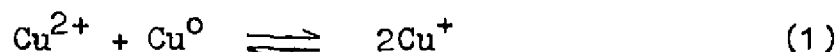


CHAPTER-I

INTRODUCTION

## I N T R O D U C T I O N

Copper(I) salts are unstable in aqueous solutions<sup>1</sup>. They can, however, be stabilized in water containing nitriles, ammonia, organic bases, cyanides, halides and gases like carbon monoxide and ethene<sup>2,3</sup>. In water + acetonitrile (H<sub>2</sub>O + AN) mixtures, the stabilization of copper(I) salts takes place because of preferential solvation of Cu<sup>+</sup> by acetonitrile<sup>2,3</sup> (AN). This strong preferential solvation and hence stabilization of Cu<sup>+</sup> by AN forms the basis for the reversible reaction:



In the presence of sufficient amount of AN, reaction (1) proceeds rapidly in the forward direction and when AN is removed from the solution, the backward reaction becomes extremely fast. When the forward reaction proceeds, the rate of the backward reaction becomes negligibly small and vice versa.

Before presenting a review of literature on the kinetics of the reversible reaction (1) or on other similar reactions in some solvent media, it is desirable to survey the literature on preferential solvation studies of Cu<sup>+</sup> in mixed solvents<sup>2-9</sup>. It will also be meaningful if the specific type of interactions<sup>9-11</sup> which are responsible for the preferential solvation of Cu<sup>+</sup> are

briefly reviewed. In the following few pages of this dissertation, therefore, a brief survey of literature on the comparative study of the solvation behaviour of  $\text{Cu}^+$  and  $\text{Ag}^+$  with other ions has been presented. Some studies on the preferential solvation of  $\text{Cu}^+$  in mixed solvents<sup>2-9</sup> and on the complexing tendency<sup>3,12-14</sup> of this ion with bases and halide ions have also been reported.

Detailed studies of the solvation of alkali metal cations in different dipolar aprotic solvents show that these cations are solvated mainly by electrostatic ion-dipole type of interactions<sup>15,16</sup> which are interactions of Born<sup>17</sup> type or its modifications<sup>18,19</sup>. Similar studies indicate that all the anions have very poor solvation in dipolar aprotic solvents<sup>20-22</sup>, though, they are strongly solvated in protic solvents<sup>23,24</sup>. The solvation of  $\text{Ag}^+$  and  $\text{Cu}^+$  in some solvents is similar to that possessed by alkali metal cations and takes place by the simple electrostatic ion-dipole type of interactions<sup>16,20,25</sup>. In some other solvents  $\text{Ag}^+$  and  $\text{Cu}^+$ , in addition to, electrostatic ion-dipole interactions, are solvated by an entirely different and specific type of interaction which is primarily of covalent character<sup>15,16</sup>. The behaviour of  $\text{Ag}^+$  and  $\text{Cu}^+$  in AN is a well known example of this special type of interaction<sup>10,11,16</sup>. It is in part due to the back bonding interaction of the  $d^{10}$  cations with the nitrile group of AN<sup>9,26</sup>. The solvation behaviour of  $\text{Ag}^+$  and  $\text{Cu}^+$  in many

more organic solvents is interesting and differs from the solvation behaviour possessed by many other ions in such solvents<sup>11,15,16</sup>.

Gill and Sekhri<sup>7</sup> and Gill and Cheema<sup>6</sup> have recently reported the conductance of  $\text{CuNO}_3$  in AN + benzene and the conductance and viscosity of  $\text{CuClO}_4 \cdot 4\text{AN}$  in AN + N,N-dimethylformamide (AN + DMF) mixtures respectively. They observed that  $\text{Cu}^+$  was preferentially solvated by AN in AN + benzene mixtures and by AN in DMF-rich region and by DMF in AN-rich region of the AN + DMF mixtures. In another study Gill and Cheema<sup>5</sup> reported the conductance of  $\text{CuClO}_4 \cdot 4\text{AN}$  in a large number of solvent mixtures of DMF with organic bases like pyridine and picolines and with other organic solvents like hexamethylphosphotriamide, dimethylsulphoxide (DMSO) and 1,1,3,3-tetramethylurea. They compared the solvation behaviour of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cu}^+$  and  $\text{Ag}^+$  in these mixed solvents and observed that the solvents more basic than DMF had preferential solvation for  $\text{Cu}^+$  in these solvent systems. The solvation behaviour of  $\text{Cu}^+$  and  $\text{Ag}^+$  was found to be different from the behaviour shown by alkali metal cations. These studies indicated the specific type of interaction possessed by  $\text{Cu}^+$  and  $\text{Ag}^+$  with some organic solvents<sup>5</sup>.

