

# Stoichiometry and Stability Constant Values for Copper (II) Chelates with Ethylene Diamine in Deep Eutectic Solvents (DES) (Ethaline) Solutions

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**How to cite this paper:** El Ttaib, K., Benhmid, A. and Hasan Omar, R. (2024) Stoichiometry and Stability Constant Values for Copper (II) Chelates with Ethylene Diamine in Deep Eutectic Solvents (DES) (Ethaline) Solutions. *Open Journal of Applied Sciences*, 14, 2592-2609.

<https://doi.org/10.4236/ojapps.2024.149171>

**Received:** August 17, 2024

**Accepted:** September 23, 2024

**Published:** September 26, 2024

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## Abstract

In this study we used the deep eutectic solvents (ionic liquids) to investigate the reaction between copper (II) with ethylene diamine (en). Two of the existing methods for analyzing spectrophotometric measurements have been applied for establishing, the stoichiometry and whenever possible, the stability constants of the chelates formed. The method of continuous variations was necessary to determine first whether, the metal ion and the ligand ethylene diamine form one or more than one chelate, when more than one chelate formed, the results obtained depend on the wavelength and for meaningful conclusions the wavelengths were carefully selected. 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 studied. The stability constants,  $K_1$  and  $K_2$  for the copper (II) chelates were calculated, though reliable, and are comparable to literature values.

## Keywords

Cu(II), Ethylene Diamine (en), Deep Eutectic Solvents, Job's Method, Ionic Liquids and Stability Constant

## 1. Introduction

Molten salts at high temperature have long been applied for metal production and metals such as Li, Na, Ti and Al have been electroextraction for molten salts [1]-[3]. The major limitation, with elevated temperature molten salts is markedly the temperature which leads to a difficult operation and confines the range of

substrates that can be used. In attempts to minimise the melting temperature of salts several studies focussed on Li<sup>+</sup>/K<sup>+</sup>/AlCl<sub>3</sub> eutectics which have melting points close to 100°C [4]. The use of quaternary ammonium salts particularly pyridinium and imidazolium salts has pushed the melting point down to setting conditions. The term “ionic liquids” has been used to distinguish between high temperature and low temperature systems.

Ionic liquids are made of simple anions, as opposed to a mixture of anions in equilibrium. Their discovery is ascribed to Wilkes and Zaworotko who produced 1-ethyl-3-methylimidazolium tetrafluoroborate and acetate for the first time [5]. It is this type of ionic liquid which has dominated the literature ever since. Anions such as BF<sub>4</sub><sup>-</sup> and BF<sub>6</sub><sup>-</sup> were used in early stages because of their stability in wide range of electrical potential compared to aqueous media [6] [7], however, they were noticeably difficult to hydrolyse yielding HF [8], and liquids with more nonpolar anions such as trifluoromethanesulphonate (CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>) and bis-(trifluoromethanesulphonyl)imide [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] have subsequently become famous [9].

Ionic liquids are salts that have a melting temperature below 100°C. Generally one of the ionic constituents is organic, most commonly the positive ion. The ions have a high irregular structure. By conscientiously chosen from the components it is possible to manipulate the properties of the liquid.

It is generally agreed that the first ionic liquid was [EtNH<sub>3</sub>] [NO<sub>3</sub>], and had a melting point of 12°C. Ionic liquids as a low temperature alternative are currently a favoured area of research. Ionic liquids are systems with an anionic and a cationic component which are liquid below 100°C [10]. The definition is used to distance these fluids with high temperature molten salts but is completely arbitrary. Ionic liquids have been of great interest, due to them having many advantageous properties from molten salts, yet negating the difficulties of high temperature. The contingency to select a possible ligand as the anionic component permits control over speciation and thus redox properties of metal solutes to a much greater extent than in 1 ChCl:2 EG (ethylene glycol) (ethaline) based liquid media since extremely high activities of the ligands can be achieved.

Ionic Liquids have clearly been declared to be green solvents, remarkably for their low vapour pressure in contrast with molecular alternatives. In the application of ionic liquids to metal deposition and other applications, 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 [11] [12]. 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 less hazard and these include functionalised imidazoles [13], lactams [14], amino acids [15] and choline [16] although it is only the last of these which have been extensively applied to metal deposition, catalysis and synthesis. Deep eutectic solvents (ionic liquids) can be used on a bulk scale for metal deposition due to; low cost where it can compete in the market, non-toxic means friendly environment, pre-registered

for reach and water insensitive. The majority of discrete anions do not meet some or all of mentioned requirements and so allow deep eutectic ionic liquids more felicitous in large scale industrial applications.

The systems studied so far described can be expressed in terms of the general formula  $\text{Cat}^+ \text{X}^- \cdot z \text{Y}$ , where  $\text{Cat}^+$  is in principle any ammonium or phosphonium cation, X is generally a halide anion (usually  $\text{Cl}^-$ ). They are based on equilibria set up between  $\text{X}^-$  and a Lewis or Brønsted acid Y, z refers to the number of Y molecules which complex  $\text{X}^-$ .

