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Redox Properties of a Rhenium Tetrazolato Complex in Room Temperature Ionic Liquids: Assessing the Applicability of the Stokes–Einstein Equation for a Metal Complex in Ionic Liquids

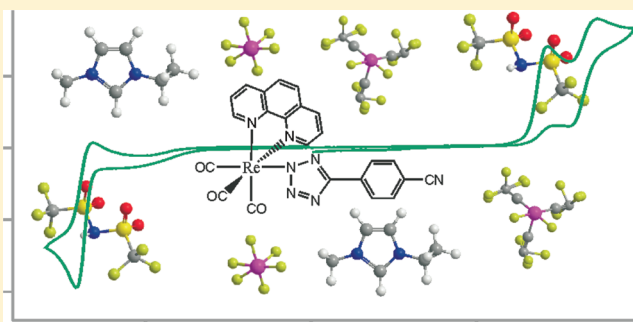
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S Supporting Information

ABSTRACT: The redox properties of a rhenium-tetrazolato complex, namely *fac*-[Re(CO)₃(phen)L] (where L is 5-(4'-cyanophenyl)tetrazolate), have been studied by cyclic voltammetry in a range of common room temperature ionic liquids (RTILs) with different anions and cations. In all eight RTILs, one reduction and two oxidation peaks are observed. It is believed that the reduction peak corresponds to ligand reduction and the two oxidation peaks are two one-electron oxidations of the metal from Re(I) to Re(II) and Re(II) to Re(III). The redox potentials of the metal oxidations appear to be unchanged with the solvent; however, the potential for the reduction peak is more negative in RTILs containing the [P_{14,6,6,6}]⁺ cation, suggesting a stabilization effect of the electrogenerated intermediate with the other RTIL cations studied (imidazolium and pyrrolidinium). Potential step chronoamperometric experiments were used to calculate diffusion coefficients of the complex in RTILs, and it was found that *fac*-[Re(CO)₃(phen)L] diffuses very slowly through the RTIL medium. A plot of diffusion coefficient against the inverse of viscosity of the RTIL solvent showed a linear trend, suggesting that the Stokes–Einstein relationship generally applies for this complex in RTILs, but the coefficient on the denominator is likely to be closer to 4 (the “slip” limit) than 6 (the “stick” limit) when taking into account the hydrodynamic radius.



1. INTRODUCTION

Room temperature ionic liquids (RTILs) are liquids at room temperature and are composed entirely of ions.^{1,2} They possess several typical properties such as intrinsic conductivity, wide electrochemical windows, high viscosity, high polarity, high thermal stability, and the ability to dissolve a wide range of compounds.^{1,2} Since the nature of the anion and cation can be easily changed, RTILs are highly “tunable” solvents and can be opportunely modified toward a specific application. As such, they have been explored as replacement solvents in a range of applications such in gas sensors,^{3,4} fuel cells,⁵ lithium batteries,⁶ solar cells,⁷ light emitting electrochemical cells (LEECs),⁸ and organic light emitting devices (OLEDs)⁹ and have widely been used as solvents in fundamental electrochemical reactions.^{10–13} In this work, we have employed RTILs as the electrochemical solvent for a number of reasons. First, their wide electrochemical windows allow the study of redox reactions at high potentials, which may not be accessible in conventional organic solvent/electrolyte systems. Second, as a consequence of their extremely low volatility, they can be placed under vacuum conditions, to allow purging of dissolved impurities (e.g., oxygen/water), but with no evaporation of the solvent.¹⁴ Additionally,

the use of a specially designed small-volume electrochemical “T-cell”¹⁵ means that only microliter quantities of solvent are required for experiments. It is worth noting that this reduces the cost of the RTIL solvent required per experiment and also reduces the quantity of the electroactive species required for analysis. This is a huge advantage especially when the specific electroactive species are available in small quantities due to expensive starting materials or difficulties in their preparation and isolation.

In the last 30 years, rhenium(I) complexes of the type *fac*-[Re(CO)₃(diim)L]^{0/+}, where *diim* is a bidentate conjugated aromatic system such as 1,10-phenanthroline (*phen*) and L is either an anionic or neutral monodentate ancillary ligand, have become of great interest due to their phosphorescence properties as well as their potential use in nuclear medicine.^{16,17} Due to their inert nature arising from their low spin *t*_{2g}⁶ electronic configuration as well as their favorable photophysical properties, they have drawn a lot of attention from areas such as