Conductance and viscosity measurements using  $\text{CuClO}_4 \cdot 4\text{AN}$  have been recently made in AN + methanol<sup>27</sup> and AN + acetone<sup>28</sup> mixtures. These studies also indicate preferential solvation

of  $\text{Cu}^+$  by AN in both of these solvent systems.

Parker and coworkers<sup>2,4</sup> from proton magnetic resonance studies of the solutions of  $\text{Na}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Cu}^+$  and  $\text{Ag}^+$  salts in  $\text{H}_2\text{O} + \text{AN}$  and  $\text{H}_2\text{O} + 3\text{-hydroxypropanenitrile}$  mixtures of varying compositions showed that the inner solvation shells of  $\text{Na}^+$  and  $\text{Cu}^{2+}$  were almost entirely composed of water, but more than half of the solvation sites of  $10^{-2} \text{ mol dm}^{-3}$  solutions of  $\text{Cu}^+$  or  $\text{Ag}^+$  were occupied by AN or by 3-hydroxypropanenitrile in 15 mol % nitrile in water + nitrile mixtures.

$^{63}\text{Cu}$ -NMR spectra of  $\text{Cu}(\text{AN})_4\text{X}$  ( $\text{X} = \text{ClO}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ) and  $\text{Cu}(\text{Py})_4\text{X}$  ( $\text{X} = \text{ClO}_4^-$ ,  $\text{BF}_4^-$  and  $\text{Py} = \text{Pyridine}$ ) in solution were reported at different temperatures and concentrations by Ochsenbein and Schlaepfer<sup>29</sup>. The influence of temperature on the line width and chemical shift indicated an equilibrium of  $\text{Cu}(\text{AN})_4^+$  and  $\text{Cu}(\text{Py})_4^+$  with another complex of lower symmetry. The preferential solvation of  $\text{Cu}^+$  by pyridine in AN + pyridine mixtures was indicated.

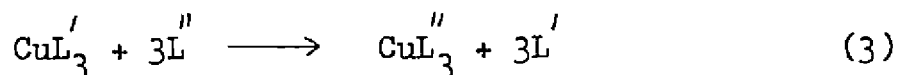
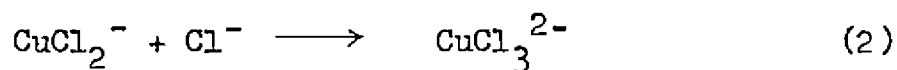
Parker and coworkers<sup>2,3</sup> measured free energies of transfer of  $\text{Cu}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$  and  $\text{Na}^+$  from water to  $\text{H}_2\text{O} + \text{AN}$  mixtures using emf and solubility methods. They found that the free energy of transfer for  $\text{Ag}^+$  and  $\text{Cu}^+$  became more negative while that of  $\text{Cu}^{2+}$  and  $\text{Na}^+$  became more positive when the amount of AN increased in the mixtures. This showed strong preferential solvation of  $\text{Ag}^+$

and  $\text{Cu}^+$  by AN and that of  $\text{Cu}^{2+}$  and  $\text{Na}^+$  by water. These authors<sup>3</sup> also measured the reduction potentials of  $\text{Pt}/(\text{Cu}^{2+}, \text{Cu}^+)$ ,  $\text{Cu}^{2+}/\text{Cu}$  and  $\text{Cu}^+/\text{Cu}$  electrodes in water containing AN, 3-hydroxypropanenitrile, ammonia, pyridine, thioamides, cyanides, halides, thiosulphates and some gases like carbon monoxide, ethene and propene. The free energies of transfer of  $\text{Cu}^+$  from water to water containing these additives were calculated; which from water to water containing additives became more negative showing thereby that  $\text{Cu}^+$  was stabilized in the presence of additives. The order of stabilization of  $\text{Cu}^+$  was reported to be:

$$\text{CN}^- \gg \text{S}_2\text{O}_3^{2-} > \text{Me}_2\text{NCHS} > \text{KI} > \text{NH}_3 > \text{C}_5\text{H}_5\text{N} > \text{KBr} > \text{KCl} > \text{C}_3\text{H}_5\text{OH} \gg \text{AN}, \text{CO}, \text{C}_2\text{H}_4 > \text{C}_3\text{H}_6.$$

Ahrland and Tagesson<sup>12</sup> studied the bromide, iodide and thiocyanate complexes of  $\text{Cu}^+$  in aqueous solutions containing  $\text{NaClO}_4$  of ionic strength  $5 \text{ mol dm}^{-3}$  using potentiometric and solubility measurements. They observed that at low  $\text{Cu}^+$  concentrations, mononuclear complexes predominated. The solubility of these mononuclear complexes decreased and the stability increased in the order:  $\text{Br}^- > \text{I}^- > \text{SCN}^-$ . At higher metal concentrations the polynuclear complexes were formed in appreciable concentrations. In another study, Ahrland and coworkers<sup>13</sup> using calorimetric measurements obtained thermodynamic information on the reaction of copper(I) salts with halide ions, which stabilized  $\text{Cu}^+$  in aqueous solutions.

