

Electrochemistry of $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{phen})_3]^{2+}$ inserted in Nafion membranes studied in the ionic liquid HMImPF₆

M. J. Gálvez-Vázquez^{1,2}, J.L. Gárate-Morales¹, J. R. Cerna-Cortez¹ and R. Aguilar-Sánchez^{1,*}

¹ Facultad de Ciencias Químicas, Benemérita Universidad Autónoma de Puebla, 72570, Puebla, México.

² University of Bern, Department of Chemistry and Biochemistry, Freiestrasse 3, CH-3012 Bern, Switzerland.

*E-mail: rocio.aguilar@correo.buap.mx, ras747698@gmail.com

Received: 25 July 2020 / Accepted: 23 October 2020 / Published: 31 October 2020

The electrochemical properties of tris(2,2'-bipyridine)ruthenium (II) dichloride ($[\text{Ru}(\text{bpy})_3]^{2+}$), and tris(1,10-phenantroline)ruthenium (II) dichloride ($[\text{Ru}(\text{phen})_3]^{2+}$) complexes inserted in Nafion membranes were studied in the ionic liquid (IL) 1-hexyl-3-methylimidazolium hexafluorophosphate (HMImPF₆). The wide potential window provided by the IL, allows for the study of the redox properties without using organic solvents. The voltammetric patterns revealed reversible reduction waves for bpy and phen ligands and for the oxidation signal of Ru(II)/Ru(III) similar to those observed in aqueous and organic solvents.

Keywords: Nafion, $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{phen})_3]^{2+}$, ionic liquid, voltammetry.

1. INTRODUCTION

Several technological applications such as batteries, fuel cells, sensors and actuators, transducers, and wet molecular electronics, depend on electron transfer chemical reactions and the possibility to perform them in humid environments. Irrespective of the active chemical elements in solution or on a surface, the desired properties are induced by an applied load and registrations of the changes in electrical parameters are made. In an electrochemical environment, voltages as low as 2-3 V are enough to drive properties such as catalysis, and luminescence, among others. However, a big drawback for the application of systems working in wet environments is related to the volatility and electrochemical decomposition of the solvent. During the last two decades, ionic liquids have been foreseen as potential alternatives to conventional solvents in a wide variety of catalytic [1], synthetic [2], sensing [3, 4] and electrochemical applications [5, 6]. They exhibit practically no vapor pressure, they are not volatile, and their physical and chemical properties can be tuned by varying the chemical structure of the

component ions. These properties make them attractive for applications in electrochemical “quasi-liquid” environments.

Additionally, a key point in the construction of, for example, biosensors [7] and dye-sensitized solar cells [8], is the surface immobilization of photo-active chemical elements such as Ru-complexes. Due to its excellent chemical and physical properties, Nafion [9] has been widely explored as a host for Ru-complexes, since it avoids the quenching of their luminescent properties in aqueous solutions [10, 11]. Several reports have been giving attention to the light emission of Ru species bound to Nafion coated electrodes [12]. However, the performance and properties of Nafion highly depend on their swelling and wetting properties [12], and then limitations due to the evaporation of the solvent and the electrolysis of water may be significant for possible applications. With exception of the references [13, 14] where the electroluminescent properties of $[\text{Ru}(\text{bpy})_3]^{2+}$ have been investigated in 1-butyl-3-methylimidazolium hexafluorophosphate (BMIPF₆) in presence of triethylamine [14], the majority of the studies so far have been carried out in aqueous solutions and volatile organic compounds (VOC) [15, 16, 17]. However, it is important to investigate whether or not the properties of the redox-active species inserted in polymer hosts are the same in these viscous electrolytes.

Herein, we describe the electrochemical properties of Ru-complexes in 1-hexyl-3-methylimidazolium hexafluorophosphate ionic liquid using glassy carbon (GC)/Nafion modified electrodes in which the Ru-complexes have been loaded. The knowledge gained can be used to probe electron and mass transfer processes and ion transport within the polymer films on electrodes in ionic liquids. The results may serve to illuminate some aspects of the complex interplay between the molecular structure of such materials and their ability to carry out the electron transfer events necessary for several applications.