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sensing, light emitting electrochemical cells, biological labeling, and electron-transfer in biomolecules.¹⁶ Their emissive properties originate from metal-to-ligand charge transfer (MLCT) transitions, typically ascribed to the promotion of an electron from a metal-localized t_{2g} orbital to the π^* system of the **diim** ligand.¹⁸ The photophysical properties of these complexes can be readily tuned in terms of emission color by manipulating the electronic properties of the **diim** ligand, e.g. attaching electron withdrawing or donating substituents, and/or by manipulating the properties of the metal center via the chemical nature of the ancillary ligand **L**.^{16,18} The detailed investigation of the photophysical mechanisms governing *fac*-[Re(CO)₃(**diim**)**L**]^{0/+} complexes (and in general phosphorescent metal coordination complexes) is often achieved by complementing spectroscopic with electrochemical techniques, the latter often involving the use of cyclic voltammetry.^{19,20} This technique allows a deeper understanding of the redox processes involved in the complex, including whether their localization is predominantly on the metal or on the coordinating ligands. This information can then be directly related to the origin of excited states arising from MLCT transitions, since these can be formally described as oxidations on the metal centers with concomitant reduction of the ligands.²¹ Generally cyclic voltammetric measurements are performed in solutions of organic solvents, such as acetonitrile, containing the metal complex.²² These solvents must be free of water (thus often requiring a proper dedicated apparatus in the case of water-miscible solvents such as acetonitrile) and degassed to avoid the interference of dissolved O₂ molecules on the redox processes of the complex. Moreover, they sometimes have a limited potential window with the possible consequence of limiting the detection of the number of redox processes. Lastly, a supporting electrolyte is required for the experiment and the choice of the specific electrolyte is critical for the detection and the quality of the electrochemical processes. RTILs have been scarcely considered as solvents for the cyclic voltammetry of such metal complexes, nevertheless they can represent an advantageous alternative to traditional organic solvents due to their intrinsic properties.

In this work, we have used electrochemical techniques to understand the electronic properties of a neutral Re–tetrazolato complex, namely *fac*-[Re(CO)₃(**phen**)**L**] where **L** is 5-(4'-cyanophenyl)tetrazolate as schematized in Figure 1,

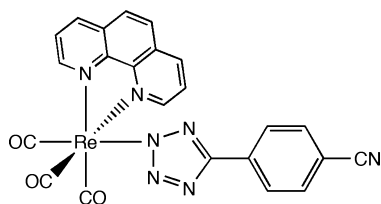


Figure 1. Chemical structure of the *fac*-[Re(CO)₃(**phen**)**L**] complex employed in this work.

using room temperature ionic liquids as electrochemical solvents. Complexes of these types have been reported before, including their detailed photophysical investigation.²³ In addition to studying the redox properties of *fac*-[Re(CO)₃(**phen**)**L**], this work also investigates the fundamental behavior of RTILs as electrochemical solvents. In the past, it has been found that the Stokes–Einstein equation:²⁴

$$D = \frac{k_B T}{6\pi\eta a} \quad (1)$$

applies only for some species in RTILs.¹⁰ In this equation, D is diffusion coefficient, k_B is the Boltzmann constant, T is the temperature, η is the viscosity, and a is the hydrodynamic radius of the diffusing particle. In RTILs, this equation works well in cases where the size of solvent molecules is similar to the diffusing species (e.g., ferrocene and cobaltocenium,²⁵ which are similar in size to RTIL ions). However, it does not apply for smaller molecules (e.g., oxygen, sulfur dioxide, hydrogen molecules) in RTILs.^{3,26,27} It is worth noting that Licence and co-workers have shown a general dependence on the diffusion coefficient of the electroactive species with the inverse of the viscosity, but that the denominator of eq 1 lies somewhere between 4 and 6 (the “slip” and “stick” coefficients) for ferrocenemethanol and 1-ferrocenylmethylimidazole in ionic liquids.^{28,29} We have therefore investigated if the Stokes–Einstein equation applies for the chosen Re–tetrazolato metal complex in RTILs. A number of RTILs with different viscosities have been employed and diffusion coefficients of the Re–tetrazolato complex in each RTIL are calculated. The results from this investigation will reveal more information on the fundamental behavior of inorganic metal complexes in RTILs and the suitability of RTILs as electrochemical solvents for such compounds.

2. EXPERIMENTAL SECTION

2.1. Chemical Reagents. The complex *fac*-[Re(CO)₃(**phen**)**L**] was synthesized via direct addition of 4-(1H-tetrazol-5-yl)benzonitrile³⁰ to *fac*-[Re(CO)₃(**phen**)Cl]²⁰ in refluxing acetonitrile and in the presence of triethylamine, following a slightly modified procedure reported elsewhere (see the Supporting Information (SI) for details).²³ Ferrocene (Fe(C₅H₅)₂, Aldrich, 98%), acetonitrile (MeCN, Fischer Scientific, 99%), and tetra-*N*-butylammonium perchlorate (TBAP, Fluka, 99%) were used as received without further purification. The RTILs 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C₄mim][NTf₂]), 1-ethyl-3-methylimidazolium (trifluoromethyl-sulfonyl)imide ([C₂mim][NTf₂]), *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([C₄mpyr][NTf₂]) and trihexyl tetradecylphosphonium bis(trifluoromethylsulfonyl)imide ([P_{14,6,6,6}][NTf₂]) were synthesized according to standard literature procedures^{31,32} and kindly donated by the group of Professor Christopher Hardacre at Queens University, Belfast. The RTILs 1-hexyl-3-methylimidazolium trifluorotris(pentafluoroethyl)phosphate ([C₆mim][FAP]), tris(hexyl)tetradecylphosphonium trifluorotris(pentafluoroethyl)phosphate ([P_{14,6,6,6}][FAP]), 1-butyl-3-methylimidazolium hexafluorophosphate ([C₄mim][PF₆]), 1-butyl-3-methylimidazolium tetrafluoroborate ([C₄mim][BF₄]) were purchased from Merck at ultra high purity electrochemical grade (halide content less than 100 ppm). All RTILs were used as received. The chemical structure of the RTILs anions and cations employed in this work are shown in Figure 1 of the Supporting Information.