The melting point of two component mixtures is dependent upon the size of the interaction between the components. For ideal mixtures (non-interacting components) the freezing point will vary linearly with mole fraction whereas large negative deviations can occur when the components interact strongly with each other. The composition at which the minimum freezing point occurs is known as the eutectic point and this is also the temperature where the phases simultaneously crystallize from molten solution.

One of the key advantages of these types of ionic liquids is easy to prepare. The liquid formation is generally slightly endothermic and necessitates simply mixing the two components with light 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:  $\text{Y} = \text{MCl}_x$ ,  $\text{M} = \text{Zn}$  [17]-[20],  $\text{Sn}$  [21],  $\text{Fe}$  [22],  $\text{Al}$  [23],  $\text{Ga}$ ,  $\text{In}$  [24]

Eutectic Type 2:  $\text{Y} = \text{MCl}_x \cdot y\text{H}_2\text{O}$ ,  $\text{M} = \text{Cr}$  [25],  $\text{Co}$ ,  $\text{Cu}$ ,  $\text{Ni}$ ,  $\text{Fe}$

Eutectic Type 3:  $\text{Y} = \text{RZ}$ ,  $\text{Z} = \text{CONH}_2$  [24],  $\text{COOH}$  [26],  $\text{OH}$

Eutectic Type 4:  $\text{MCl}_x + \text{RZ} = \text{MCl}_{x-1}^+ \cdot \text{RZ} + \text{MCl}_{x+1}^-$ ,  $\text{M} = \text{Al}$ ,  $\text{Zn}$  and  $\text{Z} = \text{CONH}_2$ ,  $\text{OH}$  [27]

To date the only  $\text{Cat}^+$  species studied have been based on pyridinium, imidazolium and quaternary ammonium moieties. In general, as with the chloroaluminate and discrete anion systems, the imidazolium based liquids have the lowest freezing points and viscosities and higher conductivities. The depression of freezing point is related to the strength of interaction between the anion and complexing agent although this has not really been quantified as yet due primarily to a lack of thermodynamic data about the individual components.

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

scale processes.

Deep Eutectic Solvents (DES) 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 [28] [29], although the applications to inorganic synthesis and particularly in the area of template growth of solids is more extensive [30]-[35]. DESs have also been used as media for biocatalysts as several enzymes have been found to be stable in these liquids [36]-[40]. 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 [41]-[43]. There are also reports of DESs being used as electrolytes in dye sensitised solar cells [44] [45].

A fourth type of eutectic has been described involving just a metal salt and a hydrogen bond donor [46]. It was shown that  $ZnCl_2$  when mixed with acetamide or urea could also form eutectics which had all the properties of ionic liquids.

The nature of Type III eutectics which is used in this study is that we use a simple hydrogen bond donor to complex the simple anion (usually chloride). Most of the scientific research to date has interested on simple amides, alcohols and carboxylic acids. The first reported eutectics were those formed between choline chloride and amides such as urea and acetamide. 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  $303^\circ C$  and  $135^\circ C$  respectively. By combining these two compounds in a ratio of 1:2 (choline chloride: urea), the product formed has a freezing point of  $12^\circ C$  which is a depression of freezing point of  $178^\circ C$ . For comparison the freezing point depression for the choline chloride-zinc chloride system was much larger ( $272^\circ C$ ) [47] due to the covalent bonds formed in the metal 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 character of this molecule decreases 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, also because one of the supplements of chicken feed. 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 [48] for this salt is close to zero because almost no waste products are formed during this reaction.

## 2. Optical Methods

One spectacular consequence of complex formation is the change in spectral properties. Observations of color and reaction-related color changes of coordination

complexes have been important throughout the history of the field.

The excitation of electrons of both metal and ligand is influenced by their interaction. Excitation of transition metal electrons is easy and consequently they absorb in the visible region. Any chemical compound is colored if light of a wavelength conjugate to that color is absorbed. The color of the complex derives, of course, from the wavelength of light transmitted.

Spectrophotometric methods are particularly used to advantage for studying complexation equilibria and determination of the amount of complex-forming constituents, as it is suited to the selective determination of very small concentrations of species without changing the composition of the solution. The basic condition for application of spectrophotometric method, as is true for all analytical methods based on the measurement of light absorption, is that the Beer-Lambert law is obeyed by the constituents to be determined. If adequate selectivity in the spectrophotometric determination of a given substance is to be achieved some practical considerations must also be taken into account. For example, it is necessary to choose a suitable wavelength at which the measurement is taken. The absorption coefficient of the substance being determined should be high, and those of other species present be negligible. The errors in spectrophotometric measurements are the result of chemical, instrumental factors or deviations from Beer's law.

