ORIGINAL PAPER

Electrochemical studies on [M(diars)$_2$X$_2$]$^+$ where [X = Cl, Br; M = Os, Re, Ru, Rh; diars = o-phenylenebis (dimethylarsine)] at bare and Nafion modified electrodes

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Abstract The voltammetric behaviour of the M(III/II) redox couple of the complexes of the general formula [M(diars)$_2$X$_2$]$^+$ where M = Os, Re, Ru, Rh and diars = o-phenylenebis-(dimethylarsine) has been investigated in aqueous and aqueous/ethanol solvents at bare and Nafion modified electrodes. The formal reduction potential falls within the range of 0.097–0.0920 V and increases with the dielectric constant of the solvent. In acertonitrile, both the oxidized and reduced forms of the complex showed no adsorption at the surface of the glassy carbon electrode as shown by cyclic voltammetry. The electrochemistry is consistent with a quasireversible one electron transfer between the di and tri cationic forms of the complexes. A current-enhancement of ~2 was observed at Nafion-modified glassy carbon over the bare electrode. Well defined voltammograms were obtained at Nafion-modified glassy carbon with a detectable signal down to 10^{-9} M range by differential pulse voltammetry. Electrochemical detection of dopamine in presence of [Os(4-mediars)$_2$Cl$_2$]$^+$ at Nafion modified electrode indicates an increase in peak current. This shows that this complex acts as biochemical-sensor for dopamine.

1 Introduction

o-Phenylenebis(dimethylarsine), [o-C$_6$H$_4$(As–CH$_3$)$_2$]$_2$ (diars) is a versatile ligand which is capable of stabilizing a range of common and uncommon oxidation states and stereo-chemistries for almost all the transition elements [1]. Diars complexes have attracted interest in the field of radiopharmaceuticals due to the selective uptake of [Tc(diars)$_2$Cl$_2$]Cl in the brain tissue of test animals [2, 3]. Cationic technitium (^{99}Tc) complexes that incorporate tertiary arsine ligands are developed as potential myocardial imaging agents [4, 5] and are especially benefited from application of electrochemical and spectroelectro chemical techniques [6]. The analogous complexes of the radioactive isotope of Rhenium, ^{186}Re have been investigated with regard to their potential use in nuclear medicine [7, 8]. The electrochemistry of [Re(diars)$_2$Cl$_2$]Cl in glassy carbon and Nafion modified glassy carbon electrodes has been studied with the aim of the development of sensor for in vivo use [9]. Recently homoleptic iron(II) and ruthenium(II) diarsine complexes have been synthesised and their redox properties evaluated [10, 11].

In this paper we explore the potential utility of Nafion as a polymer film to enhance the electrochemical detection of [M^{III}(diars)$_2$X$_2$]$^+$ where diars = o-phenylene bis(dimethylarsine), and M = Os, Re, Ru, Rh.

This investigation has been initiated with the spectroscopic and electrochemical evaluation of [Re(DMPE)$_3$]Cl where DMPE = 1,2-bis(dimethylphosphino)ethene at Nafion modified electrodes [12–14]. Micro electrode sensors with a coating of Nafion gel for in vivo detection of

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[Re(DMPE)₃]Cl were also developed [15]. The perfluoro sulfonated cation exchange polymer Nafion [16–18] is employed to selectively preconcentrate large cationic species with hydrophobic ligands and to improve their detection limits [19, 20].

Differential pulse voltammetric technique [21–23] is employed to find detectable signals at very low concentration using Nafion coated glassy carbon electrodes. Film thickness variation and interference from other electroactive species have also been studied.

