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The Role of Cations in the Reduction of 9-Fluorenone in Bis(trifluoromethylsulfonyl)imide Room Temperature Ionic Liquids

Irene Reche, Iluminada Gallardo, and Gonzalo Guirado*

Departament de Química, Universitat Autònoma de Barcelona, 08193-Bellaterra, Barcelona, Spain

Abstract: A report is presented on some fundamental electrochemical studies based on the effects of cations on the determination of the standard potential values for five bis(trifluoromethylsulfonyl)imide Room Temperature Ionic Liquids (RTILs) in the electrochemical reduction of 9-fluorenone, a well-known redox probe. The standard potential values obtained can be related with the solvation process of the electrogenerated fluorenone radical anion. The accurate determination of the above-mentioned values for RTILs, which are composed of unsymmetrical organic cations and a weakly-coordinating inorganic anion, can be used as a good starting point for establishing the basis of the design for new more environmentally friendly and energetically efficient electrosynthetic routes, as well as new optoelectronic devices based on fluorenone chemistry in those ionic solvents.

Keywords: Ionic Liquids; Electrochemistry; Diffusion Coefficient; Solvation Effects; 9-Fluorenone

1. Introduction

Electrochemistry is a rather neglected technology in the context of organic chemicals manufacturing but the green chemistry revolution opens a new door to its better exploitation. [1] The benefits of using the electrochemical approaches have been pointed out several times, [2] since they usually include: mild chemical and process conditions, easy to control, high process selectivity, novel chemistry available and safer operation. The electrons are inexpensive reagents compared to the commonly used reducing or oxidizing agents, and the electrodes can be regarded as heterogeneous catalysts that are easily separated from the products. Taking into account the above-mentioned concepts, the main drawback associated with the electrochemical processes are, from a "green" point of view,

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the use of either protic or aprotic organic polar solvents containing supporting electrolytes in high concentrations. [3]

This problem could be addressed by using "Greener" Solvents. In this sense Room Temperature Ionic Liquids (RTILs) can be designed to be a potentially attractive "greener" alternative to replace classical electrolyte solutions in a large number of electrochemical applications. [4] It is important to highlight that RTILs are solvents composed by ions, which ensures a high ion concentration, and usually provides conductivities from 0.1 to 18 mS cm^{-1}. Moreover, the electrochemical window of some ILs can be up to 7 V, depending on the chemical nature of the cation and anion.[5-7] Hence, the most active fields in electrochemistry, together with RTILs, is currently focused on electrodeposition, [8-10] supercapacitors, [11] batteries, [12-14] and the study of the heterogeneous electron transfer of electroactive organic compounds in RTILs. [15-21] It is important to note that the "stabilization" of radicals and radical anions has been observed in few cases (such as nitroderivatives, [15, 16] halogenated compounds, [22, 23] acetophenone, [24] stilbene, [25] and superoxide ion [26]). Following this approach, it is possible to determine electrocatalytic properties of some RTILs, understanding as electrocatalytic properties the fact that the same reduction or oxidation process can take place at a lower potential value depending on the composition of the RTILs. [1, 27] This effect on the standard potential value (E°) of the electroactive compound studied is basically due to solvation effects of the RTIL.

Thus, the aim of this study is to explore the interesting possibilities that the use of electrochemical techniques in ILs offer. Some fundamental studies are presented in order to estimate diffusion coefficients and the accurate determination of standard potential shifts, depending on the RTILs used in the electrochemical reduction process of 9-fluorenone (**1**). It was decided to use **1**, as a redox probe, since it is a well-known one, electron fully, reversible system at the radical anion level. [28] It is worth mentioning that **1** is currently being used for electrochemical tuning of the optoelectronic properties of several conjugated polymers. [29] Thus, knowledge of the electrochemical behavior of **1** in ILs would be a good starting point for combining the optoelectronic properties of **1** in those new solvents in order to design new tunable materials or devices. In spite of the potential interest of those studies for further applications, as far as we are aware only one has been previously published. [30] It was decided to perform our electrochemical investigations using silver as working electrode due to the electrocatalytic properties that have been recently reported for this material. [31] The combine use of silver and RTILs will undoubtedly help in the design of new, more efficient, electro-synthetic routes. [27, 32] It is also worth mentioning that five RTILs, composed of unsymmetrical organic cations and a weakly-coordinating inorganic anion, such as bis(trifluoromethylsulfonyl)imide, have been selected for the studies of the electrochemical reduction of 9-fluorenone (redox probe, **1**), Scheme 1.

