Electron Transfer Kinetics in a Deep Eutectic Solvent

*Fangchen Zhen, Lucie Percevault, Ludovic Paquin, Emmanuelle Limanton, Corinne Lagrost, Philippe Hapiot**

Univ Rennes, CNRS, ISCR – UMR 6226, F-35000 Rennes, France

ABSTRACT. Electron transfer (ET) kinetic rate constants k_s in Ethaline (1:2 Choline Chloride + Ethylene Glycol) have been measured for two common redox couples (ferrocene/ferrocenium and ferrocyanide/ferricyanide) on a glassy carbon electrode and compared with ET kinetics in ionic liquids and classical organic solvents in the same conditions (acetonitrile and water). A particular care has been taken to treat ohmic drop in DES. For both couples, we found that ET rate constants are just a little lower than those measured in classical solvents (around 50% or less). These results contrast with ET rates in ionic liquids where electron transfers are considerably slower (100 times lower). Data are discussed as function of the solvent relaxation time using Marcus Theory for an adiabatic electron transfer.

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1. Introduction

Since their initial proposition,[1,2] Deep Eutectic Solvents (DES) are receiving an increasing interest as new class of solvent for numerous applications ranging from synthesis, electrochemistry to extraction, etc.[3] Common DES are often composed of a salt and a hydrogen bond donor. Such DESs are frequently presented as an improvement of ionic liquids and they are considered as possible electrolytic media because they have an inherent ionic conductivity associated to excellent solubilizing properties. Moreover, they are easy to prepare, low cost and possibly environmental friendly.[3]

Electron transfers (ET) rate in these media is a key parameter for many proposed electrochemical applications. For example, ET strongly influences the response time of sensor or the current density in an energy storage device. Interest of ET studies in DES is not limited to electrochemistry because the analysis of the charge transfer kinetics provides information about the solvation of a solute. In the search of the best DES, it could help in the definition of criteria for an optimized DES. In the framework of the Marcus-Hush theory,[4,5] the electron transfer kinetics is for a large part driven by the dynamics and solvent reorganization that accompany the electrochemical process.[6,7,8,9] This explains that numerous publications have addressed this question in ionic liquids (see for example references[10,11,12,13,14]) and more recently in DESs.[14,15,16,17,18,19,20] In ionic liquids, the electron transfer of a redox couple is considerably decreased when passing from a classical organic solvents to a ionic liquid, generally by a ratio 10-100 depending on the outer-sphere character of the electron transfer.[8-13] Concerning the DES, well-defined cyclic voltammograms in Ethaline or Reline were reported for “outer-sphere redox” couple like ferrocene/ferrocenium[14-17,19] but also for highly charged couple like ferro/ferricyanide,[14,19] suggesting fast electron transfers. However, recent reports about electron

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transfer kinetics in DESs have reached a different conclusion. The standard electron transfer rates constants k_s were reported to be significantly lower in DES (below 10^{-3} cm s^{-1}) than in molecular solvents and in the same range or below the values reported in ionic liquids.[14-17] In a recent publication, Akolkar *et al.* have highlighted the possible difficulties and pitfalls for such kinetics measurements in DES. They explained the need of an accurate treatment of the uncompensated ohmic drop.[21] Accurate characterizations of fast electron transfer kinetics require the use of short experimental times, for instance high scan rates in transient cyclic voltammetry.[6,22,23] Despite the relatively good conductivity of DES, their inherent conductivities remain lower than those found in classical organic or aqueous electrolytic solvents and their viscosities are generally higher.[2] A lower conductivity means a higher resistance of the solution and thus larger distortions due to the ohmic drop, R_uI (where R_u is the uncompensated resistance at the working electrode connection that contains all sources of resistances between the working electrode and the tip of the reference electrode and I is the current passing through the working electrode). Because, the current in cyclic voltammetry increases with the scan rate, the ohmic drop becomes a major problem when high scan rates are required.[22] Additionally, the larger viscosity of DES results in lower diffusion coefficients of the solubilized redox couples and in a lower mass transfer rates from the solution to the electrode. For this reason, we need using high scan rates for measuring a large standard electron transfer rate constant, k_s in DES. If we combine all these difficulties due to the low conductivity of DES and the small diffusion coefficients of solute in DES, accurate examination of a fast electron transfer in such media is a challenging task.

Briefly, there are two general approaches for considering the ohmic drop in electrochemical methods.[22,23] The first ones rely on post-treatment corrections by full simulations of voltammograms or are based on semi-integral and potential scale correction, impedance

