

Full Length Research Paper

Redox and spectral behaviour of copper (II)-chloro and bromo complexes in some nonaqueous solvents

E. J. Ukpong^{1*}, N. W. Akpanudo¹ and J. Prasad²

¹Department of Science Laboratory Technology, Akwa Ibom State College of Agriculture, P. M. B 1001, Abak, Nigeria.
²Chemistry Department, Allahabad University, Allahabad, India.

Accepted 22 January, 2010

The redox behaviour of 3×10^{-3} M each of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CuBr}_2 \cdot \text{H}_2\text{O}$ have been investigated at Platinum (Pt) electrode and 1×10^{-3} M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ at glassy carbon (GCE) electrode in dimethylformamide (DMF), dimethylsulfoxide (DMSO), acetonitrile (AN) and ethanol/0.1 M tetrabutylammonium perchlorate (TBAP) using cyclic voltammetry. For CuCl_2 System, E_{pc_1} and E^0 are more positive, ΔE_p is smaller and I_{pa_1}/I_{pc_1} is $>$ at GCE than at Pt electrode, exception being ethanol where opposite trend is observed. In ethanol, two reduction steps c_1/a_1 due to $\text{Cu}^{2+}/\text{Cu}^+$ couple while a_2/c_2 due to Br^-/Br_2 couple are observed in CuBr_2 system. The electron paramagnetic resonance (EPR) features of copper (II) chloro species in DMF and DMSO show splitting of the g_{\parallel} in frozen solution. For frozen CuBr_2 system, the spectral features in DMF, DMSO and ethanol are characterized by four small peaks in the g_{\parallel} and one g_{\perp} signal as found for CuCl_2 in ethanol. However, splitting of the g_{\parallel} peak occurs in AN which was not observed in similar solvent for CuCl_2 .

Key words: Redox, spectral, voltammograph, EPR, nonaqueous, cupric halide.

INTRODUCTION

Comparison of stability constants of the chloro and bromo complexes of Cu (II) and Cu (I) in organo solvents with the corresponding constants in water have been reported, (Ukpong and Prasad, 2005). This illustrates the importance of solvents in complex ion stability. The present cyclic voltammetric studies are an attempt to investigate the redox behaviour of these halo species of copper (II/I) in some organo solvents. The EPR studies have also been carried out in order to investigate the number of Cu (II) species in frozen solution of these solvents.

MATERIALS AND METHODS

Electrochemical

The cyclic voltammetric measurements were carried out with a BAS Model CV-1B (Indiana USA) instrument having an electrochemical cell with a three-electrode system. The working electrodes were

glassy carbon, (GC) and platinum (Pt). Platinum wire was used as an auxiliary electrode, while a saturated calomel electrode, (SCE) as reference electrode with $E^0 = 0.242\text{V}$ vs. NHE. The cyclic voltammograms were recorded on an X-Y recorder.

All the cyclic voltammetric experiments were done in an inert atmosphere achieved by purging the cell solution with nitrogen gas for about 20 min and maintained over the cell solution during recording of the voltammograms. The nitrogen was purified by bubbling through alkaline vanadous sulphate solution and passing through a calcium sulphate drying tube bubbling through the cell solution. Sodium perchlorate (NaClO_4), sodium bromide (NaBr) were Analar grade while TBAP was obtained from Aldrich (USA). M/100 standard solutions of analytical reagent (Analar) grade $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CuBr}_2 \cdot \text{H}_2\text{O}$ were prepared in spectroscopy grade nonaqueous solvents. Freshly prepared solutions were used for the electrochemical studies, while all experiments were carried out in $25 \pm 1^\circ\text{C}$ in 0.1 M TBAP supporting electrolyte.

EPR

The EPR spectral measurements were obtained using a Varian E-line X-band spectrometer equipped with a dual cavity and operating in a 9.152 - 9.232 GHz range with 100KHz modulation. The g -values were calibrated with TCNE, that is, tetracyanoethylene ($g=2.0028$) sealed in a quartz capillary as an external standard and

*Corresponding author. E-mail: jimmukpong@yahoo.com.