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Scheme 1. Chart of Structures.

ROOM TEMPERATURE IONIC LIQUIDS
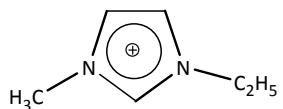
[EMIM] = 1-Ethyl-3-Methylimidazolium

[BMIM]= 1-Butyl-3-Methylimidazolium
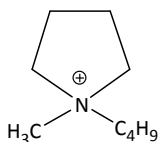
[BMPyr]= 1-Butyl-1-Methylpyrrolidinium
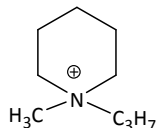
[PP13]= 1-Methyl-1-Propylpiperidinium
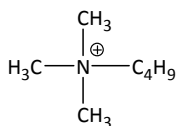
[N1114]= *N*-trimethyl-*N*-butylammonium

Redox Probe (9-Fluorenone)

1
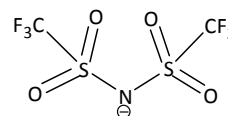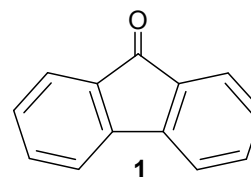
TFSI= Bis(trifluoromethanesulfonyl)imide

2. Experimental Section

2.1. Chemicals

N,N-dimethylformamide (DMF) is stored in an inert atmosphere, and molecular sieves were purchased from Across. *N*-tetrabutylammonium tetrafluoroborate (TBABF$_4$, Fluka, puriss.) is used without further purification. 9-Fluorenone (**1**) is purchased from Aldrich. All the commercially available reactants, including RTILs, are of the highest purity available and are used without further purification. However, since the diffusion coefficient is dependent on the ILs water contents [33], when it was required the purchased RTILs were dried under vacuum using activated molecular sieves for 72 h in order to guarantee that the amount of water present was always less than 100 ppm.

2.2. Cyclic Voltammetry Experiments

An electrochemical conical cell equipped with a methanol jacket, which makes it possible to fix the temperature by means of a thermostat, is used for the set-up of the three-electrode system. For cyclic voltammetry experiments, the working electrode is, in all cases, a silver disk of a diameter of 1.6 mm. It is polished using a 1 μm diamond paste. The counter electrode is a Pt disk of a diameter of 1 mm. All of the potentials are reported versus an aqueous saturated calomel electrode (SCE) isolated from the working electrode compartment by a salt bridge. The salt solution of the reference calomel electrode is separated from the electrochemical solution by a salt-bridge ended with a frit, which is made of a ceramic material, allowing ionic conduction between the two solutions and avoiding appreciable contamination. Ideally, the electrolyte solution present in the bridge (pure RTIL in the Ionic Liquid experiments) is the same as the one used for the electrochemical solution, in order to minimize junction potentials.

Solutions were prepared using *N,N*-dimethylformamide (DMF) as a solvent, and they were purged with nitrogen before and during the measurements. The concentration of **1** was ~10^{-3} M; while the supporting electrolyte concentration was 0.1 M of TBABF$_4$.

The cyclic voltammetry experiments were performed at c.a. 7-12 mM of electroactive substance concentration. The electrochemical cell used is the same as the one described above for aprotic polar solvents. Experiments were performed at 20.0 ± 0.5 ºC under N$_2$ atmosphere. At the end of the process the RTILs were suitably recovered and recycled to start a new set of experiments.

