The Interaction of Nickel (II) ion with Ethylene Diamine (en) Chelate using Ethaline (ionic liquid) as Solvent

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ABSTRACT

For this experiment, this is the first time using 1 choline chloride (ChCl) : 2 ethylene glycol (EG)based liquid (ethaline) to study the interaction between Ni (II) with ethylene diamine. Two of the optical methods for analyzing spectrophotometric measurements have been utilized for determination of, the stoichiometry and whenever possible, the stability constants of the chelates formed. Job`s method was necessary to determine whether, the metal ionion and the ligand ethylene diamine form one or more than one chelate, when more than one chelate formed, the results obtained depend on the maximum wavelength and for meaningful conclusions the wavelengths were carefully chosen. The empirical formulae of the chelates were further substantiated by the molar ratio method. The effect of time and temperature on the formation and stability of these chelates in solution is also investigated. The stability constants, K_1, $K_2$and K_3 for the nickel (II) chelates were calculated by both optical methods, though reliable, and are comparable to literature values.

Keywords: Ni (II), en, ionic liquid, deep eutectic solvent (DES), Job`s method, molar ratio, stability constant and UV spectra

INTRODUCTION

The transition elements are classically defined as those which, the elements have been partially filled d- or f- subshells. However, a broader definition the elements which have been partially filled d- or -subshells in any of their commonly occurring oxidation states, includes the coinage metal ions[1], Cu, Ag and Au as transition elements. Cu(II) has a 3d configuration, Ag, (II) ion a 4d configuration and Au (III) ion a 5d configuration. From a purely chemical point of view it is also appropriate to consider these elements as transition elements, since their chemical behavior is, on the whole quite similar to that of other transition elements. Thus, with the above broad definition in mind, one finds that the majority of all known elements are transition elements.
The transition elements display all the properties common to metal ions. They have relatively low ionization potentials, they are good conductors of heat and electricity and they are lustrous, malleable and ductile too. The fact that they have small sizes and high electro positivity renders them a high charge to size ratio; a fact responsible for their ability to form a large group of binary compounds, commonly known as coordination compounds, with a large variety of ligands. In this respect, transition elements display a marked ability to react with a large variety of ligands above and beyond that expected on the basis of normal valence rules.

Werner's[2] recognition of the existence of two types of valence, primary and secondary, was a major breakthrough in the history of coordination compounds. Recently, however progress in the chemistry of transition elements has occurred across two broad fronts, classical coordination chemistry and organometallicchemistry, which have been tended by two separate schools of chemists.There are no universally valid principles on the basis of which the relative values of formation constants of complexes of different metal ion ions with the same ligand, or of the same metal ion ions with different ligands can be predicted.Ligands supply the electron density for the covalent bond formation. The strength of this link partly depends on the nature of the donor atom directly attached to the metal ion atom, and partly on the nature of the complexing agent.The nature of the complexing agent varies considerably from inorganic to organic species. The organic species usually contain one or more non-metal ionlic elements of group IV, V or VI which are electron donating atoms. The potential part of an organic species differs greatly; some are aromatic as catechol and some are basic such as amines and diamines aliphatic or aromatic.

The nature of the donor atom has a distinct influence on the strength of the ligand and eventually on the stability of the metal ion complex. In an extended form of the spectrochemical series it is also seen that the position of the ligand depends largely on the donor atom in the order:

$$\text{Halogen} \approx S < O < N < P$$

Thus, the nitrate which donates through 0 is a weaker ligand than the nitrite which donates through N. An even more striking example is in the thiocyanate, SCN, group with a weak ligand field when coordinated through S and a much stronger field when coordinated through N. These features govern the effect of ligands by their contribution to the crystal field stabilization energy, but this term may only be a minor contribution to the overall stabilization and it is also therefore necessary to not to equate strong crystal field unthinkingly with metal ion complex stability[3].

Within a particular transitional group the tendency of complex formation increases, in a way, with the availability of d-electrons for hybridization. Data available on the correlation of stability of transition metal ion complexes indicated a considerable increase along the series Mn, Fe, Co, Ni, Cu, and that in every case the stability drops off with Zn. It seems, therefore, that the values of the stability constants increase in a regular manner with some property related to the atomic number, and that the regular variation of this property reaches a discontinuity in the case of In. It is important to note that there is a regular increase in the number of 3d-electrons and that in all cases excepting Zn^{2+} the d-orbitals can take part in homopolar bond formation. Thus, it seems that covalent bond formation involving d-orbitals is of primary importance among the factors affecting the stability of these chelates. The above order of stability of metal ionion chelates is part of a more extensive order[4], known as the Irving-Williams order. It was also particularly noted that the Zn (II) chelates are much less stable then Cu (II) chelates[4]. It is also interesting to note that, in general agreement with the above the relative stabilities of glycine chelates of the transition metal ions as determined by Ley[5], from conductance measurements, fall in the order:

$$\text{Cu} > \text{Ni} > \text{Co, Zn} > \text{Cd}.$$

Atomic structure is found to affect the tendency of the metal ionion towards complex formation. Metal ion ions with an inert gas structure show a lower coordination tendency than those with pseudo-inert gas structure.

Ionic liquids

High temperature molten salts have long been used for metal ion extraction and metal ions such as Li, Na, Ti and Al have been electrowin for molten salts[6,78]the main limitation with high temperature molten salts is clearly the operation temperature which makes operation difficult and limits the range of substrates that can be used. In an endeavour to reduce the melting temperature of salts numerous studies focussed on Li^+/ K^+/ $AlCl_3$ eutectics which have freezing points close to 100^oC.[9] The use of quaternary ammonium salts particularly pyridinium and imidazolium salts has pushed the freezing point down to ambient conditions. The term "ionic liquids" has been used to distinguish between high temperature and low temperature systems.

Ionic Liquids have clearly been reported to be green solvents most notably for their low vapour pressure compared to molecular alternatives. In the application of ionic liquids to metal ion deposition the green credentials of this methodology could also come from a significant reduction in the volume of low level 1 ChCl: 2 EG based liquid (ethaline) streams that would need to be processed. Today, it is generally recognised that this is only part of the picture since many ionic liquids do have significant toxicity. Some ionic liquids have been designed to contain ions which are known to have lower toxicity and these include functionalised imidazoles,[10] lactams,[11] amino acids[12] and choline[13] although it is only the last of these which have been extensively applied to metal ion deposition.

The requirements for ionic liquids to be used on a bulk scale for metal ion deposition are that they need to be; low cost, non-toxic, pre-registered and water insensitive[14,15,16].

The majority of discrete anions do not achieve all of these criteria and so it is more likely that eutectic based ionic liquids will be more applicable for bulk-scale electro deposition.

The systems studied so far described can be expressed in terms of the general formula

$Cat^+ X^- z\ Y$.

Where Cat^+ is in principle any ammonium or phosphonium cation, X is generally a halide anion (usually Cl^-). They are based on equilibria set up between X^- and a Lewis or Brønsted acid Y; z refers to the number of Y molecules which complex X^-.

One of the key advantages of these types of ionic liquids is the ease of manufacture. The liquid formation is generally mildly endothermic and requires simply mixing the two components with gentle heating. Another key advantage is that they are water insensitive which is very important for practical electroplating systems. The final key advantage of eutectic based systems is that because they are simple mixtures of known chemicals they do not have to be registered as new entities as they revert to their constituent components upon excessive dilution in water.