They studied the following reactions:



Their results showed that these complexes were enthalpy stabilized. The complex formation reaction became more exothermic as the ligand became softer i.e. in the sequence:  $\text{Cl}^- < \text{Br}^- < \text{I}^-$  which, of course, was also the order of increasing stability of the complexes. In a recent study by Ahrlund and coworkers<sup>30</sup> using potentiometric and calorimetric methods, the thermodynamics of copper(I) halide complex formation was studied in DMSO at ionic strength of  $1 \text{ mol dm}^{-3}$  produced by  $\text{NH}_4\text{ClO}_4$ . These authors showed that  $\text{Cu}^+$  and its complexes were highly solvated by DMSO and were fairly stabilized in this solvent. The formation of  $\text{CuCl}_2^-$  was found to be an exothermic process while  $\text{CuBr}_2^-$  and  $\text{CuI}_2^-$  were formed in slightly endothermic reactions. The entropy changes in all the cases were large and positive.

Solubility of copper(I) chloride in copper(II) chloride-copper(I) chloride-hydrochloric acid-water system was determined by Pochtarev and coworkers<sup>14</sup> between  $20\text{-}30^\circ\text{C}$ . These authors

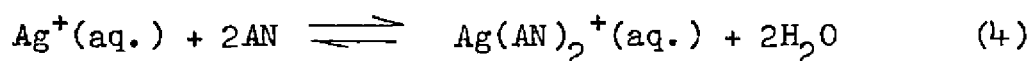
reported that solubility of cuprous chloride decreased as the temperature increased. The decrease in solubility with increase of temperature was explained to be due to the dissociation of  $\text{CuCl}_2^-$  and  $\text{CuCl}_3^{2-}$  complexes formed in the solution.

A survey of literature on the studies of copper(I) salts as given above shows that preferential solvation studies of  $\text{Cu}^+$  in mixed solvents are rare in the literature<sup>2-9</sup>. Such studies using silver(I) salts, however, have recently been reported by a number of workers. As the solvation behaviour of  $\text{Ag}^+$  and  $\text{Cu}^+$  is similar, therefore, it will be meaningful if some preferential solvation studies of  $\text{Ag}^+$  are also briefly reviewed, so that some additional information about preferential solvation of  $\text{Cu}^+$  can be indirectly obtained in those solvent mixtures where preferential solvation data on  $\text{Ag}^+$  are available and on  $\text{Cu}^+$  are lacking.

During recent years many investigations of silver salts have been reported in mixed solvents using conductance<sup>31-34</sup>, solubility<sup>35-38</sup>, emf<sup>35-38</sup>, transport numbers<sup>39-44</sup> and NMR<sup>35,44</sup> measurements. In all these studies  $\text{Ag}^+$  was found to possess strong preferential solvation by one of the solvents. Rodehueser and Schneider<sup>35</sup> from solubility and NMR measurements using  $\text{Ag}_2\text{SO}_4$  and  $\text{AgClO}_4$  in DMSO and methanol mixtures found that  $\text{Ag}^+$  was more strongly solvated by DMSO as compared to methanol. Studies of  $\text{Ag}_2\text{SO}_4$  in methanol + N-methylformamide mixtures from



solubility and emf measurements were attempted by Kalidas and Schneider<sup>36</sup>. Their results showed preferential solvation of  $\text{Ag}^+$  by N-methylformamide in the mixtures. Gill and coworkers<sup>32,33,45</sup> from conductance and viscosity studies of  $\text{AgClO}_4$  and  $\text{AgNO}_3$  in acetone + DMF mixtures found that  $\text{Ag}^+$  was preferentially solvated by DMF upto 20 mol % DMF in the mixtures. In another study Gill and Cheema<sup>34</sup> reported that  $\text{Ag}^+$  had very strong preferential solvation by all the bases and by AN in binary mixtures of DMF containing 1 mol % of pyridine,  $\alpha$ -picoline,  $\beta$ -picoline,  $\gamma$ -picoline and AN. Griffiths and coworkers<sup>46-48</sup> from conductance studies of  $\text{AgNO}_3$  and  $\text{AgClO}_4$  showed preferential solvation of  $\text{Ag}^+$  by AN, pyridine, picolines and by other organic bases in binary mixtures of these bases with acetone and methanol. Cox and Parker<sup>49</sup> and Chantooni and Kolthoff<sup>50</sup> from solubility measurements of some silver salts determined medium activity coefficients of  $\text{Ag}^+$  between water and AN and found that  $\text{Ag}^+$  showed strong preferential solvation effects by AN. Strehlow and Koepf<sup>31</sup> from conductance and viscosity measurements of the solutions of  $\text{AgNO}_3$  in  $\text{H}_2\text{O}$  + AN mixtures found that  $\text{Ag}^+$  had preferential solvation by AN. They proposed the following equilibrium for the complex formation between  $\text{Ag}^+$  and AN:



Rao and coworkers<sup>51</sup> from conductance studies of silver acetate in  $H_2O + AN$  mixtures showed that  $Ag^+$  was preferentially solvated by AN while acetate ion was preferentially hydrated in these mixtures. Janardhanan and Kalidas<sup>38</sup> also studied preferential solvation of silver acetate in water, methanol and their mixtures with DMSO by employing emf and solubility measurements. These authors found that  $Ag^+$  was preferentially solvated by DMSO and acetate ion by water or methanol. The selective solvation of silver bromate and iodate was studied by Janardhanan and Kalidas<sup>37</sup> in aqueous DMSO solutions by emf and solubility measurements. The results were interpreted in terms of heteroselective solvation of both the salts; the  $Ag^+$  being preferentially solvated by DMSO and the halate ions selectively hydrated in the mixtures.

Oliver and Janz<sup>52</sup> studied the behaviour of  $AgNO_3$  in  $H_2O + AN$  mixtures by Raman spectra using He-Ne ( $6328 \text{ \AA}$ ) and  $Ar^+$  ( $4880 \text{ \AA}$ ) lasers as excitation sources. The variations in relative intensities of the bands with concentration were interpreted relative to ion-pair formation and selective solvation of ions in this mixed solvent system. The studies indicated that  $Ag^+$  was preferentially solvated by AN and  $NO_3^-$  by water.

The work reported by Parker and coworkers<sup>2,3,9,53-62</sup> on (i) preferential solvation of  $Cu^+$  in  $H_2O + AN$  mixtures,

(ii) stabilization of copper(I) salts in water containing nitriles, ammonia, organic bases and other copper(I) stabilizers and (iii) the industrial importance of the stabilized copper(I) solutions is of great interest. These authors, from studies for many years on this subject, have suggested useful methods for the economical electrorefining of copper. In some of their investigations they have reported the kinetics of the leaching processes and have established new methods for leaching copper salts in solution directly from the copper ores<sup>54,59</sup>. In addition, they have also reported the kinetics of the reduction of copper salts in  $H_2O + AN$  mixtures at a number of electrodes<sup>2,3,61</sup>. Exhaustive studies by Parker and coworkers<sup>2,3</sup> have also shown that in acidic  $H_2O + AN$  and water + 3-hydroxypropanenitrile mixtures of appropriate concentrations, copper(I) sulphate solution as concentrated as  $\approx 3 \text{ mol dm}^{-3}$  could be prepared and stabilized. These solutions have practical importance as they provide a cheaper and quicker hydrometallurgical method for the electrorefining of copper metal as compared to other recent electrochemical methods of copper refining outlined below.

Muir and Parker<sup>62</sup> studied the refining of copper via one-electron process using cuprous chloride in brine or cuprous sulphate in aqueous AN solutions. This process offered significant energy savings over conventional processes involving

cupric sulphate solutions. Electrochemical recovery of copper from industrial by-product of copper compounds was made by Vasudevarao and coworkers<sup>63</sup>. They reported that copper upto 99.82% purity could be prepared by their method. Electrorefining of copper<sup>64</sup> from cupric sulphate solutions containing glue and chloride ions showed that electrorefining was improved and the purity of copper metal was increased by adding 2-5 mg per litre of the products from the condensation of thiourea and aliphatic acid amino amides to the bath. Lalaeva<sup>65</sup> studied the electrolysis of copper containing solutions from concentrates for copper powder production. The effect of the concentration of copper, sulphuric acid and current density (c.d.) on the technological indicators of the process, the grain size composition and the purity of the powder was examined. The c.d. providing the required purity of powder was satisfactory upto  $2000 \text{ A/m}^2$ , and a further increase in c.d. led to contamination of the copper powder. The effect of c.d. on current efficiency in the electrorefining of copper was studied by Orekhov and coworkers<sup>66</sup>. A c.d. value of  $300 \text{ A/m}^2$  gave 87-89% current efficiency, increased the yield of copper and decreased the operating cost by 3.5-5.5%.

