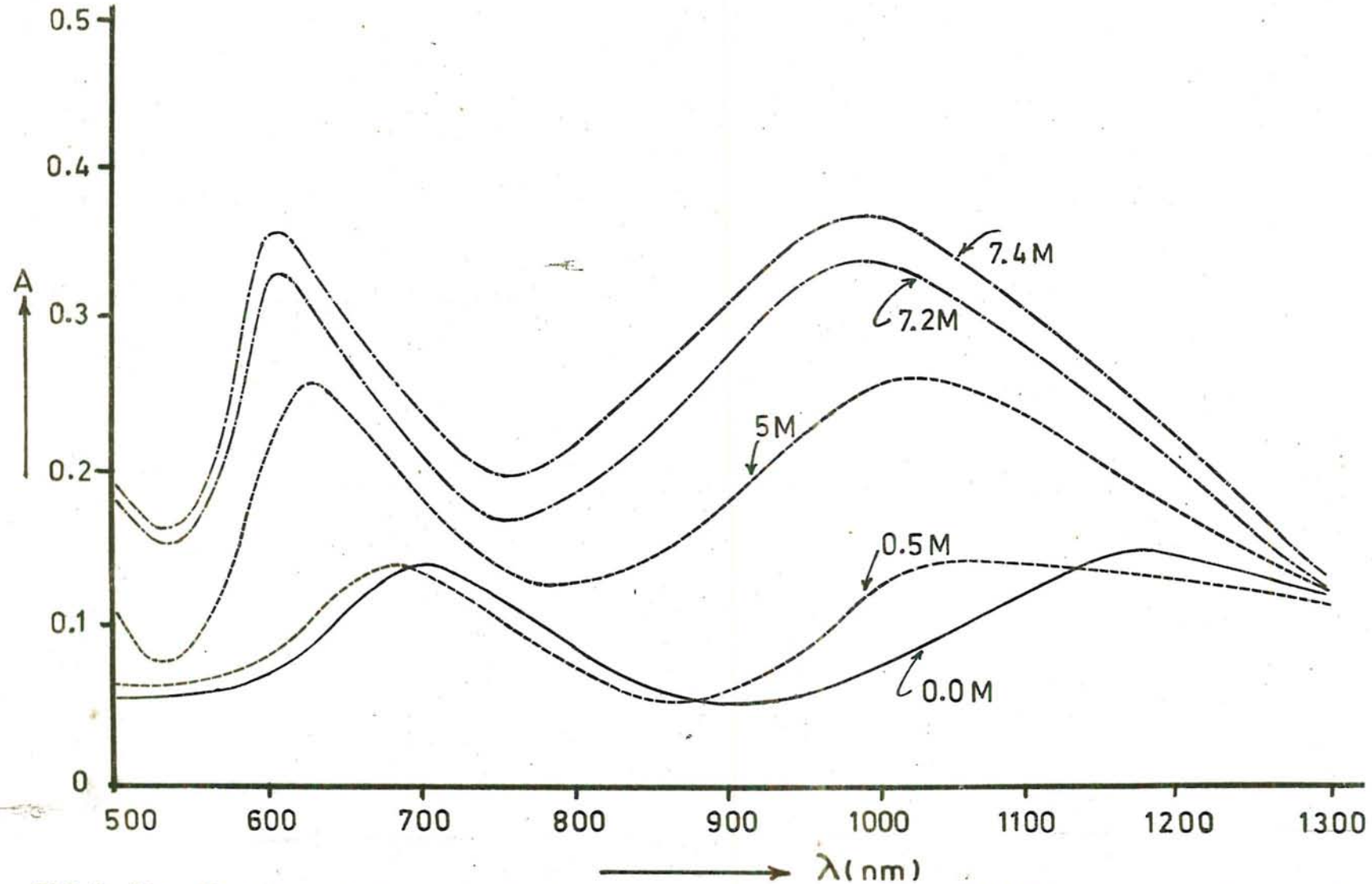


FIG: 2. The Spectra of $Ni(NO_3)_2.6H_2O$ in varying cocentrations of $NaNO_2$ at room temperature

TABLE NO. 3

System: $Cr(NO_3)_3 \cdot 9H_2O$ — $NaNO_2$

Concentration of $Cr(NO_3)_3 \cdot 9H_2O$ = 0.01M

Maximum concentration of $NaNO_2$ obtained = 7.5M

Temperature: 298^oK

S. No.	Concentration of NO_2^- (Moles/litre)	Absorption maximum λ_{max} (nm)	Absorption maximum ϵ (litres/mole cm)	Molar conductance of $Cr(NO_3)_3 \cdot 9H_2O$ ($Ohms^{-1}$)	Molar conductance of $NaNO_2$ ($Ohms^{-1}$)	Molar conducatance of $Cr(NO_3)_3 \cdot 9H_2O + NaNO_2$ ($Ohms^{-1}$)
1.	0.00	410 576	18 18	190	—	190.0
2.	0.50	420 582	20 20	190	50.0	52.0
3.	1.00	420 580	41 30	190	48.0	49.0
4.	2.00	420 575	43 41	190	43.0	44.0
5.	3.00	— 570	— 42	190	35.3	35.8
6.	4.00	— 565	— 41	190	29.0	29.3
7.	5.00	— 560	— 40	190	23.8	24.1
8.	6.00	— 558	— 40	190	20.8	21.2
9.	6.50	— 557	— 38	190	19.7	19.8
10.	6.60	— 556	— 38	190	19.5	19.6
11.	6.70	— 556	— 36	190	19.4	19.4
12.	6.80	— 556	— 40	190	19.3	19.2
13.	6.90	— 556	— 51	190	19.1	18.9
14.	7.00	— 556	— 70	190	18.9	18.8
15.	7.50	— 556	— 82	190	18.0	17.9
16.	7.20*	— 576	— 18	190	20.0	20.28

*After boiling the solution.

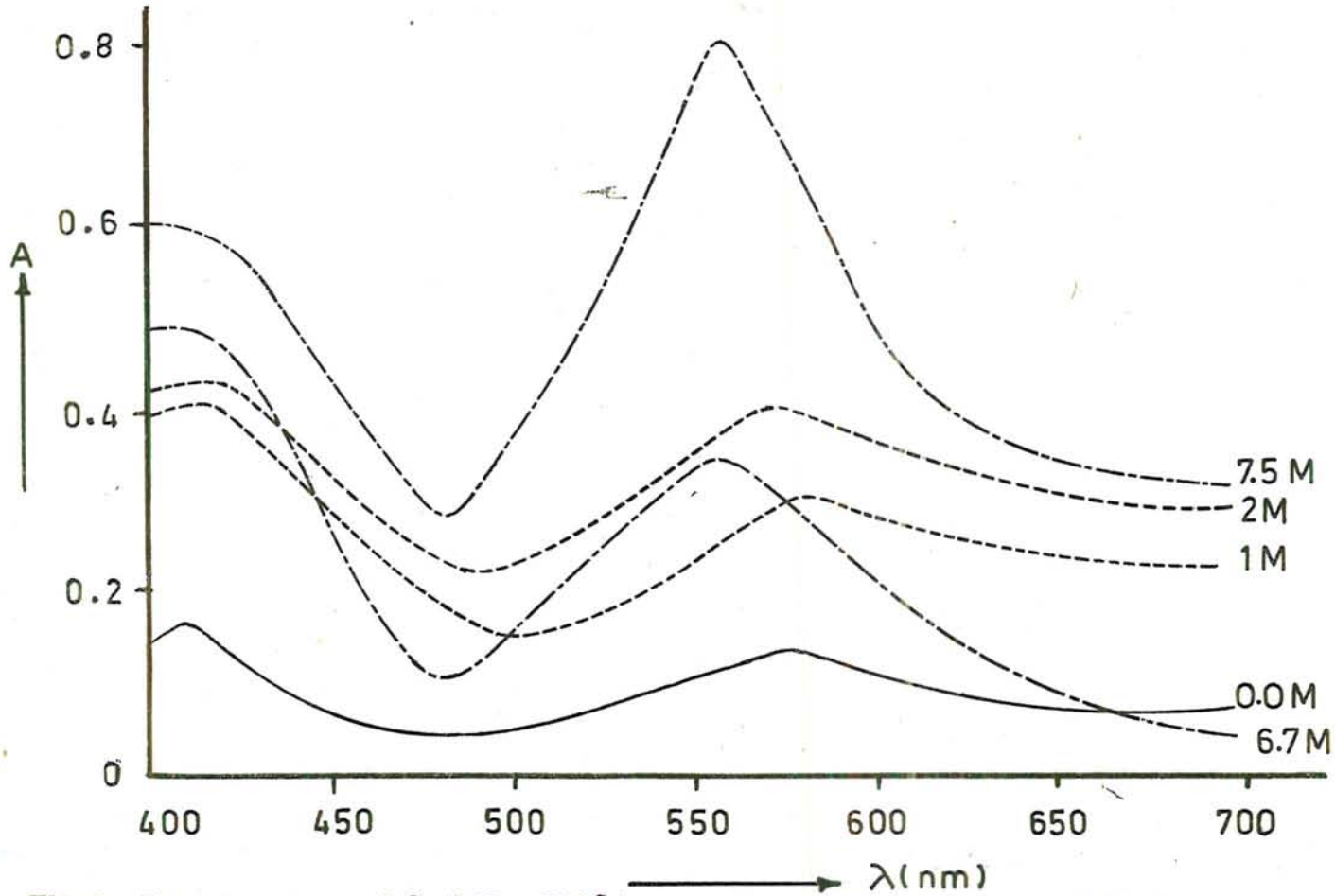


FIG:3. The Spectra of $Cr(NO_3)_3.9H_2O$ in varying concentrations of $NaNO_2$ at room temperature.

TABLE NO. 4

System: $CoSO_4 \cdot 7H_2O$ — $Na_2S_2O_3$

Concentration of $CoSO_4 \cdot 7H_2O$ = 0.01M

Maximum concentration of $Na_2S_2O_3$ obtained = 3.0M

Temperature 298°K

S. NO.	Concentration of S_2O_3 (Moles/litre)	Absorption maximum λ_{max} (nm)	Absorption maximum ϵ (litres/mole cm)	Molar conductance of $CoSO_4 \cdot 7H_2O$ ($Ohms^{-1}$)	Molar conductance of $Na_2S_2O_3$ ($Ohms^{-1}$)	Molar conductance of $CoSO_4 \cdot 7H_2O + Na_2S_2O_3$ ($Ohms^{-1}$)
1.	0.00	515	5.0	460	—	460.0
2.	1.00	520	10.0	460	69.0	71.0
3.	1.50	523	17.0	460	57.7	58.5
4.	2.00	525	22.0	460	46.5	46.9
5.	2.30	590	37.0	460	43.2	43.7
6.	2.50	645	50.0	460	39.8	39.9
7.	2.80	650	57.5	460	36.4	36.4
8.	2.90	657	100.0	460	35.8	39.8
9.	3.00	657	130.0	460	35.0	33.6

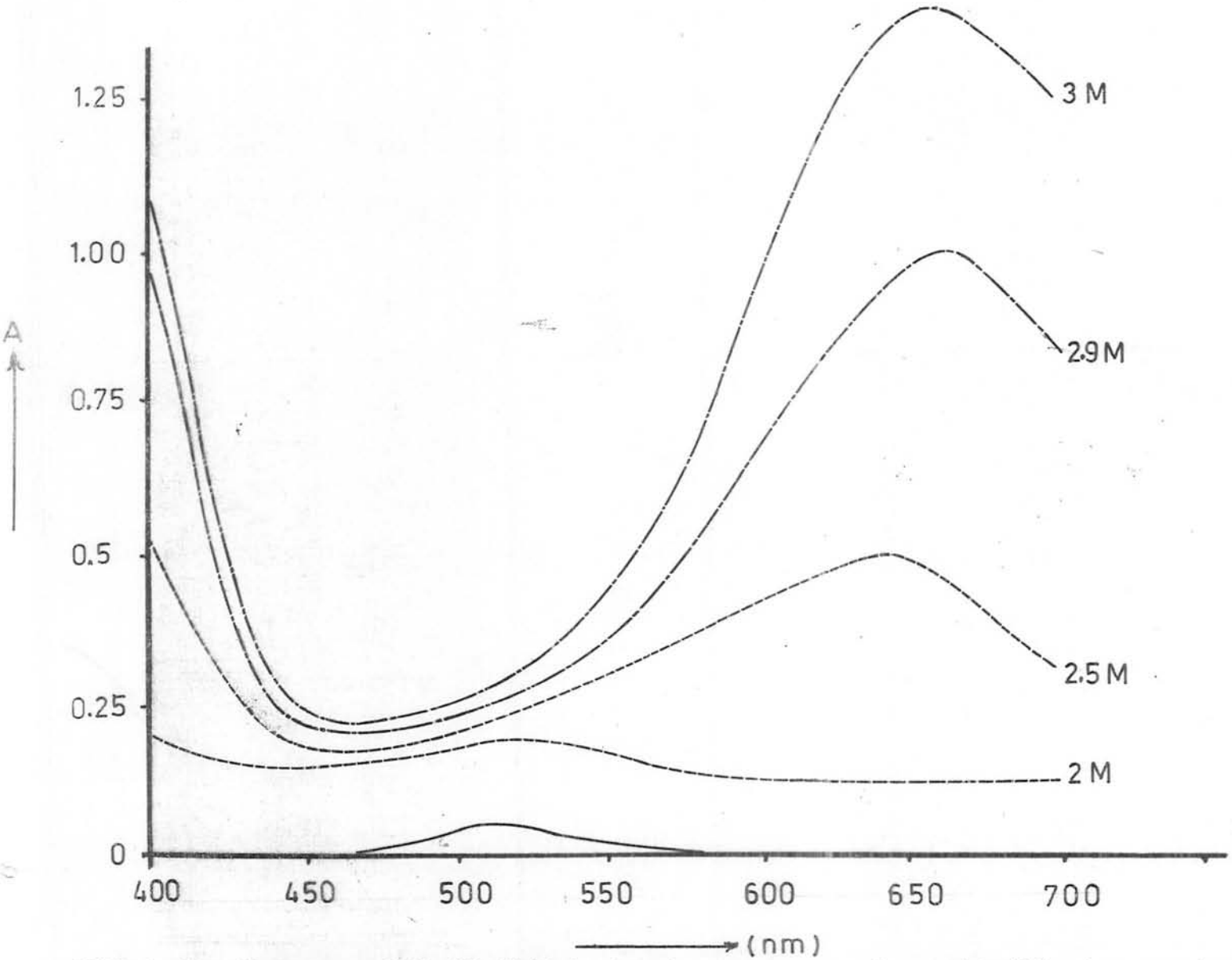


FIG: 4. The Spectra of $CoSO_4.7H_2O$ in varying concentrations of Na_2SO_3 at room temperature

TABLE NO. 5

System: $NiSO_4 \cdot 6H_2O$ — $Na_2S_2O_3$

Concentration of $NiSO_4 \cdot 6H_2O$ = 0.01M

Maximum concentration of $Na_2S_2O_3$ obtained = 3.0M

Temperature: 298°K

S. No.	Concentration of $S_2O_3^{--}$ (Moles/litre)	Absorption maximum λ_{max} (nm)	Absorption maximum ϵ (litres/mole cm)	Molar conductance of $NiSO_4 \cdot 6H_2O$ ($Ohms^{-1}$)	Molar conductance of $Na_2S_2O_3$ ($Ohms^{-1}$)	Molar conducatance of $NiSO_4 \cdot 6H_2O + Na_2S_2O_3$ ($Ohms^{-1}$)
1.	0.00	390 730	5 2	120	—	120.0
2.	1.00	389 725	3 3	120	69.0	70.0
3.	2.00	392 720	4 3	120	46.5	46.7
4.	2.50	394 715	10 4	120	39.8	40.2
5.	2.80	394 705	18 7	120	36.4	36.4
6.	2.90	380 394 690	22 9	120	35.8	35.6
7.	3.00	380 394 690	28 35	120	35.00	34.7
8.	3.00*	380 394 690	25 10	120	39.0	38.0

*After boiling the solution.