The ionic liquids described can be subdivided into four types depending on the nature of the complexing agent used.

Eutectic Type 1 $Y = MCl_X$, M = Zn,[17,18,19,20] Sn,[21]

Eutectic Type 2 $Y = MCl_X.yH_2O$, M = Cr,[22] Co, Cu, Ni, Fe

Eutectic Type 3 Y = RZ, Z = $CONH_2$,[23] COOH[24], OH

Eutectic Type 4 $MCl_x + RZ = MCl_{x-1}^{+}\cdot RZ + MCl_{x+1}^{-}$ M = Al, Zn and Z = $CONH_2$, OH[25]

In current years, the advantages of ionic liquids (ILs) in inorganic nanomaterials synthetic processes have been gradually realized and have received more and more attention due to their unique physical and chemical properties[26,27,28,29,30]. Various approaches to the fabrication of inorganic nanomaterials with unprecedented and sometimes unique structures and properties have been reported in ILs. The most fascinating objective is that it cannot only replicate traditional inorganic particulates, nevertheless also supply routes towards new inorganic particulate with features that cannot or hardly be produced by applying traditional processes. Because of the significance and the rapid expansion of ILs in inorganic nanomaterials, this will open the door for the researchers to dig deep in this field or types of these kinds of tunable solvents in all type of research areas. The inorganic–organic hybrids such as metal ion–organic frameworks synthesized in ILs have been reviewed recently by Parnham and Morris[31].

Deep eutectic solvents(DES) are easy to synthesise, economically viable to produce on a large scale, relatively insensitive to water, exhibit high metal ion solubility, pre-registered for reach and can be recycled make them useful in wide range of application, such as metal ion plating, electro-polishing and metal ion recycling. Type III eutectics have the ability to dissolve high concentrations of metal ion oxides which allows them to be used for metallurgy.As a consequence they can be applied to large-scale processes.

Deep Eutectic Solvents have been used by a variety of groups in a range of applications which are summarised briefly here. The largest number of applications has been in the field of synthesis. In the same way that ionic liquids have been used as bulk solvents for synthesis, the same is true for DESs. There are a limited number of applications in organic synthesis,[32],[33] although the applications to inorganic synthesis and particularly in the area of template growth of solids is more extensive.[34,35,36,37,38,39] DESs have also been used as media for biocatalysts as several enzymes have been found to be stable in these liquids.[40,41,42,43,44,45,46] There are two reports of DESs based on choline chloride and glycerol being used for the purification of biodiesel through the extraction of excess glycerol.[47]There are also reports of DESs being used as electrolytes in dye sensitised solar cells[48,49.]

The novelty of Type 3 eutectics is that they use a simple hydrogen bond donor to complex the simple anion (usually chloride). The majority of the work to date has focussed on simple amides, alcohols and carboxylic acids. The first reported eutectics were those formed between choline chloride and amides such as urea and acetamide.[24]These materials have been called Deep Eutectic Solvents to differentiate them from ionic liquids with discrete anions. A eutectic forms when there is a large interaction between the two species in the mixture. An example of this is the choline chloride: urea mixture. By themselves they have freezing points of 303°C and 135°C respectively. By combining these two compounds in a ratio of 1:2 (choline chloride: urea), the product formed has a freezing point of 12°C which is a depression of freezing point of is 178 °C. For comparison the freezing point depression for the choline chloride-zinc chloride system was much larger (272 °C)[50]due to the covalent bonds formed in the metal ion chloride case. The main reason behind choline chloride being such a useful quaternary ammonium salt is to do with the fact it is an asymmetric quaternary ammonium salt with a polar functional group, but is also small. The asymmetric nature of this molecule reduces the freezing point of the ionic-molecular liquid, as does the polar functional group. Abbott*et.al*has published extensively on the subject of choline chloride $HOC_2H_4N^+ (CH_3)_3Cl^-$ (ChCl) because it is non-toxic and readily available as a bulk commodity chemical. Its common use stems in part from its simple manufacture; an efficient gas phase reaction between trimethylamine, ethylene oxide and HCl. This means that the Sheldon E factor[51] for this salt is close to zero because almost no waste products are formed during this reaction.

EXPERIMENTAL

Although much worthy research has been dedicated recently to the development of new instrumental techniques, the use of chemical reactions still remains the true basis of numerous methods of detection, separation and determination. In this respect the reaction of organic reagents with inorganic substances are very important in inorganic analysis.

There are many solution properties which change measurably as a result of complex formation and which are very informative on the existence and stability of the different species present in solution. A careful consideration is necessary, however, as to whether the effects of complex formation are quantitatively reflected in the measured property. The choice of an adequate method is a prerequisite for obtaining reliable equilibrium or stability constants. Following is an outline of some of the methods frequently used for the determination of stoichiometry and stability of metal ion complexes.

MOLAR RATIO METHOD

This method was introduced by Yoe and Jones[52] and is considered a more reliable method in the case of successive complex formation. A series of solutions is prepared in which the total concentration of the metal ion is kept constant and the concentration of the ligand is varied under similar conditions. A plot of absorbance as a function of the ratio of moles of ligand to moles of the metal ion is prepared. This plot is expected to give a straight line from the origin to the point where equivalent amounts of the constituents are present. The curve will then be- come horizontal, if only one complex of high stability is formed (Figure la). This is because all of one constituent is used up, and the addition of more of the other constituent can produce no more of the absorbing complex.
A complex that undergoes, appreciable dissociation in solution, however, gives a continuous curve which becomes approximately parallel to the molar ratio axis only when an appreciable excess of the variable component is added, (Figure 1b), and results obtained by extrapolation of this curve are unreliable[53], Harvey and Manning[54,55]found that in some cases such a curve can be made to break up sharply at the perfect molar ratio, if the ionic strength of the solutions is adjusted by addition of an inert electrolyte.

In the case of successive complex formation of different absorbances more than two linearly intersecting parts are observed in the graph; (Figure 1c). The corresponding point at themolar ratio axis to each intersecting point gives directly the ligand to metal ionion ratio in each complex.

A series of solutions which contain a constant amount of metal ionion solution and varying amounts of ligand solution were prepared. The initial concentration of both metal ion and ligand was kept the same. Deep eutectic solvent (ethaline) was added to make the total volume 5.00 cm^3. Absorbance of the solutions were recorded similarly.

CONTINUOUS VARIATION METHOD

A series of solutions of varying mole fractions of metal ionion and ligand were prepared keeping the total volume 5.0 cm^3. To determine the wavelength of maximum absorption, three samples of different mole fractions of metal ionion and ligand from the series were selected. The solution absorbance was then measured at the wavelengths where only the complex absorbs as a function of the mole fraction of the metal ionion.