Two optical methods were used in this research which are continuous variation (Job's) method and molar ratio method

### 3. Materials and Preparation of Ionic Liquids

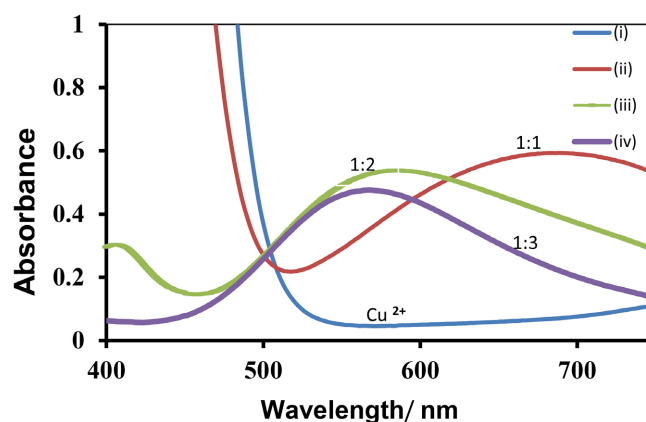
Choline chloride [ $\text{HOC}_2\text{H}_4\text{N}(\text{CH}_3)_3\text{Cl}$ ] (ChCl) (-Choline Chloride/Glenthman LLFE SCIENCES/1 kg Prod code GV0479-99%) was, when necessary, recrystallised from absolute ethanol, filtered and dried under vacuum. Ethylene glycol (EG) (Ortanal + 99%), was used as received. The mixtures were formed by stirring the two components together (in a 1:2 molar ratio of ChCl: hydrogen bond donor) at  $60^\circ\text{C}$  until a homogeneous, colourless liquid formed. The metal salts; Copper sulphate pentahydrate (Riedel-de haen 99%) 1 kg, Nickel (II) Chloride hexahydrate (Scharlau 90%)/NI0139, ethylene diamine/Merck-Schuchardt 96%/1 L/Art 800947 were used as received. The concentrations of the metal salts ethylene diamine, were in the range between  $0.004\text{ mol}\cdot\text{dm}^{-3}$  to  $0.05\text{ mol}\cdot\text{dm}^{-3}$ . Balance/METTLER TOLEDO (AB54-S)/5 digit/ 10 mg minimum SNR 1125180005/Made in Switzerland.

### 4. Speciation

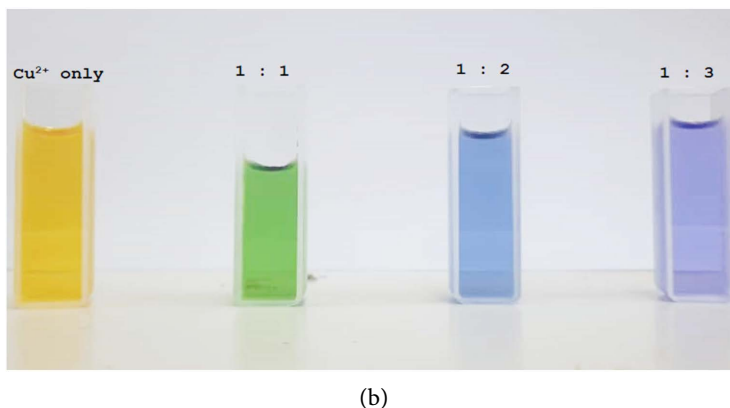
A DRAWELL model 8600RN split beam spectrophotometer made in China was used with the cell path length equal to 10 mm. Values for  $\lambda_{\text{max}}$  were determined using the spectrophotometer's built-in peak-pick feature, using uv/vis analyst software.

## 5. Results and Discussions

It has been observed in **Figure 1(a)** and **Figure 1(b)** that the reaction of Cu(II) with ethylene diamine produces two distinct different colors, depending on the number of moles of Cu(II) and number of moles of ethylene diamine in 1 ChCl:2 EG (ethylene glycol) based liquid (ethaline) solutions. It was, therefore, necessary to determine first whether, Cu(II), the diamine reagent form one or more than one complex. Two of the existing spectrophotometric methods have been applied to establish the empirical formulae or formula of the resulting complex or complexes. The method of continuous variations was first applied to establish whether one or more complexes are formed in the solution. The results were further substantiated by the molar ratio method. In the continuous variations method, a series of a ChCl:2EG ionic liquids (ethaline) was prepared in which the mole fractions of Cu(II) ion and ethylene diamine were varied between 1.00 and 0.00 at a constant total concentration under similar, temperature and ionic strength are concerned. Four of those solutions with different mole fractions were selected and their absorption spectra were measured in the range of 750 to 400 nm, **Figure 1(a)**. The spectra (i), (ii), (iii) and (iv) in **Figure 1(a)** refer to the Cu(II) in a ChCl:2EG ionic liquid, the 1:1 chelate and the 1:2 chelate, respectively. The ethylene diamine in the ratio of 1:3 spectrum was also recorded for the solution. It is quite evident from **Figure 1(a)** that the 1:2 and 1:3 chelates exhibit maximum absorption at the same wavelength, 575 nm; the absorbance being higher for the 1:2 chelate. The 1:1 chelate, on the other hand, absorbs at a distinctly longer wavelength, 660 nm, as compared to the 1:2 chelate. These spectra revealed that the 1:3 chelate,  $[\text{Cu}(\text{en})_3]^{2+}$ , is not formed and that the only ones are the 1:1 and 1:2 chelates are formed by Cu(II) and ethylene diamine. This conclusion is in general agreement with the fact that under normal conditions the removal of the fifth and sixth molecules of water from the ion  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  is not easy because of the  $d^9$  configuration renders the Cu(II) ion subject to Jahn-Teller effect [49]. These conclusions were further substantiated by the continuous variations and molar ratio methods.



