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Ion-exchange voltammetry of tris(2,2′-bipyridine) nickel(II), cobalt(II), and Co(salen) at polyestersulfonated ionomer coated electrodes in acetonitrile: Reactivity of the electrogenerated low-valent complexes

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Abstract

The electrochemical behaviour of [Ni(bpy)$_3$(BF$_4$)$_2$], [Co(bpy)$_3$(BF$_4$)$_2$], and Co(salen) (where bpy = 2,2′-bipyridine, and salen = *N*,*N*′-bis(salicylidene)ethylenediamine) is studied at a glassy carbon electrode modified with the poly(estersulfonate) ionomer Eastman AQ 55 in acetonitrile (MeCN). It is shown that the nickel complex is strongly incorporated into the polymer. The reduction of the divalent nickel compound features a two-electron process leading to a nickel(0) species which is released from the coating because of the lack of electrostatic attraction with the ionomer. Yet, the neutral zerovalent nickel-bipyridine complex is reactive towards ethyl 4-iodobenzoate and di-bromocyclohexane despite the presence of the polymer. The activation of the aryl halide occurs through an oxidative addition, whereas, an electron transfer is involved in the presence of the alkyl halide making the catalyst regeneration much faster in the latter case. The electrochemical study of [Co(bpy)$_3$(BF$_4$)$_2$] shows that incorporation of the cobalt complex into the polymer is efficient, provided excess bpy is used. This excess bpy does not interfere with the electrocatalytic activity of the cobalt complex incorporated in the AQ coating and efficient electrocatalysis is observed towards di-bromocyclohexane and benzyl-bromide as substrates. Finally, replacement of the bpy ligand with the macrocycle *N*,*N*′-bis(salicylidene)ethylenediamine, salen, leads to the incorporation of the non-charged Co^{II}(salen) complex into the AQ 55 polymer showing the relevancy of hydrophobic interactions. The reaction between the electrogenerated [Co^{I}(salen)]$^-$ with 1,2-dibromocyclohexane exhibits a fast inner sphere electron transfer.

Keywords: Ion-exchange voltammetry; Polyestersulfonate ionomer; Catalysts immobilisation; Electrocatalysis; Acetonitrile

1. Introduction

The preparation and use of polymer modified electrodes have been the subject of increased research over the past decades due to the possibility of immobilizing redox centers, and especially catalysts or catalyst precursors, on the electrode surface. Among the numerous existing methods for electrode modification, the use of ion-exchange polymers is an elegant route. The procedure relies on coating the electrode surface with a thin film of an ion-exchange polymer and following incorporation of ion redox species of interest as counterion. This strategy was introduced by Oyama and Anson [1] who have initially reported on films of poly(vinylpyridine) adsorbed on carbon electrodes, and by Rubinstein and Bard who used electrodes coated with the perfluorinated ionomer Nafion [2]. Since then, the ability to prepare electrodes modified with thin films of a variety of ion exchange polymers [1–4] has given rise to a new electroanalytical technique named ion-exchange voltammetry [5,6], which takes advantage of the preconcentration capabilities of the coating. Such a preconcentration–immobilization procedure has found numerous applications in a variety of fields ranging from electroanalysis [6,7] to electrocatalysis [8,9] and photoelectrochemistry [10–12].

Electrodes modified with ion-exchangers have been used and applied mainly for studies and determinations in aqueous solutions. However, it has been demonstrated that the use of the polyestersulfonated ionomer AQ 55 (Scheme 1), produced by Eastman, opens new perspectives since it is stable in organic solvents such as acetonitrile, in which more commonly employed polyanionic coatings, e.g. Nafion, exhibit poor stability.

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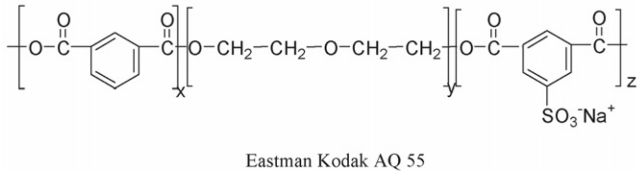

Scheme 1.

Indeed, the use of an aprotic solvent allows the study of reactants that are insoluble or unstable in aqueous solutions. Moreover, the wider potential range in aprotic media allows the detection of analytes that are undetectable in aqueous solution because their redox electrochemistry is out of the potential window accessible in water. Additionally, from a mechanistic viewpoint, unusual oxidation states as well as reactive organometallic intermediates are stabilised in aprotic solvents.