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MATERIALS

Choline chloride [$HOC_2H_4N\ (CH_3)_3Cl$] (ChCl) (-Choline Chloride / Glenthman LLFE SCIENCES /1 kg Prod code GV0479 -99 %) was, when necessary, recrystallised from absolute ethanol, filtered and dried under vacuum. Ethylene glycol (EG) (Ortanal + 99 %), was used as received. The mixtures were formed by stirring the two components together (in a 1: 2 molar ratio of ChCl: hydrogen bond donor)at 60 ^{o}C until a homogeneous, colourless liquid formed.The metal ion salts Nickel (II) Chloride hexahydrate (**Scharlau** 90%) **/** NI0139, ethylene diamine / Merck- Schuchardt 96% / 1L / Art 800947 were used as received. The concentrations of metal ion salts and ethylene diamine were in the range between 0.004 mol dm^{-3} to 0.05 mol dm^{-3}.Balance / METTLER TOLEDO (AB54-S)/5 digit/ **10 mg** minimum SNR 1125180005 / Made in Switzerland.

UV visible spectrophotometer

A Shimadzu model uv-1601 spectrophotometer made in China was used with the cell path length equal to 10mm. Values for λ_{max} were determined using the spectrophotometer's built-in peak-pick feature, using UV- probe software.

RESULTS AND DISCUSSION

The ligand ethylene diamine produces three different colours with nickel (II) depending on the number of moles of ligand per mole of the nickel (II) ions. This color reaction forms the basis for the application of spectrophotometric methods for the determination of the empirical formulae of the colored chelates of nickel (II) with ethylene diamine and their approximate stability constants.The method of molar ratio was applied first to establish the empirical formulae for the colored chelates of nickel (II) and ethylene diamine. A series of solutions was prepared in which the mole fractions of nickel (II) and ethylene diamine were varied between 0.00 and 1.00 at constant total volume and under exactly similar conditions.Four of these solutions with different mole fractions were selected and their absorption spectra were then measured in the range 750 to 400 nm, as shown in **Figure 2a**and **Figure 2b** represents the photo of the colour of Ni (**II**) complexes formed after the successive addition of ethylene diamine. The spectra (i), (ii), (iii) and (IV) refer to Ni(**II**) ions in 1 ChCl: 2 EG based liquid (ethaline) solution, the 1:1 chelate, the 1:2 chelate and the 1:3 chelate, From these spectra it has been concluded that Ni(**II**) ions react with ethylene diamine to form the chelates $[Ni(en)\ (H2O)_4]^{2+}$, $[Ni(en)_2(H_2O)_{2]}^{2+}$ and $[Ni(en)_3]^{2+}$ in 1 ChCl: 2 EG based ionic liquid (ethaline) solutions, depending on the number of moles of ligand per mole of metal ionion and with maximum wavelength of 626 nm, 604 nm and 587 nm, respectively. The absorption of the $[Ni\ (H_2O)\ _6]^{2+}$ ion is centered at maximum wavelength 650 nm. The successive shift to higher energy on moving from Ni (**II**) ions to the 1:3 chelate is in accordance with the stronger ligand field of the chelating ligand as compared to H_2O.

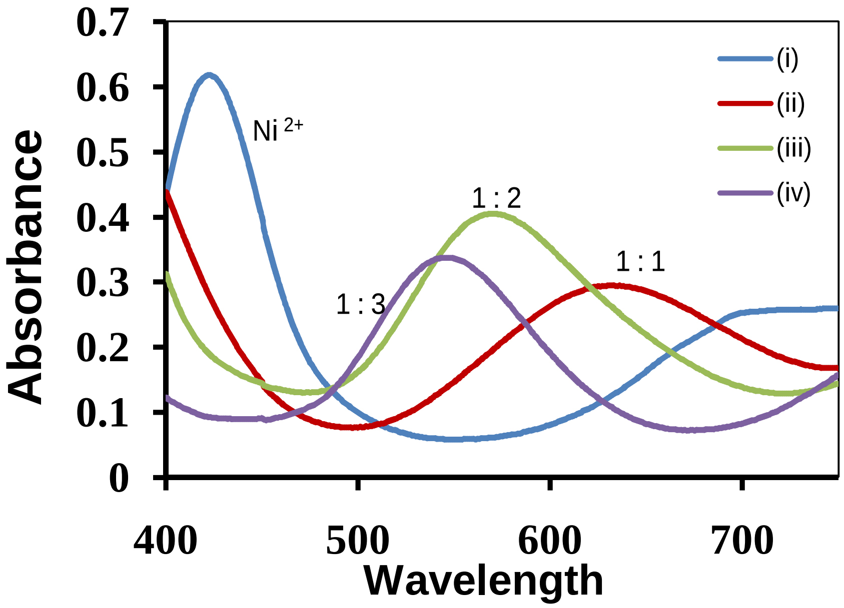

Figure 2a shows the visible absorption of nickel chelate with ethylene diamine in ionic liquids.

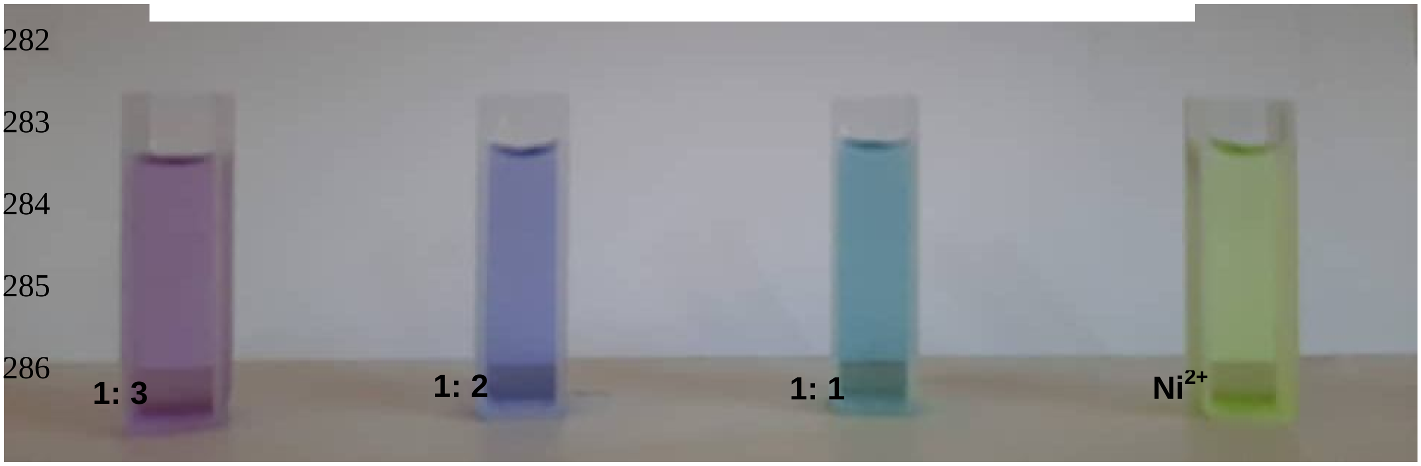

Figure 2b represents photo the colour change after successive addition of ethylene diamine (en) substance to Ni^{+2} in ionic liquids.

The 1:1 Chelate; [Ni en $(H_2O)_4]^{2+}$

The molar ratio method was first applied to confirm the fact that Ni (II) ions react with ethylene diamine in 1 ChCl: 2 EG based liquid (ethaline) solutions to form a stable complex in the ratio of 1:1.

