

Evaluation of a Ru-bipod Complex as a Redox Transducer for Membrane-Based Voltammetry of Anions**

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Molecular redox compounds show promise for the development of solid contact ion selective electrodes (SC-ISEs) for anion determinations. In this work, a hydrophobic bis-tridentate Ru-bipod complex was studied as a molecular redox transducer in voltammetric SC-ISEs. Thin film voltammetric behavior was achieved in films comprised of the Ru-bipod complex, polyvinylchloride (PVC) and a plasticiser, nitrophenyloctylether (NPOE). Importantly, the choice of plasticiser had a significant effect on the SC-ISE response of the Ru-bipod complex; *i.e.*, voltammetric responses of the Ru-bipod complex in NPOE films were sharper and more intense than in bis(2-ethylhexyl)

sebacate (DOS) films. Moreover, addition of tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH 500) to the membrane had an unfavorable impact on detection of anions due to oxidation of this salt in the film. Although the thin film electrode showed close-to-Nernstian behavior in anion responses, the detection responses in the presence of very hydrophilic anions such as sulfate ion were shifted to higher potentials (> 1 V) with a subsequent loss of sensitivity. Overall, the Ru-bipod complex operates as a simple transducer in SC-ISEs with benefits in anion detection.

Introduction

Detection methods based on ion transfer between aqueous samples and polymeric membranes have developed rapidly due to their clinical and environmental applications.^[1] In some cases, zero current potentiometry has been replaced by dynamic electrochemical methods to improve limits of detection, selectivity and recalibration frequency.^[2] Additionally, conventional configurations of ion selective electrodes (ISEs) with fragile internal solutions have been replaced by more promising solid contact ion selective electrodes (SC-ISEs)^[3] in which the sensing thin polymeric layer is directly in contact with a conductive electrode and with an ion-to-electron transducer material. This approach was introduced by Shi and Anson^[4] to evaluate electron transfer chemistry of redox-active substances (e.g. ferrocene) dissolved in a thin layer of organic solvent interposed between a graphite surface and an aqueous phase. Subsequently, Bond and co-workers used the redox behavior of 7,7,8,8-tetracyanoquinodimethane to control ion transfer into

such thin films.^[5] To maintain electro-neutrality in the film, redox reactions are accompanied by ion transfer. Using voltammetric approaches, the oxidation and reduction potentials of the redox compound within the thin film depend on the identity and the concentration of transferring ions in the contacting aqueous phase and provides a suitable analytical signal.

A key component in the thin films used in SC-ISEs is the redox-active material. Some of the most widely-used such materials are conducting polymers like poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(3-octylthiophene) (POT) which are commonly applied in SC-ISEs.^[6] However, their low redox capacity, significant difference between anodic and cathodic currents, lack of device-to-device reproducibility, and electrochemical instabilities specifically in anion sensing have driven the search for alternative ion-to-electron transducers.^[7] A range of electroactive materials has been used in SC-ISEs, such as ferrocene derivatives, cobalt and osmium complexes, and cationic [6]-helicenes.^[8] Generally, these materials are directly dissolved in the membranes or covalently attached to the sensing layers.^[9] Ferrocene (Fc) has been applied to sense heparin or carbonate but it did not behave reversibly and was unstable in the thin film, specifically in the presence of chloride.^[8b] Another approach to improve the stability of Fc was its immobilization as a monolayer on glassy carbon electrodes^[1c] but this approach limits the choice of redox materials to those suitable for surface attachment.^[10] As an alternative redox probe, a promising osmium complex produced more stable and reversible responses compared to Fc.^[8c] However, the electrochemical response of this complex was strongly dependent on the background electrolytes and their concentrations relative to the osmium complex.

Although several studies reported reliable and stable SC-ISEs, knowledge about the ion-to-electron transduction mechanism is incomplete, and there is an on-going need to

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investigate new redox compounds to broaden the range of materials for the development of improved sensing methods. In this regard, ruthenium (Ru) complexes are a promising alternative to initiate ion transfer at membrane-sample interfaces, because studies have suggested that their redox potentials and solubility in organic phases can be changed by judicious design of the coordination sphere.^[11] This property of Ru complexes brings flexibility as redox materials in ion-to-electron transduction systems. Very recently, a heteroleptic Ru complex was investigated in a three-phase junction (liquid-liquid-solid) system.^[12] The complex exhibited sensitivity to different anions in this system and its redox potential was tunable by changing the aqueous phase pH. However, the three-phase junction system with an organic liquid phase (e.g. nitrobenzene) is unsuitable for development of sensors.^[12]

Another key component in thin film SC-ISEs is the organic solvent or plasticizer, which usually occupies 60–70% (m/m) of the membrane.^[13] For this reason, it is important to investigate the effect of plasticizers on the voltammetric responses of redox-active materials in thin films. A number of reports discuss the impact of plasticizers on sensitivity and selectivity of traditional ISEs.^[14] Important characteristics of plasticizers in ISE membranes include their proportion, lipophilicity, exudation from the polymeric layer, and vapour pressure.^[15] Additionally, since the plasticizer is the major component of membranes, its dielectric constant is an important factor^[15] and can determine the dielectric properties of the polymeric membrane.^[16]