This notwithstanding, very few studies dealt with the use of AQ 55 coated electrodes in non-aqueous media, all aimed mainly to study fundamentals of ion-exchange and redox reactions of cations incorporated in the coating [13–18]. It was shown that cationic complexes such as $[Ru(bpy)_3]^{2+}$, $[Fe(bpy)_3]^{2+}$, $[Os(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridyl), $Ru(bpz)_3{}^{2+}$ (bpz = 2,2′-bipyrazine) [14], $Ru(phen)_3{}^{2+}$, $Ru(pdon)_3{}^{2+}$ (phen = 9,10-phenatroline; pdon = 9,10-phennatroline-1,6dione) [15] are successfully pre-concentrated and immobilized on glassy carbon electrodes coated with AQ 55, in acetonitrile solution. It was shown that the potential window accessible at AQ coated electrodes in acetonitrile solutions extends from −1.75 to +1.90 V versus a KCl saturated Ag/AgCl reference electrode [14]. The ion-exchange equilibrium at AQ 55 modified electrodes in acetonitrile is ruled mainly by the steric hindrance both of the electroactive species and of the supporting electrolyte cation [13,17].

In the present study, we examine the possibility to immobilize in the AQ coating some nickel(II) and cobalt(II) complexes of the type $[Ni(bpy)_3(BF_4)_2]$, $[Co(bpy)_3(BF_4)_2]$, or Co(salen), in order to test their possible use as precursors for electrogenerated catalysts for electrosynthesis purposes in non-aqueous media. This approach could open interesting perspectives for the development of new electro-synthesis schemes more sustainable both environmentally and economically, since even partial immobilization of the catalyst in the electrode coating by ion-exchange preconcentration would allow one to use very small amounts of expensive and toxic catalysts. Note that the polyestersulfonated ionomer coating Eastman AQ 55 is cheap, bio-degradable and non-toxic [19]. To the best of our knowledge this is the first report describing electrocatalysis (for synthetic purposes) at electrodes coated with ionomers in acetonitrile solutions.

2. Experimental

2.1. Chemicals

Acetonitrile (MeCN) was purchased from SDS (analytical grade), stored under argon, and used without further purification. *N*,*N*′-Bis-(salicylidene)ethylenediaminocobalt(II), Co(salen), was from Aldrich. Nickel- and cobalt-bipyridine complexes, i.e. $Ni(bpy)_3(BF_4)_2$ and $Co(bpy)_3(BF_4)_2$, were prepared respectively from $Ni(BF_4)_2{\cdot}6H_2O$ and $Co(BF_4)_2{\cdot}6H_2O$ with 3 molar equivalents of 2,2′-bipyridine (Aldrich) in ethanol. The solution was stirred overnight. The precipitate was then filtered, washed with ethanol, and dried at 70 °C under vacuum for 24 h. 1,2-Dibromocyclohexane, benzylbromide, and ethyl 4-iodobenzoate, were from Aldrich. Tetrabutylammonium tetrafluoroborate ($TBABF_4$) used as the supporting electrolyte was prepared from $NaBF_4$ and *n*-$TBAHSO_4$, recrystallized from ethyl acetate-hexane and dried at 60 °C. In some experiments, tetrabutylammonium perchlorate ($TBAClO_4$) (Aldrich) was used as the supporting electrolyte.

2.2. Instrumentation

Cyclic voltammetry experiments were performed at room temperature under an argon atmosphere, in a three-electrode cell using an EG&G model 273A potentiostat. A saturated calomel electrode (SCE-Tacussel) or a silver/silver chloride electrode was used as the reference which was separated from the solution by a bridge compartment filled with the same solvent/supporting electrolyte used in the cell. The counter electrode was a gold wire or a platinum coil. The glassy carbon-working electrode (3 mm diameter) was purchased from Radiometer Analytical.

2.3. Preparation of the modified electrode and experimental protocol

Prior to coating, the glassy carbon electrode (3 mm diameter) was pad felt polished with aqueous alumina (0.3 μm) suspension. Residual polishing material was removed from the surface by ultrasonication in a water bath for 5 min.

The AQ 55 dispersion (approximately 17%, w/v) was prepared by treating the proper amount of the finely grinded AQ55 resin with warm water (45 °C), under vigorous stirring until a homogeneous and transparent phase was obtained. The exact concentration of the polymer in the dispersion was determined by drying and weighing a known volume of this dispersion. The mirror polished surface of the GC was then coated by applying 12 μL of a water dispersion of AQ55, finally diluted to 1% (w/v), with a microsyringe. The water was let to evaporate at room temperature. The coated electrode was then heated at 60 °C, for 1 h before use [14]. Some modified electrodes were also prepared by deposition of 5 μL of an acetone/water dispersion obtained by 1:1 (v/v) acetone dilution of the AQ55 17% aqueous dispersion. The latter films are stable and present good cation-exchange capabilities even omitting the thermal curing step [17].