2.2. Instrumental. A gold microelectrode (made in house and kindly donated by the group of Professor Richard Compton at Oxford University, UK) was polished in a figure-8 motion on soft lapping pads (Buehler, Illinois) prior to each experiment with decreasing particle size of alumina (3 μm, 1 μm, 0.25 μm respectively). The working electrode was modified with a section of disposable micropipet tip into which microliter quantities of the RTIL can be placed. The electrode was then inserted into the “T-cell”,¹⁵ a specially designed cell used to study electrochemical properties of samples under atmospheric conditions (see Figure 2

of the Supporting Information). A silver wire of 0.5 mm diameter was inserted from the top and acted as a combined counter and reference electrode. The T-cell was placed inside an aluminum Faraday cage and connected to vacuum pump (Edwards high vacuum model ES50) to remove dissolved atmospheric impurities naturally present in the RTIL.

For experiments on the Re complex, ~0.6 mg was weighed into a vial and dissolved in 100 μL of the selected RTIL, to give an approximate concentration of 10 mM. A 30 μL portion of this solution was directly pipetted onto the μ -electrode. For experiments involving the addition of ferrocene (Fc), 20 mM of Fc was first made in 10 mL acetonitrile. A 15 μL portion of this solution was added to 30 μL of RTIL and mixed under a nitrogen atmosphere in the cell. The cell was then placed under vacuum to evaporate the MeCN to leave the desired concentration (5 mM) of ferrocene in the RTIL.

All voltammetric and chronoamperometric experiments were performed using a PGSTAT302N potentiostat (Eco-Chemie, Netherlands) interfaced to a PC with GPES (General Purpose Electrochemical System) software, fixing the step potential at 0.01 V. The gold microelectrode diameter was calibrated electrochemically by examining the steady-state current of a 2 mM of ferrocene in acetonitrile containing 0.1 M TBAP. This gave a nominal radius of 11.8 μm when a value of $2.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ was adopted for the diffusion coefficient of Fc in MeCN.³³

2.3. Chronoamperometric Experiments. Chronoamperometric transients were achieved using a sample time of 0.01 s. The potential was held at 0 V for 20 s for pretreatment, after which the potential was stepped to the required value and the current was measured for 10 s. Fitting of the experimental data was achieved using the nonlinear curve fitting function available in Origin 8.6 (Herne Scientific Software, Australia), following the Shoup and Szabo approximation.³⁴ The equations used in this approximation are sufficient to describe the current response to within an accuracy of 0.6% and are given below:

$$I = -4nFDcr_d f(\tau) \quad (2)$$

$$f(\tau) = 0.7854 + 0.8863\tau^{-1/2} + 0.2146e^{-0.7823\tau^{-1/2}} \quad (3)$$

$$\tau = \frac{4Dt}{r_d^2} \quad (4)$$

where n is the number of electrons transferred, F is Faraday's constant, D is the diffusion coefficient, c is the initial concentration of the Re–tetrazolato complex, r_d is the radius of the microdisk, and t is the time. The software was instructed to perform 10 iterations on the data, fixing the value for the electrode radius, which was previously calibrated. When the experimental data had been optimized, a value for the diffusion coefficient and the product of the number of electrons multiplied by the concentration was obtained.

3. RESULTS AND DISCUSSION

In this work, the electronic properties of the *fac*-[Re(CO)₃(phen)L] complex in RTILs will be studied in detail, and any similarities/differences in the electrochemical behavior in different RTILs will be explored. First, cyclic voltammetry will be presented in one chosen RTIL ([C₂mim][NTf₂]) to describe the electrochemical reaction mechanism. Then, the behavior in eight different RTILs with a range of cations and anions will be presented. Finally, the applicability of the

Stokes–Einstein equation for this large inorganic metal complex in ionic liquids will be addressed.