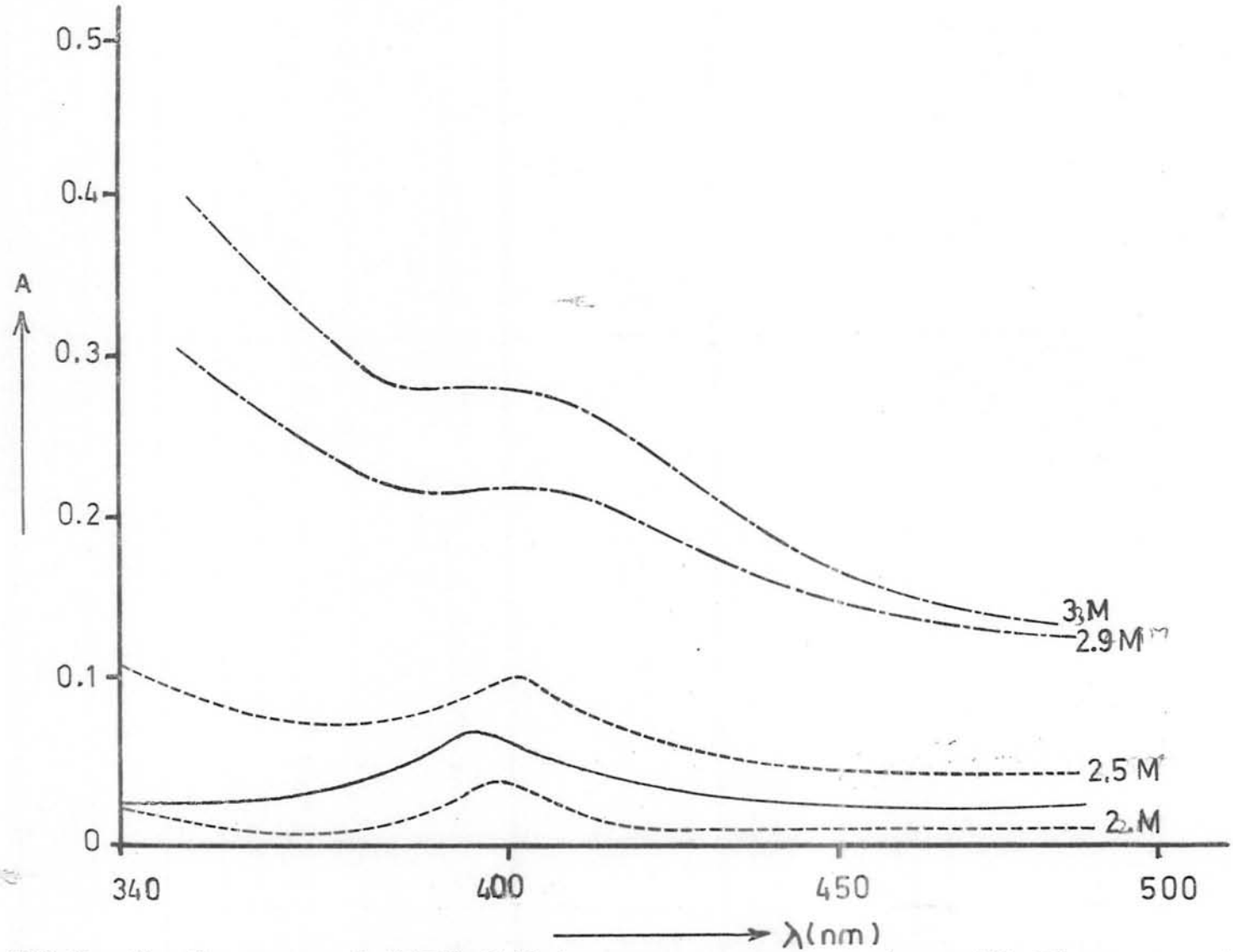


FIG:5a. The Spectra of $NiSO_4.6H_2O$ in varying concentrations of Na_2SO_3 at room temperature

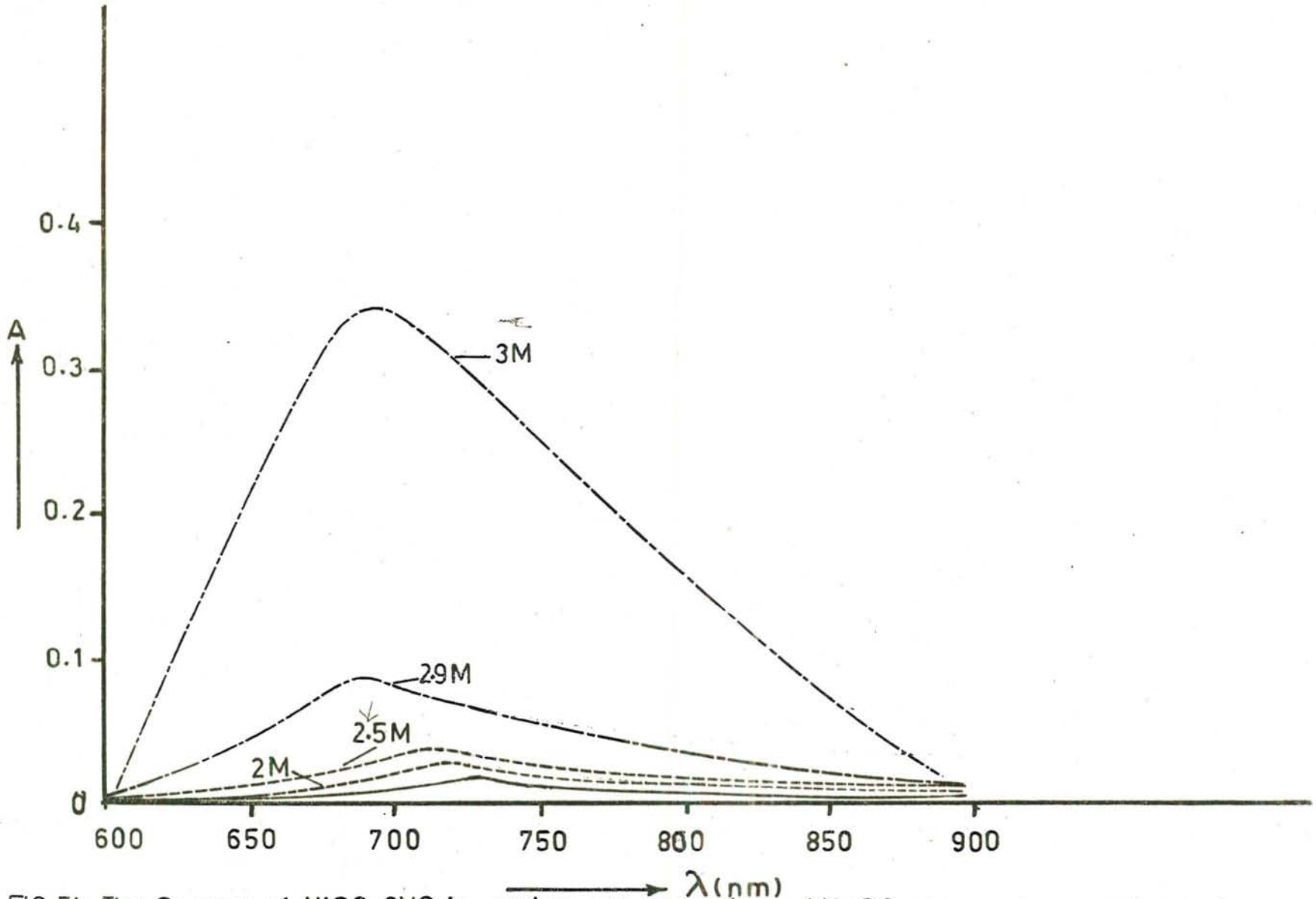


FIG:5b. The Spectra of $NiSO_4 \cdot 6H_2O$ in varying concentrations of $Na_2S_2O_3$ at room temperature

TABLE NO. 6

System: $CoSO_4 \cdot 7H_2O$ — Na_2SO_3

Concentration of $CoSO_4 \cdot 7H_2O$ = 0.01M

Maximum concentration of Na_2SO_3 obtained = 0.10M

Temperature: 298°K

	Concentration of $NaSO_3$	Absorption maximum		Molar conductance of $CoSO_4 \cdot 7H_2O$	Molar conductance of Na_2SO_3	Molar conductance of $CoSO_4 \cdot 7H_2O + Na_2SO_3$
		λ_{max}	ϵ			
	(Moles/litre)	(nm)	(litres/mole cm)	($Ohms^{-1}$)	($Ohms^{-1}$)	($Ohms^{-1}$)
1.	0.00	265 515	3.0 5.0	460	—	460.0
2.	0.01	285 615	7.0 6.0	460	170.0	200.0
3.	0.05	283 515	8.0 7.0	460	136.0	138.0
4.	0.06	280 515	175.0 7.5	460	133.3	130.0
5.	0.10	280 515	249.0 8.0	460	119.0	115.0

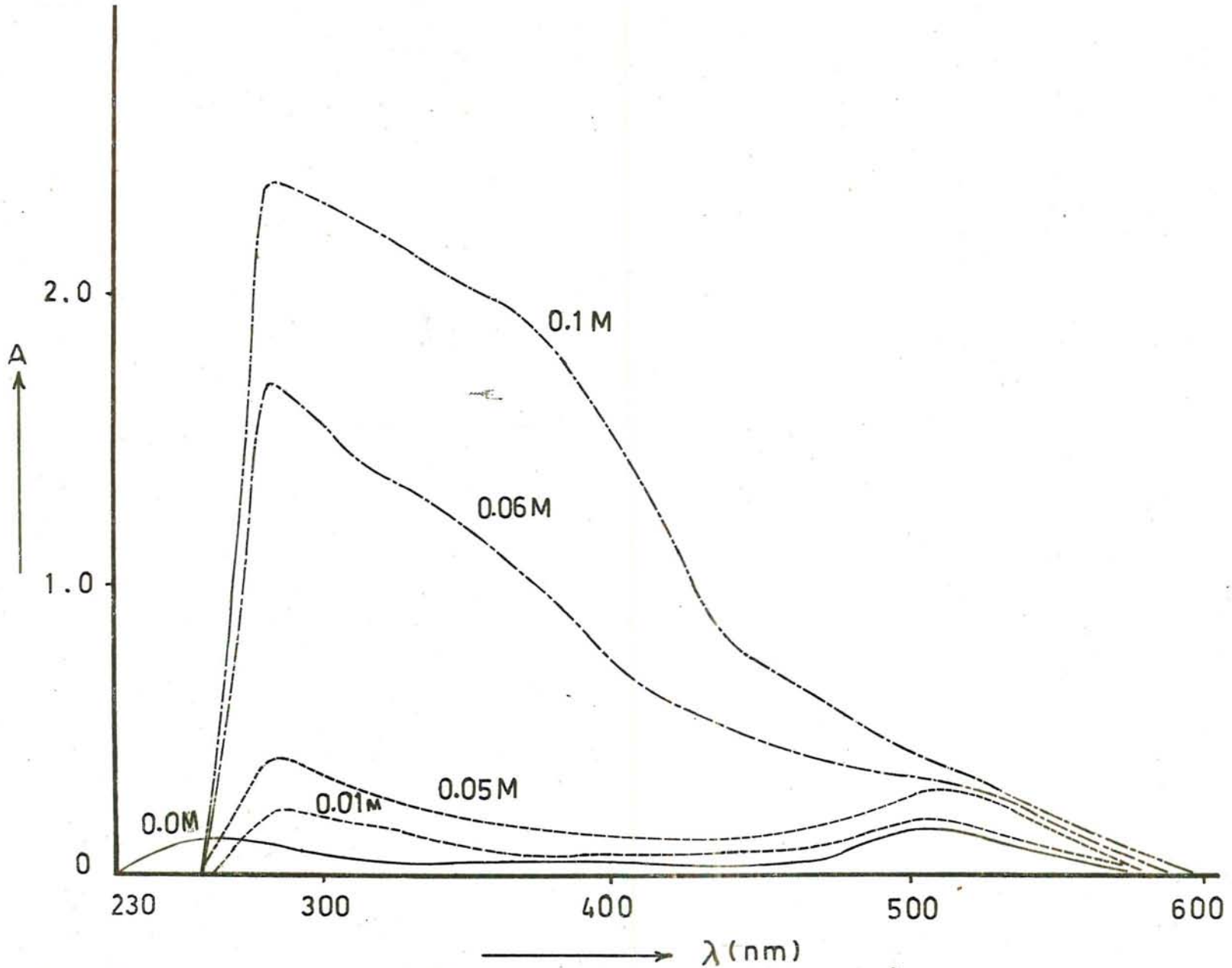


FIG: 6. The Spectra of $CoSO_4.7H_2O$ in varying concentrations of Na_2SO_3 at room temperature