The freshly prepared AQ 55 coated electrode was, at first, dipped in 0.01 M $TBABF_4$ acetonitrile solution; by this way, the Na^+ counter ions initially present in the coating, are substituted by the TBA^+ cations; this process can be accelerated by stirring. The electroactive compound was then added and allowed to partition into the AQ 55 film. The equilibrium process was followed by periodically scanning through the redox wave of the electroactive compound. The partition equilibrium is considered to have been achieved when the peak current reaches a constant value; unless otherwise indicated, voltammograms reported in the following were obtained under such ion-exchange equilibrium conditions.

3. Results and discussion

3.1. Ion-exchange voltammetry of $Ni(bpy)_3(BF_4)_2$

The cyclic voltammetry of a 2 mM solution of $Ni(bpy)_3$ $(BF_4)_2$, in acetonitrile (MeCN), at a uncoated glassy carbon electrode, is shown in Fig. 1 (light line).

Unlike the electrochemical behaviour of tris(2,2′-bipyridyl) ruthenium(II), iron(II), and osmium(II) complexes which exhibits two successive mono-electronic transfers [14], the reduction of the nickel(II) compound involves a two-electron process leading to the formation of a nickel(0) complex [20–22]. It was shown that the electrochemical reduction of $[Ni^{II}(bpy)_3]^{2+}$ to $[Ni^0(bpy)_3]$ is followed by a fast loss of a bpy ligand to give $[Ni^0(bpy)_2]$ [19,20], the latter species being in equilibrium with a solvent molecule to give $[Ni^0(bpy)(MeCN)]$ [22]. These equilibria explain the presence of a second small oxidation wave on the reverse scan. Accordingly, the addition of free bpy leads to a single oxidation wave (O_1) since $[Ni^0(bpy)_3]$ becomes the predominant species under these conditions (see Fig. 3). The reversible response observed at positive potentials, near 1.8 V corresponds to the $Ni(bpy)_3{}^{2+/3+}$ couple. The peak current for the oxidation of the nickel(II) complex (wave O_2) is halved with respect to R_1 in agreement with a mono-electronic process.

Really the reduction of $Ni(bpy)_3(BF_4)_2$, at a uncoated electrode, involves two mono-electronic transfers at similar potentials; this prompted us to examine whether these two processes could be eventually more separated in potential at a polymer modified electrode so leading to the formation of a monocationic compound liable to be stabilized by electrostatic interactions with the AQ film, as for the analogous Ru(II), Fe(II), and Os(II) complexes. Fig. 1 (dark line) shows the cyclic voltammogram obtained at a AQ 55 modified electrode (AQME), for a 130 more diluted solution of $Ni(bpy)_3(BF_4)_2$, and recorded after an equilibration time of around 30 min.

Under these conditions, the peak current R_1 is as high as that obtained at a bare glassy carbon electrode indicating a strong incorporation of the nickel complex into the polymer. Moreover, wave R_1 is shifted towards a more negative potential value ($E_{R_1} = -1.42$ versus -1.32 V) and is located in the same potential range observed for Ru(II), Fe(II), and Os(II) complexes [14]. However, though the reduction of the nickel complex tends to split, the reduction process remains roughly bielectronic. More importantly, it is worth noting that the return peak associated to R_1 is smaller at a AQME than at a bare glassy carbon electrode suggesting that the electrogenerated neutral nickel(0) species are partially released from the coating owing to the absence of electrostatic attractions with the sulfonate exchange sites. Besides, the peak current of R_1 decreases rapidly after three consecutive voltammetric scans (not shown). Note also that the loading of $Ni(bpy)_3{}^{2+}$ in the AQ55 coating increases slightly in the presence of excess bpy, however, the major problem, that is the release of the Ni(0) species, remains unsolved.

It is interesting to note that voltammograms recorded at 100 mV s^{-1} at a AQME show diffusional tailing characteristic of semi-infinite linear diffusion in the film, whereas, a surface confined process is observed at slower scan rates, e.g. 5 mV s^{-1}. This is because the thickness of the diffusion layer is smaller than the film thickness at the higher scan rate (namely, 100 mV s^{-1}), while it becomes comparable with the coating thickness at the lower scan rate (5 mV s^{-1}); under the latter condition, the exhaustive reduction of all the complex incorporated in the coating is indeed performed within the scan time [6]. Note also that, under these conditions, i.e. at long time-scales, the reoxidation peak disappears completely, so confirming a total complex loss via the electro-formation of the nickel(0) neutral species.