Table 1. Cyclic voltammetric parameters at Pt electrode for 3×10^{-3} M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and at GCE Electrode for 1×10^{-3} M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in some nonaqueous solvents at $\nu = 25\text{mVs}^{-1}$.

| Solvent | E_{pc_1}/mV | E_{pa_1}/mV | $I_{pc_1}/\mu\text{A}$ | $I_{pa_1}/\mu\text{A}$ | E^0/mV | $\Delta E/\text{mV}$ | I_{pa_1}/I_{pc_1} |
|---|----------------------|----------------------|------------------------|------------------------|--------------------|----------------------|---------------------|
| Ethanol | + 405 | + 520 | 6.2 | 6.2 | + 462 | 115 | 1.0 |
| | + 360 ^a | + 525 ^a | 6.0 ^a | 5.5 ^a | + 442 ^a | 165 ^a | 0.91 ^a |
| DMSO | + 195 | + 395 | 4.0 | 3.2 | + 295 | 200 | 0.80 |
| | + 245 ^a | + 385 ^a | 3.0 ^a | 3.0 ^a | + 315 ^a | 140 ^a | 1.0 ^a |
| DMF | + 280 | + 540 | 6.5 | 5.2 | + 410 | 260 | 0.80 |
| | + 425 ^a | + 510 ^a | 5.0 ^a | 5.5 ^a | + 468 ^a | 85 ^a | 1.10 ^a |
| AN | + 435 | + 600 | 4.9 | 5.5 | + 518 | 165 | 0.86 |
| | + 490 ^a | + 605 ^a | 7.25 ^a | 6.5 ^a | + 552 ^a | 115 ^a | 0.89 ^a |
| For $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in DMSO/0.1M TBAP - 20 + 105 | | | 9.95 | 4.75 | + 42 | 125 | 0.48 |

a: Values are given for 1×10^{-3} M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ at the GCE working electrode; all potentials are measured in mV vs. SCE.

placed in the ESR cavity alongside the sample. The frozen (77K) 4×10^{-3} M solutions of analytical reagent (Analar) grade $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CuBr}_2 \cdot \text{H}_2\text{O}$ prepared in spectroscopy grade non-aqueous solvent were placed in a Varian liquid nitrogen Dewar flask for EPR spectral measurements.

RESULTS AND DISCUSSION

Table 1 shows the cyclic voltammetric parameters for copper (II) chloro complex species in ethanol, DMSO, DMF and AN at GCE and Pt electrodes. It can be observed that the cathodic peak potential, E_{pc_1} and formal electrode potential (E^0) are more positive, the magnitude of ΔE_p ($E_{pa_1} - E_{pc_1}$) is smaller and the peak current ratio, I_{pa_1}/I_{pc_1} is greater at GCE than at Pt electrode, exception being alcohol where opposite trend is observed. This indicates that the reduction is easier and the electrode process appears to be more reversible at GCE in a given organic solvent. In different solvents, E_{pc_1} as well as E^0 increases (becomes more positive) in the following sequence: At Pt electrode; DMSO < DMF < ethanol < AN and at GCE: DMSO < ethanol < DMF < AN. This shows that copper (II) chloro complex species are more stabilized in DMSO and less stabilized in AN. Molroux and Elving (1978) have observed that the electrode process is affected by electrode material. It could be noted (Table 1) that the reduction potential E_{pc_1} shifts in the negative direction with increasing donor number (Gutman, 1967) of the solvent (ethanol excepted). It can also be seen that the reduction potential for square planar $[\text{Cu}(\text{DMSO})_4](\text{ClO}_4)_2$ solvated complex (Marcorrigiano et al., 1978) is significantly more negative (that is, difficult reduction) as compared to that for Cu (II)

- chloro solvated species (Elleb et al 1982) in DMSO/0.1M TBAP. This suggests that the chloride ions preferentially stabilize copper (I) while DMSO stabilize preferentially copper (II) as ClO_4^- ion is a very weakly coordinating ligand.