(a)

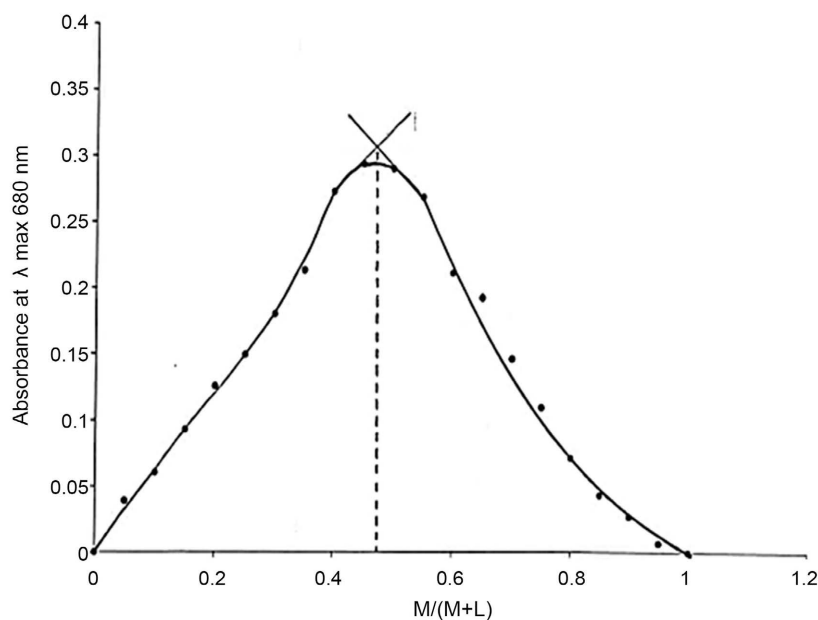


**Figure 1.** (a) The visible absorption of Copper (II) chelates with ethylene diamine (en) in deep eutectic solvent (ethaline); (b) The photo of the 1:1 and 1:2 Cu(II)-diamine complex) in deep eutectic solvent (ethaline).

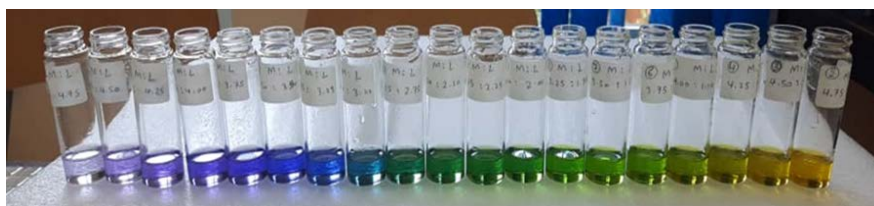
### The 1:1 Chelate, $[\text{Cu(en)}]^{2+}$

A first look at **Figure 1(a)** reveals that at the wavelength corresponding to maximum absorption of the 1:1 chelate (maximum wavelength = 660 nm), the 1:2 Cu(II)-diamine complex also absorbs. However, it is necessary to measure the absorbance of the 1:1 chelate at a slightly longer wavelength so as to move as far as possible from the **isosbestic** point. The wavelength = 680 nm was deemed suitable for that purpose. The method of continuous variations was first applied to establish the formula of the 1:1 chelate; the results were then confirmed by the molar ratio method. A series of solutions, 0.02 M in both metal ion and chelating ligand was prepared according to the method of continuous variations which is depicted in **Figure 2**. In the above series of solutions, the temperature maintained at 26°C. The range of the colour reactions between Cu(II) and ethylene diamine is shown in **Figure 3**. The maximum absorbance was observed at the mole fraction of 0.50 indicating that when Cu(II) and ethylene diamine are mixed in the ratio of 1:1, they form a stable complex.

According to Beck [50], if a 1:1 complexes are formed aqueous medium, *i.e.*  $M = L$ , and the curve shows inflections and parabolic portions for values of  $M/L$  near 0 and 1, this indicates that  $M = L > 1$ . The absence of such inflection and parabolic portions indicates that  $M = L = 1$ , fortunately this is not the case in deep eutectic solvent (ionic liquids), furthermore another key advantage of the ionic liquids upon the water as a solvent. In **Figure 2**, the chelate absorbs at 680 nm wavelength. Therefore for the 1:1 chelate formed by Cu(II) ions and ethylene diamine  $M = L = 1$ . It is evident that from **Figure 2** that the 1:1 complex is reasonably symmetrical in the 1 ChCl:2 EG based liquid (ethaline) solutions. The stability constant of the ethylene diamine chelate was calculated from **Figure 2**, the result calculated in this investigation,  $\text{Log } K_1 = 9.5$ , 27°C, is fairly in good agreement with the literature value ( $\text{Log } K_1 = 10.5$ ). The tiny difference between the value obtained in this research and the published work [51] value could be due to the experimental settings at which the values were achieved.