Despite the electroformation of a neutral nickel complex at the level of R_1, it was interesting to check the reactivity of the zero-valent complex generated in the polymer. Accordingly, and by analogy with already reported results in homogeneous solution, the reactivity of the zero-valent nickel species was tested in the presence of an aryl halide [23]. In Fig. 2 are shown cyclic voltammograms obtained at an AQ 55 modified electrode at a scan rate of 0.1 V s^{-1}. The light curve reveals the partially reversible two-electrons Ni(II)/Ni(0) redox couple. With

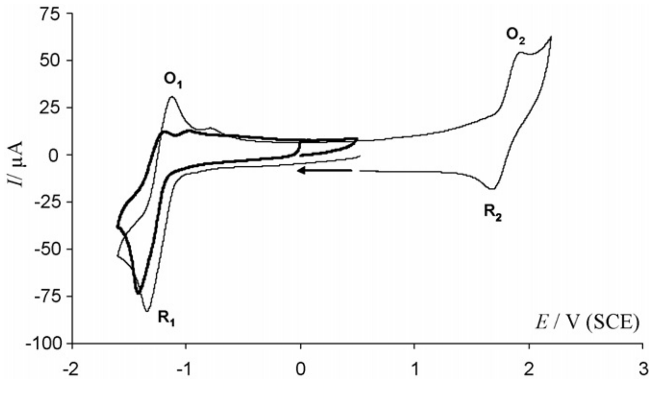

Fig. 1. Cyclic voltammograms recorded at 0.1 V s^{-1} in acetonitrile + TBABF$_4$ (0.01 M) solutions containing $[Ni(bpy)_3](BF_4)_2$: 15 μM, AQ55 modified electrode (AQME) working electrode (dark line); 2 mM, uncoated glassy-carbon electrode working electrode (light line).

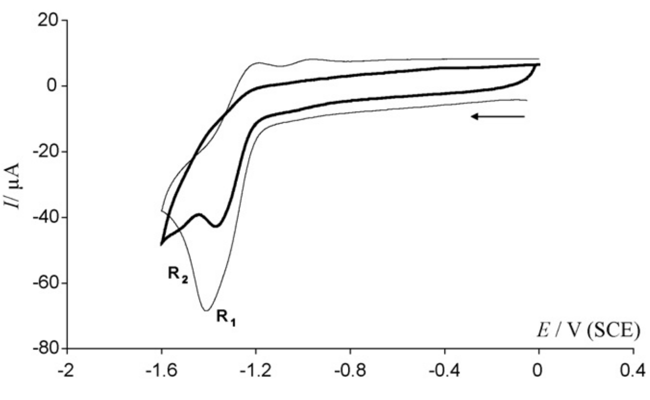

Fig. 2. Cyclic voltammograms recorded at 0.1 V s^{-1} in acetonitrile + TBABF$_4$ (0.01 M) solutions containing $[Ni(bpy)_3](BF_4)_2$: 15 μM, AQME working electrode; in the absence (light line) and the presence of excess (15 mM) ethyl 4-iodobenzoate (dark line).

the addition of ethyl 4-iodobenzoate the return peak associated to R_1 disappears completely and a new small reduction wave R_2 appears at a more negative potential ($E_{R_2} = -1.5$ V). This behaviour is consistent with a reaction between the electrogenerated nickel(0) species and the aryl halide. By analogy with the reactivity of similar zero-valent nickel species in homogeneous solution, an arylnickel(II) complex would be obtained by oxidative addition and would be reduced at the level of the new reduction wave R_2 [24,25]. Note that the peak current of R_1 is smaller after addition of the aryl halide. This is due to a catalyst loss since the two voltammetric scans have been recorded in a close interval.

Importantly, these results show that the electrogenerated nickel(0) species remains reactive towards ethyl 4-iodobenzoate even in the presence of the AQ 55 polymer. However, the activation of aromatic halides under such conditions is not fully satisfactory because of the slow regeneration of the catalyst precursor, which depends on the chemical processes rates that follow the oxidative addition.

In that context, we decided to replace the aromatic halide with an alkyl halide which is supposed to react faster with the electrogenerated Ni(0). As shown in Fig. 3, the addition of increasing amounts of *trans*-1,2-dibromocyclohexane (DBCH) leads to both an increase in the peak current of R_1 and a decrease of I(O_1). These features are characteristic of a catalytic reaction in which the Ni(0) species acts as an electrochemical mediator. By analogy with cobalt complexes [26–28], the reaction of Ni(0) with alkyl vicinal dibromides exhibits a fast inner sphere electron transfer reaction regenerating rapidly the starting nickel catalyst.