TABLE NO. 7

System: $Ce(NO_3)_2 \cdot 6H_2O$ — $\bar{N}O_3$ (as KNO_3 and $Ca(NO_3)_2 \cdot 4H_2O$)

Concentration of $Ce(NO_3)_2 \cdot 6H_2O$ = 0.01M

Maximum concentration of $\bar{N}O_3$ ions obtained in KNO_3 = 3.0M and in $Ca(NO_3)_2 \cdot 4H_2O$ = 12.0M

Temperature 298°K

S. NO.	Concentration of $\bar{N}O_3$ (Moles/litre)	Absorption maximum λ_{max} (nm)	Absorption maximum ϵ (litres/mole cm)	Molar conductance of $Ce(NO_3)_2 \cdot 6H_2O$ ($Ohms^{-1}$)	Molar conductance of KNO_3 ($Ohms^{-1}$)	Molar conductance of $Ce(NO_3)_2 \cdot 6H_2O + KNO_3$ ($Ohms^{-1}$)
1.	0.00	510	6.00	300	—	300.0
2.	0.50	510	6.50	300	79.8	87.0
3.	1.00	510	7.00	300	69.5	71.5
4.	2.00	510	9.00	300	45.0	45.8
5.	3.00	510	10.00	300	45.0	45.8
	As $Ca(NO_3)_2 \cdot 4H_2O$				$Ca(NO_3)_2 \cdot 4H_2O$	of $Ce(NO_3)_2 \cdot 6H_2O + Ca(NO_3)_2 \cdot 4H_2O$
6.	1.00	510	6.00	300	45.8	55.5
7.	2.00	510	6.01	300	40.5	49.0
8.	3.00	510	6.02	300	35.8	38.9
9.	4.00	510	6.03	300	32.5	36.2
10.	5.00	510	6.04	300	25.0	28.2
11.	6.00	510	6.05	300	21.7	22.0
12.	7.00	510	6.06	300	19.2	19.7
13.	8.00	510	6.07	300	17.4	17.8
14.	9.00	510	6.08	300	15.6	15.7
15.	10.00	510	6.09	300	13.6	13.8
16.	11.00	510	6.10	300	11.2	11.4
17.	12.00	510	6.10	300	10.7	10.8

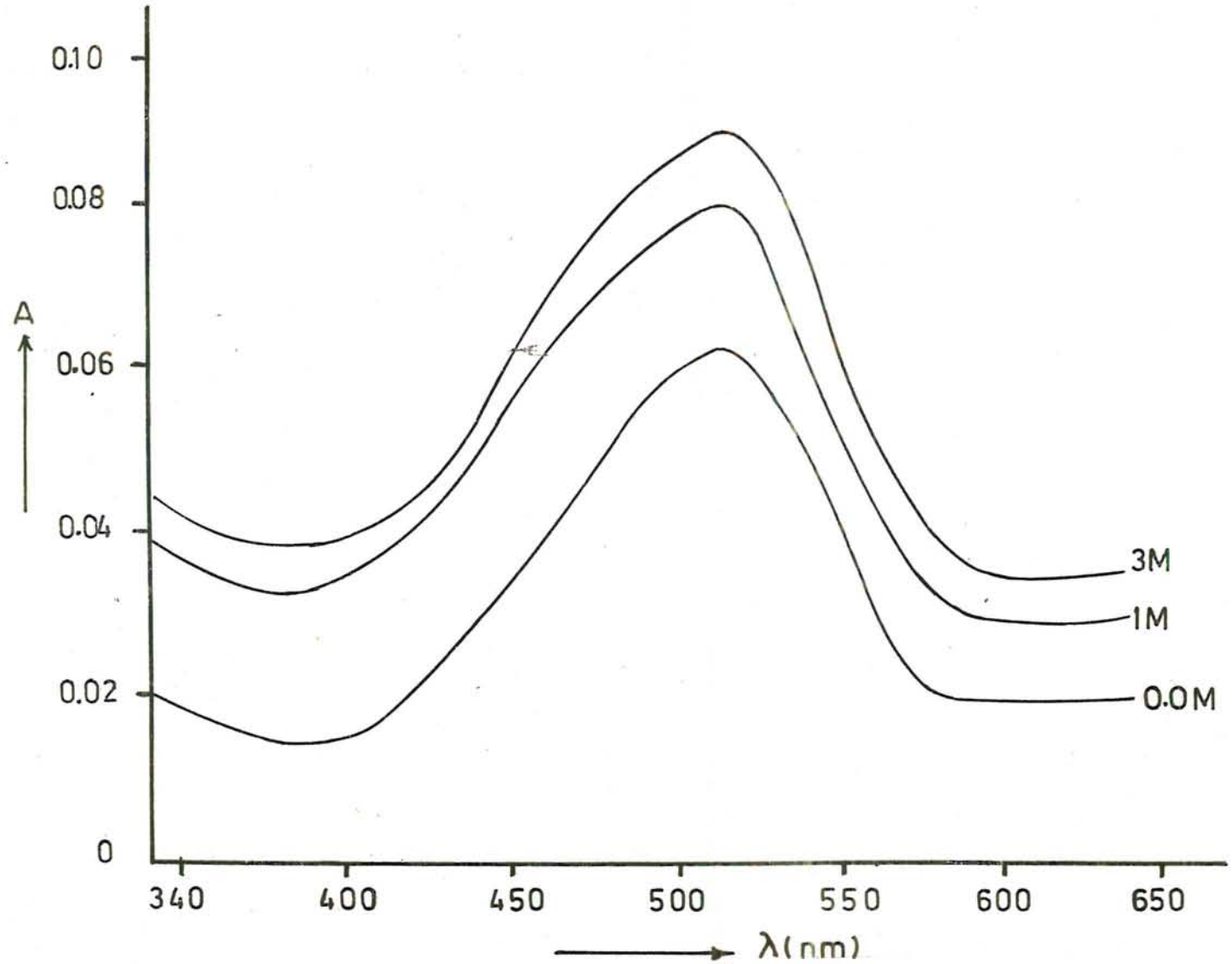
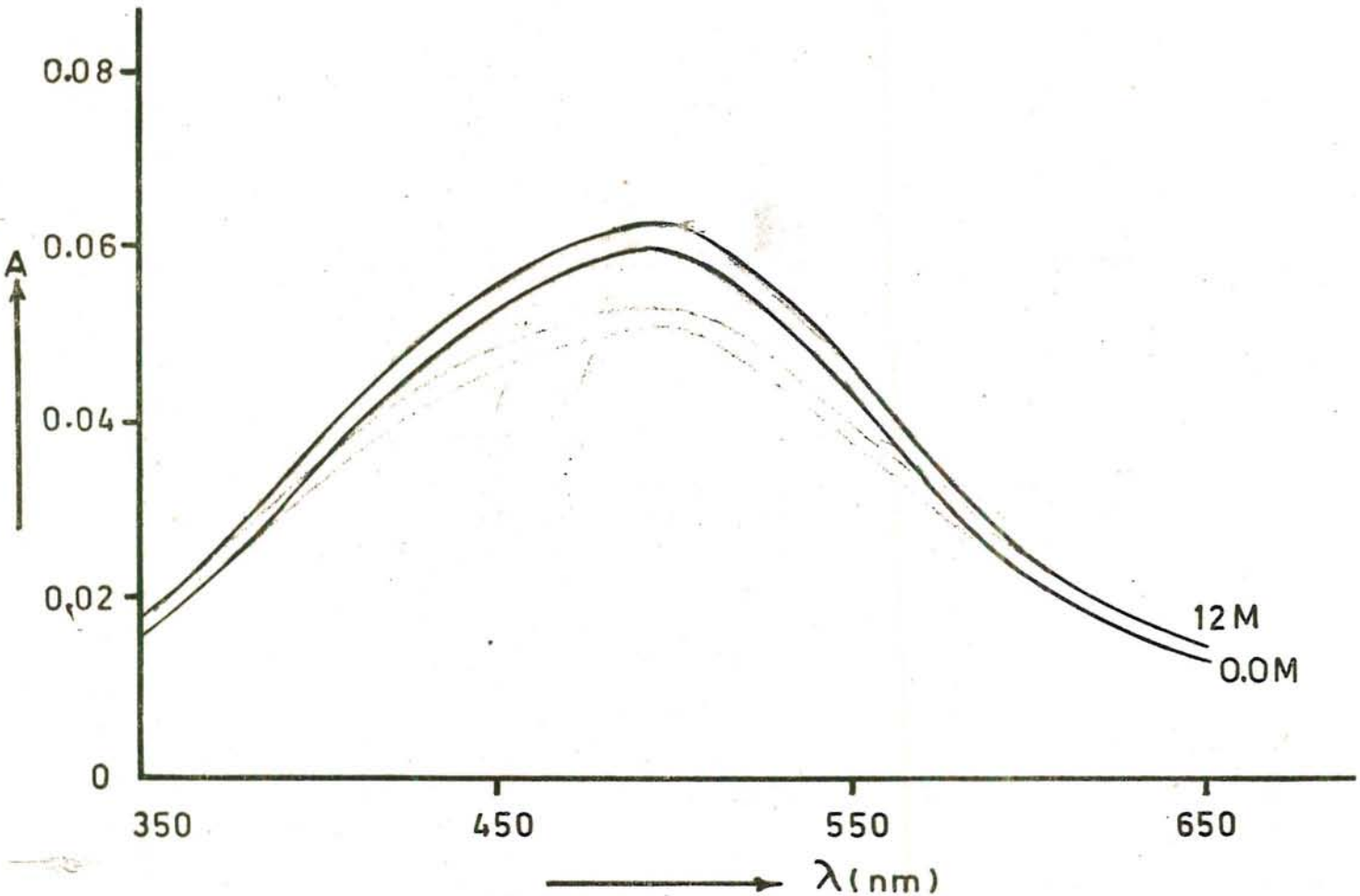


FIG: 7a. The Spectra of $Co(NO_3)_2 \cdot 6H_2O$ in varying concentrations of KNO_3 at room temperature



FIG; 7b. The Spectra of $Co(NO_3)_2 \cdot 6H_2O$ in varying concentrations of $Ca(NO_3)_2$ at room temperature

TABLE NO. 8

System: $Ni(NO_3)_2 \cdot 6H_2O - \bar{N}O_3$ ions (as KNO_3 and $Ca(NO_3)_2 \cdot 4H_2O$)

Concentration of $Ni(NO_3)_2 \cdot 6H_2O$ = 0.005M for KNO_3 and 0.05M for $Ca(NO_3)_2 \cdot 4H_2O$

Maximum concentration of $\bar{N}O_3$ ion obtained in KNO_3=3.0M and in $Ca(NO_3)_2 \cdot 4H_2O$ = 12.0M

Temperature: 298°K

S. No.	Concentration of $\bar{N}O_3$ (Moles/litre)	Absorption maximum λ_{max} (nm)	Absorption maximum ϵ (litres/mole cm)	Molar conductance of $Ni(NO_3)_2 \cdot 6H_2O$ ($Ohms^{-1}$)	Molar conductance of KNO_3 ($Ohms^{-1}$)	Molar conductance of $Ni(NO_3)_2 \cdot 6H_2O + KNO_3$ ($Ohms^{-1}$)
	As KNO_3					
1.	0.00	398 700 1175	3.5 1.5 1.5	170	—	170.00
2.	0.50	398 700 1175	4.0 1.8 1.8	170	79.8	80.00
3.	1.00	398 700 1175	5.5 2.2 2.2	170	69.5	69.90
4.	2.00	398 700 1175	7.0 2.5 2.5	170	54.5	54.75
5.	3.00	398 700 1175	8.0 2.8 2.8	170	45.00	45.23

Contd..

S. No.	Concentration of NO_3 As $Ca(NO_3)_2 \cdot 4H_2O$ (Moles/litre)	Absorption maximum λ_{max} (nm)	Absorption maximum ϵ (litres/mole cm)	Molar conductance of $Ni(NO_3)_2 \cdot 6H_2O$ ($Ohms^{-1}$)	Molar conductance of $Ca(NO_3)_2 \cdot 4H_2O$ ($Ohms^{-1}$)	Molar conductance of $Ni(NO_3)_2 \cdot 6H_2O + Ca(NO_3)_2 \cdot 4H_2O$ ($Ohms^{-1}$)
6.	1.00	398 700 1175	5.6 3.5 3.5	118	45.8	48.20
7.	2.00	398 700 1175	5.6 3.5 3.5	118	40.5	42.00
8.	3.00	398 700 1175	5.6 3.5 3.5	118	35.8	37.60
9.	4.00	398 700 1175	5.6 3.5 3.5	118	32.5	34.50
10.	5.00	398 700 1175	5.6 3.5 3.5	118	25.0	26.70
11.	6.00	398 700 1175	5.6 3.5 3.5	118	21.7	22.33
12.	7.00	398 700 1175	5.6 3.5 3.5	118	19.2	19.90
13.	8.00	398 700 1175	5.6 3.5 3.5	118	17.4	18.10
14.	9.00	398 700 1175	5.6 3.5 3.5	118	15.6	15.90
15.	10.00	398 700 1175	5.6 3.5 3.5	118	13.6	13.90
16.	11.00	398 700 1175	5.6 3.5 3.5	118	11.2	11.40
17.	12.00	398 700 1175	5.6 3.5 3.5	118	10.7	10.80