A series of solutions 0.25 M in both metal ion and ligand was prepared in the usual manner according to the molar ratio method. The absorbance of the above solutions was measured at maximum wavelength 640 nm and a temperature of 27 °C. The plot of the complex absorbance, corrected for excess metal ion and/or excess ligand, against the mole ratio of ligand to metal ion, L/M, is represented in **Figure 3.**

If only one complex of high stability is formed in solution, one would expect the plot to give a semi straight line from the origin to the point where the equivalent amounts of constituents are present. The curve will then become horizontal since all of one constituent is used up and the addition of more of the other constituent can produce no more of the absorbing complex, unless the constituent which is in excess itself absorbs at the same wavelength. In such cases, the curve will show a positive slope after the equivalence point, but of smaller magnitude than that prior to equivalence.

The stability constant Log K_1 is calculated in this investigation from **Figure 3** andwas found Log K_1= 6.87, 27°C which is fairly in good agreement with the literature value[4](Log K_1 =7.52). The little difference between the value obtained in this study and the published work value could be due to the experimental settings at which the values were achieved.

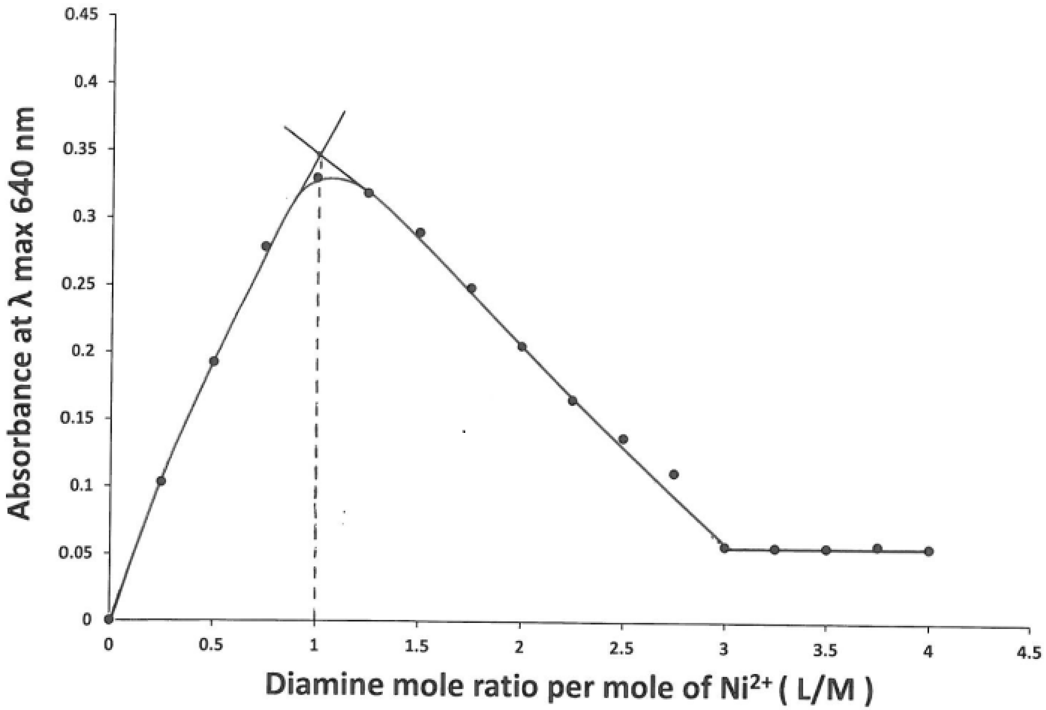

Figure 3 depicts the plot of absorbance against ethylene diamine (en) mole ratio per a mole of Ni (II) in ethaline.

Another series of solutions 0.25M in both metal ion and ligand was prepared according to the Job`s method. The temperature was maintained at 26°C. The absorbance of the above solutions was measured at 640 nm wavelength. The net absorbance was then plotted against the mole ratio as shown in **Figure 4.** From **Figure 4**,the value of Log K_1 =6.52 which is obtained using deep eutectic solvent (ethaline) as solvent have been found reliable, the calculation of the stability of formation constant (K_1) of 1:1 Ni- diamine complex was found consistent.

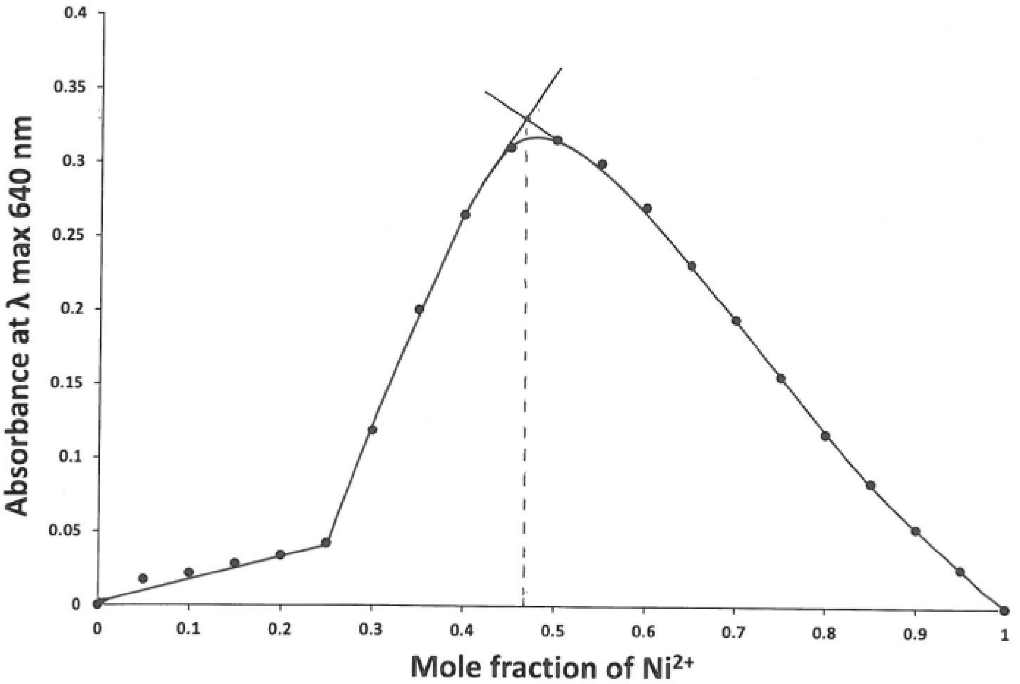

Figure 4 shows the plot of absorbance versus mole fraction of Ni (II) in deep eutectic solvent (ethaline).

It is very interesting to observe that the value ofthe stability constant of the 1:1 Ni (II)-diamine complex obtained by the molar ratio (Log K_1 = 6.87) is in consistent with the value calculated by using continuous variation method (Log K_1 = 6.52) and more over are bothare close to the literature value in aqueous media[4]. The slight difference between the values obtained in this study and the literature values could be attributed to the experimental conditions at the values were calculated.

EFFECT OF CONCENTRATION

The effect of the concentrations of both Ni(II) ion and ethylene diamine (en) ligand have been investigated using molar ratio method on the extent of the 1 : 1 Cu-diamine complex. It has been noticed that the successive increase in absorbance at mole fraction = 1 as the initial concentration of both metal ionion and the ligand increase.