Cyclic Voltammetry experiments of **1** in DMF and in RTILs were performed at different scan rates from 0.1 V s^{-1} to 1 V s^{-1}. At this scan rate range neither the peak potential values nor the ΔE_p were scan rate dependent, so it is fair to think that all the redox systems are under thermodynamic control. Thus, the Eº value is calculated as the half-sum between

forward and reversed peak potentials from a single voltammogram. The E° values shown in all the Tables are the average of three independent sets of experiments. The error associated with these standard potential values is less than 5 mV. The ohmic drop can be one of the main sources of error when RTILs are used as solvents, since they are more resistive media than aprotic polar solvents with 0.1 M concentration of supporting electrolyte. In order to minimize the ohmic drop effects, the electrode used as working electrode is 1.6 mm diameter and the scan rates investigated were in the range $0.1 – 1$ V s^{-1} . Positive feed-back iR compensation was used throughout. Typically compensated resistances were 0.5-2.0 kΩ, depending on the electrode location in the electrochemical cell.

Due to the low conductivity and larger viscosity of RTILs and, in order to facilitate direct comparison between the cyclic voltammograms of redox probes in the different media, the current values were plotted as arbitrary units. [15, 22]

2.3. Instrumentation

The cyclic voltammetry at low scan rates was performed using a PAR 273A potentiostat controlled by a computer. Power Suite software was used for data acquisition and data handling.

3. Results and Discussion

3.1. Cyclic Voltammetry of 9- Fluorenone in DMF + 0.1 M TBA BF₄

Before starting with the electrochemical studies in RTILs, it was decided to establish the electrochemical properties of 9-fluorenone (**1**), a well-known one electron reduction probe, in DMF using a silver electrode as a cathode.

Hence, several solutions of **1** in DMF containing 0.1 M of TBABF$_4$, as supporting electrolyte, were analyzed using cyclic voltammetry. Cyclic voltammograms, at low scan rates, indicate that neither the peak potential value nor the ΔE_p are scan rate dependent, so it is reasonable to think that the redox systems are under thermodynamic control. The E° value is an average value, calculated as the half-sum between forward and reversed peak potentials from the recorded voltammograms at different scan rates, using at least three independent series of experiments (Table 1, Figure 1a).

Table 1. Standard Potential, Anodic and Cathodic Peak Potential (in V vs. SCE) and ΔE_p for **1** in DMF[a] at 20 °C using Silver as a Working Electrode. Scan Rate: 0.1 V s^{-1}.

Solvent	E° (V)	E_{pc}(V)	E_{pa}(V)	ΔE_p (mV) [b]	E° (DMF)-E°(RTIL)
DMF[a]	-1.220	-1.265	-1.175	66	-
[EMIM]TFSI	-1.289	-1.320	-1.258	62	69 mV
[BMIM]TFSI	-1.290	-1.333	-1.248	67	70 mV
[BMPyr] TFSI	-1.309	-1.352	-1.266	68	89 mV
[PP13]TFSI	-1.312	-1.354	-1.270	70	92 mV
[N1114]TFSI	-1.347	-1.385	-1.309	68	127 mV

[a] The DMF solution contains 0.1 M of *N*-tetrabutylammonium tetrafluoroborate (TBABF$_4$)