2. EXPERIMENTAL

2.1 Chemicals

Ruthenium complexes; $\text{C}_{36}\text{H}_{24}\text{Cl}_2\text{N}_6\text{Ru}\cdot x\text{H}_2\text{O}$ ($[\text{Ru}(\text{phen})_3]^{2+}$, Dichlorotris(1,10-phenanthroline) ruthenium (II) hydrate, 98%), $\text{C}_{30}\text{H}_{24}\text{Cl}_2\text{N}_6\text{Ru}\cdot 6\text{H}_2\text{O}$ ($[\text{Ru}(\text{bpy})_3]^{2+}$, Tris(2,2'-bipyridyl)ruthenium (II) chloride hexahydrate), 5% Nafion ion-exchange resin solution, HMImpF₆ ionic liquid were all purchased from Sigma-Aldrich and used without further purification. Water-based solutions were prepared in deionized Milli-Q water (18M Ω). The Ru-complex-ionic liquid solutions were prepared by dissolving the corresponding Ru-complex in HMImpF₆ under sonication for about 1 hour. Either the HMImpF₆ ionic liquid and Ru-complex/HMImpF₆ solution was dried 18 hours at 90 °C under vacuum.

2.2 Electrode preparation

A glassy carbon (GC) electrode was used as substrate to deposit a Nafion membrane from solution. First, the electrode was polished using diamond paste of 3 and 0.25 μm diameter successively, followed by rinsing with acetone and abundant deionized water in an ultrasonic bath. Then, one aliquot

of a 5% Nafion solution was deposited onto the previously polished electrode surface, and the solvent was allowed to evaporate at room temperature. Incorporation of the Ru-complex into the Nafion film was accomplished by exposing the GC/Nafion electrode to 1 mM aqueous solution of the corresponding Ru-complex for 12 hours, and then it was dried 24 hours at room temperature and transferred to the electrochemical cell containing HMImPF₆. For the studies with the bare electrode, it was polished as above, dried with ultra-high purity argon and immediately transferred to the cell containing HMImPF₆.

2.3 Spectroscopic measurements

The absorption spectra of ionic liquids containing Ru-complex were measured in a quartz cell employing an UV-Vis spectrophotometer Varian Model Cary-50. Previously, the solutions were prepared at a concentration of 1 mM Ru-complexes dissolved by sonication in HMImPF₆.

2.4 Electrochemical measurements

All the electrochemical measurements were performed in a three-electrode cell purged with ultra-high purity Ar, and the gas flow was maintained during the measurements at room temperature. The cell was dried in an oven at 150 °C and it was assembled while still hot under argon atmosphere. A GC, a GC/Nafion or a GC/Nafion/Ru-complex electrode was used as working electrode. Platinum wires were used either as counter and quasi-reference electrodes. Before each measurement, the Pt electrodes were rinsed in concentrated H₂SO₄, thoroughly washed with deionized water, flame annealed for 10 minutes, cooled under Ar atmosphere and immersed into the electrochemical cell. The electrochemical measurements were performed with an Epsilon (Bioanalytical Systems) potentiostat–galvanostat. The BASi-Epsilon EC (ver. 2.13.77) software was used for control and data acquisition.

3. RESULTS AND DISCUSSION

3.1 UV-vis spectroscopy of Ru-complex dissolved in HMImPF₆

The UV-vis spectra of [Ru(bpy)₃]²⁺ and [Ru(phen)₃]²⁺ in HMImPF₆ are shown in Fig 1A and 1B respectively. The spectrum of ionic liquid alone is added for comparison (dashed line). The absorption maximum occurring at 450 nm for [Ru(bpy)₃]²⁺ arise from metal to ligand charge transfer promoting a metal d electron to a ligand antibonding π^* orbital. In the case of [Ru(phen)₃]²⁺ it can be observed two absorption maxima at 410 and 446 nm. Similar spectra have been obtained for these complexes in sulfuric acid and methylene chloride [16, 17] and other types of ionic liquids [18]. These spectroscopic characteristics let us assume that the Ru-complexes maintain their optical properties in HMImPF₆.