2 Experimental

2.1 Materials

The general structure of the metal complexes (1–6) studied are given in Fig. 1. The metal complexes such as [Os(4-mediars)₂Cl₂]BF₄, [Re(diars)₂Cl₂]BF₄, [Ru(diars)₂Br₂]BF₄, [Ru(4-mediars)₂Cl₂]BF₄, [Rh(diars)₂Cl₂] were further purified by recrystallisation from ethanol [24]. Analytical grade mono potassium phosphate and disodium phosphate were used to prepare a buffer with a pH of 7.2 by mixing appropriate volumes of each of the phosphate salts. To prepare fresh ethanol/buffer solutions the complex was dissolved in absolute ethanol followed by dilution with the buffer to make a stock solution of 10^{-3} M. A 5% weight Nafion (E.W. 1100) in a mixture of lower aliphatic alcohols and 10% water was purchased from Aldrich Chemical Co. L. Ascorbic acid and Dopamine were used for interference studies. All solutions were prepared using double distilled water. HPLC grade acetonitrile was the solvent employed with 0.1 M, tetrabutyl ammonium perchlorate (TBAP) as supporting electrolyte. No significant electroactive impurities were detected in either the solvent or supporting electrolyte.
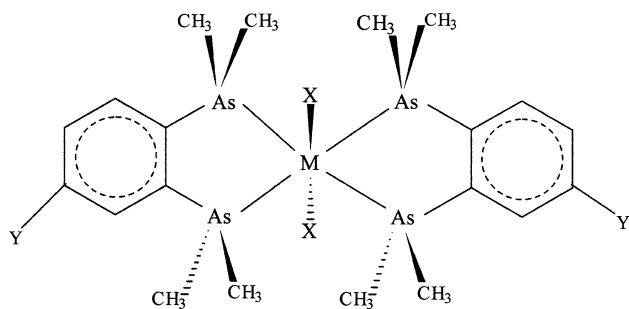

Fig. 1 Structure of *o*-phenylenebis(dimethylarsine) metal complexes. Complex 1: M = Ru, X = Cl, Y = CH₃, complex 2: M = Ru, X = Cl, complex 3: M = Ru, X = Br, complex 4: M = Rh, X = Cl, complex 5: M = Os, X = Cl, Y = CH3, complex 6: M = Re, X = Cl

2.2 Instrumentation and procedure

Electrochemical measurements were performed with BAS-50A electrochemical analyzer. A three electrode assembly of glassy carbon electrode (working), platinum electrode (auxiliary) and Ag/AgCl (reference) was used. Glassy carbon was resurfaced with alumina. Solutions were prepared in HPLC grade acetonitrile and ethanol containing 0.1 M tetrabutyl ammonium perchlorate (TBAP) as supporting electrolyte. Each solution was bubbled with nitrogen before use and blanketed with N₂ during voltammetric measurements. The redox potentials given are against Ag/AgCl unless otherwise mentioned. DPV was employed for these complexes in CH₃CN to concentration 10^{-9} M.

2.3 Preparation of Nafion coated electrode

Nafion, an ion-exchange polymer which is very resistant to chemical attack, even by strong oxidants at elevated temperature has found increasing use as a membrane material. A 5% Nafion solution was diluted to 2% solution using ethanol. To prepare the Nafion-coated electrode, a known volume of 2% Nafion solution in ethanol was coated on the surface of clean, pretreated glassy carbon electrode with a microsyringe and the solvent was allowed to evaporate in air at room temperature for about 10 min. Prior to use, the electrode was soaked for 30 min either in distilled water or in supporting electrolyte solution [25]. Using known values of the volume and density of the Nafion solution and the surface area of the electrode, the thickness of the Nafion film was calculated as 6.2 μm [16]. In the thickness variation study, the thickness of the Nafion film was changed by using varying volumes of the Nafion solution deposited onto the electrode tip. Aliquots of 5 μl were applied until a total volume of 5, 10, 15 and 20 μl, respectively were obtained. The deposited aliquot was allowed to dry for 5 min at room temperature to evaporate the solvent before the next aliquot was applied. Solutions were purged with nitrogen before measurement and blanketed with nitrogen during measurement.