Also, the peak current ratio, I_{pa_1}/I_{pc_1} for $[\text{Cu}(\text{DMSO})_4](\text{ClO}_4)_2$ species is <1, indicating that Cu (I) solvated species is chemically unstable as compared to Cu (II) complex species (Elleb et al., 1980, 1982).

Kaddish et al. (1978) concluded that coordinating solvents shifted the iron (III) reduction potential in a positive direction whereas strongly coordinating anions shifted the potential in a negative direction in the case of TPPFex complexes. Further, it has been observed that as the solvent donicity (donor number) increases from 15, the iron (III/II) potential shifts negatively with increased donor number.

A close look at Table 2 shows that E_{pc_1} and E^0 for bromo-copper (II) solvated species becomes more positive in the order: DMSO < DMF < ethanol < AN as also found in the case of chloro-copper (II) solvated species at Pt electrode (Table 1). Further, the current ratio, $I_{pa_1}/I_{pc_1} > 1.0$ in ethanol and DMF, indicates that the electrogenerated Cu (I) complex species is adsorbed at the surface of the Pt electrode. However, a comparison of the magnitude of E_{pc_1} , E^0 , and ΔE_p is smaller for Cu (II) - bromo complex. This indicates that the reduction is easier and the electrode process is more reversible in Cu (II) - bromo complex system than that in Cu (II) - chloro complex system at Pt electrode.

Figure 1 shows voltammograms for $\text{CuBr}_2 \cdot \text{H}_2\text{O}$ in ethanol at scan rate $\nu = 25\text{mVs}^{-1}$ and at Pt electrode. A close look at Figure 1A scanned from + 0.70 to - 0.1 V

Table 2. Cyclic voltametric parameters at Pt electrodes for 3×10^{-3} M $\text{CuBr}_2 \cdot 2\text{H}_2\text{O}$ in some nonaqueous solvents at $\nu = 25 \text{ mVs}^{-1}$.

| Solvent | E_{pc_1}/mV | E_{pa_1}/mV | $i_{pc_1}/\mu\text{A}$ | $i_{pa_1}/\mu\text{A}$ | E^0/mV | $\Delta E/\text{mV}$ | i_{pa_1}/i_{pc_1} |
|---------|----------------------|----------------------|------------------------|------------------------|-----------------|----------------------|---------------------|
| Ethanol | + 445 | +575 | 6.5 | 7.0 | +510 | 130 | 1.10 |
| DMSO | + 200 | +335 | 3.60 | 3.20 | +268 | 135 | 0.88 |
| DMF | + 395 | +545 | 6.25 | 7.50 | +470 | 150 | 1.20 |
| AN | + 525 | +630 | 7.0 | 6.25 | +577 | 105 | 0.89 |

All potentials given in mV vs. SCE.