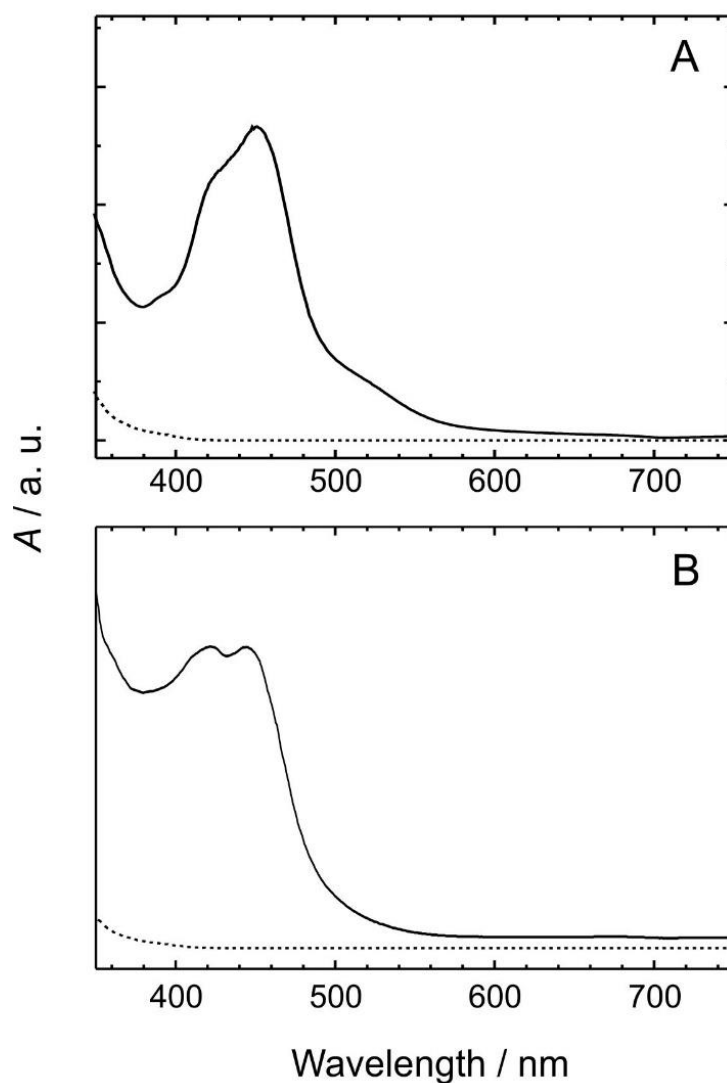


Figure 1. UV-vis absorption spectra of complexes A) $[\text{Ru}(\text{bpy})_3]^{2+}$ and B) $[\text{Ru}(\text{phen})_3]^{2+}$ registered in HMImPF_6 at room temperature (solid line) and compared to Ru-complex free HMImPF_6 (dashed line).

3.2 Electrochemical studies

3.2.1 Cyclic voltammetry of bare GC and GC/Nafion electrode in HMImPF_6

The electrochemical characteristics of the bare GC and the GC/Nafion electrodes in HMImPF_6 recorded at 0.1 V s^{-1} are shown in Figure 2. The voltammogram in Figure 2A was started from 0 V and scanned to positive values up to 2 V.

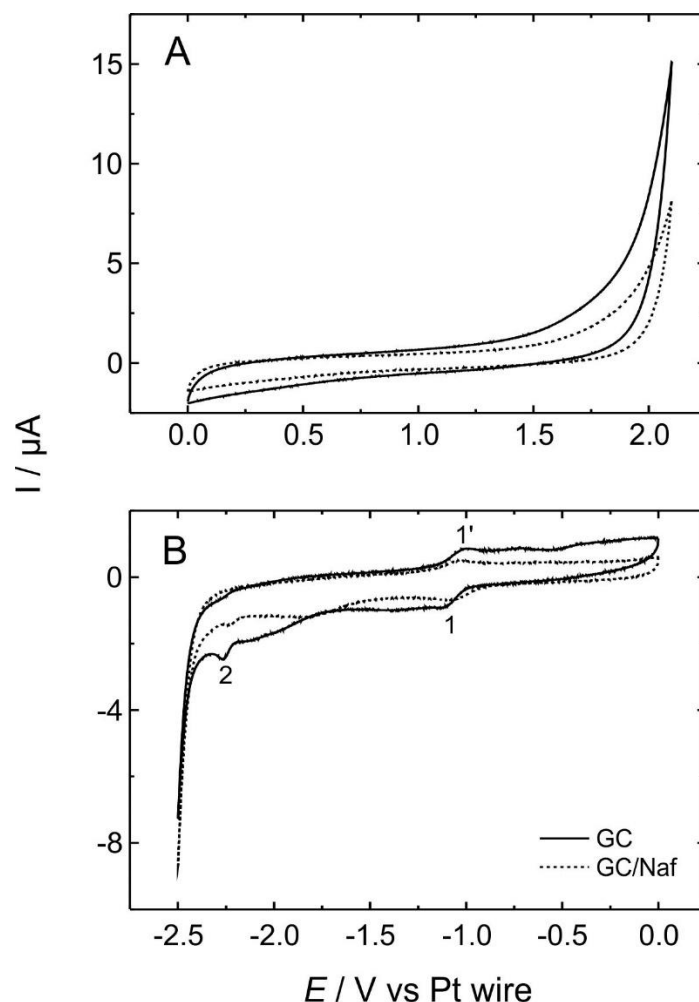


Figure 2. Cyclic voltammograms of bare GC (solid line) and Nafion modified-GC (dashed line) electrodes at A) positive (up to 2 V) and B) negative potentials (up to -2.5 V) in dry HMImpF₆ electrolyte. Scan rate: 50 mV s⁻¹.