Under these conditions, direct reduction of DBCH occurs at −2.1 V, so the catalysis results in a 0.6 V decrease in overpotential. Note that the use of excess bpy allows faster incorporation of the nickel complex in the polymer as observed for the analogue cobalt compound (see below) and favours the electron transfer.

These results prompted us to extend the study to different systems, such as the cobalt-bipyridine one. Indeed, it has been recently discovered that the electrochemical reduction of $CoBr_2$(bpy) allows the generation of a cationic cobalt(I) species, $Co^I(bpy)^+$, stable on the time scale of cyclic voltametry (few seconds), and able to activate aromatic halides [29].

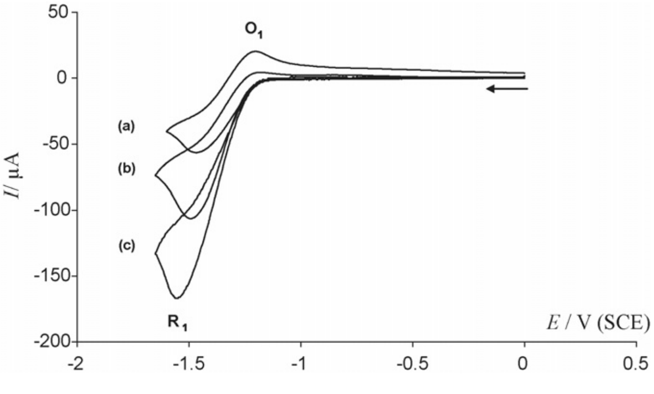

Fig. 3. Cyclic voltammograms recorded at 0.1 V s^{-1} in acetonitrile + $TBABF_4$ (0.01 M) of $Ni(bpy)_3BF_4$ (30 µM) + excess bpy (1.4 mM) at a AQME working electrode: in the absence (a) and in the presence of 2.66 mM (b), and 5.32 mM (c) of di-bromocyclohexane.

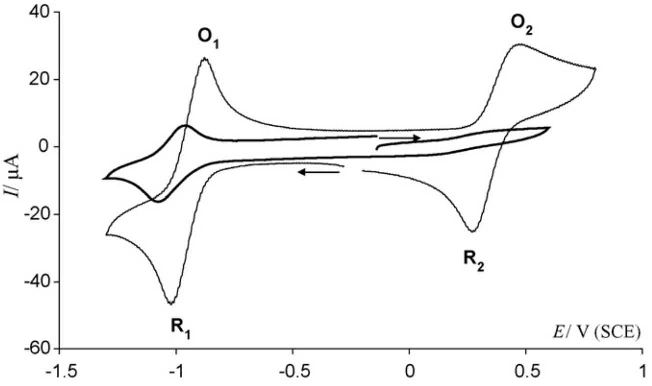

Fig. 4. Cyclic voltammogram recorded at an AQME in 30 µM $Co(bpy)_3^{2+}$ + acetonitrile solution containing $TBABF_4$ (0.01 M) and excess 2,2′-bipyridine (2.61 mM) (dark line), and cyclic voltammogram of $Co(bpy)_3(BF_4)_2$ (2 mM) at 0.1 V s^{-1} in acetonitrile + $TBABF_4$ (0.01 M) recorded at a bare graphite electrode (light line).

3.2. Ion-exchange voltammetry of $Co(bpy)_3(BF_4)_2$

First of all, and in the continuity of the nickel-bipyridine system, we studied the electrochemical behaviour of $Co(bpy)_3(BF_4)_2$. Surprisingly, and unlike the behaviour exhibited in Nafion [16], the cyclic voltammogram of this compound at a concentration of 30 µM and recorded at an AQME gives a very small response. However, the appearance of signals both at the negative and positive potentials are much more visible if excess 2,2′-bipyridine is added indicating a faster and a stronger incorporation of the cobalt complex (Fig. 4, dark line).

The responses of the $Co(bpy)_3^{2+/+}$ and $Co(bpy)_3^{3+/2+}$ couples within the AQ 55 coating appear at −1.02 and 0.21 V, respectively, instead of −0.95 and 0.33 V at a uncoated glassy carbon electrode, in agreement with already reported results (Fig. 4, light line) [16].

Therefore, at the modified electrode the $E_{1/2}$ values ($E_{1/2} = (E_{pf} + E_{pb})/2$, where E_{pf} and E_{pb} are the peak potentials recorded in the forward and backward scans, respectively), of the two sets of waves display negative shifts with respect to data obtained at a bare electrode.