3.1. Cyclic Voltammetry for the Oxidation and Reduction of the *fac*-[Re(CO)₃(phen)L] Complex in [C₂mim][NTf₂]. Figure 2 shows typical cyclic voltammetry for the reduction and oxidation of *fac*-[Re(CO)₃(phen)L] in the RTIL

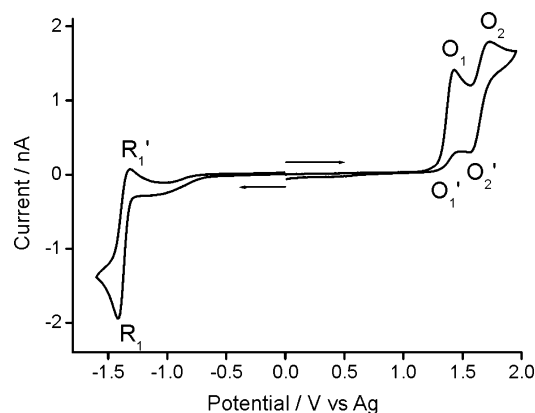
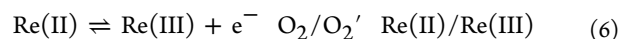
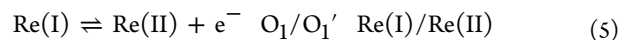


Figure 2. Typical cyclic voltammetry for the oxidation and reduction of ~10 mM of *fac*-[Re(CO)₃(phen)L] in [C₂mim][NTf₂] on a gold microelectrode (radius 11.8 μm) at a scan rate 100 mV s⁻¹. Arrows indicate the direction of the scan.

[C₂mim][NTf₂] on a gold microelectrode (radius 11.8 μm) at a scan rate of 100 mV s⁻¹. The voltammetric curve consists of one reduction and two oxidations, and all three peaks have a corresponding reverse peak (i.e., all are reversible redox couples). The reduction peak at ~-1.4 V is ascribed to a one-electron reduction of the **phen** ligand, in accordance to previously reported data on analogous Re complexes.¹⁹ The two oxidation peaks (at ~+1.4 and ~+1.7 V) are assigned to the double oxidation of the Re metal center, according to the following equations:



However, it cannot be excluded that the tetrazolato ligand effectively contributes to one or both of the oxidation processes, as we have previously shown that in these types of complexes an extended delocalization is present between the t_{2g} orbitals centered on the rhenium cation and the π system of the tetrazole ring.²³ Cyclic voltammetry was also carried out at a range of scan rates to obtain information on the diffusional behavior of the complex in [C₂mim][NTf₂] and the electrochemical reversibility of the peaks. Voltammetry at a range of scan rates for all three peaks is presented in Figure 3 of the Supporting Information, and corresponding plots of peak current vs the square root of scan rate are given in Figure 4 (SI). A very good linear relationship was observed between peak current and square root scan rate for both the reduction peak and the first oxidation peak, indicating that both processes are diffusion controlled, as observed for other metal complexes in RTILs (e.g., ferrocene and cobaltocenium).²⁵

All three peaks initially appear to be chemically reversible due to the presence of back peaks (labeled R_1' , O_1' , and O_2'). However, the peak height for the reverse peaks R_1' and O_1' are smaller than for R_1 and O_1 (approximately 80–85% of the size) suggesting that there may be some follow-up chemistry

(homogeneous reaction) after the electrochemical step. This could be a reaction with some impurity in the RTIL (e.g., trace water) or dimerization of the metal complex, which has been reported previously for analogous rhenium complexes in acetonitrile.³⁵ However, this homogeneous reaction appears to be slow on the electrochemical time scale, particularly for O_1/O_1' , since the peak currents are approximately similar in height at higher scan rates (see Figure 3b Supporting Information). The peak-to-peak separations (ΔE_{pp}) for R_1/R_1' , O_1/O_1' , and O_2/O_2' at 100 mV s⁻¹ was found to be 100, 109, and 160 mV, respectively, comparable to that for Fc/Fc⁺ (110 mV, see Table 1) suggesting relatively fast kinetics for R_1/R_1' and O_1/O_1' , but

Table 1. Peak-to-Peak Separations (ΔE_{pp}) from Cyclic Voltammetry at 100 mV s⁻¹ for the Three Redox Couples of *fac*-[Re(CO)₃(phen)L] in Various Ionic Liquids^a

RTIL	viscosity at 298 K/cP ¹⁰	ΔE_{pp} (R_1/R_1')/mV	ΔE_{pp} (O_1/O_1')/mV	ΔE_{pp} (O_2/O_2')/mV	ΔE_{pp} (Fc/Fc ⁺)/mV
[C ₂ mim][NTf ₂]	34	100	109	160	110
[C ₄ mim][NTf ₂]	52	101	106	104	95
[C ₆ mim][FAP]	74	99	94	121	92
[C ₄ mpyr][NTf ₂]	89	90	100	111	82
[C ₄ mim][BF ₄]	112	102	112		105
[C ₄ mim][PF ₆]	371	99	112	211	99
[P _{14,6,6,6}][NTf ₂]	450	89	129		109
[P _{14,6,6,6}][FAP]	464		102	226	95

^a ΔE_{pp} for Fc/Fc⁺ is also included as a comparison.

slower kinetics for O_2/O_2' (i.e., this process is electrochemically quasi-reversible).

3.2. Cyclic Voltammetry for *fac*-[Re(CO)₃(phen)L] in a Range of RTILs. In the previous section, the behavior of *fac*-[Re(CO)₃(phen)L] in one ionic liquid was presented. Now, the behavior of this complex in eight different ionic liquids is studied, to see if the nature of the ionic liquid changes the electrochemical behavior or reaction mechanism of the species. This can give information about any possible physical interaction (e.g., Coulombic attraction) or any reaction of the RTIL cation or anion with the Re complex or electrogenerated intermediates.