In this potential interval, no redox signals could be detected but only a flat response until the oxidative decomposition of HMImpF₆ may take place about 2.0 V [1, 6]. Figure 2B shows the response of the same electrodes at negative potential values. It can be observed a reversible small signal (1/1') at about -1.1 V. Since IL absorbs water easily from the environment, these signatures can be related to the reduction of the presence of small quantities of water. Further scanning the potential to negative values, a cathodic peak about -2.2 V was observed which is due to the adsorption of the imidazolium (HMImp⁺) cation preceding its electroreduction [19] at slightly more negative potentials.

3.2.2 Electrochemical studies of GC/Nafion/Ru-complex electrodes in HMImpF₆

The electrochemistry of [Ru(bpy)₃]²⁺ inserted in Nafion membranes is well known in aqueous solutions [20-23] at positive potentials. However, because re-cast Nafion membranes are not stable in

organic solvents, the electrochemical activity of Ru-complex inserted in this polymer at negative potentials has been far less investigated.

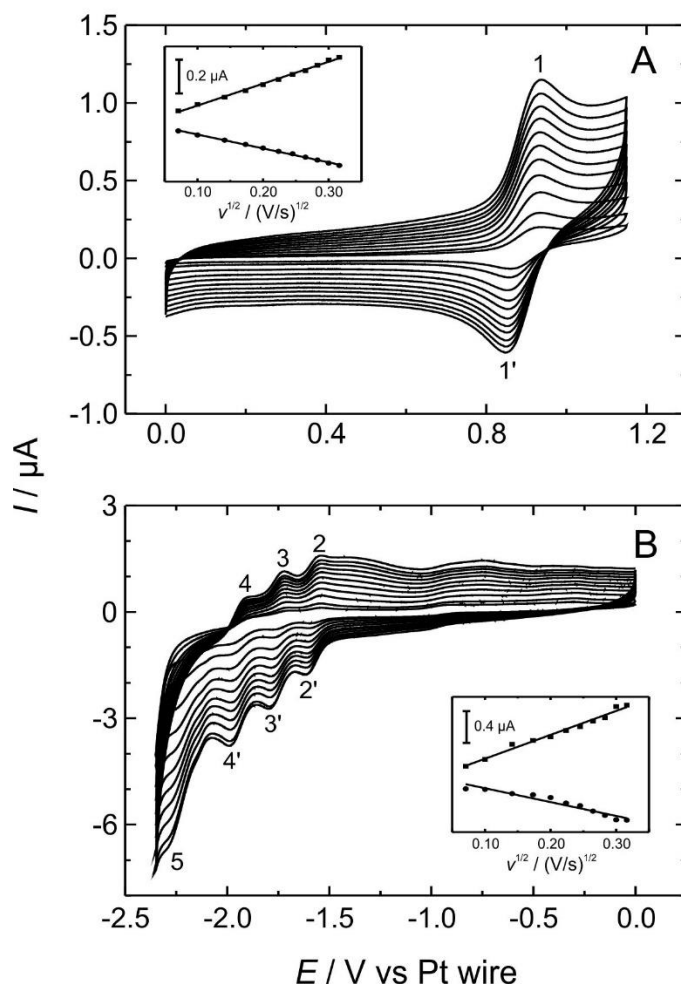


Figure 3. Cyclic voltammograms of modified GC/Nafion/[Ru(bpy)₃]²⁺ electrode in HMImpF₆ at several scan rates ranging from 10–100 mV s^{−1}, in a potential interval from A) 0 to 1.2 V and B) 0 to −2.3 V. Inset A) linear dependence of anodic and cathodic current versus scan rate. Inset B) representative current versus scan rate dependence for the redox pair marked as 3/3' in the corresponding figure.