Additionally, contrary to what was observed at a bare electrode, the peak current obtained for the oxidation of $Co(bpy)_3^{2+}$ is much lower than that obtained for its reduction. By analogy to the Anson's work concerning the incorporation of $Co(bpy)_3^{2+}$ in Nafion [16], the apparent diffusion coefficient of $Co(bpy)_3^{2+}$ in the presence of the electrogenerated $Co(bpy)_3^{+}$ complex would be larger than that in the presence of $Co(bpy)_3^{3+}$. The difference would be attributable to the much larger self-electron exchange rate constant for the reduction allowing thus a significant contribution from electron hopping, whereas, physical diffusion would be the only transport mechanism of the electrochemical charges during the oxidation process.

Notwithstanding the presence of excess bpy, as shown in Fig. 5, the addition to the electrolyte solution of di-bromocyclohexane changes dramatically the voltammetric picture.

Under the latter conditions, and as observed previously with the nickel complex, the current of the reduction peak

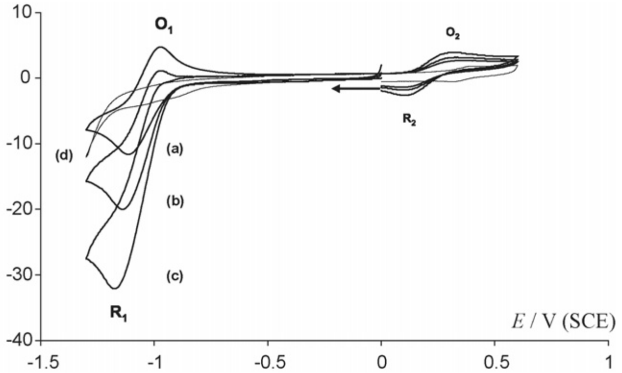

Fig. 5. Cyclic voltammograms recorded at 0.1 V s^{-1} in acetonitrile + $TBABF_4$ (0.01 M) of $Co(bpy)_3(BF_4)_2$ (30 µM) + excess bpy (1.4 mM) at a AQME working electrode: in the absence (a) and in the presence of 1.33 mM (b), and 2.66 mM (c) of di-bromocyclohexane. Scan (d) follows scan (c) after polishing the glassy carbon electrode.

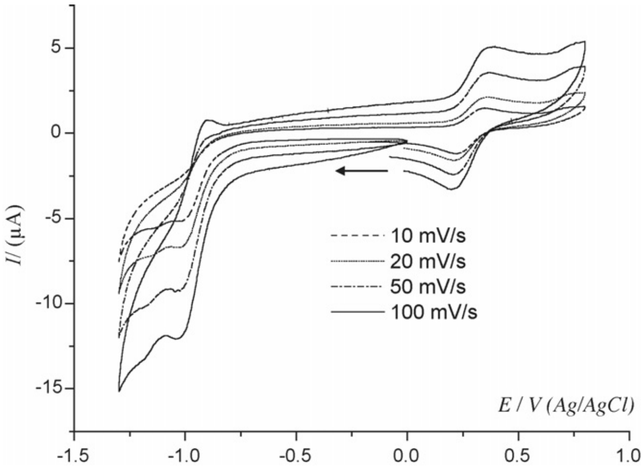

Fig. 7. Cyclic voltammograms recorded at various scan rates in acetonitrile + $TBAClO_4$ (0.001 M) of $Co(bpy)_3BF_4$ (30 µM) + excess bpy (1.4 mM) at a AQME working electrode in the presence of 20 mM benzyl-bromide.

R_1 increases, such an increase doubling when the concentration of the organic halide is doubled. At the same time, the reoxidation peak O_1 decreases, up to disappearing completely after the second addition of the halide. Here again, these are clear evidences of the occurrence of an electrocatalytic cycle involving electrogenerated $Co(bpy)_3{}^+$ and the organic halide. Importantly, the catalytic wave totally disappears after polishing the electrode indicating the relevance of the preconcentration phenomena (Fig. 5, scan (d)). A similar situation is found using benzyl-bromide as the substrate despite a slower electron transfer (Figs. 6 and 7). The exam of the scan rate dependence of the CVs shows that the catalytic behaviour is indeed more evident at lower scan rates (10–20 mV s^{-1}), where the reduction peak tends to acquire a sigmoidal shape and the reoxidation peak fully disappears.

