Investigation of Catalytic Effect Nitrite on Electrochemical Reduction of Cobalt Dimethylglyoxime Complex by Polarographic and Voltammetric Techniques

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The voltammetric and polarographic behaviour of Cobalt Dimethylglyoxime (Co-DMG) complex on a hanging mercury drop electrode (HMDE) and static mercury drop electrode (SMDE) has been studied by several techniques including Square wave voltammetry (SWV), Differential pulse polarography (DPP) and stripping techniques. Polarographic and voltammetric curves recorded at HMDE and SMDE provide information about electrode reaction mechanism. Catalytic effect of nitrite on the electrochemical reduction mechanism of the complex have been explained.

1. INTRODUCTION

Cobalt is biologically essential trace element. Although usually cobalt is found in natural waters and food in trace concentrations, their variations occurring due to the natural processes or antropogenic activities can cause deficiency and toxicity problems. The quantitative determination of trace amounts of cobalt plays an important role in the field of environmental analysis, process control and medicine [1-4].

Modern stripping voltammetric methods belong to the most sensitive analytical techniques thanks to the adsorption or electrochemical accumulation of electroactive substances on the electrode

surface, as well as the exploitation of the catalytic reactions. The presence of dioximes (e.g. DMG, α-benzyl dioxime (α-BD), α-furyl dioxime (α-FD) or cyclohexanedione dioxime (nioxime)) in the solution during determination of Co(II) by means of catalytic adsorptive stripping voltammetry (CAdSV) leads to the formation of a complex of a metal with the active ligand, which is accumulated adsorptively at the electrode surface. The analytical signal is the sum of reduction currents of the central metal ion and the surrounding two dioxime ligands [4–7].

Adsorptive stripping voltammetry (AdSV) has become popular for metal speciation studies because they have very low limits of detection, extremely high sensitivity and the ability to differentiate between different physico-chemical forms of metals. It has been shown that adsorption can be used as a pre-concentration step to increase the sensitivity of the electroanalytical determinations particularly for elements such as cobalt their electrode process being irreversible in non-complexing media. To reduce the detection limit of cobalt determination by AdSV, a long period of accumulation or catalytic processes in the presence of nitrite are exploited. Catalytic systems are often exploited in voltammetric determinations for cobalt determinations the Co(II)-dioxime-nitrite systems are most commonly used. Recently, they have been reported a highly sensitive and selective method for the determination of cobalt by catalytic adsorptive cathodic stripping voltammetry. The method was based on adsorptive accumulation of cobalt-ligand complex onto a hanging mercury drop electrode, followed by reduction of the adsorbed species by voltammetric scan. The reduction current has been seen to enhance dramatically by the presence of nitrite [4-10,16-17]. Bobrowski and co-workers also studied a bromate based catalytic determination [18]. The high selectivity and sensitivity of this method made us investigate the actual mechanism, which is involved in such an electrochemical system.

This work deals with the determination of electrochemical behaviour of cobalt-dimethylglyoxime (Co-DMG) in different electrolyte media. The polarographic and voltammetric behaviour at the SMDE and HMDE has been studied in aqueous by using SWV and DPP techniques. At the same time, catalytic effect of nitrite, on the Co-DMG complex were investigated depended on different parameters. It has been determined optimum conditions by using SWV, DPV and stripping techniques. This study contributes to previous studies on the electrochemistry of Co-DMG complex.

2. EXPERIMENTAL

Cobalt nitrate $Co(NO_3)_2.6H_2O$ (Merck) and dimethylglyoxime was purchased from Aldrich and was used without further purification. Phosphoric acid, acetic acid, boric acid, ammonia and tartrate, sodium hydroxide were of purity p.a. Buffer solutions used were Britton Robinson (B-R) buffer (pH 9.0), acetate buffer (pH 4.5), phosphate buffer (pH 7.0) and borate buffer (pH 9.0) ammonia buffer (pH 9.2) and tartrate buffer (pH 9.2). All solutions were prepared using ultra pure water obtained by passing deionized water through a Milli-Q water purification system.

The polarographic and voltammetric experiments were performed using a Metrohm 757 VA Computrace Electrochemical Analyser at room temperature. This consisted of a Multi Mode Electrode (DME, SMDE and HMDE), a Ag/AgCl reference electrode and Pt wire auxiliary electrode.