In Figure 3 it is shown the electrochemical behavior of a GC/Nafion/[Ru(bpy)₃]²⁺ electrode in HMImpF₆ when the potential is scanned between 0 and 1.2 V at different scan rates. At approximately 0.895±0.005 V, it was found a pair of well-defined anodic and cathodic peaks (1/1') corresponding to the reversible oxidation-reduction of the [Ru(bpy)₃]^{2+/3+} redox pair. The voltammograms resemble a diffusion-like controlled reaction with broad peaks that arise from a mass-transport limitation of the reactant within the Nafion film similar to what has been found in aqueous electrolyte [22–25]. With the variation of the scan rate *v*, the splitting of the anodic and cathodic peak potentials (ΔE) ranges from 75 to 90 mV which is not far from the reported for a Nernstian behaviour in aqueous solution and indicate that the electron transfer is fast enough in the ionic liquid. The small variations in ΔE , as well as the I_a/I_c

ratios (1.3) at all scan rates, are understandable in terms of the high viscosity of the ionic liquid. Through the use of a well-established method [26], we calculated the apparent heterogeneous rate constant (k_{app}) from the ΔE values at various scan rates and we noted that its value was one order of magnitude lower ($6 \pm 2 \times 10^{-5} \text{ cm s}^{-1}$) than that reported in aqueous solution ($1 \times 10^{-4} \text{ cm s}^{-1}$) [23]. We should ascribe the observed kinetic phenomena to the polymer environment and the high viscosity of HMImpF₆.

The analysis of the voltammograms at several scan rates is shown in the inset of Figure 3. The anodic and cathodic peak currents show a linear dependence to $v^{1/2}$ over a range of 0.005 – 0.1 V which is indicative of a redox reaction controlled by diffusion for the GC/Naf/[Ru(bpy)₃]²⁺ electrode in HMImpF₆. Diffusion control in polymer-modified electrodes has been reported before [27]. From this dependence we calculated that the *apparent* diffusion coefficient for the anodic ($1.0 \pm 0.1 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) and the cathodic branch ($4.7 \pm 0.3 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$) are asymmetric, implying that self-exchange electron hopping is happening between the halves of the redox couple and the ionic liquid is not playing a significant role on this phenomena. These values are similar to those reported for [Ru(bpy)₃]²⁺ inserted in Nafion and studied in aqueous solutions [28]. This asymmetry in the diffusion coefficients has been reported for other redox couples as ferrocene [29] in ionic liquids.

At very negative potentials (Figure 3B), [Ru(bpy)₃]²⁺ produces three reversible one-electron waves at -1.57, -1.75, and -1.94 V respectively, due to ligand reduction (2/2', 3/3', 4/4') [30] in analogy to studies in dimethylformamide (DMF) [31] and acetonitrile [32]. The difference between the peak potentials was $65 \pm 5 \text{ mV}$ and the pattern and reversibility of the redox peaks can be associated to the reduction of the bipyridine ligands of the complex [33] because of the nearly identical nature of the redox orbitals for the one-, two- and three-electron reduction products. This fair behavior would tell us that the mechanism of electron transfer is by hopping between the redox centers inside the polymer and the slow relaxation process of HMImpF₆ [34] is not affecting the kinetics of charge transfer as far as only energetic aspects are concerned. The inset of figure 3B shows the linear dependence of current (peak 3/3' as representative) with scan rate and the calculated cathodic and anodic apparent diffusion coefficients were $5 \pm 0.2 \times 10^{-10}$ and $1.5 \pm 0.2 \times 10^{-10}$ respectively.

The luminescence properties of Ru-complexes strongly depend on the type of ligand; the greater the shielding of the excited portion, the smaller the solvent perturbations on the emission spectrum. For instance, the bulky phenyl group (phen) is very effective at shielding the excited state from solvent perturbations [35]. For practical applications is important to study different ligands since they can have a profound impact in the spectral characteristics of Ru-complexes [33] and any alteration of the ligand structure could potentially produce different chemical properties, so it is important to demonstrate that the redox properties of the ligand are not altered by the ionic liquid. Figure 4 displays the cyclic voltammograms obtained with a GC/Nafion/[Ru(phen)₃]²⁺ electrode at positive and negative potentials in HMImpF₆. Since cyclic voltammetric waves reflect the kinetics and thermodynamics of various processes that contribute to the redox reactions, it is expected that the diffusional waves are less defined for the case of more hydrophobic and bigger phenantroline ligands. The relationship between current and scan rate is shown in the inset of Figure 4A and the corresponding diffusion coefficients were $4.8 \pm 0.3 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ and $1.8 \pm 0.2 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$. This suggests that distance between redox centers contributes to a lower efficiency and diffusion coefficient if the mechanism is electron hopping through these redox species [28].