Table1. Calibration Curve Data forNickel (II) Ethylene diamine Complex (1:1)

Molar Concentration of Ni(II) –en Complex	Absorbance
0	0
0.0125	0.099
0.025	0.183
0.0375	0.266
0.0500	0.358
0.0625	0.436

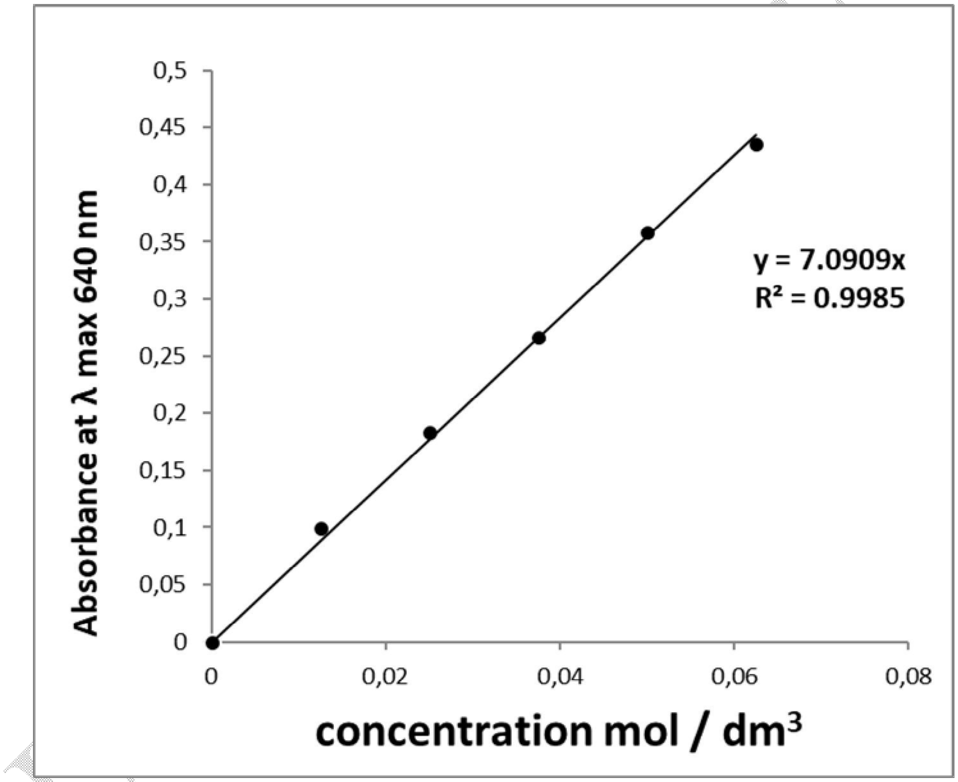

Figure 5 shows the plot of [Ni (en)] $^{2+}$ complex absorbance versus its concentrations.

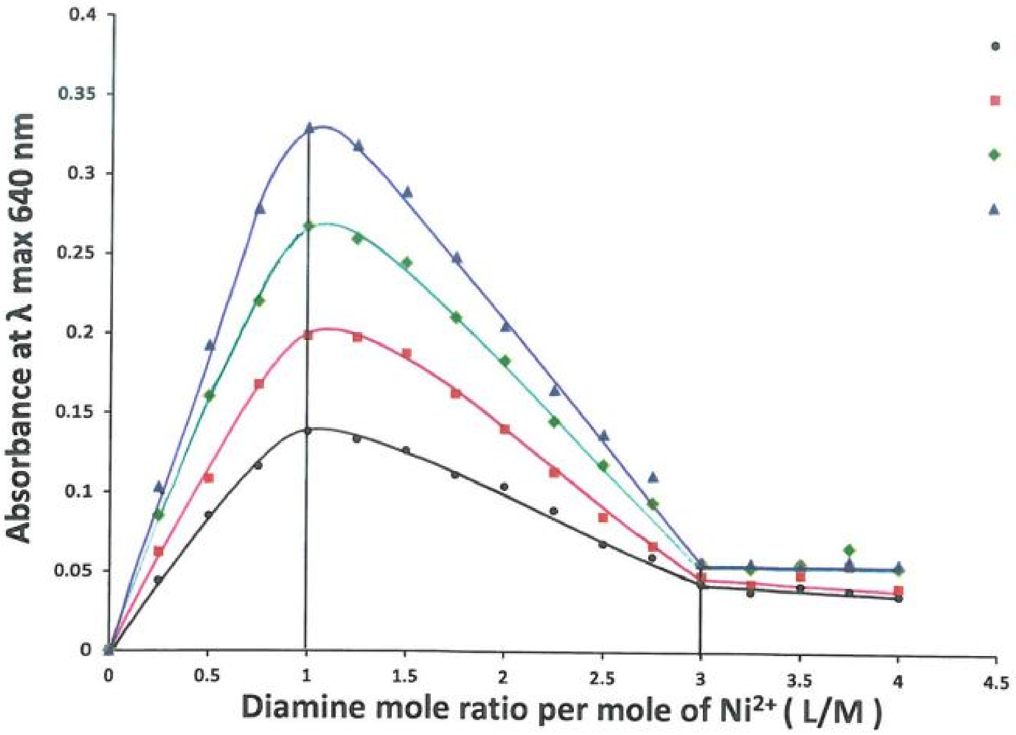

Figure 6 depicts the plot of absorbance against ethylene diamine (en) mole ratio per a mole of Ni (II) in ethaline.

The absorbance of the complex increases remarkably with increase of initial concentration of both Ni (II) ion and ethylene diamine. The plot of absorbance versus molar ratio of ethylene diamine, L / M for different initial concentration is depicted in **Figure 6**. It was found that the Ni (II) ion-diamine complex obey Beer`s lawobey Beer`s law, which is shown in **Figure 5**

The 1:2 Chelate; $[Ni\ (en)_2\ (H_2O)_2]^{2+}$

The molar ratio method was first applied to establish the fact that Ni (II) ions and ethylene diamine react under the specified conditions to form a stable complex in the ratio of 1:2.A series of solutions was prepared according to the molar ratio method. The concentration of these solutions was exactly. 0.20 M in both metal ion and ligand. The absorbance of these solutions was measured at maximum wavelength 565 nm and 27˚C.The plot of the net absorbance corrected for excess metal ion and/or ligand against the mole fraction of ligand -L/M- is shown in Figure7.