All solutions were de-aerated for 5 min oxygen-free nitrogen prior to polarographic and voltammetric measurements.

3. RESULTS AND DISCUSSION

The nature of electrochemical behaviour of Cobalt(II), dimethylglyoxime and Cobalt-dimethylglyoxime complex were investigated by using SWV, DPP techniques in Britton-Robinson buffer (pH 2.0-12.0), acetate buffer (pH 3.5-6.0), phosphate buffer (pH 6.0-8.0) and borate buffer (pH 8.0-10.0) ammonia buffer (pH 8.5-10.5) and tartrate buffer (pH 8.5-10.5) solutions. Voltamograms and polarograms were recorded by square wave voltammetry (SWV) mode at hanging mercury drop electrode (HMDE) and differential pulse polarography (DPP) mode at static mercury drop electrode(SMDE).
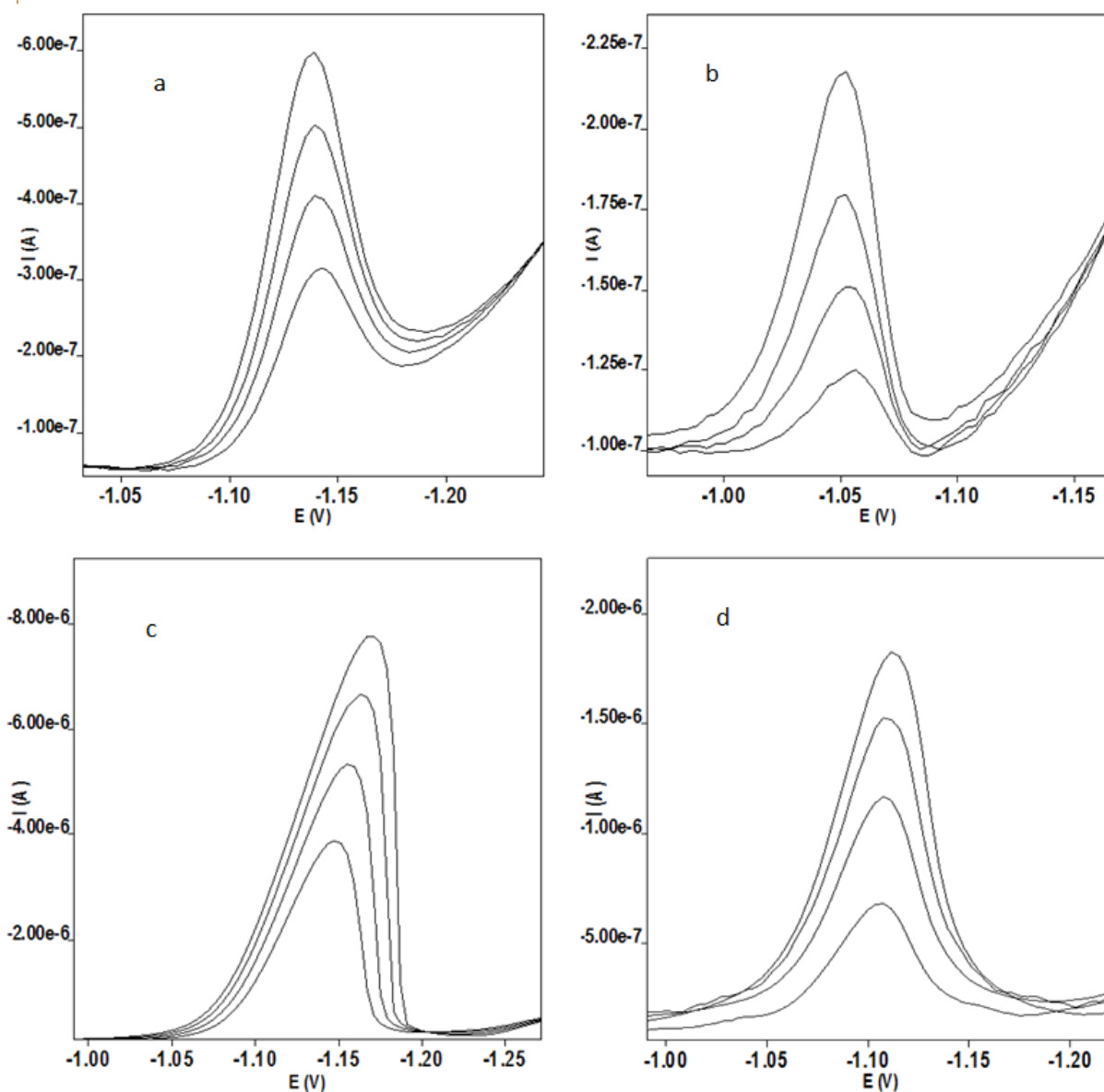
Figure 1. SWV voltammograms of 10^{-7} M Co(II)-DMG complex a) ammonia buffer in non nitrite media b) tartrate buffer in non nitrite media c) ammonia buffer in nitrite media d) tartrate buffer in nitrite media

