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Investigation of Electrochemical Behavior of Co(II)-Disulfiram Complex at the Surface of Gold Electrode in Different Non-Aqueous Media

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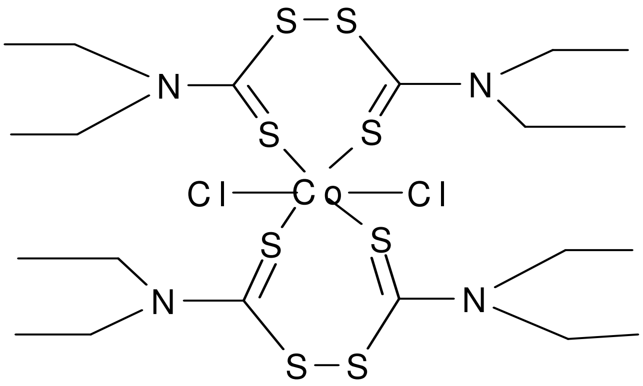
The redox properties of a Co(II)- Disulfiram complex has been examined using cyclic voltametry in different non-aqueous media such as dimethylsulfoxid (DMSO), dichlromethane(CH_2Cl_2) and mixed solvents at the surface of gold , pelatin and glassy carbon electrodes. It has been found that, this compound 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 voltamograms. Effect of scan rate and dielectric constants of solvents on redox behavior of complex was investigated.

Keywords: Disulfiram Complex, Electrochemical Behavior, Solid Electrodes, Cyclic voltammetry

1. INTRODUCTION

Dsulfiram (bis(diethylthicarbamoyl) disulfide or Antabuse (Scheme. 1) is a dithiocarbamate drug used clinically in the treatment of alcoholism [1]. It inhibits the enzyme aldehyde dehydrogenase that leads to the accumulation of acetaldehyde, a byproduct of alcohol metabolism, producing unpleasant and aversive side effects on alcohol consumption [2-3]. It addition disulfiram, inhibits dopamine-β-hydroxylate (DBH) [4-5].

In the literature review, there are papers in the synthesis, characterization and study of the electrochemical behavior of new Schiff-base [6-10] and other compounds at the surface of different solid electodes and medias [11-15]. As a part of our continuing work on dissymmetric tetradentate Schiff base complexes containing N, S and O donor atoms [16-17] and our research group in the recent years [18-22]. We now report, the electrochemical studies of transition metal complex containing thiolate coordination is an important area of study with implication in bioinorganic and medical chemistry.



Scheme. 1. Chemical structure of Co(II)-Disulfiram complex

2. EXPERIMENTAL PART

2.1. Reagents and techniques

All the chemicals and solvents used for the syntheses were of reagent grade and were obtained commercially from Merck Company. The solvents were purified by standard methods. The Co(II)-complex received as gift and was used after recrystalization.

2.2. Electrochemistry

Cyclic voltammetric 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. Au 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 mixture $(CH_3)_2SO$) and (CH_2Cl_2) solution with 0.1 M tetrabutylammunium perchlorate as the supporting electrolyte.

3. RESULTS AND DISCUSSION

3.1. The effect of scan rate

This complex reduction, is irreversibly in different solvents. With increasing scan rates shows a negative peak potential shift, as well as an increase in current intensity. The typical plot of I_p vs. $\upsilon^{\frac{1}{2}}$ for 0.0001 M complex under N_2 saturated at the surface of gold electrode was shown in Fig. 1A. As seen from Fig. 1 suggesting that at sufficient overpotential the reaction is diffusion-limited. Also, a plot of the scan rate-normalized current ($I/\upsilon^{1/2}$) vs. scan rate exhibits the indicative shape typical of an EC nature process (Fig.1C). The Ep_c of the reduction peak was also dependent on scan rate. The plot of Ep_c vs. log υ was linear having a correlation coefficient of 0.9951 and this behavior was consistent with the EC nature of the reaction. Figure.2 shows a Tafel plot was drawn from data of the rising part of the current voltage curve recorded at scan rate of 300 mVs^{-1}.