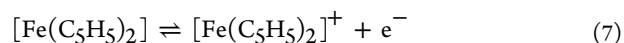
Figure 3 shows cyclic voltammetry for the reduction and oxidation of *fac*-[Re(CO)₃(phen)L] on a gold microelectrode (radius 11.8 μm) at a scan rate of 100 mV s⁻¹ in eight different RTILs. As can be observed, the voltammetric behavior is relatively similar in all eight RTILs and the electrochemical reaction mechanisms appear to be the same. All three redox couples are present in all eight ionic liquids, but the peaks for O_2/O_2' are not so clear in [C₄mim][BF₄] and [P_{14,6,6,6}][NTf₂], probably due to the peak being too close to the breakdown of the [BF₄]⁻ anion at high potentials, and due to impurities (e.g., trace water) in the case of [P_{14,6,6,6}][NTf₂]. For [C₄mpyr][NTf₂] and [P_{14,6,6,6}][FAP], the height of peak R_1' is much smaller than for R_1 , suggesting follow-up chemistry is occurring to a greater extent in these ionic liquids. However, there is no

obvious relationship between the RTIL anion/cation and the extent of follow-up chemistry.

Table 1 shows the peak-to-peak separations for all three redox couples obtained from Figure 3, along with the separations of the Fc/Fc⁺ redox couple (voltammograms not shown) for comparison. For R_1/R_1' , ΔE_{pp} is relatively consistent for all RTILs studied, suggesting that the nature of the solvent does not affect the kinetics of this process. There is slightly more variation with O_1/O_1' and a much larger variation seen for O_2/O_2' , particularly for the more highly viscous RTILs (where ΔE_{pp} is more than 200 mV for O_2/O_2'). There is also some slight variation for Fc/Fc⁺ in the ionic liquids, but generally the separations of Fc/Fc⁺ are similar to R_1/R_1' and O_1/O_1' , suggesting that both of these processes are fast 1-electron transfers. Ideally, a 1-electron transfer process would have a ΔE_{pp} of ~60 mV,²⁴ but this is rarely observed in ionic liquids (even for traditionally “fast” redox couples such as Fc/Fc⁺) due to additional contributions from outersphere electron transfer in these more viscous solvents.¹⁰

3.2.1. Redox Potentials vs the Ferrocene/Ferrocenium (Fc/Fc⁺) Redox Couple. In order to determine if the nature of the RTIL solvent affects the potential of the redox processes, a stable internal redox couple was added to the solution in-situ. The ferrocene/ferrocenium (Fc/Fc⁺) redox couple has been suggested as an internal reference couple in ionic liquids because it has a potential independent of electrode composition, analyte concentration and scan rate.²⁵ In addition, ferrocene conveniently oxidizes in a potential range where the other peaks from the *fac*-[Re(CO)₃(phen)L] complex do not oxidize/reduce.

Figure 4 shows typical cyclic voltammetry for the oxidation and reduction of the Re–tetrazole complex in the presence of ferrocene in [C₄mpyr][NTf₂] on a 11.8 μm radius gold electrode at a scan rate of 100 mV s⁻¹. The voltammetry is reported against a silver wire reference electrode. Ferrocene is reversibly oxidized by one-electron to Fc⁺ at ~0.5 V according to the following equation:



The same experiment was carried out for all eight ionic liquids. The potentials of the *fac*-[Re(CO)₃(phen)L] processes R_1 and O_1 were calculated vs the midpoint of the Fc/Fc⁺ redox couple, and the results are presented in Table 2. The results show that the potential does not vary significantly for O_1 , with a maximum variation of 40 mV over all eight ionic liquids, which is relatively small. This suggests that the oxidation potential of the metal is not affected by the nature of the solvent. However, for R_1 , there is a larger variation in potential (~140 mV), most notably in the case of RTILs containing [P_{14,6,6,6}]⁺ cations. This suggests that the electrogenerated species (negatively charged complex) may have a different interaction with the positively charged [P_{14,6,6,6}]⁺ cations and that the reduction of *fac*-[Re(CO)₃(phen)L] is slightly more difficult in RTILs containing this cation. This could be due to the imidazolium and pyrrolidinium cations (which are more planar than the tetraalkylphosphonium cation) having a stabilization effect on the electrogenerated intermediate. Anomalous behavior of electroactive species in ionic liquids containing the [P_{14,6,6,6}]⁺ cation has also been observed previously for oxygen reduction³⁶ and for the ratios of diffusion coefficients of ferrocene/ferrocenium and cobaltocenium/cobaltocene¹⁰ in ionic liquids.