Optimum peak potentials were obtain at ammonia buffer (pH 9.2) and tartrate buffer (pH 9.2) solutions. Polarograms and voltammograms of Co-DMG complex are shown in Fig.1.

Differential pulse voltammetric and Square wave voltammetric measurements of Co-DMG complexes showed that there are no significant differences in their electrochemical techniques. This could be explained by similarity in the reduction properties of their chelate complex. In generally the reaction mechanism of the Co(HDMG) complex are given as below;

$$[Co(HDMG)_2]_{adsorbed} + 2H^+ \longrightarrow Co(0) + 2[H_2DMG]_{desorbed}$$
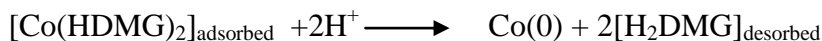
Two protons are involved in the rate-determining step of the $Co(HDMG)_2$ reduction. Therefore, pH changes should influence the cobalt reaction process.

This was proved by experiments at different pH and buffer media Britton-Robinson buffer (pH 2.0-12.0), acetate buffer (pH 3.5-6.0), phosphate buffer (pH 6.0-8.0), borate buffer (pH 8.0-10.0), ammonia buffer (pH 8.5-10.5) and tartrate buffer (pH 8.5-10.5) solutions in various supporting electrolytes. It has been found that, ammonia buffer at pH 9.2 as the optimum solution media for the Co-DMG complexes determination as shown Figure 1.a and 1.c. Therefore, it has been studied systematically in ammonia buffer media. Under these conditions, the E_p for $Co(DMG)_2$ appears at ~-1.10 V, and the polarographic wave is well defined [4,5,7,13]. The well-defined $Co(HDMG)_2$ peaks allowed estimation of areas without any difficulties.