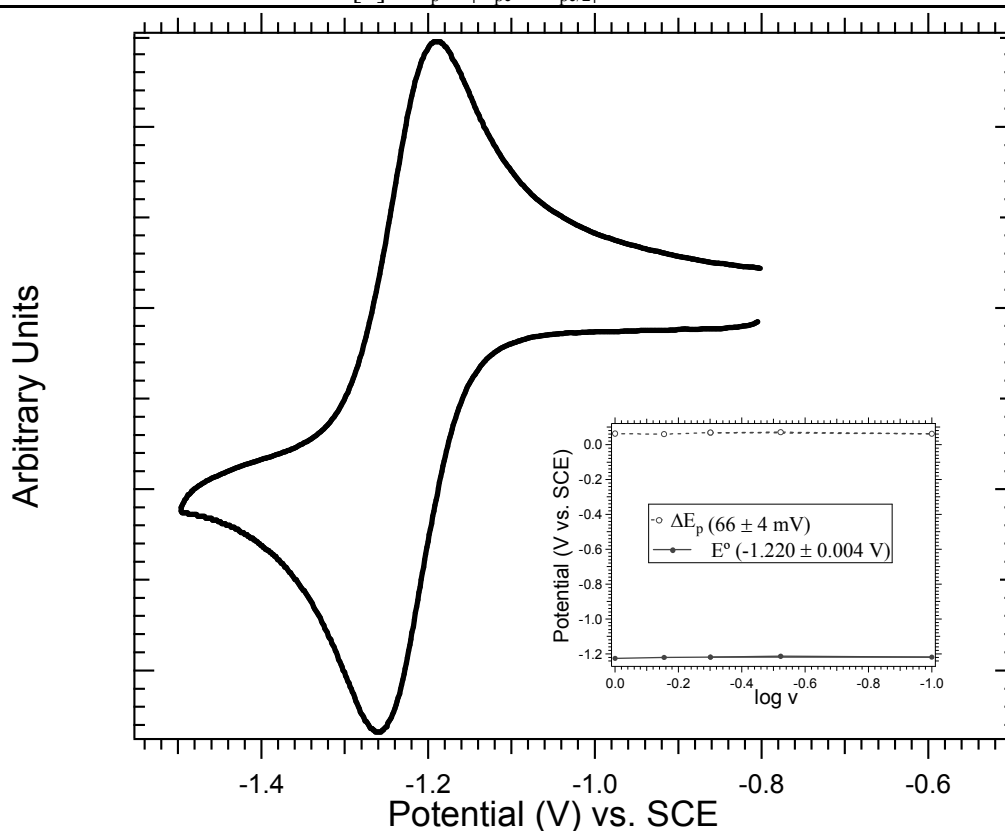[b] $\Delta E_p = |E_{pc} - E_{pc/2}|$ in mV

Figure 1. Cyclic Voltammogram (scan rate of 0.5 Vs^{-1}) of **1** showing the reduction of 7.6 mM solution of **1** in DMF + 0.1 M TBABF$_4$ on a silver electrode. Inset: Variation of the E° and ΔE_p of **1** at different scan rates. The solid and dotted lines represent the fitting of the experimental data for each value.

3.2. Cyclic Voltammetry of *1* in bis(trifluoromethylsulfonyl)imide RTILs

Cyclic voltammograms, at low scan rates, show that there is no dependence either on the peak potentials or the ΔE_p with the scan rate, which allow us to conclude that the redox systems are under thermodynamic conditions (Table 1). The typical cyclic voltammograms of the reduction of **1**, within the different RTILs investigated, reveal a strong dependence on the E° value with the RTIL. The E° values for the electrochemical reduction of **1** are calculated as the half-sum between forward and reversed peak potentials, from three independent series of experiments (Figure 2). The current values obtained for the reduction process of **1** under our experimental conditions were within the microampere range for all the RTILs investigated.
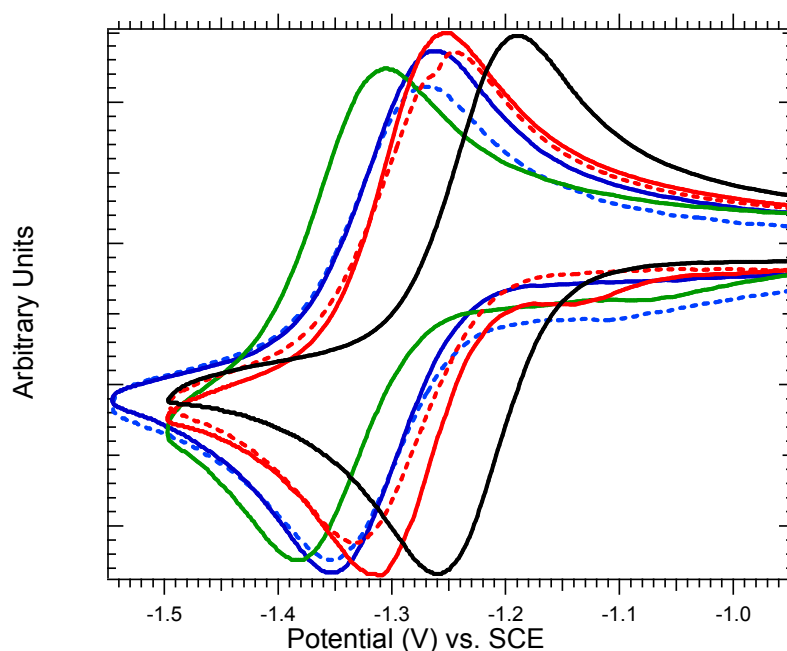