In this work, we have investigated a hydrophobic homoleptic bis-tridentate Ru-bipod complex $[\text{Ru}(\text{bipod})_2]^{2+}$ (see Figure 1) (where bipod is 2,6-bis(1-(2-octyldodecyl)benzimidazol-2-yl)pyridine)) as a redox-active ion-to-electron transducer in thin polymeric films. The redox chemistry of Ru(II/III) complexes with

bis-tridentate ligands has been well-documented.^[11,17] Ligand modifications, such as terpyridyl and bis(benzimidazolyl)pyridine as tridentate ligands, can not only control the oxidation potential, but also lead to improved solubility in various media, such as within polymers and plasticizers, and when immobilised on solid surfaces.^[11,17] The aim of this study was to investigate a new material suitable for use in ion-to-electron transduction and to assess its suitability for anion detection in a SC-ISE sensing system. Cyclic voltammetry was used to characterize the anion responses with thin film compositions incorporating the Ru-bipod complex. Furthermore, the effect of plasticizers on the ion-to-electron transduction system was evaluated by use of two plasticizers with different dielectric constants (nitrophenyloctylether, NPOE, ϵ_r , 23.6 and bis(2-ethylhexyl) sebacate, DOS, ϵ_r , 3.9).

Experimental section

Reagents

Potassium chloride, potassium hexafluorophosphate, potassium nitrate, potassium perchlorate, potassium sulfate, tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH500), bis(2-ethylhexyl)sebacate (DOS),^[14a] 2-nitrophenyloctylether (NPOE), anhydrous tetrahydrofuran (THF), high molecular weight poly(vinyl chloride) (PVC) and the sulfate ionophore (S.I.) were purchased from Sigma Aldrich in analytical grade. Aqueous solutions were prepared in deionized water (resistivity 18.2 M Ω cm; from a USF Purelab with UV system). 2-Octyl-1-dodecanol (Sigma-Aldrich) and Ruthenium(III) trichloride hydrate (Heraeus GmbH) were used without further purification. 1-Bromo-2-octyldodecane was prepared from 2-octyl-1-dodecanol according to a published method.^[18]

Instrumentation and measurements

A three-electrode electrochemical cell was used for all measurements, comprising a thin film-coated glassy carbon (GC) disc working electrode (3 mm diameter) (CH Instruments), a Ag/AgCl/3M NaCl reference electrode (BASi), and a platinum disc as counter electrode. The cell was placed in a Faraday cage. Electrochemical experiments were conducted with an Autolab PGSTAT302N electrochemical workstation (Metrohm, The Netherlands) with NOVA software. A CH1900b potentiostat (CH Instruments Inc., USA) was used to estimate the uncompensated resistance. The organic thin films were spin-coated onto GC electrodes using an inverted overhead stirrer (model IKA RW20). ¹H NMR, ESI-MS, MALDI-TOF-MS, and UV-VIS spectra were recorded with a JNM-ECA 500 (JEOL) spectrometer, a JEOL JMS-T100 LC AccuTOF, Shimadzu MALDI-TOF AXIMA-CFR mass spectrometer, and Hitachi U-3210 UV-vis spectrophotometer, respectively.

Film preparation

Building on prior reports of thin film preparation,^[8c-e] various thin film membrane compositions were formulated (Table S1, supplementary information). For each formulation, all components (total mass 12.5 mg) were dissolved in 0.5 mL THF. Then 20 μ L of this cocktail was spin coated on a GC electrode with an inverted overhead stirrer at 1500 rpm for one minute. The electrode was then immediately used for measurements. The thickness of the

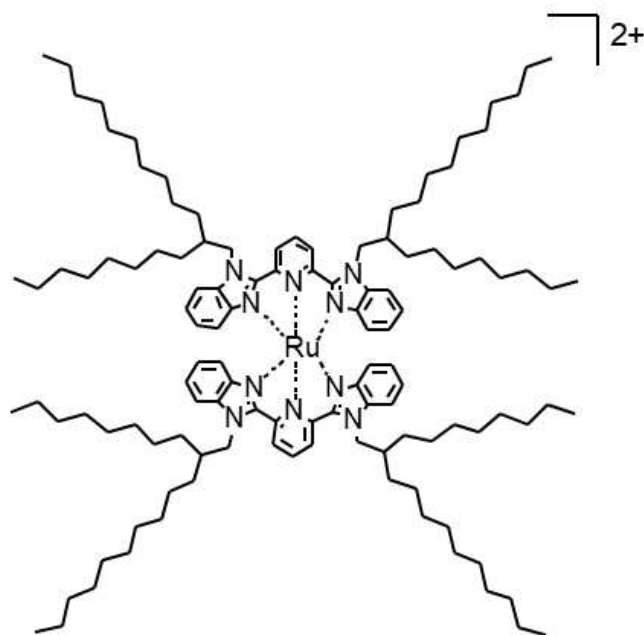


Figure 1. Structure of the Ru-bipod complex investigated, the hydrophobic homoleptic bis-tridentate Ru-bipod complex $[\text{Ru}(\text{bipod})_2]^{2+}$ (where bipod is 2,6-bis(1-(2-octyldodecyl)benzimidazol-2-yl)pyridine)).

spin-coated films was assessed by estimating the volume of the mixture remaining on the surface after spinning from the charge under the voltammetric peaks (Table S2) and considering the density^[19] of PVC-NPOE membranes; the estimated film thickness is $0.9 \pm 0.3 \mu\text{m}$ ($n = 15$).