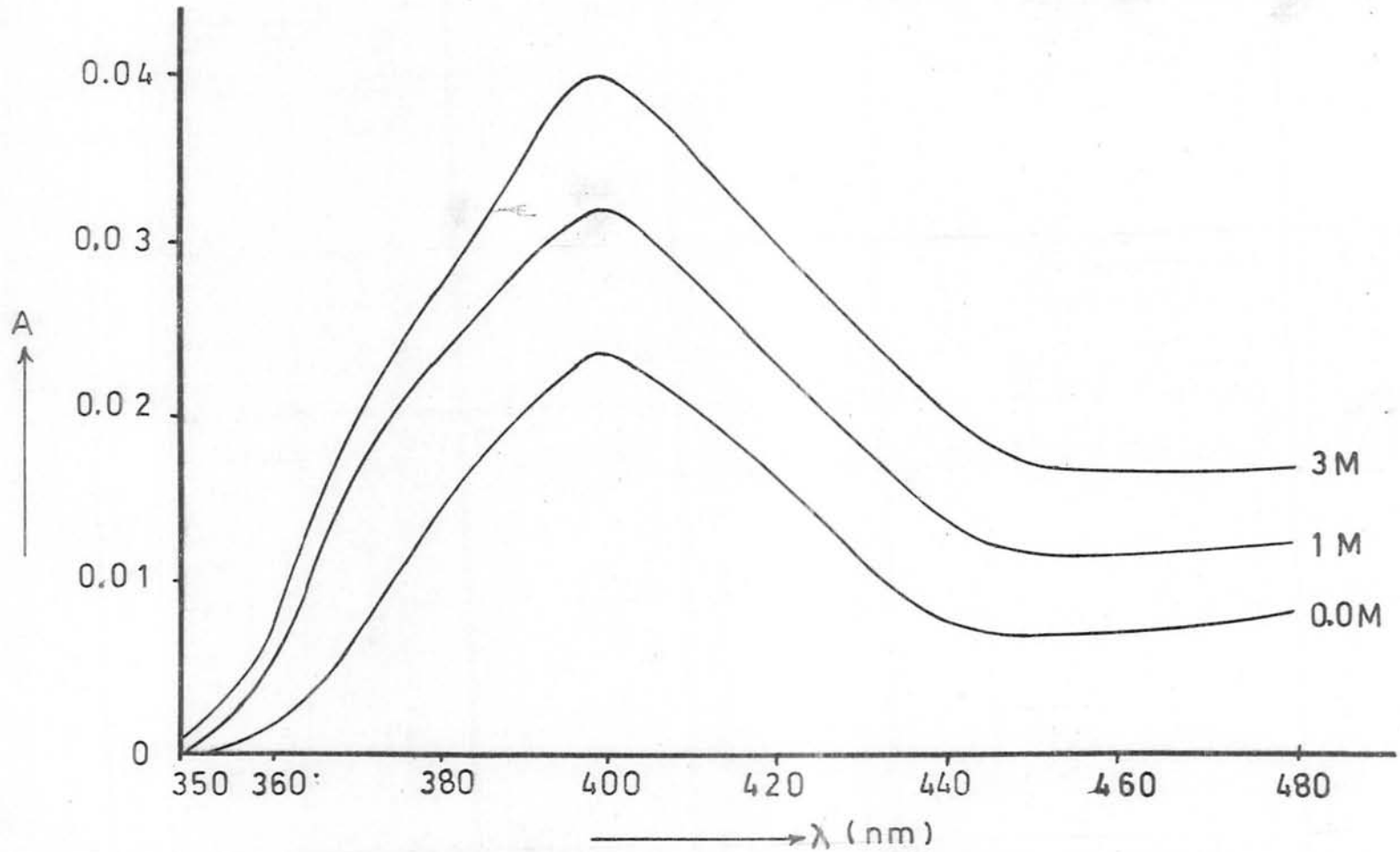


FIG: 8a. The Spectra of $Ni(NO_3)_2 \cdot 6H_2O$ in varying concentrations of KNO_3 at room temperature

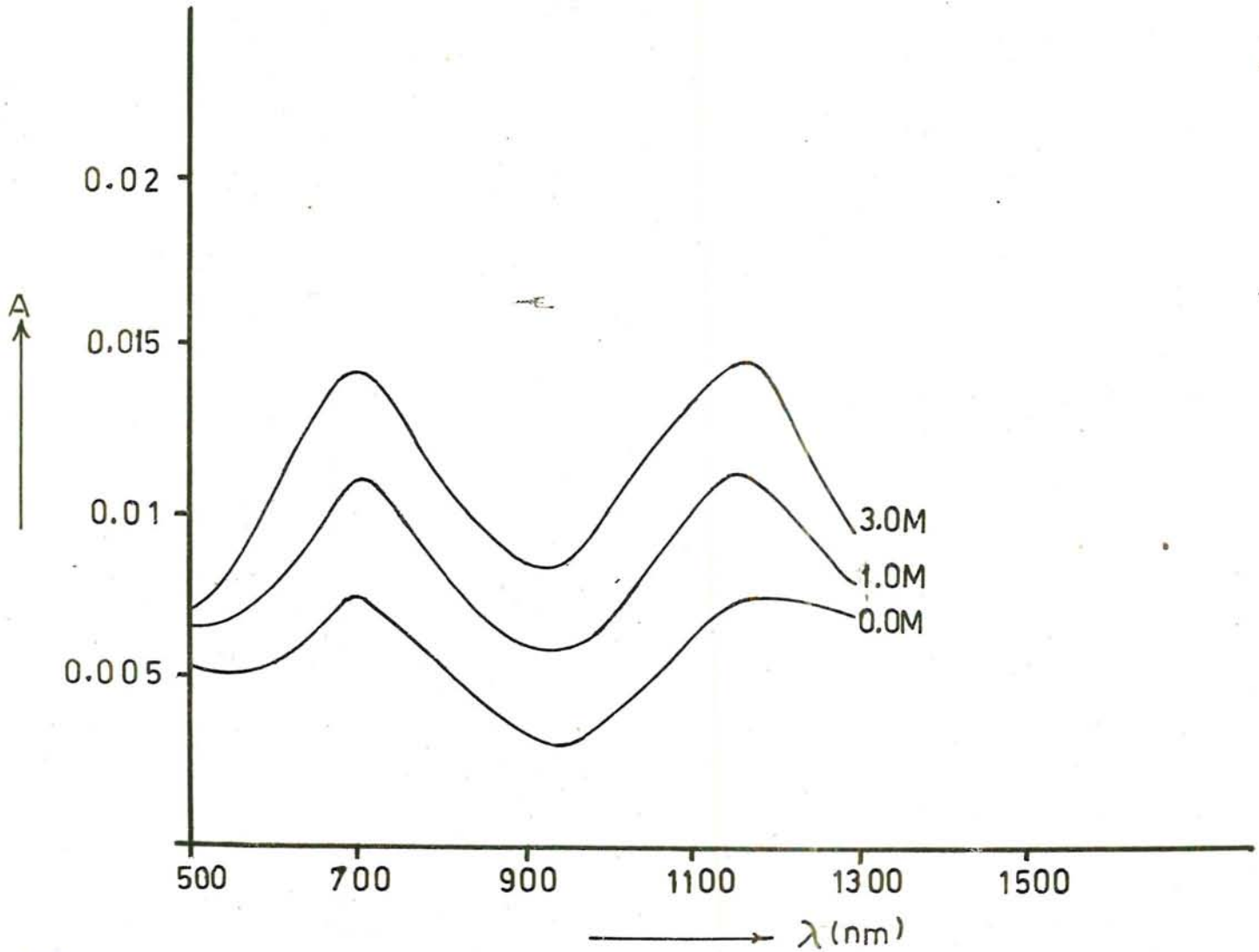


FIG: 8b. The Spectra of $Ni(NO_3)_2 \cdot 6H_2O$ in varying concentrations of KNO_3 at room temperature

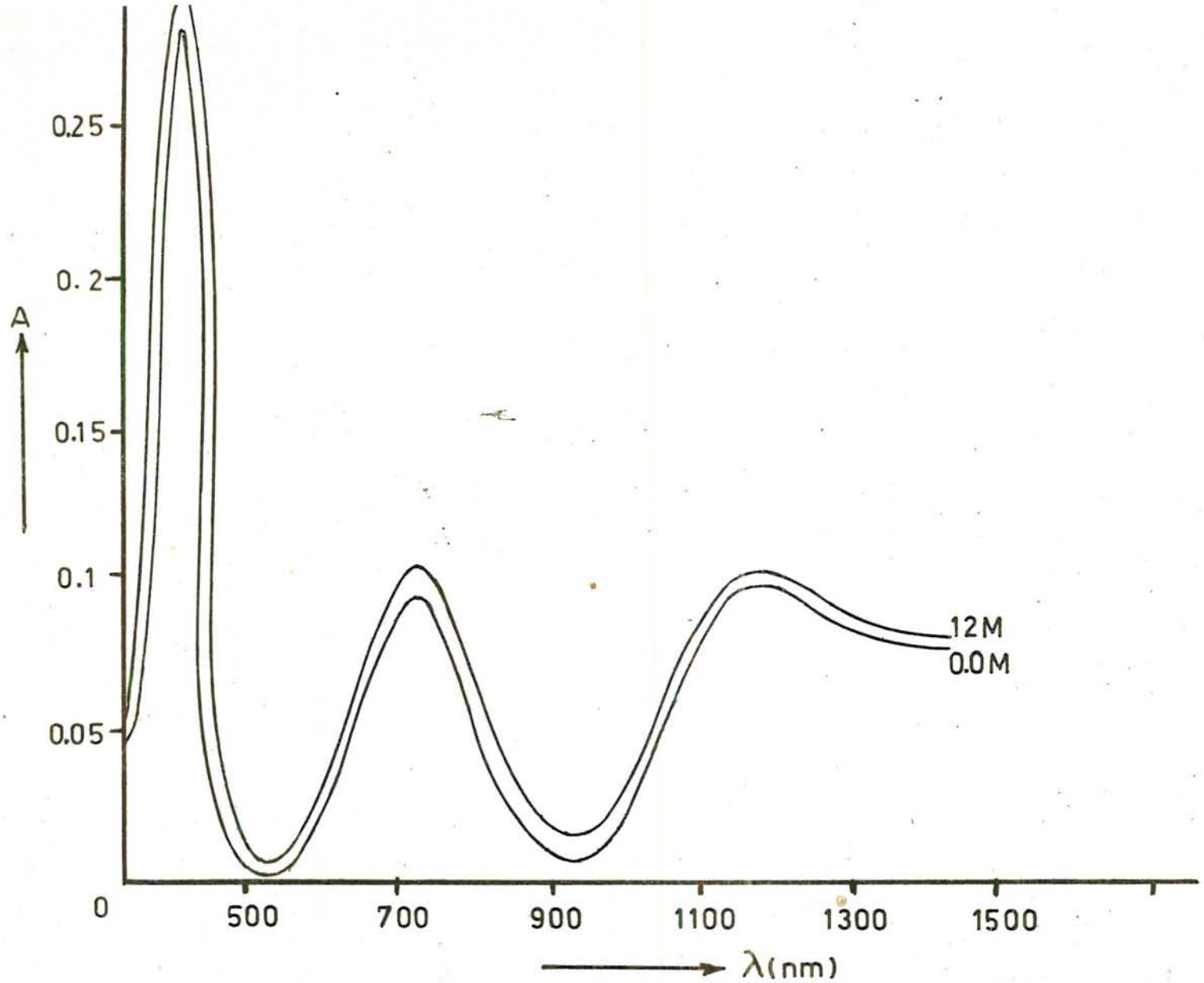


FIG: 8c. The Spectra of $Ni(NO_3)_2 \cdot 6H_2O$ in varying concentrations of $Ca(NO_3)_2 \cdot 4H_2O$ at room temperatur

TABLE NO. 9

System: $Cu(NO_3)_2 \cdot 3H_2O$ — $Ca(NO_3)_2 \cdot 4H_2O$

Concentration of $Cu(NO_3)_2 \cdot 3H_2O$ = 0.02M

Maximum concentration of NO_3^- ions obtained = 12.0M

Temperature 298°K

S. No.	Concentration of NO_3^- (Moles/litre)	Absorption maximum λ_{max} (nm)	Absorption maximum ϵ (litres/mole cm)	Molar conductance of $Cu(NO_3)_2 \cdot 3H_2O$ ($Ohms^{-1}$)	Molar conductance of $Ca(NO_3)_2 \cdot 4H_2O$ ($Ohms^{-1}$)	Molar conductance of $Cu(NO_3)_2 \cdot 3H_2O + Ca(NO_3)_2 \cdot 4H_2O$ ($Ohms^{-1}$)
1.	0.00	820	11.0	34.0	—	34.0
2.	1.00	820	11.5	34.0	45.8	48.9
3.	2.00	820	12.0	34.0	40.5	43.5
4.	3.00	820	12.2	34.0	35.8	38.5
5.	4.00	820	12.4	34.0	32.5	34.9
6.	5.00	820	12.8	34.0	25.0	27.8
7.	6.00	820	13.0	34.0	21.7	24.0
8.	7.00	820	13.2	34.0	19.2	22.1
9.	8.00	820	13.5	34.0	17.4	19.6
10.	9.00	820	13.8	34.0	15.6	17.8
11.	10.00	820	14.2	34.0	13.6	15.3
12.	11.00	820	14.6	34.0	11.2	13.0
13.	12.00	820	15.0	34.0	10.7	11.5