Figure 2. Cyclic Voltammograms on a silver electrode (scan rate of 0.5 Vs^{-1}) of **1** (7.6 mM) showing the reduction in: DMF + 0.1 M TBABF$_4$ (black), [EMIM]TFSI (red solid line), [BMIM]TFSI (red dotted line), [BMPyr]TFSI (blue solid line), [PP13]TFSI (blue dotted line) and [N1114]TFSI (green).

3.3. Solvation Effects of 9-Fluorenone Radical Anion on Bis(trifluoromethylsulfonyl)imide RTILs

It has been previously reported by some of us, and other research groups, that the Eº values obtained for the reduction process of several redox probes on RTILs are strongly associated with the solvation process of the electrogenerated radical anions. [15-16, 22-26] For simplicity we will analyze the data by considering a concerted solvation process when the radical anion is electrogenerated, [34] which implies that the difference between the Eº values (Eº (DMF)-Eº(RTIL)) can be related to the $\Delta_{\text{ion-pair solvation}}G^\circ$. [35]

The Eº values for the formation of 9-fluorenone anion radical ($\mathbf{1}^{\cdot-}$) in RTILs are negatively shifted with respect to the reference value obtained in DMF (Table 1, Figure 3) for all the RTILs investigated. Thus, the solvation process of $\mathbf{1}^{\cdot-}$ appears to be more effective in the case of using tetrabutylammonium salts at low concentrations, 0.1 M in DMF, than in RTILs in spite of there is a high concentration of cations. [37-39] A plausible explanation for those differences can be attributed to the excess of bis(trifluoromethylsulfonyl)imide anion (TFSI), which will interfere in the solvation of the $\mathbf{1}^{\cdot-}$ by the cation moiety of the RTIL. Thus, at this point it may be concluded that the anion does not act as a mere spectator. The size of the anion will strongly interfere in the solvation process, so the use of RTILs composed of smaller anions should help in order to perform the electrochemical reduction at less negative potentials. [15]

When either [EMIM]TFSI or [BMIM]TFSI are used as a solvents, the electrochemical reduction of **1** takes place at less negative potential values (Eº). Thus, the presence of the imidazolium cation in the RTIL composition renders a better solvation of $\mathbf{1}^{\cdot-}$. This result can be easily rationalized by taking into account that the imidazolium cations are able to strongly interact with $\mathbf{1}^{\cdot-}$ by π-π intermolecular forces, since it may be possible to form a face-to-face ion-pair between the π-system imidazolium moiety and the aromatic rings of **1** anion radical. [15] Moreover, it is worth considering that the electrostatic attractive molecular forces will be enhanced after the reduction of **1** by the appearance of new coulombic interactions between opposite charges or charge densities (cation-anion forces) and by the increase in the strength of the hydrogen bond between the H of the imidazolium moiety located in position 2 and the C=O group of **1** (where the negative charge density will be mainly located). It is reasonable to believe that all the above-mentioned intermolecular forces are acting in a concerted manner, giving rise to a positive cooperative effect between the bonding sites.