3 Results and discussion

3.1 Cyclic voltammetry

A typical cyclic voltammogram of complex 1 in acetonitrile at bare glassy carbon electrode is shown in Fig. 2. The electrochemical parameters obtained from the voltammograms at bare and Nafion modified electrodes are summarized in Table 1. The values of i_{pa} and i_{pc} were almost identical indicating a single reversible process. The separation of the anodic and cathodic peak potenial
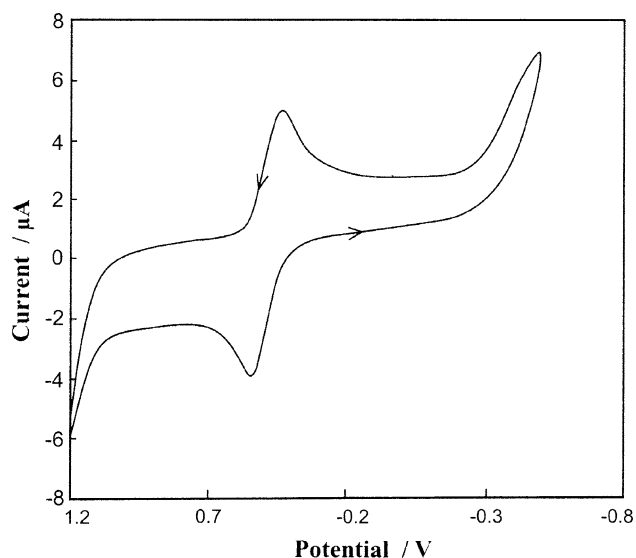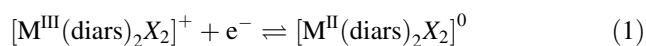
Fig. 2 Cyclic voltammogram of 1 mM [Ru(4-mediars)$_2$Cl$_2$]$^+$ in acetonitrile scan rate, 100 mV s^{-1}

Fig. 3 Cyclic voltammogram of 1 mM [Ru(diars)$_2$Cl$_2$]$^+$ in acetonitrile. Scan rate, 100 mV s^{-1}

($\sim$120 mV) indicates quasi-reversible redox process. Hence the electrochemical process may be depicted as

$$[M^{III}(\text{diars})_2 X_2]^+ + e^- \rightleftharpoons [M^{II}(\text{diars})_2 X_2]^0 \tag{1}$$

The cyclic voltammograms of complexes 2 and 5 are shown in Figs. 3 and 4, respectively. The effect of scan rate was also investigated and is shown typically for the complex, [Ru(diars)$_2$Br$_2$] in Fig. 5a. A plot of the cathodic peak current versus scan rate is linear for scan rates ranging from 50 to 150 mV s^{-1} and follows the Randles–Sevcik equation

$$i_p = (2.69 \times 10^5)\, \eta^{3/2}\, AD^{1/2}\, Cv^{1/2}, \tag{2}$$

i_{pa} and i_{pc} increase as $v^{1/2}$ increases, as seen in Fig. 5b for the complex 1.