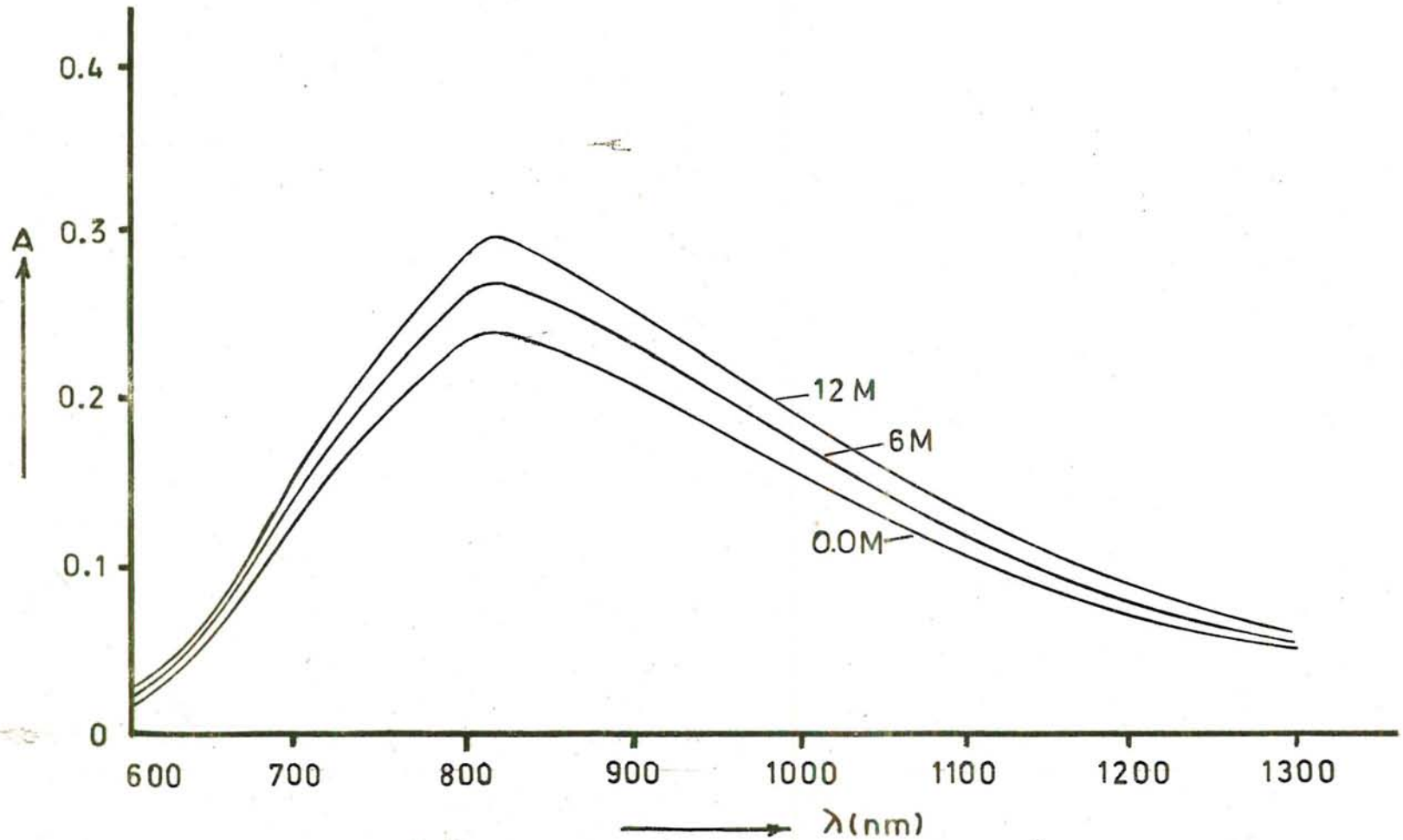


FIG:9. The Spectra of $Cu(NO_3)_2.3H_2O$ in varying concentrations of $Ca(NO_3)_2.4H_2O$ at room temperature.

TABLE NO. 10

System: $Co(SO_4) \cdot 7H_2O$ — $MgSO_4$

Concentration of $CoSO_4 \cdot 7H_2O$ = 0.01M

Maximum concentration of $MgSO_4$ obtained = 3.8M

Temperature: 298°K

S. No.	Concentration of SO_4 (Moles/litre)	Absorption maximum λ_{max} (nm)	Absorption maximum ϵ (litres/mole cm)	Molar conductance of $CoSO_4 \cdot 7H_2O$ ($Ohms^{-1}$)	Molar conductance of $MgSO_4$ ($Ohms^{-1}$)	Molar conductance of $CoSO_4 \cdot 7H_2O + MgSO_4$ ($Ohms^{-1}$)
1.	0.00	515	5	460.0	—	460.0
2.	0.5	515	5	460.0	33.0	41.7
3.	1.0	515	5	460.0	27.2	34.7
4.	1.5	515	5	460.0	22.5	30.2
5.	2.0	515	5	460.0	18.2	25.5
6.	2.5	515	5	460.0	15.7	21.2
7.	3.0	515	5	460.0	13.0	19.1
8.	3.5	515	5	460.0	11.7	16.7
9.	3.8	515	5	460.0	9.34	11.53

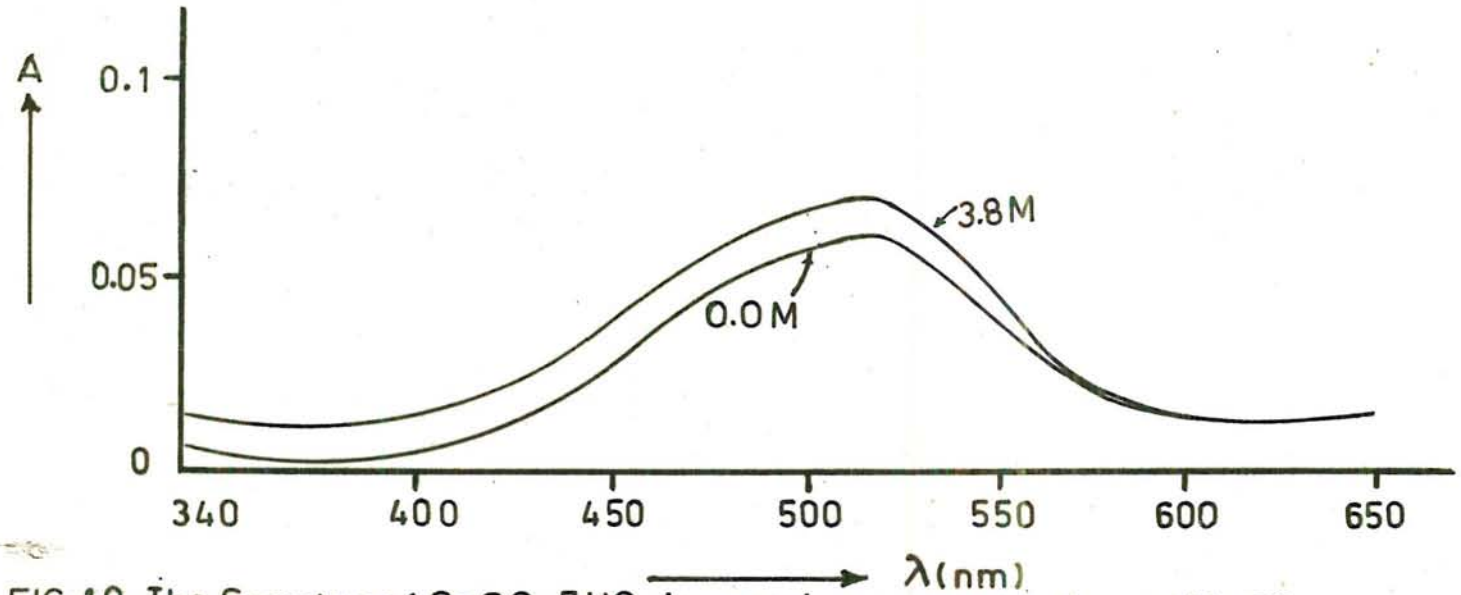


FIG:10. The Spectra of $CoSO_4 \cdot 7H_2O$ in varying concentrations of $MgSO_4$ at room temperature

TABLE NO. 11

System: $NiSO_4 \cdot 6H_2O$ — $MgSO_4$

Concentration of $NiSO_4 \cdot 6H_2O$ = 0.01M

Maximum concentration of $MgSO_4$ obtained = 3.8M

Temperature 298°K

S. No.	Concentration of SO_4 (Moles/litre)	Absorption maximum λ_{max} (nm)	Absorption maximum ϵ (litres/mole cm)	Molar conductance of $NiSO_4 \cdot 6H_2O$ ($Ohms^{-1}$)	Molar conductance of $MgSO_4$ ($Ohms^{-1}$)	Molar conductance of $NiSO_4 \cdot 6H_2O + MgSO_4$ ($Ohms^{-1}$)
1.	0.00	394 730 1160	6.2 2.0 3.5	120	—	120.0
2.	0.50	394 730 1160	6.2 2.0 3.5	120	33.0	36.5
3.	1.00	394 730 1160	6.2 2.0 3.5	120	27.2	30.1
4.	1.50	394 730 1160	6.2 2.0 3.5	120	22.5	26.0
5.	2.00	394 730 1160	6.2 2.0 3.5	120	18.2	21.9
6.	2.50	394 730 1160	6.2 2.0 3.5	120	15.7	18.2
7.	3.00	394 730 1160	6.2 2.0 3.5	120	13.0	15.7
8.	3.50	394 730 1160	6.2 2.0 3.5	120	11.7	12.5
9.	3.80	394 730 1160	6.2 2.0 3.5	120	9.34	9.42

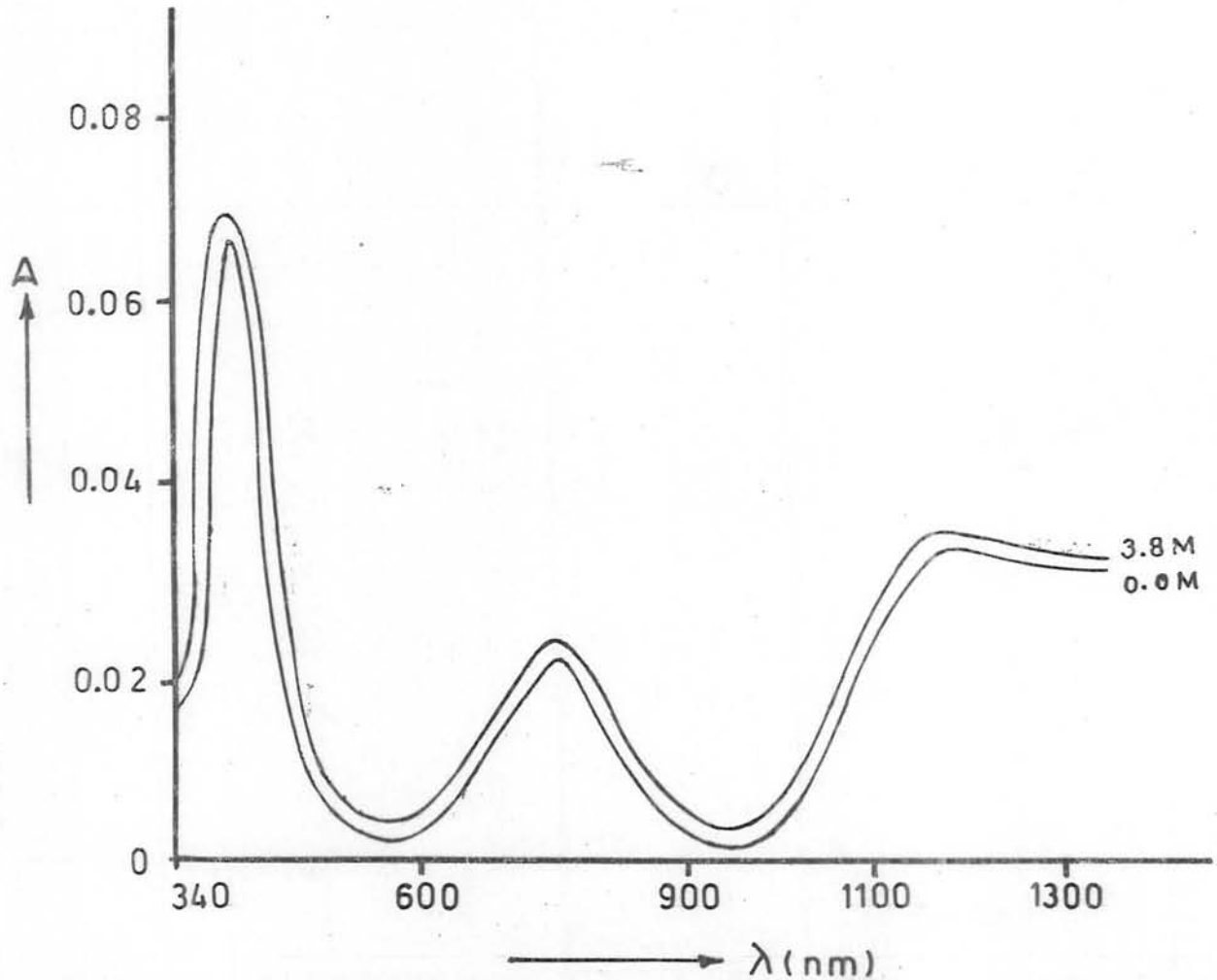


FIG:11. The Spectra of $NiSO_4 \cdot 6H_2O$ in varying concetrations of $MgSO_4$ at room temperatue

TABLE NO. 12

System: $CuSO_4 \cdot 5H_2O$ — $MgSO_4$

Concentration of $CuSO_4 \cdot 5H_2O$ = 0.01M

Maximum concentration of $MgSO_4$ obtained = 3.8M

Temperature 298^0K

S. No.	Concentration of SO_4 (Moles/litre)	Absorption maximum λ_{max} (nm)	Absorption maximum ϵ (litres/mole cm)	Molar conductance of $CuSO_4 \cdot 5H_2O$ ($Ohms^{-1}$)	Molar conductance of $MgSO_4$ ($Ohms^{-1}$)	Molar conductance of $CuSO_4 \cdot 5H_2O + MgSO_4$ ($Ohms^{-1}$)
1.	0.00	820	13.0	375.0	—	375.0
2.	0.50	820	13.01	375.0	33.0	35.0
3.	1.00	820	13.02	375.0	27.2	29.7
4.	1.50	820	13.03	375.0	22.5	24.9
4.	2.00	820	13.04	375.0	18.2	20.5
6.	2.50	820	13.05	375.0	15.7	17.4
7.	3.00	820	13.06	375.0	13.0	14.5
8.	3.50	820	13.08	375.0	11.7	12.2
9.	3.80	820	13.10	375.0	9.34	9.86