Finally, it can be also concluded that the use of BMIM cations instead of EMIM cations does not affect the solvation of the corresponding **1** anion radical. The presence of a more bulky group in position 1 of the imidazolium moiety does not increase the distance between the imidazolium and fluorenone aromatic rings. At the same time the positive solvation effect due to coulombic and hydrogen bond intermolecular forces will be also operating. Hence, the butyl change should be in a perpendicular plane with respect to π-π system.
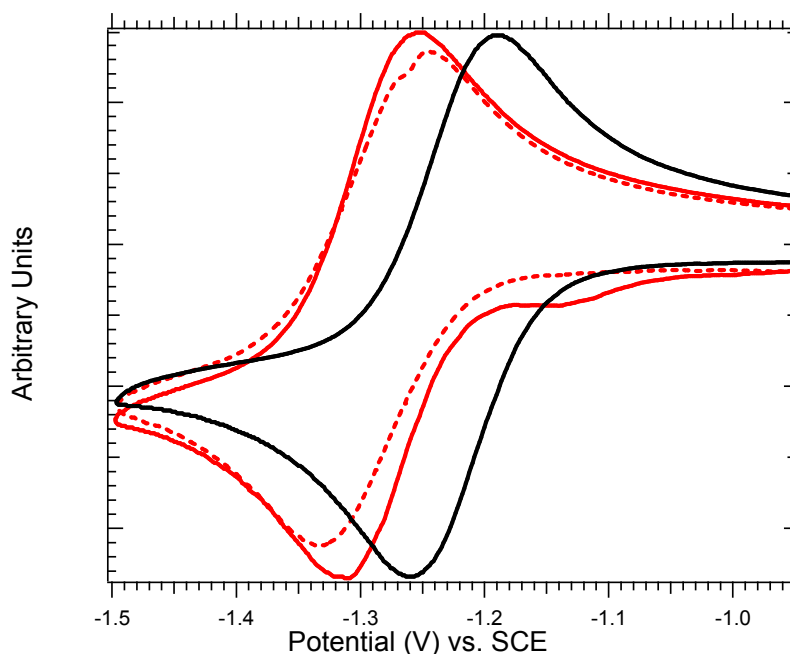

Figure 3. Cyclic Voltammograms on a silver electrode (scan rate of 0.5 Vs^{-1}) of **1** (7.6 mM) showing the reduction in: DMF + 0.1 M TBABF$_4$ (black), [EMIM]TFSI (red solid line), [BMIM]TFSI (red dotted line).

In the case of [BMPyr]TFSI, [PP13]TFSI, and [N1114]TFSI, the cyclic voltammetry experiments reveal that **1** anion radical is negatively shifted with respect to the imidazolium RTILs (Table 1, Figure 4), so the ion-pairing effect appears to be less effective than in the case of imidazolium RTILs. It is also worth noting that the solvation between **1** anion radical and [BMPyr], [PP13], and [N1114] is mainly related to coulombic interactions. In those systems, it is not possible to have a contribution to the solvation energy, either by hydrogen bonding (since the cations do not have acidic hydrogens) or π-π intermolecular interactions (since the cations are non-aromatic), thus large solvent separation ion pairs are formed. A careful analysis of the E° values of **1** in [BMPyr]TFSI, [PP13]TFSI, and [N1114]TFSI also reveals that the ion-ion interactions between **1**$^{\cdot-}$ and the corresponding

