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Cyclic Voltammetric Investigations of Newly Synthesized Cd(II) 4'-(4-methylphenyl)-2,2':6',2"-Terpyridyl Complex in DMF solution

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The redox properties of a newly synthsized Cd(II)- terpyridine complex has been examined using cyclic voltammetry in non-aqueous media of DMF solvent at the surface of gold, pelatin and glassy carbon electrodes. It has been found that, this compound exhibits one electron reduction peak with the EC mechanism. The charge transfer coefficients (α) and the diffusion coefficients (D values) for this compound in various solvents were obtained on the basis of voltammograms.

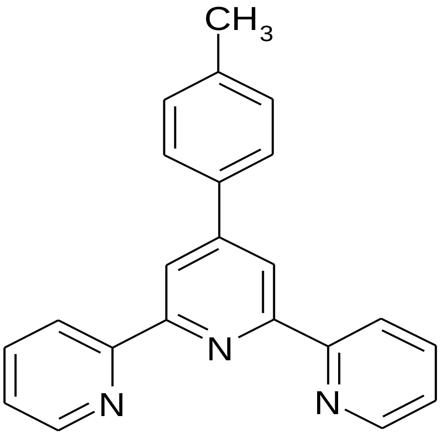
Keywords: Cd(II)- terpyridine; Electrochemical Behavior ; Solid Electrodes; Cyclic Voltammetry ; DMF

1. INTRODUCTION

2,2' :6',2″-Terpyridine (terpy) and its derivatives form one of the most widely studied classes of ligands in coordination chemistry [1-2]. The popularity of terpy as a ligand is easy to understand. It is commercially available and straightforward to synthesise, while several types of derivatised terpy, particularly those substituted at the 4'-position, are also readily accessible [3]. Terpy can bind to both low- and high-oxidation state metal ions; almost always in tridentate fashion [2, 4].

Chemists have great interest in the design, synthesis and exploring the properties of coordination polymers. 2,2' :6',2″-Terpyridine (terpy) and its derivatives have been intensively explored because of their versatility as building blocks for supramolecular assembles and polymers [5] and the interesting electronic, photonic, magnetic, reactive and structural properties shown by the transition metal complexes of these ligands [6]. In the last decades, special attention has been drawn to the 4' functionalized terpyridine ligands, since the appended substituents may be utilized not only to tailor the electronic properties of the ligand and its metal complexes, but also to incorporate new functionalities through further derivative reactions, as well as to introduce terpyridine complexes into polymers [7-8].

We have newly reported the crystal structures of 4'-chloro-2,2':6',2"-terpyridine lead(II) complexes with different crystallographic symmetry and molecular structures, where hydrogen bonding and π-π interactions play significant roles in the forming the resultant supramolecular networks [9-10]. To extend our studies in the field of surface electrochemistry [11-15]and study in the coordination and supramolecular chemistry of the tridentate ligand, 4'-(4-methylphenyl)-2,2':6',2"-terpyridine (Mephtpy) Scheme.1, we present in this paper the, the electrochemical studies of transition metal complexes formulated as: $[Cd(Mephtpy)I_2]$ (**1**) .



Scheme. 1. Chemical structure of terpyridine derivative (Mephtpy)

2. EXPERIMENTAL PART

2.1. Reagents and techniques

All the chemicals and solvents used for the synthesis were of reagent grade and were obtained commercially from Merck Company with the exception of the cadmium nitrate, which was obtained from Aldrich. The solvents were purified by standard methods.

2.2. General synthesis procedure

4'-(4-methylphenyl)-2,2':6',2"-terpyridine (Mephtpy), is commercially available from Aldrich and was used as received. All chemicals were reagent grade and have been used without further purification. FT-IR spectra (4000 400 cm^{-1}) were recorded with a Shimadzu FT-IR prestige 21 spectrophotometer on KBr disks. Elemental analyses (CHN) were performed using a Carlo ERBA model EA1108analyzer. ^{1}H and ^{13}C- NMR spectra were recorded with a Bruker spectrometer at 250 MHz in [D6]DMSO. Thermal analyses were carried out on a Perkin–Elmer instrument (Seiko Instruments).