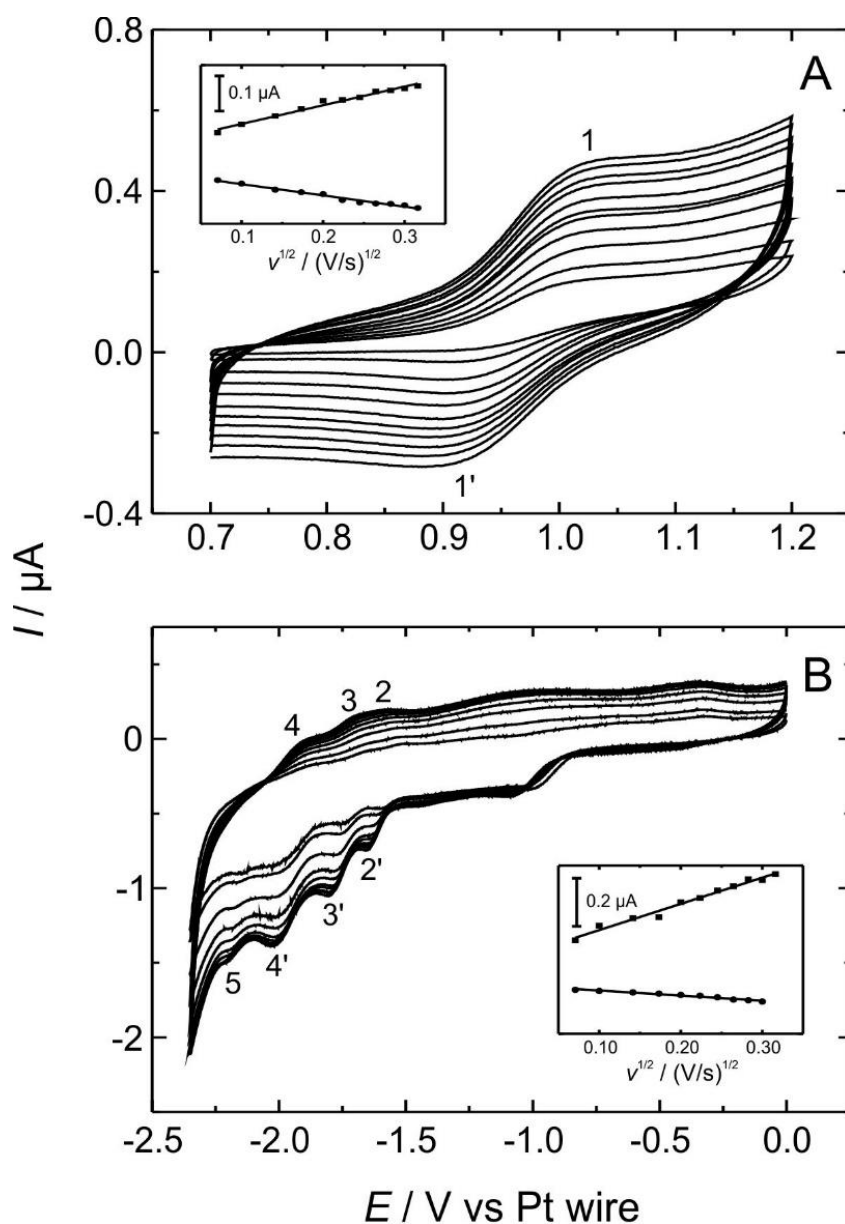


Figure 4. Cyclic voltammograms of modified GC/Nafion/[Ru(phen)₃]²⁺ electrode in HMImpF₆ at several scan rates from 10-100 mV s⁻¹ in a potential interval from A) 0.7 to 1.2 V and B) 0 to -2.3 V. Inset A) linear dependence of anodic and cathodic current versus scan rate. Inset B) representative current versus scan rate dependence for the redox pair marked as 4/4' in the corresponding figure.