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spectroscopy including the ohmic drop. Post-treatment techniques generally require an independent measurement of R_u and could be long to obtain if multiple parameters are needed in the treatment.[6,23] The properties of the working and the reference electrodes must remain perfectly stable during the experiments, which could be difficult to achieve in some experimental situations.[18,24] A second type of approach is based on the direct corrections of the ohmic drop by using a potentiostat equipped with an electronic ohmic drop compensation circuit (positive feedback) or by simply using a microelectrode to decrease the ohmic drop.[25,26] In similar situation, we used these different approaches that present their own advantages and inherent difficulties.[22] A large literature exists about the conditions needed for obtaining an efficient positive feedback[25,26] or more specifically about difficulties in DES investigations.[21] Semi-integral correction procedures were used for cyclic voltammetry of $FeCl_3$ in common DESs for which k_s value of 0.017 cm s^{-1} was measured in Glyceline.[18] In this paper, the authors show the importance of a correct treatment of the ohmic drop for the determination of ET rate constants and diffusion coefficients in a low conductivity DES like Glyceline.[18] We could also emphasize that the influence of the ohmic drop on a recorded voltammograms could be difficult to detect on a single curve. Then, the characteristics of the cyclic voltammograms could incorrectly be ascribed to a slow ET rate, particularly when the measurement is made at a single scan rate or in a too narrow range of scan rates.[22]

In this work, we prefer using the methodology based on direct electronic compensation and a millimetric electrode. This permits an immediate view of the corrected curves and does not required a separate measurement of R_u when the conditions of bandpass of the potentiostat and cell times are respected.[22,25,26] Using a millimetric electrode offers more choice of electrode materials than a microelectrode, notably for carbon electrodes. Glassy carbon (GC) electrodes

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were used in this study. GC is a well-adapted electrode material for electrochemical analysis in DES notably because of the stability of GC and the high electrochemical windows in a medium that could contain high quantity of water.[27] We used a 1-millimeter diameter glassy carbon electrode as a working electrode. Electron transfer kinetics were investigated for two redox couples, ferrocene/ferrocenium and ferrocyanide/ferricyanide in a widely used DES, Ethaline, which is a 1:2 mixture of choline chloride and ethylene glycol. We chose these two common redox couples that are often considered as standard couples. They present different charges, ferrocyanide ion or $[Fe(CN)_6]^{4-}$ is four times negatively charged and prone to specific interactions with the cation of the DES as observed for negatively charged species in the ionic liquids.[12,28,29] As discussed in several publications, the presence of chemical moieties on the surface of GC electrode could also influence the ET kinetics notably in the case of $[Fe(CN)_6]^{4-}$.[27] For a better comparison between experiments, all experiments were performed with the same GC electrode that was prepared and cleaned in the same manner.

Residual water could play a major role in the properties of DES even if the effect is not totally understood; so all experiments were made with a careful control of the residual water and after drying the DES as much as possible (typically residual water measured by Karl-Fischer coulometric technique is less than 0.5 wt % (around 0.31 mol L^{-1}).

2. Experimental Section.

Electrochemical measurements were performed with a home-built potentiostat using a conventional 3-electrode setup and allowing a fast electronic compensation of the ohmic drop.[25,26] The counter-electrode was a large Pt wire and the working electrode a 1-millimeter diameter

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glassy carbon disk electrode. The reference electrode was a quasi-reference electrode made with an Ag wire.

Faradaic peak current, I_p was measured after correction of the baseline that was estimated under the faradaic peak by a linear extrapolation of the background current determined at the beginning of the voltammogram. Diffusion coefficients D were derived assuming a reversible electron transfer at low scan rate using $I_p = 0.446\, FSC^{\circ}\sqrt{D}\sqrt{\frac{Fv}{RT}}$ (F is the Faraday constant, S the electrode surface area, C the initial concentration of the redox couple, R the gas constant, v the scan rate and T the absolute temperature).[6,23] In all experiments, the peak current I_p was found to vary linearly with the square root of the scan rate. (See Figures S1 and S2 in the Supporting Section) Such results demonstrate a linear diffusion process for the mass transport to the electrode. Apparent heterogeneous electron transfer standard rate constants, k_s, were extracted from the variation of ΔE_p versus the scan rate considering the Butler-Volmer law6 and uncorrected from the double layer effect. Working curves for the variation of the ΔE_p were calculated as a function of the dimensionless parameter $\Lambda = \frac{k_s}{\sqrt{D}}\sqrt{\frac{RT}{aFv}}$ using the Kissa 1D package developed by C. Amatore and I. Svir and taking α as 0.5 for the transfer coefficient.[30] Curves are shown in Figure S6 of the SI and show that similar working curves are obtained for α between 0.3 and 0.6 when the system is reversible or quasi-reversible. Single parameter adjustment of the theoretical curve with the experimental data provides the value of $\frac{k_s}{\sqrt{D}}$ and then of k_s using the D value derived from the variation of I_p with $v^{1/2}$. We show the original voltammograms with the potential scale versus the quasi-reference electrode on Figures 1 and 3 to show the quality of the data and for an easier comparison of the data with literature. Notice that the measurement of the rate constant k_s only

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requires the measure of the peak-to-peak difference ΔE_p and not of the absolute peak potential and that we do not extract $E°$ from this experiments. The procedure is thus almost insensitive to a possible drift of the potential of the Ag quasi-reference electrode but presents the advantage of using a low impedance reference electrode.

As reported and discussed in several publications, the kinetics of the electron transfer for a molecule like ferrocyanide is sensitive to the surface state of the carbon electrode.[27] To maintain a similar surface state on a series of measurements, the working electrode was just cleaned for each series of voltammograms. Each voltammogram was recorded at least 3 times and averaged allowing an estimation of the error on E_p around ± 5mV.