Electrochemical study of the production of pure copper powders was made by Fofanov and coworkers<sup>67</sup>. These authors studied the production of copper powders by reduction of divalent

copper(II) salts with trivalent titanium in acidic solutions. The effect of concentrations of the system components and of the presence of complexing agents and surfactants on the reduction process and on the size of copper grains was studied by plotting electrolytic polarization curves. Mellor<sup>68</sup> described a process for the recovery of copper from aqueous solutions containing  $\text{Cu}^{2+}$ ,  $\text{Cu}^+$  and  $\text{Cl}^-$ , obtained from the etching of copper layers in printed circuit fabrication. By treating with cupric chloride solution in an electrolytic cell, the  $\text{Cu}^+$  was oxidised to  $\text{Cu}^{2+}$  at the anode and  $\text{Cu}^+$  was reduced to elemental copper at the cathode. A continuous process for the production of pure copper powder in an electrochemical reactor with tangential inlet electrolyte was studied in reference to the technological aspects, e.g. c.d., sulphuric acid concentration,  $\text{Cu}^{2+}$  concentration etc. by Stankovic and coworkers<sup>69</sup>. The copper sulphate concentrations were 0.016, 0.032, 0.048 and 0.064 mol  $\text{dm}^{-3}$  and the sulphuric acid concentrations were 0.5, 1.0 and 1.5 mol  $\text{dm}^{-3}$ . A two-step process was used and after the copper powder was obtained it was washed with water and alcohol and finally dried in a nitrogen gas atmosphere at 423<sup>o</sup>K.

Shiga and coworkers<sup>70</sup> studied the electrolytic purification of copper by adding the condensation product of formaldehyde and naphthalene sulfonic acid to an acidic copper salt solution. They found that the copper metal purified by this method had only

small quantities of metal impurities like Bi, Pb, Sb, As and Ag. Studies by Clark<sup>71</sup> showed that copper could be recovered in pure state from solutions by electrorefining method. They found that using titanium meshes connected to copper hanger bar as anode and copper metal as cathode, pure copper metal containing Zn < 10, Sn < 2, Pb < 2, Fe < 5, Ni < 1, Mn < 1, Bi < 2, Sb < 5, As < 2 and Te < 5 ppm could be recovered with a current density of 186 A/m<sup>2</sup>.

Fajardo and coworkers<sup>72,73</sup> proposed a method of electrowinning of copper from cuprous sulphide leaching in solutions of H<sub>2</sub>O + AN mixtures using copper cathode and graphite anode. The current efficiency of the process was determined by weighing the cathode and using a copper coulometer. The addition of AN was found not to be too relevant in the cathodic efficiency but was important in relation to energy requirements.

Satchell<sup>74</sup> developed a method for electrochemical production of copper from sulphide ores of copper. The sulphide ore was treated with oxygen and an aqueous leaching solution of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> to form a leach liquor which contained sulphato and carbonato amine complexes of copper. After heating this leach liquor to form ammonia and carbon dioxide and treating the strongly alkaline material to precipitate sulphates and evolve additional ammonia, copper was recovered by electrolysis.

Illangovan and Vasu<sup>75,76</sup> reported that acidic Fe<sup>3+</sup> was an

efficient leachant for chalcopyrite ( $\text{CuFeS}_2$ ). They utilized galvanic cementation process consisting of iron anode (in acidic ferrous chloride solution) and copper cathode (in leach solution) to produce pure copper. The process was simple, less expensive and could be used to deposit 76% of the original copper concentration in  $\sim$ 24 hours.

During the recent years a large number of kinetic investigations have been carried out for the study of the equilibrium in copper-copper ions system in mineral acids and in salt solutions of varying ionic strengths. Kinetic investigations have also been made on the reduction of copper salts at the electrodes. Such studies have also been attempted for the leaching processes of copper salts from various ores of copper. Although, kinetic investigations for many of these reactions are well established but the kinetics of the reversible reaction (1) in  $\text{H}_2\text{O} + \text{AN}$  mixtures have not been investigated in the literature so far.

Makarov<sup>77</sup> studied the equilibrium in copper-copper ions-sulphuric acid system. The concentration of  $\text{Cu}^+$  formed at equilibrium was established by the regression analysis of the experimental data. The author reported that the formation of  $\text{Cu}^+$  in the system was a first order reaction and the rate constant was independent of  $\text{Cu}^{2+}$  concentration. Naboichenko and Khudyakov<sup>78</sup> studied the rate of formation of  $\text{Cu}^+$  during the

reduction of  $\text{Cu}^{2+}$  by hydrogen gas in sulphuric acid solutions. They showed that  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  deposited metallic copper autocatalytically.

Kozin and coworkers<sup>79</sup> showed that  $\text{Cu}^+$  was formed in the  $\text{Cu-CuCl}_2\text{-HCl}$  system and was carried completely into the solution as  $\text{CuCl}_2^-$ . The equilibrium concentration of  $\text{CuCl}_2^-$  was dependent on the concentrations of  $\text{Cu}^{2+}$  and  $\text{Cl}^-$  in the solution.