3.1. Catalytic Effect of Nitrite

In this work, it has been investigated catalytic effects of nitrite on cobalt-dimethy-glyoxime complex by using polarographic and voltammetric techniques. Preliminary, the change of the peak current depending on nitrite concentration has been investigated by using SWV and DPP techniques. Polarograms and voltammograms have been given in Figure 2.
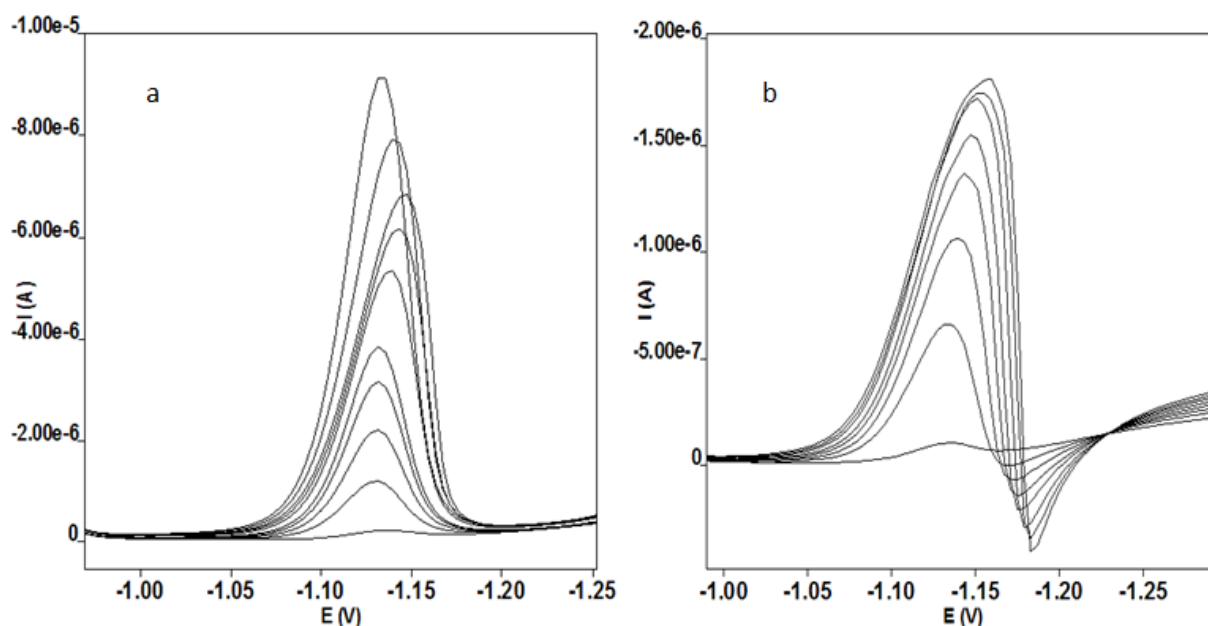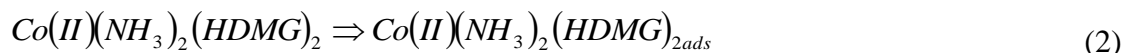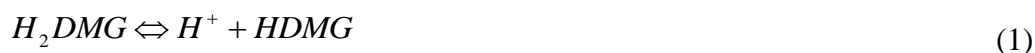

Figure 2. The change of peak current of 10^{-7} M the Co-DMG complex dependent on nitrite concentration at ammonia buffer pH 9.2 a)SW Voltammograms b) DP polarograms
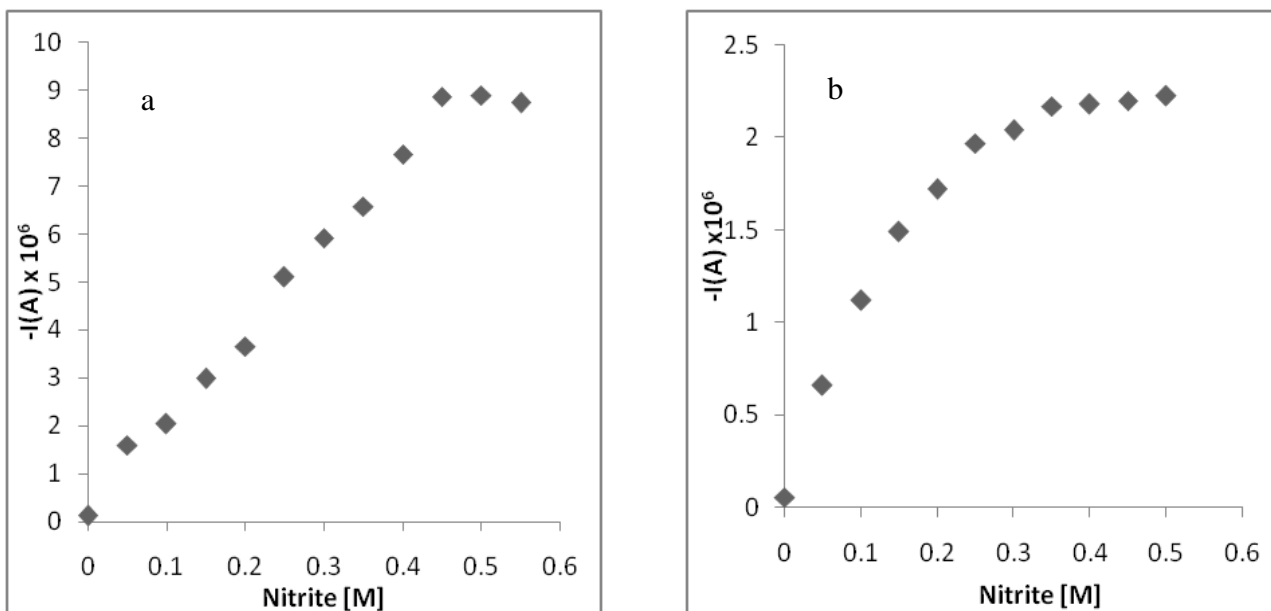
Figure 3. The change of peak current of 10^{-7} M the complex dependent on nitrite concentration at ammonia buffer pH 9.2   a) SWV b) DPV