Repetitive cycling did not affect either the peak potential or the peak currents, and no evidence of adsorption at the electrode was found. The cyclic voltammogram was run for complex 5 in ethanol, acetonitrile and ethanol-buffer
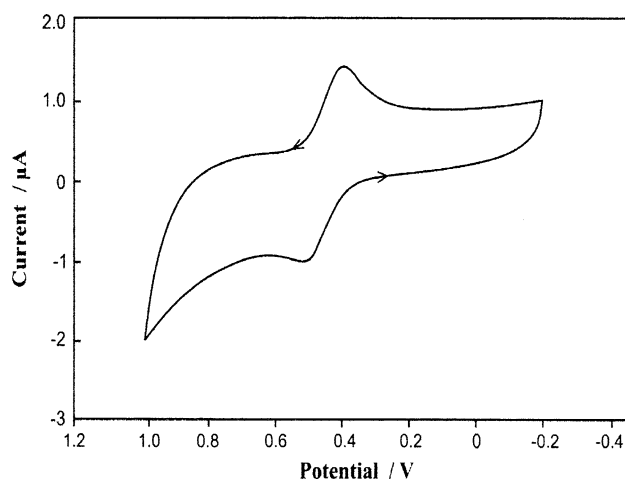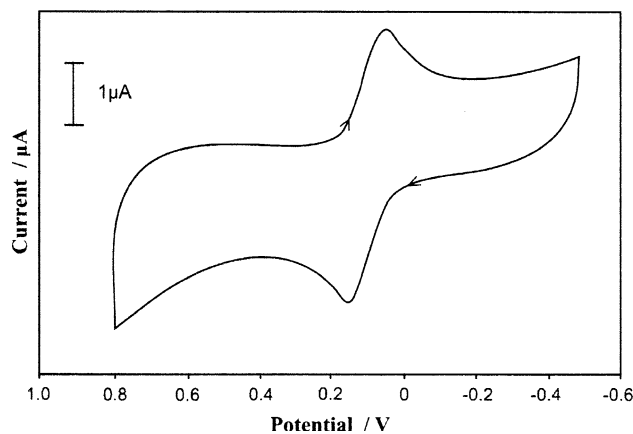

Fig. 4 Cyclic voltammogram of 1 mM [Os(4-mediars)$_2$Cl$_2$]$^+$ in ethanol at glassy carbon electrode. Scan rate, 100 mV s^{-1}

mixture. The redox potential was found to increase with increase in the dielectric constant. In EtOH–phosphate buffer, the oxidation peak was less prominent and the peak

Table 1 Electrochemical data for [M^{III}(diars)$_2$X$_2$]$^+$ (M = Os, Ru, Rh)

Solvent	Electrolyte	Electrode type	[Ru(4-mediars)$_2$Cl$_2$]$^+$ (1)		[Ru(diars)$_2$Cl$_2$]$^+$ (2)		[Ru(diars)$_2$Br$_2$]$^+$ (3)		[Rh-(diars)$_2$Cl$_2$]$^+$ (4)		[Os(4-mediars)$_2$Cl$_2$]$^+$ (5)	
			E$^{0'}$ (V)	ΔE$_p$ (V)	E$^{0'}$ (V)	ΔE$_p$ (V)	E$^{0'}$ (V)	ΔE$_p$ (V)	E$_{pa}$ (V)	ΔE$_p$ (V)	E$^{0'}$ (V)	ΔE$_p$ (V)
Ethanol	TBAP	GC	0.465	0.286	0.459	0.160	–	–	−0.742	–	0.097	0.142
		Au	0.502	0.126	0.457	0.142	–	–	–	–	0.100	0.125
CH$_3$CN	TBAP	GC	0.494	0.117	0.451	0.124	0.579	0.179	–	–	0.122	0.074
		Nafion GC	0.466	0.077	0.450	0.062	0.586	0.168	−0.163	–	0.092	0.079
Ethanol/water	Buffer	GC	–	–	0.434	0.100	–	–	–	–	0.065	0.088