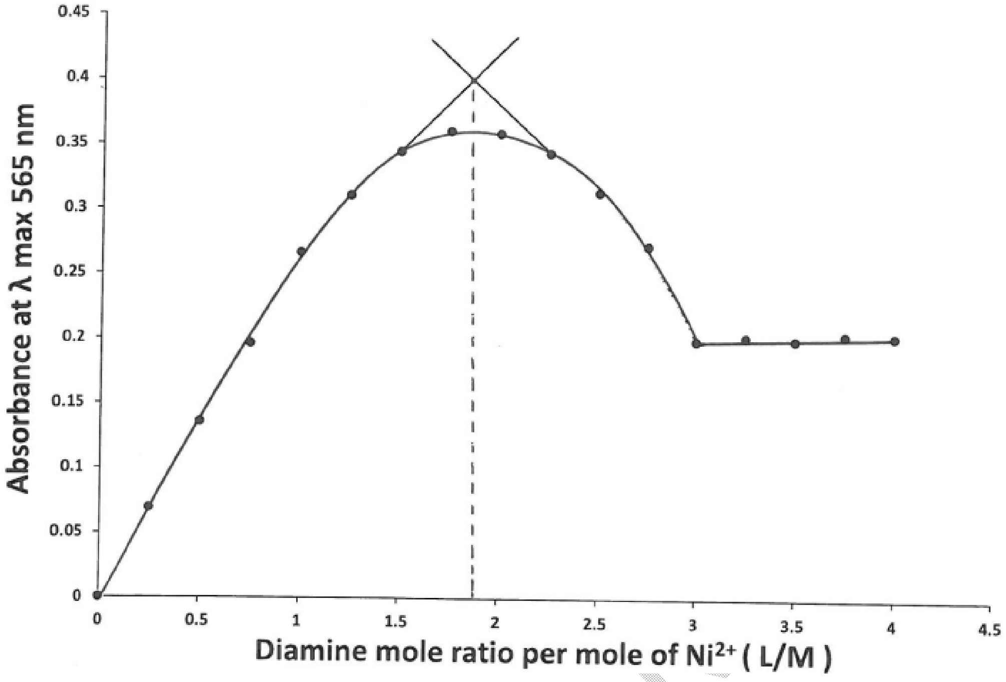

Figure 7 depicts the plot of absorbance against ethylene diamine (en) mole ratio per a mole of Ni (II) in ethaline.

The profile of **Figure 7** indicates a stepwise formation of more than one complex where the mole ratio of Ni (II) equal three comprehensibly indicating the possibility between Ni(II) and the diamine ligand in 1 ChCl: 2 EG based liquid (ethaline) solution. The value of the stability constant was obtained from **Figure 7** (Log K_2**=** 5.18), which is comparable to the value obtained in aqueous media (Log =6.28)[4].The method of continuous variations was also applied to confirm the results outlined above. A series of solutions 0.20 M in both metal ion and ligand was prepared under the same conditions of temperature and ionic strength. The plot of net absorbance versus mole fraction of the metal ion is shown in **Figures 8a**,further confirmed by the image of the successive colour change as a function of mole fraction of Ni (II) ion, this is shown in **Figure 8b** the straight lines resulting from the extrapolation of the two legs of **Figures 8a** intersect each other at a mole fraction of 0.33 indicating the formation of a 1:2 chelate. Also, it has been observed that a break at mole fraction equal to 0.5 indicating the stepwise complex formation of 1 : 1 Ni(II) and ethylene diamine complex, which is shown in**Figures 8a**.The stability constant of the 1:2 chelate was determined from **Figure 8a** has the value Log K_2 = 4.48The value obtained by continuous variation was found uncertain; this could be attributed to the asymmetrical bell curve due to stepwise complex formation of 1:1 complex. But the value of K_2 calculated using molar ratio method was found is in good agreement with literature values.

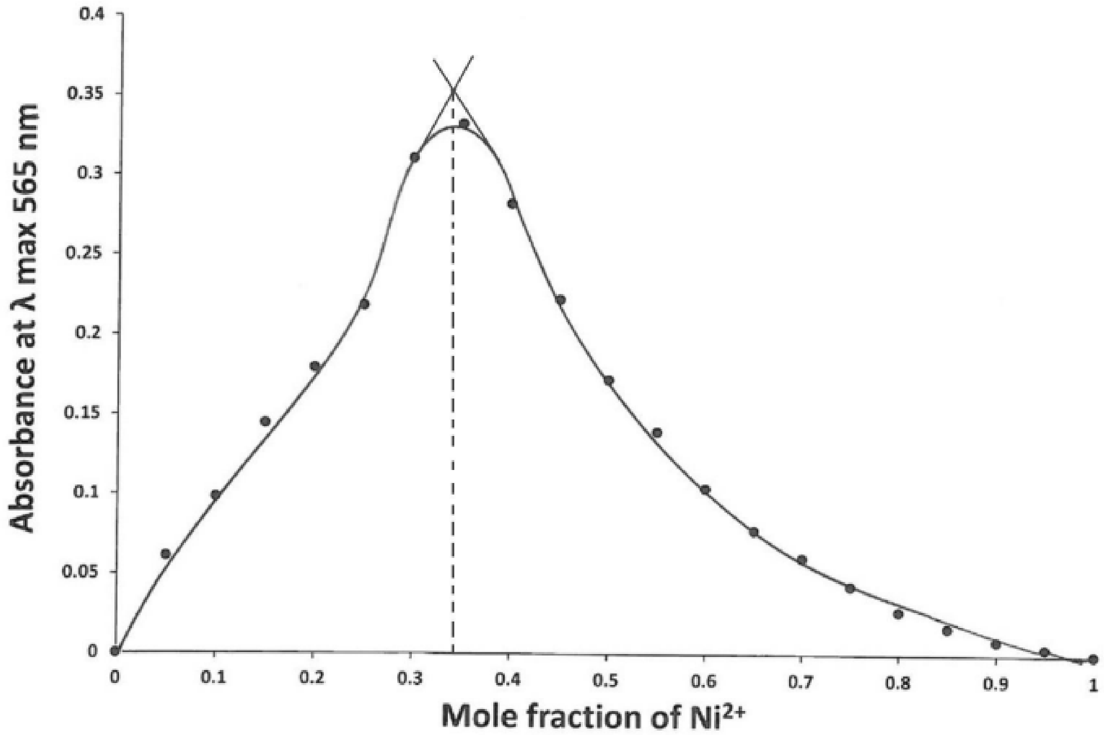

Figure 8a shows the plot of absorbance versus mole fraction of Ni (II) in deep eutectic solvent (ethaline).

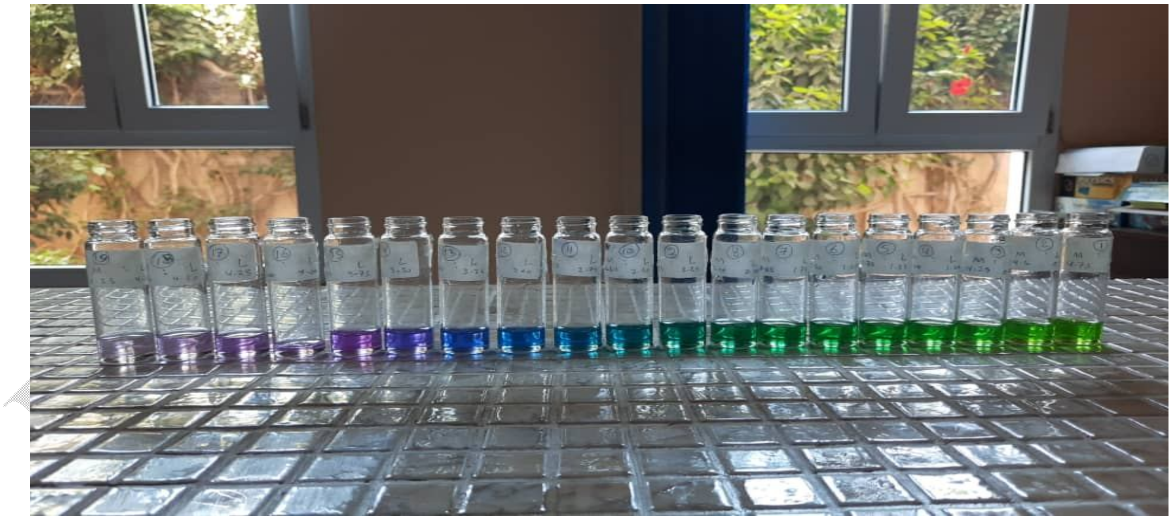

Figure 8b represents photo the colour change after successive addition of ethylene diamine (en) substance to Ni^{+2} in ionic liquids (continuous variation method).