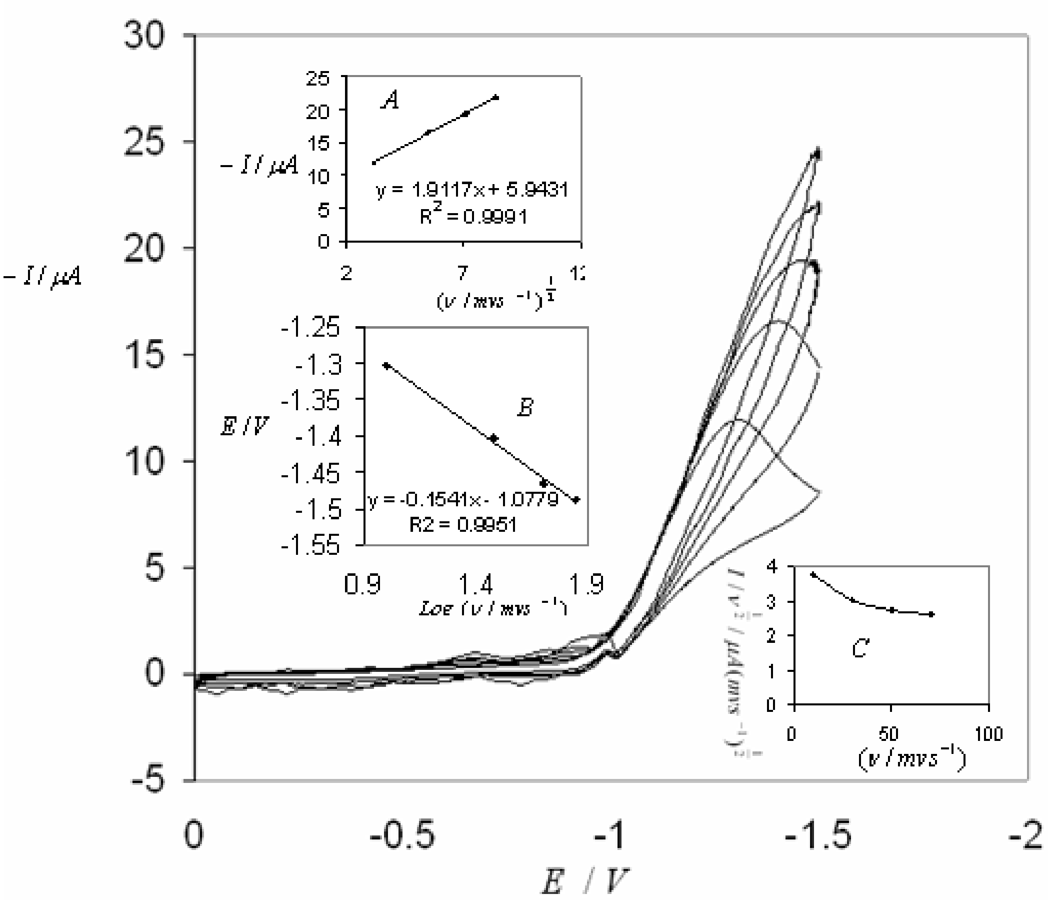


Figure.**1.** Cyclic voltammograms recorded in DMSO at the Au electrode in the presence of 0.1mM Co (II) disufiram complex.Insete: (A) Varation of the cathodic current with the square root of scan rate, (B) Plot of Epc vs. log scan rate, (C) Varation of the scan rate normalized current $\left| I_P / v^{\frac{1}{2}} \right|$ with scan rate

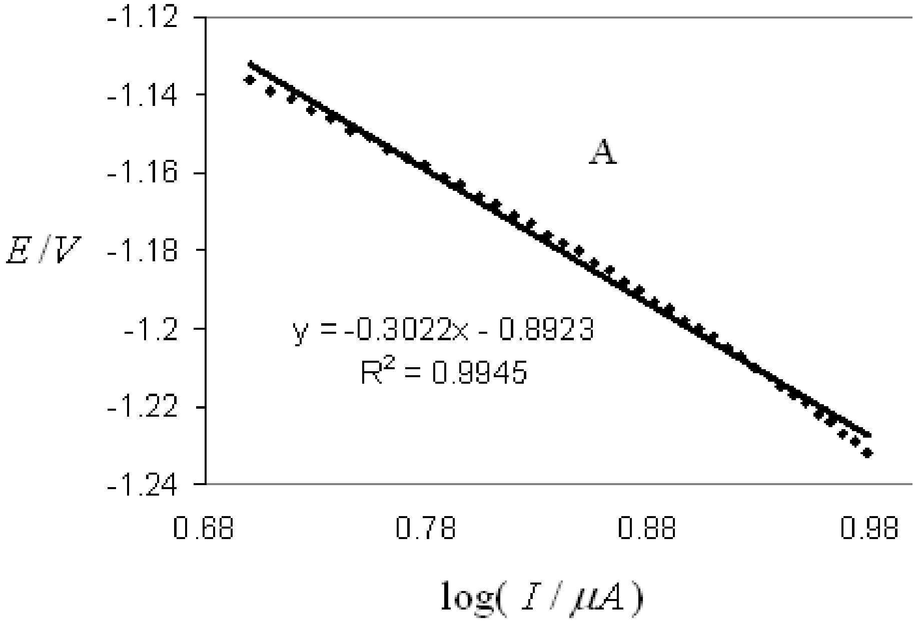


Figure.2. Tafel plot derived from the current-potential curve recorded at scan rate 300 mVs^{-1}

3.2. The effect of solvent

The cyclic voltammograms of [Co (complex)] are solvent dependent. The behavior of this compound in $(CH_3)_2SO$) is more intricate. In all different solutions such as dichlromethane and mixed solutions one irreversible catodic wave observed. The typical results cyclic voltametric data for Co(II)-disulfiram complex in $(CH_3)_2SO$) solution at the surface of Au electrode in (0.1 M TBAP) [a] are shown in Table 1.