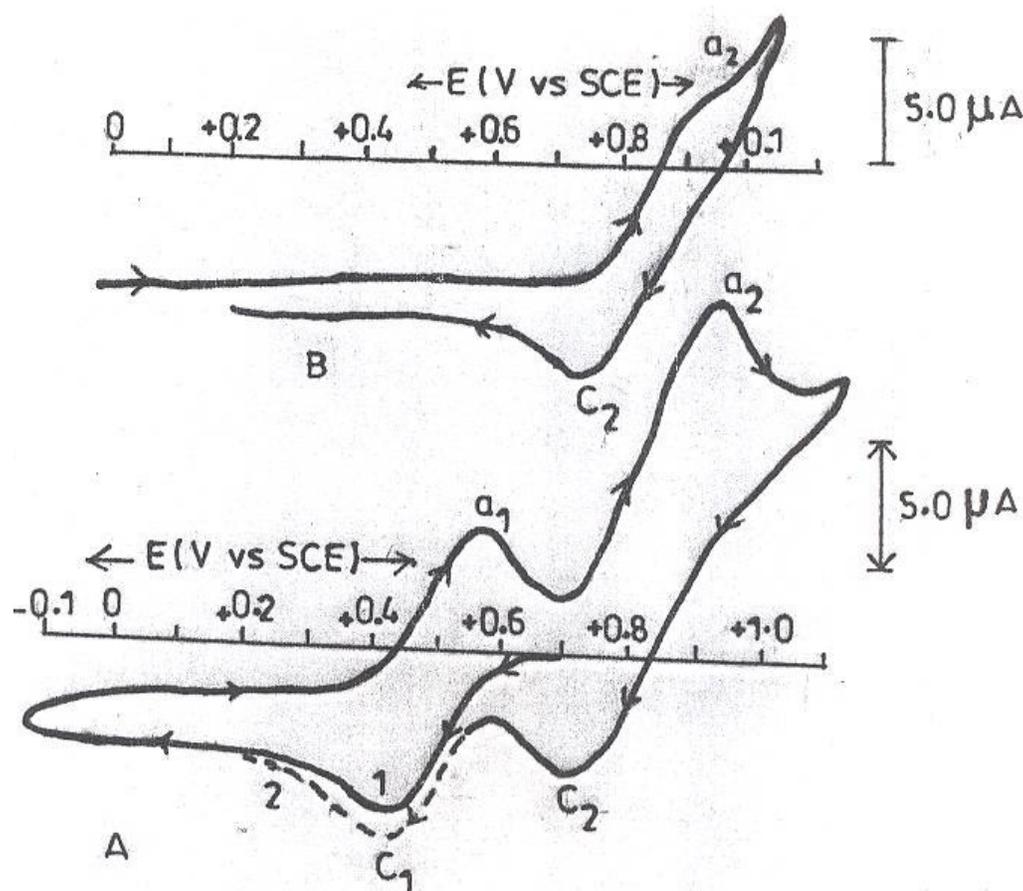


Figure 1. (A) CV of 3×10^{-3} $\text{CuBr}_2 \cdot \text{H}_2\text{O}$ in 0.1 M BAP; in ethanol; (B) CV of 3×10^{-3} M NaBr and 0.2 M NaClO_4 in 75% alcohol - aqueous media both at $\nu = 25 \text{ mVs}^{-1}$ at Pt electrode.

depicts two redox steps marked c_1/a_1 and c_2/a_2 with formal potential E^0 of 510 mV ($i_{pc_1} = 445$, $E_{pa_1} = 575$ mV) and 820 mV ($E_{pc_2} = 715$ mV; $E_{pa_2} = 920$ mV) respectively. In order to investigate this observation, a positive scan from OV vs. SCE of the medium containing 3×10^{-3} M NaBr and 0.2 M NaClO_4 in 75% alcohol-aqueous media at scan rate 25 mVs^{-1} has shown an anodic peak c_2 at +920 mV and in the reverse cycle, its corresponding cathodic peak c_2 at +720 mV. On the basis of these observations, it is concluded that the redox step c_1/a_1 is

due to $\text{Cu}^{2+}/\text{Cu}^+$ couple while the step a_2/c_2 is due to Br^-/Br_2 couple (Figure 1B).

It is relevant to mention that the principal experimental complication in the study of copper (II) bromine complexation is auto decomposition into copper (I) bromide or its complexes and bromine. In solution, the decomposition is more rapid. Dochlemann and Fromherz (1935) reported that as much as 19% of the copper was in the mono valent state in aqueous solutions with high lithium bromide concentration. It has been found that with cupric