It is very impressive to observe that the value of the stability constant of the 1:2Cu (II)-diamine complex obtained by the molar ratio is in good agreement with the literature value in aqueous media[4]. The slight difference between the values obtained in this study and the literature values could be attributed to the experimental conditions at the values were calculated.

Furthermore, many values have been published for the formation constants of various metal ion-ligand systems, especially in past and recent years, but the experimental methods and precision attained have varied considerably. Some authors have worked at unspecified "room temperature" and with solutions in which the ionic strength must have varied appreciably in aqueous media which is not in our case as solvent with high ionic strength (ionic liquids solvents) during the experiments and can only be estimated approximately from their Figures[56]

EFFECT OF INITIAL CONCENTRATION

Again the molar ratio method was introduced to explore the effect of initial concentration of both metal ion and ligand on the extent of formation of the 1:2 Ni-diamine complexes in deep eutectic solvent.
It was observed that the 1:2 Ni (II)-diamine complex obeys Beer`s law. A plot of absorbance the 1:2 Ni (II)-diamine complex versus concentration at maximum wavelengths of 565nm summarized in Table 2 show linearity as evident in Figure 9.

Table2. Calibration Curve Data forNickel (II) Ethylene diamine Complex (1:1)

Molar Concentration of Ni(II) –en Complex	Absorbance
0	0
0.0125	0.112
0.025	0.21
0.0375	0.304
0.0500	0.403
0.0625	0.501

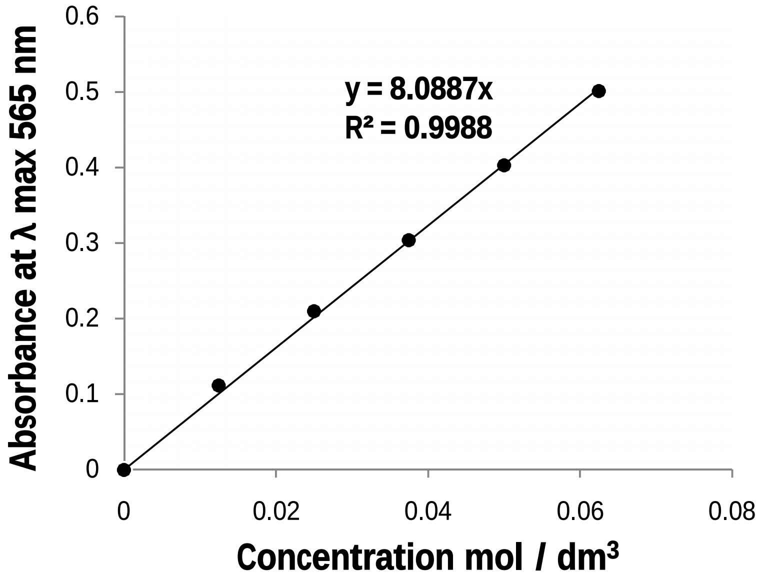

Figure 9 shows the plot of $[Ni\ (en)_2]^{2+}$ complex absorbance versus its concentrations.

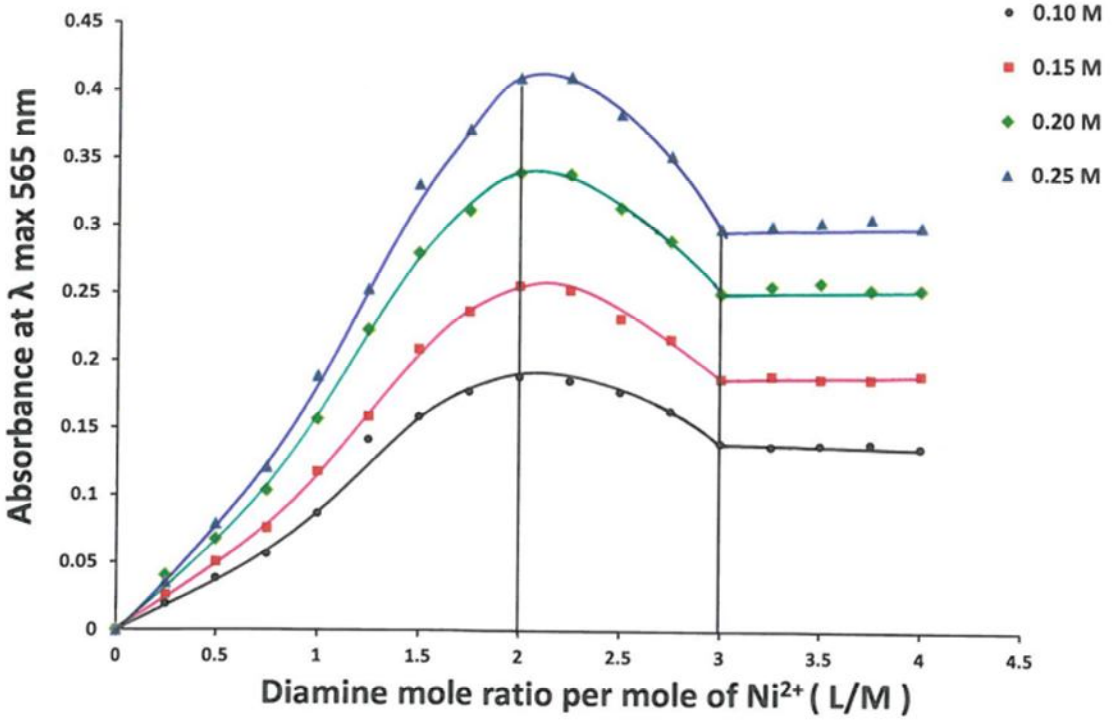

Figure 10 shows the plot of absorbance against ethylene diamine (en) mole ratio per a mole of Ni (II) in ethaline.

It has been noticed that the break in **Figure 10**, at mole fraction = 3 which becomes more apparent as the initial concentrations of both metal ionion and the ethylene diamine increase.

The 1:3 Chelate; $[Ni\ (en)_3]^{2+}$

The Molar ratio method was used to determine the stoichiometry and stability constant of the 1:3 chelate if possible. The absorbance of the solutions was measured at maximum wavelength 530 nm, the temperature was exactly 26˚C,and the data is shown in **Figure 11** which reveals the plot of net absorbance of the complex against diamine ratio to Ni (II) (L/M).