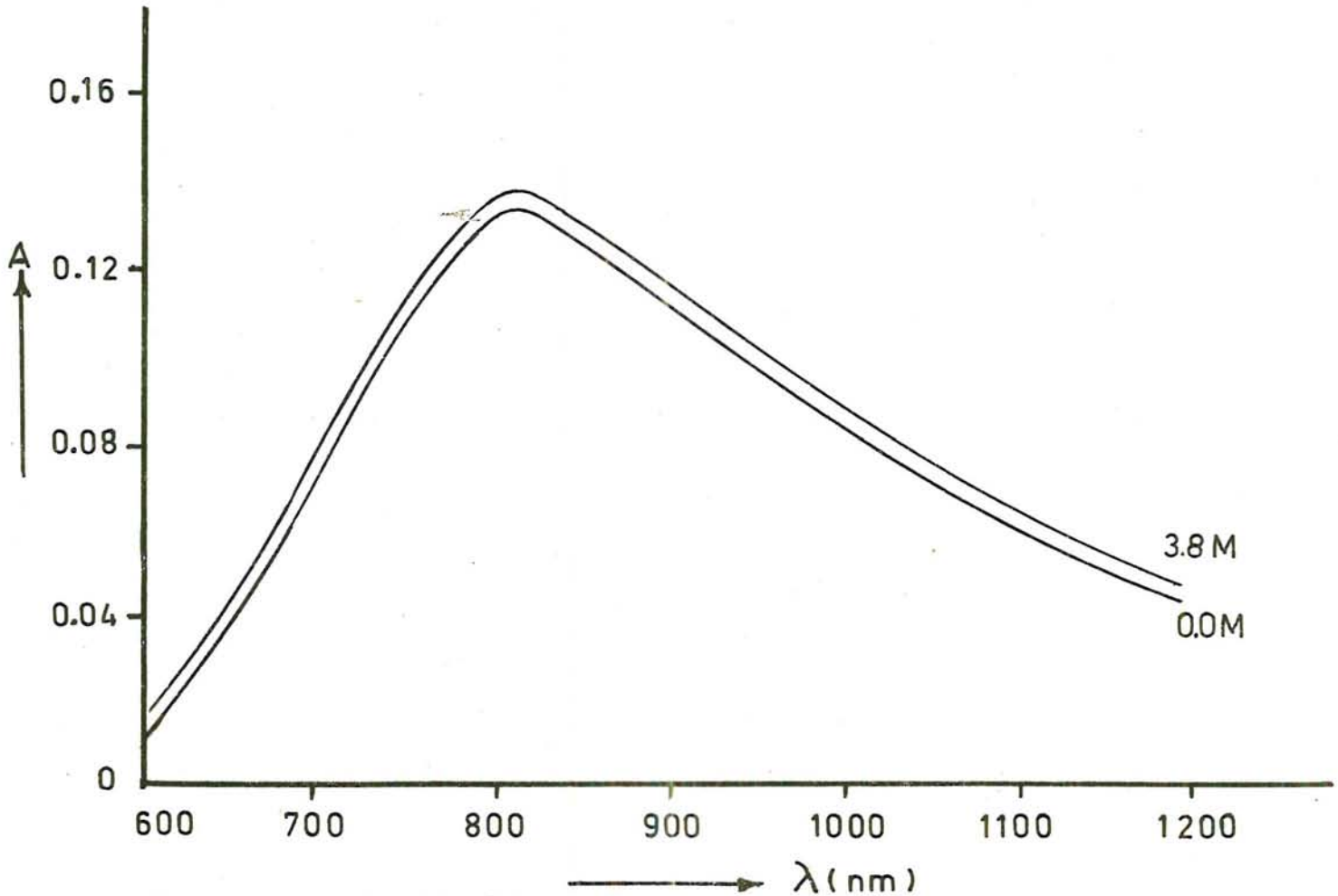


FIG:12. The Spectra of $CuSO_4 \cdot 5H_2O$ in varying concentrations of $MgSO_4$ at room temperature

TABLE NO. 13

System: $Cr_4(SO_4)_5(OH)_2$ — Na_2SO_3

Concentration of $Cr_4(SO_4)_5(OH)_2$ = 0.0045M

Maximum concentration of Na_2SO_3 obtained = 1M

Temperation 298°K

S. No.	Concentration of SO_3^{--} (Moles/litre)	Absorption maximum λ_{max} (nm)	Absorption maximum ϵ (litres/mole cm)	Molar conductance of $Cr_4(SO_4)_5(OH)_2$ ($Ohms^{-1}$)	Molar conductance of Na_2SO_3 ($Ohms^{-1}$)	Molar conductance of $Cr_4(SO_4)_5(OH)_2 + Na_2SO_3$ ($Ohms^{-1}$)
1.	0.00	420 590		51.1	—	51.1
2.	0.01	420 590		51.0	170.0	190
3.	0.1	420 590		51.0	119.0	120.0
4.	0.5	420 590		51.0	77.0	79.0
5.	1.00	420 590		51.0	58.0	58.5

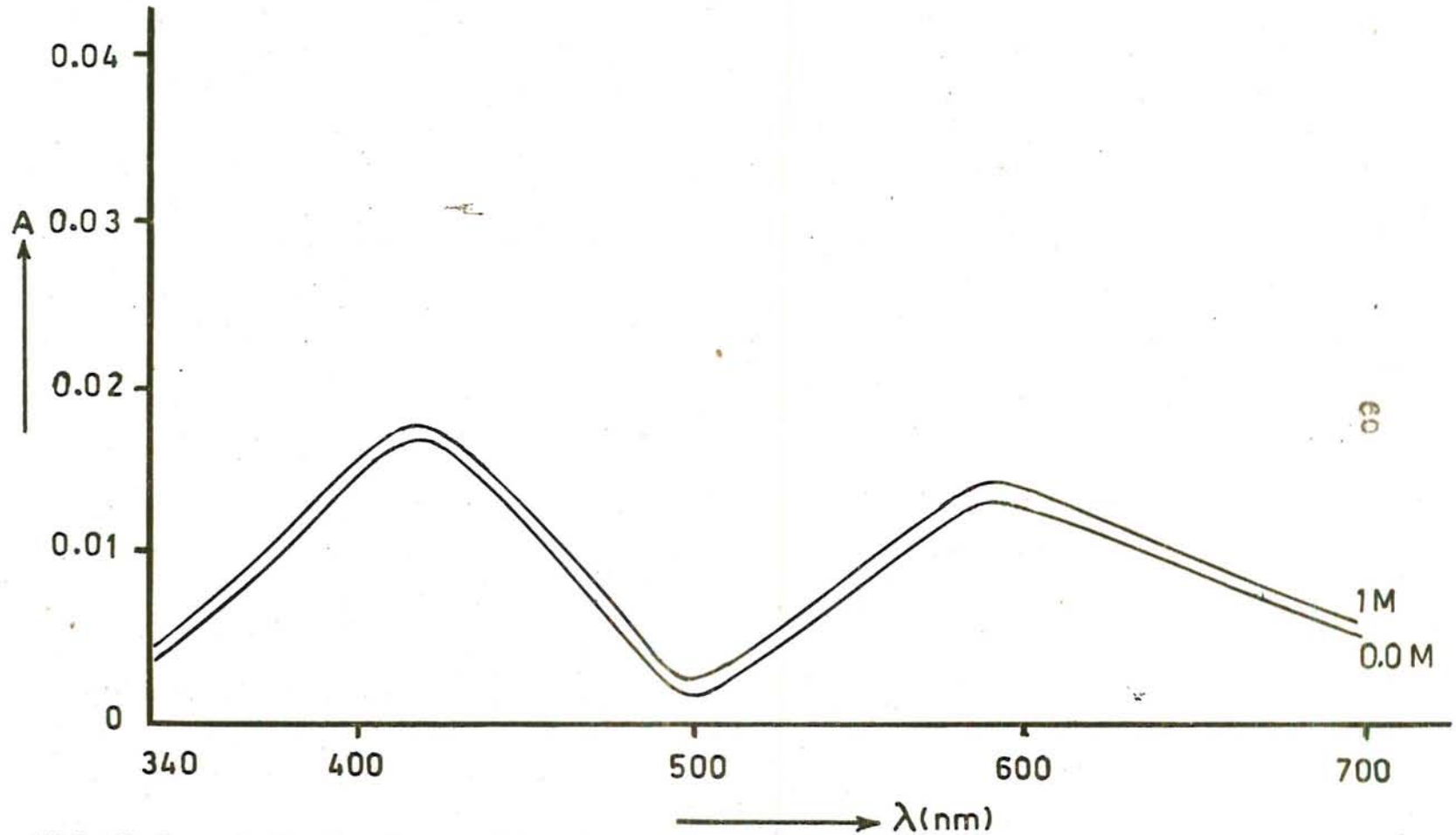


FIG:13. The Spectra of $Cr_4(SO_4)_5(OH)_2$ in varying concentrations of Na_2SO_3 at room temperature

TABLE NO. 14

System: $Cr_4(SO_4)_5(OH)_2$ — $MgSO_4$

Concentration of $Cr_4(SO_4)_5(OH)_2$ = 0.0045M

Maximum concentration of $MgSO_4$ obtained = 4M

Temperature 298°K

S. No.	Concentration of SO_4 (Moles/litre)	Absorption maximum λ_{max} (nm)	Absorption maximum ϵ (litres/mole cm)	Molar conductance of $Cr_4(SO_4)_5(OH)_2$ ($Ohms^{-1}$)	Molar conductance of $MgSO_4$ ($Ohms^{-1}$)	Molar conductance of $Cr_4(SO_4)_5(OH)_2 + MgSO_4$ ($Ohms^{-1}$)
1.	0.00	420 590	18.0 15	51.1	—	51.1
2.	0.01	420 590	18.0 15	51.1	130.0	150.0
3.	0.05	420 590	18.0 15	51.1	84.0	86.0
4.	0.15	420 590	18.0 15	51.1	61.3	62.67
5.	0.20	420 590	18.0 15	51.1	49.5	50.0
6.	0.30	420 590	18.0 15	51.1	45.3	47.0
7.	0.40	420 590	18.0 15	51.1	35.0	37.5
8.	0.50	420 590	18.0 15	51.1	33.0	33.6
9.	1.0	420 590	18.0 15	51.1	31.0	32.0
10.	2.0	420 590	18.05 15.05	51.1	21.0	22.0
11.	3.0	420 590	18.05 15.05	51.1	14.5	15.0
12.	3.8	420 590	18.1 15.05	51.1	9.3	9.47

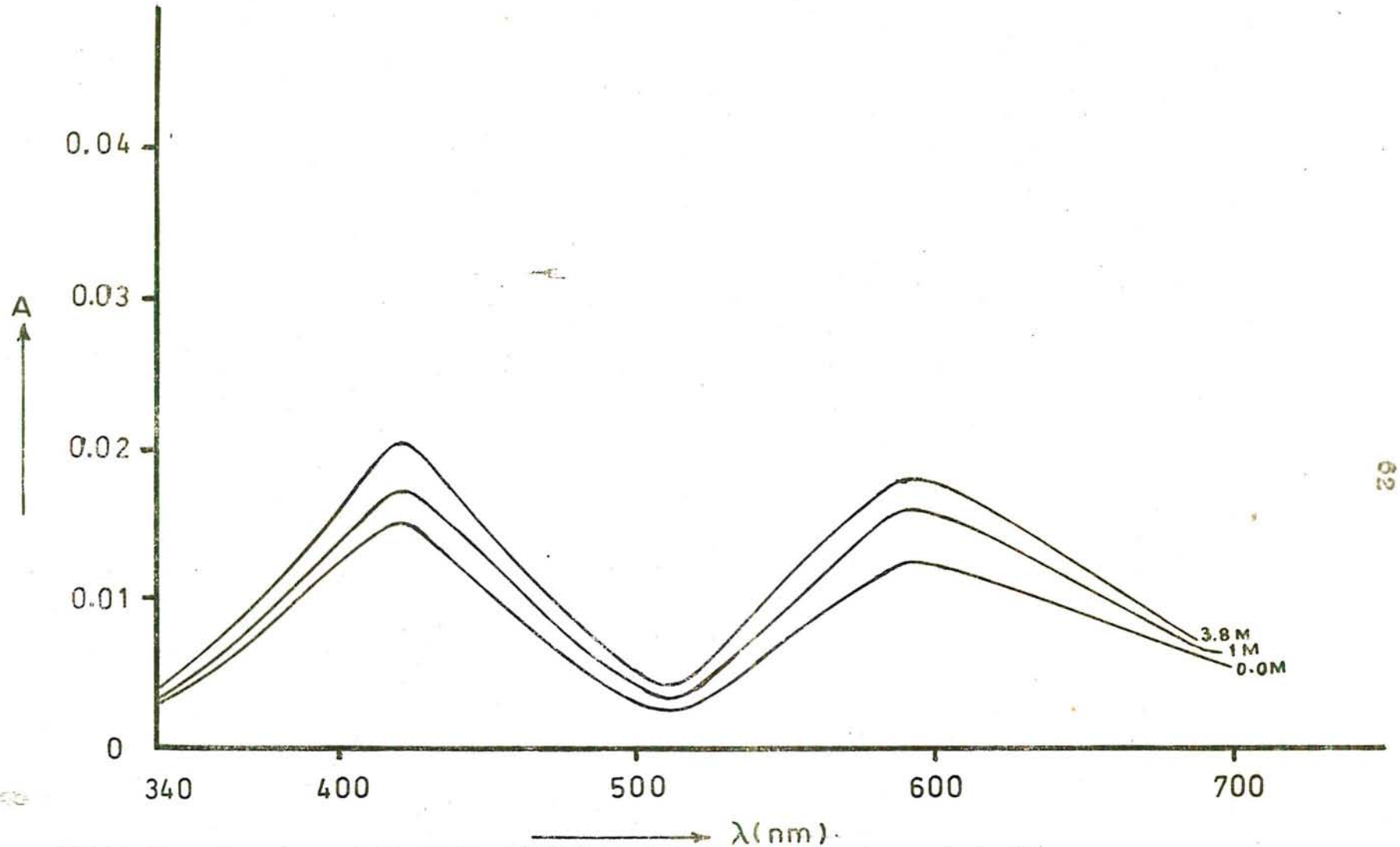


FIG:14. The Spectra of $Cr_4(SO_4)_5(OH)_5$ in varying concentrations of $MgSO_4$ at room temperature

RESULTS AND DISCUSSION

The present work deals with a study of the absorption spectra in the UV, VIS and NIR regions of a number of systems containing small amounts of transition metal salts and high concentrations of certain, anions in aqueous solution. The transition metal ions studied for the complex formation were cobalt (II), nickel (II), copper (II), chromium (III) and iron (III) salts while concentrated solutions of nitrite, nitrate, sulphate, sulphite and thiosulphate ions were present in the systems under investigation.