Catalytic effect of nitrite ions on the current of Co-DMG complex provides a significant enhancement of the voltammetric response and consequently a considerable decrease of the detection limit of the complex as shown figure 2 and 3. The effect of nitrite concentration, were investigated to obtain suitable conditions for the determination of the complex. The effect of the nitrite concentration on the peak heights for Co-DMG in the ammonia buffer solution containing is illustrated in Fig. 2 and 3. Initially the signals increase linearly and at higher concentration of nitrite concentration the plot for complex slightly levels off. The last step of optimization comprised examination of the influence of nitrite concentration on the Co-DMG peak current. It increases linearly with increasing nitrite concentration up to 0.1 M, and then more slowly, up to 0.75 M. The concentration of 0.5 M was selected for further experiments, as it was a good compromise between the sensitivity of the Co-DMG response and the blank value for cobalt, which increases with the nitrite concentration. Especially, as shown Figure 2 and 3 linear range area of SWV data is bigger than DPV studies. Therefore, optimum concentration of the nitrite ion and suitable technique has been chosen 0.5 M and SWV as below studies. In this method, cobalt is usually accumulated on the electrode in the form of Co-DMG complexes and the analytical signal is obtained as a result of reduction of the accumulated complex. Although various cobalt complexes have been used for accumulation of cobalt, its complex with dimethylglyoxime (DMG) has been most widely used [5-7,13-15,19].
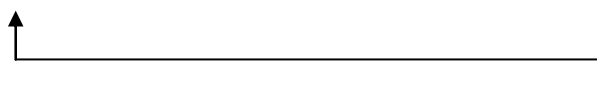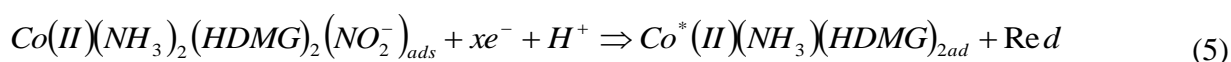
Considering literature studies, catalytic effect of nitrite on the complex is commonly given as the following reaction mechanism [6,7]. Parameters of adsorbed complexes at the electrode/solution interface would be necessary to distinguish between these mechanisms

$$H_2DMG \Leftrightarrow H^+ + HDMG \tag{1}$$

$$Co(II)(NH_3)_2(HDMG)_2 \Rightarrow Co(II)(NH_3)_2(HDMG)_{2ads} \tag{2}$$

$$Co(II)(NH_3)_2(HDMG)_{2ads} + NO_2^- \Rightarrow Co(II)(NH_3)(HDMG)_2 NO_2^- ads + NH_3 \tag{3}$$

or

$$Co(II)(NH_3)_2(HDMG)_{2ads} + NO_2^- \Rightarrow Co(II)(HDMG)_2 \left(NO_2^-\right)_{2ads} + 2NH_3 \tag{4}$$

and

$$Co(II)(NH_3)_2(HDMG)_2 \left(NO_2^-\right)_{ads} + xe^- + H^+ \Rightarrow Co^*(II)(NH_3)(HDMG)_{2ad} + \text{Re}d \tag{5}$$

$$Co^*(II)(NH_3)(HDMG)_{2ads} + NO_2^- \Rightarrow Co(II)(NH_3)(HDMG)_2 NO_2^- ads \tag{6}$$

H_2DMG **:** dimethylgloxime molecule
HDMG **:** anion form of the molecule
Red **:** reduction product
$Co^*(II)(NH_3)(HDMG)_{2ads}$**:** electroactive complex in solution media

Hydrogen ions are involved in the rate-determining step of the $Co(HDMG)_2$ as shown reduction reaction mechanism Therefore, the reaction process of the complex is dependent on pH. Other mechanism are also discussed in the literature [6,7].

3.2. Stripping Studies

To obtain suitable conditions for the stripping determination of Co-DMG, the influence of deposition time and deposition potential effect were investigated.