The syntheses described in the present article are essentially simple and straightforward in concept, but frequently presenting difficulties in execution, because of limited solubility of the desired species, if a usefully crystalline product is desired. This has been overcome in many cases by making use of the often appreciable temperature dependence of solubility found here. For the less soluble species, suitable crystalline products have been accessed by the method of Ref. [16] wherein the reactants are placed under an appropriate solvent in the separate arms of a sealed branched tube with its lower end containing cadmium(II) salt reactant held at a relatively high temperature in an oil bath, while the branch is at room temperature. Frequently, crystalline material usable for X-ray studies deposits in the branch, often only after an extended period. In most of the present systems, the ligand in the branch held at room temperature was very readily soluble in the solvent, so the success of the procedure was also possibly a reflection of the slow rate of liquid phase diffusion.

*2.3. Preparation and crystal growth of [Cd(Mephtpy)I_2] (**1**)*

4'-(4-methylphenyl)-2,2':6',2''-terpyridine (0.323 g, 1 mmol) was placed in one arm of a branched tube and cadmium(II) nitrate (0.308 g, 1 mmol) in the other. Methanol was carefully added to fill both arms, the tube was then sealed and the ligand-containing arm immersed in a bath at 60°C while the other remained at ambient temperature. After three days, the crystals that had deposited in the cooler arm were filtered off, washed with solvent, and air dried. Yield: 75.4%. Analysis: found: C: 38.41, H: 2.50, N: 6.09%. Calculated for $C_{22}H_{17}CdI_2N_9$: C: 38.32, H: 2.48, N: 6.11%. IR (cm^{-1}) selected bonds: 3062(w), 2950(w), 1582(s), 1569(m),1557(s), 1476(s), 1150(m), 794(m). ^{1}H NMR (DMSO, δ): 8.948 (s, 2H), 8.776 (d, 2H), 8.313 (m, 4H), 8.11(d, 2H), 7.886 (t, 2H), 7.409 (d, 2H), 3.246 (s, 3H) ppm. ^{13}C NMR (DMSO, δ): 154.22, 150.58, 149.57, 141.19, 137.34, 131.19, 130.59, 127.87, 127.16, 125.61, 124.43, 121.08, 21.38 ppm.

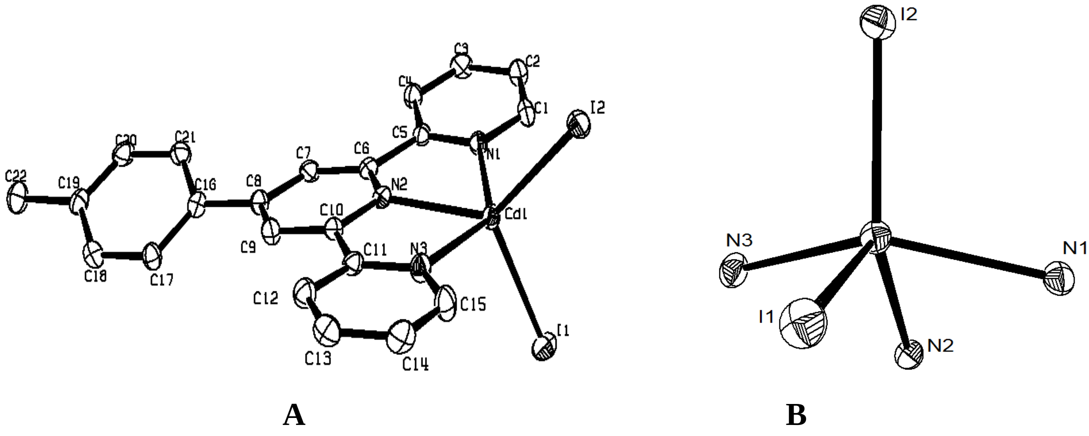


Figure 1. (a) ORTEP plot for complex **1** with 50% thermal ellipsoids (the hydrogen atoms are omitted for clarity). (b) ORTEP view of the CdN3I2 coordination sphere of complex **1**

2.4. Electrochemistry

Cyclic voltametric measurements and microelectrolysis at controlled potential experiments were performed using a potentiostate – galvanostat Auto-Lab instrument equipped with a three electrode system in an undivided cell. Glassy Carbon polished electrodes were used as working electrodes. The reference was an aqueous saturated calomel electrode (SCE), separated from the bulk of the solution by a bridge filled with solvent and supporting electrolyte. Solutions in the bridge were changed periodically to avoid aqueous contamination from entering the cell via the SCE. The auxiliary electrode was a Pt-wire coil. All solutions were deoxygenated by passing a stream of pre-purified N_2 into the solution for at least 10 Min prior to recording the voltamogram. Voltammetric measurements were performed at room temperature in dimetylformamide (DMF) with 0.1 M tetrabutylammunium perchlorate as the supporting electrolyte.