Synthesis of Ru-bipod complex

The Ru-bipod complex (Figure 1) was synthesized as described in the Supporting Information (Figure S1) and characterized by ESI-MS, ¹H NMR and cyclic voltammetry (Figures S2, S3 and S4, respectively).

Results and Discussion

The synthesis and characterization of the new Ru-bipod complex (Figure 1) as a molecular redox transducer for thin voltammetric sensing membranes are reported here. The membranes contain the complex which acts as an ion-to-electron transducer. By imposing an oxidizing potential, oxidation of Ru-bipod in the film is accompanied by anion transfer into the membrane to compensate the positive charge resulting from oxidation of the complex. Subsequent reduction of that oxidized complex drives anion expulsion from the membrane back into the aqueous phase.

Synthesis and electrochemical characterization of the Ru-bipod complex

The tridentate ligand, 2,6-bis(1-(2-octyldecyl)benzimidazol-2-yl)pyridine (bipod) was synthesized by alkylation of 2,6-bis(benzimidazol-2-yl)pyridine with 1-bromo-2-octyldecane (Figure S1). The homoleptic bis-tridentate Ru-bipod complex was obtained by the reaction of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ with bipod (Figure S1) in a mixture of glycerol and tert-butanol at 150°C .^[20] The structure of the bis-tridentate Ru-bipod complex is shown in Figure 1. The complex was soluble in dichloromethane and in toluene, but insoluble in water. The cyclic voltammetry (CV) of the Ru-bipod complex in acetonitrile electrolyte solution at different scan rates was undertaken. The complex exhibited a reversible one-electron process at $+0.49 \text{ V}$ ($\Delta E_p = 59 \text{ mV}$) vs. Fc^+/Fc (Figure S4) which was diffusion-controlled. Two one-electron reductions were observed at -1.65 V vs. Fc^+/Fc ($\Delta E_p = 53 \text{ mV}$) and -1.84 V vs. Fc^+/Fc ($\Delta E_p = 67 \text{ mV}$), in which the second reduction process involved a large anodic desorption peak (Figure S4).

Cyclic voltammetry confined in thin films

The electrochemical behavior of redox molecules in organic solution is very similar to that in polymeric sensing films.^[8c] As reported previously for SC-ISEs, the membrane response can be tuned to be responsive to either cations or anions. In this study, the membrane compositions were adjusted to be responsive to anions.^[8c] The Ru-bipod complex was easily dissolved in the

hydrophobic membrane formulations. These thin films were responsive to anions, regardless of the presence or absence of ETH500 as lipophilic background electrolyte. Once a sufficiently positive potential is imposed, the Ru-bipod complex is oxidized and anions are extracted from the aqueous electrolyte solution into the membrane to compensate this unbalanced positive charge. This phenomenon is reversed when the complex is reduced, resulting in anion expulsion from the membrane to the aqueous phase. A generalized reaction scheme for this process is as follows (where M(II), M(III) represent the Ru-bipod complex in different oxidation states):

- at the electrode | film interface: $\text{M(II)} \rightarrow \text{M(III)} + \text{e}^-$
- at the film | aqueous interface: $\text{anion}_{(\text{aq})} \rightarrow \text{anion}_{(\text{film})}$

Figure 2 (solid line) shows a typical CV of the Ru-bipod complex within a polymeric thin film. It shows oxidation and reduction processes with features as expected for a thin film, including reversibility, narrow peak width at half-height (90 mV),^[21] and low peak-to-peak separation (close to 0 mV). No oxidation or reduction was observed in the absence of aqueous phase anions (Figure 2, dashed line). Although the CV behaviour strongly depends on the characteristics of the redox-active species, it is also affected by the composition of the polymeric membranes. Different PVC-based membrane compositions were evaluated (Table S1). Consecutive CVs for each membrane formulation were recorded in the presence of aqueous 10 mM KPF_6 (Figure S5). The best CV response was achieved with a film formulation that contained 65 mmol/kg of the Ru-bipod complex (Figure 2). It seems that in contrast to earlier reports in which lipophilic background electrolyte (i.e. ETH500) can promote fulfilment of electroneutrality in anion sensing,^[8c,e] here no evidence was found for lower resistance and better sensitivity in the presence of ETH500 (Figure S5). In addition, the responses toward different anions (i.e. a Hofmeister series response) indicated better selectivity in the absence of ETH500