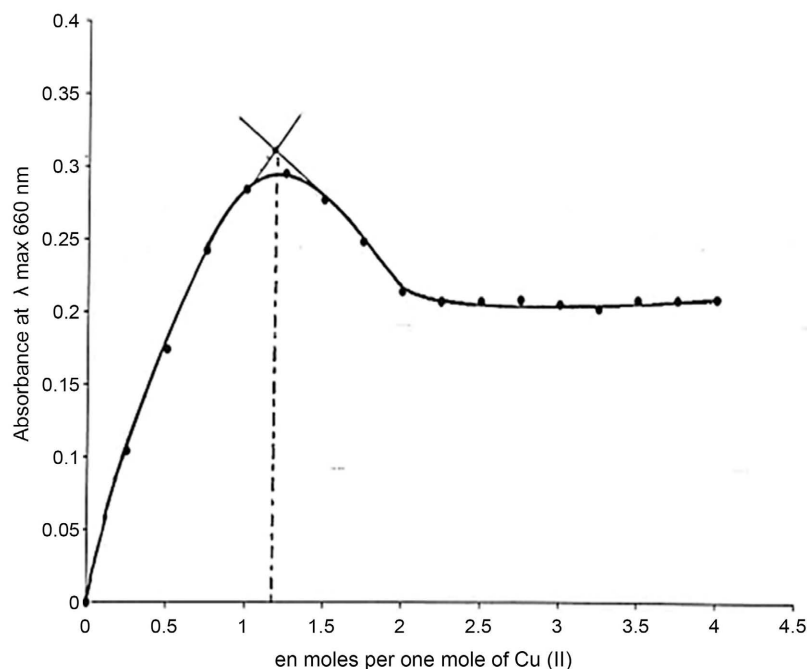


**Figure 2.** The plot of absorbance versus mole fraction of Cu(II) in deep eutectic solvent (ethaline).



**Figure 3.** The colour change with successive addition of ethylene diamine (en) to Cu(II) in ionic liquids.

Another series of solutions 0.02 M in both metal and ligand was prepared according to the molar ratio method. The temperature was maintained at 26°C. The absorbance of the above solutions was measured at 660 nm wavelength. The net absorbance was then plotted against the mole ratio of the ligand per mole of metal ion, L/M, which represented in **Figure 4**. Surprisingly, the data 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 Cu- diamine complex is consistent. On the other hand this is not the case in the aqueous media where results obtained by extrapolation of such curves are uncertain and the complex in aqueous medium undergoes appreciable dissociation. Harvy [52] and Manning [53] [54] found that in such cases the curve may be made to break sharply at the perfect mole ratio if the ionic strength of the solution was carefully adjusted by addition of inert electrolyte. One of the key advantage of the ionic liquids they possess high ionic strength and another feature their capability to dissolve most of the metal ions. Again from the curve in **Figure 4** it was possible to calculate the stability constant of the 1:1 Cu(II)-diamine complex and the value obtained is equal  $\text{Log } K_1 = 9.4$ .



**Figure 4.** The plot of absorbance against ethylene diamine (en) mole ratio per a mole of Cu(II) in ethaline.

It is very interesting to observe that the value of the stability constant of the 1:1 Cu(II)-diamine complex obtained by the molar ratio is in very good agreement with the value calculated by using continuous variation method and more over both they are close to the literature value in aqueous media. 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.

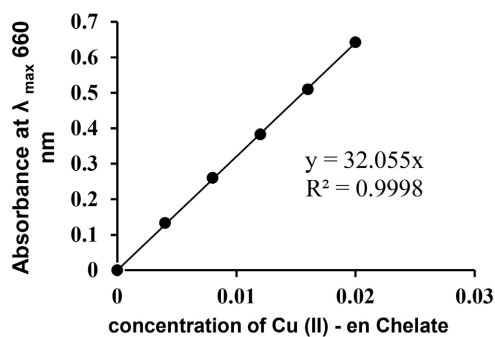
#### Effect of Initial Concentration

The molar ratio method was used to study the effect of initial concentration of both metal and ligand on the extent of formation of the 1:1 Cu-diamine complex.