3.2.2. Stokes–Einstein Behavior of *fac*-[Re(CO)₃(phen)L] in RTILs. Potential step chronoamperometry was carried out in order to calculate diffusion coefficients of *fac*-[Re(CO)₃(phen)L]

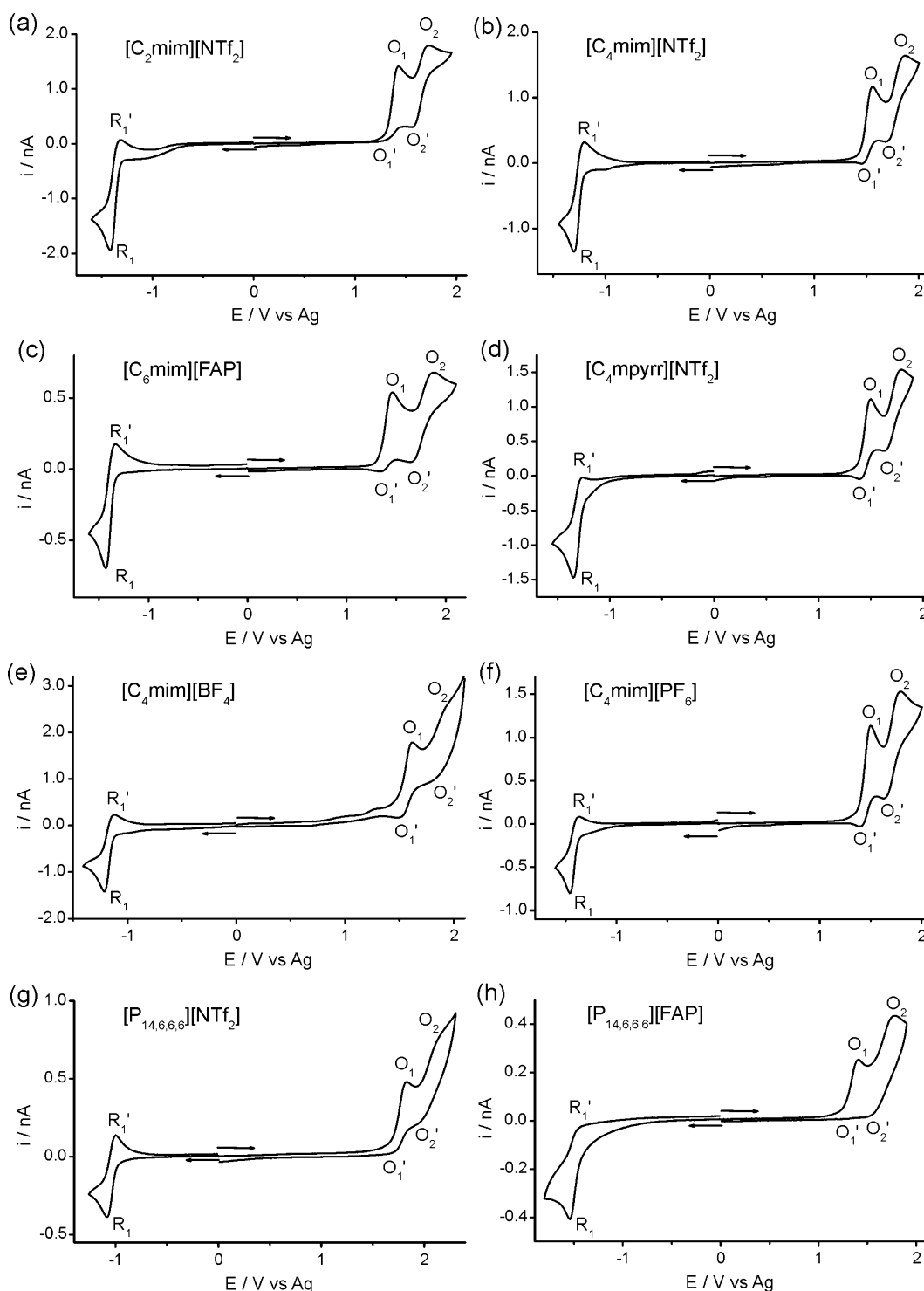


Figure 3. Typical cyclic voltammetry for the oxidation and reduction of ~ 10 mM of $fac\text{-}[\text{Re}(\text{CO})_3(\text{phen})\text{L}]$ in eight different RTILs on a gold microelectrode (radius $11.8 \mu\text{m}$) at a scan rate of 100 mV s^{-1} .

in all eight RTILs. The diffusion coefficient was determined using the Shoup and Szabo expression,³⁴ using computer software to find the best fit to the experimental data. Figure 5 shows the experimental (—) and fitted theoretical (○) chronoamperometric transients for the first oxidation process of $fac\text{-}[\text{Re}(\text{CO})_3(\text{phen})\text{L}]$ in $[\text{C}_4\text{mim}][\text{NTf}_2]$. The same process was repeated in the remaining seven RTILs (results not shown) and similar shapes and excellent fitting was observed. The calculated diffusion coefficients of $fac\text{-}[\text{Re}(\text{CO})_3(\text{phen})\text{L}]$ from

this analysis are presented in Table 3, in order of increasing viscosity of the RTIL solvent. The results indicate that there is a large variation in diffusion coefficient as the ionic liquid is changed. As can also be observed, the Re complex diffuses very slowly in all eight RTILs compared to other inorganic metal complexes such as ferrocene (e.g., D_{Fc} is $5.3 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ in $[\text{C}_2\text{mim}][\text{NTf}_2]$ ²⁵ compared to $D_{\text{Re-tetrazole}}$ which is $8.1 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$), but similar to very large polyoxometalate ions such as $[\text{Mo}_6\text{O}_{19}]^{2-}$ (where $D = 1.4 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ in $[\text{C}_4\text{mim}][\text{PF}_6]$).³⁷