We used a homemade potentiostat equipped with a positive feedback electronic compensation following an adder scheme[23,25] that has been published before and used in several studies (See Scheme 3 in the reference).[25] Potentiostat was built with Burr-Brown OPA111AM Low Noise Precision operational amplifiers. Potential scan and signal digitalization were controlled by a PC-computer equipped with a fast National Instruments DAQ card and a SCB-68 block for digital data acquisition. As discussed before, when the band pass of the potentiostat circuit using the ohmic drop compensation is much below than the electrochemical cell-time, over-compensation is not possible as the system oscillates when R_u tends to zero. (For a detailed discussion see references).[25,26] This procedure avoids an independent measurement of the uncompensated resistance R_u and allows readjusting the compensation in case where the characteristics of the working electrode have been modified.

Ferrocene, potassium ferrocyanide and potassium ferricyanide were of the highest available purity grade from commercial source (Aldrich) and used without further purification. Solutions in Ethaline were prepared by heating the solution with a gradual increase of the temperature up to

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60°C in an ultrasonic bath. We found that concentrations around 3 x 10^{-3} mol L^{-1} are accessible without the appearance of a precipitate when the solution was cooled down to room temperature. Such concentrations were sufficient to record currents with a good ratio between the signal and background currents and noise.

Potassium ferricyanide or ferrocyanide are not well soluble in ionic liquids and the use of other salts are required like $BMP_3[Fe(CN)_6]$ where BMP is 1-butyl-1-methylpyrrolidinium. $BMP_3[Fe(CN)_6]$ was prepared according to a procedure derived from literature[28,29] starting from the Ag salt. Briefly, $Ag_3[Fe(CN)_6]$ was prepared by treating $K_3[Fe(CN)_6]$ (1 eq., dissolved with 2-3 mL water) with $AgNO_3$ (3-4 eq.) in methanol and stirred overnight at 30°C. $BMP_3[Fe(CN)_6]$ was then obtained by cation exchange between $Ag_3[Fe(CN)_6]$ and BMP-Br in methanol by stirring overnight. The process was followed by change of the color of the solution from brown to green. Then, the reaction mixture was concentrated under reduced pressure; the resulting precipitate was filtered and dried under vacuum overnight. Ethaline was prepared from commercially available compounds obtained from Aldrich according to general published procedures.[16,17] Mass fraction of residual water was measured by using a coulometric Karl-Fischer titration (831KF Coulometer – Metrohm and using Hydranal® Coulomat E solution from Fluka) for each sample and after each series of experiments and was found less than 0.5 wt % (around 0.31 mol L^{-1}).

3. Results

Ferrocene Oxidation in Ethaline. As seen on Figure 1, Ferrocene/ferrocenium couple displays well-defined cyclic voltammograms in Ethaline even at high scan rates on a glassy carbon electrode.

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Typical voltammograms of ferrocene oxidation in Ethaline and using the electronic direct compensation are shown at low (0.5 and 2 V s^{-1}) and high scan rates (25 and 200 V s^{-1}).