3. RESULTS AND DISCUSSION

3.1. The surface effect of electrode

For investigation the surface effect on the electrochemical behavior of these compounds their cyclic voltamograms were recorded at the surface of different solid electrodes such as pelatin (Pt), gold (Au) and glassy carbon (GC). The typical results for 0.001 M solution of Co(II)-complex are shown in Fig.2.

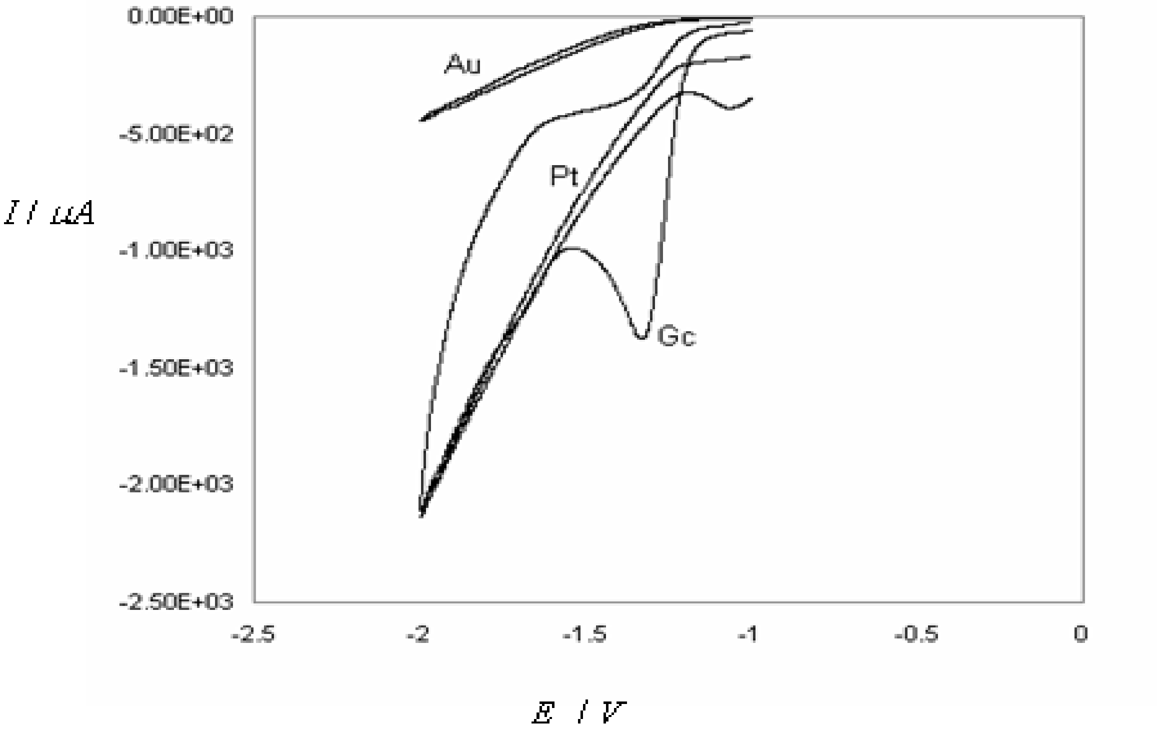
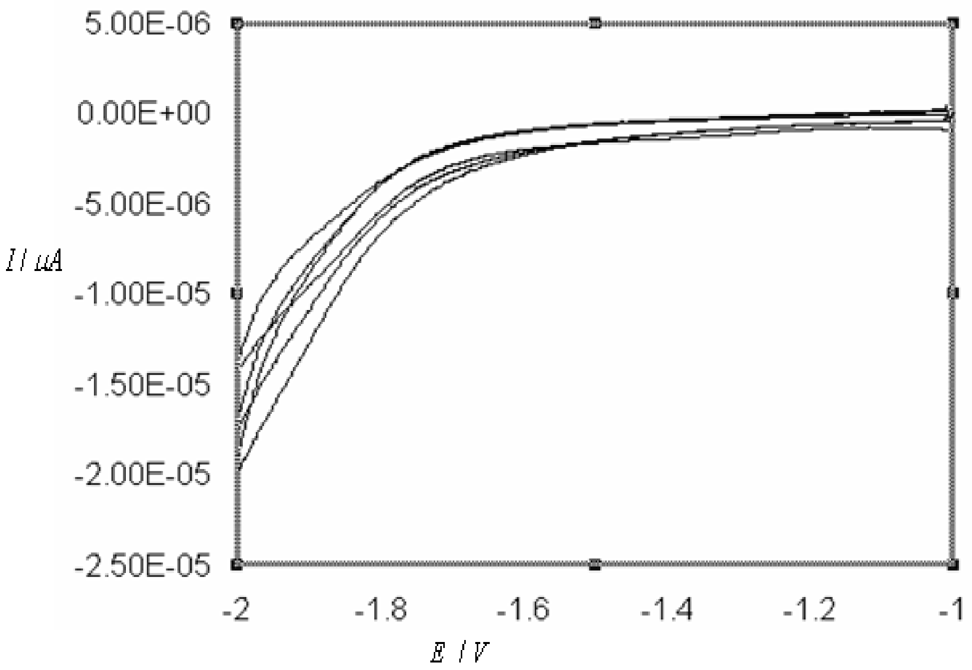
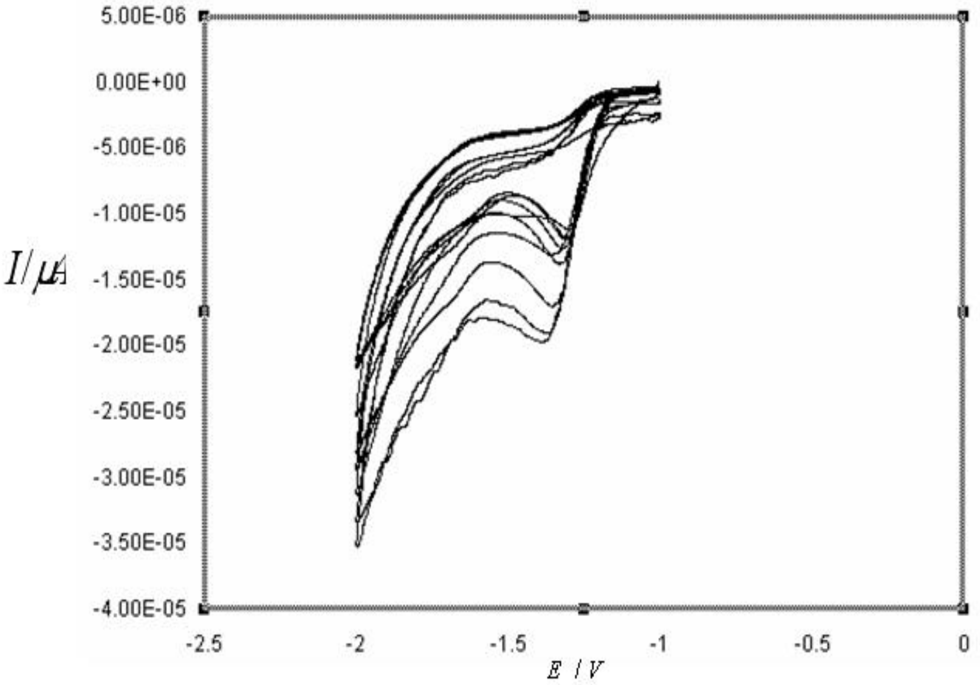