Ciavatta and coworkers<sup>80</sup> studied the equilibrium between  $\text{Cu}^{2+}\text{-Cu-Cu}^+$  in aqueous  $\text{NaClO}_4$  and  $\text{Na}_2\text{SO}_4$  ionic media of varying ionic strengths by passing  $\text{Cu}^{2+}$  solutions through a column packed with finely divided copper metal. The effluent liquid phase was made to percolate at a rate low enough for equilibrium to be attained and the number of equivalents of reducing agents was determined by constant coulometry. The equilibrium constant at infinite dilution was evaluated by applying the specific interaction theory to the experimental results and the value of  $\log K^0$  was found to be -5.73.

Kinetic studies of the reaction of copper with cupric chloride solutions was reported by Ivascan and Bandrabur<sup>81</sup>. A mathematical model was proposed to explain the kinetic results. The effects of temperature and concentration of cupric chloride on the reaction rate were also studied.

Parker and coworkers<sup>61</sup> have recently reported the kinetics



of  $\text{Cu}^{2+}/\text{Cu}^+$  sulphate and chloride systems in water containing various cosolvents at mercury, platinum and glassy carbon electrodes using cyclic voltametry. They found that the two-electron process:  $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}^0$  was normally observed in water in the absence of  $\text{Cu}^+$  stabilizing ligands. In the presence of copper(I) stabilizing bases like nitriles<sup>82</sup> and ammonia<sup>83</sup> in water, however, the electroreduction has been found to take place in two stages i.e.  $\text{Cu}^{2+} + \text{e}^- \rightleftharpoons \text{Cu}^+$  and  $\text{Cu}^+ + \text{e}^- \rightleftharpoons \text{Cu}^0$ . Parker and coworkers<sup>61</sup> also observed that in alkaline ammonia + ammonium chloride solutions the reduction of  $\text{Cu}^{2+}$  as well as that of  $\text{Cu}^+$  was very fast at mercury electrodes. The reduction of  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  in  $\text{H}_2\text{O} + \text{AN}$  mixtures was the fastest at platinum electrode and slowest at the glassy carbon electrode. In addition, these authors observed that the electrode processes were faster in chloride solutions than in sulphate solutions and the rate of electron transfer for the  $\text{Cu}^{2+}/\text{Cu}^+$  couple on platinum electrode in  $\text{H}_2\text{O} + \text{AN}$  mixtures containing sulphuric acid decreased with the increase of AN content in the order  $30\% > 50\% > 85\%$ .

A kinetic study of the  $\text{Cu}^{2+}/\text{Cu}^+$  system in chloride media at the glassy carbon electrode was reported by Kiekens and coworkers<sup>84</sup>. The kinetic parameters indicated a quasireversible process.

Rotating disc electrode and cyclic voltametry studies of the  $\text{Cu}^{2+}/\text{Cu}^+$  couple in hydrochloric acid was studied by Cofre and

Bustos<sup>85</sup>. These studies indicated the existence of two possible mechanisms for the redox reaction depending on the potential sweep rate. At low sweep rates, the degree of electrode coverage was high and the reaction followed a mechanism:  $\text{Cu}^{2+}(\text{sol.}) \rightleftharpoons \text{Cu}^{2+}(\text{adsorbed}); \text{Cu}^{2+}(\text{adsorbed}) + e^{-} \longrightarrow \text{Cu}^{+}(\text{adsorbed}); \text{Cu}^{+}(\text{adsorbed}) \rightleftharpoons \text{Cu}^{+}(\text{sol.})$ . At high sweep rates the degree of electrode coverage was relatively small and the mechanism proposed for the redox reaction in that case was:  $\text{Cu}^{2+}(\text{sol.}) + e^{-} \longrightarrow \text{Cu}^{+}(\text{adsorbed}) \rightleftharpoons \text{Cu}^{+}(\text{sol.})$ .

Buisson and coworkers<sup>86</sup> studied spectrophotometrically the kinetics of the reduction of  $\text{CuL}_2^{2+}$  (L = 2,2'-bipyridyl) to  $\text{CuL}_2^{+}$  in water containing various amounts of  $\text{Cu}(\text{ClO}_4)_2$ , the ligand and  $\text{HClO}_4$ . At low acid concentrations the reaction proceeded by two pathways; the first was independent of the  $\text{Cu}^{+}$  species whereas the second was autocatalyzed by  $\text{Cu}^{+}$  species by a mechanism exhibiting inverse dependence on the acid concentration. A third acid-catalyzed pathway became significant at high acid concentrations.