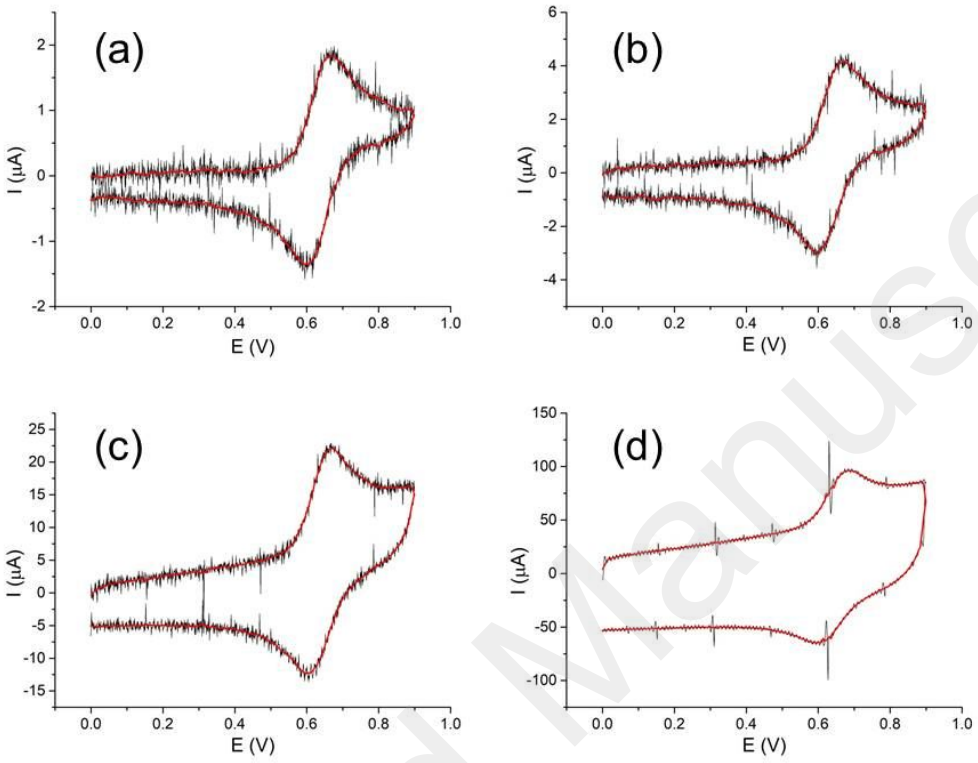


Figure 1. Cyclic voltammograms of the oxidation of a solution of ferrocene in Ethaline (C° = 2 10^{-3} mol L^{-1}) on a 1-mm diameter glassy carbon electrode at 0.5 (a), 2 (b), 25 (c), 200 (d) V s^{-1}. Red lines are smooth lines. T= 298 K.

As explained above, to determine a value of electron transfer standard rate constant, k_s, we performed the measurement in a large range of scan rates notably to check that the electron transfer controls the electrochemical process without interference of another process and that ohmic drop correction is correctly treated. These experiments were performed for different initial concentrations of ferrocene and found to be similar, which confirm the quality of the ohmic drop compensation (see Figure S3 in the SI). Both slow electron transfer and ohmic drop increase the value of ΔEp, but their relations with the scan rates are different. A good agreement between

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experiments and the theoretical curve allowing us to validate the quality of the ohmic drop compensation.[22,24,25]

Variations of ΔE_p as a function of the scan rates were examined at different temperatures in Ethaline and then compared with the values obtained in Acetonitrile (ACN) using the same glassy carbon electrode (see Figure 2).

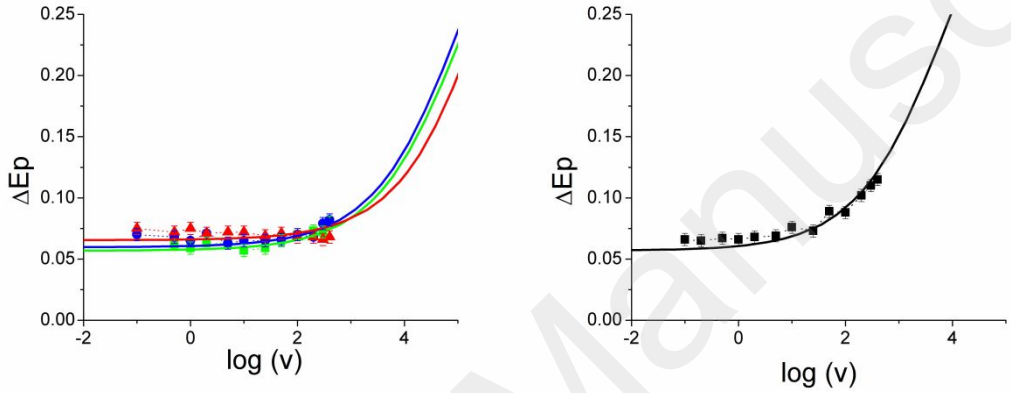


Figure 2. Cyclic voltammetry investigations of the oxidation of a 2 10^{-3} mol L^{-1} ferrocene solution in Ethaline (left) and in ACN (+ 0.1 mol L^{-1} nBu_4NPF_6) (right). Variations of ΔEp as function of the log(v) (v : scan rate in V s^{-1}) at different temperatures: in Ethaline, T= 298 (green), 313 (blue), 343K (red); in acetonitrile at T= 298K. Lines are the theoretical variations assuming a Butler-Volmer law and taking $\alpha = 0.5$ as transfer coefficient (see text).

In ACN, a considerable increase of ΔE_p is observed for scan rates higher than 100 V s^{-1}, which corresponds to a change in the kinetics passing from a diffusion control at low scan rate to an electron transfer control at the higher scan rate.[6,22] Measurements were repeated for different initial concentrations of ferrocene and similar variations were systematically obtained as expected (See Figure S3 in the SI). Such an observation confirms that the ohmic drop was effectively compensated. From the fitting of the experimental data with the theoretical curve, it is possible to derive the value of k_s was found equal to 1.5 cm s^{-1}. This value falls in the range of reported

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values under similar experimental conditions.[10] In contrast, in Ethaline, ΔE_p displays very little change up to the highest usable scan rates (400 V s^{-1}). It shows that the system is reversible and remains controlled by the diffusion of molecules from the solution to the electrode even at short timescale. A small increase of ΔEp is just visible for the experiments performed at the highest scan rates and temperature. However, it is difficult to clearly conclude that the kinetics is approaching a control by the electron transfer because of the narrow range of the change and we could only derive a lower limit for the heterogeneous electron transfer rate constant as $k_s >> 0.16$ cm s^{-1}. Such estimations of k_s are higher than reported data but these data were obtained without taking into account the ohmic drop.[14,16,17] As a first remark, we could observe that the k_s values in Ethaline are just slightly slower than the rate constants measured in an organic solvent like ACN. They are also much higher than the values reported in common ionic liquids where k_s around 10^{-2} cm s^{-1} are generally obtained (See discussion below).[11,13]