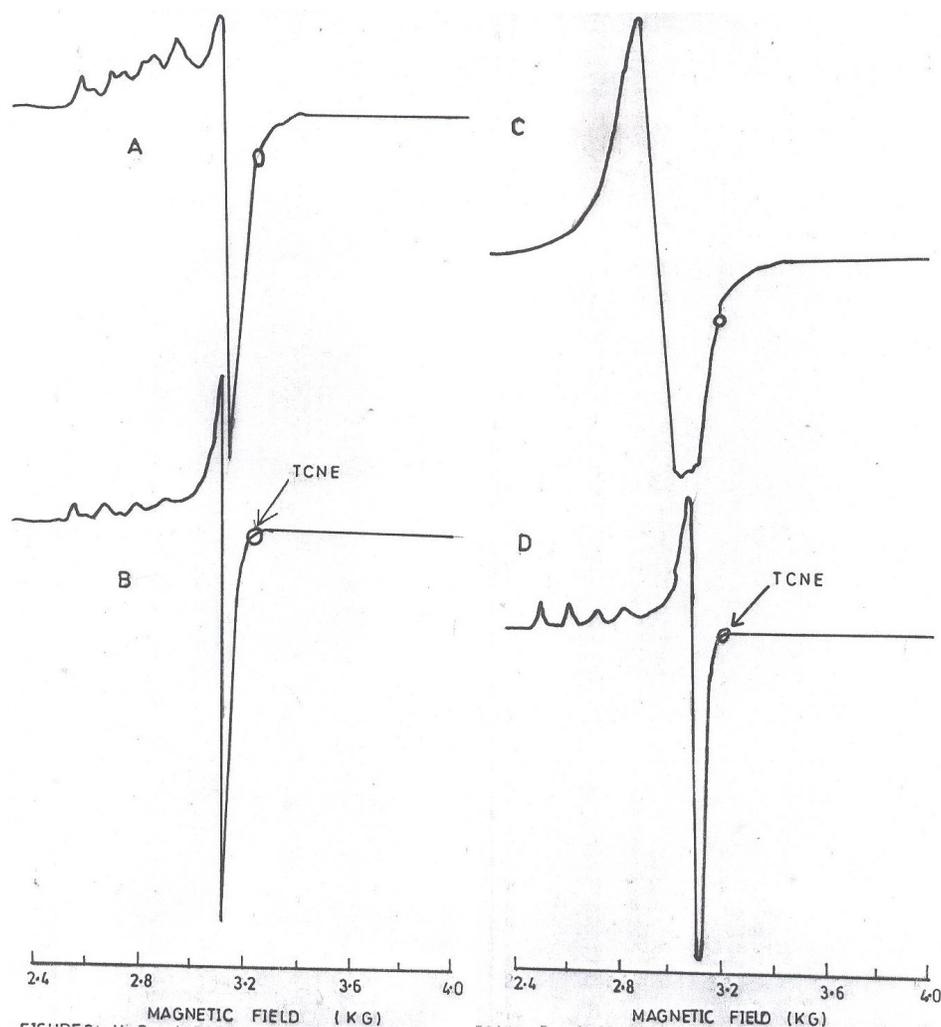


Figure 2. X-Band EPR spectra of nonaqueous solution for 4×10^{-3} M $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ at 77K. (A) DMF, (B) DMSO, (C) AN, (D) Ethanol.

bromide in acetonitrile at room temperature, about half the copper is reduced in 25 h. If the solution is boiled, a mixture of bromine and acetonitrile is distilled off and the reaction proceeds to completion. On addition of water to the solution, remaining undistilled cupric bromide is precipitated.

The 77K (liquid nitrogen temperature) electron paramagnetic resonance (EPR) studies of 4×10^{-3} M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CuBr}_2 \cdot \text{H}_2\text{O}$ has been done in frozen nonaqueous solutions (ethanol, DMF, DMSO and AN). The EPR features of copper (II) - chloro species in DMF and DMSO are similar both in g_{\parallel} and g_{\perp} regions, here splitting of the g_{\parallel} peaks can be noticed (Figures 2A and B). The splitting of the g_{\parallel} signals indicates the presence of more than one Cu (II) species in frozen solution. On the basis of their UV-visible and near IR spectral studies (Elleb et