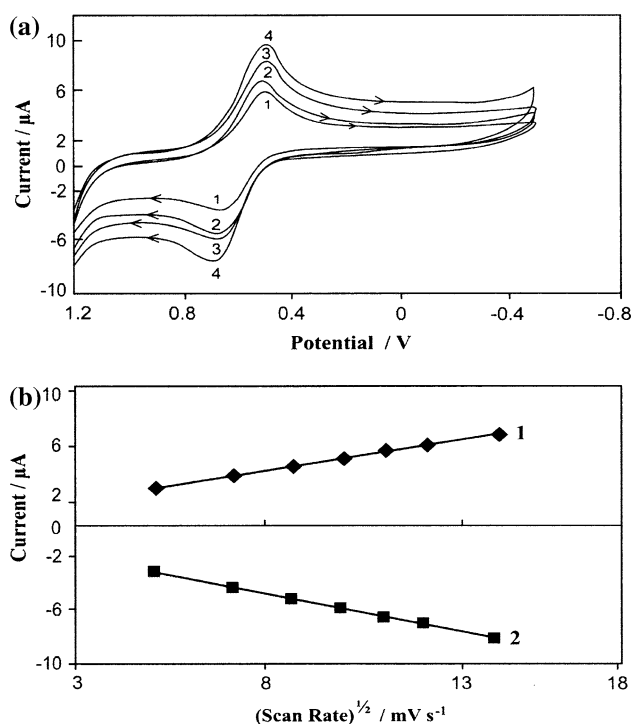E$^{0'}$, the average of the cathodic and anodic peak potentials; GC, glassy carbon electrode; scan rate, 100 mV s^{-1}

(a)

(b)

Fig. 5 Cyclic voltammograms of (**a**) 1 mM $[Ru(diars)_2Br_2]^+$ in CH_3CN at various scan rates (v = 50, 75, 100, 150 mV s^{-1}). (**b**) Plot of i_{pc} versus $v^{1/2}$ (1) and i_{pa} versus $v^{1/2}$ (2) from cyclic voltammograms of $[Ru(4-mediars)_2Cl_2]^+$

current diminished, confirming adsorption of the reduction product.

3.2 Effect of substituents and counter ions on the reduction potential

For complexes with identical equatorial ligands the $E^{0'}$ of the dibromo complex is more positive than that of the corresponding dichloro complex [26]. The redox potentials for the couple M^{III}/M^{II} vary according to the nature of the anions present [13]. This is revealed by the complexes 1–3. The $E^{0'}$ of complex 1 is about 128 mV more positive than that of complex 3. The electron releasing methyl group of the diars ligand increases the reduction potential of complex 1. This is illustrated from the redox data of complex 1 and 2 (Table 1). The complex 4 showed an irreversible peak with E_{pc} = −0.163 V for the couple $Rh^{III} \rightarrow Rh^{II}$. Table 2 describes the effect of scan rate on $E^{0'}$ and i_p for 10 mM solution of complex 1 in CH_3CN. The ratio of the anodic peak current to cathodic peak current, i_{pa}/i_{pc} did not vary with the scan rate. The average peak potential ($E^{0'}$ = 0.498 ± 4 mV) was also independent of scan rate (Table 2).

The incorporation of complex 1 into a Nafion film modified glassy carbon electrode was observed voltammetrically by continuously cycling the potential between

Table 2 Effect of scan rate on $E^{0'}$ and i_p for $[Ru(4-mediars)Cl_2]BF_4$ (10 mM in CH_3CN)

N (mV s^{-1})	i_{pa} (μA)	i_{pc} (μA)	i_{pa}/i_{pc}	$E^{0'}$ (V)
25	−3.02	+3.01	1.00	0.498
50	−4.2	+4.1	1.02	0.494
75	−4.99	+4.89	1.02	0.500
100	−5.67	+5.58	1.01	0.502
125	−6.23	+6.15	1.01	0.501
150	−6.76	+6.68	1.01	0.501
200	−7.84	+7.57	1.03	0.502

+1.2 and −0.8 V. The peak current increased as the electroactive species were incorporated into the film. The $E^{0'}$ showed a positive shift of about 28 mV at the Nafion modified electrode, indicating that $[Ru(4-mediars)_2Cl_2]^0$ is stabilized by Nafion, relative to $[Ru(4-mediars)_2Cl_2]^+$ [14]. This may be attributed to a strong hydrophobic interaction between the complex and the Nafion.