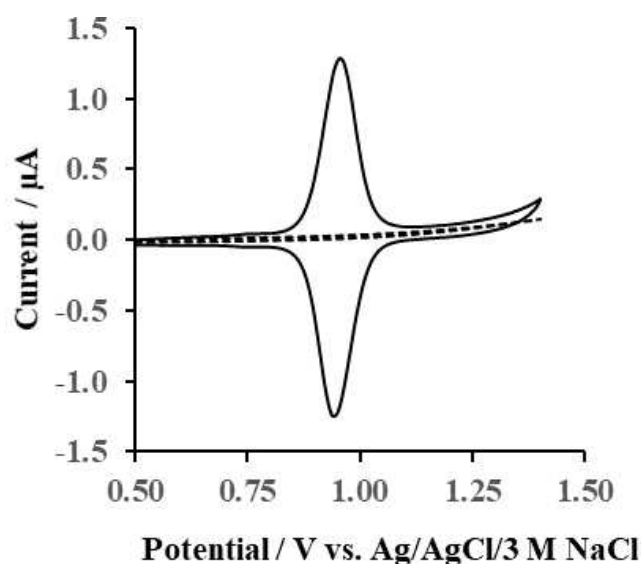


Figure 2. Cyclic voltammetry obtained using membrane M5 (Table S1, containing 65 mmol/kg Ru-bipod complex, 33% PVC and 66% NPOE) SC-ISE in aqueous media in the presence (solid line) of 10 mM KPF_6 and in the absence (dashed line) of deliberately added electrolyte. Scan rate: 10 mV/s .

(Figure S6), i.e. the responses to the presence of different anions are better separated along the potential axis. Also, with the exception of sulfate, there is a linear relationship between the CV mid-point potential of the membrane response with the hydration energies of the anions studied (Figure S7). However, that sulfate does not fit this linear response can be attributed to its double-negative charge, while the other anions have a single negative charge. Thus, the observed voltammetric response is a combination of the oxidation of the Ru-bipod complex and the transfer of counter-anion into the membrane film; the latter depends on the Gibbs energy of transfer of the anion into the thin film organic phase.^[22] Accordingly, hydrophilic anions result in a higher overall potential for this process of combined electron and ion transfers.

Since the composition of plasticizer in the polymeric membranes is more than 60%(m/m), the dielectric constant of the plasticizer determines the dielectric constant of the membrane and has a crucial impact on ISE performance.^[23] To investigate this impact, two plasticizers with different dielectric constants were studied (Figure S8). Evaluation of the peak-width at half-height and peak-to-peak separation at low scan rate (10 mV/s) indicated that there is a dramatic impact on these parameters for membranes prepared with either NPOE or DOS, but with the same composition otherwise (Figure S8). The membrane with NPOE shows a more promising response than the one with DOS. In thin films, the peak-width at half-height can be attributed to electrostatic effects produced by neighbouring charged species in the films,^[24] for example, interactions between oxidised and reduced forms of the redox couple. The magnitudes of these interactions determine whether peak-widths at half-height are less than, equal to, or greater than the theoretical value $90.6/n\text{mV}$.^[21] The greater peak-width at half-height in the presence of DOS (133 mV) can be attributed to the difference in dielectric constants of the two plasticizers (i.e. 23.6 and 3.9 for NPOE and DOS, respectively)^[25] because, in the thin film membrane with lower dielectric constant, the Ru-bipod complexes can experience greater neighbouring electrostatic interactions between charged species. Additionally, CVs of the membranes containing NPOE or DOS at different scan rates (Figure 3a and 3b, respectively) revealed a substantial shift in peak potentials with scan rate in the DOS-based membrane. The relationship between the peak current and scan rate is linear in the NPOE-based film, which exhibits a typical thin film behaviour (Figures 3c), whereas the DOS-based film showed a linear relationship with square root of scan rate (Figure 3d). Since all procedures to prepare the membranes with either plasticizer were identical, the reasons for this difference in scan rate behaviour are unclear at present. This deviation might be attributed to ohmic drop,^[8c] but the uncompensated resistance for the DOS-based thin films was low (2 k Ω) and similar to that for the NPOE-based films (1.7 k Ω). These results are in agreement with theoretical studies that indicated ohmic drop of thin films can be neglected.^[26] Another reason for the difference might be the kinetics of electron transfer of the Ru-bipod complex at the film-electrode interface or kinetics of anion transfer at the membrane-water interface. Since voltammetric and potentiometric studies of PF_6^- transfer showed Nernstian

behaviour, the transfer of this ion at the water-membrane interface is fast and assumed not to be the limiting factor.^[5a,27]

The differences in voltammetric behaviour that the redox transducer (Ru-bipod) experiences in the NPOE-based and DOS-based thin films can be attributed to the interactions in the membrane with plasticizers with higher or lower dielectric constants. This is seen in the CVs in the presence of these plasticizers (Figure 3). In the membrane with lower dielectric constant, charged species more easily influence each other because they have weaker interactions with the solvent (plasticizer). In contrast, in the membrane with higher dielectric constant, both oxidized and reduced species are partially impacted by the solvent (plasticizer), and their interactions with each other is lower than in the membrane with lower dielectric constant. These interactions negatively impact the voltammetric behavior so that with higher neighbouring interactions (i.e. in lower dielectric constant film, DOS), the voltammetric response is less than ideal. In contrast, in the thin film with lower neighbouring interactions (i.e. higher dielectric constant film, NPOE), a voltammetric response closer to ideal was achieved. These observations agree with other reports in which electrostatic interactions or ionic interactions can result in increased ion pairing between similarly-sized organic molecules; this effect is more pronounced in lower dielectric constant solvents so that greater electrostatic interactions in the film result in poorer voltammetric responses.^[28]