Ferrocyanide oxidation. Cyclic voltammetry were recorded for the oxidation of ferrocyanide in Ethaline using the same experimental conditions (see Figure 3). Well-defined voltammograms are recorded at low scan rates as previously reported19 but also at high scan rates (up to 400 V s^{-1}) suggesting a fast electron transfer. Variations of ΔE_p were recorded for two temperatures and compared with the data in aqueous media used as a reference electrolyte (See Figure 4). A good agreement between the experimental and theoretical variations of ΔE_p are observed for all experiments, indicating that the electron transfer controls the kinetics at the highest scan rates. By adjusting the position of the theoretical curve with the experimental points, we derived the value of $k_s/D^{1/2}$ then the value of k_s after determination of D from the $I_p/v^{1/2}$ variation (See Table 1). The values are then standardized using the values of the diffusion coefficient D for ferrocene and

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ferrocyanide reported in the literature to limit the error due to the effective area of the working electrode.

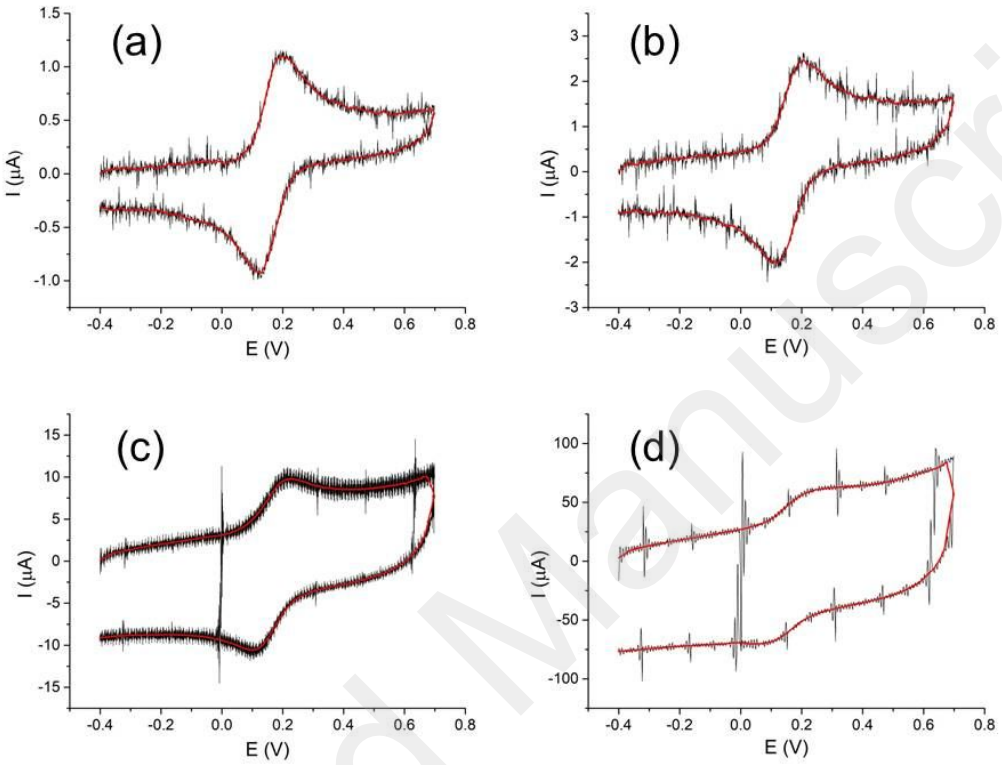


Figure 3. Cyclic voltammograms of the oxidation of a 2 10^{-3} mol L^{-1} solution of ferrocyanide in Ethaline on a 1-mm diameter disk glassy carbon at 0.5 (a), 2 (b), 25 (c), 200 (d) V s^{-1}. Red lines are smooth lines.

For a final comparison, the behaviors of the ferro/ferricyanide couple were examined and k_s determined in two common ionic liquids 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMP-TFSI) and 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF_4) and using the same glassy carbon electrode (See Figures S4-S6 in the supplementary section). In BMP-TFSI, ΔE_p variations follow the curve expected for a simple electron transfer and Butler-Volmer law. ΔE_p values are much larger than those recorded in

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Ethaline in the same conditions, showing a much slower electron transfer. In EMIM-BF_4, the variations of ΔE_p with the scan rate slightly deviate from the theoretical variations expected for a simple electron transfer. This suggests that another process is associated to the electron transfer in this ionic liquid, probably a complexation or strong ion pairing association of the ferro/ferricyanide anion with the cation of the ionic liquid.[12,13] In this work dedicated to DES, we just consider these data to estimate an apparent k_s for an easiest comparison in Table 1.