3.3 Differential pulse voltammetry

Differential pulse voltammetry was employed at Nafion-modified glassy carbon electrodes to determine the detection limits of the complexes. Differential pulse voltammograms were run at modified electrode in 10^{-9} M concentration range, in acetonitrile, at a scan rate of 20 mV s^{-1}. Table 3 summarises the data obtained from differential pulse voltammetry. The cathodic differential pulse voltammogram for the complex 5 indicated a peak at +121 mV (Fig. 6c). The voltammogram was also run with the Nafion modified electrodes. A shift in peak potential (+106 mV) as well as an enhancement in peak current (2-fold) was noticed. This negative shift from +121 (bare) to 106 mV (modified) reveals that the oxidation is thermodynamically easier for this complex in Nafion [27, 28].

Table 3 Voltammetric parameters from differential pulse voltammetry in acetonitrile

Compound	Bare GC electrode		Nafion coated GC electrode	
	E_{pc} (mV)	i_{pc} (μA)	E_{pc} (mV)	i_{pc} (μA)
$[Ru(4-mediars)_2Cl_2]^+$	500	6.67	468	7.81
$[Ru(diars)_2Cl]^+$	−464	1.66	−450	2.21
$[Ru(diars)_2Br_2]^+$	576	6.85	572	7.2
$[Rh(diars)_2Cl_2]^+$	−116	0.589	−128	0.626
$[Os(4-mediars)_2Cl_2]^+$	+121	1.9	+106.8	3.39
$[Re(diars)_2Cl_2]^+$	−441	+3.72	−395.5	7.48
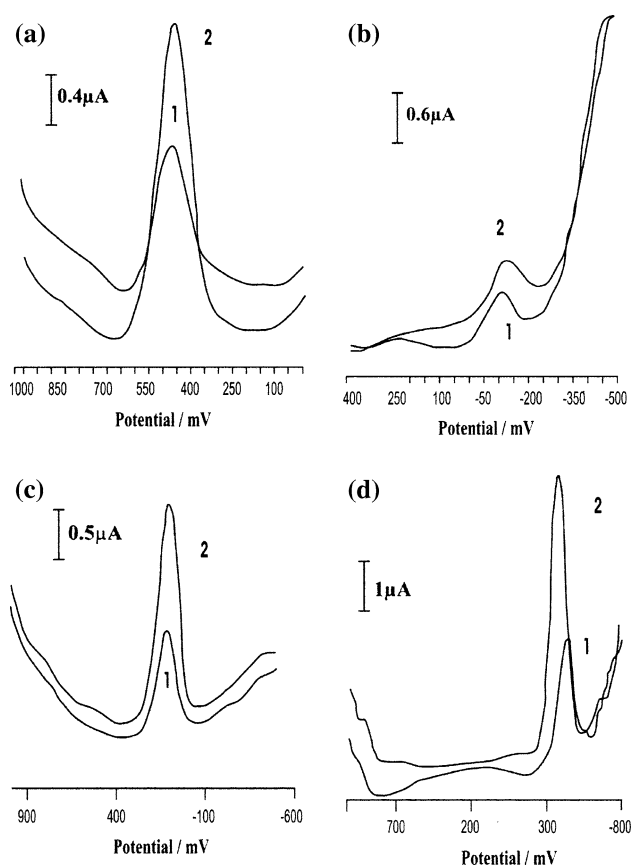
Fig. 6 Differential pulse voltammograms of (**a**) 1×10^{-9} M [Ru(diars)$_2$Cl$_2$]$^+$, (**b**) 1×10^{-9} M [Rh(diars)$_2$Cl$_2$]$^+$ (**c**) 1×10^{-9} M [Os(4-mediars)$_2$Cl$_2$]$^+$, (**d**) 1×10^{-9} M [Re(diars)$_2$Cl$_2$]$^+$ at bare (1) and Nafion modified (2) glassy carbon electrodes. Scan rate 20 mV s^{-1}

3.4 Effect of film thickness

A modifier can change the properties and functions of the electrode surface. Hence the influence of the Nafion concentration on the peak current was investigated and the results are shown in Fig. 7b. The peak current reached a maximum when the Nafion film thickness was 6.3 μm. When the film thickness >6.3 μm, a decrease in peak current was observed, indicating increase in electrical resistance [30]. The sensitivity decreased substantially with the film thickness.