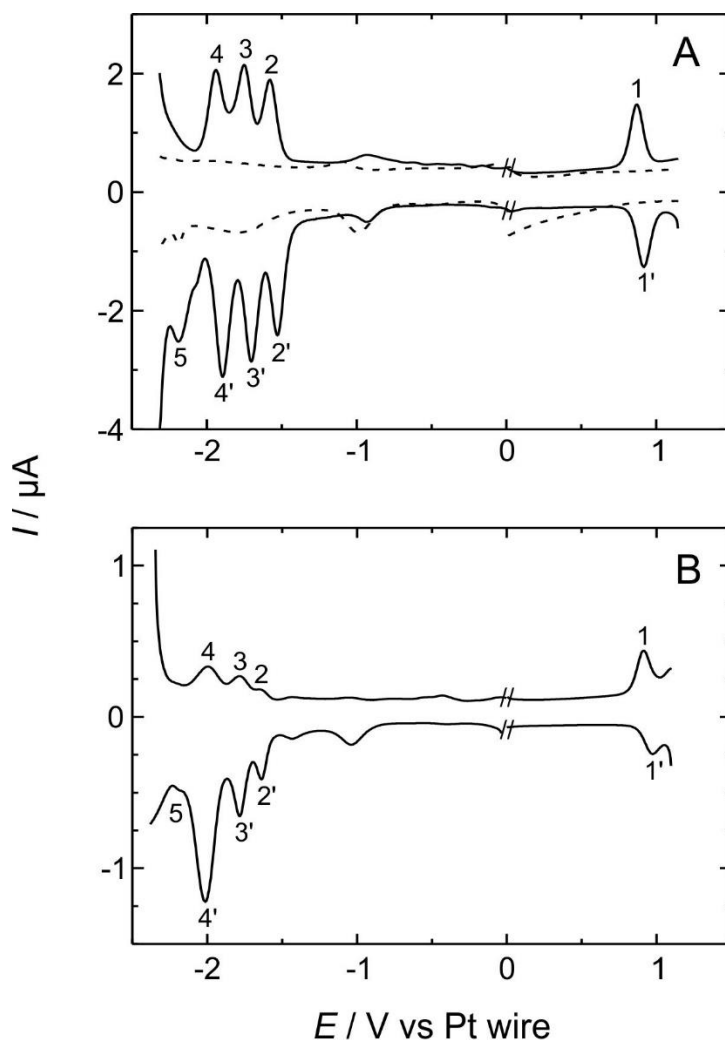


Figure 5. Differential pulse voltammograms of modified A) GC/Nafion/[Ru(bpy)₃]²⁺ and B) GC/Nafion/[Ru(phen)₃]²⁺ electrodes in HMImpF₆. The response of the GC/Nafion electrode is added in A) for comparison (dashed line). Scan rate: 20 mV s⁻¹; pulse amplitude: 50 mV; pulse duration: 200 ms.

At negative potentials (Fig 4B) the reduction signals of phenantroline ligand can be observed. These waves and potential values have been rarely reported [32]. Differential pulse voltammograms in Figure 5, show better resolved waves and for both Ru complexes it was seen a small signal at about -2.1 V. Here is important to note that for Rubpy it has been reported one additional ligand reduction but the species formed is unstable and rapidly vanishes in DMF [33].

4. CONCLUSION

The electrochemical properties of the [Ru(bpy)₃]²⁺ and [Ru(phen)₃]²⁺ studied in HMImpF₆ are similar to those reported in aqueous (positive potentials) and organic solvents (negative potentials). HMImpF₆ presents a good electrochemical stability which makes possible to investigate the

electrochemistry of bipyridine and phenantroline ligands at negative potentials without the need of using organic solvents and then it can be proposed as a green electrolyte alternative in applications where evaporation and electrochemical stability of the solvent is a key issue.

ACKNOWLEDGEMENTS

This work was supported by CONACyT (243030, 104361) and VIEP-BUAP (2019-0284). M. J. Galv  z-V  zquez thanks CONACyT (18069 and 330362) for financial support.