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cations of the ionic liquids, [BMPyr], [PP13], and [N1114], have a weak directionality, with the stabilization energy of the ion-pair basically being related to the distance between the opposite charges. As a consequence, the E° value of **1** in [BMPyr]TFSI and [PP13]TFSI are quite similar since the steric hindrance and pre-organization factors are also quite similar. In the case of [N1114]TFSI, the presence of a more bulky cation leads to the formation of less "tight" interactions between **1·⁻** and [N1114], which can experimentally be seen as an increase in the E° potential value.
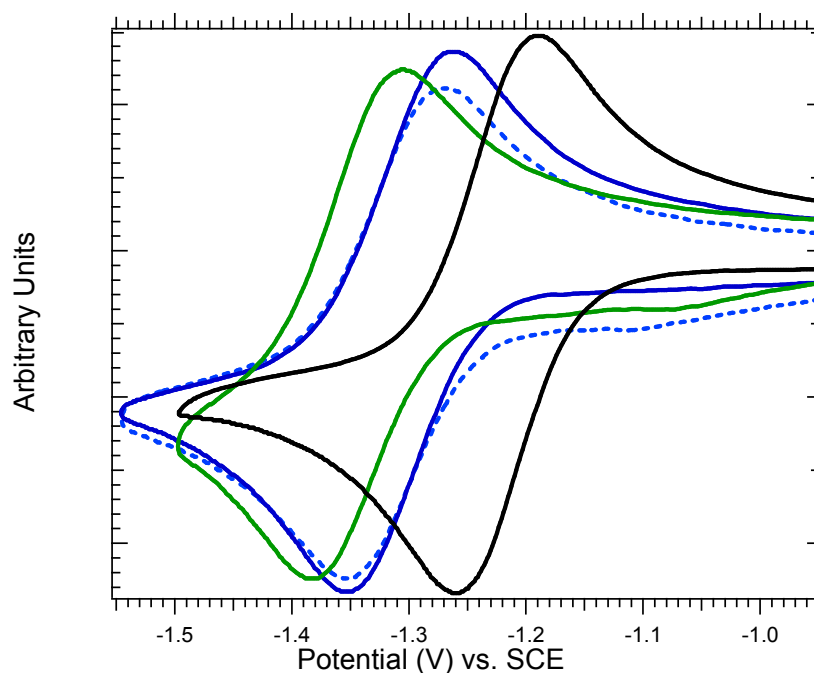

Figure 4. Cyclic Voltammograms on a silver electrode (scan rate of 0.5 Vs⁻¹) of **1** (7.6mM) showing the reduction in: DMF + 0.1 M TBABF₄ (black), [BMPyr]TFSI (blue solid line), [PP13]TFSI (blue dotted line) and [N1114]TFSI (green).

3.4. Determination of the 9-Fluorenone Diffusion Coefficient using Cyclic Voltammetry

In terms of mechanism analysis, the peak current, potential and width values of a cyclic voltammogram are parameters commonly used for characterizing and identifying a reversible redox system. If a redox process is reversible, the peak potential is independent of scan rate and concentration, providing an easy access to the standard potential E° (mean of the cathodic and anodic peak potentials). Moreover, one of the most useful features of

the peak current is its proportionality to concentration and, even more important, its proportionality to the square root of the scan rate. The peak current is given by equation 1 for a one electron process, where S is the electrode surface area, C° is the concentration of reactant, v is the scan rate of the cyclic voltammogram and D is the diffusion coefficient of the molecule. Hence, fitting our experimental data (I_{pc} vs. $v^{1/2}$) to this equation, it is possible to have access to the diffusion coefficient values of **1** in four RTILs through the determination of the slope values (Figure 5, Equation 1).[3, 28]

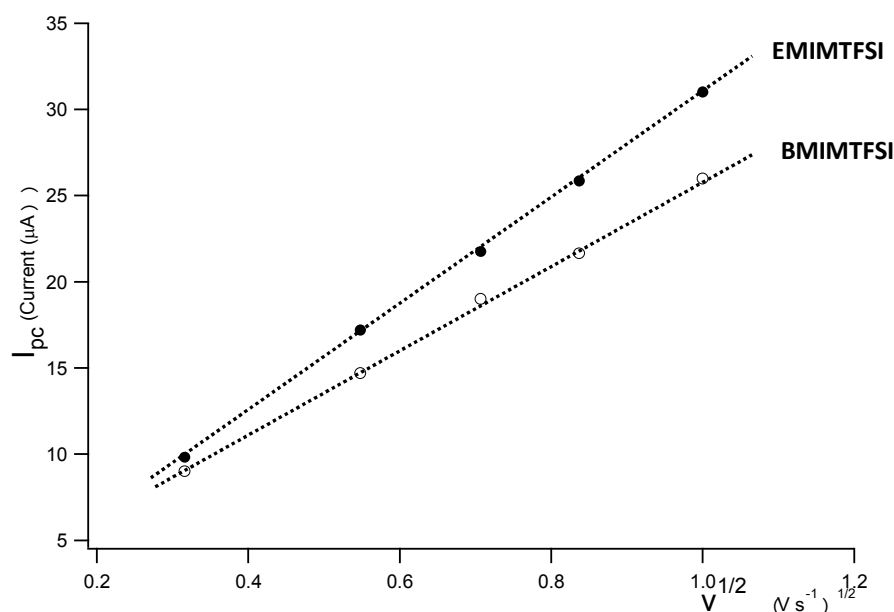$$i_p = 0.446 FSC^0 \sqrt{D} \sqrt{\frac{Fv}{R\,T}} \tag{1}$$