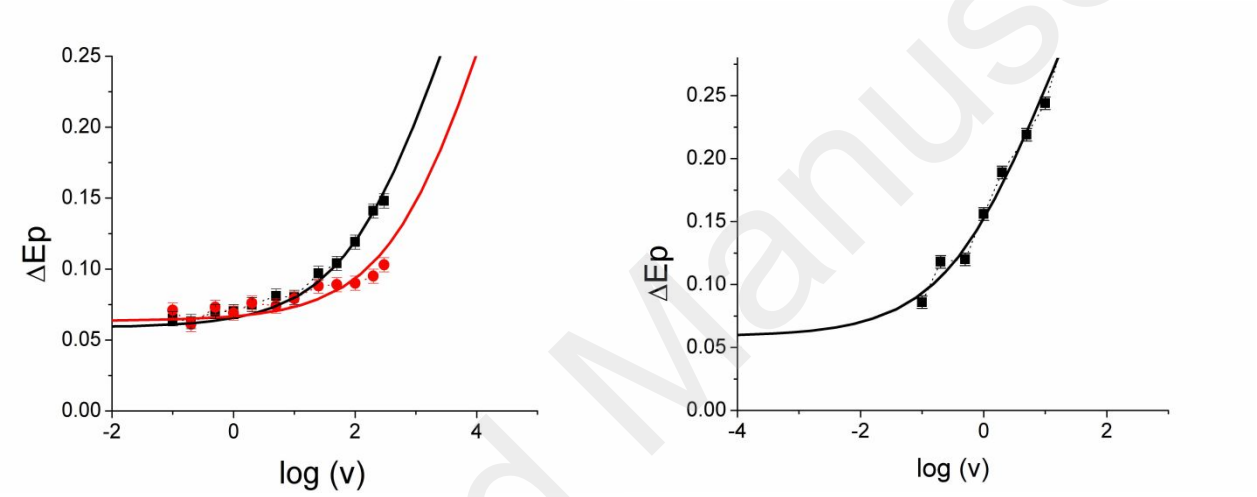


Figure 4. Cyclic voltammetry investigations of the oxidation of a 2 10^{-3} mol L^{-1} ferrocyanide solution in Ethaline (left) and in water (+ 0.1 mol L^{-1} KCl) (right) on a 1-mm diameter glassy carbon electrode. Variations of ΔEp as function of the log(v) (v the scan rate in V s^{-1}) at different temperatures: in Ethaline T= 308 K (black) and 333 K (red); in water at 308 K (right). Lines are the theoretical variations assuming a Butler-Volmer law and taking $\alpha = 0.5$ as transfer coefficient.

Same observations could be done for the ferrocene/ferrocenium couple. Rate constants could be compared to the numerous studies in common ionic liquids where low k_s values are reported for the oxidation of the ferrocene (0.2-0.01 cm s^{-1} range)[12,13] in contrast to the large k_s in organic solvents (higher than 1 cm s^{-1}) as measured here in ACN with a carbon electrode. To go further in

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the analysis, it is useful to use the Marcus formalism as done in several studies related to electron transfers in molecular solvents but also in ionic liquids. (See for example [7,8,31,32])

Table 1. Calculated parameters and comparison of k_s measured in different media.

Compound/Solvent	T (K)	D ($cm^2\ s^{-1}$)	$k_s/D^{1/2}$ ($s^{-1/2}$)	k_s ($cm\ s^{-1}$)	k_s [d] ($cm\ s^{-1}$)	τ_L [e] *(ps)*
Fc/ACN	298	$2.8_5\ 10^{-5}$	300	1.6	$1.4_5 \pm 0.3$	≈ 0.2
Fc/EMIM-TFSI	298	$3.3_5\ 10^{-7}$ [a]	-	-	0.15-0.21[a,b]	6.7
Fc /Ethaline	298	$2.2\ 10^{-7}$	360	> 0.17	$> 0.15_5$	4.0
Fc/Ethaline	313	$4.0_5\ 10^{-7}$	345	> 0.22	> 0.20	-
Fc/Ethaline	343	$8.7\ 10^{-7}$	500	> 0.47	> 0.43	-
Ferrocyanide/Water	308	$8.5\ 10^{-6}$	8.9	$2.6\ 10^{-2}$	$(2.4 \pm 0.5)\ 10^{-2}$	≈ 0.2
Ferrocyanide/Ethaline	308	$1.2\ 10^{-7}$	46	$1.6\ 10^{-2}$	$(1.5 \pm 0.3)\ 10^{-2}$	4.0
Ferrocyanide/Ethaline	333	$2.3\ 10^{-7}$	77	$3.7\ 10^{-2}$	$(3.4 \pm 0.7)\ 10^{-2}$	-
Ferricyanide/BMP-TFSI	303	$1.1\ 10^{-8}$	0.95	$1.0\ 10^{-4}$	$(9.1 \pm 2)\ 10^{-5}$	22
Ferricyanide/EMIM-BF_4	303	$2.7\ 10^{-8}$	8.5	$\approx 1.4\ 10^{-3}$ [c]	$\approx 1.3\ 10^{-3}$	5.0

[a] From Compton *et al.*[33,34]. [b] From Hapiot *et al.*[35] [c] *Ep/log(v)* variation does not follow a simple Butler-Volmer Law. Estimation. [d]Values from this work were corrected with D taken from literature. Ferrocene in ACN at 298K: $2.37\ 10^{-5}\ cm^2\ s^{-1}$.[36] Ferrocyanide in water at 298K: $7.1\ 10^{-6}\ cm^2\ s^{-1}$.[37] [d]See Table S1 in SI for details.