al., 1980, 1982) concluded that $\text{CuCl}(\text{DMF})_3^+$ and $\text{CuCl}_3(\text{DMF})^-$ are the solvated species in DMF solution while $\text{CuCl}(\text{DMSO})_3^+$ and $\text{CuCl}_3(\text{DMSO})^-$ are solvated species in DMSO solution. Interestingly, however, a single g_{\perp} EPR signal is observed in AN (Figure 2C). In alcohol, the EPR spectrum (Figure 2D, Table 3) is characterized by relatively larger g_{\parallel} and smaller value of A_{\parallel} . The g_{\parallel} values of copper (II)-chloro complex species in these nonaqueous solvents increase in the order DMF (2.380) < DMSO (2.402) < ethanol (2.415).

It could be noticed that the EPR spectral features of copper (II)-bromo complex species (Dochlemann and Fromherz, 1935; Braterman, 1963; and Ishiguro et al., 1987) in DMF, DMSO and alcohol (Figure 3A) are characterized by four small peaks in the g_{\parallel} and one intense g_{\perp} in acetonitrile (Figure 3B), indicating that more than

Table 3. Cryogenic EPR spectral parameters for 4×10^{-3} M solutions of cupric halides in some nonaqueous solvents.

| Solvent | $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ | | | | $\text{CuBr}_2 \cdot \text{H}_2\text{O}$ | | | |
|---------|---|-------------|----------------|--|--|-------------|----------|--|
| | g_{\parallel} | g_{\perp} | g_{av} | A_{\parallel} $\text{Cu}_G(\times 10^4 \text{cm}^{-1})$ | g_{\parallel} | g_{\perp} | g_{av} | A_{\parallel} $\text{Cu}_G(\times 10^4 \text{cm}^{-1})$ |
| DMF | 2.380 ^a 2.337 ^b | 2.080 | 2.177 2.166 | 110 ^a (122) 120 ^b (130) | 2.388 | 2.080 | 2.183 | 120(134) |
| DMSO | 2.402 ^a 2.354 ^b | 2.080 | 2.188 2.172 | 110 ^a (123) 120 ^b (132) | 2.402 | 2.080 | 2.188 | 110(123) |
| AN | | 2.157 | | | 2.420 ^a | 2.080 | 2.194 | 110 ^a (124) |
| Ethanol | 2.415 | 2.080 | 2.192 | 110(124) | 2.433 | 2.080 | 2.198 | 100(114) |

a: value corresponding to A_1 and A_2 ; b, value corresponding to B_1 and B_2 .

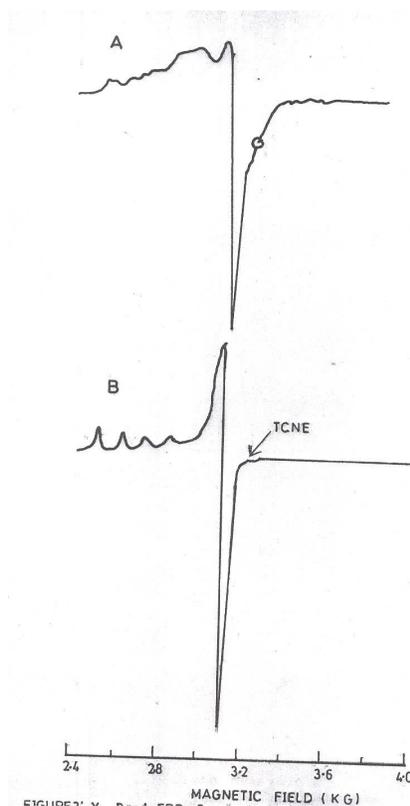


Figure 3. X-Band EPR spectra of non-aqueous solution for 4×10^{-3} M $\text{CuBr}_2 \cdot \text{H}_2\text{O}$ at 77K. (A) Ethanol, (B) AN,

one copper (II)-bromo solvated complex species are present in solution. Braterman (1963) characterized a green specie, $\text{CuBr}_3 \cdot 2$ solvent having the trigonal bipyramidal structure in various organic solvents particularly acetonitrile, which is obtained at bromide concentrations

lower than those needed to form purple specie, CuBr_4^{2-} . Spectrum of 10×10^{-3} M bromide in acetonitrile has shown that half of the copper(II) is present as CuBr_3^- , some 10% as CuBr_4^{2-} and the remainder ($\cong 40\%$) as Cu^{2+} .