Table 1. Cyclic voltammetric data in DMSO and (CH_2Cl_2+DMSO) 50% solutions for Co(II) disufiram complex on Au electrode [a]

$v\ ^{V}/_{s}$	*DMSO In*				50% $(CH_3)_2SO + CH_2Cl_2$ *In*			
	E_P-	$-I_P$	$-E_{\frac{P}{2}}$	$\alpha_C n_\alpha$	E_P-	$-I_P$	$-E_{\frac{P}{2}}$	$\alpha_C n_\alpha$
0.01	1.303	11.9	1.11	0.165	1.347	22.5	1.142	0.23
0.03	1.403	16.9	1.159	0.2	1.435	32.2	1.173	0.182
0.05	1.466	19.4	1.19	0.19	1.483	38.5	1.2	0.17
0.07	1.488	21.9	1.212	0.175	1.487	42.1	1.222	0.18
0.1	b	b	b	b	b	b	b	b
0.2	b	b	b	b	b	b	b	b

[a] All potentials are referred to Ag/AgCl(3 M KCl)
[b] The catodic wave is not detected at high scan rate

In both solvents the current-scan rate responses in cyclic voltammetry experiments for complex, depicted as I versus $\upsilon^{1/2}$ Eq.(1) representation [23], are straight lines.

$$I_P = (2/99\times10^5)n(\alpha_c n_\alpha)^{1/2} AC^* D^{1/2} v^{1/2}$$

By using the slope equation, the diffusion coefficients for reduction (D) was calculated and are summarized in Table 2 from slope equation.

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

Table 2. Diffusion coefficient values data for Co(II)-complex in different solutions

$In(cH_2Cl_2 + (CH_3)_2SO)90\%$			$In(CH_2Cl_2 + (CH_3)_2SO)80\%$		$In(cH_2Cl_2 + (CH_3)_2SO)50\%$		$(CH_3)_2SO$ 100 %
SlOP	$D(cm^2/s)\times10^{-5}$	SlOP	$D(cm^2/s)\times10^{-5}$	SlOP	$D(cm^2/s)\times10^{-5}$	SlOP	$D(cm^2/s)\times10^{-5}$
3/0002	5/5	3/5427	8/7	3/9148	9/9	1/9117	2/3

Analysis of D shows that the values in (CH_2Cl_2 + $(CH_3)_2SO$) are higher than those obtained in $(CH_3)_2SO$. Solvent dependence can easily be accounted for by differences in solvent dielectric constant [23-27]. The complex has smaller D values in the solvent with high dielectric constant, $(CH_3)_2SO$). Voltammetric measurements were performed at room temperature in mixture $(CH_3)_2SO$) and (CH_2Cl_2) solution with 0.1 M tetrabutylammunium perchlorate as the supporting electrolyte.

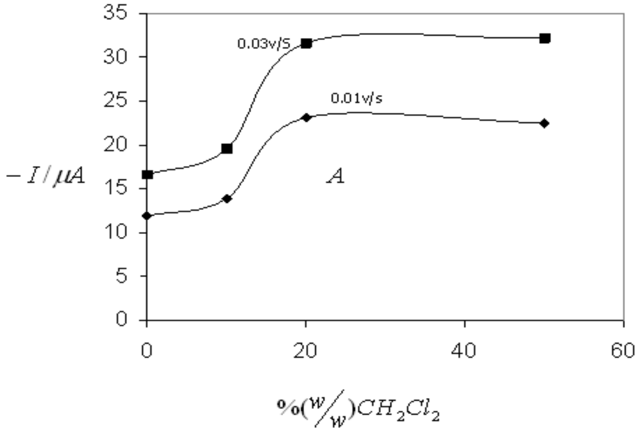


Figure.3. Dependence of peak current on % of solvent for 0.1 mM Co(II) Disulfiram complex at two scan rate of 10 and 30 mV/s^{-1} on Au electrode

The amount of $(CH_3)_2SO$) -(CH_2Cl_2) (%w/w) content was varied. The catodic peak potential and catodic peak current decreased on increasing the amount of CH_2Cl_2 (Fig3&4) . But well resolved catodic peak were obtained at 50%($(CH_3)_2SO$)-(CH_2Cl_2) media**.** The balance between the solubility and conductivity was achieved by using this system.