Electron transfer kinetics of NPOE-based films

Based on thin film behaviour, the rate of electron transfer of the Ru-bipod complex dissolved in the NPOE-based membrane was estimated by Laviron's model.^[29] The separation of anodic and cathodic peaks with increasing scan rates (Figure 4) was employed to estimate kinetic parameters,^[29] according to Eq. (1) and (2) together with Eq. (3), (4) and (5) in the supporting information:

$$E_{p,c} = E^0 - \frac{2.3RT}{\alpha nF} \log \left[\frac{\alpha nFv}{RTk_{app,c}} \right] \quad (1)$$

$$E_{p,a} = E^0 - \frac{2.3RT}{(1-\alpha)nF} \log \left[\frac{(1-\alpha)nFv}{RTk_{app,a}} \right] \quad (2)$$

where $E_{p,c}$ and $E_{p,a}$ are the cathodic and anodic peak potentials, respectively, E^0 is the formal potential calculated by averaging the anodic and cathodic peak potentials at low scan rates, v is the scan rate, α is the electron transfer coefficient, k_{app} is the apparent rate constant of electron transfer, R is the ideal gas constant, T is the temperature, F is the Faraday constant, and n is the number of electrons transferred. Note that this approach cannot be applied to the DOS-based films as these did not show a linear relationship between the peak current and scan rate. By plotting $E_{p,c} - E^0$ and $E_{p,a} - E^0$ versus the logarithm of the scan rate at higher scan rates, where $E_p - E^0 > 100$ mV (Figure 4), α and $1-\alpha$ can be determined from the slopes of the linear fits (Figure 4). The resulting kinetic data are shown in