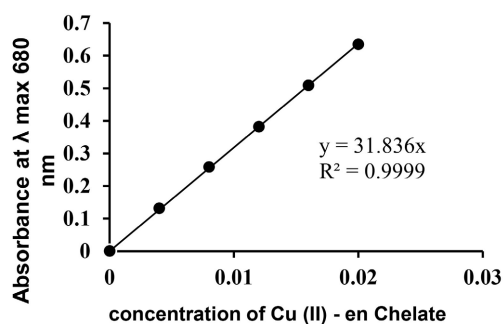
It is interesting to observe that the 1:1 Cu(II)-diamine complex clearly obeys Beer's law in the range of concentration shown in **Table 1**. A plot of absorbance the 1:1 Cu(II)-diamine complex against concentration at two maximum wavelengths 660 nm and 680 nm summarized in **Table 1** It is interesting to observe that the linearity as evident in **Figure 5(a)** and **Figure 5(b)**

**Table 1.** Calibration curve data for copper (II) ethylene diamine complex.

Concentration (mol/dm <sup>3</sup> )	Absorbance at $\lambda_{\max}$ 660 nm	Absorbance at $\lambda_{\max}$ 680 nm
0.00	0.00	0.00
0.002	0.133	0.133
0.004	0.260	0.258
0.006	0.383	0.382
0.008	0.510	0.509
0.012	0.642	0.635



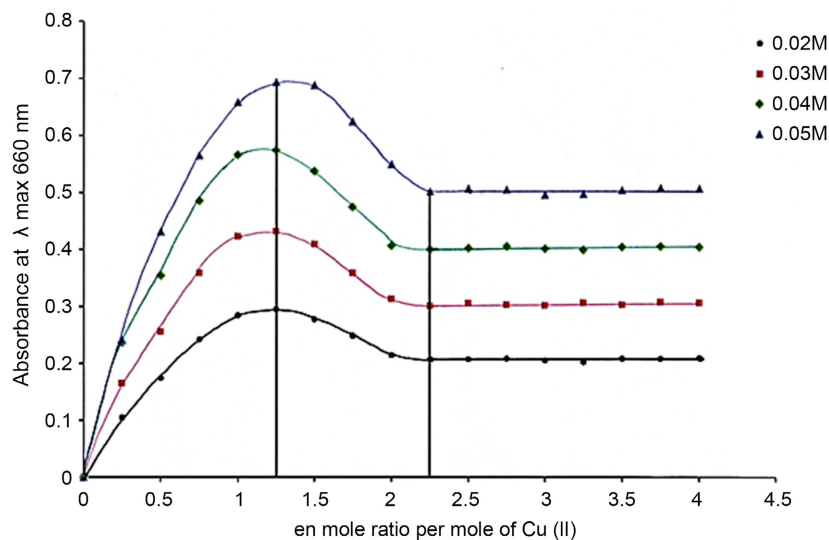
(a)



(b)

**Figure 5.** (a) and (b) show the graph of Cu(II) diamine chelate against its concentration.

The absorbance of the complex increases considerably with increasing of initial concentration of both metal ion and ligand in the range 0.002 M to 0.020 M. The results are summarized in **Table 1**. The plot of absorbance against molar ratio of ethylene diamine L/M, for different initial concentrations, is shown in **Figure 6**, along with the stepwise complex of mole ratio of 1:2 metal to ligand ( $[\text{Cu}(\text{en})_2]^{2+}$ ).

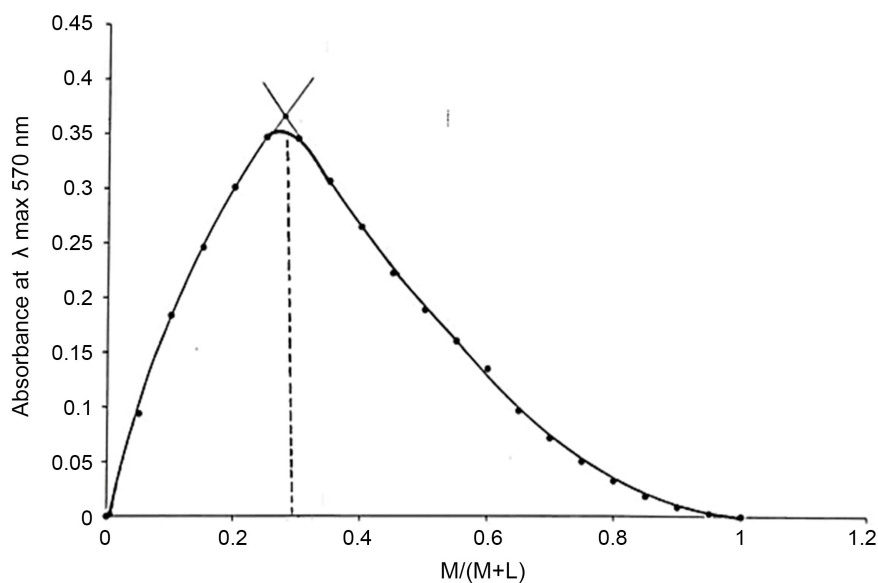


**Figure 6.** The plot of absorbance versus mole ratio of (en) per mole of Cu(II) in deep eutectic solvent as a function of concentration.

It has been observed that the break in **Figure 6** at mole fraction = 2 becomes more evident as the initial concentration of both copper (II) ion and the ethylene diamine increases.