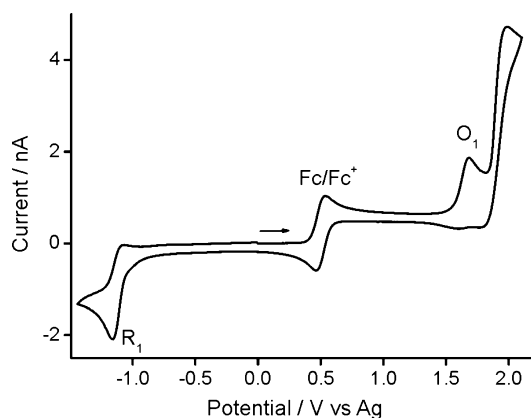


Figure 4. Cyclic voltammetry for ~ 10 mM of $\text{fac-}[\text{Re}(\text{CO})_3(\text{phen})\text{L}]$ in the presence of ~ 5 mM ferrocene in the RTIL $[\text{C}_4\text{mpyrr}][\text{NTf}_2]$ on a gold microelectrode (radius $11.8 \mu\text{m}$) at a scan rate of 100 mV s^{-1} .

Table 2. Peak Potentials from Cyclic Voltammetry at 100 mV s^{-1} for the First Reduction and First Oxidation Peak of $\text{fac-}[\text{Re}(\text{CO})_3(\text{phen})\text{L}]$ versus the Midpoint of the Fc/Fc^+ Redox Couple

RTIL	$E_p(R_1)$ vs $\text{Fc}/\text{Fc}^+/\text{V}$	$E_p(O_1)$ vs $\text{Fc}/\text{Fc}^+/\text{V}$
$[\text{C}_2\text{mim}][\text{NTf}_2]$	-1.64	1.20
$[\text{C}_4\text{mim}][\text{NTf}_2]$	-1.65	1.19
$[\text{C}_6\text{mim}][\text{FAP}]$	-1.67	1.20
$[\text{C}_4\text{mpyrr}][\text{NTf}_2]$	-1.66	1.18
$[\text{C}_4\text{mim}][\text{BF}_4]$	-1.61	1.21
$[\text{C}_4\text{mim}][\text{PF}_6]$	-1.62	1.19
$[\text{P}_{14,6,6,6}][\text{NTf}_2]$	-1.75	1.17
$[\text{P}_{14,6,6,6}][\text{FAP}]$	-1.73	1.20

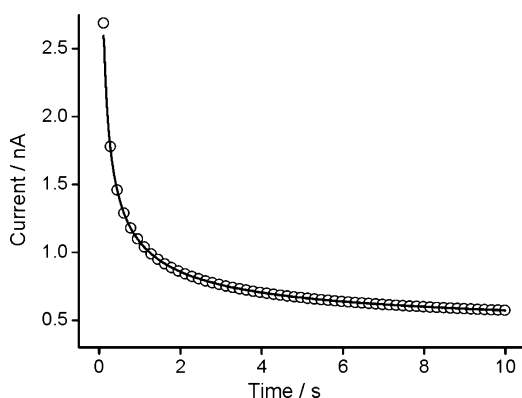


Figure 5. Experimental (—) and fitted theoretical (O) chronoamperometric transients for the oxidation of ~ 10 mM of $\text{fac-}[\text{Re}(\text{CO})_3(\text{phen})\text{L}]$ in $[\text{C}_4\text{mim}][\text{NTf}_2]$ on a gold microelectrode (radius $11.8 \mu\text{m}$). The potential was stepped from 0 to $+1.65 \text{ V}$ and measured for 10 s with a pretreatment time of 20 s at 0 V.

The diffusion coefficient of the $\text{fac-}[\text{Re}(\text{CO})_3(\text{phen})\text{L}]$ complex is significantly smaller than D_{Fc} in all eight RTILs studied.