Initially the signals increase linearly and at higher concentration the plot for Co-DMG slightly levels off, indicating that the saturation surface metal-complex concentration is gradually reached.

The next investigated factor, accumulation potential has decisive influence on the effectiveness of the Metal–DMG adsorption at the electrode surface. The dependence of the accumulation potential on the stripping currents have been studied. The peak currents for the complex remain stable in the potential interval from -0.3V to -0.9 V, then decreases. Adsorption efficiency and matrix effect for the complex increases dramatically while the deposition potential was changed at below and above -0.6 V.

Thus optimum accumulation potential of -0.6 V can be recommended for DPV and SWV techniques. However, for the precise and sensitive determination of the complex, the value of -0.6 V would be more suitable [12,14]. The value of 50 mV was chosen for pulse height further study, since it ensured the suitable peak currents for the complex investigated.

3.3. Deposition time

For procedure exploiting the deposition in ammonia buffer solution media the effect of the deposition time was studied at deposition potentials -0.6 V. Prolongation of the deposition time from 10 to 120 s the complex peak increased linearly up to 50 s and then increased nonlinear manner up to 240 s for DPV and SWV but linear range are SWV bigger than DPV. Such a different dependency for deposition potential of -0.6 V may attributed to square wave nature of applied voltage. The contribution of anodic current part which leads to much linear dependency and makes possible a lower detection limit. For the effect of deposition