3.5 Evaluation of catalytic effect of complex 5

Monoamines such as dopamine (DA), norepinephrine (NE) and 5-hydroxy tryptamine (5-HT) are regarded as important neuro transmitters. Extreme abnormalities of DA levels leads to brain disorders such as Parkinson's diseases and Schizophrenia [31, 32]. Hence currently there is vast interest in the development of rapid and simple methods for the determination of the concentration of DA. DA can be determined by electrochemical methods because it is an electrochemically active compound. However, a major problem encountered in the detection is the interference from ascorbic acid (AA), because AA (10^4 mol dm^{-3}) largely coexists with DA (10^{-8}–10^{-6} mol dm^{-3}) in brain tissue; therefore it is very difficult to determine DA directly [33, 34]. DA exists as a cation and AA exists as an anion at the physiological pH, 7.4. This problem may be overcome
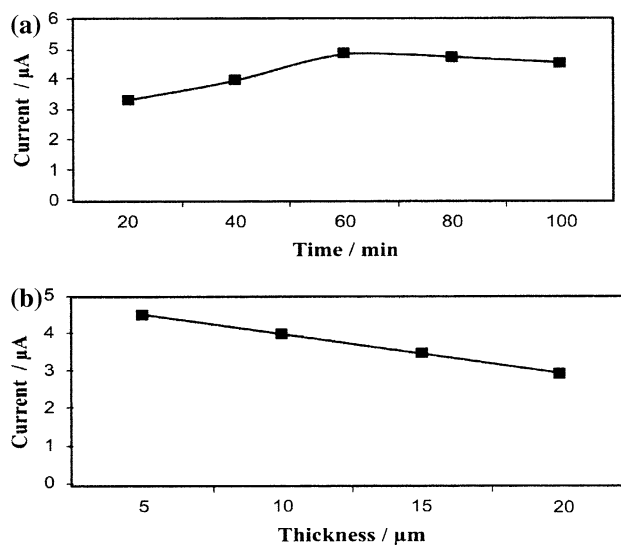
Similar voltammogram recorded for complex 6 is shown in Fig. 6d. For complex 2 (Fig. 6a), the DPV peak was observed at −441 mV. With modified Nafion electrode, there was a slight reduction (∼6 mV) in the potential. For ruthenium complexes, a small shift (14 mV) in the reduction potential was noticed at the Nafion modified electrode, compared to the bare one. For complex 4 (Fig. 6b), the cathodic differential pulse voltammogram showed a peak at −116 mV. This was shifted to −128 in Nafion modified glassy carbon electrode. But the increase in current was minimum for the rhodium complex.

Differential pulse voltammetry was also used to determine the amount required for maximum uptake for the complexes into the Nafion film. The partitioning of complex 5 in the Nafion film was measured by immersing a Nafion modified electrode in a stirred solution of complex 5 and measuring the peak current from cyclic voltammety. Figure 7a shows the result of peak current versus immersion time for an electrode immersed in 1×10^{-4} solution of complex 5. Maximum uptake occurred at about 60 min, evidenced by the plateauing of the current plot [29].