Figure 2. Cyclic voltammograms of 0.001 M [Cd -complex] in 0.1 M TBAP– (DMF) between 0.0 and -2.5 V in the scan rates 50 mV/S at the surface of different solid electrodes



A



B

Figure 3. Cyclic voltammograms recorded in dimetylfomamide (DMF) solution at the GC electrode A: in the absence of 0.1mM Cd (II) B: in the presense of 0.1mM Cd (II)-complex

The typical results cyclic voltammetric data for Cd(II)-disulfiram complex in dimetylfomamide (DMF) solution at the surface of GC electrode in (0.1 M TBAP) [a] are shown in Table 1.

Table 1. Cyclic voltammetric data in dimetylfomamide (DMF) solution for Cd(II) -terpyridine complex on GC electrode [a]

$\nu\left(\frac{v}{s}\right)$	In DMF							
	0.01	0.015	0.02	0.025	0.03	0.035	0.045	0.055
$-E_p/V$	1.305	1.317	1.32	1.332	1.339	1.364	1.376	1.391
$-I_p/\mu A$	11.1	11.7	11.8	12.5	13.7	16.9	19	19.7

[a] All potentials are referrad to Ag/AgCl (3MKCl)

The typical plot of I_p vs. $v^{\frac{1}{2}}$ for 0.0001 M complex under N_2 saturated at the surface of Glassy Carbon electrode was shown in Fig. 4.