time concentration range has been selected as 1×10^{-12} and 1×10^{-7} mol/L and it was found that the cobalt peak increases linearly with the deposition time to 50s. In further experiments, the accumulation time of 30 s was used, which ensures high sensitivity of cobalt ion and short time of analysis. Voltammetric data have been given in Figure 4 and 5. The peak current of the complex significantly rises with presence of nitrite in both techniques and this allows to detection of cobalt below 10^{-11} M concentration. The detection limit for deposition time of 30 s was found as 2.10^{-12} mol/L.
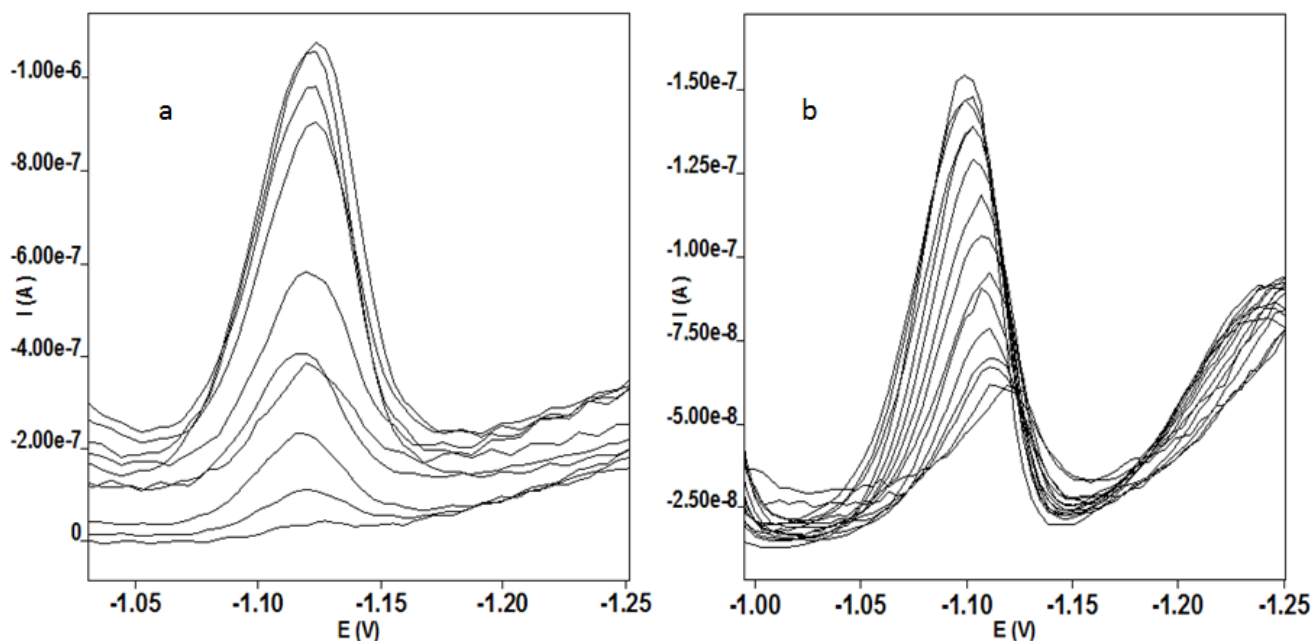
Figure 4. Voltammograms of a 2.10^{-12} M Co(II)-DMG complex in ammonia buffer and 0.5 M nitrite media a) AdsSWV b) AdsDPV
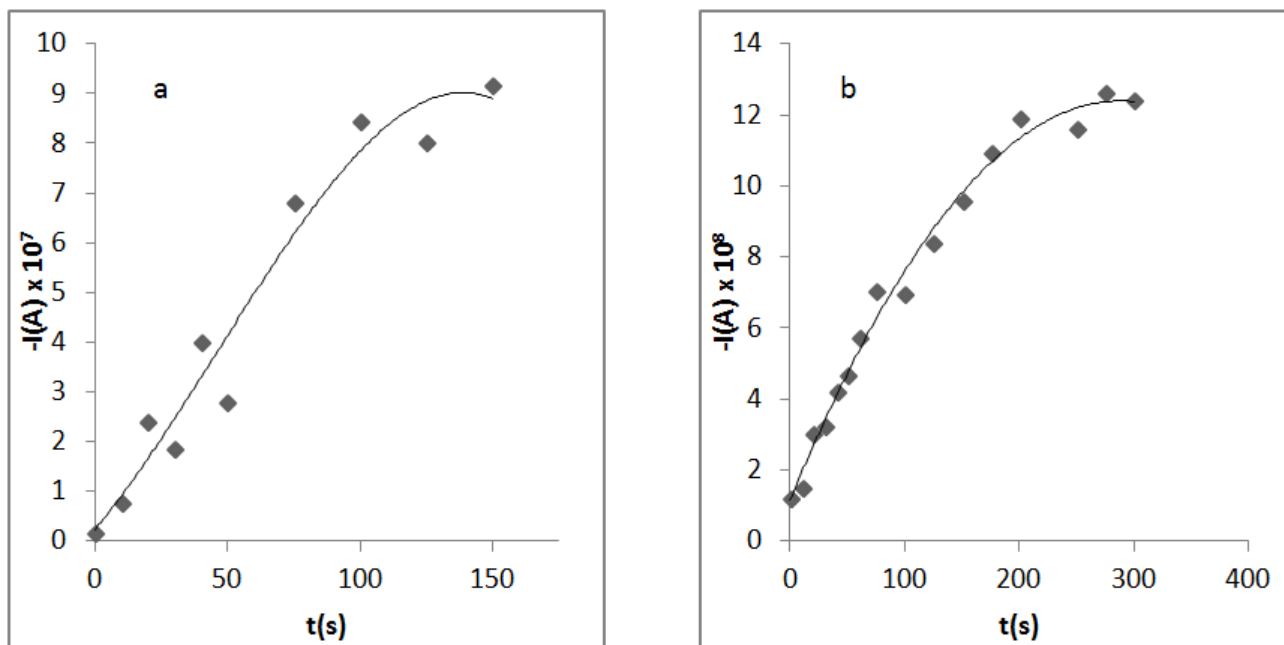
Figure 5. Dependent on time calibration curve graph of 2.10^{-12} M Co(II)-DMG in ammonia a) AdsSWV b) AdSDPP

4. CONCLUSION

In this investigation, The voltammetric and polarographic behaviour of Cobalt Dimethylglyoxime (Co-DMG) complex on a hanging mercury drop electrode (HMDE) and static mercury drop electrode (SMDE) has been studied by several techniques including Square wave voltammetry (SWV), Differential pulse polarography (DPP), and stripping techniques. The electrochemical response of the complex was determined by experimental conditions such as pH, deposition potential, time and concentration. From the polarographic and voltammetric data optimum conditions were found pH 9.2 and a deposition potential value of -0.6 V. A detection limit of 2.10^{-12} M is achievable for deposition time of 30 s in ammonia buffer media.

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