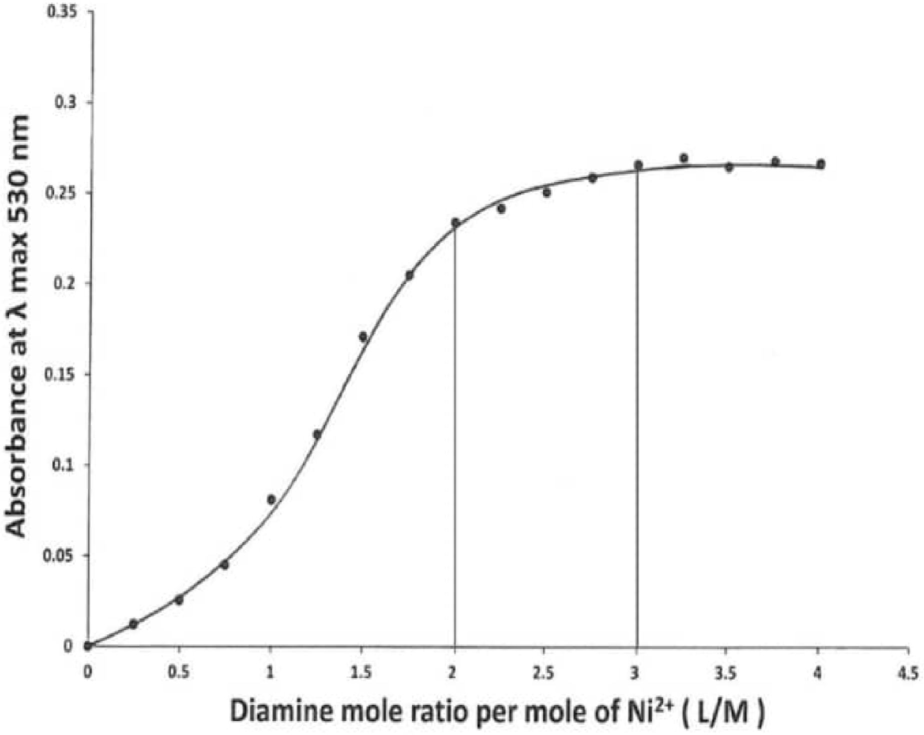

Figure 11 reveals the plot of absorbance against ethylene diamine (en) mole ratio per a mole of Ni (II) in ethaline.

The complications arising from stepwise formation of complexes in deep eutectic solvent (ionicliquid) is observed in Figure 11. Thecurve in mentionedFigure shows more than linear intersecting parts breaking off at ligand to metal ion ratio of approximately 2.00 and 3.00; a conclusion which confirms the formation of 1: 2 and 1: 3 complexes. In view of these complications, attempts to calculate the stability constant using Figure 11 will be uncertain.

A series of solutions 0.20 M in both metal ion and ligand was prepared in the usual manner according to continuous variations under the same conditions as in the molar ratio method. The absorbance of the solutions at maximum wavelength 530 nm at 27 °C. The plot of net absorbance against the mole fraction of the metal ion is shown in Figure 12.

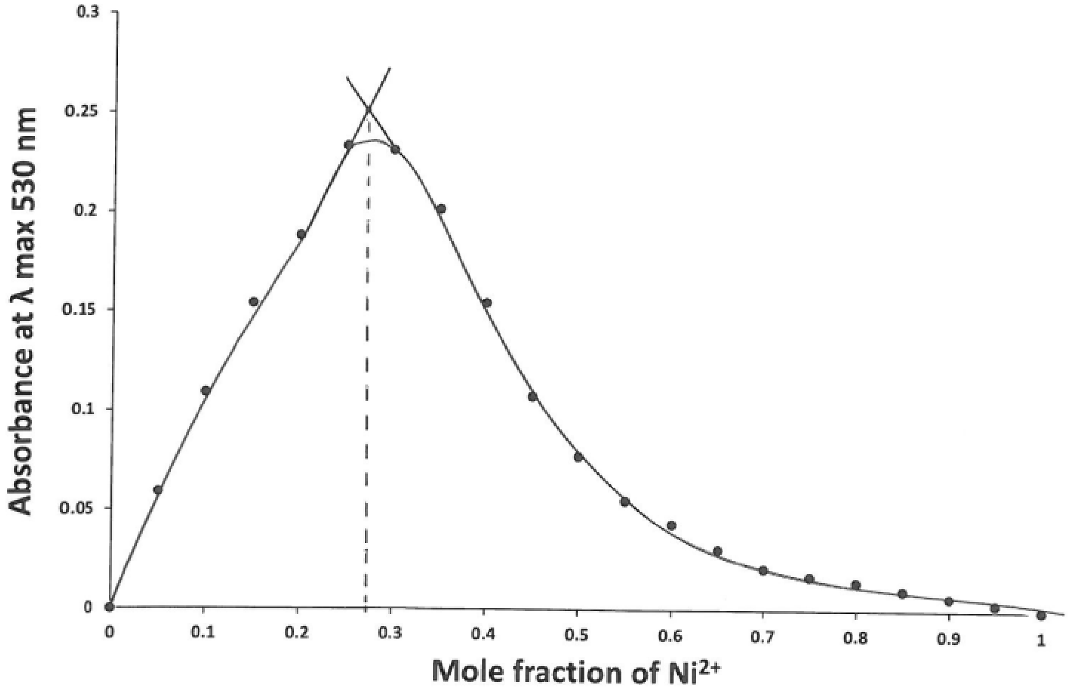

Figure 12 shows the plot of absorbance versus mole fraction of Ni (II) in deep eutectic solvent (ethaline).

Figure 12 reveals that the 1:3complexesare reasonably symmetrical inthe 1 ChCl: 2 EG based liquid (ethaline) solutions.The stability constant of the ethylene diamine chelate was calculated from Figure 12 was found Log K_3 = 4.81which consistent with the literature value[4](Log K_3=4.26) . Furthermore ethylene diamine was used as complexing agent (brightener) in the electro deposition of metal ions such as nickel resulting even distribution of nickel coating and bright finish[57].

Complex	1 : 1	1 : 2	1 : 3
Molar Ratio	Log K = 6.87	Log K = 5.18	Log K = Unreliable
Job`s Method	Log K = 6.52	Log K = 4.48	Log K = 4.81

CONCLUSION

The reaction of Ni (II) ion with ethylene diamine chelate in is 1 ChCl: 2 EG based on liquid (ethaline) has been investigated using spectrophotometric methods. Three complexes instantaneously are formed the first 1 : 1 mole ratio ,the second 1 : 2 mole ratio at maximum and the third 1 : 3 mole ratio at maximum wavelengths 626 nm , 604 nm and 587 nm respectively. The empirical formula and stability constant for the three complexes were determined by continuous variations and molar ratio methods. The values of stability, constants K_1, $K_2$and K_3were found in good agreement with the values obtained in aqueous solution, despite the different settings and methods which is encouraged to use the ionic liquids in coordination chemistry researches. The effect of concentration of the complexes formed $[Ni\ (en)]^{2+}$, $[Ni\ (en)_2]^{2+}$ and $[Ni\ (en)_3]^{2+}$ was also studied and revealed that the three complexes obey Beer`s law. The absorbance increases considerably as the concentration increases. For $[Ni\ (en)]^{2+}$it has been observed that there is a break at mole ratio 3 as the initial concentration of both the metal ion and the chelate increases. Also it has been noted that the value of stability constant K_3 calculated from molar ratio method is undertrained, this may attributed to isosbestic point. The deep eutectic solvent type III (ionic liquids) is found to be an excellent solvent in coordination chemistry. That will allow expansion into the research area, for example inorganic synthesis, organic synthesis and catalyst etc.

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