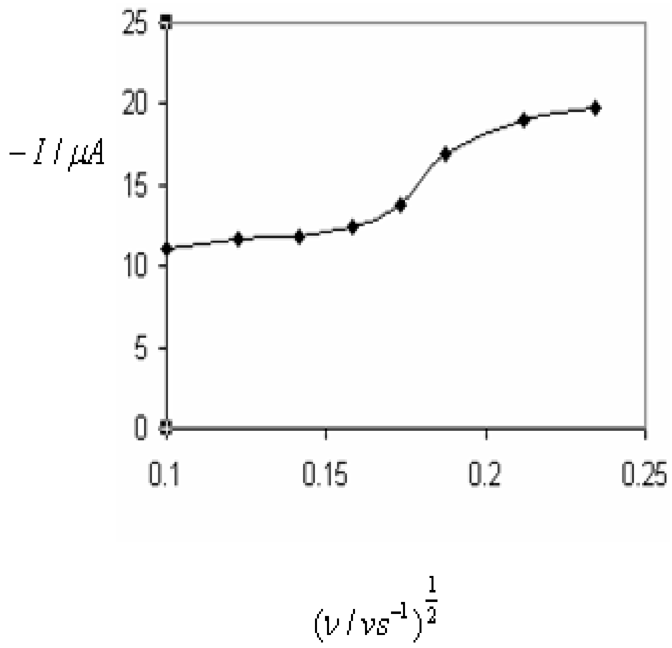


Figure. 4. Varation of the cathodic current with the square root of scan rate

As seen from Fig. 4 in pure DMF solution the current-scan rate responses in cyclic voltammetry experiments for Cd(II)-complex, depicted as i versus $\upsilon^{1/2}$ Randles-Sevick Eq.(1) representation [21-24], are straight lines that exhibits deviations from linearity in higher scan rates.

$$I_P = \left(2/99\times10^5\right)n\left(\alpha_c n_\alpha\right)^{1/2} A C^* D^{1/2} \nu^{1/2}$$

These deviation from linearity suggest a change from diffusion–controlled process to a mixed controlled process [25].

By using of the linear regin with the slope equation, the diffusion coefficients for reduction (D) was calculated .

$$SLOP = \left(3/01\times10^{5}\right)n\left(\alpha_c n_\alpha\right)^{\frac{1}{2}} AC^{*}D^{1/2}$$

A plot of the scan rate-normalized current $\left| I_P / \nu^{\frac{1}{2}} \right|$ vs. scan rate as shown in Fig. 5. exhibits the indicative shape of an EC nature process.