4. Discussion

The Marcus theory for electron transfer based on a dielectric continuum solvent was originally developed for polar solvent. The applicability of the model to ionic liquids was highly questioned but based on simulations it was concluded that Marcus Theory is applicable to ET in ionic liquids if specific solvation of the molecules by the ions are neglected.[8,9] By analogy, we could use the same approach for discussing the electron transfer rates in an ionic DES like Ethaline.

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In the Marcus theory, the standard rate constant corrected by the effect of the double layer for an adiabatic electron transfer is given by:[7,8]

$$k_s = \frac{K_p}{\tau_L}\left(\frac{\Delta G_{Os}^{\#}}{4\pi RT}\right)^{1/2} \exp\left[-\left(\frac{\Delta G_{Os}^{\#} + \Delta G_{is}^{\#}}{RT}\right)\right]$$

where K_p is the equilibrium constant for a precursor complex and τ_L is the longitudinal relaxation time that is the relaxation time of the solvent normalized by the ratio of the static ε_s and high frequency ε_{op} relative permittivities, $\Delta G_{Os}^{\#}$, $\Delta G_{is}^{\#}$ are the standard Gibbs activation energy of the outer sphere and inner sphere contributions. According to Marcus theory, $\Delta G_{Os}^{\#}$ could be evaluated considering solvation by a dielectric continuum solvent by the following equation: [7,8]

$$\Delta G_{Os}^{\#} = \frac{N_{av}e^2}{32\pi\varepsilon_o}\left(\frac{1}{a} - \frac{1}{d}\right)\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right)$$

where N_{av} is the Avogadro constant, e, the electron charge, ε_o, the permittivity of the vacuum, a the equivalent radius of the redox molecule and d its distance to its electrical image through the electrode plane. For redox molecules like ferrocene of ferrocyanide, the oxidized and reduced forms of the molecules are very similar and thus the inner-sphere contribution $\Delta G_{is}^{\#}$ to the total activation energy is negligible versus the outer-sphere contribution $\Delta G_{Os}^{\#}$; it means that most of the activation energy comes from the solvent reorganization. In a first approximation, we could neglect for a given molecule the variations of $\left(\frac{1}{a} - \frac{1}{d}\right)$ with the electrolyte as done previously.[8] We could also neglect the variation of the Pekar's factor $\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right)$ that varies only by a small amount in $\Delta G_{Os}^{\#}$ for the considered polar media (see Table S1 in SI). From this simplification, k_s and $1/\tau_L$ follow a similar trend for a given redox molecule, and correlations have been reported in several

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publications.[7] The relaxation times τ_L are derived from dielectric loss measured by dielectric spectroscopy techniques.[38,39] Several studies were dedicated to ionic liquids (see for example [40] for investigation of imidazolium-based ionic salts and reference used for Table S1 in SI) but Ethaline was only recently investigated by dielectric spectroscopy in a wide range of frequencies and temperatures.[38] Authors have observed that a single relaxation time describes the re-orientational dipolar motions for Ethaline with times close to those of the molecular component.[38,39] Relaxation times were fitted using a VFT law (Vogel-Fulcher-Tammann) in the whole range of investigated temperatures.[38] Using this correlation, dipolar relaxation time for Ethaline could be estimated to be around 71 ps at 298K leading to τ_L=4 ps. This τ_L is in the range of data reported for ionic liquids with low viscosity like EMIM-TFSI. Similar diffusion coefficients of ferrocene (and thus viscosities) are also reported in EMIM-TFSI and Ethaline. (See Table 1) Considering these estimations of τ_L, we could predict that k_s for ferrocene in Ethaline should be larger than k_s in EMIM-TFSI but slower than k_s in acetonitrile. If this prediction remains compatible with our observations, we could emphasize that the ET in Ethaline is relatively fast and faster than in most of the ionic liquids. For the ferro/ferricyanide couple, a better comparison is possible. It is remarkable that the rate constant k_s measured in Ethaline (1.5 10^{-2} cm s^{-1}) is of the same order as values measured in water (2.4 10^{-2} cm s^{-1}) despite totally different media, different diffusion coefficients and relaxation times of the solvent. This value could also be compared with k_s in the two ionic liquids where a large slowdown of the electron transfer is observed with k_s in the range of 10^{-4} - 10^{-3} cm s^{-1}. This is illustrated in Figure 5 that shows a plot of k_s with $1/\tau_L$. k_s in Ethaline is more than one order of magnitude larger than its estimation from the longitudinal relaxation times. A first remark to explain these results concerns the applicability of the Marcus theory to DES and the possibility of a specific solvation by the

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ions of the DES of the molecule notably by the residual water or the ions of the DES. As mentioned before for ionic liquids, this would result in an additional contribution to the reorganization energy and a smaller rate constant.[8] Another possible explanation is that a faster relaxation process controls the solvation reorganization of the molecule upon electron transfer in DES. From Figure 5, a reorganization with relaxation time around or lower than 0.4 ps is required to explain the data and such process may have not been seen in the dielectric spectroscopy experiments. A better description of the solvation arrangement and the role of the different components (water, ions, Ethylene Glycol) around the redox molecule in DES are necessary. This was predicted by molecular dynamics in ILs (see for example 32 and references therein) but not in DES.