Fig. 8 shows that the signal relevant to incorporated $Co(bpy)_3{}^{2+}$ is retained even after transfer in pure supporting electrolyte, with no cobalt complex nor bpy dissolved in the acetonitrile solution. As typically found in ion-exchange voltammetry, the signal is lower after the transfer than in the loading solution, however, the incorporated $Co(bpy)_3{}^{2+}$ complex retains its electroactivity as well as its electrocatalytic capabilities towards benzyl-bromide coupling, as shown by the electrocatalytic wave observed after the addition of 16 mM substrate.

Note that the electrocatalytic behaviour is retained at least for 3 h after dipping the AQME in the test solution, where only benzyl-bromide was added to the electrolyte. All these evidences indicate the suitability of the $Co(bpy)_3{}^{2+}$ incorporated in the AQ55 coating for the activation of suitable organic halides, and a good electrocatalytic activity of the $Co(bpy)_3{}^{2+}$ complex incorporated in the film. Interestingly, the process requires the presence of excess bpy in order to initially promote the incorporation and electroactivity of the $Co(bpy)_3{}^{2+}$ at the AQME, however, such an excess bpy does not hinder the catalytic activity nor is required in electrocataltyic test following the loading of the modified electrode.

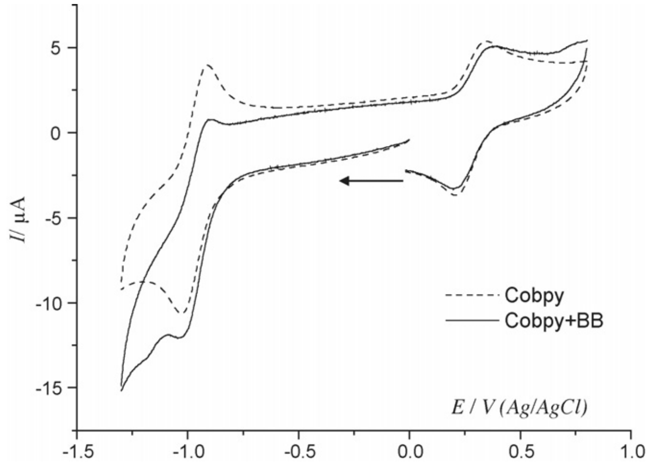

Fig. 6. Cyclic voltammograms recorded at 0.1 V s^{-1} in acetonitrile + $TBAClO_4$ (0.001 M) of $Co(bpy)_3BF_4$ (30 µM) + excess bpy (1.4 mM) at a AQME working electrode: before (dashed line), and after (solid line) the addition of 20 mM benzyl-bromide (BB).

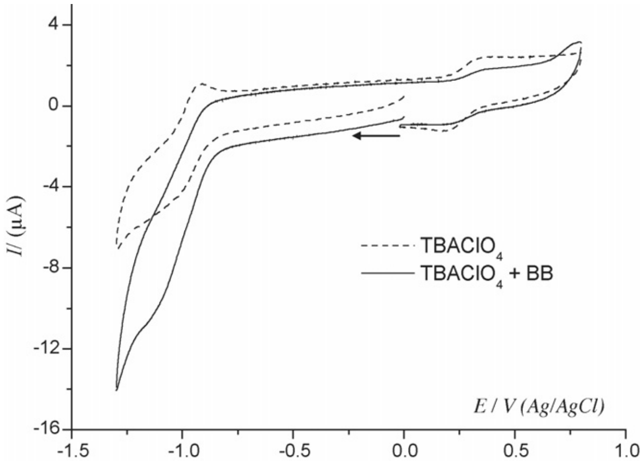

Fig. 8. AQME loaded in 0.001 M $TBAClO_4$ acetonitrile solution containing 30 µM $Co(bpy)_3(BF_4)_2$ and 1.4 mM bpy, transferred into pure supporting electrolyte: before (dashed line) and after (solid line) addition of 16 mM benzyl-bromide (BB) in the cell. $\nu = 0.1$ V s^{-1}.

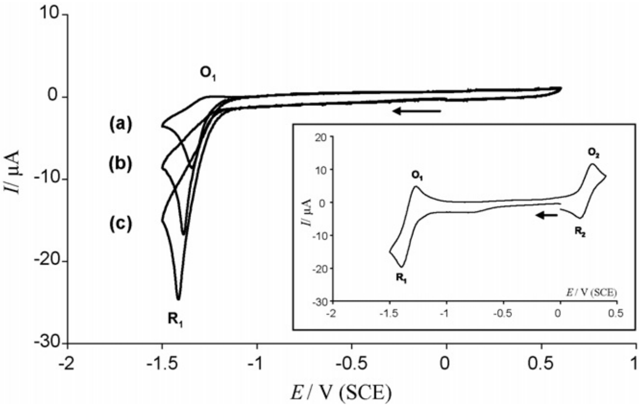

Fig. 9. Cyclic voltammograms recorded at 0.05 V s^{-1} in acetonitrile + TBABF$_4$ (0.01 M) solution containing cobalt(II)-salen: 20 µM, AQME, in the absence (a), and in the presence of 10 (b), and 20 (c) molar equivalents of DBCH. Insert: cyclic voltammogram recorded at a bare glassy carbon electrode, at 0.05 V s^{-1} in acetonitrile + TBABF$_4$ (0.01 mol dm^{-3}) solution containing cobalt(II)-salen (0.8 mM).