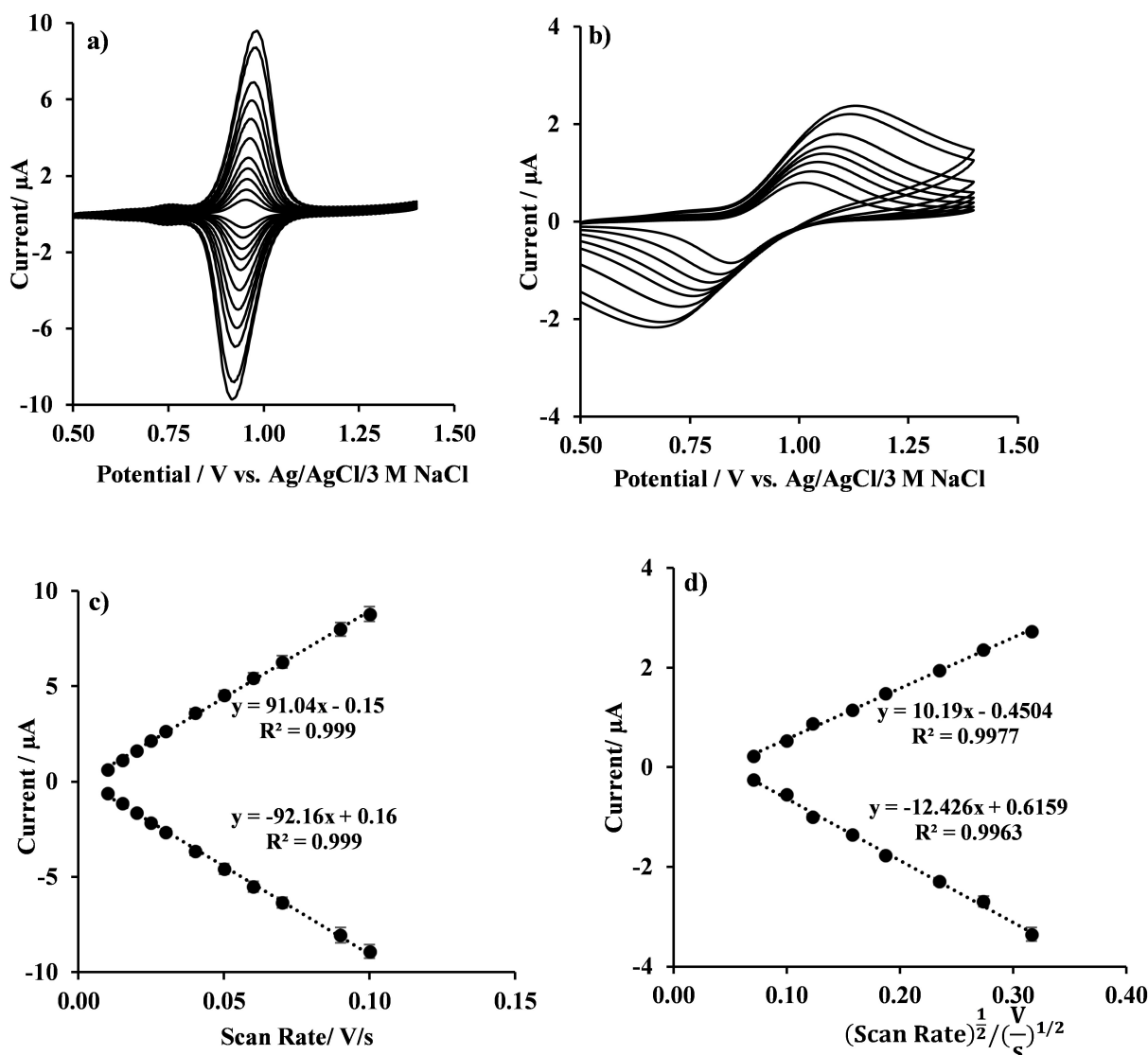


Figure 3. Cyclic voltammograms in 10 mM KPF_6 using thin film membrane SC-ISEs with either a) NPOE (membrane M5, 65 mmol/kg Ru-bipod, 33% PVC, 66% NPOE) or b) DOS (membrane M4, 65 mmol/kg Ru-bipod, 33% PVC, 66% DOS) at different scan rates (10, 15, 20, 25, 30, 40, 50, 60, 70, 90 and 100 mV/s). The scan rate dependencies of cathodic and anodic peak currents for thin films prepared with c) NPOE or d) DOS (data are averages with error bars of ± 1 standard deviation, $n=3$).

Table 1. The low transfer coefficient and non-unity sum of α and $1-\alpha$ is attributed to the structure of the polymeric membrane and is consistent with highly defective film structures on electrodes, as reported previously.^[30] By extrapolating the linear fits to determine the corresponding intercept (Figure 4), anodic and cathodic critical scan rates (v_a and v_c , respectively) are obtained. Then, by using equations 3, 4 and 5 (Supplementary Information), anodic, cathodic and total elec-

tron transfer rate constants ($k_{app,a}$, $k_{app,c}$ and $k_{app,ET}$, respectively) are calculated (Table 1). Since the measured response potentials are a combination of electron transfer and ion transfer, this analysis assumes that ion transfer at the film-aqueous interface is not limiting, consistent with reversible ion transfer of PF_6^- .^[5a,27]

Table 1. Kinetic parameters for Ru-bipod in thin films with NPOE as plasticizer, calculated from the data in Figure 4.

	$1-\alpha$	α	v_a (V/s)	v_c (V/s)	$k_{app,a}$ (s^{-1})	$k_{app,c}$ (s^{-1})	$k_{app,ET}$ (s^{-1})
Ru-bipod (NPOE)	0.34 (± 0.02)	0.42 (± 0.03)	0.37 (± 0.02)	0.26 (± 0.06)	4.9 (± 0.18)	4.4 (± 0.15)	4.7 (± 0.10)

α : electron transfer coefficient; v_a and v_c : anodic and cathodic critical scan rates, respectively; $k_{app,a}$ and $k_{app,c}$: anodic and cathodic electron transfer rate constants, respectively; $k_{app,ET}$: total electron transfer rate constant.

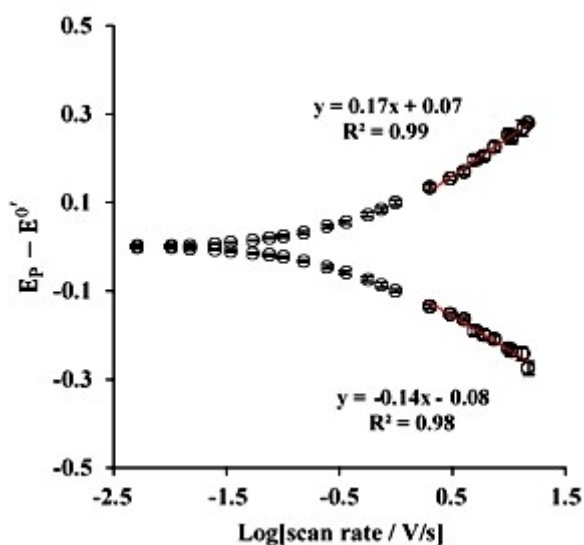


Figure 4. Plot of the oxidation and reduction peak potentials of the Ru-bipod complex in membrane M5 (65 mmol/kg Ru-bipod, 33% PVC, 66% NPOE) as a function of logarithm of scan rate, recorded in the presence of aqueous 10 mM KPF_6 . Linear regression data shown for the higher scan rates where $E_p - E_0' > 100$ mV. Error bars are ± 1 standard deviation, $n=3$.