Fig. 7 (**a**) Plot of peak current versus deposition time for 1×10^{-4} M [Os(4-mediars)$_2$Cl$_2$]$^+$ in acetonitrile at a Nafion-modified electrode. (**b**) Plot of peak current versus film thickness from 1×10^{-6} M [Os(4-mediars)$_2$Cl$_2$]$^+$ in CH$_3$CN at Nafion-modified electrode. Scan rate, 20 mV s^{-1}, soak time, 20 min
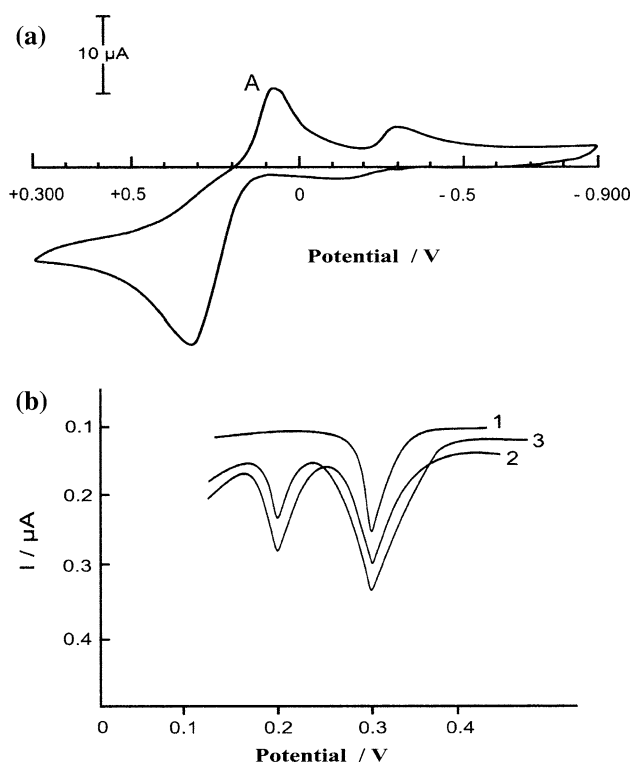
(a)

(b)

Fig. 8 (a) Cyclic voltammogram of 10^{-6} M dopamine at a Nafion modified glassy carbon electrode, scan rate 100 mV s^{-1}. (b) Anodic differential pulse voltammogram of (1) dopamine (10^{-7} M) and ascorbic acid (10^{-2} M) (2) 1:1 mixture of complex 5 an dopamine (10^{-7}) in sodium phosphate buffer at a Nafion modified glassy carbon electrode; deposition time 20 min: Scan rate 20 mV s^{-1}. (3) 1:2 mixture of complex 5 and dopamine in phosphate buffer

by coating the electrodes with a thin film of Nafion. Since differential pulse voltammetry can improve the selectivity and sensitivity of the determination, it could be employed to study the interference of AA and other compounds. In this section an attempt to study the electrochemical behaviour of dopamine in the presence of ascorbic and the osmium diars complex is described.

Figure 8a shows the cyclic voltammograms of DA at a Nafion modified GCE. At the bare glassy carbon electrode DA exhibited poor electrochemical response. Differential pulse voltammogram of mixture of 10^{-2} M AA with 10^{-8} M DA at Nafion modified electrode is shown in Fig. 8b(1). Ascorbic acid had no interference as it is excluded by the Nafion film. Figure 8b(2) shows the DPV at Nafion modified electrode for the 1:1 mixture of [Os(diars)$_2$Cl$_2$]BF$_4$. Figure 8b(3) shows the 1:2 mixture of complex 5 and dopamine in phosphate buffer. In the presence of osmium complex enhancement of current is noted for DA. This increase is consistent with an increase in the concentration of osmium complex, thus confirming the catalytic effect on the oxidation of DA. No such activity was observed for other complexes.

4 Conclusion

The electrochemistry of six metal diars complexes was studied using cyclic voltammetry and differential pulse voltammetry at both bare and Nafion modified electrodes. Cyclic voltammetry is consistent with a one electron quasi-reversible reduction process. The reduction potential increases with increase in dielectric constant. The differential pulse voltammetric studies indicate a negative shift in the redox potential and a 2-fold enhancement of peak current. Complex 5 was studied in the presence of dopamine and an enhancement of the peak was noticed, indicating that complex 5 may have potential as an electrochemical sensor for the detection of dopamine.

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