3.3. Ion-exchange voltammetry of Co(salen)

We also examined the possibility of replacing the bipyridine ligand with the *N,N′*-bis(salicylidene)ethylenediamine macrocycle. Fig. 9 (insert) depicts the cyclic voltammogram recorded with a glassy carbon electrode at 50 mV s^{-1} in acetonitrile containing 0.01 M TBABF$_4$ for the cobalt(II)-salen complex. As already reported, two sets of waves corresponding to the cobalt(II)-salen-cobalt(I) salen (R_1/O$_1$) and cobalt(II)-salen-cobalt(III)-salen (O$_2$/R_2) couples are observed [30,31].

The cyclic voltammogram of a 40-times more diluted solution of cobalt(II)-salen obtained at a Eastman Kodak AQ55 modified electrode is also shown in Fig. 9 (scan (a)). Although cobalt(II)-salen is a neutral complex, this voltammogram shows that it is incorporated into the AQ55 coating. This clearly shows the relevancy of hydrophobic interactions with the polymer that contains hydrophilic regions surrounded by hydrophobic domains [32]. Note that wave R_1 corresponding to the reduction of cobalt(II)-salen presents the typical shape of thin layer conditions. However, under these conditions wave R_1 is not totally reversible (compare with the reversibility obtained in the absence of polymer). The electrogenerated $[\mathrm{Co^I L}]^-$ (L = salen), which is known to be a super nucleophile is therefore partially released.

More interestingly, the addition of 1,2-dibromocyclohexane leads to a catalytic increase in the peak current of R_1, and the small oxidation wave O$_1$ totally disappears in the same range of time. Here gain, the reaction of Co(I) with alkyl vicinal dibromides exhibits a fast inner sphere electron transfer reaction regenerating the starting cobalt(II)-salen [26–28].

Importantly, comparison with a similar experiment performed at a bare glassy carbon electrode instead of a coated one shows comparable catalytic activity, so indicating that the polymer does not prevent or inhibit the process.

4. Conclusion

The use of the poly(estersulfonate) Eastman AQ 55, aimed at immobilizing catalyst precursors, is an elegant and promising way to achieve electrocatalysis in non-aqueous media. Experimental evidences indicate that both the Ni(bpy)$_3{}^{2+}$ complex is strongly incorporated in the AQ55 coating and the reduced species can react with aryl or alkyl halides added as substrates in the electrolyte solution. The activation of the aryl halide occurs through an oxidative addition, whereas, an electron transfer is involved in the presence of the alkyl halide making the catalyst regeneration much faster in the latter case. At variance with the case of the Ni(bpy)$_3{}^{2+}$ complex where the catalytic species is a neutral "Ni^0", which is slowly released from the coating, for the Co(bpy)$_3{}^{2+}$ case the catalytically active species is the cation Co(bpy)$_3{}^+$ (obtained by reduction of Co(bpy)$_3{}^{2+}$), which is stably retained by the sulfonic groups of the AQ 55 coating. The addition of extra bipyridine allows the acceleration of the initial loading of the Co(bpy)$_3{}^{2+}$ complex. But, once incorporated, the presence of free bipyridine is not required to retain both the electroactivity and electrocatalytic capabilities of the cobalt complex.

The case of the cobalt(II)-salen complex, indicates that hydrophobic interactions can play an important role for the immobilization of organometallic complexes. Thanks to these hydrophobic strength it was indeed possible to incorporate the neutral cobalt(II)-salen complex and to observe an efficient inner sphere electron transfer process between the electrogenerated Co$^{\mathrm{I}}$ macrocycle and an alkyl vicinal dibromide.

Although further studies are required for fully understanding the details of the role played by excess bipyridine ligand and hydrophobic interactions in the incorporation of the catalyst precursors, the electrocatalytic systems here studied can open new interesting prospects in electrorganic synthesis, particularly considering that they allow one to lower the amount and to recycle the organometallic compounds required for the catalysis.

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