#### The 1:2 Chelate; $[\text{Cu}(\text{en})_2]^{2+}$

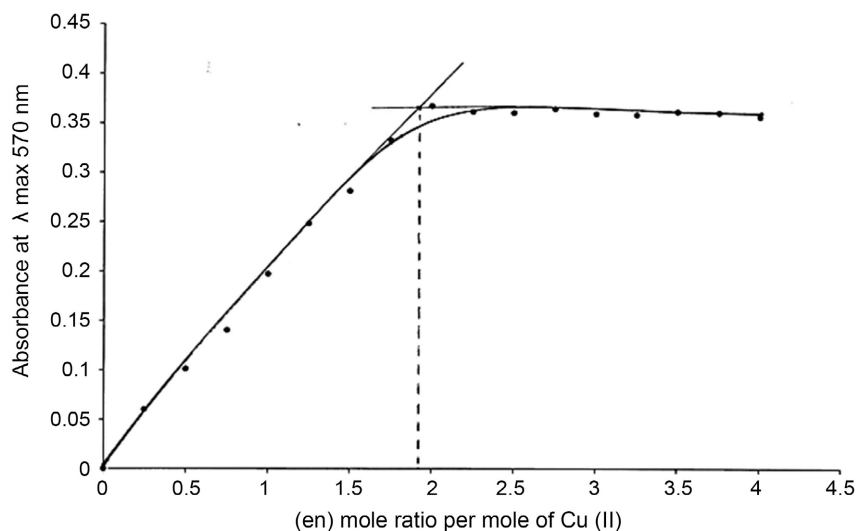
A series of 1 ChCl:2 EG based ionic liquid (ethaline) solutions was prepared according to the continuous variations method. The mole fractions of Cu(II) ions and ethylene diamine were varied between 1.00 and 0.00, keeping the total volume of the solutions constant. The observed absorbance was corrected for the absorbance of the corresponding reference and the net absorbance was then plotted against the mole fraction of the metal ion as illustrated in **Figure 7**. It is evident from **Figure 7**, that the maximum absorbance was observed at the mole fraction of 0.33 of Cu(II) indicating a 1:2 ratio of Cu(II) to ethylene diamine in the complex, however, **Figure 7** shows a break at the mole fraction of 0.5 clearly indicating that the possibility of step wise formation of a 1:1 complex between Cu(II) and the diamine ligand. The stability constant of the 1:2 chelate was calculated from **Figure 7** and found,  $K_2 = 8.73 \times 10^7$  ( $\text{Log } K_2 = 7.94 \approx 8.0$ )



**Figure 7.** The plot of absorbance versus mole fraction of Cu(II) in deep eutectic solvent (ethaline).

This result was further confirmed by the molar ratio method. A series of solutions was prepared in which the volume of the Cu(II) solution 0.02 M, while the volume of the ethylene diamine 0.02 M was varied under similar conditions. The total volume of all the solutions, however, was kept constant. The absorbance of the solutions measured at wavelength 570 nm and 26°C. After correcting for absorbance of the corresponding reference, the net absorbance was then plotted against the mole ratio of the ligand per mole of metal as shown in **Figure 8**. The two straight lines resulting from the extrapolation of the legs of the curve intersect each other at a mole ratio of 1:2 metal to ligand respectively, confirming the

formation of a 1:2 chelate between Cu(II) and ethylene diamine. The stability constant of the ethylene diamine chelate was calculated from **Figure 8**, the result evaluated in this study,  $K_2 = 2.4 \times 10^8$ ,  $\text{Log } K_2 = 8.4$



**Figure 8.** The plot of absorbance versus mole ratio of (en) per mole of Cu(II) in deep eutectic solvents.

Many values have been published for the formation constants of various metal-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 our case as solvent with high ionic strength (ionic liquids solvents) during the experiments and can only be estimated approximately from their Figures [55].

Most of the stability constants of metal complexes with diamine ligands in aqueous solutions have been determined by the potentiometric pH method. The value obtained in this study  $\text{Log } K_2 = 8.4$ ,  $26^\circ\text{C}$  is consistent with the literature values [46] ( $\text{Log } K_2 = 9.05$ ). The slight difference between the value obtained in this study, and the literature values could be attributed to the experimental conditions at which the values were obtained.

Also it is very delightful to notice that the value of stability constant of the 1:2 Cu(II)-diamine complex in ethaline using the molar ratio curve in **Figure 8**; was found consistent with value obtained by the continuous variations method.