Stability evaluation during potential cycling

Our eventual goal is to use these films in SC-ISE sensors. Hence, the stability of the polymeric film during repetitive potential cycling was evaluated (Figure S9a). In the presence of 10 mM KPF_6 , there was no significant change in the peak current for both forward and reverse peaks. However, in the presence of 10 mM KNO_3 or K_2SO_4 (Figures S9b and S9c, respectively), significant loss in signal occurred during 50 cycles and shows instability in presence of more hydrophilic anions. It was also observed that in the presence of K_2SO_4 (Figure S9c) there is a

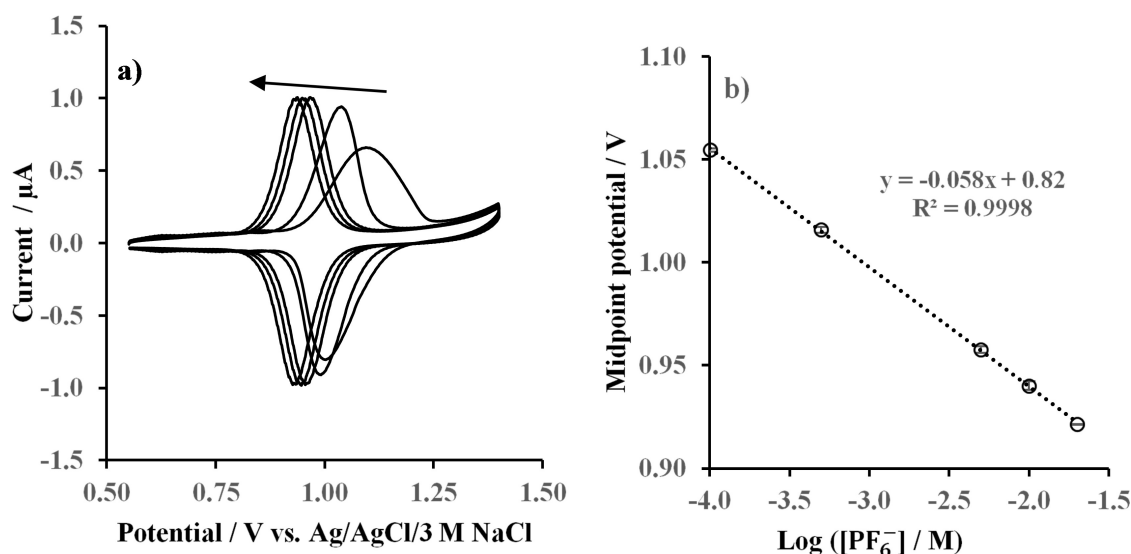


Figure 5. Cyclic voltammograms for increasing concentrations of a) different concentrations of KPF_6 with membrane M5 (65 mmol/kg Ru-bipod, 33% PVC, 66% NPOE). b) Relationship between log of concentration and midpoint potential, with a Nernst slope for PF_6^- . Error bars are ± 1 standard deviation, $n=3$. Scan rate: 10 mV/s.

combination of two or three peaks instead of a single sharp peak as seen with KPF_6 . The origin of this feature is unclear at present, but might be attributed to transfer of different species or to leaching of the Ru-bipod complex to the aqueous phase, as shown previously^[8c] with an osmium complex. Chemical reaction between Ru-bipod and sulfate cannot be excluded. The instability could be attributed to the high potential required in the presence of aqueous phase sulfate, close to 1.25 V. The impact of this high potential is shown by comparison of the first scans of membrane M5 and M11 (without and with sulfate ionophore, respectively) in the presence of 10 mM sulfate (Figures S10c and S10d), and also the first scans of M10 and M5 (with and without ETH500) (Figures S11a and S11b, respectively). These indicate that sulfate ionophore and ETH500 are oxidised^[31] in the membrane. The measured oxidation charges are shown in Table S2. It is clear that the oxidation charge is substantially greater in the presence of ETH500 or sulfate ionophore than in their absence, indicating that these membrane components are subjected to oxidation within the films. In this regard, the composition of the membrane with background electrolyte and this sulfate ionophore is not suitable for detection of anions, especially more hydrophilic anions such as sulfate.

Potentiometric behaviour of thin films

The potentiometric responses and selectivity of Ru-bipod thin film membranes were assessed in the presence of more hydrophobic anions (PF_6^- , ClO_4^- and NO_3^-), because more stable electrochemical responses were achieved with these. Gradual addition of PF_6^- and NO_3^- to the aqueous phase provoked a shift of the peak potentials in a negative direction (Figure 5 and 6, respectively). The membranes show close-to-Nernstian behaviours in the presence of PF_6^- (Figure 5b) and NO_3^-