References

1. O. Fontaine, C. Lagrost, J. Ghilane, P. Martin, G. Tripp  , C. Fave, J.-C. Lacroix, P. Hapiot, H.N. Randriamahazaka, *J. Electroanal. Chem.*, 632 (2009) 88.
2. S. Zahmatkesh, *Amino Acids*, 40 (2011) 533.
3. M. Ge, G. Hussain, D. B. Hibbert, D. S. Silvester, Chuan Zhao, *Electroanalysis*, 31 (2019) 66.
4. O. Oter, K. Ertekin, S. Derinkuyu, *Mater Chem. Phys.*, 113 (2009) 322.
5. M. Watanabe, M.L. Thomas, S. Zhang, K. Ueno, T. Yasuda, K. Dokko, *Chem. Rev.*, 117 (2017) 7190.
6. N.E. Mart  nez-Romero, R. Aguilar-S  nchez, Y.-C. Fu, M. Homberger, U. Simon, *Electrochim. Acta*, 231 (2017) 44.
7. H. Wang, Y. Yuan, Y. Zhuo, Y. Chai, and R. Yuan, *Anal. Chem.*, 88 (2016) 2258.
8. R.N. Sampaio, A.V. M  ller, A. Polo and G.J. Meyer, *ACS Appl. Mater. Inter.*, 9 (2017) 33446.
9. K.A. Mauritz and R. B. Moore, *Chem. Rev.*, 104 (2004) 4535.
10. Y. Jenkins, A.E. Friedman, N.J. Turro, J.K. Barton, *Biochemistry*, 31 (1992) 10809.
11. R. M. Hartshorn, J.K. Barton, *J. Amer. Chem. Soc.*, 114 (1992) 5919.
12. P.C. Lee and D. Meisel, *J. Amer. Chem. Soc.* 102 (1980) 5477.
13. B. Quinn, Z. Ding, R. Moulton and A.J. Bard, *Langmuir*, 18 (2002) 1734.
14. Zheng L. Chi Y. Dong Y, Zhang L. and G. Chen, *J. Phys. Chem. C*, 112 (2008) 15570.
15. B. Quinn, Z. Ding, R. Moulton and A.J. Bard, *Langmuir*, 18 (2002) 1734.
16. B.N. Bideh, C. Rold  n-Carmona, H. Shahroosvand and M.K. Nazeeruddin, *J. Mater. Chem. C*, 4 (2016) 9674.
17. B. Durham, J. V. Caspar, J. K. Nagle and T. J. Meyer, *J. Am. Chem. Soc.*, 104 (1982) 4803.
18. Y. Toshimitsu, Y. Katayama and T. Miura, *Electrochimica Acta*, 82 (2012) 43.
19. P.A. Suarez, C. S. Consorti, R.F. de Souza, J. Dupont, R. S. Gon  alves, *J. Braz. Chem. Soc.*, 13 (2002) 106.
20. I. Rubinstein and A. J. Bard, *J. Amer. Chem. Soc.*, 102 (1980) 6641.
21. I. Rubinstein and A. J. Bard, *J. Amer. Chem. Soc.*, 103 (1981) 5007.
22. C. R. Martin, I. Rubinstein and A. J. Bard, *J. Amer. Chem. Soc.*, 104 (1982) 4817.
23. D. A. Buttry and F. C. Anson, *J. Amer. Chem. Soc.*, 104 (1982) 4824.
24. I. Rubinstein and A. J. Bard, *J. Amer. Chem. Soc.*, 102 (1980) 6641.
25. I. Rubinstein and A. J. Bard, *J. Amer. Chem. Soc.*, 103 (1981) 5007.
26. E. Laviron, *J. Electroanal. Chem.*, 101 (1979) 19.
27. R.J. Nowak, F.A. Schultz, M. Umana, R. Lam, R.W. Murray, *Anal. Chem.*, 52 (1980) 315.
28. W.L. Gellett, K.L. Knoche, N.P.W. Rathuwadu, J. Leddy, *J. Electrochem. Soc.*, 163 (2016) H588.
29. E. I. Rogers, D. S. Silvester, D. L. Poole, L. Aldous, C. Hardacre, R. G. Compton, *J. Phys. Chem. C*, 112 (2008) 2729.
30. Y. Ohsawa, M. K. DeArmond, K. W. Hanck, D. E. Morris, D. G. Whitten and P.E. Neveux Jr, *J. Am. Chem. Soc.*, 105 (1983) 6522.
31. D. E. Morris, K. W. Hanck and M. K. DeArmond, *J. Am. Chem. Soc.*, 105 (1983) 3032.

32. N.E. Tokel-Takvoryan, R.E. Hemingway and A.J. Bard, *J. Am. Chem. Soc.*, 95 (1973) 6582.
33. C. M. Elliot, E. J. Hershenhart, *J. Am. Chem. Soc.*, 104 (1982) 7519.
34. X. Li, M. Liang, A. Chakraborty, M. Kondo, M. Maroncelli, *J. Phys. Chem. B*, 115 (2011) 6592.
35. E. R. Carraway, J. N. Demas, B. A. DeGraff, J. R. Bacon, *Anal. Chem.*, 63 (1991) 337.

© 2020 The Authors. Published by ESG (www.electrochemsci.org). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).