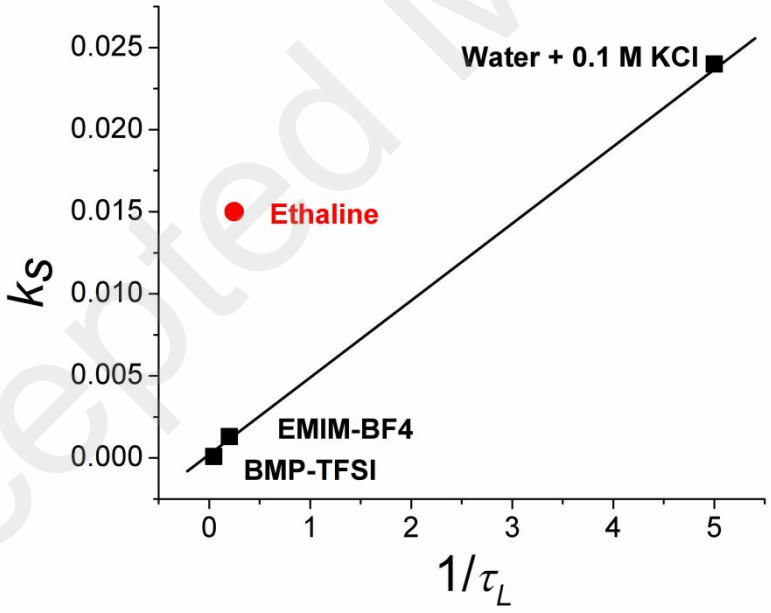


Figure 5. Variations of k_s for the ferrocyanide/ferricyanide couple versus $1/\tau_L$, τ_L, being the longitudinal relaxation time of the solvent. k_s in cm s^{-1} and τ_L in ps.

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Finally, we could remind that the values derived from the Marcus model are uncorrected from the double layer effect. This correction could be different according to the different media especially if a specific adsorption of ions or of the redox molecule occurs on the electrode surface.[8]

5. Conclusion

Electron transfer rate constant measured in Ethaline are close to the values reported in organic solvent for Ferrocene or in water for ferrocyanide oxidations. Ethaline appears to be more similar to a molecular solvent than to an ionic liquid.[11-13] We could connect this observation with another observation concerning the small variations of the diffusion coefficients with the charge of the solute as observed previously in Ethaline and in Reline.[19] This behavior is in sharp contrast to the observations in ionic liquids where diffusion coefficients vary with the charge carried by the solute because of specific interactions between the molecules and the ions of the ionic liquids.[22] These results fall also in line with recent FTIR studies concerning the oxidation of ferrocyanide in Reline where it was observed that the DES components are not considerably affected during the electrochemical process.[20]

Our work clearly evidences the importance of a careful treatment of the ohmic drop. We found much larger electron transfer rate constant values (sometimes by several orders of magnitude) than recently reported values in ionic liquids and in DES where ohmic drop was not considered.[14,16,17] Such ohmic drop issues in electrochemical measurements were previously highlighted by other groups.[18,21] Herein, we use on-line (or direct) compensation with transient voltammetry on a millimetric electrode in combination of a single-parameter fitting of a working curves with the experimental data. For the present study in DES, the methodology used here is particularly well-adapted since it limits the alteration of the electrode during the recording of the

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voltammograms, allowing an easy use of different electrode materials and an immediate qualitative view of the experiment.

When considering DES for electrochemical applications, a fast electron transfer is a strong advantage for example in energy storage systems or electrochemical sensors where the current density or time response is a key parameter. From the present results, electrochemical properties in a DES like Ethaline appear more similar to those observed in a molecular solvent than in an ionic liquid.

Supporting Information. The section presents additional cyclic voltammetry experiments in ionic liquids and in Ethaline (variation the peak current with the scan rate), details about the calculations of the longitudinal relaxation time τ_L used in Table 1 and the theoretical curves for the calculations of k_s from ΔE_p.

Corresponding Author

*Corresponding author. Email: philippe.hapiot@univ-rennes1.fr

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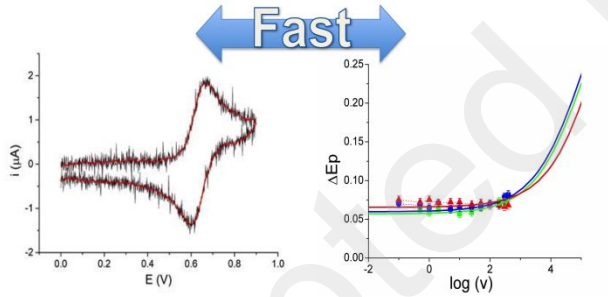
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