The trend in g_{\parallel} values for Cu (II)-bromo complex species in these nonaqueous solvents is similar to that for Cu (II)-chloro complex species (Table 3). It may also be noted that g_{\perp} values are independent ($g_{\perp}=2.080$) of the nature of the nonaqueous solvents for both copper (II)-chloro and bromo complexes. Also a comparison of Tables 2 and 3 shows that the frozen solution spectra exhibit axial spectra ($g_{\parallel}>g_{\perp}$) that are characteristic of copper(II) complexes (Bertini and Scozzafava, 1981).

Conclusion

The voltammetric results of the copper (II)-chloro and bromo complexes confirm observations of earlier works with different techniques, especially the experimental complication in the study of copper (II) bromine complexation. The same observation goes for the spectral behaviour. However, it is interesting to note that copper (II)-bromo complex shows splitting of the g_{\parallel} peak in AN, whereas this is not observed in similar solvent for CuCl_2 system.

ACKNOWLEDGEMENT

The authors acknowledge with thanks, the receipt of financial assistance as a fellowship from the University Grants Commission (U.G.C), New Delhi, India, for carrying out this research work.

REFERENCES

- Bertini I, Scozzafava A (1981). In *Metal Ions in Biological Systems*, H. Seigel (Ed.), Marcel Dekker, Inc; New York, 12(2) 31-74.
- Braterman PS (1963). Copper (II) Bromide Complexes: A Discussion of the Tetrabromocuprate (II) Spectrum. *Inorg. Chem.* 2: 448.
- Dochlemann E, Fromherz H (1935). Absorption Spectra and Chemical Bonding in complexes of Copper (II). *Z. Phys. Chem. Abt. A.* 171: 371.
- Elleb M, Meullemeestre, Schwing-weill MJ, Vierling F (1982). Stability, Electronic Spectra and Structure of Copper(II) Chloride Complexes in Dimethylsulphoxide, 21: 1477.
- Elleb M, Meullemeestre, Schwing-weill MJ, Vierling F (1980). Stability, Electronic Spectra and Structure of Copper(II)Chloride Complexes in N, N-Dimethyl formamide 19: 2699-2704.
- Gutmann RV (1967). *Coordination Chemistry in Non-Aqueous Solutions*, Springer-Verlag, Wien and New York. pp.170-173.
- Ishiguro SI, Ozutsumi KI, Naggy L, Ohtaki H (1987). Calorimetric and Spectroscopic Studies of Bromo Complexes of Copper (II) in N, N-Dimethyl formamide; *Bull. Chem. Soc. Jpn.* 60: 1691-1698.
- Kadish KM, Beroiz D, Bottomley LA (1978). Reactions of Pyridine with series of para-substituted Tetraphenylporphyrin-cobalt and iron complexes. *Inorg. Chem.* 17: 1124-1129.
- Marcotrigiano G, Menabue L, Pellacani GC (1978). Spectroscopic and Electrochemical Study of Copper and Zinc Complexes in Nonaqueous Solvent. *J. Trans. Met. Chem.* 3(1): 108-112.
- Molroux J, Elving PJ (1978). Effects of Adsorption, Electrode Material and Operational Variables on the Oxidation of Dihyronicotinamide Adenine Dinucleotide at Carbon Electrodes *Anal. Chem.* 50(8): 1056-1062.
- Ukpong EJ, Prasad J, Asuquo J (2005). Cyclic Voltammetry of Chloro and Bromo Complexes of Copper(II) in aqueous halide ion concentrations. *J. Chem. Soc. Nigeria* 30(2): 171-180.