Figure 6 shows a plot of $D_{\text{Re-tetrazole}}$ against the inverse viscosity of the RTIL solvent. As the viscosity of the RTIL increases, the diffusion coefficient decreases and a good linear trend is observed (Figure 6). The linear trend suggests that the general form of the Stokes–Einstein relationship (eq 1) applies reasonably well for the inorganic Re–tetrazole complex in RTILs (i.e., D is proportional to η^{-1}), analogous to that observed for ferrocene and cobaltocenium.²⁵ However, the coefficient on

Table 3. Viscosity of Eight RTILs and Diffusion Coefficient of $\text{fac-}[\text{Re}(\text{CO})_3(\text{phen})\text{L}]$ Calculated from Chronoamperometric Fittings to the Shoup and Szabo Equation³⁴

ionic liquid	viscosity at 298 K/cP ¹⁰	$D_{\text{Re-tetrazole}}/\times 10^{-12} \text{ m}^2 \text{ s}^{-1}$
$[\text{C}_2\text{mim}][\text{NTf}_2]$	34	8.1
$[\text{C}_4\text{mim}][\text{NTf}_2]$	52	5.8
$[\text{C}_6\text{mim}][\text{FAP}]$	74	4.2
$[\text{C}_4\text{mpyrr}][\text{NTf}_2]$	89	3.8
$[\text{C}_4\text{mim}][\text{BF}_4]$	112	3.2
$[\text{C}_4\text{mim}][\text{PF}_6]$	371	1.3
$[\text{P}_{14,6,6,6}][\text{NTf}_2]$	450	1.0
$[\text{P}_{14,6,6,6}][\text{FAP}]$	464	1.3

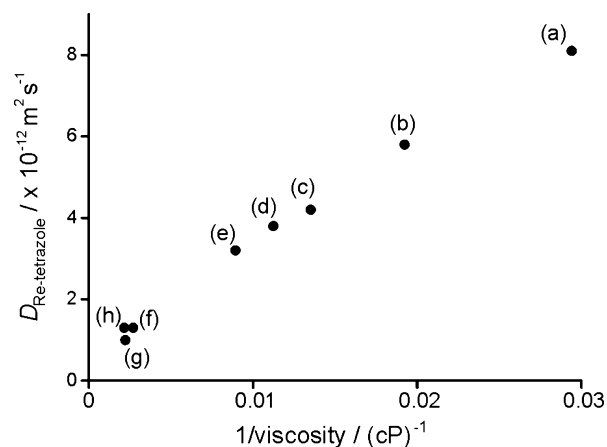


Figure 6. Stokes–Einstein plot of diffusion coefficient (D) of $\text{fac-}[\text{Re}(\text{CO})_3(\text{phen})\text{L}]$ versus the inverse of viscosity for eight different ionic liquids (a) $[\text{C}_2\text{mim}][\text{NTf}_2]$, (b) $[\text{C}_4\text{mim}][\text{NTf}_2]$, (c) $[\text{C}_6\text{mim}][\text{FAP}]$, (d) $[\text{C}_4\text{mpyrr}][\text{NTf}_2]$, (e) $[\text{C}_4\text{mim}][\text{BF}_4]$, (f) $[\text{C}_4\text{mim}][\text{PF}_6]$, (g) $[\text{P}_{14,6,6,6}][\text{NTf}_2]$, and (h) $[\text{P}_{14,6,6,6}][\text{FAP}]$. The data was obtained from Shoup and Szabo fitting to chronoamperometric experiments and is included in Table 3.

the denominator likely lies closer to the slip limit (4), since the calculated hydrodynamic radius (a) is $\sim 8 \text{ \AA}$ for the slip limit (4) and 12 \AA for the stick (6) limit. a for the Re–tetrazolato complex was found to be between ~ 10 and 14 \AA from X-ray structural determination on analogous Re–tetrazolato complexes.²³ It should be noted that when the size of the diffusing species is very different to the size of the RTIL ions, this equation does not apply (e.g., for small molecular gases such as H_2 , O_2 and SO_2) in RTILs.¹⁰ There is relatively little information on the behavior of inorganic metal complexes in RTILs,^{12,37,38} and this result will add new knowledge and understanding to this area.

4. CONCLUSIONS

Cyclic voltammetry for the complex $\text{fac-}[\text{Re}(\text{CO})_3(\text{phen})\text{L}]$ has been studied in a range of RTILs with different anions and cations. The electrochemical mechanism appears to be the same in all ionic liquids, with one reduction peak (reduction of the phenanthroline ligand) and two oxidation peaks (two one-electron oxidations of the metal) observed. All three peaks display some degree of reversibility, with slower kinetics observed for the second metal oxidation. The peak potential for the metal oxidation appears to be unaffected by the solvent, but peak potentials for the ligand reduction suggest that this process is slightly more difficult in ionic liquids containing $[\text{P}_{14,6,6,6}]^+$ cations. Very slow diffusion coefficients were

observed for this complex in all RTILs, suggesting slow movement of the complex through the solvent, which is not unexpected for such a large molecule. A linear trend between diffusion coefficient and the inverse of solvent viscosity was observed for this inorganic complex in ionic liquids. This study also confirms that RTILs are a viable alternative to traditional organic solvents for electrochemical studies of redox processes in inorganic/organometallic coordination compounds.

■ ASSOCIATED CONTENT

■ Supporting Information

Figures showing the synthesis of the Re–tetrazolato complex, RTIL anion/cation structures, electrochemical cell, voltammetry at a range of scan rates, plots of peak currents vs square root of scan rate, and a table of peak-to-peak separations at different scan rates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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