Usually saturated solutions of alkali or alkaline earth metal salts at room temperature were prepared in water and their concentrations were determined by literature methods. A number of solutions of varying concentrations of these anionic salts were obtained by appropriate dilutions of their saturated solutions. Then accurately weighed amounts of respective transition metal salts were dissolved in aliquote portions of each standard anion solution. The solutions were left in dark for several hours or preferably overnight so that equilibrium was achieved. The pure anionic solutions were used in the reference cells of the spectrophotometer while those containing transition metal ions and anionic salts were filled in the sample cell and their absorption spectra were recorded. Similarly the conductance of the two sets of solutions containing only anion salts and those containing both anionic solutions and transition metal ions were measured at room tempera-

ture. Finally the solutions were boiled for a short time (10-15 minutes) and then cooled to room temperature. Their absorption spectra and conductance were measured again, assuming that the substitution of anions for coordinated water was completed at higher temperatures, and the complexes with maximum number of anions coordinated with the metal ion was produced under such conditions.

Since the various salts have different solubilities in water, a limiting maximum concentration of anions was obtained for each solution. The concentrations of saturated solutions of various salts were in the range 3.0 - 12.0 moles/litre. The concentrations of the transition metal salts used were maintained in the range 0.0045 – 0.05 moles/litre.

The transition metal ions are in fact aquated complexes and their salts invariably crystallise with 4-6 moles of co-ordinated water. In aquous solutions of the transition metal ions, complex ions of the type $\left[M(H_2O)_{4-6}\right]^{n+}$ are present and the absorption spectra is essentially due to these ions. If large number of anions particles (i.e. high concentrations) are introduced in such a system, these anions will be able to displace water from the coordination sphere of the metal ions and a number of complex ion species such as $\left[M(L)\ (H_2O)_5\right]^{n-1}$, $\left[M(L)_2\ (H_2O)_4\right]^{n-2}$, $\left[M(L)_3\ (H_2O)_3\right]^{n-3}$ ....etc. will be produced depending upon the concentration of the anionic ligands. The relative amount of each specie present in the solution depends upon the stability of each complex ion. Further the substitution of anions for water in the coordination sphere of the metal ions is also dependent upon the magnitude of crystal

field splitting effects produced by the anionic ligands. Thus ligands such as NO_2^-, CN^- etc. which produce very strong crystal field splitting as compared to that produced by H_2O, should easily displace water in the coordination sphere in the metal ions where as weak ligands such as NO_3^- & SO_4^{--} should face difficulty in replacing coordinated water due to their small crystal field effects. Both of these factors are responsible for the negative effects observed in certain systems. In some cases perhaps the concentration of anions was not enough (because of their lower solubility in water) to expell even a single molecule of coordinated water from the coordination sphere of the transition metal ions.

The shift in the absorption maximum (λ_{max}) of the transition metal ion in solution was observed upon the addition of anions in the system. This shift in the absorption maximum continued with the increasing concentration of the anions. There was no further shift in the absorption maximum above certain concentration of the anions in the solution. Further addition of the anions only slightly affected the extinction coefficient (absorptivity) of the absorption band. In certain cases, the absorption maxima of the transition metal ion did not change upon the addition of anions in the system but the extinction coefficient was largely affected. These changes observed in the position of the absorption band or molar extinction coefficient could only be attributed to the formation of new complex ion species in solution.

When the conductance of the anionic solutions were compared with that of solutions of the same concentration contai-

ning anions and transition metal ions, a relative decrease in the number of ions in solution. If a new complex ion is formed in solution, the number of charge carrying species decrease as shown:

$$[M(H_2O)_6]^{n+} + 6NO_2^- \rightleftharpoons [M(NO_2)_6]^{(n-6)-} + H_2O$$

1 ion + 6 ions = 1 ion

Thus a decrease in conductance should be observed. The observed decrease in conductance of the anionic solutions in the presence of metal ions indicate the presence of a complex ion in solution.

The conductance behaviour of solutions is a complex phenomenon. The strong electrolytes are considered to be highly dissociated into ions at infinite dilutions whereas the ionization rapidly decreases with increasing concentrations. In concentrated solutions, the activity coefficients are very much away from unity. Thus in concentrated solutions it is necessary to obtain activities instead of concentrations of the electrolytes. Moreover, in very much concentrated solutions, ion pair formation becomes more and more prominent.

This behaviour is shown by strong electrolytes like $NaNO_2$ or Na_2SO_4. In these studies concentrations were used instead of activities and decrease in conductance was observed at higher concentrations of salts. Further when small amounts of transition metal salts such as $Co(NO_3)_2 . 6H_2O$ or $Ni(NO_3)_2 . 6H_2O$ (0.01M) were added to the concentrated solutions of anions, the conductance does not change appreciably. This also shows that apart from complex formation, ion pairs are

also produced. Thus conductance measurements could only be used as supporting evidence for the complex formation in these systems.

The systems investigated by us can be divided into three groups.

1. Systems which show the formation of anionic complexes.
2. Systems which show no evidence of the complex formation.
3. Systems where certain interaction take place between the anionic solutions and the metal ions.

These systems are discussed in the following paragraphs:

1. Systems giving evidence of complex formation:

In these systems the addition of anions to metal complexes show a marked shift in the absorption band maximum when the reaction is complete. The complex formation is evident by the fact that no more change in absorption maximum occurs. Similarly it is observed that the conductance of the resulting solution is less than the conductance of the anions added, which indicates the presence of less than the expected number of ions in the solution.

The following systems show a change in the absorption spectra of transition metal ions in the presence of large amounts of anions.

1. $Co(NO_3)_2 \cdot 6H_2O$ — $NaNO_2$
2. $CoSO_4 \cdot 7H_2O$ — Na_2SO_3
3. $CoSO_4 \cdot 7H_2O$ — $Na_2S_2O_3$

4. $Ni(NO_3)_2 \cdot 6H_2O$ — $NaNO_2$
5. $NiSO_4 \cdot 6H_2O$ — $Na_2S_2O_3$
6. $Cr(NO_3)_3 \cdot 9H_2O$ — $NaNO_2$

It is evident that nitrite ion interacts with cobalt (II), nickel (II) and chromium (III) ions where as thiosulphate forms complexes with cobalt (II) and nickel (II) ions. Sulphite ions interact with only cobalt (II) ions and indicate the formation of a complex in solution. These systems are discussed below.

i. Interaction of nitrite ions with metal salts:

The concentration of a saturated solution of nitrite ions was found to be slightly less than 8 moles/litre. Therefore, the complex formation was studied in the regularly varying concentrations of nitrite ions upto maximum of 7.5M of this ion. The change in spectra of transition metal ions occurr even at very low concentrations of nitrite ion. In the lower concentrations of nitrite ion, there is a large shift in absorption band of cobalt (II) (i.e. 510 to 389 nm) which then shifts to higher wavelength region with increasing concentrations of anions and attain equilibrium position at 408 nm. Ultimately when the solution is boiled and its spectrum is taken again, the band position is again shifted to 387 nm. Both the absorption bands observed in aquous $Ni(NO_3)_2 6H_2O$ are shifted to lower wavelength regions in the presence of nitrite ions. The bands regularly shift to the lower wavelength regions and remain constant at 608 and 990 nm. at a 2.0M concentration of anions. Further a slight change in the band position of this system were observed after boiling the

solution.

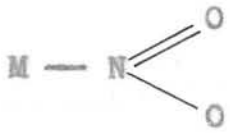
The absorption band at 576 nm. of $[Cr(H_2O)_6](NO_3)_3$ first slightly shifts to higher wavelength regions with increasing concentrations of anions and then towards lower wavelengths upon further increase in concentration (above 2.0M) of the anions. Finally there is very little change in the band position (centered at 556 nm.) when the concentration of the anions is more than 5.0M. In this case the absorption band is shifted to its original position i.e. 576 nm. which is due to $[Cr(H_2O)_6]^{3+}$ ion in solution, upon boiling the mixture.

When the molar conductances of the mixtures, containing transition metal salt and nitrite ions, are compared with that of the pure nitrite solution of the same concentrations, first a slight increase and then a regular decrease in conductance is observed. The conductances of boiled solutions are slightly higher than the solutions containing only anions.

These observations indicated that at lower concentrations of anions in the systems, coordinated water, is partially substituted by anions in the coordination sphere of metal ions. As the concentration of anionic ligands is increased in the solution, more and more anions substitute for water molecules. The metal ions i.e. cobalt (II), chromium (III) and nickel (II) all have a maximum coordination number of six and this is maintained during these reactions at room temperature.

The nitrite ion is a strong ligand and produces a very large amount of crystal field splitting. In the spectrochemical series, nitrite ion is at a very high order as compared to

any other ion or water molecule. So it is understandable that nitrite can easily replace water in the solution of a complex ion. There are two nitrate ions also present in the system, but these do not compete with the nitrite group for complex formation. This is due to the poor coordination power of nitrate ion, which is present at a very low order in the spectrochemical series. Further nitrite ion usually acts as a monodentate ligand but is capable of coordinating either through an oxygen or a nitrogen atom as shown:



I

II

A number of metals prefer to coordinate with this ion through nitrogen atom while other prefer to coordinate through oxygen atom. Cobalt (III) is a unique ion which forms complexes with this ion having bonding through either of the two donor atoms, thus forming two isomers. An example of this type of isomeric complexes is furnished by the synthesis of $[Co(NH_3)_5\ ONO]\ Cl_2$ (orange) and $[Co(NH_3)_5\ NO_2]Cl_2$ (yellow.) The later compound is more stable. In solid form the former is slowly converted to the later. On the other hand chromium prefers to coordinate through oxygen donor atoms. If nitrogen containing ligands are present in the systems containing chromium ion in aqueous solution, only hydrated chromic oxide precipitates out. The nickel (II) ions form stable complexes with nitrogen containing ligands but can also coordiante with oxygen donors as well.

In the light of these considerations it is reasonable to

assume that in $Co(NO_3)_2\ 6H_2O - \bar{N}O_2$ system, the nitrite ligand, is coordinated to the metal ion through nitrogen atoms while in chromium (III) system the metal ligand bonds are produced through oxygen atoms. In $Ni(NO_3)_2\ 6H_2O - \bar{N}O_2$ system the metal is also bonded to nitrogen atom of the anion. The absorption spectra of these ions provide proof for these considerations. The presence of absorption band at 408 nm. indicate that the complex should have a yellow color, which is of course true. All of the coordination compounds of bivalent and trivalent cobalt ions with nitrogen donor ligands are yellow in color an have absorption maximum in this region of the spectrum. These may be written as $[CoN_6]^{n+}$ where N denotes for the coordinating atom of the ligand. A few examples are cited to substantiat this fact:

$[Co(phen)_3]^{2+}$	yellow	$[Co(en)_3]^{3+}$	yellow
$[Co(dipy)_3]^{2+}$	"	$[Co(NH_3)_6]^{3+}$	"
$[Co(en)_3]^{2+}$	"	$[Co(NH_3)_5\ NO_2]^{2+}$	Brown
$[Co(NH_3)_6]^{2+}$	"	$[Co(en)_2(NO_2)_2]^{+}$	"

On the other hand the coordination compounds of cobalt (II) or cobalt (III) containing oxygen as donor atom are green or pink in color and those containing both types of ligands have colors ranging from pruple to red. A few examples to illustrate these phenomenon are:

$[Co(CO_3)_3]^{3-}$	green	$[Co(gly)_3]$	red
$[Co(OX)_3]^{3-}$	"	$[Co(EDTA)_3]^{-}$	purple

$[Co(MLT)_3]^{3-}$ green $[Co(NH_3)_4(H_2O)_2]^{3+}$ red

$[Co(acac)_3]^{3-}$ " $[Co(en)_2(OX)]^{+}$ "

Similar variation in colors are observed for complexes of chromium (III) and nickel (III) due to coordination of different atoms to the metal ions. The chromium (III) complexes of the type $[CrN_6]^{n\pm}$ are always yellow whereas $[CrO_6]^{n\pm}$ type complexes have purplesh green color and mixed ligands form compounds having color in between those two extremes. Similarly octahedral complexes of nickel (II) containing nitrogen ligands such as $[Ni(phen)_3]^{2+}$, $[Ni(dipy)]^{2+}$ are red in color while others containing metal oxygen bonding such as $[Ni(H_2O)_6]^{2+}$ are green. Thus simply by comparing the colors produced in these systems and their absorption spectra with other complexes of known composition, we can decide about the nature of metal-ligand bonding.

As stated earlier the number of absorption bands and their extinction coefficients are affected by the symmetry and geometry of the complex ions. In all of these systems, new bands were not developed. Only the absorption bands present in the spectrum of aquous solutions of metal ions were shifted to larger or shorter wavelength regions. This shows that the metal ions retained their earlier geometry even in very concentrated solutions of anions. These three metal ions are known to have an octahedral geometry in aquo complexes which is retained at all concentrations of nitrite ions. At lower concentrations of nitrite ions, probably mixed complexes of the type $[M(NO_2)_x(H_2O)_{6-x}]$ where x = 1-6, are formed due to

the very high concentration (55.5M) of solvent present in the solution. Above certain limits of concentrations of anions, sufficient number of anionic species are present to displace all of the coordinated water molecules and so the predominent complex ions $[M(NO_2)_6]^{x-}$ are the only species present in the system. The chromium (III) nitrite system has probably produced a mixed complex of the type $[Cr(NO_2)_4(H_2O)_2]^{1-}$.

The extinction coefficients are in the order cobalt (II) chromium (III) nickel (II) in the systems. The extinction coefficient in cobalt (II) system seems to be higher than that expected for an octahedral complex. The higher extinction coefficient in the cobalt (II) — nitrite ion system can be explained if we consider the fact that nitrite ions have a strong absorption band centered at 355 nm. When a complex of this ion is formed with cobalt (II) ion, the band present at 408 nm. has stolen some energy from this strong UV band. This phenomenon of energy stealing is quite common in coordination compounds. The extinction coefficients associated with the absorption bands of other two complex ions are thos expected for the octahedral complexes.