Figure 5. Plot of cathodic peak current (I_{pc}) vs. Square-root of scan rate ($v^{1/2}$).

For all the RTILs investigated the diffusion coefficient values of **1** are in the range from 2.48 to 5.64 x 10^{-7} cm^2 s^{-1}, that is two orders of magnitude lower than in DMF + 0.1 M TBABF$_4$ (1x10^{-5} cm^2 s^{-1}) at 20 ºC. A careful analysis of the data also reveals that in the case of [EMIM]TFSI the diffusion coefficient is 4.34 x 10^{-7} cm^2 s^{-1} , almost twice the value of [BMIM]TFSI (2.48 x 10^{-7} cm^2 s^{-1}). This, result can be explained by taking into account the Stokes-Einstein equation, [40-41] and the fact that the viscosity of the [EMIM]TFSI is 35.55 cP (at 298 K), whereas it is 61.14 cP (at 298 K) for [BMIM]TFSI. [42]

4. Conclusion

We have established the dependence of the Eº values, depending on the electrochemical media selected for the most common used bis(trifluoromethylsulfonyl)imide room temperature ionic liquids for the electrochemical reduction of 9-fluorenone, a reversible redox probe. We have analyzed the effect on the standard potential displacement (Eº) at the first reduction level, establishing the influence of the ionic liquid composition (anionic and cationic moieties) in the ion-pair formation. The formation of more effective solvent separation ion-pairs is seen when imidazolium ionic liquids are used. It has also been observed that when the room temperature ionic liquids are composed of large anions, such as the bis(trifluoromethylsulfonyl)imide, makes it more difficult to form tighter ion-pairs between the fluorenone anion radical and the cation moiety of the ionic liquid. As a consequence, the anion of the room temperature ionic liquid does not act as a mere spectator and thus, it should be taken into account in the solvation process between the electrogenerated radical anion and the cation of the room temperature ionic liquids where the electrochemical reaction is performed. It has been also confirmed that the diffusion coefficient values are lower in ionic liquids in comparison with *N,N*-dimethylformamide. Moreover, there appears to be a linear relationship between the diffusion coefficient of fluorenone, and the viscosity of the solvent for the all room temperature ionic liquids investigated. Further investigations in terms of calculation of the Stokes radius, coordination number surrounding fluorenone and fluorenone anion radical in the above-mentioned ionic liquids using Raman Spectroscopy will be done in a foreseeable future. Finally, it is important to mention that the results described in this manuscript can potentially be used to improve the performance of electrode processes for a wide variety of organic compounds. The energy required for performing the process could be optimized, not only for establishing new electro-synthetic conditions but also to design electrochemical and optoelectronic devices based on chemical and electrochemical properties of fluorenone in room temperature ionic liquids.

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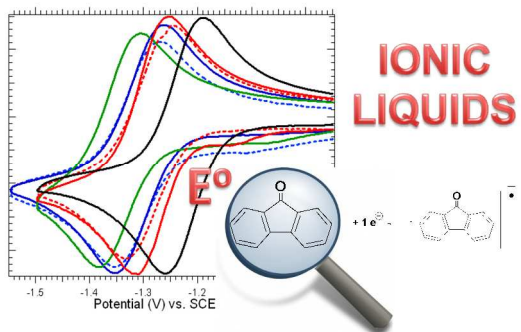
Comprehensive study of the electrochemical reduction of 9-fluorenone in various Room Temperature Ionic Liquids using Silver Electrode as a Cathode Material