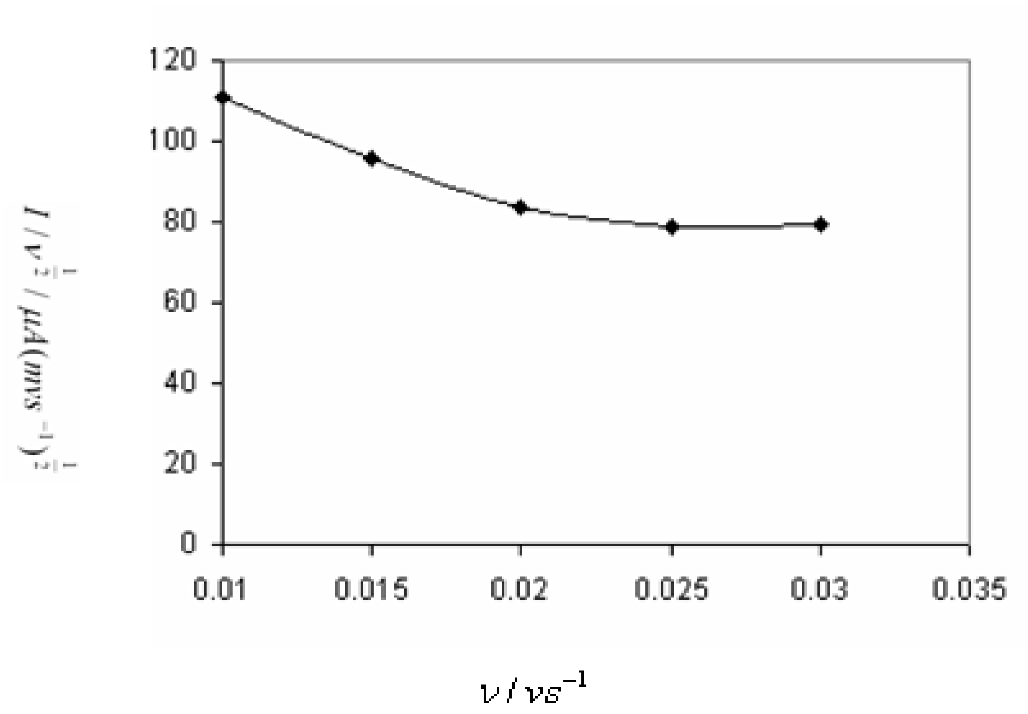


Figure. 5. Varation of the scan rate normalized current $\left| I_P / \nu^{\frac{1}{2}} \right|$ with scan rate

Also, the Ep_c of the redox peak was also dependent on scan rate. The plot of Ep_c vs. log υ was linear having a correlation coefficient of 0.9922 and this behavior was consistent with the EC nature of the reaction.

3.2. Evalution of α_c and n_α

Figure.6 shows a Tafel plot was drawn from data of the rising part of the current voltage curve recorded at scan rat of $5mVs^{-1}$ and can be used to obtain information on the rate-determing step. A slope of 0.1001 $mVdecade^{-1}$ is obtained which indicated that the rate determing step is one electron transfer ($n_\alpha = 0.88 \approx 1.0$) assuming a trasfer coefficient of $\alpha_c = 0.41$.

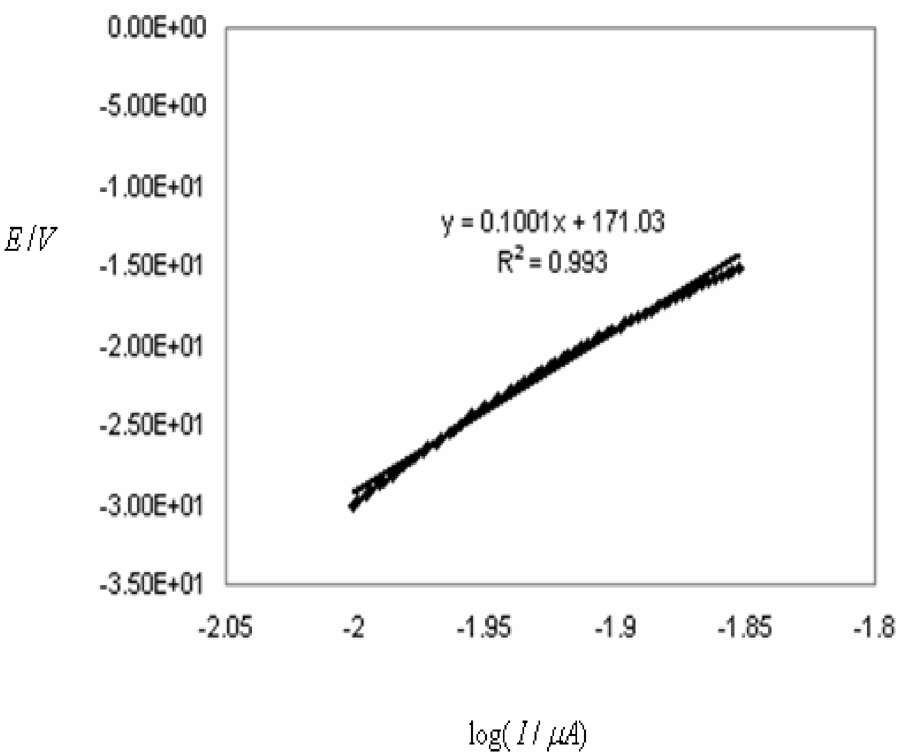


Figure.6. Tafel plot derived from the current-potential curve recorded at scan rate $5 mVS^{-1}$

From the slope of Ep_c vs. log υ, the tafel slope b, can also be obtained from the following eqation:

$$Ep = b/2 \log \upsilon + \text{constant}$$

The evaluated slope of Ep_c vs. log υ is 0.0704 mV, therefore b= 0.1408. the value of the slope also which indicated that the rate determing step is one electron transfer (n_α =0.82≈ 1.0) assuming a trasfer coefficient of $\alpha_c = 0.41$.

4. CONCLUSION

The results obtained in this work demonstrated newly synthesized Cd(II)-terpyridine complex at the surface of unmodified glassy carbon electrode undergoes electron reductive process with EC nature mechanism. The number of elercron in the rate determing step was one with charge transfer coeffiecnt 0.41.

5. AKNOWLEDGMENT

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