The mechanism of the reactions canbe explained by successive replacement of coordinated water molecules by nitrite ions with the increasing concentration of ligands as:

$$[M(H_2O)_6]^{n\pm} \rightleftharpoons [M(OH_2)_5]^{n\pm} \overset{L}{\rightleftharpoons} [M(OH_2)_5L]^{(n-1)\pm}$$

$$[M(H_2O)_5L]^{(n-1)\pm} \rightleftharpoons [M(OH_2)_4L]^{(n-1)\pm} \overset{L}{\rightleftharpoons} [M(OH_2)_4L_2]^{n\pm2}$$

$$[M(H_2O)_xL_{6-x}]^{n\pm} \rightleftharpoons [M(H_2O)_{x-1}L_{6-x}] \overset{L}{\rightleftharpoons} [M(H_2O)_{x-1}L_{6-(x-1)}]$$

In this sequence the reaction with $[Cr(H_2O)_6]^{3+}$ ion stops at a step like $[Cr(H_2O)_2(NO_2)_4]^-$ due to the fact that $Cr - OH_2$ bond is quite strong and the concentration of NO_2 ions compared to solvent is not enough to displace all the coordinated water molecules.

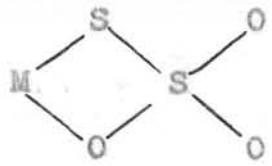
ii. Interaction of $S_2O_3^{2-}$ ions with metal ions:

The maximum concentration of a saturated solution of $Na_2S_2O_3$ was obtained as 3.0 moles/litre. This is due to the higher molecular weight and lower solubility of the compound. Inspite of lower solubility of this ion as compared to nitrite ion, the complexes were formed with cobalt (II) and nickel (II) salts. This is also due to the strong crystal field splitting effects of this ion. The maximum ratio of concentration of ligand to transition metal ion was achieved as 300 : 1.

A dilute aqueous solution of cobalt (II) sulphate has an absorption band at 515 nm. which is progressively shifted to 657 nm. by increasing the concentration of thiosulphate ion in the system. The extinction coefficient is also increased and attains a value of 130 litre mole^{-1} cm.$^{-1}$ in the highest concentration of the anion solution. Similarly the visible region band centered at 730 nm. of $NiSO_4.6H_2O$ solution in shifted to 690 nm. at highest concentration of thiosulphate ion. The other band at 390 nm. is very little affected upon coordination. The extinction coefficients of both of the bands (centered at 515 and 730 nm.) are also very much affected. The intensity of color of the resultant solutions is increased and shifted to the red side of the spectrum.

The conductance of the mixed solutions are progressively decreased with the increase in the concentration of anionic ligands in the solution. This also shows the decrease in number of ions due to the complex formation in the solution.

Thiosulphate ion usually acts as a bidentate ligand and studies have shown that the metal to ligand bonds are formed through an oxygen and a sulpher atom only as shown:



III

Thus four membered chelate rings are formed upon the coordination of thiosulphate ion with metals. These chelates are less stable as compared to the commonly observed five or six membered chelates. Further oxygen and sulpher belong to the same group of the periodic table and have similar properties. Sulpher atom is less electronegative than oxygen and so prefers to coordinate with class B metal atoms.

Again in these systems the number of absorption bands is not increased upon coordination which indicates the retention of octahedral environment around the metal ions. For octahedral cobalt (II) and nickel (II) metal complexes in solutions of thiosulphate ions, the maximum stoichometry of $[M(S_2O_3)_3]^{4-}$ should be attained. Of course complex ions with mixed ligands such as $[M(S_2O_3)(H_2O)_4]$ and $[M(S_2O_3)_2(H_2O)_2]^{2-}$ are also possible. There is very little possibility of formation of $[M(S_2O_3)(H_2O)_4]$ complex since it carries no charge and should be insoluble in water. The $[M(S_2O_3)_2(H_2O)_2]^{2-}$ ion should have different symmetry due to which the splitting or

broadening of absorption bands would occur. Of course no splitting of absorption bands is observed at any concentration of thiosulphate ions. Probably a little broadening of these absorption bands is due to these lower symmetry species present in very small concentration in solution.

The conductance of these systems also indicate the formation of anionic complexes which decreases the number of ions in solution.

iii. Interaction of Sulphite ions with cobalt (II) sulphate:

The maximum concentration of sulphite ions in solutions is obtained as a 0.1 moles/litre. This concentration is probably not enough to displace the complex ion equilibrium in the desired direction, although sulphite ion produces very strong crystal field effects and so should be considered as a strong ligand. The complex formation was evidenced in the presence of cobalt (II) sulphate when the ratio of the ligand to metal ion concentration was maintained at 10 : 1. In this case the visible absorption band present at 515 nm. in the spectra of cobalt (II) sulphate remained unchanged upon complex formation. A new band was developed at 280 nm. in the UV region upon the addition of sulphite ions in the system. The extinction coefficients of the two bands were increased to a large extent. Further a decrease in the molar conductance of the mixed solutions was also observed.

These observations provide strong evidence for the complex formation. The sulphite ions act as monodentate ligands occupying only one coordination position, either through oxygen

or through sulpher. The recent studies centered on the complexing of this ion show that sulphite ion is usually bonded to metal atoms through its sulpher atom. In the present studies we can easily assume a bond formation through sulpher atom. Probably the complete displacement of the coordinated water does not occur because of the relatively lower concentration ratio between water and sulphite ions. The predominent species present in the solution may be assumed as $[Co(SO_3)_2\ (H_2O)_4]^{2-}$ ion, which could give rise to this spectra. The formation of precipitation after about 12 hours may be attributed to the formation of an uncharged $[Co(SO_3)\ (H_2O)_5]$ species which could also be produced by heating the solution. In this case also $\overset{--}{SO_4}$ ions being lower in the spectrochemical series do not compete with $\overset{--}{SO_3}$ ions for complex formation.

2. <u>Systems that give no evidence of complex formation</u>:

The following systems do not show any indication of complex formation.

1. $Co(NO_3)_2 \cdot 6H_2O$ — $\overset{-}{NO_3}$ ions (as KNO_3 and $Ca(NO_3)_2\ 4H_2O$)
2. $Ni(NO_3)_2 \cdot 6H_2O$ — $\overset{-}{NO_3}$ ions (" " ")
3. $Cu(NO_3)_2 \cdot 3H_2O$ — $Ca(NO_3)_2 \cdot 4H_2O$
4. $CoSO_4 \cdot 7H_2O$ — $MgSO_4$
5. $NiSO_4 \cdot 6H_2O$ — $MgSO_4$
6. $CuSO_4 \cdot 5H_2O$ — $MgSO_4$
7. $Cr_4(SO_4)_5(OH)_2$ — $MgSO_4$
8. $Cr_4(SO_4)_5(OH)_2$ — Na_2SO_3

All the above systems do not show any evidence of complex formation as their spectra remains the same even after addition of maximum concentration of anions possible under experimental conditions. The extinction coefficients of the absorption bands also remained unchanged. It is further supported by the fact that the conductance of the resulting solutions after the addition of anions is always greater than the conductance of the solutions containing only anions, showing no decrease in the number of ions. In these systems the complex formation of cobalt (II), nickel (II), chromium (III), and copper (II) with sulphate, nitrate and sulphite ions were studied.

In most of these studies solutions containing high concentrations of anions such as NO_3^-, SO_4^{--}, or SO_3^{--} could not be achieved mainly due to limited solubilities of their alkali metal salts. For the nitrate ion solution, calcium nitrate was used which could provide 12M nitrate ion solution but no complex formation was observed in these systems. The effect of low solubilities badly affected a very promising system i.e. $Cr_4(SO_4)_5(OH)_2$ — SO_3^{--} ion. In this case the saturated solution was found to be only 1 mole/litre, which was not sufficient to shift the equilibrium of complex ion species to the desired direction.

The nitrate and sulphate ions are very poor coordinating agents. These two ions are present well below water in the spectrochemical series. This means that aquo complexes of these metal ions are more stable than nitrato or sulphato complexes. As a result the anionic complexes of these ligands

by displacing water in the coordination sphere of metals such as cobalt (II), nickel (II), chromium (III) and copper (II) are not formed. This is evident from the absorption spectra and conductance measurements of these systems.

3. Systems showing an Interaction between the added anions and Transition Metal ions:

In the following systems the addition of transition metal ion solutions on different concentrations of anions lead to some sort of reaction. These reactions occured at room temperature. Due to the interaction between the anions and metal ions, measurement of absorption spectra and conductance could not be done on the following systems:

1. $Cu(NO_3)_2 \cdot 3H_2O$ — $NaNO_2$
2. $Fe(NO_3)_3 \cdot 9H_2O$ — $NaNO_2$
3. $CuSO_4 \cdot 5H_2O$ — Na_2SO_3
4. $CuSO_4 \cdot 5H_2O$ — $Na_2S_2O_3$
5. $Cr_4(SO_4)_5(OH)_2$ — $Na_2S_2O_3$

In most of these systems oxidation reduction reactions have occured and thus changed the whole systems, In two cases where thiosulphate ions were used for complexation, probably decomposition of thiosulphate occured. We shall discuss these systems individually.

The solution containing blue hydrated copper (II) ions were decolorized upon the addition of either nitrite or sulphite

ions in larger concentrations. A green precipitate was first formed in $CuSO_4$ solution upon the addition of sulphite ions which was decolorized and dissolved upon further increase in concentration of anions in the system.

It is a well known fact that nitrite and sulphite ions are reducing agents. Similarly copper (II) can easily be reduced to copper (I) which is colorless due to completely filled 3d orbitals. Thus the decolorization of the blue color of copper (II) ion in the presence of nitrite or sulphite is mainly a redox process. The green precipitate first appeared at lower concentration of sulphite ions in copper (II) solution in probably due to the formation of a very instable complex species $Cu(SO_3)_2^{2-}$ which immediately dissociates to produce copper (I) ions in the solution. The reduction of copper (II) to copper (I) by means of H_2SO_3 or HSO_3^- ion and then precipitation as $Cu_2(SCN)_2$ is a well established method for the estimation of copper in solution.

When large concentrations of nitrite ions were added to yellow ferric nitrate, a vigorous reaction occured with the evolution of brown fumes. The solution became reddish probably due to nitrous fumes.

The violent reaction is mainly due to the reduction of Fe (III) to Fe (II) and then decomposition of nitrite and nitrate ions is solution. The reaction may be represented as:

$$Fe^{3+} + NO_3^- + 7NO_2^- \longrightarrow Fe^{2+} + NO_3^- + NO + N_2O$$

$$NO + O_2 \longrightarrow NO_2\uparrow$$

It is also well known that ferric can easily be reduced to ferrous ions by means of a number of reducing agents such as cobalt (III) acetate, stannous chloride.

When thiosulphate was added to a solution of copper (II) ions, first a black precipitate was formed in about half an hour. When the mixture was left for 12 hours, the black precipitate was changed to white precipitate. This is probably due to firstly the formation of an unstable CuS_2O_3 compound which decomposes with time to produce black CuS (cupric sulphide) and SO_3^{--} ions in solution. The sulphite ions produced white precipitate of copper tetrathionate. The assumed sequence of reactions is shown below:

$$Cu^{2+} + S_2O_3^{--} \rightarrow CuS_2O_3 \text{ (unstable)}$$

$$CuS_2O_3 \rightarrow CuS + SO_3^{--}$$

$$CuS + SO_3^{--} + H_2O \rightarrow Cu^{+} + SO_4^{--} + H^{+}$$

$$Cu^{+} + 2S_2O_3^{--} + H_2O \rightarrow CuS_4O_6 \text{ (white)} + OH^{-}$$

$$H^{+} + OH^{-} \rightarrow H_2O$$

A colloidal dirty white precipitate was formed upon the addition of thiosulphate ion to a solution of basic chloric sulphate. The colloidal particles were found to be that of sulpher. In this system thiosulphate decomposed to produce colloidal sulpher and sulphite ions. These sulphite ions produced unstable chromium (II) ion by reduction of chromium (III). The unstable chromium (II) is again converted to chromium (III) with time. This is again a combined decumposition and oxida-

tion reduction reaction in nature.

It is revealed from these studies that anionic complexes are formed at room temperature by increasing the concentration of particular type of anions in aquous solutions. The conditions necessary for the formaion of coordination compounds can be summerized as:

1. The entering anionic ligand should produce stronger crystal field effects as compared to the aquo complexes i.e. the entering ligand should be higher in order than water in the spectrochemical series.

2. The anionic ligand should be stable and should not decompose in solution.

3. The entering ligand should neither oxidize nor reduce the metal ion.

4. The ligand should not interact with the transition metal ions thus producing any other intermediate compounds.

Examples of all these conditions have been furnished in the preceding discussion.

The absorption spectra of these systems have successfully provided information about the geometry of the complexes formed.

The conductance measurements, although not of very much help, have also provided some evidence for the formation of complexes.

SUMMARY

The formation of anionic complexes by the interaction of transition metal ions with high concentrations of anionic ligands at room temperature are studied. The transition metal ions studied for complex formation include chromium (III), cobalt (II), nickel (II), iron (III) and copper (II) ions where as nitrite, nitrate, sulphite, sulphate and thiosulphate are the anions used for this purpose.

The formation of complexes was studied by means of their absorption spectra and conductance measurements. The nitrite ions form stable complex anions with cobalt (II), nickel (II) and chromium (III) nitrates. Similarly thiosulphate ion forms complexes with cobalt (II) and nickel (II) whereas sulphite ions form coordination compounds only with nickel (II) ions. Nitrates and sulphates do not form complexes with any of these metal ions.

Nitrite ions interact and reduce a number of metal ions such as copper (II), and iron (III) to their lower oxidation state species. Similarly copper (II) is also reduced by sulphite ions under these conditions. Thiosulphate ion is decomposed to give sulpher and sulphite ions and then reduce the metal ions such as copper (II) and chromium (III) present in the solution.

In most of these studies, the absorption bands of aquous transition metal ions are shifted towards higher or lower

wavelength regions. Intensity of the absorption bands is also increased in these systems. On the basis of these studies, the metal ions are assumed to retain octahedral environment of ligands around them as $[ML_6]^{6-n}$ where M is for metals like cobalt (II) and nickel (II) and L is for anions like NO_2^- and $SO_3^=$. In certain cases mixed complexes of the type $[Ni(SO_3)_2\ (H_2O)_2]^{2-}$ are also responsible for changes observed in absorption spectra.

The conductance measurements have indicated the formation of complex ions thus decreasing the number of ions in solution. The conductometric evidence is just a supporting evidence to the spectrophotometric studies.

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