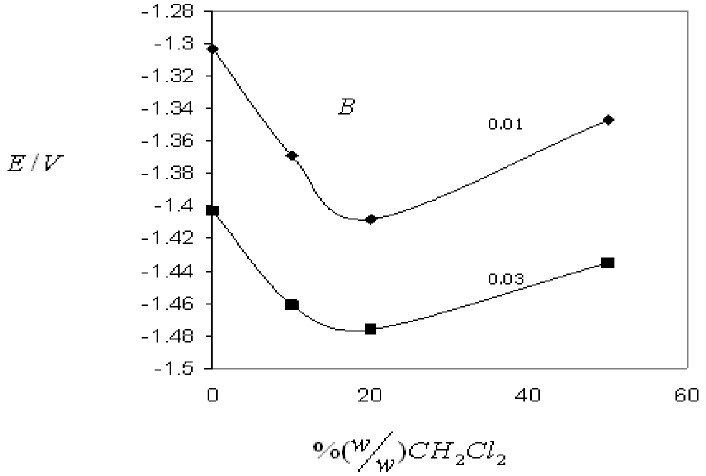


Figure.4. Dependence of peak potential on % of solvent for 0.1mM Co(II) Disulfiram complex at two scan rate of 10 and 30 mV/s^{-1} on Au electrode

3.3. Chronoamperometric studies

Chronoamperometric measurements of Co(II) Disulfiram complex at Au electrode were done by setting the working electrode potential at -0.99V and used for the measurements of the diffusion coefficient of Co(II) Disulfiram complex. In Chronoamperometric studies, the current for the electrochemical reaction of an electroactive material that diffuses to an electrode with a diffusion coefficient (D) is described the Cottrell equation [25]:

$$I = \frac{nFAD^{\frac{1}{2}}C^{*}}{(\pi t)^{\frac{1}{2}}}$$

Where D is the diffusion coefficient and C* is tht bulk concentration in mol cm^{-1}. Under diffusion control, a plot of I vs. t$^{-1/2}$ will be linear ,and from the slope the value of D can be obtained.

Fig.5 shows a Chronoamperogram of a Co(II) Disulfiram complex in Acetonitrile (AN) solution, recorded for a Au electrode.The inset of fig.5 B shows the expermintal plot of I vs. t$^{-1/2}$ for a Co(II) Disulfiram complex in Acetonitrile (AN) solution, recorded for a Au electrode. From the slope of this plot, we calculated a diffusion coefficient of 6.95×10^{-5}cm^{2}s^{-1} for a Co(II) Disulfiram complex in Acetonitril (AN) solution at Au electrode.

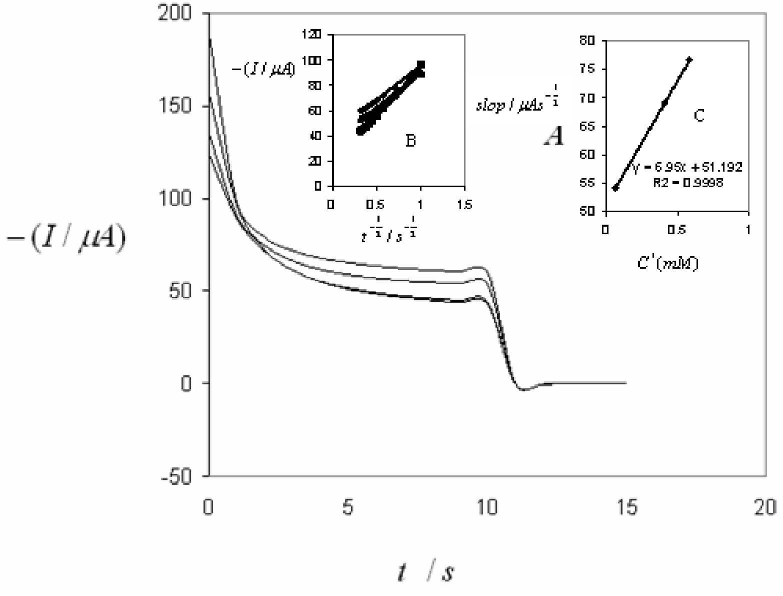


Figure.5. Chronoamperometric response at Au electrode for different concentrations of Co(II) Disulfram ؛ a)0.1 , b)0.3 , c)0.5 , d)0.7 mM.first and second potential Steps were -0/99 and 0 mV respectively. B) Plots of Ip vs.t obtained from chronoamperograms . C) Plot of the slope of straight lines against the complex concentration.

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