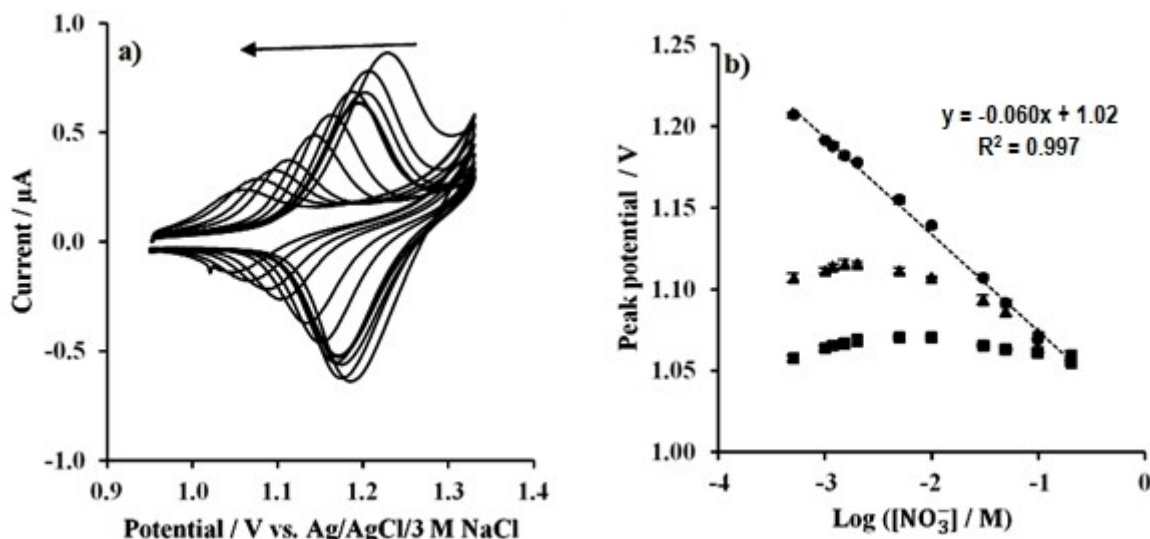


Figure 6. Selectivity study of solid contact electrode with membrane M5 (65 mmol/kg Ru-bipod, 33% PVC and 66% NPOE) in the presence of different concentrations of a) NO_3^- (0.5, 1, 1.2, 1.5, 2, 5, 10, 30, 50, 100 and 200 mM); the arrow shows changing potential with increasing concentration, and b) relation of mid-point potential to logarithm of NO_3^- concentration ($n=3$): NO_3^- without interference (circles), NO_3^- ions in presence of 0.1 mM ClO_4^- (triangles) and NO_3^- ions in presence of 0.1 mM PF_6^- (squares). Error bars are ± 1 standard deviation, $n=3$. Scan rate: 10 mV/s.

(Figure 6b), with response slopes of -58 mV/dec and -60 mV/dec for PF_6^- and NO_3^- , respectively. As mentioned earlier, the thin films show instability to repeated scanning in the presence of NO_3^- (Figure S9b). The deterioration of the peak currents in the presence of different concentrations of nitrate (Figure 6a) may be associated with leaching of the Ru-bipod complex from the thin film, analogous with earlier studies,^[8c,d] or to reactions of Ru-bipod with nitrate within the membrane. Despite the decrease in current, there is a Nernstian response to nitrate ions.

The fixed interference method was used to investigate the selectivity of the membrane for nitrate anions over perchlorate and hexafluorophosphate anions. In this method,^[8d,32] CVs were recorded at different concentrations of nitrate without interference (Figure 6a) and in the presence of 0.1 mM ClO_4^- (Figure S11a) or 0.1 mM PF_6^- (Figure S11b). Plotting the midpoint potential from these CVs versus the logarithm of nitrate concentration (Figure 6b) for these three solutions indicates poor selectivity for nitrate over perchlorate or hexafluorophosphate; calculated selectivity coefficients $K_{\text{NO}_3^-, \text{ClO}_4^-}$ and $K_{\text{NO}_3^-, \text{PF}_6^-}$ were $25(\pm 1)$ and $50(\pm 4)$, respectively. Selectivity coefficient values for NO_3^- over PF_6^- and ClO_4^- by potentiometric methods reported in other studies are more promising than the values found here.^[27,33] Thus, it seems that selectivity of thin films without ionophore is not satisfactory for application of SC-ISEs, and degradation of the thin film occurs in mixed solution experiments. Such membranes without selective ionophores are responsive to more hydrophobic anions in mixed solutions.

Conclusions

In this study, a Ru-bipod complex was investigated as a redox transducer within a thin polymeric film for detection of anions.

The complex showed reversible and stable voltammetric responses in the presence of more lipophilic anions, while in the presence of sulfate and chloride the response was unstable. It was also shown that background electrolyte (ETH500) or sulfate ionophore in the polymeric thin film were susceptible to oxidation in the film. Nevertheless, thin film behaviour was demonstrated by scan rate dependence in the presence of lipophilic anions for thin films containing NPOE plasticizer. The kinetics of charge transfer of the Ru-bipod complex in NPOE-based thin films was determined. The voltammetric behaviour of thin film membranes containing NPOE (higher dielectric constant) was better than that with membranes containing DOS (lower dielectric constant). Moreover, the Ru-bipod complex showed close-to-Nernstian responses to anions (except sulfate and chloride). Based on the results presented, the Ru-bipod complex enables anion detection, but the design of new complexes with lower redox potentials is needed to achieve more stable responses in the presence of ionophores, as oxidation of a commercially-available sulfate ionophore was observed in this work.

Supporting Information

Synthesis and characterisation of the Ru-bipod complex, compositions of membranes, kinetic equations employed, and voltammograms of electrolyte oxidation and sulfate ionophore oxidation.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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