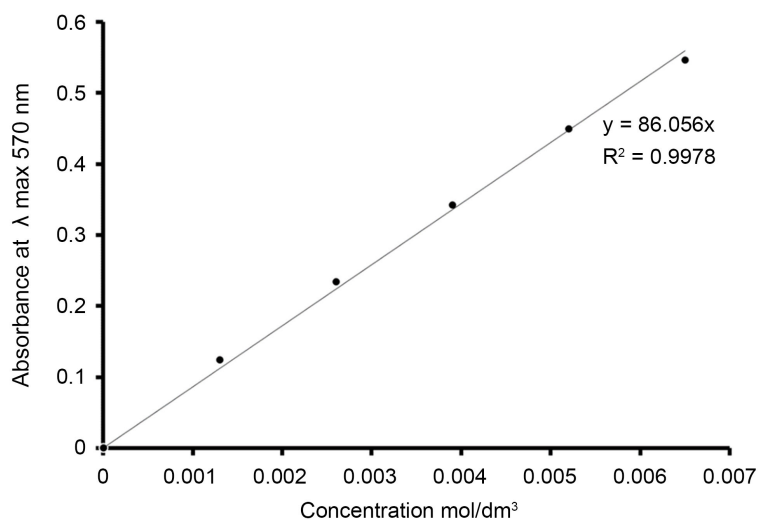
#### **Effect of Initial Concentration**

Again the molar ratio method was applied to probe the effect of initial concentration of both metal and ligand on the extent of formation of the 1:2 Cu-diamine complex in deep eutectic solvent.

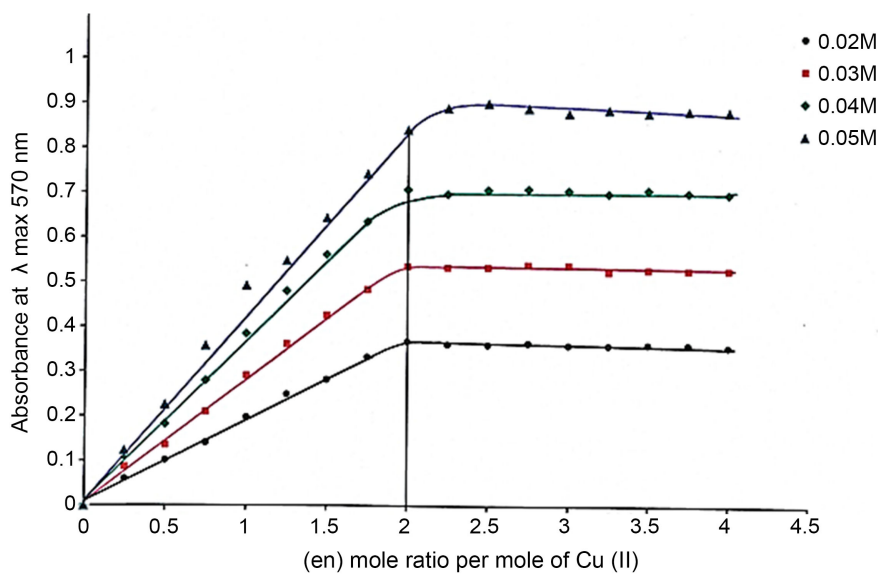
It was noticeable that the 1:2 Cu(II)-diamine complex obeys Beer’s law. A plot of absorbance of the 1:2 Cu(II)-diamine complex versus concentration at maximum wavelengths 750 nm summarized in **Table 2** which shows the linearity as evident in **Figure 9**.

**Table 2.** Calibration curve data for copper (II) ethylene diamine complex.

Concentration (mol/dm <sup>3</sup> )	Absorbance
0.00	0.00
0.002	0.124
0.004	0.234
0.006	0.342
0.008	0.450
0.012	0.547



**Figure 9.** The graph of Cu(II) diamine chelate deep eutectic solvent against its concentration.



**Figure 10.** The plot of absorbance versus mole ratio of (en) per mole of Cu(II) in deep eutectic solvent as a function of concentration.

The absorbance of the complex increases considerably with increase of initial concentration of both metal and ligand in the range 0.002 M to 0.005 M. The results are summarized in **Table 2**. The plot of absorbance against molar ratio of ethylene diamine, L/M for different initial concentration is shown in **Figure 10**. However, it has been observed that no break in **Figure 10** at a mole fraction 1.00 confirming step wise complex 1:1 Cu diamine complex is not established.

## 6. Conclusion

The reaction of Cu(II) ion with ethylene diamine chelate in deep eutectic solvents (DES) has been investigated using Job's and molar ratio methods. Two complexes instantaneously are formed: the first 1:1 mole ratio and the second 1:2 mole ratio at maximum wavelengths 660 nm and 575 nm respectively. The empirical formula and stability constant for both complexes were determined by continuous variations and molar ratio methods. The values of stability, constants  $K_1$  and  $K_2$  were found in good agreement with values obtained in aqueous solution, despite the different conditions, and methods which is encouraged to use the ionic liquids in coordination chemistry studies. The effect of concentration of both complexes  $[\text{Cu}(\text{en})]^{2+}$  and  $[\text{Cu}(\text{en})_2]^{2+}$  was also studied and revealed that both complexes obey Beer's law. The absorbance increases considerably as the concentration increases. For  $[\text{Cu}(\text{en})]^{2+}$ . It has been noted that there is a break at mole ratio 2 as the initial concentration of both the metal and the chelate increases. The 1 ChCl:2 EG based liquid (ethaline) (ionic liquids) is found to be an excellent solvent in coordination chemistry.

## Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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