Recently, the effect of some cations on the kinetics and mechanism of electrodeposition and electrodisolution of copper was studied by Stankovic<sup>87</sup> by the galvanostatic method. The measured kinetic parameters indicated that the presence of  $\text{NH}_4^{+}$  had an inhibitory effect, the presence of  $\text{Na}^{+}$  and  $\text{Mn}^{2+}$  had no effect, while  $\text{Zn}^{2+}$  produced a catalytic effect on the kinetics

of both dissolution and deposition of copper. The effect of  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  on the equilibrium in the copper-copper ions-sulphuric acid system was studied by Makarov and Suleimanova<sup>88</sup> using the method of fixed  $\text{Cu}^+/\text{Cu}^{2+}$  redox potential in nitrogen atmosphere. The rate constant for  $\text{Cu}^+$  accumulation was determined. The authors found that the presence of  $\text{Ni}^{2+}$  or  $\text{Zn}^{2+}$  did not affect significantly the first order rate constant of  $\text{Cu}^+$  formation.

Dzhusupov and coworkers<sup>89,90</sup> studied the kinetics of the reduction of copper sulphide in DMF and propylene carbonate. Galvanostatic discharge curves were shown in solutions of  $0.8 \text{ mol dm}^{-3} \text{ LiClO}_4$  in DMF and  $1 \text{ mol dm}^{-3} \text{ LiClO}_4$  in propylene carbonate at different c.d. values. They reported that the mechanism of copper sulphide reduction in aprotic solvents did not correspond to the earlier known two-stage and one-stage mechanisms, but was more complex and had dependence on the nature of the solvent.

Swinbourne and Harris<sup>91</sup> studied the kinetics of copper(I) sulphide chlorination. The reaction of  $\text{Cl}^-$  with  $\text{Cu}_2\text{S}$  cylinders was investigated to elucidate the reaction mechanism. The reaction was topochemical and the main product was cuprous chloride. These authors observed that sulphide core did not change significantly in diameter, but copper concentration in the core decreased as the reaction progressed and the core

transformed from  $\text{Cu}_2\text{S}$  to  $\text{Cu}_{2-x}\text{S}$  (digenite) and  $\text{CuS}$  precipitated at the sulphide chloride interface. The reaction rate was controlled by the diffusion of  $\text{Cu}^+$  in the sulphide core. The temperature effect on the reaction rate was also studied and it was found that the temperature was the only external variable which affected the reaction rate.

Kinetics of the oxidation of chalcocite ( $\text{Cu}_2\text{S}$ ) to form  $\text{CuS}$  and hence  $\text{Cu}^{2+}$  using oxygen in buffered aqueous ammonia solution at pH 10.5 at  $30^\circ\text{C}$  was recently reported by Parker and coworkers<sup>57</sup>. The rate of the oxidation was followed by determining the increase in the concentration of  $\text{Cu}^{2+}$  formed with time. The authors observed that the increase in oxygen pressure increased the rate of oxidation of  $\text{CuS}$  in  $7 \text{ mol dm}^{-3}$  aqueous ammonia buffered with  $1.5 \text{ mol dm}^{-3}$  ammonium sulphate. The plot of  $\log K_S$  against  $\log P(\text{O}_2)$  was found to be linear with slope 0.45 over 20 to 70% oxidation of  $\text{CuS}$ . This indicated the order of dependence of the rate on oxygen as 0.45. These authors also studied the effect of aqueous ammonia and hence the effect of pH on the reaction rate. The increase in concentration of ammonia increased the stability of the  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  complex. A plot of  $\log K_S$  against  $\log (\text{NH}_3)$  for the oxidation of  $\text{CuS}$  was also linear with slope 0.7. This showed an order of this reaction in ammonia to be 0.7.

Some workers<sup>54,92,93</sup> have studied the kinetics of the

leaching of chalcocite ( $\text{Cu}_2\text{S}$ ), covellite ( $\text{CuS}$ ) and other copper minerals with iron(III) sulphate or chloride in water. Studies with rotating discs showed that  $\text{Cu}_2\text{S}$  reacted rapidly at first and the rate of leaching was proportional to  $\text{Fe}^{3+}$  concentration. When half the copper was leached, the leaching process became slow and the rate of leaching became independent of the concentration of  $\text{Fe}^{3+}$ .  $\text{CuS}$  and chalcopyrite ( $\text{CuFeS}_2$ ) were found to be leached of their copper more slowly than the blaubleibender-covellite ( $\text{Cu}_x\text{S}$ ,  $x = 1 - 1.1$ ). The greater reactivity of blaubleibender-covellite was explained to be due to its defective crystal structure and many active sites.

The reaction kinetics of  $\text{Cu}_2\text{S}$ -Cu system melts with hydrogen gas was studied between  $1150-1300^\circ\text{C}$  by Liu and coworkers<sup>94</sup>. They gave the rate equations in the sulphur-rich single phase, in the miscibility gap and in the copper-rich phase as functions of sulphur concentration and hydrogen gas partial pressure. The activities of sulphur in copper in the melt were calculated by mathematical models. They reported that the reaction rates and activities of sulphur which they calculated were valid when the hydrogen gas flow was between 200 to  $300 \text{ ml min}^{-1}$ .

Ghali and coworkers<sup>95</sup> studied the anodic dissolution characteristics of commercial and synthetic covellite in hydrochloric acid. The dissolution was strongly influenced by the pH and the chloride ion concentration. The dissolution rate

could be accelerated by the formation of  $\text{CuCl}_2^-$  complex at high chloride concentrations, whereas at lower concentrations of hydrochloric acid, the electrochemical oxidation to sulphate was predominant.

#### AIM OF THE PRESENT WORK

A detailed survey of the literature reveals that during the last few years a considerable amount of work has been done on (i) electrorefining of copper, (ii) study of the kinetics of the reduction processes involving copper salts at the electrodes and (iii) leaching of copper salts from various copper ores. In most of these investigations methods for the recovery of pure copper from crude samples in large scale have been presented. A limited number of attempts, however, have been made to investigate systematically the preferential solvation of  $\text{Cu}^+$  in mixed solvents, on which most of these studies are based. The kinetics of the reversible reaction (1), which forms the basis for the development of a novel, cheaper and quicker hydrometallurgical method for the purification of copper in large scale have also not been investigated in  $\text{H}_2\text{O} + \text{AN}$  mixtures.

Measurement of molar conductances of electrolytes in mixed solvents provides limiting molar conductances at infinite

dilution ( $\Lambda_o$ ). From these  $\Lambda_o$  values, limiting ionic conductances at infinite dilution ( $\lambda_i^o$ ) can be calculated. The evaluation of solvated radii of ions from the  $\lambda_i^o$  values and the examination of these solvated radii as a function of solvent composition can be used to provide information regarding preferential solvation of ions in mixed solvents. With this aim in mind molar conductances of  $\text{Bu}_4\text{NBPh}_4$ ,  $\text{Bu}_4\text{NClO}_4$  and  $\text{CuClO}_4 \cdot 4\text{AN}$  have been measured in several  $\text{H}_2\text{O} + \text{AN}$  mixtures at  $25^\circ\text{C}$  so that some information regarding preferential solvation of  $\text{Cu}^+$  in  $\text{H}_2\text{O} + \text{AN}$  mixtures could be obtained from conductance measurements and the results could be compared with those of Parker and coworkers<sup>2-4</sup> derived from emf and NMR measurements.

The major aim of the present investigation, however, was to study the kinetics of the reversible reaction (1) in  $\text{H}_2\text{O} + \text{AN}$  mixtures under varying conditions with the result the optimum conditions for the forward and the backward reactions in turn could be available. It was also expected that once the optimum conditions for the forward and the backward reaction of the reversible reaction (1) in turn had been established, this work would provide a novel, simple, quick and economical method for the purification of copper in large scale. The kinetic studies of the reversible reaction (1) were expected to throw light on the following points:

- i) Whether there was a complete conversion of  $\text{Cu}^{2+}$  into  $\text{Cu}^+$

when reaction proceeded in the forward direction and whole of  $\text{Cu}^+$  was converted into  $\text{Cu}^{2+}$  when the backward reaction took place?

- ii) What was the maximum time period in which there was maximum conversion of  $\text{Cu}^{2+}$  into  $\text{Cu}^+$  and vice versa in the reversible reaction?
- iii) Whether the rate of the reaction was dependent upon the amount of AN? If the rate of the reaction was dependent upon the concentration of AN, then what was the appropriate composition of the mixture of water with AN at which the rate of the reaction was maximum?
- iv) Was there any appropriate concentration of copper sulphate and  $\text{Cu}_2\text{SO}_4$  at which the reaction velocity of the forward and the backward reactions respectively was maximum?
- v) Whether varied amounts of sulphuric acid had any effect on the rate of the forward reaction?
- vi) At what temperature the rate of the forward as well as of the backward reactions in turn was maximum?
- vii) Whether there was any effect of the particle size and hence of the surface area of copper crystals on the rate of the forward reaction?
- viii) Whether the rate of the forward reaction was affected by the change of stirring speed with which the solutions were stirred?



ix) How did the rate of the forward reaction depend upon  $\text{Cu}^{2+}$  concentration and of the backward reaction on  $\text{Cu}^+$  concentration?